Evaluation of Performance of Sono 3-Kolshi Filter for Arsenic Removal from Groundwater Using Zero Valent Iron Through Laboratory and Field Studies

A.K. M. MUNIR and **S. B. RASUL**
Sono Diagnostics Centre
Environment Initiative, Kushtia, Bangladesh

M. HABIBUDDOWLA
140 Northwood Road,
Frankfort, KY 40601, USA

M. ALAUDDIN
Department of Chemistry,
Wagner College, Staten Island New York, USA,

A. HUSSAM
Department of Chemistry, George Mason University,
Virginia, Fairfax, VA 220 30, USA
and
A.H. KHAN
Department of Chemistry, University of Dhaka,
Dhaka - 1000, Bangladesh

Abstract

A three-pitcher (locally known as '3-Kolshi') water filtration system made from locally available materials was tested for its efficacy in removing arsenic, other trace metals and anions from the groundwater of Bangladesh and the disposal of the filtering materials after the breakthrough was studied. In this filter, the first Kolshi has cast iron turnings, and sand, the second Kolshi has wood charcoal and sand as the active ingredients. About 6000 L of groundwater containing 80 - 1900 μg/L of arsenic was filtered. The filtered water contained about 10 μg/L As(total), no detectable As(III), and significantly reduced major, minor and trace

metals. The filtration process was monitored for a year by measuring As (total), As(III), 23 other metals, 9 anions, pH, conductivity, temperature and flow rate. The complete conversion of Fe^0 to nonmagnetic hydrous ferric oxide (HFO) as the most active component for arsenic removal is indicative of an oxidizing environment sustained by continuous diffusion of air through the porous Kolshi. All parameters indicate that the water quality meets and exceeds USEPA, WHO, and Bangladesh standards. The effect of flow rate on arsenic removal has been studied separately for three tube wells with arsenic concentration of 166-212, 211-238 and 1435-1642 μg/L (ppb) over a period of 48 months. The results demonstrate that the optimum flow rate is about 7 L/hr for achieving an arsenic concentration down to the level of 7-13 ppb from the initial level of about 200 ppb. The optimum flow rate is 8.4 L/hr for achieving an arsenic concentration of about 20 ppb from the initial level of 1600 ppb. Any possibility of pathogenic contamination during the use of the system as a household utility can be removed with a 4-litre hot water cycle, once in a week. This contamination is not inherent to the system. Leaching experiment on solid wastes from 3-Kolshi filter, with rain water at pH 4 and 7, showed no release of arsenic above 16 µg/L of the leachate, which is the detection limit of ICP-AES method for arsenic. The release of other trace metals was also not very significant.

At its present capacity, five people can use the system for about five months at a consumption rate of 50 L/day. Regeneration of the system to its original efficiency can be achieved by changing the sand in the Kolshi. These low-cost units (ca. US $ 5.0- 6.0) are being used by people in the arsenic affected areas of Bangladesh in large numbers. Further studies on the improvement of the design and the initial treatment of the filtering materials are in progress.

INTRODUCTION

Recent measurements show that in many parts of the Ganges and Bhrahmmaputra basin more than 60% of the shallow and deep tubewell water contains arsenic above the WHO guideline value of 10 µg/L and more than 30% of the tubewells contains arsenic above the Bangladesh standard of 50 µg/L (Chatterjee, *et. al.,* 1995; Das *et. al.,* 1995). It is estimated that of the 125 million people of Bangladesh, between 35-77 million are drinking groundwater containing more than 50 µg/L of arsenic. The contaminated water is widely hand-pumped from a depth of 30 - 200 feet using shallow tubewells. According to WHO estimate, there are about 2.5 million tubewells, although the unofficial estimate is about 10 million (Smith *et. al.* 2000). The prolonged drinking of this water has caused serious health hazard in the form of hyperkeratosis on the palms and feet (Choudhury *et. al.,* 1998). Long term exposure to low concentrations of arsenic has been reported to cause cancer of bladder, skin and other internal

organs (International Agency for Research on Cancer, 1980). The health hazard caused by drinking arsenic affected water can be arrested by drinking arsenic-free water because the biological half-life of arsenic appears to be between ten hours and four days (National Research Council, 2000; Goyer *et. al.,* 1996; Tam *et. al.,* 1979). There are no known cures for arsenicosis. Since 97% of population depend on groundwater, provision of safe drinking and cooking water warrants immediate development of water purification systems appropriate for rural Bangladesh.

This work is motivated by the urgency of the current crisis and the need for a simple and low-cost technique for the removal of arsenic from the groundwater of Bangladesh. Considering the vulnerability of vast population to adverse health effects of arsenic, developing an appropriate, affordable household filtration system is a major step in combating the current calamity. Recently, we have reported such a method and the physicochemical basis for the purification of arsenic contaminated groundwater (Khan *et. al.,* 2000). The arsenic filtration system assembled by using locally available materials has been widely accepted and promoted by various non-governmental organizations in the arsenic affected areas of Bangladesh in large numbers (est. 20,000 units are in use). This paper presents the results of a one-year critical evaluation of the 3- Kolshi filtration system based on measurements of As(III), As(total), 23 major, minor and trace metals, 9 anions, pH, conductivity and flow rate.

