Water-Soluble Polymers: Optimization of Arsenate Species Retention by Ultrafiltration

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ABSTRACT: The liquid-phase polymer-based retention (LPR) technique was employed to study the retention of arsenate species by poly(vinylbenzyl trimethylammonium chloride), P(ClVBTA), and poly[2-(acryloyloxy)ethyltrimethylammonium chloride], P(ClAETA). The effect of parameters such as polymer concentration, time exposure, competition of sulfate and phosphate anions, and the use of natural systems as drinking water on the retention of As(V) species was analyzed. The mole ratios of polymer : As(V) of (31 : 1), (20 : 1), (10 : 1), (6 : 1), and (3 : 1) by using the washing method at pH 8 and 6 were assayed. The retention capacity was a function of polymer concentration and pH. The optimum mole ratio of polymer : As(V) was (20 : 1) for all pHs studied and all polymeric structures. The polymer's activity recovery assays were performed by washing at pH 2 and 3. A 95% As(V) elimination was achieved from polymers. A study of competition in the presence of other anions was performed at the same polymer : As(V) ratio (20 : 1). At pH 8 and at the same concentration of arsenate anions, sulfate, and phosphate anions, no important competition on arsenic retention was observed. Assays for P(ClVBTA) at pH 8 and mole ratio of polymer : As(V) (20 : 1), (40 : 1), and (60 : 1) using drinking water showed that the efficiency was higher under these conditions for the three As(V) retention cases. An unbuffered system with drinking water was tested for washing and enrichment methods by determining the maximum saturation capacity of the P(ClVBTA) polymer. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2327–2333, 2009

Key words: radical polymerization; water-soluble polymers; membranes

INTRODUCTION

Arsenic is known worldwide as a highly toxic element even at low levels. The permissible level according to the WHO[1] is <10 μg/L. In an aqueous environment, inorganic arsenic species [arsenite As(III) and arsenate As(V)] are more abundant and present the lowest oxidation state, making removal difficult. The presence of arsenical water in several countries, such as India, Chile, France, and Argentina, make it necessary to find adequate removal methods. In an international workshop[2] on arsenic contamination and safe water held in Bangladesh, the efficacy of arsenic removal technologies applied to groundwater was discussed. The consensus was that all technologies are potentially useful, and the selection of a particular method should be based on the specific conditions in each region.

One methodology uses metallic oxides as absorbents, mainly iron, aluminum, and hydroxides in a two-phase system.[3,4] Both arsenite and arsenate present high affinity for iron oxides in soil and subsurface environment.[5] The adsorption characteristics of As(V) and As(III) on titanium dioxide-loaded Ambulate XAD-7 resin have been studied,[6] showing favorable As(III) adsorption in comparison with As(V) in column adsorption experiments from pH 5 to 10. These applications assume that As(III) has been oxidized before its removal. As(III) oxidation is possible in the presence of manganese oxide-coated sands or by advanced oxidation processes. Although many of the two-phase methods such as flocculation, precipitation, and adsorption on inorganic oxides have been developed and used,[1] and their applications can be related to problems of heterogeneous reactions and interphase transfer.

A promissory technique is related to filtration membranes. One reported method leaves groundwater for a few hours in a container with soluble iron, and then collects the water by decanting.[7] The modification is a simple three-pitcher filtration assembly with iron chips and core sand in the first pitcher, wood charcoal and fine sand in the second pitcher, and the filtered water is collected in the third pitcher.[6]

We have previously reported[8–10] the retention properties of arsenic ions from an aqueous solution using liquid-phase polymer-based retention (LPR) technique. The retention properties using the washing method at constant ionic strength and different

