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Water-Soluble Polyelectrolytes with Ability to Remove Arsenic

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Summary: Arsenic species can be removed from aqueous solutions using the liquid-phase polymer-based retention, LPR, technique. The LPR technique removes ionic species by functional groups of water-soluble polyelectrolytes (WSP) and then using a ultrafiltration membrane that does not let them pass through the membrane, thus separating them from the solution. The ability of WSP with groups $(R)_4N^+X^-$ to remove arsenate ions using LPR was studied. The interaction and arsenate anion retention capacity depended on: pH, the quaternary ammonium group's counter ion, and the ratio polymer: As(V), using different concentrations of As(V). Water-soluble polychelates were also used for one-step retention of As(III) in solution. The complex of poly(acrylic acid)-Sn, 10 and 20 wt-% of metal gave a high retention of As(III) species at pH 8, although the molar ratio polychelate: As(III) was 400:1. The enrichment method was used to determine the maximum retention capacity (C) for arsenate anions in aqueous solutions at pH 8. In similar conditions, the values of C were 142 mg g^{-1} for P(ClAETA) and 75 mg g^{-1} for P(SAETA). The combined treatment of arsenic aqueous solutions by electrocatalytic oxidation (EO) to convert the species of As(III) to As(V) with the LPR technique quantitatively removed arsenic.

Keywords: membranes; metal-polymer complexes; water-soluble polymers

Introduction

Arsenic is toxic to all living organisms, thus creating potentially serious environmental concerns. The tremendous environmental impact of these highly toxic contaminating agents urges the scientific community to improve the methods for both the determination of arsenic in water and food and the development of appropriate technologies to remove traces of arsenic from drinking water, wastewaters and industrial effluents, to reach acceptable levels.

The main arsenic species present in natural waters are arsenate (oxidation state V) and arsenite ions (oxidation state III) related to the arsenic acid (H_3AsO_4) and arsenous acid (H_3AsO_3) respectively. The forms, concentrations, and relative proportions of As(V) and As(III) in water vary significantly depending of changes of pH and oxidation potential.

The arsenic extraction efficiency strongly depends on the ability to convert As(III) species into more easily extractable As(V) forms, which is the first step to an efficient extraction process.[1] The main obstacle to this conversion lies in the high irreversibility of the electrochemical oxidation of As(III) into As(V) at bare electrodes. This problem could be solved by a catalytic system that can promote the

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oxidation of As(III) into As(V) in the solvent's stability domain, which is thermodynamically possible. The oxidation of As(III) could be quantitatively performed, using catalysts or electrode materials possessing appropriate catalytic properties, resulting in the successful treatment of polluted water.

Many polymeric materials play a key role in different removal systems for contaminating species. Water-insoluble polymers are widely investigated and applied to recover metals from aqueous solutions.[2–5] There are various natural and synthetic products that show ion exchange properties. Organic resins are the most used as ion exchangers due to their high chemical and mechanical stability and high ion exchange capacity. These resins are widely used to purify demineralized water and are also applied in chemical synthesis, biomedicine, pharmaceutics, food processing, hydrometallurgy, industry and agriculture.[6–8] These polyelectrolytes have importance in the biological field and in polycomplexes formation used in bioseparation, biocides, and materials for medical use.[9–12]

Among the latest materials developed for arsenic removal are water-soluble cationic polyelectrolytes, which are combined with a filtration membrane to remove arsenate from aqueous solutions. With a suitable choice of monomers, it is possible to provide the polymer with certain characteristics, such as water solubility, binding ability, and selectivity.[13,14] The most studied ligands in the case of polyelectrolyte are amines, ammonium, carboxylic acids, sulfonic acids, amides, alcohols, amino acids, etc..[15–18] For polyelectrolytes with ammonium groups, the interaction is between the nitrogen of the ammonium group and the oxygen anion arsenate, forming a dipole according to Figure 1.

A large number of soluble and hydrophilic polymers, which are functionalized and provide high capacity separation of ions in solution through a membrane filter, have been identified and characterized. The liquid-phase polymer-based retention (LPR) method[14,19–21] involves the interaction of ionic species with the functional groups of high molecular weight polymers that are soluble in water followed by the use of a ultrafiltration membrane that subsequently separate them.

According to that, polyelectrolytes containing ammonium groups have been synthesized and assayed to remove arsenate ions by LPR technique.

Experimental Part

Synthesis and Characterization of Polyelectrolytes

The polyelectrolytes were synthesized by radical polymerization using ammonium persulfate (1 mol-%) as initiator. The polymers were characterized by FT-IR and ^{1}H-NMR spectroscopy which corroborates that the polymerization reaction occurred.

Polymers with quaternary ammonium salts with counter ions groups as methyl sulphate, chloride, bromide and hydroxide (see Fig. 2) were studied to remove arsenate ions.

