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Removal of Eriochrome black-T by adsorption on to eucalyptus bark using green technology

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The efficiency of eucalyptus bark as a low cost adsorbent for removing an azo dye from an aqueous solution has been investigated in batch mode. The azo dye, Eriochrome black-T (EBT) is removed by adsorption over field waste eucalyptus bark after minimum chemical treatment. The investigations are carried out to study the effects of pH, adsorbate concentration, adsorbent dosage, contact time and temperature. The thermodynamic parameters were obtained from Langmuir and Freundlich adsorption isotherm models. The kinetic studies showed that the adsorption reaction is of first order. A fixed-bed column has been designed, and necessary parameters have been calculated by applying a mass transfer kinetic approach. Experiments are also performed for the recovery of loaded dye through chemical regeneration of spent columns.

Keywords: Azo dye, Eriochrome black-T, Adsorption, Eucalyptus bark, Kinetics, Thermodynamics

Pigments and dyes are widely used in the textile, paper and leather dyeing, printing, pharmaceutical, and cosmetic industries. About 10,000 different dyes weighing approximately 0.7 million tons are produced annually for various industrial processes[1]. Textile effluents have complex composition with variety of dyes, surfactants; bleaching agents and ionic impurities. A considerable percentage of these dyes go into the effluent during the dyeing process as they are highly soluble in water. Many of these have been identified[2] as toxic or even carcinogenic. Discharge of these toxic substances into water bodies pollute the water and make it unfit for aquatic life. Most of the dyes are hazardous to aquatic flora and fauna. The degradation products of dyes are also undesirable and toxic. Further, the dyes make penetration of sunlight to reach the lower layers impossible, thus affecting the possibility for aquatic plants to perform photosynthesis[3]. Polluted water not only damages plants and animals but also is harmful to the environment. A majority of these dyes are stable to light and oxidation. Biological treatment would be cost effective, but most dyes are resistant to bacterial degradation. Thus, this treatment may remove BOD, COD, and suspended solids but is ineffective in removing the color of dyes. Due to environmental awareness also it is necessary to eliminate hazardous dye from the increasing effluents before discharge to the main stream. Many physico-chemical methods such as adsorption, coagulation, precipitation, filtration, and oxidation have been attempted for the treatment of effluent containing dyes. The potential of various methods for the removal of chemical dyes from the effluents have been explored, and the adsorption process has been found to be the most effective.

Some other methods like reverse osmosis, precipitation, electro flotation, flocculation[4,5] have also been used for textile industry effluent treatment. Adsorption is still one of the best known techniques. This method is successful even at low concentration of the dye. Commercially available activated carbon as an adsorbent has yielded excellent results[6]. However, taking into account the high costs involved in the preparation and regeneration process, the feasibility of alternate adsorbents has been studied recently.

In recent years, attention is being paid to low cost, non-conventional adsorbents like bottom ash[7], deoiled soya[8], hen feathers[9], bagasse[10], coir pith[11], wool[12],

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orange and banana peels[13], rice husk[14], hazelnut shell[15] and neem sawdust[16]. Adsorbents are very important for color removal from waste water. Activated carbon with appropriate pore size distribution[17] can give the best adsorption capacity but is ineffective against vat dyes. Thus adsorption by low cost adsorbents is simple, cost effective and efficient tool to remove dyes from textile effluents[18] and is now the need of hour.

Eucalyptus citriodora tree commonly grown in India, sheds off its bark often. The bark of this tree is rich in tannin and polyphenolic compounds[19]. In the present paper, this bark has been used for removal of EBT which is used for dyeing silk, wool, nylon, multifibres after pretreatment with chromium salts. So the dye containing effluent also contains heavy metal chromium. Pure EBT is also used as an indicator in complexometric titrations for estimation of Ca^{2+}, Mg^{2+} and Zn^{2+} ions and for biological staining. This dye is hazardous as such and its degradation products like Naphthaquinone are still more carcinogenic. Therefore, it would be worthwhile to develop a cost effective low-cost adsorbent from waste biomass, which in turn would assist in environmental decontamination processes.