METHODOLOGY

Filtration System Setup

The filtration system described here and in our earlier report (Khan *et. al.,* 2000) is based on fired unglazed clay pitchers (hereafter called by its local Bengali name 'Kolshi') used by more than 80% of the population as a reservoir for drinking and cooking water. Figure 1 shows the photograph of the filtration system used in this study. In a three Kolshi (3-Kolshi) filtration system, the Kolshis (top, middle, and bottom) are placed on top of each other in a steel or bamboo frame for ease of maintenance. Each Kolshi has a volume of about 18 liters. The top and middle Kolshi has small holes (~ 0.5 cm diameter) which are covered with pieces of synthetic (polyester) material from inside. The holes are made for free flow junction nozzles connected from outside. These nozzles can be easily altered to adjust flow rate.

Figure 1: **Picture of a 3-Kolshi-filtration setup. This particular setup was used to filter 6000 L of arsenic contaminated groundwater. The computerized electrochemical analyzer for the measurement of arsenic is shown in the background,**

About half kilograms of small brickette pieces (grade A red bricks, 2-3 cm pieces) were spread on the clothes. The middle Kolshi was then filled with 2 kg sand (from local Garai river), 1 kg wood charcoal (ca. 1 cm pieces from cooking wood) and 2 kg brickette pieces. The top Kolshi has 3-kg of cast iron turnings (from local machine shop or iron works) placed uniformly on the brickette and 2 kg of sand on top of the iron turnings. All the filtering materials are pre-cleaned to remove any unwanted dirt before the filter unit is assembled. Tubewell water is poured slowly on the top Kolshi and collected at the bottom Kolshi. The filtration system is used for pure drinking water after discarding initial 3-4 batches (ca. 10-L each) of water. Experience shows that covering the middle and bottom Kolshis with small pieces of synthetic clothes placed on perforated earthen covers (available from the same Kolshi makers), can prevent accidental

leakage and dust. Users are advised to follow general precautions such as the placement of the filtration unit in a secured place, always keeping the top opening of the Kolshis covered with clean clothes and practice hygiene rules in handling drinking and cooking water. The filtered water was collected for analysis by decanting into pre-washed HDP (high-density polyethylene) sample collection bottles and analyzed immediately for As(III) and As(total) by the computerized electrochemical analyzer.

Analytical methods and procedure

Details of analytical methods and procedure for the measurement of As(III), As(V), Fe(soluble), pH, E_h, and conductivity were described earlier (Khan *et. al.,* 2000). It should be noted that water samples were collected before and after filtration in acid pre-washed HDP bottles and promptly analyzed for As(III), As(total), and Fe (total) without further filtration. This ensures almost real time analytical data for actual drinking water. Samples for ICPAES (Inductively Coupled Plasma Atomic Emission Spectroscopy) analysis of 24 metals were preserved in 250-mL HDP bottles acidified with 1.0 mL concentrated HCl (AnalaR) without a headspace. Samples for anion analysis were preserved without acid.

Selective measurements of As(III) were performed by a computer controlled electrochemical analyzer (Model HQ-2040, Advanced Analytics, Virginia, USA) following a modified EPA method [Method 7063: Arsenic in Aqueous Samples and Extracts by Anodic Stripping Voltammetry (ASV) (Pyles, *et. al.,* 1999)]. As(total) was measured by the same technique after chemical reduction of As(V) to As(III). Detail procedure, analytical merits and method validation are described elsewhere (Khan *et. al.,* 2000; Rasul *et. al.,* 1999; Davis *et. al.,* 1978; Sun *et. al.,* 1997). A continuous flow hydride generation atomic absorption spectrometer (Buck Scientific, Model 210 VGP at Intronics Technology Center, Dhaka, Bangladesh), a Perkin-Elmer model 5100 Zeeman-effect atomic absorption spectrometer with a graphite furnace (AASGF-Z), and model A-60 autosampler (at GMU, USA) were used for regular measurement checkup and cross validation of field measurements. A 24-trace metal profile of water samples before and after filtration was measured by a direct reading Echelle ICPAES with radial and axial view (Leeman Labs, NH, USA). The anion analysis of preserved water samples was performed by a Lachat QuickChem Model 6000 Ion Chromatograph (Zellweger Analytics, WI, USA). Total alkalinity, and the concentrations of H_2CO_3 (aq), CO_3^{2-} and HCO_3^- were determined from acid base micro-titration of groundwater.

To study the effect of flow rate on arsenic removal efficiency, two tubewells from the same area were selected, one having the initial concentration of total arsenic of about 200 ppb and the other, about 1400 ppb. Other parameters such as pH and conductivity were almost the same for the two samples.

The analytical quality control of the method is maintained through quality control chart of analysis with the same method over a period, apart from independent method approach of analytical validation.

RESULTS AND DISCUSSION

Nature of groundwater

In Bangladesh, the groundwater chemistry is not very well known. The development of any filtration system requires a relatively clear understanding of the composition of the water being filtered. The present work was carried out in Kushtia Sadar with a population of about 400,000 thousand in 316 km^2 (Stat, 1994). It is now known that over 40% of the tubewells in Kushtia are contaminated with arsenic (total) above 50 μg/L, of which 43-98% is present in the as more toxic As(III) (Rasul *et. al.,* 1999). Table 1 shows the composition of six replicates of anoxic groundwater obtained from two tubewells used for the present filtration studies. The elemental compositions are shown as the concentration range and the anion compositions are the average of three replicates. Except for the total arsenic concentrations (80 -1900 μg/L), the water from these wells are representative of the drinking water from this area. Typically, the groundwater has high soluble iron that, upon leaving for 2-6 hours in an oxic environment, forms a brownish colloidal hydrous ferric oxide making the water turbid. Spectrophotometric measurement of turbidity at 450-nm shows 30% decrease in transmittance from a clear solution in 4 hours (Rasul *et. al.,* 2000). The water is also high in calcium and magnesium and thus can be regarded as hard water. The choice of these two tubewells for the present study was prompted by the high concentrations of arsenic and other minerals that clog many commercial filters and constitute a stringent test for the long-term effectiveness of the 3-Kolshi filtration system. Table 1 also lists the composition of the 3-Kolshi filtered tubewell water as discussed later.