Removal of Arsenate by LPR Technique

The arsenic species removal capacity of polymers based in ammonium salts has been studied in solution by the LPR technique, (see Figure 3).[19,22–28] This method is performed in homogeneous media and largely avoids mass transfer or

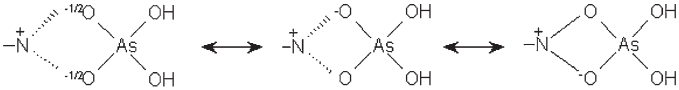
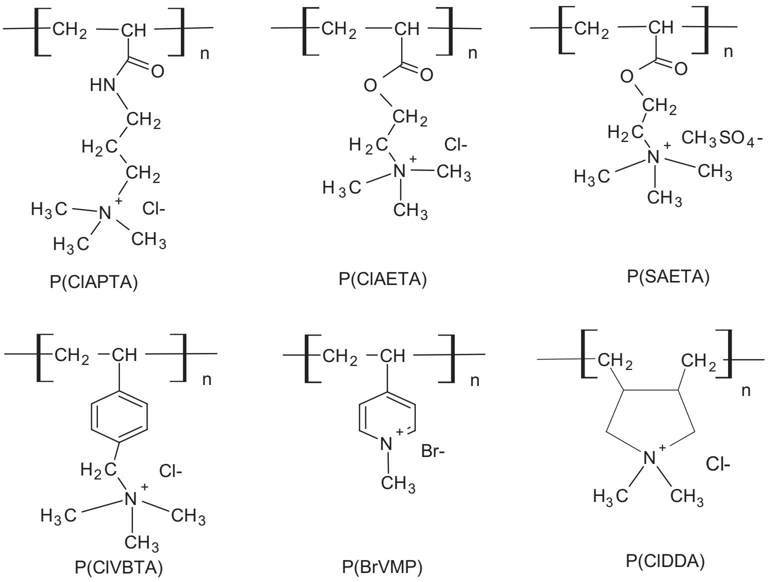


Figure 1.
Electrostatic interaction of quaternary ammonium group of cationic polyelectrolyte with oxy-anion arsenate.[19]



P(ClAPTA) P(ClAETA) P(SAETA)

P(ClVBTA) P(BrVMP) P(ClDDA)

Figure 2.
Structures of WSPs: poly[3-(acryloylamine) propyl] trimethyl ammonium chloride, P(ClAPTA), poly[2-(acryloyloxy) ethyl] trimethylammonium chloride, P(ClAETA), poly[2-(acryloyloxy) ethyl] trimethylammonium methyl sufate, P(SAETA), poly(ar-vinyl benzyl) trimethylammonium chloride, P(ClVBTA), poly(4-vinyl-1-methyl-pyridinium)bromide, P(BrVMP), and poly(diallyl dimethyl ammonium) chloride, P(ClDDA).

diffusion phenomena that occur in heterogeneous methods. In LPR experiments, fractions of polymer with high molecular weight (100,000 Da) are used to interact with anions. Membranes of poly(ether sulfone) are used because they have an exclusion limit of 10,000 Da, which is below that of the polymer. A solution of polymer/arsenate is placed in the cell and then washed with distilled water at constant volume and defined pH.

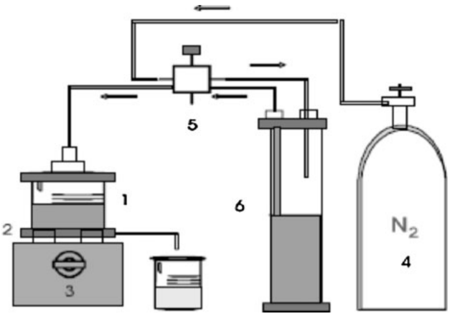


Figure 3.
(1) Filtration cell with polymeric and/or metal ion solution; (2) membrane filtrate; (3) magnetic stirrer; (4) pressure trap; (5) selector; (6) reservoir with water.[14]

In order to systematize the study of polymer interactions with ions in solution using the ultrafiltration technique, two quantities were defined: 1) retention and 2) filtration factor. Retention (Rz) is the fraction of remaining ions in the cell:

$$\mathrm{Rz} = \mathrm{Mz}^{\mathrm{c}}/\mathrm{Mz}^{\mathrm{init}} \tag{1}$$

Where Mz^{c} is the absolute amount of ions that are inside the cell and $\mathrm{Mz}^{\mathrm{init}}$ is the absolute amount of ions to be removed at the start of the experiment. The filtration factor (Z) is the ratio between the total volume of filtrate and the volume of the solution inside the cell:

$$\mathrm{Z} = \mathrm{V_f}/\mathrm{V_o} \tag{2}$$

Using the experimental data, we can then draw a graph (retention profile) in which Rz is represented as a function of Z.

Results and Discussion

Application of LPR Technique to Arsenic Removal

The Effect of pH on the Retention of Arsenate
It is known that the inorganic species As(V) coexists in an aqueous medium according following equilibrium constants:[23]

$$H_3AsO_4 \leftrightharpoons H^+ + H_2AsO_4^- \quad (pKa_1 = 2.22) \tag{3}$$

$$H_2AsO_4^- \leftrightharpoons H^+ + HAsO_4^{-2} \quad (pKa_2 = 6.98) \tag{4}$$

$$HAsO_4^= \leftrightharpoons H^+ + AsO_4^{-3} \quad (pKa_3 = 11.53) \tag{5}$$

The effect of pH on arsenate retention has been studied. The removal of As(V) in the form of mono and divalent oxy-anions was determined using the LPR with different cationic polyelectrolytes through the washing method in a range from acidic to basic pH.