pHs were evaluated for water-soluble poly[3-(metha-cryloylamine)propyltrimethyl ammonium chloride], P(ClMPTA), and copolymer poly [3-(meth-acryloylaminepropyl) trimethylammonium chloride-*co*-acrylic acid], P(ClMPTA-*co*-AA). The performance of P(ClMPTA) at basic and neutral pH was optimum. Studies with the copolymer at different mole ratios [(1 : 1), (1 : 2), and (2 : 1) polycation/polyanion] showed the concerted action of polycation and polyanion on arsenic retention ability.[8] The polymeric structures[9] of quaternary ammonium salt with different ion exchange groups, such as methyl sulfate, chloride, bromide, and hydroxide, presented different properties to remove arsenate anions from aqueous solution, where the type of the voluminous quaternary ammonium group influenced the arsenic retention. Recently, studies with two cationic polymers,[10] which were synthesized by radical polymerization and containing different anion exchanger groups, Cl^- and $(OSO_3CH_3)^-$, have presented different arsenate ion retention properties. More recently, we have prepared a series[11] of water-soluble metal–polymer complexes to retain As(III) from an aqueous solution in one step. The complex of poly(acrylic acid) with 10 and 20 wt % of tin in the structure presented the highest retention for As(III) species at pH 8.[11]

The aim of this article is to optimize the operative variables for As(V) retention using the poly[2-(acryloyloxy)ethyltrimethylammonium chloride], P(ClAETA), and poly(vinylbenzyltrimethylammonium chloride), P(ClVBTA). The influence of polymer concentration, the exposure time prior filtration, the recovery activity of polymers desorbing the species As(V), and the retention behavior in the presence of other anions were studied. In addition, polymer performance in drinking water contaminated with 37 ppm of As for several polymer : As(V) ratios was also studied.

EXPERIMENTAL PART

Reagents

The monomers 2-(acryloyloxyethyl)trimethyl ammonium chloride, ClAETA, and (vinyl benzyl)trimethylammonium chloride, 99%, (ClVBTA) were used as received (from Aldrich, Milwaukee, USA). Ammonium persulfate (AP, from Aldrich, Milwaukee, USA) was used as the polymerization initiator. A pattern solution of 46 mM of $Na_2HAsO_4 \times 7H_2O$ (Merck, Stuttgart, Germany) was used.

Homopolymer synthesis

Two homopolymers were synthesized by solution radical polymerization. Specifically, 5 g of each monomer and 1 mol % of AP were dissolved in 40 mL of water, and then the reaction mixture was stirred at 70°C over N_2 for 24 h. The products were completely solubilized in water, and subsequently the solutions were freeze-dried. The polymers obtained were dissolved in water, purified using an ultrafiltration membrane, and then fractionated with ultrafiltration membranes with different exclusion molecular mass cutoff, MMCO (10,000; 30,000; 50,000; and 1,00,000 Da) to get different fractions, using the material collected with 10,000 Da to perform all the LPR runs. This membrane's MMCO ensures that the polymer is of a sufficient molecular size and has an adequate time to perform the ultrafiltration runs. For this reason, a polyethersulfone membrane with 10,000 Da was used.

The polymer fraction was characterized by FTIR and ^{1}H-NMR spectroscopy and TG-DSC. The ^{1}H-NMR spectra of monomers and homopolymers were comparatively analyzed. ^{1}H-NMR spectroscopy corroborated that the copolymerization reaction occurred because of the absence of the signals at 5.44 and 5.68 ppm corresponding to the ethylene and vinyl protons of the monomers. The polymerization yield was 97.2% for P(ClAETA) and 98.0% for P(ClVBTA). The polymer P(ClAETA) showed to be highly hydroscopic.

Procedure

Using the washing method, the experiments performed at different mole ratios of polymer : As(V) are summarized in Table I. The mole ratio (20 : 1), 0.2 mmol of the polymer in the range above 10,000 Da was dissolved in twice-distilled water and added to the cell solution together with the solution containing 0.01 mmol of arsenic.

The solutions were brought to 20 mL of total volume and the pH was adjusted by adding 0.1M NaOH. The pH reservoir's washing water was at the same pH of the cell. Filtration runs were performed under a total pressure of 3.5 bar, room temperature, using a ultrafiltration membrane with an exclusion rating of 10,000 g mol^{-1}. The total volume (20 mL) in the cell was kept constant. Fractions of 20 mL were collected by filtration, and the metal ion concentration was analyzed by AAS.

The enrichment method to determine the polymer's maximum retention capacity was performed with drinking water, using 0.5 mM of As(V) solution and 0.2 mmol of P(ClVBTA) at 300 mL of total filtrate volume. One blank experiment without polymer was also performed.

