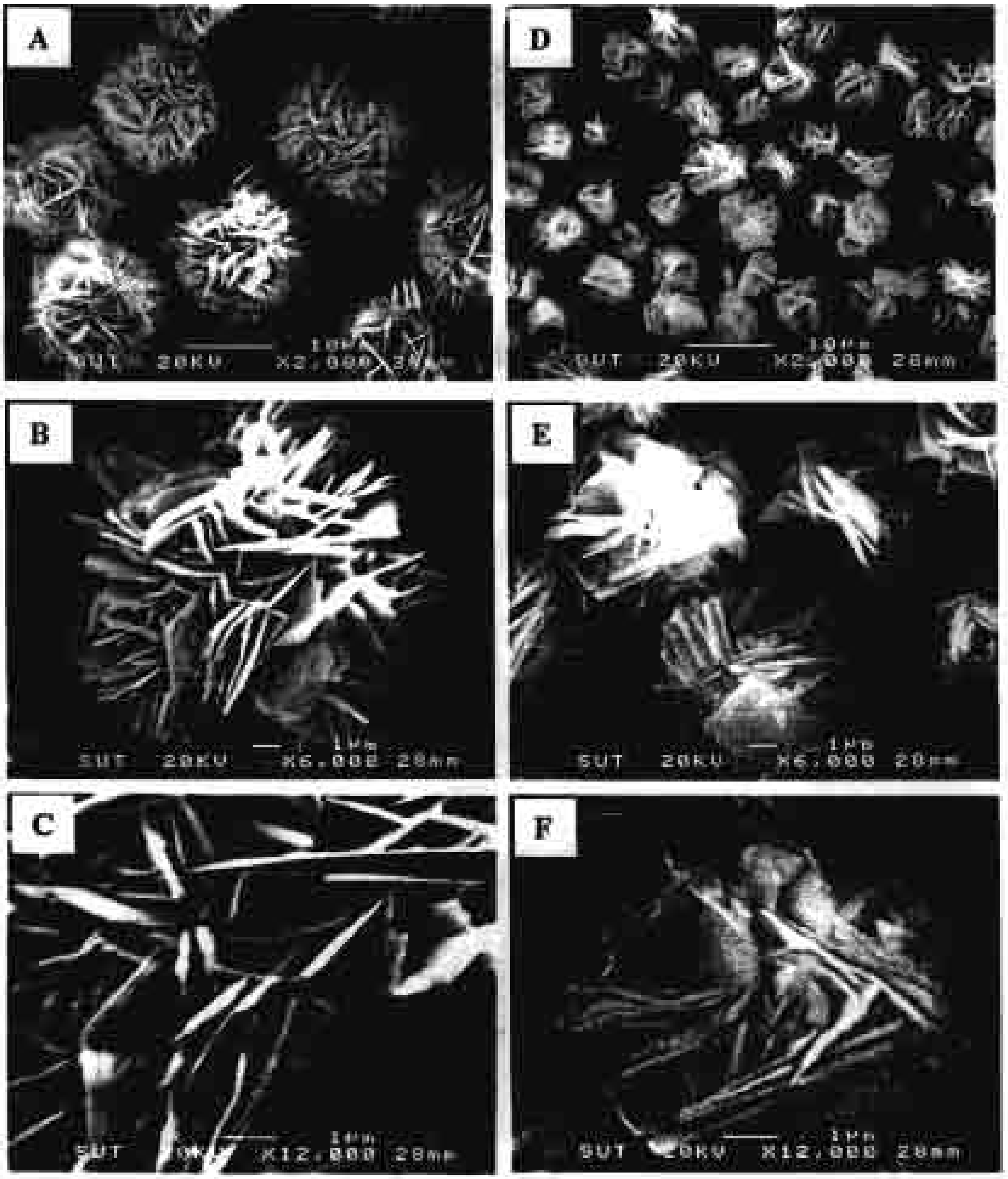

Figure 38. SEM micrographs of copper arsenate particles formed in the absence of QUAT (A-C), and in the presence of 0.2 M QUAT (D-F).

Discussion

Dispersion Stability

In the without polyelectrolyte, the average particle size of main peak of copper arsenate increases from 8.6 to 18.5 μm with decreasing copper to arsenate concentration ratios from 3.0 to 0.50. Copper arsenate in the absence of QUAT shows bimodal particle size distributions with a major and a minor at smaller particle sizes peak. In the small particle, Brownian motion is caused by random variations of in the incessant diffusion of particles and due to the velocity difference under gravity and centrifugal force (Okuyama, 1997). The small size of particle leads to slow sedimentation. While resulting from agglomeration by Brownian motion and collision between particles lead to growth of the particle. The sedimentation rate increases with increasing temperature, increasing salt concentration, and increasing copper to arsenate concentration ratio. The copper arsenate particles form soft and loosely packed sediments with large sedimentation volume. The sedimentation rate of copper arsenate is slower than barium hydrogen arsenate monohydrate due to the average particle size of copper arsenate is smaller than the average particle size of barium hydrogen arsenate monohydrate (Pookrod, Haller & Scamehorn, 2003) under the same condition. The average particles increase from 14 to 67 μm with decreasing barium to arsenate concentration ratios.

In this results show that the morphology of copper arsenate in addition of QUAT gives more densely packed due to more face-to-face contact of adjacent plates as compared to copper arsenate formed in the absence of QUAT (Figure 6.13). In the presence of QUAT, the average particle size of copper arsenate particles decreases with average diameter ranging from 7.5 to 4.6 μm at the main peak (compared to 11 μm in the absence of QUAT). This phenomenon was observed in QUAT dispersion behavior of barium chromate (Soponvuttikul, Scamehorn & Saiwan, 2003). The average particle diameter of barium chromate was 2 μm without polymer and decreased to 0.9 μm in the presence of QUAT (0.2 M). Another sample, the adsorption of SDS or cellulose on CT112 (Terayama, Okumura, Sakai, Torigoe & Esumi, 2001). The particle diameter of CT112 in the presence of 1 mM SDS or 0.2 g/L cellulose was 10 μm (compared to 47 μm in the absence of additive). As QUAT concentration increases, polymer adsorption on the copper arsenate particles increases, sedimentation rate increases, electrophoretic mobility increases, average particle size decreases, viscosity increases, and the particle size distribution broadens. The copper arsenate in the presence of QUAT leads to development of multimodal size distribution. The distributions consisted of a smaller peak (approximately 0.8-2 µm) remains close to the primary particle (approximately 11 µm) while the coarse shifts progressively to larger sizes with increasing polymer concentration (approximately 65-163 µm) This behavior has been observed in barium chromate in the added of QUAT (Soponvuttikul, Scamehorn & Saiwan, 2003) and in the addition of nonionic and anionic polymer on alumina (Rattanakawin & Hogg, 2001). In practice, the phenomenon is often noted as a combination of high settling rates and very high supernatant turbidity (Hogg, 1999).

