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ORIGINAL PAPER

Removal of arsenate from ionic mixture by anion exchanger water-soluble polymers combined with ultrafiltration membranes

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Abstract This study shows the influence of Cl^-, SO_4^{2-}, NO_3^-, SiO_3^{2-}, Na^+, and Ca^{2+} on arsenate removal by anion exchanger polymers using the liquid-phase polymer-based retention (LPR) technique. The LPR was carried out in the presence of anion exchanger soluble polymers containing quaternary ammonium salts. These polymers were characterized by NMR. Compared with As(V) removal from deionized water, the results showed that in the presence of ionic mixture, the As(V) removal capacity decreased. However, P(ClVBTA) showed As(V) removal ability of 91 % when the ionic mixture was used. Polymers with chloride exchanger groups showed a higher ability to remove arsenate than the polymer that contains methyl sulfate as anion exchanger group. At higher arsenate concentration (47.6 mg L^{-1}), arsenate retention by the water-soluble polymers ranged between 58 and 91 %. This removal capacity increased gradually reaching 100 % retention when the arsenate concentration in the cell was minimum (5.5 mg L^{-1}). The values of maximum retention capacity were 264 mg g^{-1} for P(ClMPTA), 260 mg g^{-1} for P(ClVBTA), and 200 mg g^{-1} for P(ClAPTA) at the total filtrate volume of 300 mL. The charge–discharge process found to be suitable for saturate the polymer with As(V) and then eluting As(V) for regenerating the extracting capacity of polymer.

Keywords Arsenic · Interfering ions · Anion exchanger polymers · Maximum retention capacity

Introduction

It is widely known that arsenic is a toxic element and its complete removal from aqueous environments is still a challenge. This urges the scientific community to

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improve as well as to develop appropriate technologies to remove traces of arsenic from drinking water, wastewaters, and industrial effluents in order to reach acceptable levels.

Arsenic is one of the most toxic elements that can be found and the human population can be exposed to arsenic through food, water, and air. It can also enter food chain causing wide spread distribution throughout the plant and animal kingdoms [1]. The World Health Organization (WHO) [2] established a maximum permissible limit of arsenic in drinking water as 10 $\mu g\ L^{-1}$. In northern Chile, arsenic is the most harmful environmental pollutant in the area. The arsenic is of natural origin but is also released in the environment due to the exploitation of copper [1].

In aqueous environment, the arsenic exists mainly in four oxidation states (+5, +3, 0, −3), being As(III) (arsenite ion) more toxic than As(V) (arsenate ion), but arsenate is more abundant [3]. The coexistence of inorganic anions is controlled by factors such as pH, redox potential, and solubility [4, 5].

The arsenic can be removed from water using different methods like ion-exchange, adsorption with reagents impregnated resins and metal-loaded chelating resins, chemical precipitation–coagulation, membrane processes like reverse osmosis, and complexation among others [6–8].

The newly developed materials for arsenic removal are the anion exchanger soluble polymers that are combined with ultrafiltration membrane to remove arsenates from aqueous solutions [9–16]. This method is known as liquid-phase polymer-based retention (LPR) or polymer-enhanced ultrafiltration (PEUF), and it involves the use of a ultrafiltration membrane that separates the ionic species interacting with the functional groups of water-soluble polymers with high-molecular weights thus preventing them from passing through the membrane [14].

The LPR technique has a great capacity to separate arsenate oxy-anions from solution using the adequate anion exchanger polymer. The interactions in the system are produced mainly by the anion exchange between the counterion of the polymers and the arsenate anions at basic pH, as can be corroborated by the polymers' higher retention capacity at pH 8 where divalent As(V) species are predominant [10, 11]. Previous results indicate that the retention capacity is also limited by the polymer concentration. The optimal polymer:arsenate molar ratio for complete separation is 20:1 [12]. We have demonstrated that this kind of anion exchanger polymers can remove arsenate ions more efficiently than that of arsenite ions directly from aqueous solution in a wide pH range. In order to remove arsenite, we have combined the exhaustive electrooxidation of As(III) to As(V) with LPR technique obtaining the complete arsenic removal even using the same water-soluble polymer like supporting electrolyte and extracting agent [13–15].

In our research group, several arsenic removal studies have been carried out by LPR technique using deionized water in single ion systems. However, environmental arsenic is always accompanied in contaminated water by other ions, so that source water's effects on the adsorbent efficiency must be explored [8].

This study of arsenic removal was performed by LPR technique using water-soluble polymers, containing quaternary ammonium salts and different counterions at pH 8.5, from aqueous solution in the presence of the following interfering ions: Cl^-, SO_4^{2-}, NO_3^-, SiO_3^{2-}, Na^+, and Ca^{2+}.

The competitive effect of interfering ions was analyzed using polymer:arsenate 20:1 mol ratio and the influence of arsenate concentration on retention capacity was also determined in these conditions.

The maximum retention capacity (MRC) was determined by the enrichment method for each polymer and this regeneration was obtained by the charge–discharge process.

Experimental

Preparation of anion exchanger soluble polymers

The different anion exchanger polymers were prepared by free-radical polymerization using the same conditions. Approximately 5 g of each monomer and 1 mol% ammonium persulfate (AP, Aldrich), used as an initiator of polymerization, were dissolved in 40 mL of water under an inert atmosphere. The reaction mixture was kept at 70 °C under N_2 for 24 h.

The following monomers were used for the free-radical polymerization: (ar-vinyl benzyl)trimethylammonium chloride solution (ClVBTA) (99 wt% in water; Aldrich), [2-(acryloyloxy)ethyl] trimethylammonium chloride solution (ClAETA) (80 wt% in water; Aldrich), [2-(acryloyloxy)ethyl] trimethylammonium methyl sulfate solution (SAETA) (80 wt% in water; Aldrich), [3-(methacryloylamino)-propyl]trimethylammonium chloride solution (ClMPTA) (50 wt% in water; Aldrich, St. Louis, MO) and [3-(acryloylamino)-propyl]trimethylammonium chloride solution (ClAPTA) (50 wt% in water; Aldrich, St. Louis, MO).

