A comparison of conventional and non-conventional treatment technologies on arsenic removal from water

H.H. Ngo*, S. Vigneswaran*, J.Y. Hu*, O. Thirunavukkarasu** and T. Viraraghavan**

* Faculty of Engineering, University of Technology, Sydney, Australia (E-mail: *H.Ngo@uts.edu.au*)

** Faculty of Engineeering, University of Regina, Regina, Saskatchewan, Canada S4S OA2

Abstract In this study, four treatment methods were used to remove arsenic from water, namely: (i) chemical precipitation, (ii) arsenic adsorption onto iron-oxide-coated sand, (iii) high-rate saturated floating-medium flocculator/filter and (iv) membrane hybrid system (adsorption-microfiltration). The results indicated that more than 90% of total arsenic was removed by using $FeCl_3$ (40 mg/L) as coagulant. The removal efficiency was 10% lower when polysilicato-iron (PSI, 2.5 mg/L) was used as a flocculant. The results of both the batch and column adsorption studies showed that iron-oxide-coated sand can effectively be used to achieve very high levels of arsenic removal (less than 5 μm/L as As in drinking water). Arsenic was removed up to 78% from the packed polystyrene beads filter with in-line $FeCl_3$ addition at a high loading rate of 30 m^3/m^2.h. When powder activated carbon (PAC) was used in the membrane hybrid system, 87% removal of arsenic was achieved. A mixing time of 2.7 min with the mixing intensity of 87.8 s^{-1} were used. A very high filtration (permeate flux of 760 L/m^2.h) was observed with a membrane of pore size of 0.2 μm.

Keywords Adsorption-microfiltration hybrid system; arsenic removal; chemical precipitation; high-rate saturated floating-medium filter; iron-oxide-coated sand

Introduction

Arsenic in ground water and surface water is recognized as a toxic metal that has fatal effects on human health and environment. Arsenic enters into aquifers and wells through natural activities, and to the water cycle as a result of anthropogenic activities. Arsenic contamination of subsurface waters can be geological whereas the dissolution of, or desorption from iron oxide, and oxidation of arsenic pyrites may result in high arsenic concentration in groundwater (Welch *et al.*, 1999). The presence of organic or inorganic arsenic compounds is mainly in 4 oxidation states (arsenite –3, monomethyl arsenic acid, dimethyl arsenic acid +3 and arsenate +5). The significant toxicity was mainly attributed to inorganic arsenic compounds and trivalent species (arsenic III) (Eisler, 1994). It is believed that arsenic can cause urinary tract, bladder, lung and skin cancer, gastrointestinal disorders, muscular weakness, loss of appetites, nerve tissue injuries, blackfoot disease (National Research Council, 1999; Cheng *et al.*, 1994).

There are many methods to remove arsenic from water such as coagulation, lime softening, activated alumina, adsorption, ion exchange, filtration and membrane technologies such as nanofiltration and reverse osmosis, etc. However, to explore suitable treatment technology, which can satisfy drinking water guidelines or criteria and economic points of view, further studies are very necessary. In this study, arsenic removal by conventional treatment methods such as chemical precipitation process (coagulation process) and adsorption process (iron-oxide-coated sand (IOCS) as absorbent) and by non-conventional treatment such as high-rate saturated floating-medium flocculator/filter and membrane hybrid system (adsorption-microfiltration) was investigated.

Coagulation is the simplest conventional treatment process for arsenic removal in which chemicals are added to form precipitates or flocs that are removed by a subsequent sedimentation or filtration process. The most common coagulants used are alum, ferrous

sulfate, ferric chloride and ferric hydroxide. Previous study showed that ferric chloride led to better arsenic removal compared with ferrous and aluminum sulfate (Scott *et al.*, 1995).