Measurements

Arsenic concentration was measured in the filtrate by atomic absorption spectrometry (AAS) using a Perkin Elmer 3100 spectrometer. The amount of

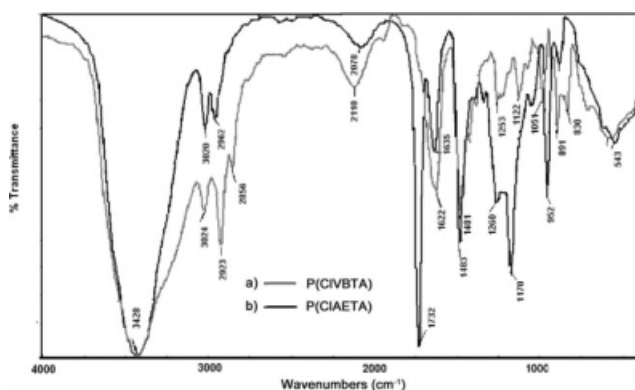**Effect of the Polymer : As(V) Ratio on As(V) Retention for the Two Polymers at pH 8 (volume in cell 20 mL)**

Mol ratio Polymer : As(V)	Mol of polymer	Mol of As(V)	As(V) in feed (ppm)	P(ClVBTA) R (%), pH 8	P(ClAETA) R (%), pH 8
(31 : 1)	7×10^{-4}	2.25×10^{-5}	84.0	70.0	84.0
(20 : 1)	7×10^{-5}	3.45×10^{-6}	13.0	100.0	100.0
(20 : 1)	2×10^{-4}	1.00×10^{-5}	37.5	100.0	100.0
(10 : 1)	7×10^{-5}	6.90×10^{-6}	25.8	88.0	59.0
(6 : 1)	7×10^{-5}	1.12×10^{-5}	42.0	77.0	60.0
(3 : 1)	7×10^{-5}	2.25×10^{-5}	84.0	54.0	14.0

arsenic species retained was determined by its difference with the initial arsenic concentration. pH was controlled by a pH meter (H. Jürgen and Co).

The Fourier transform infrared spectra (FTIR) were recorded with Magna Nicolet 550 and Nexus Nicolet spectrometers. For quantitative analysis, 1 mg of the sample per 100 mg of KBr was employed. The NMR spectra were recorded in D_2O at room temperature with a multinuclear Bruker AC 250 spectrometer 250 MHz. The thermal behavior was studied under N_2 using a thermogravimetric analyzer with a TGA 625 from Polymer Laboratories. The heating rate was $10°C$ min^{-1}. Sample weight: 0.5–3 mg.

RESULTS AND DISCUSSION

The cationic polymers were synthesized by solution radical polymerization. The polymers were characterized by FTIR and ^{1}H-NMR spectroscopy. The FTIR spectra were recorded in the range 400–4000 cm^{-1}. The spectra showed the following main characteristic absorption bands (in cm^{-1}): 1735 (C=O) of ester bond, 1175 (C—O) of ester. P(ClVBTA) shows the distinctive asymmetric stretching and symmetric stretching absorption bands (cm^{-1}), 1641–1408 ν(C=C) aromatic ring. A common absorption band for both structures, placed at 1483–1481, is the bend-

ing band of the quaternary ammonium groups, —$N^+(CH_3)_3$ (see Fig. 1).

^{1}H-NMR spectra of monomers and homopolymers were recorded in D_2O. The polymerization reaction occurred, demonstrated by the absence of the signals at 5.44 and 5.68 ppm corresponding to the protons of the carbon–carbon double bond of the monomer. The solvent's signal appears at 4.7–4.9 ppm. The characteristic signals for each polymer are as follows:

P(ClVBTA): Vinyl protons of chain: δ = 2.0 ppm (2 H[1]). δ = 2.5 ppm (1 H[1]). Protons of side groups: δ = 3. ppm (9 H[1]) for the quaternary ammonium group; δ = 4.35 ppm (2 H[1]); δ = 6.5 ppm (1H[1]) and 7.4 ppm (1 H[1]) aromatic ring (see Fig. 2).