The results were expressed in the retention profile (see Fig. 4), which shows the retention rate, R, versus filtration factor Z of different water-soluble cationic polyelectrolytes at different pH. In general, the As(V) is more easily retained at pH between 6 and 9 that at a lower pH.

At pH 3, monovalent anionic species ($H_2AsO_4^-$) are in equilibrium with the coupled salt. It is assumed that the polarity of the functional group should be a parameter to control the selectivity of ion exchange. At pH 6, the oxy-anionic monovalent ($H_2AsO_4^-$) and divalent ($HAsO_4^{2-}$) species exist in equilibrium. The polymer's interaction capacity is due to the presence of a positively charged quaternary ammonium group. These interactions are produced through the ion exchange between the counter ion chloride of quaternary ammonium salt and the arsenate anions. This explanation can be corroborated by the higher retention capacity of the polymers at basic pH, predominantly divalent species. In this study, we used the washing method with polymer: As(V) 20:1 mole ratio. The polymers removed between 80–100% of ion arsenate at pH between 6 and 9, where arsenate is oxy-anionic divalent species.

Other assays with copolymer poly[(3-methacryloylamine) propyl]trimethyl ammonium chloride-*co*-acrylic acid, P(ClMPTA-*co*-AA) were performed at different mole ratios (1:1, 1:2 and 2:1), differing in its ability to remove arsenate.[19]

Studies of the concerted action of water-soluble copolymers that have anionic and cationic ion-exchange sites to retain As(V) from an aqueous medium are presented. These P(ClMPTA-*co*-AA) copolymers were synthesized at feed mole ratios of cation: anion monomer units of 1:1, 1:2, and 2:1. The action of the copolymer versus pH and its arsenic retention capacity are shown in Figure 5a. At feed mole ratio of 1:1, the copolymer loss its ability to bind anions independently on the pH. This result can be explained by an interaction of the COO^- group of the P(AA) with the -$N^+(R_3)$ groups of P(ClMPTA) by charge transfer that should have blocked both functional groups.

The crosslinking by both hydrogen and covalent bonds between polycations and polyanions inhibited the copolymers' function of anion retention, independently of whether the mole ratio was 1:2 or 2:1. It has been said that monomer units form ''complexes'' taking this form because arsenate retention is negligible. At pH 6, when most of the carboxylic acid groups of P(AA) were carboxylate anions groups and therefore able to participate in the formation of complexes, such conditions could not be totally satisfied. This result suggests that some of the additional active sites were dissociated by the extraction of protons from the aqueous solution without being incorporated into the domain of the polymer chains. Therefore, a great part of quaternary ammonium groups were free and available to bind with the arsenate of the solution when the mole ratio of the copolymer composition was not equimolar. This effect was higher when the ratio of polycations to polyanions was