The concentrations of anions, NO_2^- , NO_3^- , SO_4^{2-} , Cl^- , F^- , Br^- , and PO_4^{3-} , listed in Table 1, were obtained by ion chromatography of water preserved without acid. The concentration of these anions may be underestimated due to the precipitation of groundwater, which has affected the multivalent anions (SO_4^{2-} and PO_4^{3-}) more than the monovalent anions (Cl^- , F^- , NO_2^- , and NO_2^-). The concentrations of CO_3^{2-} , $H_2CO_3(aq)$, and HCO_3^- were based on acid-base titration of fresh groundwater (Snoeyink *et. al.,* 1980). To understand the chemical speciation of groundwater, a computational geochemical model, MINEQL+ (Schecher *et. al.,* 1998) was used with the inputs as shown in Table 1.

Table 1: Composition of typical groundwater from two tubewells and the 3-Kolshi filtered tubewell water.

Species and Parameters	Groundwater mg/L	3-Kolshi water mg/L
Aluminum, Al	<0.015-0.052	<0.015-0.033
Antimony, Sb	<0.013-0.017	<0.013
Arsenic. As (total)	0.08-1.900	0.012 0.010
As(III)	0.073 -1.170	<0.002
Barium, Ba	0.161-0.170	0.05 - 0.063
Beryllium, Be	<0.001	<0.001
Cadmium, Cd	<0.001	<0.001
Calcium, Ca	111-117	56 - 65
Chromium, Cr	<0.002	<0.002
Cobalt, Co	<0.002	<0.002
Copper, Cu	0.004-0.009	0.005
Iron, Fe	6.77-7.19	0.010 - 0.49
Lead, Pb	<0.004-0.005	<0.004 - 0.006
Magnesium, Mg	21.4-23.1	19 - 27
Manganese, Mn	0.69-0.74	< 0.002
Molybdenum, Mo	0.001-0.003	0.001-0.003
Nickel, Ni	<0.002	<0.002
Potassium, K	1.88-2.45	1.88-2.45
Selenium, Se	<0.012	<0.012
Silver, Ag	<0.002	<0.002
Sodium, Na	18.2-20.4	20.1 - 92.4
Strontium, Sr	0.280-0.297	0.18-0.37
Thallium, Tl	<0.067	<0.067
Tin, Sn	<0.002-0.01	<0.002-0.01
Vanadium, V	<0.001	0.004-0.009
Zinc, Zn	0.012-0.021	0.011
pH	6.9-7.2	7.7 0.2
Conductivity S-cm)	570 46	365 66
Temperature,oC	27-29	27 - 30
NO2(-)	0.469	< ic
NO3(-)	0.980	0.823
SO4(2-)	0.424	2.43
Cl(-)	3.273	5.9 - 110
Br(-)	<ic	0.028
F(-)	0.27	0.47
PO4(3-)	0.023	0.068
CO3(2-)	0.29	1.47
H2CO3(aq)	148	18.3
HCO3(-)	560	432

<ic : below the detection limit of ion chromatographic system.

The speciation model shows Ca^{2+}, Fe^{2+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Sr^{2+}, Zn^{2+}, Cl^-, CO_3^{2-}, F^-, SO_4^{2-}, NO_3^-, and NO_2^- as the major components and $H_3AsO_3(aq)$, $HASO_4^{2-}$, $H_2ASO_4^-$, $CaHCO_3^+$, $CaCO_3$ (aq), $MgCO_3$ (aq), $MgHCO_3^+$, $MnHCO_3^+$, $H_2CO_3(aq)$, and HCO_3^-, as the major species (concentration >10-6 M) under anoxic condition. The model also predicts that the concentration of Fe(total), Mn(total), Al, Ca, Ba, and CO_3^{2-} exceeds their solubility product limits for minerals - hematite   -Fe_2O_3), bixbyite ($Mn(OH)_3$), diaspore ($Al(OH)_3$, $2H_2O$), Calcite ($CaCO_3$), and Dolomite ($CaMg(CO_3)_2$), and thus precipitate out under oxic condition (Rasul *et. al.,* 2000). Similar oxic conditions prevail in the 3-Kolshi filtration system.