P(ClAETA). Vinyl protons of the main chain: δ = 2.0 ppm (2 H[1]). δ = 2.5 ppm (1 H[1]). Protons of side groups: δ = 3.75 ppm (2 H[1]); δ = 4.5 ppm (2 H[1]); δ = 3.18 ppm (9 H[1]) for the quaternary ammonium group (see Fig. 3).

Figures 4 and 5 clearly indicate a strong weight loss (around 85 %) of the polymer at 267 or 278°C. Thus, the DSC endotherm at these temperatures is not only attributed to polymer melting but also with polymer melting with simultaneous decomposition and subsequent weight loss.


Figure 1 FTIR (KBr) spectra of the homopolymers: (a) P(ClVBTA) and (b) P(ClAETA).
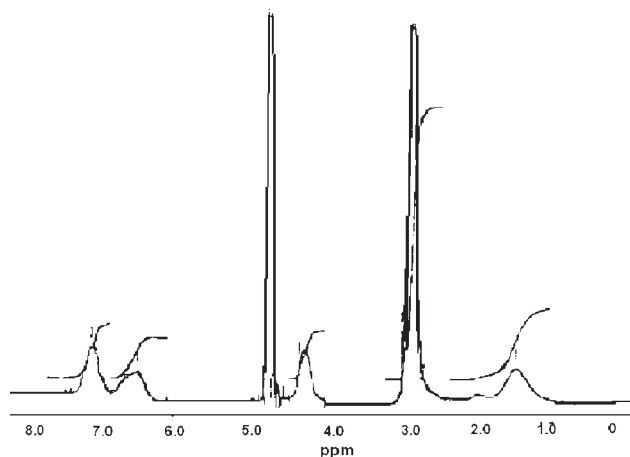
Figure 2 ^{1}H-NMR spectrum (250 MHz, D_2O, room temperature) of P(ClVBTA).
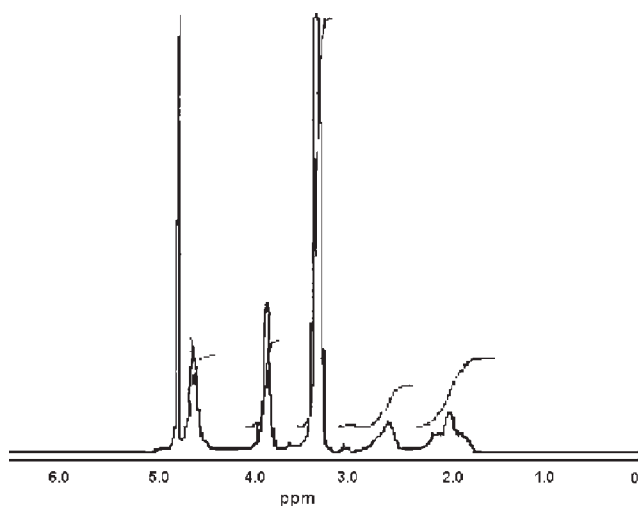
Figure 3 ^{1}H-NMR spectrum (250 MHz, D_2O, room temperature) of P(ClAETA).

The LPR technique allows the separation of the polymer-As(V) complex since membrane's MMCO is higher than As(V)'s molecular weight, and hence there is no possibility for the separation of free arsenic. Therefore, As(V) separation does not depend on the membrane property but reflects the formation of some complex with polymer resulting in As(V) separation. The rate and the extent of As(V) retention depends on the polymer's concentration, and hence the extent of As(V) retention in ultrafiltration.