QUAT adsorption increases with decreasing copper to arsenate concentration ratios. This phenomenon was also found in adsorption of QUAT on barium hydrogen arsenate monohydrate (Pookrod, Haller & Scamehorn, 2003) due to attractive and repulsive interactions between the polymer and local charged sites of particles. Copper arsenate solid surface consists of polar groups lead to produce an electric field that induces dipoles in the adsorbed molecules. The electrophoretic mobilities of copper arsenate particle with and without adsorbed QUAT are given as a function of copper to arsenate concentration ratio in Figure 6.6. The particles alone remain negatively charged at low stoichiometric ratio of copper arsenate, whereas with 0.2 M QUAT adsorbed they become positively charged.

When the salt concentration is increased, the average particle size at the main peak decreases in both the absence and in the presence of polymer. The dispersion is more stable to the addition of polyelectrolyte in the presence of NaCl compared to in the absence of polyelectrolyte. An increase in sedimentation of copper arsenate with increasing electrolyte concentration and decrease in viscosity is observed. Adsorption of polymer on copper arsenate also decreases with increasing electrolyte concentration. A similar result is found in the adsorption of QUAT on barium arsenate (Pookrod, Haller & Scamehorn, 2003) and also in adsorption of low molecular weight anionic poly(styrene sulphonate) on $CaCO_3$ and adsorption of cationic quaternized poly(vinylpyridine), at pH 8 on TiO_2 (Adam & Rodd, 1983; Esumi, 1999). Addition of salt screens the electrostatic repulsion of neighboring adsorbed QUAT molecules which tends to increase adsorption. The electrostatic attraction between polymer and surface, however, is also weakened, because the salt ions (Na^+) compete with the polymer for surface sites, tending to decrease the adsorption (Figure 6.11) (Esumi, 1999; Hoogeveen, Stuart & Fleer, 1996). An explanation for this has been proposed (Liu, Min & Ducker, 2001).

From Figure 6.12 the average particle diameter decreases and adsorption of polyelectrolyte on copper arsenate particles increases with increasing QUAT concentration. The sedimentation rate of copper arsenate and viscosity of QUAT in water increases with increasing QUAT concentration.

Conclusions

Conclusions

Arsenic Removal Using Polyelectrolyte-Enhanced Ultrafiltration

The polyelectrolyte-enhanced ultrafiltration method, using cationic polyelectrolyte poly(diallyldimethyl ammonium chloride) with an average molecular weight of 240,000 Daltons, was used to investigate the removal of arsenic(V) from dilute aqueous solution. Arsenic rejection as high as 99.95 % was observed from solution with starting arsenic concentration of 100ppb. An increase in pH results in an increase in arsenic rejection by PEUF. Arsenic rejection increased with increasing polyelectrolyte-to-arsenic concentration ratio because of the increase in the number of positively charged sites on the QUAT per unit volume, increasing the fraction of arsenic anion bound to polyelectrolyte.

The arsenic rejection is found to decrease with increasing salt concentration and increased valence of the added anion. The PEUF is effective where ionic strength is low. The arsenic reject also decreases with increasing ionic strength. The magnitude of rejection reduction due to the presence of salt decreases in the Na_2SO_4 > NaH_2PO_4 > Na_2SiO_3, $MgCl_2$, $CaCl_2$ > $NaCl$ > $NaHCO_3$ at the same molar concentration of these salts. The deleterious effect of added electrolytes on arsenic complex binding to the QUAT can be understood as due to competitive binding of competing anions with arsenate on the polymer. Another way of explaining the effect is that the electrical double layer is compressed around the polymer as ionic strength increases, reducing the electrical potential on the polymer. The divalent anions reduce arsenic rejection more than the monovalent anion because these 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 anion.

Arsenic retention increased and relative flux decreased with increased polyelectrolyte concentration in the retentate. Gel concentrations (polymer concentration at which flux becomes zero) was found to be 655 to 665 mM, (approximately 5.98 to 6.07 wt%). These high gel points mean that high water recoveries (> 99%) are achievable in this separation process.

Polyelectrolyte-enhanced ultrafiltration process can achieve to remove arsenate from dilute water solutions. Moreover, in this work the interaction between QUAT and the barium arsenate or copper arsenate particles produced in this recovery process and their environment is useful preparation for further development of the process.

Crystallization of Arsenate with Barium(II)

Barium hydrogen arsenate monohydrate ($BaHAsO_4 \cdot H_2O$) particles formed by mixing solutions of $BaCl_2 \cdot 2H_2O$ and $Na_2HAsO_4 \cdot 7H_2O$ and characterized by using XRD, FT-IR, and SEM/EDX. The morphology of barium arsenate formed plate-like crystal. At the stoichiometric ratio of 1.0, the zeta potential is zero. To study the effect of polymer on aqueous dispersion of barium arsenate was investigated the amount adsorbed of QUAT on barium arsenate, zeta potential, electrophoretic mobility, viscosity, particle size, and sedimentation of barium arsenate. The adsorption of QUAT onto barium arsenate particles increases with increasing polymer concentration, decreasing ionic strength, and decreasing barium to arsenate ratio. The elcetrophoretic mobility barium arsenate increases with increasing QUAT concentration. The reversal of the signs in the electrophoretic mobility from negative to positive (at barium to arsenate concentration ratio of 0.25) supports strongly the excess adsorption of polymer on barium arsenate. QUAT promotes crystal growth of barium arsenate crystal morphology. The average particle size of barium arsenate particles in the absence of polymer is about 67 µm, smaller than particles in the presence of polymer (average particle size about 94 µm). As a consequence, slower settling of the smaller particles occurs in the presence of polymer. The sedimentation of barium arsenate increase with increasing barium to arsenate ratio, increasing salt concentration, increasing temperature, and decreasing polymer concentration. The viscosity increases with increased polymer concentrations, decreased temperatures, decreased ionic strengths, and decreased barium to arsenate concentration ratios.

