IAEA-TECDOC-1598

Radiation Treatment of Polluted Water and Wastewater

IAEA
International Atomic Energy Agency

September 2008

IAEA-TECDOC-1598

Radiation Treatment of Polluted Water and Wastewater

IAEA
International Atomic Energy Agency

September 2008

The originating Section of this publication in the IAEA was:

Industrial Applications in Chemistry Section
International Atomic Energy Agency
Wagramer Strasse 5
P.O. Box 100
A-1400 Vienna, Austria

RADIATION TREATMENT OF POLLUTED WATER AND WASTEWATER
IAEA, VIENNA, 2008
IAEA-TECDOC-1598
ISBN 978–92–0–107408–9
ISSN 1011–4289

Printed by the IAEA in Austria
September 2008

FOREWORD

Strategies to tackle environmental pollution have been receiving increasing attention throughout the world in recent years. Radiation processing using electron beam accelerators and gamma irradiators has shown very promising results in this area. Radiation processing in wastewater treatment is an additive-free process that uses the short lived reactive species formed during the radiolysis of water for efficient decomposition of pollutants therein.

The rapid growth of the global population, together with the increased development of agriculture and industry, have led to the generation of large quantities of polluted industrial and municipal wastewater. The recognition that these polluted waters may pose a serious threat to humans has led technologists to look for cost effective technologies for their treatment. A variety of methods based on biological, chemical, photochemical and electrochemical processes are being explored for decomposing the chemical and biological contaminants present in the wastewaters. Studies in recent years have demonstrated the effectiveness of ionizing radiation such as, gamma rays and electron beams or in combination with other treatments, in the decomposition of refractory organic compounds in aqueous solutions and in the effective removal or inactivation of various microorganisms and parasites. The application of electron beam processing for drinking water, wastewater and groundwater treatment offers the promise of a cost effective process.

The installation of the first full scale electron beam plant in Daegu, Republic of Korea, to treat 10 000 m^3 day^{-1} textile wastewater has demonstrated that the process is a cost effective technology when compared to conventional treatment. The regular operation of this facility provides operational data on reliability and additional data for a detailed economic evaluation.

The IAEA has been supporting activities in this area by organizing advisory group meetings, consultants meetings, symposia and Technical Committee meetings. Following the recommendations of scientists and consultants, the IAEA established a Coordinated Research Project on Remediation of Polluted Waters and Wastewater by Radiation Processing during the years 2002 to 2006, with the aim of establishing optimal treatment methodologies to treat drinking water and wastewater by using ionizing radiation from gamma rays and electron beam accelerators.

This publication describes the most important results and achievements of the participating groups during the course of this Coordinated Research Project and will be of value for research groups working in the field of radiation technology for the treatment of aqueous effluents, and will serve as a basis for both pre-feasibility study and technology implementation.

The IAEA wishes to thank all the participants for their valuable contributions, and W. Cooper of the University of California at Irvine for compiling this IAEA-TECDOC. The IAEA officer responsible for the Coordinated Research Project and this publication was M.H. de Oliveira Sampa of the Division of Physical and Chemical Sciences.

EDITORIAL NOTE

CONTENTS

REPORTS BY THE PARTICPANTS IN THE COORDINATED RESEARCH PROJECT

SUMMARY

1. INTRODUCTION

“Over 70 per cent of the Earth's surface is covered with water, but less than 3 per cent of that is fresh water — most of it locked up in glaciers, ice caps, the atmosphere and deep groundwater reservoirs. Just 13 per cent of the globe's total fresh water is readily available to meet human needs. In the meantime, worldwide demand for water is doubling every 21 years, according to the FAO. As industrial, agricultural and domestic pollution threatens finite supplies, water is becoming an increasingly precious resource that must be managed judiciously.” (IAEA Technical Cooperation — A Partner in Development, ‘Managing Water Resources’)

Water as a resource may very well become a dominant factor in planning in the not so distant future. The application of electron beam processing for drinking water, wastewater and groundwater treatment offers the promise of a cost effective process to insure adequate availability of that resource worldwide. Therefore this CRP intends to focus on these areas where there appears to be highest probability for the successful application of the process.

Potable water is the cornerstone of development and essential for sustainable growth. The first consideration for drinking water is to produce water that has been disinfected. The most common process used throughout the world in the disinfection of drinking water has been the use of chlorine. However, it is now known that the use of chlorine leads to the formation of chemicals known as disinfection by-products. These disinfection by-products may be carcinogenic or have other toxicological effects associated with consumption. Also, new pathogens are being found that are not easily inactivated using chlorine. Therefore, there is a major effort in the water treatment industry worldwide to find alternatives to chlorine.

In addition to disinfection there is an increasing problem with the presence of toxic chemicals in source waters (that is, waters used as sources of drinking water). These source waters may be surface waters or groundwater. Surface waters often are influenced by the discharge of treated wastewater and the biological and chemical quality compromised. Groundwaters used as a source of drinking water may also be contaminated. In general, if the quality of groundwater is compromised it is the result of chemical contamination.

Studies of the ionizing radiation from gamma rays and electron beam machines and its potential application in solving environmental problems have only recently begun in earnest. The process holds great promise; however, it appears that additional studies are warranted to provide additional data to potential users. The underlying scientific basis for the application of the process to solving environmental problems is as well established as any technology that is in use. However, because the ‘market’ is so diverse (the electron beams are relatively capital intensive and the technology innovative) few treatment plants exist. Continued studies are necessary to increase the general awareness of the process in the environmental engineering community.

There are a number of features that make this an attractive process to pursue for eventual application. Several of these advantages in the application of electron beam processing for solving environmental problems are:

(1) Both oxidizing and reducing reactive species are formed in relatively the same proportion in aqueous media.
(2) The process can be used simultaneously for control of biological and chemical hazards.
(3) The process is a physical process and requires no additional chemicals.
(4) The process is rapid, allowing for maximum flexibility in plant design.
(5) The accelerators only require electricity to operate.
(6) The systems are totally automated for ease of operation.

In the development of any innovative treatment process there are numerous obstacles that must be overcome before extensive implementation occurs. One of these obstacles is providing adequate data to assure engineers that the process, if applied properly, will not fail. In the case of electron beam systems the application to environmental problems is new; however, the systems (hardware) have been used successfully for 30 or more years in other applications. This is a significant hurdle because of the initial capital investment in a system. As with other 'radiation' technologies there is also a significant public perception aspect to implementing the technology.

Drinking water

The decade of the 1980s was declared the decade of water by the United Nations. The objective was to attempt to provide potable water to all of the peoples of the world. The goal was lofty and unfortunately not achieved. There exists a significant percentage of the population that is without potable drinking water.

Chlorine, the most widely accepted disinfectant in drinking water treatment, is known to have some disadvantages, namely in the formation of by-products that have adverse health effects, and the fact that it is less effective with some of the new, emerging organisms of public health concern. Active research in many areas of the world is focused on studying alternatives to the chlorination process.

Where chlorine is used one alternative is to use the electron beam process to destroy the disinfection by-products (DBPs). There has been some headway in studies focused on the electron beam to destroy these DBPs. However, more work is needed to determine if this feasible treatment strategy is likely to become a cost effective alternative.

The ionizing radiation (gamma rays and electron beams) process has been shown to be extremely effective in killing bacteria of widely differing genera, inactivating viruses of many different kinds, and more recently, in waters of differing quality (particularly those high in suspended material), in killing *Cryptosporidium*. However, more studies in this area are warranted to expand the database to other possible biological threats to drinking water.

Another area that deserves additional study is the use of toxicity tests, e.g. genotoxicity, to assess new and innovative water treatment alternatives. It is very difficult, if not impossible, to analyze all of the compounds in drinking water either before or after treatment. An alternative method that has been suggested is that of applying genotoxicity to source waters and to follow the water through different water treatment processes to see how they affect this parameter. Genotoxicity can be thought of as a sum-parameter for the toxicity of particular waters. In general, as the genotoxicity goes down or is eliminated, the water quality increases. The use of radiation technology with electron beam machine has been shown to lower the genotoxicity of one water sample, where conventional treatment processes did not. Further studies are needed to determine whether this can be generalized. If so, then water authorities would rapidly accept the radiation technology process using electron beam machines.

Wastewater

Wastewater treatment is typically divided into primary and secondary treatment. Primary treatment refers to the reduction of solids in the waste stream. Secondary treatment refers to lowering biochemical oxygen demand and suspended solids. In the case where tertiary treatment is used, the focus is the reduction of macronutrients, nitrogen and phosphorous.

After wastewater treatment, the effluent is discharged to a receiving stream that, in many cases, serves as the source of drinking water for those living downstream. Therefore, adequate treatment is necessary to ensure a high quality source for those downstream.

In some cases, chlorine is used as a final treatment process to minimize the biological 'load' of the wastewater. However, it is widely acknowledged that this is of minimal impact on the bacterial quality of secondary wastewater, not effective at all on primary wastewater, and produces halogenated by-products that may have harmful effects. Many wastewaters are discharged with no chlorine added and, in fact, probably in the wide majority of cases, with little or no treatment at all. If any wastewater is to be considered for reuse for agriculture or discharged to the environment, better and more efficient methods of disinfection are needed. The electron beam process holds great promise as a treatment process because of its flexibility and its ability to treat waters that contain suspended solids.

Another more recent problem that has been recognized is that of persistent organic pollutants (POPs), endocrine disruptors and chemicals that have biological activity. The standard biological treatment processes commonly used for wastewater treatment are not capable of treating many of these complex organic chemicals that are being found in increasing quantities in the wastewater. For example, biologically active compounds such as hormones pass through the treatment processes and are discharged directly into the receiving stream. A typical example of a hormone that is passed through the plant is estrogen. Another example that has recently been recognized is the addition of growth hormones to animal feed and the eventual discharge of hormones into streams that serve as sources of drinking water.

Typically POP compounds are only slightly soluble in water and are not treated by traditional wastewater treatment processes. Once in the environment they are bio-magnified as they move up the food chain. An example of a POP would be DDT, although no longer used in most countries. They are found at very low concentrations and are often very difficult to analyze in a wastewater matrix.

Endocrine disruptors are a diverse group of compounds that mimic biologically active compounds and can exert biological activity in organisms in receiving waters. Little is known about their fate in conventional treatment systems; however, it is probably safe to assume that many of these compounds are not treated effectively by traditional biological methods.

Groundwater

“Ninety-six per cent of the country (Egypt) is desert and only 4 per cent habitable,” explains T. Hassan, head of desert studies at the Research Institute for Groundwater (RIGW), a government scientific body located on the outskirts of Cairo, “But 96 per cent of the Egyptian people live on that tiny portion of habitable land within a kilometre or two of the river banks.”

As Egypt's population and demands for food and water have been continually expanding, national authorities have sought means to reclaim desert lands for productive use. The main constraint to further large scale reclamation, however, is that the waters of the Nile, albeit bountiful, are reaching their capacity.

“There are many restrictions now imposed on how Nile water can be utilized in agriculture, and many of the shallow wells near the river are unsafe for drinking,” explains F. Abdel Rahman Attia, the director the RIGW and a key advisor to the government on water policies. “Groundwater is finally being recognized as the critical factor in Egypt's water balance. Indeed, it's the primary issue.” (IAEA Technical Cooperation — A Partner in Development, ‘Managing Water Resources’).

Groundwater serves as the source of drinking water in many areas of the world. As the use of chemicals (industrialization) has increased, contamination of groundwater has also increased. The extent of the contamination is not well documented mainly because traditional water quality investigations do not include examination of the groundwater for complex organic compounds. By way of example, the recent discovery of the extensive contamination by methyl *tert*-butyl ether (MTBE) in groundwaters in the United States of America has shown how extensive the undetected problem may be. Therefore, by analogy it is likely that there is extensive groundwater contamination in IAEA Member States. (MTBE is used to enhance the level of oxygen in gasoline to reduce the levels of carbon monoxide and to increase the octane value of the fuel.)

In some locations around the world (the arid regions in the Middle East as an example), groundwater storage of treated wastewater is currently being explored for water reuse. It is necessary that this water be of a high quality both chemically and biologically before it is discharged into subsurface reservoirs.

The ionizing radiation (gamma rays and electron beams) process offers a possible solution for the treatment of contaminated groundwater and simultaneous disinfection of the water.

Emergency management

An important consideration, often overlooked in water treatment, is the need for water in times of emergencies. These emergencies may be from natural disasters, hurricanes, earthquakes and volcanic eruptions; or from human-made disasters such as conflicts between peoples.

Processing of water using ionizing radiation can lead to water that has minimal biological risk. Bacteria, viruses and other higher forms of life (e.g. parasites) can be controlled using the radiation processing in waters that have other treatment. In an emergency this may be all that is required for short term consumption of the drinking water; thus, in one step providing a source of drinking water for the people.

OBJECTIVES OF CRP

The overall goal of this CRP was to develop potential applications of radiation processing treatment in Member States in the area of water, wastewater and groundwater treatment.

Specific objectives included:

- Consider issues associated with radiation induced disinfection and decontamination of water.
- Consider issues associated with radiation-induced disinfection and decontamination wastewater, and for reuse, (e.g. agricultural or groundwater injection).
- Consider the treatment of groundwater as a source of drinking water
- Consider the treatment of highly contaminated groundwater for remediation and eventual uses of the water resource.
- Development of alternative methods for assessing the toxicity of treated water, e.g. genotoxicity.
- Studies may be conducted in the laboratory as long as the waters are simulations of ‘real world’ samples being studied to better define potential limitations of the treatment process.

2. ACHIEVEMENTS

2.1. Austria

Three different advanced oxidation processes (ozonation at pH 7.5, electron beam irradiation and a combination ozonation/electron beam irradiation) had been applied to study decomposition of aqueous naphthalene-1,5-disulfonic acid (1,5-NDSA) with regard to mineralization and formation of biodegradable intermediates. Formation of biodegradable intermediates could not be indicated for any of the processes used, single electron beam irradiation treatment was the most efficient process for mineralization of organic carbon contained in aqueous 1,5-NDSA. Applied to a real wastewater effluent from a mixed municipal/industrial, wastewater electron beam irradiation with a radiation dose of 2 kGy was sufficient to reduce the concentrations of all naphthalene sulfonic acids and some of the alkylphenol ethoxylates by about two orders of magnitude. Moreover, high energy electrons effectively inactivate indicator bacteria in effluents from municipal wastewater treatment plants and eliminate simultaneously any estrogenic activity originating from natural and synthetic hormones also contained in the wastewater effluents. Inactivation of bacteria and bacterial spores by electron beam irradiation was found to be practically unaffected by the water matrix and suspended solids. There is a strong indication from literature data that these findings are also relevant to viruses of concern (like poliovirus) in water hygiene. Cost analysis of the irradiation process based on actual numbers from the first full scale wastewater treatment plant in the Republic of Korea indicated a total cost of about 0.2 US$/m^3 treated water for 2 kGy irradiation dose.

2.2. Brazil

The programme in Brazil on radiation treatment of wastewater studied the removal and degradation efficiency of toxic and refractory pollutants (organic compounds mainly from industrial origins) and the disinfecting of pathogenic microorganisms in wastewater, industrial effluents and sludge. This project also embraced engineering expertise on the design and construction of a wastewater treatment pilot plant in the IPEN electron beam facility in order to develop and test wastewater irradiation devices, to study in continuous run the degradation of pollutants and inactivation of microorganism and to perform economical feasibility studies to scale up for a mobile demonstration plant to operate on a commercial basis as a demonstration facility. Concerning the human resources, ten technicians were trained (generating three PhDs, and five MSc theses) focusing on the aspects of engineering, chemistry and toxicity related to this application.

2.3. Ecuador

The flower industry in Ecuador uses a large quantity of pesticides for flower growing. Many of the pesticides are toxic and non-biodegradable, which may lead to contamination of receiving waters of the different effluents. This study was focused on the possibility of using electron beam radiation to decrease the concentration of pesticides in effluents both from flower cultivation and from treatment of flowers.

The research was initiated by a survey of twelve flower plantations located in the provinces of Pichincha and Cotopaxi (Ecuador), with the purpose of knowing the class of used pesticides; its form of utilization before, during and after fumigation process; the class of staff working in flower industry and the methods of effluents treatment they are using. The information on importation of pesticides and exportation of different classes of flowers was gathered, as well as the flower sales, with the purpose of selecting the pesticides to be studied. The study of electron beam influence was realized with 6 pesticides considered toxics (diazinon, procloraz, imidacloprid, dimetoato, carbofuran and metiocarb).

The studied variables were irradiation dose, pesticide concentration, aeration and pH effect. Besides pH changes, formation of nitrites, nitrates, sulphates, sulfides, ammonium ion and cyanides, after irradiation process of pesticides in aqueous solutions, were analyzed.

In general, the degradation data obtained for pesticides was 99% for pesticides (procloraz, imidacloprid, carbofuran and dimetoato), and 67% for metiocarb pesticide, when the pesticide concentration was 50 ppm and 5 kGy irradiation dose.

2.4. Hungary

The high-energy radiation-induced degradation of different textile dyes such as Apollofix-Red (AR–28), Reactive Black 5, H-acid, (4-amino-5-hydroxynaphthalene-2,7-disulfonic acid, **I**) and of its derivative, 4-hydroxynaphthalene-2,7-disulfonic acid (**II**) was studied in aqueous solution by using pulse radiolysis with kinetic spectroscopic detection for transient measurements and also by gamma radiolysis with UV-VIS spectroscopy and gradient HPLC separation with diode array detection for following the destruction of the dye molecules and measuring the products. The reactions of hydrated electron (e_{aq}^-) and hydroxyl ($^\bullet$OH) radical were investigated separately. The $^\bullet$OH reacts with the unsaturated bonds of the molecules. In the further reactions of the $^\bullet$OH adduct radicals, the AR-28 molecules partly reform with a slightly modified structure. The once reacted AR-28 molecules also have high reactivity towards the $^{\bullet}OH$ radicals. For these reasons the efficiency of $^{\bullet}OH$ radicals in discoloration of the solution is relatively low. It is below 0.5. The efficiency is much higher, close to unity for the e_{aq}^{-}. The reaction of e_{aq}^{-} with AR-28 leads to an immediate destruction of the color giving center. The intermediates of water radiolysis attack the azo functionality of the reactive Black 5 and this resulted in the efficient decoloration of aqueous dye solutions independent of the pH of the solution. It appears that the $^{\bullet}OH$ attacks mainly the benzene ring of the dye. The reaction of e_{aq}^{-} and $^{\bullet}OH$ with **I** and **II** leads mainly to the formation of cyclohexadienyl type radicals; however, with **I** H-atom elimination from the NH_2 group is also observed yielding aniline-type radicals. The cyclohexadienyl and also the anilino type radicals decay on the millisecond timescale. In the $^{\bullet}OH$ reactions, as a first step of decomposition, hydroxylated molecules and quinone type compounds are formed that absorb light in the UV-visible region. These molecules at higher doses with further decomposition of the ring structure were transformed to open chain alcohols, carboxylic acids, etc. In the case of e_{aq}^{-} the primarily formed products have absorption spectra shifted to the low wavelength region indicating the destruction at least one of the aromatic rings. At 0.25 mmol dm^{-3} concentration 4–6 kGy dose is sufficient to destruct the starting compounds.

2.5. Jordan

Irradiation processing was shown to be efficient in treatment and disinfection of microbiologically contaminated drinking water supplies. An irradiation dose of 1 kGy was found to be optimal in controlling the microbiological content of raw drinking waters containing up to 1000 *E. coli* per 100 mL.

An irradiation dose of 1.5 kGy was found to be efficient in controlling the microbiological content of domestic wastewater treatment plant effluents to meet the requirements and guideline values for wastewater reuse for unrestricted irrigation. The dose of 2 kGy is recommended to eliminate the process of microbiological re-growth after irradiation processing.

The irradiation dose required for microbiological disinfection of wastewater was dependent on microbiological load of irradiated water. The physical parameters such as TSS and turbidity, and seasonal variations between summer and winter periods had minor effects on the efficiency of wastewater disinfection by irradiation. Irradiation processing was effective in the deactivation of nematode eggs, where 96% of the nematode eggs were deactivated at a dose of 5 kGy. However, doses up to 2 kGy were not effective in controlling algae blooms in surface waters.

More than 98% of THMs can be removed from drinking water supplies containing up to 100 μg/L THMs, when applying an irradiation dose of 1 kGy. However, this dose was not sufficient in removing THM precursors and THMs could be formed in the presence of chlorine. To control the THM re-formation in drinking water networks, higher irradiation doses up to 10 kGy should be applied to remove the THM precursors from the irradiated waters.

2.6. Republic of Korea

A pilot plant for treating 1000 m^3 of textile dying wastewater per day with electron beam irradiation was constructed and operated continuously since October 1998. This plant was combined with biological treatment and has shown a reduction of chemical additive consumption, and also a reduction in retention time, with an increase in removal efficiencies of COD_{Cr} and BOD_5. On the basis of data obtained from pilot plant operation, construction of an industrial scale plant was started in 2004 and finished in December 2005 with the support of the International Atomic Energy Agency and Korean Government. This plant is located on the area of an existing wastewater treatment facility in Daegu, Republic of Korea, and its capacity 10 000 m^3 of wastewater per day using one 1MeV, 400kW accelerator combined with the existing biotreatment facility. The achievement was presented in the 50th General Conference of IAEA in 2006.

FIG. 1. Industrial e beam plant for textile dying wastewater in Daegu, Republic of Korea.

The electron beam process was introduced to investigate the effect of radiation on the disinfection of coliform bacteria in the effluent from the municipal wastewater treatment plant. Unchlorinated secondary effluent was irradiated at different doses, 0.2–1.0 kGy with a 1 MeV, 40 kW electron accelerator. Nearly 100% reduction in *E. coli* and total coliform bacteria was achieved with a dose of 0.8 kGy. Even with the lower dose of 0.2 kGy, the *E. coli* and total coliform bacteria were successfully inactivated to the level of the new guideline for discharged effluent that has been effective from 2003 in the Republic of Korea. Based on the data obtained in the experiments, an industrial scale plant with 0.2 kGy for the flow rate of 100 000 m^3 effluent per day has been designed. The overall cost for plant construction is approximately US$ 4.0 M, and the operation cost is around US$ 1M per year. This is quite applicable when compared to other advanced oxidation techniques such as Ozonation, UV techniques, etc.

The Advanced Radiation Research Institute was opened in Jeong-Eup, Republic of Korea, in 2006 for research and promotion of radiation technologies and, in this center, a Co-60 irradiation facility (300 KCi), a 10 MeV electron accelerator, a 30 MeV Cyclotron and ion beam facilities are in operation. Researches on the radiation application to polymer engineering, food sciences, agricultural engineering, environment sciences and material engineering are the major directions of the new Institute. Application to more various fields with various radiation sources will be available, and it will extend the application of radiation technology in the near future.

FIG. 2. The Advanced Radiation Research Institute has opened in Jeong-Eup city, Republic of Korea.

In the Republic of Korea, major problems in water/wastewater treatment are the industrial wastewaters; nowadays however, more concerns are on the re-use of water resources and remediation of contaminated resources. Therefore, the re-use of effluent from municipal wastewater treatment plants and office buildings are actively studied with electron beam. Also, the remediation of wastewater-containing hazardous wastes and contaminated groundwater, as well as the control of algal bloom in lakes, are studied with gamma ray and e beam. Some of them are in operation with small scale pilot plants in a laboratory.

2.7. Poland

A careful optimization of measuring conditions allowed the use of HPLC as a convenient method for monitoring the effectiveness of processes for the radiolytic degradation of organic pollutants and formation of products from these processes. The complete radiolytic degradation of dicamba at concentrations of 110 ppm in aqueous solution required irradiation doses of about 5 kGy. The efficiency of degradation, in contrast to 2,4-D was not affected by the presence of 50 ppm nitrate; however, the concentration of the main toxic decomposition products phenol and 2-chlorophenol was affected by the presence of nitrate. It was found that in numerous systems, that addition of ozone or hydrogen peroxide to irradiated solutions may improve the effectiveness of radiolytic degradation of organic pollutants, including pesticides and phenols. The presence of inorganic scavengers, commonly occurring in natural waters and wastes, affects the consumption of oxygen during the irradiation process, essential for its effectiveness. In the presence of nitrate and hydrogen carbonate, oxygen is consumed at higher irradiation doses than in pure solutions in distilled water.

The results obtained indicate that in numerous cases radiolytic degradation may be a suitable and effective method for treatment of industrial wastes. The results obtained in these studies for pesticides 2,4-D, MCPA and carbendazim indicate that radiolytic degradation may be a suitable and effective method for treatment of industrial wastes. In many cases the experimental data on effectiveness of radiolytic decomposition of target compounds were compared with results of kinetic modeling based on rate constants of radical reactions involved with good or satisfactory agreement.

2.8. Portugal

In the framework of the CRP on Remediation of Polluted Waters and Wastewaters by Radiation Processing, the Portuguese group has been conducting studies at lab scale on several kinds of samples originated from municipal and industrial wastewater treatment. The objective was to understand the effect of main physical parameters, such as the type of radiation, dose rate and absorbed dose on biological and chemical factors of the wastewater. To compare the effect of gamma radiation (60-Co facility-UTR) versus electron beam (LINAC energy 9 MeV), dosimetry studies were developed by means of a Fricke reference dosimeter, and an ionometric system was also applied to the electron beam. Equivalent locals for specific irradiation geometry (polyethylene bags 10 cm × 10cm) were found in the LINAC and UTR facility with an absorbed dose rate of approximately 1 $kGy.h^{-1}$. Biological and chemical effects studies were performed with wastewater samples irradiated in the polyethylene bags at absorbed doses ranging from 0.5 kGy up to 30 kGy depending on the studies' purposes. Microbiological studies were performed based on conventional methods and molecular biology techniques. Chemical studies were performed using several techniques such as Fourier transform infrared spectroscopy (FTIR), instrumental neutron activation analysis (INAA) and ionic chromatography in order to study the influence of ionising radiation in the ions' dynamic at liquid and solid phases of the wastewater.

The overall preliminary results obtained on the biological, chemical and economical studies lead us to choose agricultural wastewater and gamma irradiation for future work. Therefore, we continue to develop more specific studies on agricultural wastewater to implement the technology as a tool in the treatment process and focus on gamma irradiation process. For these studies, the legislated indicator parameters, such as biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total suspended solids (TSS) were also determined. Summarizing: achieved results showed that gamma radiation could be used in two ways for the wastewater treatment: 1) Lower dose rates for helping bioremediation, leading to faster treatment in the lagoons; and 2) Higher dose rates for disinfection during the tertiary phase. A lab scale wastewater treatment system where gamma radiation is applied directly in the treatment is being assembled. A special design will allow the application of low doses at low dose rate to induce molecular bound breaks, and higher absorbed doses at higher dose rates will be applied for manure disinfection purposes. Under the Projects CRP 12017 and TC POR/8/010, sponsored by IAEA, there were also achieved six graduation theses, four of them in Escola Superior Agrária de Santarém (Portugal) that is a Polytechnic High School and two in the Faculdade de Ciência e Tecnologia, Universidade Independente (Portugal); two Master of Science on Environment Management (Universidade dos Açores, Portugal), and Microbiology (Upsala University, Sweden).

2.9. Turkey

In this study, the possibility of using gamma rays to degrade or decolorize reactive dyes in water was investigated. Two different reactive dyes (reactive blue 15 and reactive black 5) in aqueous solutions were irradiated with doses 0.1 to 15 kGy at 0.14 and 2.87 kGy/h dose rates. The change of absorption spectra, pH, chemical oxygen demand (COD), and the degree of decoloration (per cent reduction in optical density) were examined in the presence of air and H_2O_2.

The absorption bands at 664, 640, 340, 260 and 596, 392, 312 nm for RB15 and RB5, respectively, decreased rapidly with increasing irradiation dose. The degree of decoloration of each dye solution with irradiation dose was estimated as 100 per cent for the lower concentration (50 ppm) dye solutions. The complete decoloration was observed after 1 and 15 kGy doses for RB5 and RB15, respectively. Solutions of RB5 and RB15 solutions decreased in pH from 6.15 and 6.98 to 3.40 and 3.68 with the irradiation dose, repectively. The COD reduction for all the dye solutions was approximately 76–80% at 1kGy and 15 kGy for RB5 and RB15. The COD reduction and the change of pH for all the dye solutions examined were similar to each other.

The effect of pH, N_2, N_2O on the degradation and decoloration process was studied. The degradation and decoloration in the presence of nitrous oxide occured faster than in air and nitrogen-saturated solutions. The degree of decoloration for RB5 increased with the increasing irradiation dose and dose rate, but above 2 kGy/h dose rate, the degree of decoloration is independent of the dose rate and irradiation dose. The degree of decoloration increased up to 100% for the nitrous oxide-saturated RB5 solution from 80% for the nitrogen-saturated RB5 solution at 0.8 kGy irradiation dose and at 2 kGy/h dose rate. Although the absorptions at maximum wavelength (596 nm) decreased with increasing irradiation dose for nitrogen-saturated RB5 aqueous solutions, for nitrous oxide-saturated RB5 aqueous solutions they decreased and shifted to lower wavelength. This suggests that the skeleton of the RB5 molecule is mainly destroyed by the attack of the OH radicals. AR and RB5 dyes are destroyed in the pH range from 7 to 4 with a reduced sensitivity at lower and higher pH range.

In the second dye group, Apollofix type dyes were chosen. Two different Apollofix dyes, Apollofix Red (AR) and Apollofix Yellow (AY), in aqueous solutions were irradiated in air with doses 1.0 kGy to 8.0 kGy at 0.14 kGy/h dose rate. The change in absorption spectra, pH, chemical oxygen demand (COD), and the degree of decoloration (per cent reduction in optical density) were examined in the presence and absence of H_2O_2. The absorption bands at 534 nm and 420 nm for AR and AY were observed to decrease rapidly with increasing irradiation dose. The degree of decoloration of each dye solution with irradiation dose was estimated as 100 per cent for the lower concentration (50ppm) dye solutions. The complete decoloration was observed after 3.0 kGy and 1.0 kGy doses for AR and AY, respectively. The COD and BOD reduction and the change of pH for all dye solutions on irradiation showed similar behavior.

In another study, the possibility of using gamma rays to degrade some pesticides in water was investigated. Four different pesticides (4-chloro phenoxyacetic acid (4-CPA), 2.4-dichloro phenoxyacetic acid (2,4-D), 2.4-dichloro phenoxyacetic propionic acid (2,4-DP), 2.4-dichloro phenoxyacetic butanoic acid (2,4-DB) in aqueous solutions were irradiated with doses 0.1kGy to

10.0kGy at 0.07kGy/h dose rate. The change of absorption spectra and the degree of degradation (per cent reduction in optical density) were examined in the presence of air. The absorption bands for 224, 228, and 229 nm for (4-CPA), (2,4-D), (2,4-DP), (2,4-DB) were decreased rapidly with increasing irradiation dose. The degree of degradation of each pesticide with irradiation dose was estimated for all pesticide concentrations (3–75 ppm). The highest degradation was observed after 1.0 kGy dose for all pesticides. Solutions of (4-CPA), (2,4-D), (2,4-DP), (2,4-DB) decreased in pH from 6.13, 6.33, 6.15, 6.67 to 3.34, 3.12, 3.39, 3.91 with the irradiation. This suggests that the skeleton of the pesticide molecule is mainly destroyed. The irradiated samples were analyzed by GC-MS-MS.The results obtained were compared and evaluated.

2.10. United States of America

Absolute rate constants for the free radical induced degradation of trichloronitromethane (TCNM), chloropicrin, were determined using electron pulse radiolysis and transient absorption spectroscopy. The rate constants for the hydroxyl radical $^{\bullet}$OH and the hydrated electron, e_{aq}^{-} reactions were $(4.97 \pm 0.28) \times 10^{7}$ M^{-1} s^{-1} and $(2.13 \pm 0.03) \times 10^{10}$ M^{-1} s^{-1}, respectively. The mechanisms of the free radical reactions with TCNM were also investigated using ^{60}Co gamma irradiation at various times (absorbed doses). From the measured disappearance of TCNM, and the appearance of the major reaction products nitrate and chloride ions, a detailed degradation mechanism was developed. The reaction rate constants and mechanism were combined in a kinetic computer model that was used to describe the major free radical pathways for the destruction of TCNM in solution. These data are applicable to other advanced oxidation/reduction processes.

3. CONCLUSIONS

The participants agree that this CRP has resulted in better understanding of the use of ionizing radiation in treating waters for various purposes. It was also recognized that there are a number of areas that need considerable additional work.

- The installation of the first full scale electron beam plant in Daegu, the Republic of Korea, to treat 10 000 m^3 day^{-1} textile wastewater has demonstrated that the process is a cost effective technology when compared to conventional treatment. The continuous operation of this facility will provide operational data on reliability and additional data for a detailed economic evaluation.
- The electron beam processing of wastewater based on an economic feasibility study in comparing UV and ozonation was shown to be the most cost effective process for the control of *E. coli* at flows greater than 5000 m^3 day^{-1}.
- Radiation processing of secondary and tertiary effluents from municipal wastewater treatment plants has shown that the destruction of organic compounds, elimination of estrogenic activity and efficient reduction in the number of microorganisms occurs simultaneously.
- Radiation processing of effluents of various qualities was shown to be very efficient at removing extremely low concentrations of estrogens (estrogenic activity).
- The disinfection of sludge for beneficial reuse has been demonstrated at full scale using gamma irradiation. It is likely that this application will be accomplished using electron beam processing in the future.
- Ionizing radiation at low dose rates has been demonstrated to increase the efficiency of lagoon treatment systems.
- Studies conducted have shown that the destruction of selected dyes and pesticides are efficiently removed using radiation processing. The combination of ionizing radiation with oxidants, such as ozone or hydrogen peroxide, further improved the removal efficiency. It has also been shown that the addition of TiO_2 prior to irradiation improved the destruction efficiency of a pesticide.
- Fundamental studies have resulted in the determination of bimolecular reaction rate constants for several pollutants. Complimentary studies have also been conducted on the elucidation of destruction mechanisms of some compounds.

- Kinetic models describing the removal of organic compounds, including the formation and destruction of reaction by-products, have been formulated. These models appear to predict the formation of reaction by-products and could be used to guide analytical methodology and economic evaluation of the radiation processing.
- Even after successful removal of pollutants from water by irradiation, the treated water may still contain toxic by-products not detectable by chemical methods. Therefore, other methods that provide estimates of toxicity need to be employed to fully characterize the treated water.
- It appears that the most appropriate areas of future investigations include:
  - Wastewater reuse and recycling
  - Wastewater disinfection
  - Sludge (biosolids) treatment for agricultural application
  - Water, wastewater, municipal and industrial wastewater effluents, municipal landfill leachates and other materials that are highly contaminated with recalcitrant compounds such as:
    - Pesticides
    - Textile dye wastes
    - Endocrine disruptors
    - Surfactants
  - Process optimization.

PUBLICATIONS RESULTING FROM THE COORDINATED RESEARCH PROJECT

Poland

DRZEWICZ, P., BOJANOWSKA-CZAJKA, A., TROJANOWICZ, M., NAŁĘCZ-JAWECKI, G., SAWICKI, J., WOŁKOWICZ, S., Application of ionizing radiation to degradation of organic pollutants in waters and wastes, *Polish J. Appl. Chem.,* **47**(3) (2003) 127–136.

DRZEWICZ, P., TROJANOWICZ, M., ZONA, R., SOLAR, S., GEHRINGER, P., Decomposition of 2,4-dichlorophenoxyacetic acid by ozonation, ionizing radiation as well as ozonation combined with ionizing radiation, *Rad. Phys. Chem.,* **69** (2004) 281–287.

DRZEWICZ, P., BOJANOWSKA-CZAJKA, A., NAŁĘCZ — JAWECKI, G., SAWICKI, J., WOŁKOWICZ, S., ESWAYAH, A., TROJANOWICZ, M., Application of Ionizing Radiation for Degradation of Pesticides in Environmental Samples, *Annual Report of Institute on Nuclear Research and Technology* (2002) 46–49.

TROJANOWICZ, M., DRZEWICZ, P., BOJANOWSKA-CZAJKA, A., NAŁĘCZ-JAWECKI, G., SAWICKI, J., WOŁKOWICZ, S., ESWAYAH, A., Application of ionizing radiation for removal of pesticides from groundwater, Chapter in *IAEA Report of the 1st Research Coordination Meeting on Remediation of Polluted Waters and Wastewater by Radiation Processing, Lisbon, Portugal, 15–18 October 2002.*

DRZEWICZ, P., NAŁĘCZ-JAWECKI, G., TROJANOWICZ, M., BOJANOWSKA-CZAJKA, A. SAWICKI, J., GRYZ, M., GŁUSZEWSKI, W., WOŁKOWICZ, S., Application of selected toxicity tests for monitoring of degradation of selected pesticides using ionizing radiation, *Chemosphere*, 57 (2004) 135–145.

DRZEWICZ, P., BOJANOWSKA-CZAJKA, A., GŁUSZEWSKI, W., NAŁĘCZ-JAWECKI, G., SAWICKI, J., LISTOPADZKI, E., TROJANOWICZ, M., Degradation of pesticide 2,4-D by γ -radiation combined with hydrogen peroxide, *Annual Report of Institute on Nuclear Research and Technology*, (2003) 43–46.

JANKOWSKA A., BIESAGA, M., DRZEWICZ, P. TROJANOWICZ, M., PYRZYNSKA, K., Chromatographic separation of chlorophenoxy acid herbicides and their radiolytic degradation products in water samples, *Water Res*., 38 (2004) 3259–3264.

BOJANOWSKA-CZAJKA, A., DRZEWICZ, P., NAŁĘCZ-JAWECKI, G., SAWICKI, J., KOZYRA, C., TROJANOWICZ, M., Radiolytic degradation of herbicide 4-chlror-2-methylphenoxyacetic acid (MCPA) by g-radiation for environmental protection, *Annual Report of Institute on Nuclear Research and Technology*, (2004) 42–46.

DRZEWICZ, P., GEHRINGER, P., BOJANOWSKA-CZAJKA, A., ZONA, R., SOLAR, S. NAŁĘCZ-JAWECKI, G., SAWICKI, J., TROJANOWICZ, M., Radiolytic degradation of herbicide dicamba for environmental protection, *Arch. Environ. Contam. Toxicol*., 48 (2005) 311–322.

BOJANOWSKA-CZAJKA, A., DRZEWICZ, P., KOZYRA, C., NAŁĘCZ-JAWECKI, G., SAWICKI, J., SZOSTEK, B., TROJANOWICZ, M., Radiolytic degradation of herbicide (4-chloro-2-methylphenoxy)acetic acid (MCPA) by γ-radiation for environmental purposes *Ecotoxicol. Environ. Safety*, 65 (2006) 265-277.

BIESAGA, M., STAFIEJ, A., PYRZYŃSKA, K., DRZEWICZ, P., TROJANOWICZ, M., Chromatographic determination of products of radiolytic degradation of chlorophenoxy acid herbicides, *Chem. Anal.(Warsaw),* 50 (2005) 863–866.

BOJANOWSKA-CZAJKA, A., DRZEWIUCZ, P., ZIMEK, Z., NICHIPOR H., NAŁĘCZ-JAWECKI, G., KOZYRA, C. TROJANOWICZ, M., Radiolytic degradation of herbicide 4-chloro-2-methylphenoxyacetic acid for environmental protection, *Annual Report of Institute on Nuclear Research and Technology*, 2005, 43–47.

BOJANOWSKA-CZAJKA, A., DRZEWICZ, P., NAŁĘCZ-JAWECKI, G., SAWICKI, J., TROJANOWICZ, M. , Zastsowanie promieniowania jonizującego do degradacji wybranych pestycydów w wodach i ściekach. *Postępy Techniki Jądrowej* (in Polish), 49 (2006) 26–31.

Turkey

ŞOLPAN, D., GÜVEN O., Decoloration and degradation of some textile dyes by gamma-irradiation. *Rad. Phys. Chem*., 65 (2002) 549–558.

ŞOLPAN, D., GÜVEN O., TAKACS E., WOJNAROVITS, L., DAJKA K., High Energy Irradiation Treatment of aqueous solutions of azo dyes: Steady State Gamma Radiolysis Experiments. *Rad. Phys. Chem* 67 (2003) 531–534.

DAJKA K., TAKACS, E., ŞOLPAN D., WOJNAROVITS L., GÜVEN, O., High Energy Irradiation Treatment of aqueous solutions of C.I.Reactive Black 5 azo dye: Pulse Radiolysis Experiments' *Rad. Phys. Chem* 67 (2003) 535–538.

United States of America

COLE, S.K., COOPER, W.J., FOX, R.V. GARDINALI, P.R. MEZYK, S.P., MINCHER, B.J., O'SHEA, K.E., Free Radical Chemistry of Disinfection-By-Products 2. Rate Constants and Degradation Mechanisms of Trichloronitromethane (Chloropicrin). *Environ. Sci. Technol.* (In press).

COOPER, W.J., CRAMER, C.J., MARTIN, N.H., MEZYK, S.P., O'SHEA K.E., VON SONNTAG C., A Proposed Free Radical-Mechanism for the Destruction of Methyl- *tert*-Butyl Ether (MTBE) *via* Advanced Oxidation Processes. *Chem. Rev.*

REPORTS BY THE PARTICIPANTS IN THE COORDINATED RESEARCH PROJECT

EFFLUENT POLISHING BY MEANS OF ADVANCED OXIDATION*

P. Gehringer, H. Eschweiler
ARC Seibersdorf Research GmbH, Seibersdorf, Austria

S. Weiss, T. Reemtsma
Technical University of Berlin, Berlin, Germany

Abstract

Three different Advanced Oxidation Processes (ozonation at pH 7.5, electron beam irradiation and a combination ozonation/electron beam irradiation) have been applied to study decomposition of aqueous naphthalene-1,5-disulfonic acid (1,5-NDSA) with regard to mineralization and formation of biodegradable intermediates. Formation of biodegradable intermediates could not be indicated for any of the processes used, single electron beam irradiation treatment was the most efficient process for mineralization of organic carbon contained in aqueous 1,5-NDSA. Applied to a real wastewater effluent from a mixed municipal/industrial wastewater electron beam irradiation with a radiation dose of 2 kGy was sufficient to reduce the concentrations of all naphthalene sulfonic acids and some of the alkylphenol ethoxylates by about 2 orders of magnitude. Moreover, high energy electrons effectively inactivate indicator bacteria in effluents from municipal wastewater treatment plants and eliminate simultaneously any estrogenic activity originating from natural and synthetic hormones also contained in the wastewater effluents. Inactivation of bacteria and bacterial spores by electron beam irradiation was found to be practically unaffected by the water matrix and suspended solids. There is a strong indication from literature data that these findings are also relevant to viruses of concern in water hygiene like poliovirus. Cost analysis of the irradiation process based on actual numbers from the first full scale wastewater treatment plant in the Republic of Korea indicated a total cost of about 0.2 US$/m³ treated water for 2 kGy irradiation dose.

1. INTRODUCTION

Due to their wide application in various chemical processes, sulfonated aromatic compounds have been produced in large quantities for a long time. Many of these compounds are poorly biodegradable. Of the naphthalene sulfonates, naphthalene-1,5-disulfonate (1,5-NDSA) is most persistent and regularly found in surface waters and bank filtrate [1, 2]. Even under the improved conditions of a membrane bio reactor, 1,5-NDSA was not degraded and could not be removed from municipal wastewater [3]. 1,5-NDSA reacts with ozone. However despite a reaction rate constant of $k = 41\ M^{-1}s^{-1}$ for the direct reaction with ozone [4], a low reactivity of 1,5-NDSA to ozone was stated by Rivera-Utrilla et al. (2002) [5]. This is most likely due to the formation of intermediates, which obviously react more slowly with ozone than the parent compound; thus increasing the ozone demand for total mineralization of 1,5-NDSA. Breithaupt et al. (2003) [6] reported that the ozone demand for total mineralization of 1,5-NDSA was twice as high as demand for removal of 1,5-NDSA. The same authors also studied a combined ozone/biology treatment in order to reduce the high ozone demand for total mineralization of 1,5-NDSA. They found less ozone demand for the combined process, but recorded the formation of non-biodegradable intermediates, which certainly limits the efficacy of the combined process.

Caldera et al. (2001) [4] studied ozonation of aqueous 1,5-NDSA in ultra pure water at different pH values. These laboratory experiments demonstrated enhanced mineralization of 1,5-NDSA with increasing pH values, indicating advanced oxidation could be more effective for mineralization of 1,5-NDSA than direct ozone reaction. No studies dealing with the efficacy of Advanced Oxidation Processes (AOPs) under realistic conditions, (i.e. in real wastewater), exist to date.

The primary goal of this study was **(i)** to evaluate AOPs with regard to mineralization of aqueous 1,5-NDSA and formation of biodegradable intermediates during decomposition, respectively and;

---

* The results given in this paper were previously published in part in Ozone: Sci & Eng. and, moreover, presented at the Ozone World Congress, Strasbourg, France, 2005.

moreover, **(ii)** to demonstrate for the AOPs showing the best results in these studies its applicability to real wastewater. As an AOP, ozonation pH ~7.5, electron beam irradiation, and ozone in combination with electron beam irradiation were chosen. The addition of ozone before or during irradiation converts the reducing species formed during water radiolysis into OH radicals [7] and enhances consequently the OH radical yield from water radiolysis by a factor of 2. In the present study, therefore, three different AOPs have been used. (1) Ozonation at pH ~7.5 (providing beside OH radicals additionally some molecular ozone for pollutant decomposition) (2) electron beam irradiation (providing beside OH radicals additionally solvated electrons e_{aq}^- for pollutant decomposition) and (3) combination of ozone and electron beam irradiation (providing, almost exclusively, OH radicals for pollutant decomposition).

With regard to electron beam irradiation, it is well known that ionizing radiation is quite effective for inactivation of microorganisms which are always contained in secondary and tertiary effluents, respectively. Consequently, using electron beam irradiation for detoxification of wastewater effluents, reduction of microorganisms also occurs. Although there are only a few studies dealing with this special subject, it has already been demonstrated that both coli forms and coliphages could be effectively inactivated in secondary effluents by means of ionizing radiation (Farooq et al. (1993) [8]; Slifko, (1999) [9]). Therefore, another intention of this study was **(iii)** to examine the influence of wastewater quality (water matrix) on radiation- induced inactivation of some indicator bacteria relevant in water hygiene using effluents of different quality from municipal wastewater treatment plants.

Besides the microbiological pollution of wastewater effluents, the appearance of natural hormones like the estrogens estrone, 17ß-estradiol and 17α-ethynylestradiol in secondary effluents became a serious problem due to the proven estrogenic effect on fish and the concern for accumulation in the environment (Routledge et al. (1998) [10]). As a consequence, estrogens have been recently added to the National Toxicology Programme's list of cancer-causing agents in the United States (Anonymus, (2003) [11]). No data has been published yet describing the effect of ionizing radiation on estrogens contained in an aqueous system.

To study **(iv)** simultaneously the inactivation of some indicator bacteria and the effect of irradiation to some estrogens usually contained in secondary effluents from municipal wastewater treatment plants; and moreover to provide **(v)** a cost evaluation of an electron beam irradiation process for wastewater based on a reasonable radiation dose and numbers derived from the calculation of the first full scale-plant for wastewater irradiation in operation in the Republic of Korea[12].

2. MATERIALS AND METHODS

Naphthalene-1,5-disulfonic acid tetra hydrate (Sigma-Aldrich, 97%) dissolved in Seibersdorf tap water (pH 7.5; 297 mg/L bicarbonate; 23 mg/L chloride; 3 mg/L nitrate; 91 mg/L sulphate; 4 mg/L oxygen and 0.9 mg/L DOC) was used to study the changes in Biological Oxygen Demand (BOD) and Dissolved Organic Carbon (DOC) related to 1,5-NDSA decomposition. 1,5-NDSA concentration was determined by means of UV spectroscopy at 287 nm using a Cary 3C UV-Visible spectrophotometer (Varian Australia Pty Ltd). BOD was measured by means of a procedure described in [13] and DOC by means of a Dohrmann DC-190-ASM (Rosemount Analytical).

The effluent (pH 7.6; COD [Chemical Oxygen Demand] 113 mg/L; BOD 41 mg/L; TSS [Total Suspended Solids) 35 mg/L] from Rubi Wastewater Treatment Plant (27 000 m^3/day municipal/industrial wastewater, located about 20 km outside Barcelona, Spain) was analyzed before and after treatment for naphthalene disulfonic acids (1,3-NDSA; 1,5-NDSA; 1,6-NDSA; 1,7- NDSA; 2,6-NDSA and 2,7-NDSA), for naphthalene monosulfonic acids (1-NSA and 2-NSA) and benzothiazole sulfonic acid BTSA using the following procedure: HPLC analyses were carried out with an HP 1100 series liquid chromatography system (Agilent, Germany) consisting of a membrane degasser, a binary high-pressure gradient pump, an automatic sampler, a column thermostat and a diode array detector. Separations were obtained by ion-pair chromatography with tributylamine

(TrBA) using a Luna Phenyl Hexyl column (150 mm × 2 mm; 3 µm particles, Phenomenex Aschaffenburg, Germany) with gradients formed from eluent A (water/methanol 80/20) and eluent B (water/methanol 5/95) both with 1 mM TrBA and 1 mM acetic acid. The chromatographic system was coupled to a Quattro LC triple stage quadrupole mass spectrometer (Micromass, Manchester, UK) equipped with an orthogonal Z-spray electrospray interface that was operated in the negative ion mode.

Secondary and tertiary effluent from municipal wastewater treatment plants has been used to study inactivation of indicator bacteria by means of electron beam irradiation. Their characteristics are given in the appropriate figures. The secondary effluent was also used to investigate decomposition of estrogens by electron beam irradiation. The concentration of the natural estrogens contained in the secondary effluent was sufficient for experiments. About 20 ng/L of the synthetic 17α-Ethynylestradiol was spiked to the effluent before irradiation.

Chemical analyses of the estrogens have been performed by Ion Trap-GC/MS/MS after preconcentration and derivatisation. In addition, estrogenic activity of the wastewater samples was checked using a recombinant yeast estrogen screen (Routledge and Sumpter, (1996) [14], in the modification of De Boever et al. (2001) [15]). Moreover, several experiments with spores of *Bacillus subtilis* have been performed irradiating them in freeze-dried state or suspended in Vienna tap water (0.8 mg/L DOC; 159 mg/L bicarbonate; 8 mg/L oxygen and 4.6 mg/L nitrate) and a natural swampy water (15 mg/L DOC; 235 mg/L bicarbonate; 9.4 mg/L oxygen and 0.5 mg/L nitrate) as well. Spores of *Bacillus subtilis* ATCC 6633 were produced in liquid enrichment medium, heated at 80°C for 10 minutes to inactivate the vegetative cells, washed by centrifugation, and suspended in sterile deionized water (Sommer et al. (1993) [16].

Ozone was made from pure oxygen using a laboratory ozonizer (E. Sander Ltd., Germany) with a gas flow of 20 L/h. The average ozone concentration in the gas flow was about 12 mg O_3/L O_2. For ozonation experiments, a cylindrical glass vessel with a fixed ceramic frit over the whole diameter of about 10 cm was used. Gaseous ozone was introduced at the bottom of the vessel, the small volume between the frit, and the bottom of the vessel was filled with glass pellets to reduce the volume of water below the frit to a minimum. 1.5 litres of aqueous solutions has been treated in each experiment. A process photometer (Sigrist model KAS 500) was employed to determine ozone concentration in the oxygen flow. OH radical generation from aqueous ozone at a pH value ~7.5 was checked with p-chlorobenzoic acid (>98%, Merck-Schuchard) dissolved in Seibersdorf tap water. Concentration of aqueous p-chlorobenzoic acid was determined by UV spectroscopy at 235 nm.

γ irradiations have been performed in an AECL Gammacell 220 cobalt-60 source having an average dose rate of about 0.9 Gy/s. The experimental set-up has been described elsewhere (Sommer et al. (2001) [17]). For electron beam irradiation an ICT-500 electron beam accelerator (500 kV; 25 mA; 1.2 m scan width) manufactured by High Voltage Eng., USA has been used. Irradiations have been performed with constant water flow varying the beam current for dose adjustment. For details, see Gehringer et al. (2003) [18].

3. RESULTS AND DISCUSSION

3.1. Decomposition of aqueous 1,5-NDSA by AOPs

Despite some new results concerning the kinetics of the ozone/p-chlorobenzoic acid reaction in aqueous solution[19], it may still be assumed that aqueous p-chlorobenzoic acid (p-CB) reacts only with OH radicals and not significantly with molecular ozone or secondary oxidants and other reaction species, respectively. Consequently, aqueous p-CB was used to check the efficacy of ozone at pH ~7.5 with regard to OH radical generation. It was found that at pH ~7.5 almost all of the 11 mg/L p-CB available was decomposed by about 15 mg O_3/L, while at pH ~2 just 3 mg/L, (i.e. just about 25% of the available pCB) was decomposed. Therefore, ozonation at pH~7.5 was considered to generate sufficient OH radicals for competition with the other AOPs.

Figure 1 shows the decomposition of aqueous 1,5-NDSA by ozonation with regard to DOC reduction and BOD formation, respectively. It is obvious that total decomposition of 1,5-NDSA does not mean total mineralization of the organic carbon originally present. After 99% decomposition of 1,5-NDSA just about 65% of the original organic carbon has been mineralized. Moreover, there is an indication that mineralization is slowed down or even stopped with continuous ozonation. Most likely some intermediates formed during the oxidative decomposition of 1,5-NDSA react more slowly with OH radicals (and/or ozone) than the parent component. About 35% of the original DOC are still present after total destruction of 1,5-NDSA. The intermediates formed from 1,5-NDSA besides the partial mineralization of the 1,5-NDSA are obviously non-biodegradable because no significant BOD increase could be recorded in any stage of the 1,5-NDSA decomposition.

Breithaupt et al. (2003) [6] also found partial mineralization of aqueous 1,5-NDSA after its total destruction by ozonation, but they found only about 35% mineralized, (i.e. almost a factor of 2 less), when compared to our results. However, the experimental conditions were quite different and could be the reason for the different results. Moreover, their statement about formation of biodegradable intermediates from 1,5-NDSA decomposition by ozonation is not supported by our results.

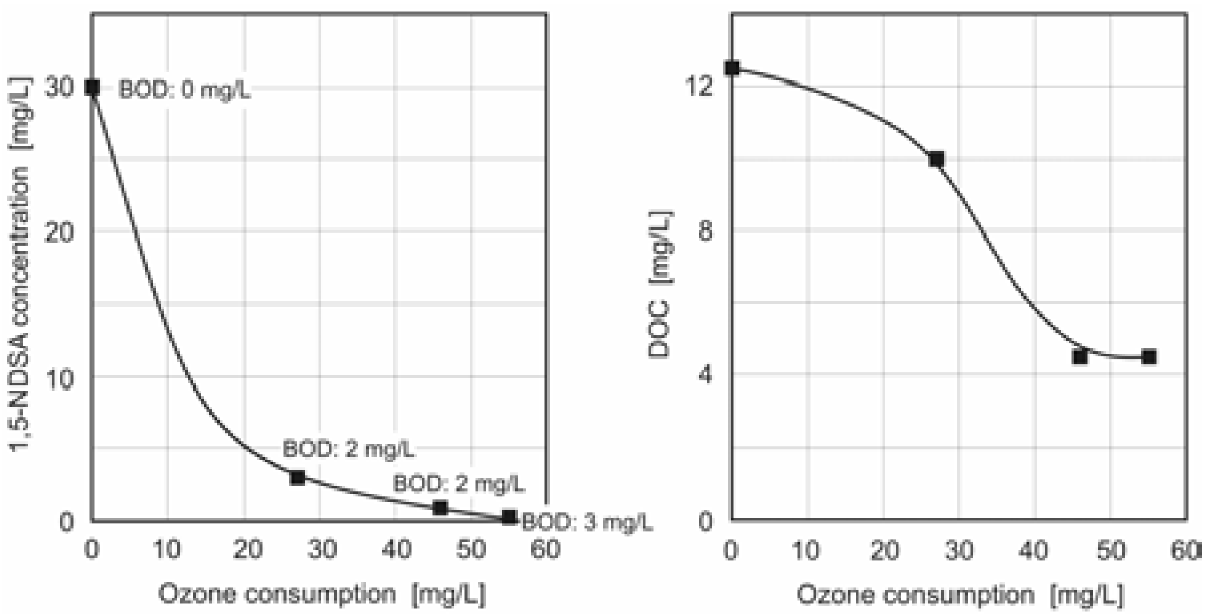


FIG. 1. Decomposition of 1,5-NDSA in tap water by means of ozonation at pH 7.5 as a function of ozone dose.

Figure 2 shows decomposition of aqueous 1,5-NDSA by electron beam irradiation, as well as DOC reduction and BOD formation as a function of the radiation dose. With a radiation dose of 10 kGy, about 96% of the original 1,5-NDSA is decomposed and about 83% of the initially present organic carbon is mineralized at this dose. In this dose range DOC reduction follows approximately pseudo first order reaction kinetics without any indication of a plateau in the graph, (i.e. intermediates formed during 1,5-NDSA decomposition do not slow down the decomposition process as was observed for ozonation). BOD during 1,5-NDSA decomposition, clearly indicated that no biodegradable intermediates were formed during decomposition of aqueous 1,5-NDSA by electron beam irradiation at any time.

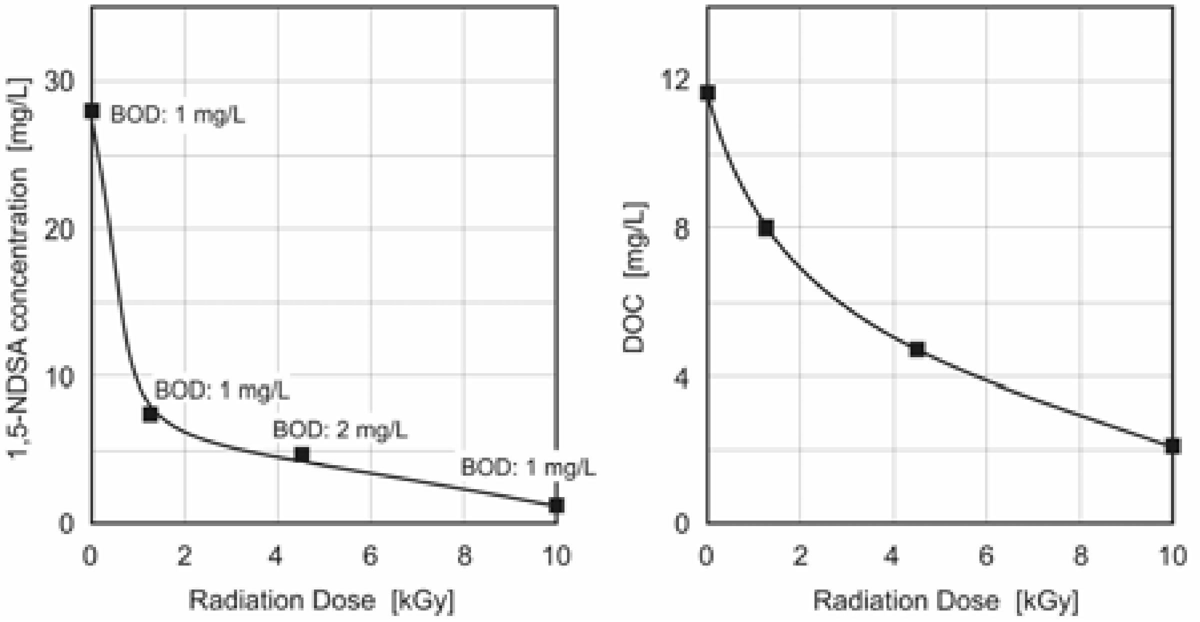


FIG. 2. Decomposition of 1,5-NDSA in tap water by means of electron beam irradiation as a function of radiation dose.

The yield of OH radicals formed by electron beam irradiation in water by water radiolysis is 2.7×10^{-7} mol/J [20]. Accordingly, a radiation dose of 10 kGy is equivalent to the formation of 2.7 mmol/L OH radicals. From data given in Fig. 2, it can be calculated that under the conditions given about 35 mol OH radicals are needed to mineralize the carbon of 1 mol aqueous 1,5-NDSA. Ozonation at pH7.5 decomposes about 99% of aqueous 1,5-NDSA when a dose of 55 mg/L ozone is applied (Fig. 1). Supposing an OH radical yield of 0.5 mol OH/mol O_3, an OH radical concentration of about 0.575 mmol/L OH radicals is calculated from 55 mg/L O_3. Consequently, the potential contribution of OH radicals for total decomposition of aqueous 1,5-NDSA by ozonation must be significantly lower as compared with electron beam irradiation. Thus, decomposition of aqueous 1,5-NDSA by ozonation at pH7.5 is mainly due to ozone reactions, and OH radicals play only a minor role. Under these conditions, ozonation at pH7.5 is not an AOP. This also explains the different form of the DOC reduction curve of both processes discussed.

Figure 3 shows the decomposition of aqueous 1,5-NDSA by a combined ozone/electron beam irradiation process as a function of the radiation dose. The ozone dose which corresponds with an individual radiation dose is given at each point in the graph. For example, the point in the graph indicated by 48 mg O_3/L means that this sample was irradiated with 5 kGy and simultaneously with the irradiation 48 mg O_3/L was consumed in the aqueous solution during irradiation. After irradiation no residual ozone is left in the aqueous phase. Addition of ozone during irradiation converts the reducing species formed by water radiolysis besides the OH radicals into OH radicals [7] and increases the OH radical yield from 2.7×10^{-7} mol/J to about 5.4×10^{-7} mol/J. Moreover, possible reactions of reducing species which could intervene in the decomposition mechanism are largely eliminated by their conversion into OH radicals.

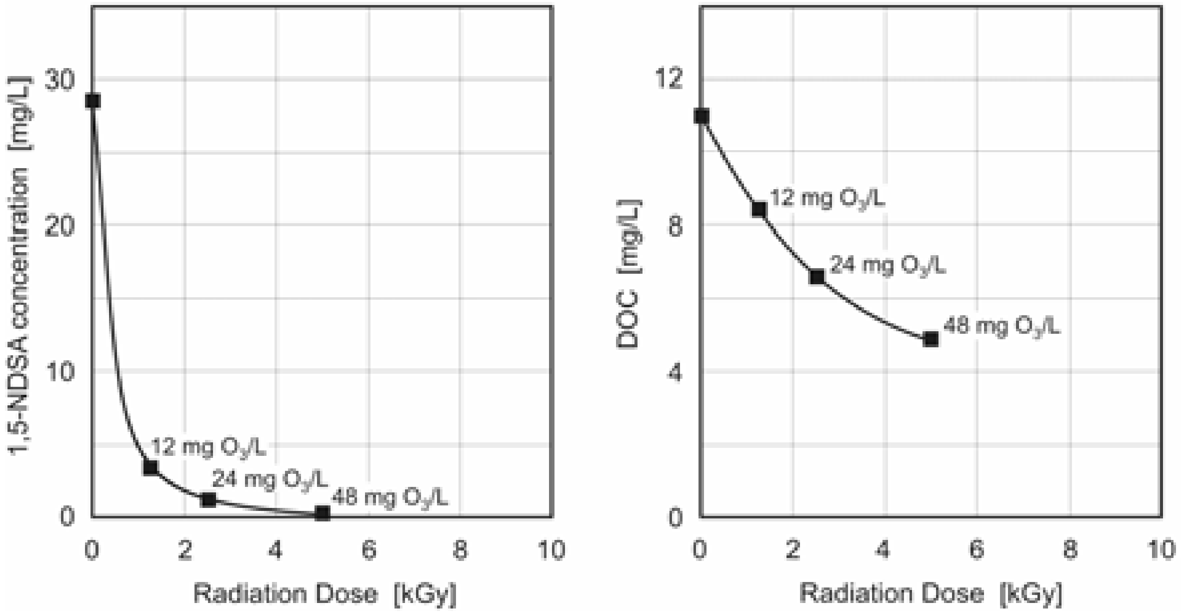


FIG. 3. Decomposition of 1,5-NDSA in tap water by means of a combined ozone/electron beam irradiation treatment as a function of radiation and ozone dose, respectively. Ozone concentrations are given within the graphs indicating the amount of ozone introduced during electron beam irradiation at the appropriate radiation dose.

The results obtained with the combined ozone/electron beam process confirm the results obtained with single electron beam irradiation regarding OH radical demand for total decomposition of aqueous 1,5-NDSA. Doubling of the OH radical yield from water radiolysis by ozone addition resulted in bisection of the radiation dose requirement for total 1,5-NDSA decomposition as compared with single electron beam irradiation. However, 5 kGy combined with 48 mg O_3/L results again in an OH radical demand of 2.7 mmol/L for total decomposition of 28 mg/L aqueous 1,5-NDSA. With regard to mineralization of 1,5-NDSA, the combined ozone/electron beam process is less effective than the single electron beam irradiation process. After total decomposition of the aqueous 1,5-NDSA, the corresponding DOC reduction was only about 60% for the combined process, while 83% DOC reduction was achieved by the single electron beam irradiation process. It is quite unexpected, and it is difficult to understand that the higher OH radical concentration of the combined process did not lead to an improved mineralization.

In consequence, under the conditions given, single electron beam irradiation clearly is the best process for mineralization of 1,5-NDSA in water. It has been, therefore, applied to a real wastewater originating from Rubi Wastewater Treatment Plant in Spain. Besides NDSAs and NSA, some alkylphenol ethoxylates (APEOs) — another group of ubiquitous pollutants in the aquatic environment — have been analyzed. A few selected results will be presented here, and a more detailed study will be published elsewhere.

According to the results presented in Table 1, a reasonable reduction of about 1–2 orders of magnitude for all the pollutants analyzed could be recorded for the electron beam irradiation already at a radiation dose of 2 kGy; while at 5 kGy all NDSAs analyzed were reduced below limit of detection (LOD). Two kGy reduced APEOs by one order-of-magnitude, with 5 kGy a reduction of 2 orders of magnitude was achieved. Ozonation at pH7.5 with an ozone dose of about 22 mg O_3/L resulted in a reduction of about a factor of 2 for the NDSAs and BTSA, while NSAs were decomposed somewhat better. For APEOs, ozonation was quite efficient. Twenty-two mg O_3/L resulted in a reduction of almost 2 orders of magnitude.

3.2. Radiation induced inactivation of bacteria and bacterial spores.

Electron beam irradiation of a secondary and a tertiary effluent, respectively, for inactivation of some coli forms naturally contained in wastewater effluents have been performed (Figure 4). The inactivation curves obtained in the two different effluents did not show any significant difference, although solute concentration and amount of total suspended solids (TSS) of the effluents were significantly different (e.g. BOD and TSS differ by one order of magnitude). This finding is somewhat unexpected because, under the conditions given, coli form inactivation must be mainly due to OH radical attack and OH radicals, on the other hand, does certainly react with most of the solutes contained in the effluents. Thus, to verify this finding, additional experiments with *B. subtilis* spores were performed.

In these experiments *B. subtilis* spores were used in freeze-dried state and suspended in tap and swampy water. The outcome of these experiments presented in Figure 5 confirmed the earlier findings with coli form inactivation. No significant effect of the surrounding medium on the radiation-induced spore inactivation could be noticed although the media were significantly different, even much more, as compared to coli form inactivation in various effluents. The consequence of inactivation of both suspended *B. subtilis* spores and coliforms in water must originate intracellularly, (i.e. endogenous damage is responsible for the radiation induced inactivation of spores and bacteria). The water radicals formed outside the cell in the bulk water do not contribute to spore or bacteria inactivation. Inactivation becomes independent of water quality!

TABLE 1. ELECTRON BEAM IRRADIATION TREATMENT AND OZONATION, RESPECTIVELY, OF AN EFFLUENT FROM RUBI WASTEWATER TREATMENT PLANT, SPAIN, FOR REDUCTION OF NAPHTHALENE MONOSULFONIC ACIDS (NSAs), DISULFONIC ACIDS (NDSAs), BENZOTHIAZOLE SULFONIC ACID (BTSA) AND SOME ALKYLPHENOL ETHOXYLATES (APEOs) INCLUDING METABOLITES

Pollutants	Before Treatment	Treatment Processes		
		Electron Beam Irradiation		Ozonation 22 mg O_3/L
		2 kGy	5 kGy	
	Concentration in ng/L			
2,6-NDSA	723	41	<LOD	317
1,5-NDSA	528	28	<LOD	256
2,7-NDSA	1743	58	<LOD	763
1,6-NDSA	3711	124	<LOD	1855
1,3-NDSA	520	7	<LOD	208
1,7-NDSA	3264	82	<LOD	1511
Σ NDSAs	10488	340	<LOD	4912
1-NSA	1620	27	2	317
2-NSA	2749	65	17	386
Σ NSAs	4369	92	19	703
BTSA	358	58	20	189
Σ (APEOs + metabolites)	273630	13693	2410	6102

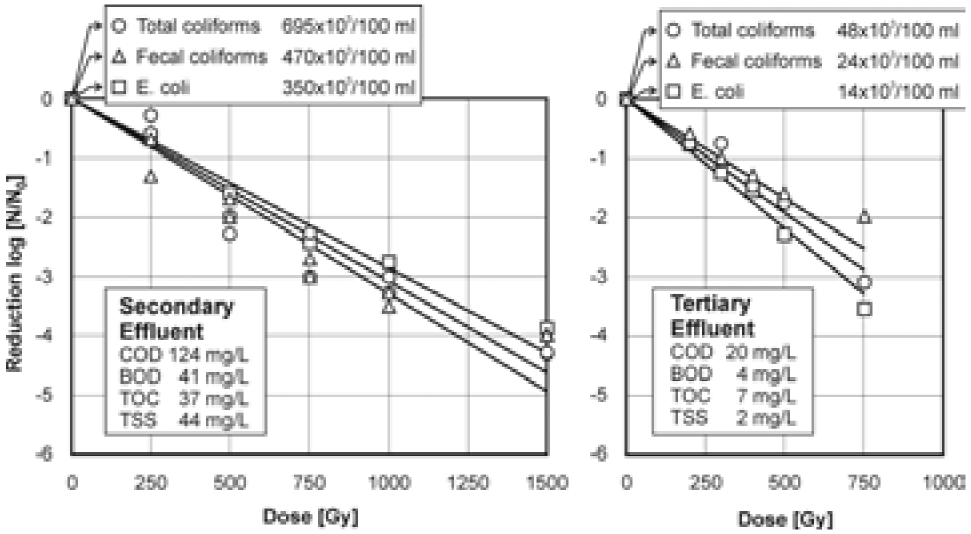


FIG. 4. Radiation induced inactivation of some coliforms in different effluents by means of electron beam irradiation.

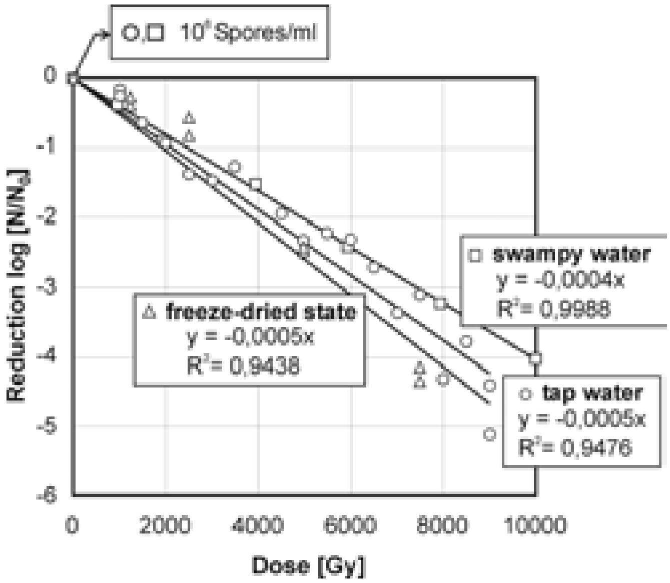


FIG. 5. Radiation-induced inactivation of dry and in water suspended B. subtilis spores by means of gamma irradiation.

Sinskey et al. (1976) [21] studied inactivation of five representative enteric viruses (Adenovirus, Reovirus, coxsackievirus B, Poliovirus and Echovirus) suspended in different aqueous systems by high energy electrons. Poliovirus and coxsackievirus B were found to be most resistant to ionizing radiation among these five viruses investigated. No appreciable differences in inactivation kinetics were detected when poliovirus was suspended in distilled water, waste treatment plant effluent, and amino acid glycine. This result suggests that ordinary amounts of organic matter encountered in wastewater do not significantly alter virus-inactivating effectiveness of a given radiation dose. Obviously, not only bacteria and bacterial spores, but also the enteric virus representative of water hygiene is inactivated endogenously by ionizing radiation. Thus, contrary to chemical and UV disinfection, ionizing radiation as a disinfectant should be largely independent of wastewater quality.

3.3. Radiation-induced decomposition of some estrogens in secondary effluents by electron beam irradiation.

The secondary effluent used for experiments to study coliform inactivation by electron beam irradiation (see Figure 4) also contained concentration levels of natural hormones high enough to induce estrogenic effects in aquatic organisms (Table 2). Therefore, this effluent was also used to study the effect of ionizing radiation to eliminate estrogenic activity. However, about 20 ng/L of the synthetic hormone 17α-ethynylestradiol, often found in effluents from municipal wastewater treatment plants, was not contained in this sample and was added to the effluent before irradiation. Both chemical analysis and recombinant yeast estrogen screens indicated a pronounced estrogenic activity of the original effluent. Chemical analysis, moreover, detected a rather high estrone concentration. Due to the chemical analysis of the individual hormones, a radiation dose of 1 kGy was sufficient to remove all the hormones identified below the limit of detection, which was in the present case generally1.5 ng/L. However, the bio-test still recorded a small residual estrogenic activity with samples irradiated with 1 kGy. At 2 kGy, even the bio-test did not show any estrogenic activity at all.

Accordingly, a somewhat higher radiation dose than 1 kGy should be applied in the present case to eliminate any estrogenic activity most likely due to the unusually high estrone concentration. Generally speaking, a dose of about 1 kGy should be sufficient for total elimination of the estrogenic activity in secondary effluents under usual conditions.

The effect of irradiation on the water matrix in the dose range applied resulted in some reduction of BOD, about 20% or less, (i.e. some mineralization of easily oxidable components contained in the wastewater will occur). Formation of hazardous products is quite unlikely. Contrary to chemical disinfection processes, water disinfection by means of ionizing radiation represents a clean technology.

TABLE 2. THE EFFECT OF ELECTRON BEAM IRRADIATION ON HORMONES CONTAINED IN A SECONDARY EFFLUENT FROM A MUNICIPAL WASTEWATER TREATMENT PLANT

Radiation dose Gy	Concentration in ng/L in the effluent				Relative estrogen activity due to recombinant yeast estrogen screen
	Estrone	17α-estradiol	17β-estradiol	17α-ethynyl estradiol*	
0	110	32	6.6	20	+ + + + + +
1000	nd	nd	nd	nd	+
2000	nd	nd	nd	nd	0
3000	nd	nd	nd	nd	0

nd...not detected; 0...no estrogenic activity detectable; + + + + + + very high estrogenic activity;
+ estrogenic activity just above detection limit; *added to the effluent before irradiation.

3.4. Cost assessment for wastewater irradiation by means of electron beam accelerators

A pollutant reduction by 2 orders of magnitude for the aromatic sulfonic acids and one order of magnitude for the APEOs should be sufficient for a final treatment of effluents from municipal wastewater treatment plants.

Moreover, it has been demonstrated that an electron beam irradiation with a radiation dose of 1–2 kGy would be sufficient to totally eliminate any estrogenic activity originating from estrogens and their metabolites, which is always detectable in municipal wastewater effluents. Additionally, at the same time as the elimination of the estrogens, fecal coliform, present in large numbers in municipal wastewater effluents, could be reduced by several orders of magnitude by electron beam irradiation with 1–2 kGy radiation dose. Electron beam irradiation of effluents from municipal wastewater treatment plants represents a highly efficient technology for effluent treatment as a final step before discharging the effluents into the aquatic environment.

In 2004, construction of the first full scale wastewater treatment plant for industrial wastewater based on electron beam irradiation started, and the plant has been in operation since spring 2006. Therefore, data about cost of an electron beam irradiation plant for wastewater treatment is available now [12]. Tables 3 and 4 show a cost assessment for a possible wastewater irradiation plant using a 400 kW accelerator sufficient to irradiate a wastewater flow of about 575 m^3/h with a radiation dose of 2 kGy.

Cost for such a high power accelerator is about 2 million US$. Due to the other items given in Table 3, the overall capital requirement for such a plant should be approximately 4 million US$. Table 4 shows capital and operation cost. Total capital cost was calculated to be 520 k$/year, and operational cost was estimated to be about 460 k$/year. The resulting total cost of about 0.2 US$/$m^3$ for the effluent treatment indicates that the electron beam irradiation process is also cost effective and competitive to other treatment processes.

TABLE 3. CAPITAL REQUIREMENT FOR THE CONSTRUCTION OF AN ELECTRON BEAM IRRADIATION FACILITY TO TREAT 575 m^3/h WASTEWATER EFFLUENT WITH A RADIATION DOSE OF 2 kGy

Items	Cost in kU$	Remarks
Electron accelerator — 1MeV, 400kW, 3 windows	2000	Cost for Land, R&D, Approval from Authorities are not included
Shielded Room (concrete) Auxiliary equipment Transportation and Installation Water handling system	1500	
Others — documentation, tax, insurance etc.	500	
Total Capital Requirement	*4000*	

TABLE 4. CAPITAL COST AND OPERATION COST ASSESSMENT OF AN ELECTRON BEAM IRRADIATION FACILITY FOR TREATING 575 m^3/h WASTEWATER EFFLUENT WITH A RADIATION DOSE OF 2 kGy

	Items	Cost in kU$/year	Remarks
Capital Cost	Interest	320	8%
	Depreciation	200	20 a
	Total Capital Cost	*520*	
	Capital cost (8500 h/year, 575 m^3/h)	0.1 $/$m^3$	
Operation Cost	Electricity ((0.05 U$/kWh)	340	800 kW
	Labor	100	3 shift
	Maintenance, etc.	20	
	Total Operation Cost	*460*	
	Operation cost (8500 h/year, 575 m^3/h)	0.1 $/$m^3$	

4. CONCLUSIONS

Ozonation at pH7.5, electron beam irradiation and combined ozonation/electron beam irradiation effectively decomposes aqueous 1,5-NDSA, but the efficacy of these processes regarding mineralization of the organic carbon contained in 1,5-NDSA is different. Under the conditions given, single electron beam irradiation mineralizes the organic carbon of aqueous 1,5-NDSA more efficiently than the two other processes mentioned. The higher OH radical concentration generated by the combined ozone/electron beam irradiation process does not result in improved mineralization of the organic carbon. Ozonation at pH7.5 represents the process with the lowest OH radical production and least efficient mineralization of 1,5-NDSA. Most likely, ozone reactions, or secondary oxidants other than OH radicals formed from ozone, are mainly responsible for decomposition of 1,5-NDSA when ozonation at pH7.5 is applied. Consequently the three processes studied for decomposition of aqueous 1,5-NDSA differ considerably with OH radical concentration; nevertheless, in none of these processes formation of biodegradable intermediates during decomposition of 1,5-NDSA could be recorded.

Since radiation-induced inactivation of indicator bacteria *B. subtilis* spores and, most likely, some enteric virus, relevant to water hygiene, proceeds endogenously in wastewater disinfected using ionizing radiation, therefore it is largely independent of solute and suspended solid content of the wastewater. Simultaneously, with such a disinfection process, some natural and synthetic hormones usually also contained in secondary effluents will be totally removed. It is thought that the formation of hazardous products is quite unlikely.

Electron beam irradiation decomposes at a rather low radiation dose of 2 kGy, the whole spectrum of naphthalene sulfonic acids, and is quite efficient in the complex matrix of a real wastewater effluent originating from a wastewater treatment plant for mixed municipal/industrial wastewater. Besides naphthalene sulfonic acids, alkylphenol ethoxylates and their metabolites were simultaneously decomposed by electron beam irradiation treatment.

Since it was also shown that electron beam irradiation of effluents with a radiation dose of 2 kGy is sufficient to eliminate estrogens and their metabolites when contained in the effluents in usual concentration and, moreover, to reduce fecal coliforms at the same time by several orders of magnitude, electron beam irradiation represents an emerging technology for final effluent treatment. With total cost of about 0.2 US$/m^3 the electron beam irradiation treatment process is cost effective and should be competitive to other technologies technically less attractive.

ACKNOWLEDGEMENTS

This work was financially supported in part by the European Union, Project P-THREE EVK1-2002–00116)

REFERENCES

[1] REEMTSMA, T., JOCHIMSEN J., JEKEL, M., ‘Persistence of Sulphonated Polyphenols in the Biological Treatment of Industrial Wastewater”, Vom Wasser **81** (1993) 353–363.

[2] LANGE, F.T., WENZ, M., BRAUCH, H.J., ”The Behaviour of Aromatic Sulfonates in Drinking Water Production from River Rhine Water and Bank Filtrate”, Anal. Methods Instrum. **2(5)** (1995) 277–284.

[3] DE WEVER, H., personal communication (2004).

[4] CALDERARA, V., JEKEL, M., ZAROR, C., ”Kinetics of ozone reactions with 1-naphthalene, 1,5 naphthalene and 3-nitrobenzene sulphonic acids in aqueous solutions”, Wat. Sci. Techn. **44(5)** (2001) 7–13.

[5] RIVERA-UTTRILLA, J., SANCHEZ-POLO, M., ZAROR, C.A., “Degradation of naphthalenesulfonic acids by oxidation with ozone in aqueous phase”. Phys. Chem. Chem. Phys. **4** (2002) 1129–1134.

[6] BREITHAUPT, T., REEMTSMA, T., JEKEL, M., STORM, T., WIESMANN, U., ”Combined Biological Treatment/Ozonation of Wastewaters for the Mineralisation of Non-Biodegradable Naphthalene-1,5-Disulfonic Acid”, Acta Biotechnol. **23(4)** (2003) 321–333.

[7] GEHRINGER, P., ESCHWEILER, H., “The use of radiation-induced advanced oxidation for water reclamation”, Wat. Sci. Technol. **34** 343–349.

[8] FAROOQ, S., KURUCZ, C.N., WAITE, T.D., COOPER, W.J., “Disinfection of wastewaters: high-energy electrons vs gamma irradiation”, Wat. Res. **33(9)** (1993) 2053–2058.

[9] SLIFKO, T.R., ROSE, J.B., NICKELSON, M., COOPER, W.J., “Inactivation of waterborne micro organisms by high energy electron beam: a large scale study”, Proc. 1999 Int. Symp. On Waterborne Pathogens (1999) Milwaukee, Wisconsin (USA) Aug. 29–Sept. 1, (1999).

[10] ROUTLEDGE, E.J., SHEAHAN, D., DESBROW, C., BRIGHTY, C., WALDOCK, M., SUMPTER, J.P., “Identification of Estrogenic Chemicals in STW Effluent. 2. In Vivo Responses in trout and roach”, Environ. Sci. Technol. **32** (1998) 1559–1565.

[11] ANONYMUS, “NGWA Conference focus on endocrine-disrupting chemicals” Water & Wastewater Int. **18** (2003) 5.

[12] HAN, B., personal communications (2004).

[13] OENORM EN 1899-1, “Wasserbeschaffenheit–Bestimmung des Biochemischen Sauerstoffbedarfs nach n Tagen (BSBn)“.

[14] ROUTLEDGE, E.J., SUMPTER, J.P., “Estrogenic activity of surfactants and some of their degradation products assessed using a recombinant yeast screen”, Environ. Toxicology and Chemistry **15(3)** (1996) 241–248.

[15] DE BOEVER, P., DEMARE, W., VANDERPERREN, E., COOREMAN, K., BOSSIER, P., VERSTRAETE, W., “Optimization of a Yeast Estrogen Screen and Its Applicability to Study the Release of Estrogenic Isoflavones from Soygerm Powder”, Environ. Health Perspectives **109(7)** (2001) 691–697.

[16] SOMMER, R., CABAJ, A., “Evaluation of the efficiency of a UV plant for drinking water disinfection”, Wat. Sci. Tech. **27** (1993) 357–362.

[17] SOMMER, R., PRIBIL, W., APPELT, S., GEHRINGER, P., ESCHWEILER, H., LETH, H., CABAJ, A., HAIDER, T., “Inactivation of bacteriophages in water by means of non-ionizing (UV-253.7 nm) and ionizing (gamma) radiation: a comparative approach”, Wat. Res. **35(13)** (2003) 3109–3116.

[18] GEHRINGER, P., ESCHWEILER, H., LETH, H., PRIBIL, W., PFLEGER, S., CABAJ, A., HAIDER, T., SOMMER, R., “Bacteriophages as viral indicators for radiation processing of water: a chemical approach”, Appl. Rad. Isot. **58** (2003) 651–656.

[19] RIVAS, F.J., BELTRAN, F.J., ACEDO, B., GARCIA ARAYA, J.F., CARBAJO, M., ”Kinetics of the Ozone-p-Chlorobenzoic Acid Reaction”, Ozone: Sci. Eng. **27(1)** (2005) 3–9.

[20] WOODS, R.J., PIKAEV, A.K., ”Applied Radiation Chemistry: Radiation Processing”, John Wiley & Sons, New York, Chichester, Brisbane, Toronto, Singapore (1994) 4.

[21] SINSKEY, A.J., SHAH, D., METCALF, T.J., ”Biological Effects with High Energy Electrons”, Proc. 3rd National Conf. on Sludge Management Disposal and Utilization”, Miami Beach, Florida, December 14–16 (1976), 160 –163.

THE STATUS OF RADIATION PROCESS TO TREAT INDUSTRIAL EFFLUENTS IN BRAZIL

P.R. Rela, M.H.O. Sampa, C.L. Duarte, F.E.D. Costa, C.S. Rela, S.I.Borrely,
M.N. Mori, E.S.R. Somessari, C.G. Silveira
Radiation Technology Centre — CTR,
Instituto de Pesquisas Energéticas e Nucleares — IPEN,
São Paulo, Brazil

Abstract

The use of ionising radiation has great ecological and technological advantages, especially when compared to physiochemical and biological methods. It has great efficiency to destroy microorganism andi it breaks down organic compounds, generating substances that are easily biodegraded and it is not necessary to add chemical compounds. The Radiation Technology Centre — CTR at the Institute for Energetic and Nuclear Research (IPEN) started in 1992 marked the development of an alternative technology for wastewater and industrial effluent treatment, mainly for the degradation of pollutants using the radiation from a high-energy electron beam. This technology has been extensively studied by many research centres. The objective of this programme in Brazil is to use the existing gamma and electron beam to study the removal and degradation efficiency of toxic and refractory pollutants (organic compounds mainly from industrial origins) and the disinfecting of pathogenic micro-organisms in wastewater, industrial effluents and sludge. This programme also embraces the design and construction of a wastewater treatment pilot plant in the IPEN electron beam facility. Its function is to develop and test water irradiation devices, to test in continuous run the degradation of polutants and inactivation of microorganism and to perform economical feasibility study to scale up for a movable demonstration plant to operate on a commercial basis.

1. INTRODUCTION

Environmental pollution has become a significant worldwide concern. Industrial development has generated halogenated hydrocarbons, used as solvents, dielectric fluids and many other products in industrial processes, delivering to the environment injurious effluents often without any treatment. Applications on land of pesticides, fertilizers by the agriculture, as well as the large quantities of domestic wastewater generated in most regions of the country has introduced pollution into the air, land and waters, risking the quality of the water used for human consumption. Many contaminants biodegrade slowly and may become dangerous to people, plants and animals. Damage to human health related to improper treatment of residues has led to strict environmental protection laws and, consequently, the need for research in the treatment of effluents. [1]

The variables involved in the environment's recuperation are numerous, mainly by the great variety of chemical compounds and raw materials used by industry. Most of the pollutants in industrial wastewater are chemically and biologically resistant; thus, the application of conventional treatment is often not sufficient. Besides, the reduction of microorganisms in wastewater treatment plants with chlorination was found insufficient, and it may generate the formation of carcinogenic chlorinated hydrocarbons. The same phenomenon was observed with the chlorination of drinking water, containing humic substances which will promote trihalomethanes formation regarded as toxic or carcinogenic. [2, 3]

Sao Paulo State in Brazil presents the main industrial park of the country, and in the Metropolitan Region (SPMR). There are metallurgical (including mechanical and automobile), textile, food, chemical, electrical, cellulose and paper industries contributing nearly 80% of organic and inorganic load discharged without any kind of treatment, delivering these effluents directly to the main river of Sao Paulo city, Tietê.

Considering these aspects, the Government of Sao Paulo State and Industries are concentrating a major effort in a decontamination programme of the main rivers and water reservoir located close to industrial areas, with new wastewater treatment plant construction. Since these plants can present a low efficiency for the removal of refractory pollutants, mainly organochloride compounds, there is a requirement for an alternative technology to be used in conjunction with the conventional treatment to improve the reduction of pollutants [4]. The best way, in some cases, would be the treatment at the industrial site before disposal at the wastewater treatment plant, which discharges the wastewater directly into the environment. The main development to be achieved will be a technique reliable and economically available to greatly reduce the emission of industrial pollutants.

Usually, the conventional techniques used to treat these effluents are employed to reduce the volume and toxicity of the effluents. The available techniques are coprecipitation, adsorption on charcoal and resins, oxidation, flotation, biodegradation, incineration, radiation and recycling.

One of the most widely used methods to treat organic compounds is adsorption on activated carbon. However, this process only transfers the contaminant from liquid to solid phase. In this treatment the organic compounds are not degraded, and the used (spent) activated carbon has to be decontaminated or properly stored.

