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Preeyaporn Pookrod[a]; Kenneth J. Haller[a]; John F. Scamehorn[b]
[a] School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, Thailand [b] Institute for Applied Surfactant Research, The University of Oklahoma, Norman, Oklahoma, USA

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Removal of Arsenic Anions from Water Using Polyelectrolyte-Enhanced Ultrafiltration

Preeyaporn Pookrod,[1] Kenneth J. Haller,[1,]* and John F. Scamehorn[2]

[1]School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, Thailand
[2]Institute for Applied Surfactant Research, The University of Oklahoma, Norman, Oklahoma, USA

ABSTRACT

Polyelectrolyte-enhanced ultrafiltration (PEUF), using cationic poly (diallyldimethyl ammonium chloride) polyelectrolyte, was used to investigate the removal of arsenic(V) from dilute aqueous solutions. In PEUF a water-soluble polyelectrolyte of opposite charge to that of the target ion binds the charged arsenate complex. The solution is then treated by ultrafiltration with membrane pore sizes small enough to block the polymer. Only the residual unbound arsenate at the concentration in the retentate (solution not passing through membrane) is present in the

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*Correspondence: Dr. Kenneth J. Haller, School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, Thailand; Fax: 66-44-224185; E-mail: haller@ccs.sut.ac.th.

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permeate solution passing through the membrane. Arsenic rejections as high as 99.95% are obtained and increase with increasing polymer concentration and decrease with increasing ionic strength (added salt concentration). Arsenic rejection increases with increasing pH (pH of 6.5–8.5) as the $HAsO_4^{2-}/H_2AsO_4^-$ ratio in solution increases, improving arsenate binding to the polymer. Gel point concentration (polymer concentration at which flux becomes zero) was found to be 655–665 mM (approximately 5.98–6.07 wt%), consistent with previous PEUF studies. These high gel points mean that high water recoveries (>99%) are achievable in this separation process.

Key Words: Arsenic; Polyelectrolyte-enhanced ultrafiltration; Maximum contaminant level; Arsenic remediation.

INTRODUCTION

Arsenic is toxic to all living organisms, thus creating potentially serious environmental concerns. Arsenic is a metalloid in group VA of the periodic table. It exists naturally in the earth's crust, rock, soil, water, air, plants, and animals. Arsenic is found in natural surface water and groundwater because of release of arsenic compounds from minerals. Arsenic occurs in a variety of forms and oxidation states. The main arsenic species present in natural waters are arsenate ions (oxidation state V) and arsenite ions (oxidation state III).[1–7] Arsenate and arsenite are part of the arsenic acid (H_3AsO_4) and arsenous acid (H_3AsO_3) systems, respectively. Arsenic(III) and arsenic(V) are significantly different in their chemical behavior. The dissociation constants of the species of the two oxidation states of arsenic are as follows:[6]

Arsenous Acid/Arsenite:

$$H_3AsO_3 \longrightarrow H^+ + H_2AsO_3^- \quad pKa_1 = 9.23$$
$$H_2AsO_3^- \longrightarrow H^+ + HAsO_3^{2-} \quad pKa_2 = 12.13$$
$$HAsO_3^{2-} \longrightarrow H^+ + AsO_3^{3-} \quad pKa_3 = 13.40$$

Arsenic Acid/Arsenate:

$$H_3AsO_4 \longrightarrow H^+ + H_2AsO_4^- \quad pKa_1 = 2.22$$
$$H_2AsO_4^- \longrightarrow H^+ + HAsO_4^{2-} \quad pKa_2 = 6.98$$
$$HAsO_4^{2-} \longrightarrow H^+ + AsO_4^{3-} \quad pKa_3 = 11.53$$

The p*K*a is the pH at which the dissociation of the reactant is 50% complete. Therefore, arsenic occurs in water in different forms depending upon the pH and oxidation potential of the water. Figure 1 illustrates the effect of redox potential (Eh) and pH on arsenic species in aqueous systems.[8] At high redox potentials arsenic can be stabilized as a series of pentavalent (arsenate) oxyarsenic species: H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}. However, under most reducing (acid and mildly alkaline) conditions and low redox potential, the trivalent arsenic species (H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-}) become stable.[1] A National Arsenic Occurrence Survey determined arsenic species in samples from 21 surface water sources and 49 groundwater sources. In samples with detectable soluble arsenic, an average of two-thirds of the soluble arsenic was contributed by arsenic(V) and one-third by arsenic(III).[4] In strongly reducing aquifers, arsenic(III) typically dominates in groundwater. In seawater, the arsenic is typically dominated by arsenic(V) at a pH around 8.2. Ratios of arsenic(V)/arsenic(III) are in the range of 10–100 in open seawater. Arsenic(V) is also generally the dominant species in lake and river