The products were dissolved in water, purified with ultrafiltration membranes of poly(ethersulfone), and fractionated by ultrafiltration membranes with different molar mass cut-offs (MMCO) range (10000, 30000, 50000, and 100000 Da).

The polymerization yields (mass %) at these conditions are summarized in the Table 1.

The structures of the polymers are shown in the Fig. 1.

Characterization of polymers by ^{1}H-NMR spectroscopy

The NMR spectra were recorded with a multinuclear Bruker AC 250 spectrometer at 250 MHz at room temperature using D_2O as the solvent. The ^{1}H-NMR spectra of

Table 1 Polymerization yield in mass over a fraction above than 10,00,00 g mol^{-1}

Polymer	Amount of initiator (AP)	Amount of monomer	Polymerization yield (mass%)
P(ClVBTA)	54 mg (2.40×10^{-4} mol)	5.05 g (2.40×10^{-2} mol)	90 %
P(ClAPTA)	70 mg (3.20×10^{-4} mol)	5.01 g (3.20×10^{-2} mol)	99 %
P(SAETA)	50 mg (2.32×10^{-4} mol)	5.02 g (2.30×10^{-2} mol)	77 %
P(ClAETA)	60 mg (2.58×10^{-4} mol)	5.00 g (2.50×10^{-2} mol)	95 %

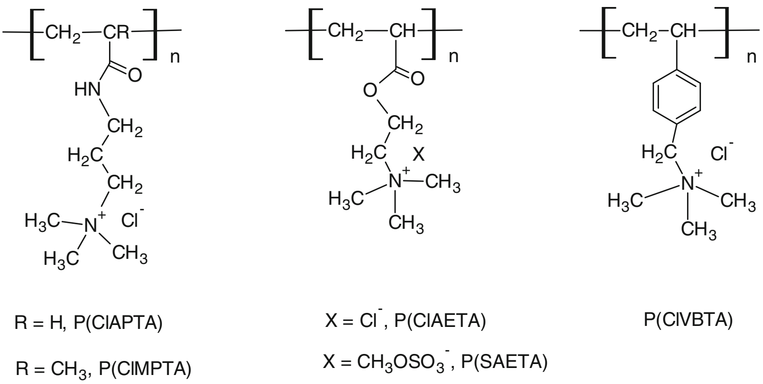

Fig. 1 Structures of the anion exchanger polymers

the monomers and homopolymers were analyzed comparatively, and the absence of the signals at 5.44 and 5.68 ppm, corresponding to protons of the vinylic bond, indicated that the polymerization was done. The ^{1}H-NMR assignments of the homopolymers were as follows.

P(ClVBTA) Protons of the main chain: $\delta = 1.5$ ppm (2H) (a) and $\delta = 2.0$ ppm (1H) (b). Protons of the side groups: $\delta = 4.24$ ppm (2H) (e) and $\delta = 7.03$ ppm (2H) (d) and $\delta = 6.54$ ppm (2H) (c) for the aromatic ring and $\delta = 2.79$ ppm (9H) (f) for the methyl protons of quaternary ammonium group (see Fig. 2).

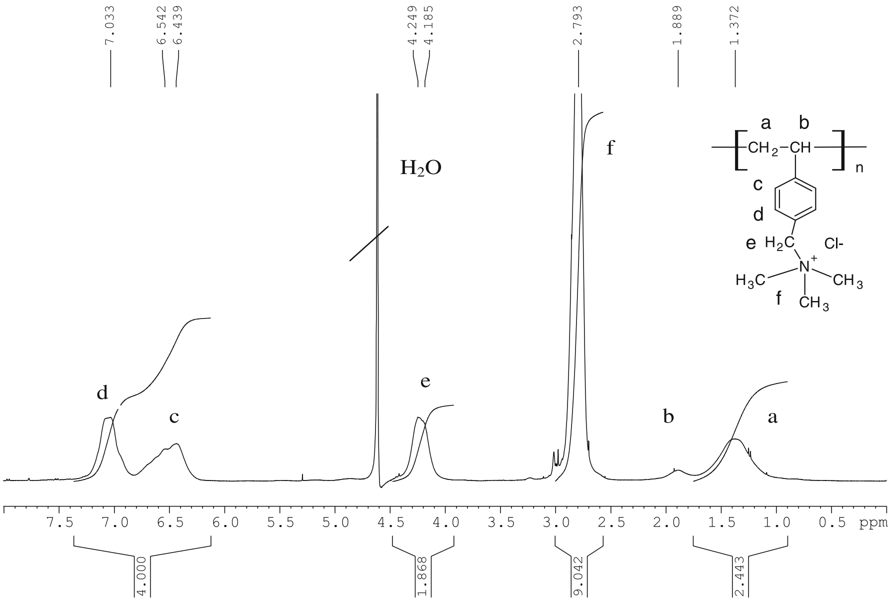

Fig. 2 ^{1}H-NMR (250 MHz, D_2O) at room temperature for P(ClVBTA)