This manuscript reports the efficiency of field waste eucalyptus bark in removing EBT with variation of some experimental parameters.

Experimental Procedure

Materials

Eriochrome black-T, (C.I. number 14645); sodium-4-[(1 - hydroxynaphthalen - 2yl - hydrazinylidene]-7-nitro-3-oxo Y-naphthalene-1-sulfonate was obtained from Qualigens – Glaxo India Ltd. The structure of Eriochrome black-T is given in Fig. 1.

Eucalyptus bark used in the present work was collected in spring 2009 from adult trees from the Eucalyptus cloning centre Philaur, Punjab, India. The collected bark was washed with permuted water several times to remove the dirt particles and water soluble materials followed by treatment with 1% (w/v) NaOH. The washing process was continued till the wash water contained no color and was then completely dried in an oven at 353 K for 24 h. The dried bark was then cut into small pieces, crushed, and sieved to eliminate fine particles (<0.5 mm). The obtained material was washed repeatedly with distilled water (conductivity 500 μS cm^{-1} and pH 6) until the wash water contained no color and its UV-V is absorbance (200-780 nm) was equal to zero and conductivity and pH remained constant. Finally, the obtained material was dried in an air circulating oven at 353 K for 24 h and stored in the desiccator until further use.

Characterization of the adsorbent

Surface chemistry of the Eucalyptus bark such as specific surface area, pore volume distribution, and pore diameter were measured using the nitrogen gas adsorption technique using an ASAP 2010 micro pore analyzer with liquid nitrogen at 77 K. The surface area was calculated using the BET method[20,21]. Pore volume was determined by the BJH method[22,23]. The acidity and basicity of the adsorbent were determined by the Boehm titration method[24-28] as reported elsewhere. The zero point charge of the activated Eucalyptus bark was determined by the solid addition technique[29], presented in Table 1. For morphological characteristics, scanning electron micrograph of the adsorbent eucalyptus bark was carried out. The sample was also characterized by X-ray diffractometry using a X'PERT PRO PANalytical with Cu-K_α radiation. FTIR spectra were also determined using Perkin Elmer spectrophotometer.

Methods

The concentrations of EBT before and after the adsorption processes were monitored using a UV-Visible spectrophotometer at λ_{max} 623 nm. Equilibrium isotherms were determined by contacting

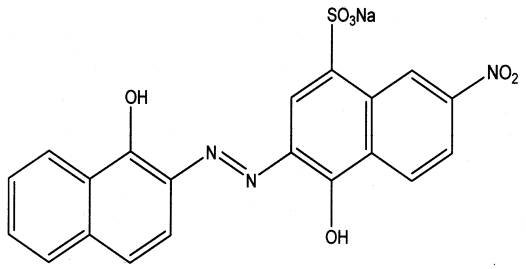

Fig. 1– Molecular structure of EBT, C.I Number14645

Table 1– Physicochemical properties of Eucalyptus bark

Surface area (m^2g^{-1})	20.47
Bulk density (g mL^{-1})	0.689
Pore volume (cm^3 g^{-1})	0.0534
Pore size distribution (nm)	200-1400
Zero point charge (pH_{pzc})	2.2
Total surface acidity (mmol g^{-1})	0.769
Total surface basicity (mmol g^{-1})	0.1456

a fixed mass of eucalyptus bark (1.250 g) with 100 mL of EBT solutions in beakers. A range of EBT concentrations (25-300 mg L^{-1}) were tested. All experiments were conducted in triplicate, and sometimes repeated again and the mean values have been reported.