Crystallization of Arsenate with Copper(II)

The crystals of copper arsenate ($NaCu_6(AsO_4)_4Cl \cdot 4H_2O$) were prepared by adding solution of $CuCl_2 \cdot 2H_2O$ and $Na_2HAsO_4 \cdot 7H_2O$. The composition of crystals was studied by SEM/EDX, EDX, and FT-IR. Copper arsenate morphology formed more spherical crystal agglomerates. The zeta potential of copper arsenate is zero at the stoichiometric ratio of 1.5. The effect of polyelectrolyte on the dispersion stability of the suspension of copper arsenate particles were also studied. The adsorption of QUAT on copper arsenate particles increases with increasing polymer concentration, decreasing ionic strength, and decreasing copper to arsenate ratio. Electrophoretic mobility also increases with adding QUAT. Polymer adsorption on copper arsenate particle can enhance the dispersion stability through electrostatic and/or steric stabilization mechanism, leading to a slower sedimentation rate due to repulsive forces. The sedimentation rate of the crystals increases with increasing polymer concentration, increasing electrolyte concentration, and increasing temperature The sedimentation rate generally increases with increasing average particle size except when QUAT concentration increases, where increasing viscosity offsets increased particle size effects. The viscosity of the supernatant solution increases with increasing polymer concentration, decreasing ionic strength, decreasing temperature, and decreasing copper to arsenate ratio. Copper arsenate in the absence of QUAT shows bimodal particle size distributions with the main and smaller sizes (average particle size about 11 and 0.9) distribution peak, while particles in the presence of polymer show multimodal distributions with smaller, main, and larger particle sizes (average particle size about 0.7 to 12 μm, 4.6 to 7.5 μm, and 65 to 163 μm). The average particle size of main peak decreases with increasing polymer concentration, increasing salt concentration, decreasing temperature, and decreasing copper to arsenate concentration ratio.

7.2 Suggestions for Future Work

Arsenic removal

At high levels of added salt can be quite deleterious to arsenic removal by PEUF, just as they are harmful to ion exchange efficiency. Thus, this separation technique may not be economically feasible for some sources of drinking water, but 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 which 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 (Tuncay, Christian, Tucker, Taylor & Scamehorn, 1994a, 1994b).

Implications for PEUF Process

In the presence of QUAT, barium arsenate forms larger crystals (average particle size about 94 μm) than in the absence of QUAT (average particle size about 67 μm). In contrast, the particle size diameter of barium chromate in the presence of QUAT (about 0.9 μm) is smaller than in the absence of QUAT (about 2 μm) (Soponvuttikul, Scamehorn & Saiwan, 2003). In the chromate case a difficult separation was made worse by the addition of polyelectrolyte, requiring the investigators to resort to batch settling to remove the barium chromate precipitate (Soponvuttikul, 2003). The arsenate case is highly favorable, not only because the average particles formed during the precipitation are initially quite large, but also because they become much larger when formed in the presence of the polyelectrolyte. Furthermore, the particles become larger still when formed in the presence of added electrolyte. Thus, the large particle size and high sedimentation rate of barium arsenate augments regeneration of polyelectrolyte from the PEUF process in a steady-state crystallization process with gravity settling. The time required for complete settling of the particles increased when QUAT was added due to the enhanced dispersion stability for the smallest particles. One potential solution to this technological problem is to take advantage of the high positive electrophoretic mobility of the particles on the presence of QUAT; adding an electric field across the solution could cause the dispersed particles to settle rapidly.

Copper arsenate forms smaller crystals (approximately 7 μm) than in the absence of added polymer (approximately 11 μm) Comparison to barium arsenate, particle size diameter of barium arsenate in the presence of polyelectrolyte (about 94 μm) is larger than in the absence of polyelectrolyte (about 67 μm). Average particle size of copper arsenate is smaller than barium arsenate, but still larger than barium chromate. In the presence of QUAT, copper arsenate is more stable dispersion than barium arsenate. Sedimentation of copper arsenate is slower than barium arsenate, but no fine particles in the suspension, so settling requirement time of copper arsenate is more quickly than barium arsenate. In copper arsenate, increasing temperature and/or increasing added electrolyte decreases dispersion stability. In this work show that copper arsenate in the presence and in the absence of QUAT need to be high settling rate and large particle size. Adding an electric field could help particles to settling rapidly due to high positive electrophoretic mobility as the same in barium arsenate.

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Output

Publications

1. Pookrod, P.; Haller, K. J.; Scamehorn, J. F. Removal of Arsenic Anions from Water Using Polyelectrolyte-Enhanced Ultrafiltration. Sep. Sci. Tech. 2003, accepted.
2. Pookrod, P.; Haller, K. J.; Scamehorn, J. F. Copper Arsenate Precipitation in the Presence of Cationic Polyelectrolyte. Langmuir 2003, in preparation.
3. Pookrod, P.; Haller, K. J.; Scamehorn, J. F. Precipitation of Barium Arsenate in the Presence of Cationic Polyelectrolyte. Langmuir 2003, in preparation.

Presentations

1. Pookrod, P.; Haller, K. J. Polyelectrolyte-Enhanced Ultrafiltration for the Removal of Arsenic from Water *The 26th Congress on Science and Technology of Thailand*, October 2, 2000, Bangkok Thailand.
2. Pookrod, P.; Haller, K. J.; Scamehorn, J. F. Retention of Arsenate from Dilute Aqueous Solutions by Polyelectrolyte-Enhanced Ultrafiltration. *Royal Golden Jubilee-Ph.D. Congress II*, April 22-22, 2001, Phattaya, Thailand.
3. Pookrod, P.; Haller, K. J.; Scamehorn, J. F. Removal of Arsenic Anions from Water Using Polyelectrolyte-Enhanced Ultrafiltration. *222nd American Chemical Society (ACS) National Meeting*, August 26-30, 2001, Chicago IL.
4. Pookrod, P.; Haller, K. J.; Scamehorn, J. F. Effect of pH and Ionic strength on Arsenic Rejection Through Ultrafiltration Membrane. *Royal Golden Jubilee-Ph.D. Congress III*, April 25-27, 2002, Phattaya, Thailand.
5. Pookrod, P.; Haller, K. J.; Scamehorn, J. F. Application of Polyelectrolyte-Enhanced Ultrafiltration to the Removal of Arsenic from Aqueous Solution. *The 3rd National Symposium on Graduate Research*, July 18-19, 2002, Nakhon Ratchasima, Thailand.
6. Pookrod, P.; Haller, K. J.; Scamehorn, J. F. Regeneration of Polyelectrolyte by Precipitation Process. *The 28th Congress on Science and Technology of Thailand*, October 24-26, 2002, Bangkok Thailand.