Previous studies[9,10] for P(ClVBTA) and P(ClAETA) showed, in general, that As(V) species are more efficiently retained at higher pH (8 and 6 than 4), where the divalent $HAsO_4^{-}$ anions predominate and the number of effective active sites for the homopolymers is high. Now, the influence of the polymer's concentration while optimizing the reaction conditions was studied. Different mole ratios of polymer : As(V) (31 : 1), (20 : 1), (10 : 1), (6 : 1), and (3 : 1) were prepared. The polymer's quantity was in the range of 10^{-4}–10^{-5} mol in a total volume cell of
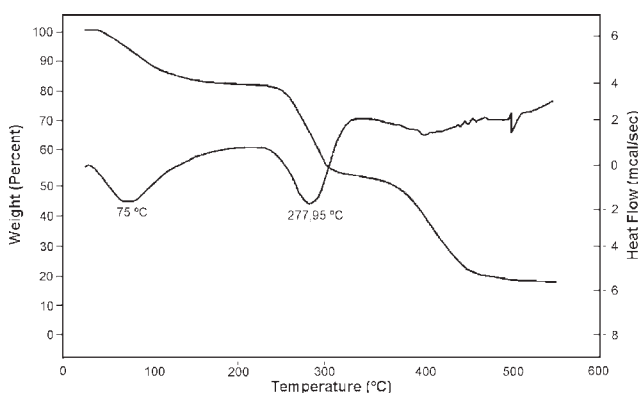

Figure 4 TG-DSC of P(ClVBTA) (heating rate 10°C/min under N_2).
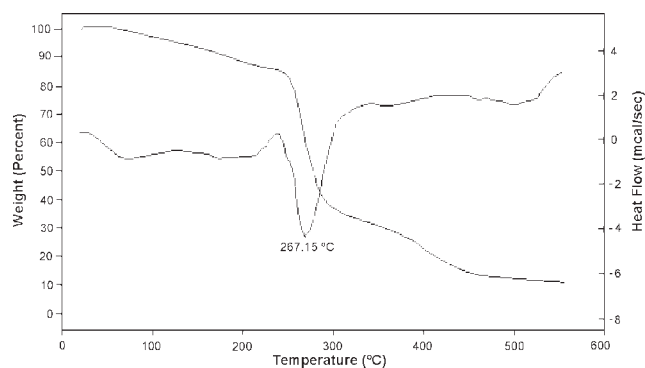
Figure 5 TG-DSC of P(ClAETA) (heating rate 10°C/min under N_2).

20 mL. In general, a constant 7×10^{-5} mol of polymer at pH 8 or 6 was used. The results for P(ClVBTA) and P(ClAETA) by washing method at constant ionic strength at pH 8 are shown in Figures 6 and 7, respectively. These retention profiles show the arsenic retention (R) versus the filtration factor (Z), which is defined as the ratio of the filtrate volume (V_f) to the cell volume (V_0).