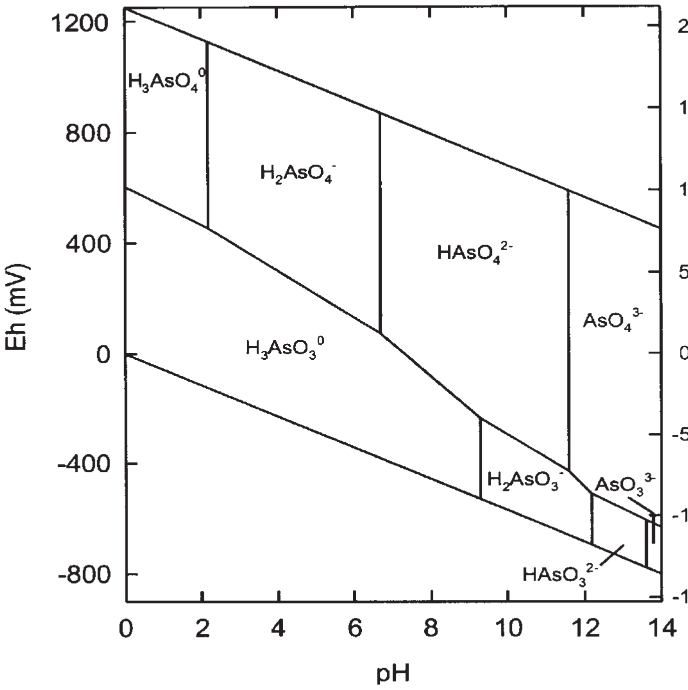

Figure 1. Redox potential (Eh) vs. pH diagram for aqueous arsenic species in the As-O_2-H_2O system at 25°C and 1 bar total pressure. The hypothetical electron activity at equilibrium, pe, is used interchangeably with Eh, $pe = (F/2.3RT)Eh$. *Source*: Reprinted with permission from Ref.[8], Copyright 1988, Springer-Verlag.

waters. Proportions of arsenic(III) and arsenic(V) vary according to changes in input sources, redox conditions, and biological activity.[5] The toxic effect of arsenic species depends on their chemical form, with toxicity in the order: arsine > arsenite > arsenate > monomethyl arsonic acid > dimethyl arsinic acid. Studies on long-term human exposure show that arsenic in drinking water is associated with liver, lung, kidney, bladder, and skin cancers.

Within the United States, a maximum permissible concentration of 50 ppb ($\mu g/L$) for arsenic in drinking water was first established by the Public Health Service in 1942. Over the past two decades, there has been reevaluation of the appropriate maximum contaminant level (MCL) of arsenic in drinking water[9,10] because it is classified as a human carcinogen. In 2001 the US Environmental Protection Agency implemented the new 10-ppb standard for arsenic in drinking water to be effective in 2006.[11,12]

There are several methods to remove arsenic from aqueous solution, including chemical precipitation–coagulation, adsorption, lime softening, ion exchange, and membrane processes.[13,14] Chemical precipitation–coagulation is a simple and economical method. Iron(III) or alum,[15–21] lanthanum salts,[22] metal hydroxides,[23,24] and a combination of Fe–Mn salts[25,26] have been used as precipitants or coagulants. Adsorption studies have been conducted to characterize the removal of arsenite and arsenate with various solid phases, including lanthanum compounds,[27] activated aluminas,[28] iron compounds,[29–33] natural solids,[34] ores,[35,36] and clay minerals.[37–39] Activated and nonactivated carbons[40] or materials like fly ash[41] obtained from inexpensive or waste materials have been studied for use in arsenic removal. As an alternative treatment, adsorption by iron oxide-impregnated activated carbon,[42] iron oxide-coated sand,[43] manganese dioxide-coated sand,[44] and molybdate-impregnated chitosan[45] has been demonstrated to be effective in arsenic removal. Colloid flotation,[46,47] emulsion liquid membrane separations,[48] reverse osmosis,[49] microfiltration,[49] ultrafiltration,[49–53] and nanofiltration[49,54,55] as well as ion exchange (of arsenate and arsenite)[56–61] have been demonstrated to be capable of removing arsenic from water.