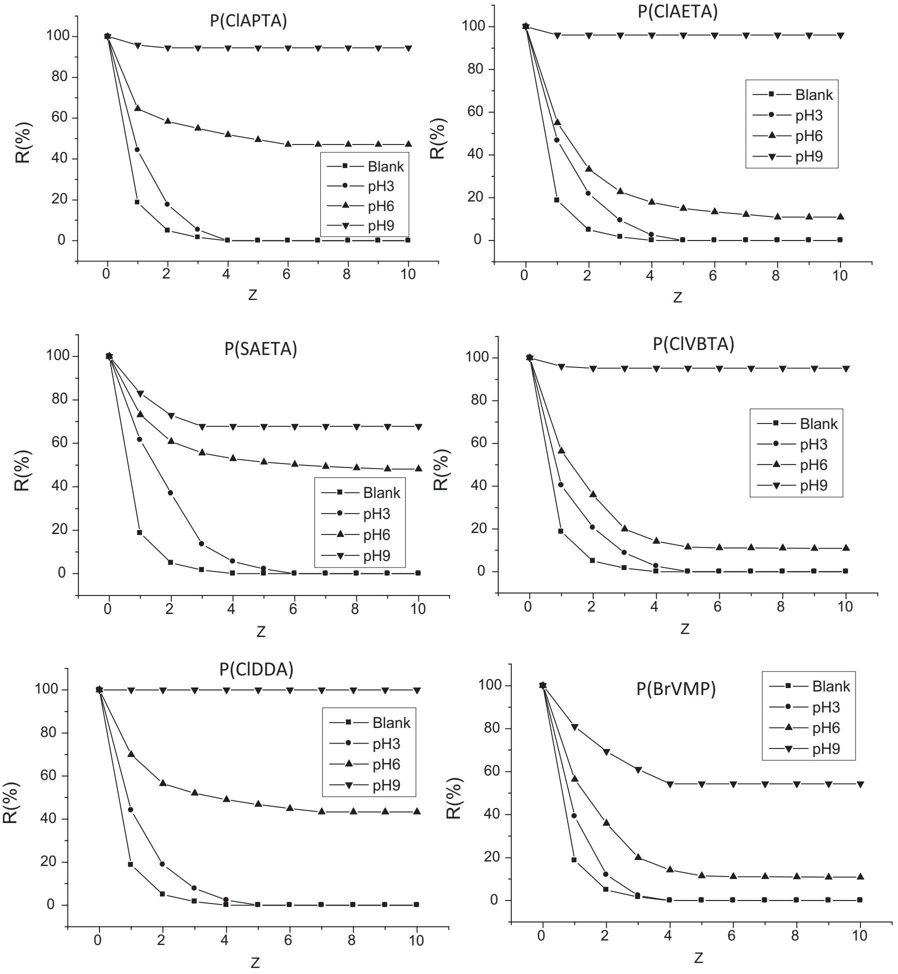


Figure 4.
Retention profile of As(V) using water-soluble polylectrolytes at different pH, with 0.2 mmol polymer to 0.01mmol As(V) ion.

higher than 1, when most of the $–N^+(CH_3)_3$ were free to interact with arsenate anions, increasing the retention ability as shown in Figure 5.

At pH 8, the arsenate ion retention increased to 30% at $Z = 10$ for both copolymers without an equimolar ratio. It is known that increasing the ionic strength (> pH) produced a reduction in electrostatic interaction of the polymeric complexes because of the screening effect of microsalts or due to the accelerating dissociation of weak polyelectrolytes. This effect could improve the ability of the quaternary ammonium group in the copolymer.

Influence of Anion Exchanger Group of Polymer on Arsenate Retention

Poly[2-(acryloyloxy)ethyl]trimethylammonium chloride P(ClAETA) and poly[2-(acryloyloxy)ethyl]trimethylammonium methyl sulfate P(SAETA) have similar structures, except for the exchanger group chloride (Cl^-) and methyl sulphate ($OSO_3CH_3^-$), respectively. All assays were performed using the washing method and the polymer: arsenate, 20:1 mole ratio. Both

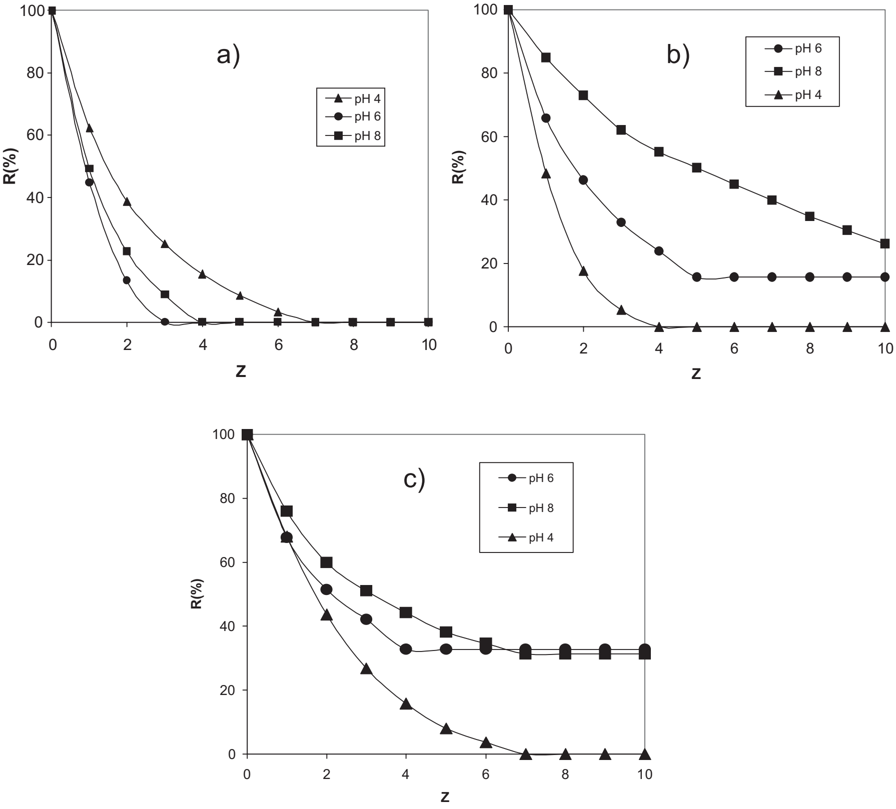


Figure 5.
Retention profile of As(V) for poly[(3-methacryloylamine) propyl]trimethylammonium chloride–*co*–acrylic acid] [P(ClMPTA-*co*-AA] at a) 1: 1, b) 1: 2 and c) 2: 1 ratio with 0.2 mmol polymer and 0.01 mmol As(V) ion.[20]

polymers studied were capable of interacting and removing arsenate species at pH 8 (see Fig. 6). It is notable that polyelectrolytes with chloride exchanger groups, such as P(ClAETA) showed a greater ability to remove arsenate in comparison with P(SAETA), which contains methyl sulphate as anion exchanger group. Polymers with chloride anion exchanger groups have a high capacity to remove arsenate's oxy-anions (100%) at basic pH.

These results can be attributed to the easy release of the chloride anion in comparison with methyl sulfates, which are associated with the quaternary ammonium groups. Monovalent ions, such as methyl sulfate are strongly retained by hydrophobic sites of quaternary ammonium groups due to the difference in size, solubility and polarity. Larger and polarized ions produce a disruption in the local water structure, favoring an easy association with the quaternary ammonium group. Specifically, monovalent ions will be polarized and retained better in comparison with chloride due to the high hydrophobicity of the anion exchanger site.