The absorbance measured was then converted to concentration. The dye uptake was determined by using following equation.

$$q_e = \frac{(C_0 - C_e)V}{W} \quad \ldots (1)$$

Where C_o is initial dye concentration and C_e is equilibrium dye concentration in mg L^{-1}, V is volume of solution (L) and W is the mass of the adsorbent used (g). The optimum adsorbent dosage in each mesh size was then standardized. To understand the maximum uptake of the adsorbent and its behaviour at very high dye concentrations, solutions of various concentrations ranging from 50 to 5000 mg L^{-1} were prepared in separate 100 mL flasks. The standardized adsorbent dosage was transferred to each of the conical flasks. These flasks were placed in the orbital shaker for 24 h, and the residual concentration of dye was measured after centrifuging.

The initial concentration of EBT solution was 250 mg L^{-1} for all the experiments, except for those carried out to examine the effect of the initial concentration of EBT. For kinetic studies, the batch method was used because of its simplicity. 1.250 g of eucalyptus bark was contacted with 100 mL of EBT in a beaker and agitated vigorously by a mechanical stirrer using a water bath maintained at a constant temperature. The stirring speed was kept constant at 400 rpm. The samples of the mixture were withdrawn at suitable time intervals, and filtered through a paper filter and were analyzed by UV visible spectrophotometer (Shimazdu 2101 PC) for the dye concentration.

Sorption experiments were carried out to investigate the effect of pH by using a volume 100 mL of solution of dye having 250 mg L^{-1} of EBT concentration with a sorbent mass of 1.250 g at 303 K in the pH range 2.0 to 11.0 using Toshnival (India) pH meter; model CL-46. The solution pH was adjusted using 0.01N HCl and 0.01N NaOH solution. The samples were withdrawn at regular intervals and the residual concentration of dye in the aqueous phase was analyzed after filtration.

Results and Discussion

Analysis of eucalyptus bark

The physic-chemical properties of Eucalyptus bark are given in Table 1. The bark was analyzed for cellulose[30], hemicellulose[31], lignin[32], reducing sugars[33] and nitrogen[34] which are given in Table 2. From Table 2, it is clear that the total organic matter in the bark is 92.7%.

The eucalyptus bark was analyzed by scanning electron micrographs as shown in Fig. 2. SEM is widely used to study the morphological features and surface characteristics of the adsorbent materials. In the present study, SEM of eucalyptus bark reveals surface texture and porosity. The X-ray diffraction analysis of the eucalyptus barks was carried out and shown in Fig. 3, revealed the appearance of peaks centered at $2\theta = 14.0$; 22.5, indicated the existence of amorphous hemicelluloses and cellulose respectively in the sample. FTIR spectra (not shown here) revealed substituted ammonium salts (2370 cm^{-1}), substituted

Table 2– Chemical analysis of Eucalyptus bark

Component	Percentage by weight
Cellulose	39.7
Hemicelluloses	18.5
Free Sugars	6.0
Total carbohydrates	60.5
Lignin	29.5
Ash	4.0
Total nitrogen	1.8
Water extractable	14.7
Alcohol extractable	7.9
Total organic matter	92.7

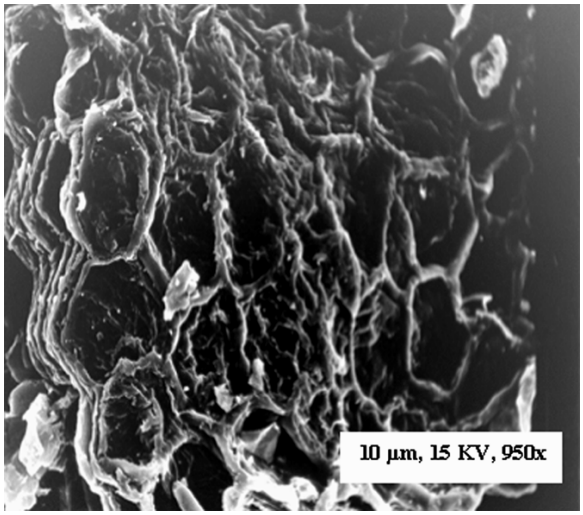

Fig. 2– Scanning electron micrograph of eucalyptus bark

phenols (3343.4 cm^{-1}) and straight organic chains (896.6, 778.9 cm^{-1}) in bark as main functional groups on the surface of bark.

