The Removal of Arsenic from Contaminated Water using a Hybrid Membrane Process

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Abstract

The objective of this study is to develop a method to reduce arsenic concentrations in contaminated water. This work is also aimed at increasing the specificity of membrane separation processes. Arsenic in contaminated waters is often present in the form of negatively charged oxyanions. These are relatively small molecules which cannot be separated directly by ultrafiltration. Oxyanions can be captured by polyelectrolytes and separated by ultrafiltration. Results will be presented on the use of two polyelectrolytes; polyethylenimine (PEI) and poly-diallyl dimethyl ammonium chloride (DADMAC) at various feed concentrations. A semi-continuous process utilizing PEI in a circulation loop was tested. The results indicate that better than 99.6 % recovery (permeate concentration <0.001 μg/L) can be achieved based on an initial arsenic concentration of 300 μg/L. The results indicate that this treatment method is suitable as a main treatment process for drinking water or a polishing step after arsenic precipitation.

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Key words: Arsenic, membrane, polymer binding, ultrafiltration.

Introduction

Arsenic constitutes a major environmental problem in many locations. It is the 20th most common element in the earth's crust and the 12th most common in our body. In addition to its well known acute toxicity, it is a potent cancerogen. The effects of arsenic contamination in drinking water is well documented; Chili, Taiwan, Mongolia (Bagla and Kaiser, 1997) and Argentina (Science News, 1995). When present in drinking water, it represents an increased risk for bladder cancer (Science News, 1995). In India, more than one million people are affected by the contamination of groundwaters with arsenic. Over 200,000 people exhibit skin lesions; depigmentation, keratosis, and hyperkeratosis which can evolve into cancer. This major public health problem is caused by the contamination of deep wells dug in the early 1960's. A gradual decrease in the groundwater levels caused by the increasing need for irrigation water and the use of phosphate fertilizers has facilitated the release of arsenic into the wells. Certain wells can contain up to 3,700 μg/L of arsenic (Bagla and Kaiser, 1997).

The inorganic forms of arsenic As(V) and especially As(III) are the most toxic. In light of such public health problems legislators in the United-States have proposed a drop in the drinking water standard from 50 μg/L to 2 or 5 μg/L. What is the acceptable limit for drinking water? According to certain toxicologists minute quantities of arsenic can have long term effects. This approach would impose much lower limits than the present Canadian (25 μg/L, Canadian Council of Ministers of the Environment, 1991), American (50 μg/L, Code of Federal Regulations, 1990) and European (50 μg/L, Boisset, 1997) levels.

The debate rages on in the United-States as to what level is actually permissible in drinking water. The cost of stricter limits is estimated to be in excess of 6 billion US dollars (News, 1994).

Arsenic

In natural waters, arsenic can be found under many different forms depending on the pH and oxidation potential of the water. Groundwater is often reducing. Under these conditions we find the trivalent form As(III) as arsenous acid which dissociates according to;

$H_3AsO_3 \Leftrightarrow H^+ + H_2AsO_3^-$ pKa = 9.22 (1)
$H_2AsO_3^- \Leftrightarrow H^+ + HAsO_3^{2-}$ pKa = 12.31 (2)

Current practice has shown that the trivalent form is difficult to separate using conventional wastewater treatment methods. For this reason, As(III) is usually transformed into As(V) by oxidation with chlorine (Kartinen et Martin, 1995). The pentavalent form of arsenic is present as arsenic acid which ionizes as follows (Gulledge et O'Connor, 1973);

$H_3AsO_4 \Leftrightarrow H^+ + H_2AsO_4^-$ pKa = 2.2 (3)
$H_2AsO_4^- \Leftrightarrow H^+ + HAsO_4^{2-}$ pKa = 6.97 (4)
$HAsO_4^{2-} \Leftrightarrow H^+ + AsO_4^{3-}$ pKa = 11.53 (5)

The pH of drinking water ranges between 6 and 9. For As(III), equations 1 and 2 indicate that at pH 6 the non ionized form H_3AsO_3 is prevalent while at pH 9 a mixture of H_3AsO_3 and the ionized form $H_2AsO_3^-$ are present in solution. While for As(V), in the same pH range, the ionized forms $H_2AsO_4^-$ et $HAsO_4^{2-}$ are present which are more easily separated using processes which respond well to ions such as reverse osmosis, ion exchange, and electrodialysis.