The hydrophobic nature of the monovalent anion ($OSO_3CH_3^-$), which contains a methyl group, may explain this arsenate removal efficiency as due to the difficulty of exchanging this large group.[25]

Effect of Polymer: As(V) Mole Ratio on Arsenate Retention

The removal was optimized by changing the ratio (in mole) polymer: arsenate. Using the washing method with the polymers P(ClAETA) and P(ClVBTA), we studied the influence of polymer concentration

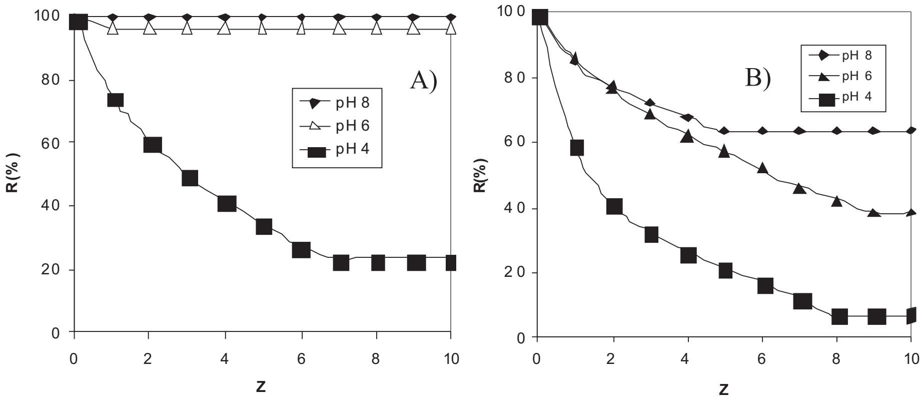


Figure 6.
Retention profile of As(V) by (A) P(ClAETA) and (B) P(SAETA) at pH 8, using 30 mg L^{-1} of As(V) and mole ratio of (20:1) polymer: As(V) ($1{,}6 \times 10^{-4}$ mol: 8×10^{-6} mol).

compared to arsenate. Different polymer: As(V) molar ratios, 31:1, 20:1, 10:1, 6:1 and 3:1 were prepared at pH 8. The results for As(V) retention R (%) with a filtration factor of $Z = 10$ for P(ClVBTA) and P(ClAETA) using the washing method are presented in Table 1. It can be observed that the retention capacity is limited by the polymer concentration when using an arsenic concentration of order 10 - 84 mg/L for two range orders of magnitude: 2×10^{-4} and 7×10^{-5} mol of polymer.

For complete arsenate removal, the results indicate an optimum molar ratio of 20:1.

Arsenite Retention Properties of Water-Soluble Metal–Polymers

A series of water-soluble polychelates have been prepared and used for one-step retention of As(III) form the solution. The complex of poly (acrylic acid)-Sn, 10 and 20% by weight of metal, introduced a high retention of species of As(III) at pH 8, the molar ratio polychelate: As (III) was 400: 1.[23]

The As(III) retention profile, as a function of pH for poly(AA) indicates that the poly(AA)'s retention properties for the arsenite anions are negligible, independent of pH. However, the poly(AA)-Sn samples present different behavior, confirming that the selectivity depended on tin salt concentration, solution pH, and the mole polymer-As(III) ratio. At pH 8, the predominating species in solution are the non-dissociated As(III) salts in equilibrium with monovalent ($H_2AsO_3^-$) anions, although the presence of As(V) species is not discarded. With poly(AA)-Sn complex at 10 wt-% theoretical tin content, high performance is obtained with nearly 90% of retention at a mole Sn-As(III) ratio close to 20: 1 and a poly(AA)-Sn: As(III) ratio of 400: 1.

Table 1.
Behavior of different molar ratio polymer: As(V) in the removal of arsenate using P(ClVBTA) and P(ClAETA) at pH 8.

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

The effect of the metal–polymer complex concentration is shown in Figure 7 for 3, 5, 10, 20 wt-% of tin content, respectively. Assays with poly(AA)-Sn: As(III) mole ratios of 20: 1, 100: 1, 200: 1, 400: 1, and 600: 1 were performed. A higher tin content improved retention performance. At a constant tin content of 3 wt-%, the retention is negligible. At 5, 10, and 20 wt-%, the retention improved with the highest yield at 600: 1 and 400: 1 mol ratios. The optimum Sn-As(III) ratio found close to 20: 1.

The retention R = 80% indicates that As(III) species are strongly bound at basic pH, such as sample 400: 1 at 10 and 20 wt-% tin content. In the second case, As(III) probably suffers a partial oxidation to As(V) due to the sample's higher tin content. However, assays for speciation progress in solution show that the majority remains as As(III) with traces of As(V), less than 10 wt-% in the filtrate solution. It is assumed that the functional groups' polarity should be one parameter controlling selectivity. The polymer's binding capacity is attributed to the surface metal polymer complexes. This bond is presumably between (positively charged) tin and the oxygen of the arsenite or arsenate forming a dipole.