7. Dungkeaw, W.; Pookrod, P.; Haller, K. J. Precipitation and Characterization of Barium Arsenate. *The 28th Congress on Science and Technology of Thailand*, October 24-26, 2002, Bangkok Thailand.

8. Pookrod, P.; Haller, K. J.; Scamehorn, J. F. Arsenic Removal And Polyelectrolyte Recovery by Polyelectrolyte-Enhanced Ultrafiltration Process. *American Institute of Chemical Engineers (AIChE) Annual Meeting*, (Proceeding). November 3-8, 2002, Indianapolis IN.

9. Scamehorn, J. F.; Pookrod, P.; Haller, K. J. Removal of Arsenic Anions from Water Using Polyelectrolyte-Enhanced Ultrafiltration. *226nd American Chemical Society (ACS) National Meeting*, September 7-11, 2003, New York, NY

Appendices

Manuscript 1

Polyelectrolyte-Enhanced Ultrafiltration for Removal of Arsenic from Aqueous Solutions

REMOVAL OF ARSENIC ANIONS FROM WATER USING POLYELECTROLYTE-ENHANCED ULTRAFILTRATION

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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 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 to 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 to 665 mM, (approximately 5.98 to 6.07 wt%) consistent with previous PEUF studies. These high gel points mean that high water recoveries (>99%) are achievable in this separation process.

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:

$H_3AsO_3 \longrightarrow H^+ + H_2AsO_3^-$ $pKa_1 = 9.23$

$H_2AsO_3^- \longrightarrow H^+ + HAsO_3^{2-}$ $pKa_2 = 12.13$

$HAsO_3^{2-} \longrightarrow H^+ + AsO_3^{3-}$ $pKa_3 = 13.40$

Arsenic Acid/Arsenate:

$H_3AsO_4 \longrightarrow H^+ + H_2AsO_4^-$ $pKa_1 = 2.22$

$H_2AsO_4^- \longrightarrow H^+ + HAsO_4^{2-}$ $pKa_2 = 6.98$

$HAsO_4^{2-} \longrightarrow H^+ + AsO_4^{3-}$ $pKa_3 = 11.53$

The pKa 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^-, $HAsO_3^{2-}$, 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 10-100 in open seawater. Arsenic(V) is also generally the dominant species in lake and river 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 (μg/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 (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) have 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 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 which 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 2.4x10^5 Daltons, was purchased from Calgon 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 was 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 which 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 percent (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 percent (w/v) sodium borohydride ($NaBH_4$) dissolved in a 0.05 percent (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 ([QUAT]/[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 units 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 Figure 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 Figure 3. An increase in pH from 6.5 to 8.5 results in an 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 Figure 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% to 99.95% shown in Figure 3 correspond to a permeate arsenic concentration of 4.22 to 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 Figure 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 [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 which 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).

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 Figure 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).

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

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 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 which 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 to 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 Figures 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 Figure 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. 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 permeate [arsenic] would be < 10 ppb from the data in Figure 3 and Figure 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.

ACKNOWLEDGEMENTS

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List of Figures and Table

Table1. Gel concentration of QUAT (mM)), Best Fit, and Range of Values Within 95% Confidence Level.

	Initial [QUAT]/[ANION]		
Anion	5	10	20
Chromate[a]	838 (778-913)	718 (670-776)	581 (549-621)
Sulfate[a]	885 (780-1035)	719 (663-790)	582 (549-621)
Nitrate[a]	797 (701-938)	574 (547-604)	559 (536-586)

	Initial [QUAT]/[ANION]		
Anion	50	100	150
Arsenate[b]	665 (568-805)	655 (583-818)	658 (575-836)

a. Ref. 68. b. This work.

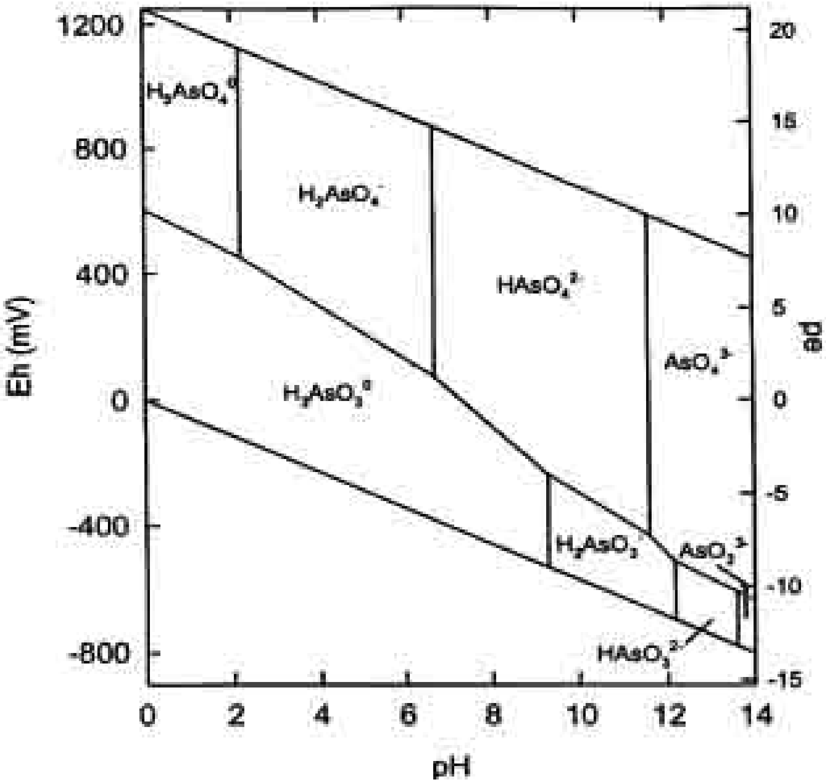

Figure 1 Redox potential (Eh) *vs* pH diagram for aqueous arsenic species in the As-O_2-H_2O system at 25°C and 1 bar total pressure. The hypothetical electron activity at equilibrium, pe, is used interchangeably with Eh, pe = (F/2.3RT)Eh. Reprinted with permission from ref. 8, Copyright 1988, Springer-Verlag.