Separation Technologies for Arsenic Removal

Several technologies can be used to remove arsenic from contaminated water. The main methods can be regrouped into four categories; precipitation, ion exchange, membrane processes, and adsorption (Kartinen and Martin, 1995). Precipitation can be performed using alum, lime softening, or ferric salts such as sulfate, chloride or hydroxide. All precipitation methods remove arsenic at levels of 20 to 80 % without chlorine oxidation and 90 % with chlorine oxidation. These separations are based on 300 to 400 $\mu g/L$ feed which implies a residual concentration of 30 to 40 $\mu g/L$. Such a level would not meet existing Canadian drinking water standards. Two types of membrane processes have been tested, reverse osmosis and electrodialysis (ED) (Kartinen and Martin, 1995). Reverse osmosis has shown limited ability in removing As(III) (40-80% separation). However, it was very effective in separating As(V) with 97 % removal efficiency. In ED 97 % separations are also reported.

However, RO membranes have poor tolerance to oxidants such as chlorine. RO and to a lesser extent ED and nanofiltration (NF) remove all solutes, which implies the need for post treatments to meet municipal drinking water standards.

Hybrid Methods - Ultrafiltration

Certain methods exist to separate organic substances and heavy metals by chelation followed by ultrafiltration. In the case where fouling is at a minimum, this technology combines the retention of reverse osmosis, and the low operating pressures and high flowrates of UF. Many volatile organic compounds have been captured in micelles and successfully separated by UF (Christian, 1989). In a similar technique, 10 mg/L of powdered activated carbon are added to the feed of a UF system. During the treatment of drinking water from the river Seine, this process has successfully reduced the concentration of atrazine in drinking water from 1.8 $\mu g/L$ to below the detection level (<20 ng/l) (Baudin and Anselme, 1995).

The objectives of this work are to develop a separation method which can be operated with minimum energy (low pressure, minimum tangential flow) and polymer requirements.

Two modes of operation are possible;

I) A conventional mode where a very low dose of polymer is added to the feed stream.

II) A semi-continuous system where, a fairly high concentration of polymer is contained in a closed loop and the loop fed with contaminated water. After a set recovery is reached, polymer in the loop can be either regenerated or precipitated. Treatment can then continue with either regenerated or fresh polymer in the loop. This system is illustrated in Figure 1.

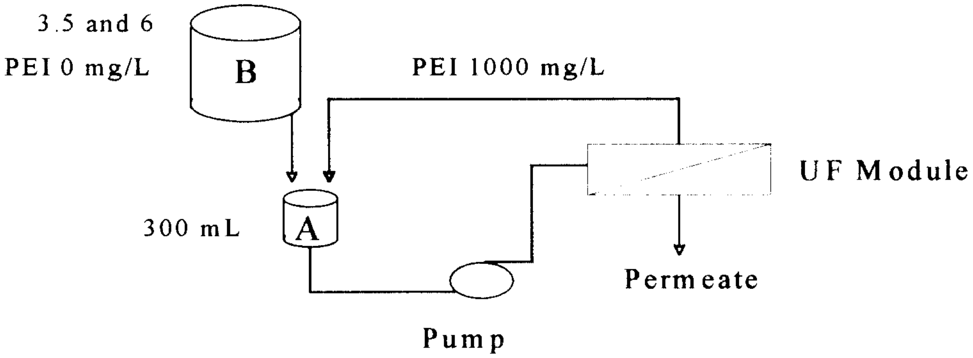

Figure 1. Semi-continuous process for arsenic removal.

Two synthetic cationic polymers, soluble in water were selected; polyethylenimine (PEI) and poly-diallyl dimethyl ammonium chloride (DADMAC). The preference for either process will be defined by the separation of arsenic as a function of polymer concentration. In order to determine this, arsenic separation was determined at three concentrations for both PEI and DADMAC. All experiments were performed in the presence of 1000 mg/L of NaCL, to obtain experiments which would be representative of the competition of ions in groundwater. The results from these experiments were then used to select options I) or II) above and experiments on the process were performed.

Experimental

1) Effect of polymer concentration on arsenic retention.