Table I shows the retention profile R (%) at a filtration factor, Z = 10. The retention capacity is limited by the polymer concentration if an arsenic concentration in the range 10–84 ppm is used. A typical ratio (20 : 1) was adequate. Contrary to expected results, the highest mol ratio of 31 : 1 produced a lower retention. This result could be due to a large excess of arsenic in the medium (84 ppm) with respect to the polymer mass used. The arsenic rejection did not follow a linear dependence of polymer and arsenic concentration. On the other hand, the effect of the polyelectrolyte's conformational changes cannot be discarded. A polymer excess can perhaps induce changes of correlative positions of
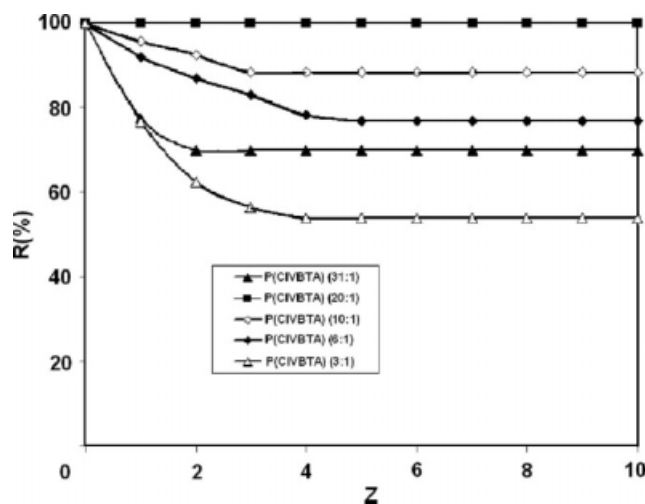
Figure 6 Retention profiles for As(V) at pH 8 using P(ClVBTA). Polymer : As(V) mol ratio: ▲, 31 : 1; ■, 20 : 1; ◆, 10 : 1; ◇, 6 : 1–3 : 1.
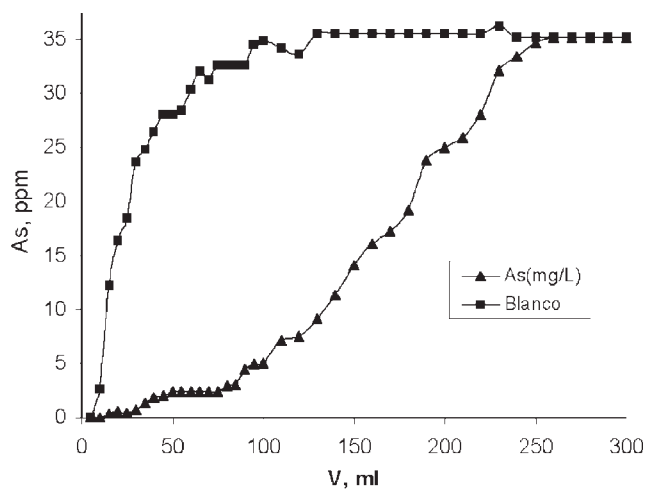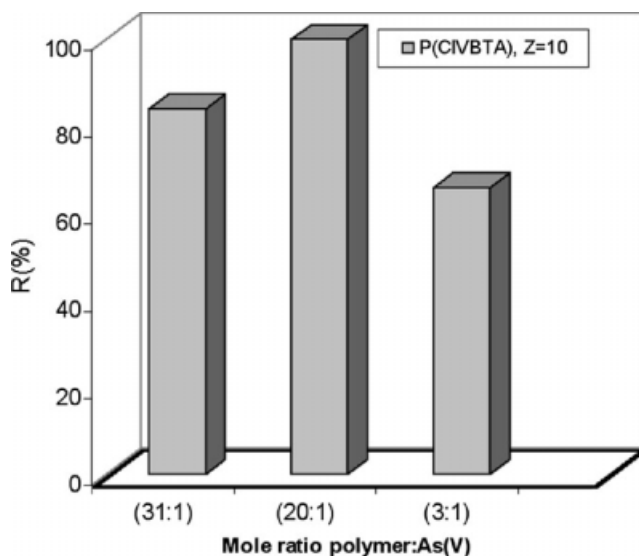
Figure 7 Retention profiles for As(V) at pH 8 using P(ClAETA). Polymer : As(V) mol ratio: ▲, 31 : 1; ■, 20 : 1; ◆, 10 : 1; ◇, 6 : 1–3 : 1.

complementary reactive sites. It may be due to the arrangement of chains that form densely packed coils decreasing electrostatic interactions. In the case of poly(diallyldimethyl ammonium chloride) for a feed arsenic concentration of 100 ppb, it has been found that the arsenic rejection in a mol ratio (50 : 1) was higher for 0.3 mM than that 72.9 mM polyelectrolyte concentration.[12]

It is remarkable that the polycation maintains the high efficiency for As(V) species recovery, even in strongly higher arsenic concentration. The majority of authors have worked at the limit or slightly above of 0.05 or 1 ppm for arsenic species removal from water.[6]

Figure 8 shows the performance of P(ClVBTA) at pH 6 and Z = 10 for the characteristic polymer :

Figure 8 Retention profiles for As(V), using P(ClVBTA) at pH 6, and different polymer-As(V) mol ratios.
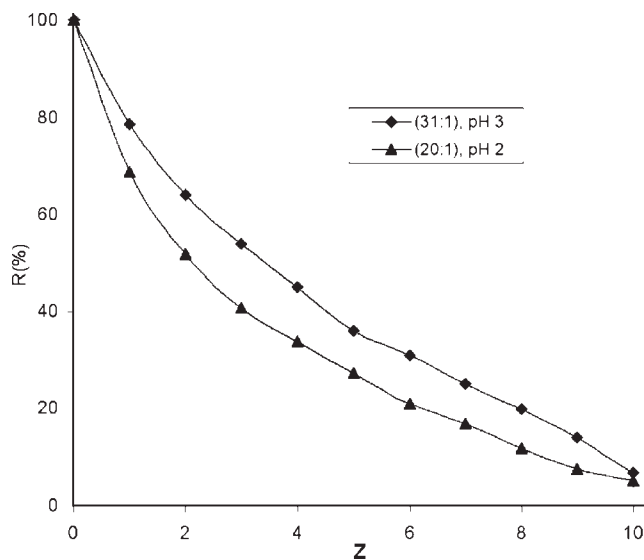
Figure 9 Removal profile of As(V) from P(ClVBTA) at pH 2 and 3, after essays of retention using (31 : 1) and (20 : 1) mole ratio polymer : As(V), pH 8.