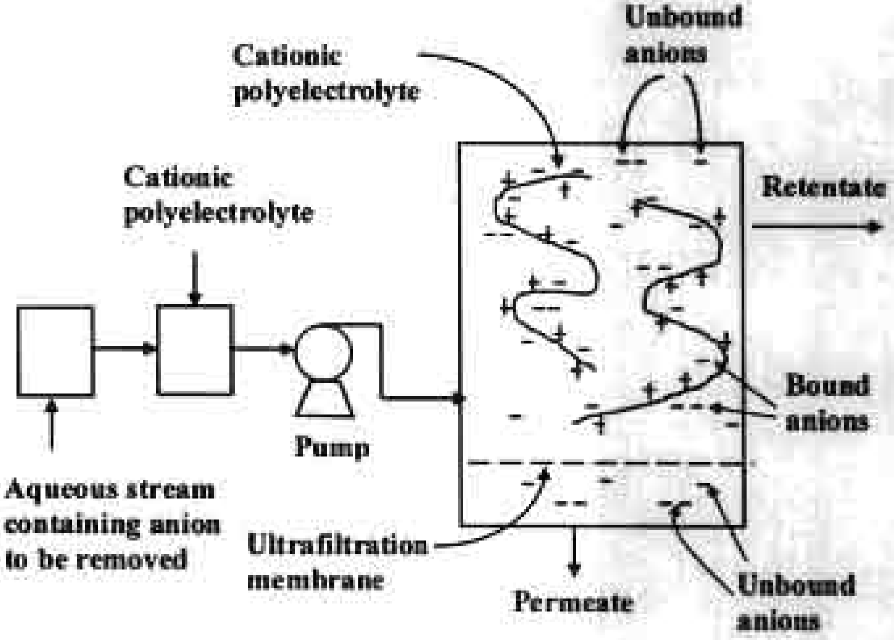

Figure 2 Schematic diagram of polyelectrolyte-enhanced ultrafiltration (PEUF) to remove anionic arsenic species from water.

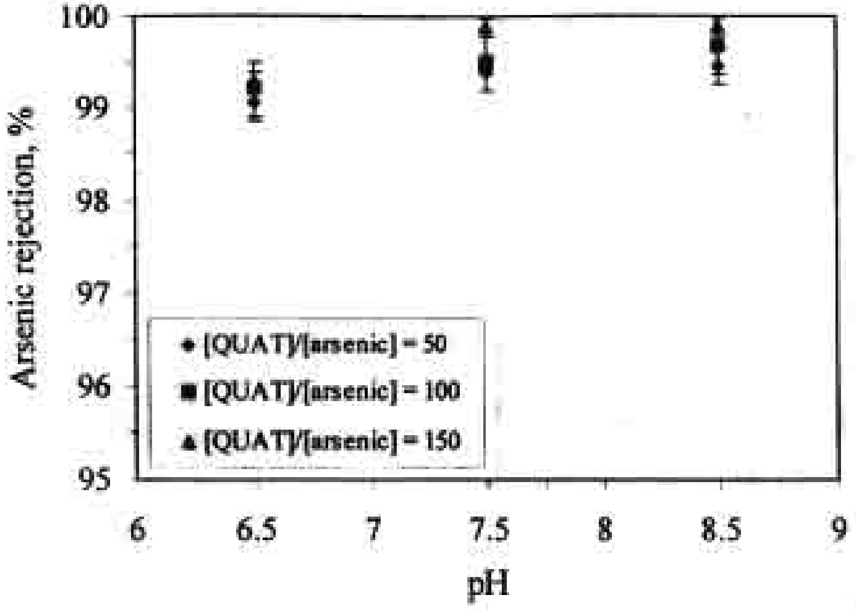

Figure 3 Rejection of arsenate as a function of pH with retentate [arsenic] = 150 ppb.

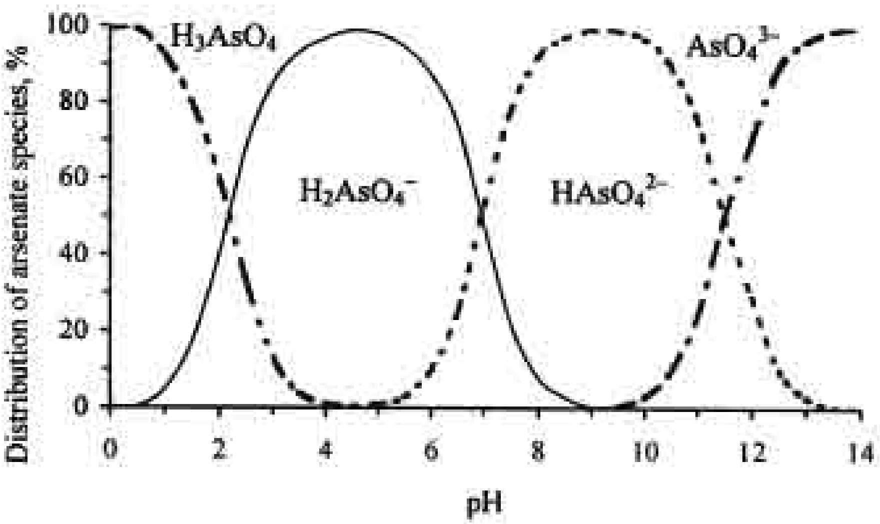

Figure 4 Arsenate speciation as a function of pH (after Coleman, ref.71).

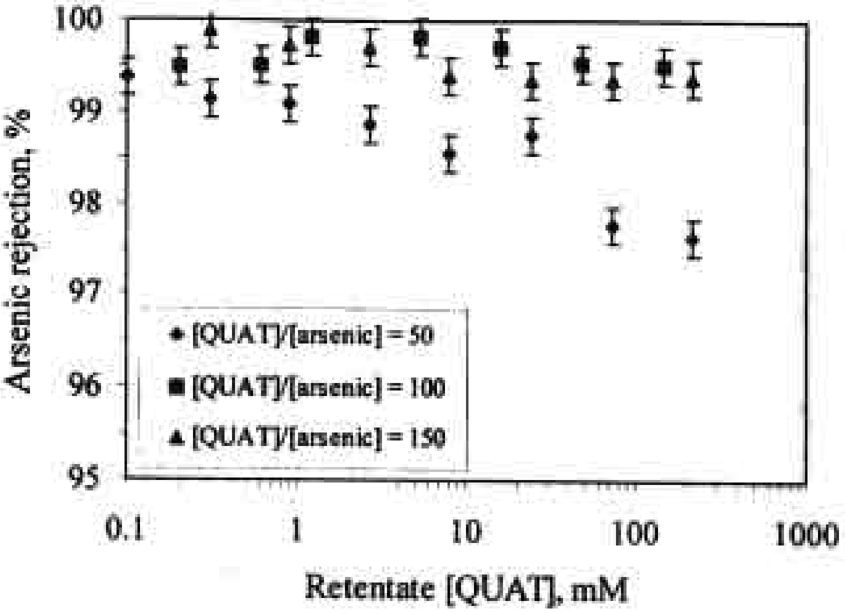

Figure 5 Rejection of arsenic as a function of retentate [QUAT] at pH 7.5.