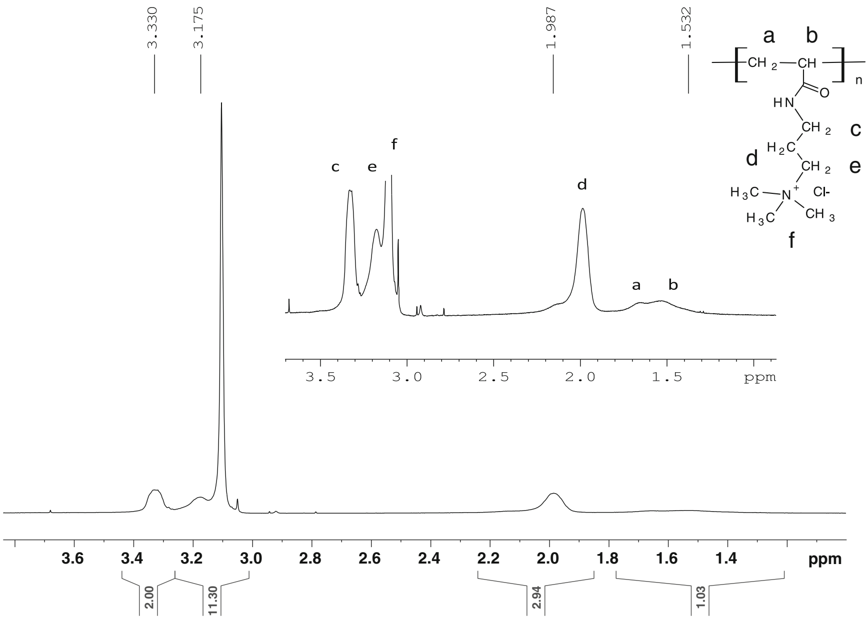

Fig. 3 ^{1}H-NMR (250 MHz, D_2O) at room temperature for P(ClAPTA)

P(ClAPTA) Protons of the main chain: $\delta = 1.5$ ppm (1H) (b), $\delta = 1.7$ ppm (2H) (a), protons of side groups: $\delta = 2$ ppm (2H) (d), $\delta = 3.17$ ppm (2H) (e), $\delta = 3.3$ ppm (2H) (c) and $\delta = 3.1$ ppm (9H) (f) for the quaternary ammonium group (see Fig. 3).

In order to distinguish the CH_2 of this structure, the technique called "distorsionless enhancement by polarization transfer" (DEPT-NMR) was used. This technique is useful to distinguish among signals due to CH_3, CH_2, CH, and quaternary carbons. A DEPT experiment was done in two stages. The first one was to run an ordinary ^{13}C-NMR spectrum to locate the chemical shifts of all the carbons: δ (ppm): 23.5 (–CH_2) (d), 37.0 (–CH_2)(c), 43.1 (–CH), 54.0 (–CH_3), 64.1 (–CH_2) (e) (see Fig. 4a). At the second stage, a DEPT-135 was run using conditions under which CH_3 and CH resonances appear as positive signals, and CH_2 appears as negative signals, which are as a peak below the baseline (see Fig. 4b). The signal corresponding to CH (a) was difficult to determine probably because it is in the main chain.

P(ClAETA) Protons of the main chain: $\delta = 1.8$ ppm (2H) (a) and $\delta = 2.43$ ppm (1H) (b). Protons of the side groups: $\delta = 3.72$ ppm (2H) (c), $\delta = 4.5$ ppm (2H) (d) and $\delta = 3.20$ ppm (9H) (e) for the quaternary ammonium group (see Fig. 5).

P(SAETA) Protons of the main chain: $\delta = 1.8$ ppm (2H) (a) and $\delta = 2.43$ ppm (1H) (b). Protons of the side groups: $\delta = 3.72$ ppm (2H) (c), $\delta = 4.5$ ppm (2H) (d) and $\delta = 3.20$ ppm (9H) (e) for the quaternary ammonium group. The difference between P(ClAETA) and P(SAETA) signals correspond to $\delta = 3.69$ ppm (3H) for the $CH_3OSO_3^-$ group (f) in the case of the last one (see Fig. 6).

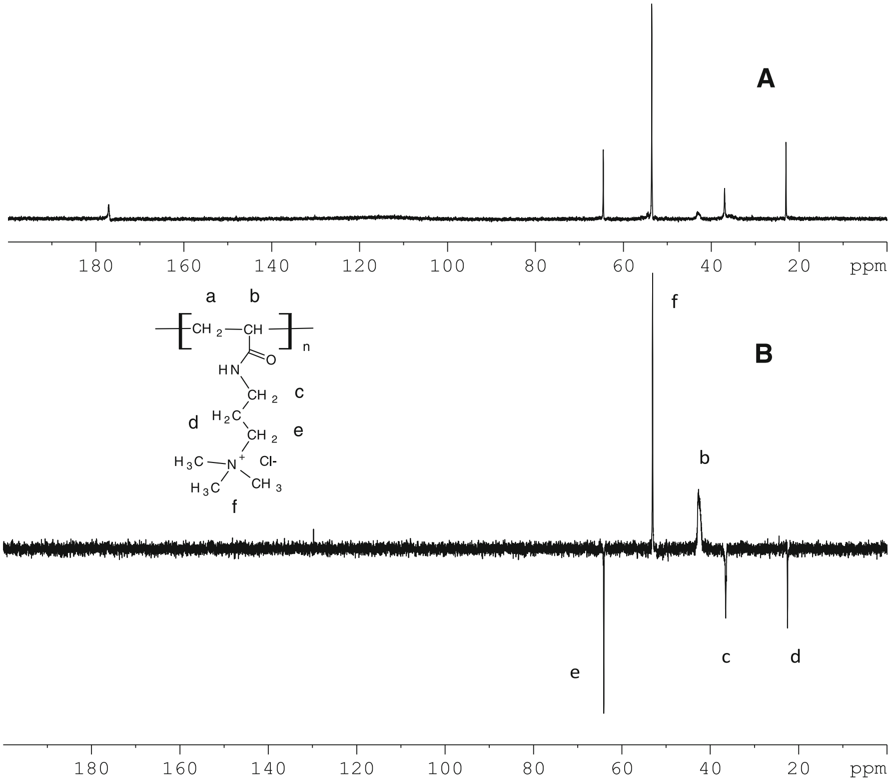

Fig. 4 **a** ^{13}C-NMR spectrum and **b** DEPT-135 experiment of P(ClAPTA)

LPR procedure

When arsenic ions and anion exchanger soluble polymer are placed in contact and diafiltered by ultrafiltration, arsenic ions with high interaction rates with the polymer are retained whereas ions with low interaction rates are eluted through membrane to permeate stream. Consistently, the ions retained by the polymer do not pass through the membrane (see Fig. 7).