Depending on the pH value, ionized poly(AA) may form complexes with D_{2h} or D_{4h} (dimers) symmetry. At higher pH values, the poly(AA) chain has a drawn shape due to electrostatic repulsion of charged carboxylate groups; thus, metal ions are binding with either one or two neighbor groups. At pH 4.8, the macromolecular globule contracts and the metal ions are able to coordinate with 2–4 carboxylic acid groups. The pHs 8, 6, and 4 are studied. The retention is lower than that at pH 8, with a maximum value of R = 30%. The highest retention, 80%, is

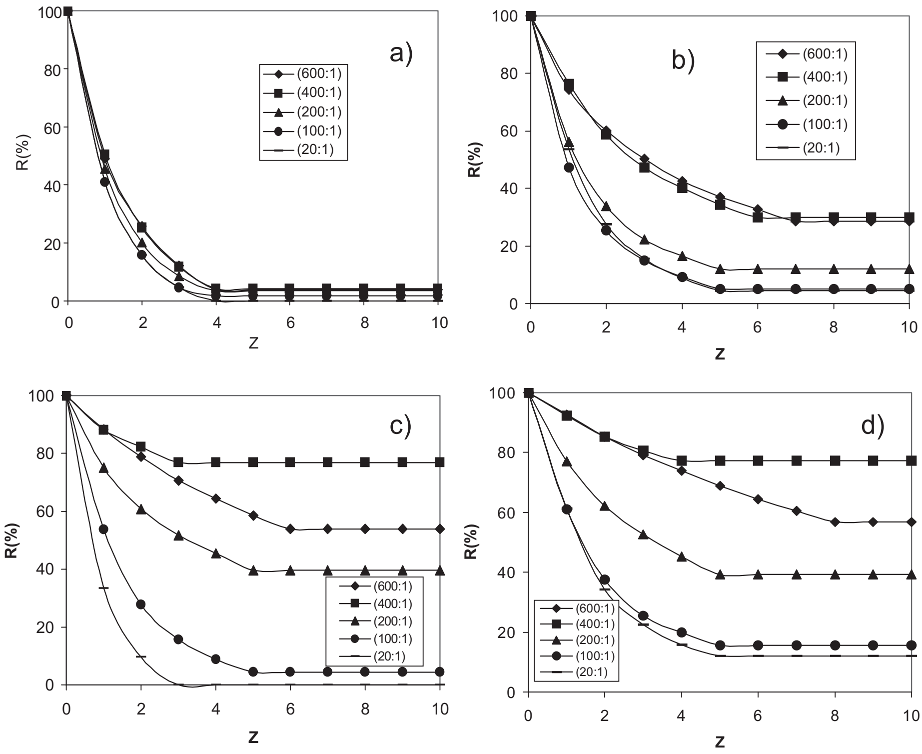


Figure 7.

Retention profiles for As(III) at pH 8, using poly (AA)-Sn with a) 3 wt-% tin, b) 5 wt % tin, c) 10 wt % tin, d) 20 wt % tin. Polymer: As(III) mol ratio: ◆600:1,■ 400:1, ▲200:1, •100:1, -- 20:1.[24]

found for poly(AA)-Sn with 20 wt-% tin content. It is suggested that the media's conditions, in the presence of oxygen from the air and water, could produce oxidation of As(III) in filtrate solution. Nevertheless, the speciation by hydride abstraction shows a high percent of As(III) in solution and the polymeric solution with an arsenic total quantification close to that in the feed of As(III).

Maximum Retention Capacity of Arsenate

To determine the polymer's maximum arsenate retention capacity, the enrichment method was used which consists in using the maximum polymer concentration with the arsenate anion to reach saturation. The maximum retention (enrichment method) is defined as:

$$C = (M\ V)/Pm \qquad (6)$$

Where Pm is the amount of polymer (g), M is initial concentration of As(V) (mg L^{-1}), V is the volume of filtrate (volume set) containing As(V) (mL) that passes through the membrane. C was calculated in the total volume of filtrate (300 mL). The enrichment factor E is determined as follows:

$$E = (P\ C)/M \qquad (7)$$

The results with P(ClAETA) using the enrichment method to determine C for arsenate anions in aqueous solutions at pH 8 are shown in Figure 8. In similar conditions, the values of C were 142 mg g^{-1} for P(ClAETA) and 75 mg g^{-1} for P(SAETA). Assuming a quantitative retention of As(V), the enrichment factor was determined (E = 3.5 for P(ClAETA) and E = 2.5 for P(SAETA)). The type of anion exchanger was an important factor in arsenate retention.[25]

Off-Line Coupled Electrocatalytic Oxidation and Liquid Phase Polymer Based Retention (EO-LPR) Techniques to Remove Arsenic

Electrochemistry and membrane ultrafiltration methods (electro-oxidation and liquid phase polymer based retention, LPR, technique respectively) were off-line coupled to remove As(III) inorganic species from aqueous solutions. The main objective is to achieve an efficient extraction of arsenic species by associating a polymer-assisted liquid phase retention procedure, based on the As(V) adsorption properties of cationic water-soluble polymers, with an electrocatalytic oxidation process of As(III) into its more easily removable analogue As(V). The electrocatalytic oxidation of As(III) to As(V) was performed in the presence of different water-soluble poly(quaternary ammonium) salts acting also as supporting electrolyte, *i.e.*, P(ClMPTA), P(ClVBTA), or P(BrVMP).