The oxidation process has attracted many researches because of the capacity to mineralise organic compounds. The most efficient oxidation is the use of OH radicals. There are various methods of generating OH radicals such as the use of ozone, hydrogen peroxide, ultraviolet and the interaction of ionising radiation with water (AOP — Advanced Oxidation Process), which is the most simple and efficient method for generating OH radicals in situ. [4, 6, 7].

Radiation processing is an ecological and technological advantage compared to physiochemical and biological methods, because it breaks down organic compounds, generating substances that are easily biodegraded. It is not necessary to add chemical compounds.

This technology has been extensively studied by many research centres [1–7]. Following this tendency, The Radiation Technology Centre — CTR at the Institute for Energetic and Nuclear Research (IPEN) started in 1992 the development of an alternative technology for wastewater and industrial effluent treatment (mainly for the degradation of pollutants using the available radiation sources, gamma cell irradiator and particulary a medium energy industrial electron beam).

A research programme was established in order to study the removal and degradation efficiency of toxic and refractory pollutants (organic compounds mainly from industrial origins) and the disinfecting of pathogenic micro-organisms in wastewater, industrial effluents and sludge.

A wastewater treatment pilot plant was designed and constructed in the existing building at the IPEN electron beam facility to develop and optimize devices and related items to be used with this technology, such as the underbeam delivery system real time dosimetric system to control the irradiation process[8]. The use of this pilot plant performing radiation process tests of real effluent is for the economical feasibility studies and provides information to scale up for a movable demonstration plant to operate on a commercial basis. Figure 1 shows the flowchart of this programme.

2. OBJECTIVE

Brazil has several gamma and EB facilities for different industrial applications (sterilisation of medical products, wire and cable crosslinking, packaging, etc.), but no environmental application on a large scale.

The use of electron beam technology in environmental areas such as to treat sludge, groundwater, surface water and municipal wastewater has been moving slowly because the industry and government are always conservative in adoption of new technology, especially when they cannot observe the efficiency and cost effectiveness of treatment in a full scale facility [1].

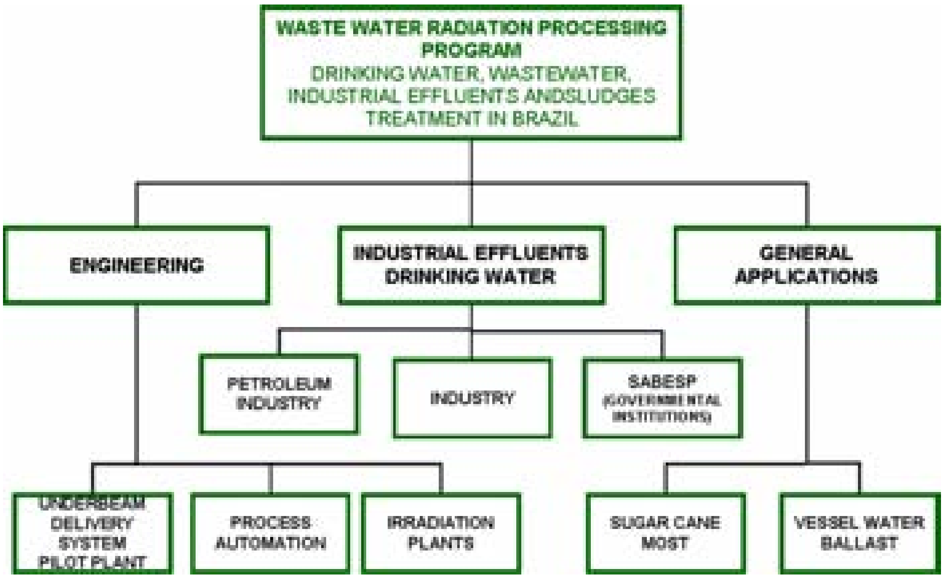


FIG. 1. Wastewater programme developed by IPEN.

Since the efficiency of the industrial wastewater treatment using EB has been demonstrated on a small scale, the strategy is that this technology becomes accepted and embraced by industry and environmental engineers. Thus, reducing negative social, environmental and economic consequences of discharging inadequately treated wastewater, from the chemical process industry, and to consolidate the use of electron beam processing on industrial wastewater treatment in Brazil, transferring the technology for the implementation of facilities in industries and governmental sanitation companies.

3. EXPERIMENTAL

3.1. Drinking Water Treatment Tests

Experiments were made using the irradiation technology to treat the potable waters. Firstly, trihalomethanes in samples from Sao Paulo city were studied. A pilot plant was used with a flow rate of 1.3m ^{3}/h, the energy was fixed on 1.5 MeV, the current was varied to obtain the desired dose, and the organic compounds were analyzed by Gas Chromatography. Table 1 shows the trihalomethane concentrations and its reduction with irradiation doses and the pH variation.

TABLE 1. THM´S REDUCTION WITH THE DOSES

Dose (kGy)	$CHCl_3$ (µg/L)	$CHBrCL_2$ (µg/L)	$CHBr_2Cl$ (µg/L)	$CHBr_3$ (µg/L)	pH
0	77,99	12,25	3,16	168,32	7,64
2	9,80	n.d.	n.d.	n.d.	5,81
3	7,11	n.d.	n.d.	n.d.	4,53
4	8,90	n.d.	n.d.	n.d.	4,20
5	6,78	n.d.	n.d.	n.d.	4,94
6	3,72	n.d.	n.d.	n.d.	4,22

n.d. not detected (below detection limits)
$CHCl_3$ = chloroform; $CHBrCl_2$ = bromodichloromethane;
$CHBr_2Cl$ = dibromochloromethane; $CHBr_3$ = bromoform

This table shows that a dose of 2 kGy may remove approximately 87.4% of Chloroform, while the increase of the dose to 6 kGy provokes a nearly 92.5% removal. Other experiments were performed with high chloroform concentrations, varying from 145 μg/L to 780 μg/L, and the results showed reduction efficiency near 95% at the doses below 6 kGy. [9]

Other experiments were done using samples from a public drinking water treatment plant located in Sao Paulo city. This plant receives water from a Guarapiranga reservoir that has major pollution caused by clandestine domestic wastewater and garbage that has resulted in the occurrence of seaweed proliferation. Particularly in the summer time it is possible to note alterations in the taste and odor of public drinking water distributed in the city. [10]

The main compounds responsible for the taste and odour are as geosmin (trans-1-10-dimethyl-transdecalol)-GEO and methylisoborneol (2-methylisoboneol) — MIB. The activated charcoal used since 1977 by the company that treats the drinking water has decreased, due to the high intensity of the seaweed growth. This material has the disadvantage of generating great volumes of residue.

Experiments were done using a gamma irradiation with a Co-60 source (gamma cell type, 11 000Ci) in a batch system using the dose: 0.5 kGy, 1.0 kGy, 2.0 kGy and 3.0 kGy. Three kinds of samples containing close to 100 ng/L and 1, 000 ng/L of GEO and MIB were submitted to the irradiation. They were sampled from the capture region of the water treatment station (WTS), after the sedimentation process in the WTS and delivered water in the exit of WTS.

The irradiation efficiency of the duplicate samples was evaluated by the chemical analysis before and after the irradiation process with doses: 0.5 kGy and 1.0 kGy. The irradiated samples were submitted to an acute toxicity test using *Vibrio fisheri*, Microtox test 1.

The results of quantitative analyzes of GEO and MIB in the three water samples before and after irradiation are showed in the Figure 2.

At concentrations of approximately 100 ng/L of GEO and MIB, after the sedimentation process and the final water, there was total removal at a doses of 0.5 kGy. Raw water samples presented lower reduction with the same delivered dose. With samples where concentrations were close to 1000 ng/L, higher doses were necessary to remove 90% of these compounds. However, for final water to be delivered to the population, 1.0 kGy dose was enough to remove 99%. It was not observed acute toxicity in the samples before neither after irradiation, showing that no toxic substances were formed after the irradiation process.

3.2. Sewage and Sludge Disinfection Tests

Combining biological and radiation treatment of domestic sewage and sludge collected at the different wastewater treatment plants, a number of tests were carried out to investigate disinfection and removal of organic matter. [11]

The electron beam radiation technology was applied to raw sewage, secondary biological sewage, chlorinated wastewater and sludge. The irradiations were performed in batch system, and the disinfection was determined by the elimination of indicators bacteria (i.e. total and fecal coliforms) enumerated by Most Probable Number technique, NMP/100mL, through the lactose fermentation. The enumeration of total aerobic bacteria, plating count with Difco-Nutrient Agar, was also conducted as an evaluation of raw domestic sewage and dehydrated sludge.

The sewage samples were collected in a Lagoon System-Sewage Treatment Plant which discharges approximately 30L/s of chlorinated effluent without sludge generation. This Lagoon System is composed of double lagoons classified as anaerobic and facultative. The influent reach the station, pass successively through the collecting well (**A)** anaerobic lagoon (**B**) facultative lagoon (**C**) and chlorination tank (**D)**.

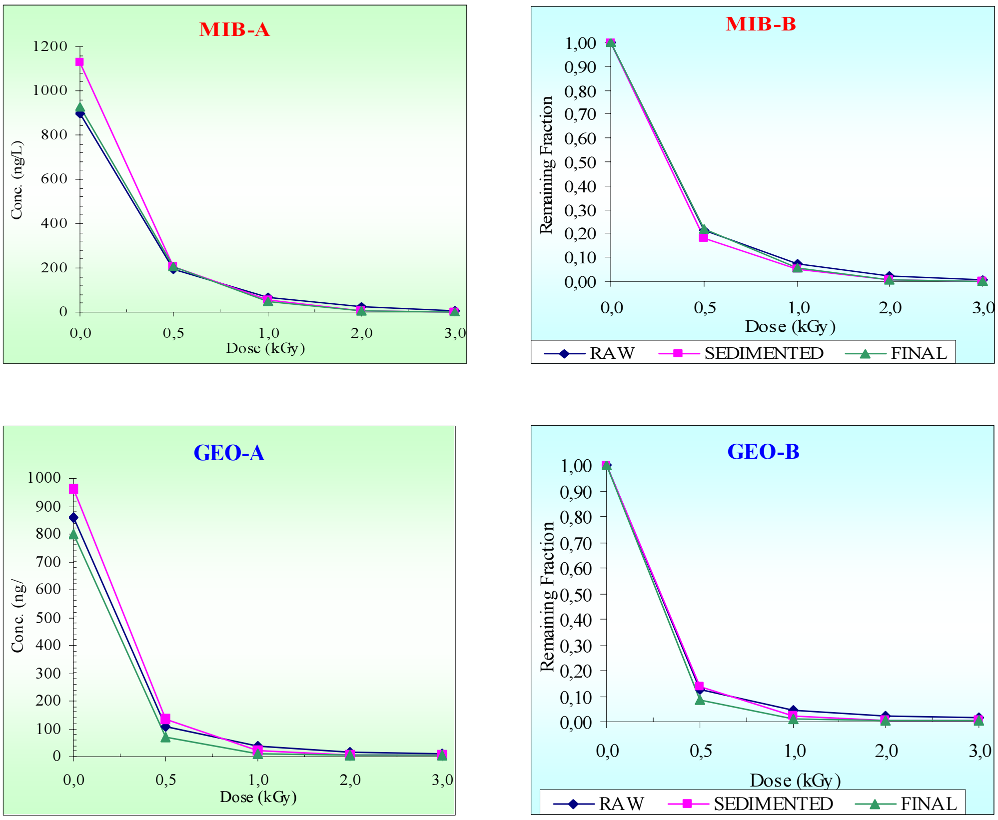


FIG. 2. Removal of Geosmine and methilisoborneol of drinking water samples at the different steps of the treatment plant.

The effect of radiation on the elimination of indicator bacteria (i.e., total and fecal coliform) showed a 5 log reduction at 3.0 kGy dose applied to raw sewage. The higher oxygen concentration in facultative lagoon C due to the presence of algae, resulted in a higher efficiency of the same 3.0 kGy radiation dose at that site. The final effluent, although chlorinated, was contaminated by total coliforms which were completely eliminated by irradiation as shown in Figure 3 [11].

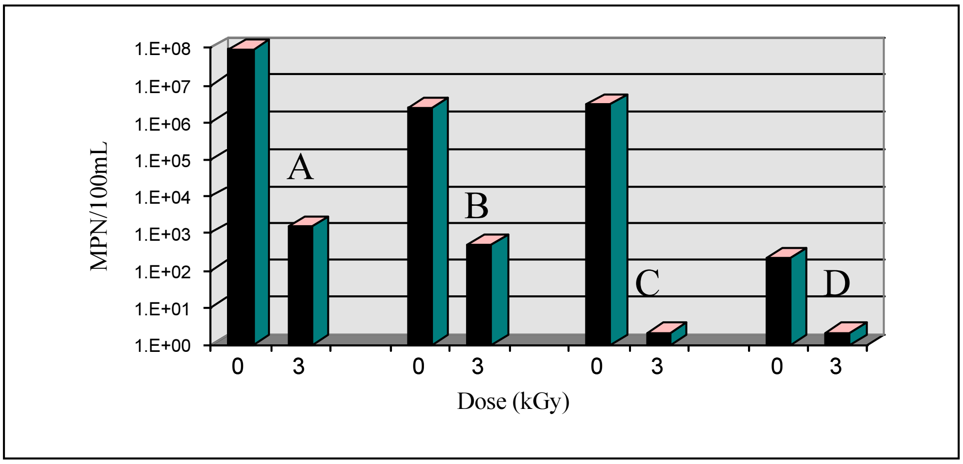


FIG. 3. Reduction of total coliforms by 3.0kGy irradiation dose applied to raw sewage, secondary and chlorinated effluents.

Sewage sludge was collected from a conventional treatment station, which includes anaerobic digestion and generates approximately 200 ton/day of dehydrated sludge. The results showed a reduction of 3 cycle log and a total elimination of aerobic bacteria by 10 kGy and 15 kGy radiation dose. Other experiments demonstrated that doses between 5.0 kGy and 6.0 kGy are enough to reduce pathogenic bacteria to an acceptable level. The level of decontamination will depend on the application of the sludge as a soil conditioner.

3.3 Industrial Wastewater Treatment Tests

IPEN has been studying radiation improvement for effluents since 1992 with samples originally from Governmental Wastewater Treatment Plant. This plant collects the greatest volume delivered from industrial wastewater from Sao Paulo and samples from chemical and petrochemical industries.

At first, samples from Governmental Wastewater Treatment Plant were performed in a batch system with irradiation doses from 0.5 kGy to 10 kGy. The following analyzes were performed: apparent colour, true colour, total suspended solids, turbidity biochemical oxygen demand (BOD) and the chemical oxygen demand (COD), before and after irradiation. [12]

As can be seen in Table 2, a significant reduction in the apparent and true colour with a 5 kGy dose was observed in raw wastewater, primary, and secondary effluent from biological treatment. Between 5 kGy and 50 kGy an increase in colour values of the samples from raw wastewater and primary effluent was noted, mainly in apparent colour values. When effluents from secondary treatment (activated sludge) received different doses, the values of apparent and true colour decreased as a function of doses. The opposite was noted for turbidity and total suspended solids. These results are presented in Table 3.

In the second stage using IPEN's pilot plant, studies were performed with standard solutions of the most widely used organic compounds in Brazilian industries such as chloroform, bromoform, trichloroethylene (TCE) and perchloroethylene (PCE). The results in Table 4 indicate a 4.0 kGy dose removed approximately 70% of chloroform, while increasing the dose to 8.0 kGy caused degradation close to 85%. In the case of bromoform, the degradation was close to 95%; TCE, about 99%; and PCE, 95%. When air mixing (flow: 4mL/min) was used, the degradation rates increased.

TABLE 2. EFFECTS OF DOSE ON APPARENT COLOUR OF INDUSTRIAL WASTEWATER

DOSES (kGy)	Raw Wastewater	Primary Effluents	Biological Treatment Effluents
0	3200 253*	3000 550*	90 153*
5	80 49*	500 250*	82 20*
10	120 59*	1300 250*	45 15*
50	600 250*	1600 280*	7.5 < 2.5*

* Irradiated samples

TABLE 3. IRRADIATION EFFECTS ON CONVENTIONAL PARAMETERS AFTER SECONDARY TREATMENT ACTIVATED SLUDGE)

Doses (kGy)	Apparent Colour	True Colour	BOD (mgO_2/L)	COD (mgO_2/L)	Total Suspended solids(mg/L)	Turbidity (UF)
0	1100	58.0	35	313	28	2
0.5	75	5.5	62	289	28	8
1.0	52	5.5	47	287	44	17
2.0	37	6.0	58	253	86	20
3.0	30	4.5	40	235	108	22
4.0	23	2.0	34	235	110	26

TABLE 4. ORGANIC COMPOUNDS DEGRADATION IN RELATION TO IRRADIATION DOSES

	$CHCl_3$		$CHBr_3$		TCE		PCE	
Doses (kGy)	No air (ppb)	Air (ppb)	No air (ppb)	Air (ppb)	No air (ppb)	Air (ppb)	No air (ppb)	Air (ppb)
0	193.8	264.0	330.7	529.2	107.4	189.0	93.9	130.6
4.0	70.0	70.3	57.9	45.8	7.7	ND	15.4	22.3
6.0	47.0	49.5	31.9	45.8	4.4	ND	9.9	11.7
8.0	33.0	32.1	20.3	25.0	ND	ND	7.2	7.4

ND — not detected

3.4. Electron Beam Irradiation Process Combined With Conventional Treatment

Other tests were performed using samples of industrial wastewater collected at the Public Wastewater Treatment Plant in Sao Paulo State. A large amount of industrial wastewater comes from chemical industries, and its quality, quantity and colour characteristics changes every day, resulting in a low efficiency of the wastewater treatment plant. This allowed the discharge of dangerous products to the environment. This plant has a capacity of 1.5 m^3/s, receiving about 80% of wastewater from industrial sources (chemical, pharmaceutical, textile and dye industries) and 20% from domestic origin. This plant has a secondary treatment using activated sludge, and the treatment process has two phases — liquid and solid (sludge) The final effluent remains coloured and contains some organic compounds even after biological treatment, and goes into the Tiete River, obstructing its reuse for industrial applications. [13, 14]

These experiments were performed with the objective of using the electron beam technology combined with the biological treatment in order to get better performance with this plant. To verify in which stage of the plant the EB processing could be more efficient, five points were selected for sampling — from main industrial receiver unit influent (RUI), coarse bar screens effluent (CB), medium bar screens effluent (MB), primary sedimentation effluent (PS) and final effluent (FE).

The electron beam irradiation was performed in a batch system using a Dynamitron II Electro Beam Accelerator 1.5MeV, using a conveyor velocity of 6.7m/min. The beam with 2cm width was scanned in 120cm length. The samples were placed in a Pyrex vessel, and the thickness of layer was 4mm.

The composed samples (four samplings collected each two hours during 12 hours) were collected from each selected point during eight months. The samples were irradiated with the doses 5 kGy, 10 kGy and 20 kGy. The following analyzes were performed: Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), dissolved and volatile solids dried at 550 ^{0}C and total solids dried at 103–105 ^{0}C, Trihalomethanes (THM's), tetrachloroethylene (PCE), trichloroethylene (TCE), benzene, toluene, xylene, phenol, Organic acids. The evaluation of the irradiation treatment efficiency was verified by the chemical analysis of the duplicate samples before and after irradiation.

The average concentration of the samples for the main organic compounds present in different steps of the WWTP, before and after electron beam irradiation, are in Table 5. The variation between the sampling was about 50%. The receiver unit (RUI) and the coarse bar screen (CB) points receive, exclusively, industrial effluent, before the medium bar screens (MB), the plant receives about 20% in volume of domestic effluent. In this way, the average of all organic compounds analysed was higher in the two first steps, requiring high doses for degradation. Besides the others, contaminants present such as solids, metals and dyes contributed to the necessity of higher doses.

These experiments showed that for RUI and CB, it was necessary to have a 20 kGy dose to degrade about 99% of all organic compounds, but for the other steps such as MB and PS, 99% degradation was obtained at 10 kGy dose. For the Final Effluent (FE), a low dose (2kGy) is enough to degrade the remaining organic compounds and dyes after the biological treatment. The coloration still remained in the effluent, and the radiation processing contributed to color degradation (FIG. 4).

TABLE 5. ORGANIC COMPOUNDS REMOVAL BY IRRADIATION AND BY GRANULAR ACTIVATED CARBON (GAC)

Compound (%)	Dose (kGy)					GAC
	5	10	20	30	50	
Benzene	93	97	99	99	>99	>99
Toluene	89	99	>99	>99	>99	>99
1,2 Dichlorethene	89	94	96	99	>99	>99
Chloroform	96	97	98	99	>99	>99
Bromoform	99	>99	>99	>99	>99	>99
Trichlorethylene	99	99	>99	>99	>99	>99
Methyl Isobutyl ketone	76	94	97	>99	>99	>99

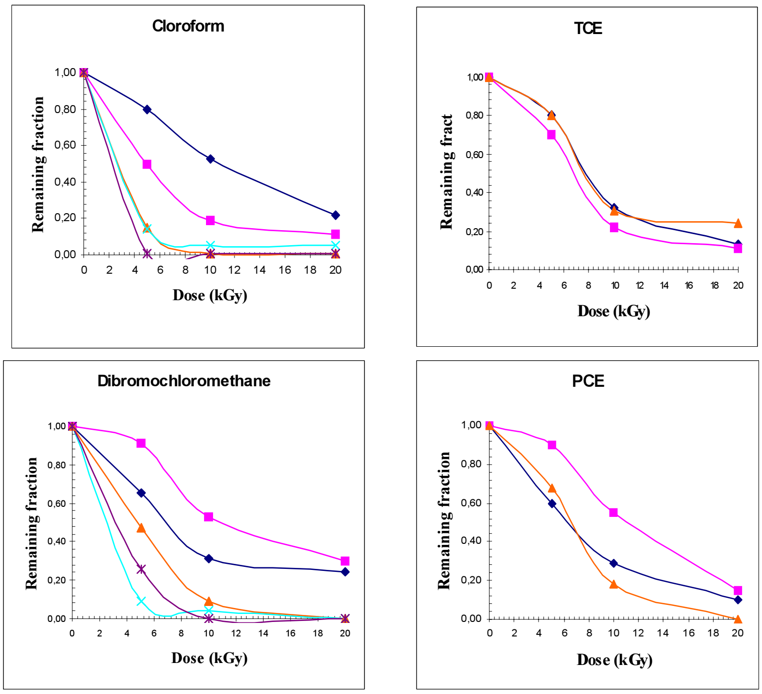


FIG.4. Degradation of the organic compounds present at the different steps of WWTP after electron beam irradiation.

Concerning the conventional parameters such as COD, BOD, TOC, Total Solid, Total Volatile Solid and pH, it was verified that there were no significant changes in these values after the irradiation. As expected, most of the pH values decreased after the irradiation from the formation of smaller organic acids.

To evaluate the by-products from radiation processing mass spectrometry and organic acid analysis were conducted. The results of the mass spectrometry analysis showed that no volatile by-products were formed after irradiation. However, using a high performance liquid chromatography, an increase at ppm level the concentration of the organic acids: oxalic, tartaric, ascorbic and formic, mainly in the RUI and CB points was observed.

The electron beam irradiation should be efficient in destroying aromatic organic compounds, trihalometanes, PCE and TCE and colour present in industrial effluent. The necessary irradiation dose depends on the concentration of the pollutant in the effluent.

These studies showed that in this WWTP, there are two possibilities to use the electron beam irradiation process:

- in the reception of industrial effluent — delivering high dose (20 kGy) in order to maintain the good performance of the wastewater treatment plant and
- in the Final Effluent — delivering a low dose (5 kGy) to enhance the clarification, making possible the reuse of treated wastewater to industrial applications.

3.5. Electron Beam Irradiation Process Compared to Adsorption with Activated Carbon

Comparison studies using the electron beam process and adsorption with activated carbon (AC) to treat industrial effluents were performed. The objective was to predict how the electron beam treatment of industrial effluents could be considered an available and competitive technology since the activated carbon has demonstrated its effectiveness in removing organic compounds in wastewater treatment plants.

Seven organic compounds were chosen as surrogate standards to represent a wide variety of organic pollutants which may be present in wastewater and in real samples from a petrochemical plant. Electron beam treatment was performed at IPEN´s EB facility using the doses 5, 10, 20, 30 and 50 kGy. The activated carbon process was performed in a fixed-bed absorber glass column (3 cm internal diameter and 17.5 cm length), and the utilized EBCT (empty bed contact time) was 3 minute.

Table 5 shows the efficiency in organic compound removal using EB technology, where the samples were irradiated at different doses and adsorption with activated carbon using a fix bed column was used.

The irradiation experiments performed allow selecting the dose of 20 kGy as reasonable results for the surrogate standard solution and the dose of 50 kGy for the real effluent. It is important to point out that the dose for real effluents was not optimized, and, according the results, lower doses below 50 kGy would be reasonable for the organic compound reduction.

The results showed that the organic removal efficiency was similar in both methods. The costs using EB were higher than adsorption of activated carbon but it should take in account that the contaminants were transferred to the granular activated carbon, with the regulations becoming more restrictive. It is necessary to consider the high incineration temperature of the spent carbon to ensure a proper ultimate disposal, increasing the cost of the process.

3.6. IPEN’S Pilot Plant

A pilot plant was set up to treat wastewater and industrial effluents in the Electron Beam Facility on the IPEN. The Electron Beam Accelerator is a 1.5 MeV Dynamitron type from Radiation Dynamics Inc. USA. The accelerating voltage ranges from 500 keV to 1.5 MeV and the beam current from 1 mA to 25 mA. The beam with a frequency of 100Hz can scan an area of 60 cm length and 2 cm width [9].

This pilot plant (Fig. 5) was set up to process up to 70 L/min with an average dose rate of 5 kGy. Two tanks with 1200-liter capacity are used for storage and collect the liquid and two pumps are used to homogenize and pump the liquid through the irradiation device. A sample system allows sample collection just before and after irradiation. A real time calorimetric system was developed at IPEN to control the dose rate delivered to the stream flowing under the electron beam.

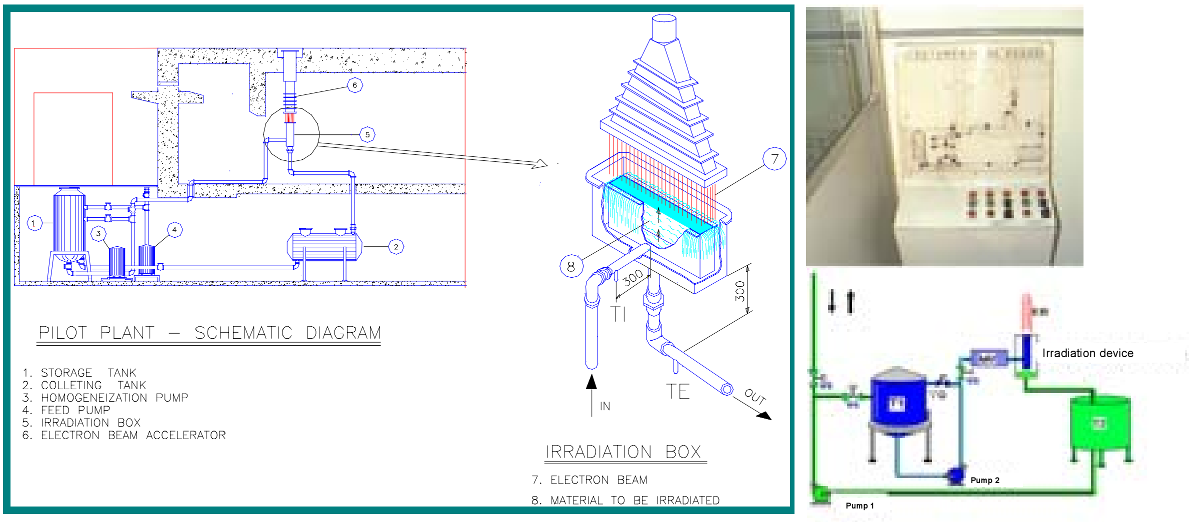


FIG. 5. IPEN´s pilot plant — schematic diagram.

3.6.1. Hydraulic system

The hydraulic system where the water is presented to the electron beam governs the efficiency of this technology. The development of *an up-flow irradiation device,* theoretically alleviates the dependence of energy transfer to the stream with the beam accelerating voltage (penetration capability).

Three models of up-flow stream irradiation device were tested. The models and the position of the irradiation device under the EB machine are represented in Fig. 6 [10]. The sequence of the development started by model 1 was upgraded to models 2 and 3. The model 3 fitted with a titanium foil window allows the irradiation device to work as a closed system. In this configuration, hazardous liquids can be processed safely, avoiding the spread of gaseous by-products to the environment and allowing sampling of the gas formed during the irradiation process. It also re-injects the gas in the influent stream to be submitted to the electron beam treatment.

3.6.2. Dosimetric system

For a better control of parameters involved during liquid waste radiation processing, an on-line calorimetric system was developed [11]. The absorbed dose was obtained by measuring the temperature difference of the water stream before and after the irradiation device. The dosimetric system is based on a two Wire Current Output Temperature Transducer, WCOTT, model, GE-ADJ590J, from Intersil. These were located in the influent and effluent pipes, close (35 cm) before and after the irradiation device. The temperature transducers are connected via an interface to a PC computer that continuously reads and records the temperatures and transforms the values to the equivalent dose delivered to the stream. Figure 7 shows the electric circuit diagram.

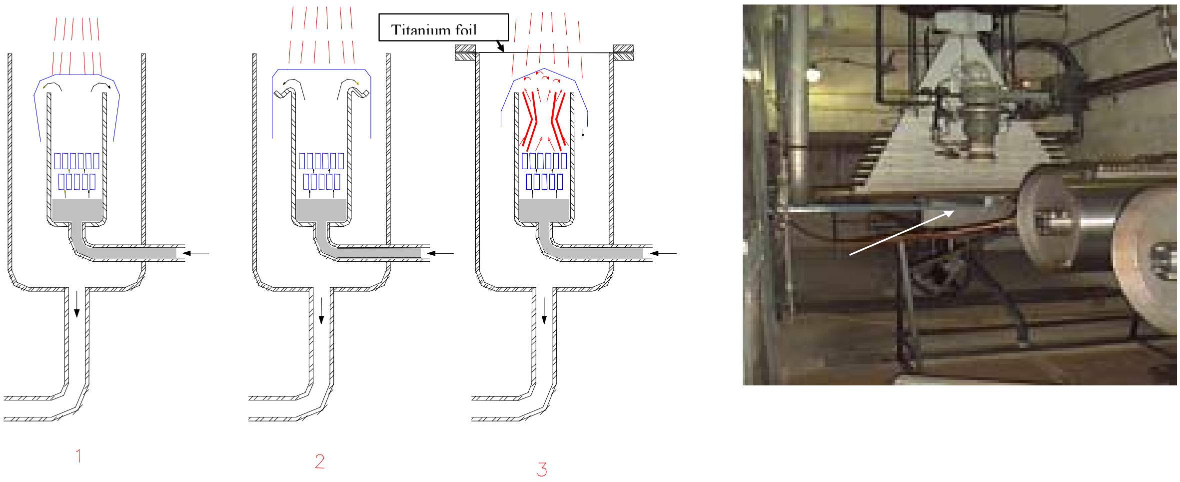


FIG. 6. Models of up flow stream irradiation devices.

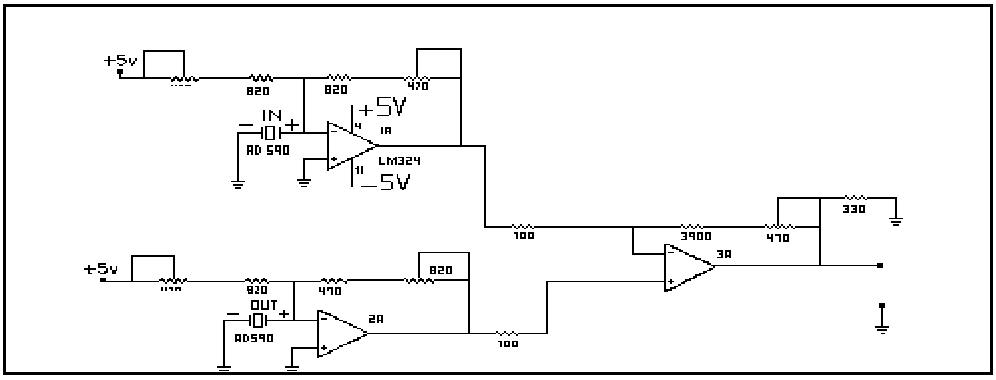


FIG. 7. Dosimetric system electric circuit diagram.

To evaluate the consistency of the dose registered by the calorimetric system, experiments were performed using aqueous chemical dosimeters, where the colour degradation of a commercial textile dye named 'Duacouro' similar to Acid Red 265 was measured by the UV-Visible spectrophotometer at 500nm [12].

3.6.3. Hydraulic system efficiency studies

For each irradiation device, a series of tests were carried out in different operating conditions to determine the maximum efficiency of the system. The efficiency was determined by the relation between the absorbed dose of the stream registered in the calorimeter and the delivered dose from electron beam accelerator (without losses). Using 200 hours of the IPEN's pilot plant, the best results for the efficiency of the developed irradiation prototypes are shown in Table 6.

TABLE 6. EFFICIENCY OF THE PROTOTYPES

	MODEL 1	MODEL 2	MODEL 3	
			OPEN SYSTEM	SELF-CONTAINED SYSTEM
EB energy (MeV)	1.5	1.5	1.5	1.5
Flow (L/min)	45	45	54	54
Efficiency (%)	33	72	76	67

Besides the best efficiency results, Model 3 was a versatile device wherein different kinds of effluents (especially the hazardous wastes) could be processed. The tests were performed in two configurations (1) without the titanium foil window becoming the hydraulic circuit opened to the environment and (2) fitted with the foil becoming a self-contained system.

4. ONGOING ACTIVITIES

4.1. Experiments with real effluent from industries and effluents from Municipal Wastewater Treatment (WWTP) Plants

To acquire the necessary data to support the conclusions regarding technical feasibility and cost of water treatment under optimized conditions, the following data were required:

- data on optimized operating parameters such as electron energy, dose, flow rate, current, and voltage;
- data on wastewater composition and toxicity pre - and post — treatment;
- data and other technical and economical information for feasibility studies for applications at a large scale;
- perform a model feasibility study for each particular case.

The continuec use of the stationary pilot plant set up at IPEN was to carry out feasibility studies using EB technology, especially on optimization, mainly for the irradiation device that governs the efficiency of the energy transfer from the electrons to the effluent and for defining the requirements for the optimum operating parameters for the treatment in industrial applications.

4.2. Project for mobile EB treatment plant

The main objective of this project will be to use the mobile system as a demonstration facility that moves to the treatment point, becoming a ready-to-use and self-powered sustained unit for treatment services where effluent was generated. This will facilitate the logistics and promote the use of EB technology for wastewater and other liquid product treatment. Fig. 8 shows the configuration of the mobile unit.

4.3. Main Features

The concept of a mobile facility was engineered according to the radio-protection limits permitted for the workers (operators) and with respect to the limits of the load allowed to be transported on the country road. The design performs well and is based on the interaction of the EB with the effluent. The design includes the under beam system developed by the engineering group and a selection of a robust accelerator to sustain the severity condition during the transport of the irradiation unit.

EB Characteristics

- Accelerating voltage: 600 kV
- Beam Current: 83 mA
- Power: 50 kW
- Scan width: 1.3 m
- Blower: fitted with a cooling air system that allows the recycling of the air, protecting the emission of ozone to the atmosphere.

Irradiation Device

- Type: ‘Up Flow Stream’ — developed by IPEN-Brazil. This device can be fitted with a titanium foil window becoming the hydraulic circuit self-contained, protecting the environment.

Truck Trailer

- Capacity: 40 ton- 03 axis

- Dimensions: 14 m × 2.6 m and 2.9 m high

  Autonomous power supply
- Diesel- generator: 150 kW

  Dosimetric System
- On-line calorimetric system with four wire current transducer (WCOTT from Intersil-General Electric)

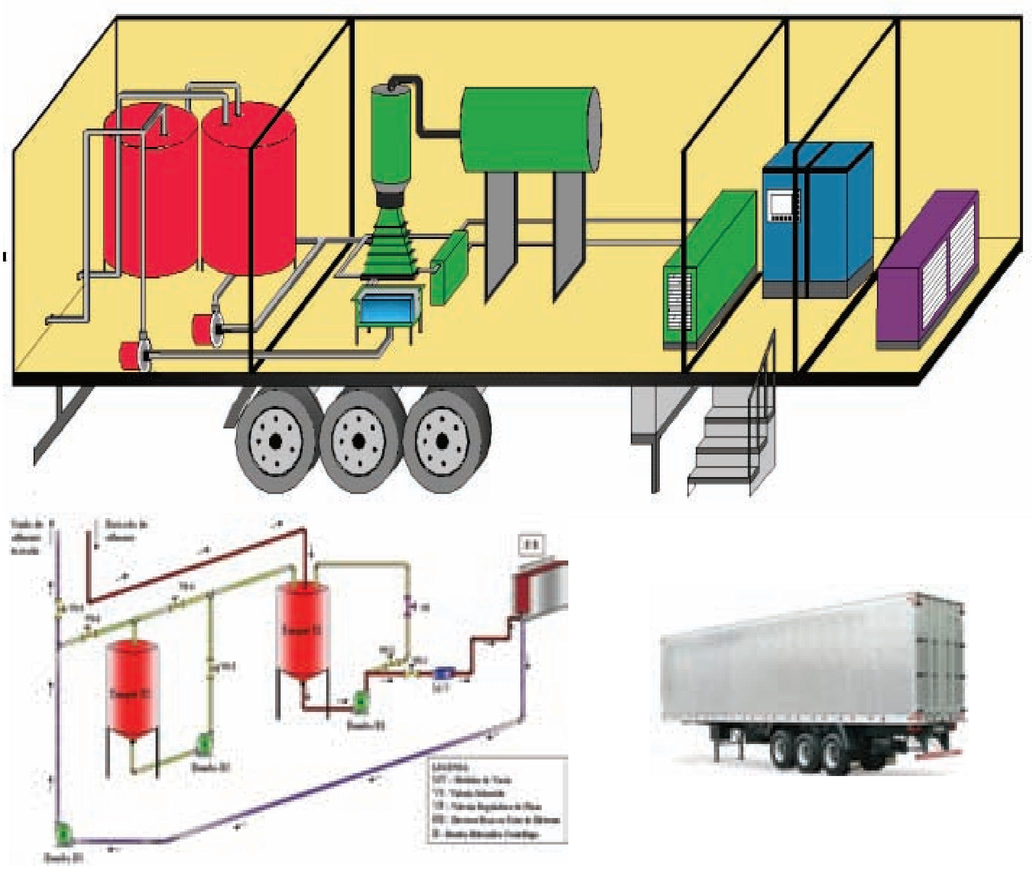


FIG. 8. Mobile irradiation facility.

4.4. Approach with potential clients

During the developments at IPEN, there was strong interest from Brazilain companies, especially petroleum companies and chemical industries. There was also interest from governmental treatment companies concerning studies on wastewater treatment (industrial and domestic) and drinking water (odorific substances and THM).

The following areas of potential interest are also being contacted:

- decontamination of airport and hospital wastewater effluent
- leachates treatment from landfills
- disinfection of water as a replacement chlorination for food industry
- reuse of specific industrial wastewater effluent
- dewatering of sludge in WWTP
- use of the liquid irradiation process to increase the production efficiency in sugar (cane sugar) and alcohol plants
- use of liquid irradiation process to treat vessel water ballast

5. CONCLUSIONS

The developed programme in Brazil on radiation treatment of wastewater studied the removal and degradation efficiency of toxic and refractory pollutants (organic compounds mainly from industrial origins) and the disinfecting of pathogenic microorganisms in wastewater, industrial effluents and sludge.

This programme also embraced an engineering expertise on the design and construction of a wastewater treatment pilot plant in the IPEN electron beam facility, develop and test wastewater irradiation devices, to study in continuous run the degradation of pollutants and inactivation of microorganism and to perform economical feasibility studies to scale up for a mobile demonstration plant to operate on a commercial basis as a demonstration facility. Concerning human resources, 10 technicians were trained (3 Ph. D.'s, 5 M. Sc.'s thesis) were developed focusing the aspects of engineering, chemistry and toxicity related to this application.

There are factors that still influence further developments and applications, such as legislation of environmental protection becoming more restrictive in several countries and the efficacy of this technology to treat recalcitrantes effluents. The design and construction of mobile irradiation facility using EB will permit a ready-to-use facility for treatment services and demonstrate the availability of the treatment in locals where the liquid waste is generated or stored.

REFERENCES

[1] WAITE, T.D., Overview of electron beam irradiation. In: Second International Symposium on Environmental Applications of Advanced Oxidation Technologies, Coral Gables, FL February (1996).

[2] COOPER, W.J., CADAVID, E.M., NICKELSEN, M.G., LIN, K., KURUCZ, C.N., WAITE, T.D., Removing THMS from drinking water using high-energy electron-beam irradiation. *J.Am. Water Works Assoc.* **85** (9) (1993) 106–112.

[3] GETOFF, N. "Advancements of Radiation Induced Degradation of Pollutants in Drinking and Wastewater", Appl. Radiat.Isot. 40 (7), (1989) 585–594.

[4] SAMPA, M.H.O., RELA, P.R., DUARTE, C.L., "Industrial Wastewater Treatment in Brazil Using Electron Beam Accelerator" Editors: William J._Cooper, Kevin E. O'Shea and Randolph D. Curry, in "Environmental Applications of Ionizing Radiation," John Wiley & Sounds, Inc., 33 (1998) 521–530.

[5] GEHRINGER, P., PROKSCH, E., ESCHWEILER, H., SZINOVATZ, W., "Oxidation of volatile chlorinated contaminants in drinking water by a combined ozone/electron beam treatment. Proceeedings of 10th Ozone World Crongress, vol. 2, Monaco, Mach (1991).

[6] GEHRINGER, P., ESCHWEILER, H., *Advanced oxidation for groundwater remediation and for soil decontamination.* INTERNATIONAL ATOMIC ENERGY AGENCY, Final report of a co-ordinated research project 1995–1999. IAEA-TECDOC-1225, Vienna, Austria (2001) 5–12.

[7] GETOFF, N., Radiation and photoinduced degradation of pollutants in water. A comparative study. *Radiat. Phys.Chem.* **37**(5) (1991) 673–680.

[8] RELA, P.R., SAMPA, M.H.0., DUARTE, CL.L., COSTA, F.E., SCIANI, V., "Development of an up-flow irradiation device for electron beam wastewater treatment". *Radiation Physics and Chemistry*, vol. **57** (3–6) 2000 (657–660).

[9] SAMPA, M.H.O., BORRELY, S.I., SILVA, B.L., VIEIRA, J.M., RELA, P.R., CALVO, W.A.P., NIETO, R.C., DUARTE, C.L., PEREZ, H.E.B., SOMESSARI, E.S.R., LUGÃO, A.B., The use of electron beam accelerator for the treatment of drinking water and wastewater in Brazil. *Radiat. Phys.Chem.* **46,** No. 4–6 (1995) 1143–1146.

[10] DUARTE, C.L., SAKAGAMI, M.K., MAUTONE, C.A., SAMPA, M.H.O., BORRELY, S.I., SOMESSARI, E.S.R., Removal of Oodrific substances in drinking water caused by seaweed using ionizing radiation. ANES — Americas Nuclear Energy Symposiujm, October, 16–18, Miami, Fla, (2002).

[11] BORRELY, S.I., CRUZ, A.C., DEL MASTRO, N.L., SAMPA, M.H.O., SOMESSARI, E.S. Radiation Processing of Sewage and Sludge. A review. *Progress in Nuclear Energy*, **33,** No. ½, (1997) 3–21.

[12] SAMPA, M.H.O., RELA, P.R., DUARTE, C.L., Industrial Wastewater Treatment in Brazil Using na Electron-Beam Accelerator. In Environmental Applications of Ionizing Radiation (ed. by Cooper, W.J., Curry, R.D., O'Shea, K.E.) John Wiley & Sons, Inc., USA, 23 (1998).

[13] SAMPA,M.H.O., RELA, P.R., DUARTE, C.L., BORRELY, S.I., OIKAWA, H., SOMESSARI, E.S., SILVEIRA, C.G., COSTA, F.E., *Electron Beam Wastewater Treatment in Brazil.* INTERNATIONAL ATOMIC ENERGY AGENCY, Final report of a co-ordinated research project 1995–1999. IAEA-TECDOC-1225, Vienna, Austria (2001) 65–86.

[14] DUARTE, C.L., SAMPA, M.H.O., RELA, P.R., OIKAWA, H., CHERBAKIAN, E.H., SENA, H.C., ABE, H., SCIANI, V., "Application of electron beam irradiation combined to conventional treatment to treat industrial effluents". Radiat.Phys.Chem., 57 (3–6) (2000) 513–518.

EFFECT OF ACCELERATED ELECTRON BEAM ON PESTICIDES REMOVAL OF EFFLUENTS FROM FLOWER PLANTATIONS

T. Ramírez, M. Armas, M. Uzcátegui
Escuela Politécnica Nacional, Nuclear Science Department
Quito, Ecuador

Abstract

The flower industry in Ecuador uses a great quantity of pesticides for flower growing. Many of them are toxic and non-biodegradable, which contaminates the different effluents. The study of this research is focused on the possibility of using electron beam radiation in order to decrease the concentration of pesticides in effluents. The research is initiated with a survey of twelve flower plantations in Ecuador. The information on importation of pesticides and exportation of different classes of flowers was carried out, as well as the flower sales. The study of electron beam influence was realized with 6 pesticides considered toxic (Diazinon, procloraz, imidacloprid, dimetoato, carbofuran and metiocarb). The studied variables were irradiation dose, pesticide concentration, aeration and pH effect. Besides pH changes, formation of nitrites, nitrates, sulfates, sulfides, ammonium ion and cyanides, after irradiation process of pesticides in aqueous solutions were analyzed. In general, the obtained degradation of pesticides was 99% for the pesticides procloraz, imidacloprid, carbofuran and dimetoato, and 67% for metiocarb pesticide when the pesticide concentration was 50 ppm and 5 kGy irradiation dose.

1. INTRODUCTION

Pesticides are chemical or biological products used in direct form, in aqueous solutions or mixtures for preventing, fighting, eliminating and mitigating the insects, mushrooms, bacteria, acarus, mollusks, rodents, grass and any other form that can affect directly or indirectly cultivation and agricultural products [1].

In general, all types of pesticides are toxics for the environment, animals and people. These chemical compounds produce bioaccumulation in soil, irrigation water, plants, animals and people [2].

The ways of entrance of pesticides to the human body and animal's organism are through the skin, respiratory and digestive systems [3].

Ecuador imports a great quantity of pesticides, which in 2002, reached 27 500 tons of pesticides.

On a world-wide level, Ecuadorian flowers are esteemed for their quality, which has converted Ecuador to a country very competitive in the international market of flowers. Flower production constitutes the second product of export in the country, with roses the principal flower [3].

The value for sales of export flowers is very relevant, so, in 2002 reached to US $291 112 000. The USA buys the greatest amount of Ecuadorian flowers followed by the Russian Federation and the Netherlands.

Ecuador has destined more than 3000 hectares (7413 acres) to the flower cultivation of the most varied flowers to be sent to the different markets.

In flower production, effluents transport pesticide residues from flower plantation. Mainly, these effluents are constituted by washing water from fumigation equipment and from pesticide storage tanks, where fumigation solutions and post harvest water are prepared.

Effluents are usually discharged into the septic wells. This procedure can affect the ecosystem by means of groundwater. This risk must be attended to by using some treatment to reduce the quantity of pesticides to permissible levels. In consequence, this research has the purpose of studying the pesticides removal from irrigation waters and washing water used in flower plantations by means of electron beam radiation.

2. TECHNICAL SURVEY

Necessary surveys were development for the following reasons:

1. Determining the pesticide types that are being used, their handling before, during and after fumigation and the treatment type that the plantations are using for their contaminated effluents having pesticide residues.

2. Getting the pertinent information about the ionizing radiation effects on pesticides from different flower plantations.

Twelve of the most important flower plantations were surveyed. The main results of the survey are:

- 93% of employees are workers, 4% technicians and 3% professionals ·
- The average production of rose stems in a year was 645, 400 stems/hectare/year.
- Analyzing the pesticides used in flower plantations and considering their different toxicological grades, it can be concluded that the main relevant pesticides for this study are those which have a toxicity grade of I and II. In the case of insecticides, the greater amount of pesticides used in the production of flowers has a toxicological grade II with a percentage of 35.7% [1].
- 50% of the plantations decontaminate their effluents with oxidation pools which permit the reuse of water.
- 69.23% of plantations desire to decontaminate their wastewater for reuse to prevent the contamination of groundwater and 30.77% of plantations do not see the need of doing any treatment of effluents contaminated with pesticides.

3. EXPERIMENTAL PART

3.1. Selection of pesticides

The selection of six commercial pesticides to be studied in the present research project is the result of the survey applied to several flower plantations and to bibliographic references [5, 6]. The active ingredients of selected commercial pesticides were carfuran, diazinon, dimetoato, imidacloprid, metiocarb and procloraz.

3.2. Analysis of pesticides and formed ions in irradiation process

The analysis of pesticide concentration before and after irradiation process was carried out by High Pressure Liquid Chromatography (HPLC) in an inversed-phase system, using Varian column ODS2 and a UV detector. The optimal calibration curves for each pesticide were initially studied, considering the analysis of the following parameters of HPLC operation: column type, temperature, movil phase composition, mobile phase flow, wavelength and concentration range of pesticides [6].

The maximum pesticide concentrations, using HPLC technical, was determined as a function of the linear part of the calibration curve for each pesticide under the optimal HPLC operation conditions.

For carbofuran, the linear tendency is up to 100 ppm. In similar form, the maximum detectable concentration was established. The maximum values considered of the other pesticides were 250 ppm Diazinon, 200 ppm Procloraz, 50 ppm Metiocarb, 100 ppm Dimetoato and 170 ppm Imidacloprid. In all cases, the minimum detectable value was 1 ppm.

The formation of chemical species (ions) after irradiation process, such as sulfates, phosphates, nitrites, nitrates, cyanides, sulfides, chlorides and ammonium ion, were analyzed using a HACH DR–2000 spectrophotometer and HANNA 8521 pH-meter. The analysis of chemical species formed in each pesticide after irradiation is shown in Table 1.

TABLE 1. ANALYZED IONS IN EACH PESTICIDES SOLUTION AFTER IRRADIATION

Pesticide	Analyzed ions
Diazinon	Nitrites, nitrates, ammonium, cyanide, phosphates, Sulfides, sulfates.
Procloraz	Nitrites, nitrates, ammonium, cyanide, chloride.
Dimetoato	Nitrites, nitrates, ammonium, cyanide, phosphates, Sulfides, sulfates.
Metiocarb	Nitrites, nitrates, ammonium, cyanide, Sulfides, sulfates.
Carbofuran	Nitrites, nitrates, ammonium, cyanide
Imidacloprid	Nitrites, nitrates, ammonium, cyanide, chloride.

3.3. Study of irradiation effect on pesticide in aqueous solutions

Preparation of pesticides solutions

The irradiation study on commercial pesticides was performed considering the pesticide concentration, the irradiation dose and the influence of aeration.

The maximum concentration of the pesticide solution to be used in the irradiation process was determined at 400 ppm [7, 8].

According to several studies of pesticide irradiation in aqueous solutions, performed by some authors, the irradiation dose is within an interval of 2 and 10 kGy [9]. Then, the irradiation doses established for the present study were 20, 10, 5 and 2 kGy.

With the purpose of irradiating the pesticide solutions without air flow, the homogenized pesticide solution with a determined concentration was introduced into an 18 × 18cm polyethylene sheath, containing 300 ml solution. Then, it was proceeded to seal them by eliminating the most quantity of air into the sheath. The pesticide solutions to be irradiated in such conditions were placed in a metallic box, specially designed to bubble some air into the solutions during the irradiation process.

Polyethylene bags with the pesticide solution were put in aluminum boxes for transport to the irradiation window for irradiating.

Analysis of pesticides degradation in aqueous solution by radiation

The irradiation dose was fixed according to the main operation parameters of the accelerator:

Electron beam energy	8.3 MeV
Electron beam Power	2 kW
Electron beam Intensity	1000 mA
Frequency of electron beam pulse	100 Hz
Duration of electron beam pulse	6 µs
Velocity of conveyor	Variable

With the purpose of analyzing the pesticides after irradiation, it proceeded to extract the pesticide (active ingredient) by liquid- liquid extraction, using dichlomethane as an HPLC solvent type. The phase extracted with the solvent is evaporated to dryness. Then, 6 ml of acetonitrile/ water solution (70/30 (v/v)) was added to the dry residue.

The detection of pesticides was carried out by a UV detector under the optimal parameters once standardized the HPLC equipment.

The retention times of each selected pesticide were used to identify the peaks in the chromatogram and the peak area was used for determining its quantification.

The calibrated curves established for each studied pesticide were used for determining the pesticide concentration before and after the irradiation process.

Besides, the formation of nitrate ions, nitrites, sulfates, ammonium ion, chlorides, sulfides and phosphates during the radiation process, as well as the pH measurements after the irradiation, were analyzed.

3.4. Influence of pH on the pesticides degradation in aqueous solutions

pH changes of the aqueous solutions were carried out using 0.1 N sodium hydroxide or HCl 0.1 N, depending on fixed pH, using HANNA pH-meter. The new pH values were 4.5 and 8.0.

Pesticides concentration due to the electron radiation effect was carried out with an HPLC system in phase reverse using a Shimadzu chromatograph with UV detector and a column VARIAN ODS2 of 25 cm high.

The aqueous samples of the six pesticides considered in this research study with the pH indicated above were irradiated at 2, 5 and 10 kGy, maintaining constant the pesticide concentration of 100 mg/l, in all cases.

Besides, concentration of chemical species such as nitrates, nitrites, sulfates, ammonium ion, chlorides, sulfides and phosphates formed by the radiation effect, as well as the pH after the irradiation process, were analyzed.

3.5. Irradiation of flower plantation effluents

The previously developed study corresponds to the radiation effect on a single pesticide. However, in the flower plantation effluents, there are many other pesticides and other pollutants that can change the behavior of the pesticides degradation by the electron effect. Water samples were taken from four flower plantations: DENMAR S.A., MARLEDIAN, PETYRO'S and TAMBOROSES S.A. Water samples from the irrigation process were taken with the purpose of knowing the pesticides pollution and their degradation using electron beam radiation. The sampling points for each flower plantation are shown in figure 5.

The irradiation dose applying to the selected samples was 5 kGy, considering as the optimal dose in order to obtain a high degradation of the six analyzed pesticides.

The pesticides degradation on the ions formation was analyzed following the procedures exposed in item 3.3.

4. RESULTS

4. 1. Analysis of pesticide degradation

The irradiation results of 6 pesticides are shown in Figure 1, where the degradation percentage as a function of the irradiation dose to different pesticide concentrations with and without aeration is reported.

4.2. Results of radiation effect on concentration of ions in aqueous solution after the irradiation process of pesticides

4.2.1. pH Measurements on irradiated pesticide solutions

Due to the destruction of the pesticide structure by electron beam irradiation, the pH decreases in all pesticide solutions after irradiation by the effect of water radiolysis and the formation of chemical species (ions). The initial pH of all pesticide solutions was 5.5.

The influence of electron beam radiation on the pH of pesticide solutions at different pesticide concentration with and without aeration is shown in Figure 2 for imidacloprid and dimetoato pesticides, as an example.

4.2.2. Formation of ions during the irradiation of the pesticide solutions

The irradiation of six pesticide solutions using electron beam produces the formation of inorganic species by depending of the chemical structure of pesticide. The ions formed during the irradiation of pesticide solutions were nitrites, nitrates, ammonium, sulfates, sulfides, phosphates and chlorides. Cyanide ions were not present in any pesticide solutions studied.

The influence of electron beam radiation on ions formed during the irradiation of pesticide solutions at different pesticide concentration with and without aeration is shown in Figure 2 with diazinon as an example. The chloride concentration is shown in Figure 3 as an example.

After observing the behavior of each pesticide solution irradiated with electron beam is concluded the following:

1. Pesticide degradation by radiation effect

- When aqueous solutions of the six pesticides, with an initial concentration of pesticide of 100 to 400 ppm, were irradiated it was observed that a high degradation percentage is reached when the irradiation dose was 5 kGy. Irradiated solutions with an initial concentration of 50 ppm for diazinon and procloraz pesticides have high degradation percentage at 2 kGy.

- Generally, when the pesticide solutions are irradiated with or without aeration, high initial concentrations of pesticides give small degradation percentages.

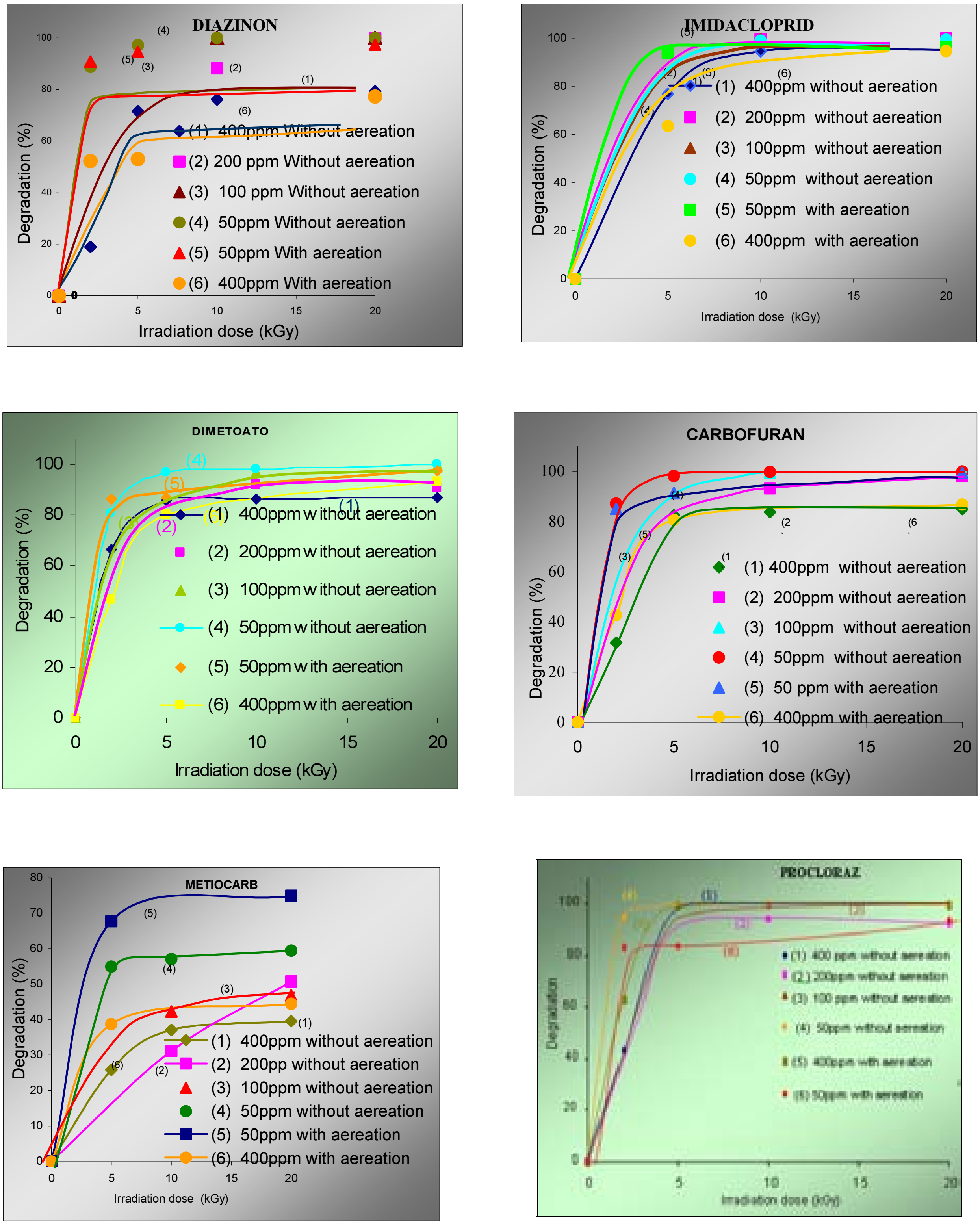
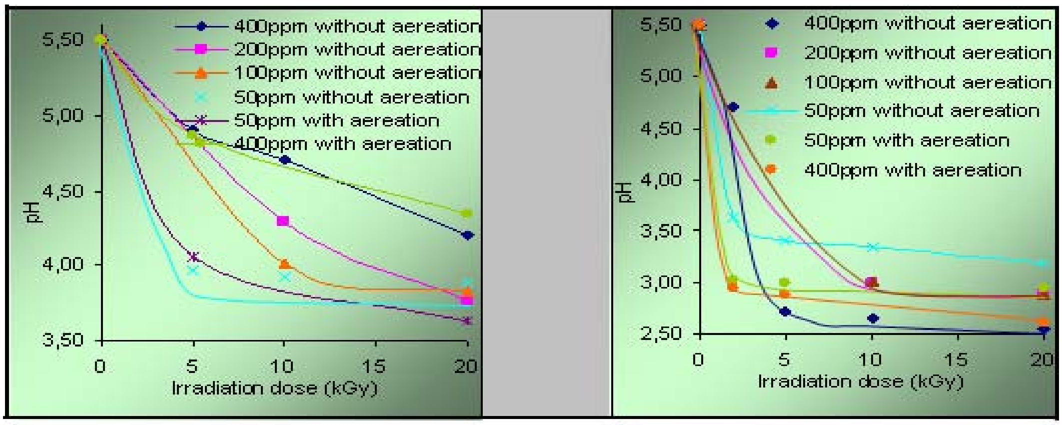


FIG. 1. Influence of electron beam on degradation percentage of Diazinon, imidacloprid, dimetoato, carbofuran, metiocarb and procloraz pesticides, as a function of irradiation dose to different concentrations of pesticide, with and without aeration.



Imidacloprid **Dimetoato**

FIG. 2. Influence of electron beam on pH of Imidacloprid and dimetoato pesticides to different concentrations of pesticides as a function of irradiation dose, with and without aeration.

- Each pesticide presents a different behavior when it is irradiated with and without aeration. The influence of the aeration process does not improve degradation for diazinon, imidacloprid and dimetoato pesticides, since their degradation percentages are practically similar at the same dose of irradiation and concentration. However, Carbofuran and procloraz pesticides present an increase on degradation percentage from 5% to 10% at 5 kGy dose, with aeration and at the same operation parameters. Finally, the metiocarb pesticide solution presents the highest degradation (up to 99.9%).

- In all cases, to increase concentration of pesticide in the solution, the degradation percentage is smaller at the same irradiation dose, with or without aeration.

  For initial concentrations smaller or equal to 50 ppm diazinon and procloraz pesticides, the degradation increase is proportional to the irradiation dose up to 2 kGy dose. Over this dose, the degradation velocity is asymptotic. If the pesticide concentration is equal to or higher than 100 ppm, the degradation increases up to 5 kGy dose. Over this dose, the degradation reaches an asymptotic tendency.

- For initial concentrations of dimetoato, imidacloprid, metiocarb and carbofuran pesticides, in the range from 50 to 400 ppm, the degradation increase is proportional to the irradiation dose up to 5 kGy dose. Over this dose, the degradation reaches an asymptotic form.

- When the irradiation dose is increased to 20 kGy, the degradation percentage of diazinon, carbofuran and procloraz pesticides has two reaction kinetics zones well differentiated.
  a) An accelerated degradation zone up to 2 kGy dose when the pesticide concentration is 50 ppm or less; and an accelerated degradation zone up to 5 kGy dose for higher or equal concentrations of 100 ppm pesticide.

b) A retarded zone of degradation between 2 and 20 for pesticides with concentrations equal to or smaller than 50 ppm, and a retarded zone for pesticides with concentrations higher than 100 ppm.

- The irradiated aqueous solutions of imidacloprid, dimetoato and metiocarb pesticides present two zones of reaction kinetic that relate their degradation percentages as a function of the irradiation dose.
  a) An accelerated degradation zone up to 5 kGy dose within an interval of concentration from 50 to 400 ppm.
  b) A retarded degradation zone between 5 and 20 kGy for all pesticide concentrations.

- Procloraz, imidacloprid, carbofuran, diazinon and dimetoato pesticides are much more radiosensibles than metiocarb.

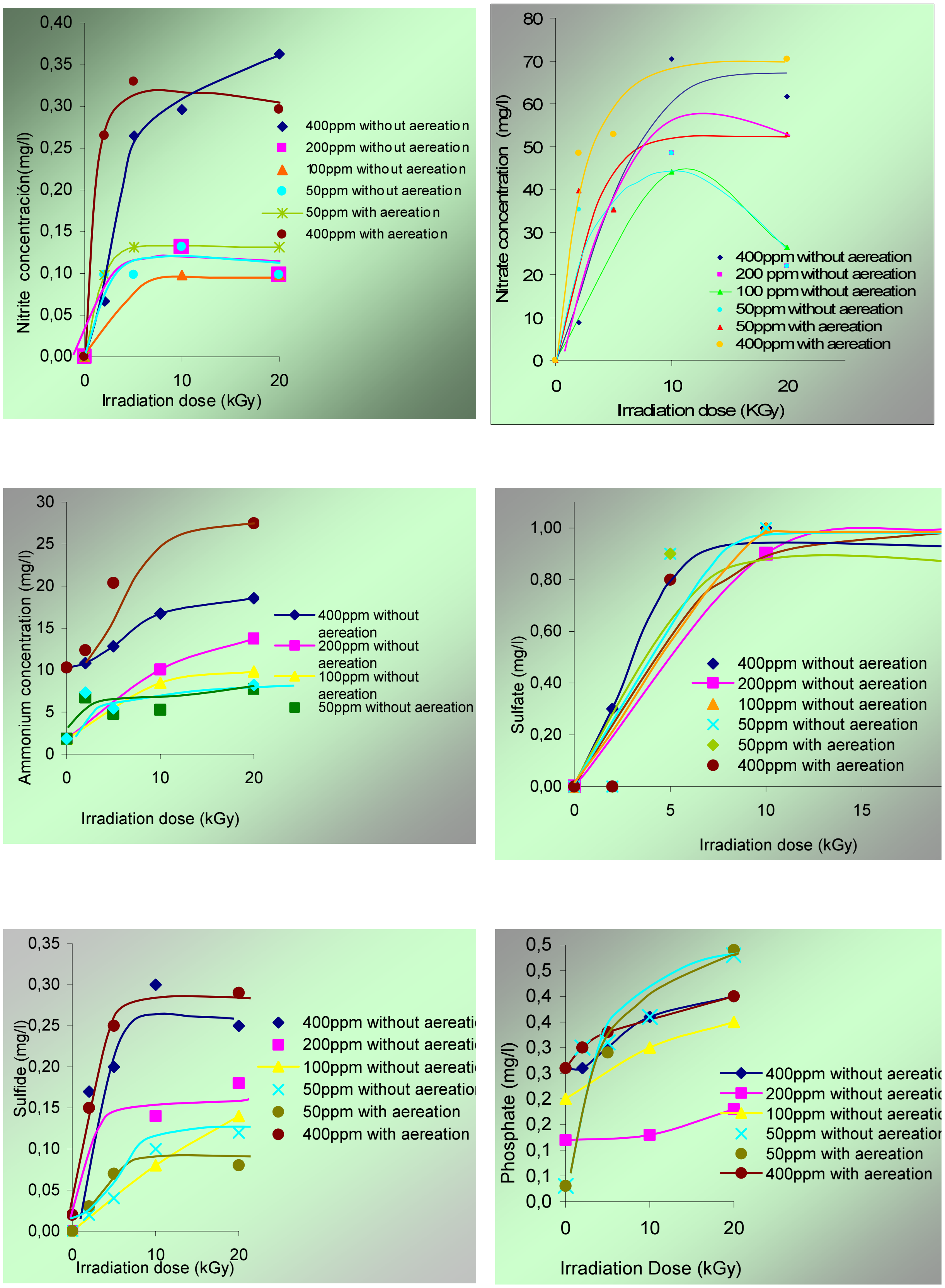


FIG. 3. Influence of electron beam on ion concentration of Diazinon pesticide, as a function of irradiation dose, with and without aeration.

2. Ions formed by electron beam effect

Ion formation by radiation effect on different pesticides studied in this research project depends on chemical structure, irradiation dose, the initial concentration of pesticide, dose rate and thickness of pesticide solution mainly.

A useful correlation between the pesticide degradation and the concentration of formed ions was found.

Formation of nitrite ions

Nitrogen included in the structure of the analyzed pesticides is converted to nitrite ions by the radiation effect. The concentration of nitrite is increased with both the irradiation dose and the pesticide concentration.

The maximum concentration of nitrite ions obtained was 0.52 ppm in an irradiated solution of Imidacloprid pesticide when the initial concentration was 400 ppm of pesticide at 20 kGy dose with aeration.

Formation of nitrate ions

Due to the structure of the analyzed pesticides, the formation of nitrate ions was found in the aqueous solutions of pesticides irradiated.

When the concentration of a pesticide and the irradiation dose are increased, the nitrate concentration is also increased. The maximum concentration of nitrate ions was 120 ppm when 400 ppm dimetoato pesticide was irradiated at 20 kGy.

Formation of ammonium ions

The concentration of ammonium ions is greater when aqueous solution concentration of pesticides studied and irradiation dose are increased. The greatest concentration of ammonium ions is reached when the aqueous solutions of analyzed pesticides were irradiated to 400 ppm pesticide. The maximum concentration of ammonium ions was 31.99 ppm, which is obtained when 400 ppm dimetoato pesticide was irradiated at 20 kGy. The formation of ammonium ions varies significantly with the aeration with and without aeration.

Formation of sulfate ions

The formation of sulfate ions is obtained when aqueous solutions of Diazinon, Dimetoato and Metiocarb pesticides were irradiated due to their chemical structures.

The concentration of sulfate ions is higher while the irradiation dose is increased by reaching an asymptotic tendency for the pesticides mentioned above, obtaining maximum formation of sulfate ions at 10 kGy.

Formation of sulfide ions

Due to the presence of sulfur in chemical structure of Diazinon, Dimetoato and Metiocarb pesticides, the irradiated aqueous solutions of these pesticides have sulfide ions.

The concentration of sulfide ions is increased with both the irradiation dose and the pesticide concentration, reaching the maximum concentration when the irradiation dose is 20 kGy for these three pesticides. The maximum concentration of sulfide ions is obtained when 400 ppm Metiocarb pesticide was irradiated at 20 kGy with aeration.

The concentrations of sulfide ions have a small increment when the aqueous solutions of pesticide were irradiated with and without aeration.

Formation of phosphate ions

According to the chemical structure, Diazinon and Dimetoato pesticides can produce phosphate anions after of irradiation process.

The formation of phosphate ions in irradiated solutions of pesticides mentioned above is greater when both the pesticide concentration and the irradiation dose are increased. The concentrations of phosphate ions did not increase very significantly when aqueous solutions of diazinon and dimetoato pesticides were irradiated with and without aeration.

Formation of chloride ions

Due to the chemical structure of Imidacloprid and Procloraz pesticides, chloride ions are formed after irradiation.

The concentration of chlorides is greater when both the dose of irradiation and the pesticide concentration are increased. The maximum concentration of chloride ions was 42 ppm when 400 ppm Imidacloprid solution was irradiated at 20 kGy.

4.3. Results of pesticides degradation in aqueous solution by pH effect

The results of pesticides degradation in aqueous solutions by pH effect, using electron beam, are shown in Table 2, considering a constant concentration of a 400 ppm pesticide. The results of formed ions are shown in Table 3 for pH4.5 as an example. The concentrations of formed ions in aqueous pesticide solutions at pH = 5.5 during the irradiation process are exposed in item 4.2.1.

In general, when pH is changed from 5.5 to 4.5, the degradation of diazinon, metiocarb and imidacloprid pesticides in aqueous solutions increase in a range from 12% to 20% at 5 kGy dose, which is considered the optimal dose for the irradiation. For the other pesticides, the degradation changes are not significant. The same consideration was found when the pH is changed from 5.5 to 8.0. The chemical species and product of electron radiation effect, does not have significant changes with the pH variation of aqueous solutions studied.

TABLE 2. INFLUENCE OF pH ON PESTICIDES DEGRADATION IN AQUEOUS SOLUTION AT DIFFERENT IRRADIATION DOSE

Pesticide	Degradation (%)								
	pH = 4.5			pH = 5.5			pH = 8		
	2 kGy	5 kGy	10 kGy	2 kGy	5 kGy	10 kGy	2 kGy	5 kGy	10 kGy
DIAZINON	92.8	96.4	97.9	37.2	72.9	77.8	59	78.5	88.9
PROCLORAZ	53.9	92.1	96.5	62.8	99.6	99.8	58.3	99.2	99.7
METIOCARB	26.8	50.0	55.9	25.2	38.2	40	53.1	50.7	58.2
DIMETOATO	75.5	87.2	98.7	42.4	82.8	86.5	84.8	92.0	98.6
IMIDACLOPRID	52.3	94.5	99.3	39.2	78.8	95.2	83.7	94.9	99.8
CARBOFURAN	53.2	92.2	99.4	31.7	82.6	83.2	57.3	90.5	98.9

TABLE 3. IONS FORMED DURING IRRADIATION PROCESS OF PESTICIDES IN AQUEOUS SOLUTION AT pH4.5 AND AT DIFFERENT DOSE IRRADIATION

Pesticide	Dose (kGy)	Ions concentration (mg/l)						
		Chlorides	Nitrates	Ammonium	Sulfates	Sulfides	Phosphates	pH
DIAZINON	2	…..	8.8	2.5	2	0.09	0.0	3.19
	5	-----	9.7	3.3	8	0.08	0.08	3.17
	10	-----	19.4	4.3	8	0.09	0.14	3.08
PROCLORAZ	2	4.3	7.0	4.8	-----	-----	-----	3.81
	5	8.2	21.1	7.0	-----	-----	-----	3.46
	10	6.2	49.2	10.0	-----	-----	-----	3.27
METIOCARB	2	-----	4.8	2.1	2	0.012	-----	3.98
	5	-----	5.1	2.2	5	0.011	-----	3.85
	10	-----	5.7	2.3	7	0.014	-----	3.27
DIMETOATO	2	-----	8.8	3.3	1	0.08	0.05	3.2
	5	-----	9.6	4.3	9	0.09	0.82	3.07
	10	-----	19.3	9.2	17	0.10	1.66	2.87
IMIDACLOPRID	2	4.2	1.7	3.4	-----	-----	-----	3.86
	5	10.5	6.2	6.6	-----	-----	……	3.85
	10	12.1	15.1	7.0	-----	-----	-----	3.75
CARBOFURAN	2	-----	5.4	2.4	-----	-----	-----	5.23
	5	-----	6.7	3.5	-----	-----	-----	5.87
	10	-----	7.3	3.9	-----	-----	-----	5.40

4.4. Results of Irradiation in flower plantations

4.4.1. Analysis of pesticides degradation in effluents from flower plantations

The chromatogram comparison of irradiated and non irradiated samples from different effluents permits to determine the pesticides degradation in the flower plantation effluents. In general, pesticide concentrations decrease when they are irradiated.

The degradation study of the pesticides was carried out with samples taken from the four plantation effluents mentioned above. As an example, the chromatogram comparison before and after irradiation in Tamboroses plantation are shown in Figure 4.

The degradation percentages of the pesticides in the post-harvest water samples due to the electron beam incidence are at the range of 6.7 to 88.3% with 5 kGy irradiation dose. The analytes degradation in the irradiated samples from the stem washing process is between 16.42 and 62.74%.

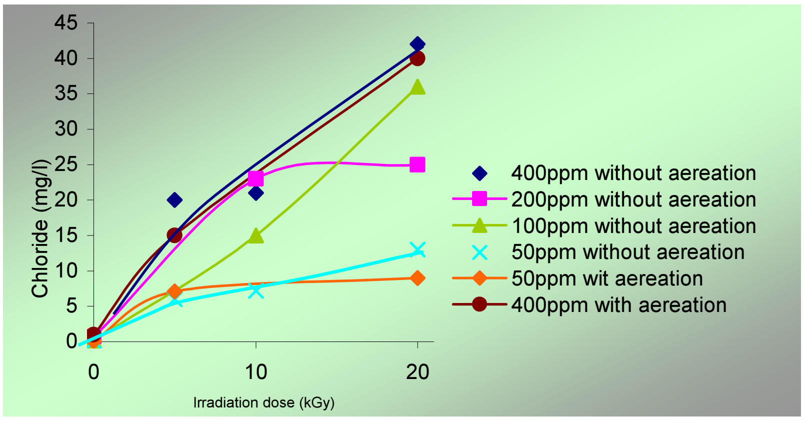


FIG. 4. Influence of electron beam on chloride concentration of imidacloprid pesticide as a function of irradiation dose, with and without aeration.

Irradiated water samples from Petyro`s flower plantation were from irrigation water, from post harvest effluent and from effluent of oxidation pool. By comparing the chromatograms of the water samples before and after irradiation a decrease of pesticide concentration and the formation of other chemical compounds was observed. The pesticides degradation in irrigation water from Petyro`s plantation with an electron accelerator has values from 22.2% to 54.5%. The incidence of electron beam on post-harvest samples produces degradation in the range of 44.0 to 98.7% with 5 kGy irradiation dose.

Pesticide degradation in irradiated samples from an oxidation pool reaches up to a range of 12.8 to 96.9%. Methiocarb pesticides, at 99.4 ppm concentration in an oxidation pool was found, and after irradiation, this concentration decreases to 82.9 ppm.

The chromatograms comparison of post-harvest water samples from Denmar flower plantation, before and after irradiation, shows the pesticide degradation and chemical compounds formed in the water sample. The degradation percentages of pesticides are within the interval of 51.1 to 92.5% with 5 kGy irradiation dose.

The chromatogram comparison of water samples from Marledian plantation, before and after irradiation, permits to establish that the incidence of electron beam degrades the pesticides and other chemical compounds present in the sample. The degradation percentage of pesticides is 43% for output channel sample and 46.7% for input channel sample.

4.4.2. pH measurements in flowers plantation effluents during irradiation process

pH was one of the analyzed parameters in the water samples from the plantations and its measurements were carried out using pH-meter HI 8521 properly calibrated. pH results are shown in Figure 17.

The water samples of the reservoirs from the four flower plantations present a pH greater than the water from post harvest.

The water from the plantation channels of Pichincha Province (Denmar and Marledian plantations) presents a basic pH, while the water from the plantation channels of Cotopaxi Province (Petyro´s and Tamboroses plantations) has a pH approximately neutral. The pH of irradiated samples from the four flower plantations after irradiation process decreases.

4.4.3. Analysis of ions in water samples of effluent from flower plantations

Ions to be analyzed in the water samples of affluent and effluents of flower plantations were selected considering the same ions mentioned in Item 3.2. The results pH, nitrites, nitrates, ammonium ion, sulfates, sulfides, phosphates and chlorides for different effluents of Tamboroses Plantation are shown in figure 5 as an example.

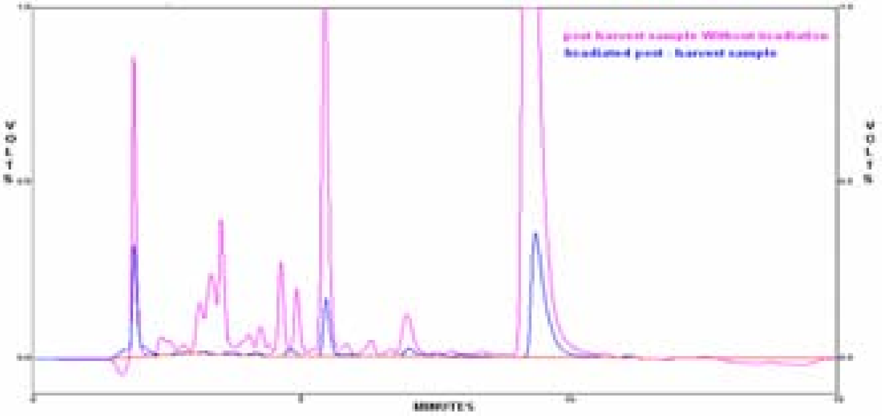


FIG. 5. Chromatograms Comparison of post harvest samples from Tamboroses plantation, before and after irradiation.

Nitrite concentrations in analyzed water samples from the flower plantations present the following characteristics:

- The channel water that flows to the plantations has 0.01 ppm nitrite concentrations in Petyro´s plantation up to 0.37 ppm in Denmar plantation.
- Nitrite concentrations in the post harvest samples without irradiation are between 0.17 and 0.28 ppm.

Nitrate concentration in the water samples from flower plantations, after irradiation, is greater than initial concentration in the water sample without irradiation. The most difference of nitrate concentration is in the stem-washing effluent from Tamboroses plantation with 3.66 ppm nitrate concentrations. The following was observed:

- Nitrate concentrations in the channel water from the four flower plantations change from 4.84 ppm in Petyro´s plantation to 12.70 ppm in Denmar plantation.
- In the post-harvest water samples from four flower plantations, the smallest nitrate concentration was 16.5 ppm in Denmar plantation and the greatest concentration was 44.0 ppm in Tamboroses plantation.
- The irradiated samples with electron beam present an increase in the concentration of nitrate ions.
- The maximum difference on concentration of nitrate ions, comparing the irradiated samples with the non irradiated samples, was 42.3 ppm in the irrigation water from Petyro`s plantation.

Concentration of ammonium Ions in the water samples from the four flower plantations shows the following:

- Concentration of ammonium ions in the channel water from Tamboroses and Denmar plantations is in the range from 0.1 to 0.21 ppm.
- The smallest concentration of ammonium ion in the analyzed post-harvest effluents from Tamboroses plantation was 1.94 ppm, and the greatest ammonium ion concentration was 4.32 ppm in the Denmar plantation.
- The water samples irradiated with the electron accelerator present an increase of concentration of ammonium ions.
- The maximum difference of concentration of ammonium ions related with irradiated and non irradiated samples was 4.26 ppm in the stem washing samples from Tamboroses plantation.

Concentration of sulfate ions in the water samples from the four flower plantations shows the following:

- Sulfate ions were found in the input channel water to the flower plantations from 4 ppm in Tamboroses plantation to 39 ppm in Petyro`s plantation.
- Sulfate concentration in the post-harvest effluent from the flower plantations reaches values of 17 ppm in the Tamboroses plantation and 320 ppm in Petyro`s plantation.
- Sulfate concentration presents an increase when it is irradiated with electron beam.
- The maximum difference of concentration was 18. 5 ppm in the post harvest samples from Denmar plantation, comparing the results of irradiated and non irradiated samples.

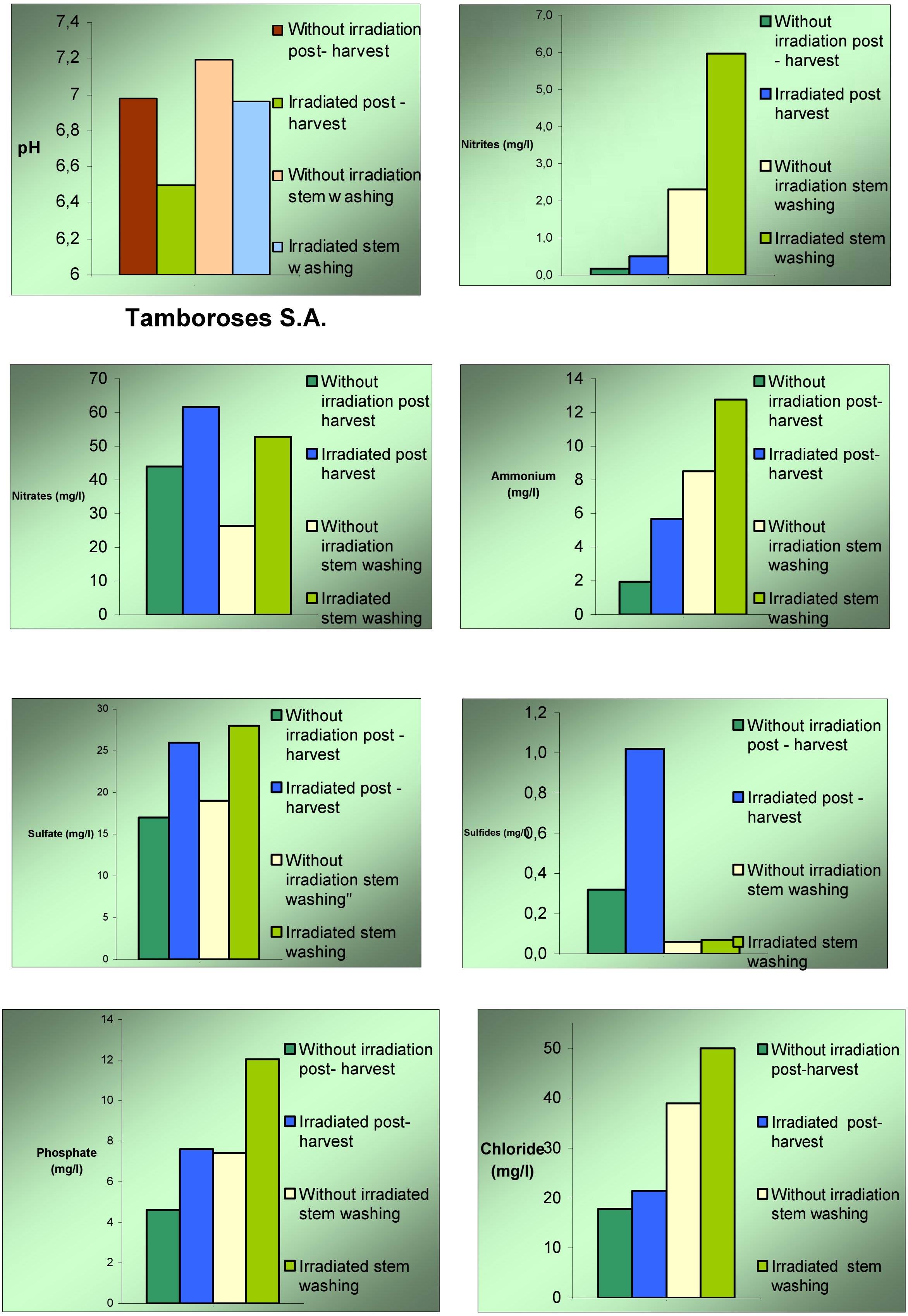


FIG. 6. Potential hydrogen, concentration of nitrites, nitrates, ammonium ion, sulfates, sulfides, phosphates and chlorides in different effluents of Tamborose Plantation, before and after irradiation.

Sulfide concentration in the irradiated and non irradiated samples from the four flower plantations shows the following:

- Concentrations of sulfide ions analyzed in the channel water from the flower plantations are not important, since those values oscillate between 0.0 and 0.01ppm.
- The maximum concentration of sulfides in the post harvest effluents from the flower plantations analyzed was 0.32 ppm in Tamboroses plantation and 0.06 ppm in Denmar plantation.
- An increase of concentration of sulfide ions is obtained in irradiated samples from flower plantations.
- The maximum difference of concentration was 0.7 ppm, comparing the sulfide concentration in the effluents before and after irradiation for the post- harvest samples from Tamboroses plantation.

Phosphate concentration in both affluent and effluents from the four flower plantations shows the following:

- Phosphate concentrations in the water channels from the four flower plantations reach to values of 0.78 ppm in Petyro`s plantation and 3.3 ppm in Tamboroses plantation.
- Phosphate concentration in the post harvest effluents has values from 0.3 ppm in Petyro`s plantation and 4.6 ppm in Tamboroses plantation.
- The results of phosphate concentration analyzed in the effluents of flower plantations have an increase after irradiating with accelerated electrons.
- The greater concentration of phosphates in the irradiated samples was found in the stem washing from Tamboroses plantation, while the difference between the phosphate concentration, before and after irradiation, was 4.6 ppm.

Chloride concentration in the analyzed water samples from four flower plantations shows the following:

- The water channels that plantations are using have chlorides 2.3 ppm in Denmar plantation and 24.6 ppm in Tamboroses plantation.

Chloride concentration in the post harvest effluent from the flower plantation reaches 17.7 ppm in Petyro`s plantation and 45.0 ppm in Denmar plantation.

- An increase in chloride ion concentration is obtained when the water samples from flower plantations are irradiated.

Cyanide Ions were not found in all samples treated in this study.

5. CONCLUSIONS

- When the aqueous solutions of the six commercial pesticides (diazinon, dimetoato, procloraz, metiocarb, imidacloprid and carbofuran) were irradiated with initial pesticide concentrations at a range of 400 to 100 ppm, it was observed that the optimal conditions for the irradiation of these pesticides were the following:
    - Irradiation: without aeration
    - Irradiation dose: 5 kGy.
- When the initial concentration of pesticide in aqueous solutions under the irradiation process is greater, the degradation percentage is smaller.

- The most radiosensible pesticide is procloraz, which reaches a degradation percentage of 99% with a 50 ppm pesticide concentration and a 5 kGy irradiation dose without aeration.
- Of the studied commercial pesticides, the least sensible pesticide to the radiation is the metiocarb pesticide, which has a maximum degradation percentage of 67.7% with a 50 ppm pesticide concentration and a 5 kGy irradiation dose with aeration.
- The aerated of solutions of the commercial pesticides during the irradiation does not improve the pesticide degradation, except for the metiocarb pesticide solutions, which were irradiated with aeration and its degradation percentage was increased up to 18%.
- With the initial concentrations of pesticide in the range of 50 to 400 ppm, the rates of pesticide degradation were increased with the increase of the irradiation dose up to 5 kGy. After that, the degradation rates decrease with the increase of the irradiation dose, reaching an asymptotic form for higher doses.
- The concentration of analytes formed in the pesticide solutions (nitrites, nitrates, ammonium ion, sulfates, sulfides, phosphates and chlorides) was increased after the irradiation process.
- pH of the irradiated aqueous solutions decreases.
- The pesticides degradation in irradiated effluents from flower plantations Denmar S.A, Marledian, Petyro`s and Tamboroses S.A. was reached to a maximum of 92.5%.
- The changes of pH in pesticide solutions do not have a significant effect on the formed ions during the irradiation process.
- Irradiation with the accelerated electron beam is a good alternative to reduce the pesticide contamination in the effluents of flower cultivation.