The main features of a LPR system (by Amicon) are a filtration cell with a magnetic stirrer containing a membrane filter of poly(ethersulfone) with a known exclusion rating and reservoir and a pressure source, e.g., a nitrogen bottle). The LPR equipment was previously described [14].

In LPR, two kinds of experiments were studied. The first one is a washing method which is an elution method based on the continuous diafiltration by addition of solvent at constant volume. Before carrying out ultrafiltration, the pH of the ionic solution was adjusted to 8.5. The resulting mixture polymer/arsenate in the presence of interfering ions (Cl^-, SO_4^{2-}, NO_3^-, SiO_3^{2-}, Na^+, Ca^{2+}) was stirred for 1 h at room temperature, and then placed in the ultrafiltration cell. The solution was submitted to ultrafiltration and washed with reservoir twice-distilled water at the

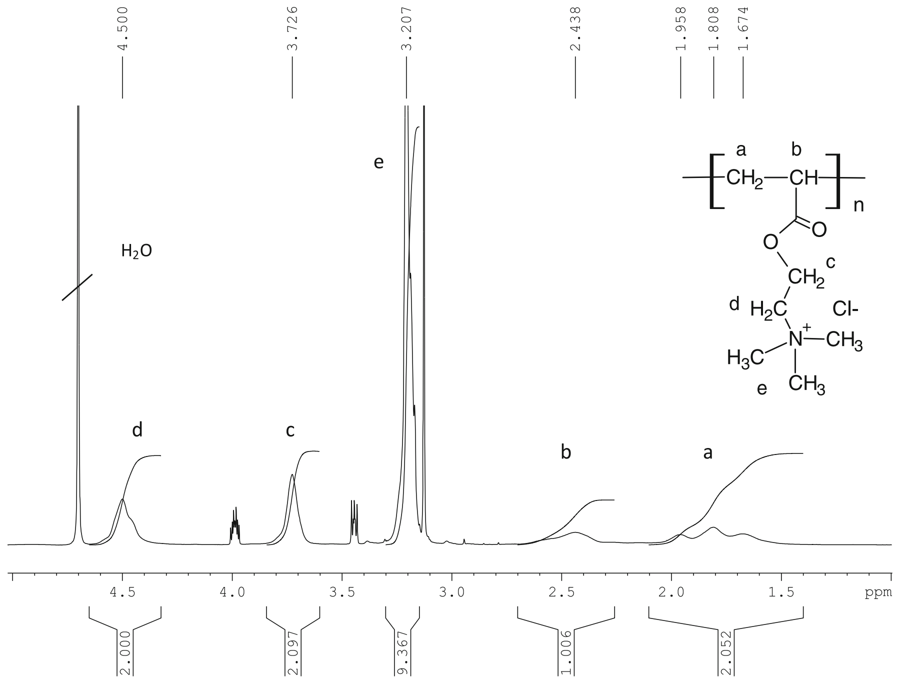

Fig. 5 ^{1}H-NMR (250 MHz, D_2O) at room temperature for P(ClAETA)

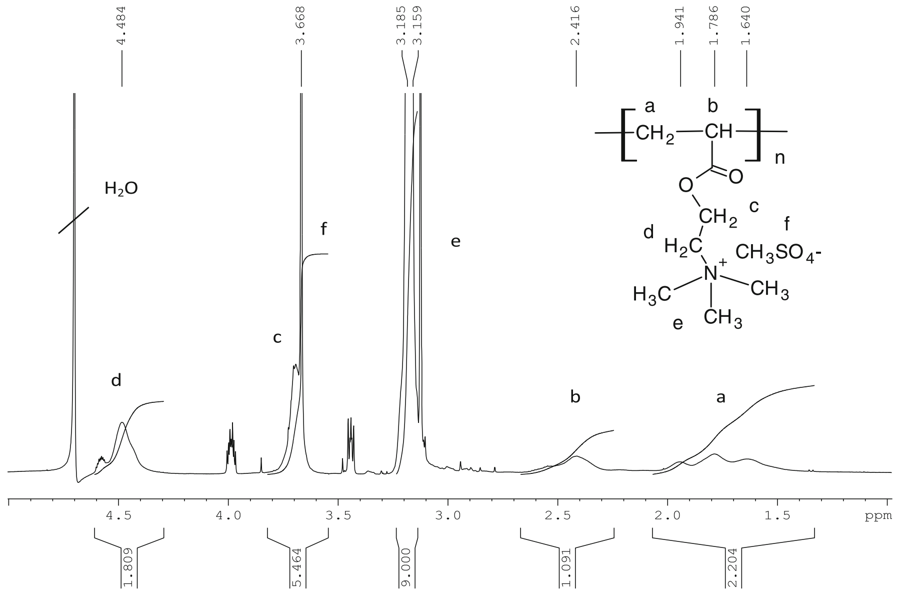

Fig. 6 ^{1}H-NMR (250 MHz, D_2O) at room temperature for P(SAETA)