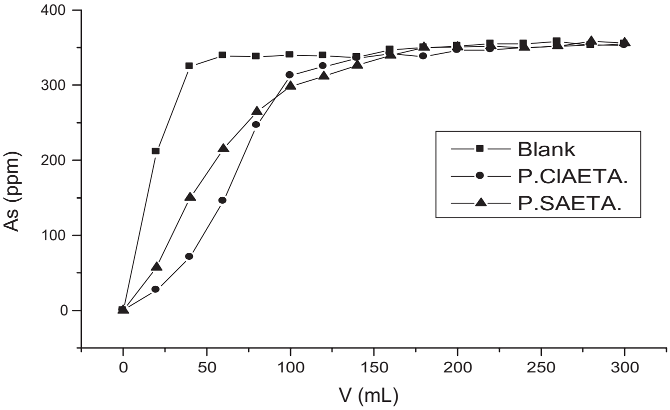


Figure 8.
Maximum capacity of retention C using P(ClAETA) and P(SAETA) at pH 8. Mole ratio: 0.8 mmol of polymer and 4 mM of As(V).

After complete electrocatalytic conversion of As(III) into As(V), the mixtures were introduced into a LPR cell to remove the As(V)-polymer adducts. Using P(ClMPTA), P(ClVBTA), or P(BrVMP) ammonium salts in a polymer:As(III) 20:1 mol ratio at pH 8, complete (100%) arsenic retention was achieved (see Fig. 9). Moreover, the As(V) retention efficiency turned out to be directly related to the net charge consumed during the electrochemical conversion of As(III) to As(V).[24]

Macroscopic electro-oxidation of As(III) to As(V) at a platinum gauze electrode was carried out in the presence of the polyelectrolytes P(ClVBTA), P(ClMPTA), and P(BrVMP) in unbuffered aqueous solutions. Electrolyses were performed at a constantly applied potential between +0.8 to +0.9 V vs. Ag/AgCl until the theoretical charge required for the two-electron oxidation of As(III) to As(V) was consumed. Similar results were obtained by oxidation at +0.8 or +0.9 V, but the electrolysis time was largely reduced at an applied potential of +0.9 V. The initial solutions were basic (pH 9–10), but the pH decreased continuously as the consumed charge increased, reaching a value of 3–4 at the end of the electrolysis. The progress of the macro-scale oxidation of As(III) to As(V) could be readily judged from the height of the As(III) oxidation peak recorded at a platinum disc microelectrode.

Before performing the ultrafiltration process to remove complexed As(V) species from the electrolyzed solution, pH was adjusted to 8 with 0.1 M NaOH and stirring was maintained for about 1–4 h. This mixture is then washed with the reservoir's water solution, which should reproduce the same pH and ionic strength values, wherein the volume was adjusted to 20 mL. Ultrafiltration runs were performed under a total pressure of 3.5 bar using a ultrafiltration membrane of polyethersulfone with an exclusion rating of 10,000 Da. Fractions of 20 mL were collected up to a total volume of 200 mL. The arsenic concentration in the filtrate was determined by atomic absorption spectrometry. A blank assay was also performed with a solution of polymer and As(III), 20:1 mole ratio, which had not been previously electrochemically oxidized. This ratio was selected to ensure an excess of the repeat polymer unit. The results of the

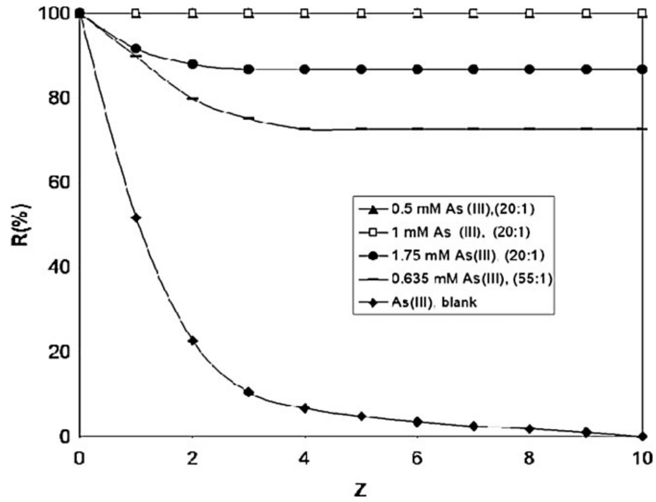


Figure 9.

Arsenic retention by P(ClVBTA) as supporting electrolyte and polychelatogen at pH 8, at different concentrations of As(III); (▲) 0.5 mM, (-) 0.635 mM, (□) 1.0 mM, (●) 1.75 mM in the electrolysis cell; polymer:As(III) molar ratio 20:1; solutions were previously electrolyzed onto a Pt gauze electrode (E.app +0.9 V vs Ag/AgCl) up to the consumption of the theoretical charge for the complete oxidation of As(III) to As(V)[24].