Fixed-bed treatment systems such as adsorption and ion exchange are becoming increasingly popular for arsenic removal in small-scale treatment systems because of their simplicity, ease of operation and handling, regeneration capacity and sludge-free operation. Iron oxides play an important role in removing arsenic from water and wastewater (Benjamin *et al.*, 1996; Edward and Benjamin, 1989). In column studies with IOCS (Benjamin *et al.*, 1996), a complete removal of arsenic (75 µm/L) in the influent was observed despite the fact that the influent contained 800 mg/L sulfate. However, the information on IOCS for arsenic removal is still limited, especially on the effectiveness of IOCS for arsenate and arsenite removal and the effect of different coating procedures on arsenic removal and retention of the coating.

A new high-rate flocculation-filtration system was successfully developed for water and tertiary wastewater treatment at the Environmental Engineering R & D Laboratory (EERDL), University of Technology, Sydney (Ngo *et al.*, 1997; Ngo and Vigneswaran, 1999; Vigneswaran *et al.*, 1999). This system consists of a floating-filter medium of polystyrene and/or polypropylene beads. It operates at very high input rates under down-flow conditions. This system, while achieving superior pollutant removal, results in minimum clogging of filter beds. Thus, it can be operated for longer periods with lower energy requirements. An automatic backwash arrangement (frequent but short duration of backwash) is provided to clean the medium. A series of on-site trials of this treatment system in wastewater treatment plants showed its high applicability in water reuse.

The application of membranes to water treatment is being actively considered in many countries especially due to their capability in producing high-quality water. A recent study on an adsorption–microfiltration hybrid system for water treatment showed that it was very effective in removing organics and herbicides from water (Ngo *et al.*, 2000; Bikar, 2000). This hybrid system consists of a microfiltration module modified to incorporate in-line powdered activated carbon (PAC) addition. PAC was mixed continuously in a spiral-mixing device for a predetermined time before its entry to the membrane unit.

Conventional technologies

Arsenic removal by chemical precipitation process

The experimental set-up in EERDL, UTS, consists of a jar test apparatus with six vertical paddles lined up to a common horizontal drive shaft. The paddles were motor driven with a variable speed control and a speed indicator. Six 1 L beakers were used as the reactor basin. Arsenic trichloride standard solution (Ajax Chemicals, each mL contains 1.00 mg As) was used to prepare the synthetic arsenic solution. An artificial arsenic suspension was prepared by dissolving a predetermined concentration (500 µg/L) of As in kaolin clay suspension (mixture of tap water with a turbidity of 10 NTU). The coagulants used were polysilicato-iron (molar ratio of silica and iron is 3 to 1 from Suido Kiko Kaisha, Japan) and commercial and ferric chloride (AJAX). Different concentrations of chemicals were added to the arsenic suspensions. During these tests, the contents of the jars, after coagulant addition, were rapidly mixed with chemicals for 1 minute at a speed of 100 rpm (velocity gradient G $\approx$ 1,000 sec^{-1}). This was then followed by a slow mixing at 40 rpm for 30 minutes (velocity gradient G $\approx$ 100 sec^{-1}). The suspensions were then allowed to settle for 60 minutes. The performance of the tests was assessed in terms of total arsenic. Total arsenic was measured using ICPMS, Elan 6100DRC (Perkin Elmer). The surface charge characteristics of the particles were also measured using Malvern Zetasizer (Zeta 4000).

As can be seen from Table 1, the arsenic removal efficiency was highest (92%) when using 40 mg/L of FeCl$_3$. In these experiments, the pH of the suspension remained between 6

Table 1 Total arsenic removal at the different concentrations of FeCl$_3$ and PSI (initial As concentration in the suspension = 500 μg/L)

a) Coagulant: FeCl$_3$

FeCl$_3$ concentration (mg/L)	10	20	30	40	50	60
Arsenic removal (%)	74	78	83.2	92	66	64

b) Coagulant: PSI

FeCl3 concentration (mg/L)	0.5	1.0	1.5	2.0	2.5	3.0
Arsenic removal (%)	62	64	66	70	76	74

and 7. The results show that the optimum PSI concentration was 3 mg/L. Here too, the pH of the suspension was between 6 and 7. It is expected that the better removal efficiency can be achieved at the optimum pH value. Hence, a series of experiments was also carried out at different pH. The optimum pH for FeCl$_3$ and PSI in arsenic removal was between 9 and 12 and 4 and 5 respectively. This is due to the charge of the interacting particles being effectively neutral (the zeta potential value tend towards zero) and the solids removal being significantly high (> 85%) (Table 2).