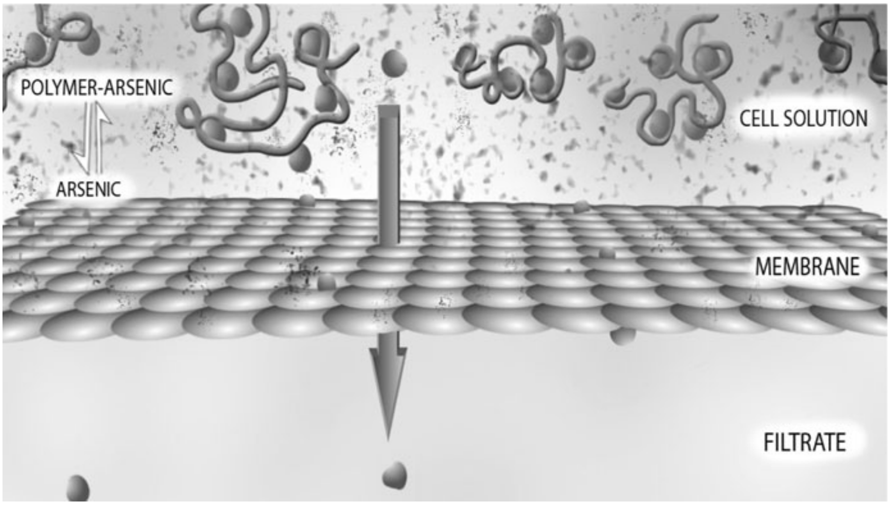

Fig. 7 Principle of LPR technique

same pH. Ultrafiltration was performed under a total pressure of 3.5 bar using an ultrafiltration membrane of poly(ethersulfone) with MMCO of 10,000 Da. Total cell volume was kept constant during the filtration process. Fractions of 20 mL were collected up to a total volume of 200 mL. All experiments were performed with a solution of polymer and As(V) (20:1 polymer:As(V) mole ratio). Results of the As(V) uptake are systematically presented as the percentage of retention *R*(%) versus the filtration factor *Z* (volume of filtrate/volume of the cell).

The second mode is the enrichment method, which is a concentration method based in the continuous diafiltration by addition of solvent with interfering ions and arsenic at constant volume. This method is used to determine the MRC of the water-soluble polymer.

A solution containing the arsenate and interfering ions is passed from the reservoir through the ultrafiltration cell containing a polymer solution. Both cell and reservoir solutions were adjusted to the same values of pH 8.5. The enrichment method was used in aqueous solution, using 4×10^{-3} M of As(V) solution and 8×10^{-4} mol of anion exchanger soluble polymers at 300 mL of total filtrate volume. In the charge–discharge process, the washing method at basic-acid pH was alternately used.

In both cases, washing and enrichment methods, a blank experiment (in the absence of the anion exchanger polymer) is necessary to evaluate the interaction of the membrane with arsenate ions. The membranes were placed in water for approximately 24 h for membrane hydration, and then were previously washed with ethanol according to indication of manufacturer. Washing with twice-distilled water was realized after each filtration step.

Arsenic concentration was measured in the filtrate by atomic absorption spectrometry (AAS) using a Perkin Elmer 3100 spectrometer and Perkin Elmer AAnalyst T200. The quantity of arsenic species retained was calculated as the difference with the initial concentration. The pH was measured by a pH meter (H. Jürgen and Co). A solution of 1,000 mg L^{-1} of $Na_2HAsO_4{\cdot}7H_2O$ (Merck) was used. The pH was adjusted by adding 0.1 M NaOH or HNO_3 (by Merck) and the interfering ions solution was obtained using the following salts: $Ca(NO_3)_2$, $CaCl_2$, Na_2SO_4, and Na_2SiO_3 (by Merck).

Results and discussion

Removal of arsenate ions by the washing method

In order to study the removal of arsenate ions from ionic solution using the ultrafiltration technique, two factors should be defined: (1) retention (*R*), which is the fraction of arsenate ions remaining in the cell and (2) filtering factor.

$$R = [\mathrm{As_{cell}}]/[\mathrm{As_{init}}] \tag{1}$$

where $[\mathrm{As_{cell}}]$ is the absolute amount of arsenate ions that are retained in the cell and $[\mathrm{As_{init}}]$ is the absolute amount of arsenate ions at the start of the experiment. The filtration factor (Z) is the ratio between the total permeate volume (V_f) and the retentate volume (V_o):

$$Z = V_\mathrm{f}/V_\mathrm{o} \tag{2}$$

Depending on the experimental data, a graph (retention profile) in which *R* is represented as a function of *Z*, can be drawn.

Effect of interfering ions on arsenate retention

In order to determine the influence of other interfering anions on arsenate removal, the ionic mixture containing different concentrations of Cl^-, SO_4^{2-}, NO_3^-, SiO_3^{2-}, Na^+, and Ca^{2+}, was used at pH 8.5 (see Table 2). These concentrations were used in order to simulate the natural water of northern Chile.

In this study, we used the washing method at variable ionic strength by adding the polymer, arsenate anions, and the ionic mixture to the ultrafiltration cell at pH 8.5. Twice-distilled water at the same pH was flowed from the reservoir to the cell. In separate experiments for each polymer, we used a polymer:As(V) mole ratio of 20:1 inside of ultrafiltration cell.

First, we proved that some anion exchanger soluble polymers present the highest retention of arsenate species by the LPR technique when no other anions are present in the solution. These polymers were capable of interacting and removing arsenate species preferably at basic pH.

Table 2 Concentration of different interfering ions used in the ionic mixture at pH 8.5

Ions	Cl^-	SO_4^{2-}	NO_3^-	AsO_4^{3-}	SiO_3^{2-}	Na^+	Ca^{2+}
Concentration (mg L^{-1})	90	140	1	1–47.6	25	55	40

On the other hand, arsenate retention is found to decrease in the presence of interfering salts in all the studied cases. The decrease of As(V) removal capacity at $Z = 10$ in the presence of ionic mixture was as follows: P(ClAPTA) decreased the ability of As(V) removal from 94 to 82 % (see Fig. 8a); P(ClAETA) from 96 to 58 % (see Fig. 8b); P(SAETA) from 68 to 14 % (see Fig. 8c). However, P(ClVBTA) decreased its ability of As(V) removal from 96 to 91 % in the presence of ionic mixture (see Fig. 8d).

The effect of added salts on arsenic binding to the polymer can be understood as due to the competition between arsenate and other anions for binding sites on the polymer [16]. The affinity of anions to bind onto the polymer is similar to the behavior observed in the ion-exchange resin containing ammonium groups when removing arsenic by ion-exchange process [17]. This behavior can be explained by the electrical double layer that is compressed around the polymer as the ionic strength increases in the system, thus reducing the polymer's electrical potential. The divalent anions should produce more competition than the monovalent anions because the divalent anions bind more strongly to the polymer's charged sites [18].