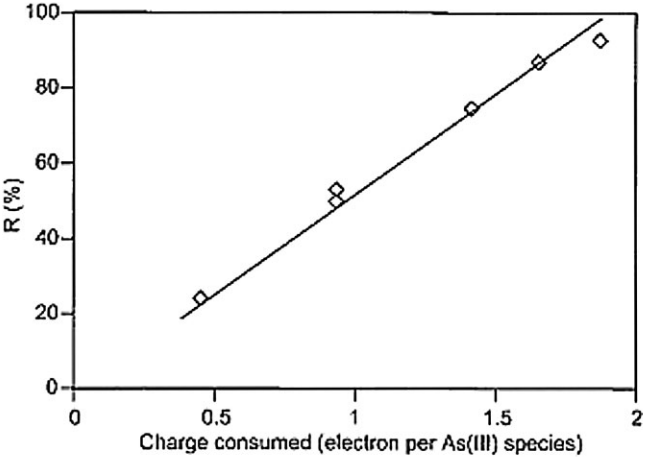


Figure 10.
Arsenic retention as a function of the charge passed during the electrolysis (massive Pt electrode, Potential applied +0.9 V of 1mM As(III) solutions containing P(ClVBTA) as polyelectrolyte; P(ClVBTA): As(III) mol ratio 20:1.[24]

As(V) uptake are systematically presented as the percentage of retention R (%) vs. the filtration factor Z (volume of the filtrate/volume of the cell) (see Fig. 9).

Moreover, an important point is that the entire process can be conducted in the same reactor without any additives except for the complexing polycationic polymer, which also serves as supporting electrolyte.

A serie of experiments have been performed to estimate the effect of the oxidation of As(III) to As(V) species on arsenic removal efficiency using LPR. In all these experiments, P(ClVBTA) was used as a capturing and supporting polyelectrolyte. Several As(III) solutions were oxidized at an applied potential of +0.8 V or +0.9 V. Electrolysis were stopped after the consumption of 0.5, 1, 1.5, 1.75, and 2 electrons per As(III) species. Then, arsenic retention using the LPR technique was determined for every electrolyzed solution (see Fig. 10), calculating the retention factor (R) obtained for electrolyzed (+0.9 V) arsenic solutions (0.5 and 1×10^{-3} mol L^{-1}) containing P(ClVBTA) as polyelectrolyte as a function of the consumed charge during electrolysis. In all these experiments, the polymer: As(III) mol ratio was 20:1. After electrolysis, the solutions' pH was adjusted to 8 and arsenic was removed by ultrafiltration. Similar results were obtained using a lower oxidation potential (+0.8 V). The linear increase of arsenic retention as a function of the electrolysis charge (regression linear factor $r^2 = 0.98$), reaching 100% after the consumption of 2 electrons per As(III) species, clearly demonstrates that the arsenic removal efficiency is directly related to the oxidation of As(III) to As(V). These experiments also demonstrate that the combination of LPR with an electrocatalytic oxidation process is an efficient, straightforward procedure to remove arsenic from contaminated aqueous solutions.

Our combined method, electro-oxidation EO-LPR avoids the use of chemical oxidants.

Preliminary studies indicate that it is possible to improve these results using electrodes modified with catalytically active materials based on nano/micro particles of noble metals (Pt, Pd and Au)[26] or metal oxide,[27] among others, dispersed in polymer films covering the surface of carbon electrodes.

Conclusion

The liquid-phase polymer-based retention (LPR) technique has proved to be a convenient technique to retain significantly anions arsenate solution using a polymer with quaternary ammonium groups. The retention capacity of the arsenate depended on pH, counter ion, quaternary ammonium group, and the polymer concentration.

The retention behavior with copolymers P(ClMPTA-*co*-AA) showed that the interaction rate increased with the pH for copolymers with mole ratios of 1:2 and 2:1, the difference in activity of polycations was more remarkable at pH 6. The highest values were obtained at pH 8 with 1:2 and 2:1.

P(SAETA) containing bulky counter ions ($OSO_3CH_3^-$) showed a lower retention capacity of arsenate ions. Thus, the nature of the anionic exchanger groups appears to be an important factor in the arsenate retention by these water-soluble polymers.

The arsenic anions' retention behavior depended on the pH, polymer concentrations, and tin content. The adequate Sn-As(III) mole ratio, close to 20:1 or 40:1, presented the highest yield in all cases. A good retention was found at pH 8 and 4. Additionally, the retention results with As(V) in the feed presented a similar retention behavior to values found for As(III) at $Z=10$. Therefore, the water-soluble metal-polymer complexes prepared can remove arsenic in its two oxidation states from water.

Treatment of aqueous solutions with arsenic previously subjected to an electrocatalytic oxidation (EO), to convert the species of As(III) to As(V), quantitatively removed arsenic from aqueous solutions by LPR technique. This study demonstrated that water soluble polymers can be used as As(V) removal reagents in ultrafiltration and support electrolytes for electrocatalytic conversion process, which is a decisive advantage, since their application does not require the addition of other reagents (such as salts medium) in homogeneous electrocatalytic processes.

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