REFERENCES

[1] Universidad Laica Vicente Rocafuerte, “Pesticides”, Seminary on the use and handling of pesticides in tropical Plantations, Ecuador (1986) 25–26.
[2] PRIMO, E., CARRASCO, J., “Química Agrícola”, volumen II, editorial Alhambra, first edition, Spain (1977) 1–2.
[3] Vademécum, Florícola, Edifarm, second edition, Ecuador (2001) 389–390.
[4] Data base of Central Bank of Ecuador, year 1978–2005.
[5] DOLE, M., “The Radiation Chemistry of Macromolecules”, Academic Press, New York (1972) 336–338.
[6] M., TROJANOWICZ, P., DRZEWICZ, “Monitoring of toxicity and determination of products in degradation of selected pesticides using ionizing Radiation”, Report on Remediation of polluted water and wastewater of radiation processing, International Atomic Energy Agency, Warsaw, Poland (2004).
[7] PAZMIÑO, O., CASTRO, R., Ecuadorian Service Laboratory of SESA (Minister of Agriculture) and Toxicology Laboratory of Ecuadorian Atomic Energy Commission.
[8] Technical specification of pesticides Diazinon, Dimetoato, Procloraz, Carbofuran, Metiocarb, Imidacloprid of suppliers.
[9] DESSOUKI, A.M., ABDEL AAL, S.E., SOKKER, Y.H.H. “Degradation of Some Pesticides in Aqueous Solution by Electron Beam and Gamma Irradiation”, Seventh Conference of Nuclear Sciences & Applications, Cairo, Egypt, 6–10 Febrero (2000).

IRRADIATION TREATMENT OF TEXTILE DYE CONTAINING WASTEWATER

[a]E. Takács[a], L. Wojnárovits [a], T. Pálfi [b], S.S. Emmi[b]
[a]Institute of Isotopes, Budapest, Hungary
[b]Istituto per la Sintesi Organica e la Fotoreattività (ISOF), CNR, Bologna, Italy

Abstract

In the framework of the CRP are the high-energy radiation-induced degradation of an H-acid containing azo dye Apollofix-Red (AR-28), H-acid, (4-amino-5-hydroxynaphthalene-2,7-disulfonic acid, I) and its derivative, 4-hydroxynaphthalene-2,7-disulfonic acid (II) was studied in aqueous solution by using pulse radiolysis with kinetic spectroscopic detection for transient measurements and also by gamma radiolysis with UV-VIS spectroscopy and gradient HPLC separation with diode array detection for following the destruction of the dye molecules and measuring the products. The reactions of hydrated electron (e_{aq}^-) and hydroxyl ($^{\bullet}OH$) radical were investigated separately. The $^{\bullet}OH$ reacts with the unsaturated bonds of the molecules. In the further reactions of the $^{\bullet}OH$ adduct radicals, the AR-28 molecules partly reform with a slightly modified structure. The once reacted AR-28 molecules also have high reactivity towards the $^{\bullet}OH$ radicals. For these reasons, the efficiency of $^{\bullet}OH$ radicals in discoloration of the solution is relatively low it is below 0.5. The efficiency is much higher close to unity for the e_{aq}^-. The reaction of e_{aq}^- with AR-28 leads to an immediate destruction of the colour giving center. The reaction of e_{aq}^- and $^{\bullet}OH$ with I and II leads mainly to the formation of cyclohexadienyl type radicals; however, I H-atom elimination from the NH_2 group is also observed yielding anilino type radicals. The cyclohexadienyl and the anilino type radicals decay in a millisecond. In the $^{\bullet}OH$ reactions, as a first step of decomposition, hydroxylated products and quinone type compounds formed that absorb in the UV-visible region. These molecules at higher doses by further decomposition of the ring structure transform to open chain alcohols, carboxylic acids, etc. In the case of e_{aq}^- the primarily formed products have absorption spectra shifted to the low wavelength region, indicating the destruction at of least one aromatic ring. At 0.25 mmol dm^{-3}, concentration 4–6 kGy dose is sufficient to destruct the starting compounds.

1. INTRODUCTION

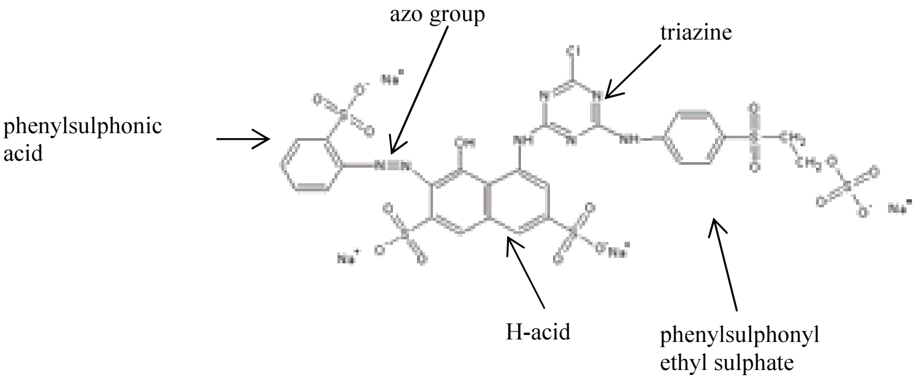
The azo dyes are very stable and resistant to chemical processes. Thus, it is important to remove these dyes from industrial effluents. Conventional methods (mechanical screening, sedimentation, biological treatment, biofilters) alone are usually not very effective in decolouration and degradation of these compounds. Several methods can be used in combination with the conventional techniques to solve this problem. In the so-called advanced oxidation processes (AOP's), hydroxyl radicals are the mainoxidants for the degradation of organic pollutants [1, 2].

Environmental remediation using radiation chemistry is one of the most promising techniques among AOP's [3–6]. UV-peroxide, ozonation, the photo-Fenton process, photocatalysis, and sonolysis are some of the other popular methods employed to oxidize the organic compounds (see for example [1, 2]). These methods are based on the generation and use of hydroxyl radicals as the primary oxidant for the degradation of organic pollutants.

Most papers published in the field of radiation treatment of wastewater report on decolouration of the wastes by $^{\bullet}OH$ radicals [7, 8], and only a few papers deal with the reaction of e_{aq}^- and H atom. The products of decomposition were rarely separated and identified individually; therefore, we know very little about the mechanism of decomposition [9, 10].

In the present paper, we summarize the results obtained in our laboratory on the radiation degradation of azo dyes. They are synthetic organic dyes used in the textile, cosmetic, paper, drug and food-processing industries. They are brightly coloured compound's, and their colour is dependent on the chromophore and the extent of conjugation. The H-acid containing dyes belongs to the class of reactive dyes having a usually brilliant deep red colour.

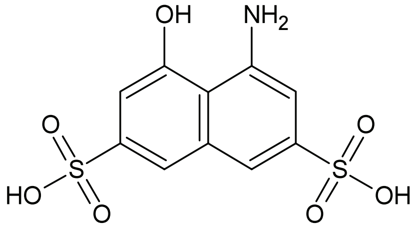
The degradation of Apollofix-Red SF-28 (AR-28), a mono azo compound having maximum absorbances at 514 nm and 532 nm with $\varepsilon_{532} = 31400\ \mathrm{mol^{-1}\ dm^{3}\ cm^{-1}}$ [11–13], was followed both by UV-VIS spectroscopy and gradient ionpair HPLC with diode array detection [14].



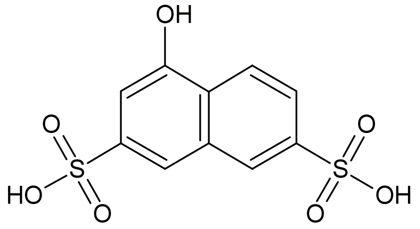
Apollofix-Red SF-28

The dye molecule is relatively large. Several degradation products are expected in its irradiation. We were especially interested in transformations altering the colour-giving part of the molecule (phenylsulphonic acid–azo group–H-acid). Changes in the other part of the molecule, on the phenylsulphonyl ethyl sulphate group, connected to the triazine ring through an amine group, just slightly modify the color.

The reactions of H-acid, (4-amino-5-hydroxynaphthalene-2,7-disulphonic acid, **I**) and its derivative, 4-hydroxynaphthalene-2,7-disulphonic acid (**II**), are also discussed.



4-amino-5-hydroxynaphthalene-2,7-disulphonic acid
(H-acid, **I.**)



4-hydroxynaphthalene-2,7-disulphonic a
(**II.**)

Reverse phase ion pair chromatography is widely used to separate sulphonated aromatic compounds [15]. In our analyzes, tetrabutyl ammonium hydrogensulphate was used as ionpar forming reagent. By this method, it is possible to separate molecules with different numbers of sulpho groups. The elution times are in reverse order with the number of sulpho groups in the molecule. The method also allows separating compounds substituted with hydroxy or amino groups in different positions.

2. EXPERIMENTAL

2.1. Chemicals

AR-28 was obtained from Taiheung Corporation (Kyunggido, South Korea) and was used without purification. Its structure and stability were checked by NMR and FTIR spectroscopy. **I** and **II** were manufactured by Sigma-Aldrich Co. and were used after purification. Usually 0.085 $\mathrm{mmol\ dm^{-3}}$ concentration solutions were used in the experiments. We used perchloric acid, sulphuric acid or sodium hydroxide to set the pH of the solutions.

Metanol (HPLC grade) and tetrabutyl-ammonium-hydrogen sulfate (TBAHS) were obtained from Sigma-Aldrich, and *tert*-butanol from Spektrum-3D.

2.2. Radiolysis

Deoxygenation of the solutions was carried out by bubbling with appropriate gases for 25 minutes before irradiation and continued during the experiments.

The gamma radiolytic experiments were carried out using a ^{60}Co irradiation facility with a dose rate of 3.0 kGy h^{-1} as determined by Fricke dosimetry ($G(Fe^{2+}) = 15.6\ (100\ eV)^{-1}$). The solutions were irradiated in Pyrex glass containers. The solutions were analyzed before and after the reaction by using a Jasco 550 UV-VIS spectrophotometer and HPLC system.

The reactive transient intermediates were recorded by using pulse radiolysis facilities. The set-up of the Institute of Isotopes works with 800 ns pulses of 4 MeV electrons. The changes in the absorbance were followed with UV-VIS kinetic spectrophotometry in 2 cm cells [16]. Some pulse radiolysis experiments were also carried out in Bologna with the 20 ns pulses of the 12 MeV electron accelerator of the Istituto per la Sintesi Organica e la Fotoreattivita [17] in 5 cm cell. The dose/pulse values were generally between 5 and 20 Gy and were determined by tiocyanate dosimetry.

2.3. HPLC analysis

The chromatographic system consisted of a Jasco PU-2089Plus quaternary gradient pump, a Jasco MD-2015Plus diode-array Multiwavelenght Detector and a Nucleosil 100 C18 column (Teknokroma®) (pore size 5 µm, length 15 cm, diameter 0.4 cm). Gradient-elution ion-pair separations were made using 50 mmol dm^{-3} aqueous solution of TBAHS at pH6.1 and methanol. All mobile phases were filtered using a Millipore 0.45 µm filter and were degassed by ultrasonication before use. The separations were made at room temperature using injection volume of 10 µl and flow-rate of 0.8 ml/min.

2.4. The reaction systems

The radiolytic reactions were investigated by applying the standard radiation chemical techniques. The radiolysis of water supplies hydrated electron (e_{aq}^-), hydroxyl radical ($^\bullet OH$) and hydrogen atom (H) reactive intermediates with G-values (species $(100\ eV)^{-1}$) shown in equ. (1). In order to reduce the number of reactive intermediates, the reactions of $^\bullet OH$ radicals were studied in N_2O saturated solutions. In such solutions, the hydrated electrons are converted to $^\bullet OH$ radicals (Reaction (2)) [18]. When the e_{aq}^- reactions were investigated, the solutions were bubbled with N_2 for deoxygenation and contained 0.5 mol dm^{-3} *tert*-butanol in order to transform the $^\bullet OH$ radicals to less reactive $^\bullet CH_2C(CH_3)_2OH$ radicals (3). H atoms react with a low rate coefficient with *tert*-butanol (4).

$$H_2O \rightsquigarrow e_{aq}^-, {}^\bullet OH, H \qquad G(e_{aq}^-) = 2.7;\ G({}^\bullet OH) = 2.7;\ G({}^\bullet H) = 0.6 \qquad (1)$$

$$e_{aq}^- + N_2O + H_2O \rightarrow N_2 + OH^- + {}^\bullet OH \qquad k_2 = 7 \times 10^9\ mol^{-1}\ dm^3\ s^{-1} \qquad (2)$$

$${}^\bullet OH + CH_3C(CH_3)_2OH \rightarrow H_2O + {}^\bullet CH_2C(CH_3)_2OH \qquad k_3 = 6 \times 10^8\ mol^{-1}\ dm^3\ s^{-1} \qquad (3)$$

$$H + CH_3C(CH_3)_2OH \rightarrow H_2O + {}^\bullet CH_2C(CH_3)_2OH \qquad k_4 = 1 \times 10^6\ mol^{-1}\ dm^3\ s^{-1} \qquad (4)$$

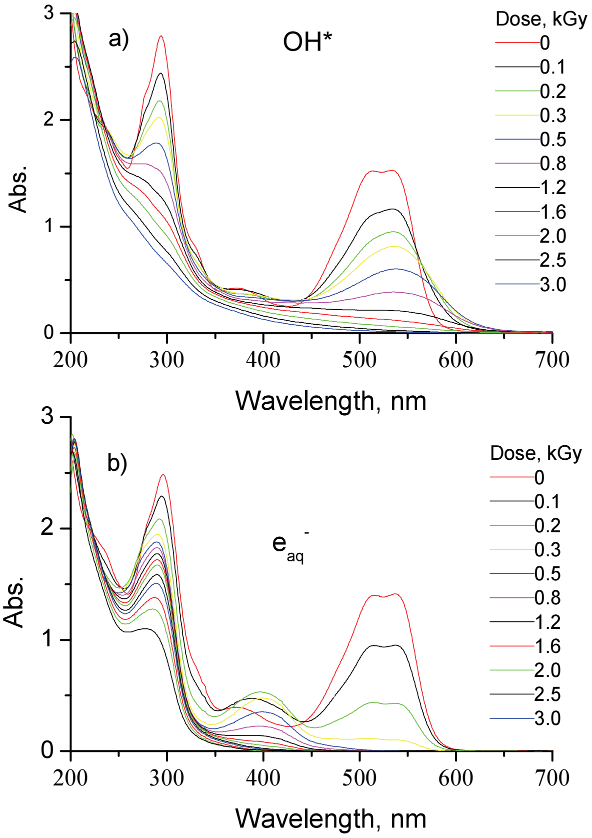


FIG. 1. Discolouration of 8.5 × 10^{-5} mol dm^{-3} concentration aqueous AR-28 solutions in the reactions of hydroxyl radicals in N_2O saturated solutions a), and in the reactions of hydrated electrons in N_2 saturated 0.5 mol dm^{-3} tert-butanol containing solution b) (gamma irradiation).

3. RESULTS

3.1. Apollofix-Red SF-28 (AR-28)

3.1.1. Absorption spectra and separation

Figure 1 (0 dose) shows the absorption spectrum taken in 8.5 × 10^{-5} mol dm^{-3} solution of AR-28 without irradiation. In addition to the double peak band between 450 nm and 600 nm, mentioned already in the Introduction, the spectrum has another intensive band at λ_{max} = 297 nm with $\varepsilon_{max} \approx$ 50000 mol^{-1} dm^{3} cm^{-1}. Using TBAHS as eluent for the HPLC separation of unirradiated AR-28 in aqueous solution, we obtained two components AR-28 I and AR-28 II, and no other resolvable peaks were observed. These two components had practically the same absorption spectrum with different elution times; however, the ratio of the two peaks could be influenced by different procedures. For instance, in alkaline solutions the intensity of AR-28 I peak decreased, and this decrease was compensated by the increase of the intensity of the AR-28 II peak. Therefore, we assume that one of the peaks, AR-28 I, belongs to Apollofix-Red SF-28 with the formula shown in the Introduction, and the other belongs to its derivative with hydrolysed sulphonyl group from the ethyl moiety [15]. Since this part of the molecule is not in conjugation with the H-acid part, the hydrolysis practically does not influence the visible absorption spectrum.

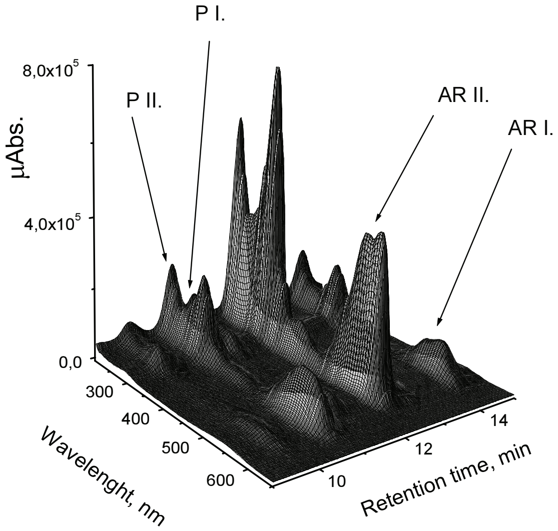


FIG. 2. Three dimensional HPLC chromatogram showing the separation of components in N_2O saturated solution irradiated with 0.6 kGy dose.

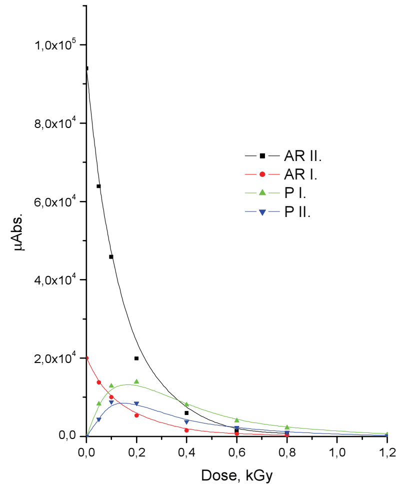


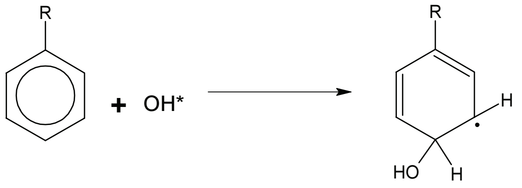
FIG. 3. Destruction of AR-28 molecules and formation of degradation products in OH radical reactions as detected by HPLC at 530 nm.

3.1.2. Reactions of $^\bullet$OH

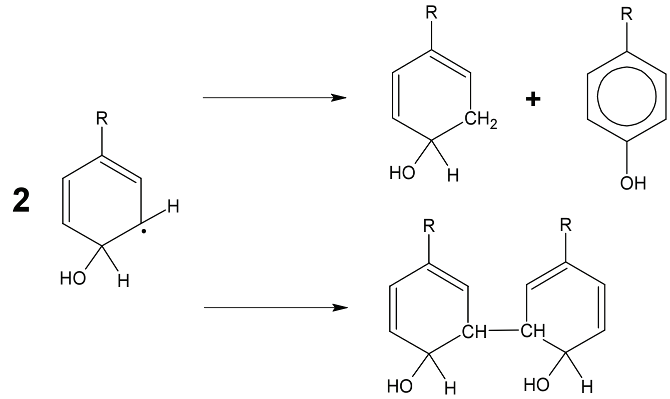
In the irradiated solution, besides the AR-28 I and AR-28 II components, another two major components and several other minor components were detected (Fig. 2.). One of the intermediate products (P I) has practically the same absorption spectrum as the starting compounds; whereas, in the case of the other product (P II), the spectrum is slightly shifted to longer wavelengths, as compared to the spectra of the non-reacted molecules.

The destruction of AR-28 I and AR-28 II, and the formation of the degradation products, P I and P II, as a function of absorbed dose were measured by HPLC (Fig. 3). The absorbances of AR-28 I and AR-28 II decrease quickly with the dose of irradiation. P I and P II show maximum absorbances at 0.2 kGy dose. Especially at higher doses other components were also observed on the HPLC chromatograms. Above 1.5 kGy dose, all of the compounds that show absorbance in the VIS range disappeared.

From the dose dependence curves, it seems that the reactivity of the intermediate products towards the $^{\bullet}$OH radicals is similarly as high as that of the starting compounds. This is obvious also from Fig. 1a, which shows the absorbances measured both in irradiated and unirradiated solutions. This dose dependence can be due to a stepwise destruction of colour giving center in the molecule. Finally, we obtain compounds having no light absorption in the visible range.



(5)



(6a)

(6b)

Large molecules, like AR-28, have several places for the attack by $^{\bullet}$OH radicals. It is well known that $^{\bullet}$OH radicals attack the aromatic rings with practically diffusion-limited rate coefficients, forming cyclohexadienyl-type radicals [19]. The reaction of this radical with another cyclohexadienyl radical (or with any other radical present) may regenerate the aromatic ring structure. Above, we show these reactions on the example of R group (alkyl group or halogen atom) substituted benzene.

In the disproportionation reaction (6a), an aromatic molecule containing an additional OH group also forms. If similar reaction of the $^{\bullet}$AR-28-OH adduct radical takes place, we obtain an AR-28 molecule that has an additional OH group attached to one of the aromatic rings. If this ring belongs to the conjugated phenylsulphonic acid–azo group–H-acid part of the molecule, the absorption spectrum is slightly shifted to longer wavelength; thus, we obtain P II. However, if the product formation takes place after $^{\bullet}$OH addition to the aromatic ring on the phenylsulphonyl ethyl sulphate part of the molecule, the final product OH-group-containing molecule (P I) will practically have the same visible absorption spectrum as AR-28 since the chromophoric group, that is the conjugated part of the molecule, is not altered. As Fig.1a shows, the absorbance in the visible range gradually decreases with the increasing dose of irradiation. At the same time there is a shift of the band to longer wavelengths supporting the idea of incorporation of an OH group into the chromophoric part of the molecule.

OH addition to a triazine ring, based on analogies [20], is a slow reaction. The $^{\bullet}$OH radicals may add to the azo group. This reaction probably immediately leads to the destruction of the intensive color in the visible range [21].

Transient absorption spectra were taken at several time delays after the electron pulse in N_2O-saturated solution where the $^{\bullet}$OH radical reacts with the dye molecules (Fig. 4). Due to the specialities of the pulse radiolysis on the y axis of the figure Δ-absorbances are shown, i.e. absorbance differences between the irradiated solution and the unirradiated one taken at given time intervals after the pulse. These Δ-absorbances can be positive when the absorbance of the intermediate formed during the pulse is higher than the absorbance of the depletion of the absorbance of the dye at the wavelength of the measurement. Such positive Δabsorbances are seen in the 330–460 nm range and above 600 nm on Fig. 4. The cyclohexadienyl-type radicals show characteristic bands between 300 and 400 nm. In the transient spectrum, there is an intensive fading after the pulse in the visible part of the spectrum between 460 and 585 nm with an initial yield of c.a. G = 3 (100 eV)$^{-1}$. In this range, there is an intensive absorbance in the unirradiated sample. After the initial fading, some part of the color is regenerated during the time of the transient recording (~9 ms). The fading can be attributed to the reaction of the $^{\bullet}$OH radical with the chromophoric part of the molecule, and the regain of the absorbance is probably attributed to the regeneration of the aromatic structure.

The time dependence of the transient absorbance at 355 nm obtained in pulse radiolysis experiments is shown in Fig. 5. The AR-28 concentration of the starting solution was 8.5×10^{-5} mol dm^{-3}, and with the dose/pulse 20 Gy applied, an initial $^{\bullet}$OH radical concentration of $\sim 1 \times 10^{-5}$ mol dm^{-3} was introduced into the system. Under these conditions the build-up is finished in about 10 μs, suggesting a rate coefficient of 1.2×10^{10} mol^{-1} dm^{3} s^{-1} for the reaction between AR-28 and $^{\bullet}$OH radical. As the figure shows, the absorbance changes were not finished in the 9 ms time window of the measurement, and changes were observed even 1 s after the pulse.

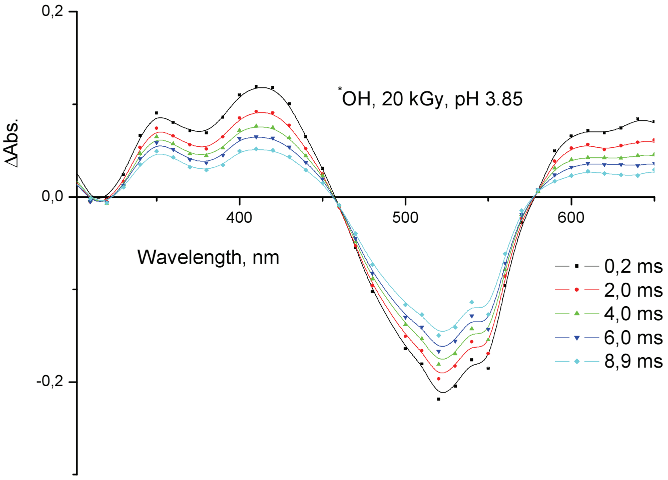


FIG. 4. Transient absorption spectra taken at various intervals after 20 Gy pulses of accelerated electrons in 8.5×10^{-5} mol dm^{-3} AR-28 solutions saturated with N_2O.

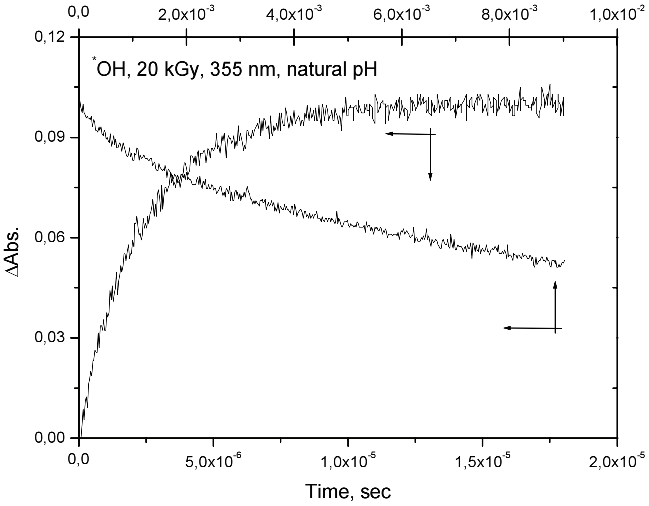


FIG. 5. Time dependence of the absorbance build-up and decay measured in pulse radiolysis experiments in 8.5×10^{-5} mol dm^{-3} AR-28 containing N_2O saturated solution with 20 Gy/pulse dose, at 355 nm, natural pH. The fast build-up was measured with the Bologna LINAC. Tthe trace of the slow decay was taken in Budapest. Both measurements were normalized to 2 cm cell length.

3.1.2. Reactions of e_{aq}^-

The HPLC chromatogram of the sample obtained in irradiating N_2-saturated AR-28 solution containing 0.5 mol dm^{-3} tert-butanol with a dose of 0.6 kGy is shown on Figure 6. By comparing Fig. 6 and Fig. 2 reveals that products formed during e_{aq}^- reactions have less absorbance in the visible range than the products formed in the case of $^{\bullet}OH$ reactions. It is obvious from Fig. 1b and 7 that e_{aq}^- is highly effective in destroying AR-28. It seems that while the $^{\bullet}OH$ reaction does not necessarily causes the destruction of the colour centre, in the e_{aq}^- reaction the colour giving center of the molecule is altered, resulting in decolouration of the dye solution.

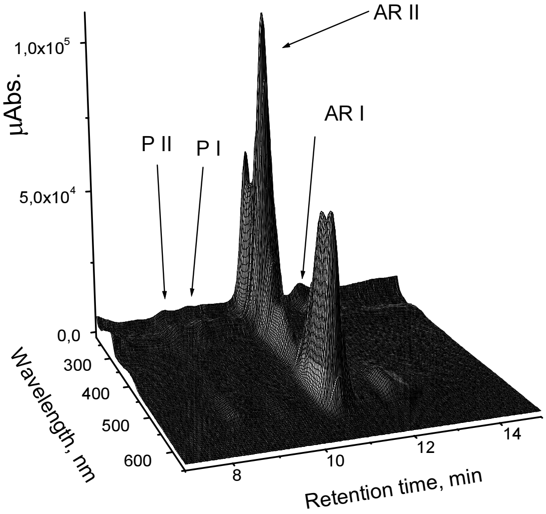


FIG. 6. Three dimensional HPLC chromatogram showing the separation of components in N_2 -saturated solution containing 0.5 mol dm^{-3} tert-butanol, irradiated with 0.6 kGy dose.

Based on the analogous reactions taking place in azobenzenes [9, 22], the hydrated electrons react with the azo group quickly, and the radical anion quickly protonates, forming a hydrazyl radical:

$$\text{-N=N-} + e_{aq}^- \longrightarrow \text{-N}^{\bullet}\text{-N}^-\text{-} \xrightarrow{+H_2O} \text{-N}^{\bullet}\text{-NH-} + OH^- \qquad (7)$$

The effective fading may be due to a fast reaction of e_{aq}^- with the unreacted AR-28 molecules, as well as to the low reactivity of the e_{aq}^- with the transformed molecules.

The transient absorption spectra formed in the reaction of e_{aq}^- with AR-28 were similar to those observed in the reaction of $^{\bullet}OH$ radical. It also shows the intensive decoloration between 450 and 585 nm; however, the absorbance above 600 nm was much weaker here than in the case of the $^{\bullet}OH$ adduct spectrum. Also, the regeneration of the absorbance in the visible range was smaller. This is in agreement with our conclusion based on the final product measurements that in the case of e_{aq}^- reactions there is an immediate destruction of the colour giving center.

The destruction of AR-28 I and AR-28 II by e_{aq}^-, and the formation of the degradation product, P I, as a function of absorbed dose were measured by HPLC (Fig. 7). The absorbances of AR-28 I and AR-28 II decrease quickly with the dose of irradiation. P I and P II show maximum absorbances at 0.2 kGy dose. Above 0.8 kGy dose, all of the compounds that show absorbance in the VIS range disappeared.

In Fig. 8, the concentration of AR-28 molecules, as measured by HPLC, is shown as a function of the amount of $^{\bullet}OH$ or e_{aq}^- reactive intermediates produced in the system. The amount of reactive intermediates produced was calculated based on the absorbed dose by using radiation chemical yields of $G(e_{aq}^-) = 2.7\ (100\ eV)^{-1}$ and $G(^\bullet OH) = 5.4\ (100\ eV)^{-1}$. The figure clearly shows that e_{aq}^- is much more effective in transforming AR-28 to products than $^\bullet$OH radical. The initial efficiency (i.e., the efficiency at low dose) for the e_{aq}^- is close to unity, and the same value for the $^\bullet$OH radical is less than 0.5. (The higher reactivity of e_{aq}^- as compared to $^\bullet$OH, is in disagreement with results on some other azo dyes [3, 8] which may reflect the effect of the molecular structure.) These findings are of theoretical and practical importance.

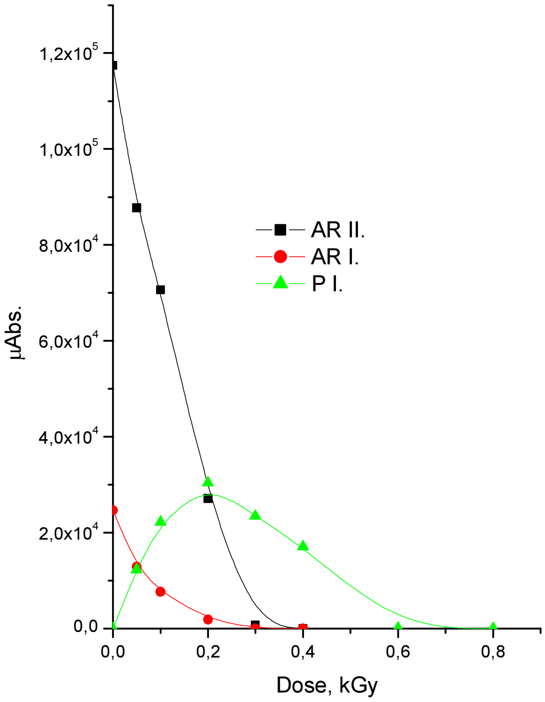


FIG. 7. Destruction of AR-28 molecules and formation of degradation products in e_{aq}^- reactions as detected by HPLC at 530 nm.

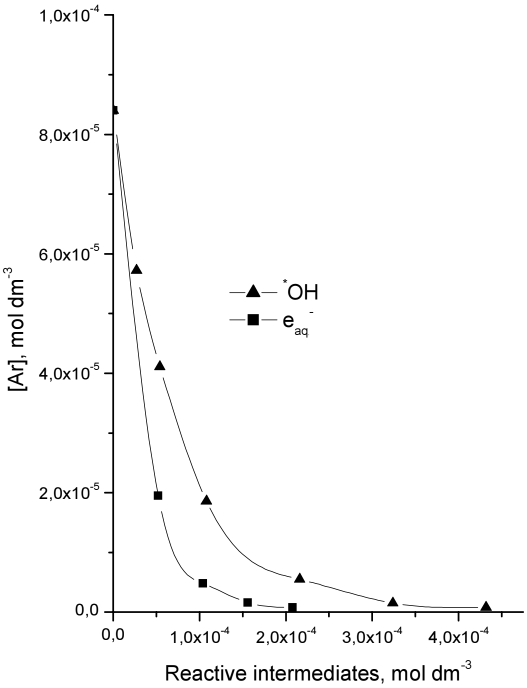


FIG. 8. AR-28 concentration as a function of the number of moles of OH or e_{aq}^- reactive intermediates of water radiolysis produced in 1 dm^3 solution.

3.2. H-acid (4-amino-5-hydroxynaphthalene-2,7-disulfonic acid, I) and its derivative (4-hydroxynaphthalene-2,7-disulfonic acid, II)

3.2.1. Absorption spectra and separation

The absorption spectra of compounds **I** and **II** are shown in Fig. 9. The shapes of both spectra were changing with the pH of the solution. The inset of Fig. 1 shows the pH dependence of absorbance for **I** at 375 nm. This compound has two acid-base transitions. One of them with $pK_1 = 3.54$ is connected with deprotonation/protonation of the amino group, and the other at $pK_2 = 8.64$ is due to the ionization of the phenolic OH group. Compound **II** has only one acid/base transition, due to ionization of the phenolic OH group with $pK_1 = 8.9$. We made our measurements at pH ≈ 5 where the neutral forms are predominant for both compounds.

With the applied separation method, we achieved good resolution of the products from the starting compounds **I** and **II** eluted at 13 and 17 minutes, respectively. We show the dose dependencies of the absorbancies (at the maximum absorbance) of the starting compound and those of the main products formed in the reaction between $^{\bullet}OH$ radicals and **I** or **II** ($c = 0.25$ mmol dm^{-3}) on Figures 10 and 11, respectively.

On Figure 10, the PI, PIII and PIV product formation *in $^{\bullet}OH$ radical reaction with **I*** already starts at small doses, and the curves go over a maximum at about 1 kGy dose. There is a delay in the formation of PII and the maximum is shifted to about 3 kGy. The decay of H-acid and the formation of PI, and PIV show some parallelism; however, in the case of PII, we may assume that its formation is connected with decay, either of PI or PIV product. Product PII is probably due to a secondary decomposition. Because of the lack of authentic samples, we were not able to individually identify the compounds formed. We directly proved that **I** does not transform to **II**.

The spectra of H-acid and the products have strong absorption bands with single (H-acid) or double (products) peaks between 200 and 300 nm. All of the product spectra have wider bands above 300 nm than H-acid (Fig. 10, Inset). In the case of H-acid, the second maximum is around 350 nm and should be connected to the aromatic system. The long wavelength bands of the products are between 400 and 700 nm. Such wide structureless bands in the visible range are usually connected to quinoidal systems [23]. Solution containing **I** due to irradiation turned to red. By increasing the dose, this red colour disappeared.

The products formed from **I** completely disappear at ~ 6 kGy dose (Fig. 10). The methanol eluent used in the HPLC measurement has a considerable light absorbance at < 250 nm, complicating the observation of products being present after higher dose irradiation. The new (secondary or tertiary) products have light absorptions below 250 nm. In this range, such simple compounds as the hydrocarbons and alcohols have their characteristic light absorptions. The kinetic curves of the products of ***II** formed in $^{\bullet}OH$ radical reaction* on Fig. 11 are similar to the dose dependencies of the products from **I** on Fig. 10. PI and PII form quickly and decay relatively quickly. There is some retardation in the formation of the PIII and PIV. Their transformation to further products is relatively slow. We may suppose that PIII and PIV are secondary products. The PI–PIV products formed in $^{\bullet}OH$ radical reaction with **II** have very low absorbances, complicating the evaluation of the results. This low absorbance is probably due to some decrease of the electron conjugation in the molecule. We may assume that in one of the aromatic rings of the naphthalene moiety, one of the double bonds is saturated, ceasing in this ring the aromatic conjugation.

In the solutions saturated with N_2 containing *tert*-butanol, when *e_{aq}^- reacts with the solute,* we found considerable distractions of compounds **I** and **II** (see Fig. 12). However, the efficiencies were smaller than those found in the reaction of $^{\bullet}OH$ radical. The spectral and kinetic characteristics of the intermediates formed in e_{aq}^- and in $^{\bullet}OH$ reactions, as we showed previously, are different. At the same time, the chromatograms reveal different final products. The absorption spectra of the stable products formed in e_{aq}^- reactions are shifted to the low wavelength region, where the identification of the products spectra is difficult due to the strong absorption of the eluent. The low wavelength absorption here may again mean that a double bond in one of the rings is saturated during the first final product-forming reactions. The shift of the spectrum is due to the decrease of conjugation.

Fig. 12 compares the dose dependence curves of **I** and **II** disappearance in e_{aq}^- and $^{\bullet}OH$ reaction as measured by the HPLC method. The *G*-values calculated from the initial slopes and the efficiency values are collected in Table 1.

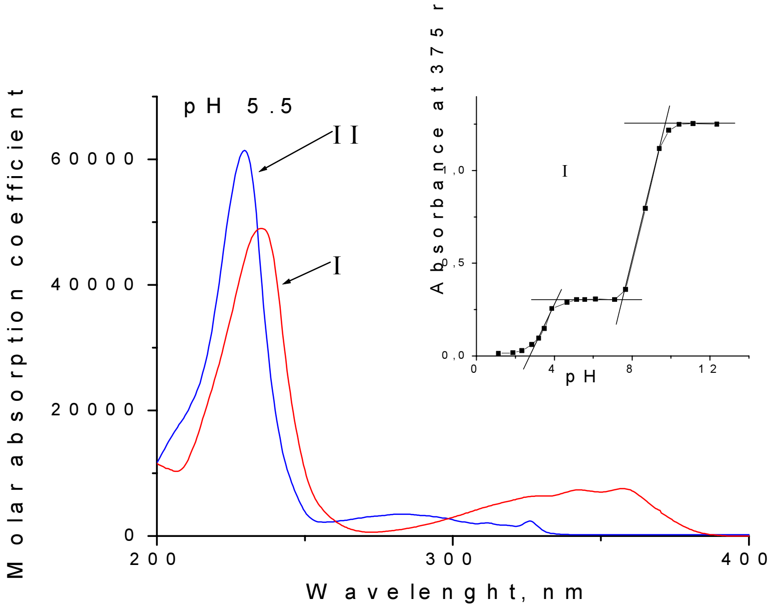


*FIG. 9. Absorption spectra of **I** and **II** at pH5.5. In the Inset we show the pH dependence of absorbance of **I** at 375 nm.*

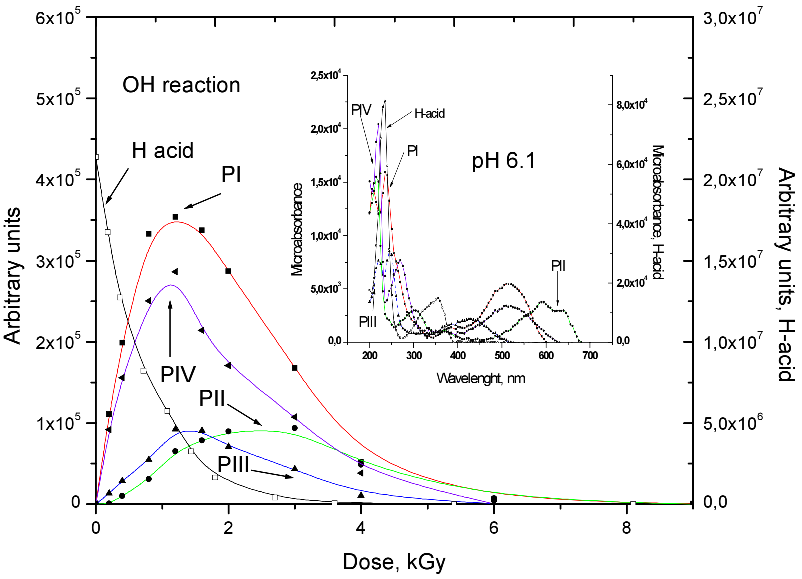


*FIG. 10. Dose dependences of the absorbancies of the starting compound and the products formed in the reaction between $^{\bullet}OH$ radicals and **I**, c = 0.25 mmol dm^{-3}. PI: maximum at 236 nm, t = 11.3 min, PII: maximum at 592 nm, t = 15.8 min, PIII: maximum at 334 nm, t = 16.5 min, PIV: maximum at 240 nm, t = 21.5 min, H-acid: maximum at 233 nm, t = 13.4 min. The Inset shows the absorption spectra of the main compounds formed and that of the H-acid.*

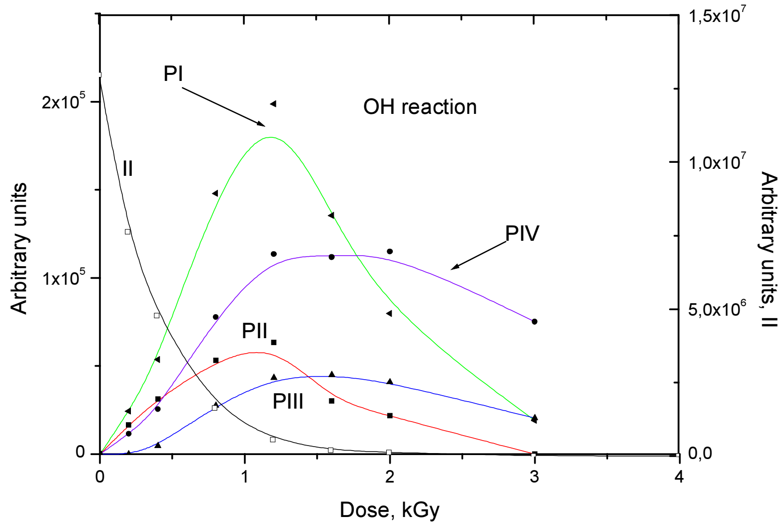


*FIG. 11. Dose dependences of the absorbancies of the starting compound and the products formed in the reaction between $^{\bullet}$OH radicals and **II**, c = 0.25 mmol dm^{-3}. PI: maximum at 240 nm, t = 15.1 min, PII: maximum at 242 nm, t = 10.7 min, PIII: maximum at 334 nm, t = 16,5 min, PIV: maximum at 213 nm, t = 12.6 min, **II**: maximum at 235 nm, t = 17.7 min.*

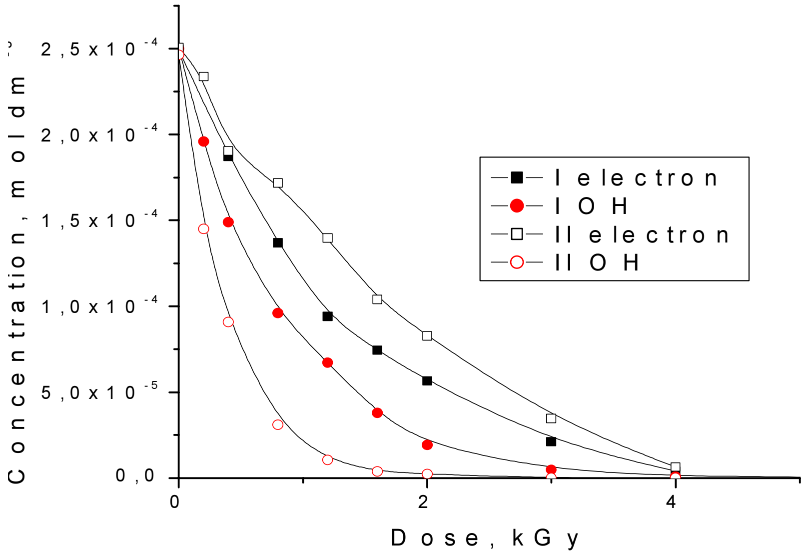


*FIG. 12. Dose dependence of the disappearance of **I** and **II** in the reaction with hydroxyl radicals (G ≈ 5.4) and hydrated electrons (G ≈ 2.7).*

TABLE 1. INITIAL *G* VALUES AND EFFICIENCIES (*G*(DISAPPEARANCE)/*G*(WATER RADIOLYSIS INTERMEDIATE)) OF DISAPPEARANCE

Water intermediate	Compound	*G*(disappearance) (100 eV)$^{-1}$	Efficiency
$^{\bullet}$OH	I	2.7	0.5
	II	5.4	0.9
e_{aq}^{-}	I	1.5	0.6
	II	1.1	0.4

3.2.3. Observation of intermediates

A very strong overlap of the absorption spectra of the intermediates that form in pulse radiolysis, and the absorption spectra of the starting compounds **I** and **II** complicates the measurements. In the reaction of water radiolysis intermediates with the compounds studied, some of the starting molecules disappear, decreasing the absorbance in the 300–400 nm range (fading), but the newly formed intermediates show light absorbance in the same region, giving an opposite effect. In the Inset of Fig. 13 as an example, we show the uncorrected spectrum taken in N_2O saturated H-acid containing solution. In order to obtain the transient absorption spectra of the intermediates, we applied a method (described in one our former works, [24]) that corrects the fading. The absorption spectra of the intermediates formed in $^{\bullet}$OH radical reactions of **I** and **II** are different (Fig. 13a) similarly to the UV-VIS spectra of the starting compounds (see Fig. 9). However, the spectra of intermediates formed in the reaction of **I** and **II** with e_{aq}^{-} are similar (Fig. 13b). The build-up of the intermediates was very fast, and completed within a few μs (the rate coefficients can be estimated to be above 10^9 mol^{-1} dm^3 s^{-1}). The decay of the transients was on the ms timescale. Intermediates formed from **II** in $^{\bullet}$OH reaction decayed faster than the intermediates of **I**. The decay of the intermediate formed from **I** in e_{aq}^{-} reaction is about three times faster than that of the intermediate formed from **II**. It is just the opposite trend that was observed in $^{\bullet}$OH reaction.

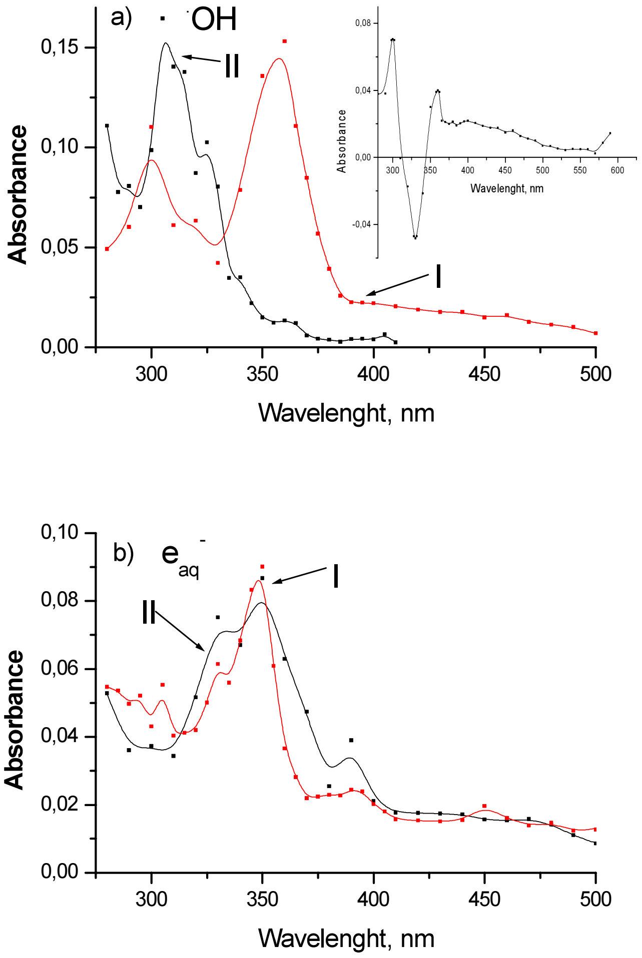
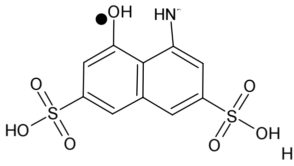
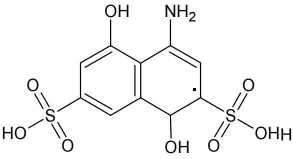


*FIG. 13. Absorption spectra of the intermediate species formed in solution of **I** and **II**, respectively, 5 μs after the pulse. Spectra measured **a**, in N_2O saturated system, **b**, in N_2 + 0.5 mol dm^{-3} tert-butanol containing system. 21 Gy/pulse, c = 0.1 mmol dm^{-3}. Inset: uncorrected absorption spectrum taken in solution of **I**.*

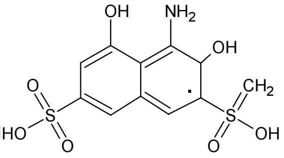
Hydroxyl radicals produced upon water radiolysis are electrophylic oxidants; therefore, they attack the electron-rich sites of the molecules, (as mentioned in the previous part in the case of AR-28). Such sites are the rings at any position as well as the $-NH_2$ group. By addition to the rings several isomeric cyclohexadienyl-type radicals are expected. Below we show the anilino type radical that is produced when an H-atom is eliminated from the $-NH_2$ group as well as two cyclohexadienyl-type radicals that probably form in $^{\bullet}OH$ radical addition to the more electron rich ring of **I**.



A



B



C

The spectrum of the intermediates that is observed in the reaction between $^{\bullet}OH$ and **I** with a strong, well-resolved absorption peak at about 360 nm (Fig. 13a) based on the analogy with aniline [25] most probably belongs to ortho OH adduct cyclohexadienyl type radical (C). The primarily formed a C cyclohexadienyl-type radical by water elimination and is expected to transform to anilino type radical (A). In the case of **II,** the peak around 320 nm is probably due to cyclohexadienyl-type radical absorption.

The $^{\bullet}OH$ radicals in destroying **II** have an efficiency of close to 1 (Table I). In the reaction with **I,** the efficiency is only half of this value. Since the $^{\bullet}OH$ radicals under the conditions applied react entirely with the solute molecules, we assume that the intermediates formed in the reaction of **II** in the further reactions are nearly entirely transformed to new products. As it was mentioned before, a considerable part of the chemical changes in the system takes place through the additional reaction of the $^{\bullet}OH$ radicals to the naphthalene central part of the molecules forming cyclohexadienyl type radicals (in Equ. (8), cyclohexadienyl-type radicals are indicated as $\mathbf{II}^{\bullet}$-OH). These $^{\bullet}OH$ adduct radicals in disproportionation (Equ. 9a) reform the naphthalene structure that contains one OH substituent more than the starting compounds (**II**(-H)-OH), in addition to **II**(+H)-OH that probably have cyclohexadiene or quinoidal structure.

$$\mathbf{II} + {}^{\bullet}\mathrm{OH} \longrightarrow \mathbf{II}^{\bullet}\text{-OH} \qquad (8)$$

$$\begin{tikzcd} & \mathbf{II}(+\mathrm{H})\text{-OH} + \mathbf{II}\,(-\mathrm{H})\text{-OH} \qquad (9a) \\ \mathbf{II}^{\bullet}\text{-OH} \arrow[ur] \arrow[dr] & \\ & \text{Dimer} \qquad (9b) \end{tikzcd}$$

In the $^{\bullet}OH$ radical-induced decomposition of **I** both the cyclohexadienyl and anilino- type radicals play a role. In aniline radiolysis, the aniline-type radicals are suggested to decay in radical-radical reactions, yielding mainly dimer products, (for instance hydrazobenzene [25, 26]). Such reactions do not restore the starting structures, similarly to the reaction of two OH-adduct cyclohexadienyl radicals. However, in the cross-reaction, (i.e. in the reaction of an anilino type radical and cyclohexadienyl-type radical, the aniline-type radical picks up a hydrogen atom from the cyclohexadienyl-type radical, producing H-acid and hydroxy-H-acid. This back reaction may give partial explanation for the relatively low efficiency factor (Table 1). In the $^{\bullet}OH$ radical-induced transformation of aniline, oxygen-containing products with quinine type structures were also detected. Compounds with similar structures probably also form in the reaction of **I**. These compounds — as it is typical for quinones — have wide absorption bands in the visible region as experimentally observed (Fig. 10, Inset).

The maxima appearing around 350 nm in the reaction system where the hydrated electrons are the main attacking species (Fig. 13b) most possibly belong again to the absorption of different cyclohexadienyl type radicals.

$$\text{H-acid} + e_{aq}^{-} + \text{H}^{+} \longrightarrow \text{H-acid}^{\bullet}\text{-H} \qquad (10)$$

The cyclohexadienyl type radicals formed following the electron scavenging and a subsequent protonation in equ. (10) (H-adduct cyclohexadienyl type radicals) are certainly different from the OH-adduct cyclohexadienyl-type radicals. The hydrated electron probably adds to the ring containing the OH group, due to the electron withdrawing property of the –OH and $–SO_3H$ groups attached to the benzene ring. The preferred radical site is on a carbon atom close to the $–SO_3H$ substituent. A possible structure is shown below in example **I**.

The lower efficiency of e_{aq}^{-} reactions, as compared to the reactions of $^{\bullet}$OH radicals, in destroying the compounds, requires some explanation. The fast build-up of the transient absorbance in pulse radiolysis suggests that the majority of hydrated electrons also react with the solute.

The self-termination reaction of two H-acid H-adduct cyclohexadienyl type radicals the disproportionation is in competition with the combination (see Equ. (11). In disproportination, (Equ. 11a) one of the radicals may transform to a compound in which one of the double bonds is saturated. The product thus formed has only one aromatic ring and probably has a low extinction coefficient above 300 nm. The other radical may reform the starting molecule, decreasing the efficiency. The combination (Equ. 11b) yields a dimer molecule, again with low extinction coefficient above 300 nm.

$$\begin{tikzcd}
 & \text{H-acid + H-acid(+H)-H} & \text{(11a)} \\
2\text{H-acid}^{\bullet}\text{-H} \arrow[ur] \arrow[dr] & & \\
 & \text{Dimer} & \text{(11b)}
\end{tikzcd}$$

In the scheme H-acid$^{\bullet}$-H, is a radical that can also form when an H-atom is added to H-acid. H-acid(+H)-H is a compound that has two extra H-atoms as compared to H-acid.

4. CONCLUSIONS

We have shown that in the case of AR-28 $^{\bullet}$OH reacts with the unsaturated bonds of the molecule. In the further reactions of the $^{\bullet}$OH adduct radicals, the AR-28 molecules partly reform with a slightly modified structure. The products formed in the first reaction of $^{\bullet}$OH and AR-28 molecules also have high reactivity towards the $^{\bullet}$OH radicals. For these reasons, the efficiency of $^{\bullet}$OH radicals in discolouration of the solution is below 0.5. The efficiency is much higher, close to unity for e_{aq}^{-}. The reaction of e_{aq}^{-} with AR-28 leads to an immediate destruction of the colour giving center.

In the case of H-acid (**I**) and its derivative (**II**), we found that they can be efficiently destroyed by the $^{\bullet}$OH and e_{aq}^{-} intermediates formed during water irradiation. The reaction of these water radicals with the molecules studied leads mainly to the formation of cyclohexadienyl type radicals; however, with the H-acid, H-atom elimination from the $–NH_2$ group was also observed, in the reaction anilino type radical formed. The cyclohexadienyl-type radicals and the anilino type radical decayed in a millisecond. In the case of compound **I,** the e_{aq}^{-} intermediate decayed faster, while in the case of **II** the decay of $^{\bullet}$OH intermediate was more rapid. In the $^{\bullet}$OH reactions as a first step of decomposition hydroxylated molecules and quinone type compounds that absorb the light in the UV-visible region formed. These molecules at higher doses by further decomposition of the ring structure transformed to open chain alcohols, carboxylic acids, etc. In the case of e_{aq}^-, even the primarily formed products had spectra shifted to the low wavelength region, indicating the destruction of aromatic conjugation in at least one of the C_6 rings. At a concentration of 0.25 mmol dm^{-3}, 4–6 kGy dose was sufficient to destroy the starting compounds. However, for complete mineralization, much higher doses are needed.

ACKNOWLEDGEMENTS

We express our thanks to the Hungarian Science Foundation (OTKA K 60 096). Support of the International Atomic Energy (contact No. 302-F2-HUN-12015) is also acknowledged.

REFERENCES

[1] LEGRINI, O., OLIVEROS, E., BRAUN, A.M., “Photochemical process for water treatment”, Chem. Rev. **93** (1993) 671–698.

[2] PERA-TITUS, M., GARCIA-MOLINA, V., BANOS, M.A., GIMENEZ, J., ESPLUGAS, S., “Degradation of chlorophenols by means of advanced oxidation processes: a general review”, Appl. Catal. B. Environment **47** (2004) 219–256.

[3] “Electron Beam Purification of Water and Wastewater, Environmental Application of Ionizing Radiation”. (COOPER, J., CURRY, R.D., O’SHEA, K.E., Eds.) Wiley, New York. (1999).

[4] HAN, B., KO, J.I., KIM, Y., CHUNG, W., CHOI, J.S., KANG, H.J., CHOI, C.K., PIKAEV, A.K., MAKAROV I.E., PONOMAREV, A.V., “Electron beam treatment of textile dyeing wastewater”, In Proc. of Symp. Radiation Technology in Emerging Industrial Applications, IAEA. Vienna (2003) 187-194.

[5] MAKAROV, I.E., PONOMAREV, A.V., HAN, B., “Demonstration plant for electron-beam treatment of Taegu dye industry complex wastewater” EMERGING APPLICATIONS OF RADIATION PROCESSING. IAEA-TECDOC-1386. (2004) 138–152.

[6] EMMI, S.S., TAKÁCS, E., “Advanced oxidation processes for water remediation: The E-beam method” L’Actualité Chimique submitted (2007).

[7] DELAAT, J., CHRAMOSTA, N., DORE, M., SUTY, H., POUILLOT, M., “Rate constants for reaction of hydroxyl radicals with some degradation by-products of atrazine by O_3 or O_3/H_2O_2”, Environ. Technol. **15** (1994) 419–428.

[8] SOLPAN, D., GÜVEN, O., TAKÁCS, E., WOJNÁROVITS, L., DAJKA, K., “High-energy irradiation treatment of aqueous solutions of azo dyes: steady-state gamma radiolysis experiments,” Radiat. Phys. Chem. **67** (2003) 531–534.

[9] KRAPFENBAUER, K., WOLFGER, H., GETOFF, N., HAMBLETT, I., NAVARATNAM, S., “Pulse radiolysis and chemical analysis of azo dyes in aqueous solution I. *p*-phenyloxazoaniline“, Radiat. Phys. Chem. **58** (2000) 21–27.

[10] GETOFF, N., “Factors influencing the efficiency of radiation-induced degradation of water pollutants”, Radiat. Phys. Chem. **65** (2002) 437–446.

[11] BREDERECK, K., SCHUMACHER, C., “Structure reactivity correlations of azo reactive dyes based on H-acid. I. NMR chemical shift values, pK_a values, dyestuff aggregation and dyeing behaviour”, Dyes and Pigments **21** (1993) 23–43.

[12] BREDERECK, K., SCHUMACHER, C., “Structure reactivity correlations of azo reactive dyes based on H-acid. II. Dye degradation by hypochlorite”, Dyes and Pigments **21** (1993) 45–66.

[13] BREDERECK, K., SCHUMACHER, C., “Structure reactivity correlations of azo reactive dyes based on H-acid. III. Dye degradation by peroxide”, Dyes and Pigments **21** (1993) 121–133.

[14] WOJNÁROVITS, L., PÁLFI, T., TAKÁCS, E., EMMI, S.S., “Reactivity differences of hydroxyl radicals and hydrated electrons in distracting azo dyes”, Radiat. Phys. Chem. **74** (2005) 239–246.

[15] HOLCAPEK, M., JANDERA, P., ZDERADICKA, P., "High performance liquid chromatography-mass spectrometric analysis of sulphonated dyes and intermediates", J. Chrom. **A926** (2001) 175–186.

[16] FÖLDIÁK, G., HARGITTAI, P., KASZANYICZKI, L., WOJNÁROVITS, L., "A computer controlled pulse radiolysis laboratory", J. Radional. Nucl. Chem., Articles **125** (1988) 19–28.

[17] EMMI, S.S., D'ANGELANTONIO, M., POGGI, G., BEGGIATO, G., CAMAIONI, N., GERI, A., MARTELLI, A., PIETROPAOLO, D., ZOTTI, G., "The spectral caharacterization of tiophene radical cation generated by pulse radiolysis", Res. Chem. Intermed. **24** (1998) 1–14.

[18] BUXTON, G.V., GREENSTOCK, C.L., HELMAN, W.P., ROSS, A.B., "Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($^{\bullet}OH/^{\bullet}O^{-}$) in aqueos solution", J. Phys. Chem. Ref. Data **17** (1988) 518–886. Updated version. http://www.rcdc.nd.edu.

[19] WOJNÁROVITS, L., "Radiation Chemistry" (VERTES, A., NAGY, S., KLENCSAR, Z., Eds), NUCLEAR CHEMISTRY, Kluwer, Dordrecht 3 (2003) 1–55.

[20] KARPEL VEL LEITNER, N., BERGERA, P., GEHRINGER, P., "γ-irradiation for the removal of atrazine in aqueous solution containing humic substances", Radiat. Phys. Chem. **55** (1999) 317–322.

[21] VINODGOPAL, K., KAMAT, P., "Hydroxyl-radical-mediated oxidation: A common pathway in the catalytic, radiolytic, and sonolytic degradation of textile dyes", (COOPER, J., CURRY, R.D., O'SHEA, K.E., Eds) ENVIRONMENTAL APPLICATIONS OF IONIZING RADIATION, Wiley, New York (1999) 587–599.

[22] FLAMIGNI, L., MONTI, S., "Primary processes in the reduction of azo dyes in alcohols studied by pulse radiolysis method", J. Phys. Chem. **89** (1985) 3702–3707.

[23] GÓRSKI, Z., ROLEWSKI, P., SŁAWIŃSKA, D., SŁAWIŃSKI, J., "Chemiluminescence imaging of the formation and photodegradation of humic acid derived from 5-hydroxy-1,4-naphthoquinone (Juglone)", Electronic Journal of Polish Agricultural Universities, Environmental Development, **7** Issue 2. (2004) Available online http://www.ejpau.media.pl/series/volume7/issue2/environment/art-04.html

[24] WOJNÁROVITS, L., PÁLFI, T., TAKÁCS, E., "Irradiation treatment of textile dyes: Apollofix Red." Res. Chem. Intermediat. **31** (2005) 679–690.

[25] SOLAR, S., SOLAR, W., GETOFF, N., "Resolved multisite OH-attack on aqueous aniline studied by pulse radiolysis", Radiat. Phys. Chem. **28** (1986) 229–234.

[26] CHRISTENSEN, H., "Pulse radiolysis of aqueous solutions of aniline and substituted anilines", Int. J. Radiat. Phys. Chem. **4** (1972) 311–333.

THE E BEAM INDUCED DECOMPOSITION OF PESTICIDES IN WATER: A GAMMA AND PULSE RADIOLYSIS INVESTIGATION ON CARBOFURAN

S.S. Emmi[1], G. De Paoli[1], E. Takács[2], S. Caminati[1], T. Pálfi[2]
[1]Istituto per la Sintesi Organica e la Fotoreattività (ISOF), CNR, Bologna, Italy,
[2] Institute of Isotopes, CRC, Hungarian Academy of Sciences, Budapest, Hungary

Abstract

The reactivity of carbofuran (CF) with OH was measured directly by means of pulse radiolysis matched with kinetic UV-vis absorption spectrometry. The hydroxylation attack of CF proceeds with a rate constant $k_1 = 6.6 \times 10^9\ M^{-1}s^{-1}$, similar to that of benzene forming hydroxycyclohexadienyl radicals ($k_{benzene + OH} = 7.8 \times 10^9\ M^{-1}s^{-1}$). It reacts, instead, 30 times slower with the methyl-carbamic acid methyl ester used to probe the reactivity of the carbamic part of the molecule. These kinetic observations and the spectral features in the region 280–330 nm of the hydroxylation products, which resemble those of a cyclohexadienyl type radical, have led to the conclusion that OH and CF form dienyl type radicals, HO-CF$^\bullet$. In deaerated atmosphere, HO-CF$^\bullet$ decays in a millisecond time regime via a second order process. In the presence of oxygen, the peroxidation reaction channel prevails, forming HO-CF-OO$^\bullet$ ($k \approx 10^7\ M^{-1}s^{-1}$). As monitored after γ radiolysis, oxygen participation makes the global decomposition six times more efficient than in anaerobic solutions (N_2O saturated).

1. INTRODUCTION

Carbofuran (CF) (Methyl-carbamic acid 2,2-dimethyl-2 ,3-dihydro-benzofuran-7-yl ester, $C_{12}H_{15}NO_3$), is a hydrogenated benzofuran ester of the carbamic acid. It is vastly employed as an insecticide and nematocide in North America and in some European countries to preserve corn fields, beetroot, rice, potato, alfalfa, onion, garlic, etc. Its action directly inhibits the acetyl cholinesterase in parasite's metabolism.

It is toxic by contact and ingestion, and lethal over the level of 5–14 mg/kg (LD_{50}, rats). The Maximum Contamination Level (MCL) for drinkable water, as established by the EPA (USA), corresponds to 0.18 µmol/L (0.04 ppm). This molecule is adsorbed and weakly bound to the plant tissue and to the ground. Its mobility is then enhanced, such that it may contaminate areas far away from the application zone. The overall decomposition of carbofuran by the hydroxyl radical has been previously investigated by means of photochemical and photocatalytic Advanced Oxidation Processes (AOPs) [3, 4, 5, 6]. Scanty data, instead, regard its decomposition initiated by E beam or γ radiation [7], despite the ability of electron accelerators to produce high concentrations of OH radicals in very short times. Besides that, the bimolecular rate constants values of CF with OH and other water and oxygen radicals are needed in view of the understanding of its degradation mechanism. Therefore we decided to employ pulse radiolysis spanning a nanosecond-millisecond time region to define the above reactions. γ radiolysis was employed as well to evaluate the global efficiency of the decomposition process in various conditions (i.e. in the presence and absence of oxygen).

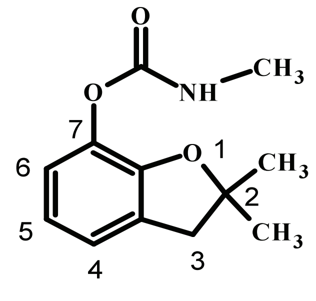


FIG. 1. Carbofuran.

TABLE 1. CARBOFURAN MAIN FEATURES [1, 2]

IUPAC NAME	2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate
SOLUBILITY	700 ppm (equivalent to 3.16 mM) in water at 25°C
STABILITY	690 weeks at pH5, 1 week at pH8 (half-life)
ACTION	inhalation, contact, and ingestion
WHERE	cultivation of beetroots, corns, potatoes, onions and garlic
CARCINOGENICITY	not classified
ACUTE TOXICITY (oral, Letal Dose)	LD_{50} = 5–14 mg/kg (rats)
MAXIMUM CONTAMINATION LEVEL	MCL_{H2O} = 0.18 μM (0.04 ppm)

2. EXPERIMENTAL SECTION AND CARBOFURAN PROPERTIES

Preliminary investigations on the main properties of CF were carried out up to 1 mM concentration. The apolar character of the aromatic group affects the whole molecule, such that solubilization in water follows a slow kinetics. Most experiences have been made at pH ≈ 5.5–6.0 to simulate the natural environment in which the CF shows a high stability. Spectral measurements after γ irradiation were usually done in a 1 cm quartz cell against air, whereas for pulse radiolysis, a 5 cm optical suprasil cell was generally used. The Linear accelerator and pulse radiolysis system at ISOF were applied, their features being described elsewhere [8]. A 20 ns electron pulse was generally employed. The UV-Vis a spectrum of an aqueous solution of CF (shown in Figure 2). It is characterized by a large absorption band in the UV, which may be finely resolved in two peaks, at 275 and 278 nm, of equivalent intensities. Also, at higher energies, a shoulder is evidenced around 216 nm.

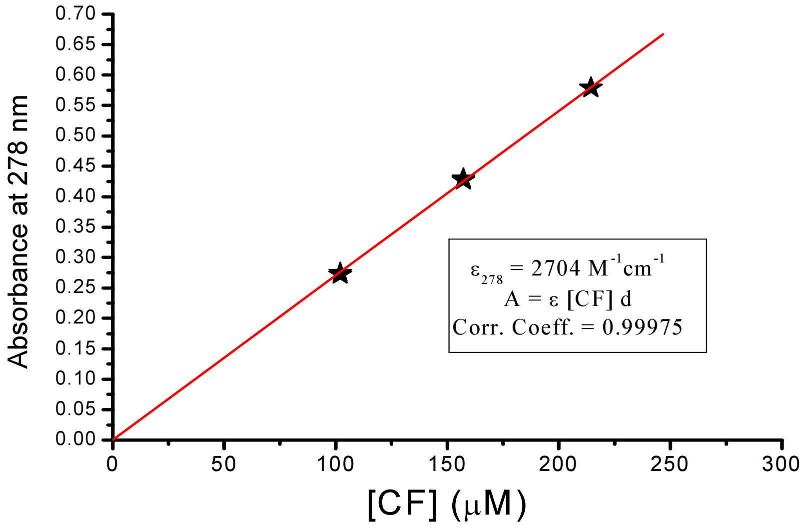


FIG. 2. Lambert-Beer plot to calculate the molar absorption coefficient of CF, 1cm cell.

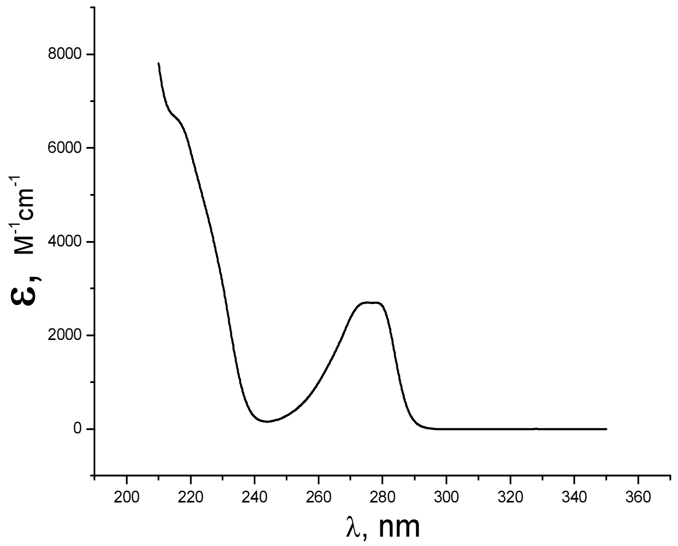


FIG. 3. UV-Vis spectrum of Carbofuran in water.

To our knowledge, the molar absorption coefficient of CF has not been reported. Therefore, a linear regression plot of the Lambert-Beer relationship (A = ε. [CF].d) between absorbances A and concentrations of CF (Figure 3) gave the molar absorption coefficient at 278 nm (i.e. ε_{278} = 2704 dm^3 mol^{-1} cm^{-1}). The CF spectrum in Figure 2 is plotted in terms of molar absorption coefficients normalized to the ε_{278} just calculated.

3. STUDIES IN THE ABSENCE OF OXYGEN

Reaction with the OH radical

Hydroxyl radical was produced by a standard procedure, consisting in the irradiation of aqueous solutions saturated with N_2O. In these conditions aqueous electron is converted into OH, whose yield sums up to 5.4 molecules/100 eV (G_{eaq} + G_{OH}). The system works as an almost mono-radical oxidizing environment. Actually, a minor quantity (ca. 10%) of H atoms is left and its reactions are usually very similar to those of hydroxyl, although it cannot be properly considered an oxidant. For the present purposes, we may neglect its presence.

γ irradiation

The effectiveness of hydroxyl radical oxidative degradation of the pesticide was verified by comparing the spectra of a solution of Carbofuran before and after an γ irradiation treatment. Figures 4a and 4b show that irradiation modifies the spectrum, the change depending on the initial concentration of Carbofuran and the irradiation dose. While low doses (ca. 1 kGy) induce the formation of intermediate degradation products, as revealed by new absorptions growing around 300 nm (Figure 4a), doses relatively high (ca. 14 kGy) apparently promote the molecular destruction, pointed out by the bleaching of both the characteristic absorptions at 275 and 278 nm (Figure 4b). The residual absorption in the UV zone at $\lambda \leq 235$ nm accounts for the presence of final degradation products (for instance, amides and dienes are known to absorb in this spectral area).

A step-by-step increase of dose remarks that degradation proceeds via a complex mechanism. Two main stages are identified. At low doses (about 750 Gy for the above-mentioned solution), the OH radicals directly interact with CF, producing absorption changes proportional to the dose applied. The main characteristic changes may be outlined as (1) a shoulder growth at 220 nm, (2) two isosbestic points, and (3) a slight bleaching of the main peak, while a new band appears on its right side (Fig. 5).

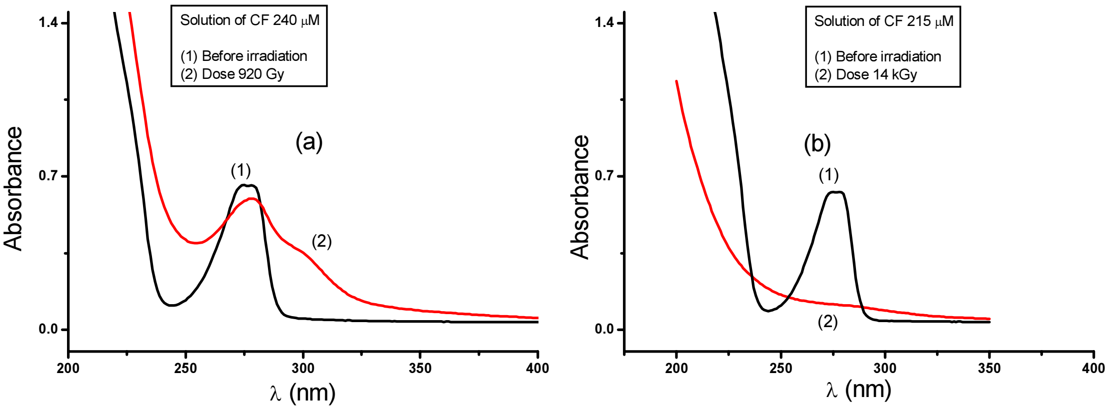


FIG. 4. γ irradiation of CF in N_2O saturated solutions at low (a) and high (b) doses, 1 cm cell.

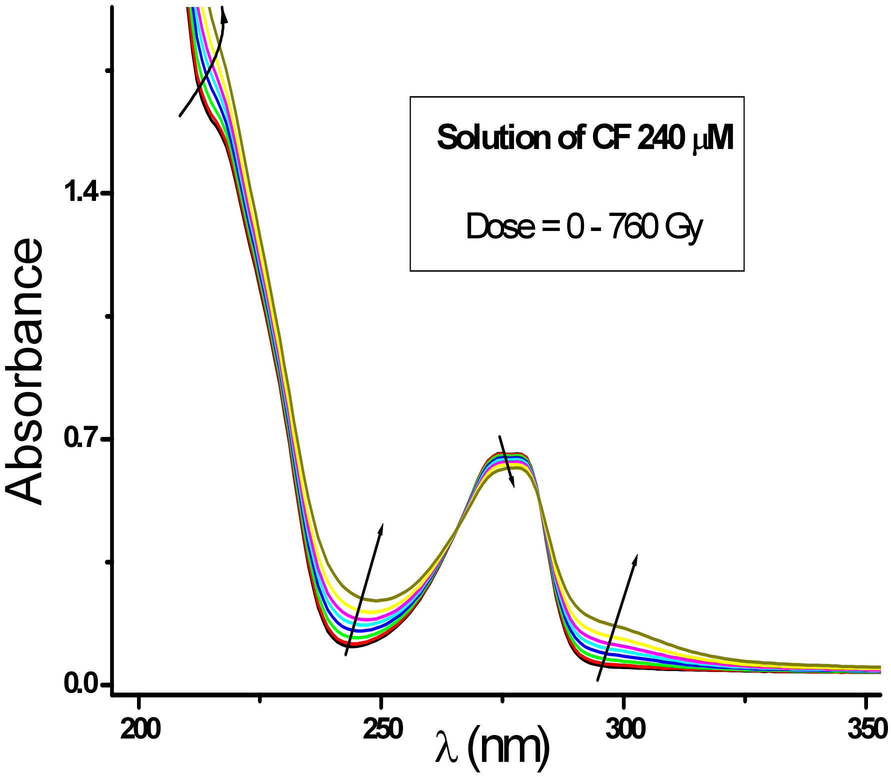


FIG. 5. Incremental dose irradiation in saturated N_2O atmosphere. Notice the two isosbestic points and the direction of change, 1 cm cell.

A further increase of dose (second stage) induces complex changes in the system. Figures 6a and 6b illustrate the detailed dynamics of these changes, showing an up-and-down behaviour of the optical density. It increases first (Figure 6a), then decreases (Figure 6b), later proceeding towards the total disappearance of the main peak (see again Figure 4b). It is then concluded that, up to 760 Gy, OH directly reacts with CF, producing partially destructured intermediates which then slowly accumulate. At the attainment of the proper concentration, a direct reaction of intermediates with OH takes place, such that further irradiation leads to the complete breakdown of the pesticide molecule. The destructured products do not absorb in the UV-vis region. As a first conclusion, it can be stated that the oxidative degradation of carbofuran by OH is effectively able to destroy the pesticides through a complex mechanism which involves intermediates of a short and long lifetime. It then generates products with completely different spectroscopic features than the original molecule.

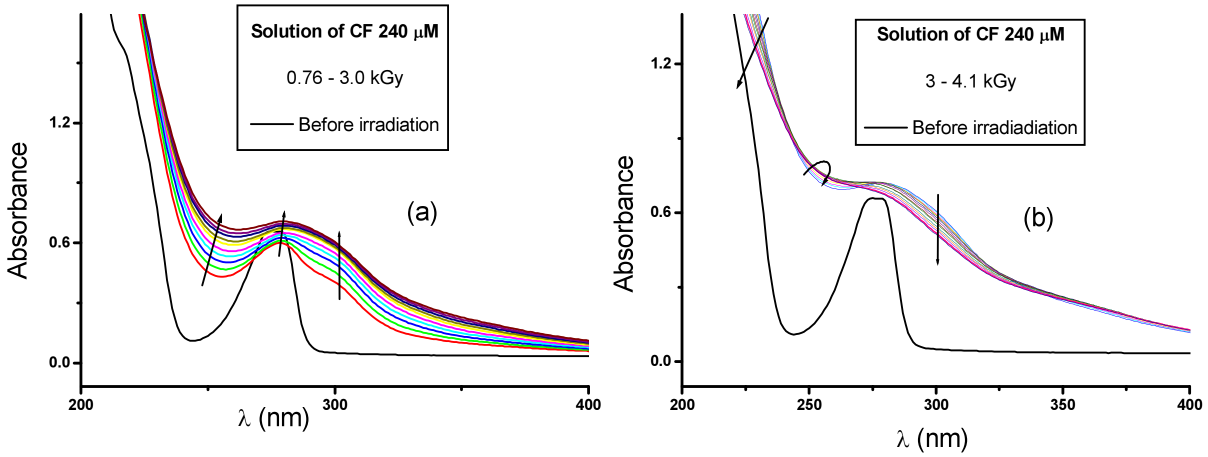


FIG. 6. Incremental dose irradiation: further evolution of the system of Figure 5 at doses up to 4.1 kGy.

Pulse radiolysis

Time resolved methods may help in disclosing the kinetics of the micro-milliseconds lifetime intermediates above. Therefore, we undertook a comprehensive pulse radiolysis study of N_2O aqueous solutions containing growing concentrations of CF. The reaction of OH with CF is easily monitored through an absorption buildup at 300 nm. By irradiating with a constant dose of 4 Gy, an asymptotic plot of ΔA_{max} vs. [CF] can be constructed (Figure 7). From that, it is seen that a plateau value is reached at the threshold value of [CF] = 25 μM. Just beyond that value, OH is quantitatively captured by CF, such that no further increase of optical signal can be obtained. Quite diluted solutions of CF are therefore suitable to be investigated with kinetic spectrophotometry.

Kinetic analyzes

The reaction of CF with OH radical induces optical density changes substantially pertaining to two different time regimes. The faster regime spans the μs time scale after the electron pulse (*short times*), while the slower regime falls in the milliseconds time scale (*long times*). At 'short times' after the pulse, the formation of a transient product is observed by an optical signal growing around 300 nm. A typical curve is shown in Figure 8. As we will see afterwards, this signal describes the kinetics of the addition of OH to Carbofuran.

At 300 nm, a pseudo-first order kinetic treatment has been carried out. From Figure 7, we know that OH is completely scavenged by CF above 25 μM using a dose of 4 Gy; therefore, by plotting the values of the observed rate constant k_{obs} vs [CF], in the range 50–250 μM, a $k_{bim} = 6.6 \times 10^9\ M^{-1}s^{-1}$ is obtained. Figure 9 shows the linear fitting of these values.

The transient spectrum

By irradiating a typical solution of carbofuran 100 μM, a transient spectrum appears 9 μs after the pulse, as it is shown in Figure 10.

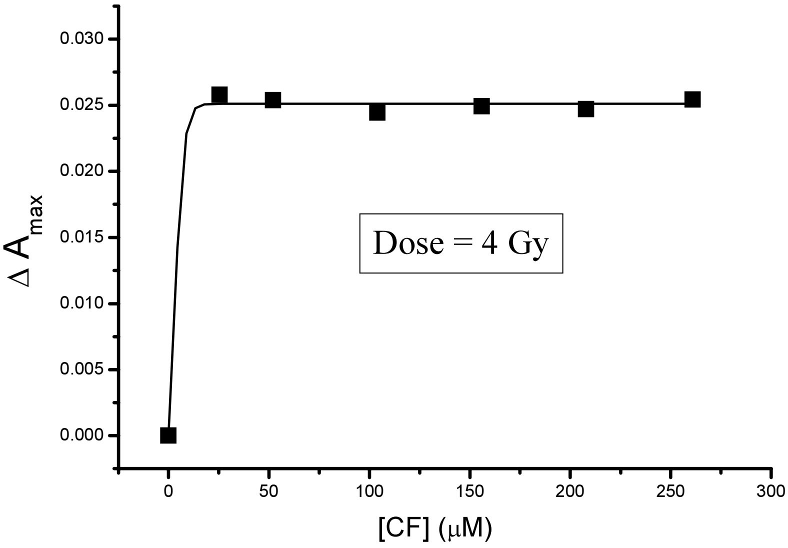


FIG. 7. OH scavenging in dependence of CF concentrations.

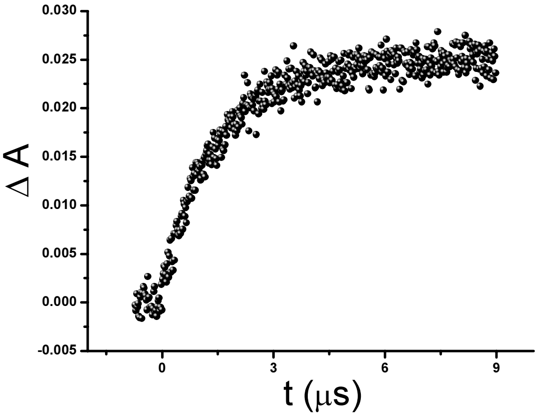


FIG. 8. Product build up of the reaction OH + CF at 300 nm, 5 cm cell.

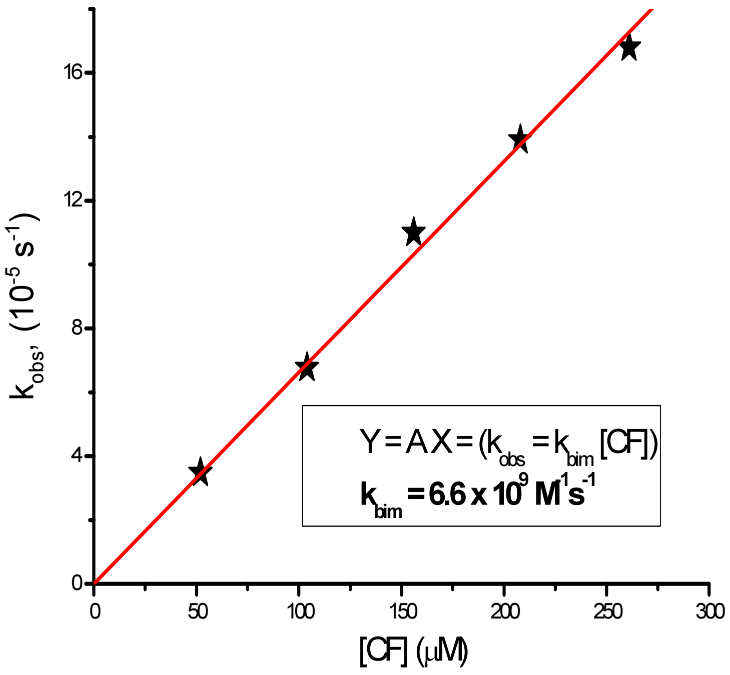


FIG. 9. Observed pseudo-first-order rate constant for OH + CF at 300 nm as a function of [CF].

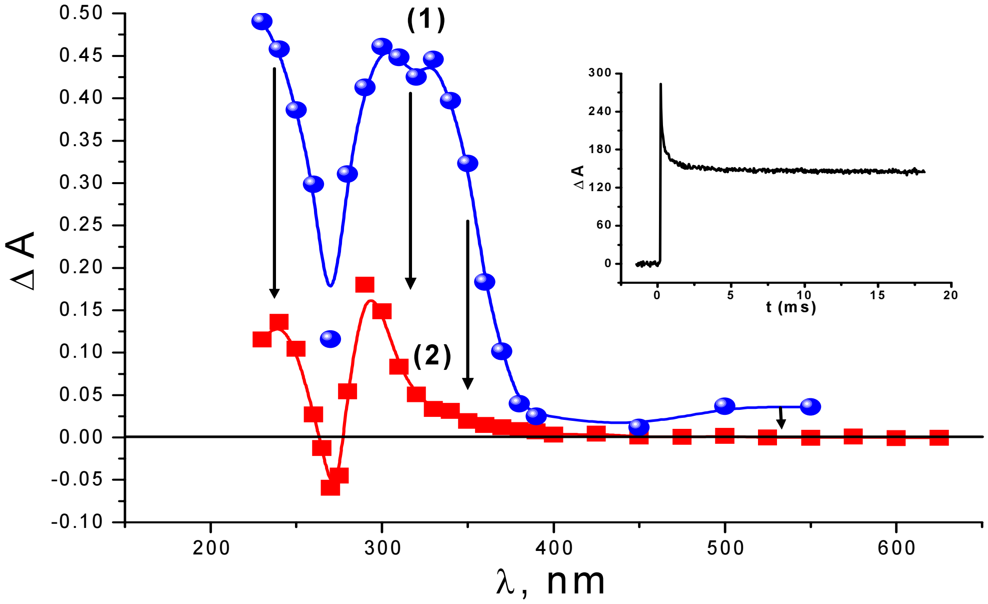


FIG. 10. (1): observed spectrum 9 μs after the pulse, dose = 11.5 Gy. (2 : observed spectrum 9 ms after the pulse, dose = 62.4 Gy. [CF] = 100 μM, 5 cm cell. Inset: decay of $CF^{\bullet}$ in the absence of oxygen at 300 nm.

For the identification of the intermediate responsible of this spectrum, we thought to consider the OH reactivity and transient spectra related to the carbamic acid methyl ester (CAME, Figure 11), studied under the same conditions as those of CF. In the CAME case, a significant structural difference with respect to carbofuran is represented by the absence of the benzofuranic part. It is in fact substituted by a methyl group. Now, from this study it comes out that the OH radical reactivity with CAME is 40 times slower than that with CF, (i.e. $k_{OH+CAME} = 1.7 \times 10^8$ $M^{-1}s^{-1}$). Moreover, no UV bands are growing during this reaction. We concluded that the benzofuranic part opens a different reaction channel, likely an interaction between the OH radical and the π system. As a matter of fact, cyclohexadienyl radicals are known to have characteristic bands in the 300 nm area, such that the assumption of a hydroxylation on the aromatic ring of CF sounds reasonable. From OH attack on CF a mixture of cyclohexadienyl-type-radical forms (positions 4, 5, and 6 in Figure 1 are available), which will be called HO-CF$^\bullet$ in the following of the paper.