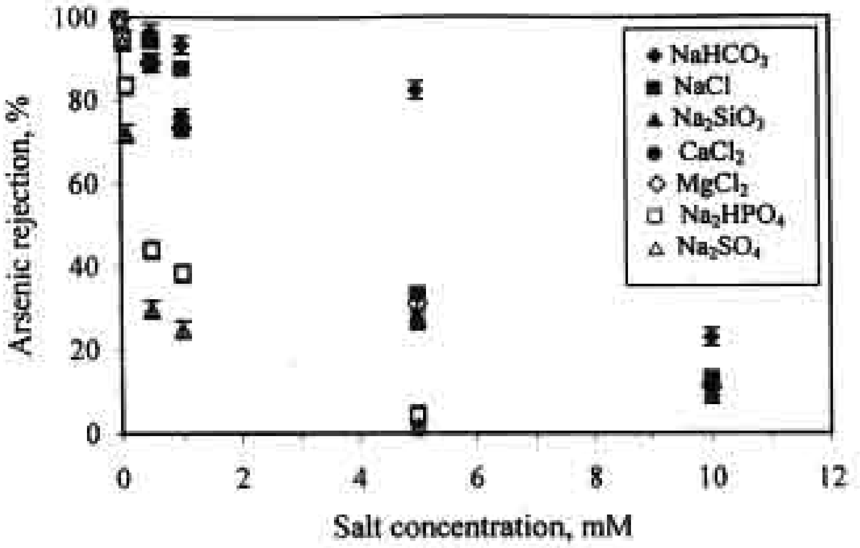

Figure 6 Effect of added electrolyte concentration on arsenic rejection for various salts.

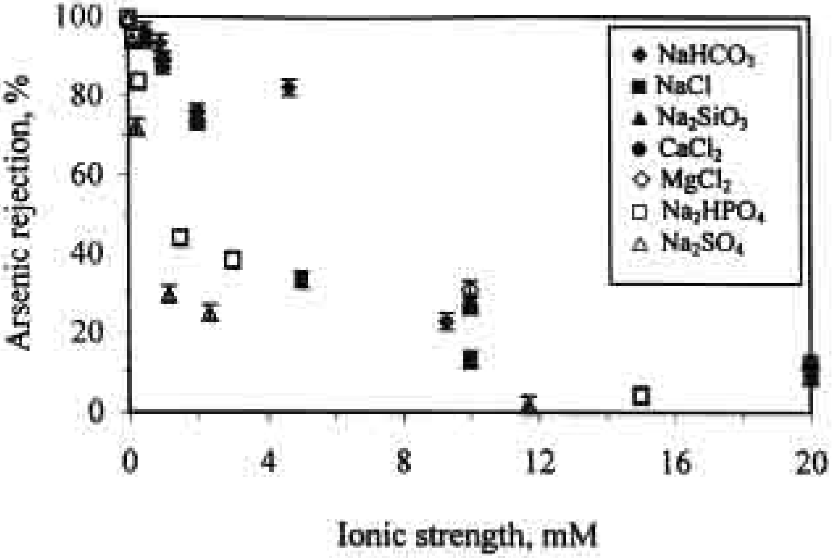

Figure 7 Effect of ionic strength on arsenic rejection for various salts.

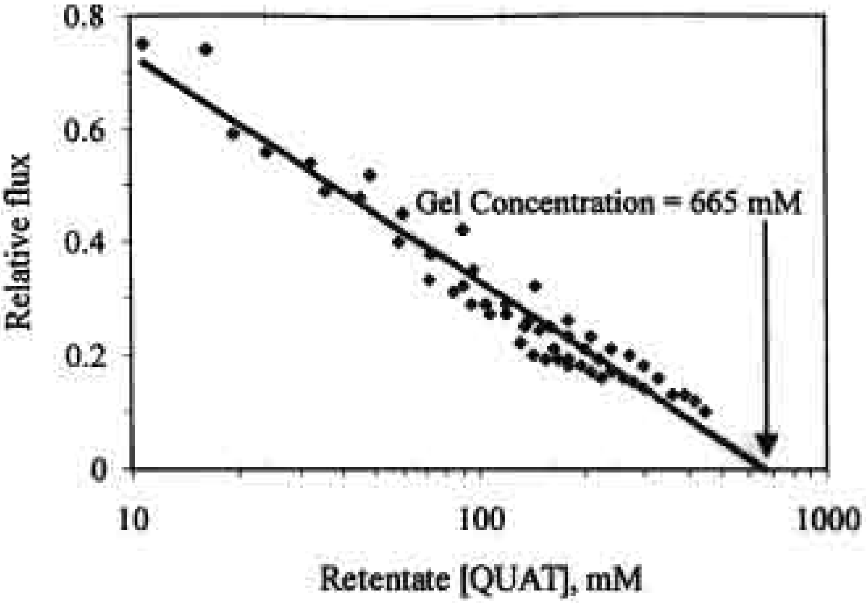

Figure 8 Relative flux as a function of retentate [QUAT] at a [QUAT]/[arsenic] ratio of 50.