Effect of pH

To determine the effect of pH on the removal of the dye, its adsorption was studied at varied pH range of 2.0-11.0 and is shown in Fig. 4. The figure clearly indicates that maximum uptake of dye takes place at pH 2.0 and 8.0. The dye EBT is a diprotic dye with pKa values of 6.6 and 11.6. The dissociation of dye takes place depending upon pH values. At low pH only one proton is dissociated thus there is less negative charge on the dye surface. At acidic pH the phenolic groups and amino groups on the eucalyptus bark surface are protonated which attracts the anionic dye due to electrostatic forces of interaction. This suggests that chemisorption is the mode of adsorption at low pH. The same fact is supported by pH_{zpc} measurement. At pH 6.0 both protons are dissociated thus maximum repulsions are present between adsorbate and adsorbent thus minimum removal is established. At slightly basic pH, the phenolic group is slightly ionized which enhances the diffusion of dye molecule into the adsorbent, further increase in pH causes repulsions due to equal electrical charges on the surface of adsorbent and adsorbate. Thus, at pH 8.0 good adsorption is obtained. For all other experiments pH 8.0 is used as it is supposed to be more close to pH of textile effluent.

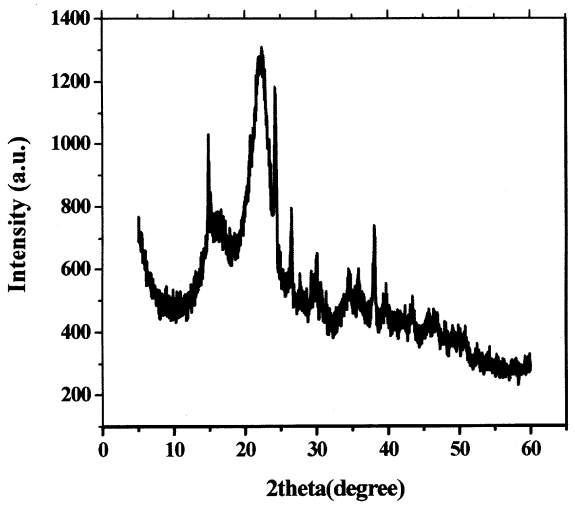

Fig. 3– X-ray diffraction pattern of eucalyptus bark

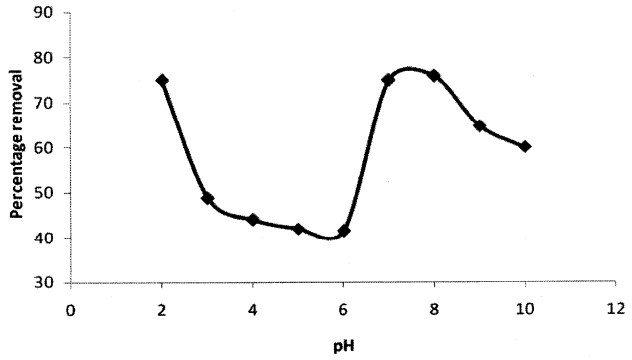

Fig. 4– Effect of pH on removal of EBT by eucalyptus bark (initial dye concentration 250 mg L^{-1}, adsorbent dose 12.50 g L^{-1}, agitation time 2 h, temperature 303 K)

Variation in the adsorbent dosage

To investigate the effect of adsorbent dose on adsorption of EBT on eucalyptus bark, the experiments were conducted with different adsorbent doses and it was found that with an increase in the dose, the adsorption increases. A significant increase is observed at adsorbent dose of 0.125 g. Any further addition of adsorbent did not cause a significant change in adsorption as at lower adsorbent dosage the number of dye molecules are relatively higher, compared to availability of adsorption sites. Further, the rate of adsorption does not register a proportionate increase as per the experimental results. In view of this it is justified that with the increase in adsorbent dose the increase in adsorption is not proportionately high. The results are shown in Fig. 5.