HO-CF$^\bullet$ lives for milliseconds, as illustrated in the inset of Figure 10. Its disappearing is in acceptable agreement with second order kinetics, indicating a bimolecular rate constant,$k_{300\text{-self-decay}} = 5.85 \times 10^8$ $M^{-1}s^{-1}$. This decay likely represents the dimerization or disproportionation of the cyclohexadienyl radical. The products of this reaction yet show very weak absorptions, reported in Figure 10 as well (in order to obtain this spectrum, the dose was increased 5 times, with respect to the short time spectrum).

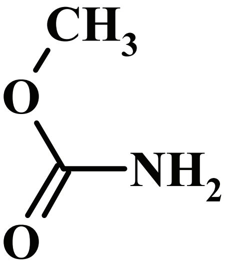


FIG. 11. Carbamic acid methyl ester.

4. STUDIES IN THE PRESENCE OF OXYGEN

Reactions and transient spectrum

So far, we examined the products of carbofuran hydroxylation in water in a saturated nitrous oxide atmosphere. The irradiation of this system represents a unique method to characterize the first steps of the OH attack to the pesticide. Actually, since our definitive goal is to clarify the oxidative abatement of pesticides in an aerated system, a further set of experiments was carried out by adding oxygen to the system above.

In the presence of O_2, the hydroxycyclohexadienyl radical self-decay is partially inhibited by its peroxidation. Due to the necessity of e_{aq}^- conversion into OH, a mixed atmosphere of N_2O and O_2 was used, thus changing the radical yields, N_2O and O_2, in fact, compete in scavenging e_{aq}^-. The OH yield decreases more and more as the O_2 content increases, being substituted by $O_2^{\bullet -}$. Therefore, peroxidation kinetics become complex and, for the purpose of this work, we decided it was not worth a thorough kinetic analysis. However, it is interesting to remark that oxygen capture by the carbofuran hydroxycyclohexadienyl radicals occurs approximately 10 times faster than it's self-decay. Typical profiles of HO-CF$^\bullet$ peroxidation, at increasing O_2 concentrations, are shown in Figure 12.

The spectrum of the hydroxylated carbofuran peroxyl radical, HO-CFOO$^\bullet$, was obtained in saturated O_2 atmosphere (1.25 mM), and it is shown in Figure 13. The characteristic spectral feature of a peroxyl radical is represented by the peak in the 240 nm area. The remaining absorption band around 290 nm appears to be a residual HO-CF$^\bullet$ contribution, likely due to a rapid C-O bond-forming/bond-breaking equilibrium. It is not surprising, in fact, to find that oxygen addition to dienyl type radicals is a reversible process, since the forming carbon-oxygen bond in these systems may be weak.

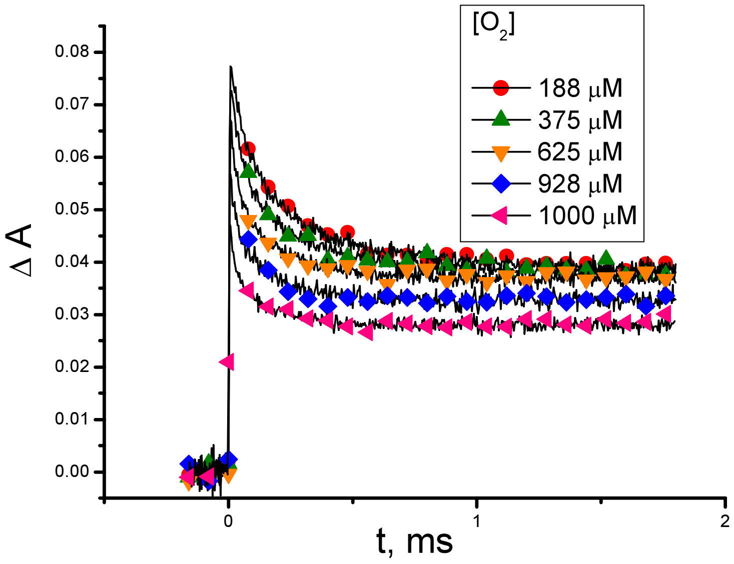


FIG. 12. Peroxydation reaction of HO-CF$^{\bullet}$ at increasing O_2 concentrations, λ = 300 nm, 5 cm cell, dose = 11.0 Gy.

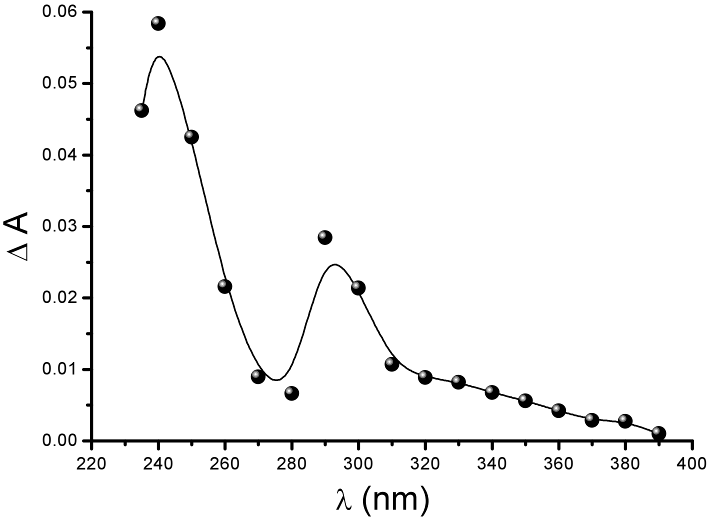


FIG. 13. Observed transient spectrum of the hydroxylated carbofuran peroxyl radical HO-CFOO$^{\bullet}$, 0.9 ms after the pulse, [O_2] = 1.25 mM, pH5.5, 5 cm cell, dose = 12 Gy, 20 ns pulse length.

γ irradiation

The oxygen effect on the overall oxidative degradation has been studied by irradiating solutions of CF with gamma rays under continuous O_2 bubbling; that is, samples were in an O_2 saturated environment. Each sample was monitored spectrophotometrically before and after the irradiation. Oxygen takes an active part in the degradation of CF and accelerates it substantially. This is shown in Figure 14 (a) and 14 (b), where two identical samples, irradiated with the same dose of 760 Gy, are compared. The sample on the left is without O_2 (N_2O saturated), while the sample on the right contains O_2 (O_2 saturated).

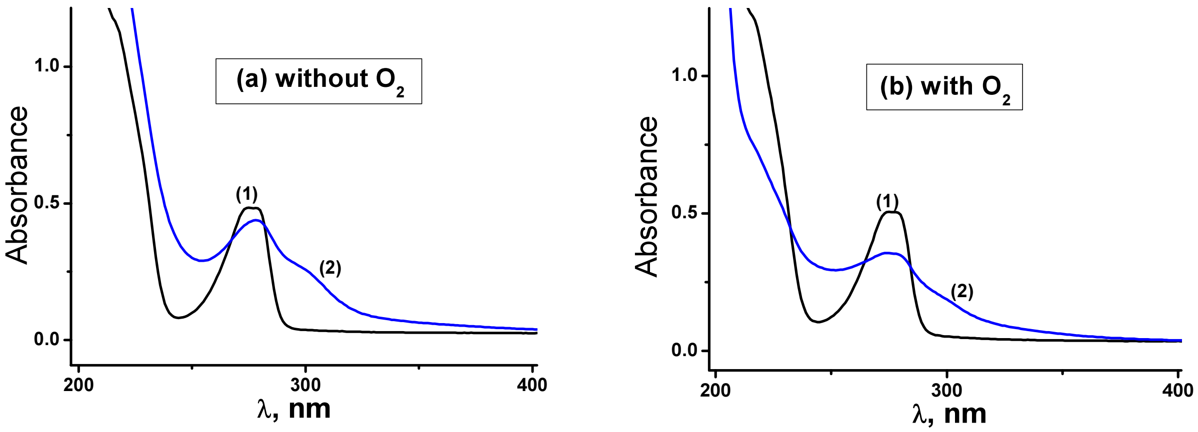


FIG. 14. Continuous irradiation of an aqueous solution of [CF] 160 μM, dose 760 Gy, 1 cm cell, (1) before irradiation, (2) after irradiation.

Although the spectral features in Figure 14 do not allow us to distinguish the forming products, their changes are visibly more pronounced in the case of O_2. How processes and products differ, in the absence and presence of O_2, is more evident from the detailed spectral studies reported in Figure 15(a) and 15(b), as dose is incremented to reach a total bleaching. In Figure 15, 200 μM CF solutions are irradiated with step-by-step growing doses. In a first phase (up to 760 Gy, Figure 15a), the 278 nm absorbance decreases, and new bands grow right and left of it; then higher doses (from 760 to 2350 Gy, Figure 15b) progressively remove the absorbances until they are almost completely bleached. The products from CF degradation demonstrate absorbance below 235 nm.

At low doses (Figure 15a), three isosbestic points appear, while in N_2O saturated solutions they were only two (compare with Figure 6). The shoulder at 220 nm progressively disappears, whereas in the absence of oxygen, an increase of absorption was observed (Figure 6).

Few conjectures may be advanced about mechanism, regarding the initial irradiation stages, when intermediates and final products do not compete with CF for oxidizing radicals.

Since CF is stable in the natural environment (pH ≈ 5.5–6), a direct action of oxygen may be ruled out. Irradiation conditions produce mainly two radicals, OH e $O_2^{\bullet-}$. Since we specifically verified that $O_2^{\bullet-}$ does not react at all with CF, the only initial active agent of CF decomposition in oxygenated environment is the hydroxyl radical. Its addition to the aromatic π system produces various hydroxyl-substituted cyclohexadienyl radicals, which, as seen by pulse radiolysis, are inhibited to recombine by the presence of oxygen. The peroxidation pathway, in fact, tends to prevail, giving rise to a degradation chain mechanism which leads to the complete destructuration of carbofuran. It is interesting to remark that in a saturated oxygen atmosphere, the yield of OH is ½ that of an N_2O atmosphere; however, oxygen enhances the degradation efficiency almost by a factor of 6. It sounds reasonable to conceive a role for the superoxide radical as well. Although it is unreactive towards CF, $O_2^{\bullet-}$ may in fact take an active part at a later stage by reacting with the intermediates.

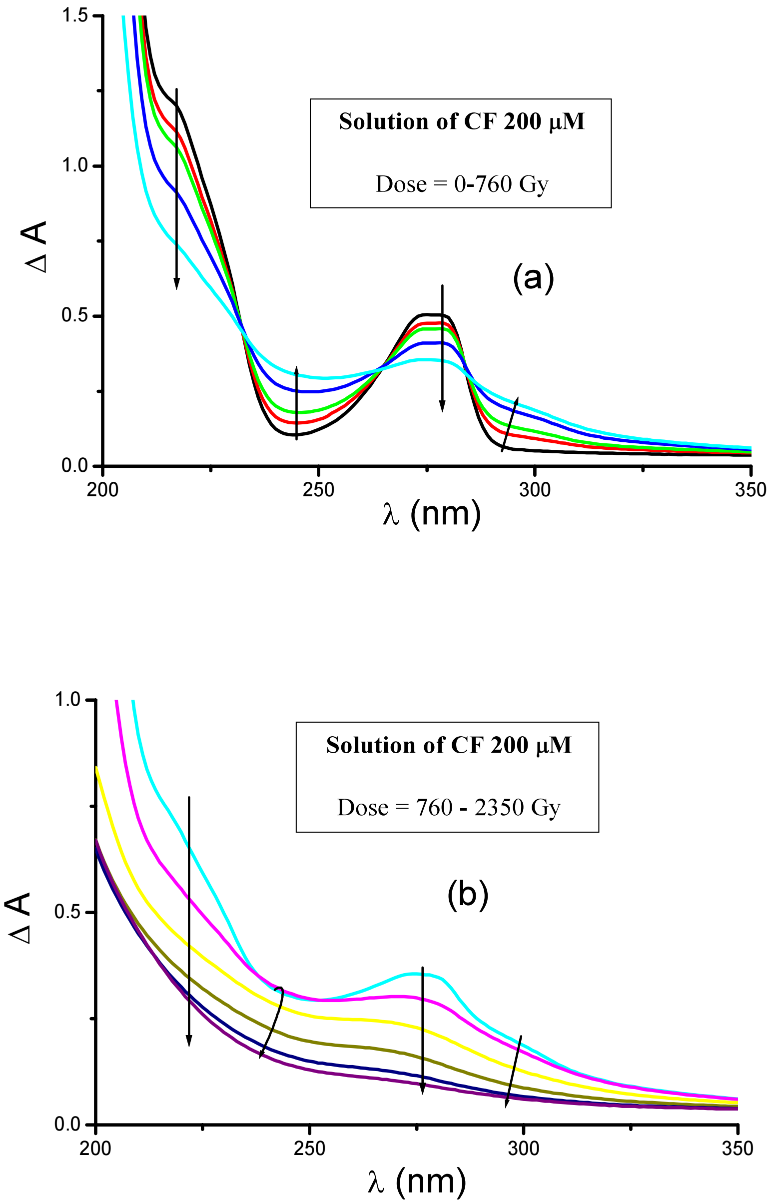


FIG. 15. Irradiation at incremental doses in saturated O_2 atmosphere, 1 cm cell. (a) Notice the trends and the three isosbestic points. (b) Spectral changes at higher doses.

5. CONCLUSIONS

The treatment with ionizing radiation (e beam and γ rays) of carbofuran in deaerated (nitrous oxide saturated) and oxygenated atmosphere has demonstrated to lead to its decomposition. Pulse radiolysis highlighted the various phases of OH radical attack, revealing the initial formation of cyclohexadienyl type radicals. In the absence of oxygen, these radicals recombine. Recombination is instead prevented when oxygen is present, since peroxyl radicals are preferentially formed. It appears that $O_2^{\bullet-}$ takes part in the degradation process as well, by reacting with the secondary products. No reaction was, in fact, seen of $O_2^{\bullet-}$ with CF itself. In both systems, with and without with oxygen, the decomposition of CF is effective, since it can be understood by the complete bleaching of the typical absorption spectrum of CF. Although the late intermediates and final products of the two systems have not been identified so far, they are different, as it is shown by their spectral changes. The major efficiency of the oxygenated system is proven by comparing samples of CF in both environments. The system containing oxygen, in fact, requires the 17% (1/6) of the dose needed in the N_2O atmosphere for similar concentrations. Preliminary measurements in a heterogeneous phase containing 1% of TiO_2 suggest that this catalyst may improve the efficiency by a further factor of 2.

REFERENCES

[1] a) MUCCINELLI, M., “Prontuario dei fitofarmaci”, 6th ed., Edagricole, Bologna, Italy (1990), 165 b) BARON, R.L., “Carbamate Insecticides”. In Handbook of pesticide toxicology. Hayes, W.J., Jr. and Laws, E.R., Jr., Eds. Academic Press, New York, NY, (1991) 3–6.

[2] MEAR A.-M., LE SAINT, J., PRIVAT, M., “Adsorption mechanism of carbofuran on silica: Structure, kinetics, and solubility influence”, Ecotox. Environ. Saf., 35 (1996) 163–173.

[3] DE BERTRAND, N., BARCELÓ, D., “Photodegradation of carbamic pesticides aldicarb, carbaryl and carbofuran in water”, Anal. Chim. Acta., 254 (1991) 235–244.

[4] BACHMAN, J., PATTERSON, H.H., “Photodecomposition of the carbamate pesticide carbofuran: kinetics and the influence of dissolved organic matter”, Environ. Sci. Technol., 33 (1999) 874–881.

[5] BENITEZ, F. J., ACERO, J. L., REAL F. J., “Degradation of carbofuran by using ozone, UV radiation and advanced oxidation processes”, Journ. Hazard. Mat., B89 (2002) 51–65.

[6] WANG, Q., LEMLEY, A. T., “Oxidative degradation and detoxification of aqueous carbofuran by membrane anodic Fenton treatment”, Journ. Hazard. Mat., B98 (2003) 241–255.

[7] ŞOLPAN, D., “The degradation of some pesticides in aqueous solutions by gamma radiation”, IAEA 2nd RCM Report on “Remediation of polluted waters and wastewater by radiation processing”, Warsaw, Poland 13–18 June (2004).

[8] S.S. EMMI, M. D’ANGELANTONIO, G. POGGI, G. BEGGIATO, N. CAMAIONI, A.GERI, A. MARTELLI, D. PIETROPAOLO, G. ZOTTI, “The spectral characterization of thiophene radical cation generated by pulse radiolysis”, Res.Chem.Intermed., 24 (1998) 1–14.

REMEDIATION OF POLLUTED WATERS AND WASTEWATER BY IRRADIATION PROCESSING IN JORDAN

H. Amro, R. Tuffaha, S. Zenati, M. Jneidi

Water Authority of Jordan
Amman, Jordan

Abstract

This paper presents the results of the applied research carried out within the frame of the IAEA Coordinated Research Project (CRP) No. 11964 on remediation of contaminated drinking waters and wastewater to improve their quality by irradiation processing. The obtained results show that an irradiation dose of 1 kGy is capable of controlling the microbiological content of contaminated drinking water supplies containing e-coli counts up to 1000/100 ml. It is also found that an irradiation dose of 1 kGy capable of removing up to 98% of the THM contained in drinking water with THM concentration of 100 µg/L. To remove THM precursors from drinking water, irradiation dose of 5 kGy and higher should be applied. The ideal irradiation dose for disinfection of treated wastewaters was found to be 1.5 kGy. At this dose, the irradiated wastewaters will be suitable for wastewater reuse in unrestricted irrigation.

1. INTRODUCTION

Jordan is characterized by an arid to semiarid climate with very limited water resources. The country mainly depends on groundwater as a major source for drinking water supplies. These resources are affected by continual quality degradation due to effects of overexploitation, increasing emissions of anthropogenic pollution sources like agriculture activities, chemical and organic wastes, septic tank disposal, infiltration of effluents of wastewater sewage treatment plants, waste water reuse, etc. The high diversity of pollutants of different origins and natures, accompanied with variations of their physical, chemical and biological characteristics, requires new fundamental approaches in water treatment and water quality improvement. Water disinfection by chlorination can cause formation of carcinogenic chlorinated organic compounds. The reduction of microorganisms in wastewater treatment plants by chlorination was found to be insufficient. [1]

Radiation processing can contribute to solving these problems. Radiation energy treatment for clean water supply and for wastewater treatment is under study in many technologically advanced countries, as well as in some developing countries. Greater application of this technology may rest on not only the development of improved technical processes, but also on greater public acceptance of radiation energy technology as environmental engineering needs grow and health hazard fears subsides.

This paper presents the results of the experimental investigations and research carried out on improving the water quality by irradiation in the following areas:

a) Improving the chemical quality of the drinking water by decomposition of halogenated (Chlorinated) organic contaminants and removal of trihalomethanes;
b) Improving the microbiological quality of the contaminated drinking water resources and the effluents of the wastewater treatment plants by disinfection and control of the microorganisms which present a hazard for public health and the environment.

2. PROJECT SCOPE AND OBJECTIVES

The main objective of this project is to assess potential applications of radiation processing treatment in the area of contaminated waters and wastewater in Jordan through:

1- Advanced methods and technology of water processing to have water with minimal biological risk. Improving the microbiological quality of the contaminated drinking water resources and the effluents of the wastewater treatment plants by disinfection and controlling microorganisms leads to protect public health and conserve the environment.

2- As a subject of integrated water resources management, especially with increasing water demand and a shortage of the available water supplies, the re-use of treated wastewater becomes an important subject. Remediation of municipal wastewater, including treatment and proper disinfection, allows this important water resource to be utilized for industrial and agricultural purposes.

The scope of the research project is to study the use of irradiation technology (electron beam or gamma radiation) to treat and improve the water quality in the following areas:

1- Improving the quality of drinking water supplies containing considerable concentrations of Trihalomethanes (THMs) by decomposition and removing these compounds from water by irradiation.

2- Improving the water quality of microbiologically contaminated drinking water supplies, using irradiation technology for water decontamination and disinfection.

3- Use of the ionization radiation for remediation of polluted waters and disinfection of treated wastewaters.

3. THEORY AND BIBLIOGRAPHY

3.1. Background

There are many forms of radiation, but only high-energy radiation can produce ions or charged particles after being absorbed by matter. This type of radiation is called ionizing radiation and comprises gamma rays from decaying radio nuclides as Cobalt-60, X rays generated by X ray generators, and machine generated electrons by electron accelerators. In other words, among the electromagnetic spectrum, the visible light can break only the weakest intermolecular bonds and Ultraviolet (UV) light somewhat breaks stronger bonds, while X rays and gamma rays are powerful enough to expel orbiting electrons from atoms of the irradiated matter to produce free radicals and charged ions (radiolysis).

The total amount of ionizing radiation absorbed by matter forms the radiation dose. The radiation is considered as pockets of energy or photons, which are characterized by their energy E given by:

$$E = h \times c/\lambda = h \times \nu$$

Where:

E: Energy of photon (radiation energy)
h: Blanks constant (6.626×10^{-27} erg.sec)
λ: Wave length of the radiation (cm)
ν: Frequency of the radiation (sec^{-1})
c: Velocity of the light (3×10^{10} cm/sec.)

The energy unit commonly used for radiation is the electron volt (eV). One electron volt is equal to the kinetic energy acquired by an electron being accelerated through a potential difference of one volt ($1 \text{ eV} = 1.602 \times 10^{12}$ ergs). The absorbed dote D is the amount of energy absorbed per unit mass of irradiated matter at a point of region of interest. The unit of measurement of absorbed dose is called Gray (Gy), which is equal to the absorption of one Joule of energy per kilogram of matter being irradiated.

If the energy of radiation employed is high enough (more than 14.5 MeV), it may produce induced radioactivity in the irradiated material. Therefore the maximum permissible energy levels of irradiation sources are: 10 MeV for accelerated electron beams, and 5 MeV for gamma and X rays. These energy levels are very low to induce radioactivity in irradiated water or food. [3]

3.2. Radiation Chemistry and Water Radiolysis

When matter absorbs gamma or X rays, Compton scattering is the most important mechanism that occurs when the gamma- photons lie in the energy range of 0.5 to 5 MeV. Part of photon energy is used to eject an electron from an atom of the absorber while the remainder is retained. The ejected electron, carrying a large portion of the original energy of the photon, also loses energy through ionization and excitation of the molecules of the absorber.

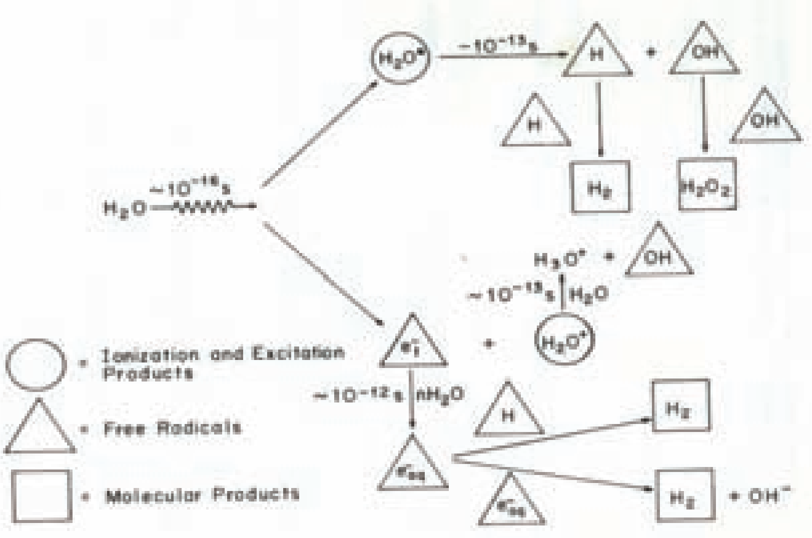


FIG. 1. Radiolysis products of Water. Schubert 1974

When water is irradiated, a number of radiolysis products are formed, as shown in Figure 1. [1, 8].

The most common products formed are hydroxyl radicals OH, hydrated electrons hydrogen atoms H, hydrogen molecules H2, hydrated protons H3O, and hydrogen peroxide H_2O_2. These reactions can be simply be expressed by the following equation. [4]

$$H_2O \text{®}\rightarrow [2.7]\ OH^* + [2.6]\ e^-_{(aq)} + [0.6]\ H^* + [0.45]\ H_2 + [0.71]\ H_2O_2 + [2.7]\ H_3O^+$$

The numbers in the equation are the number of molecules reacting or produced per 100 eV of absorbed energy. The only stable product of water radiolysis is hydrogen and hydrogen peroxide, which are themselves consumed by the radicals formed and mostly lost prior to consumption. The hydrogen peroxide is an oxidizing agent of much less importance than the highly reactive hydrated electron intermediates and short-lived free radicals that can react with other materials existing in the water media. These radicals can lead to the formation of new compounds different from those initially present. The hydroxyl radicals are a powerful oxidizing agent while hydrated electrons are a strong reducing agent. As a result, both oxidation and reduction reactions can occur upon the irradiation of water.

The radiolysis of organic compounds can also occur in a very complex form. Recent studies have shown that irradiation of water is capable of destroying organic compounds. Proksch (et al [4]) showed that when perchloroethylene (PCE) is present in water in mg/L concentrations, nearly 100% of the organic chloride would be degraded to chloride after irradiation. Haberl, R (et al [7]) showed that irradiation in the presence of ozone was able to destroy up to 30% of both the chemical oxygen demand (COD) and the biological oxygen demand (BOD). He found that the concentration of the absorbable oxidant was reduced by at least 60% as a result of enhancing the biodegradability of the effluent due to the distraction of toxic chlorinated organics. When irradiating drinking water or river water, part of the primary species of water radicals are consumed by carbonates, phosphates, nitrates and humic compounds available in water. Some concern may rise due to the decomposition of some organic compounds in case of their presence, such as chlorinated alphatic and aromatic compounds. Presence of ozone can lead to much higher decomposition efficiency and reduction in the required irradiation dose. Getoff et al. [5] studied the radiolysis and degradation of several organic compounds in aerated water, such as 1,2- dichloroethane, $CHCl_3$, CCL_4, chlorinated organic phenol 4-Cl–phenol, and concluded that organic compounds can be degraded using radiation processes. These processes and a proper irradiation dose lead to the formation of CO_2 and H_2O as a final decomposition product.

3.3. Radiation effects on Living Organisms

It is presumed that the biological effects of radiation are due to the chemical changes within the living organism. These chemical changes may kill or inactivate the microorganisms.

For a living biological system, chromosomal DNA is the most critical target for irradiation. The nucleic acid molecules are affected by ionization and excitation. Indirect effects on DNA include excitation of water molecules, which then make contact with the chromosomal material. The sequences of events following irradiation can occur in different ways depending on the dose. A sufficiently high dose can prevent recovery of living organisms from radiation injury.

The effect of radiation cannot be simply described for all organisms, since these effects are related to the nature of the organism, especially to its complexity, as shown in Table 1.

TABLE 1. THE EFFECT OF IRRADIATION ON LIVING ORGANISMS

Dose (Gy)	Effect on living organisms
1–0.1	No acute effect
1.2–11	Lethal to humans
8–500	Sprouting inhibited
10–1000	Lethal to insects
50–100000	Sterilization of micro organisms

The correlation of radiation sensitivity is roughly inversely proportional to the size of the microorganism. Viruses, the minutest living entities, are the most radiation-resistant entities (some surviving as many as 100 kGy, while humans at the other size range and complexity suffer death with only 5 Gy. Single cell organisms are more vulnerable to the radiation damage than multicell organisms. Studies on food irradiation show that radiation doses between 5 to 25 kGy result in extensive distraction of salmonella and other common food-born microorganisms. Viruses, represent significant health hazards in food water supplies and wastewater including those causing hepatitis and poliomyelitis, but can also be inactivated by irradiation. Pathogenic protozoa and parasitic helminthes mostly can be killed or rendered noninfectious at doses about 1 k Gy. [6]

4. DISINFECTION OF MICROBIOLOGICALLY CONTAMINATED DRINKING WATER

4.1. Methods and Tools

Ain Hazzier Spring is a shallow spring, located 5 kilometers to the south of Salt City. The spring is subject to anthropogenic contamination as a result of different human activities in the catchments area upstream of the spring. The spring water, which is microbiologically contaminated, is used to supply part of Salt City with drinking water after water processing with filtration and chlorination.

Samples were collected routinely from the raw water of the spring to study the effect of irradiation on the microbiological content and to find the effective dose required for disinfection of such type of water. The collected samples were irradiated using a Co-60 research gamma irradiator for 100, 300, 500, 750, 1000 and 2000 Grays (Gy). The samples were collected in duplicate, and the sampling campaign was repeated six times with time interval of one month. The collected samples before and after irradiation were analyzed for their microbiological content at ISO-17025 accredited; central laboratories of Water Authority of Jordan (WAJ). The analysis included the following parameters: Total Coliform Count (TCC), Thermo-toleriant Coliform Count (TTCC), and Escherichia coli (E-coli). The method used for the above microbiological analysis was the multiple tube fermentation technique. Sampling and analytical methods used were according to the standard methods for examination of water and wastewater (20th edition, 1998). For the purpose of studying the efficiency of the absorbed dose in controlling the bacterial re-growth after irradiation, the samples, before and after irradiation, were kept for one week at room temperature (25 C°). After the holding time, the samples were again analyzed for the same microbiological parameters.

4.2. Results and discussion

The results of microbiological analysis of the samples collected from Ain Hazzier Spring are shown in Table 2. Each reported result is the average result of 12 samples (n = 12).

TABLE 2. MICROBIOLOGICAL RESULTS OF AIN HAZZIER SPRING BEFORE AND AFTER IRRADIATION

Dose (Gy)	TCC	TTCC	E- coli
0	4516.9	913	571.8
100	282.8	219	219
300	83	18.43	16.12
500	9.59	2	2
1000	2	2	2
2000	2	2	2

The relationship between an irradiation dose and a microbiological count is shown in Figure 2. The irradiated raw water is slightly contaminated, but the E-coli content is less than 1000 counts. The results show that irradiation dose of 500 Gy is a sufficient dose for water disinfection, while the E-coli count reduced to less than 2.

The results of the microbiological re-growth after 7 days are shown in Table 3 and illustrated in Figure 3. The irradiation dose of 500 Gy was found not sufficient to stop the bacterial growth after irradiation. Therefore, it is recommended to use irradiation dose of 1 kGy to insure complete disinfection of the treated water.

From the above results, we can conclude that the dose of 1 kGy is the optimum dose that can be used to achieve both goals to complete water disinfection and insure no bacterial regrowth in the drinking water network.

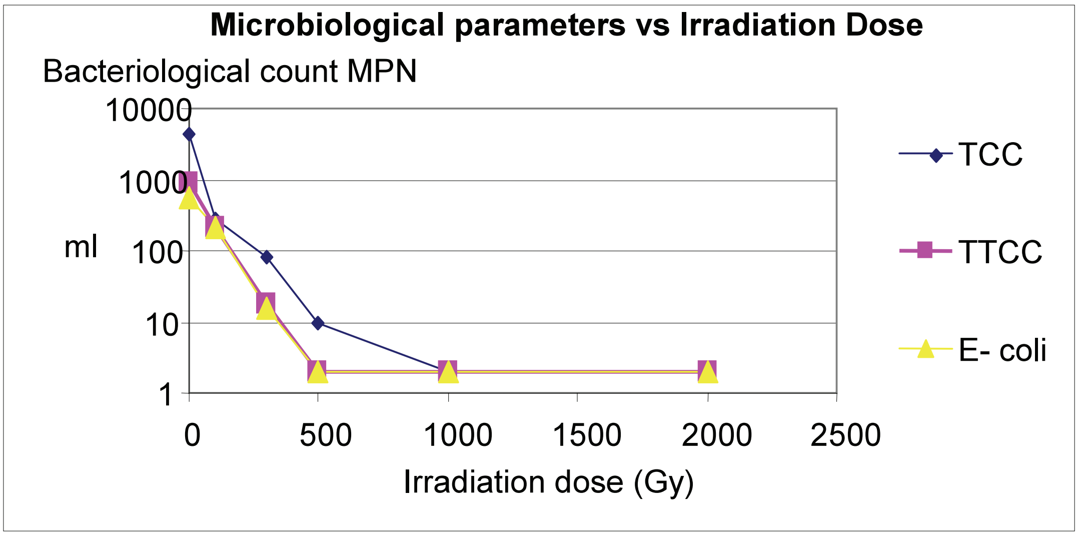


FIG. 2. Microbiological parameters before and after irradiation.

TABLE 3. THE RESULTS OF THE BACTERIAL RE-GROWTH AFTER 7 DAYS OF IRRADIATION

Dose (Gy)	0-day E- Coli	7-days E- Coli	7-days TTCC	7-days TCC	7-days TTCC
0	571.8	10.91	12.76	148.8	12.76
100	219	178.8	357.7	606.6	357.7
300	16.12	14.14	14.14	33.9	14.14
500	2	3.7	3.7	9.2	3.7
1000	2	2	2	2	2
2000	2	2	2	2	2

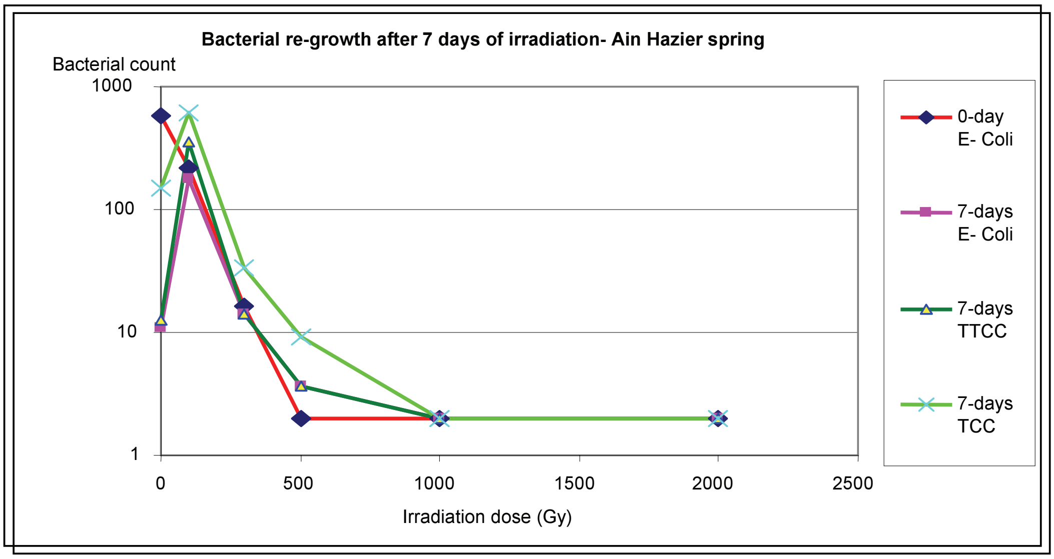


FIG. 3. The relationship between bacterial re-growth after 7 days and irradiation dose.

5. WASTEWATER TREATMENT AND DISINFECTION

5.1. Methods and Tools

Irradiation processing was carried out on wastewater samples collected from Baqaa Wastewater Treatment Plant (WWTP) to determine the optimum dose required for water disinfection and to study the factors affecting the irradiation efficiency and bacterial re-growth. The samples were collected from the plant influent and effluent during the summer and winter. The samples were irradiated with different irradiation doses using a Co-60 research gamma irradiator and measured for microbiological and chemical content before and after irradiation. For the study of the effect of the irradiation dose on the bacterial re-growth, sufficient quantities of nutrient media were added to the samples before and after irradiation. The samples were kept in room temperature for seven days. All collected samples were measured using the multiple tube fermentation method for TCC, TTCC, and E-coli. Other physical, chemical and biochemical parameters were measured, according to the book of the standard methods for examination of water and wastewater (20th edition, 1998). The irradiation doses applied were: 0.3, 0.5, 0.75, 1, 1.5, 2, 3, 5, and 10 kGy.

5.2. Results and Discussion

5.2.1. Optimal disinfection dose

To examine the effect of ionization radiation on the disinfection of the highly contaminated wastewater, samples from the influent of the Baqaa WWTP were collected and irradiated with doses up to 10 kGy. The microbiological results for the samples are shown in Table 4 and plotted in Figure 4.

TABLE 4. IRRADIATION RESULTS OF BAQAA WWTP INFLUENT

Dose (Gy)	TCC	E.coli
0	16000000	16000000
1000	16000000	1700000
5000	23	2
10000	23	2

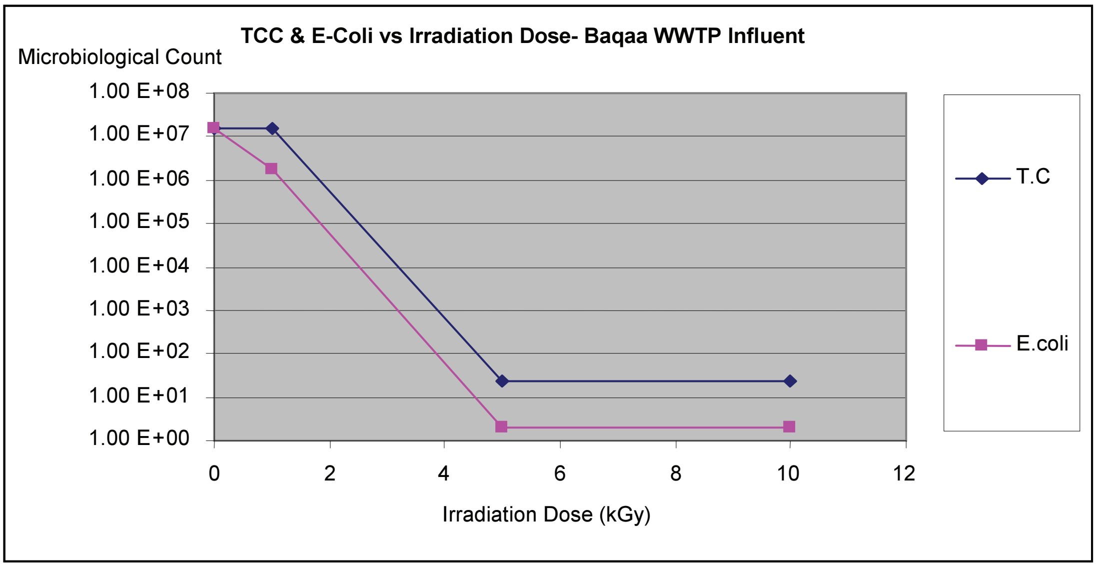


FIG. 4. Results of irradiation with different doses on microbiological content- Baqaa WWTP influent.

The irradiation dose of 5 kGy was found to be sufficient in controlling the microbiological content of the highly contaminated wastewater of the plant influent. Comparing these results with the results obtained from disinfection of the slightly contaminated drinking water, where a dose of 0.5 kGy was sufficient to control microbiological content of that water, it can be concluded that the irradiation dose required for water disinfection is proportional to the microbiological load of the irradiated water.

More detailed experiments were carried out on wastewater disinfection, where about 210 samples were collected from the effluent of Baqaa WWTP during different seasons, (i.e. in summer and winter) as well as during different physical, chemical, and biological loads. The analytical results of the samples before and after irradiation are shown in Table 5, where the presented results represent the geometric mean values of all samples.

The results show that an irradiation dose of 1.5 kGy is capable of controlling the E-coli content to less than 10 counts. Using an irradiation dose of 2 kGy is possible to reduce the microbiological content of irradiated waters to a very low number (E-coli count to about 2 counts/100 mL), as shown in Figure 5.

5.2.2. Bacterial regrowth

To study the effect of different irradiation doses on the microbiological regrowth of the irradiated samples, a simulated microbiological regrowth test (SMRT) carried out by adding a nutrient to the irradiated samples. The results of SMRT test for samples irradiated with different doses and kept for 7 days are shown in the Table 6 and illustrated in Figure 6.

TABLE 5. MEAN VALUE OF MICROBIOLOGICAL RESULTS BEFORE AND AFTER IRRADIATION

Dose (kGy)	E-coli	TCC	TTCC
0	2416667	1.16E+07	4.16E+06
1	31.2	374.6	269.6
1.5	3.4	16.8	27.6
2	2.1	6.4	3.6

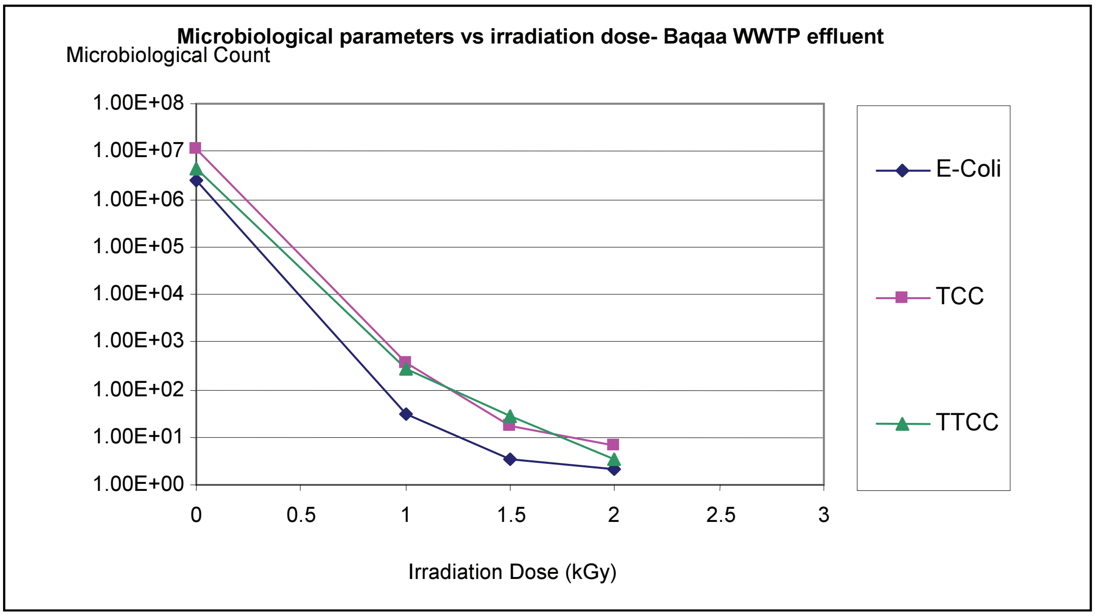


FIG. 5. Microbiological parameters versus irradiation doses- Baqaa WWTP effluent.

TABLE 6. E-COLI COUNT OF SMRT AFTER IRRADIATION WITH DIFFERENT DOSES AND 7 DAY HOLDING TIME

Time	Before Irradiation	Irradiation with 1 kGy	Irradiation with 1.5 kGy	Irradiation with 2 kGy
0-day	500000	47	2.4	8
3-days	15500	1.2	1.2	1
7-days	1150	2.8	1	1

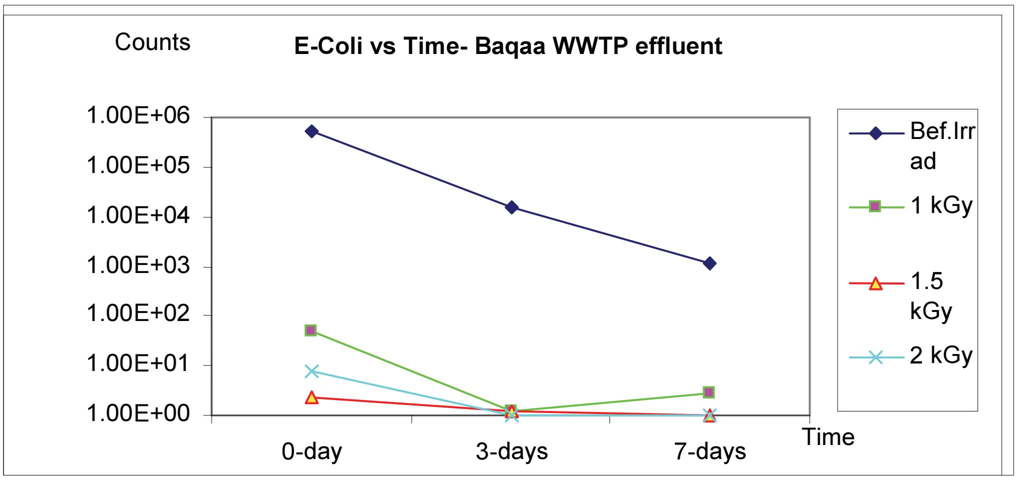


FIG. 6. E-coli re-growth at 1, 1.5 & 2 kGy irradiation doses.

The results show no bacterial regrowth happens at an irradiation dose of 1.5 kGy or more. Microbiological regrowth did not occur in samples after irradiation perhaps due to the lack of nutrients. When a sufficient amount of nutrients was added to the samples after irradiation, the microbiological regrowth happened, and E-coli count reached its initial values as shown in Table 7.

At the same time, the microbiological regrowth was found inversely proportional to the applied irradiation dose as illustrated in Figure 7. This can be explained that at higher irradiation doses, more bacteria are killed and less bacteria survive. Therefore, higher irradiation doses are required to achieve complete disinfection and full control of microbiological content of the irradiated wastewater.

TABLE 7. E-COLI CONTENT OF IRRADIATED SAMPLES WITH AND WITHOUT NUTRIENT ADDITION

Time (days)	Bef.Irrad.	Bef.Irrd+ Nt	1 kGy	1 kGy+ Nutr.	1.5 kGy	1.5 kGy+ Nutr.	2 kGy	2 kGy+ Nutr.
0	5000000	2400000	220	300	80	11	8	4
3	30000	16000000	30	24000000	8	16000000	1	240000
7	16000	1.6E+08	13	35000000	17	17000000	1	1700000

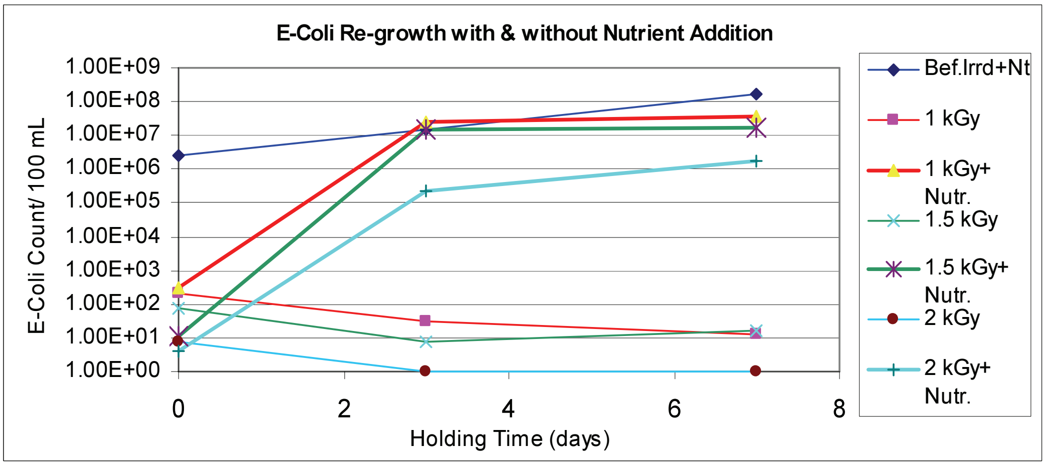


FIG. 7. E-coli regrowth in irradiated samples with and without nutrient addition.

5.2.3. Factors affecting the irradiation efficiency of wastewater disinfection

To determine the factors affecting the efficiency of wastewater disinfection by irradiation, about 65 samples were collected from the effluent of Baqaa wastewater treatment plant during summer and winter periods. The collected samples were irradiated with different doses and analyzed for microbiological content (E-coli count), as well as some physical and chemical parameters such as Total Suspended Solids (TSS), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), and turbidity.

Table 8 below includes the COD and TSS monitoring data of Baqaa WWTP effluent collected in 2005. The reported results represent the mean values of all samples.

The plot of the data is shown in Figure 8, which shows a close relationship between TSS and COD of the plant effluent. The variations of the results between summer and winter period do not show any clear effect of the seasonal variations on water quality of the plant effluent.

To study the effect of TSS of the irradiated water on the efficiency of water disinfection, samples with different TSS were collected from plant effluent irradiated with a dose of 1.5 kGy and measured for E-coli count. The results are presented in Table 9 and illustrated in Figure 9 and show that the dose required for water disinfection is slightly affected with the increase in TSS of the irradiated water.

TABLE 8. THE TSS AND COD RESULTS OF BAQAA WWTP EFFLUENTS- 2005

Months	No	COD	TSS
1	1	117	49
2	2	161	104
3	3	123	30
10	4	121	10
11	5	48	46
12	6	48	36
4	7		53
5	8	126	37
6	9	125	12
7	10	89.5	36
8	11	187	120
9	12	145	168

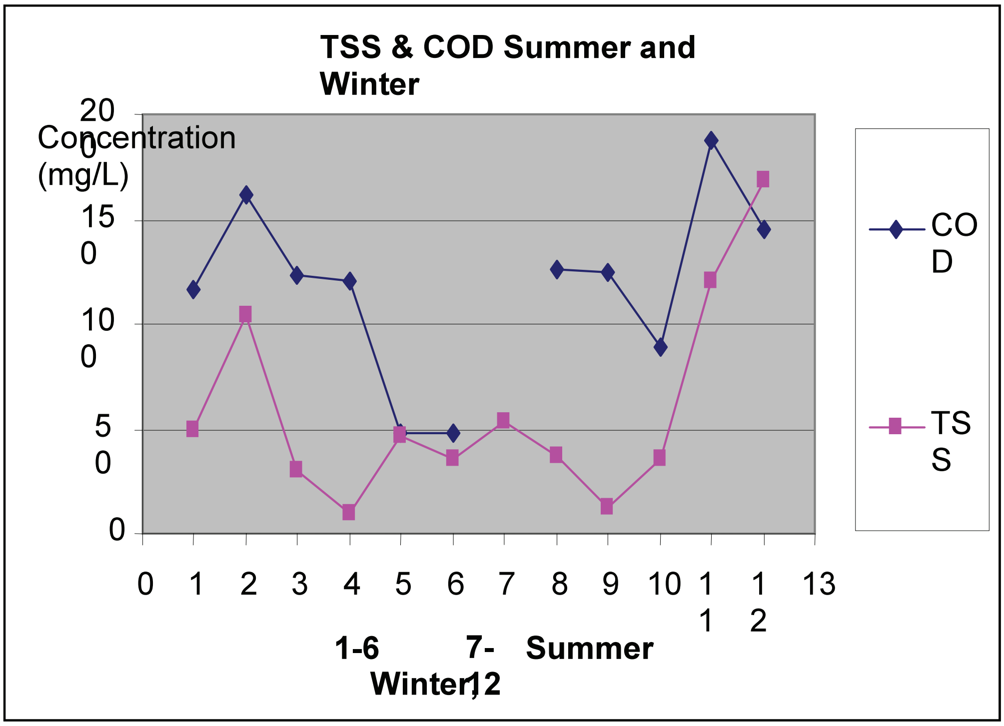


FIG. 8. TSS and COD of Baqaa WWTP effluent during summer and winter times.

TABLE 9. E-COLI COUNT AFTER SAMPLE IRRADIATION WITH 1.5 kGy WITH DIFFERENT WATER TSS

TSS of water	li before irradi	E-coli after irrad.(1.5 kGy)
12	1.00E+06	4
62	1.60E+06	8
120	1.60E+07	48

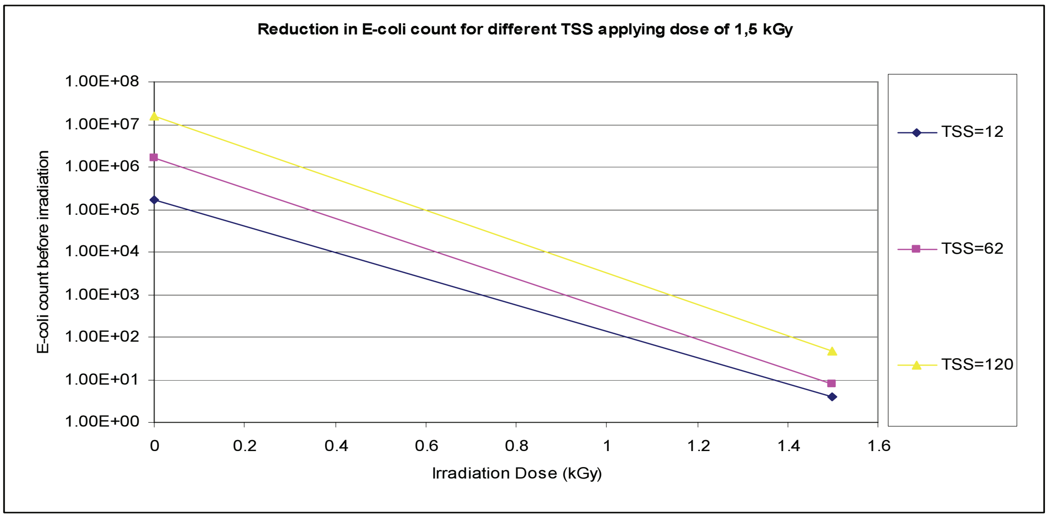


FIG. 9. The effect of TSS on the efficiency of water disinfection.

To study the effect of seasonal variations on the efficiency of water disinfection, water samples from plant effluent were collected during summer and winter periods, irradiated with different doses and measured for *E. coli* content. The results are shown in Table 10 and plotted in Figure 10.

The results show that the dose required for water disinfection is seasonally dependent, and a higher dose is needed during the summertime as compared to the wintertime. This could be explained as the result of a higher E-coli content of the row water during summer as compared to winter, as shown in Figure 10.

TABLE 9. E-COLI COUNT OF IRRADIATED WATER WITH DIFFERENT DOSES DURING SUMMER AND WINTER PERIODS

Dose (kGy)	*E. coli* count (Summer)	*E. coli* count (Winter)
0	6.00E+06	1.60E+05
0.5	1200	240
0.75	130	32
1	8	4
1.5	4	<1
2	<1	<1

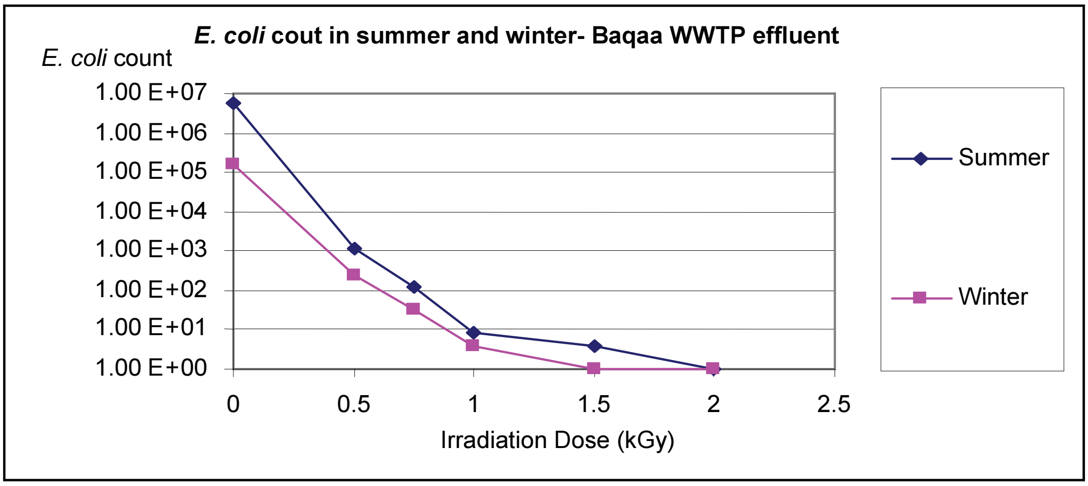


FIG. 10. The effect of seasonal variations on water disinfection for samples irradiated with a dose of 1.5 kGy.

6. DEACTIVATION OF NEMATODE EGGS BY IRRADIATION

6.1. Methods and Tools Used

To study the effect of irradiation processing on deactivation of nematode eggs, 3 triplicate samples were collected. Each sample contained 4 bottles. To each bottle, sterilized water and 3 egg masses of the parasitic nematode *Meloidogyza javanica* were added and incubated up to 7 days. The first bottle of each sample was un-irradiated, while the other 3 bottles were subject to irradiation with 1, 2, 3, 4, and 5 kGy. Within the incubation period, samples were examined and counted for nematode larvae's hatching using a binocular microscope. Forty-two samples, total, were analyzed.

6.2. Results and Discussion

The results of the experiments where shown in Table 11. The relationship between the irradiation dose and the number of deactivated nematode eggs is shown in Figure 11. It is found that at irradiation dose of 1 kGy, only about 65% of the nematode eggs in the irradiated samples were deactivated, while at a dose of 5 kGy, the per cent of the deactivated nematode eggs is over 98%.

TABLE 11. NUMBER OF ACTIVE NEMATODE EGGS IN WATER SAMPLES BEFORE AND AFTER IRRADIATION WITH DIFFERENT DOSES

Patch No	Number of samples	0 kGy	1 kGy	2 kGy	3 kGy	4 kGy	5 kGy
1	4	11	11	10	2	-	-
2	4	19	2	2	1	-	-
3	4	52	14	14	14		
4	6	50	17	15	12	5	0
5	6	72	28	20	19	7	1
6	6	22	6	8	6	2	0
7	6	40	14	10	10	4	0
8	6	85	33	28	20	8	2
Average	42	43.9	15.6	13.4	10.5	5.2	0.6

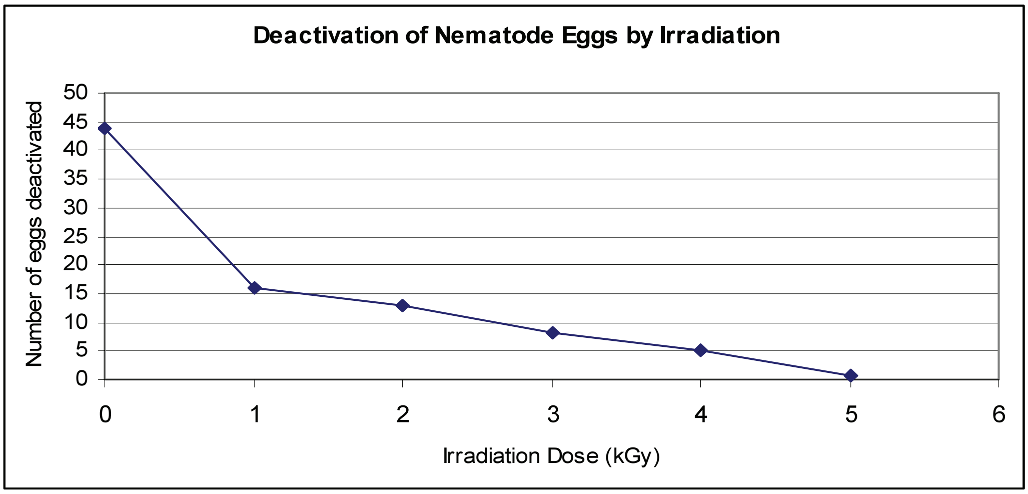


FIG. 11. The effect of Gamma radiation on deactivation of nematode eggs.

7. ALGAE CONTROLL BY IRRADIATION

Experiments were carried out to study the effect of irradiation on controlling the algae blooms in surface waters. The water samples were collected from King Abdalla Canal during summer and winter periods. The samples were irradiated with 0.5, 1, 1.5, and 2 kGy.

The plankton count in Unit/mL and Chlorophyl-a in µg/L is carried out for the samples before and after irradiation. The analytical results are shown in Table 12. The results illustrated in Figure 6 show that irradiation doses up to 2 kGy were insufficient in controlling the algae blooms and in destroying the plankton in the irradiated water.

TABLE 12. THE RESULTS OF IRRADIATION EFFECT ON PHYTOPLANKTON COUNT AND CHLOROPHYL-A CONCENTRATIONS

Irrad. Dose (kGy)	Plancton Count 'summer' (Unit/mL)	Plankton Count 'winter' (Unit/mL)	Chlorophyl-a 'summer' (µg/L)	Chlorophyl-a 'winter' (µg/L)
0	1011	216	13.9	4.6
0.5	642	231	14.3	5.1
1	818	214	13.2	6.2
1.5	825	120	15	5.6
2	931	231	14.3	5.9

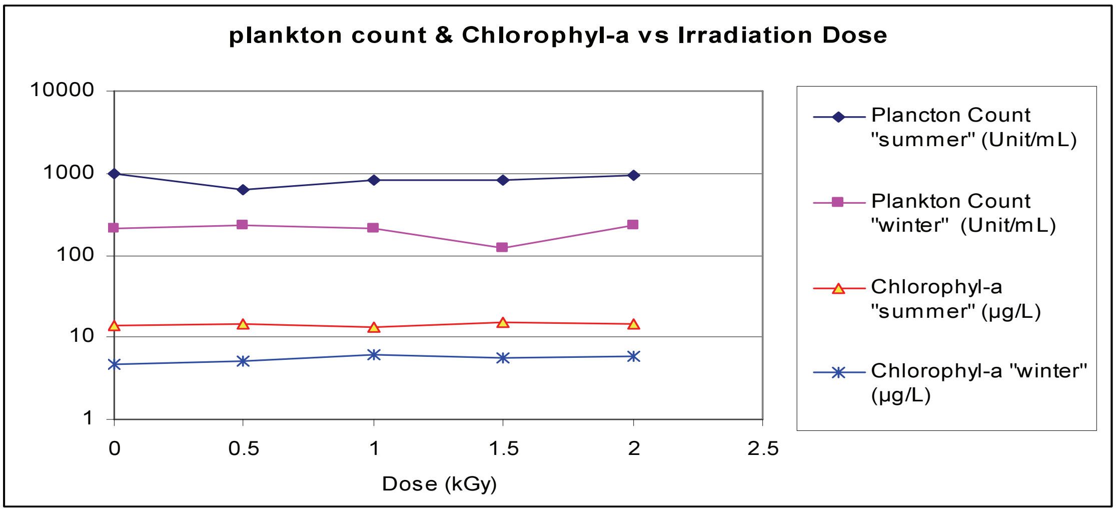


FIG. 12. The effect of gamma radiation on Phytoplankton and concentration of Chlorophyll-a in water.

8. THM REMOVAL FROM DRINKING WATER

8.1. THM Sampling and Processing

Experiments with removal of THM compounds from drinking water supplies were carried out on water samples collected from Dabouq reservoir, which represents the effluent of the Zai drinking water treatment plant. In this plant, surface water from King Abdulla Canal passes several treatment processes like oxidization, coagulation and filtration. The plant effluent (the treated water) is disinfected by chlorination. The residual chlorine, with presence of organic substances such as humic and fulvic acids together with high concentrtions of bromide, lead to formation of trihalomethanes. Brominated compounds contribute a high fraction of the total THMs formed in this water. The bromoform alone contributes to more than 90% of the total THMs concentrations. This is due to the fact that the reaction of the bromine with humic and fulvic acids is much faster compared to that of chlorine. This reaction is temperature dependent, while in the summertime THM concentrations can exceed the maximum allowable level of 100 ppm, which is set by the World Health Organization (WHO).

Samples were collected on a monthly basis to consider the effect of water quality and seasonal variations on THM formation. Samples were collected in 40 ml special glass bottles and kept cool at 4ºC immediately after collection and after irradiation processing. For the samples measured directly, sodium thiosulphate was added upon sample collection. Irradiation was carried out using research Co-60 gamma irradiator at Jordan Nuclear Energy Commission laboratories. Irradiation doses applied ranges between 100 Gy and 10 kGy. For THM Simulated Distribution System test (SDS-THM), each sample was collected in duplicate, one to be measured after applying the required irradiation dose, and the other after applying the same dose, but with addition of chlorine after irradiation processing. Samples were measured before irradiation as well as after irradiation, within the time interval of 0, 1, 3, 5, and 7 days. THM analyzes were carried out at Central Laboratories of Water Authority of Jordan using a Thermo Quest Trace Gas Chromatograph GC 2000 equipped with anelectron capture detector and headspace sample injection system. The anion analysis was carried out using Dionex DX-120 ion chromatograph. Samples for inorganic analysis were collected in polyethylene bottles, for which the following analyses were carried out: pH, EC, Cl, Br, NO_2, NO_3, ClO_2, BrO_3, TOC.

8.2. Results and Discussion

The analytical results of the chemical parameters, with respect to irradiation dose are shown in Table 13.

TABLE 13. CHEMICAL PARAMETERS OF IRRADIATED DRINKING WATER WITH RESPECT TO IRRADIATION DOSES

Dose (Gy)	PH (units)	EC (µs/cm)	Cl (mg/L)	Br (mg/L)	NO_2 (mg/L)	NO_3 (mg/L)	ClO_2 (mg/L)	TOC (mg/L)
100	7.18	1177	249	1.48	<0.20	2.1	<0.10	2.16
300	7.33	1184	247	1.54	<0.20	2.2	<0.10	3.92
500	7.2	1180	249	1.68	<0.20	2.2	<0.10	2.18
1000	7.35	1183	249	1.68	<0.20	2.1	<0.10	2.3
2000	7.17	1180	250	1.75	<0.20	2.1	<0.10	2.14

The results show that irradiation doses up to 10,000 Gy have no significant influence on the concentrations of the measured inorganic chemical compounds present in the irradiated water samples. Bromide was the exception. Its concentration in irradiated water increased with the increase of irradiation dose. Nitrite (NO_2) was not detected in the water samples before and after irradiation. Nitrate (NO_3) concentrations were not affected by irradiation doses up to 10 kGy.

The irradiation process was found to have different effects on the organic compounds present in the water. While irradiation doses up to 10,000Gy have no reduction in total organic carbon (TOC) concentrations, THM compounds were found very sensitive to the irradiation processing. Figure 13 shows the THM concentrations before and after water irradiation at different irradiation doses (from 100 Gy up to 10 kGy).

The mean THM values of all collected samples before and after irradiation are shown in Table 14 and illustrated in Figure 14.

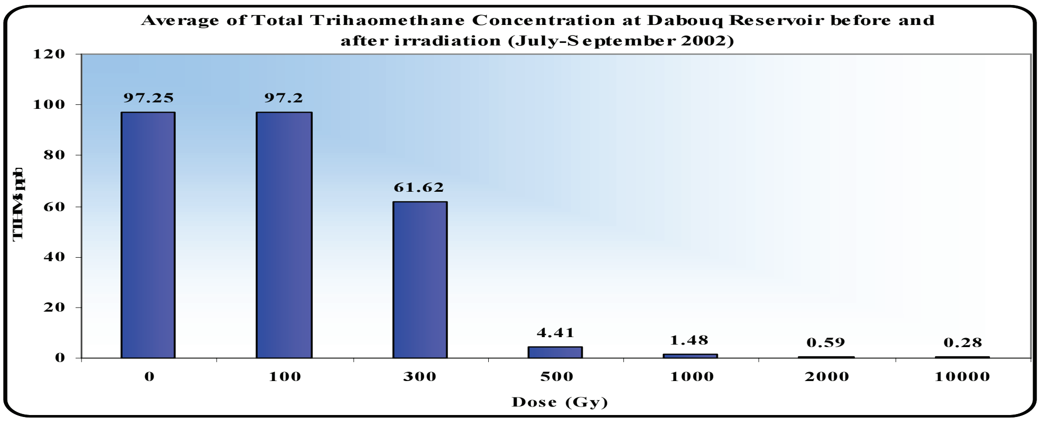


FIG. 13. THMs concentrations before and after water irradiation at different irradiation doses.

TABLE 14. PER CENT OF THM REMOVED APPLYING DIFFERENT IRRADIATION DOSES

Applied dose (kGy)	Initial THM concentration (µg/L)	% THM removed
0	98	0
0.1	97	1.0
0.3	65	33.7
0.5	22	77.6
0.75	8	91.8
1	1.8	98.2
2	1	99.0

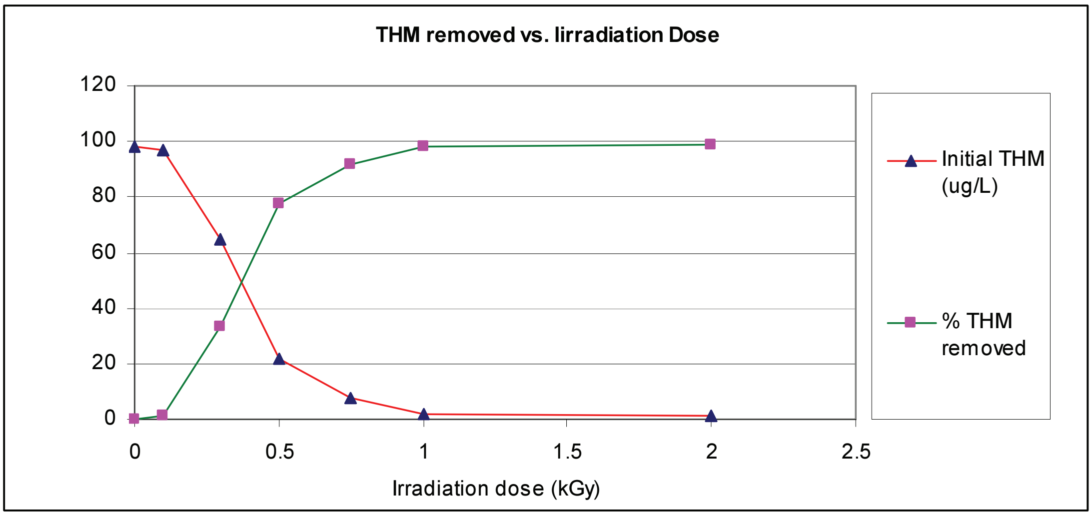


FIG. 14. The effect of irradiation processing on THM removal from drinking water.

The irradiation dose of 100 Gy found no influence on the THM's degradation, while at doses of 1 kGy, the THM concentration removed was more than 98% of its initial value. This dose could be considered the optimal irradiation dose for THM removal from waters containing up to100 µg/L of THMs.

To estimate the values of the THM's re-formed in the distribution system after disinfection, SDS-THM tests were performed on the samples taken from the Dabooq reservoir and irradiated with different irradiation doses. The results of the SDS test are shown in Figures 15 and 16.

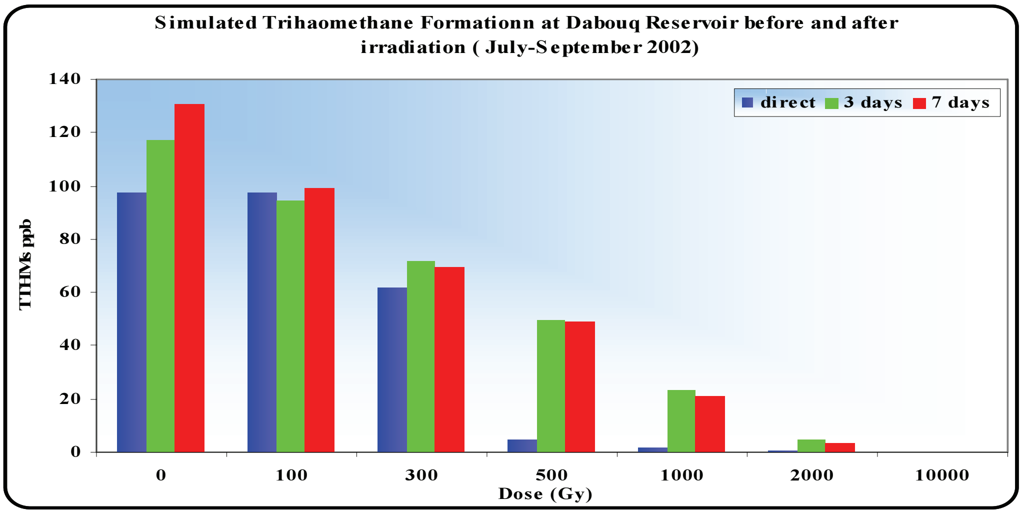


FIG. 15. Results of the SDS-THM test before and after irradiation.

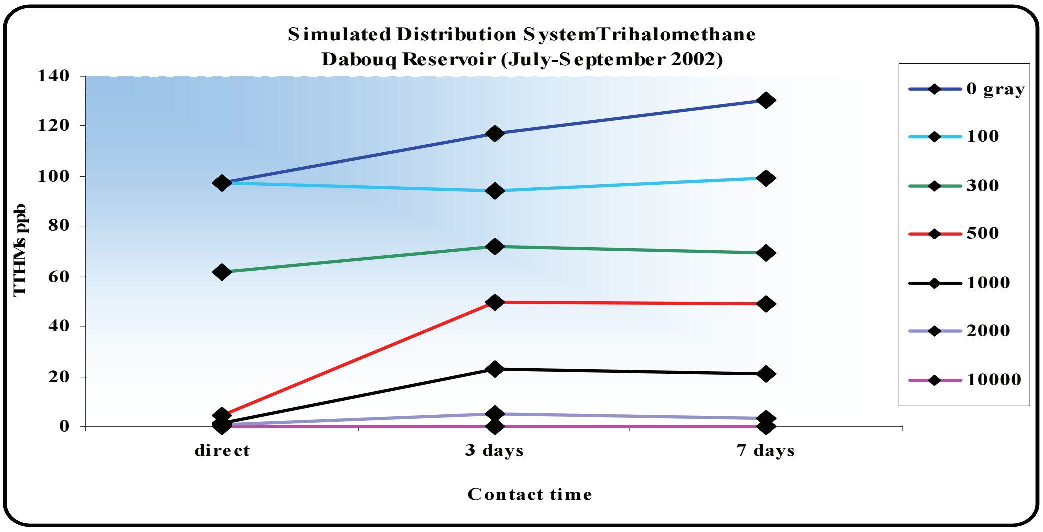


FIG. 16. Results of the SDS-THM test before and after irradiation.

For non-irradiated samples, the THM's concentration increased from initial value of 97 µg/L to 117 µg/L after 3 days and to 131 µg/L after 7 days. With irradiation dose of 500 Gy, the THMs value increased from 4.4 µg/L to 49.7 µg/L after 3 days, and to 49 µg/L after 7 days. For 1000 Gy dose, the THM concentration increased from 1.5 µg/L to 23 µg/L after 3 days and to 21 µg/L after 7 days. At 2000 Gy dose, the THM concentration increased from 0.6 µg/L to only 4.9 µg/L after 3 days and to 3.4 µg/L after 7 days. At irradiation dose of 2 kGy and higher, the THM re-formation is very small.

From the above mentioned results, one can conclude that the irradiation dose of 1 kGy is a reasonable dose in both aspects; removal of the initial concentration of the THMs, and achieving low levels of THM re-formation in the distribution system.

The low THM re-formation could be explained as a result of the destruction of the residual chlorine in the irradiated water. In the case of the water distribution system, the water has to contain enough residual chlorine to keep the water safe. Therefore, further experiments were carried out on the SDS-THM test by addition of sufficient amounts of chlorine to the samples after irradiation. The results obtained are shown in Table 15 and illustrated in Figure 17.

TABLE 15. THE RESULTS OF THE SDS-THM TEST AFTER CHLORINE ADDITION AFTER IRRADIATION OF THE SAMPLES. THE THM RESULTS ARE IN µg/L

Time (days)	Bef.Irrd+Cl	1 kGy	1 kGy+ Cl	3 kGy	3 kGy +CL	10 kGy	10 kGy +Cl
0	124.43	31.77	42.75	2.32	3.55	0.01	12.56
1	146.49	34.6	139.2	4.68	109.47	0.01	27.44
3	174.6	27.7	184.93	2.28	152.85	0.01	35
5	188.63	32.5	200.27	3.99	177.13	0.01	49
7	205.8	31.4	222.33	3.55	232.15	0.01	60.82

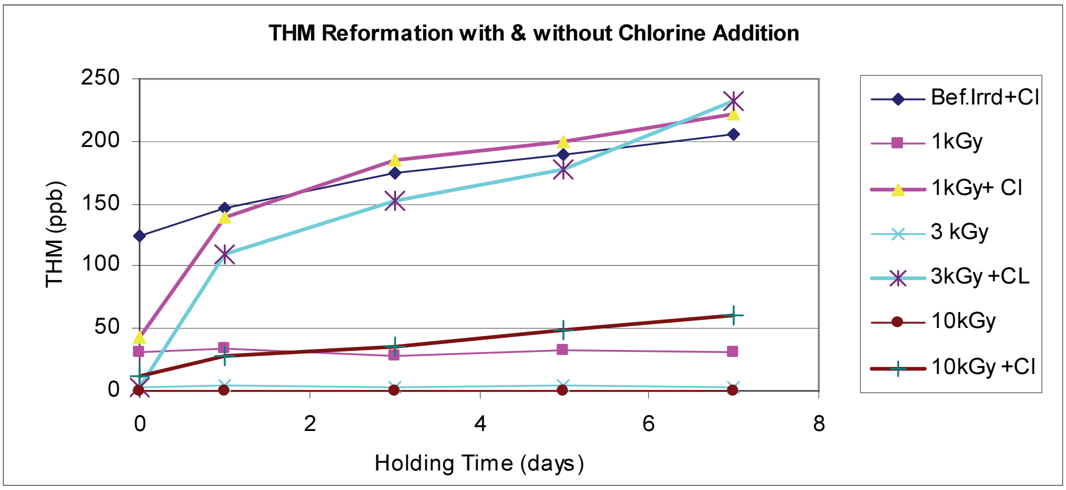


FIG. 17. THM re-formation after chlorine addition to the irradiated samples.

The results show that THM concentration of non-chlorinated samples probably remains unchanged after 7 days of irradiation. When a sufficient amount of chlorine is added to the samples, THM’s re-formed again and increased with time to reach concentrations exceeding their initial values. The THM reforms as a result of the reaction between the added chlorine and the THM precursors which still exist in water. THM re-formation was found to be very small for the samples irradiated with a dose of 10 kGy. This means that at such high irradiation doses, most THM precursors were destroyed or removed from water.

To identify the effect of seasonal variations in re-formation and removal of THMs, water samples were collected in Dabooq reservoir in summer and winter periods, irradiated and measured for THM concentration before and after irradiation. An SDS-THM test was carried out on samples irradiated with a dose of 3 kGy, chlorinated, and kept in room temperature for 7 days. The analytical results of the experiments are shown in Table 16.

The results shown in Figure 18 indicate that the THM re-formation is a temperature- dependant process with the highest THM concentrations reached during summer time.

TABLE 16. THE EFFECT OF SEASONAL VARIATIONS ON THE THM FORMATION

Time	Bef.Irrd	Bef.Irrd+C (Summer)	After Irrad. (3 kGy)	3 kGy +Cl (Summer) t= 35°)	After irrad. 3 kGy	3 kGy+Cl (Winter) (t=10°)	Before Irrad+Cl (Winter)
0	99.42	124.43	2.32	3.55	65	2	56
1	97.25	146.49	4.68	109.47	72	60	90
3	126.65	174.6	2.28	152.85	75	94	111
5	139.07	188.63	3.99	177.13	80	92	120
7	138.66	205.8	3.55	232.15	82	95	135

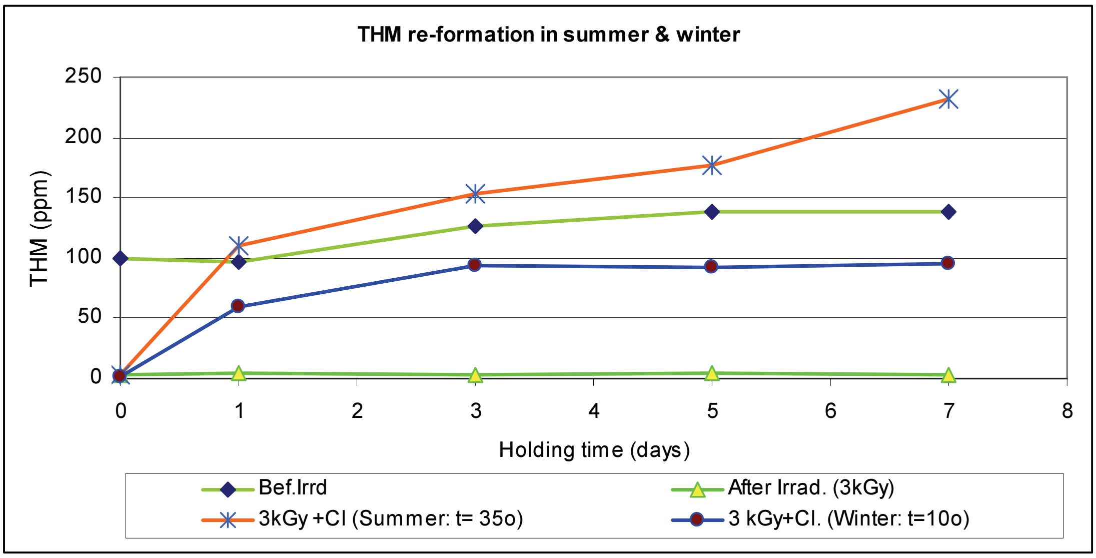


FIG. 18. The effect of seasonal variations on THM re-formation.

9. CONCLUSIONS

1- Irradiation processing was found efficient in treatment and disinfection of microbiologically contaminated drinking water supplies. Irradiation dose of 1 kGy was found optimal in controlling the microbiological content of drinking waters containing up to 1000 e-Coli counts.

2- Irradiation dose of 1.5 kGy was found efficient in controlling the microbiological content of domestic wastewater treatment plant effluents to meet the requirements and guideline values for wastewater reuse for unrestricted irrigation.

3- The irradiation dose required for wastewater disinfection depends on the microbiological load of irradiated water. The physical parameters, such as water TSS and turbidity, and seasonal variations between summer and winter periods were found to have minor effect in the irradiation efficiency of wastewater disinfection.

4- Irradiation processing was found an effective method in the deactivation of nematode eggs where 96% of the nematode eggs deactivated at a dose of 5 kGy.

5- Ionization doses up to 2 kGy were found inefficient in controlling the algae blooms in surface water sources.

6- More than 98% of THM compounds can be removed from drinking water supplies containing up to 100 μg/L THMs when applying an irradiation dose of 1 kGy.

7- To control the THM's re-formation in drinking water networks, higher irradiation doses up to 10 kGy should be applied to remove the THM precursors from the irradiated waters.

REFERENCES

[1] GOTOFF, N., Radiation processing of liquid and solid industrial wastes. Applications of isotopes and radiation in conservation of the environment. IDEA, Vienna (1992).

[2] IAEA Training manual on food irradiation technology and techniques. Second edition Vienna (1982).

[3] WHO, Wholesomeness of irradiated food. Report of a joint FAD/IAEA/WHO expert committee, report series No 659, Geneva (1981).

[4] W. J., COOPER, et. al. The removial of tri- (TCE) and tetrachloroethylene (PCE) from aqueous solution using high energy electrons. Air and Waste Management Association, 43 (1993).

[5] PROKSCH, E et al. Radiation- induced decomposition of small amounts of perochloroethlene in water, app. Radiat Isot. 38 (1987).

[6] GETOFF, N, SOLARS, S., Radiation induced decomposition of chloronated phenols in water. Radiat. Phys chem 31 (1988).

[7] WHO Safety and nutritional adequacy of irradiated food. Geneva (1994).

[8] HABERL, R. URBAN, W. GEHRIAGER, P. SZINOVATZ, W. Water Science, Technology, No. 24 (1991).

[9] SCHUBERT, J., Irradiation of food and food constituents. Improvement of food quality by irradiation, IAEA, Vienna (1974).

DISINFECTION OF EFFLUENT FROM MUNICIPAL WASTEWATER PLANT WITH ELECTRON BEAM

B. Han, J.K. Kim, Y.R. Kim

EB-TECH Co., Ltd
Yuseong-gu Daejeon, Republic of Korea

Abstract

Electron beam has been introduced to investigate the effect of radiation on the disinfection of Coli-forms in the effluent from the municipal wastewater treatment plant. Unchlorinated secondary effluent was irradiated at a different dose of 0.2–1.0 kGy with a 1 MeV, 40 kW electron accelerator. It is observed that nearly 100% reduction in E-Coli and total Coli-forms was achieved with a dose of 0.8 kGy. Even with the lower dose of 0.2 kGy, the E-Coli and total Coli-forms were successfully inactivated to the level of the new guideline for discharged effluent that has been effective since 2003 in the Republic of Korea. Based on the data obtained in the experiments, an industrial scale plant with 0.2 kGy for the flow rate of 100,000m^3 effluent per day was designed. The overall cost for plant construction is approximately US $4.0 M, and the operation cost is around US $1M per year. This is applicable when compared to other advanced oxidation techniques such as Ozonation, UV techniques etc.

1. INTRODUCTION

The problems of environmental damage and degradation of natural resources are receiving increasing attention throughout the world. The increased population, higher living standards, increased urbanization and enhanced industrial activities of humankind are all leading to degradation of the environment. Increasing urbanization has been accompanied by significant water pollution. Radiation technologists have been investigating the use of high-energy radiation for treatment of wastewaters. The major advantage of radiation technology is that the reactive species are generated in-situ during the radiolysis process without addition of any chemicals. The results of practical applications have confirmed that radiation technology can be easily and effectively utilized for treating large quantities of wastewater [1–3].

Electron beam processing of wastewater is non-chemical, and uses fast formation of short-lived reactive radicals that can interact with a wide range of pollutants. Such reactive radicals are strong oxidizing or reducing agents that can transform the pollutants in the liquid wastes. The first studies on the radiation treatment of wastes were carried out in the 1950s principally for disinfection. In the 1960s, these studies were extended to the purification of water and wastewater. After some laboratory research on industrial wastewaters and polluted groundwater in the1970s and 1980s, several pilot plants were built for extended research in the 1990s. The first full-scale application was reported for the purification of wastewater at the Voronezh synthetic rubber plant in Russia. Two accelerators (50kW each) were used to convert the non-biodegradable emulsifier, ‘nekal’, present in the wastewater to a biodegradable form [1]. The installation treats up to 2,000 m^3 of effluent per day. A pilot plant of 1,000 m^3/d for treating textile-dyeing wastewater has been constructed in Daegu, Republic of Korea, with a 1MeV, 40kW electron accelerator [2], and commercial plant for 10,000 m^3/d with a 1MeV, 400kW electron accelerator was also in operation at the same site [4].

High-energy irradiation produces instantaneous radiolytical transformations by energy transfer from accelerated electrons to orbital electrons of water molecules. Absorbed energy disturbs the electron system of the molecule and results in breakage of inter-atomic bonds [5]. Hydrated electron e_{aq}^-, H atom, $^\bullet OH$ and $HO_2^\bullet$ radicals and hydrogen peroxide H_2O_2 and H_2 are the most important products of the primary interactions (radiolysis products):

$$H_2O \text{ /\/\/\-->} e_{aq}^-, {}^\bullet H, {}^\bullet OH, HO_2^\bullet, H_2O_2, H_2$$

with yields (G value, μmol/J) of 0.28(e_{aq}^-), 0.062($^\bullet H$), 0.28($^\bullet OH$), 0.072(H_2O_2).

High reactivity is characteristic of water radiolysis products [5]. The typical time of their reactions with the impurities in water is less than 1 microsecond. Hydrogen peroxide H_2O_2 and $^{\bullet}OH$ and $HO_2^{\bullet}$ radicals are oxidizing species, while H atom and e_{aq}^- are chemical- reducing in nature [1].

2. RECLAMATION OF EFFLUENT FROM MUNICIPAL WASTEWATER PLANT

Population growth, coupled with declining fresh water supplies, has necessitated development of technologies to reclaim potable water from wastewater. It is one of the critical challenges for the 21st century. The increasing levels of pollution and complexity of effluents from municipalities and industries demand effective technologies to remove pollutants to the desired levels, and current wastewater treatment technologies are often not successful for such reclamation. Some progress has been made, however, in technical approaches for producting reliable sources of quality water by use of wastewater reclamation technologies. Advanced wastewater treatment technologies are essential for the treatment of municipal wastewater to protect public health and to meet water quality criteria for the aquatic environment and water recycling and reuse. Further, when reclaimed wastewater is to be used for human consumption, disinfection is absolutely essential, and removal or inactivation of pathogenic organisms is a critical step in final treatment. Among the possible water treatment alternatives, radiation processing is a very effective option, since it can simultaneously degrade toxic organic compounds, as well as biological contaminants that are present.

Radiation disinfection of effluent from municipal wastewater treatment for reuse has been successfully demonstrated by a number of researchers. It has been demonstrated that inactivation of fecal Coli-forms in secondary effluents from municipal wastewater plants can be achieved with doses less than 1 kGy. While the efficiency of conventional disinfectants is adversely affected by the water matrix, radiation processing for bacteria inactivation is generally unaffected by the matrix. Therefore, radiation processing has a clear advantage over existing methods for municipal wastewater disinfection. Radiation processing would be technically much easier than conventional processes for wastewater disinfection. Reclamation of effluent from municipal wastewater treatment plants has been extensively studied in Austria, the Republic of Korea, Brazil, Ecuador and Jordan. In Austria, the effect of oxygen on the radiation-induced inactivation of selected microorganisms in water has been studied (see Fig. 3.6). A cost assessment based on a radiation dose of 1 kGy has indicated that for a plant capacity of about 1,150 m^3/h, the treatment of secondary effluent should cost about US $0.1/$m^3$, which should be acceptable considering the advantages that the radiation induced disinfection provides over conventional technologies[6]. A 99% reduction of microbiological content of the irradiated water was achieved at the dose of 2 kGy in Jordan, and to carry out the effective deactivation of nematode eggs, up to 3 kGy of irradiation dose was found to be required. [7] In Ecuador, irradiation with an electron accelerator resulted in the decontamination and disinfection of municipal wastewater with a reduction of 72% in COD, 80% in BOD, 72% in surfactants, and 100% in total micro-organisms and fecal Coli-forms. Regulations currently exist for concentration of E-Coli in secondary effluents in some countries, and such regulations will be adopted by a significant number of countries in the near future. Hence, radiation processing is a highly attractive technology, especially given its meeting such regulations and the advantages compared to conventional technologies. However, at present, there is no full-scale radiation treatment plant in operation.