Effectiveness of Arsenic Filtration System

Figure 2 shows the effectiveness of the 3-Kolshi filtration system for the removal of As(III) and As(total) from 6000 L of groundwater. The numbers indicate measurement at regular intervals except for the breaks at 10th and 22nd measurements. The first break was due to the change in the filter plug in the middle-Kolshi and the second break was caused by the breakage of the top-Kolshi, which was replaced with new sand. These changes, however, did not decrease the arsenic removal efficiency as shown in Figure 2. Measurements 1-5 were due to the filtration of original groundwater containing 80-100 µg/L As(total) and 75 µg/L As(III). The filtered water contained 17 µg/L As(total) and <2 µg/L As(III). At this point the same groundwater was spiked with arsenite (As(III): As_2O_3 dissolved in dilute NaOH and neutralized) and arsenate (As(V) in Na_2HAsO_4) to increase the concentrations of As(total) and As(III) at indicted levels. In order to facilitate and observe the 50 µg/L breakthrough, a 6-L groundwater spiked with 10,000 µg/L of arsenate was filtered. The resulting effluent contained arsenic at a level of 22 µg/L As(total) (not shown in Figure 2). Clearly, no breakthrough appeared. The total volume of water filtered from this tubewell was ca. 4850 L. Measurements 24-38 were made with groundwater from another tubewell (Harishankarpur, Kushtia Sadar) which was known to have a maximum of 1900 µg/L As(total) and 800 µg/L As(III). Clinically identified arsenical keratosis patients are reported in this location. Measurements 24-38 were carried out in quick successions so as to maintain the high concentration of arsenic species. Concentrations of both As(total) and As(III) were found to fluctuate in this location when water was collected at long irregular intervals as shown by the remaining data. The total volume of water filtered from this tubewell was ca. 1000 L. In all cases the filtered water contained, 12 ± 10 µg/L As(total), which is close to the WHO guideline value of 10 µg/L and no detectable As(III), irrespective of the input levels of As(total) and spiking. In continuation with our previous work, measurements of total soluble Fe, pH, conductivity and flow rate were made intermittently to judge the quality

of water. These results and the elemental composition are summarized in Table 1. We also note that the filtered water remained clear for months in clear plastic water bottles. Table 1 shows that the concentrations of Fe decreased significantly and sometimes below the detection limit of ICPAES. The concentration of Mn also decreased to less than 2 µg/L. Therefore, these two metals are quantitatively removed by the filtration system as their hydroxide precipitates. While the concentration of Ca and Ba are decreased to half, the concentration of Mg did not change. The concentration of Na also did not change (except one high reading) while the concentration of K has increased slightly. This could be an indication of a very weak dissolution or ion exchange dissolution of sand minerals (Langmuir, 1997). A slight increase in V concentration in the filtered water is an indication of presence of V in cast-iron turnings. Zinc concentration was decreased by half. The concentrations of all other trace metals did not change or remained below the detection limit of ICPAES.
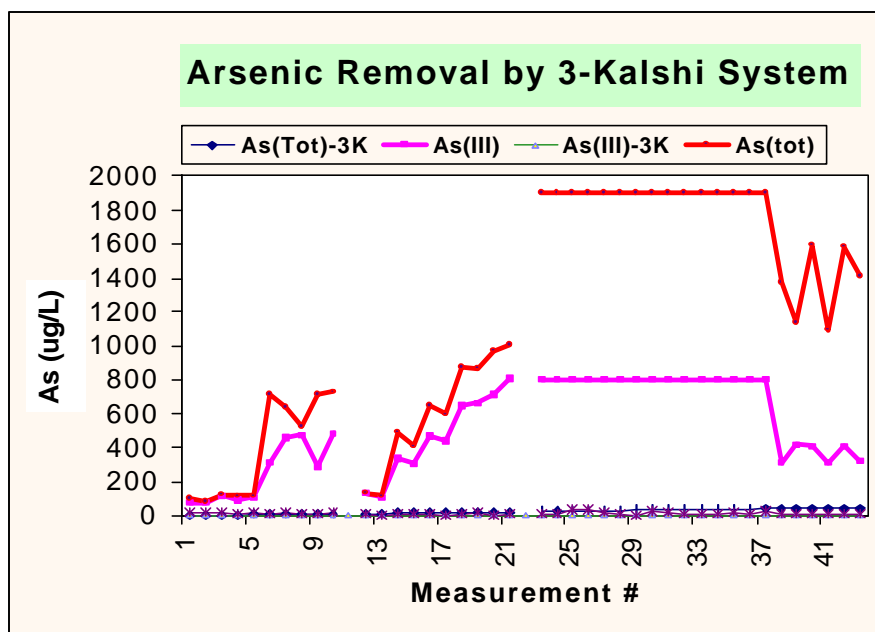

Figure 2: Arsenic removal efficiency of a 3-Kolshi filtration system. The 3-Kolshi filtered data (-3K) are shown near abscissa. See text for details data (-3K)

The pH of the filtered water increased by one unit, possibly a result of decarbonation. This is also evident from the decrease in bicarbonate concentration. A 36% decrease in solution conductivity is indicative of substantial removal of ionic components from solution. Anion concentrations in

the filtered water are generally low (except for one high reading for Cl⁻) and had no consequence either on the filtration system or on speciation. Water chemistry shown in Table 1 is in agreement with our previous findings at the early stage of filtration system development, which indicates the consistency and reproducibility of the 3-Kolshi filtration system. Except for occasional variations in non-toxic species (Na and Fe), and a change in flow rate, the 3-Kolshi system has performed well.

The 3-Kolshi system described here was used to filter about 6000 L of groundwater after which the effluent arsenic increased to about 60 μg/L As(total) without a clear rise in concentration as would be expected from classical breakthrough experiments (not shown in Figure 2). In some cases, the system may not function adequately due to clogging of the outlets and overloading of sand with fine hydrous ferric oxide (HFO: $Fe_2O_3.2\text{-}3\ H_2O$) precipitates.

Effect of the Flow Rate on Arsenic Removal

After the report of the Phase II program (Rapid Assessment-2001) as discussed below, it was realized that the control of the flow rate and its effect on arsenic removal by 3-Kolshi filter needs further improvement. Accordingly, three tube wells [one in the house of one of the authors (AKM Munir), one in his Clinic, and a third one] with arsenic concentrations of 166 - 212 μg/L, 211 - 238 μg/L, and 1435 - 1642 μg/L, respectively (varying over a period of 4-8 months, September 2000 - April 2001) were studied with 3-Kolshi filter. Flow rates were fixed at 7.2, 8.4, 9.6 and 11.8 L/hr. The filter sets were newly designed with flow rate adjustable free flow junctions. The results of this study are given in Table 2, as preliminary findings since the study is still continuing to find the breakthrough stage for different flow rates.