In these tests, 200 mls of solution were prepared containing 0.3 mg/L of arsenic, 1000 mg/L of NaCl and 1, 1000, and 5000 mg/L of DADMAC.

2) Semi-continuous system.

The feasibility of using a semi-continuous system containing a relatively high concentration of polymer was studied in this step. Figure 1 illustrates this process where a small tank A containing a relatively high amount of polymer is constantly recirculated in a UF module. A sufficient amount of contaminated water in tank B is fed to tank A to compensate the amount of permeate which has passed through the membrane.

Materials

Two polymers; polyethylenimine (PEI) (50000 - 60000 Daltons) and poly-diallyl dimethyl ammonium chloride (DADMAC) (250000 Daltons) both from Aldrich (U.S.) were used. All polymer solutions were prepared from stock solutions of 10000 mg/L. Arsenic solutions were made using the salt $Na_2HAsO_4 \cdot 7H_2O$ (As(V)).

The concentration of arsenic used during this study were made from an initial arsenic solution concentration of 1000 mg/L. Arsenic analyses were made using a hydride generator and an Atomic Absorption Spectrophotometer. De-ionized water was used in all preparations.

1) Effect of polymer concentration on arsenic retention.

A UF membrane Bioken having a molecular weight cut-off of 10000 Daltons was used in all trials. A 50 ml Amicon ultrafiltration stir cell (Beverly, U.S.A) having a 13.4 cm^2 surface area was used. The stir speed was 364 rpm. The cell was subjected to a pure nitrogen pressure of 275 kPa (40 psig) and held at room temperature (22 °C). The following procedure was used; a solution containing arsenic, 1000 mg/L of NaCl and the polymer was adjusted to pH 7.0 and placed in the stir cell. The cell was put under pressure and a period of twenty minutes was allowed to stabilize the system. The permeate collected during these twenty minutes was weighed and placed back in the cell. A sample of the cell was taken and the cell put under pressure. The first 5 mls of permeate were rejected and the next 5 mls retained as a sample. The concentrate was then sampled.

2) Semi-continuous system.

A cross flow, plate and frame module was used to simulate the semi-continuous system. The effective surface of the membrane was 64.52 cm^2 under a trans-membrane pressure of 275 kPa. Solution contained in tank A was circulated at a flowrate of 3.5 L/min. The initial solution contained in tank B was composed of 0.1 or 0.3 mg/L of arsenic and 1000 mg/L of NaCl. The initial solution in tank A contained 0.3 mg/L of arsenic, 1000 mg/L of NaCl and 1000 mg/L of PEI. In this set of experiments, no pH adjustments were made.

Results

1) Effect of polymer concentration on arsenic retention.

The results on the effect of polymer concentration are summarized in Table 1. They indicate that the concentration of polymer has a major effect on the retention of arsenic. The results for both test cells are in good agreement for the trials with DADMAC. However, for PEI, a variability in the results can be noticed between cells. This can be explained by variations in the molecular weight cut-off of the membranes used in the experiments. Such variations would affect more the separation of PEI since its molecular weight is lower than that of the DADMAC. The molecular weight of PEI is 5 to 6 times the cut-off of the membrane, whereas the molecular weight of DADMAC is 25 times that of the membrane's molecular weight cut-off. The variations in PEI can be easily explained by normal local variations in the molecular weight cut-off of the test coupons.

The linearity of both molecules would further enhance the variations. At equal weight, PEI offers more retention capacity than DADMAC. The lower molecular weight of PEI greatly favors a reduction in concentration polarization.

Table 1. The effect of concentration for PEI and DADMAC in the presence of 1000 mg/L of NaCl and an initial concentration of 0.3 mg/L of arsenic. Each results represents an average of 4 experiments on one membrane coupon.

Polymer	Polymer Concentration (mg/L)	Rejection As ± σ (%) stir cell 1	Rejection As ± σ (%) stir cell 2
DADMAC	1	23,68 ± 5,20	13,75 ± 2,42
	1000	25,65 ± 0,40	22,13 ± 5,03
	5000	47,39 ±6,68	36,54 ± 18,1
PEI	1	14,82 ± 3,28	6,06 ± 3,85
	1000	47,05 ± 0,42	92,46 ± 4,23
	5000	74,45 ± 5,59	100,00 ± 0,00

A 23 % improvement in arsenic retention was obtained by increasing the concentration of DADMAC from 1 to 5000 mg/L. While the improvement over the 1 to 5000 mg/L range was 60 and 94 % for PEI. Again we can see that the concentration of polymer has a net effect on the on arsenic retention. For the operation of this system, it is desirable to minimize the concentration of polymer and if possible to use the lowest molecular weight permissible to minimize concentration polarization.