Radiation processing for effluent treatment represents a beneficial alternative to chemical and UV treatment. Compared to chemical disinfection, it has proven to be a ‘cleaner’ technology without the formation of hazardous by-products; as compared to UV irradiation electron beam irradiation, it is technically much simpler, almost insensitive to color, suspended solids or gas bubbles in the effluent stream and, moreover, to effluent composition and fouling characteristics. Besides, it requires considerably less maintenance and is very easy to control. Studies of the remediation of contaminated groundwater using radiation have been conducted in the USA, and kinetic models and destruction mechanisms have been proposed [8]. Remediation of groundwater contaminated by pesticides has been studied in Poland and Turkey. [9, 10]

The treatment of municipal wastewater for reclamation of industries or agricultural purposes becomes a more important subject in the field of Water Resources Management. Nationwide in the Republic of Korea, over 200 sewage disposal plants are in operation and they treat up to 20 million tons of sewage per day. It covers 80% of the total discharged and 95% of the main streams in the country. Most of those existing municipal sewage disposal plants are equipped with conventional biological methods with the digestion of activated sludges, which are efficient to remove suspended solids and organic matters. However, those methods have limitations in removing nitrates and phosphates that used to be the nutrient of algae formation as well as in decreasing the number of microorganisms in effluent. For the reuse of such effluent to industries or irrigation, not only the colour, odour, and residual organics are important, but the numbers of microorganisms are also important. In the Repubic of Korea, since 2003, new guidelines of governmental authorities have been effective to control the numbers of E-Coli in the effluent from sewage plants to less than 3000 numbers in 1 ml. Therefore, advanced technologies to control the microorganisms, as well as to remove colour, odor etc., are required on the economical basis. Among the many new technologies, radiation treatment is the most promising method in both economical and technical evaluation. The treatment of municipal wastewater with electron beam is actively studied in EB TECH Co. An electron accelerator of energy 1 MeV is used in experiments. Applied doses in the experiments were measured with an ordinary or modified Fricke dosimeter and dichromatic dosimetry system.

3. CONTINUOUS FLOW IRRADIATION EXPERIMENTS

To observe the applicability of electron beam treatment for disinfection of the effluent from municipal sewage treatment plant the effectiveness of electron beam irradiation in the disinfection of wastewater, and the improvement of the water quality were measured by determining the changes in organic matter as indicated by the measurement of BOD, COD and TOC. The experiments were conducted with a 1MeV, 40kW electron accelerator at EB-TECH CO., LTD in the Republic of Korea. The absorbed doses for all of the experiments were in the region of 0.2 kGy–1.0 kGy.

The effluent used for this research was supplied by the Daejeon Municipal Wastewater Treatment Plant, and the effluent was taken after the activated sludge treatment just prior to discharge. Measurements of E-Coli, total Coli-forms and bacteria were determined by the membrane filter procedures which is the EPA standard Method. After Irradiation, the change of characteristics in effluent was measured as BOD and COD, using the EPA standard method. FIG. 1 shows the bench scale electron beam irradiation system used in this research.

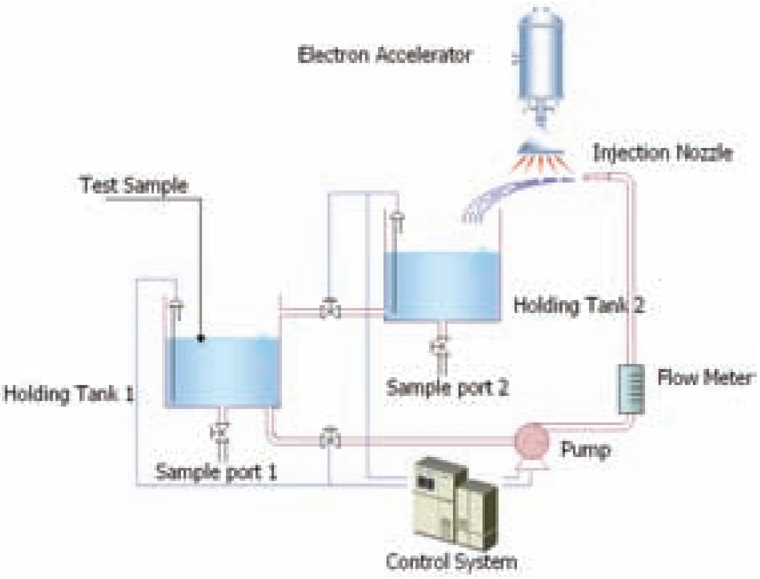


FIG. 1. Schematic diagram of experimental apparatus.

TABLE 1. SUPPLY AND DEMAND OF FRESH WATER IN THE REPUBLIC OF KOREA ($10^8 m^3$/year)

Year	1994	2001	2006	2011
Demand	29,901	33,640	34,991	36,652
Supply	32, 219	34, 290	34, 541	34,655
Shortage	-	-	450	1,997

4. RESULTS AND DISCUSSION

It is observed that nearly 100% of E-Coli and total Coli-forms were inactivated with a dose of 0.8 kGy. Even with the lower dose of 0.2 kGy, the E-Coli and total Coli-forms were successfully inactivated to the level of the guideline for effluent discharge. (See FIG. 2) Besides disinfection of total Coli-forms, approximately 50% of removal in biochemical oxygen demand (BOD) was pronounced at a dose of 0.2 kGy. More than 20% removal in suspended solids (SS) and turbidity was also observed at a dose of 1.0 kGy.

TABLE 2. CHARACTERISTICS OF SECONDARY EFFLUENT FROM MUNICIPAL PLANT

Parameters	Max.	Min.	Aver.
	2002. 7. 8–2002. 9. 6 (40day)		
BOD (mg/L)	21.2	7.2	10.1
COD (mg/L)	14.8	8.8	10.8
SS (mg/L)	12.8	1.7	5.6
E-Coli (CFU/ml)	14 000	800	4200
Total Coli-forms (CFU/ml)	820 000	140 000	440 000

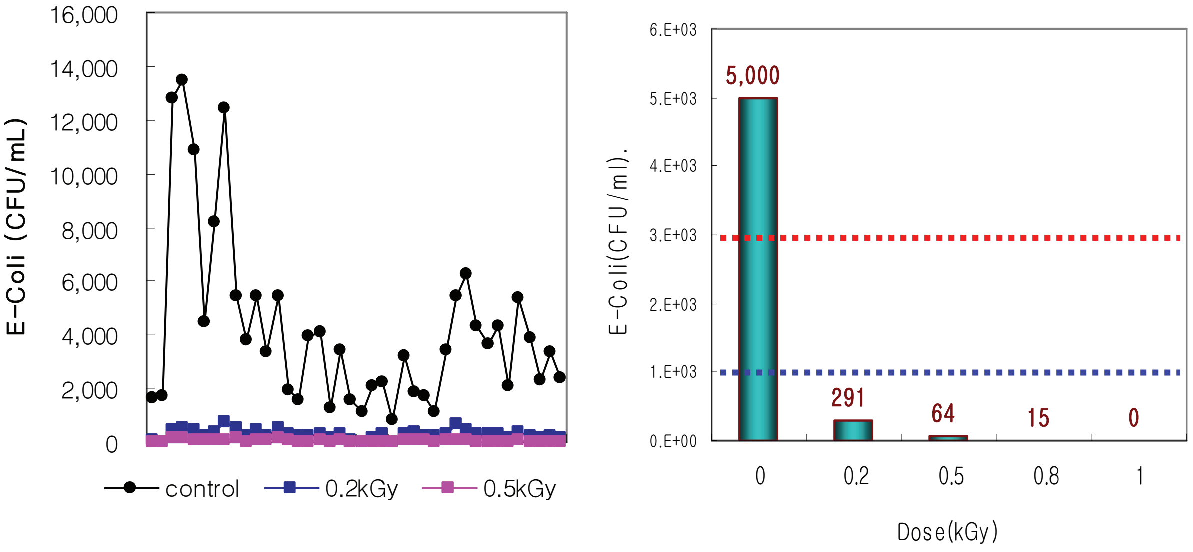


FIG. 2. Disinfection of E-Coli with different doses.

Radiation processing for effluent reclamation represents a true alternative to chemical and UV treatment. When compared to chemical disinfection, it has been shown to be a cleaner technology without the formation of hazardous by-products; as compared to UV irradiation electron beam irradiation is technically much more simple, almost insensitive to color, suspended solids or gas bubbles in the effluent stream, and moreover, to effluent composition and fouling characteristics, respectively. It needs considerably less maintenance and is very easy to control.

5. ECONOMICAL ESTIMATION OF COMMERCIAL PLANT

Based on the data obtained in the laboratory experiments, the suitable doses are determined to be around 0.2 kGy for the flow rate of 100,000m^3 effluent per day. Therefore, an accelerator, with the power of 400kW, is economical and compact for the plant. The cost for the high power accelerator is around US \$2.0~2.5M and building, piping, and other equipment and construction works could be estimated at US \$1.0~1.5M. Even by considering the additional cost for tax, insurance and documentation as US \$0.5M, the overall cost for plant construction is approximately US \$4.0~4.5M, as is stipulated in Table 3. This does not include cost for land, R & D and cost for the authority approval. The expected construction period is 17 months in civil and installation works and 3 months for trial operation.

TABLE 3. CONSTRUCTION COST OF INDUSTRIAL PLANT (UNIT: US \$M)

	Cost	Remarks
Accelerator — 1MeV, 400kW, double window	2.0~2.5	Cost for Land, R&D, Approval from Authorities are not included
Water reactor & other Raw Material	1.0~1.5	
Installation cost — welding/piping/inspection etc.		
Design		
Shield Room & Construction works		
Others — transportation, tax, insurance etc.	0.5	
Total	4.0~4.5	~ 4

TABLE 4. ECONOMIC EVALUATION OF INDUSTRIAL PLANT (UNIT: US $\$10^3$)

Items		Addition of E beam	Remarks
Operation Cost	Invest	(4,000)	
	Interest	320	8%
	Depreciation	200	20yrs
	Electricity	336	800kW
	Labour, etc.	100	3 shift
Total cost		956	~ US \$1M/yr

To estimate the operational costs, the electricity consumption is estimated and other equipment in additional 300kW to the total of 800kW. Based on the year round operation (8400hr/yr), it costs US \$336,000/yr when the cost of electricity (kWh) was assumed to be US \$0.05. The labor cost is calculated to be 3-shifts with one additional operator and is approximately US \$100,000/yr. Thus, the actual operation cost for 100,000m^3/day plants is US \$436,000/yr, and if we consider the interest and depreciation of investment, the cost comes to around US \$1M/yr. It is approximately US \$0.12/m^3 for construction and US \$0.03/m^3/yr for operation of above reuse plant. It is inexpensive compared to other advanced oxidation techniques such as Ozonation, UV techniques, etc.

6. CONCLUSIONS

Radiation disinfection appears to be an alternative method to replace the traditional chlorination method of treating effluent from municipal plants. This would improve the economics of the disinfection process and would also reduce the residual organics. Nearly 100% reduction in E-Coli and total Coli-forms were achieved with a dose of 0.8 kGy. Even with the lower dose of 0.2 kGy, the E-Coli and total Coli-forms were successfully inactivated to the level of the new guideline (less than 3,000 numbers in 1 ml) for discharged effluent.

Construction cost for the plant of 100,000 m^3/day is around US $4.0~4.5M and operation cost is around US $1M/yr. It is quite reasonable when compared to other advanced oxidation techniques.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the support of the International Atomic Energy Agency (IAEA) and the Ministries of Science and Technology (MOST) of the Korean Government.

REFERENCES

[1] THOMPSON, J. E. et al., "Toxicity effects of γ-irradiated wastewater effluents", Water Researches 33(9), (1999) 2053.

[2] LESSEL, T., et al, "Ten year experience in operation of sewage sludge treatment plant using gamma irradiation", Radiation Physics and Chemistry, 24, (1984) 13.

[3] MAKNI, H., "Disinfection of secondary effluents by infiltration percolation", Water Science Technology, 43(12), (2001) 175.

[4] HAN, B., et al., "Electron beam treatment of textile dyeing wastewater: operation of ilot plant and industrial plant construction", Water Science and Technology, 54(11), (2005).

[5] XU, P., et al., "Wastewater disinfection by ozone: main parameters for process design", Water Research 36, (2002) 1043.

[6] GEHRINGER, P., ESCHWEILER H. and HAN B., "High energy electrons for reclamation of effluents from municipal wastewater treatment plants", *Proceedings of 5th IWA Congress,* Marrakech September (2004).

[7] AMRO, H.M., "Remediation of Polluted Waters by Irradiation Processing" Remediation of Polluted Waters and Wastewater by Radiation Processing, IAEA Warsaw, June (2004).

[8] COOPER, W.J., et al. "A Partial Free Radical-Mechanism for the Destruction of Methyl-ter-butyl ether"Remediation of Polluted Waters and Wastewater by Radiation Processing. IAEA Warsaw, June (2004).

[9] TROJANOWICZ, M., et al, "Monitoring of Toxicity and Determination of Products in Degradation of Selected Pesticides Using Ionization Radiation" Remediation of Polluted Waters and Wastewater by Radiation Processing. IAEA Warsaw, June (2004).

[10] SOLPAN, D., "The Degradation of Some Pesticides in Aqueous Solutions by Gamma-Radiation" Remediation of Polluted Waters and Wastewater by Radiation Processing. IAEA Warsaw, June (2004).

[11] TILL, S. W., et al., "Reduction of faecal Coli-form bacteria in sewage effluents using a micro-porous polymeric membrane", Water Research, 32(5), 9 (1998) 1417.

[12] STAMPI, S., et al., "Evaluation of the efficiency of per-acetic acid in the disinfection of sewage effluents", Journal of Applied Microbiology, 91(5), (2001) 833.

[13] WANG, T., et al., "Oxidant reduction and biodegradability improvement of paper mill effluent by irradiation", Water Research, 28(1), (1994) 237.

APPLICATION OF IONIZING RADIATION FOR REMOVAL OF PESTICIDES FROM GROUNDWATERS AND WASTES

M. Trojanowicz[1, 4], P. Drzewicz[1], A. Bojanowska-Czajka[1],
G. Nałęcz-Jawecki[2], M. Gryz[2], J. Sawicki[2], K. Kulisa[1], S. Wołkowicz[3],
G. Nichipor[5], Z. Zimek[1]

[1]Institute of Nuclear Chemistry and Technology, Warsaw, Poland
[2]Warsaw University of Medicine, Department of Environmental Health Sciences, Warsaw, Poland
[3]Polish Geological Institute, Rakowiecka 4, Warsaw, Poland
[4]Department of Chemistry, Warsaw University, Warsaw, Poland
[5]Institute of Radiation Physics and Chemistry Problems, National Academy of Sciences of Belarus, Minsk-Sosny, Belarus

Abstract

A careful optimization of measuring conditions allows to use hplc as a convenient method for monitoring the effectiveness of processes of radiolytic degradation of organic pollutants and formation of products of these processes. The complete radiolytic degradation of dicamba at a concentration level of 110 ppm in aqueous solution requires an irradiation dose of about 5 kGy. The efficiency of degradation, in contrast to 2,4-d, was not affected by the presence of 50 ppm nitrate; however, concentration of main toxic decomposition products phenol and 2-chlorophenol is affected by the presence of nitrate. It was found that in numerous examined systems that addition of ozone or hydrogen peroxide to irradiated solutions may improve the effectiveness of radiolytic degradation of organic pollutants, including pesticides and phenolics. The presence of inorganic scavengers, commonly occurring in natural waters and wastes, affects the consumption of oxygen during the irradiation process, essential for its effectiveness. In the presence of nitrate and hydrogen carbonate, oxygen is consumed at higher irradiation doses than in pure solutions in distilled water. The results obtained indicate that in numerous cases radiolytic degradation may be a suitable and effective method for treatment of industrial wastes. The results obtained in these studies for pesticides 2,4-d, mcpa and carbendazim indicate that radiolytic degradation may be a suitable and effective method for treatment of industrial wastes. In many cases, the experimental data on effectiveness of radiolytic decomposition of target compounds were compared with results of kinetic modeling based on rate constants of radical reactions involved with good or satisfactory agreement.

1. INTRODUCTION

The aim of this project was the investigation of the decomposition of selected pesticides and the formation of by-products during the application of ionizing radiation for the treatment of pesticides in synthetic aqueous solutions, as well as in real samples of industrial wastes. The removal of these species is a great challenge for the protection of the environment [1] The world-wide application of intensive methods in modern agriculture in the last few decades has resulted in the presence of a variety of agrochemicals in the environment. Many pesticides that are commonly used are resistant to natural degradation in the environment hence, there is great concern about possible adverse effects for human health and for the equilibrium in ecosystems [1, 2, 3]. The target pesticides examined in this project for the possibility of their degradation with the use of ionizing radiation are listed in Table 1. Their data on environmental fate and toxicological effects are listed in Table 2.

Chlorophenoxy herbicides, which have potential toxicity toward humans and animals [4], and are suspected mutagenes and carcinogens, are used world-wide largely as a plant growth regulator for agricultural and non-agricultural purposes. For instance, MCPA is used in amounts exceeding 2000 tons per year in West European countries [5]. In commercial preparations, it is used as dimethylammonium, potassium or sodium-potassium salts, very often in mixtures together with other chlorophenoxy pesticides (2,4-D,dicamba, MCPB), as well as with other groups of pesticide compounds. In aqueous solutions it occurs mainly in anionic form (pKa = 3.1), and it's reported field half time ranges from 6 to 60 days, longer than reported for 2,4-D or dicamba [6].

TABLE 1. PESTICIDES EXAMINED IN THIS PROJECT

Chemical class	Systematic name	Common name	Usage
Aryloxyalkanoic acids	2,4-dichlorophenoxyacetic acid	2,4-D	Herbicide
	3,6-dichloro-2-methoxy-benzoic acid	Dicamba	Herbicide
	4-chloro-2-methylphenoxy- acetic acid	MCPA	Herbicide
Benzimidazole	Methyl-2-benzimidazole carbamate	Carbendazim	Fungicide
Organophosphorus	Phosphoric acid, 2-chloro-1-(di-chorophenyl) vinyl dimethyl ester	Chlorfenvinphos	Insecticide, Acaricide

TABLE 2. ENVIRONMENTAL FATE AND TOXICOLOGICAL EFFECTS FROM DATA REPORTED BY EXTENSION TOXICOLOGY NETWORK (EXTOXNET) in http://extoxnet.orst.edu

Pesticide	Breakdown in water, days	Half-life in soil, days	Microtox toxicity, ppm
2,4-D	7	<7	5.7–127 53)
Dicamba	1 to several weeks	1–12 weeks	not found (?)
MCPA	14–35	14–30	75 1)
Carbendazim	not found		6–12 months
not found			
Chlorfenvinphos	80–170 1)	4–30 weeks	not found

1) data obtained in present work
2) http://www.atsdr.cdc.gov/toxprofiles

The ecological, technological and analytical literature contains a large number of works on various methods of removing those pesticides for environmental protection. Some examples of Advanced Oxidation Processes (AOPs) developed for decomposition of those compounds are listed in Table 3. Due to the common use of this herbicide, the largest number of papers on decomposition were published for 2,4-D. Among them were different variants of photochemical degradation in various conditions (e.g. [7, 8] Fenton methods (e.g. [9] and electrochemical [10]). Fewer AOP methods were reported for dicamba and some of them are alols listed in Table 3.

In the literature on degradation or removal of MCPA for environmental purposes, mostly photodegradation methods have been reported [7, 13, 16]. In electrochemical degradation, oxidation was carried out with hydroxyl radicals produced from Fenton's reaction between Fe(II) and H_2O_2 generated in anodic reaction that can be additionally accelerated using a photoperoxi-coagulation treatment under UV irradiation of solutions, providing more hydroxyl radicals [20]. Other methods reported in the literature include ultrasonic decomposition in an argon atmosphere [19], biodegradation using a microcosm technique[13], and removal of MCPA from aqueous solutions by acid-activated spent bleaching earth, which is a solid waste from the edible oil processing industry [22].

TABLE 3. SELECTED LITERATURE DATA ON ADVANCED OXIDATION METHODS (AOP) OTHER THAN IONIZING IRRADIATION EMPLOYED FOR DECOMPOSITION OF PESTICIDES EXAMINED IN THIS WORK

Pesticide	AOP method	Authors	Ref.	
2,4–D	Photochemical	Benitez et al. (2004)	[7]	
	Catalyzed ozonation	Piera et al. (2000)	[8]	
	Photocatalysis	Singh et al. (2004)	[9]	
	Photofenton	Kwan et al. (2004)	[10]	
	Electrochemical	Oturan et al. (2000)	[11]	
Dicamba	Photocatalysis	Chu et al. (2004)	[14]	($UV/H_2O_2/TiO_2$)
	Photocatalysis (UV/TiO_2)	Bianco et al. (2001)	[15]	
MCPA	Photochemical	Soley et al. (1986)	[16]	
		Zertal et al. (2001)	[17]	
		Benitez et al. (2004)	[7]	
	Phtocatalytic, TiO_2	Zertal et al. (2004)	[18]	
	Ultrasonic	Fuijita et al. (2003)	[19]	
	Electrochemical	Boye at al., (2003)	[20]	
Carbendazim	Photochemical	Pandes et al. (2000)	[23]	
		Mazellier et al. (2002)	[25]	
		Boudina et al. (2003)	[26]	
Chlorfenvinfos	Photochemical	Farre et al. (2005)	[27]	
		Meijers et al. (1995)	[28]	
		Hincapie et al. (2005)	[29]	
	Fenton’s	Barbusinski, Filipek, (2001)	[30]	

Different methods of decomposition of widely used fungicide carbendazim (methyl-2 benzimidazole carbamate), important for the environment, have been already reported in the literature. These include photodecomposition [23] or degradation by UV/H_2O_2 [24, 25]. The degradation of chlorfenvinphos, which besides carbendazim is among the most persistent pesticides in the environment, has been achieved using photocatalytic degradation under various conditions (e.g. [27, 28, 29] and Fenton's method [30]).

Among hundreds of papers published in international scientific literature on the use of ionizing radiation for decomposition of environmental pollutants in the liquid phase, only a few have been devoted to decomposition of pesticides (Table 4). Again, as it was mentioned generally about AOP methods, the largest number was published about radiolytic degradation of 2,4-D, which was also examined in this work. To our best knowledge, there were no papers published about the application of radiolytic degradation for decomposition of other pesticides investigated in a work.

TABLE 4. LITERATURE DATA ON APPLICATION OF IONIZING RADIATION FOR DECOMPOSITION OF PESTICIDES

Pesticide	Radiation	Authors	Reference
Atrazine	γ	Kerpel vel Leitner et al. (1999)	[31]
	γ	Angelini et al. (2000)	[32]
2,4 – D	γ	Zona et al. (2002)	[33]
	γ	de Campas et al. (2002)	[34]
	EB	Drzewicz et al. (2004)	[35]
	γ	Zona et al. (2002)	[36]
	γ	Kamat et al. (2002)	[37]
	γ	Kamat et al. (2004)	[38]
Lannate, fenvalerate	γ	Aal et al. (2001)	[39]

2. OBJECTIVE OF THE RESEARCH

The objective of this research was the investigation of conditions for the use of ionizing radiation for radiolytic decomposition of selected pesticides commonly used all over the world, that present a threat to the natural environment. For this study, three herbicides and one fungicide of different chemical structures have been selected. In final selections of target compounds, besides their common use in agriculture, such factors were considered as their presence in industrial wastes from their production in Poland, and also reported in the literature data for their decomposition using other Advance Oxidation Processes (AOPs) that makes it possible to compare various technologies.

Within the project, it was planned to examine the yield of degradation of pesticides in various conditions of irradiation, identification of products of radiolytic decomposition of target species, and investigation of the Microtox toxicity changes of irradiated solutions. Among the examined parameters affecting the effectiveness of irradiation, there were irradiation dose magnitude and dose rate, pH of irradiated solutions and initial concentration of target compounds. The irradiation was also examined in conditions where particular radical products of radiolysis of water predominate, and in the presence of certain commonly occurring scavengers of radiation. In order to verify the mechanisms of radiolytic processes, a computation modeling based on available or presumed rate constants of radical reactions was carried out. In conditions assumed as optimum based upon examination of pure aqueous solutions of target species', the examination of different industrial wastes was planned.

3. MATERIALS AND METHODS

3.1. Instrumentation used in experimental studies

Irradiation of synthetic aqueous solutions of target compounds and waste samples was performed using ^{60}Co γ-source Issledowatel (2.72 kGy/h).

Determination of 2,4-dichlorophenoxyacetic acid (2,4-D), 3,6-dichloro-2-methoxy-benzoic acid (dicamba), 4-chloro-2-methylphenoxyacetic acid (MCPA) and chlorophenols was carried out by reversed-phase HPLC using Shimadzu Chromatograph with a diode array UV/VIS detector, equipped with column Luna ODS2, 5 μm and guard column from Phenomenex. Injected sample volume was 20 μl. The eluent was a mixture of 2g/L citric acid solution in water, methanol and acetonitrile in ratio 65: 35:5 was used at flow rate 1 ml/L.

Determination of carbendazim and its expected degradation products was carried out by reversed-phase HPLC using a Shimadzu Chromatograph with a diode array UV/VIS detector equipped with column LUNA ODS2, 5 μm and guard column from Phenomenex. Injected sample volume was 100 μl. The determinations were carried using gradient conditions, as eluent A- the mixture of 10 mM amonium acetate and 5% ACN and as eluent B- pure ACN was used. The flow rate was 1 ml/min.

Chemical Oxygen Demand (COD) was determined according to the ISO 6060:1989 method using the setup from Behr-Labor-Technik (Dűsseldorf, Germany). Oxygen concentration was measured by a commercially available Clark electrode and Oxymeter model 3000 from WTW (Weilheim, Germany). Toxicity measurements in irradiated solutions were carried out using a commercial Microtox® test with setup from Azur Environmental (Wokingham, England).

3.1.1. Development of analytical methods needed for the project

Acidic pesticides and chlorophenols can be determined by reversed-phase HPLC with acidic buffers as a mobile phase. Although several examples of gradient elution for the determination of these compounds can be found in the literature, we optimized the isocratic mode of elution. The solution containing 2 g L^{-1} citric acid in a mixture of water, acetonitrile and methanol in the volume ratio of 40:30:30, was found in our earlier works as optimum eluent for separation of phenol and various chlorophenols. In such conditions, the increasing retention times were observed with increasing numbers of chlorine atoms in chlorophenols molecules.

In these studies, we found that when the citric acid concentration in the mobile phase was lower than 0.5 g L^{-1} (at constant 45% acetonitrile content), the retention factors for all investigated herbicides were very large (*i.e.* for 2,4,5-T k = 26.0) with asymmetric and wide peaks. The increase of citric acid concentration (up to 2.5 g/L) resulted in a large decrease of the retention factors (k = 5.86 for 2,4,5-T), but a peak of 2,4-D overlapped with MCPA. Moreover, no acceptable resolution of the 2,4-DP and MCPA, the critical pair, was achieved (resolution factor $R_s = 0.75$). With the increase of acetonitrile content in eluent the increase of the k value for the more hydrophobic compounds such as 2,4,5-T, 2,4-DP and MCPP decreased essentially. On the other hand, the k value for dicamba, the most hydrophobic compound, did not vary much. These data indicate that the elution strength of eluent with acetonitrile added increases with the increase of hydrophobicity of the analytes. The HPLC procedure has been developed for the determination of four important chlorophenoxy acids and dicamba, where baseline resolution was achieved with a mobile phase consisting of 43.7 mM acetic acid and 45% acetonitrile. The pH value of this eluent has a very pronounced effect on the chromatographic separation. An increase in pH dramatically reduces the retention of all analytes, particularly in the 2.5–3.5 range, and at pH >4 only one broad peak was recorded. The chlorophenoxy herbicides are relatively strong acids ($pK_a < 4$) and are very weakly retained by reversed-phase C_{18} in the ionized state. In order to increase the retention capacity, pH of the eluent should be lower than their pK_a values. The pH value of an acidic mobile phase used in reversed-phase liquid chromatography of investigated herbicides is, however, a compromise between the separation efficiency and the decrease in the silica-column lifetime. The pH value of 2.5 was selected as optimum and such eluent was also applied for separation of phenol and its derivatives. Better resolution, particularly for hydroquinone and pirocatechol, as well as for monochlorophenols, was obtained using a smaller content of acetonitrile (40%). These conditions allowed a satisfactory separation of five herbicides and eight phenolic derivatives in 40 min (FIG.1). Such a method for simultaneous determination of examined compounds in one run was not, so far, reported in the literature.

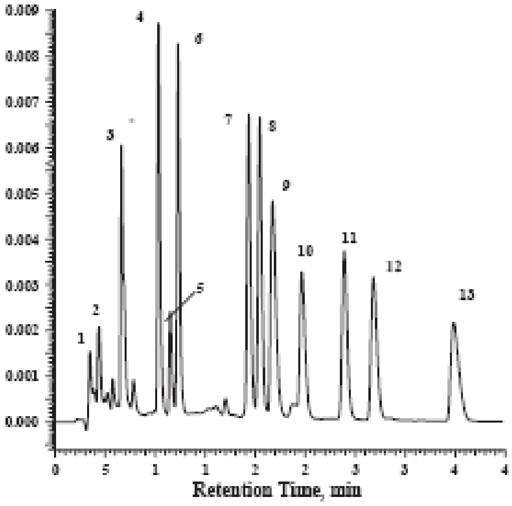
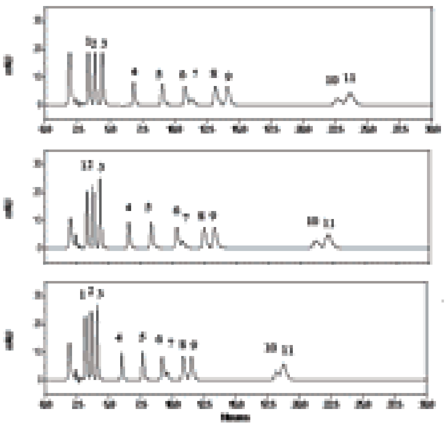


FIG. 1. Chromatogram obtained for mixture of phenol derivatives and chlorophenoxy acid herbicides containing 2.5 mg L^{-1} of each solute with UV detection at 280 nm. Eluent: 43.7 mM acetic acid with 45% acetonitrile. Column: Phenomenex C18(2) Luna 5 μm (250 × 4.6 mm), flow rate 1mL min^{-1}. Peaks: (1) hydroquinone, (2) catechol, (3) phenol, (4) 2-chlorophenol, (5) 4-chlorophenol, (6) 3-chlorophenol, (7) 4-chloro-2-methyl-phenol, (8) 2,4-dichlorophenol, (9) dicamba, (10) 2,4-D, (11) MCPP, (12) 2,4-DP, (13) 2,4,5-T.

The chromatographic determination of MCPA and products of its radiolytic decomposition was also carried out in a reversed-phase HPLC system using Shimadzu chromatograph with a diode array UV/Vis detector, using column Luna ODS 2, 5 μm, 250 × 4.6 mm and a guard column from Phenomenex (Torrance, CA, USA). The sample injection volume was 20 μL. The application of the earlier developed RP-HPLC isocratic method for simultaneous determination of 2,4-D and its main degradation products chlorophenols, was not satisfactory for the separation of MCPA and the main product of its degradation in mild conditions was 4-chloro-2-methylphenol. In order to improve the separation of these two analytes, the effect of temperature in isocratic conditions was examined, and it was found that the separation only slightly depends on temperature (FIG. 2).

The next step in optimisation of separation was to examine two different gradient procedures. The separation was optimised for a mixture of MCPA with several chlorophenols, dihydroxybenzenes and 4-chloro-2-methylphenol. The optimum separation, illustrated by chromatogram shown in (FIG. 3) for synthetic mixture, was obtained for the system with solution A containing 5% acetonitrile (ACN) in aqueous solution of citric acid g/L and B, a pure ACN. The linear change of solution A in eluent was applied from 79% to 42% in 45 minutes. For all examined solutes, a base-line resolution was obtained.



$R_{6/7}$ = 1,39
$R_{8/9}$ = 1,88
$R_{10/11}$ = 1,46

$R_{6/7}$ = 1,15
$R_{8/9}$ = 1,4
$R_{10/11}$ = 1,2

$R_{6/7}$ = 1,53
$R_{8/9}$ = 1,6
$R_{10/11}$ = 1,61

FIG. 2. Effect of temperature on separation of mixture of standards containing 10 mg/L of each solute with UV detection at 280 nm. Eluent 2 g/L citric acid with acetonitrile-gradient programme. Column: Phenomenex C18(2) Luna 5 μM (250 × 4.6 mm), flow rate 1 mL/min. Peaks: (1) hydroquinone, (2) methylhydroquinone, (3) catechol, (4) phenol, (5) salicylic acid, (6) o-cresol, (7) MPA, (8) 4-chlorophenol, (9) 3-chlorophenol, (10) MCPA, (11) 4-chloro-2-methylphenol in different temperature. A-25^{o}C, B- 40^{o}C, C- 65^{o}C. R is resolution for indicated peaks.

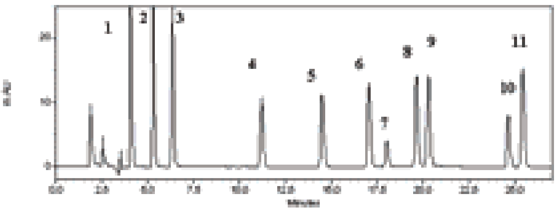


FIG. 3. Chromatogram obtained for mixture of standards containing 10 mg/L of each solute in optimized conditions with UV detection at 280 nm. Eluent 2 g/L citric acid with acetonitrile-gradient programme. Column: Phenomenex C18(2) Luna 5 μm (250 × 4.6 mm), flow rate 1 mL/min. Peaks: (1) hydroquinone, (2) methylhydroquinone, (3) catechol, (4) phenol, (5) salicylic acid, (6) o-cresol, (7) MPA, (8) 4-chlorophenol, (9) 3-chlorophenol, (10) MCPA, (11) 4-chloro-2-methylphenol.

To monitor effectiveness of radiolytic decomposition of carbendazim and studies of mechanism of this process, investigation for the development of an HPLC method enabling the simultaneous determination of carbendazim and products of its degradation observed in similar processes has been undertaken. These products include benzimidazole, 2-aminobenzimidazole, aniline, o-phenyldiamine and 2-hydroksybenzimidazole. The gradient conditions used were described in Experimental, and detection was carried out at 277 nm, since at this wavelength the separation could be observed for 2-hydroxybenzimidazol and benzimidazole. It was observed that the pH of eluent significantly affects the retention time of determined compounds and the shape of chromatograms (FIG. 4). As the optimum value, the pH 8 was selected for solution A in further measurements.

3.1.2. Preconcentration of irradiated sample

The BAKERBOND solid-phase extraction (SPE) phenyl microcolumns from Baker (Gross-Gerau, Germany) were used. The SPE columns were rinsed with two 3 ml portions of methanol and water. The pH value of the preconcentrated solution was adjusted to 2.0 with HCl and solid sodium chloride was added to a total concentration of 25 g/100 mL. After the sorption from the sample solution, the column was rinsed with 5 mL of 10 mM HCl and dried for 5 minutes purging with a stream of air. Preconcentrated analytes were eluted with a 2 mL portion of methanol. The recovery of this procedure for phenol, monochloropenols, 2,4-dichlorophenol and 2,4-D was no less than 85%.

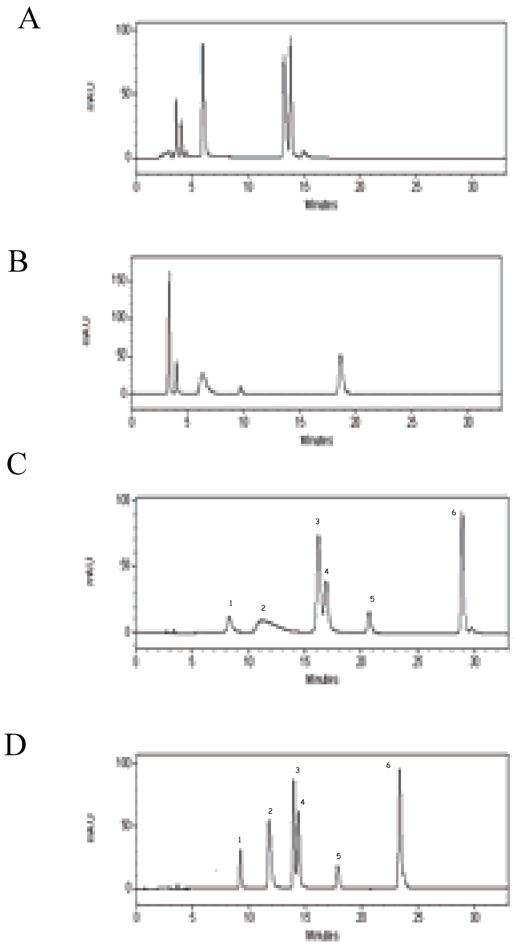


FIG. 4. Chromatograms obtained for mixture of standards containing 4 mg/L of each solute in optimized conditions with UV detection at 277 nm. Eluent 10 mM amonium acetate pH8 with acetonitrile-gradient programme. Column: Phenomenex C18(2) Luna 5 μM (250 × 4.6 mm), flow rate 1mL/min. Peak assignment: (1) 1,2-phenylenediamine, (2) 2-aminobenzimidazole, (3) 2-hydroxybenzimidazole, (4) benzimidazole, (5) aniline, (6) carbendazim.

3.2. Investigation of factors affecting the yield of radiolytic decomposition of examined pesticides

During this study, several different factors affecting the efficiency of radiolytic degradation of selected pesticides have been examined, including dose rate, a role of initial concentration of irradiated solutions, and a natural water matrix, as well as the effect of the presence of ozone and hydrogen peroxide in irradiated solutions.

3.2.1. Effect of the irradiation dose

It was found that the dose needed to complete decomposition of 2,4-D increases significantly with the value of initial concentration of herbicides, for a concentration in the range 0.045-2.2 mM for different γ irradiation doses (FIG. 5). The reported measurement has been carried out in herbicide solution prepared on groundwater matrix.

The same observations were made for water solution of carbendazim at pH7 irradiated in γ-source. The dose needed for 90% degradation of carbendazim increases linear to the initial concentration of carbendazim up to 100 μM. (FIG. 6).

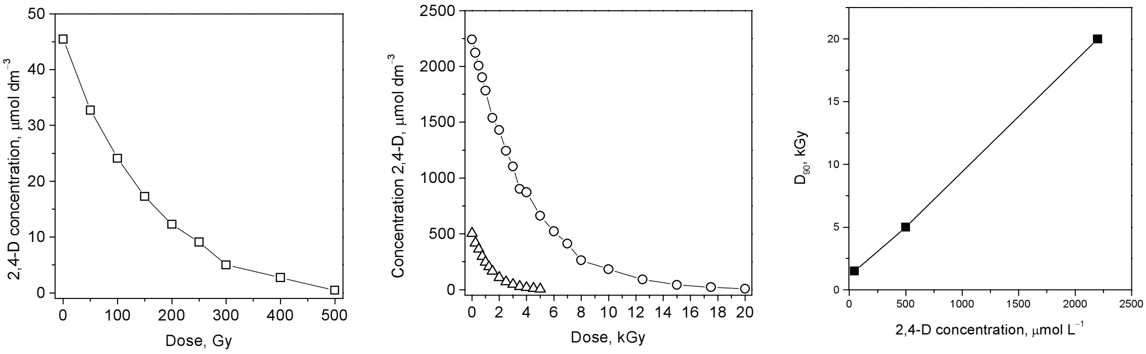


FIG. 5. The effect of 2,4-D initial concentration in γ irradiated solution in groundwater on the magnitude of the dose required for the complete decomposition of herbicide.

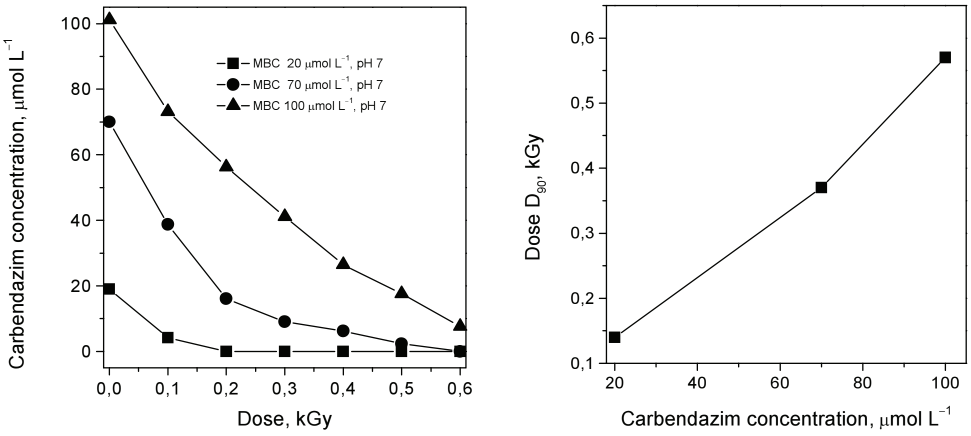


FIG. 6. The effect of carbendazim initial concentration in γ irradiated solution in distilled water on the magnitude of the dose required for 90% decomposition of herbicide.

3.2.2. Effect of the kind of radiation employed

The processes of radiolytic degradation in aqueous solutions are carried out by means of γ-radiation from ^{60}Co source, or by electron beam from accelerator, and are based on reaction of target pollutant with products of water radiolysis. Comparing the EB process with gamma radiolysis in aerated solutions, the degradation rate of 2,4-D was found to be almost the same (FIG. 7A). It was observed, however, that in the case of EB, a larger chloride amount is released (FIG. 7B). This can be explained by a faster process in case of EB and lack of equilibrium between the ambient air and irradiated solutions.

3.2.3. Effect of pH of irradiated solutions

As MCPA is a weak acid (pK_a = 3.1), the effect of pH value of irradiated MCPA solutions on the effectiveness of radiolytic decomposition was examined. Additionally, pH of industrial wastes from production of MCPA is 1,5. On the other hand, wastes containing 2,4-D and dicamba were almost neutral; hence, they were not examined at other pH values. The irradiation experiments for MCPA were carried out at pH values of 1.5 (where MCPA is almost completely protonated), 7.0 and 11.5

(where MCPA is present in anionic form). Initial solutions containing 100 ppm MCPA were irradiated with doses of up to 4 kGy. It was found that the main product of radiolytic degradation of MCPA was identified as 4-chloro-2-methylphenol in these experimental conditions. Besides 4-chloro-2-methylphenol, other products of radiolytic degradation of MCPA were catechol, phenol, o-cresol and 3-chlorophenol were identified, and their decomposition is also more effective in acidic than in neutral or alkaline solutions (FIG.8). Since industrial wastes are strongly acidic, in practical applications, no additional neutralization would be required.

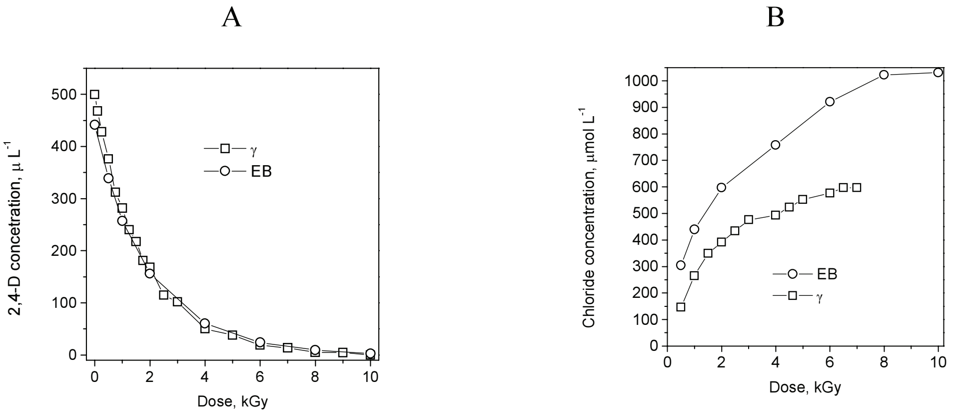


FIG. 7. Effect of kind of radiation on decomposition of 2,4-D (A) and formation of chloride (B) in irradiated 0.5 mM 2,4-D solutions.

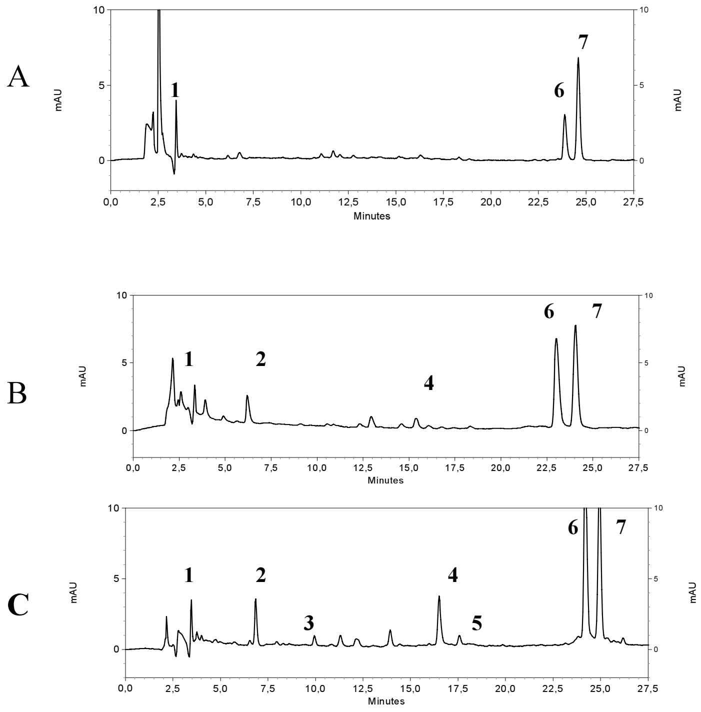


FIG. 8. Effect of pH of irradiated solutions on RP-HPLC chromatograms for 100 ppm solution of MCPA obtained after γ irradiation with 3 kGy dose. A- pH 1.5, B- pH 7.0, C- pH11.5. Peak assignments: (1) hydroquinone, (2) catechol, (3) phenol, (4) o-cresol, (5) 4-chlorophenol, (6) MCPA, (7) 4-chloro-2-methylphenol.

The most effective decomposition occurs at pH1.5 (FIG. 9A), while at the 3 kGy dose, 97% of MCPA was decomposed. Generally, the effect of pH was not very pronounced. Alkaline conditions were less favourable, but the difference in the yield of the decomposition was between pH7 and 11.5 is minor. In the case of 4-CMP, the main product of radiolytic degradation of MCPA, the most efficient removal was observed for irradiated solution of pH1.5. As can be seen in (FIG. 9B), further decomposition of 4-CMP, however, is significantly affected by the pH of irradiated solutions for doses above 2 kGy.

In preliminary experiments with carbendazim, the effect of pH on the yield of decomposition of carbendazim was examined in solutions not irradiated and γ irradiated. The observed decomposition of carbendazim solutions at different pH values is shown in (FIG.10).

In all cases, decomposition in 20 μmol L^{-1} during 2 months does not exceed 5%. The largest decomposition occurs in solutions at pH10, which can be attributed to hydrolysis of carbendazim according to the scheme in (FIG. 11). This was confirmed by detection of 2-aminobenzimidazole in analyzed solutions.

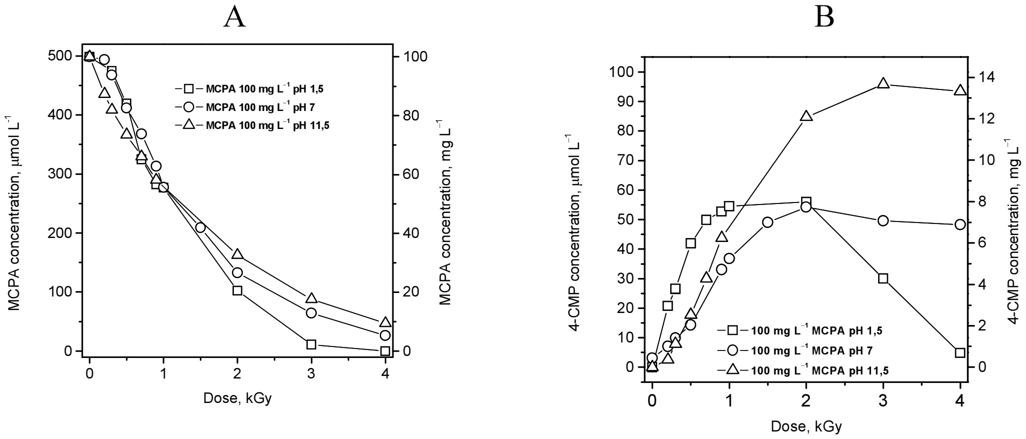


FIG. 9. (A) — decomposition of 100 ppm MCPA at different doses during γ irradiation at pH1.5 ( ), 7.0 (O) and 11.5 (Δ). (B) — formation of 4-chloro-2-methylphenol at different doses during γ irradiation of 100 ppm MCPA at pH =1.5 ( ), 7.0 (O) and 11.5 (Δ).

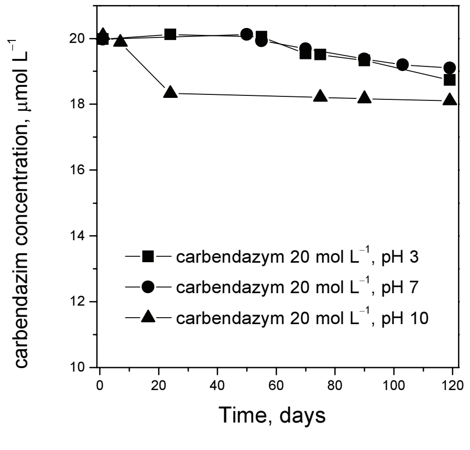


FIG. 10. Decomposition of carbendazim in aqueous solutions without irradiation at different pH.

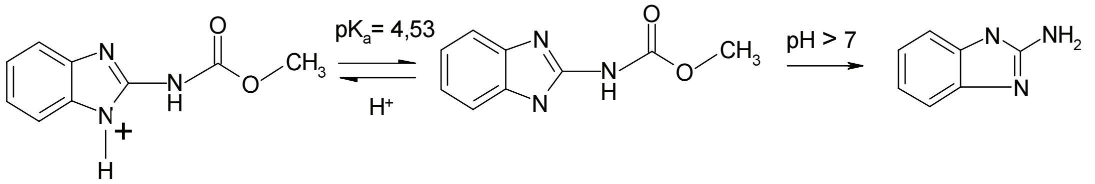


FIG. 11. Scheme of decomposition of carbendazim[23].

In γ irradiated aerated solutions of carbendazim 100 μmol L^{-1} in pH range from 3 to 10, practically complete decomposition has been observed at small doses up to 0.6 kGy. In alkaline solutions, it occurs slightly faster than that of simultaneous hydrolysis (FIG. 12). It is contrary to observations for photochemical decomposition, which was strongly affected by pH of initial solution of carbendazim [7].

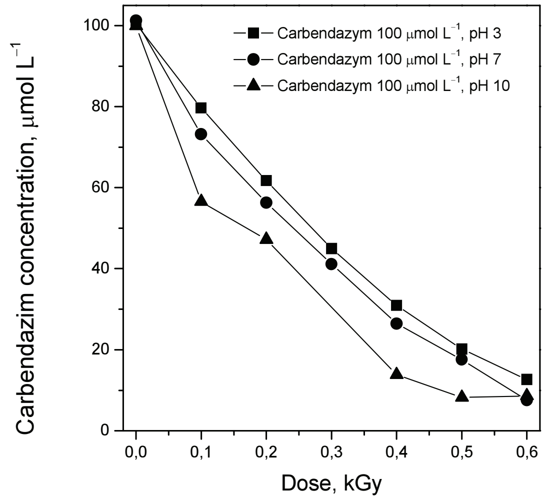


FIG. 12. The effect of pH of irradiated solutions of carbendazim on yield of decomposition at initial concentration 100 μM.

3.2.4. Irradiation in the presence of ozone

Ozonation is a commonly employed method for the treatment of waters and wastes, (e. g. to improve quality of drinking water [40]). Ozonation can also be used as a pretreatment step to biodegradation, which was recently shown for aqueous solutions.

In these studies, the effectiveness of additional ozonation irradiated dicamba solutions was examined for EB processes. The dose needed for complete decomposition of 110 mg L^{-1} dicamba in groundwater solution with continuous addition of 64 mg L^{-1} ozone was decreased from 10 to 3 kGy (FIG.13 A), and at this decreased dose, a complete release of chlorine from chloroorganic compounds was observed (FIG. 13C).The effectiveness of this combined process has also been examined for different concentrations of ozone in irradiated solutions. The presence of 64 mg L^{-1} of ozone in 110 ppm solution of dicamba in a round water matrix results in decomposition of 75% herbicide, while simultaneous irradiation with a 2.66 kGy dose results in an increased decomposition yielding 95% (FIG. 13B). As shown in (FIG. 13D), the irradiation of solutions of different content of ozone results in more efficient dehalogenation of chloroorganic compounds (dicamba and its products).

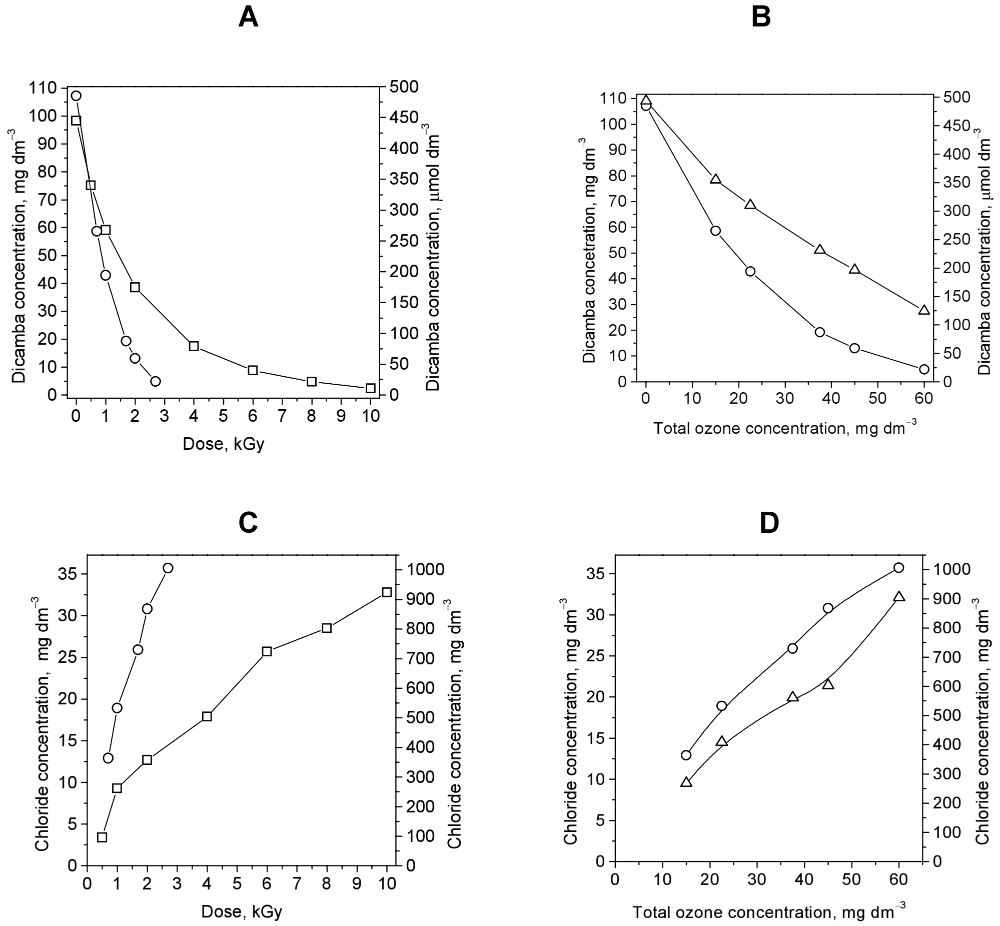


FIG. 13. The effect of ozone on EB degradation of dicamba (A,B) and of chloride release from 110 ppm dicamba solution (C,D) carried out in groundwater matrix, EB irradiation (□) EB/O_3 (O) ozonation (Δ).

3.2.5. Irradiation in the presence of hydrogen peroxide in irradiated solutions

The increased efficiency of degradation of organic compounds for combined γ or electron beam irradiation with hydrogen peroxide was already observed by Gehringer et al.[44] for tetrachloroethylene (PCE) and 1,2,2-trichloroethylene (TCE). A similar observation was reported for degradation of chloroform by γ irradiation with H_2O_2 [42]. Recently, in radiation-reduced degradation of polyvinyl alcohol, it was found that at a certain dose rate, there was an optimal dosage of H_2O_2 to facilitate the degradation, above which the H_2O_2 dosage reduced the degradation efficiency [43].

The estimation of the optimum amount of hydrogen peroxide needed to enhance the given process is difficult, since it is involved in numerous reactions with radicals formed during radiolytic degradation of target compounds and an additional problem is the self-decomposition of hydrogen peroxide to water and oxygen, which depends on pH. The first order rate constant of self-decomposition of hydrogen peroxide is 2.29×10^{-2} min^{-1} at pH7 and 7.4 10^{-2} min^{-1} at pH10 [44]. In order to decrease the rate of decomposition of hydrogen peroxide in oxygen and water, it is usually used in a solution of pH5.

Although it was reported that hydrogen peroxide does not react with 2,4-D [45], or with products of its decomposition, phenol and chlorophenols [46], the subject of this work was to examine the effect of hydrogen peroxide on the decomposition of 2,4-D. It was found that the addition of 1.7 mM H_2O_2 to irradiated solutions at pH7 allowed lower γ irradiation doses to achieve 95% of 2,5-D at initial concentration 50 mg L^{-1} from 2 to 1 kGy (FIG. 14). Simultaneously, a 50% lower toxicity of irradiated solution was observed. This illustrates the fact that during irradiation, the hydrogen peroxide added is an additional source of oxygen and hydroxyl radicals that result in more efficient degradation of 2,4-D and their products.

The possibility of chemical enhancement of radiolytic decomposition was also examined for MCPA and was carried out in the presence of 4.8 mM hydrogen peroxide, which is the stoichiometric amount needed for oxidation of 100 ppm MCPA and for smaller amounts 2.4 and 1.2 mM.

As can be seen from (FIG. 15) at doses below 4 kGy the added H_2O_2 evidently acts as a scavenger of hydroxyl radicals, giving a less efficient decomposition of MCPA, and a less effective formation of 4-chloro-2-methylphenol. The larger the concentration of H_2O_2, the larger the scavenging effect was observed.

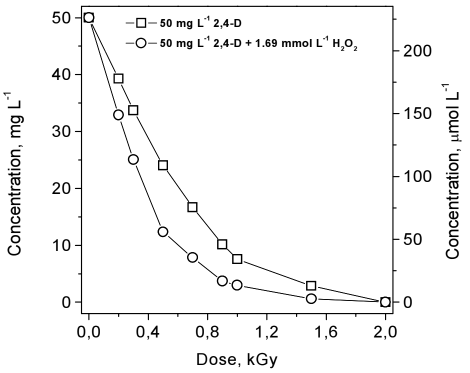


FIG. 14. Decompostion of 2,4-D at different doses during γ-irradaition of 50 mg L^{-1} without ( ) and with 1.7 mM of H_2O_2.

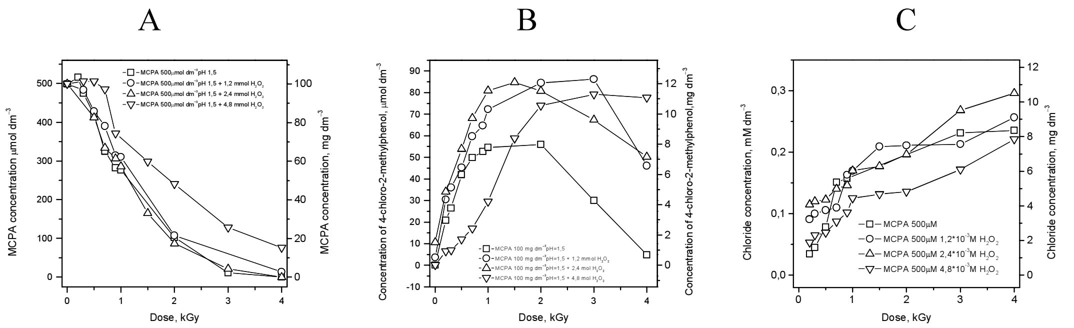


FIG. 15. Yield of decomposition of MCPA(A), formation of 4-chloro-2-methylphenol (B) and chloride (C) at different doses during γ irradiation of 100 ppm solution of MCPA without H_2O_2 ( ), in the presence of 1.2 mM H_2O_2 (O), 2.4 mM H_2O_2 (Δ) and 4.8 mM H_2O_2 (∇).

3.2.6. *Effect of scavengers on radiolytic decomposition*

Natural water may contain some potential scavengers of radicals, such as carbonate and nitrate, which can affect the degradation of pesticides. Hydroxyl radicals formed from radiolysis of water are scavenged by nitrates and carbonates or their radicals[47]. Thus, the presence of scavengers may affect the efficiency of decomposition of organic compounds.

In γ irradiation experiments, it was found that the presence of 400 mg L^{-1} bicarbonate shifted a required dose for complete degradation of 2,4-D in 50 mg L^{-1} solution from 6 to 10 kGy (FIG.16 A). This concentration of bicarbonate in an irradiated solution caused an incomplete release of chloride even at 20 kGy dose (FIG.16 B).

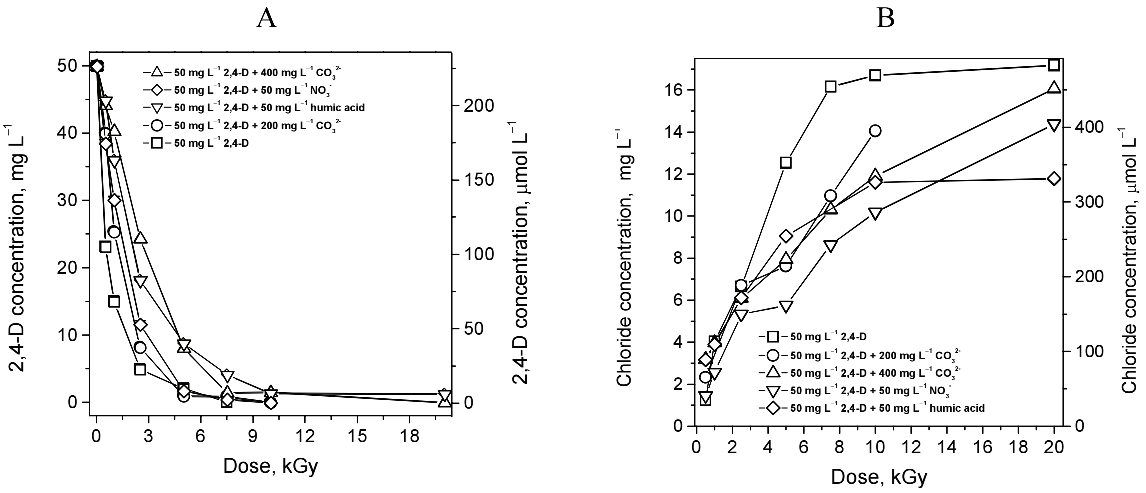


FIG. 16. Effect of dose of γ-radiation (A) on efficiency of degradation of 2,4-D (A) and on the formation of chloride ion (B), during irradiation of 2,4-D in the presence of different scavengers measured by suppressed ion-chromatography.

Other common scavengers of OH radicals in waters and waste are nitrate anions. During irradiation, nitrate is reduced to nitrite, which further reacts with OH radicals and turns back to nitrate [48]. In the absence of oxygen, nitrite can be reduced to the ammonia, which was found in our earlier study [49]. The scavenging effect of nitrate was much stronger than bicarbonate. Only 50 mg L^{-1} of nitrate gave the same effect as 400 mg L^{-1} bicarbonate.

One of the important scavengers of OH radicals in natural water is dissolved organic matter, formed from plant tissue. Humic acids are compounds present as dissolved organic matter. They are formed during degradation of cellulose, and their structure is similar to this compound. It was found that humic acid decreased the effectiveness of the degradation of 50 mg L^{-1} 2,4-D and chloride release at low doses only.

Radiolytic degradation of dicamba was also investigated in the presence of common scavengers of γ radiation. Experiments on the effects of scavengers were carried out in the presence of 50 mg L^{-1} nitrate and 400 mg L^{-1} bicarbonate in neutral solutions, where protonated bicarbonate and not carbonate predominates. The effectiveness of dicamba decomposition at doses up to 2 kGy was decreased slightly only in the presence of both examined scavengers (FIG. 17A). A pronounced effect of the presence of both scavengers, however, was found in the case of dehalogenation (FIG. 17B). Nitrate decreased dehalogenation yield by approximately 50%, which can be attributed to the contribution of carbonate radicals in the process of degradation. A similar effect was reported recently for pesticide carbendazim during photochemical decomposition in the presence of hydrogen peroxide and bicarbonate ions [25].

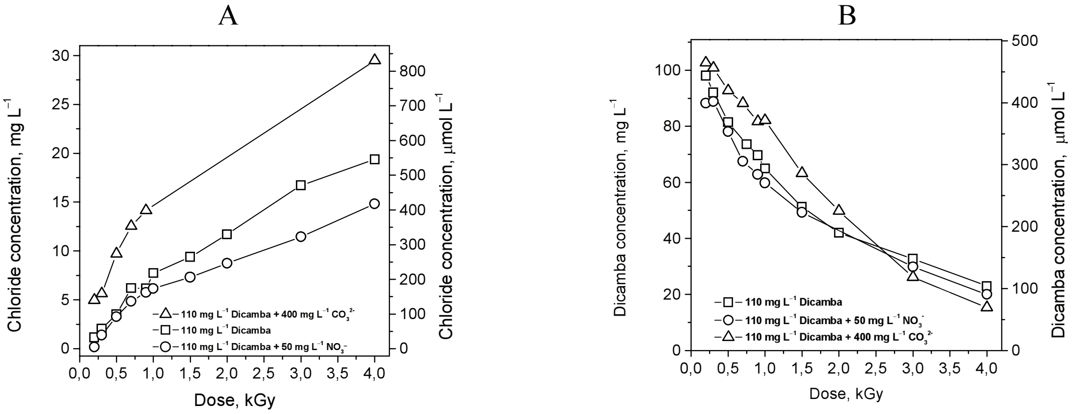


FIG. 17. Effect of dose of γ irradiation (A) on efficiency of degradation of dicamba (A) and (B) on the formation of chloride (B) ion during irradiation of dicamba in the presence of different scavengers (o) 50 mg L^{-1} of nitrate and (□) 400 mg L^{-1} bicarbonate.

3.2.7. Correlation of experimental results of radiolytic degradation with kinetic modeling data

The correlation of experimental results on yield of radiolytic decomposition of target compounds under different conditions with model kinetic calculations allowed us to conclude that the assumed mechanism of radiolytic decomposition was correct. This was recently illustrated in the literature for 2,4-D [37, 38]. In these studies such a modeling was carried out for MCPA and carbendazim.

The results of experimental data on decomposition of MCPA and changes in concentration of the main degradation product at low doses of radiation 4-chloro-2-methylphenol (CMP) have been compared for different conditions with model kinetic calculations based on known rate constants of radical reactions. The calculations have been performed with the use of software KINETIC, which was used earlier for modelling of a high temperature radiation induced reduction of NO [50], and for examination of mechanism of decomposition of 1,1-dichloroethylene in humid air under electron beam irradiation [51]. The results of modelling obtained for processes carried out at different pH values are shown in Fig. 1. The computer calculations have been carried out using the rate constants for MCPA and OH radical $k = 6.6 \times 10^9$ M^{-1}s^{-1} [7]. Similarly, the experimental results also correlated well with the model calculations (FIG.18A), indicate a minor effect of pH of irradiated solutions on yield of MCPA decomposition.

No satisfactory correlation, however, has been observed between experimental data and results of kinetic modelling for decomposition of decomposition products of CMP for radiation doses above 2 kGy (FIG.18B), this means that some other presesses take place, and only those for which rate constants have been taken are for modeling.

It has been shown that, in some cases, the effectiveness of decomposition can be improved by the addition of hydrogen peroxide to irradiated solutions and (FIG.19) shows results of model calculations for processes carried out at pH1.5 and various levels of hydrogen peroxide in irradiated solutions. A general approach to calculate the changes of MCPA and CMP concentrations in function of dose magnitude and hydrogen peroxide content is close to those observed experimentally. The best correlation between the results of calculation and experimental data has been obtained for the largest amount of hydrogen peroxide added to irradiated solution (4.8 mM).

3.2.8. Modeling for carbendazim

A similar modelling was carried out for radiolytic degradation of carbendazim in different conditions. The calculations have been carried out with the use of rate constant for reaction of carbendazim with OH radical $k = 2.2 \times 10^9$ M^{-1}s^{-1} [25]. Both in studying the effect of pH (FIG. 20) and the effect of initial concentration of carbendazim (FIG. 21) satisfactory agreement was obtained.

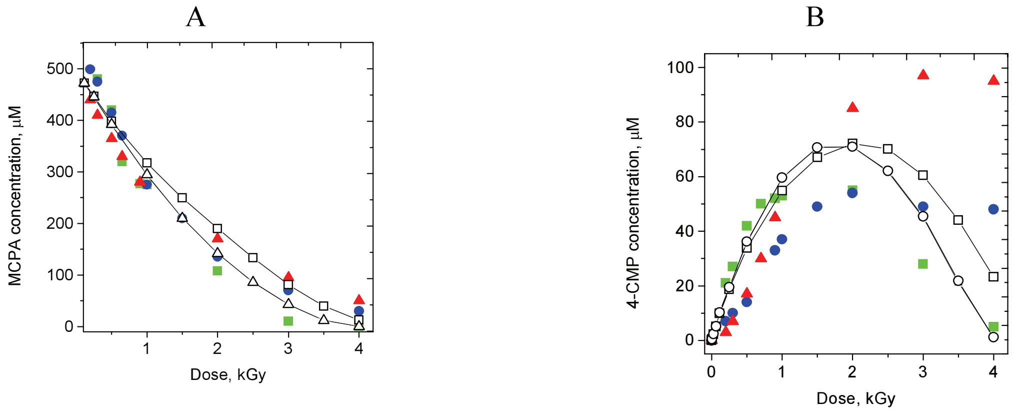


FIG. 18. Comparison of experimental data with kinetic modelling for yield of degradation of (A) MCPA of initial concentration 0.5 mM in aerated solutions of different pH, and (B) formation and decomposition of 4-chloro-2-methylphenol in irradiated solutions of MCPA. Data for pH1.5 experimental (■) and calculated (□), data for pH7.0 experimental (●) and calculated (○), data for pH11.5 experimental (▲)and calculated (△).

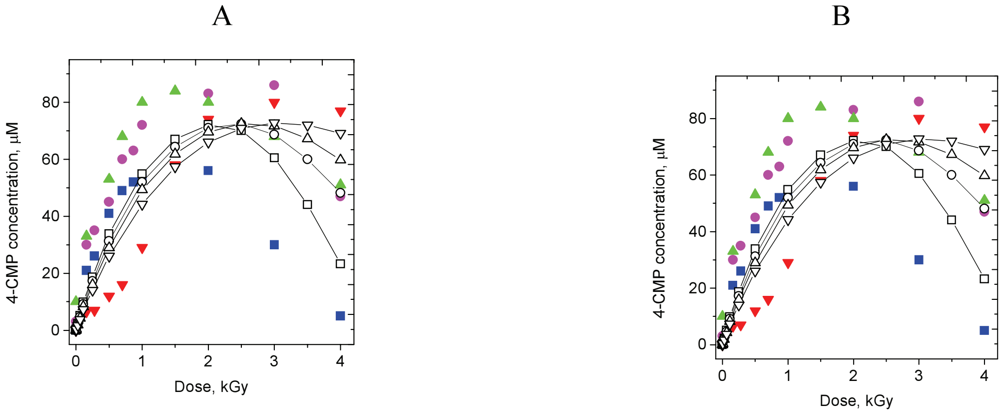


FIG. 19. Comparison of experimental data with kinetic modelling for yield of degradation of (A) MCPA of initial concentration 0.5 mM in aerated solutions of pH1.5 and different concentration of hydrogen peroxide added to irradiated solutions, and (B) formation and decomposition of 4-chloro-2-methylphenol in irradiated solutions of MCPA. Data for irradiation without H_2O_2 experimental (■) and calculated (□), data for irradiation in the presence of 1.2 mM H_2O_2 experimental (●) and calculated (○), data for added 2.4 mM H_2O_2 experimental (▲) and calculated (△), data for added 4.8 mM H_2O_2 experimental (▼) and calculated (▽).

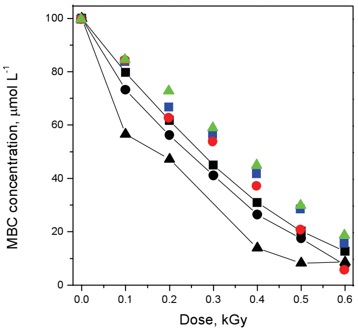
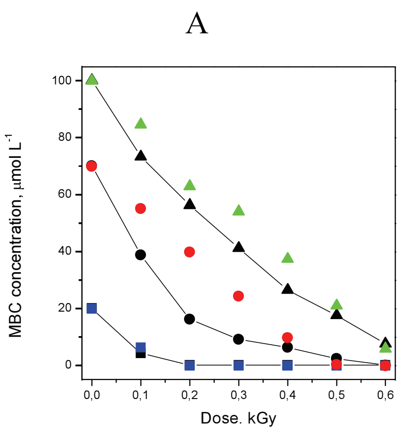


FIG. 20. Comparison of experimental data with kinetic modeling for yield of degradation of carbendazim at initial concentration 100 μM in aerated solution of different pH. Data for pH3 experimental (■) and calculated (■), data for pH7 experimental (●) and calculated (●), data for pH10 experimental (▲) and calculated (▲).



B

SYMBOL	CONDITIONS	RADICALS
■	Aqueous solutions of carbendazim pH 7, before irradiation saturated with N_2O,	•OH
●	Aqueous solutions of carbendazim pH 7, before irradiation areated	•OH, $HO_2^•$, $O_2^{•-}$
▲	Aqueous solutions of carbendazim pH 1.5 Irradiated in the presence of tert-butanol, before irradiation saturated with Ar,	•H
▼	Aqueous solutions of carbendazim pH 7. Irradiated in the presence of tert-butanol, before irradiation saturated with Ar,	e_{aq}

FIG. 21. The effect of carbendazim initial concentration in γ irradiated solution in distilled water in aerated solutions of pH7– comparison of experimental data with kinetic modeling, Data for 20 µM experimental (■) and calculated (■), data for 70 µM experimental (●) and calculated (●),Data for 100 µM experimental (▲) and calculated (▲).

Both experiments and modeling were also carried out for irradiation of carbendazim in conditions where particular active radicals were predominating, and data shown in (FIG. 22) show satisfactory agreement.

The obtained data strongly confirm that radiolytic degradation of carbendazim occurs in radical oxidation processes.

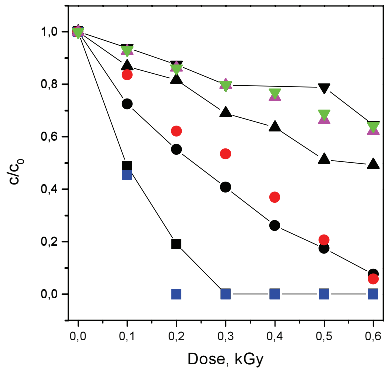


FIG. 22. Degradation of 100 µM of carbendazim in different radiolytic conditions: data for N_2O at pH7 experimental (■) and calculated (■), data for aerated solution at pH7 experimental (●) and calculated (●), data for argon saturated solution with added tert-butanol at pH1.5 experimental (▲) and calculated (▲), data for Ar + tert-butanol at pH7 experimental (▼) and calculated (▼).

3.2.9. Radiolytic degradation of examined pesticides in industrial wastes

The effect of irradiation on degradation of target compounds was also examined for samples of industrial wastes from production of examined pesticides. The synthesis of 2,4-D proceeds in three stages, first by chlorination of phenol 2,4-dichlorophenol (2,4-DCP) is obtained. In alkaline medium, a condensation of 2,4-DCP with chlorooacetic acid is carried out, and 2,4-D formed is precipitated as sodium salt. Finally, 2,4-D is transformed into acid and purified. Wastes produced in synthesis of 2,4-

D, besides organic pollutants, contain a substantial level of sodium chloride (about 0.1 g L^{-1}), which can be recycled industrially after removal of organic pollutants. For irradiation studies, the waste from the condensation stage was taken with a Chemical Oxygen Demand value of 79.2 gL^{-1} and pH8. In this sample HPLC measurements allowed us to identify and determine 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,6-dichlorophenol (2,6-DCP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and 2,4-dichlorophenoxyacid at levels shown in (FIG. 23).

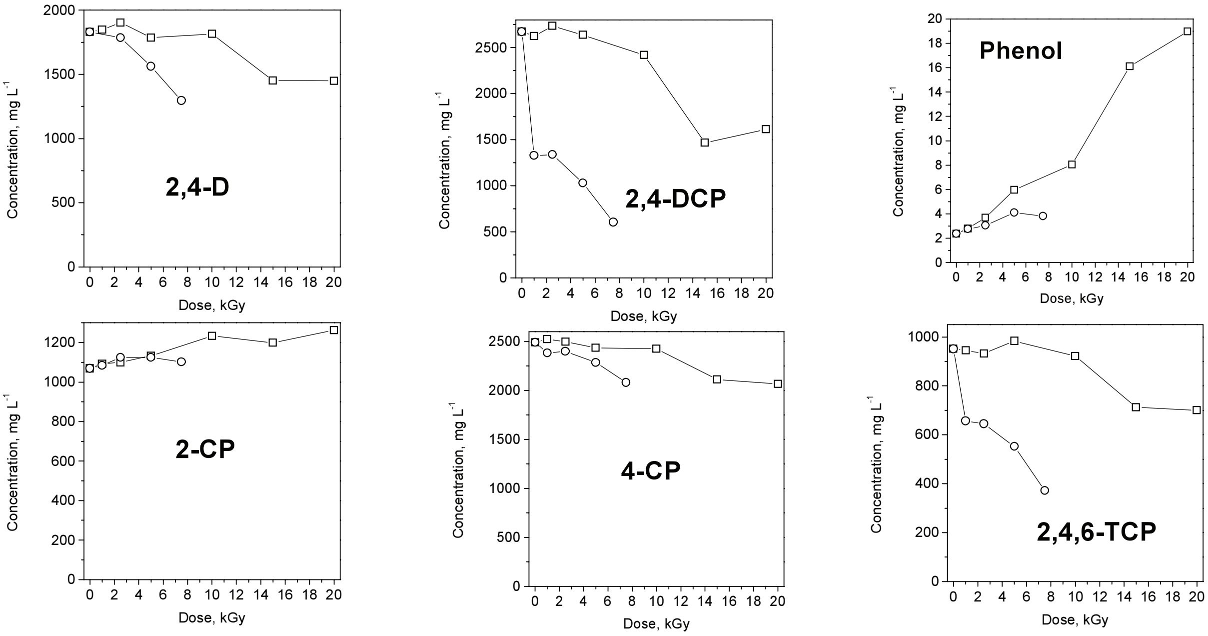


FIG. 23. Degradation of selected organic pollutants by irradiation in industrial wastes from synthesis of 2,4-D observed without addition of hydrogen peroxide (□) and in the presence (○) of 39 mM hydrogen peroxide in irradiated solutions.

The addition of 39 mM hydrogen peroxide to irradiated waste for all mentioned pollutants causes their more efficient decomposition, compared to irradiation without H_2O_2. Some of these compounds, (e.g. phenol or dichlorophenols), are products of degradation of higher chlorinated compounds; hence, increase of their content with increase of applied dose is observed. This effect, however, is evidently reduced in the presence of hydrogen peroxide.

Although it was shown to be effective in the discussed case, the addition of hydrogen peroxide to irradiated solutions containing organic pollutants is less efficient than electron beam irradiation in the presence of ozone [35]. Hydrogen peroxide is a less expensive reagent for industrial use than ozone. Further increase of efficiency of radiolytic degradation of organic pollutants in the presence of H_2O_2 requires both careful optimisation of chemical conditions of irradiation (pH, concentration of H_2O_2) and preliminary chemical neutralization of wastes prior to irradiation.

The consecutive steps of industrial synthesis of MCPA include condensation of sodium o-cresolate with chloroacetic acid in alkaline medium, which is followed by separation of 2-methylphenoxyacetic acid (MPA) by precipitation by acidification with hydrochloric acid, and chlorination of MPA that leads to obtaining MCPA. The product is filtered and dried. The wastes disposed after filtration of MCPA were taken for treatment with γ-radiation. The effect of irradiation dose up to 10 kGy on decomposition of MCPA and the product of its radiolytic degradation in irradiated waste is shown in (FIG. 24).

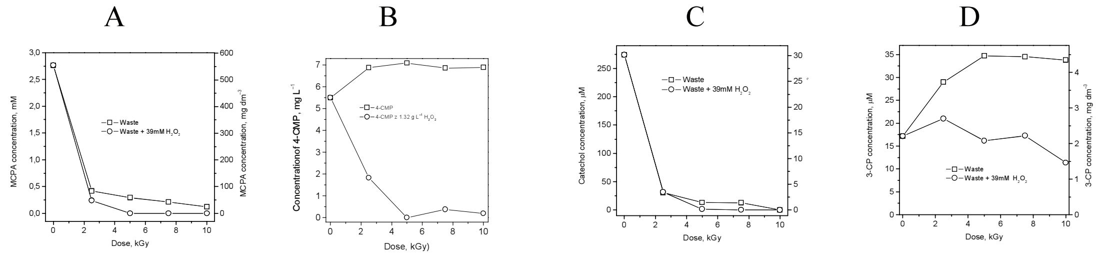


FIG. 24. Decomposition of MCPA (A) and formation of 4-chloro-2-methylphenol (B), catechol (C) and 3-chlorophenols (D) at different doses during γ irradiation waste from production of MCPA without H_2O_2 ( ), and with 39 mM H_2O_2 (o).

In raw waste, the presence of MCPA, MPA, hydroquinone, catechol, o-cresol, 3-chlorophenol, 4-chloro-2-methylphenol, together with trace amounts of 4-chlorophenol, was observed. The complete decomposition of MCPA occurs at 10 kGy dose, while in the presence of 39 mM, hydrogen peroxide decreases the dose needed to 5 kGy. Simultaneously, more efficient degradation of 3-CP and 4-chloro-2-methylphenol was observed in the presence of hydrogen peroxide. After addition of hydrogen peroxide, MPA and o-cresol were decomposed without needing irradiation.

For the examination of the effect of matrix components in wastes on the yield of the irradiation process, irradiation of pure MCPA solutions was carried out at the same level they were found in industrial waste from synthesis of MCPA. Irradiation of this solution was carried out at three different levels of added hydrogen peroxide 19, 39 and 58 mM. As it is illustrated by the data plotted in (FIG. 24), the yield of degradation of MCPA was evidently better at the same doses in waste matrix than in pure water. For synthetic aqueous solutions of MCPA, the addition of H_2O_2 at three different levels practically does not affect the yield of decomposition. One may conclude that H_2O_2 added to the wastes significantly accelerates the decomposition of 4-chloro-2-methylphenol or 4-chloro-2-methylphenol. Possibly, the decomposition of MCPA occurs in the presence of waste constituents by a different mechanism with the participation of other radical species formed during irradiation. One possible hypothesis is the participation in these processes of chloride, present in high concentrations in waste 81 g/dm3. For the reaction: $Cl^- + {}^\bullet OH \leftrightarrow ClOH^-$ there are known rate constants $K_+ = 4.3 \times 10^{10}$ $M^{-1}s^{-1}$ and in reverse direction $K_- = 6 \times 10^9$ M^{-1} s^{-1} [40]. Formation of strong oxidants $HClO_2$ and $HClO_4$ may accelerate the oxidation of MCPA in waste compared to pure aqueous solutions [52].

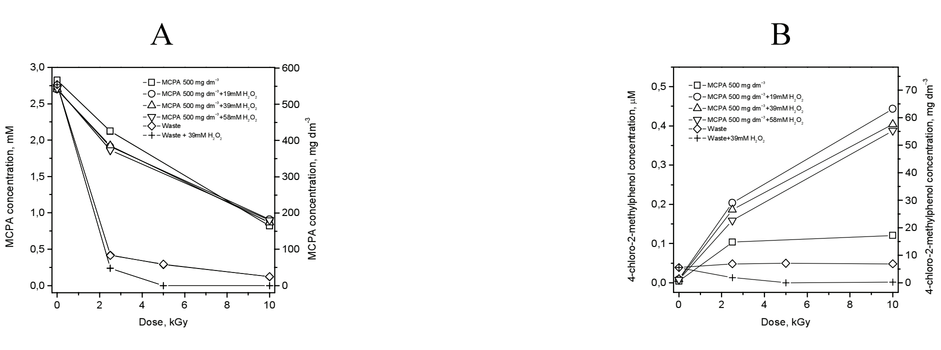


FIG. 25. Decomposition of MCPA (A) and formation of 4-chloro-2-methylphenol (B) during irradiation of solution 500 mg mg dm^{-3} MCPA ( ), 500 mg mg dm^{-3} MCPA with 19 mM H_2O_2(O), 500 mg mg dm^{-3} MCPA with 39 mM H_2O_2 (Δ), 500 mg dm^{-3} 1 MCPA with 58 mM H_2O_2 (∇), waste (◊), waste with 39 mM H_2O_2 (+).

The environmental issue of great importance is the utilization of outdated agrochemical preparations containing herbicides. Since the sixties, they have been stored in Poland, in dump sites in concrete bunkers located in different regions. Their durability, however, is limited and in many cases, environmental pollution was caused by their leakage. This illustrates that there is a need to develop the most cost effective and environment-friendly technology for complete destruction of these substances. Numerous earlier experiences with the use of radiolytic degradation which utilized heavily loaded wastes indicated that this method can find potential application for this purpose.

We examined two commercial preparations widely used currently in Poland that were Chwastox and Aminopielik, in which dicamba was present and was compared to other pesticides 4-chloro-2-methylphenoxyacetic acid (MCPA) and 2,4-D, respectively. Preparations are applied after 100-fold dilution. These preparations have been γ irradiated after the same 100-fold dilution with water, and the herbicide content after irradiation was determined chromatographically. The results of experiments with 10 kGy γ irradiation are shown in Table 5. Because of high concentration of herbicides in irradiated solutions (in reported above processes 0.11 g/L of dicamba solutions were used), one can expect a lower yield of decomposition in the same range of doses. Additionally, this is also affected by the presence of a higher concentration, which also undergoes degradation consuming a large part of radiation. The yield of dicamba degradation was 42% for the preparation with 6-fold larger amount of herbicide MCPA, degraded in 20%. The other tested preparation Aminopielik contains 13 times more 2,4-D, for which the rate constant for the reaction with OH radical is almost twice as large as for dicamba. In this case, the use of γ dose 10 kGy resulted in 12% degradation of dicamba and 31% for 2,4-D. One can expect, based on the above reported data, that additional ozonation of irradiated solutions might essentially enlarge these yields, and is possibly a basis for large-scale applications of this method.

In contrast to irradiation of pure MCPA solutions, in almost every examined case the addition of hydrogen peroxide, (in this measurement used at 39 mM (1.32 g/L) level), affected the yield of processes positively. Complete decomposition of MCPA without H_2O_2 was observed at 10 kGy, while in the presence of H_2O_2 already half of this dose was sufficient for the complete decomposition of MCPA. A substantial positive effect of the addition of H_2O_2 was observed in the case of decomposition of 3-chlorophenol, especially 4-chloro-2-methylphenol.

TABLE 5. RADIOLYTIC DEGRADATION OF HERBICIDE COMPONENTS FROM COMMERCIAL AGROCHEMICAL PREPARATIONS DILUTE 1:100 IN AQUEOUS SOLUTION BY γ IRRADIATION WITH 10 kGy DOSE

Commercial preparation	Herbicide	Initial concentration	Effectiveness of degradation,% in irradiated solution, g/L
Chwastox	MCPA	2.73	20
	Dicamba	0.48	42
Aminopielik	2,4-D	4.55	31
	Dicamba	0.34	12

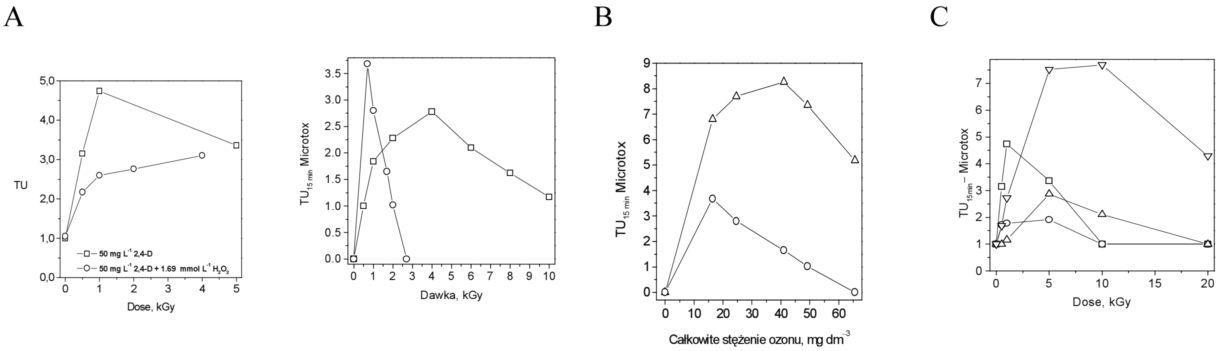


FIG. 26. Toxicity changes: A- effect of 1.7 mM hydrogen peroxide on decomposition of 50 mg dm^{-3} by γ irradiation; B — during irradiation of 0.5 mM 2,4-D solutions in groundwater in different conditions (O$_3$ (Δ), EB (□) and EB with ozonation (O)), C- during γ irradiation of 50 mg L^{-1} in the presence of (□) 200 mg L^{-1} HCO$_3$ (pH8,3) (O) 400 mg L^{-1} HCO$_3$ (pH8,3) (Δ) 50 mg L^{-1} NO$_3$ (pH7,0) (∇).

