

ARSENIC REMOVAL AND POLYELECTROLYTE RECOVERY BY  
POLYELECTROLYTE-ENHANCED ULTRAFILTRATION PROCESS

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## Abstract

The polyelectrolyte-enhanced ultrafiltration (PEUF) method, using cationic polyelectrolyte poly(diallyldimethyl ammonium chloride) with an average molecular weight of 240,000 Daltons, can remove arsenic(V) from aqueous solutions. The cationic polyelectrolyte is added to bind anionic arsenic species to form polyelectrolyte-arsenate complexes, which are separated by a subsequent ultrafiltration operation. The large polyelectrolyte-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. Arsenic was 99-99.9% removed from synthetic feed water containing 100 ppb arsenic by the PEUF process, resulting in permeate arsenic concentrations lower than 5 ppb. Thus the technique is capable of achieving the new 10 ppb standard for arsenic in drinking water to be effective in 2006. Regeneration of the polyelectrolyte from the retentate stream containing polyelectrolyte-arsenate complexes is carried out by precipitation. The arsenate anions are released from the polyelectrolyte using divalent metal ions such as copper or barium to form copper arsenate or barium arsenate. The polyelectrolyte can be reused.

## Introduction

Arsenic is toxic to all living organisms, thus creating potentially serious environmental concerns. 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) (Ferguson and Gavis, 1972). Therefore, arsenic occurs in water in different forms depending upon the pH and oxidation potential of the water.  $\text{H}_2\text{AsO}_4^-$  is dominant at pH less than about 6.9, while  $\text{HAsO}_4^{2-}$  becomes dominant above pH 6.9.  $\text{H}_2\text{AsO}_4^-$  and  $\text{AsO}_4^{3-}$  are present in extremely acidic and alkaline conditions respectively while  $\text{H}_3\text{AsO}_3$  exists primarily as the uncharged species at pH less than 9 (Smedley and Clifford, 2002). Studies on long-term human exposure show that arsenic in drinking water is associated with liver, lung, kidney, bladder, and skin cancers. To minimize these risks, the US Environmental Protection Agency implemented the new 10  $\mu\text{g/L}$  standard for arsenic in drinking water to be effective in 2006. There are several methods to remove arsenic from aqueous solution including chemical precipitation-coagulation, adsorption, lime softening, ion exchange and membrane processes (Kartinen and Martin, 1995).

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  $\text{Cu}^{2+}$  with anionic polymer (Sasaki, et al., 1989) or anionic ions like chromate

(CrO<sub>4</sub><sup>2-</sup>) with cationic polymer (Tangvijitsri, et al., 2002). 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 (Tabatabai, et al., 1995).

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 1 shows a schematic diagram of PEUF to remove anionic arsenic species from water.

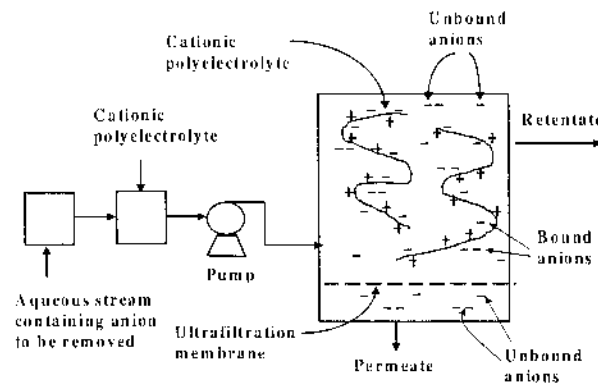


Figure 1. Schematic diagram of polyelectrolyte-enhanced ultrafiltration (PEUF) to remove anionic arsenic species from water.

In this study we separated arsenic from low concentration aqueous solution using polyelectrolyte-enhanced ultrafiltration and recovered polyelectrolyte from the retentate stream.

## Experimental

Experiments were performed in a Millipore 400 mL batch ultrafiltration stirred cell equipped with a 10 kDa molecular weight cut-off regenerated cellulose acetate membrane. 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 a small amount of HCl or NaOH. Experiments were conducted at 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. Arsenic concentrations were determined using flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS) following standard methods (Standard Methods for the Examination of Water and Wastewater, 1995). Polyelectrolyte concentrations were determined with a Leco CNS-2000 elemental analyzer.