The results indicate that given an equal weight of polymer, PEI offers a greater exchange capacity than DADMAC. The use of concentration of PEI above 1000 mg/L is not needed as retention seems to level off at this point.

2) Semi-continuous system.

The results obtained with this system are summarized in Figure 2, with PEI 1000 mg/L, NaCl 1000 mg/L and 115 μg/L As. Figure 3 represents the results obtained with PEI 1000 mg/L, NaCl 1000 mg/L and 300 μg/L As. The apparent retention is calculated from the initial feed concentration and the permeate concentration. The actual retention of the membrane is based on the concentration of arsenic in the circulation loop and the concentration of the permeate. A third curve indicates membrane flux at 275 kPa (40 psig).

During the first set of experiments an initial retention of 71.7 % was obtained which then increased to a value of 96.0 % apparent and 99.0 % actual. The concentration of arsenic in the permeate ranged from 2.5 to 5 μg/L for the test at 115 μg/L and <0.001 μg/L for the test at 300 μg/L.

During the beginning of both runs, membrane flux decreased as the retention of arsenic increased. This would indicate the formation of a gel at the surface of the membrane or the permeation of lower molecular weight PEI through the membrane. The molecular weight cut-off of UF membranes is often obtained from more globular molecules than PEI.

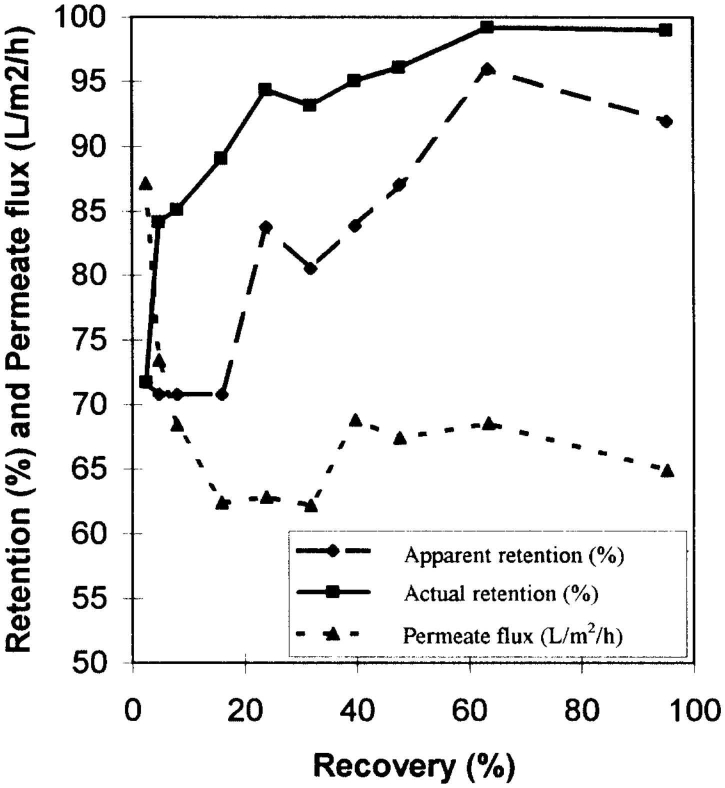

Figure 2 Arsenic retention and permeate flux vs recovery. Arsenic concentration in tank B (Fig. 1) 115 μg/L , NaCl 1000 mg/L. PEI in tank A (Fig. 1) 1000 mg/L.