3.2.10 . Changes of toxicity of irradiated solutions of pesticides

The evaluation of toxicity is mainly performed using standard tests comprising fish, crustacea, algae and bacteria. The commonly used Microtox test assesses changes in light output from a luminescent bacteria *Vibrio fisheri* as a non-specific indicator of the toxicity of the test substance. The sensitivity of the bacteria was assessed for over 1300 pure compounds [53]. The bioluminescence inhibition of the *Vibrio fisheri* test has been standardized and is commercially available in various versions (*e.g.* Microtox from SDI or ToxAlert 100 from Merck). The advantages of those toxicity tests include a short time of analysis, simplicity of operation and elimination of a need to culture the test organisms. The bacteria are provided by manufacturers in a lyophilized form, and can be stored for several months and used 'on demand'.

The aim of this work was to examine changes of toxicity, determined mostly by the Microtox test, occurring during γ and electron beam irradiation of solutions of phenoxy acid pesticides 2,4-D, dicamba and MCPA. During radiolytic degradation, several transient toxic compounds such as chlorophenols or dihydroxybenzenes may be formed. It is of great importance to find out how these processes may affect the toxicity of the irradiation solutions at various doses of radiation.

In this study, the initial increase of toxicity at low doses was observed during irradiation of aqueous solutions of 2,4-D, with the maximum about 1 kGy (FIG. 26A). This can be attributed mainly to the formation of toxic 2,4-dichlorophenol. For 2,4-D, the investigation of toxicity changes during ozonation, electron beam irradiation and combined electron beam irradiation and ozonation were also performed. In conclusion, the combined EB/O$_3$ process gives better total toxicity reduction than separate ozone or EB treatment. The combined process also reduces the dose of the irradiation and the amount of ozone needed to reduce toxicity, (FIG. 26B).

It was also found that the presence of 50 mg L^{-1} nitrate caused the highest increase of toxicity in comparison to other studied scavengers (FIG. 26C). The high toxicity of the irradiated solution can be attributed not only to the formation of toxic phenolic compounds at higher doses, but also to the formation of ammonia from the reduction of nitrate in the absence of oxygen.

In the presence of 1.7 mM of hydrogen peroxide; yield of decomposition 2,4-D, the dose needed for 95% decomposition decreased from to 2 to 1 kGy. Simultaneously, 50% lower toxicity of irradiated solution was observed (FIG. 26A). This illustrates the fact that during irradiation, the hydrogen peroxide added is an additional source of oxygen and hydroxyl radicals which results in more efficient degradation of 2,4-D and its products.

The toxicity changes of dicamba during its radiolytic degradation were examined by γ irradiation of neutral aqueous solutions of 110 mg/L (0.5 mM) saturated with air in the dose range up to 4 kGy. Irradiation was carried out in the absence and presence of 400 mg/L bicarbonate or 50 mg/L nitrate as well as in solutions prepared in groundwater that were EB irradiated and ozonated. The solutions before an after irradiation did not show any measurable toxicity, and the slight increase of toxicity can be attributed to phenolic compounds formed as a result of irradiation with limited doses, decreased with further dose increase.

The effect of pHon changes in toxicity in irradiated MCPA solutions is shown in (FIG. 27A). As expected, at a lower yield of MCPA decomposition fewer toxic species formed, at pH11.5 and smaller toxicity increase were observed at 4 kGy dose. For the most favourable conditions of pH1.5, a very large increase of toxicity was observed at low doses of 0.5 kGy, which then was constant at doses above 1 kGy, but at a value much larger than the initial toxicity level of pure MCPA solutions. The total measured toxicity depends on the sum of individual components present in the solution at different stages of radiolytic decomposition. The effect of hydrogen peroxide on the toxicity of irradiated solutions of MCPA is illustrated by results in (FIG. 27B). An increase in toxicity was observed at the highest concentration of hydrogen peroxide, where the yield of irradiation was low.

In the absence of hydrogen peroxide or at its lower concentration, at low doses, a large increase of toxicity was observed, which stabilized at higher doses. At the 4-kGy dose, however, the lowest toxicity of irradiated MCPA solution was found for irradiation without the addition of hydrogen peroxide.

In an irradiated sample of industrial waste from MCPA production without the addition of H_2O_2, the toxicity level was practically unchanged in the dose range up to 10 kGy (FIG. 27A). After the addition of hydrogen peroxide to raw waste prior to irradiation, the toxicity of waste solution decreased about 70%. Irradiation of this sample containing H_2O_2 resulted, however, in about a ten-fold increase of toxicity at doses above 2 kGy. The exact reason of this significant change is not yet known. It can be caused not only by products of radiolytic degradation of MCPA, but also by products of other reactions taking place in irradiated waste. Formation of other toxic compounds, such as chlorinated alkanecarboxylic acids, may be responsible for this effect and requires further investigation.

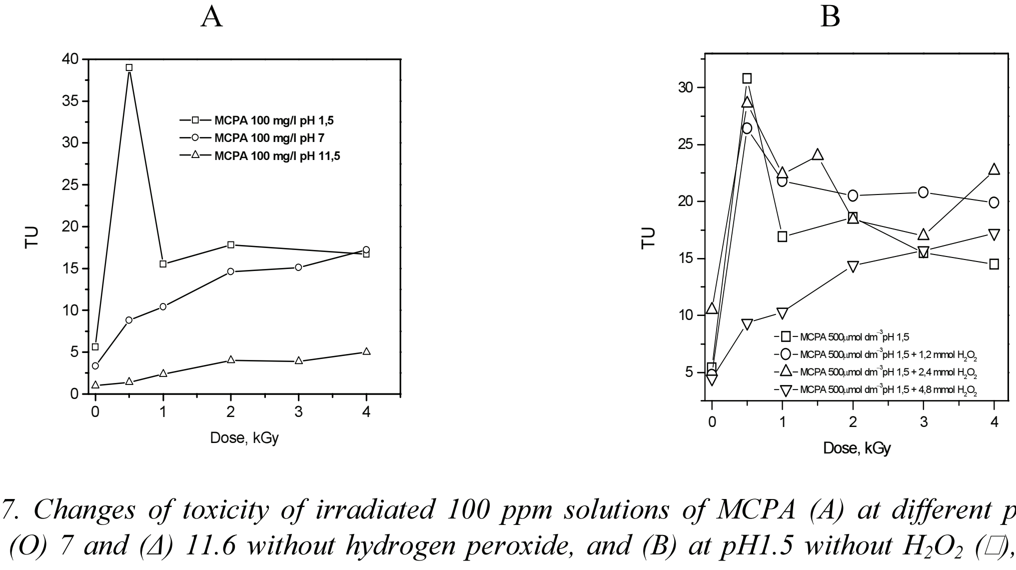


FIG. 27. Changes of toxicity of irradiated 100 ppm solutions of MCPA (A) at different pH values (□)1.6, (O) 7 and (Δ) 11.6 without hydrogen peroxide, and (B) at pH1.5 without H_2O_2 (□), with 1.2 mM H_2O_2 (O), with 2.4 mM H_2O_2 (Δ), and with 4.8 mM H_2O_2 (∇).

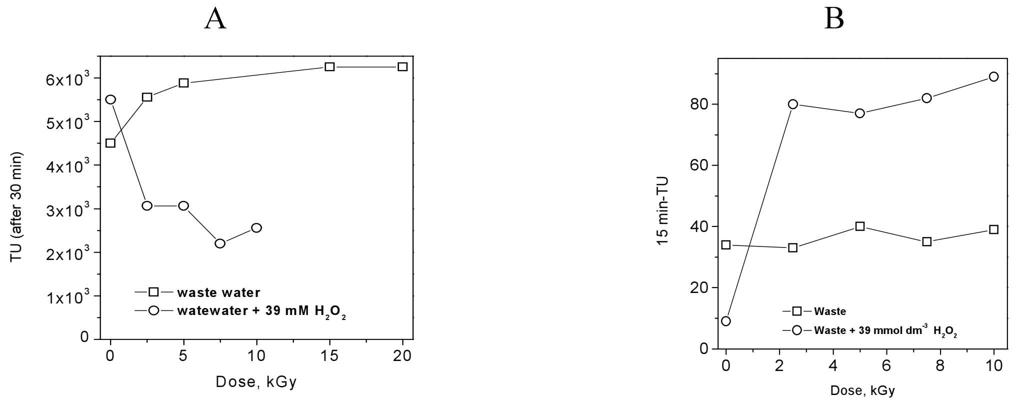


FIG. 28. Changes of toxicity of irradiated waste from production of 2,4-D(A)and MCPA(B) without H_2O_2 *(□) and with* H_2O_2 *in irradiated solution (O).*

REFERENCES

[1] GROVER, R., CESSNA, A.J., (Eds.), Environmental Chemistry of Herbicides, CRC Press, Boca Raton (1991).

[2] HODGSON, E., LEVI, P.E., Pesticides: an important but underused model for the environmental health science. Environ. Health Perspect., **104** (1996) 97.

[3] BLAIR, A., MALKER, H., CANTOR, K., BURMEISTER, L., WIKLUND, K. J., Cancer among farmers: a review. Sci. J. Work Environ. Health **11** (1985) 397–410.

[4] HOAR, S.K., BLAIR, A., HOLMES, F.F., BOYSEN, C.B., ROBEL, J.R., HOOVER, R., FRAUMENI, H., Agricultural herbicide use risk of lymphoma soft-tissue sarcoma J. Am. Med. Assoc., **256** (1986) 1141.

[5] FIELDING, M., BARCELO, D., HELWEG, A., TORSTENNSON, L., VAN ZOONEN, P., ANGELETTI, G., Pesticides in Ground and Drinking Water (Water Pollution Research Report, 27), Commission of the European Communities, Brussels (1992) 1–136.

[6] HORNSBY, A.G., WOUCHOPE, R.D., HERNER, A.E., Pesticide Properties in the Environment, Springer Verlag, New York (1996).

[7] BENITEZ, F.J., ACERO, J.L., REAL, F.J., ROMAN, S., Oxidation of MCPA and 2,4-D by UV radiation, ozone, and the combinations UV/H_2O_2 and O_3/H_2O_2 J. Env. Sci. Health, Part B-Pesticides, Food Contaminants and Agricultural Wastes, **39** (2004) 393–409.

[8] PIERA, E., CALPE, J.C., BRILLAS, E., DOMÈNECH, X., PERAL, J., 2,4-dichlorophenoxyacetic acid degradation by catalyzed ozonation: TiO_2/UVA/O_3 and Fe(II)/UVA/O_3 systems, App. Catal. B: Environ. **27** (2000) 169–177.

[9] SINGH, H.K., MUNEER, M., Photodegradation of a herbicide derivative, 2,4-dichloro-phenoxyacetic acid in aqueous solution: Res. Chem. Intermed. **30** (2004) 317–329.

[10] KWAN, C.Y., CHU, W., A study of the reaction mechanism of degradation of 2,4-dichlorophenoxyacetic acid by oxalate-mediated photoxidation, Wat. Res. **38** (2004) 4213–4221.

[11] OTURAN, M.A., An ecologically effective water treatment technique using electrochemically generated hydroxyl radical for in situ destruction of organic pollutants: Application to herbicide, 2,4-D J. App. Electrochem. **30** (2000) 475–485.

[12] BRILLAS, E., BOYE, B., DIENG, M.M., General UV-assited cathodic Fenton treatment for the mineralization of herbicides MCPA. J. Electrochem. Soc. **150** (2003) E583-E589.

[13] CLAPES, P., SOLEY, J., VINCENTE, M., RIVERA, J., CAIXACH, J., VENTURA, F., Degradation of MCPA by photochemical methods, Chemosphere **15** (1986) 395–401.

[14] CHU, W., WONG, C.C., The photocatalytic degradation of dicamba in TiO_2 suspension with the help of hydrogen peroxide by different near UV irradiations, Wat. Res. **38** (2004) 1037–1043.

[15] BIANCO-PREVOT, A., FABBRI, D., PRAMAURO, E., MORALES-RUBIO, A., DELA GUARDIA, M., Continuous monitoring of photocatalytic treatment by flow injection. Degradation of dicamba in aqueous TiO_2 dispersion, Chemosphere **44** (2001) 249–255.

[16] SOLEY, J., VICENTE, M., CLAPÉS, P., ESPLUGAS, S., Kinetic study of 4-chloro-2-methylphenoxyacetic acid photodegradation. Ind. Eng. Chem.Prod. Res. Dev., **25** (1986) 645.

[17] ZERTAL, A., SEHILI, T., BOULE, P., Photochemical behaviour of 4-chloro-2-methylphenoxyacetic acid. Influence of ph and irradiation wavelength, J. Photochem. Photobiol. A **146** (2001) 37–48.

[18] ZERTAL, A., MOLNÁR-GÁBORB, D., MALOUKIA, M.A., SEHILIA, T., BOULE, P., Photocatalytic transformation of 4-chloro-2-methylphenoxyacetic acid (MCPA) on several kinds of TiO_2. Appl. Catal. B **49** (2004) 83–89.

[19] FUJITA, T., ONA, E.P., KOJIMA, Y., MATSUDA, H., KODA, H., TANAHASHI, N., ASAKURA, Y., Ultrasonic decomposition of (4-chloro-2-methylphenoxy)acetic acid (MCPA) in aqueous solution. J. Chem. Eng. Japan **36** (2003) 806.

[20] BOYE, B., BRILLAS, E., DIENG, M.M., Electrochemical degradation of herbicide 4-chloro-2-methylphenoxyacetic acid in aqueous medium by peroxicoagulation and photoperoxicoagulation. J. Electroanal. Chem. **25** (2003) 540.

[21] HARRISON, L., LEADER, R.U., HIGGO, J.J.W., WILLIAMS, G.M., A study of the degradation of phenoxy acetic hericides at different aites in a limestone aquifer, Chemosphere **36** (1998) 1211–1232.

[22] MAHRAMANLIOGLU, M., KIZILCIKLI, I., BICER, I.O., Tuncay M., Removal of MCPA from aqueous solutions by acid-activated spent bleaching earth. J. Env. Sci. Health B **38** (2003) 813.

[23] PANDES, R., IBARZ, A., ESPLUGAS, S.,Photodecomposition of carbendazim in aqueous solution. Water Res. **34** (2000) 2951.

[24] MAZELLIER, P., LEROY, E., DE LAAT, J., LEGUBE, R., Degradation of carbendazim by UV/H_2O_2 investigated by kinetic modeling. Environ. Chem. Lett. **1** (2003) 68.

[25] MAZELLIER, P., LEROY, E., DE LAAT, J., LEGUBE, R., Transformation of carbendazim by UV/H_2O_2 system in the presence of hydrogencarbonate ions: involvement of the carbonate radical, New J. Chem. **26** (2002) 1784.

[26] BAUDINA, A., EMONELIN, C., BAALIOUAMER, A., GREMIER-LOUSTALAT, M.F., CHOVELON, J.M., Photochemical behavior of carbendazim in aqueous solution, Chemosphere, **50** (2003) 649–655.

[27] FARRE, M.J., FRANCH, M.I., MALATO, S., AYLLON, J.A., PERAL, J., DOMENECH, X., Degradation of some biorecalcitrant pesticides by homogeneous and heterogeneous photocatalytic ozonation, Chemosphere, **58** (2005) 1127–1132.

[28] MEIJERS, R.T., ODERWALD-MULLER, E.J., NUHN, P.A., N.M., KRUITHOF, J.C., Degradation of pesticides by ozonation and advanced oxidation, Ozone Sci. Eng. **17** (1995) 673–686.

[29] HINCAPIE, M., MALDONATO, M.I., OLLER, I., GERNJAK, W., SANCHEZ-PEREZ, A.A., BALLESTEROS, M.M., MALATO, S., Solar photocatalytic degradation and detoxification of EU priority substances, Catal. Today **101** (2005) 203–210.

[30] BARBUSINSKI, K., FILIPEK, K., Use of Fenton's reagent for removal of pesticides from industrial wastewater, Pol. J. Env. Stud., 10, 207–212 (2001).

[31] KARPEL VEL LEITNER, N., BERGER, B., GEHRINGER, P., γ-irradiation for the removal of atrazine in aqueous solution containing humic substances, Radiat. Phys. Chem., 55 (1999) 317–322.

[32] ANGELINI, G., BUCCI, R., CARNEVALETTI, F., COLOSIM, M., Radiolytic decomposition of aqueous atrazine, Phys. Chem., **59** (2000) 303–307.

[33] ZONA, R., SOLAR, S., GEHRINGER, P., Degradation of 2,4-dichlorophenoxyacetic acid by ionizing radiation: influence of oxygen, Wat. Res. **36** (2002) 1369.

[34] CAMPOS, S.X., VIEIRA, E.M., CORDEIRO, P.J.M., RODRIGUES-FO, E., MURGU, M., Degradation of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) dimethylamine salt by gamma radiation from cobalt-60 in aqueous solution containing humic acid, Radiat. Phys. Chem. **68** (2003) 781–786.

[35] DRZEWICZ, P., ZONA, R., GEHRINGER, P., SOLAR, S., TROJANOWICZ, M., Decomposition of 2,4-dichlorophenoxyacetic acid by ozonation, ionizing radiation as well as ozonation combined with ionizing radiation Rad. Phys. Chem. 69, 281–287 (2004).

[36] ZONA, R., SOLAR, S., SEHESTED ,K., HOLCMAN, J., MEZYK, S.P., OH-radical oxidation of phenoxyacetic acid and 2,4-dichlorophenoxyacetic acid. Primary radical steps and products, J. Phys. Chem., A **106** (2002) 6743–6749.

[37] PELLER, J., WIEST, O., KAMAT, P.V., Hydroxyl radical's role in the remediation of a common herbicide, 2,4-dichlorophenoxyacetic Acid (2,4-D) J. Phys. Chem. A, **108** (2004) 10925–10933.

[38] PELLER, J., KAMAT, P.V., Radiolytic transformations of chlorinated phenols and chlorinated phenoxyacetic acids J. Phys. Chem. A **109** (2005) 9528–9535.

[39] ABEL AAL, S.E., DESSOUKI, A.M., SOKKER, H.H., Degradation of some pesticides in aqueos solutions by electron beam and gamma-radiation, J. Radioanal. Nucl. Chem., **250**(2) (2001) 329–334.

[40] VON GUNTEN, V., Ozonation of drinking water: Part I. Oxidation kinetics and product formation, Wat. Res. **37** (2003) 1443–1467.

[41] GEHRIGER, P., ESCHWEILER, H., The dose rate effect with radiation processing of water an interpretative approach, Radiat. Phys. and Chem. **65** (2002) 379–386.

[42] WU, X.Z., YAMAMOTO, T., HATASHITA, M., Radiolytic degradation of chlorinated hydrocarbons in water, Bull. Chem. Soc. Jpn. **75** (2002) 2527–2532.

[43] ZHANG, S.J., YU, H.Q., Radiation-induced degradation of polyvinyl alcohol in aqueous solutions, Water Res. **38** (2004) 309–316.

[44] CHU, W., Modeling the quantum yields of herbicide 2,4-D decay in UV/ H_2O_2 process, Chemosphere **44** (2001) 935–941.

[45] SUN, Y., PIGNATELLO, J.J., Organic intermediates in degradation of 2,4-dichlorophenoxyacetic acid by Fe^{3+}/ H_2O_2 and Fe^{3+}/UV/ H_2O_2. J. Agric. Food Chem. **41** (1999) 1139–1142.

[46] DE, A.K., CHAUDHURI, B., BHATTACHARJEE, S., DUTTA, B.K., Estimation of $^{\bullet}OH$ radical reaction rate constants for phenol and chlorinated phenols using UV/H_2O_2 photo-oxidation, J. Hazard. Mat. **64** (1999) 91–104.

[47] BUXTON, G.V., GREENSTOCK, C.L., HELMAN, P.W., ROSS, A.B., Critical review of rate constants for reaction of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution, J. Phys. Chem. Ref. Data. **17** (1988) 513–886.

[48] LEITNER, M.C., CHEN, J.N., Pretreatment of pesticides wastewater by photocatalytic oxidation, Wat. Sci. Technol. **36** (1997) 117–127.

[49] Trojanowicz 2002

[50] NICHIPOR, H., DASHOUK, E., YERMAKOV, A., Radiat. Phys. Chem. **54** (1999) 307–315.

[51] SUN, Y., HAKODA, T., CHMIELEWSKI, A.G., HASHIMIOTO, S., ZIMEK, Z., BULKA, S., OSTAPCZUK, A., NICHIPOR, H., Radiat. Phys. Chem. **62** (2001) 353–360.

[52] GETOFF, N., Peroxyl Radicals in the Treatment of waste solutions In Peroxyl Radicals. Z.(Ed.), Peroxyl Radicals, Wiley, 483–506.

[53] KEISER, K.L.E, PALABRICA, V.S., Photobacterium phosphoreum toxicity data index, Water Pollt.Res.Com., **26** (1991) 361–366.

IMPLEMENTATION OF IONISING RADIATION ON WASTEWATER TREATMENT: THE PORTUGUESE STUDY CASE

M.L. Botelho[1], J. Branco[1], C. Freitas[1], P. Ferreira[2] , A. Belchior[1],
A. Costa[1], Í. De Sousa[1], L. Alves[1], L. Machado[1], P. Matos[1],
R. Cordeiro[1], R. Melo[1], R. Ribeiro, R. Zeinou[1],
S. Cabo Verde[1], T. Silva[1], V. Farinha[1]

[1]Nuclear and Technological Institute (ITN), Sacavém, Portugal
[2] Centro Oncológico, Linda-a-Velha, Portugal

Abstract

In the framework of the CRP on 'Remediation of Polluted Waters and Wastewaters by Radiation Processing,' the Portuguese group has been developing work at lab scale level on several kinds of samples originated from Municipal and Industrial wastewater treatment. The objective was to understand the effect of the main physical parameters such as type of radiation, dose rate and absorbed dose of biological and chemical factors of the wastewater. To compare the effect of gamma radiation (60-Co facility-UTR) versus electron beam (LINAC energy 9 MeV), dosimetry studies were developed by means of the Fricke reference dosimeter. An ionometric system was also applied to the electron beam. Equivalent locals for specific irradiation geometry (polyethylene bags 10 cm × 10cm) were found in the LINAC and UTR facility with an absorbed dose rate of approximately 1 $kGy.h^{-1}$. Biological and chemical effects studies were performed with wastewater samples irradiated in the polyethylene bags at absorbed doses ranging from 0.5 kGy to 30 kGy, depending on the studies' purposes. Microbiological studies were performed based on conventional methods and molecular biology techniques. Chemical studies were performed using several techniques such as Fourier Transform Infrared Spectroscopy (FTIR), Instrumental Neutron Activation Analysis (INAA) and ionic chromatography, in order to study the influence of ionising radiation in the ions' dynamic at liquid and solid phases of the wastewater. The overall preliminary results obtained on the biological, chemical and economical studies lead us to choose agricultural wastewater and gamma irradiation for the future work. Therefore, we continue to develop more specific studies on agricultural wastewater to implement the technology as a tool in the treatment process and, focus on gamma irradiation process. For these studies, the legislated indicator parameters, such as Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Suspended Solids (TSS) were also determined. A lab scale wastewater treatment system where gamma radiation is applied directly to the treatment is being assembled. A special design will allow the application of low doses, at a low dose rate, to induce molecular bound breaks (scissors effect), and, higher absorbed dose at a higher dose rate will be applied for manure disinfection purposes.

1. INTRODUCTION

New technologies for recycling and preserving water resources are important issues for the world. The global demand for potable water increases continuously. Between 1900 and 1995, water consumption increased over six times, which is more than twice the rate of population growth in the same period of time. Only 0.007% of the world's water is accessible for direct human use [1]. Optimization of sewage treatment by ionising radiation has been developed to ensure disinfection and increase water quality at the same time [2, 3, 4].

In 2001, the Committee on Natural Resources of the Economic and Social Council from the United Nations in 2001 issued a report showing that about 80 countries in the entire world, inhabited by about 40% of the world population, suffered from severe water supply shortages. This scarceness of water resources limits economic and social development [5]. The policy of European Community Directives is to enforce the polluter-pays principle.

In Europe, livestock agriculture has developed into a modern efficient industry. The industrialization of production; the specialization of equipment and processes; the intensive production that has led to local concentrations in animals' density; and the increased demand for food, are major socio-economic outputs of this progress. However, future prospects may be limited due to the increase of environmental pollution.

Animal wastes contribute to agricultural pollution and contaminate streams and groundwater via runoff and leaching from agricultural areas to water sources. In cases of accidental or improper management, direct disposal of wastes takes place [6]. Nitrogen compounds are one of the nutrients of major agricultural importance, yet at the same time are potential pollutants. Nitrogen-containing compounds from waste can leach to groundwater and contaminate drinking water resources [7]. All these factors will increase the probability of environmental pollution from agricultural operations, and, among others, the need for effective animal waste management is urgently felt.

To reduce pollution impact arising from intensive livestock [8], wide-ranging legislation has been introduced in most countries to protect the environment (soil, water and air). The EU Directives (*e.g.* Water Framework Directive 2000/60/EC) have been developed in approach to pollution abatement and manure management. One of the main targets of EC Directives is the polluter-pays principle, in which the polluter subsidizes the development of new strategies that aim the technical and economical profits in the treatment of residues.

Based on these trends and in the scope of the IAEA-Research Project 302-F2-POR-12017 'Impact of e beam and γ radiation on the treatment of wastewater and drinking water by radiation' studies were carried out in several kinds of wastewater from Portuguese Municipalities (e.g. Beirolas, Santarém) and Industries (e.g. food, slaughterhouse; swine exploitation and dairy). This research aims to understand the effect of ionising radiation on biological and chemical matter of the wastewater in order to choose the best treatment design and target to apply the ionising radiation. The response of ionising radiation on wastewater was studied taking into account the type of energy (gamma rays and electron beam), the dose rate, and the composition of substrata. The fields of study were chemistry, microbiology, physics and economies.

In the beginning of this project, studies were developed to compare the biological and chemical response of wastewater after irradiation to both types of ionising radiation — gamma radiation in UTR, the 60-Co source activity of 10^{16} Bq (December 2003), and electron beam type, LINAC at an energy of 9 MeV, with similar sample geometry. These comparative studies were based on previous experiments with a Fricke dosimeter with a composition of mainly water, in order to find out two equivalent locals in terms of dose rate (approximately 1 $kG.h^{-1}$). Subsequently, comparative biological responses to both types of radiation (gamma and electrons) were obtained in wastewater samples from an agro-industry (pea-washing water) and from drinking water. The number of cfu/ml obtained at equivalent doses in both inactivation processes, gamma and electron beam were not significantly different ($P > 0.05$ – Anova) for the two samples studied. After irradiation, the inactivation response of 90% of the population (D value) for the coliforms was 0.3 kGy, and for the total microorganism population was approximately 1.2 kGy in the pea washing water [9]. The D value for the total microorganism population present in drinking water samples was significantly different for each type of radiation. This could be explained by to the fact that D value is defined as the inverse of the slope of a straight inactivation line. Since the inactivation curve of the drinking water for gamma radiation does not have a linear behavior, the D value calculated could not correspond to the real value. The absorbed dose effect on an elements' dynamic of the liquid and solid phases of the wastewater samples was studied chemically. These studies were performed on eggplant and green bell pepper gamma irradiated washing waters from an agro industry. FTIR and INAA analysis showed that the functional groups founded are essentially natural to the wastewater, namely aromatic hydrocarbons and aromatic rings originated from the vegetables and chlorides from the water used in the washing process. The obtained results point out that for the absorbed dose of 10 kGy, there is no effect on the functional groups present in both phases. The INAA results point out that the concentration of the elements is higher at the solid phase, which may indicate that changes occur either by precipitation or adsorption in the chemical state of a few elements (e.g. Hg and K) [22].

To study the influence of different dose rates and the influence of substrate on the response of microorganism, experiments were performed in UTR (gamma radiation) in three locals where previous dosimetry was done by means of Fricke dosimeter. The bacterium (methilotrophic pink pigmented rods) studied has different responses to different dose rates (9 $kGy.h^{-1}$, 0.8 $kGy.h^{-1}$ and 0.08 $kGy.h^{-1}$) and distinct substrata (wastewater — WW and Tryptic Soya Broth — TSB). The determined D- values were the highest to the lowest dose rate (0.08 $kGy.h^{-1}$), with 21 kGy in TSB and 44 kGy when irradiated in WW substrata. At the highest dose rate (9 $kGy.h^{-1}$), D value showed to be significantly lower, 3 kGy in TSB and 2 kGy in WW. At a dose rate of 0.8 kGy.h^{-1}, the same bacteria showed a D value of 14 kGy in TSB and 19 kGy in WW. Results indicated that a lower dose rate may lead to a better remediation process. This fact could be more evident for the wastewater substrates if the irradiation process affects degradation, changing molecular forms into easier metabolized compounds (scissors effect). Furthermore, the large irradiation period of low dose rate irradiations may allow bacteria's repair mechanisms to respond more easily and efficiently to the lethal agent [10, 11].

Agricultural activities are one of the main sources of wastewater pollution all over the world, namely Portugal, considering that only the swine activity results in the production of 2×10^7 m^3 of slurry per year [12]. Based on this fact and on the preliminary results discussed above, more studies were carried out using gamma radiation on the agricultural wastewater, resulting because of slaughterhouse, swine and dairy activities.

In this work, three main fields of research are presented: chemistry, biology, and physics.

Chemistry — In order to study the effect of ionising radiation (UTR-^{60}Co) on the wastewater quality, its impact on nutrients and others, and the inter relation with biological and physics field results.

Biology — The impact of ionising radiation on the natural microbiota from the wastewater has been studied in terms of: a) survival of total microorganisms after irradiation, b) comparison of microorganisms types found before and after irradiation, c) inactivation studies of the survivors strains, d) comparative molecular biology studies of survivors strains at different irradiation doses, and e) Ecotoxicological studies were also performed using slaughterhouse wastewater samples.

Physics — Dosimetry studies to establish the local dose rate and to apply a lab scale process were studied during the project.

Additionally, the economical sustainability of the technology is presented, based on feasibility studies of a slaughterhouse industry. [13] The recycling of irradiated manure through its application to agricultural soils plays an important role. Besides the economical perspective, the improvement of soil characteristic quality and increasing the bioavailability of nutrients is important to underline.

2. OBJECTIVE OF THE RESEARCH.

The overall objective of this research is to show, based on the more relevant results, that the implementation of ionising radiation in agricultural wastewater treatment plants is not only possible, but is also an effective, safe and profitable way to treat wastewater.

The main gist is to implement an irradiation process for agricultural wastewater treatment that foresees: 1) the decrease of the residence time of wastewater, enhancing natural bioremediation processes; 2) the disinfection of water with consequent reuse and 3) the use of manure as a safe fertilizer with profit; thus, being a safe technology with economical benefits.

3. MATERIALS AND METHODS

Experiments were conducted to evaluate the impact of gamma radiation in different kinds of wastewater resulting from different agricultural activities, such as slaughterhouse, swine manure and dairy. The impact of gamma radiation on the slaughterhouse sludge was also studied.

Case Studies — slaughterhouse, swine and dairy industries

The slaughterhouse wastewater sample was collected from a plant that consumes about 900 cubic meters of water per day (m^3/day). The plant produces approximately 143 tons of swine meat daily. Parts of the solid residues are collected and reused. The bones, guts and excess fat removed are used to produce pet food. The pig fat and dehydrated blood are used to produce fertilizers. The wastewater takes 7 days since pre-treatment until discharge on the river and it is a treatment system of four anaerobic/aerobic lagoons.

The swine wastewater sample was collected from a pig production farm. This farm contains about 200 effectives, and the wastewater treatment system is similar to that of the slaughterhouse.

The dairy wastewater sample was collected from a dairy industry which produces cheese. Wastewater loads are typically 1–2 cubic meters per metric ton (m^3/t) of milk processed and in this case, the plant consumes 25 000 m^3/day which corresponds to 100,000 m^3/day of wastewater produced. This industry has implemented a 3-step wastewater treatment system: a) mechanical screening pre-treatment, b) biodigestors, c) sedimentation.

3.1. Sampling

The samples used for the study were untreated wastewater, submitted only to a mechanic screening pre-treatment. The samples were punctual and randomly collected, except for the slaughterhouse study where sampling was made under the slaughter worst case scenario period. Five liters of samples were collected in special bottles previously treated in order to get out chemical and biological residues (washed three times in wastewater before taking definitive samples into the bottle).

Sludge samples used for the study were untreated slaughterhouse sludge from the anaerobic lagoon. A long pipe was used to take the sludge at a number of different locations and depths. Eight sludge samples were collected randomly. The samples were placed in sterilized plastic bags, each containing about 0.5 up to 1 kg.

Samples were transported at approximately 4ºC and analyzed as soon as possible. Upon the arrival at the laboratory each recipient with a wastewater sample was mixed and was divided into aliquots and placed in 0.5 L beakers. The sludge samples were homogenized by placing the bags in a Stomaker® run at high speed for 3× at 10 minutes, with a pause of 10 minutes in between.

3.2. Irradiation

Samples were submitted to gamma radiation at the UTR. The local dose rate was previously determined by Fricke solution [14].

Wastewater samples in a 0.5 L beaker were irradiated with γ rays at the dose rates of 0.3; 0.5; 0.9, and 3 $kGy.h^{-1}$ (January 2004). Sludge samples were irradiated at a dose rate of 0.9 $kGy\ h^{-1}$ in sealed Amilon® bags with 100 mg each. In all studies, chemical and biological, it was used a correspondent and a non-irradiated sample was used as the control.

All absorbed doses applied (5 up to 35 kGy) were measured by routine dosimeters (Harwell Red Perspex, Batch HA Type 4034; and Gammachrome YR), with nominal uncertainty limits of about 5% [15]. All irradiated and non-irradiated samples were analyzed simultaneously.

3.2. Analythical Methods

COD, BOD, TSS, $N_{organic}$ and P_{total}

Five-day BOD (Respirometric Method 5210 B), COD (Tritimetric Method 5220 C), TSS (Method 2540 B), $N_{organic}$ (Macro-Kjeldahl Method, 4500-N_{org} B) and P_{total} (Ascorbic acid Method, 4500-P E.) were measured according to the Standard Methods for the Examination of Water and Wastewater [16]. COD was measured after filtration (1.2 µm pore size filter). The BOD, $N_{organic}$, and P_{total} were measured prior to filtration. The gamma irradiation efficiency was calculated in terms of the reduction of the main parameters. As an example,%COD reduction is represented by the equation%COD reduction = $[(COD_{initial} – COD_x)/COD_{initial}]*100$, where COD_x is the value measured after a given dose and $COD_{initial}$ the COD value for the non-irradiated sample.

Ionic Chromatography

To access the impact of ionising radiation on the bioavailability of the nutrients, we have measured the presence of cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+) and of anions (F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2}) in the slaughterhouse sludge solution and swine manure solution using ionic chromatography (DIONEX DX500, using CS12A and AS4A columns for cations and anions analysis, respectively). The values reported are the average of 2 replicates (standard deviation 5%).

For the slaughterhouse sludge sample, we have leached 100 mg of irradiated and non-irradiated sludge in 1000 ml of pure water, and filtered it with a 1.2 μm pore size filter measure soluble compounds only. The swine manure samples were filtered as the slaughterhouse sample in order to measure soluble compounds.

Inactivation of Microorganisms

To determine mesophilic microbiota counts before and after irradiation at several sub-lethal absorbed doses (see 3.2 Irradiation), the direct plating technique was used after tenfold dilution wherever needed. The growth conditions were as follows: aerobic incubation at 30 °C for 14 days on Tryptic Soy Agar (TSA) plates, and colony-forming units (C.F.U.) were counted after 24 h, 48 h, 72 h, 7 and 14 days.

These protocols were based on Standard Methods for the Examination of Water and Wastewater, (20th Edition, 1998). Morphological and biochemical analyses were performed in the most frequent microorganisms, and identification by API system was made [17].

Data analysis was done using Excel 2003 (e.g. regression analysis and descriptive statistics). The inactivation response of natural wastewater microbiota was assessed by the D value parameter determined based on the survival curves. Inactivation efficiency was calculated according to the equation Efficiency (%) = $[(N_0 - N_d)/N_0]*100$, where N_d is the number of survivors after irradiation at several doses, and N_0 the initial count (non-irradiated sample).

Biodegradation studies

Radiation-resistant bacteria were isolated in order to evaluate its possible biodegradative functions. With this purpose, two similar experiments were carried out. In the first one, radiation-resistant bacterium, isolated from a wastewater sample irradiated at 30 kGy (3 kGy/h), was inoculated in wastewater samples (WW) sterilized by two different processes, autoclaving (121 ºC 30') and by gamma radiation (3 kGy.h-1, 30 kGy) [18]. On a second approach another radiation-resistant strain, also isolated from an irradiated wastewater sample irradiated at 30 kGy at a lower dose rate (0.3 kGy/h), was inoculated in three kinds of substrata: 1) Tryptic Soy Broth (TSB) used in conventional bacteriology as a rich-nutrient medium, 2) irradiated wastewater at an absorbed dose of 10 kGy for a dose rate of 9 kGy.h-1 and 3) non-irradiated effluent submitted to a filtration process (nitrocellulose membranes with a pore size of 0.2 μm) [19]. For both studies, the different cultures were incubated in an orbital shaker at 30ºC at aerobic atmosphere. The bacterial growth was followed during the incubation time by turbidimetry against blank samples (same composition and treatment process but without bacteria inoculation) using a spectrophotometer (wavelength = 460 nm).

Molecular Biology studies

Four radiation-resistant bacterial isolates (R30, WOB, W0W and W0T) from the slaughterhouse wastewater samples were irradiated at 5, 13, 21 or 27 kGy and analyzed using molecular biology fingerprinting techniques (MSP-PCR, RADP-PCR and the 16S- PCR digestion) to access their genetic similarity and possible genetic alterations induced by gamma radiation.

Ecotoxicological tests

The toxicological tests were carried out in order to assess the impact irradiated slaughterhouse wastewater may have on the environment. Acute toxicity evaluation was carried out on irradiated and non-irradiated samples, expressed as EC-50 value, which means the sample concentration reduces the measured effect by 50%. The tested organisms and methods were the following: (a) Bacteria *Vibrio fischeri* in Microtox System — Basic Test Protocol — with 15 minutes exposure, and luminescence inhibition calculated; and (b) Microcrustacean *Daphnia similis*, acute test for 48h. All tests were performed in standard conditions. For the acute toxicity tests (*D. similis*), the EC-50 values were determined by trimmed Spearman-Karber method [20].

4. RESULTS AND DISCUSSION

Results obtained from all analyzed substrate point out differences in responses to the impact of gamma radiation.

4.1. Chemical studies

The effect of gamma radiation on COD and TSS values is different for the three kinds of wastewater. The COD and the TSS were measured in the irradiated and non irradiated wastewater after filtration with a 1.2 µm filter (*FIG. 1, FIG. 2*, and *FIG. 3*). The COD values are the average of 3 replicates ($\alpha = 0.05$).

As shown in *FIG. 1*, there is a decrease of the TSS values after irradiation. Contrarily, an increase of the COD values is presented. These phenomena could be explained due to the increase of species in the solution (decrease of Total Solids Suspended) that leads to a higher COD parameter at the same values of absorbed dose.

In the case of the dairy wastewater, the same phenomena are observed (*FIG. 2*), which also could be explained by the radiation-induced scissor effect that degraded the organic pollutants and the increase of chemical species soluble in the water.

However, the impact of gamma radiation on the slaughterhouse wastewater has a different effect on TSS and COD values. As shown in the *FIG. 3,* the TSS values decrease at 7 kGy and attain a plateau at higher absorbed doses. The COD values increase at 7 kGy and decrease at higher doses. The tendencies of TSS and COD parameters at 7 kGy could be explained once more by the gamma radiation scissor effects that increase the number of molecular low-weight substrates without solubilisation of organic matter. However, at higher absorbed doses, there is a decrease of the COD. This fact is likely related to the oxidation of macromolecules (e.g. hemoglobin) by the reactive species leading to a decrease of oxidizable organic matter. However, more analyses have to be conducted to better understand this behavior.

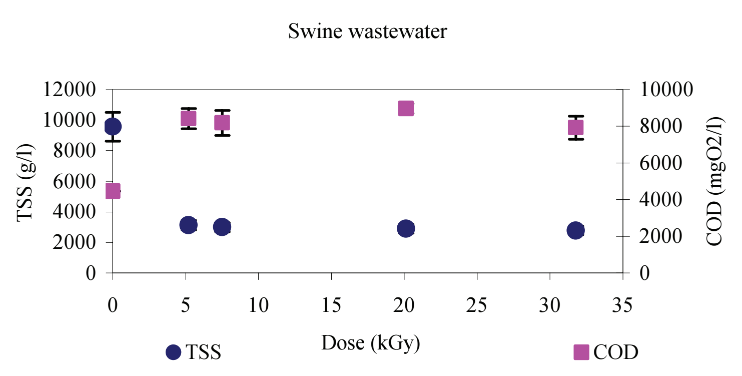


FIG. 1. COD (n=15; α=0.05) and TSS (n=5; standard error: 10%) versus absorbed dose (dose rate = 0.5 kGy/h).

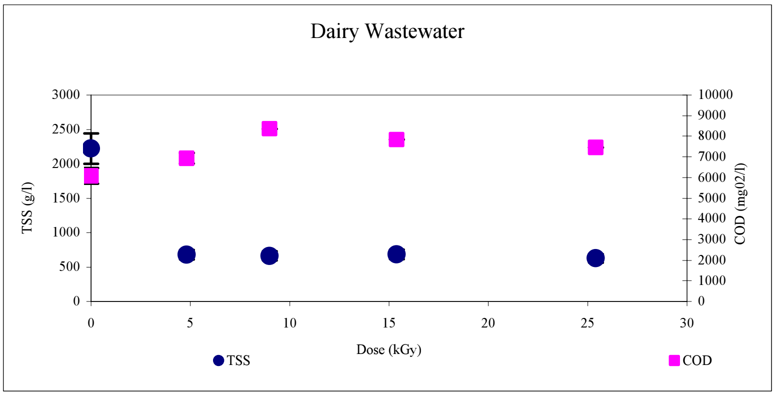


FIG. 2. COD (n=15; α=0.05) and TSS (n=5; standard error: 10%) versus absorbed dose(dose rate = 0.5 kGy/h).

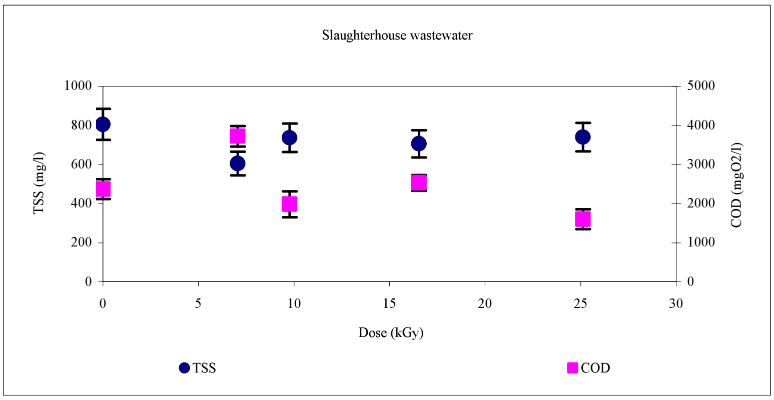


FIG. 3. COD (n=15; α=0.05) and TSS (n=5; standard error: 10%) versus absorbed dose (dose rate = 0.9 kGy/h).

The microbiological population and the chemical species are dynamically inter-dependent; thus, studies on wastewater treatment need multidisciplinary groups in order to fully understand them. In the following figures, the relation between the BOD values and the survival microorganisms (*FIG. 4, FIG. 5* and *FIG. 6*), is reported.

The reduction of BOD is related to the biodegradation of organic mater [21]. Therefore, the results point to a better water quality (the higher the dose absorbed, the lower the BOD value). As shown in *FIG. 4* there is a decrease of the BOD values and the number of the total microorganisms which means there is an increase of the water quality.

In swine wastewater BOD parameter shows the high level of the organic matter and is consistent with the results of COD (*FIG. 1*). The connection between microbiota and the parameter BOD could be explained by different hypotheses namely, by the microorganisms' radiosensitivity. Although the scissor effect was shown (higher values of BOD) microbiota data point out to an inability to use the by-products of the scissor effect.

However, in the slaughterhouse's wastewater, the BOD values increase at lower doses, which could be explained by the gamma radiation scissor effect, reported before for COD where as a consequence of the interaction with gamma radiation, the transformation of substrata into soluble small molecules better metabolized by microorganisms occurs (*FIG. 6*). Therefore, the nutrient assimilation is more easily and better done, which correlates with the increase of BOD at lower doses.

Nitrogen content is an indicator of water quality, as well as a measurement of the extent of water pollution. Thus, the macro-Kjeldhal method is applied to better understand the amounts of organic nitrogen and ammonia nitrogen in the swine and dairy wastewater (*FIG.7*).

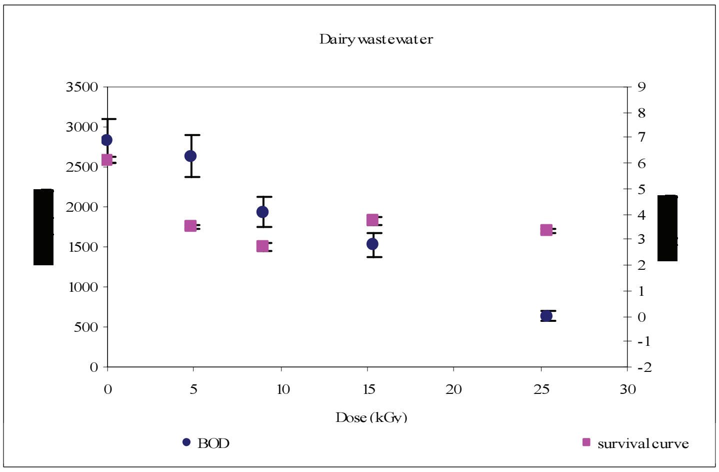


FIG. 4. BOD (n=5; standard error= 10%) and survival curve (3 ≤ n ≤ 9; α = 0.05) versus absorbed dose (dose rate = 0.5 kGy/h).

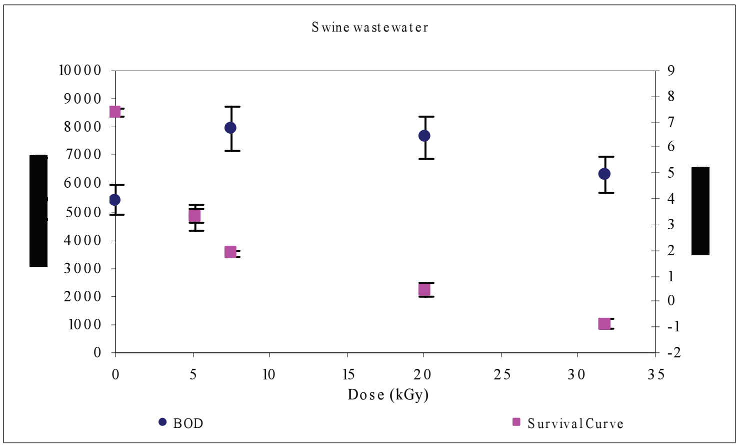


FIG. 5. BOD (n=5; standard error= 10%) and survival curve (3 ≤ n ≤ 9; α = 0.05) versus absorbed dose (dose rate =0.5 kGy).

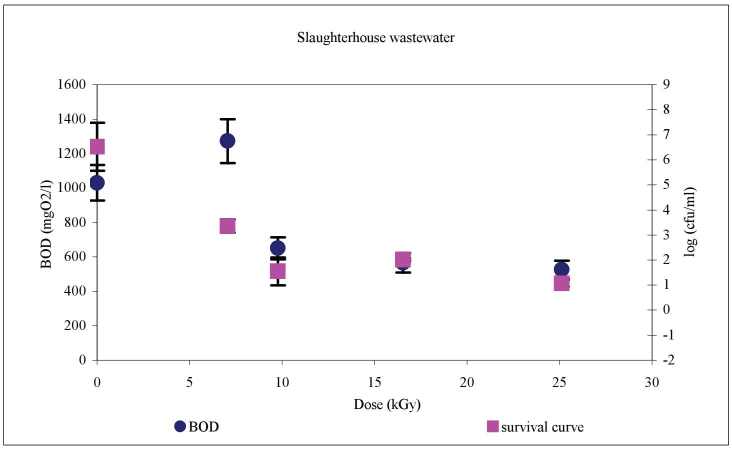


FIG. 6. BOD (n = 5; standard error = 10%) and survival curve (n = 27; α = 0.05) versus absorbed dose (dose rate = 0.9 kGy/h).

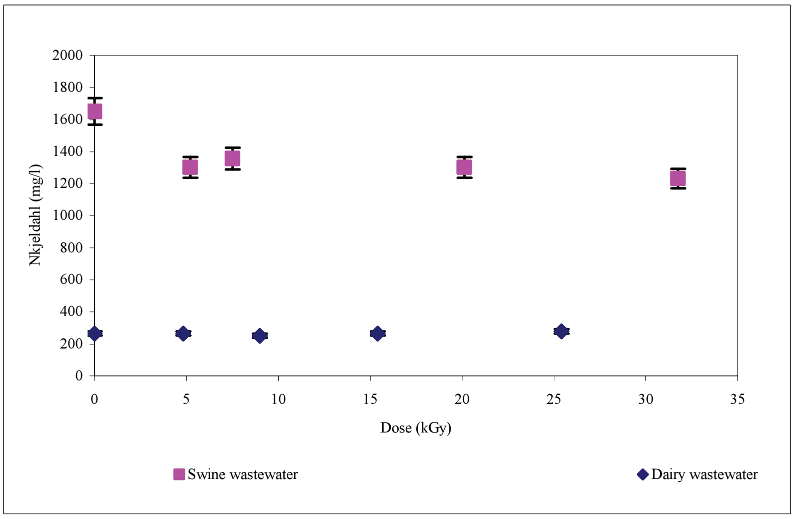


FIG. 7. $N_{Kjeldahl}$ (n=5; standard error 10%) versus absorbed dose (dose rate = 0.5 kGy/h) in swine and dairy wastewater samples.

As shown in *FIG. 7* the concentration of $N_{kjeldahl}$ in swine wastewater is higher than in dairy wastewater. The results can be related to the different kinds of substrata tested. The major swine wastewater constituents are urine, feces and feeds which are rich in nitrogen compounds such as ammonia. The source of nitrogen in the dairy wastes is mainly proteins, which are very difficult to digest. For the swine wastewater, the concentration of Kjeldahl nitrogen decreases at 5 kGy and attains a plateau at higher absorbed doses. The Kjeldahl method fails in not taking into account nitrogen in different forms, such as nitrate, nitrite and nitro. The results obtained could be related to a radiation-induced effect that could convert organic nitrogen in other compounds. *FIG. 7* also shows that there is no effect of the impact of ionising radiation on the $N_{kjeldahl}$ values for the dairy wastewater.

In *FIG. 8,* the concentrations of phosphorus obtained for the dairy and swine wastewater are presented by the ascorbic acid method.

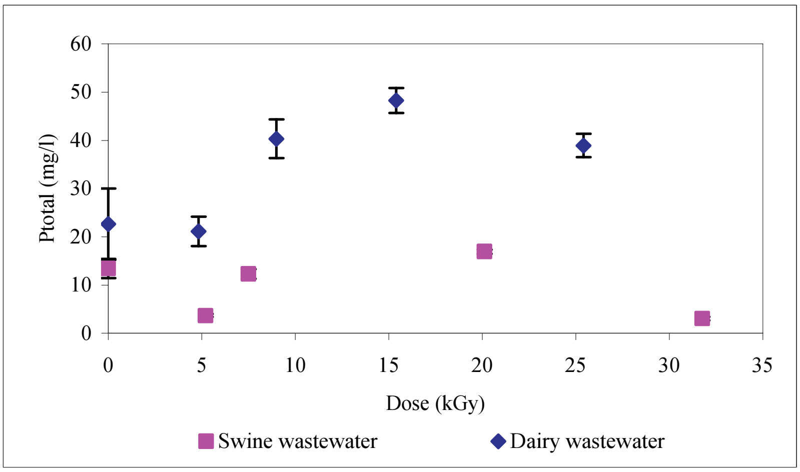


FIG. 8. P_{total} (n=5; $\alpha = 0.05$) versus absorbed dose (dose rate = 0.5 kGy/h).

The concentrations of phosphorus in the samples of swine vary significantly throughout the studied doses. For the two types of wastewater samples the same tendency of phosphorous concentration in the function of the absorbed dose was observed.

In dairy wastewater, the phosphorus source is the serum and milk from the production process, whereas in the swine manure, the origin is the rations and, consequently, the excrements of the pig. The increase of phosphorous concentration between 5 and 20 kGy may be due to the degradation of phospholipid content of wastewater samples. For the higher absorbed doses (>25 kGy) a decreasing trend was noticed. This could be explained by the precipitation of soluble phosphorous. This precipitation effect of elements by gamma radiation was previously suggested based on the results obtained by INAA analysis [22].

4.2. Ecotoxicological test

TABLE 1 summarizes the ecotoxicological results obtained for the irradiated and non-irradiated slaughterhouse wastewater, based on two biological assays performed with *Daphnia similis* and *Vibrio fisheri.*

TABLE 1. ECOTOXICOLOGICAL RESULTS FOR *V. fisheri* AND *D. similis* IN NONIRRADIATED AND IRRADIATED (DOSE RATE = 1.2 KGY/H) SLAUGHTERHOUSE WASTEWATER SAMPLES (N = 4 PER ABSORBED DOSE).

Dose (kGy)	EC-50 for Microtox (*V. fisheri*) (concentration%)	EC-50% (*D. similis*)
0	12,17 (8,52–17,39)	9,33(7,88–11,04)
7	13,04(8,34–20,38)	89,13 (85,31–93,12)
35	14,57 (4,80–44,19)	N.m.

N.m.-not measured (Microbics Corporation, 1994)

Accordingly, the non-irradiated wastewater sample presents a high level of toxicity. It is important to note that the lower the EC-50 is, the higher the toxicity. Moreover, the obtained results on the two biological assays were different. This fact could be connected to the nature of each organism used, one is a microcrustacean (*D. similis*) and the other is a bioluminescent bacterium (*V. fisheri*). Therefore, the sensibility to the toxic compounds is different, and *D. similis* could be more resistant because of its thick carapace. In general, the radiation was very effective for acute toxicity removal of the two biological systems considered in this study. The data suggested that the acute toxicity was reduced by 89% at 7 kGy.

4.3. Nutrients

There are a number of complex chemical reactions that occur in soils through the soil solution, the medium from which the nutrient plant uptake occurs. Soil solutions are composed of a variety of ion species often referred to as ion pairs, either complexed or noncomplexed. Therefore, the speciation of the soil, solution refers to determining the distribution of ions in their various chemical forms [23]. The concentration of a particular ion in the soil solution and the ability of solid components in soils to re-supply an ion that is depleted from the soil solution are both important properties of a given soil.

In this work, we have used ionic chromatography to access the impact of ionising radiation on soil solution components (ion composition). These analyses ($n = 3$; $\alpha = 0.05$) were performed in the solution of leached sludge from the slaughterhouse and in the solution phase from the swine manure after filtration, since these may be potential fertilizers (TABLE 2 and TABLE 3).

TABLE 2. SLAUGHTERHOUSE SLUDGE IONIC COMPOSITION BEFORE AND AFTER THE IMPACT OF IONISING RADIATION (0.9 KGY/H) AT DIFFERENT DOSES

		0	7	16	25
Anions (mg/L)	F^-	1.6 ± 0.2	2.1 ± 0.2	1.8 ± 0.2	1.6 ± 0.2
	Cl^-	36.4 ± 3.1	30.2 ± 2.8	27.5 ± 2.9	30.9 ± 3.0
	NO_3^-	0.2 ± 0.1	0.7 ± 0.2	n.d.	0.6 ± 0.2
	PO_4^{2-}	6.2 ± 0.8	11.8 ± 2.7	5.4 ± 0.9	4.9 ± 0.6
	SO_4^{2-}	95.5 ± 3.9	95.9 ± 3.9	102.7 ± 4.3	106.6 ± 4.5
Cations (mg/L)	Na^+	184.0 ± 26.7	382.3 ± 95.3	295.1 ± 73.5	258.9 ± 69.6
	NH_4^+	186.3 ± 57.6	182.4 ± 56.4	190.7 ± 59.1	195.6 ± 60.8
	K^+	14.4 ± 4.0	16.5 ± 9.5	12.5 ± 4.2	19.0 ± 9.3
	Mg^{2+}	4.2 ± 0.9	4.0 ± 0.5	5.5 ± 0.6	4.3 ± 0.6
	Ca^{2+}	44.5 ± 2.7	29.8 ± 3.4	38.4 ± 2.3	34.0 ± 2.7

n.d. not determined

TABLE 3. SWINE MANURE CATIONIC COMPOSITION BEFORE AND AFTER THE IMPACT OF IONISING RADIATION (0.9 KGY/H) AT DIFFERENT DOSES

		0	5	8	20	32
Cations (mg/L)	Na^+	31.1±5	28±5.3	26.8±5.4	31.7±4.9	36.4±4.7
	NH_4^+	48.8±5.7	43±54.	50.5±5.9	57.6±6.7	52.6±6.1
	K^+	40.1±4.3	39.6±4.3	38.3±4.3	436.±4.3	44.6±4.4
	Mg^{2+}	8.1±0.6	6.2±0.4	7.1±0.5	7.1±0.5	6.4±0.4
	Ca^{2+}	14.7±1.8	9.6±0.9	12.2±1.4	11.4±1.2	11.9±1.3

Table 2 shows that the major ion species in the sludge solution are Na^+, NH_4^+, Ca^{2+}, SO_4^{2-} and Cl^-. Other important species are K^+ and PO_4^{3-}. Therefore, the soil solution obtained from the sludge seems to be rich with major macronutrients, such as nitrogen and sulfate, either as ammonium sulfate $(NH_4)_2SO_4$ or sodium sulfate Na_2SO_4, whereas other important nutrients, such as calcium (CaCl) and phosphorus (K_3PO_4), are also present. Ammonium sulfate is one of the basic fertilizers used for agricultural purposes. It is very rich in calcium, and all the nitrogen is present in its nitric form. It is also important to stress the 7 kGy effect. At that dose, important fluctuations (decrease of chlorine, sulfate, calcium and ammonium; increase of sodium, potassium and phosphorus concentrations) of the ionic composition of the soil solution were observed and are currently under investigation, *e.g.* the correlation is between the sulfate decrease and its possible assimilation by plants and prokaryotes.

As shown in Table 3, the major cations in the swine manure solution are Na^+, NH_4^+ and K^+. At high absorbed doses, the concentration of nitrates increased which could be corroborated with the decrease of $N_{kjeldahl}$. Thus, the slaughterhouse sludge solution is richer in the major macronutrients than the swine manure solution. However, an anion analysis of the swine manure solution has to be conducted for better understanding of this behavior.

4.4. Inactivation studies

The effects of gamma radiation on natural microbiota wastewater samples were evaluated by means of a D value parameter and inactivation efficiency for each absorbed dose (Table 4). D value was determined based on the inverse of the slope, obtained by regression analysis of the logarithmic kinetic inactivation curve (n=15) [see *FIG 4*, *FIG 5* and *FIG. 6*].

TABLE 4. WASTEWATER'S MESOPHILIC MICROBIOTA D VALUE AND INACTIVATION EFFICIENCY TO GAMMA RADIATION AT SEVERAL DOSE RATES

					Gamma Radiation
	Sample	Dose rate (kGy/h)	Dose (kGy)	D value	Effic. (%)
Total microorganisms	Dairy Wastewater	0.5	4.82	2.7	99.76
			9.00		99.96
			15.39		99.59
			25.41		99.83
	Swine Wastewater		5.21	1.3	99.99
			7.50		>99.99
			20.13		>99.99
			31.76		>99.99
	Slaughterhouse Wastewater	3	7	2.2	99.99
		0.9	7	4.0	99.98

Microbiota from swine wastewater showed the highest sensitivity to ionising radiation in the studied circumstances. Dose rate influenced the response of microorganisms to the lethal agent as demonstrated in earlier studies [16]. However, the substrata and the type of contaminants (natural microbiota) are also determinants for the response to the lethal agent, as can be observed in D value data for microbiota of swine wastewater irradiated at a 0.5 kGy.h^{-1} dose rate.

It was noticed that the predominant bacteria that survived at higher irradiation doses were gram positive cocci for slaughterhouse samples, gram-negative cocci for dairy wastewater samples and gram negative rods for swine wastewater. The surviving microbial types are in agreement with the results obtained for D values, namely for the organisms referred [24] to as more sensitive to ionising radiation (e.g. gram negative rods).

4.5. Biodegradation studies

The biodegradation study was delineated in order to evaluate the hypothesis reported before: that a lower dose rate may lead to a better remediation process. A bacterium strain isolated from irradiated slaughterhouse wastewater samples (dose = 30 kGy; dose rate = 3 kGy/h) and identified by biochemical profiles (API system) as *Xantomonas maltophilia*, was inoculated in the original slaughterhouse effluent previously sterilized by two different treatments (gamma radiation *versus* heat-steam). Another similar experiment was performed with a strain (R30) isolated from anirradiated slaughterhouse primary effluent (dose = 30 kGy; dose rate = 0.3 kGy h^{-1}). The substrates used for this kinetic growth study were: 1) irradiated slaughterhouse effluent at 10 kGy; 2) non-irradiated slaughterhouse effluent; and 3) Tryptic Soy Broth, (TSB). For both studies, bacterial growth was followed by turbidity during incubation. The experimental results obtained reveal different rates in distinct growth phases (*FIG. 9*).

In both kinetic growth curves, the lag phase is shorter in irradiated wastewater than in the non-irradiated wastewater, indicating that the physiological adaptation to the irradiated substrate is faster. Furthermore, the exponential, or log phase, is longer in the irradiated samples than in the non-irradiated samples, demonstrating a higher rate of growth in the irradiated samples wastewater samples. The inoculated strain in the rich-nutrient medium TSB presented a typical growth curve, although it reached the stationary phase earlier with less bacterial biomass, compared with the growth presented in the irradiated effluent. These results are in conformity with the hypothesis that ionising radiation renders the nutrients more available for bacterial growth, speeding up, natural degradation and remediation processes.

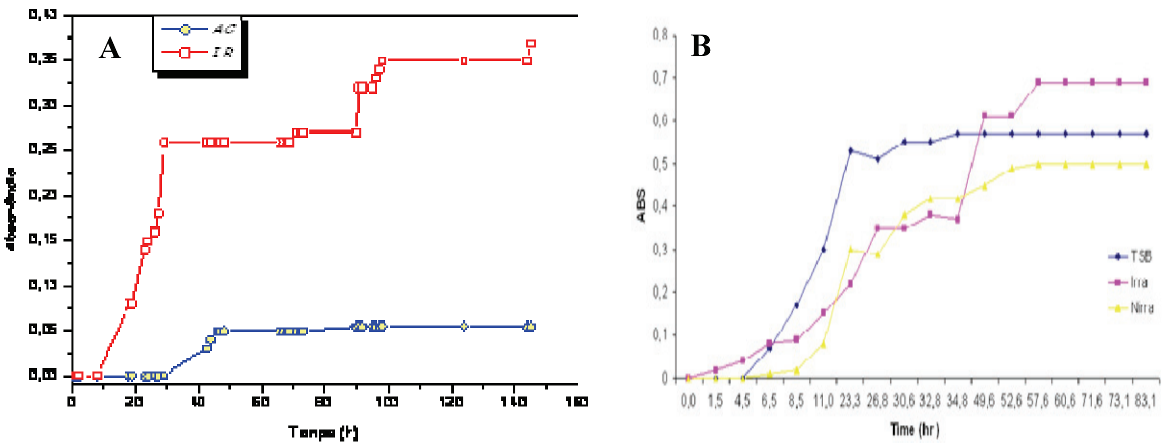


FIG. 9. Growth curve (absorvance at 460 nm in function of incubation time) of: (A) Xantomonas maltophilia in slaughterhouse wastewater sterilized by two distinct methods: Ionising radiation (IR; 30 kGy at 3 kGy/h) and Steam (AC; 121°C during 30 minutes); (B) R30 strain in nutrient rich medium TSB, irradiated slaughterhouse primary effluent (Irra.; 10 kGy at 9 kGy/h) and non-irradiated slaughterhouse primary effluent (Nirra; 0.2 µm membrane filtration).

4.6. Molecular biology studies

A dendrogram was built (*FIG. 10*), by analyzing the overall fingerprinting results generated by computer software,

The dendrogram shows a similarity above 90% between the isolates W0B and W0T, regardless of the radiation dose, indicating that they could be the same species. If there were mutations or alteration between these isolates these methods did not detect them.

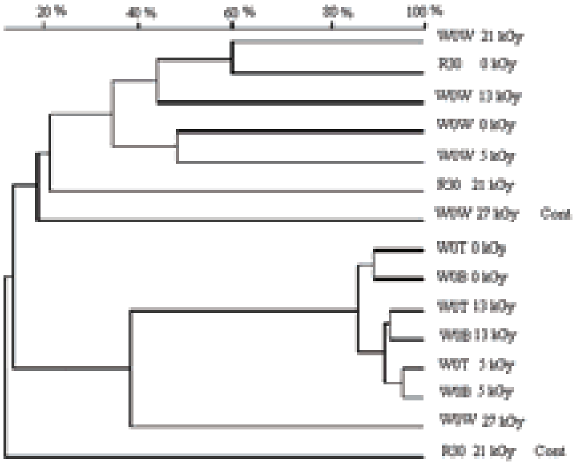


FIG.10. Dendrogram built based on the fingerprints obtained for the techniques used. Pearson correlation [0.0%–100%]. The strains are identified as W0W, W0B and R30 and with the irradiation dose submitted. The strains identified with 'Cont' are suspected contaminations. The upper horizontal bar of the dendrogram indicates the per cent similarity coefficient within strains.

These fingerprinting techniques showed that the W0W – 0 kGy and R30 – 0 kGy isolates may represent genetically distinct species. However, the W0W isolate irradiated at 21 kGy showed a higher similarity (approximately 60%) with the isolate R30 – 0 kGy. W0B and W0T isolates most likely represent the same species because these isolates were 90% similar to each other. This relation could be explained by the fact that the strain R30 – 0 kGy was selected from wastewater samples already irradiated at approximately 30 kGy. This means that the strain (R30 – 0 kGy) could have already suffered genomic alterations induced by gamma radiation under the first irradiation procedure. Since the W0W 21 kGy was also submitted to a similar dose, the genomic alterations induced could be similar to the ones that occurred with the R30 strain. This could indicate that if both strains would not be submitted to stress (gamma radiation), they could have been more closely related to each other.

5. CONCLUSIONS

Based on these results, it is predicted that combining ionising radiation with a conventional treatment process could lead to better results in treating the agro-industry wastewater. Results showed that lower dose rates can lead to better bioremediation processes in wastewater substrates due to the irradiation effect on its degradation. This would make molecular forms easier to be metabolized by bacteria, consequently diminishing the wastewater; chemical pollution and possibly the residence time spent in the lagoons. High dose rates showed to be more efficient for disinfection processes and could be applied in the tertiary treatment.

In summary, the achieved results showed that gamma radiation could be used in two ways for wastewater treatment:

1) Lower dose rates to help bioremediation, leading to faster treatment in the lagoons.
2) Higher dose rates for disinfection during the tertiary phase.

Under the Projects CRP 12017 and TC POR/8/010, sponsored by IAEA, there were several goals to be attained. Table 5 points out the goals reached and the goals to attain.

Further studies, intended to simulate an on line agricultural wastewater treatment, using ionising radiation at a lab scale are necessary. These will help to understand the radiation effects on the different kinds of wastewater, namely with the help of on-line studies that will allow to get an overall picture of the integrated wastewater treatment. Therefore, a dynamic process is planned that permits us to be a step ahead in getting a range of physical parameters connected with the biological and chemical responses desirable for a technical and economical benefit.

TABLE 5. PROPOSED OUTPUTS VERSUS ATTAINED GOALS

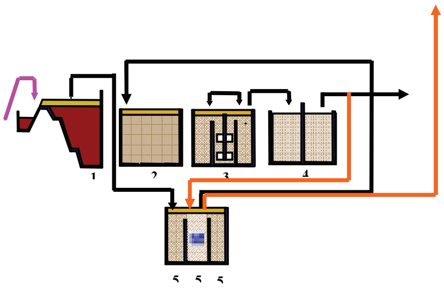
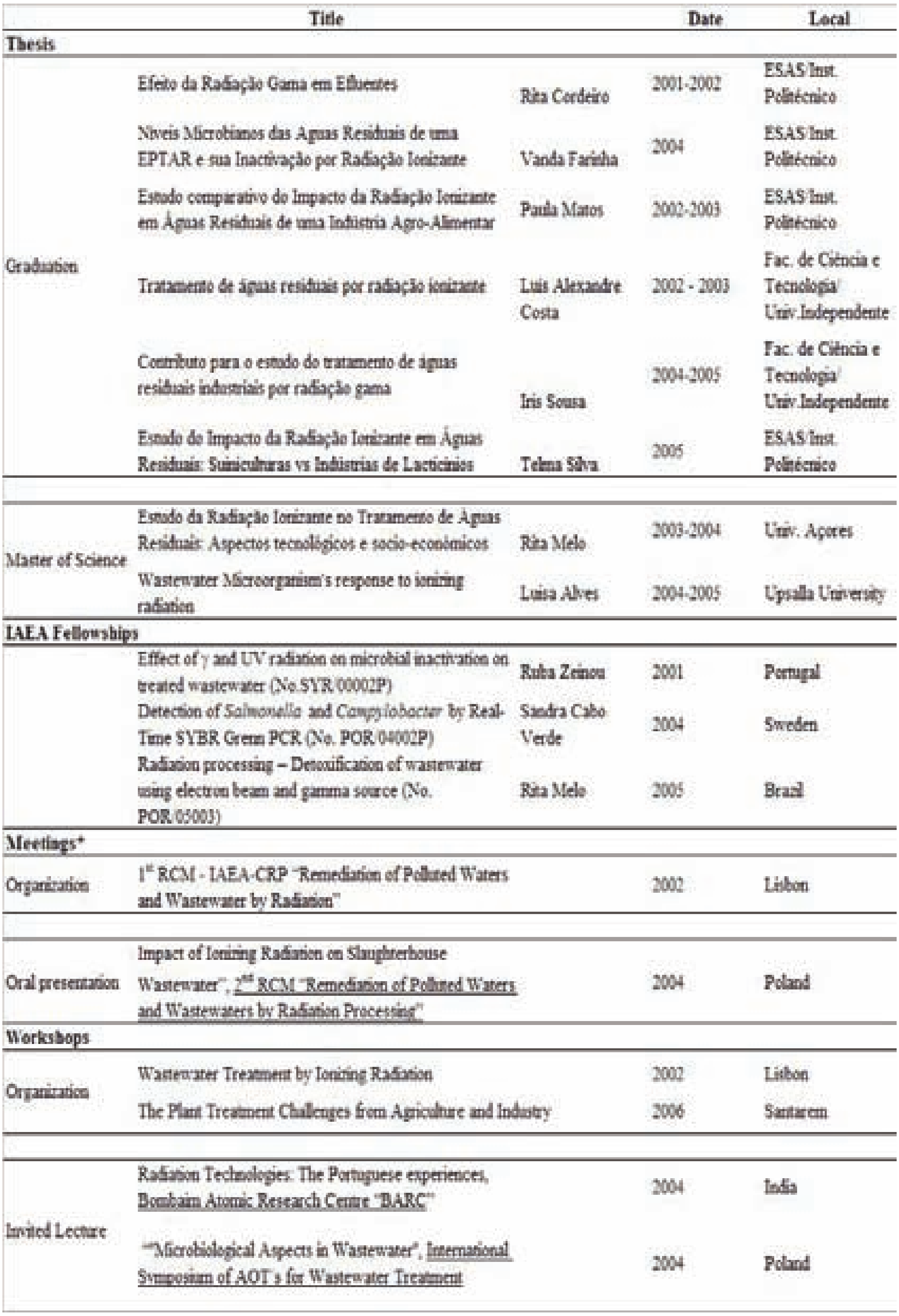
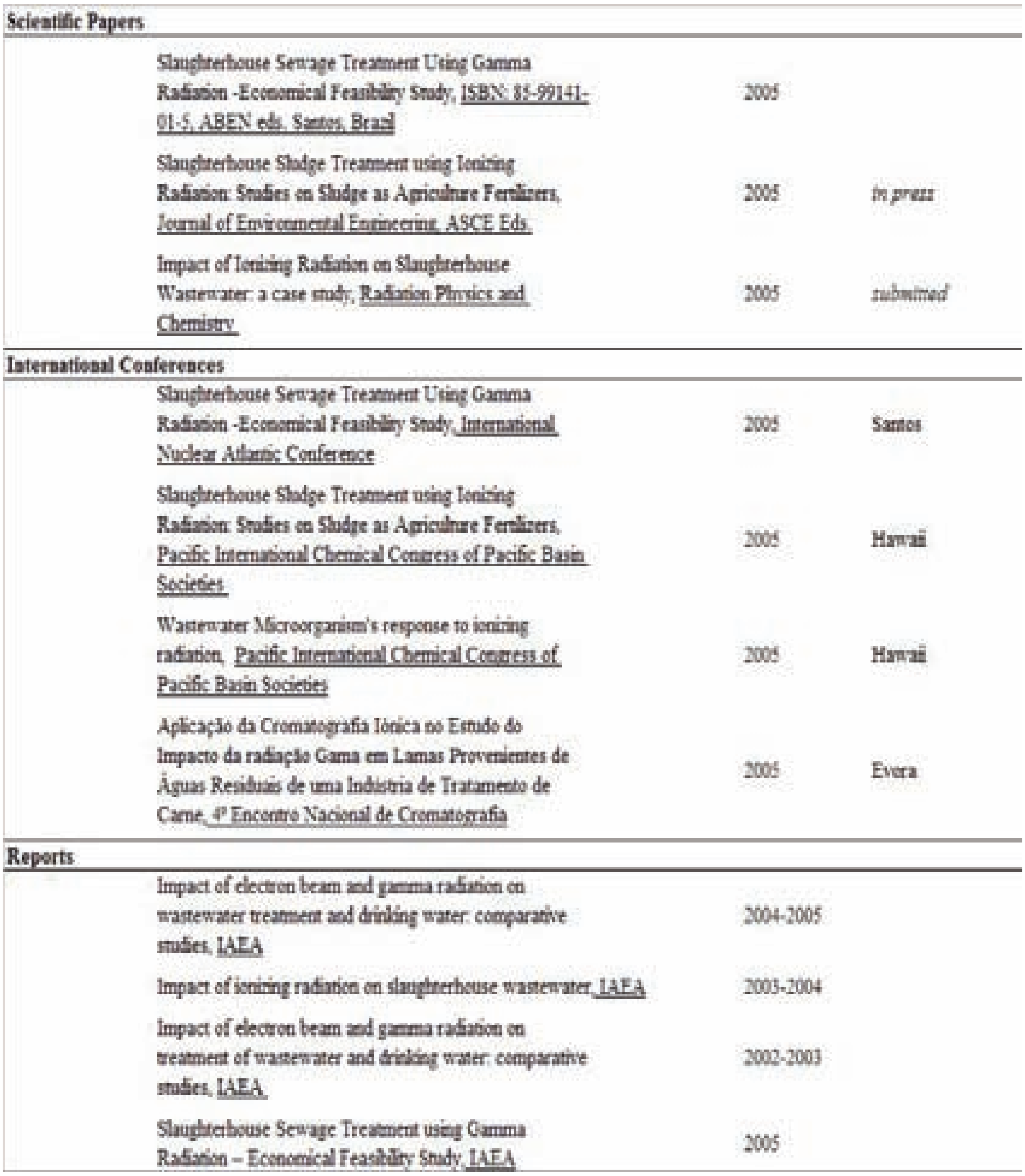
Proposed outputs	Attained
Selection of the target	In-house Industry: agro-industrial
Selection of the most suitable procedure	gamma radiation
Selection of the most adequate radiation geometry and system Plant	
Optimization of design	
Preliminary feasibility studies	
Design and construction of a model plant with radiation technology	Project to be proposed Agro Industry *in house*
Validation of microbiology, chemistry and toxicology techniques	Implemented

TABLE 6. EVENTS UNDER THE CRP AND TC ‘WASTEWATER TREATMENT USING IONISING RADIATION’ THEME (2001–2006)



	Title		Date	Local
Thesis				
Graduation	Efeito da Radiação Gama em Efluentes	Rita Cordeiro	2001-2002	ESAS/Inst. Politécnico
	Niveis Microbianos das Aguas Residuais de uma EPTAR e sua Inactivação por Radiação Ionizante	Vanda Farinha	2004	ESAS/Inst. Politécnico
	Estudo comparativo do Impacto da Radiação Ionizante em Águas Residuais de uma Indistria Agro-Alimentar	Paula Matos	2002-2003	ESAS/Inst. Politécnico
	Tratamento de águas residuais por radiação ionizante	Luis Alexandre Costa	2002 - 2003	Fac. de Ciência e Tecnologia/ Univ.Independente
	Contributo para o estudo do tratamento de águas residuais industriais por radiação gama	Iris Sousa	2004-2005	Fac. de Ciência e Tecnologia/ Univ.Independente
	Estudo do Impacto da Radiação Ionizante em Águas Residuais: Suinículturas vs Indistrias de Lacticinios	Telma Silva	2005	ESAS/Inst. Politécnico
Master of Science	Estudo da Radiação Ionizante no Tratamento de Águas Residuais: Aspectos tecnológicos e socio-económicos	Rita Melo	2003-2004	Univ. Açores
	Wastewater Microorganism's response to ionizing radiation	Luisa Alves	2004-2005	Upsalla University
IAEA Fellowships				
	Effect of γ and UV radiation on microbial inactivation on treated wastewater (No.SYR/00002P)	Ruba Zeinou	2001	Portugal
	Detection of *Salmonalla* and *Campylobacter* by Real-Time SYBR Green PCR (No. POR/04002P)	Sandra Cabo Verde	2004	Sweden
	Radiation processing – Detoxification of wastewater using electron beam and gamma source (No. POR/05003)	Rita Melo	2005	Brazil
Meetings*				
Organization	1st RCM - IAEA-CRP "Remediation of Polluted Waters and Wastewater by Radiation"		2002	Lisbon
Oral presentation	Impact of Ionizing Radiation on Slaughterhouse Wastewater", 2nd RCM "Remediation of Polluted Waters and Wastewaters by Radiation Processing"		2004	Poland
Workshops				
Organization	Wastewater Treatment by Ionizing Radiation		2002	Lisbon
	The Plant Treatment Challenges from Agriculture and Industry		2006	Santarem
Invited Lecture	Radiation Technologies: The Portuguese experiences, Bombaim Atomic Research Centre "BARC"		2004	India
	""Microbiological Aspects in Wastewater", International Symposium of AOT's for Wastewater Treatment		2004	Poland



Scientific Papers			
	Slaughterhouse Sewage Treatment Using Gamma Radiation -Economical Feasibility Study, ISBN: 85-99141-01-5, ABEN eds. Santos, Brazil	2005	
	Slaughterhouse Sludge Treatment using Ionizing Radiation: Studies on Sludge as Agriculture Fertilizers, Journal of Environmental Engineering, ASCE Eds.	2005	*in press*
	Impact of Ionizing Radiation on Slaughterhouse Wastewater: a case study, Radiation Physics and Chemistry	2005	*submitted*
International Conferences			
	Slaughterhouse Sewage Treatment Using Gamma Radiation -Economical Feasibility Study, International Nuclear Atlantic Conference	2005	Santos
	Slaughterhouse Sludge Treatment using Ionizing Radiation: Studies on Sludge as Agriculture Fertilizers, Pacific International Chemical Congress of Pacific Basin Societies	2005	Hawaii
	Wastewater Microorganism's response to ionizing radiation, Pacific International Chemical Congress of Pacific Basin Societies	2005	Hawaii
	Aplicação da Cromatografia Iónica no Estudo do Impacto da radiação Gama em Lamas Provenientes de Águas Residuais de uma Industria de Tratamento de Carne, 4º Encontro Nacional de Cromatografia	2005	Evora
Reports			
	Impact of electron beam and gamma radiation on wastewater treatment and drinking water: comparative studies, IAEA	2004-2005	
	Impact of ionizing radiation on slaughterhouse wastewater, IAEA	2003-2004	
	Impact of electron beam and gamma radiation on treatment of wastewater and drinking water: comparative studies, IAEA	2002-2003	
	Slaughterhouse Sewage Treatment using Gamma Radiation – Economical Feasibility Study, IAEA	2005	

ACKNOWLEDGEMENTS

We are grateful to the International Atomic Energy Agency (IAEA, Austria) by the supporting of the TC POR/8/010, 'Implementation of wastewater treatment by radiation in Portugal' and the CRP 302-F2-POR-12017, 'Impact of electron beam and gamma radiation in wastewater treatment: comparative studies' projects.

We are also grateful to the slaughterhouse (Centro de Abate de Suínos do Oeste), to the swine industry (Sociedade Agro-Pecuária do Mogo), and to the dairy industry (J.D. Lacticinios, Lda.) for allowing us to collect all the samples necessary for the accomplishment of this work. This work was supported by grants from the Institute of Nuclear Technology (ITN), Ministry of Science and Education, Portugal.

REFERENCES

[1] HAN, B., KIM, D.K., BOO, J.Y., KIM, J.K., KIM, Y., CHUNG, W., “Application of Electron Beam to Industrial Wastewater Treatment”, IAEA-TECDOC-1225 “Use of irradiation for chemical and microbial decontamination of water, wastewater and sludge” — Final report of a co-ordinated research project 1995–1999. 57–63. IAEA Editions. Vienna. Austria (2001).

[2] FAROOQ, S., KURUCZ, C.N., WAITE, T.D., COOPER, W.J., MANE, S.R., GREEN.ELD, J.H., “Treatment of wastewater with high energy electron beam irradiation” Water Sci. Tech, 26, (1992) 1265–1274.

[3] GETOFF, N., “Radiation-induced degradation of water pollutants-state of the art”, Radiat. Phys. Chem, 4, (1996) 581–593.

[4] AMRO, H., TUFFAHA, R., ZENATI, S., MASAADEH, M., JNEIDI, M., “Remediation of polluted Waters by Irradiation in Jordan”, Paper presented at the IAEA, on the 2nd Research Coordination Meeting (RCM) on “Remediation of polluted Waters and Watewater by Radiation Processing”, Warsaw, Poland, (14–18 June 2004) IAEA Editions, Vienna, Austria.

[5] International Atomic Energy Agency (IAEA), Report of the 1st Research Coordination Meeting (RCM) on “Remediation of polluted Waters and Watewater by Radiation Processing”, Lisbon, Portugal, 15–18 october, IAEA Editions, Vienna, Austria, (2002).

[6] KASHMANIAN, R.M., “Building support for composting in agriculture”, Biocycle, 35 (12), (1994) 67–70.

[7] BURTON, C.H., TURNER, C., “Manure Management: treatment strategies for sustainable agriculture”, 2nd Edition, Bedford, United Kingdom (2003).

[8] CRONK, J.K., “Constructed wetlands to treat wastewater from dairy and swine operations: a review”, Agriculture, Ecosystems and Environment, 58 (1996) 97–114.

[9] WOODBRIDGE, D.D., COOPER, P.C., “Synergistic effects for irradiation of fecal coliforms”, J. Water Pollut, Control Fed, 51 (1979) 2717–2723.

[10] BOTELHO, M.L., MELO, R.J., BRANCO, V., FARINHA, I., SOUSA, “Impacto f ionizing radiation on slaughterhouse wastewater: a study case”, Paper presented at the IAEA, on the 2nd Research Coordination Meeting (RCM) on “Remediation of polluted Waters and Watewater by Radiation Processing”, Warsaw, Poland, (14–18 June 2004) IAEA Editions, Vienna, Austria.

[11] BOTELHO, M.L., “Microbiological Aspects in Wastewater”, Proceeding paper presented on International Symposium of AOP’s for Wastewater Treatment (18 June 2004), Warsaw, Poland.

[12] SANTOS, A. D., “Estudo das Possibilidades de Reciclagem dos Resíduos de Tratamento de Esgoto da Região Metropolitana de São Paulo”, São Paulo, Escola Politécnica da Universidade de São Paulo (2003).

[13] MELO, R., “Estudo da Radiação Ionizante no Tratamento de Águas Residuais: aspectos tecnológicos e socio-económicos”, Master of Science thesis, Universidade dos Açores, (2005)

[14] International Atomic Energy Agency, "Manual of Food Irradiation Dosimetry", TRS 178, IAEA, Vienna, (1977).

[15] MCLAUGHLIN, W.L., BOYD, A.W., CHADWICK, K.H., MACDONALD, J.C., MILLER, A., “Dosimetry for radiation processing”, Taylor and Francis. Formby, Great Britain, (1989).

[16] CLESCERI, LENORE, S., EATON, ANDREW, D., GREENBERG, ARNOLD, E., “Standard Methods for the Examination of Water and Wastewater”, 20th edition. American Public Health Association (APHT), Washington, (1998).

[17] HOLT, J.G., KREIG, N.R., SNEATH, P.H.A, STALEY, J.T., WILLIAMS, S.T., “Bergey’s Manual of Determinative Bacteriology”, 9th Edition, Williams and Wilkins Editors, Baltimore. USA, (1994).

[18] SOUSA, I., “Contributo para o estudo do tratamento de águas residuais industriais por radiação gama”, Universidade Independente, Lisboa, (2005).

[19] ALVES, L., CABO VERDE, S., BOTELHO, M.L., “Microorganisms’ response to ionizing radiation”, Proceedings in The Chemical Congress of the Pacific Basin Societies — PACIFICHEM; Symposium on Clean and Green Technologies for a Sustainable Environment, December 15–20, Honolulu, Hawaii, (2005).

[20] HAMILTON, M.A., RUSSO, R.C., THURSTON, R.V., “Trimmed Spearman Karber Method for estimating median lethal concentrations in toxicity bioassays”, Environmental Science and Technology, 11 (1977) 714–719.

[21] WANG, T., WAITE, T.D., KURUCZ, C., COOPER, W.J., “Oxidant reduction and biodegradability improvement of paper mill effluent by irradiation”, Wat. Ref. 28 (1994) 237–241.
[22] MATOS, P., “Estudo comparativo do Impacto da radiacao ionizante em aguas residuais de uma indústria agro-alimentar”, Escola Superior Agrária de Santarém, Graduation thesis, (2003).
[23] SPARKS, D.L., “Environmental Soil Chemistry”, Academic Pr , United States, (1995).
[24] BLOCK, S.S., “Disinfection, Sterilization and Preservation”, Lea & Febiger, Philadelphia, Third Edition (1983) 27–33.

DECOLORATION AND DEGRADATION OF SOME TEXTILE DYES BY GAMMA-IRRADIATION

D. Şolpan

Hacettepe University, Department of Chemistry,
Ankara, Turkey

Abstract

In this study, the possibility of using gamma rays to degrade or decolorize reactive dyes in water was investigated. Two different reactive dyes (Reactive Blue 15 and Reactive Black 5) in aqueous solutions were irradiated with doses 0.1 kGy to 15 kGy at 2.87 kGy/h and 0.14 kGy/h dose rates. The change of absorption spectra, pH, chemical oxygen demand (COD), and the degree of decoloration (per cent reduction in optical density) were examined in the presence of air and H_2O_2. The absorption bands at 664, 640, 340, 260 nm and 596, 392, 312nm for RB15 and RB5 were decreased rapidly with an increasing irradiation dose. The degree of decoloration of each dye solution with an irradiation dose was estimated at 100 per cent for the lower concentration (50ppm) dye solutions. The complete decoloration was observed after 1 and 15 kGy doses for RB5 and RB15, respectively. The pH of RB5 and RB15 solutions was decreased from 6.15 and 6.98 to 3.40 and 3.68 with the irradiation dose. The COD reduction for all the dye solutions was approximately 76–80% at 1 kGy and 15 kGy for RB5 and RB15. The COD reduction and the change of pH for all the dye solutions was examined similaraly to each other. The effect of pH, N_2, and N_2O on the degradation and decoloration process was studied. The degradation and decoloration in the presence of nitrous oxide occured faster than in air and nitrogen-saturated solutions. The degree of decoloration for RB5 increased with the increasing irradiation dose and dose rate. Above 2 kGy/h dose rate, the degree of decoloration is independent of the dose rate and irradiation dose. The degree of decoloration increased to 100% for the nitrous oxide-saturated RB5 solution from 80% for the nitrogen-saturated RB5 solution at 0.8 kGy irradiation dose and at 2 kGy/h dose rate. Although the absorptions at maximum wavelength (596 nm) decreased with increasing irradiation dose for nitrogen-saturated RB5 aqueous solutions, for nitrous oxide-saturated RB5 aqueous solutions they decreased and shifted to lower wavelength. This suggests that the skeleton of the RB5 molecule is mainly destroyed by the attack of the OH radicals. AR and RB5 dyes are destroyed in the pH range from 7 to 4 with a reduced sensitivity at a lower and higher pH range. In the second dye group, Apollofix-type dyes were choosen. Two different Apollofix dyes, Apollofix Red (AR) and Apollofix Yellow (AY), in aqueous solutions, were irradiated in air with doses of 1.0 kGy to 8.0 kGy at 0.14 kGy/h dose rate. The change in absorption spectra, pH, chemical oxygen demand (COD), and the degree of decoloration (per cent reduction in optical density) were examined in the presence and absence of H_2O_2. The absorption bands at 534 nm and 420 nm for AR and AY were observed to decrease rapidly with an increasing irradiation dose. The degree of decoloration of each dye solution with an irradiation dose was estimated of 100 per cent for the lower concentration (50ppm) dye solutions. The complete decoloration was observed after 3.0 kGy and 1.0 kGy doses for AR and AY, respectively. The COD and BOD reduction and the change of pH for all dye solutions on irradiation showed similar behavior.