Polyelectrolyte-enhanced ultrafiltration (PEUF) is a separation process that can remove low-concentration ionic species from aqueous solution and is particularly effective for multivalent ions. This process includes the addition of water-soluble polymer followed by the ultrafiltration operation. The polymer is a polyelectrolyte of opposite charge to the target ions, causing the pollutant ions to bind to the polymer due to electrostatic attraction to form macromolecular complexes. These complexes are retained by the membrane in the retentate stream, while the uncomplexed ions pass through the membrane to the permeate stream. In previous studies, PEUF has been applied to the separation of cationic metal ions like Cu^{2+} or Cd^{2+} with anionic polymer[62–65] or anionic ions like chromate (CrO_4^{2-}) with cationic polymer.[66–68] Potential advantages of this method are the low energy requirements involved in ultrafiltration and the fact that the process can be operated in a steady-state mode.[69]

The PEUF process for arsenic removal involves addition of cationic polyelectrolyte, poly(diallyldimethyl ammonium chloride) or QUAT, to bind anionic arsenic species to form polyelectrolyte–arsenate complexes, which are separated by a subsequent ultrafiltration operation. The large QUAT–arsenate complexes are retained by the membrane in the retentate stream, while the purified water and ions that do not bind to the polyelectrolyte pass through the membrane as the permeate stream. Figure 2 shows a schematic diagram of PEUF to remove anionic arsenic species from water.

In this study the effect of arsenate ion concentration, QUAT concentration, pH, and added electrolyte concentration on arsenate rejection and flux through the membrane were investigated.

EXPERIMENTAL

Materials

Poly(diallydimethyl ammonium chloride) or QUAT, with a number average molecular weight of 2.4×10^5 Da, was purchased from the Calgon

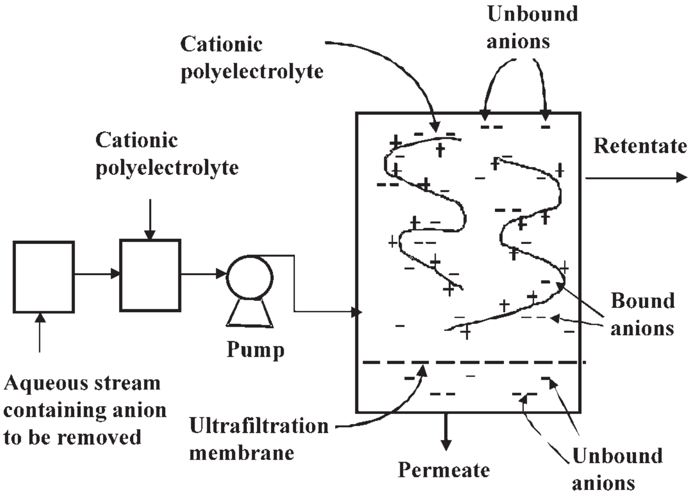

Figure 2. Schematic diagram of polyelectrolyte-enhanced ultrafiltration (PEUF) to remove anionic arsenic species from water.

Corporation (Pittsburgh, PA) as a 40% solution in water. Dilute solutions of the polymer were purified prior to PEUF experiments to remove lower molecular weight fractions using a spiral-wound ultrafiltration unit with a 10-kDa molecular weight cut-off (MWCO) membrane. Sodium arsenate (98.5%) and sodium tetraborohydride (96%) were manufactured by Fluka (Buchs, Switzerland). Sodium hydroxide was supplied by EKA (Bohus, Sweden). Arsenic standard solution was purchased from Merck (Darmstadt, Germany). Hydrochloric acid, potassium iodide (99%), L(+)-ascorbic acid (99.7%), sodium chloride (99.5%), calcium chloride (99%), sodium silicate (97%), magnesium chloride (99%), sodium sulfate (99%), sodium hydrogen carbonate (99.8%), and sodium hydrogen phosphate (99%) were obtained from Carlo Erba (Milan, Italy). Sodium metasilicate (97%) was purchased from Sigma (Singapore). All chemicals except the QUAT were analytical-grade reagent and used as received. Deionized and distilled water were used to prepare solutions.