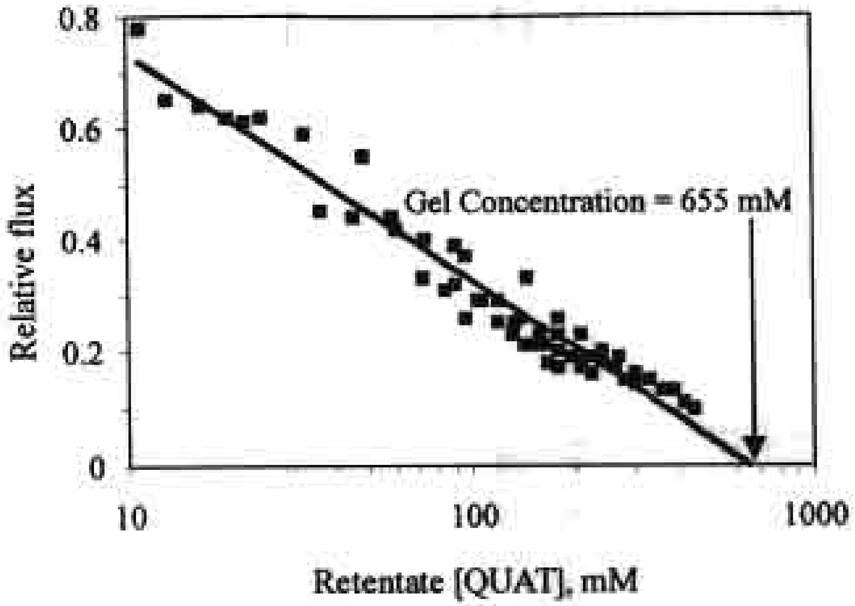

Figure 9 Relative flux as a function of retentate [QUAT] at a [QUAT]/[arsenic] ratio of 100.

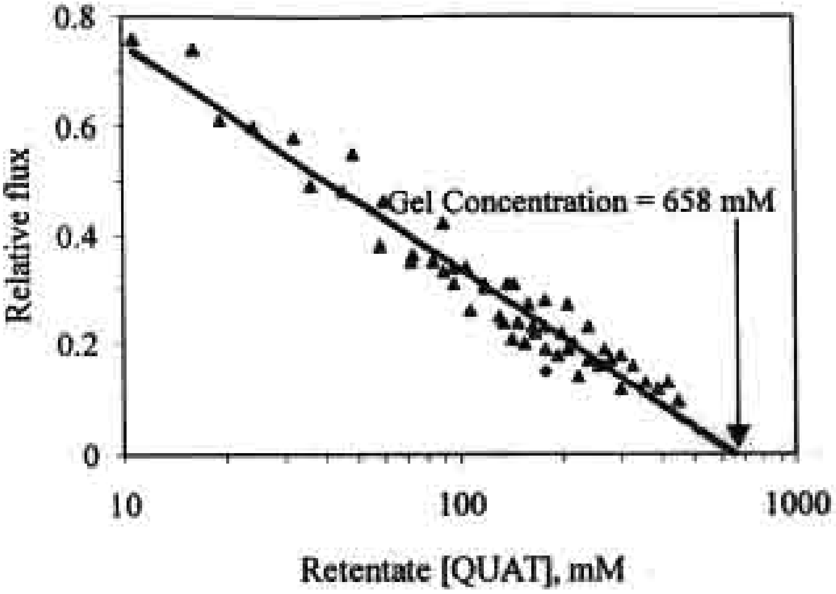

Figure 10 Relative flux as a function of retentate [QUAT] at a [QUAT]/[arsenic] ratio of 150.

Manuscript 2

Precipitation of Arsenate with Barium(II) in the Presence of Cationic Polyelectrolyte

Precipitation of Arsenate with Barium(II) in the Presence of Cationic Polyelectrolyte

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Abstract

The influence of cationic polyelectrolyte, poly(diallydimethylammonium chloride) (QUAT), on the formation and dispersion stability of barium arsenate particles is discussed here. The polymer causes an increased dispersion stability (decreased sedimentation rate) due to barriers to coalescence due to polymer adsorption and to increased viscosity. The adsorption of polyelectrolyte on the particles increases with increasing polymer concentration, decreasing ionic strength, and decreasing barium to arsenate concentration ratio. The sedimentation rate of the crystals increases with decreasing polymer concentration, increasing electrolyte concentration, and increasing temperature. The viscosity of the supernatant solution increases with increasing polymer concentration, decreasing ionic strength, decreasing temperature, and decreasing barium to arsenate concentration ratio. The barium arsenate crystallizes with a plate morphology. The average particle size increases with

increasing polymer concentration, increasing salt concentration, increasing temperature, and decreasing barium to arsenate concentration ratio. When QUAT is present during formation of the particles the entire size distribution shifts to larger particles, implying faster sedimentation. However, the very fine particles are stabilized as a dispersion by QUAT absorption and the increased viscosity leading to longer settling times for the total particulate material.

Introduction

The regulation of the stability of dispersed particles by polyelectrolytes is of high scientific and technological significance. Polyelectrolytes find widespread application in numerous products used in daily life[1], and in many industrial processes, such as water and wastewater treatment processes.[2] We are particularly interested in the polyelectrolyte enhanced-ultrafiltration (PEUF) process, which can remove ionic species from aqueous solution by using a water-soluble polyelectrolyte of opposite charge to that of the target ion to be removed. The polyelectrolyte binds the target ion, and the solution is then treated by ultrafiltration with membrane pore sizes small enough to block the polymer and polymer/ion complexes. PEUF is particularly effective for multivalent ions. PEUF with cationic poly(diallyldimethyl ammonium chloride) polyelectrolyte removes arsenic(V) naturally present in many water supplied as anionic oxide complexes, like arsenate, from dilute aqueous solutions. Only the unbound arsenate at the concentration in the retentate (solution not passing through the membrane) is present in the permeate solution passing through the membrane. Arsenic rejections as high as 99.95% were observed in PEUF.[3]

For this process of arsenate removal by PEUF to be economically competitive, the QUAT must be recovered from the retentate for reuse.[4] One promising method of recovery is addition of divalent metal ion to precipitate the arsenate.[5] After removal of the metal arsenate precipitate from solution, the concentrated QUAT solution is reused by recycling to the PEUF feed. While filtration or centrifugation can recover the solid, gravity settling is the most economical separation technique. This study of the effect of the polyelectrolyte on the sedimentation rate of barium arsenate aids in the design of this solid/liquid separation. In this paper the underlying physical chemistry of the effect of QUAT on barium arsenate particle formation and dispersion stability is probed.