1. INTRODUCTION

Since Turkey is one of the largest textile exporters, it is one of the major waste contributors that have a serious impact on the environment. Wastewater released by those industries contains toxic refractory dye at a high concentration. Disposal of effluent from textile industries has become a serious environmental concern in many countries. Most of the dyes used in the textile industry are nonbiodegradable. Therefore, effective treatment of dye waste effluent has not been achieved by ordinary processes [1, 2, 3, 4]. Earlier studies have shown that most colored materials undergo bleaching or color changes when exposed to ionizing radiation. Ionizing radiation may be promising for the treatment of textile dye waste effluents because the effect of radiation can be intensified in aqueous solution, in which the dye molecules are degraded effectively by the primary products formed from the radiolysis of water [5].

Textile dyeing wastewater is one of the major environmental problems in Turkey, much like the pollution caused by textile wastewater is a common problem faced by many countries. These types of wastewaters are generally high in biological oxygen demand (BOD), chemical oxygen demand (COD), total solids, and are strongly colored. Neither simple chemical nor simple biological treatment has proven to be adequate in removing the color and organic matter. It has been well known that dyes are not readily biodegradable and make little contribution to BOD [6]. The toxicity and mass production of dyes led to the necessity of developing new techniques. The major difficulty in treating textile wastewater containing dyes is the ineffectiveness of biological processes [7]. While physical processess, such as coagulation and adsorption, merely transfer the pollutants from wastewater to other media and cause secondary pollution, ionizing radiation proved to be more effective for the treatment of these wastewaters than conventional methods. The effect of radiation can be intensified in an aqueous solution in which the dye molecules are degraded effectively by primary products formed from the radiolysis of water. It was found that the decomposition of nonbiodegradable organic compounds can be enhanced by the addition of H_2O_2 or ozone when reactions are carried out under conditions of simultaneous application with radiation [8, 9, 10, 11]. The irradiation dose necessary for the complete decomposition of a dye depends principally on its molecular structure and reactivity towards the primary water radiolysis products, the presence of oxygen or oxidizing agents, temperature and pH, and concentration of the solution.

2. OBJECTIVE OF THE RESEARCH

The aim of this study was to explore using gamma rays for degrading or decolorizing reactive dyes in the presence and absence of H_2O_2 in water. Two different reactive dyes in aqueous solutions were irradiated with doses of 0.1 kGy to 15 kGy at 2.87 kGy/h and 0.14 kGy/h dose rates. The change of absorption spectra, pH, chemical oxygen demand (COD), and the degree of decoloration (per cent reduction in optical density) were examined as a function of irradiation dose, dose rate, and dye concentration. Synergetic effects resulting from adding additives such as oxygen and hydrogen peroxide on the degradation process were investigated.

Apollofix dyes are one of the most important classes of synthetic organic dyes in the textile industry, especially among common industrial pollutants in Turkey. Our present study provides results describing the decoloration and degradation of Apollofix Red and Apollofix Yellow, as well as commercial reactive dyes used in textile dyeing γ irradiated in the presence and absence of H_2O_2 up to 8 kGy dose.

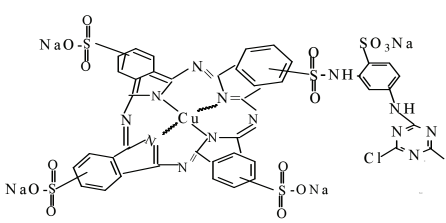
3. MATERIALS AND METHODS

3.1. Materials

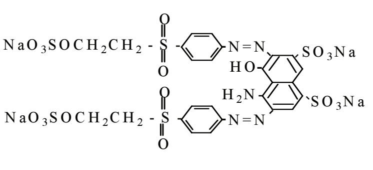
Commercial textile dyes manufactured in Germany were obtained from three major textile industries in Turkey. For this particular study, two reactive dyes: (Chrozol turquose Blue G) (Reactive Blue 15) RB15 and (Chrozol Black 5) (Reactive Black 5) RB5 were used without any further treatment. Deionized distilled water was used in the preparation of dye solutions without any contaminants.

Dyes:

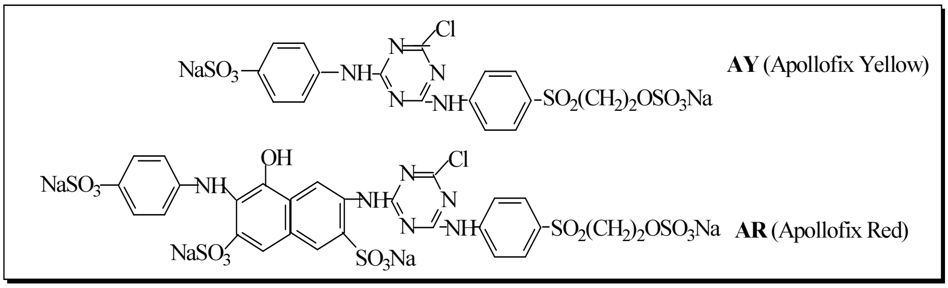
a)(Reactive Blue 15)
(Chrozol turquose blue G) **RB15**



b)(Reactive black5)
(Chrozol black5)**RB5**



Apollofix Red (AR) and Apollofix Yellow (AY) dyes used in this study are of commercial grades used directly in the textile industry in Turkey. The chemical structure of the two dyes is as follows: Deionized water was used in all preparations. All other reagents used in COD and BOD measurements were of analytical grade.



3.2. Apparatus and methods

Deionized water was used to prepare four concentrations 50, 75, 100, 150 ppm for two reactive dyes. Before and after irradiation, the pH of the solutions was measured by a JENWAY 3010 model pH meter. The UV-absorbances at the wavelength of maximum absorbance of the irradiated and unirradiated solutions were measured by a Philips PU 8715 model UV-vis spectrophotometer. Irradiation was done at doses of 0.1 kGy to 15 kGy at 2.87 kGy/h and 0.14 kGy/h dose rates. In the present work, an oxidizing and decolorizing agent was used to minimize the consumption of gamma irradiation doses. Hydrogen peroxide, as an oxidizing agent coupled with gamma irradiation, was added to the dye solutions to study the synergistic effect on the degradation of the two reactive dyes. Chemical oxygen demand was determined by using the chromic method [12]. The degree of decoloration was estimated from the reduction in optical density.

Deionized water was used to prepare a concentration range (0.050–0.200 g/L) of the two reactive dyes. The Philips 8510 model UV-vis spectrophotometer at ambient temperature was used to measure absorption spectra of the irradiated and unirradiated dye solutions. The degree of decoloration was estimated from the reduction in optical density. Before and after irradiation, the pH of the solutions was measured by a JENWAY 3010 model pH meter. Irradiations were carried out with gamma rays in an irradiation dose range (1.0–8.0 kGy) in the ^{60}Co gamma chamber using pyrex tubes in air at a dose rate of 0.14 kGy/h. Hydrogen peroxide as an oxidizing agent was added to dye solutions to obtain a synergistic effect on the degradation of the two reactive dyes. COD was determined by using the chromic method [13]. BOD_5 was measured by an Oxitop100 model BOD device [14].

4. RESULTS AND DISCUSSION

4.1. Changes of absorption spectra

The absorption spectra of the unirradiated and irradiated aqueous (Reactive Blue 15) RB15 solutions at 50ppm concentration in the absence and presence of 1.2 mM H_2O_2 concentration at 2.87 kGy/h dose rate are shown in Figures 1 and 2. RB15 showed strong absorption at 664, 640, 340, and 260 nm. The absorption bands at 664, 640, 340 and 260 nm decreased with an increasing irradiation dose and disappeared almost completely at 15 kGy (Figure 1, curve 6). The absorption band at 340 nm decreased less rapidly with increasing doses rather than those at 664 and 640 nm. These absorption spectra were similar to those for aqueous RB15 solution at 50ppm concentration in 1.2 mM H_2O_2 concentration (Figure 2). There is no absorption band at 260 nm in the presence of 1.2 mM H_2O_2 concentration. The absorption bands at 664, 640, and 340 nm decreased with the increasing irradiation dose, but the required irradiation dose to make these absorption bands disappear completely was 9.0 kGy (Figure 2, curve 7). The absorption band at 260 nm was attributed to azo groups and their auxochromic substituents. The observed changes in the absorption spectra with irradiation dose would suggest destruction of only the chromophoric groups with little or no effect on the substituted aromatic rings in the dye molecules [15]. The absorption spectra of the unirradiated and irradiated 50ppm RB5 solutions in the absence and presence of 1.2 mM H_2O_2 at 2.87 kGy/h dose rate are shown in Figures 3 and 4. While the absorption bands at 596, 392, 312 nm decreased with an increasing dose and disappeared completely at 3.0 kGy in the absence of H_2O_2. The required irradiation dose to make these absorption bands disappear was 1.0 kGy in 1.2 mM H_2O_2 concentration.

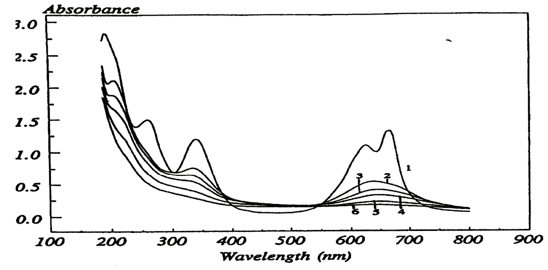


FIG. 1. *Absorption spectra of unirradiated and irradiated RB15 aqueous solutions. Dye concentration: 50 ppm, Dose rate: 2.87 kGy/h, Dose (kGy): 0 (curve 1), 2 (Curve 2), 4 (curve 3), 6 (Curve 4), 10 (Curve 5), 15 (Curve 6).*

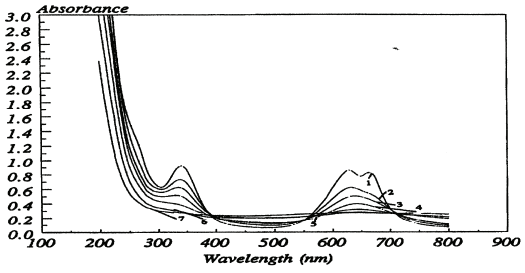


FIG. 2. *Absorption spectra of unirradiated and irradiated RB15 aqueous solutions. Dye concentration: 50 ppm, [H_2O_2]=1.2 mM, Dose rate:2.87 kGy/h, Dose (kGy): 0 (curve 1), 1 (Curve 2), 2 (curve 3), 3 (Curve 4), 5(Curve 5), 7 (Curve 6), 9 (Curve 7).*

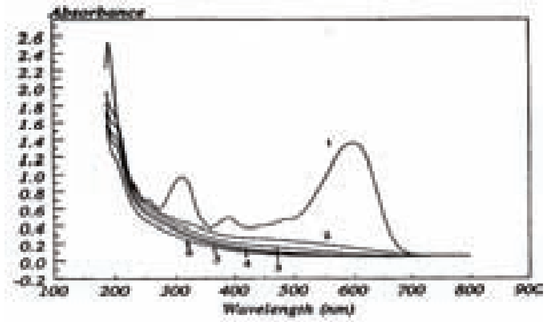


FIG. 3. *Absorption spectra of unirradiated and irradiated RB5 aqueous solutions. Dye concentration: 50 ppm, Dose rate: 2.87 kGy/h, Dose (kGy): 0 (curve 1), 1(Curve 2), 2 (curve 3), 3 (Curve 4), 4 (Curve 5), 5 (Curve 6).*

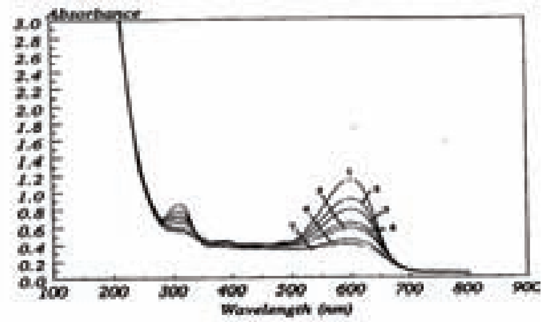


FIG. 4. *Absorption spectra of unirradiated and irradiated RB5 aqueous solutions. Dye concentration: 50 ppm, [H_2O_2]=1.2 mM, Dose rate:2.87 kGy/h, Dose (kGy): 0 (curve 1), 0.4 (Curve 5), 0.5 (Curve 6), 0.6 (Curve 7).*

4.2. Effect of irradiation dose and dose rate on decoloration and degradation

The effect of the irradiation dose in kGy and dose rate in kGy/h on the different reactive dye concentrations was studied. RB15 solutions at 50, 75, 100, and 150 ppm concentrations were subjected to different irradiation doses at 2.87 and 0.14 kGy/h dose rates. The results are shown in Figures 5 and 6. For RB5 solutions, the results are given in Tables 1 and 2. The results show that the decoloration of RB5 by irradiation was much more than that of RB15 at all of the dye concentrations. When the maximum absorbance, or the degree of decoloration (%), of two reactive dye solutions at different concentrations was compared with each other, the increase in the degree of decoloration was more rapid for the lowest concentration (50 ppm) dye solutions than for the higher concentrations. The required irradiation dose for decoloration of RB5 is lower than that of RB15. This may be attributed to the difference in the structure of both dyes. The (-N=N-) groups are very sensitive to radiation and ruptured immediately when exposed to low doses of gamma irradiation[3].The degree of decoloration of two reactive dye solutions with an irradiation dose was estimated as the reduction in optical density at corresponding wavelengths where the absorbance was strongest. The effect of the dose rate on the radiation degradation of two reactive dyes studied was investigated at two different dose rates, namely 2.87 and 0.14 kGy/h. The results are illustrated in Tables 1 and 2. It can be said that the degree of decoloration (%) is the highest for the lowest dose rate (0.14 kGy/h), and the dose rate 2.87 kGy/h showed a lower per cent decoloration.

4.3. Effect of pH on decoloration and degradation

To investigate the effect of an irradiation dose on the pH of the 50ppm RB15 and RB5 solutions at 0.14 kGy/h dose rate, pH values of the unirradiated and irradiated dye solutions were measured. Table 3 and 4 show that pH of the solutions decreased sharply with the irradiation dose. The pH of the solution was lower at the low dye concentrations than the higher dye concentrations. The change of pH depends on the structure of the the dye molecule[16].

4.4. Effect of hydrogen peroxide on decoloration and degradation

The degree of decoloration for 50ppm RB15 and 50ppm RB5 solutions containing hydrogen peroxide is shown as a function of hydrogen peroxide concentration at 10.0 kGy and 1.0 kGy irradiation dose for RB15 and RB5, respectively in Figures 7 and 8. The degree of decoloration for both solutions increased with hydrogen peroxide concentration up to about 1.2 mM. This suggests that the decoloration reaction is promoted by the addition of hydrogen peroxide[3]. Hydrogen peroxide reacts rapidly with hydrated electrons formed by the radiolysis of water, leading to the formation of OH radical:

$$H_2O_2 + e^-_{aq} \longrightarrow OH + OH^-$$

Therefore, the increase in the degree of decoloration by the addition of hydrogen peroxide would be mainly attributed to the increase of the OH radical through the reaction above, in addition to primary OH radical. This finding suggests that the OH radical destroys the dye chromophore more efficiently than the hydrated electron does. Increasing the hydrogen peroxide concentration above 1.2 mM resulted in a decrease in the degree of degradation. As the hydrogen peroxide concentration increases, a part of the OH radicals are scavenged by the excess hydrogen peroxide.

(COD) Chemical oxygen demand (COD) corresponds to the amount of oxygen required to oxidize the organic fraction of a sample that is susceptible to permanganate or dichromate oxidation in an acid solution. The COD reduction, for 50 ppm two reactive dye solutions, are summarized in Table.5. The COD reduction for two reactive dye solutions were approximately 80% and 68% at 10.0 kGy and 1.0 kGy irradiation dose for RB15 and RB5, respectively. The COD reduction for the two reactive dyes was similar to each other.

TABLE 1. THE DEGREE OF DECOLORATION AS A FUNCTION OF IRRADIATION DOSE (kGy) AT VARIOUS CONCENTRATIONS OF REACTIVE BLACK 5 (RB5) IN THE ABSENCE AND PRESENCE OF 1.2 MM H_2O_2. DOSE RATE: 2.87 kGy/h

Dose (kGy)	Concentration (ppm) 50	75	100	150
0.0	0	0	0	0
1.0	80	74	60	52
2.0	94	80	65	56
3.0	96	85	68	60
4.0	96	85	70	60
5.0	96	88	70	62
Dose (kGy)	Concentration (ppm) (in the presence of 1.2 mM H_2O_2.) 50	75	100	150
0.0	0	0	0	0
0.1	33	30	25	20
0.2	42	35	25	20
0.3	54	46	30	25
0.4	58	48	38	28
0.5	68	50	40	30
0.6	80	60	52	50

TABLE 2. THE DEGREE OF DECOLORATION AS A FUNCTION OF IRRADIATION DOSE (kGy) AT VARIOUS CONCENTRATIONS OF REACTIVE BLACK 5 (RB5) IN THE ABSENCE AND PRESENCE OF 1.2 MM H_2O_2. DOSE RATE: 0.14 kGy/h

Dose (kGy)	Concentration (ppm) 50	75	100	150
0.0	0	0	0	0
0.1	54	50	46	38
0.2	64	54	50	46
0.3	72	62	57	50
0.4	86	76	67	57
0.5	90	80	70	60
0.6	93	85	80	76
1.0	93	88	85	80
Dose (kGy)	Concentration (ppm) (in the presence of 1.2 mM H_2O_2.) 50	75	100	150
0.0	0	0	0	0
0.1	60	55	50	44
0.2	67	57	52	46
0.3	76	68	60	54
0.4	90	82	74	64
0.5	98	94	86	76
0.6	98	92	86	76
1.0	98	94	86	80

TABLE 3. THE CHANGE OF pHAS A FUNCTION OF IRRADIATION DOSE (kGy) AT VARIOUS CONCENTRATIONS OF REACTIVE BLUE 15 (RB15) IN THE ABSENCE AND PRESENCE OF 1.2 MM H_2O_2. DOSE RATE: 0.14 kGy/H SOLUTION

Dose (kGy)	Concentration (ppm)			
	50	75	100	150
0.0	6.70	6.96	6.98	6.98
1.0	4.25	4.20	4.90	4.90
2.0	3.80	4.00	4.46	4.90
4.0	3.70	3.98	4.60	4.45
6.0	3.70	3.60	4.38	4.40
10.0	3.88	4.10	3.90	4.40
15.0	3.88	4.10	3.98	4.20

Dose (kGy)	Concentration (ppm) (in the presence of 1.2 mM H_2O_2.)			
	50	75	100	150
0.0	6.70	6.70	6.98	6.98
1.0	4.00	4.20	4.90	4.90
2.0	4.10	3.98	4.00	4.46
3.0	4.10	3.98	4.00	4.40
5.0	4.20	3.60	3.96	4.38
7.0	3.86	4.10	4.10	3.98
9.0	3.68	3.90	3.88	4.10
15.0	3.68	3.90	3.88	4.10

TABLE 4. THE CHANGE OF pH AS A FUNCTION OF IRRADIATION DOSE (kGy) AT VARIOUS CONCENTRATIONS OF REACTIVE BLACK 5 (RB5) IN THE ABSENCE AND PRESENCE OF 1.2 MM H_2O_2. DOSE RATE: 0.14 kGy/H SOLUTION

Dose (kGy)	Concentration (ppm)			
	50	75	100	150
0.0	6.15	6.05	6.05	5.85
0.1	4.20	4.40	4.40	4.90
0.2	4.20	4.20	4.40	4.40
0.3	4.00	4.20	4.40	4.40
0.4	3.84	3.90	4.20	4.30
0.5	3.80	3.90	3.95	4.25
0.6	3.80	3.80	3.86	3.90
1.0	3.70	3.80	3.80	3.86

Dose (kGy)	Concentration (ppm) (in the presence of 1.2 mM H_2O_2.)			
	50	75	100	150
0.0	6.15	6.05	6.05	5.85
0.1	4.25	4.40	4.40	4.40
0.2	3.90	4.20	4.20	4.40
0.3	3.90	3.90	4.20	4.20
0.4	3.80	3.90	4.00	3.80
0.5	3.40	3.80	3.84	3.90
0.6	3.40	3.80	3.86	3.90
1.0	3.50	3.70	3.86	3.86

TABLE 5. CHANGES OF COD BY IRRADIATION. (A) COMMERCIAL REACTIVE DYES, INITIAL DYE CONCENTRATION: 50 PPM

Reactive dyes (a)	Dose (kGy)	COD Reduction (%)	
		$[H_2O_2]$= 0 mM	$[H_2O_2]$=1.2mM
Reactive Blue 15	0.0		
	2.0	46	59
	4.0	48	65
	6.0	62	78
	10.0	62	80
	15.0	70	82
Reactive Black 5	0.0		
	0.1	46	52
	0.2	48	54
	0.3	50	60
	0.5	58	64
	1.0	66	68

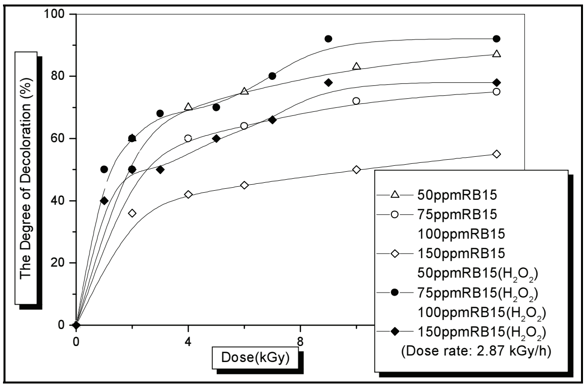


FIG. 5. The degree of decoloration as a function of irradiation dose (kGy) at various concentrations of RB15 in the absence and presence of 1.2 mM H_2O_2.

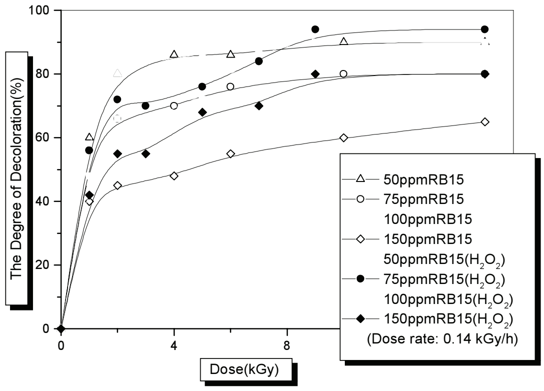


FIG. 6. The degree of decoloration as a function of irradiation dose (kGy) at various concentrations of RB15 in the absence and presence of 1.2 mM H_2O_2.

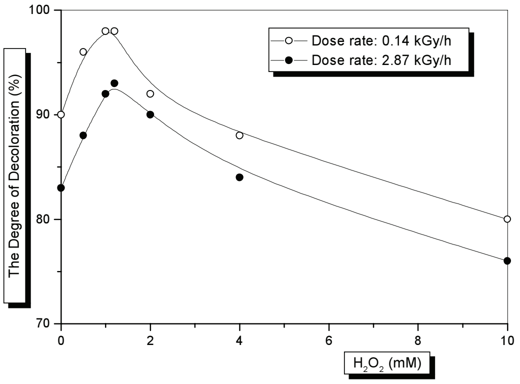


FIG. 7. Effect of hydrogen peroxide on the degree of decoloration. Irradiation dose: 10.0 kGy. RB15 concentration: 50ppm.

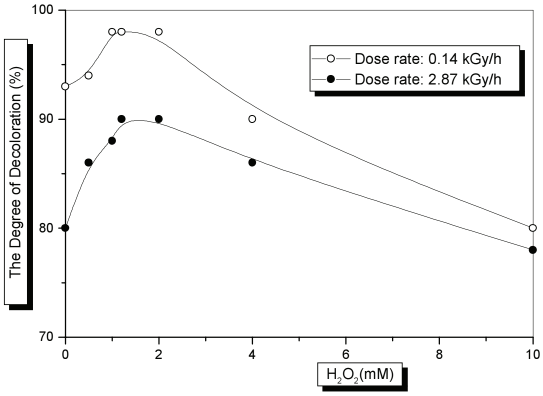


FIG. 8. Effect of hydrogen peroxide on the degree of decoloration. Irradiation dose: 1.0 kGy. RB5 concentration: 50ppm.

Figures 9–11 show the absorption spectra of RB5 aqueous solutions at 50 ppm in air and in the presence of N_2 and N_2O at 2 kGy/h dose rate. It is seen that irradiation leads to not only the decoloration of water (the decrease in optical density in visible region) but also to the considerable loss in optical density in the UV-region (the decomposition of organic compounds). The absorption spectra in Figures 9 and 10 as measured in air and for the nitrogen-saturated RB5 aqueous solutions, indicate that the absorption band at 596 nm decreased with the irradiation dose. Above 0.8 kGy irradiation dose, the absorption band of the RB5 aqueous solution in air and in the presence of N_2 at 596 nm practically disappeared. The results for nitrous oxide-saturated similar solutions are shown in Figure 11. The isosbestic point appeared at 280 nm. The degree of decoloration for the nitrous oxide-saturated solution was higher than that of the nitrogen-saturated solution and the solution in air. The required irradiation doses to make these absorption bands disappear completely were 1.6, 0.8, and 0.5 kGy in air and in the presence of N_2 and N_2O. This suggests that nitrous oxide promotes the decoloration reaction.

The decoloration of the dye solution showed that the destruction of the dyes occured. Azo dyes are characterized by nitrogen to nitrogen double bonds (-N=N-). They contain at least one to four azo groups usually attached to two radicals, of which usually both, but at least one, are aromatic groups. The color of azo dyes is determined by the azo bonds and their associated chromophores and auxochromes[17]. Azo bonds are the most active bonds in azo dye molecules, which are liable to be oxidized by a positive hole or hydroxyl radical or reduced by an electron in the conduction band[18]. The reaction of azo bonds leads to the decoloration of dyes. On the basis of the results, the radiation-induced decoloration reaction of RB5 in aqueous solutions may be represented as follows: At first, the dye solution is decolored by the attacks of active species, such as OH, hydrated electron, HO_2 and peroxides. After decoloration, the skeleton of the dye molecule is degraded to the lower molecular weight compounds, mainly organic acids, and finally to carbon dioxide.

RB5+OH→RB5OH(decoloredproduct) (1)
RB5 + OH → RB5OH’ (colored product) (2)

Dye molecules have three kinds of reactive sites (1) and (2); (a) the azo group, (b) aromatic rings connecting directly to the azo group, (c) the benzene ring, not conjugated to the azo group. The attack of the OH radical on site (c) would be independent of the decoloration reaction and would cause little change in the absorption spectra. This is represented as reaction (2) [19].

In Figure 11, the absorption band near 310 nm is attributed to the azo group. The absorption band near 230 nm is attributed to substituted aromatic rings [20, 21]. The optical density at 230 nm does not decrease with the dose as much as those at 310 nm and the isosbestic points at 224 and 263 nm. This suggests that the decoloration reaction is not necessarily accompanied by the destruction of substituted aromatic rings.

4.5. Effect of irradiation dose and dose rate on decoloration and degradation of organic dyes in the presence of N_2, N_2O and air

For RB5 aqueous solutions (50 ppm), the degree of decoloration in air and in the presence of nitrogen and nitrous oxide were plotted as a function of an irradiation dose at 2 kGy/h dose rate. The results are given in Figure 12 for RB5 aqueous solutions, respectively. The degree of decoloration increased up to 100% for the nitrous oxide-saturated RB5 solution from 80% for the nitrogen-saturated RB5 solution at 0.8 kGy irradiation dose and 2 kGy/h dose rate. The absorptions maximum at wavelength (596 nm) decreased with increasing irradiation dose for nitrogen-saturated RB5 aqueous solutions, while for nitrous oxide-saturated RB5 solutions, it decreased and shifted to a lower wavelength. This suggests that the skeleton of the RB5 molecule is mainly destroyed by the attack of the OH radicals.

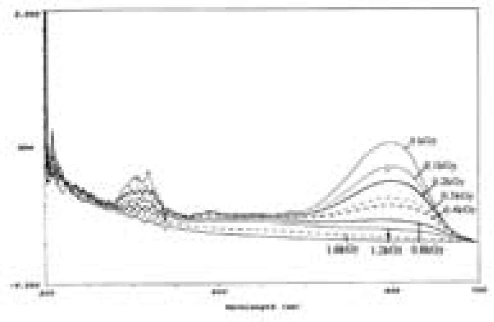


FIG. 9. Absorption spectra of unirradiated and irradiated RB5 aqueous solutions in air [Dye]=50ppm, Dose rate:2.0 kGy/h.

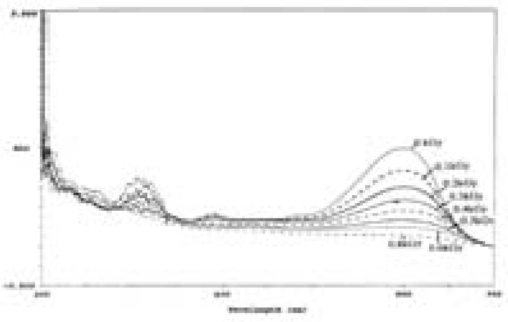


FIG. 10. Absorption spectra of unirradiated and irradiated nitrogen-saturated RB5 aqueous solutions.[Dye]=50ppm, Dose rate:2.0 kGy/h.

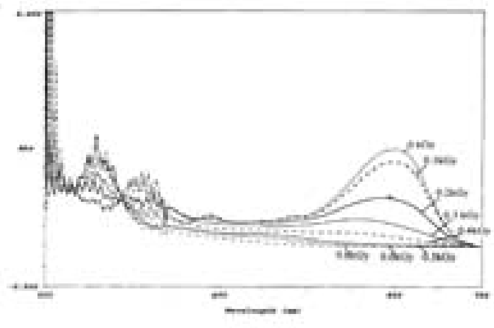


FIG. 11. Absorption spectra of unirradiated and irradiated nitrous oxide-saturated RB5 aqueous solutions. [Dye]=50ppm, Dose rate:2.0 kGy/h.

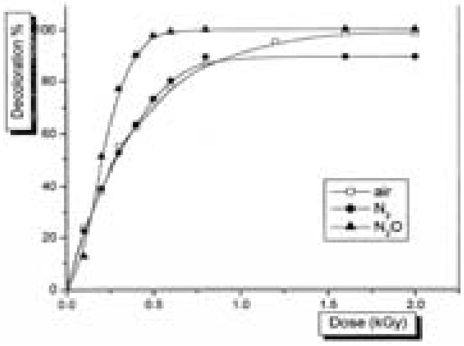


FIG. 12. Effect of additives on degree of decoloration for RB5 aqueous solutions. [Dye]=50ppm.

It is well known that nitrous oxide reacts rapidly with hydrated electrons produced in an aqueous solution by ionizing radiations; thus, leading to the formation of the OH radical [22]:

$$N_2O + e^-_{aq} \rightarrow OH + OH^- + N_2 \qquad (3)$$

Therefore, such a large G(-Dye) is attributable to an increase in the OH radical through reaction (3) in addition to the primary radical.

For a second group dye, Apollofix dyes, it was found that two dyes have main absorption bands in the visible region and some absorption bands in the UV region of the spectrum, which are attributed to the skeleton of the dye molecule. The peaks at about 220 nm wavelength are attributable to substituted aromatic rings, and these about 534 and 420 nm may be attributed to ($SO_2(CH_2)_2OSO_3Na$) groups. The absorption bands in the visible region of the spectrum are attributed to the chromophore group and its auxochromic substituents [23]. The absorption spectra were recorded for the irradiated Apollofix Red (AR) and Apollofix Yellow (AY) at different concentrations. The absorption bands at 534 nm and 420 nm decreased with increasing dose and decreasing concentration for AR and AY, respectively.

Figure 13 and Figure 14 show the change of spectrum of AR and AY after irradiation at 0.075 g/L dye concentration. The absorption in the UV and visible regions decreased as the irradiation dose increased. These decreases are obviously due to the destruction of the conjugated system. The rate of decrease of the intensity of the absorption band in the visible region (decoloration) is higher than that of the peaks in the UV region (degradation). In other words, complete decoloration (indicated by complete disappearance of the absorption band in the visible region) can be attained at doses lower than those needed for the complete degradation of the respective dyes. A similar absorption spectrum was recorded for AY dye solution in Figure 14. The decolorization primarily resulted from dye reactions with $^{\cdot}$OH radicals. In the latter, hydrated electrons reacting with a dye form a semi-reduced species, which, in turn, can partially interact with the products of dye reactions with $^{\cdot}$OH radicals to regenerate the initial dye. In aerated solutions, e_{aq}^- reacts with oxygen. The resulting $HO_2^{\cdot}$ and O_2^- radicals are characterized by low reactivity (if any) toward dyes [24]. The absorption band at 534 nm decreased with increasing irradiation dose and disappeared almost completely at 3.0 kGy irradiation dose for 0.05 g/L AR solution. For 0.05 g/L AY concentration, the required irradiation dose to make the absorption band diappear at 420 nm completely was 1.0 kGy. The degree of decoloration was determined by measuring the absorptivities in the visible region (534 nm) and (420 nm), as shown in Figures 15 and 16 for AR and AY dyes, respectively. The maximum decoloration of AR and AY dyes was reached at 100% at a dose of 3.0 kGy and 1.0 kGy, respectively, at 0.05 g/L dye concentration.

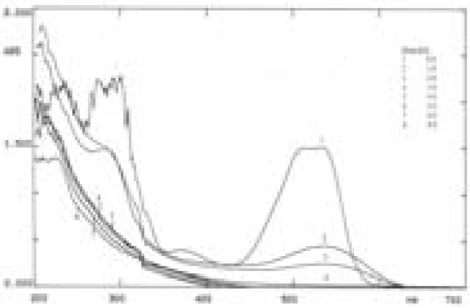


FIG. 13. Absorption spectra of aqueous AR dye solution unirradiated and irradiated to different irradiation doses. [AR] = 0.075 g/L.

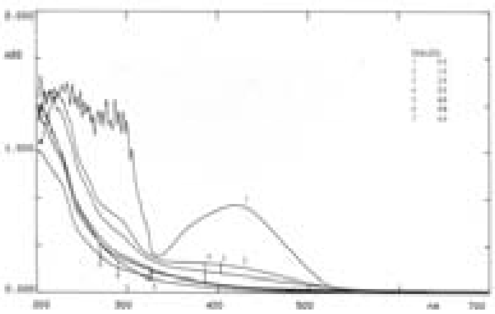


FIG. 14. Absorption spectra of aqueous AY dye solution unirradiated and irradiated to different irradiation doses. [AY] = 0.075 g/L.

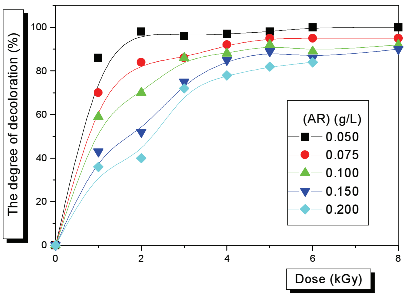


FIG. 15. Variation of the degree of decoloration of AR dye solutions as a function of irradiation dose at 534 nm.

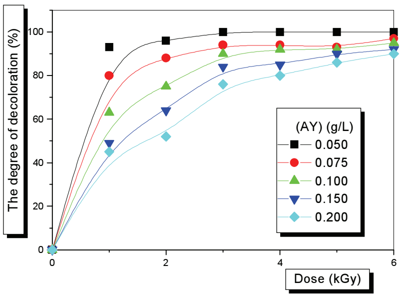


FIG. 16. Variation of the degree of decoloration of AY dye solutions as a function of irradiation dose at 420 nm.

The pH of the Apollofix dye solutions after irradiation is shown as a function of dose in Table 6 over the range of the dye concentrations 0.05–0.200 g/L. The pH of the 0.05 and 0.075 g/L dye solutions was lowered sharply, with increasing of the dose to about 2.0 kGy, while the pH of the 0.100, 0.150 and 0.200 g/L dye solutions was lowered gradually. The decrease of the pH of the dye solutions was less sensitive to the irradiation dose in the range of 3.0–8.0 kGy. The change of pH depends on the structure of the dye molecule and the sulfonic and ethylsulfonic groups in Apollofix dyes which act as an acid. These findings suggest that the change of pH for dye solutions may be attributed to the oxidizing products formed by the degradation. It is known that the oxidation of aromatic compounds induced by ionizing radiation gives some lower molecular weight aliphatic compounds such as aldehyde and organic acids [25], and that further oxidation of the organic acid formed leads to the formation of carbon dioxide [26, 27, 28].

TABLE 6. THE CHANGE OF pH AS A FUNCTION OF IRRADIATION DOSE (kGy) AT VARIOUS CONCENTRATIONS OF APOLLOFIX RED (AR) AND APOLLOFIX YELLOW (AY) DYE SOLUTION

Dose (kGy)	AR concentration (g/L)				
	0.050	0.075	0.100	0.150	0.200
0.0	4.80	4.80	4.80	4.80	4.80
1,0	4.78	4.52	4.50	4.70	4.54
2,0	4.27	4.18	4.11	4.08	4.02
3,0	4.38	4.15	4.07	4.03	4.00
4,0	4.20	4.11	4.05	3.99	3.95
5,0	3.81	3.96	3.94	3.99	3.93
6,0	3.93	3.95	3.84	3.94	3.90
8,0	3.95	3.85	3.80	3.84	3.84
Dose (kGy)	AY concentration (g/L)				
	0.050	0.075	0.100	0.150	0.200
0,0	5.04	5.12	5.15	5.15	5.34
1,0	4.29	4.65	4.52	4.58	4.53
2,0	4.18	4.25	4.45	4.42	4.47
3,0	4.01	4.24	4.14	4.11	4.32
4,0	4.00	4.14	4.14	4.03	4.10
5,0	4.00	4.01	3.98	3.97	3.98
6,0	3.97	3.98	3.90	3.93	3.93

Hydrogen peroxide is a stable product that does not require any special equipment since it is an easily storable, noncorrosive and versatile liquid. Furthermore, it is totally miscible with water. Because it has no solubility limitations, it turns out to be more advantageous in the oxidative process than chemicals such as sodium hypochlorite and ozone, which require more care in application [29]. Hydrogen peroxide can be used to decolorize the waste water, to remove a wide range of sizes, to bleach fabrics and to oxidize chrome dyes, vat dyes and some sulphur dyes. The degree of the decoloration and degradation behavior of AR and AY at different H_2O_2 concentrations was studied by irradiating aqueous dye solutions to a dose of 3.0 kGy for AR (0.200 g/L) and AY (0.200 g/L). The decoloration behavior, versus H_2O_2 concentration, is shown in Figure 17. The degree of decoloration for both solutions increased with hydrogen peroxide concentration to about 1.2 mM, suggesting that the decoloration reaction is initially promoted by the addition of hydrogen peroxide. Hydrogen peroxide reacts rapidly with hydrated electrons formed from the radiolysis of water leading to the formation of $^{\cdot}OH$ radical [26]:

$$H_2O_2 + e_{aq}^- \rightarrow {}^{\cdot}OH + OH^- \qquad (1)$$

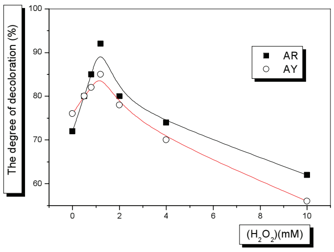


FIG. 17. Effect of hydrogen peroxide on the degree of decoloration. Irradiation dose: 3.0 kGy, [AR]=[AY]= 0.200 g/L, Dose rate: 0.14 kGy/h.

Therefore, the increase in the degree of decoloration by the addition of hydrogen peroxide would be mainly attributable to the increase of the $^{\cdot}$OH radical through the above reaction. This finding suggests that the $^{\cdot}$OH radical destroys the chromophore more efficiently than the hydrated electron does. As seen in Figure 17, the degree of decoloration decreased above 1.2 mM hydrogen peroxide. In the case of the solution containing hydrogen peroxide, the concentration of $^{\cdot}$OH radicals increases through the reaction [25]. However, as the hydrogen peroxide concentration increases, a part of the $^{\cdot}$OH radicals are scavenged by the excess hydrogen peroxide through the reactions (2), (3) and (4) [26, 27, 28, 30].

$$H_2O_2 + {}^{\cdot}OH \rightarrow HO_2^{\cdot} + H_2O \qquad (2)$$
$$H_2O_2 + HO_2^{\cdot} \rightarrow {}^{\cdot}OH + H_2O + O_2 \qquad (3)$$
$$HO_2^{\cdot}(\text{or } {}^{\cdot}OH) + HO_2^{\cdot} \rightarrow H_2O_2 \text{ (or } H_2O) + O_2 \qquad (4)$$

Therefore, the decrease in the degree of decoloration above 1.2 mM hydrogen peroxide may be attributed to the scavenging of $^{\cdot}$OH radicals by the excess hydrogen peroxide through the reactions (2), (3) and (4).

The pollution level of wastewaters is usually characterized by chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC) and dissolved carbon content. All these characteristics are group parameters, which specify the chemical and biological oxidizability of wastewater pollutants and the total carbon content of pollutants that occur in a dissolved state, respectively. Thus, COD (mg/L) is the amount of oxygen (or another oxidizing agent in terms of oxygen) required for the complete oxidation of organic matter in a test wastewater sample. BOD is the amount of oxygen consumed in the anaerobic biochemical decomposition of organic matter in the test wastewater.

TABLE 7. THE CHANGE OF COD AS A FUNCTION OF DYE CONCENTRATION IN THE PRESENCE AND ABSENCE OF H_2O_2. $[H_2O_2]$= 1.2MM. (COD DATA IN PARENTHESIS ARE USED FOR AR AND AY DYES, 8 kGy IRRADIATED BY Γ rayS.)

AR concentration (g/L)	COD (mg/L)	AYconcentration (g/L)	COD (mg/L)
0.050	946 (922)	0.050	890 (875)
0.075	950 (930)	0.075	890 (875)
0.100	970 (944)	0.100	910 (902)
0.150	1138(1050)	0.150	930(900)
0.200	310 in H_2O_2/ γ 1200(1120)	0.200	275 in H_2O_2/ γ 1000(980)

To investigate the effects of irradiation alone and both irradiation and H_2O_2 on COD, COD contents of aqueous solutions of AR and AY and 8 kGy irradiated 0.200 g/L concentration of AR and AY dyes. These were determined in the presence and absence of 1.2 mM H_2O_2 concentration. The results are given in Table 7. Comparative tests showed that H_2O_2 has only a very slight effect on COD for lower dye concentrations. COD contents were determined for the highest AR and AY dye concentrations in the presence of H_2O_2 and irradiated dye samples. The greatest effect on these dyes was performed by a simultaneous application of 1.2 mM H_2O_2 concentration and 8 kGy of gamma irradiation. The effect of the irradiation dose on AR and AY dye solutions was determined by measurement of COD values with irradiation. The results are presented in Figure 18. It was observed that COD values of AR and AY dyes studied in this work decreased with increased irradiation dose. The decrease in COD values confirms the importance of H_2O_2 in irradiation of dye solutions. Figures 18 and 19 show the change of COD and BOD contents of aqueous solutions of two Apollofix dyes before and after irradiation. It can be noticed that the solutions of AR and AY dyes were almost completely decolorized at 3.0 kGy and 1.0 kGy doses, respectively. Simultaneously, the values of COD and BOD significantly decreased. The initial AR and AY solutions had COD values equal to 1200, 1000 mg/L, and BOD values equal to 400, 330 mg/L, respectively. The gamma irradiation caused a decrease in the COD and BOD of the two dye solutions. In the presence of H_2O_2, the COD values decreased from 1200 to 310 mg/L and from 1000 to 275 mg/L, and BOD values decreased from 400 to 120 g/L and from 330 to 80 mg/L in the irradiation range (1.0–8.0 kGy for AR and AY, respectively). The BOD contents for the AR and AY dye solution were almost constantly maintained at up to 3 kGy irradiation dose in the system of γ and H_2O_2/ γ and then decreased to an 8 kGy irradiation dose. For AY dye solution, BOD contents were decreased from a 1 kGy to an 8 kGy irradiation dose range in the system of γ and H_2O_2/ γ. It can be explained that the H_2O_2/ γ system can produce only biodegradable components, like organic acids, but it cannot completely decompose the biodegradable components to the products with the dose employed.

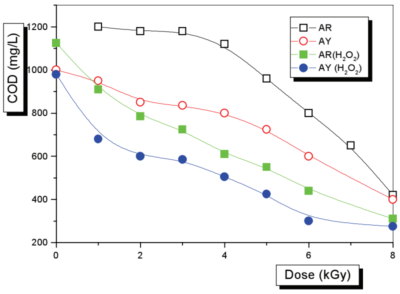


FIG. 18. COD values for AR and AY dye solutions gamma irradiation. [AR] = [AY] = 0.200 g/L, $[H_2O_2]$= 1.2 mM. Dose rate: 0.14 kGy/h. (Solid symbols are used for AR and AY concentrations containing H_2O_2.

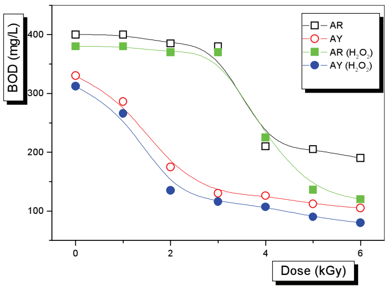


FIG. 19. BOD values for AR and AY dye solutions gamma irradiation. [AR]=[AY]= 0.200 g/L, $[H_2O_2]$ = 1.2 mM. Dose rate: 0.14 kGy/h. (Solid symbols are used for AR and AY concentrations containing H_2O_2.)

5. CONCLUSIONS

The decoloration and degradation of reactive dyes and Apollofix dyes in aqueous solutions by gamma irradiation has been demonstrated. The dye solutions are easily decolored by gamma irradiation, which may be promising for the treatment of textile dye waste water. Decoloration and degradation of textile waste water can be carried out, but the necessary dose varies with the types of the waste. The destruction of the skeleton of the dye molecule, or decoloration and degradation of the reactive dyes in aqueous solutions, can be achieved by gamma irradiation alone, or by gamma irradiation of aqueous dye solutions which contain 1.2 mM concentration H_2O_2 at lower dose rates.

REFERENCES

[1] SUZUKI, N., MIYATA, T., SAKUMATO, A., HASHIMATO, S., KAWAKAMI, W., Int. J. Appl. Rad. Isot., 29, (1978) 103–108.

[2] NAGAI, T., SUZUKI, N., Int. J. Appl. Rad. Isot., 27, (1978) 699–705.

[3] SUZUKI, N., NAGAI, T., HOTTA, H., WASHNO, M., Int. J. Appl. Rad. Isot., 26, (1975) 726–730.

[4] WALTERS, R.W., TARLETON, A.L., GRASSO, D., J. Water Pollut. Cont. Fed., **61**, 6, (1985) 789–799.

[5] GETOFF, N., LUTZ, W., Radiat. Phys. Chem., **25**, 1–3, (1985) 21–26.

[6] CLARKE, E.A., ANLIKER, R., HUTZINGER, O., The handbook of environmental chemistry, Springer, Berlin, 3A (1980).

[7] TANG, W.Z., AN, H., Chemosphere, 31 (1995) 4157.

[8] SUZUKI, N., NAGAI, T., HOTTA, H., YASHINO, H.M. Int. J. Appl. Radiat. Isotopes, 26 (1975) 725.

[9] ARAI, H., SHIMIZU, K., SUGIYAMA, M.,Proceedings of 2nd Annual Conference on Ozone and Technology in Japan, Kyoto, 21(1933).

[10] GEHRINGER, P., PROKSCH, E., SZINOVATZ, W., ESCHWEILER, H., Wat. Res. 22 (1988) 645.

[11] HOSONO, M., ARAI, H., and et al., Appl. Radiat. Isot. 44 (1993) 1199.

[12] SHEVCHUCK, I.A., A., MAKHNO, YA., DITRIKH, I.V., Khimiya i Tekhnologiya Vody, **15**, 4, (1993) 262–263.

[13] SHEVCHUCK, I.A., MAKHNO, A., DITRIKH, I.V., Khim. Technol. Vody 15 (1993) 262.

[14] Standard Methods for the Examination of Water and Wastewater, 13th ed., American Public Health Association (1971).

[15] HOSONO, M., ARAI, H., AIZAWA, M., YAMAMOTO, L., SHIMIZU, K., Int. J. Appl. Rad. Isot., **44** (1993) 199–204.

[16] PIKAEV, A.K., BLUDENKO, A.V., MAHAROV, I.E., PONOMAREV, A.V., MININ, V.N., PONOMAREV, V.I., LINNIK, O.A., Radiat. Phys. Chem., **48**, 1, (1996) 75–80.

[17] REUTERGARDH, L.B., IANGPHASUK, M., Chemosphere, 35, (1997) 585.

[18] GANESH, R., BORADMAN, G.D., MICHELSSEN, D., Wat. Res., 28, (1994) 1367.

[19] SUZUKI, N., NAGAI, T., HOTTA, H., WASHINO, M., Bull. Chem. Soc. Jap., 48(7), (1995) 2158.

[20] GILLAM, A.E., STERN, E.S., “An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry”, Edward Arnold LTD., London,(1960).

[21] DYER, J.R.,“Applications of Absorption Spectroscopy of Organic Compounds”, Prentice-Hall, Inc., New Jersey (1965).

[22] DAINTON, F.S., PETERSON, D.B., Proc.Roy.Soc., London, A267, (1962) 443.

[23] NAGAI, T., SUZUKI, N., Int. J. Appl. Radiat. Isotopes, 27 (1976) 699.

[24] VINODGOPAL, K., KAMAT, P.V., Environmental Applications of Ionizing Radiation, W.J.Cooper, R.D.Curry, K.E.O’Shea, Eds., New York; Wiley (1998) 587.

[25] SHIMADA, K., SUZUKI, N., ITATANI, N., HOTTA, H., Bull. Chem. Soc. Japan, 37 (1963) 1143.

[26] SPINKS, J.W.T., WOODS, R.J., An Introduction to Radiation Chemistry, Chapter 8, Wiley, New York (1964).

[27] BAXENDALE, J.H., WILSON, J.A., Trans.Farad.Soc., 53 (1957) 344.

[28] SUZUKI, N., NAGAI, T., HOTTA, H., WASHINO, M., Int. J. Appl. Radiat. Isotopes 26 (1965) 726.

[29] PRAT, C., VICENTE, M., ESPLUGES, S., Water Res., 22 (1988) 663.

[30] ALBEN, A.O., The Radiation Chemistry of Water and Aqueous Solutions, Van Nostrand Co., Princeton, New Jersey (1961).

THE DEGRADATION OF SOME PESTICIDES IN AQUEOUS SOLUTIONS BY GAMMA RADIATION

D. Şolpan
Hacettepe University, Department of Chemistry,
Ankara, Turkey

Abstract

In this study, the possibility of using gamma rays to degrade some pesticides in water was investigated. Four different pesticides (4-chloro phenoxyacetic acid (4-CPA), 2.4-dichloro phenoxyacetic acid (2,4-D), 2.4-dichloro phenoxyacetic propionic acid (2,4-DP), 2.4-dichloro phenoxyacetic butanoic acid (2,4-DB) in aqueous solutions were irradiated with doses of 0.1 kGy to 10.0 kGy at a 0.07 kGy/h dose rate. The change of absorption spectra and the degree of degradation (per cent reduction in optical density) were examined in the presence of air. The absorption bands at 224 nm, 228 nm, 228 nm, 229 nm for (4-CPA), (2,4-D), (2,4-DP), (2,4-DB) were decreased rapidly with an increasing irradiation dose. The degree of degradation for each pesticide with an irradiation dose was estimated for all pesticide concentrations (3–75 ppm). The highest degradation was observed after a 1.0 kGy dose for all pesticides. The pH of (4-CPA), (2,4-D), (2,4-DP), (2,4-DB) solutions was decreased from 6.13, 6.33, 6.15, 6.67 to 3.34, 3.12, 3.39, and 3.91 with the irradiation. This suggests that the skeleton of the pesticide molecule is mainly destroyed. The irradiated samples were analyzed by GC-MS-MS. The results obtained were compared and evaluated.

1. INTRODUCTION

An increase in the population of the World increases the demand for nutrients for human beings. Demands for other products increase as well due to industrial activities and result in the pollution of water with halogenated organic compounds used as solvents and halogenated pesticides used in agricultural activities. Pesticides can reach rivers and lakes via rain in means of dragging, human beings then use these water sources for drinking and for other activities. Hence, keeping these water resources clean is very important for health purposes. Some chemical and biological methods are possible to overcome water pollution. In addition to these, irradiation of the waste water is an alternative method for water treatment. In this method, no chemicals are added into the medium, and radiation can kill microorganisms and pathologic viruses, as well as degrading the toxic organic chemicals [1]. Due to the above-mentioned pollution sources, environmental and toxicological effects have increased considerably [2, 3, 4]. This is also reflected in the health of the population in industrial areas. When pesticides are released into the environment they may be broken down, or they may resist degradation, and thus remain unchanged in the environment for long periods of time. The preservation of the environment and human health from exposure to persistent organic pollutants is now a priority in developed countries. In this sense, pesticides constitute a very important group of target compounds because of their high toxicity and their unavoidable use in agricultural practices. Turkey is a country with intensive agricultural production, and the use and commercialization of organochlorinated and phenoxyacid pesticides has been gradually prohibited since 1970; however, because they were used extensively, they probably still remain in the environment.

Pesticides in their different forms (insecticides, herbicides, fungicides, etc.) are now the most common agents used in agricultural cultivations against insects which are vectors of several human diseases, pests causing severe damages in crops, weeds control, etc.; therefore, are cruel to to the economical growth of agricultural areas. However, some portions not used are washed by precipitation waters. Consequently, they are present together with their degradation by-products in surface waters and groundwaters. Among the pesticides which have been reported, weed destroying herbicides are found, to a major extent, in public water sources. More specifically, phenoxyalkyl acid derivatives such as 2,4-dichloro phenoxyacetic acid and similar types of pesticides are of great importance because of the large amounts used. The main concern is that its high solubility in water permits its detection not only during its application, but also after a long period of use.

The most frequently used analytical techniques for pesticides are gas chromatography (GC) and mass spectrometry (MS) with chemical ionization. The application of GC-MS-MS requires an adequate extraction and isolation technique, providing compound enrichment, since these compounds are present trace levels. On the other hand, a clean-up step, to obtain clean solutions and eliminate interfering compounds that limit the performance of capillary columns and the certainty of the analysis was necessary. These days, the coupling of GC and MS has become the ideal analytical tool for confirmatory analysis [5]. One of the most important developments in GC/MS has been the ion trap mass spectrometer. They offer tandem MS capabilities, which improve selectivity in the analysis of mixtures, and therefore, can lower detection limits by eliminating or minimizing chemical interferences [6, 7, 8] resulting in higher analytical sensitivity than single-stage MS analyses [9, 10, 11, 12]. Ion traps in tandem with MS, i.e. analyte-specific ions of selected mass/charge ratio are first isolated and then fragmented. MS/MS provides information for structural elucidation, which can be helpful in identifying unknowns. MS/MS allows the separation and identification of organoclorinated compounds at trace levels in the presence of many interfering compounds, even at widely different concentration levels. A large number of multiresidue extraction methods have been developed in the last 20 years. The more frequently used methods employ solvent extraction and gas chromatography (GC) with selective and sensitive detection. The more widely used extraction techniques for pesticides in ground and surface water are liquid-liquid extraction and solid-phase extraction [13].

Irradiation offers the possibility of killing any bacterial contamination and breaking down the chemical pollutants. This is another process where cobalt-60 irradiation would not be able to deliver sufficiently intense doses of radiation for the high flow rates of water needed, and electron bean radiation of a thin film of fast-flowing water is necessary to achieve results [14, 15, 16].

In this study, phenoxyacid-type of pesticides were chosen as model compounds and their radiation induced decomposition in aqueous solution was investigated. It is well known that the use of large quantities of pesticides in agricultural activities is one of the main causes of pollution of surface and groundwaters. Our work is focused on the degradation of (4-CPA), (2,4-D), (2,4-DP), and (2,4-DB), which are widely used as an insecticide throughout the world [17].

2. OBJECTIVE OF THE RESEARCH

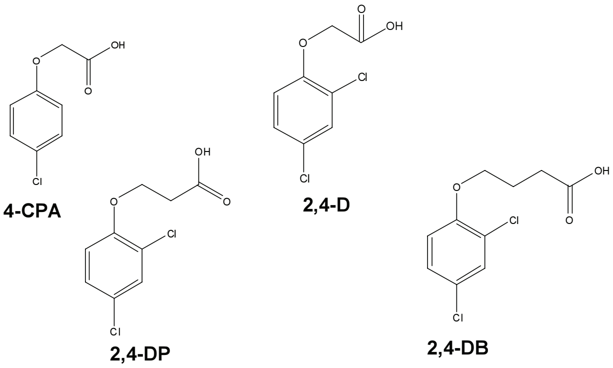
In this study, the degradation of pesticides in aqueous solutions by gamma irradiation will be demonstrated. The pesticide solutions are very easily degraded by gamma irradiation, which may be promising for the treatment of groundwater containing pesticides. The degradation of pesticide solutions can be carried out, but the necessary dose varies with the types of pesticides. The objective of this work is to do a preliminary study on the presence of organochlorinated and phenoxyacid pesticides in a predominantly agricultural, livestock and industrial regions of Turkey that are growing and developing and develope quantitative methods for the analysis of representative herbicides and their transformation products. The analysis of herbicide residues in water is typically done by gas chromatography and high-performance liquid chromatography. Most carbamates are thermally unstable. Hence, it is necessary to analyze them by liquid chromatography rather than by gas chromatography. For this reason, we decided to work on these types of pesticides.

3. MATERIALS AND METHODS

3.1. Materials

The irradiation of samples with ^{60}Co-γ rays under steady-state conditions was performed using a 'Gammacell 220' with a dose rate of 0.07 kGy/h. The irradiation treatment was carried out at about 30°C in vessels of Pyrex-glass. All chemicals used were of p.a. purity (Aldrich). Deionized distilled water was used in the preparation of pesticide solutions without contaminants. The chemical structures of the pesticides are as follows:

The herbicides used in this study



Deionized water was used to prepare eight concentrations of (3–75) mg/L for 2,4-dichloro phenoxyacetic acid and 4-chlorophenoxyacetic acid pesticides. Before and after irradiation, the pH of the solutions was measured by a JENWAY 3010 model pH meter. The UV-absorbances at the wavelength of maximum absorbance of the irradiation and unirradiated solutions were measured by a Carry 100 model UV-vis spectrophotometer. The per cent degradation was estimated by the reduction in optical density. The decomposition induced by gamma rays was followed by the determination of the cleaved chlorine as Cl^- ion [18]. The formation of various aldehydes which appear as final products was also measured [19].

Solid-phase extraction (SPE) disks, followed by gas chromatographic techniques, were used for the detection of phenoxyacetic acid pesticides [20]. The collected water samples were prefiltered through glass fiber to eliminate particulate matter. Hexane and methanol modifiers were used for better extraction. SPE using prepacked reversed-phase octadecyl (C18-bonded silica) contained in cartridges was used for sample preparation. Prior to extraction, the C18-bonded phase which contains 500mg bonded phase, were washed with methanol, hexane and next 10 mL of ultrapure water. The samples were mixed well and allowed to percolate through with a flow rate of 10–15 mL/min under vacuum. The nitrogen gas was passed through the cartridges for 10 minutes. After sample extraction, we continued for 10 minutes to dry the packing material, and the pesticides trapped in the C18-bonded phase were eluted by passing 2 mL of acetone. The pesticide residues were analyzed by the gas chromatography (GC-MS-MS) method using a Varian 3900 gas chromatograph with a Saturn 2000 Ion Trap mass spectrometer from Varian Instruments. A DB5-MS (30mx0.25mm i.d.) column, with a 0.25μm film thickness and chromatographic column was employed. The ion trap mass spectrometer was operated in the electron ionization (EI) mode, and the MS-MS option was used. The computer that controlled the system had an EI/MS/MS library specially created for the target analytes under our experimental conditions. In addition, an EI-MS library was available, [20] used for building our own MS/MS library. The carrier gas was He. The GC conditions were determined according to the EPA method.

A 50 ppm (2.26×10^{-4} mol L^{-1}) 2,4-Dichlorophenoxy acetic acid (2,4-D) sample was prepared in deionized water. Two-hundred milliliters of 50 ppm of the herbicide sample is irradiated in open bottles up to the acquired dose at 0.07 kGy/h dose rate at ambient conditions. For preconcentration and to extract of intermediates and undecomposed herbicides from aqueous media to an organic phase, the solid phase extraction method was used. Irradiated aqueous samples, 200 ml, were eluted from C18 or diol cartridges, and organic phase extraction was applied with 2 milliliters of acetone, hexane or dichloro methane. For determination of acidic groups, such as undecomposed herbicides, methyl alcohol was used for organic phase extraction. The analytes that include carboxylic acid groups cannot be observed in a GC-MS system; thus, the derivatives of these groups, such as methyl esters, have to be injected to the system. These groups were converted to methyl esters in methyl alcohol with excess concentrated sulphuric acid and methyl esters were extracted into hexane for injection into GC-MS system. EPA 8151 method was used for the determination of intermediates and methyl esters of undecomposed herbicides in GC-MS system.

4. RESULTS AND DISCUSSION

The UV absorption spectrum of a 4-chlorophenoxyacetic acid solution (50 mg/L at 0.14 kGy/h) in our experimental conditions presents a maximum of 224 nm. After the 4-chlorophenoxyacetic acid solutions were irradiated at different irradiation doses we observed a decrease of about 83% in the height characteristic peak (224 nm) of the UV 4-chlorophenoxyacetic acid spectrum. The absorption band of 224 nm decreased with an increasing irradiation dose and disappeared almost completely at 3.0 kGy (Figure 1-a). For the same experimental conditions cited above during irradiation, the absorbance of 2,4-dichlorophenoxyacetic acid solution was determined at 228 nm. Results presented in Figure 2-a indicate that the absorbance is decreased with an increasing radiation dose. The absorption spectra of the unirradiated and irradiated 50 mg/L 2,4-dichlorophenoxyacetic acid solutions in air at 0.07 kGy/h dose rate is shown in Figure 2-a. The absorption band at 228 nm decreased with increasing dose and disappeared completely at 4.0 kGy in air. The absorption spectra of 2,4-dichlorophenoxy propionic acid (Figure 3-a) and 2,4-dichlorophenoxy butanoic acid (Figure 4-a) solutions were also similar to each other.

The effect of the irradiation dose in kGy on the different concentrations of (4-CPA), (2,4-D), (2,4-DP), and (2,4-DB) solutions was studied. (4-CPA), (2,4-D), (2,4-DP), (2,4-DB) solutions at (3–75) mg/L concentrations were subjected to different irradiation doses at 0.14 kGy/h dose rate in air. The decrease in absorbance at maximum wavelengths and per cent degradation versus irradiation doses at different concentrations are shown in Figures1-b, 2-b,3-b, and 4-b and Figures 1-c, 2-c, 3-c, and 4-c.

The pH values of the unirradiated and irradiated solutions are given in Tables 1, 2, 3, and 4. When the maximum absorbance or the per cent degradation (%) of four pesticide solutions which have different concentrations are compared with each other, the increase in the per cent degradation (%) was more rapid for the lower concentration (3mg/L) of pesticide solutions than for the higher concentrations.

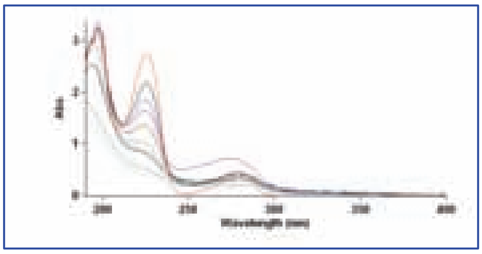


FIG. 1-a. Absorption spectra of unirradiated and irradiated 4-CPA solutions. [4-CPA]:50mg/L. (λ_{max} = 224 nm) Dose rate: 0.07 kGy/h.

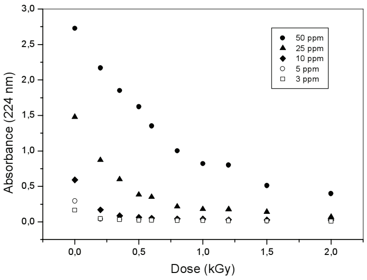


FIG. 1-b. The decrease in absorbance as a function of irradiation dose(kGy) atvarious concentrations of 4-CPA in air. Dose rate: 0.07 kGy/h.

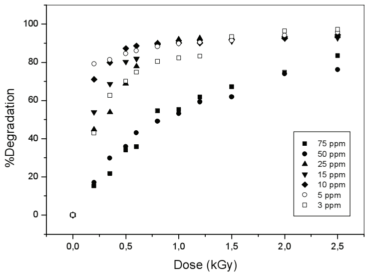


FIG. 1-c. The per cent degradation as a function of irradiation dose (kGy) at various concentrations of 4-CPA in air. Dose rate: 0.07 kGy/h.

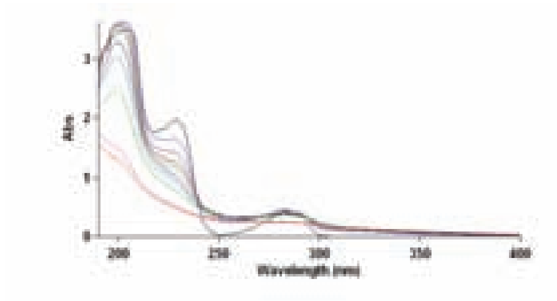


FIG. 2-a. Absorption spectra of unirradiated and irradiated 2,4-D solutions. [2,4-D]: 75 mg/L. (λ_{max} = 228 nm) Dose rate: 0.07 kGy/h.

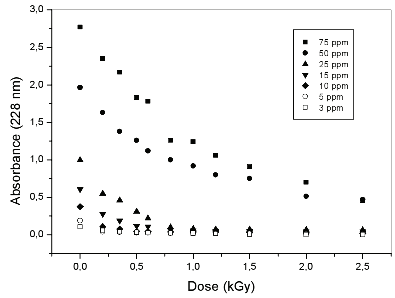


FIG 2-b. The decrease in absorbance as a function of irradiation dose(kGy) at various concentrations of 2,4-D in air. Dose rate: 0.07 kGy/h.

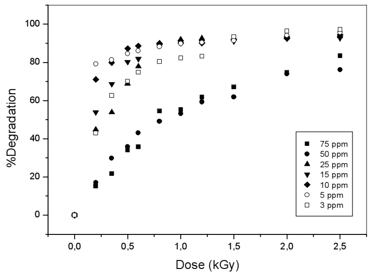


FIG. 2-c. The per cent degradation as a function of irradiation dose (kGy) at various concentrations of 2,4-D in air. Dose rate: 0.07 kGy/h.

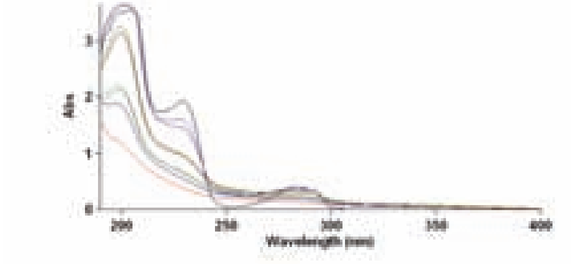


FIG. 3-a. Absorption spectra of unirradiated and irradiated 2,4-DP solutions. [2,4-DP]:50mg/L. (λ_{max} = 228 nm) Dose rate: 0.07 kGy/h.

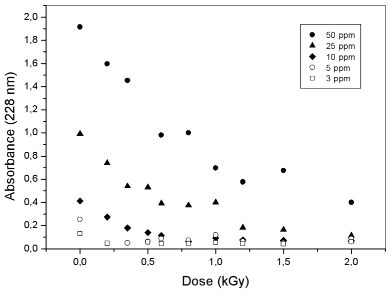


FIG. 3-b. The decrease in absorbance as a function of irradiation dose(kGy) at various concentrations of 2,4-DP in air. Dose rate: 0.07 kGy/h.

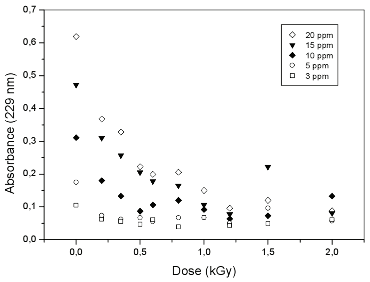


FIG. 3-c The per cent degradation of as a function of irradiation dose(kGy) at various concentrations of 2,4-DP in air. Dose rate: 0.07 kGy/h.

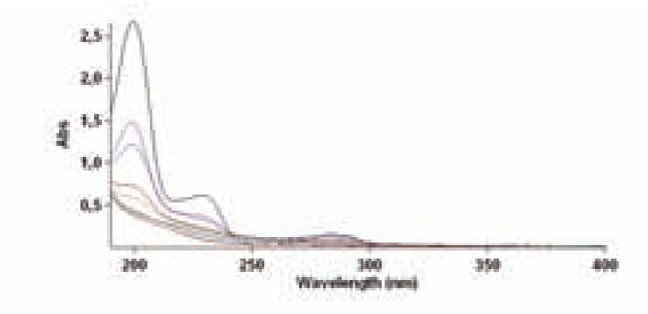


FIG. 4-a Absorption spectra of unirradiated and irradiated 2,4-DB solutions. [2,4-DB]:50mg/L. (λ_{max} = 229 nm) Dose rate: 0.07 kGy/h.

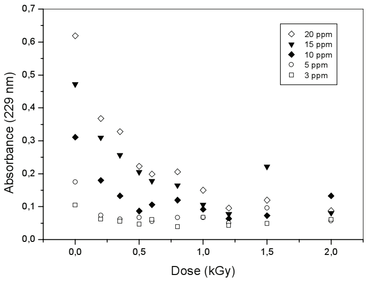


FIG. 4-b. The decrease in absorbance as function of irradiation dose(kGy) at various concentrations of 2,4-DB in air. Dose rate: 0.07 kGy/h.

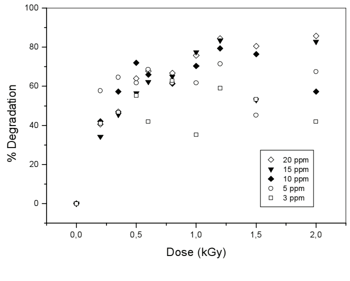


FIG. 4-c The per cent degradation as a function of irradiation dose(kGy) at various concentrations of 2,4-DB in air. Dose rate: 0.07 kGy/h.

TABLE 1. THE CHANGE OF pH AS A FUNCTION OF IRRADIATION DOSE (kGy) AT VARIOUS CONCENTRATIONS OF 4-CPA IN AIR. DOSE RATE: 0.07 kGy/h

	Concentration (ppm)				
	50	**25**	**10**	**5**	**3**
0.00	3,85	4,10	4,64	5,19	5,92
0,20	3,69	4,12	4,80	5,74	6,22
0,35	3,54	3,94	4,72	6,07	5,94
0,50	3,54	3,85	5,09	5,64	5,22
0,60	3,46	3,79	4,16	5,12	6,13
0,80	3,45	3,72	3,98	4,62	5,72
1.00	3,38	3,74	3,97	4,20	4,76
1,20	3,40	3,63	3,94	4,58	5,54
1,50	3,34	3,64	3,99	4,39	4,95
2.00	3,85	3,52	3,91	4,35	4,71

TABLE 2. THE CHANGE OF pH AS A FUNCTION OF IRRADIATION DOSE(kGy) AT VARIOUS CONCENTRATIONS OF 2,4-D IN AIR. DOSE RATE: 0.07 kGy/h

Dose (kGy)	**Concentration (ppm)**						
	75	**50**	**25**	**15**	**10**	**5**	**3**
0,0	3,87	3,90	4,15	4,43	4,91	5,60	5,90
0,20	3,44	3,67	3,75	4,26	5,24	5,70	6,33
0,35	3,49	3,54	3,75	3,92	4,56	5,01	6,1
0,50	3,40	3,60	3,57	3,78	3,99	4,65	6,01
0,60	3,42	3,47	3,66	3,82	4,06	5,86	5,93
0,80	3,28	3,58	3,57	3,65	3,92	4,42	5,64
1.00	3,31	3,43	3,52	3,76	4,87	5,45	6,05
1,20	3,19	3,42	3,53	3,70	3,91	4,46	4,97
1,50	3,19	3,40	3,52	3,71	3,92	5,23	5,93
2.00	3,27	3,34	3,49	3,67	3,83	4,29	4,22
2,50	3,12	3,32	3,51	3,72	3,98	4,37	4,54

TABLE 3. THE CHANGE OF pH AS A FUNCTION OF IRRADIE DOSE (kGy) AT VARIOUS OF 2.4-DP IN AIR. DOSE RATE: 0.07 kGy/h.

Dose (kGy)	**Concentration (ppm)**				
	50	**25**	**10**	**5**	**3**
0.00	4,16	4,62	5,34	6,15	6,15
0,20	3,75	4,11	4,38	4,94	4,75
0,35	3,72	3,89	4,26	4,33	5,03
0,50	3,67	3,83	4,02	4,21	4,32
0,60	3,54	3,77	4,02	4,27	4,41
0,80	3,64	3,88	4,11	4,63	4,48
1.00	3,53	3,80	4,08	4,34	4,34
1,20	3,49	3,67	4,01	4,21	4,20
1,50	3,49	3,67	3,99	4,14	4,37
2.00	3,39	3,65	3,99	4,08	4,12

TABLE 4. THE CHANGE OF pH AS A FUNCTION OF IRRADIATION DOSE(kGy) AT VARIOUS CONCENTRATIONS OF 2,4-DB IN AIR. DOSE RATE: 0.07 kGy/h

Dose (kGy)	Concentration (ppm)				
	20	15	10	5	3
0.00	5,33	5,50	6,02	6,47	6,67
0,20	4,43	4,49	4,50	4,62	4,98
0,35	4,18	4,23	4,26	4,50	4,52
0,50	3,97	4,18	4,23	4,42	4,50
0,60	3,98	4,10	4,26	4,44	4,37
0,80	4,09	4,20	4,23	4,38	4,52
1.00	4,00	4,07	4,19	4,40	4,43
1,20	3,91	3,96	4,10	4,20	4,23
1,50	3,93	3,97	4,10	4,27	4,39
2.00	3,91	3,96	4,10	4,20	4,23

A 50 ppm (2.26×10^{-4} mol L^{-1}) 2,4-Dichlorophenoxy acetic acid (2,4-D) sample was prepared in deionized water. The herbicide sample (200 ml of 50 ppm) was irradiated in open bottles up to the required dose at 0.07 kGy/h dose rate at ambient conditions. For preconcentration and to extract intermediates and undecomposed herbicides from aqueous media to organic phase, solid phase extraction method was used. Samples of 200 milliliters irradiated aqueous were eluted from C18, or diol cartridges, and organic phase extraction was applied with 2 milliliters of acetone, hexane or dichloro methane. For determination of acidic groups, such as undecomposed herbicides, methyl alcohol was used for organic phase extraction. The analytes that include carboxylic acid groups cannot be observed in GC-MS system; thus, the derivatives of these groups, such as methyl esters, have to be injected into the system. These groups were converted to methyl esters in methyl alcohol with excess concentrated sulphuric acid, and methyl esters were extracted into hexane for injection into GC-MS system.

The EPA 8151 method was used for the determination of intermediates and methyl esters of undecomposed herbicides in the GC-MS system. Intermediates and methyl esters of undecomposed herbicides are inejected into the GC-MS system with a split ratio of 50. The injector temperature is 270^0C.

Figure 5 shows the GC/MS/MS chromatogram and mass spectrum of the methyl ester of the unirradiated 2.4-dichloro phenoxy acetic acid after solid-phase extraction in acetone. GC/MS/MS chromatogram of the standard of phenol mixtures is given in Figure 6 and 6-a. In the Figures 7 and 7-a and the Figures 8 and 8-a, the GC/MS/MS chromatograms and mass spectra of the 0.2 and 2.5 kGy irradiated 2,4-dichloro phenoxy acetic acid after solid-phase extraction in acetone and probable degradation products from the irradiated samples are given.

We decided to investigate two regions of groundwater — Antalya and Bolu which are the agricultural and greenhouse regions. The groundwater samples were analyzed by HPLC. It was observed that the pesticides and degradation products are similar to each other. The results are given in Figures 9, 10 and 11.

One of the degradation products from the irradiated 2,4-D samples is 2,4-dichlorophenol. The amount of 2,4-dichlorophenol (2,4-DCP) was determined at various doses from 0 to 2,6 kGy. The areas of the peaks in gas chromatography were calculated for calibration and for sample analysis. The internal standard method was used to determine the amounts of 2,4-DCP. Methyl ester of 2,4-dichloro phenoxy propionic acid (2,4-DP) was used as an internal standard if the irradiated sample is 2,4-D. It was investigated that irradiation of $2{,}26 \times 10^{-4}$ mol L^{-1} 2,4-D decomposes to 2,4-DCP as one of the intermediates. Up to a dose of 0.6 kGy, an increase in the amount of 2,4-DCP was observed. Further irradiation doses, 2,4-DCP also decomposed but not linearly. At 2.6 kGy, the amount of 2,4-DCP was

0,39 × 10^{-5} mol L^{-1}; the ratio of amount of 2,4-DCP at 2.6 kGy to the amount of 2,4-DCP at 0.6 kGy is 0.043 (4.3%). These results are given in Figure 12. From these results, it can be estimated that irradiation of 2,4-D decomposes the herbicide, and form intermediates after irradiation which can also be hazardous. Sometimes intermediates may be more toxic than herbicides. To achieve this investigation, it is necessary to irradiate the aqueous herbicide sample more to decompose these toxic intermediates and further irradiation results in the decomposition of these toxic intermediates.

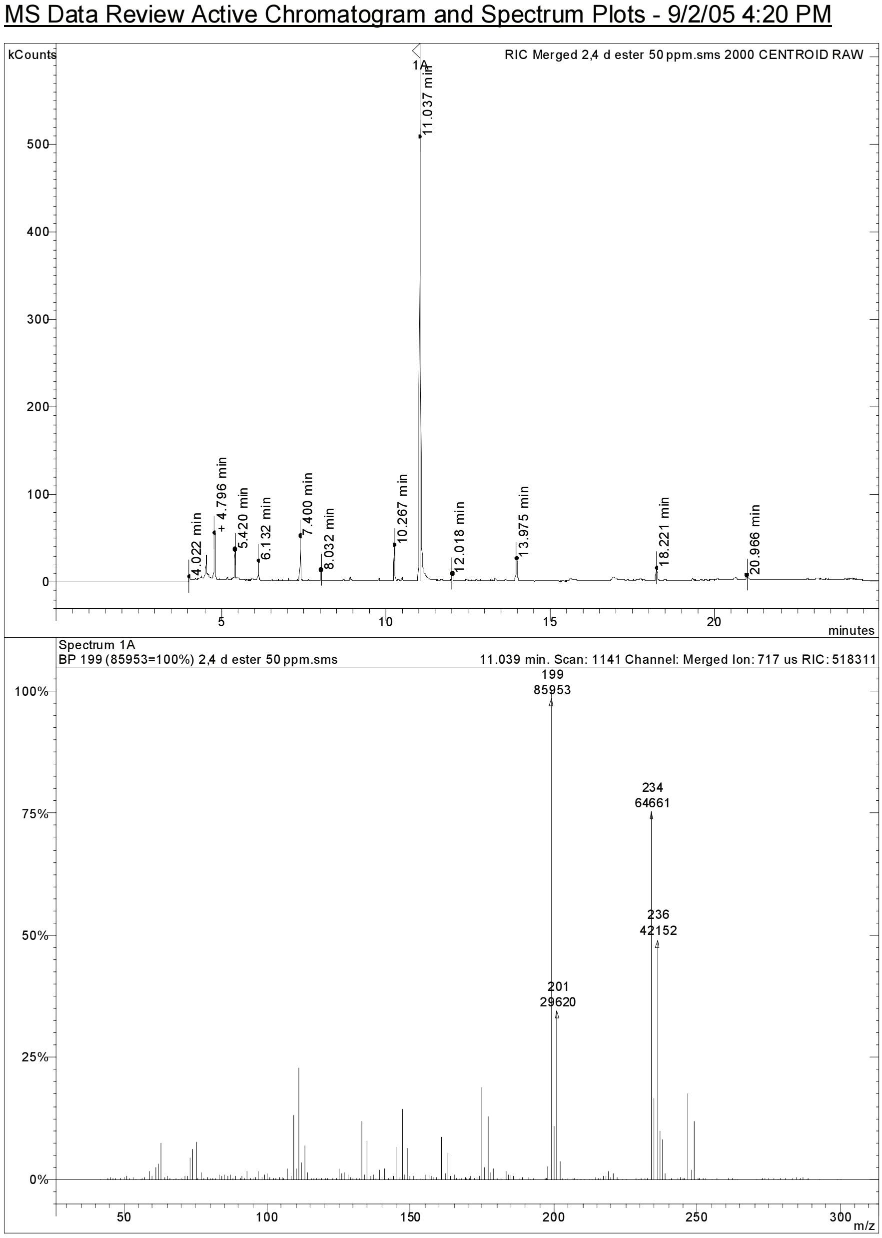


FIG. 5. GC/MS/MS chromatogram and mass spectrum of the methyl ester of the unirradiated 2.4-dichloro phenoxy acetic acid after solid-phase extraction in acetone.

Chromatogram Plot

File: g:\estimation\mix.phenols new1.sms
Sample: mix.phenols new   Operator:
Scan Range: 1 - 2715 Time Range: 0.00 - 22.99 min.   Date: 18.04.2006 17:07

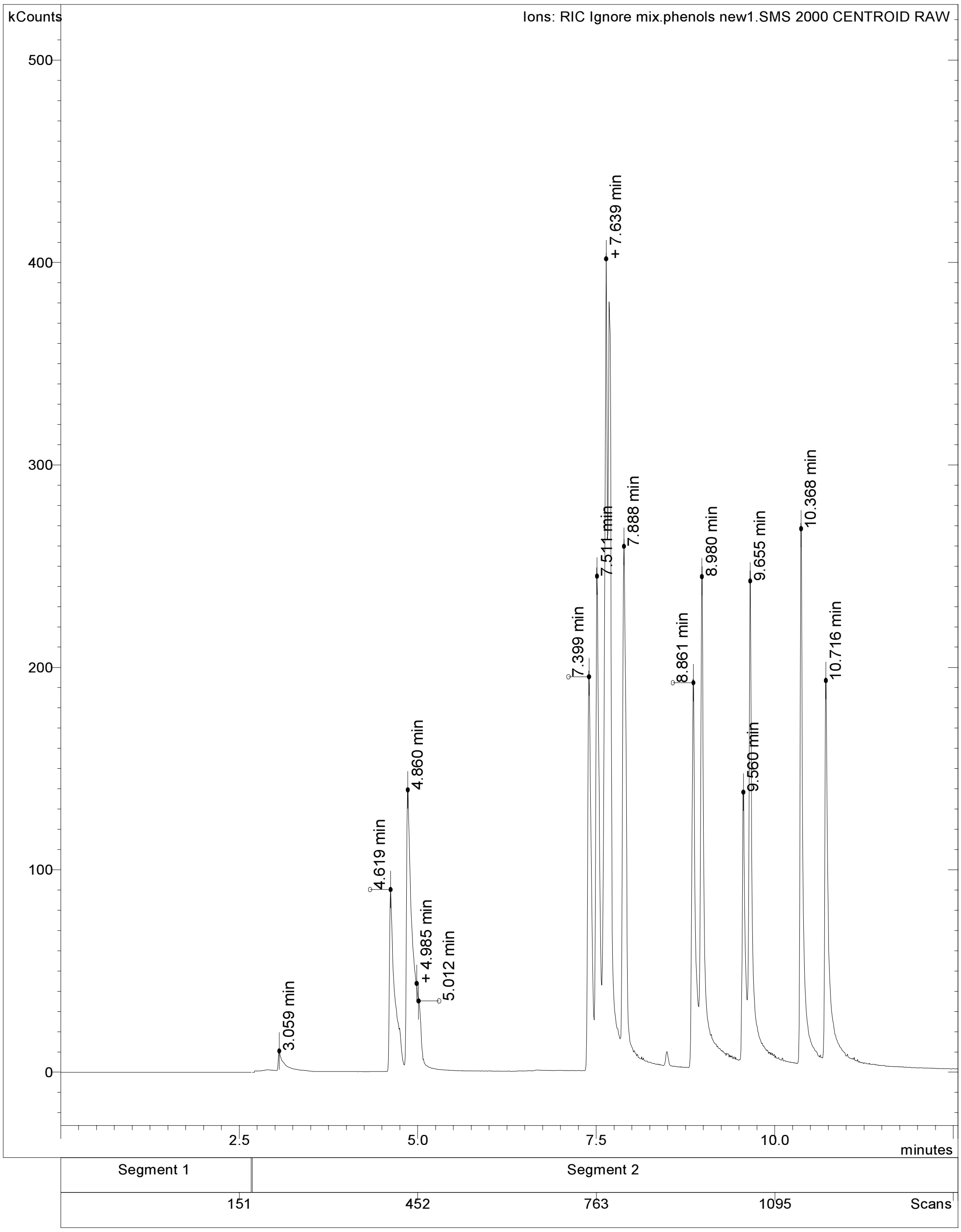
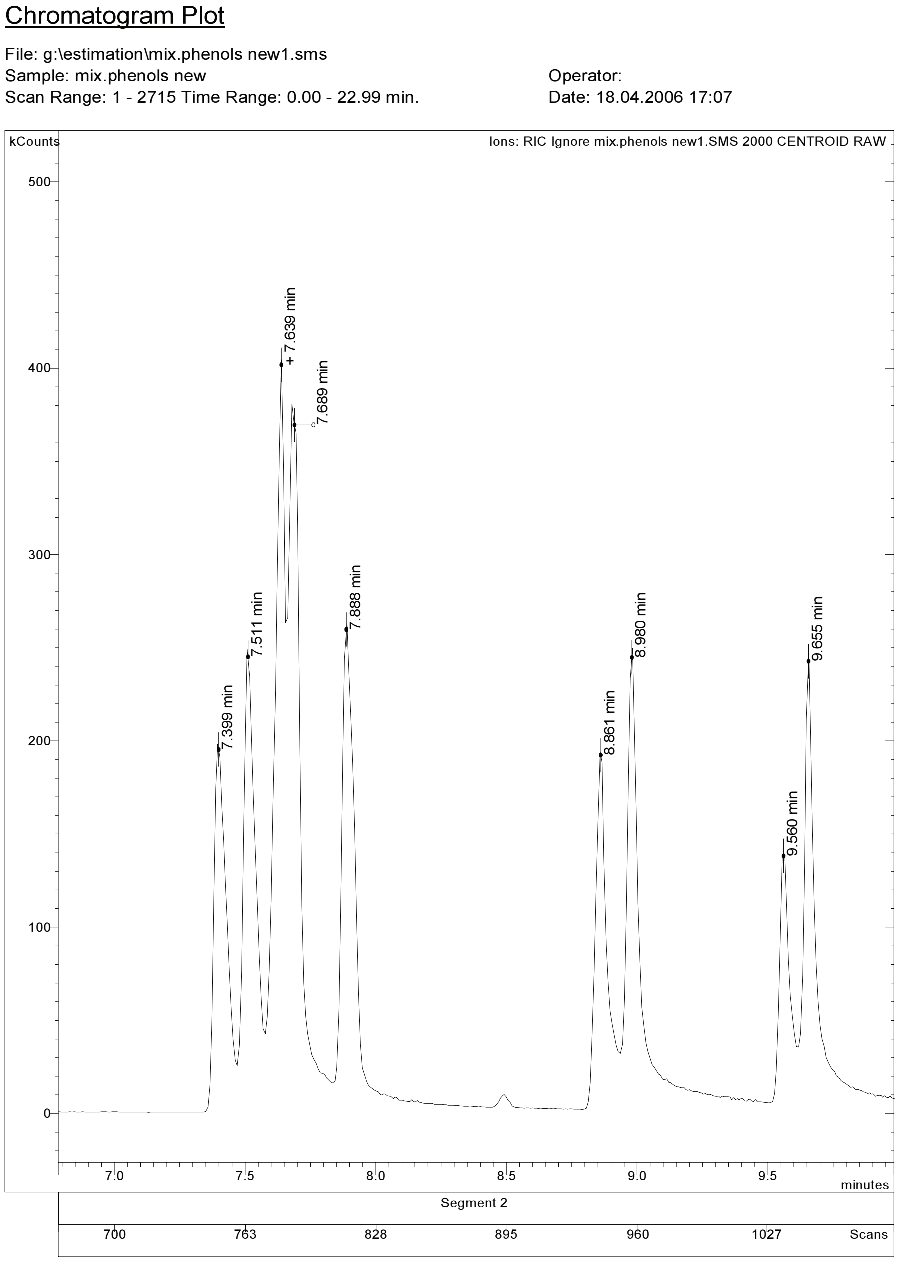


FIG. 6. GC/MS/MS chromatogram of the standard of phenol mixtures.