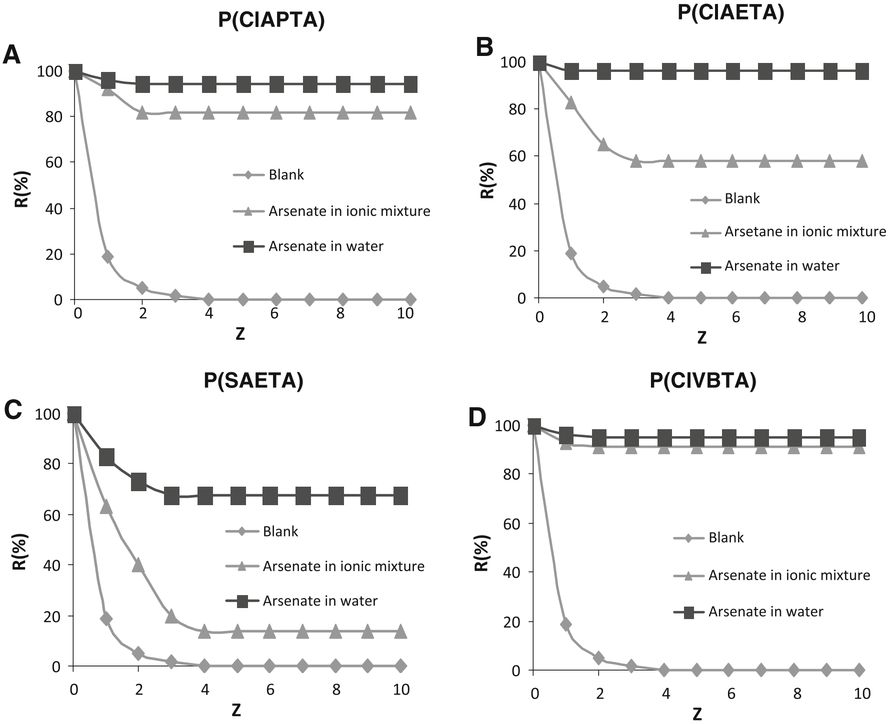

Fig. 8 Retention profile of As(V) using **a** P(ClAPTA), **b** P(ClAETA), **c** P(SAETA), and **d** P(ClVBTA) by the washing method at pH 8.5, with 2×10^{-4} mol absolute polymer and 1.2×10^{-5} mol absolute As(V) ion (47.6 ppm). Curve with *filled squares* shows the arsenic removal from water, curve with *filled triangles* shows the arsenic removal from ionic mixture solution, and curve with *filled circles* shows the blank, it means the experiment without anion exchange polymer

Therefore, the results proved that when the ionic strength increases in the cell, the retention capacity of the polymer decreases due to the competition between ions in solution. However, the arsenic retention at $Z = 10$ decreased slightly for P(ClVBTA) by washing method in the presence of interfering ions. It can be interesting alternative to remove arsenic from real samples.

Influence of polymer counterion on arsenate removal

The anion exchange between arsenate and monovalent chloride polymer counterion was higher than between sulfate counterion and arsenate. This result demonstrates that polymers with chloride exchanger groups, such as P(ClAPTA), P(ClAETA), and P(ClVBTA), show a higher ability to remove arsenate than that the polymer that contains methyl sulfate as anion exchanger group, P(SAETA), at the same conditions (see Fig. 8c). These results can be attributed to the easier release of the chloride anion in comparison with the methyl sulfate anion, which are associated with the quaternary ammonium groups [16]. Monovalent ions, such as methyl sulfates, are strongly retained by the hydrophobic sites of quaternary ammonium groups due to differences in size, solvation, and polarity. Larger, polarized ions have been reported to produce a disruption in the local structure of water, allowing an easy association with the quaternary ammonium group [14]. This behavior was the same in the presence or absence of interfering ions on arsenate removal.

Effect of arsenate concentration on retention capacity

In LPR experiments, concentration of polymer must be defined in a manner that an adequate balance between hydrodynamic properties of filtration and retention properties of polymer can be achieved.

The effect of arsenate concentration on arsenate removal in the presence of interfering ions was analyzed in 20 mL polymer ions solution. All the experiments were carried out at polymer:As(V), 20:1 molar ratio and pH 8.5. The arsenate concentration in the feed ranged from 5.5 to 47.6 mg L^{-1}, and all were in the presence of interfering electrolytes as described in Table 2.

The polymers with chloride counterions (above 10,00,00 Da) showed arsenate retention capacity more than 50 % in all the cases. At higher arsenate concentration (47.6 mg L^{-1}), arsenate retention by polymers was between 58 and 91 %. This removal capacity increased gradually reaching 100 % retention, in the case of P(ClAETA) and P(ClMPTA), when the arsenate concentration in the cell was minimum (5.5 mg L^{-1}) (see Table 3).

The effect of the conformational changes, neighbor groups or interchain distance of polymers and the influence of ionic strength cannot be discarded [19]. The filtration of arsenate ions and their subsequent release from the polymer induces an increase of the net charge on the polymer surface and then in an expansion of the chains in order to increase the total surface, minimizing the electrostatic repulsions at low arsenic concentration. Related with this, at high arsenic concentrations, the decrease on the surface charge density of the polymer induces a decrease in the

Table 3 Effect of As(V) concentration on the removal

Concentration of As(V) (mg L^{-1})	R(%) of P(ClAPTA)	R(%) of P(ClAETA)	R(%) of P(ClMPTA)	R(%) of P(ClVBTA)
47.6	82	58	90	91
15.1	85	65	82	81
10.0	100	81	62	73
5.5	65	100	100	76

Retention percentages of polymers with chloride counterions (above 10,00,00 Da) using polymer:As(V) ratio 20:1 at pH 8.5 and $Z = 10$ in the presence of Cl^-, SO_4^{2-}, NO_3^-, SiO_3^{2-}, Na^+, and Ca^{2+}

strength of the interactions with the arsenic ions, and in consequence, their easier release into the solution from the polymer domain during filtration.