Table 2: Effect of flow rate on Arsenic Removal by 3-Kolshi Filter System (period: September 2000-April 2001) (n=19, No. of measurements.)

Tube wells Water		Tube wells Water			Filtered Water		
TW	Flow Rate (L/hr)	pH	Conductivity μS/cm	As(total) μg/L	pH	Conductivity	As(total) μg/L
TW1	7.2	6.0-7.0	452 - 525	166-212	6.5-6.9	411 - 483	7-13
TW2	7.2	6.6-7.1	488 - 546	211-238	6.3-6.5	3.2 - 342	7-13
TW3	11.8	6.6-7.1	466 - 503	1438-642	6.5-6.8	443 - 558	35-114*
	8.4	6.7-6.9	492 - 499	1455-1588	6.6-6.8	442 - 459	18-20

* This was almost the break-through point at the flow rate of 11.8L/hr. At this point when the flow rate was adjusted to 8.4 L/hr., the removal efficiency of the same filter unit for the same water was recovered to the permissible level of 20 μg/L of total Arsenic, 2.5 times lower than the MCL value of 50 μg/L.

The results in Table 3 clearly indicate that by adjusting the flow rate to about 7 L/hr, maximum efficiency can be attained with arsenic content in the filtered water to be about 10 ppb, irrespective of the initial concentration of arsenic (200-1600 ppb as tested), while the other water quality parameters remain within acceptable limits. The filter units under this condition have been used for about 8 months, without any break-through yet. The filtered water satisfies the needs for drinking and cooking water, in a family of 5 members. A 4-L hot water cycle (wash) per week keeps the filter water free from pathogenic load as tested by human consumption without any health complication.

Experience shows that gentle poking of the outlet filters with a fine sewing needle can restore the flow rate. Regeneration of the system to its original efficiency can be obtained by changing the sand in the Kolshi. The drinking water production rate (6-7 L/hour) is adequate for drinking and cooking purpose of a family of 4 to 5. At this capacity, five people can use the system for five months at 50 L/day consumption. Further improvements in flow rate by redesigning the outlet system with a free flow junction are in progress. One of the present concerns with any filtration system is the disposal of the solid waste produced. We estimate that the concentration of As(total) accumulated in sand and HFO is 350 mg As/kg of solid at the break-through point. Since the filtration system requires no chemical regeneration steps (e.g., in regeneration of activated alumina column for arsenic mitigation) the wastes produced by Kolshi are self-contained. Preliminary experiments involving Dutch Total Available Leaching Procedure (TALP) of sand and mixed waste from 3-Kolshi show 15 μg/L and 25 μg/L of As(total) at pH 7 and pH 4, respectively (ASTM, 1992; Price *et. al.,* 1997). Similar results (<16 μg/L by ICPAES) were obtained for leaching with rainwater instead of deionized water. ICPAES data of same solutions shows no increase in concentrations of other metals compared to that of the filtered water (Hussam *et. al.,* 2000).

Role of Iron in Arsenic Removal

Iron is present in the filtration system as zero valent iron, Fe^0, in the top Kolshi and in groundwater mostly as soluble Fe(II) species. Since the filtered water is nearly free from iron, therefore the oxidation products of zero valent iron and the oxidation of Fe(II) species to HFO (Dzombak *et. al.,* 1990) are quantitatively retained in the top and middle Kolshi. Previously, we reasoned that arsenate was quantitatively removed by compound formation or adsorption on HFO (Khan *et. al.,* 2000). In both cases, the excess arsenic removal capacity increases linearly after each Kolshi of filtration. This is due to the accumulation of HFO formed from freshly available soluble iron in groundwater. We calculate that the excess capacity due to compound formation ($FeAsO_4$(s)) is 1.2 mg As/mg Fe and for adsorption, 0.037mg As/mg Fe. Because the excess capacity is a measure of

under used efficiency of arsenic removal, a very large volume of groundwater can be filtered before overloading the system.

The role of various forms of zero valent iron was studied by several groups as a means to remediate environmental contaminants such as arsenic, dissolved heavy metals and chlorinated hydrocarbons (Lackovic *et. al.,* 2000; Driehaus *et. al.,* 1998; Shokes *et. al.,* 999; Ponder *et. al. ,* 1999; Roberts *et. al.,* 1996). Studies by others were aimed at mitigating EPA superfund sites containing high concentrations (mg/L) of arsenic from industrial wastes and artificial waste water (Nikolaidis *et. al.,* 1998). To assess the role of Fe^0, two experiments were performed. The experiments involve one filtration column made of 50-mL plastic hypodermic syringe filled with 25.0 g sand and the other filled with 15.0 g cast-iron turnings. About 500 mL of groundwater spiked with 500 μg/L As(total) was filtered through these columns. The effluents from the sand column had 250 μg/L As(total) and that of 20 μg/L As(total) from the column containing cast iron turnings. Therefore, in comparison to sand, the Fe^0 has significant higher capacity to remove arsenic even when no visible HFO formation was observed. At the end of the present 3-Kolshi experiment, it was found that Fe^0 in the top Kolshi was turned into a solid cemented brownish iron oxide with visible pores throughout the mass. The solid mass was completely non-magnetic. It is clear that extensive oxidation of Fe^0 took place inside the Kolshi, which was sustained by a continuous diffusion of air and water vapor through the porous ceramic Kolshi. There exist various mechanistic pathways for the chemical and physical transformation of Fe^0 surface (Ponder *et. al.,* 1999; Raven *et. al., 1998,* Lackovic *et.al.,* 2000). It appears, however, HFO formation by sustained oxidation of Fe^0 and Fe(II), formation of a positively charged double-layer in presence of excess Fe(II)/Fe(III) on the HFO surface and subsequent specific adsorption of arsenate ($H_2AsO_4^-$ and $HAsO_4^{2-}$) are the primary mechanisms for the removal of arsenic (Dzombak *et. al.,* 1990; Gulledge *et. al.,* 1973; Pierce, *et. al.,* 1982). Moreover, in presence of a high concentration of Ca^{2+} the positive charge density of the HFO colloids can increase and thus enhances adsorption of arsenate: ($H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} (Wilkie et. al. 1996). It is also noted that the oxidizing environment has removed all traces of Mn(II), and NO_2^- from the groundwater.