Methods

Experiments were performed in a Millipore 400-mL batch ultrafiltration stirred cell equipped with a 10-kDa MWCO regenerated cellulose acetate membrane (Millipore, Bedford, MA). The membrane was soaked overnight in deionized water, then in 0.005 mM purified QUAT solution. A 300-mL solution of polyelectrolyte, arsenic in the form of arsenate anion, and other electrolytes were placed in the stirred cell and the pH adjusted by adding dilute HCl or NaOH. Initial arsenate concentration was fixed at 100 ppb in the effect of pH and in the effect of salt concentration experiments. Experiments were conducted at the laboratory temperature of 298 K. The solution was stirred with a cylindrical stirring bar positioned just above the membrane rotating at 250 rpm. A pressure of 414 kPa (60 psig) was applied from a nitrogen gas cylinder and the permeate solution was collected as four 50-mL aliquots in volumetric flasks until 200 mL of the solution had passed through the membrane. The rejection of arsenate was determined by analyzing the sample at the midpoint of each run where 100 mL of permeate had passed through the membrane (the second 50-mL aliquot). By knowing permeate concentrations during the run, the retentate concentration at any point in the run was calculated from material balance and double-checked by analysis of the retentate at the end of a run. In this work, the initial ratio of QUAT to arsenate was fixed; it is this ratio that is reported. Since rejection of the QUAT is essentially 100%, if rejection of the arsenic anion is high (as it is except when salt is added at high concentration), this ratio varies little throughout the experiment. Flux was determined during each run by timing every 50-mL aliquot of permeate. The flow rate is reported as a relative flux (the ratio of the observed flux to the flux of water alone under the same conditions).

Analysis

Arsenic concentrations were determined using flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS) following the *Standard Method for Examination of Water and Wastewater*, number 3114C[70] with a Perkin–Elmer atomic absorption spectrometer (Wellesley, MA) equipped with a hydride generator. The flow injection system is used to inject an exact, reproducible volume of sample into a continuously flowing liquid carrier stream. Prior to hydride generation, arsenic solutions from retentate, permeate, and calibration standards were prepared with 5% (w/v) of potassium iodide and L(+)-ascorbic acid, and addition of trace metal-grade HCl to reduce arsenic(V) to arsenic(III). Hydride generation was achieved using analytical-grade 0.2% (w/v) sodium borohydride ($NaBH_4$) dissolved in a 0.05% (w/v) sodium hydroxide (NaOH) solution.

Spectrometer calibration was performed using standard solutions and blank concentrations of standard solutions. The standard plot shows a linear relationship between absorbance and concentration, which indicates that Beer's law is valid within the concentration range used (0.5–10 ppb). Spectrometer response to arsenic (10 ppb) as a function of polyelectrolyte concentration ($[\text{QUAT}]/[\text{arsenic}] = 0–30{,}075$) was verified to be constant. Therefore, it can be concluded that FI-HG-AAS can be applied for arsenic analysis in both the permeate stream (which contains almost no polyelectrolyte) and the retentate stream (which contains high concentrations of polyelectrolyte).

Polyelectrolyte concentrations were determined with a Leco CNS-2000 elemental analyzer (Joseph, MI), which determines carbon in polymer samples by weight of the carbon element. The sample was weighed into a tared ceramic boat, along with combustion catalyst, covered with a nickel boat liner, and combusted in pure oxygen in the furnace at 1350°C. Combustion gases were collected in a ballast tank and then flowed to the detector. Carbon (as CO_2) was quantified by infrared absorption measurement.

RESULTS AND DISCUSSION

Poly(diallydimethyl ammonium chloride) or QUAT was used to remove arsenic from water by PEUF. The repeating unit of the polymer is $(H_2CCHCH_2)_2N(CH_3)_2Cl$. The QUAT concentrations are based on the moles per liter of the repeating unit and not on the total molecular weight. This permits ready comparison of experimental conditions relative to stoichiometric conditions. Due to stoichiometric considerations, arsenic to polymer ratio is a molar ratio. However, arsenic concentrations are on a weight basis (ppb) to relate to legally stipulated allowable levels.

Effect of pH on Arsenic Rejection

The ability of a membrane to retain a particular species of a solution is characterized by its rejection, R (in %), defined as the fraction of solute retained:

$$\text{Rejection}\,(\%) = \left(1 - \frac{[\text{arsenic}]_{\text{per}}}{[\text{arsenic}]_{\text{ret}}}\right)(100)$$

where $[\text{arsenic}]_{\text{per}}$ and $[\text{arsenic}]_{\text{ret}}$ are the arsenic concentrations in the permeate and retentate, respectively.