An important property of polyelectrolytes is their tendency to adsorb on solid surfaces of dispersed particles.[6] Inhibition of calcium phosphate precipitation by various polymeric additives has been studied[7]; addition of low concentration (few parts per million, ppm) of low molecular weight poly(acrylic acid) significantly retarded the precipitation of calcium phosphate in aqueous solution. The results show that cationic polymer, QUAT, does not inhibit amorphous calcium phosphate precipitation. High QUAT concentration (0.2 M QUAT) has been shown to inhibit barium chromate crystallization.[8] The adsorption of polyelectrolyte, polyphosphinoacrylates, polyacrylate, and a copolymer of maleic acid and vinyl sulfonic acid on barium sulfate was investigated.[9-10] The results showed that polyelectrolytes retarded barium sulfate crystal growth. The effect of polymer on dispersion stability and on settling of barium sulfate particles has also been studied.[11-12] In the presence of excess sodium (carboxymethyl)cellulose, barium sulfate dispersions were relatively stable to high electrolyte concentrations. In the presence of polystyrene sulfonate and polyacrylic acid, barium sulfate particles are well dispersed and no aggregation occurs. The adsorption of an amphoteric polymer or dual polymer combination of QUAT and acrylic acid on barium sulfate crystals enhances the colloid stability of barium sulfate dispersions, and the adsorption capacity of barium sulfate increases with increasing ionic strength.[13] Schwarz *et al.*[14] described the adsorption of QUAT onto silica, mica, and acidic polymer latex and have related the adsorption characteristics to the stability of the QUAT dispersions. The results show that the adsorption of QUAT increases with increasing surface charge density on the particle surface and increasing electrolyte concentration. The influence of the adsorption of cationic polyelectrolytes of different charge density, QUAT and copolymers of QUAT with N-methyl-N-vinylacetamide, on the stability of precipitated silica, sikron, and latex suspensions has been studied.[15-19] The adsorption and the thickness of the polymer layer on silica and latex increase with ionic strength and pH, with decreasing chain charge density of the polycations, and at high electrolyte concentration with the molar mass of the polymers. The dispersion stability of polymer and surfactant on a drug particle, 5-(3-ethoxy-4-pentyloxyphenyl)-2,4-thiazolidinedione, CT112, was estimated by measuring the particle size, zeta potential, adsorption isotherm, and sedimentation rate.[20] The addition of celluloses rather than sodium dodecyl sulfate (SDS) provided a highly stable suspension of CT112. In addition, mixed systems of celluloses and SDS enhanced CT112 dispersion stability more effectively.

In the present study we have investigated the effect of the barium to arsenate concentration ratio, QUAT concentration, temperature, and added electrolyte on particle size distribution, sedimentation rate, and zeta potential of the barium arsenate particles. In addition scanning electron microscopy has been used to study the morphology of the crystals formed in the absence and in the presence of polymer.

Experimental Section

Materials

Disodium hydrogen arsenate heptahydrate, $Na_2HAsO_4 \cdot 7H_2O$, (98.5%) was from Fluka (Buchs, Switzerland). Sodium chloride, NaCl, (99.5%) and barium chloride dihydrate, $BaCl_2 \cdot 2H_2O$, (97%), were from Carlo Erba (Milan, Italy). All chemicals except the QUAT were analytical reagent grade and used as received. Deionized and distilled water were used to prepare solutions.

Commercial grade poly(diallydimethyl ammonium chloride) or QUAT, a quaternary ammonium polymer, with a number average molecular weight of 2.4×10^5 Da produced by Calgon Corporation (Pittsburgh PA) as a 40% solution in water was the cationic polyelectrolyte. Dilute solutions of the polymer were purified prior to precipitation experiments using a spiral wound ultrafiltration unit with a 10 kDa molecular weight cutoff (MWCO) membrane to remove lower molecular weight fractions. A stirred cell equipped with a 10 kDa molecular weight cut-off regenerated cellulose acetate membrane (Millipore, Bedford MA) was used to concentrate the purified polymer solution up to the desired polymer concentrations for preparing stock solutions. The repeating unit of the polymer is $(H_2CCHCH_2)_2N(CH_3)_2Cl$; the QUAT concentrations are based on moles per liter of the repeating unit and not on the total molecular weight.

Methods

Sedimentation Rate Measurement

This method involves the visual observation of the sedimentation of the solid particles in the absence and in the presence of polyelectrolyte. Batch settling experiments[21-22] were conducted in screw cap test tubes and the precipitate was left undisturbed to settle throughout the period of study. The sedimentation was observed as the height of suspended solid at the base of the vessel as a function of time, measured until the height was constant.

Viscosity Measurement

The viscosity of supernatant QUAT solutions was determined using a capillary viscometer. The liquid samples of the polymer solutions were obtained from the sedimentation experiments by separating the dispersed solid by centrifugation at 4500 rpm for 10 minutes. Flow time measurements were conducted in a thermostated bath at 10, 25, and 50 ± 0.10°C. The viscosity measurements were carried out automatically with an AVS360 viscometer from SCHOTT (Germany) which uses optical sensors to measure the time taken for the solution to flow between fixed marks in a capillary tube during gravity drainage. The kinematic viscosity, in mm^2/s, was calculated from the viscometer constant, C, and the measured flow time, t, according to the equation

$$\eta = Ct$$

Relative kinematic viscosity is defined as the kinematic viscosity of a polymer solution divided by the kinematic viscosity of water.

$$\eta_r = \eta/\eta_s$$

Particle Size Measurement

The particle size distributions of barium arsenate dispersions in the absence and in the presence of QUAT were estimated with a Mastersizer S (Malvern Instrument Ltd, UK) using a small volume sample cell employing an internally mounted overhead stirrer to keep the sample suspended. The dispersions were shaken to ensure complete suspension before adding a few drops to the sample cell. Particle size distributions used average particle size parameter $d_{0.5}$, the particle size exceeded by 50% by volume of the particles.

Zeta Potential Measurement

A Zeta Meter 3.0+ (Zeta Meter Inc., Staunton, VA) was used to measure the zeta potential of barium arsenate particles in deionized water. Calculated zeta potentials from measured electrophoretic mobilities in high viscosity suspensions are unreliable, so electrophoretic mobilities are reported for the particles in the presence of 0.2 M QUAT.

Polyelectrolyte Adsorption Measurement

Adsorption isotherms were determined from depletion[15] of QUAT from the solution after equilibrium with barium arsenate (0.3g) dispersed in 30 mL of polyelectrolyte solution at various initial QUAT concentrations from 0.005 to 0.1 M. The solutions were mixed with a vortex stirrer (Barnstead/Thermolyne, Dubuque IA)