Effect of dye concentration

The adsorption experiments were then conducted with varied adsorbate doses using different initial dye concentrations ranging from 25 mg L^{-1} to 250 mg L^{-1} at 303 K, 313 K and 323 K temperatures and the behavior has been shown in Fig. 6. It is apparent from the data that adsorption increases with an increase in the concentration of dye and with the increase with the temperature.This suggests that ongoing adsorption is endothermic in nature.

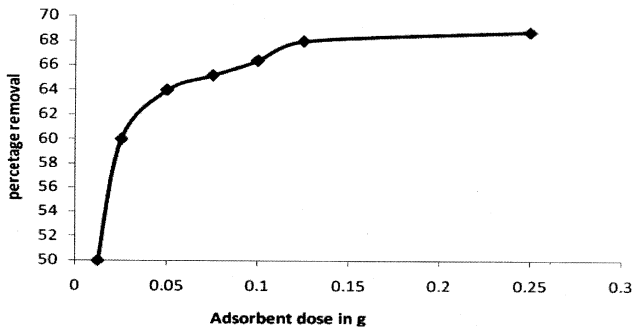

Fig. 5– Effect of adsorbent dose on percentage removal of EBT (initial dye concentration 250 mg L^{-1}, pH 8.0, temperature 303 K)

Adsorption isotherms

The Freundlich and Langmuir isotherm models have been successfully applied to the above system at various temperatures 303 K, 313 K and 323 K and thermodynamic parameters calculated accordingly. For the equilibrium concentration of adsorbate (C_e) and amount of dye adsorbed at equilibrium (q_e), the following linear forms of Langmuir and Freundlich isotherms were studied.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \quad \ldots (2)$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad \ldots (3)$$

Where Q_o and b are Langmuir constants, while K_F and n are Freundlich constants. The Freundlich and Langmuir isotherms gave straight lines and intercepts and slopes were used to determine the values of Freundlich and Langmuir parameters as given in Table 3 and the isotherms are shown in Figs 7 and 8, respectively.

Thermodynamic studies

The changes in the reaction that can be expected during the process require the brief idea of the thermodynamic parameters which were also calculated from the above data. The Gibbs free energy, $\Delta G°$ was found to be negative at all temperatures, indicating spontaneous process at all the temperatures while enthalpy $\Delta H°$, was positive suggesting endothermic and irreversible nature of the process. The positive value of entropy, $\Delta S°$ suggests favorable randomness factor though its value is small. This suggests the structural changes after adsorption of EBT takes place on bark. The thermodynamic parameters were calculated using following equations and the values of parameters are given in Table 4.

$$\Delta G° = - RT \ln b \quad \ldots (4)$$

$$\Delta H^0 = -R\left(\frac{T_2T_1}{T_2 - T_1}\right)\ln\left(\frac{b_2}{b_1}\right) \quad \ldots (5)$$

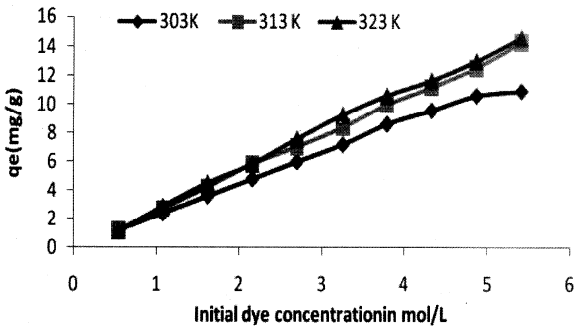

Fig. 6– Effect of dye concentration on adsorption over eucalyptus bark at different temperatures (adsorbent dose 12.50 g L^{-1}, pH 8.0)