The arsenic rejection is shown in Fig. 3 as a function of pH at feed [QUAT]/[arsenic] ratios of 50, 100, and 150 with initial arsenate concentration 100 ppb. Excellent rejections are observed, exceeding 99% for all conditions shown in Fig. 3. An increase in pH from 6.5 to 8.5 results in an

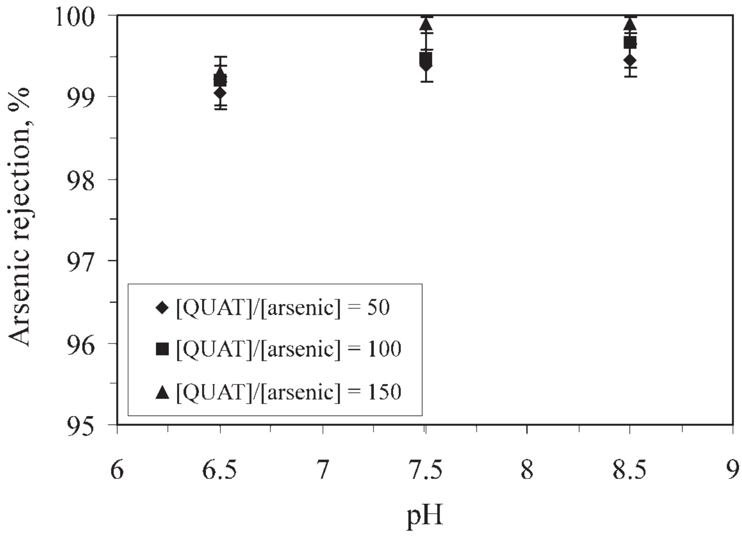

Figure 3. Arsenate rejection as a function of pH with retentate [arsenic] = 150 ppb.

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increase in arsenic rejection from 99.06 to 99.95%. Arsenate speciation is controlled by the pH of the solution. The pKa for dissociation of $H_2AsO_4^-$ to $HAsO_4^{2-}$ is 6.98. As shown in Fig. 4, for the arsenate system, the predominant species between pH 6.5 and 8.5 are $H_2AsO_4^-$ and $HAsO_4^{2-}$. At pH 6.5 and 7.5, $H_2AsO_4^-$ and $HAsO_4^{2-}$ species in solution, unbound onto the polymer exist at molar ratios of 75/25 and 22/78, respectively.[71] Comparison of arsenic rejection results at an identical initial retentate arsenate concentration of 100 ppb arsenic shows that higher rejection of arsenic is realized at pH 7.5 and pH 8.5 where arsenic(V) mainly exists in the form $HAsO_4^{2-}$ compared to pH 6.5. At the point at which the rejection is reported (the volumetric midpoint of the experiment), the arsenic concentration in the retentate is 150 ppb, based on an initial concentration of 100 ppb. Rejections of 99.06–99.95%, shown in Fig. 3, correspond to a permeate arsenic concentration of 4.22–0.20 ppb.

Effect of Retentate QUAT Concentration on Arsenic Rejection

The rejections obtained at feed [QUAT]/[arsenic] ratios 50, 100, and 150 are shown in Fig. 5 as a function of retentate [QUAT] at pH 7.5. The [QUAT]/[arsenic] ratio in the retentate at the reported midpoint value is very nearly the same as the [QUAT]/[arsenic] in the feed. As the feed ratio of [QUAT]/[arsenic] increases, the rejection increases because of the increase in the number of positively charged sites on the QUAT per unit volume, increasing the fraction of arsenic anions bound to polyelectrolyte. As the retentate

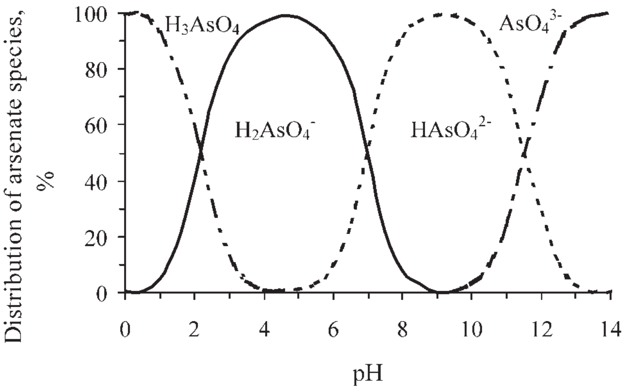

Figure 4. Arsenate speciation as a function of pH (after Coleman, Ref.[71]).