Polyelectrolyte recovery experiments were studied on a batch scale by adding copper chloride or barium chloride to solutions of the QUAT-arsenate complexes. The polyelectrolyte adsorption, sedimentation rate, and chemical analysis of copper arsenate or barium arsenate were investigated.

## Results and Discussion

### Arsenic removal by polyelectrolyte-enhanced ultrafiltration

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:

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

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

The arsenic rejection is shown in Figure 2 as a function of pH at feed [QUAT]/[arsenic] ratios of 50, 100, and 150. 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 a slight increase in arsenic rejection from 99 to 99.9%. 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. For arsenate, the predominant species between pH 6.5 and 8.5 are  $H_2AsO_4^-$  and  $HAsO_4^{2-}$ . Comparison of arsenic rejection results at identical initial retentate arsenate concentrations of 100  $\mu\text{g/L}$  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 arsenic concentration in the retentate is 150 ppb, based on an initial concentration of 100 ppb. Rejections of 99% to 99.9% shown in Figure 2 correspond to a permeate arsenic concentration of 4.22 to 0.20 ppb.

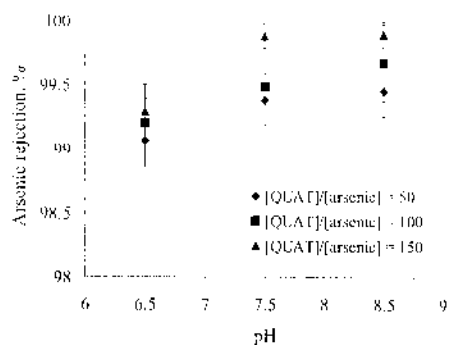


Figure 2. Rejection of arsenate as a function of pH with retentate [arsenic] = 150 ppb.

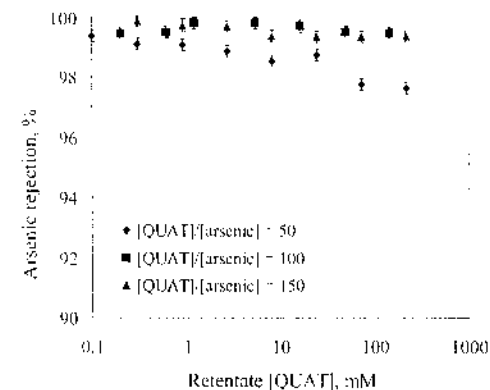


Figure 3. Rejection of arsenic as a function of retentate [QUAT] at pH 7.5.

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. 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 anion bound to polyelectrolyte. As the retentate [QUAT] or [arsenate] increases at constant feed [QUAT]/[arsenic] ratios, the rejection decreases.

#### Polyelectrolyte recovery

Economically, the cationic polyelectrolyte, poly(diallyldimethyl ammonium chloride) or QUAT must be recovered from the retentate for reuse. The method of recovery in this study was addition of the divalent metal ions copper or barium as the chloride salt to precipitate the arsenate. The chloride ion will reconstitute the polyelectrolyte with its chloride counter ion to regenerate QUAT and copper arsenate or barium arsenate can be separated as the solid waste. Copper arsenate may be economically recovered for use in the manufacture of arsenical wood preservative.

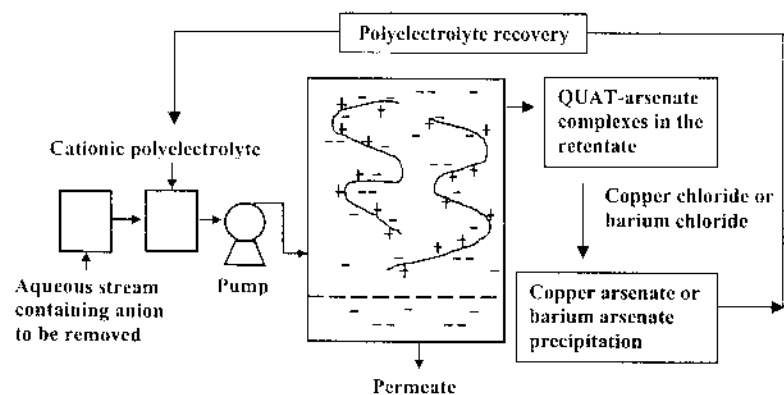


Figure 4. Polyelectrolyte-enhanced ultrafiltration with QUAT recovery using divalent metal ion precipitation.

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