MRC by the enrichment method

MRC of arsenate by the anion exchanger polymer was determined by the enrichment method. In addition to a polymer solution, this method consists the maximum concentration of the arsenate anion that the polymer can bind in order to reach its saturation. The maximum retention (enrichment method) is defined as:

$$\mathrm{MRC} = (M\,V)/Pm \tag{3}$$

where Pm is the amount of polymer (g), M is initial concentration of As(V) (mg L^{-1}), and V is the volume of filtrate (volume set) containing As(V) (mL) that passes through the membrane. The MRC of arsenate was calculated for the total filtrate volume (300 mL). Assuming a quantitative retention of As(V), the enrichment factor (E) is a measurement of the polymer's binding capacity and it is determined as follows:

$$E = P\,(\mathrm{MRC})/M \tag{4}$$

where P is the polymer concentration (g L^{-1}). Since the arsenate ion–polymer interactions are processes in equilibrium, a lower slope in the rate of increase of the arsenate concentration in the filtrate is normally observed. The differences in the slopes can easily be used to calculate the amount of arsenate ions bound to the polymer and free in solution as well as the MRC [14].

The behavior was observed in different anion exchange soluble polymers using the enrichment method in the presence of interfering ions at pH 8.5 using 8×10^{-4} mol of polymer into the ultrafiltration cell and adding a solution of 4×10^{-3} M (300 mg L^{-1}) of As(V) from the reservoir.

In similar polymeric structures, the results of MRC were different for P(ClMPTA) (see Fig. 9) and P(ClAPTA) (see Fig. 10).

The values of MRC were 264 mg g^{-1} for P(ClMPTA) and 200 mg g^{-1} for P(ClAPTA) at the total filtrate volume of 300 mL. This behavior can be attributed to the presence of $-CH_3$ in the main chain of the P(ClMPTA) instead of –H in P(ClAPTA).

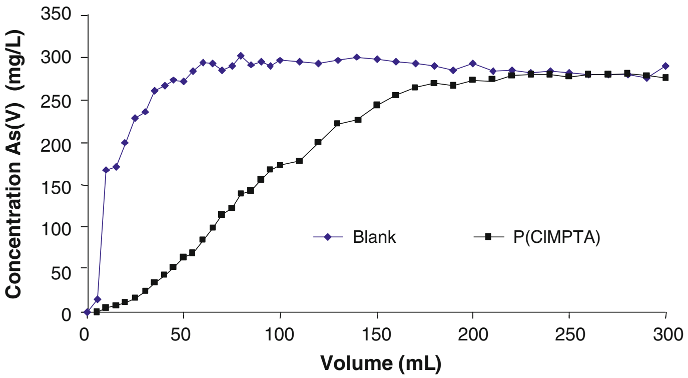

Fig. 9 MRC of arsenate using P(ClMPTA) as a extracting agent at pH 8.5. Mole ratio of 8 × 10^{-4} mol of polymer and 4 × 10^{-3} M of As(V).The blank is the experiment without polymer

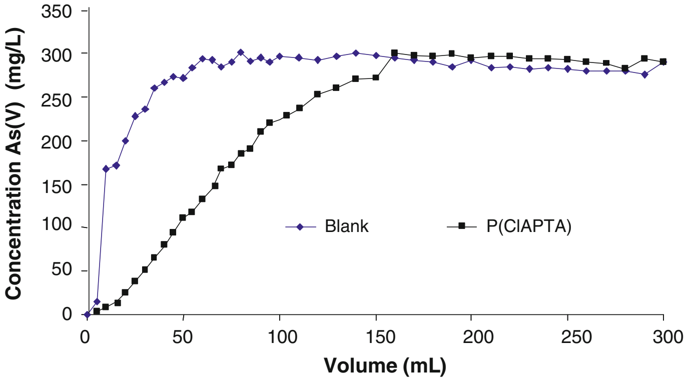

Fig. 10 MRC of arsenate using P(ClAPTA) as a extracting agent at pH 8.5. Mole ratio of 8 × 10^{-4} mol of polymer and 4 × 10^{-3} M of As(V).The blank is the experiment without polymer

On the other hand, P(ClVBTA) showed a high removal capacity through the enrichment method (see Fig. 11), being the MRC 260 mg g^{-1}.

Assuming quantitative retention of As(V) from ionic mixture, the enrichment factor was analyzed, being $E = 7$ for P(ClMPTA), $E = 6.9$ for P(ClVBTA), and $E = 5.3$ for P(ClAPTA). The type of polymer structure was an important factor in arsenate retention from ionic mixture.

Regeneration of polymer: the charge–discharge process

Once the polymer becomes exhausted (charge), the arsenic must be recovered and the polymer regenerated. A successful desorption process (discharge) must restore the polymer close to its initial properties for effective reuse [8]. We named this process as charge–discharge.

In the charge–discharge process, the enrichment method was alternately used with washing method by changing the pH from basic to acid in the reservoir. This

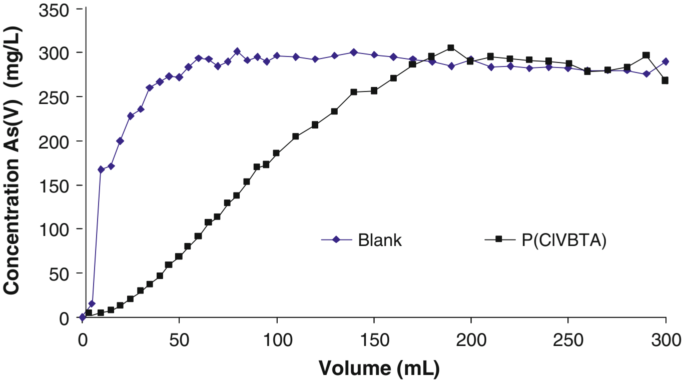

Fig. 11 MRC of arsenate using P(ClVBTA) as a extracting agent at pH 8.5. Mole ratio of 8 × 10^{-4} mol of polymer and 4 × 10^{-3} M of As(V).The blank is the experiment without polymer

process was repeated three times for each polymer in order to determine the capacity of arsenate delivery and to regenerate the extracting ability of the anion exchanger soluble polymers. Figure 12 shows the charge–discharge behavior for some polymers containing chloride counterions.