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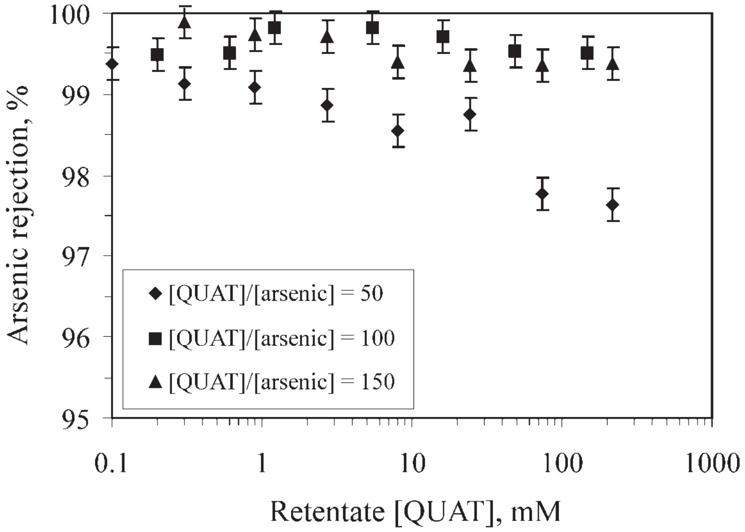

Figure 5. Rejection of arsenic as a function of retentate [QUAT] at pH 7.5.

[QUAT] or [arsenate] increases at constant feed [QUAT]/[arsenic] ratios, the rejection decreases. For example, the rejection is 99.12% in 0.3 mM QUAT and 97.76% in 72.9 mM QUAT when the initial ratio of [QUAT]/[arsenic] is 50 to 1. At an initial arsenic concentration higher than 1000 ppb, the permeate arsenic concentration is higher than 10 ppb. This same trend with concentration has also been observed for chromate, sulfate, and nitrate removal using PEUF.[68]

Effect of Added Salts on Arsenic Rejection

Figure 6 shows the effect of adding background salts to the feed on the arsenic rejection at pH 7.5, feed [QUAT]/[arsenic] ratio of 100, and initial arsenate concentration 100 ppb. The arsenic rejection is found to decrease with increasing salt concentration and increased valence of the added anion. Phosphate, silicate, and carbonate species are common oxyanions in water that can exist as mixtures of ions of different valence depending on pH. Phosphoric acid ($pK_1 = 2.16$; $pK_2 = 7.21$; $pK_3 = 12.32$), like arsenic acid, is a strong acid while carbonic acid ($pK_1 = 6.35$; $pK_2 = 10.33$)[72] and silicic acid ($pK_1 = 9.9$)[15] are weak acids. The relative ion charge distribution for the salts studied based on the pK values of $H_2PO_4^-$ to HPO_4^{2-}, H_2CO_3 to HCO_3^-, and H_2SiO_3 to $HSiO_3^-$ at pH 7.5 are 33/67, 7/93, and 99/1, respectively.[71,73]

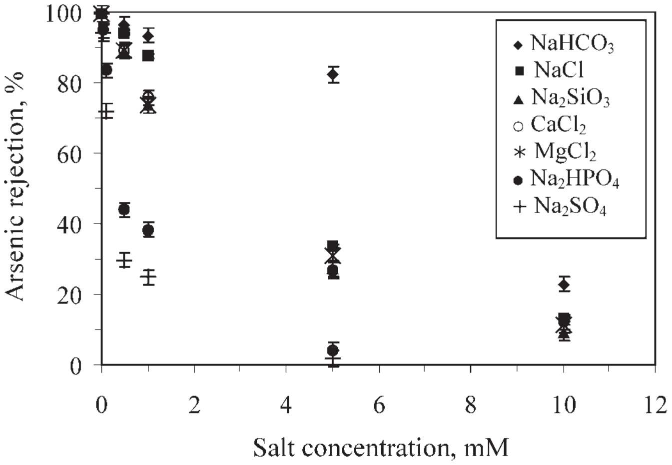

Figure 6. Effect of added electrolyte concentration on arsenic rejection for various salts.