RETENTION TIME (min)	NAME OF THE STANDARD
4.619	Phenol
4.860	2-Chloro phenol
7.399	2,3-Dichlorophenol
7.511	2,4-Dichlorophenol
7.639	Catechol
7.689	4-Chlorophenol and 3-Chlorophenol
7.888	2,6-Dichlorophenol
8.861	Resorcinol
8.980	4-Bromophenol
9.560	4-Chloro resorcinol
10.368	3,5-Dichlorophenol
10.716	3,4-Dichlorophenol



Chromatogram Plot

File: g:\estimation\mix.phenols new1.sms

Sample: mix.phenols new

Operator:

Scan Range: 1 - 2715 Time Range: 0.00 - 22.99 min.

Date: 18.04.2006 17:07

FIG. 6-a. GC/MS/MS chromatogram of the standard of phenol mixtures. The amounts of all standards are 50 ppm except resorcinol(170 ppm) and catechol(220 ppm).

Chromatogram Plot

File: g:\estimation1\0,2 kgy.sms
Sample: 0,2 kGy
Scan Range: 1 - 2776 Time Range: 0.00 - 22.99 min.

Operator:
Date: 21.04.2006 17:14

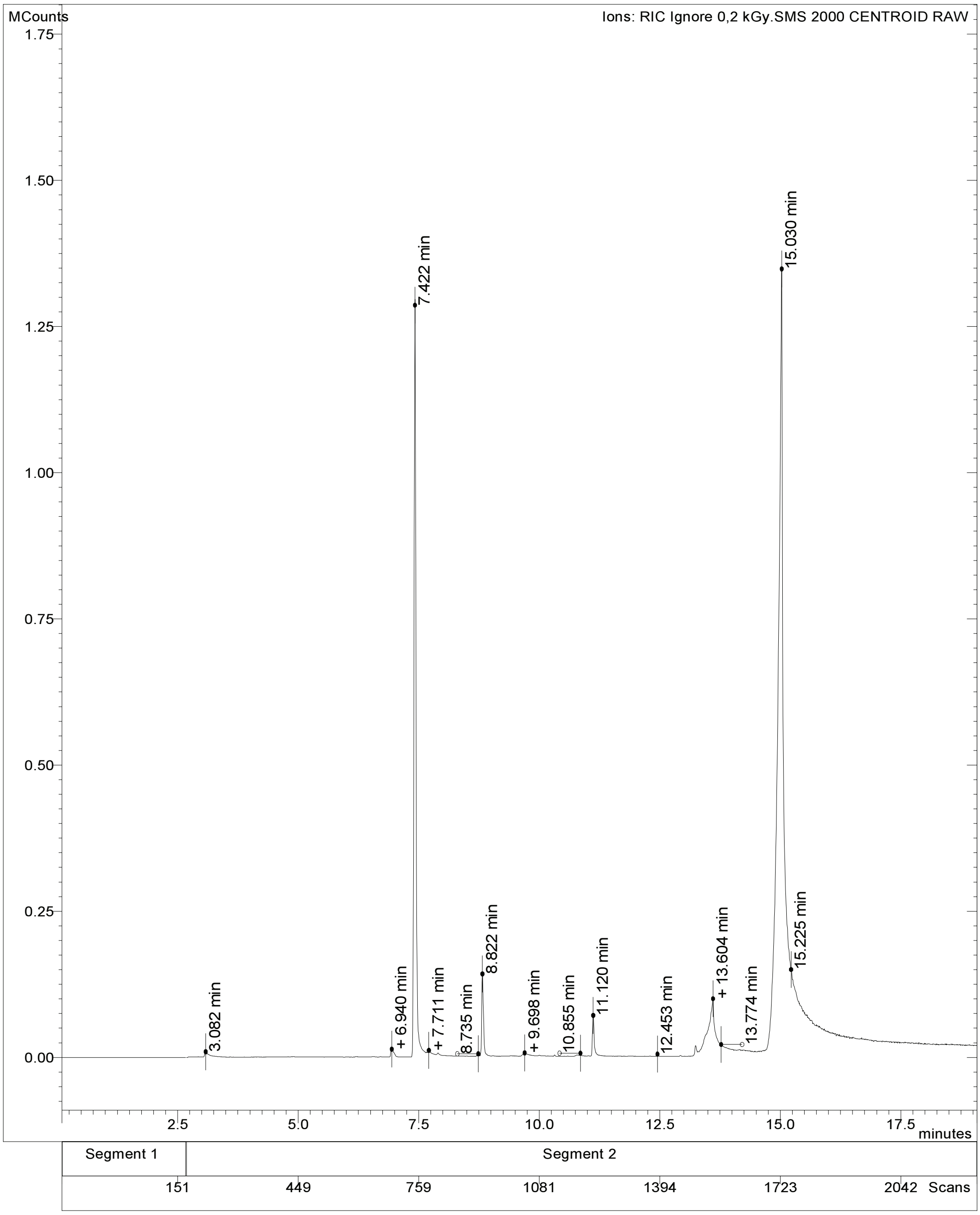
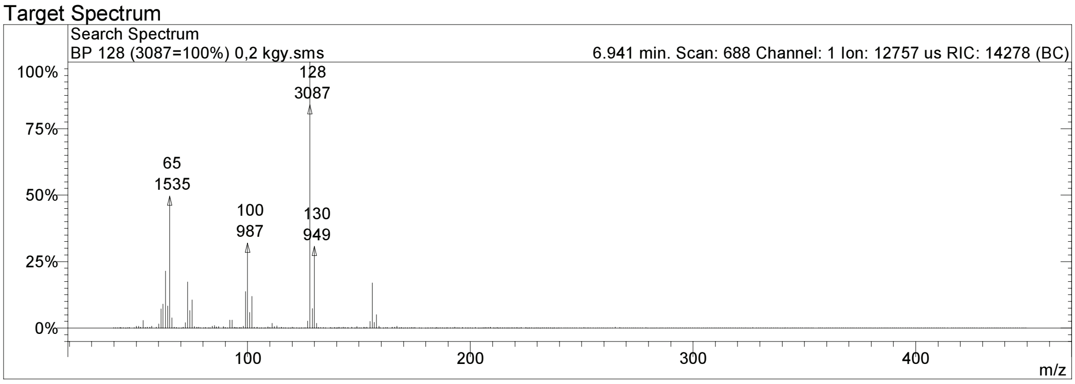


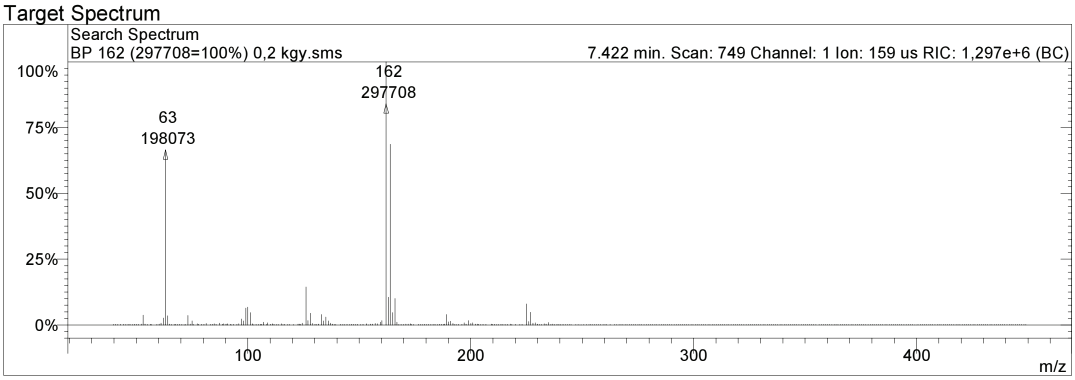
FIG. 7. GC chromatogram of the 0.2 kGy irradiated 2,4-dichloro phenoxy acetic acid (50 ppm) samples after the eluted from C18 cartridges in acetone.

Target Spectrum



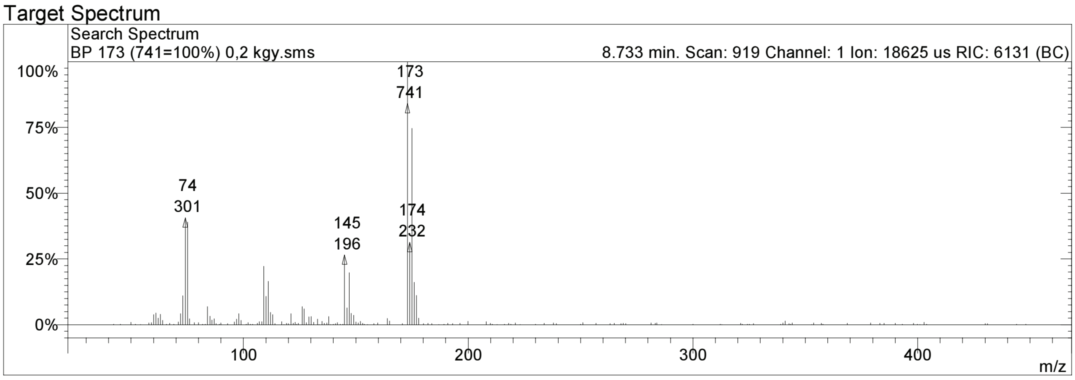
Spectrum from g:\estimation1\0,2 kgy.sms
Scan No: 688, Time: 6.941 minutes

Target Spectrum



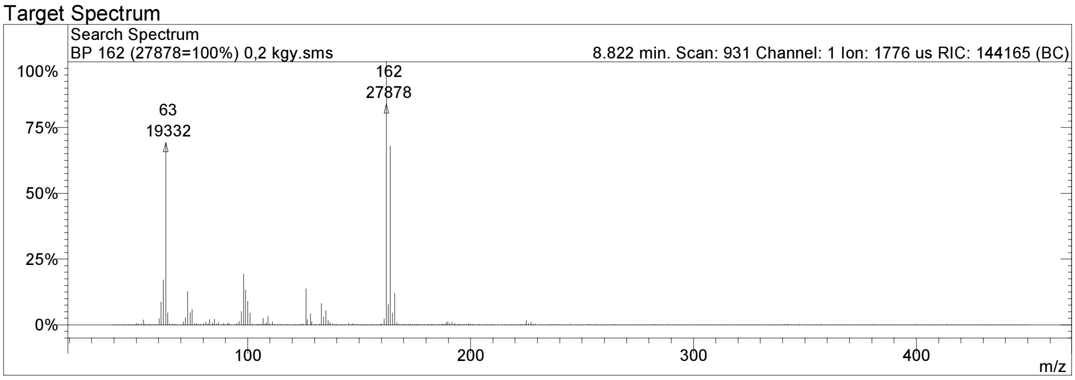
Spectrum from g:\estimation1\0,2 kgy.sms
Scan No: 749, Time: 7.422 minutes

Target Spectrum

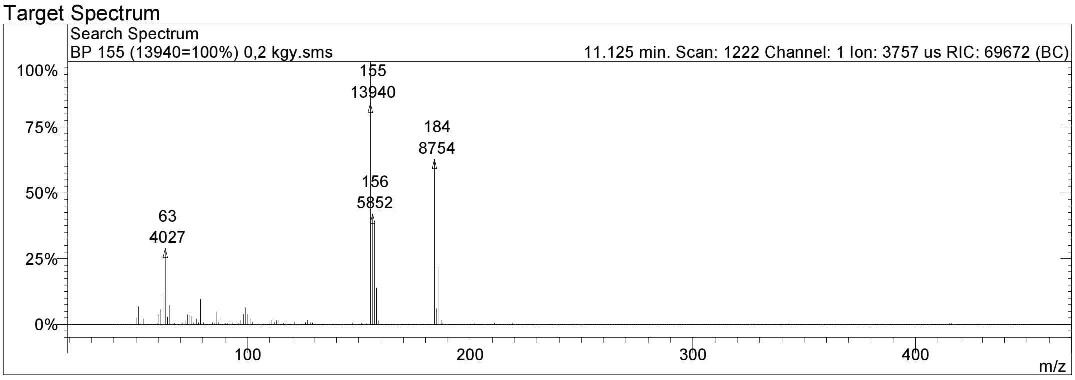


Spectrum from g:\estimation1\0,2 kgy.sms
Scan No: 919, Time: 8.733 minutes

Target Spectrum



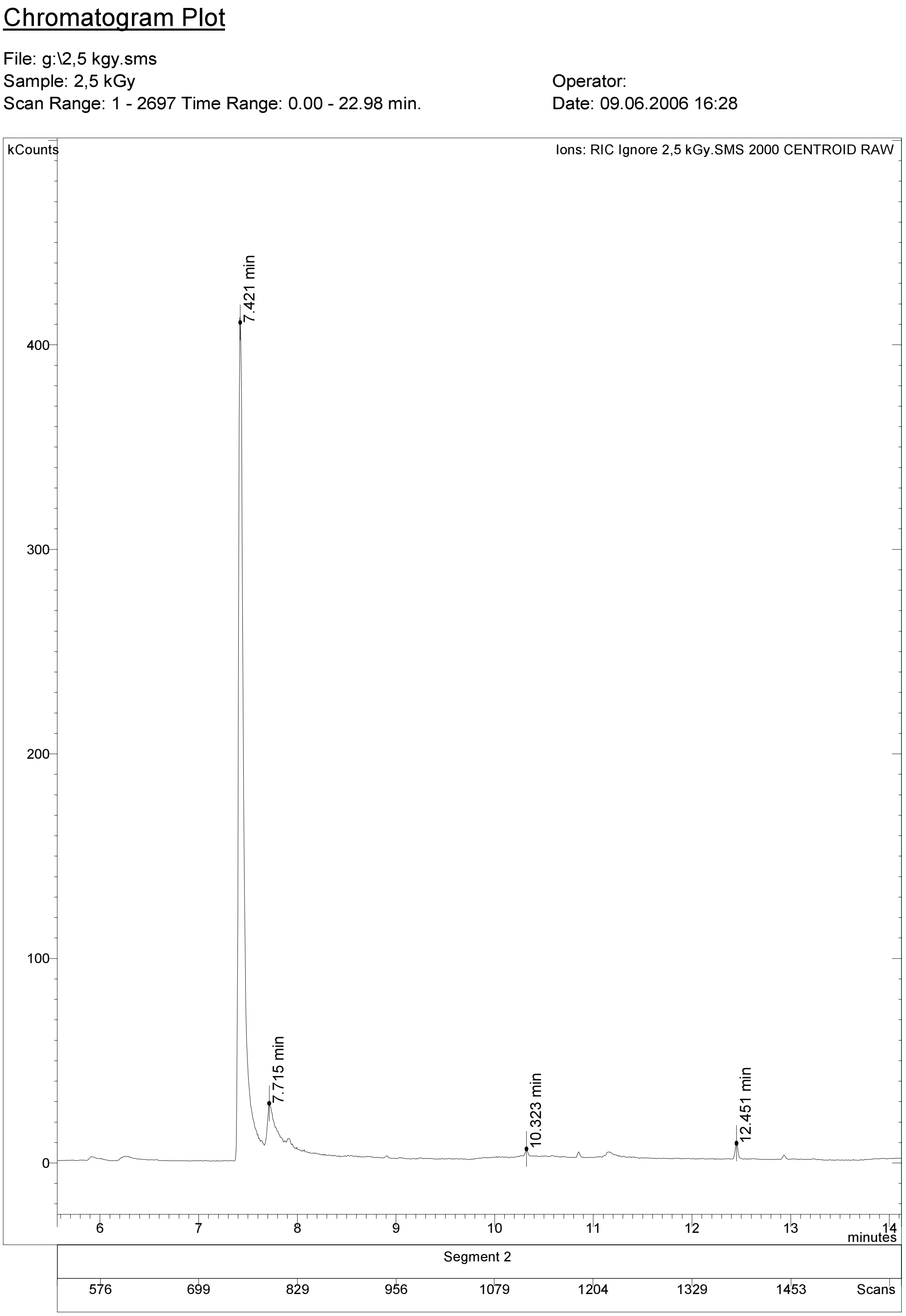
Spectrum from g:\estimation1\0,2 kgy.sms
Scan No: 931, Time: 8.822 minutes



Spectrum from g:\estimation1\0,2 kgy.sms
Scan No: 1222, Time: 11.125 minutes

FIG. 7-a. Mass spectra of the 0.2 kGy irradiated 2.4-dichloro phenoxy acetic acid (50 ppm) samples after the eluted from C18 cartridges in acetone and probable degradation products.

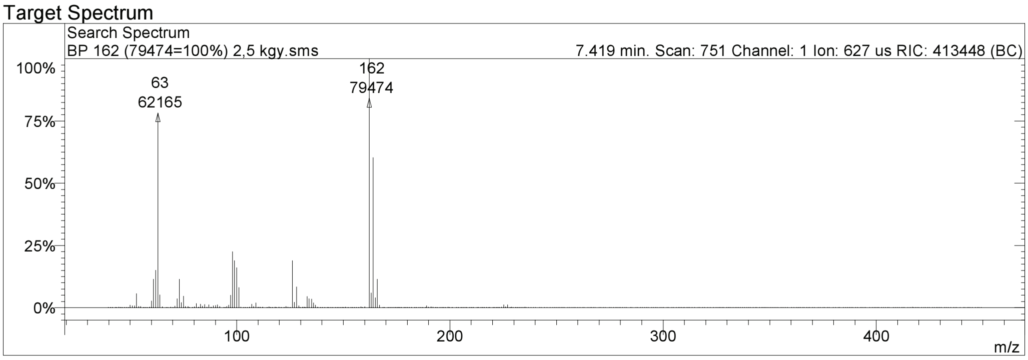
RETENTION TIME (min.)	COMPOUND
6.940	1-chloro-4-ethoxy benzene
7.422	2,4-Dichlorophenol
8.733	2,4-dichlorobenzaldehyde or 2,3-dichlorobenzaldehyde
8.822	2,5-Dichlorophenol
11.125	5-chloro,1-3 benzodioxole
13.064	Residue of 2,4-D decomposed with heat
15.030	Residue of 2,4-D decomposed with heat



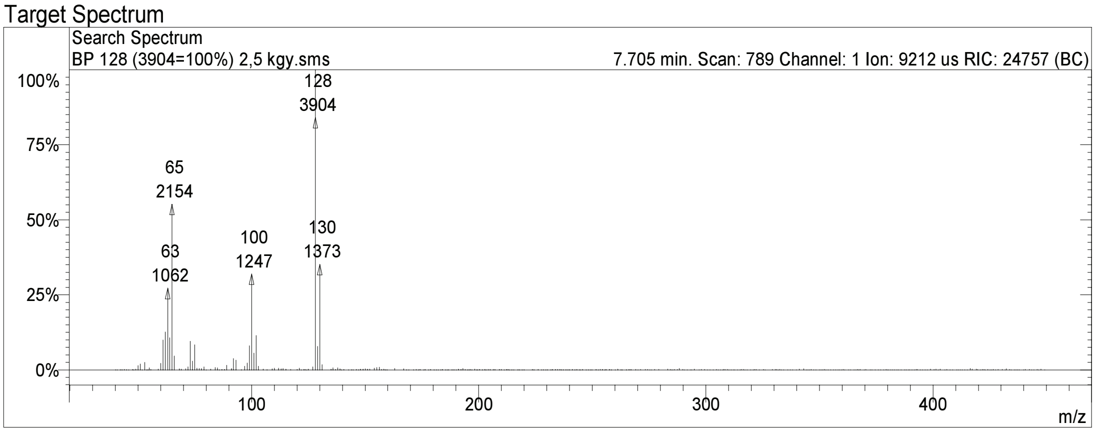
Chromatogram Plot

File: g:\2,5 kgy.sms
Sample: 2,5 kGy
Operator:
Scan Range: 1 - 2697 Time Range: 0.00 - 22.98 min.
Date: 09.06.2006 16:28

FIG. 8. GC chromatogram of the 2.5 kGy irradiated 2.4-dichloro phenoxy acetic acid (50 ppm) samples after the eluted from C18 cartridges in acetone.



Spectrum from g:\2,5 kgy.sms
Scan No: 751, Time: 7.419 minutes



Spectrum from g:\2,5 kgy.sms
Scan No: 789, Time: 7.705 minutes

FIG. 8-a. Mass spectra of the 2.5 kGy irradiated 2.4-dichloro phenoxy acetic acid (50 ppm) samples after the eluted from C18 cartridges in acetone and probable degradation products.

RETENTION TIME (min.)	COMPOUND
7, 421	2,4-Dichlorophenol
7,715	3-chlorophenol and 4-chlorophenol

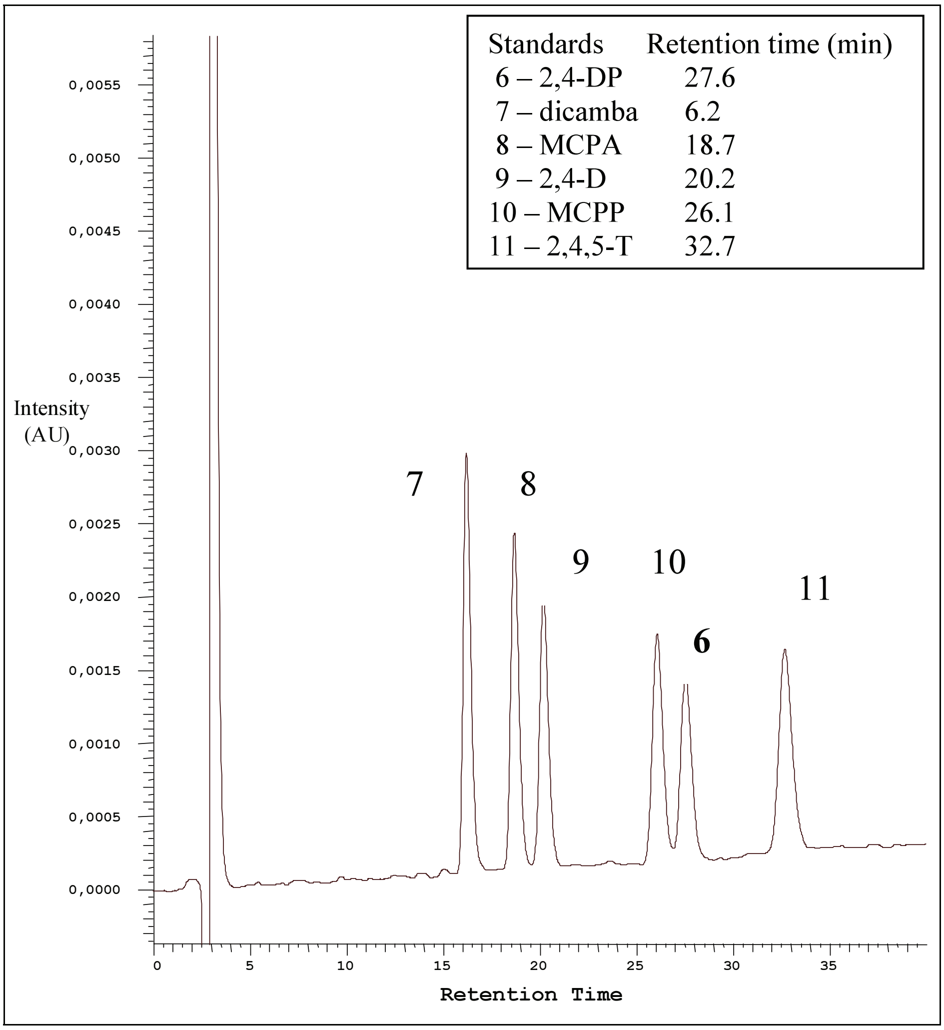


FIG. 9. Chromatogram of standard mixture of herbicides.

Standards:
MCPP (also known as Mecoprop):

(RS) 2-methyl-4-chlorophenoxy propionic acid from Riedel del Haen (Cat.No. 36147)

2,4-DP:
2-(2,4-dichlorophenoxy) propionic acid from Aldrich (Cat.No. 26,187-4)

Samples:
50 mL water sample acidified with acetic acid was preconcentrated on Waters Oasis HLB sorbent and eluted with 1 mL methanol. 40 µl eluate was injected into HPLC system.

Chromatographic conditions:
Column Phenomenex C18, 250x4.6 mm
Isocratic elution with 26 mM acetic acid and acetonitrile (60:40%).
Flow-rate 1 mL/min, UV detection at 280 nm.

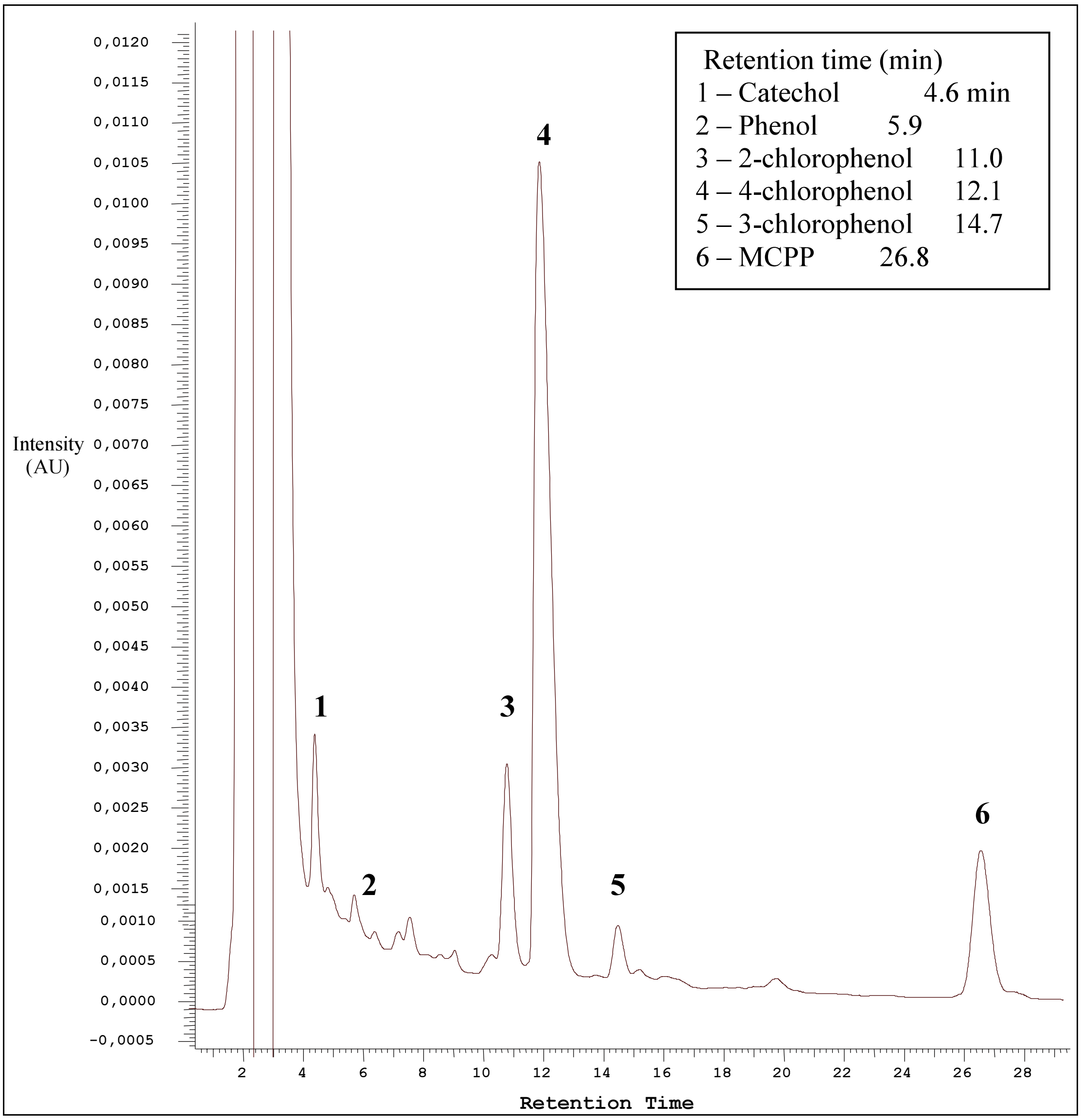


FIG. 10. Chromatogram of water sample from Antalya.

Quantitative results

Analyte	**Concentration (ppb)**
MCPP	28.0
3-chlorophenol	6.0
4-chlorophenol	13.0
2-chlorophenol	34.0
Phenol	6.0
Catechol	32.0

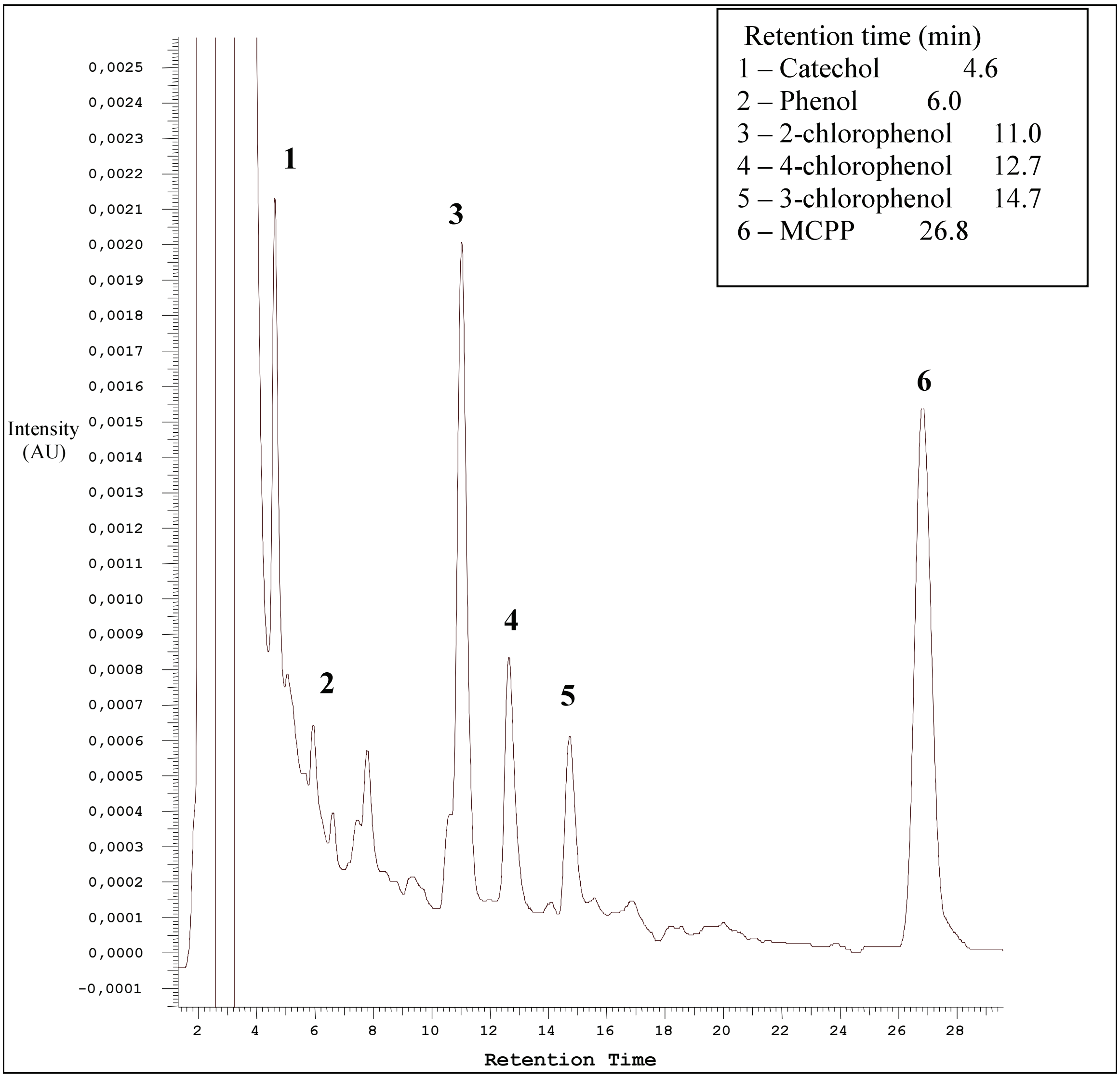


FIG. 11. Chromatogram of water sample from Bolu.

Quantitative results

Analyte	Concentration (ppb)
MCPP	30.0
3-chlorophenol	8.0
4-chlorophenol	172.0
2-chlorophenol	38.0
Phenol	9.0
Catechol	46.0

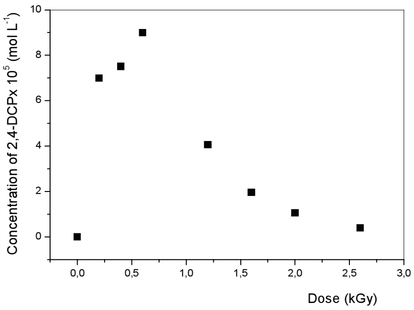


FIG. 12. The concentration of degradation product (2,4-DCP) as a function of irradiation dose. Dose rate: 0.07 kGy/h.

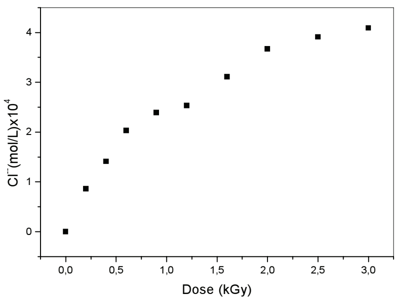


FIG. 13. The concentration of free chloride ions as a function of irradiation dose. Dose rate: 0.07 kGy/h. $[2,4\text{-}D]_{initial}$= 50 ppm, $[Cl^-]$= 16.06ppm at 0 kGy, $[Cl^-]$= 1.53ppm at 3.0 kGy

Irradiation of 2,4-D also results in the cleavege of chlorine atoms from the herbicide or from the intermediates. Free chloride ions were observed in the aqueous medium after irradiation. Chloride ions were determined at various doses from 0 to 2 kGy. The chloride electrode (Thermo Ion-plus sure flow chloride electrode) was used for calibration and for analysis of chloride ions after irradiation. It is observed that the free chloride ions in the solution increase with dose. At 2 kGy irradiation dose, 81% of the chlorine atoms in the herbicide were cleaveged. The yield of $Cl^-$was taken as an indicator for the decomposition process. The irradiation-induced decomposition process was investigated in the presence of air and was followed by determination of the formed Cl yield. The dose dependence of the Cl splitting is shown in Figure 13. The per cent degradation can be determined in this indirect method and the results are given in Figure 13. The amount of removed chloride ions is 90.5% at 3.0 kGy irradiation dose. A further irradiation may increase the amount of free chloride ions and decreases the toxicity. Sometimes, chlorinated organic compounds are more toxic than non-chlorinated organic compounds.

All decomposition products possessing (aldehydes) were determined by using spectrophotometric methods (Figure 14) and presented as aldehyde in Figure 15. The formation of acids [21], as well as aldehydes (total amount determined by titration), was also followed. The formation of the total acid is shown in Figure 16 as a function of an absorbed dose. We can say that GC/MS/MS results show that after the irradiation, 2,4-dichloro phenoxy acetic acid formed the 2,4-dichlorophenol compound and similar compounds. According to these results, we will try to investigate the amount of the by-products and determine the similar products by using a GC/MS/MS spectrometer.

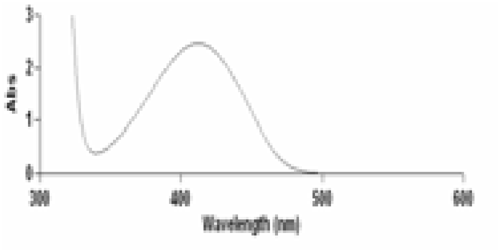


FIG. 14. Light-Absorption spectra of formaldehyde complex. λ_{max} = 412 nm

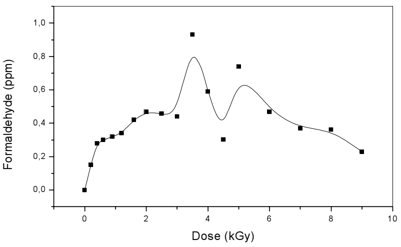
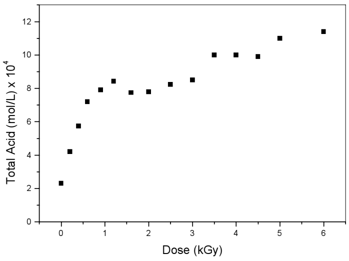


FIG. 15. Formaldehyde formation from irradiated 2,4-D solutions (50 ppm) as a function of dose.



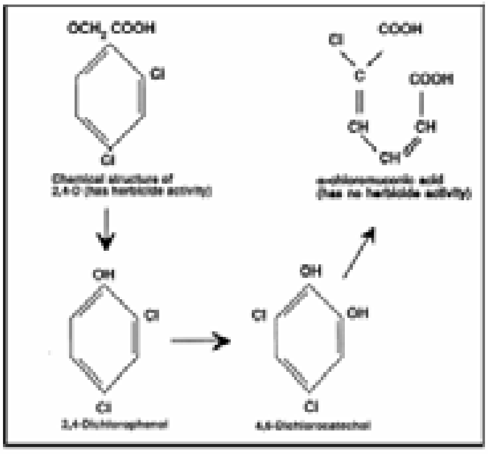


FIG. 16. The amount of total acid from irradiated 2,4-D solutions (50 ppm) as a function of dose.

5. CONCLUSIONS

The degradation of pesticides in aqueous solutions by gamma irradiation has been demonstrated. The pesticide solutions are very easily degraded by gamma irradiation, which may be promising for the treatment of groundwater containing herbicides. Degradation of pesticide solutions can be carried out, but the necessary dose varies with the type of the herbicide. The objective of this work was to do a preliminary study on the presence of phenoxyacid types of herbicides in a predominantly agricultural, livestock and industrial region developing in Turkey and to develop quantitative methods for the analysis of representative herbicides and their transformation products. The analysis of herbicide residues in water is typically done by gas chromatography and high-performance liquid chromatography. Using the determination of the intermediate products and final products, it was possible to better understand the interaction of herbicides and e^-_{aq},OH, and H. species. We can then suppose the degradation mechanism. The probable degradation of 2,4-D herbicides can be given in the above.

REFERENCES

[1] ROCK, J.J., Formation of haloforms during chlorination of natural waters, Water Treat.Exam., 23(2) (1974) 234.
[2] HUTZINGER, O., SAFE, S., ZITKO,V., The chemistry of polychlorinated Triphenyls. CRC.Press, Boca Raton, Fla.,USA (1974).
[3] FISHBEIN, L., Potential Industrial Carcinogens and mutagens, Elsevier, Amsterdam (1979).
[4] TROBEL, K., DIETER, H.J., Toxikological pick-benefit aspects of drinking water chlorination and of alternative deinfection procedures. Z.Wasser Abwasser Forsch, 23 (1990) 150.

[5] ROSELL, M.G., OBIOLS, J., BERENGUER, M.J.,GUARDINO, X., LOPEZ, F., BROSA, J., J. J. Chromatogr. A., 655 (1993) 151.

[6] LIU, Z., SIRIMANNE, SR., PATTERSON, DG., Needham,LLAnalytical Chem., 66 (1994) 3086.

[7] BUCHOLSKI, KA., BEGEROW, J., WINNEKE, G., DUNEMANN, L., J.Chromatogr. A 754 (1996) 479.

[8] KANJA, LW., SKAAVE, JU., OJWANG, SBO., MAITAI, CK., Arch.Environ.Contam.Toxicol. 22 (1992) 21.

[9] ALAWI, MA., AMMARI, N., ALSHURAIKI, Y., Arch.Environ.Contam.Toxicol. 23 (1992) 235.

[10] BORDET, F.,MALLET, J., MAURICE, L., BORREL, S., VENANT, A., Bull.Environ. Contam.Toxicol. 50 (1993), 425.

[11] ARMISHAW, P., MILLAR, RG., J. AOAC Int., 76 (1993) 1317.

[12] RIVAS, A., OLEA, N., OLEA-SERRANO, F., Trends Anal.Chem.,16 (1997) 613.

[13] KRAUTHACKER, B., ROMANIC, NS. H., REINER, E., Bull. Environ. Contam. Toxicol.,66 (2001) 334.

[14] LEITNER, N.K.V., BERGER, P., GEHRINGER, P., Radiat. Phys. and Chem., 55 (1999) 317–322.

[15] GETOFF, N., SOLAR, S., Radiat. Phys. and Chem., 28 (1986) 443–450.

[16] Kurucz, C.N., Waıte, T.D., Cooper, W.J., Nickelsen, M.G., Radiat. Phys. and Chem., 45(5) (1995) 805–816.

[17] COOPER, W.J., CURRY, R., O'SHEA, K., "Environmental Applications of Ionizing Radiation", Wiley, NewYork, (1998) 451–466.

[18] FLORENCE, T.M., "Anal. Chim. Acta", 54(1971) 373.

[19] NASH, T.J., "Biochem.", 55(1973) 416.

[20] BARCELO, D., Occurence handling and chromatographic determination of pesticides in the aquatic environment, Analyst, 116 (1991) 681.

[21] NIST/EPA/NIH Mass Spectral Library, Version 1.6d. Standard Reference Data Programme of the National Institute of Standards and Technology. Department of Commerce: Gaithersburg, MD, (1998).

FREE RADICAL CHEMISTRY OF THE DISINFECTION-BY-PRODUCT CHLOROPICRIN (TRICHLORONITROMETHANE)

W.J. Cooper[1]; S.K. Cole[2], R.V. Fox[3], P.R. Gardinali[4], S.P. Mezyk[5], B.J. Mincher[6], K.E. O'shea[4]

[1]Urban Water Research Center, Department of Civil and Environmental Engineering, University of California, Irvine, Irvine, CA, USA
[2]Civil and Environmental Engineering Department, Old Dominion University, Norfolk, Virginia, USA
[3]Idaho National Laboratory, Chemical Sciences Department — Chemistry, Idaho Falls, Idaho, USA
[4]Department of Chemistry & Biochemistry, Florida International University, University Park, Miami, Florida, USA
[5]Department of Chemistry and Biochemistry, California State University at Long Beach, Long Beach, CA, USA
[6]Idaho National Laboratory, Radiation Physics Group, Idaho Falls, Idaho, USA

Abstract

Absolute rate constants for the free-radical-induced degradation of trichloronitromethane (TCNM), chloropicrin , were determined using electron pulse radiolysis and transient absorption spectroscopy. The rate constants for the hydroxyl radical, $^{\bullet}OH$, and the hydrated electron, e_{aq}^{-} reactions were $(4.97 \pm 0.28) \times 10^{7}$ M^{-1} s^{-1} and $(2.13 \pm 0.03) \times 10^{10}$ M^{-1} s^{-1}, respectively. The mechanisms of the free radical reactions with TCNM were also investigated using ^{60}Co gamma irradiation at various times (absorbed doses). From the measured disappearance of TCNM and the appearance of the major reaction products nitrate and chloride ions, a detailed degradation mechanism was developed. The reaction rate constants and mechanism were combined in a kinetic computer model that was used to describe the major free radical pathways for the destruction of TCNM in solution. These data are applicable to other advanced oxidation/reduction processes.

1. INTRODUCTION

Disinfectants used in water treatment, such as chlorine, chloramines and ozone, react with natural organic matter to form what are collectively referred to as disinfection-by-products (DBPs). One class of DBPs, which was the focus of recent reports, are the halonitromethanes (HNMs) [1]. Of the HNMs, trichloronitromethane, (Cl_3CNO_2, chloropicrin, TCNM) appears to be the most common. Formation of TCNM occurs during the chlorination of water and in the presence of nitrite ion [2]. Ozonation and chlorination affect TCNM concentrations and it has been found as high as 6.5 nM when pre-ozonation was followed by chloramination.

Therefore, the objective of this study was to explore the utility of advanced oxidation/reduction processes for the treatment of TCNM in water. Of particular interest were the reactions of the hydroxyl radical ($^{\bullet}OH$) and hydrated electrons (e_{aq}^{-}). The bimolecular reaction rate constants for degradation of TCNM from $^{\bullet}OH$ and e_{aq}^{-} were determined using electron pulse radiolysis, while the destruction mechanism and mass balances for the reactions were studied using ^{60}Co γ-radiation. To complete the study, a kinetic computer model was employed with the results compared to experimental observations.

2. MATERIALS AND METHODS

2.1. Chemicals

Solutions of TCNM (Aldrich, Lot No. 04222TB 99.4%, and Lot No. 11320TD 99.8%, used as received, were prepared in ultra-pure deionized filtered water (≥18 MΩ) that was constantly illuminated by a UV lamp to eliminate microbes and maintain organic concentrations below 13 μM, as measured by an on-line TOC analyzer.

Sodium formate (A.C.S., Fisher Scientific Fair Lawn) and oxalic acid disodium salt (Sigma) were used to prepare calibration standards for stable product analyses. All standards and blanks were also prepared using 18 MΩ water.

2.2. Pulse Radiolysis

The radiolysis of water and distribution of products 10^{-7} s after a pulse, for pH range 3 to 11, can be described:

$$H_2O \rightsquigarrow [0.28]\,{}^\bullet OH;\ [0.06]\,H^\bullet;\ [0.27]e_{aq}^-;\ [0.05]H_2;\ [0.07]H_2O_2;\ [0.27]H_3O^+ \quad [1]$$

where, the yield or G value [X] µmol J^{-1} in equation [1] represents the number of each species formed at 10^{-7} seconds after irradiation. The linear accelerator (LINAC) electron pulse radiolysis system at the Department of Energy Radiation Laboratory, University of Notre Dame, was used for bimolecular rate constant measurements. Dosimetry for pulse radiolysis was based on the transient absorbance produced in N_2O-saturated 1.0×10^{-2} M KSCN solution at $\lambda = 475$ nm ($G\varepsilon = 5.2 \times 10^{-4}\ m^2\ J^{-1}$) with doses of 3–5 Gy per 2–3 ns pulse [3].

2.3. Bimolecular Reaction Rates

The oxidation of TCNM by reaction with the hydroxyl radical gave no significant transient absorbance over the range 260–800 nm. Therefore, this radical rate constant determination was performed using SCN^- competition kinetics, based on the competing reactions:

$$^\bullet OH + TCNM \rightarrow \text{products} \quad [2]$$
$$^\bullet OH + SCN^- (+ SCN^-) \rightarrow OH^- + (SCN)_2^{\bullet -} \quad [3]$$

This competition can be analyzed to give the expression:

$$\frac{[(SCN)_2^{\bullet -}]_o}{[(SCN)_2^{\bullet -}]} = 1 + \frac{k_2[TCNM]}{k_3[SCN^-]} \quad [4]$$

where a plot of $1/[(SCN)_2^{\bullet -}]$ against the concentration ratio $[TCNM]/[SCN^-]$ gives a straight line of slope k_2/k_3. Based on the rate constant for hydroxyl radical reaction with SCN^-, $k_3 = 1.1 \times 10^{10}\ M^{-1}\ s^{-1}$, the k_2 rate constant is readily determined [4].

To isolate the reaction of the $^\bullet OH$ with TCNM, aqueous solutions were pre-saturated with N_2O, which quantitatively converted the hydrated electron, e_{aq}^-, and hydrogen atom, $^\bullet H$, to $^\bullet OH$:[3]

$$e_{aq}^- + N_2O + H_2O \rightarrow N_2 + OH^- + {}^\bullet OH \quad k_5 = 9.1 \times 10^9\ M^{-1}\ s^{-1} \quad [5]$$
$$^\bullet H + N_2O \rightarrow {}^\bullet OH + N_2 \quad k_6 = 2.1 \times 10^6\ M^{-1}\ s^{-1} \quad [6]$$

For the determination of the reaction rate of TCNM and hydrated electrons, solutions were sparged with N_2 to remove the dissolved oxygen, and had 0.50 M *tert*-butanol added to scavenge the formed hydroxyl radicals and hydrogen atoms:

$$^\bullet OH + (CH_3)_3COH \rightarrow {}^\bullet CH_2(CH_3)_2COH + H_2O \quad k_7 = 6.6 \times 10^8\ M^{-1}\ s^{-1} \quad [7]$$
$$^\bullet H + (CH_3)_3COH \rightarrow {}^\bullet CH_2(CH_3)_2COH + H_2 \quad k_8 = 1.7 \times 10^5\ M^{-1}\ s^{-1} \quad [8]$$

The absorbance of the e_{aq}^- was then observed directly at 700 nm.

2.4. Cobalt-60 Irradiations

A ^{60}Co γ irradiator, Shepherd 109–68 at a dose rate of 122 Gy min^{-1} (Fricke dosimetry) was used for all steady state studies. Experiments were performed using nominally 1 mM TCNM solutions in aerated (measured 2.00×10^{-4} M dissolved oxygen) ultra-pure water, using sealed 47 mL glass vials at ambient temperature (20 °C) with no head-space. These TCNM solutions were irradiated for six separate doses, 1.2, 2.4, 3.6, 6.1 and 8.5 kGy, by varying the length of time in the irradiator.

2.5. Analytical Methods

The concentration of TCNM in irradiated samples was determined using a Finnigan DSQ Ultra-Trace GC/MS system. An internal standard, 1, 2-dichloropropane, was first added to 1 mL of the aqueous solution, and then liquid-liquid extraction using 1 mL portions (2 × 500 µL aliquots) of MTBE was performed. Helium was used as a carrier gas, and compounds were eluted using an oven programme of 45°C to 150 °C at 15°C min^{-1}. The lower limit of detection was 180 ± 20 nM.

Chloride and nitrate product ions were analyzed using a Dionex DX-500 ion chromatograph and had detection limits of 0.3 µM and 0.2 µM, respectively. Analytical error for Cl^- and NO_3^-, was ± 0.02 and ± 0.01 µM, respectively.

Measurement of possible organic acid by-products used HPLC/UV detection at 210 nm. The eluant was (0.1% H_3PO_4) was pumped at 0.5 mL min^{-1} through a Supelcogel C-610H column operated at 30°C. A Supelcogel H guard column and a 50 mm column packed with Amberlyst 15 resin beads were also used. The limit of detection for formate and oxalate ions was 20 µM.

2.6. Kinetic Model

The kinetic model used was developed for simulating radiation chemistry of nuclear reactors, MAKSIMA-CHEMIST and has been shown to simulate water radiolysis well [4]. The programme was coded with the basic reactions of water radiolysis and the appropriate reaction rates. This programme utilizes Gear algorithms to produce error controlled step size equations combined with order selection, and sparse algorithms for the evaluation of the Jacobian matrix as the predictor corrector equation.

During this study, the computer model was used to both assist in assigning unknown reaction rates and to conduct sensitivity analysis of the proposed mechanism. Throughout the development of the mechanisms the model was used to test the validity of the proposed reaction pathway and through this iterative process various aspects of the mechanisms were revised or then eliminated as insignificant and unknown reactions tested for relevance. That is, the ability to correlate the removal of the TCNM from de-ionized water and to predict the appearance of reaction by-products.

3. RESULTS AND DISCUSSION

Hydroxyl Radical Rate Constant. The SCN^- competition kinetics data obtained at 475 nm for various TCNM concentrations were measured previously [6], and were reconfirmed as shown in Figure 1a, with the corresponding transformed data given in Figure 1b. From the latter, a plot of the rate constant for reaction of the hydroxyl radical with TCNM was calculated as $k_2 = (4.97 \pm 0.28) \times 10^7$ $M^{-1} s^{-1}$.

Hydrated Electron Rate Constant. The reaction of TCNM reaction with the e_{aq}^- was determined using the concentration dependence of the change in the rate of decay of the hydrated electron absorbance at 700 nm [6]. Based on these data (Figure 2), the bimolecular rate constant for the reaction of e_{aq}^- was determined as $k_7 = (2.13 \pm 0.03) \times 10^{10}$ $M^{-1} s^{-1}$.

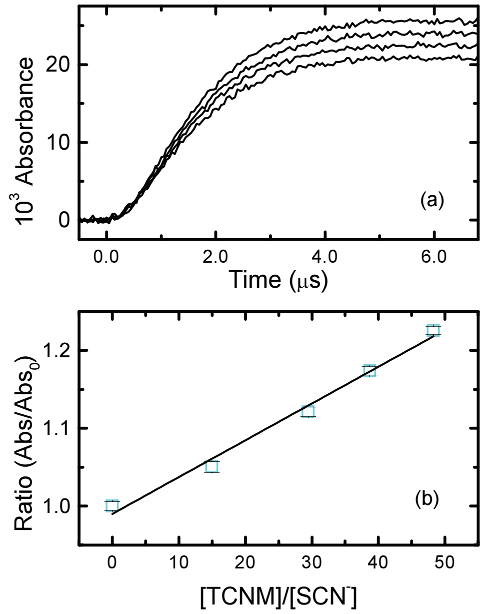


FIG. 1. Typical kinetics of $(SCN)_2^{\bullet -}$ formation at 475 nm for N_2O saturated 1.04 × 10^{-4} M KSCN solution containing 0, 5.00 mM, 3.55 mM, and 1.55 mM Chloropicrin at natural pH and 20° C. (b) Competition kinetics plot for hydroxyl radical reaction with Chloropicrin using SCN^- as a standard. Solid line is weighted linear fit, corresponding to a slope of 0.00473 ± 0.00027. This gives a second-order rate constant for Chloropicrin reaction as (4.97 ± 0.28) × 10^7 M^{-1} s^{-1}.

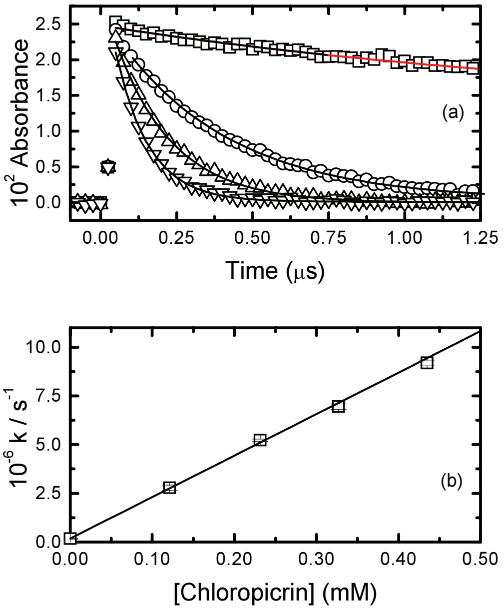


FIG. 2. a) Typical kinetic decay profiles obtained for the hydrated electron absorbance at 700 nm for the electron pulse irradiated aqueous solution at natural pH and 20° C containing zero (□), 1.12 × 10^{-4} (O), 2.32 × 10^{-4} (Δ), and 4.35 × 10^{-4} (∇) M Chloropicrin, respectively. Curves shown are the average of 15 individual pulses. Solid lines correspond to rate constant fitting with the pseudo-first-order values of 1.71 × 10^5, 2.64 × 10^6, 5.26 × 10^6, and 9.30 × 10^6 s^{-1}, respectively. (b) Second-order rate constant determination for the reaction of the hydrated electron with Chloropicrin. Single-point error bars are one standard deviation, as determined from the average of at least three kinetic traces. Solid line corresponds to weighted linear fit, giving k = (2.13 ± 0.03) × 10^{10} M^{-1} s^{-1}.

Mass Balance. Steady state ^{60}Co gamma irradiations were performed for solutions containing an initial concentration of 1.13 mM TCNM in aerated de-ionized water at room temperature. These experiments were conducted to elucidate the free-radical-induced destruction mechanism of TCNM. The measured loss of TCNM, and the corresponding formation of chloride and nitrate ions, is summarized in Table 1. Mass balance of the chloride ion was nearly achieved at 8.5 kGy, 92%. The nitrate ion at the highest dose was 79% of the initial TCNM. Oxalate and formate ions were below detection limits in all samples.

TABLE 1. SUMMARY OF EXPERIMENTAL RESULTS FOR ^{60}CO IRRADIATION OF TCNM SOLUTIONS (1.13 MM) IN ULTRA-PURE WATER AT DOSES UP TO 8.54 KGY AND KINETIC MODEL RESULTS

Dose (kGy)	Experimental			Kinetic Model		
	TCNM (mM)	Cl^- (mM)	NO_3^- (mM)	TCNM (mM)	Cl^- (mM)	NO_3^- (mM)
0	1.13	0.00	0.00	1.13	0.00	0.00
1.22	0.80	0.92	0.29	0.80	0.98	0.26
2.44	0.42	1.67	0.44	0.54	1.71	0.41
3.66	0.17	2.17	0.58	0.23	2.50	0.59
6.1	NM[a]	2.73	0.79	-[c]	3.13	0.95
8.54	BMDL[b]	3.13	0.89	-[c]	3.13	0.94

[a] not measured
[b] below method detection limit
[c] modeled data is below detection limit

Destruction Mechanism. *Solvated Electron*. Based on the measured rate constants it appeared that reductive processes involving the hydrated electron were primarily responsible for the destruction of TCNM in these steady-state experiments. Dissociative electron attachment was expected to proceed via two main reaction pathways resulting in the formation of two different carbon-centered radicals:

$e^-_{(aq)} + CCl_3NO_2 \rightarrow Cl^- + {}^{\bullet}CCl_2NO_2$ [9]
$e^-_{(aq)} + CCl_3NO_2 \rightarrow NO_2^- + {}^{\bullet}CCl_3$ [10]

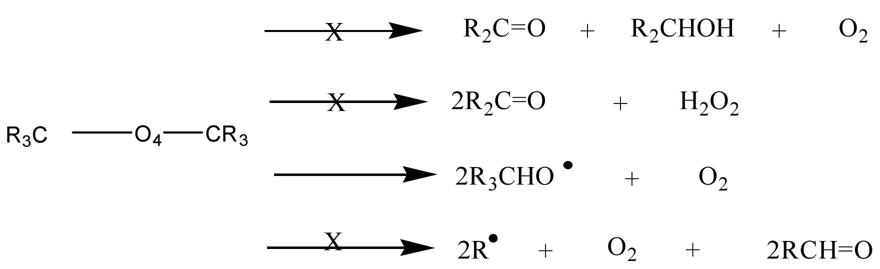
The reaction of e_{aq}^- with tetranitromethane has been shown to produce the ${}^{\bullet}NO_2$ and by analogy a similar reaction was expected with TCNM; however, during sensitivity analysis of the kinetic model this reaction did not improve the accuracy of product predictions and was therefore not considered.

In aerated solutions, carbon-centered radicals react with O_2 to give peroxyl radicals:

$O_2 + {}^{\bullet}CCl_2NO_2 \rightarrow {}^{\bullet}OOCCl_2NO_2$ [11]
$O_2 + {}^{\bullet}CCl_3 \rightarrow {}^{\bullet}OOCCl_3 \quad k_{12} = 3.3 \times 10^9\ M^{-1}\ s^{-1}$ [7] [12]

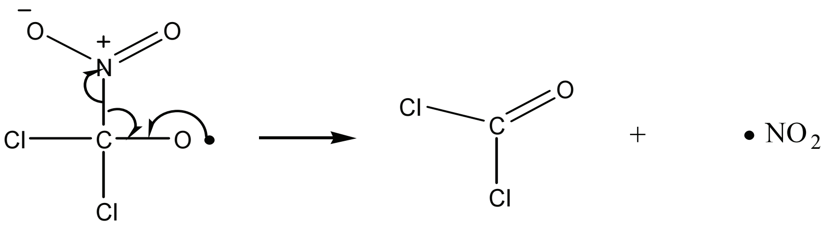
Relatively few rate constants for peroxyl radical formation have been measured; however, most of the values that have been determined are in the range $(2 - 4) \times 10^9\ M^{-1}\ s^{-1}$ [7].

In general, peroxyl radicals are relatively unreactive in aqueous solution [9]. It is known that the ${}^{\bullet}OOCCl_3$ may react via electron transfer with a suitable electron acceptor such as I^- or aromatic thiols to give ${}^{-}OOCCl_3$. In our relatively simple solutions it was not clear that such a reaction would occur. Another possibility considered was that peroxyl radicals combine to form tetroxides ($R_3C\text{-}O_4\text{-}CR_3$). These tetroxides may then react as shown in Equations 13–16:

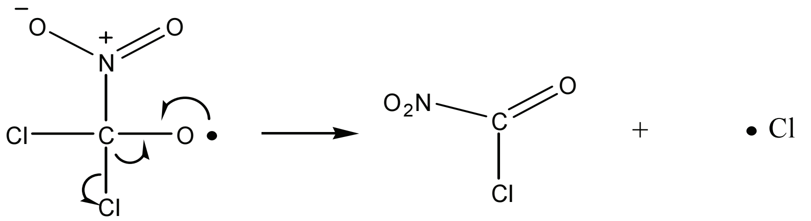


$$R_3C{-}O_4{-}CR_3 \begin{cases} \xrightarrow{\;X\;} R_2C{=}O + R_2CHOH + O_2 & [13] \\ \xrightarrow{\;X\;} 2R_2C{=}O + H_2O_2 & [14] \\ \longrightarrow 2R_3CHO^{\bullet} + O_2 & [15] \\ \xrightarrow{\;X\;} 2R^{\bullet} + O_2 + 2RCH{=}O & [16] \end{cases}$$

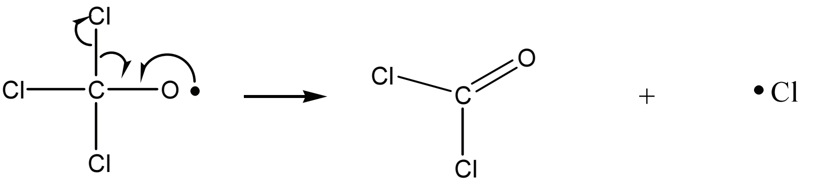
The lack of hydrogen atoms on the carbon of TCNM precludes reactions 13 and 14 from occurring, and because this is a one-carbon compound reaction 16 cannot proceed. Therefore, reaction 15 is the most likely pathway, leading to the formation of three different alkoxy radicals that would subsequently undergo intra-molecular rearrangements:



[17]



[18]



[19]

The unstable product phosgene, $COCl_2$, hydrolyzes to CO_2 and HCl [10]. Reaction 18 has not been previously reported and the $COClNO_2$ would presumably give CO_2, HCl and HNO_2.

The $^{\bullet}NO_2$ radical (reaction 17) is also produced by the reaction of the hydroxyl radical with NO_2^-:

$^{\bullet}OH + NO_2^- \rightarrow {}^{\bullet}NO_2 + OH^-$ $k_{20} = 9.6 \times 10^9\ M^{-1}\,s^{-1}$ [20]

The $^{\bullet}NO_2$ would most likely react with the hydrogen atom (58) or with O_2^-/HO_2:

$^{\bullet}NO_2 + {}^{\bullet}H \rightarrow H^+ + NO_2^-$ $k_{21} = 1.0 \times 10^{10}\ M^{-1}\,s^{-1}$ [21]
$^{\bullet}NO_2 + O_2^-/HO_2 \rightarrow H^+ + NO_2^- + O_2$ $k_{22} \sim 1 \times 10^8\ M^{-1}\,s^{-1}$ [22]

These reactions regenerate nitrite. Some of the formed $^{\bullet}NO_2$ could also react with $^{\bullet}OH$, leading to the formation of peroxynitrous acid:

$^{\bullet}OH + {}^{\bullet}NO_2 \rightarrow ONOOH$ $k_{23} = (4.5 \pm 1.0) \times 10^9\ M^{-1}\,s^{-1}$ [23]
$ONOOH \rightleftharpoons ONOO^{\bullet} + H^+$ [24]

The pK_a of ONOOH is 6.5–6.8, therefore under the acidic conditions of our irradiations the solution would be mostly in the acidic form. The mechanism for the (acid) hydrolysis of the ONOOH has been determined and reviewed in detail (which includes equation 20):

$ONOOH \rightarrow NO_3^- + H^+$ 70% [25]
$ONOOH \rightarrow {}^{\bullet}NO_2 + {}^{\bullet}OH$ 30% [26]
$2\,{}^{\bullet}NO_2 + H_2O \rightarrow NO_3^- + NO_2^- + H^+$ [27]

The overall reaction for the peroxynitrate ion decomposition is:

$ONOOH \rightarrow H^+ + NO_3^-$ $k_{28} = 1.25 \pm 0.05\ s^{-1}$ [11] [28]

Our solutions were unbuffered and with increasing radiation the pH dropped (Equation 1). Although at higher pH it is possible to have some NO_2^- formed, consequently the lower the pH the more complete the homolysis of ONOOH to only NO_3^-.

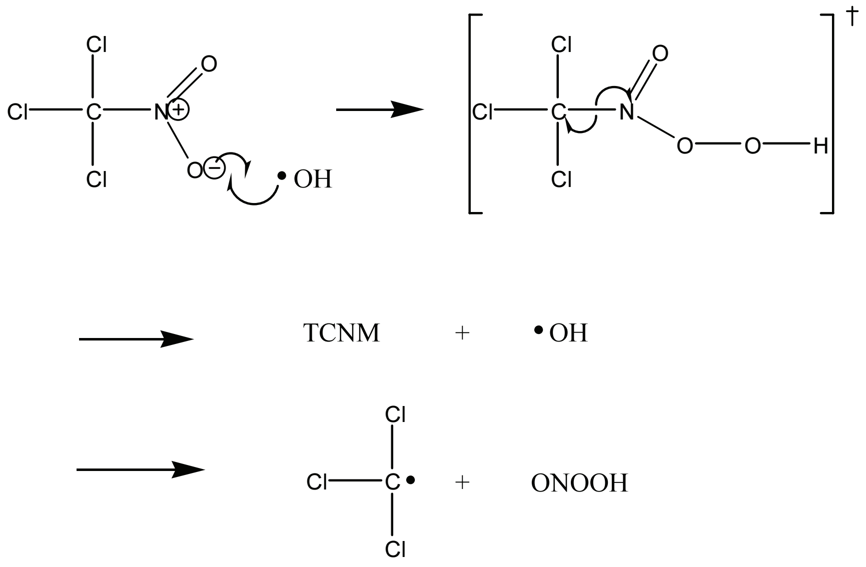
The •Cl formed in the equations 18 and 19 might be expected to react as follows, where the forward and back reactions are summarized [12]:

$e_{aq}^- + \bullet Cl \rightarrow Cl^-$ not reported [29]
$\bullet Cl + Cl^- \rightarrow Cl_2^-\bullet$ $k_{30} = (7.8 \pm 0.8) \times 10^9\ M^{-1}\,s^{-1}$ [30]
$k_{-30} = (5.7 \pm 0.4) \times 10^4\ s^{-1}$
$Cl_2^-\bullet + H_2O \rightarrow \bullet ClOH^- + H^+ + Cl^-$ $k_{31} < 100\ s^{-1}$ [31]
$\bullet Cl + \bullet Cl \rightarrow Cl_2$ $k_{32} = 8.8 \times 10^7\ M^{-1}s^{-1}$ [32]
$\bullet Cl + H_2O \leftrightarrow \bullet ClOH^- + H^+$ $k_{33} = (1.6 \pm 0.2) \times 10^5\ s^{-1}$ [33]
$k_{-33} = (2.6 \pm 0.6) \times 10^{10}\ M^{-1}\,s^{-1}$
$\bullet ClOH^- \leftrightarrow \bullet OH + Cl^-$ $k_{34} = (6.1 \pm 0.8) \times 10^9\ s^{-1}$ [34]
$k_{-34} = (4.3 \pm 0.4) \times 10^9\ M^{-1}\,s^{-1}$

The reaction of the e_{aq}^- and •Cl should proceed at diffusion controlled rates; however, the measurement of this reaction has eluded investigations (a rate of $5 \times 10^{10}\ M^{-1}\,s^{-1}$ was assumed for this reaction in the kinetic model). Radical-radical recombination of •Cl is not likely to be a major contributor to the loss of the •Cl. Therefore, reaction 30 appears to be the major loss mechanism for •Cl forming $Cl_2^-\bullet$. The reaction of the highly unstable $\bullet ClOH^-$ would proceed via hydrolysis (equation 36) with the formation of •OH and Cl^-. The chemistry of the $Cl_2^-\bullet$ has been studied extensively and when incorporated into the kinetic model significantly improved the results:

$Cl_2^-\bullet + Cl_2^-\bullet \rightarrow Cl^- + Cl_3^-$ $k_{35} = 2.0 \times 10^9\ M^{-1}\,s^{-1}$ [35]
$Cl_3^- + H\bullet \rightarrow Cl^- + Cl_2^-\bullet$ $k_{36} = 3.0 \times 10^{10}\ M^{-1}\,s^{-1}$ [36]
$Cl_2^-\bullet + H\bullet \rightarrow H^+ + 2Cl^-$ $k_{37} = 8.0 \times 10^9\ M^{-1}\,s^{-1}$ [37]
$Cl_2^-\bullet + HO_2\bullet \rightarrow O_2 + H^+ + 2Cl^-$ $k_{38} = 2.0 \times 10^9\ M^{-1}\,s^{-1}$ [38]
$Cl_2^-\bullet + O_2^-\bullet \rightarrow O_2 + 2Cl^-$ $k_{39} < 2.0 \times 10^9\ M^{-1}\,s^{-1}$ [39]
$Cl_2^-\bullet + NO_2^- \rightarrow \bullet NO_2 + 2Cl^-$ $k_{40} = 2.0 \times 10^8\ M^{-1}\,s^{-1}$ [40]

Hydroxyl Radical. Initially the •OH reaction with the TCNM was thought to be of minimal importance due to the slow reaction rate constant. Although it was possible to account for the disappearance of the TCNM when excluding this reaction, the model did not adequately predict the appearance of either the Cl^- or NO_3^-. It is well known from other chlorinated methanes that the only reaction of the ${}^{\bullet}OH$ is H abstraction, $CHCl_3$ and CH_2Cl_2, and, there is no reaction with CCl_4. Therefore, given that the ${}^{\bullet}OH$ is an electrophile and might attack the NO_2 moiety, the following mechanism was proposed for this reaction pathway:



[41]

[42]

[43]

The major question was the branching ratio of the reactions 42 and 43. From the experimental data obtained, it was not possible to evaluate the branching ratio of these reactions. From the formation of the Cl^- or NO_3^-, the kinetic model was used to optimize the branching ratio of reactions 42 and 43. The optimal value was found to be a 10:1 ratio of these two reactions, typified by using reaction rate constants of $k_{42} = 1.0 \times 10^6\ s^{-1}$ and $k_{43} = 1.0 \times 10^5\ s^{-1}$ in the modeling. This ratio implies that the overall oxidation of TCNM by $^{\bullet}OH$ is much slower than initially measured, $(4.84 \pm 0.40) \times 10^7$. However, a reevaluation of the $^{\bullet}OH$ rate constant using a new sample of TCNM, $(4.97 \pm 0.28) \times 10^7$ confirmed our original value.

Hydrogen Atom. Bimolecular reaction rates of the TCNM and H• were not evaluated; however, with a molecule such as TCNM it was apparent that it could react to give the anions:

$$TCNM + H^{\bullet} \rightarrow {}^{\bullet}CCl_2NO_2 + H^+ + Cl^- \quad [44]$$
$$TCNM + H^{\bullet} \rightarrow {}^{\bullet}CCl_3 + H^+ + NO_2^- \quad [45]$$

While hydroxyl radicals do not react with CCl_4, hydrogen atom reactions have been measured at 3.2–4.4 × $10^7\ M^{-1}\ s^{-1}$ giving Cl^- as the product. Recently, it has been shown that $H^{\bullet}$ reacts with dichloroethanes to give exclusively Cl^- in aqueous solution [13]. The precedence for reaction 45 is from the reaction of the hydrogen atom with tetranitromethane, which occurs with a rate constant of $5.5 - 26 \times 10^8\ M^{-1}\ s^{-1}$ and gives NO_2^- as a product. Thus, a second reductive destruction pathway for the loss of TCNM via $H^{\bullet}$ was added. These reactions (Equations 44 and 45) were added into the model using estimated rate constants of $2.0 \times 10^8\ M^{-1}\ s^{-1}$.

Superoxide anion radical. Sensitivity analysis using the kinetic model revealed that the reaction of $^{\bullet}NO_2$ with oxygen had a major influence on the removal rate of TCNM and predicted far more O_2 than was observed in the experimental results. Additional chemistry involving direct $O_2^{-\bullet}$ reaction with TCNM was considered. Based on the reaction of $O_2^{-\bullet}$ with tetranitromethane (TNM),

$$TNM + O_2^{-\bullet} \rightarrow O_2 + {}^{\bullet}C(NO_2)_3^- + {}^{\bullet}NO_2 \qquad k_{46} = 2.0 \times 10^9\ M^{-1}\ s^{-1} \quad [46]$$

it is possible to envisage an analogous electron transfer reaction with TCNM,

$$TCNM + O_2^{-\bullet} \rightarrow O_2 + {}^{\bullet}CCl_2NO_2 + Cl^- \quad [47]$$

Including this reaction in the kinetic model resolved the discrepancy of the reaction of $^{\bullet}NO_2$ with oxygen and by adjusting this unknown rate constant to $1.5 \times 10^8\ M^{-1}\ s^{-1}$ it was possible to increase the level of confidence in the mechanism for TCNM removal prediction and to better approximate chloride and nitrate ion formation. In fact, the model was extremely sensitive to the rate constant, grossly under predicting the removal of TCNM at 1.0 × 10^8 M^{-1} s^{-1} and over predicting the TCNM removal using a rate constant of 2.0 × 10^8 M^{-1} s^{-1}. Clearly this reaction rate should be evaluated directly.

Kinetic Model. The kinetic model developed for TCNM degradation based on the free radical work herein is summarized in Table 2. The initial computer simulation included reactions accounting for reaction of e_{aq}^- with the TCNM in water, subsequent reactions with dissolved oxygen and the formation of the reaction by-products. The best branching ratio for the reaction TCNM with e_{aq}^- (1:1), was partitioned equally between the chloride and nitrite ion producing pathways. This formulation was subsequently found unsuitable to account for the appearance of the Cl^- and NO_3^- with any accuracy.

Including the reaction for the $^{\bullet}OH$ and $H^{\bullet}$ with TCNM over-predicted the removal of TCNM; however, the calculated formation profiles of the product Cl^- and NO_3^- anions were much closer to the experimental data. As the TCNM purity was very high, side reactions of it with hydrogen-atom containing impurities were not believed to be significant.

The initial attack of the $^{\bullet}OH$ results in the formation of an adduct that can then react as shown in Equations 42 and 43. To slow the overall removal rate of TCNM, it was postulated that the intermediate adduct formed either collapses back to the starting reactants or proceeds to react at an optimal rate constant as predicted by the model and corresponds to a ratio of 90:10, respectively. This result will have to be confirmed empirically.

The model appears to be a good representation of the results for the removal of TCNM (Figure 3) and slightly under-predicts the appearance of the Cl^- (Figure 4). Based on the model both peroxynitrous acid and phosgene were formed, but even with our high initial concentration of TCNM neither of these potentially toxic by-products, were ever greater than 5 nM.

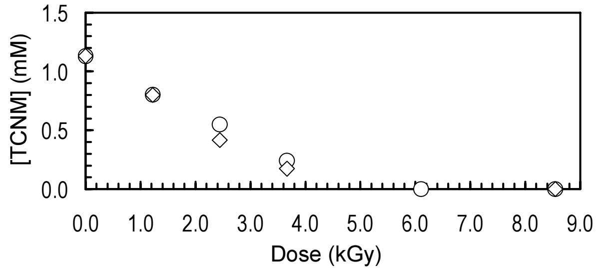


FIG. 3. Comparison of experimental (◇) and modeled (○) results for ^{60}Co irradiated $[TCNM]_0$ = 1.13 mM.

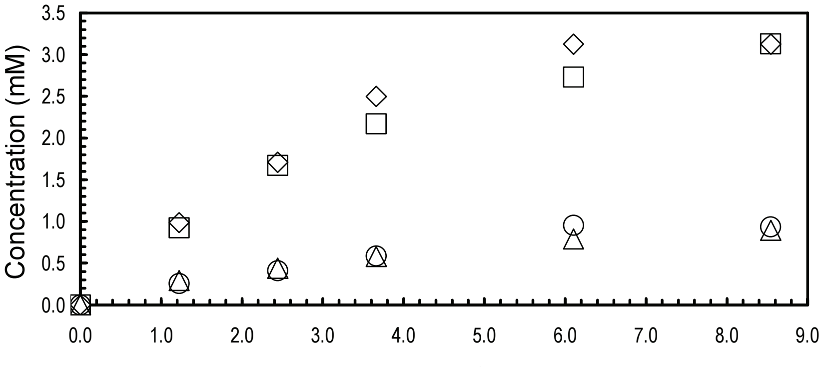


FIG 4. Concentration of chloride ions from (□) experimental results, and (◇) model results; and nitrate ions (△) experimental results, and (○) model results; versus dose ^{60}Co irradiation.

TABLE 2. LINEARIZED REACTION MECHANISM FOR THE FREE RADICAL DESTRUCTION OF TCNM. (NOTE: SOME OF THE REACTIONS DISCUSSED IN THE TEXT WERE ELIMINATED FROM THE MODEL THROUGH THE ITERATIVE SENSITIVITY STUDIES CONDUCTED.)

Equation number	Reactions									*k* $(M^{-1}\,s^{-1})$*
9	TCNM	+	e_{aq}^{-}	→	$\bullet CCl_2NO_2$	+	Cl^{-}			1.07×10^{10}
10	TCNM	+	e_{aq}^{-}	→	$\bullet CCl_3$	+	NO_2^{-}			1.07×10^{10}
11	$\bullet CCl_2NO_2$	+	O_2	→	$\bullet OOCClNO_2$					3.0×10^{9}
12	$\bullet CCl_3$	+	O_2	→	$\bullet OOCCl_3$					3.3×10^{9}
	$\bullet OOCCl_2NO_2$	+	$\bullet OOCCl_2NO_2$	→	Tetroxide A					1.0×10^{8}
	$\bullet OOCCl_3$	+	$\bullet OOCCl_3$	→	Tetroxide B					1.0×10^{8}
15	Tetroxide A				$2\bullet OCCl_2NO_2$	+	O_2			1.0×10^{6}
15	Tetroxide B				$2\bullet OCCl_3$	+	O_2			1.0×10^{6}
17	$\bullet OCCl_2NO_2$			→	$COCl_2$	+	$\bullet NO_2$			10^{5} (s^{-1})
18	$\bullet OCCl_2NO_2$			→	$CONO_2Cl_2$	+	$\bullet Cl$			10^{5} (s^{-1})
19	$\bullet OCCl_3$			→	$COCl_2$	+	$\bullet Cl$			10^{4} (s^{-1})
	$COCl_2$	+	H_2O	→	CO_2	+	$2H^{+}$	+	$2Cl^{-}$	9 (s^{-1})
	$CONO_2Cl_2$	+	H_2O	→	CO_2	+	HCl	+	HNO_2	9 (s^{-1})
20	$\bullet OH$	+	NO_2^{-}	→	OH^{-}		$\bullet NO_2$			9.6×10^{9}
23	$\bullet OH$	+	$\bullet NO_2$	→	ONOOH					4.5×10^{9}
28	ONOOH	+	H_2O	→	H^{+}	+	NO_3^{-}			1.25 (s^{-1})
29	e_{aq}^{-}	+	$\bullet Cl$	→	Cl^{-}					5.0×10^{10}
30	$\bullet Cl$	+	Cl^{-}	→	$Cl_2^{-}\bullet$					7.8×10^{9}
–30	$Cl_2^{-}\bullet$			→	$\bullet Cl$	+	Cl^{-}			5.7×10^{4} (s^{-1})
35	$Cl_2^{-}\bullet$	+	$Cl_2^{-}\bullet$	→	Cl^{-}	+	Cl_3^{-}			2.0×10^{9}
36	Cl_3^{-}	+	$H^{\bullet}$	→	Cl^{-}	+	$Cl_2^{-}\bullet$			3.0×10^{10}
37	$Cl_2^{-}\bullet$	+	$H^{\bullet}$	→	H^{+}	+	$2Cl^{-}$			8.0×10^{9}
38	$Cl_2^{-}\bullet$	+		→	O_2	+	H^{+}		$2Cl^{-}$	2.0×10^{9}
39	$Cl_2^{-}\bullet$	+		→	O_2	+	$2Cl^{-}$			$<2.0 \times 10^{9}$
40	$Cl_2^{-}\bullet$	+		→	$\bullet NO_2$	+	$2Cl^{-}$			2.0×10^{8}
41	TCNM	+	$\bullet OH$	→	Intermediate					4.97×10^{7}
42	Intermediate			→	TCNM	+	$\bullet OH$			1.0×10^{6}

43	Intermediate			→	$\bullet CCl_3$	+	ONOOH			1.0×10^5
44	TCNM	+	$H^\bullet$	→	$\bullet CCl_2NO_2$	+	H^+	+	Cl^-	1.0×10^8
45	TCNM	+	$H^\bullet$	→	$\bullet CCl_3$	+	H^+	+	NO_2^-	1.0×10^8
47	TCNM	+	$O_2^{-\bullet}$	→	$\bullet CCl_2NO_2$	+	Cl^-		O_2	1.5×10^8
	$\bullet CCl_2NO_2$	+	$\bullet CCl_2NO_2$	→	Tetroxide C					1.0×10^8
	Tetroxide C	+	e_{aq}^-	→	$2NO_2^-$	+	$4\ Cl^-$			3.0×10^{10}
	Tetroxide C	+	$H^\bullet$	→	$2NO_2^-$	+	$4\ Cl^-$			3.0×10^{10}
	NO_2-	+	$\bullet OH$	→	$\bullet NO_2$	+	OH^-			9.60×10^9
	$\bullet OH$	+	$\bullet NO_2$	→	ONOOH					4.50×10^9
	ONOOH	+	H_2O	→	H^+	+	NO_3^-			1.25×10^0
	e_{aq}^-	+	NO_2^-	→	$\bullet NO_2^-$					3.50×10^9
	e_{aq}^-	+	NO_3^-	→	NO_3^{2-}					9.70×10^9
	$\bullet OH$	+	NO_3^{2-}	→	NO_3^-	+	OH^-			3.00×10^9
	$\bullet NO_2$	+	$O_2^{-\bullet}$	→	NO_2^-	+	O_2			3.00×10^8
	$\bullet NO_2$	+	$HO_2^\bullet$	→	NO_2^-	+	O_2	+	H^+	3.00×10^8

Several reactions and intermediates that have been proposed require further verification, a task that was beyond the scope of this study. Additional studies using time resolved electron paramagnetic resonance (EPR) are being planned. It also appears that computational methodologies would also assist in better identifying the low-energy transition states and products, and could add substantially to our understanding of the details of the destruction mechanism of this relatively simple one-carbon compound.

These studies were conducted at an initial TCNM concentration of 1.13 mM, much higher than is found in drinking water. The purpose for the experimental concentration used was to form by-products (Cl^- and NO_2^-/NO_3^-) in sufficient concentration for quantitative analytical determination. It was interesting that an artifact of these experimental concentrations was likely the formation of the stable products from the radical-radical recombination of the initial carbon centered radicals, i.e. hexachloroethane and possibly dinitrotetrachloroethane. These reactions were included in the actual model as they were necessary for mass balance. These reactions were determined insignificant and ultimately not shown as they would not be formed at the environmental concentrations reported for TCNM (5.5 nM).

ACKNOWLEDGEMENTS

Work performed at the Radiation Laboratory, University of Notre Dame, was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. Partial support is also acknowledged from the WaterReuse Foundation Grant WRF04-017, and McKim & Creed, PA.

REFERENCES

[1] RICHARDSON, S.D., Water analysis: Emerging contaminants and current issues. *Anal. Chem. 75* (2003) 2831–2857.

[2] HOIGNÉ, J., BADER, H., The formation of trichloronitromethane (chloropicrin) and chloroform in a combined ozonation/chlorination treatment of drinking water. *Wat. Res. 22* (1988) 313–319.

[3] MEZYK, S.P.; COOPER, W.J.; MADDEN, K.P., BARTELS, D.M., Free radical destruction of n-nitrosodimethylamine in water. *Environ. Sci. Technol. 38* (2004) 3161–3167.

[4] ASMUS, K.-D., Pulse radiolysis methodology. *Methods in Enzymology*, *105* (1984)167–178.

[5] CARVER, M.B., HANLEY, D.V., CHAPIN, K.R., MAKSIMA-CHEMIST, A programme for mass action kinetic simulated manipulation and integration using stiff techniques. Chalk River Nuclear River Laboratories Report, Atomic Energy of Canada, Ltd. 6413 (1979) 1–28.

[6] MEZYK, S.P., HELGESON, T., COLE, S.K., COOPER, W.J., FOX, R.F., GARDINALI, P.R., MINCHER, B.J., Free radical chemistry of disinfection by-products 1. Kinetics of hydrated electron and hydroxyl radical reactions with halomethanes in water. *J. Phys. Chem.* 110, (2006) 2176–2180.

[7] MÖNIG, J., BAHNEMANN, D., ASMUS, K.-D., One-electron reduction of CCl_4 in oxygenated aqueous solutions. A CCl_3O_2• free radical mediated formation of Cl^- and CO_2. *Chem.-Biol.* 47 (1983) 15–27.

[8] NETA, P., HUIE, R.E., ROSS, A.B., Rate constants for reactions of peroxyl radicals in fluid solutions. *J. Phys. Chem. Ref. Data*, 19 (1990) 413–513.

[9] VON SONNTAG, C., SCHUCHMANN, H.-P., Peroxyl radicals in aqueous solutions. In *Peroxyl Radicals*; Alfassi, Z.B. (Ed.), John Wiley & Sons New: York, 1997 (173–234).

[10] MERTENS, R., VON SONNTAG, C., LIND, J., MERENYI, G., A kinetic study of the hydrolysis of phosgene in aqueous solution by pulse radiolysis. *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1259–1261.

[11] GOLDSTEIN, S., LIND, J., MERÉNYI, G., Chemistry of peroxynitrites as compared to peroxynitrates. *Chem. Rev. 105* (2005) 2457–2470.

[12] YU, X.-Y., BAO, Z.-C., BARKER, J.R., Free radical reactions involving Cl•, Cl_2^-•, and SO_4^-• in the 248 nm photolysis of aqueous solutions containing $S_2O_8^{2-}$ and Cl^-. *J. Phys. Chem.*, 108, (2004) 295–308.

[13] PIMBLOTT, S., MILOSAVLJEVIC, B.H., LAVERNE, J.A., Radiolysis of aqueous solutions of 1,1- and 1,2-dichloroethane. *J. Phys. Chem.* 109 (2005) 10294–10301.

LIST OF PARTICIPANTS

AMRO, H.
Ministry of Water and Irrigation,
Water Authority of Jordan,
POB 2412,
Amman 11183,
JORDAN
Tel: +962-777-854303
Fax: +962-6-5825275
Email: amro_303@yahoo.com

BOJANOWSKA-CZAJKA, A.
Institute of Nuclear Chemistry and Technology,
ul. Dorodna 16,
03-195 Warsaw,
POLAND
Tel: +48-22-504-1000
Fax: +48-22-811-1532
Email: anna.bojanowska@ichtj.waw.pl

BOTELHO, M.
Ministerio da Ciencia e da Tecnologia,
Instituto Tecnologico e Nuclear,
Sector da Fisica,
Estrada Nacional No. 10, Apartado 21,
2686-953 Sacavem,
PORTUGAL
Tel: +351-21-994-6078
Fax: +351-21-994-1525
Email: mlb@itn.pt

COOPER, W.
Urban Water Research Center,
Department of Civil and Environmental Engineering,
University of California, Irvine,
Irvine, CA 92697-2175,
UNITED STATES OF AMERICA
Tel: +1-949-824-5620
Fax: +1-949-824-3672
Email: wcooper@uci.edu

EMMI, S.
Istituto per la Sintesi Organica e la Fotoreattivita,
National Research Council,
ISOF-CNR Via P. Gobetti 101,
40129 Bologna,
ITALY
Tel.: +39 051 639-9774
Fax: +39 051 639-9848
Email: salvatore.emmi@isof.cnr.it

GEHRINGER, P.[*]
ARC Seibersdorf research GmbH,
A-2444 Seibersdorf,
AUSTRIA

HAN, B.
EB-TECH CO., LTD.,
550 Yongsan-dong Yuseong-gu,
Daejon, 305-500,
REPUBLIC OF KOREA
Tel: +82-42-930-7501
Fax: +82-42-930-7500
Email: bshan@eb-tech.com

MELO, R.
Estrada Nacional 10,
2689-953 Sacavem,
PORTUGAL
Tel.: +351-21-994-6080
Fax: +351-21-994-1525
Email: ritamelo@itn.pt

RAMIREZ, T.
Escuela Politecnica Nacional,
Instituto de Ciencias Nucleares,
Ladrón de Guevara s/n,
Quito,
ECUADOR
Tel/Fax: +593-2255-8456
Email: trajanoramirez@hotmail.com

RELA, P.
Instituto de Pesquisas Energeticas e Nucleares,
IPEN-CNEN/SP,
Av. Lineu Prestes, No. 2242,
Cidade Universitaria,
Sao Paulo/SP, 05508-900,
BRAZIL
Tel: +55-11-3816-9125
Fax: +55-11-3816-9186
Email: prela@ipen.br ; prela06@yahoo.com.br

SAMPA, M.H.O.
Industrial Applications & Chemistry Section,
Division of Physical and Chemical Sciences,
International Atomic Energy Agency,
Wagramer Strasse 5, P.O. Box 100,
A-1400 Vienna,
AUSTRIA
Tel: +43-1-2600-21744
Fax: +43-1-2600-7-21744
Email: M.Sampa@iaea.org

---

[*] Current Address:
Radetzkystr. 18/6; A-1030 Vienna; AUSTRIA
Tel: +43-1-718-29-08; Fax: +43-1-718-29-08
Email: peter.gehringer@aon.at

SOLPAN, D.
Hacettepe University,
Department of Chemistry,
06532 Beytepe,
Ankara,
TURKEY
Tel: +90-312-297-7990
Fax: +90-312-299-2163
Email: solpan@hacettepe.edu.tr

TAKACS, E.
Institute of Isotopes,
Hungarian Academy of Sciences,
POB 77,
1525 Budapest,
HUNGARY
Tel./Fax: +36-1-392-2548
Email: takacs@iki.kfki.hu