Leaching of Arsenic and Other Trace Metals from 3-Kolshi Waste

At the break-trough point of the 3-Kolshi filter (6000 L, at the flow rate of 5 L/hr and initial concentration of 1400 ppb of arsenic), the arsenic content in the waste (sand + HFO) from the first and the second Kolshi was estimated to be 350 mg/kg of the solid. This material was used in column to perform leaching experiments with rainwater (pH=4 and 7), following the EPA protocols. The distribution of different trace elements including arsenic in the leachates is given in Table 3.

The analysis of the leachates was done with ICP-AES. The detection limit of the method is 0.005 mg/L for other trace metals while for arsenic it is 0.016 mg/L. These results thus indicate that surface dispersion of the wastes from 3-Kolshi filter will not contaminate the natural environment above the background level.

Table 3: Trace Element Distribution of leachates from 2 and 3- Kalshi Wastes by EPA Protocols. Measurement by Inductively Couple Plasma Atomic Emission Spectroscopy (ICP-AES)*

Element	Conc. (mg/L) at pH = 7 3-K, Sand	Conc. (mg/L) at pH = 4 3-K, Sand	Conc. (mg/L) at pH = 7 2-K, Sand + Iron	Conc. (mg/L) at pH = 4 2-K, Sand + Iron
Al	0.028	0.02	0.049	0.014
As	<0.016	<0.016	<0.016	<0.016
Ag				
Ba	0.002	0.007	0.006	0.009
Be				
Ca	2.65	8.39	4.89	8.13
Co				
Cr				
Cu	0.005	0.018	0.007	0.008
Fe	0.02	0.031	0.041	0.051
Mg	0.2	1.03	0.519	0.831
Mn	0.013	0.081	0.005	0.047
Mo			0.001	
Ni	0.002	0.009	0.003	0.005
Pb			0.005	
K	0.82	1.26	0.608	0.527
Na	2.64	0.750	3.35	1.85
Se				
Sr	0.006	0.017	0.014	0.02
Sn	0.007	0.011	0.003	0.006
Tl				
V				
Zn	0.011	0.038	0.013	0.021

*Blank spaces show concentration below the detection limit (bdl) of the ICP-AES. bdl are generally below 0.005 mg/L. For As the bdl is 0.016 mg/L or 16 ppb. Kalshi wastes were collected and extracted at SDCEI, Kushtia according to EPA protocol. ICP-AES measurement was done at the NREPC, Kentucky, USA by Mr. M. Habibuddowla.

Quality of Filtered Water

Table 4 shows the inorganic quality parameters of filtered water in comparison to the requirements set by USEPA, WHO and Bangladesh guideline values. Clearly, the water obtained from the 3-Kolshi filtration system meets and exceeds

international drinking water standards. Recently, the 3-Kolshi filtration system underwent a series of tests commissioned by the technical advisory group of Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP) and found to perform consistently well throughout, passing the 50 µg/L threshold at all wells where it was tested (Rapid Assessment, 2001).

Table 4: Drinking water Inorganic Quality Parameters: Comparison of 3-Kolshi Water with those of USEPA, World Health Organization (WHO) and Bangladesh Standards

Constituent	USEPA (MCL)	WHO, Guideline	Bangladesh Guideline	3-Kolshi water
Arsenic (total)- mg/L	0.05	0.01	0.05	0.012 ± 0.010
Iron (total) - mg/L	0.3	0.3	.3 (1.0)	0.010 - 0.49
Sodium - mg/L		200		20.1- 92.4
Calcium - mg/L			75 (200)	59.1 ± 7.5
Copper - mg/L	1.3 1.	0 - 2.0	1.5	0.005
Manganese - mg/L	0.05	0.1 - 0.5	0.1 (0.5)	<0.001
Zinc - mg/L	5	3.0	5 (15)	0.011
Aluminum -mg/L	0.05-0.2	0.2	0.1(0.2)	<0.015- 0.033
Lead -mg/L	0.015	0.01	0.10	<0.004 -0.006
Chromium, mg/L	0.1	0.05	0.05	<0.002 <0.013
Cadmium, mg/L	0.005	0.003	0.01	<0.001
Barium, mg/L	2.0	0.7	1.0	$.063 \pm 0.01$
Antimony, mg/L	0.006	0.005		<0.013
Molybdenum, mg/L		0.07		0.003
Nickel, mg/	0.1	0.02		<0.002
Selenium, mg/L	0.050	0.01		<0.012
Silver, mg/L	0.1			<0.002
pH	6.5-8.5	6.5-8.5	6.5-8.5	7.7 0.2
Sulfate, mg/L	250		100	2.43
Fluoride, mg/L	4.0		1.0	0.47
Chloride, mg/L	250	250	200 (600)	5.9 - 110
Bromide, mg/L	10		10	0.028
Nitrite, mg/L	1			0.001 (< ic)
Phosphate, mg/L			6	0.068
Total dissolved solids (TDS), mg/L	500	1000	500 (1500)	208