The reduction of rejection due to the presence of the added salts decreases in the order $Na_2SO_4 > NaH_2PO_4 > Na_2SiO_3$, $MgCl_2$, $CaCl_2 > NaCl > NaHCO_3$. The deleterious effect of added electrolytes on arsenic complex binding to the QUAT can be understood as due to competition between arsenate and other anions for binding sites on the polymer. The affinity of anions to bind onto the polymer has behavior similar to that in ion-exchange resin containing ammonium groups observed in arsenic removal by ion exchange.[57] Another way of explaining the effect is that the electrical double layer is compressed around the polymer as ionic strength increases,[74] reducing the electrical potential on the polymer. The divalent anions reduce arsenic rejection more than the monovalent anions because the divalent anions bind more strongly to the charged sites on the polymer and also compress the electrical double layer around the polymer more effectively than the monovalent anions.

The effect of added salts on arsenic rejection is shown in Fig. 7, where the salt concentration is plotted as ionic strength instead of molarity. The ionic strength is calculated based on ion charge distribution for the salts.[71]

$$I = \frac{1}{2}\Sigma c_i z_i^2$$

where I is ionic strength, c_i is the concentration of ion i in moles per liter, and z_i is the valence charge of ion i. The ionic strength is summed over all cations and anions in solution, but the contribution of the polyelectrolyte is

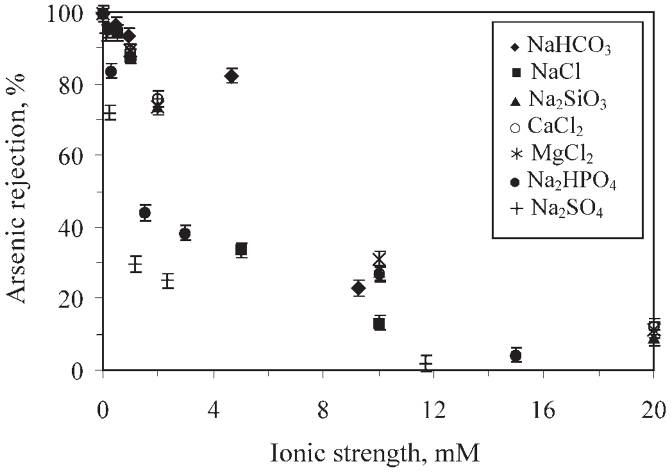

Figure 7. Effect of ionic strength on arsenic rejection for various salts.

complicated to include and is unnecessary for the simple arguments about salt effects to be made here. While the data for the different salts do not exactly coincide, there is agreement in the general trend for salts of different valence. High levels of added salt can be quite deleterious to arsenic removal by PEUF, just as they are harmful to ion-exchange efficiency. For example, at a sulfate concentration of 10 ppm (typical of some groundwaters), arsenic rejection is reduced from 99.48% to 94.20%. While this separation technique may not be economically feasible for some sources of drinking water, the characteristics of drinking water sources vary so widely that there are many cases where ionic strength is low and PEUF is effective. A technique that could conceptually achieve high arsenic rejection at high ionic strength is to use a ligand, which specifically complexes the arsenic-containing compound and binds to the polymer. This process is called ligand-modified polyelectrolyte-enhanced ultrafiltration (LM-PEUF) and has been shown to effectively remove cationic heavy metals with high selectivity.[75,76] Development of the required anion-specific ligands is underway in our laboratories.

Flux Through Membrane

As solution passes through the membrane, solutes rejected or partially rejected by the membrane will have a higher concentration near the membrane surface than in the bulk solution. The gel layer formed by this concentration polarization reduces flux rates and can either increase or decrease solute rejection. Relative flux is flux/flux of pure water. Figures 8–10 show the relative flux as a function of the logarithm of retentate [QUAT]. The flux decreases with increasing [QUAT] in the retentate solution. Extrapolation of these data on a semilogarithmic plot, as is commonly done, gives gel point concentrations for [QUAT]/[arsenic] ratios of 50, 100, and 150 of approximately 665, 655, and 658 mM, respectively. Previous studies have found gel concentrations of QUAT in the presence of three anions in the range of 559–885 mM under similar conditions to those studied here (Table 1).[68] Thus, the QUAT in the arsenate anion system has gel polarization behavior similar to QUAT used in removal of chromate, sulfate, and nitrate by PEUF.

The relatively high polymer concentrations required to substantially reduce flux, as seen in Figs. 8–10, permit the use of PEUF with both high rejections and high water recovery (permeate/feed ratio). An advantage of removal of arsenic using PEUF, compared to some other pollutants, is that feed concentrations of the arsenic are often quite low (≤100 ppb). So, if one chooses a [QUAT]/[arsenic] feed ratio of 100 and a feed [arsenic] of 100 ppb, for example, and arbitrarily assumes that the retentate will be treated until the relative flux is reduced to 0.4, the effluent retentate [QUAT] would be 72.9 mM (from Fig. 9). This means that the retentate would be concentrated by a factor of 547 and the permeate/feed volume (or flow) ratio would be 0.998.