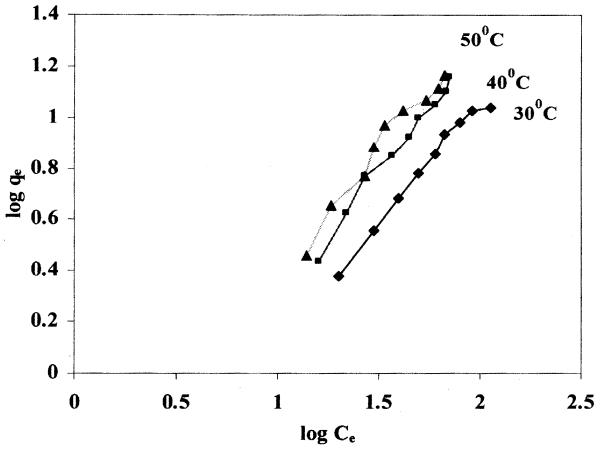

Fig. 7– Freundlich adsorption isotherm for adsorption of EBT over eucalyptus bark at different temperatures

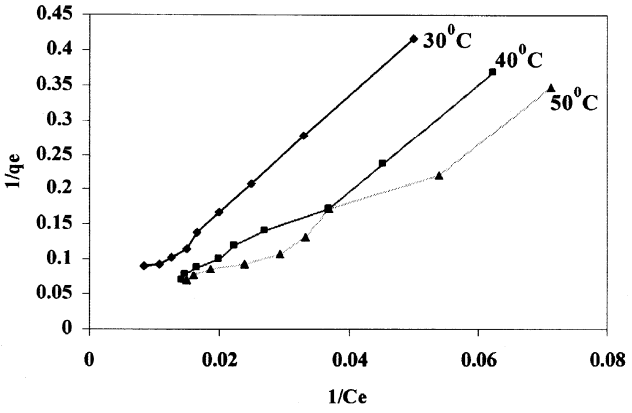

Fig. 8– Langmuir adsorption isotherm of adsorption of EBT over eucalyptus bark at different temperatures

Table 3– Freundlich and Langmuir parameters for adsorption of Eriochrome black-T over eucalyptus bark at different temperatures

Temperature (K)	*K*F	*n*	Q_o(mol/g)×10^{-3}	*b*(L/mol)
303	0.2123	1.0399	0 .1135	1.8399
313	0.2175	0.9969	0.1232	1.5927
323	0.2432	1.0144	0.1367	1.5229

Table 4 – Values of thermodynamic parameters for adsorption of Eriochrome black-T over eucalyptus bark

Temperature (K)	ΔG (J mol^{-1})	$\Delta H°$ (J mol^{-1})	ΔS (JK^{-1} mol^{-1})
303	-1536.22	+3764.66	+15.1532
313	-1211.40		
323	-1129.82		

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad \ldots (6)$$

Where b, b_1, b_2 are Langmuir constants at 303 K, 313 K and 323 K, respectively.

To investigate the favorability of a process the dimensionless separation factor R_L was also calculated (Eq. (7)) and found to be less than 1. The values are 0.5899, 0.6233 and 0.6338 at 303 K, 313 K and 323 K, respectively indicating that the adsorption of Eriochrome black-T over eucalyptus bark process is favourable.

$$R_L = \frac{1}{(1 + bC_0)} \quad \ldots (7)$$

Kinetic studies

The rate of removal of EBT has been studied as a function of time as can be seen in Fig. 9. The equilibrium was attained in 2 h. Adsorption rate constant study was carried out with the famous Lagergran rate equation (Eq. (8)).

$$\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \quad \ldots (8)$$

The time versus log (q_e-q_t) plots as shown in Fig. 10 was found to be linear suggesting that the sorption followed the first order kinetics. The slope of the plot gave the value of rate constant and it was found to be 5.337×10^{-4} s^{-1}. The plot of q_t versus $t^{1/2}$ was found to be linear with a slope K_d= 0 .0746 mg g^{-1} s$^{-0.5}$ (Fig. 11).