a. Bangladesh standard values are given as maximum desirable concentration with maximum permissible concentration in parentheses. TDS for 3-kolshi was calculated from the conductivity data excluding silica present in the filtered water. '<' symbol indicates below the detection limits of ICPAES. Anions - SO_4^{2-}, F^-, Cl^- Br^-, NO_3^-, and PO_4^{3-} were measured by ion chromatography of samples collected at 5000 L of filtration.
b. <ic - below the detection limit of ion chromatography.
c. Secondary maximum contaminant level

The report shows average arsenic concentration 9-16 µg/L As(total) in the filtered water and an average flow rate of 5.0 L/hour irrespective of water chemistry from four distinctly different locations (Sitakundu, Hajiganj, Iswardi, and alaroa) in Bangladesh. These results are consistent with our present and previous findings. In the Phase II of Rapid Assessment Program, Sono 3-Kolshi filter passed 100% of the treated water below 50 ppb of arsenic (~ 10 ppb) on the average with the initial mean value of 450 ppb and with the flow rate of 3.3 L/hr. The water quality parameters do not include information on the presence of pathogenic bacteria because groundwater is presumed to be free from such bacterial load. The pathogenic contamination of the filtered water as reported in Phase II of the rapid assessment program, is not intrinsic to the system. It is due to the user's conditions of operation of the system. It can however, be completely removed by a 4-litre hot water cycle per week on the system. Many such 3-Kolshi systems are now in regular use (Fig. 3) throughout Bangladesh including SDCEI, and authors home. The 3-Kolshi water is clear, light tasting and free from the metallic taste of groundwater generally associated with high iron and calcium, and without any health complication arising from regular consumption of this filtered water.

Figure 3 : One 3-Kolshi filter unit in domestic use.

CONCLUSIONS

The arsenic filtration system presented here is promising because it is based on a clear physicochemical principle, uses locally available materials and without adding chemicals. A possible scale up of the system to a community based rural and urban pure drinking water supply has been planned. We believe the 3-Kolshi system can be very effective for filtration of toxic groundwater in Bangladesh and in many parts of the world where clay pitchers are used for preserving drinking water.

ACKNOWLEDGMENTS

REFERENCES

American Society for Testing and Materials. 1992. *ASTM Designation: D 3987-85, Standard Test Method for Shake Extraction of Solid Waste with Water, AST*M, West Conshohocken, PA, 4p.

Chatterjee, A., Das, D., Mandal, B. K., Chowdhury, T. R., Samanta, G., and Chakraborti, D. 1995. Arsenic in groundwater in six districts of West Bengal, India: the biggest arsenic calamity in the World. Part 1 - arsenic species in drinking water and urine of the affected people. *Analyst,* 120**,** 643- 650.

Choudhury, U. K., Biswas, B. K., Dhar, R. K., Samanta, G., Mandal, B. K., Chowdhury, T. R., Chakraborti, D., Kabir, S. and Roy, S. 1998. *Proc. Third. Int. Conf. on Arsenic Exposure Health Effects, San Diego. pp. 165.*

Das, D., Chatterjee, A., Mandal, B. K., Samanta, G., Chakraborti, D. and Chanda, A. 1995. Arsenic in groundwater in six districts of West Bengal, India: the biggest arsenic calamity in the World. Part 2 - arsenic concentration in drinking water, hair, nail, urine, skin-scale and liver tissue (biopsy) of the affected people. *Analyst.* **12**0, 917-924.

Davis, P. H.,Dulude, G. R., Griffin, R. M., Matson, W. R., and Zink, E. W. 1978. Determination of total arsenic at the nanogram level by high-speed anodic stripping voltammetry. *Anal. Chem.* **50,** 137-143.

Driehaus, W., Jekel, M. and Hildebrandt, U. J. 1998. Granular ferric hydroxide - a new adsorbent for the removal of arsenic from natural water. *Water SRT-Aqua,* **47(1),** 30-35.

Dzombak, D. A. and Morel, F. M. M. 199*0. Surface Complexation Modeling: Hydrous Ferric Oxide.* Wiley- Interscience, New York. pp 89-95.

Gulledge, J. H. and O'Connor, J. T. 1973. Removal of arsenic (V) from water by adsorption on alumina and ferric hydroxide. *Jour. AWWA.* **65, S** 548-552.

Goyer, R. A. 1996. *Toxic effects of metals. In Casarett and Duull's. Part II. The Basic Science of Poisoning,* 5 th ed. Klaassen, C. D., Ed., McGraw-Hill, New York. 696-698.

Hussam, A, Habibuddowla, M., Alauddin, M., Khan, A. H., Munir, A. K. M., and Rahman. M. 2000. *Trace Element Distribution of Wastes from Simple Arsenic Filtration Units.* Prepublication Report. Sono Diagnostic Center Environment Initiative, Kushtia, Bangladesh.

International Agency for Research on Cancer. 1980. Some Metals and Metallic Compounds; IARC *Monographs on Evaluation of Carcinogenic Risk of Chemicals to Humans," IARC: Lyons, France, 23 (1980).*

Khan, A. H., Rasul, S. B., Munir, A. K. M., Habibuddowla, M., Alauddin, M., Newaz, S. S. and Hussam, A. 2000. Appraisal of a simple arsenic removal method for groundwater of Bangladesh. *J. Environ. Sci. and Healt*h. **A 35(7),** 1021-1041.