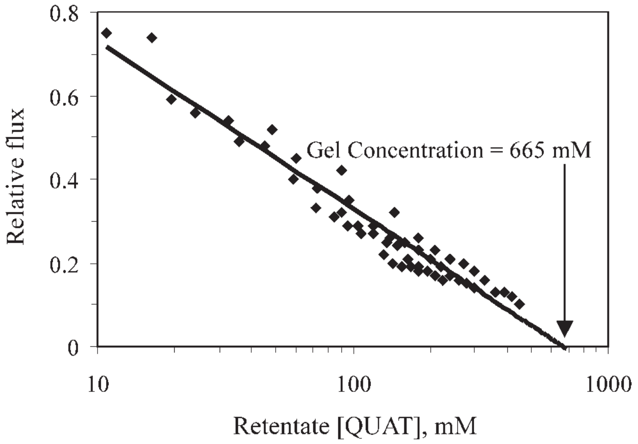

Figure 8. Relative flux as a function of retentate [QUAT] at a [QUAT]/[arsenic] ratio of 50.

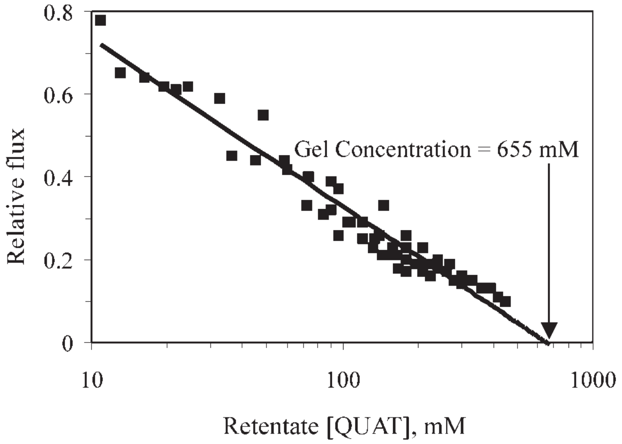

Figure 9. Relative flux as a function of retentate [QUAT] at a [QUAT]/[arsenic] ratio of 100.

The overall permeate [arsenic] would be an integrated average of that between the feed as retentate and final retentate composition as the retentate becomes concentrated during the process (as a function of time for a batch process and as a function of position along a membrane cartridge in a continuous, steady-state process). But, in our example, without doing a detailed calculation, the

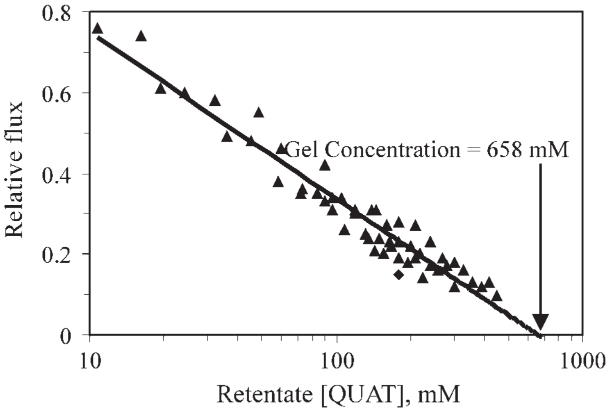

Figure 10. Relative flux as a function of retentate [QUAT] at a [QUAT]/[arsenic] ratio of 150.

Table 1. Gel concentration of QUAT (mM), best fit, and range of values within 95% confidence level.

Initial [QUAT]/[ANION]	Anion			
	Chromate[a]	Sulfate[a]	Nitrate[a]	Arsenate[b]
5	838 (778–913)	885 (780–1035)	797 (701–938)	
10	718 (670–776)	719 (663–790)	574 (547–604)	
20	581 (549–621)	582 (549–621)	559 (536–586)	
50				665 (568–805)
100				655 (583–818)
150				658 (575–836)

[a] Ref.[68].
[b] This work.

permeate [arsenic] would be <10 ppb from the data in Figs. 3 and 5. So, at least in the case of arsenic as the only electrolyte present, low permeate [arsenic], high water recovery, and high flux (low membrane area) can be simultaneously achieved, so PEUF is very promising for arsenic removal from drinking water.

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