As(V) mole ratio. The similarity of the results at basic pH 8 indicates that retention is probably more a function of the arsenate species' thermodynamic equilibrium than the polymer structure's conformational changes in solution.

The exposure time of As(V) in aqueous polymer solution required to reach the (exchange bond) species equilibrium was studied for 5, 15, 30, 60 min, 4 h, and 24 h of contact time prior to the ultrafiltration essays. These times did not include the ultrafiltration time, which was kept constant at 200 min in all cases. P(ClVBTA) in mole ratio (20 : 1) at pH 8 required a shorter contact time (above 15 min) to reach the necessary equilibrium of 0.2 mmol of polymer in contact with 37 ppm of As(V) and to maintain maximum retention. At 5 min, the retention was 93%. Nevertheless, for mole ratio (3 : 1) at pH 8 using 0.07 mmol of polymer, a selectivity of only 26% was reached after 4 h of contact time. This last case's selectivity after 24 h of contact time was of 66%. For P(ClAETA), it is concluded that 1 h of contact is enough to reach the equilibrium retention.

To remove the retained arsenic(V) from the polymer and reuse the polymer, the following experiment was performed: the polymer As(V) solution was washed with water buffered at pH 2 and 3. The ultrafiltration cell was used similarly to the washing method. The assay products with P(ClVBTA) in mole ratio polymer : As(V) (20 : 1) and P(ClVBTA) in mole ratio (31 : 1) at pH 8 were used. From the polymer recovery profile, it is possible to determine that it is near 95%, which is considered very high at Z = 10 (see Fig. 9). It is assumed that the polymers' retention capability is recovered, and that the strongly acidic media conditions did not

TABLE II
Effect of the Presence of Sulfate and Phosphate on the Arsenic Retention of P(ClVBTA), Polymer : As(V) mol Ratio : 20 : 1.0, pH 8

Mol ratio polymer : As(V)	As(V) in the feed (mol/L)	As(V) in P (ClVBTA) (mol/L)	Arsenic permeated (mol/L)	SO_4^{-2} in the feed (mol/L)	HPO_4^{-2} in the feed (mol/L)
(20 : 1)	5×10^{-4}	4.32×10^{-4}	6.80×10^{-5}	5×10^{-4}	–
(20 : 1)	5×10^{-4}	4.00×10^{-4}	1.00×10^{-4}	–	5×10^{-4}
(20 : 1)	5×10^{-4}	4.00×10^{-4}	1.00×10^{-4}	5×10^{-4}	5×10^{-4}

significantly affect the polymer's active sites because an acidic pH of 3 and 2 is used in radical polymer synthesis. In the future, it is necessary to improve polymer activity recovery in the assays through retention and desorption As(V) cycles.

The polycationic exchanger presents the highest arsenate species retention in the absence of other anions. The results of the arsenic retention assays in the presence of divalent anions SO_4^{-2} or HPO_4^{-2} at pH 8 by washing method are summarized in Table II. A mole ratio of As(V) : S or As(V) : P(V) (1 : 1) and mole ratio of polymer : As(V) (20 : 1) were used with 37.5 ppm of arsenic and 2.1 g/L of P(ClVBTA) in the feed. The results showed that the polymer retains nearly 86% of the arsenic. An important difference in anion competition was not found, and this result can be mainly attributed, in this case, to the excess of polymer mass used.