Arsenic removal by adsorption onto iron-oxide-coated sand

Raw water containing arsenic was collected from Kelliher Water Treatment Plant, Kelliher, Saskatchewan, Canada, and used in the column study. The major physicochemical characteristics of the raw water are as follows: pH 7.4; iron 2.1; manganese 1.2; nitrate 2.9; sulfate 318; copper 0.04; zinc 0.01; lead 0.002; cadmium 0.001; barium 0.011; and chromium 0.001 (all values except pH are in mg/L). Iron-oxide-coated sand 2 (IOCS-2), prepared through a high-temperature coating process, was used in the column study to remove arsenic from the raw water. In the preparation of IOCS-2, coating of iron oxide was achieved on the red flint filter sand purchased from Watergroup Canada Ltd., Regina, Canada. Effective coating of iron oxide was achieved in two steps and the details are given elsewhere (Thirunavukkarasu *et al*., 2001a).

In the column study, a glass column of 16 mm diameter and 400 mm height was used. The column was packed with 21 mL of IOCS-2, and raw water was pumped through the packed column with a peristaltic pump; the flow rate to the column was kept at 21.5 mL/min (5 m/h or 2 gpm/ft^2) that yielded an empty bed contact time (EBCT) of 1 minute. Samples from the column test were collected at regular intervals and speciated to find soluble As, As(III), and As(V) as per the speciation protocol; the speciation protocol used in the study was similar to that of Thirunavukkarasu *et al*. (2001b), except that anion exchange resin (Dowex 1X8 – 50, Sigma Chemical Co., MO, USA) of 20–50 mesh size was used instead of 50–100 mesh size. All samples were analysed for arsenic using Varian type SpectrAA–600 Zeeman GFAAS equipped with GTA 100–graphite tube atomizer and

Table 2 Effect of pH on zeta potential (As = 500 μg/L, turbidity = 10 NTU)

a) Coagulant: FeCl$_3$

pH	1	2	3	4	5	6	7	8	9	10	11	12
ZP,mV	−2.3	−2.2	−1.2	16.1	15.4	24.2	23.9	10.2	−1.7	−1.8	−1.9	−4.9

b) Coagulant: PSI

pH	1	2	3	4	5	6	7	8	9	10	11	12
ZP,mV	−5.9	−3.3	3	1.1	−2	−9.8	−3.3	−10	−3.7	−8.5	−6.9	−3.7

programmable sample dispenser. The iron content of IOCS-2 was determined by acid digestion as per the procedure described in AWWARF (1993).

The initial total As, soluble As, and particulate As were determined as 177.3, 169.8, and 7.5 µg/L, respectively. The speciation of raw water sample showed that the concentration of As(III) was nearly 2.2 times higher than that of As(V), which indicated the dominance of As(III) species in the raw water. In the column study using Kelliher water, the concentration of soluble As, As(III), and As(V) remaining in solution is shown in Figure 2.

The results showed that As(V) predominated after 28 hours of column operation, which indicated the oxidation of As(III) to As(V). The column continued to remove soluble As to a value less than 5 µg/L for a period of 28 hours, and the number of bed volumes achieved up to 5 µg/L of soluble As in the effluent was 1,720, which was higher than the bed volumes achieved using activated alumina (Simms and Azizian 1997) and ion-exchange resin (Clifford *et al.*, 1999). The results of soluble As were fitted into the Thomas model (Reynolds and Richards, 1996), and the maximum solid phase concentration "q_0" (overall arsenic adsorption capacity) was estimated at 0.3 mg/g IOCS-2. The results of acid digestion results showed that the iron content of IOCS-2 was 45 mg/g IOCS-2; by expressing the results in terms of Fe content, "q_0" was estimated to be 0.2 mmol/g Fe (11.2 mmol As/mol Fe).