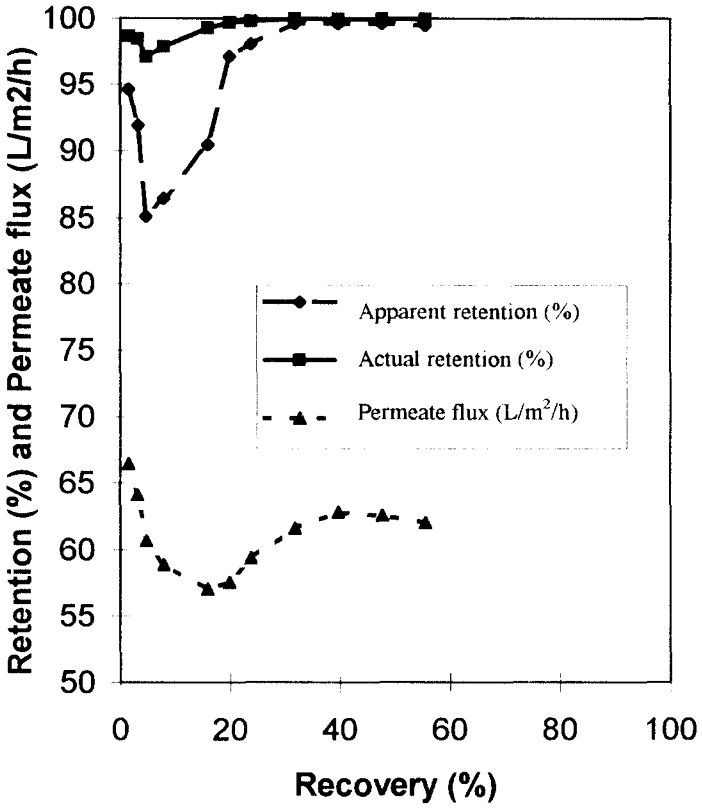

Figure 3 Arsenic retention and permeate flux vs recovery. Arsenic concentration in tank B (Fig. 1) 300 μg/L , NaCl 1000 mg/L. PEI in tank A (Fig. 1) 1000 mg/L.

PEI is polydisperse and highly linear, lower molecular weight polymer could easily pass through the membrane until a gel is formed on the surface of the membrane.

Permeate flowrate is relatively constant after 20 % recovery. The experiment at 115 μg/L was stopped after 95 % recovery was reached. This recovery is reasonably high for membrane processes such as RO and ED.

Conclusions

- The use of a semi-continuous process utilizing PEI and a UF membrane is an effective method for the removal of arsenic from contaminated waters.
- The proposed process can be used as the main treatment technology or a polishing step after precipitation.
- The method permits a retention greater than 99% at 95 % recovery.
- The efficiency of the process increases with increasing arsenic concentration.
- The process can meet and exceed the proposed EPA levels of 2 to 5 μ g/L.

Acknowledgments

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N.S.E.R.C.

References

Bagla, P., and Kaiser, J., "L'arsenic contamine dangereusement le eaux indiennes", La Recherche, vol. 295, p 42, February 1997.

Baudin I.; Anselme C.; "Combining PAC and ultrafiltration", World Water and Environmental Engineering, November (1995).

Boisset, M., "La toxicité de l'arsenic", La Recherche, vol. 295, p. 44, February 1997.

Canadian Council of Ministers of the Environment (CCME), "Interim Canadian Environmental Quality for Contaminated Sites", Report CCME EPC-CS34, Canadian Council of Ministers of the Environment, Environmental Quality Guidelines Division, Water Quality Branch, Environment Canada, Ottawa, Ontario, September 1991.

Christian, S.D.; Scamehorn, J.F.; "Use of Ultrafiltration to remove dissolved organics from aqueous streams", dans Surfactant-Based Separation Processes, Scamerhorn, J.F.; Harwell, J.H. Ed., Chap. 1, Marcel Dekker, New York, N.Y., 1989.

Code of Federal Regulations, Title 40, Part 257, U.S. (July 1990).

Gulledge, S., et O'Connor J., "Removal of As(V) from water by Adsorption on Alumina and Ferric Hydroxide", American Water Works Association Journal, vol 65(8), pp.548-552, August 1973.

Kartinen, E.O. and Martin, C.J., "Overview of arsenic removal processes", Desalination, Vol 103, 1995, pp. 79-88.

News, "Compliance with Arsenic Regulations Could Cost Billions", Civil Engineering, p19, September 1994.

Science News, "Waterborne arsenic poses a cancer risk", Science News, 1996, v 149, n. 8, p. 119.