The first step was the charge (C1) of the polymers with As(V) by enrichment method at pH 8.5. This first charge of As(V) was done in order to reach 100 % of retention at the optimum conditions for all the polymers. The charge was performed until 300 mL in the presence of interfering ions into the ultrafiltration cell and reservoir at constant volume (20 mL).

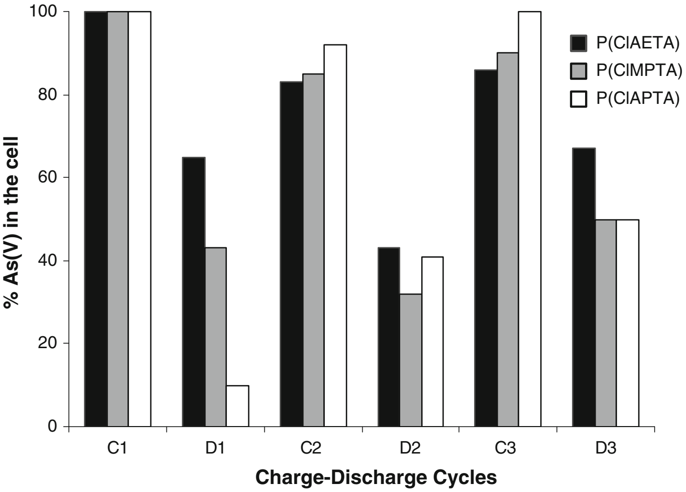

Fig. 12 Charge–discharge process of arsenate ions by P(ClAETA), P(ClMPTA), and P(ClAPTA) using basic-acid pH solution from the reservoir. (*C1*) first charge of As(V) at pH 8.5. (*D1*) first As(V) discharge from polymers at pH 3. (*C2*) second charge of As(V) at pH 8.5 (*D2*) second discharge at pH 3. (*C3*) third charge of As(V) at pH 8.5 (*D3*) third discharge at pH 3

After the first charge (C1), the discharge (D1) was performed from the polymer:As(V) solution. This solution was washed into ultrafiltration cell with reservoir water buffered at pH 3, in a similar way to the washing method using 1×10^{-1} HNO_3. The polymer activity can be recovered in the media's strongly acid conditions and that this did not significantly affect the polymer's active sites because acid pH was used in the radical polymerization.

The first discharge (D1) of arsenate was more effective using P(ClAPTA) than P(ClMPTA) or P(ClAETA). The elution capacity of P(ClAPTA) was 90 % of As(V) previously retained. In the case of P(ClAETA) and P(ClMPTA), the elution of As(V) from polymer to filtrate was lower around 35 and 57 %, respectively.

The second charge (C2) at pH 8.5 did not reach the polymers' MRC when compared with the first charge process (C1). All the polymers lost slightly the capacity to remove arsenate. This result was probably due to the presence of more species in the solution when the pH was adjusted from basic to acid in the discharge process (D1) and from acid to basic in the second charge process (C2). However, P(ClAPTA) reached 92 % of As(V) retention in the second charge (C2).

The second discharge (D2) at pH 3 showed not the same behavior than first discharge (D1), releasing lower amount of arsenate ions to the filtrate in the case of P(ClAPTA) (59 %). However, in this elution, P(ClAETA) and P(ClMPTA) showed better elution capacity compared with the first discharge (D1), releasing 57 and 68 %, respectively.

The third charge (C3) at pH 8.5 was better for all polymers, compared with the second one (C2). The P(ClAPTA) reached again 100 % of As(V) retention, even in the presence of interfering ions. The P(ClAETA) and P(ClMPTA) showed arsenate retention of 86 and 90 %, respectively. In this step, the regeneration of anion exchanger water-soluble polymer achieved the highest value.

Finally, third discharge (D3) of As(V) from the polymer at pH 3 was 33 % for P(ClAETA), 50 % for P(ClAPTA) and P(ClMPTA).

Conclusions

In order to determine the influence of other interfering anions on arsenate removal by LPR technique, the ionic mixture containing Cl^-, SO_4^{2-}, NO_3^-, SiO_3^{2-}, Na^+, and Ca^{2+} was used at pH 8.5. Arsenate retention is found to decrease in the presence of interfering salts in all the studied cases. However, P(ClVBTA) decreased its ability of As(V) removal from 96 to 91 % in the presence of ionic mixture.

Polymers with chloride exchanger groups, such as P(ClAPTA), P(ClAETA), and P(ClVBTA), show a higher ability to remove arsenate than the polymer that contains methyl sulfate as anion exchanger group, P(SAETA), at the same conditions. This behavior was the same in the presence or absence of interfering ions on arsenate removal.

At higher arsenate concentration (47.6 mg L^{-1}), arsenate retention by polymers was between 58 and 91 %. This removal capacity increased gradually reaching 100 % retention, in the case of P(ClAETA) and P(ClMPTA), when the arsenate concentration in the cell was minimum (5.5 mg L^{-1}).

The values of MRC were 264 mg g^{-1} for P(ClMPTA), 260 mg g^{-1} for P(ClVBTA), and 200 mg g^{-1} for P(ClAPTA), at the total filtrate volume of 300 mL. The enrichment factor was $E = 7$ for P(ClMPTA), $E = 6.9$ for P(ClVBTA), and $E = 5.3$ for P(ClAPTA).

The charge -discharge process found to be suitable for saturate the polymer with As(V) and then eluting As(V) for regenerating the extracting capacity of polymer. It can be interesting alternative to remove arsenic from real samples.

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