Non-conventional technologies
Arsenic removal by a high rate floating medium flocculator/filter (HRFMF)
Several experiments were conducted using an HRFMF system, which consists of a feeding system, a rapid mixing device, and a Perspex filter column. Details are given elsewhere (Ngo and Vigneswaran, 1999; Vigneswaran *et al.*, 1999). Polystyrene beads (of 1.9 mm diameter and 50 kg/cm^3 density) were used as the filter medium. The floating medium was packed in the column with a porosity of approximately of 0.36 and restrained by a grid (stainless steel mesh). It was operated mainly under downflow saturated flow conditions. Arsenic trichloride standard solution (Ajax Chemicals, each mL containing 1.00 mg As) was used to prepare the synthetic arsenic solution. An artificial arsenic suspension was prepared by dissolving a predetermined concentration of As in kaolin clay suspension (mixture of tap water with a turbidity of 10 NTU). The performance of the tests was assessed in terms of total arsenic removal. Arsenic was measured using ICPMS, Elan 6100DRC (Perkin Elmer). The coagulants used were polysilicato-iron (molar ratio of silica
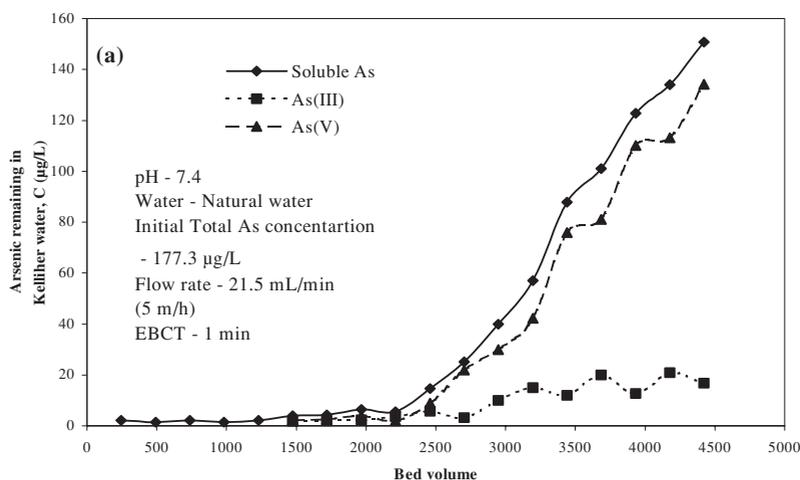

Figure 1 Arsenic concentration remaining in Kelliher water using IOCS-2

and iron is 3 to 1 from Suido Kiko Kaisha, Japan) and commercial ferric chloride (Ajax). During the experiments, the filtration rate in the filter was maintained constant at $30\ m^3/m^2.h$.

Figure 2 summarizes the performance of HRFMF system when using $FeCl_3$ and PSI as a sole flocculant. The results indicated that at a high filtration velocity of $30\ m^3/m^2.h$, the filter was still able to give reasonable arsenic and turbidity removal. In-line addition of $FeCl_3$ resulted in a better performance. For example, the average arsenic and turbidity removal were 78% and 94% when $FeCl_3$ was used as a flocculant (compared with 67% and 88% with PSI as a flocculant). The higher arsenic removal can be achieved if the filtration rate reduces and larger filter depth is applied.