The polycationic system with drinking water contaminated by adding 37 ppm of As(V). was also studied. This form was used to observe if a change in the retention ability in a natural system occurs in the presence of others ions, mainly SO_4^{-2} (120 mg/L). The groundwater composition[13] presents trace amounts of SO_4^{-2}, S^{-2}, F^-, and Cl^- anions. Ultrafiltration by washing method was applied. Several polymer : As(V) mol ratios (20 : 1), (40 : 1), and (60 : 1) were used, buffering the drinking water at pH 8 and NaOH as electrolyte. Table III shows P(ClVBTA)'s arsenic retention properties. Even with the absence of arsenic in the filtrate, the yield was close to 83% for different mol ratios.

This approach in a natural medium (drinking water at pH 7.14) shows that the profile retention decreased to 93%, with a small percentage of arsenic in filtrate. It is concluded that the difference between buffered and unbuffered solutions does not show an influence on retention properties.
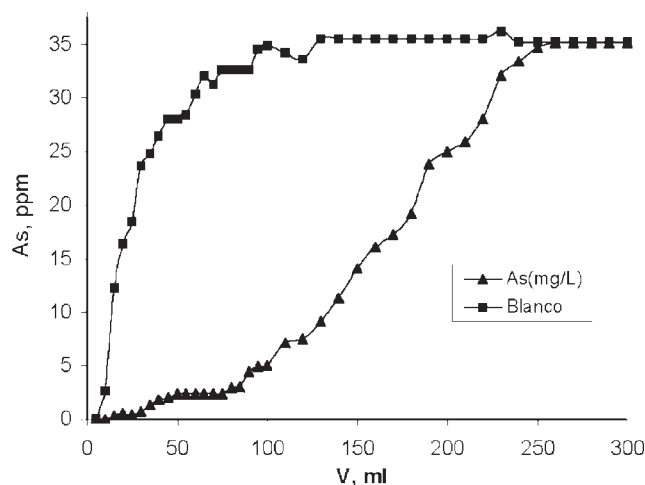
The polymer's maximum retention capacity (C) was evaluated with drinking water at pH 7.14 (see Fig. 10). The result on P(ClVBTA) was 157 mg/g. Assuming a quantitative retention of As(V), the enrichment factor (E) of 8.8 provides a measurement of the polymer's binding capacity.

CONCLUSIONS

The polycations P(ClVBTA) and P(ClAETA) were polymer reagents that effectively retained As(V) from an aqueous solution. Nevertheless, it is necessary to find the operative parameters (pH, reactive concentration, temperature, ionic strength) for optimum performance. In general, P(ClVBTA) and P(ClAETA) more efficiently retained As(V) species at higher pH (8 and 6 rather than 4), where divalent $HAsO_4^-$ anions are the predominant species. In a buffered system, the effect on arsenic retention depended on the mole ratio (10 : 1), (6 : 1), and (3 : 1). An optimum polymer : As(V) mole ratio of (20 : 1) was found, which depended slightly on ionic strength because the addition of sulfate or phosphate anions did not result in an important difference in arsenic retention, ˜86% in P(ClVBTA), which is

TABLE III
Drinking Water Contaminated with As(V): The Effect of Different P(ClVBTA) Concentrations on Retention

Mol ratio Polymer : As(V)	Polymer (g/L)	As(V) feed (mol/L)	As(V) in P(ClVBTA) (mol/L)	Arsenic permeated (mol/L)
(60 : 1)	6	4.938×10^{-4}	4.17×10^{-4}	7.68×10^{-5}
(40 : 1)	4	4.938×10^{-4}	3.96×10^{-4}	9.78×10^{-5}
(20 : 1)	2.1	4.938×10^{-4}	3.56×10^{-4}	1.38×10^{-4}

Figure 10 Maximum retention capacity (MRC) of P(ClVBTA) at pH 7.14, 0.2 mmol of polymer 0.5 mM of As(V).

attributed mainly to the polymer's concentration. Drinking water assays indicated a similar high-retention performance for polymer : As(V) mole ratios of (60 : 1), (40 : 1), and (20 : 1). The saturation and binding capacity of P(ClVBTA) in drinking water was 157 mg/g and $E = 8.8$, respectively.

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