Thus, this step is slow followed by fast steps like particle diffusion and adsorption of dye on the surface of bark. The probable mechanism for this process was diffusion film mechanism. The rate is therefore controlled by the step where an equilibrium is attained between liquid film over the surface of bark and dye molecules.

$$q_t = K_d\, t^{1/2} + \text{constant} \quad \ldots (9)$$

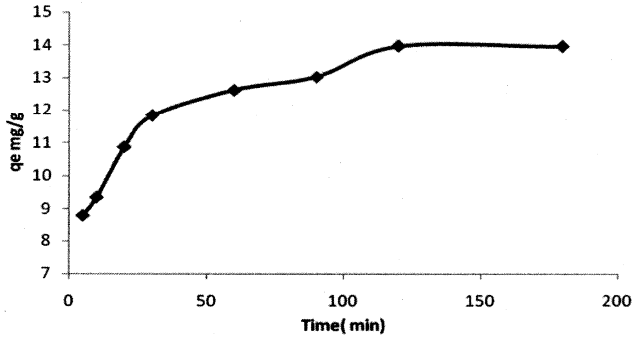

Fig. 9– Effect of contact time on adsorption of EBT on eucalyptus bark (initial dye concentration 250 mg L^{-1}, pH 8.0, temperature 303 K)

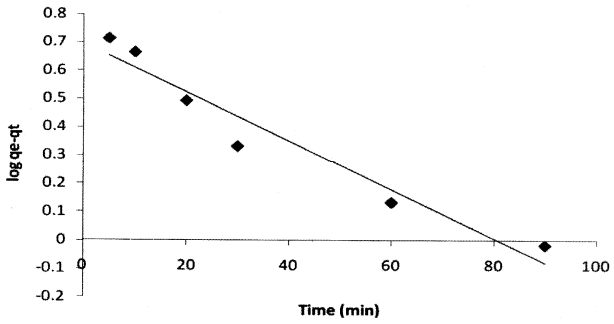

Fig.10– Lagregran plot for the adsorption of EBT over eucalyptus bark at 303 K

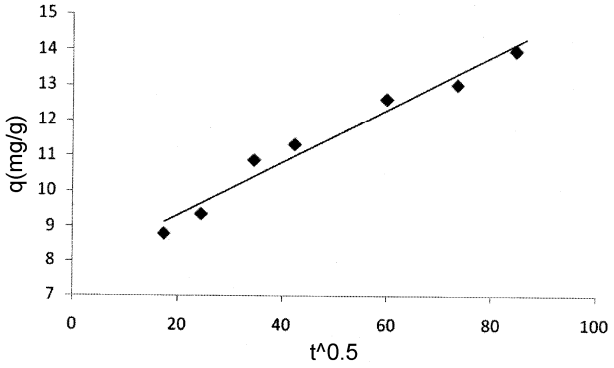

Fig. 11– Intra-particle diffusion film mechanism for adsorption of EBT over eucalyptus bark

Column studies

The continuous flow adsorption experiment was conducted in an acrylic column consisting of two columns: each column had an internal diameter of 5 cm and a length of 30 cm. The eucalyptus bark was packed in the column between glass wool and glass beads, which prevented the wash out of the bark. The particle size was 0.150-1.110 mm with a bed depth of 30 cm and filling weight of 30.0 g in each column.

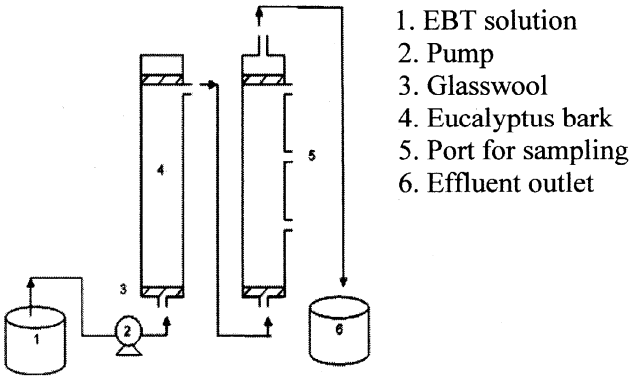

Fig. 12 – A schematic diagram of fixed-bed column of Eucalyptus bark for EBT adsorption