Arsenic removal by adsorption – membrane hybrid system

The experimental set-up consisted of a helicoidal mixing device and a Millipore flat plate microfiltration module. Details are given elsewhere (Ngo *et al*., 2001). A helicoidal tube-mixing device was employed to uniformly mix the PAC with the suspension. It was made by winding PVC tube with diameter of 6 mm around a column 110 mm in diameter. The tube length and flow rate were changed to vary the mixing time and the velocity gradient (G). The feed solution was prepared by mixing a known amount of arsenic and kaolin clay in tap water. A wood-based PAC with norminal size of 80% finer than 75 µm was used. The PAC was fed into a mixing device along with the feed solution. After mixing with PAC, the solution and PAC were then delivered to the CFMF cell. The membranes used were PVDF (polyvinyl fluoride) membrane with nominal pore sizes of 0.22 µm. In each experiment, new membranes were used to obtain reproducible results. The transmembrane pressure was controlled at 20 kPA by two valves and pressure transducers at two points. To evaluate the PAC-CFMF performance, the permeate flux as well as arsenic were measured at regular intervals during the experiments. The arsenic was measured using ICPMS, Elan 6100DRC, Perkin Elmer.

A series of experiments was conducted with 500 µg/L As solution using PAC as an adsorbent and membrane with a pore size of 0.22 µm. The PAC concentration and a velocity gradient G were kept constant at 260 mg/L and $87.8\ s^{-1}$. Figure 3 shows the performance of the PAC-CFMF hybrid system at the mixing time of 2.7 minutes. The arsenic removal was 87%. The system also produced an effluent with a turbidity of less than 1 NTU. The average permeate flux was 771 $L/m^2.h$ which is high and economical (Figure 3). The arsenic removal efficiency decreased with the decrease in the mixing time (about 7% lower for a mixing time of 1.3 minutes). The results also indicated that the higher the influent arsenic concentration, the lower arsenic removal efficiency and the lower the permeate flux. For example, with the influent arsenic concentration increased to 1,000 µg/L, only 72% of arsenic was removed and the flux was less than 700 $L/m^2.h$.

H.H. Ngo *et al.*

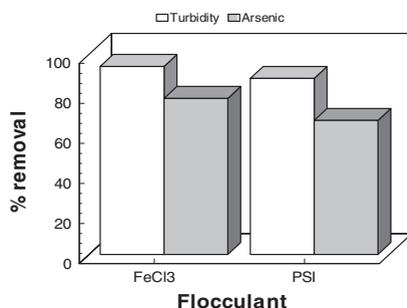**Figure 2** Percentage total arsenic removal for the HRFMF at two different flocculants ($v = 30m^3/m^2.h$, influent turbidity = 10 NTU, influent arsenic = 500 µg/L, filtration time = 120 minutes)

123

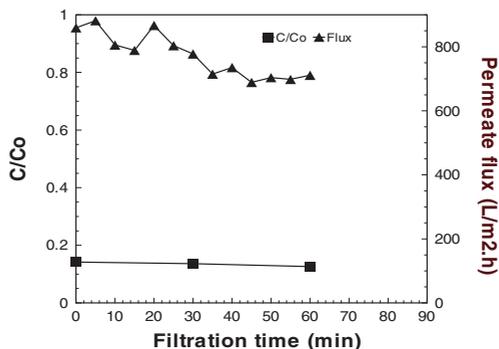**Figure 3** Performance of PAC-CFMF (PAC conc. = 260 mg/L, mixing time = 2.7 min, G = 87.8 s^{-1}, influent As = 500 µg/L, membrane pore size = 0.22 µm, transmembrane pressure = 20 kPa)

Table 3 A techno-economical comparison between the four treatment methods

Treatment method	Arsenic removal	Cost		
	(>75% removal)	Low	Medium	High
Chemical precipitation	X		X	
Adsorption/IOSC	X		X	
HRFMF	X	X		
PAC-CFMF	X			X

Comparison

Based on the results, a simple techno-economic comparison was made (Table 3).

Conclusions

The selection of an appropriate treatment process for arsenic removal from water depends on many factors such as the composition of water source and the other constituents, pH and cost. The results of this study indicated that both conventional and non-conventional treatment technologies are suitable for arsenic removal from water. Although coagulation with ferric chloride was found to be more effective than PSI, PSI produces much smaller amounts of sludge containing arsenic (hazardous in nature). IOCS can be effectively used to achieve a low level of arsenic (< 5 µg/L) in drinking water supplies. A high-rate floating-medium filter is suitable for technical and economic points of view. The membrane hybrid system is applicable when high quality effluent is warranted. To achieve high quality effluent in large quantities, further study on hybrid systems such as floating-medium filters coupled with microfiltration or IOSC are recommended.