Khan, A. H., Rasul, S. B., Munir, A. K. M., Habibuddowla, M., Alauddin, M., and Hussam, A. 2000. On Two Simple Arsenic Removal Methods for Groundwater of Bangladesh. *Bangladesh Environmental Network Conference, Dhaka, Bangladesh, January 14 (2000).*

Lackovic, J. A., Nikolaidis, N. P. and Dobbs, G. 2000. Inorganic Arsenic Removal by Zero-Valent Iron. *Environ. Eng. Sci.* **17(1),** 29-39.

Langmuir, D. 1997. *Aqueous Environmental Geochemistr*y. Prentice Hall, New Jersey. pp. 334- 337.

Nikolaidis, N., and Dobb, G. 1998. *Arsenic Remediation Technology - AsRT.* Environmental Research Institute, University of Connecticut, United Technologies Research Center, and Apex Environmental Inc., http/www.eng2.uconn.edu/-nikos/asrt- brochure.html.

National Research Council. 200*0. Arsenic in Drinking Water.* National Academic Press, Washington, D. C. USA. pp. 164.

Pierce, M. and Moore, C. B. 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Re*s. **16, S** 1247-1253.

Ponder, S. M., Darab, J. C. and Mallouk, T. E. 1999. Remediation of Cr(VI) and Pb(II) by nanoscale Fe-zero. *Environ. Sci. Techno*l. **es 9911420.** ASAP Web Edition**..**

Price, W.A. 1997. *DRAFT Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage at Minesites in British Columbia, British Columbia Ministry of Employment and Investment, Energy and Minerals Division, Smithers, B*C, (April), 143p

Pyles, S. and Miller, E. L. 1999. *Quantifying Arsenic in Aqueous Solutions by Anodic Stripping Voltammetry.* EMSL-LV.ORD/USEPA; www.epa.gov /testmethods/ 7xxx.http/.

Rapid Assessment of Household Level Arsenic Removal Technologies, *Phase I-Final Draf Report, Jan 2001, WS Atkins International Limited for BAMWSP/DFID/Water Aid. Dhaka, Bangladesh.*

Rasul, S. B., Ahmed, N., Munir, A. K. M., Washe, S., Khaliquzzaman, M., Khan, A. H. and Hussam, A. 1999. Speciation of Arsenic in Groundwater of Bangladesh. *Arsenic in Bangladesh Groundwater; World's Greatest Arsenic Calamity, International Conference. Wagner College, NY, Feb. 27-28, (1999).*

Rasul, S. B., Munir, A. K. M., Ahmed, N., Washe, S., Alauddin, M., Khan, A. H., Khair, M. A.

and Hussam, A. 1999. *Electrochemical Measurement and Speciation of Inorganic Arsenic in Groundwater of Banglades*h. Prepublication Report. Sono Diagnostic Center Environment Initiative, Kushtia, Bangladesh.

Rasul, S. B., Munir, A. K. M., Habibuddowla, M., Khan, A. H., Alauddin, M., and Hussam, A. 2000. *Natural Attenuation of Arsenic in Groundwater of Bangladesh: Experimental Measurement and Chemical Speciation Mode*l. Prepublication Report, Sono Diagnostic Center Environment Initiative, Kushtia, Bangladesh.

Raven, K. P., Jain, A. and Loeppert, R. H. 1998. Arsenite and arsenate adsorption on ferrihydrite:Kinetics, equilibrium, and adsorption envelopes. *Environ. Sci. Technol.* **3**2, 344-349.

Roberts, L. A., Totten, L. A., Arnold, W. A., Burris, D. R. and Campbell, T. *J.* 1996. Reductive Elimination of Chlorinated Ethylenes by Zero-Valent Metals. *Environ. Sci. Technol.* **30(8),** 2654-2659.

Schecher, W. D. and McAvoy, D. C. 1998. *MINEQL+: A Chemical Equilibrium Program for Personal Computers, User's Manua*l, *Version 4.0.* Environmental Research Software, Hallowell, ME 04347.

Shokes, T. E. and Moller, G. 1999. Removal of dissolved heavy metals from acid rock drainage using iron metal. *Environ. Sci. Techno*l. **3**3, 282-287.

Smith, A. H., Lingas, E. O. and Rahman, M. 2000. *Contamination of drinking-water by arsenic in Bangladesh: a public health emergency.* Bulletin of the World Health Organization, **78(9),** 1093-1103.

Snoeyink, V. L. and Jenkins, D. 1980. *Water Chemistr*y. John Wiley and Sons. New York.

Sun, Y-C., Mierzwa and Yang, M-H. 1997. New method of gold-film electrode preparation for anodic stripping voltammetric determination of arsenic (III and V) in seawater. *Talant*a. **4**4, 1379-1387.

Statistical Pocketbook of Bangladesh. 1994. *Bangladesh Bureau of Statistics, Government of Bangladesh (1994).*

Tam, G. K. H., Charbonnean, S. M., Bryce, F., Pomroy, C., Sandi, E. 1979. Metabolism of inorganic arsenic (74 As) in human following oral injestion. *Toxicol. Appl. Pharmaco*l., **50,** 319-322.

Wilkie, A. J. and Herrin*g*, J. 1986. Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes. *Colloid and Surfaces A: Physicochem. Eng.Aspect*s. **10**7, 97-110.