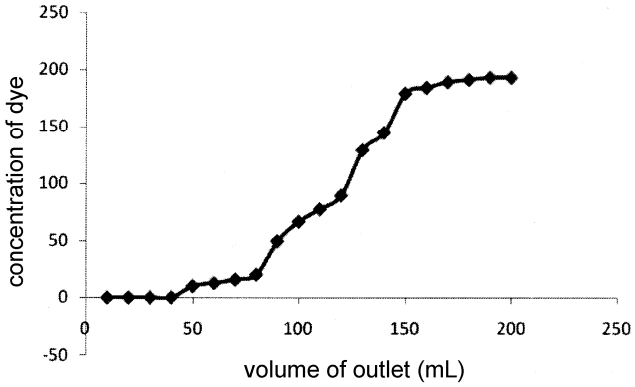

Fig. 13 –Breakthrough curves representing removal of EBT through fixed bed column of eucalyptus bark (pH 8.0, temperature 303 K, dye concentration 250mg $L^{-1)}$

The packed density or bulk density (ρ_s) of the adsorbent in the column was approximately 0.1188 g cm^{-3}. The column had three 0.5 cm (internal diameter) septa ports through which the samples were collected at time intervals using a syringe with a needle. Before operation, the bed was rinsed with distilled water and left overnight to ensure a closely packed arrangement of particles with no void, channels, or cracks. A schematic of a fixed-bed column of eucalyptus bark for EBT adsorption is shown in Fig. 12. The EBT of concentration 250 mg L^{-1}, pH 8.0 was fed through the fixed-bed column in an up-flow mode to avoid channeling of the simulated effluent and compaction. The roller pump (EYELA Roller pump RP-1000) was used to control the flow rate at the inlet and the outlet. The effluent samples were collected at specified time intervals and measured for the remaining dye by a colorimetric method, which was spectrophotometrically analyzed at a wavelength of 540 nm. The flow to the column was continued until the effluent EBT concentration (C_e) approached the influent EBT concentration (C_0), $C_e/C_0 = 0.97$.

The concentration of collected volume was determined spectrophotometrically (Fig. 13), and the sigmoid type of curve was obtained. The column was assumed to be exhausted when 90% dye was obtained in output. The column was then regenerated with four aliquots of acetone (30 mL each). The column was finally washed with hot water and successfully used for removal of dye for six cycles. The acetone containing dye was recovered by distillation at 323 K using air condenser. The dye was recovered after the process unchanged as is evident from its break through curves in Fig. 13. The capacity of column was compared with batch capacity and was found greater.

Conclusions

This study shows that EBT dye can be successfully removed from the aqueous solution by adsorption on eucalyptus bark. This adsorbent was found to be useful and valuable mean for controlling water pollution due to dyes. The following conclusions can be drawn from this study:

(i) The batch adsorption experiments show that the adsorption of the EBT over eucalyptus bark is dependent on pH, amount of adsorbent, concentration, contact time, and temperature, and almost 77.33% could be accomplished at low concentrations, whereas at higher concentrations, the adsorption was slightly decreased to 68% for eucalyptus bark at all temperatures.

(ii) The thermodynamic parameters obtained in both cases confirm the feasibility of the process at each concentration.

(iii) The results of kinetic experiments show that the adsorption proceeds via film diffusion at higher and lower concentrations.

(iv) The column capacity for each process was found to be higher than the batch capacity. The recovery of the dye was achieved by eluting with acetone due to high solubility of dye in acetone through the column, and adsorbent can be regenerated.

(v) The eucalyptus bark is inexpensive and can be used as excellent adsorbents.

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