Acknowledgements

References

AWWARF (AWWA Research Foundation) (1993). *NOM adsorption onto iron oxide-coated sand*, AWWA, Denver, Colorodo.

Benjamin, M.M., Sleten, R.S., Bailey, E.P. and Bennet, T. (1996). Sorption and filtration of metals using iron oxide coated sand. *Wat. Res.*, **30**(11), 2609–2602.

Bidkar, A. (2000). Herbicides removal by adsorption hybrid systems. PhD thesis, UTS.

Cheng, R.C., Liang, S., Wang, H.C. and Beuhler, M.D. (1994). Enhance coagulation for arsenic removal. J. *AWWA*, **86**(9), 79–90.

Clifford, D.A., Ghurye, G. and Tripp, A.R. (1999). Development of anion exchange process for arsenic

removal from drinking water, In: *Arsenic exposure and health effects*, (eds. W.R. Chappell, C.O. Abernathy and R.L. Calderon), pp. 379–388. Elsevier, New York.

Edwards, M. and Benjamin, M.M. (1989). Adsorptive filtration using coated sand: a new approach for treatment of metal bearing wastes, *J. Wat. Poll. Control Fedn*, **61**(9), 1523–1533.

Eisler, R. (1994). A review of arsenic hazards to plants and animals with emphasize on fishery and wildlife resources. In: *Arsenic in the environment*. Part II: *Human health and ecosystem effects* (J.O. Nriagu, ed.), Wiley, New York, pp. 185–259.

National Reseach Council (1999). *Arsenic in drinking water*, National Academy Press, Washington DC.

Ngo, H.H., Vigneswaran, S., Kwon, D.Y., Maheswaran, S. and Kancharla, V. (1997). Comparison of settling pond and buoyant medium packed bed filtration system in prawn farm effluent treatment. In: *Proc. Asian WaterQual'97, 6th Asia-Pacific Regional Conference, Seoul*, vol. 1, pp. 848–855.

Ngo, H.H and Vigneswaran, S. (1999). High rate floating medium filter in domestic and industrial wastewater treatment and reuse. In 18th Federal Convention AWWA, 1999.

Ngo, H.H., Vigneswaran, S., Kim, S.H., Bidkar, A. and Moon, H. (2000). Microfiltration-adsorption hybrid system in organics removal from water. *Water Science and Technology*, **41**(10–11), 51–57.

Scott, N.K., Green, F.T., Do, D.H. and McLean, J.S. (1995). Arsenic removal by coagulation. *J. AWWA*, **87**(4), 114–126.

Simms, J. and Azizian, F. (1997). Pilot-plant trials on the removal of arsenic from potable water using activated alumina. In: *Proceedings of the AWWA WQTC*, Denver, Colorado.

Reynolds, T.M. and Richards, P.A. (1996). Unit operations and processes in environmental engineering. PWS Publishing Company, Boston.

Thirunavukkarasu, O.S., Viraraghavan, T. and Subramanian, K.S. (2001a). Arsenic removal from drinking water using iron oxide-coated sand. *Water, Air, and Soil Pollution* (submitted).

Thirunavukkarasu, O.S., Viraraghavan, T. and Subramanian, K.S. (2001b). Removal of arsenic in drinking water by iron oxide-coated sand and ferrihydrite-batch studies. *Water Quality Research Journal of Canada*, **36**(1), 55–70.

Vigneswaran, S., Ngo, H.H., Kwon, D.Y. and Hu, J.Y. (1999). A new high rate filtration system in water recycle. In: *Proc. Civil and Environmental Engineering Conference, New Frontiers & Challengers*, Bangkok, Vol.1, 1–7.