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ORIGINAL PAPER

Liquid-phase polymer-based retention and coupled electrocatalytic oxidation to remove Arsenic in the presence of competitive species

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Abstract The goal was to remove arsenate species in the presence of competitive anions by coupling of liquid-phase polymer-based retention, LPR, a procedure based on the selective As(V) adsorption properties of cationic water-soluble polymers, with an electro-catalytic oxidation process (EO) of As(III) into its more easily removable As(V). The electro-catalytic oxidation of As(III) to As(V) was performed with an organic supporting electrolyte, poly[3-(methacryloylamine)propyl)]trimethyl ammonium chloride, P(ClMPTA), which is recognized as an efficient reagent in removing divalent arsenate species. The bulk electro-catalytic conversion of As(III) to As(V) was carried out with a Pt-gauze electrode, and the resulting mixtures were introduced into a LPR cell to remove the As(V)-polymer adducts. Using P(ClMPTA) and ammonium salts at a 20:1 polymer:As(III) molar ratio at pH 8, complete (100%) Arsenic retention was achieved. For binary mixtures of Arsenic with competitive anions (e.g., SO_4^{2-}, HPO_4^{2-}, NO_3^-, and NO_2^-), the retention profile varied in the range 100–70%. In addition, the As(V) retention efficiency was found to be directly related to the consumed charge in the mol ratio As(III) in solution with competitive anionic species.

Keywords Arsenic · Electro-oxidation-LPR (EO-LPR) techniques · Membranes · Quaternary ammonium polyelectrolyte · Competitive species

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Introduction

In recent years, much attention has been focused the development of new analytical techniques that allow easy detection and removal of Arsenic compounds. This requires highly sensitive methods, especially in aqueous media where the Arsenic concentration is below 1 μM (75 μg/L). The voltammetric techniques provide accurate measurements of low concentrations at the μg/L level with rapid analysis and low cost instrumentation [1, 2] and the development of new electrodes with electro-catalytic properties has also been widely investigated [3–11]. As(III) detection by materials in the nanometer range, such as gold nanoparticles modified glassy carbon electrodes [10] and Pd, Pt nanoparticles deposited on conductor polymer film [11], shows great sensitivity and a lower oxidation potential than with a bulk metal electrode, because electrochemical oxidation of As(III) can be chemically performed in the presence of catalysts such as the noble metals Pt, Pd, Au, Ag, Ir, and Ru [5–11]. However, there is little information in the literature about the application of arsenite electro-oxidation [12, 13] in bulk, where the product of oxidation is also treated for removal, despite there being many commercially available Arsenic removal techniques such as adsorption, ion exchange, coagulation and precipitation, involving pre-oxidation with chlorine, ferric chloride, and potassium permanganate [14].

In the conventional oxidation process with chemical dosing, one drawback is the resulting by-products from reactions with natural organic matter [14]. Another disadvantage is the strong oxidation which could partly oxidize the natural organic matter, while also introducing a pre-oxidation step that increases operational complexity and reduces the process's overall gain. The fixed–bed adsorption process is known to be operationally simple, with the main limitation being the sorbent, which must be stable and regenerable and have a high selectivity toward the contaminant. Although, fixed–bed adsorption with activated alumina is preferable for As(V) at pH 5–6 with a low level of competitive anions, it does not effectively remove As(III) [15]. As a result, the iron oxide/hydroxide and polymer/inorganic hybrids beds are currently being extensively studied and appear to be promissory for arsenite and arsenate retention [16, 17].

Greenleaf et al. [18] observed that the presence of a quaternary ammonium functional group in the anion exchange fibers enhanced permeation of arsenate within the fiber, which was followed by selective binding onto hydrated iron oxide. In addition, the use of poly quaternary ammonium salt on different forms in order to enhance ion removal is a promising research area. Recently, the authors have reported [19–21] arsenate removal by a polyelectrolyte of quaternary ammonium salts using the liquid-phase polymer-based retention (LPR-technique), with this method also being applied to the soluble metal complexes poly(acrylic acid)-tin(II) [22, 23]. Retention and removal from aqueous solution was performed in one step, thus minimizing the problems associated with two phases.

In this study, the authors report on the benefits obtained by combining electrochemistry and membrane filtration methods for the determination and removal of toxic metal ions from water using platinum electrodes. This off-line combined method [12, 13] avoids the addition of a third component, while the use of a poly quaternary ammonium salt has a double effect, as an organic supporting electrolyte and as a retention agent, and thereby reducing processing costs. The aim was to selectively separate Arsenic species in the presence of HPO_4^{2-}, SO_4^{2-}, NO_3^-, and NO_2^-, using liquid phase retention assisted by polymers (LPR-P technique), by combining the selective adsorption properties of the cationic water-soluble polymers that showed remarkable retention properties toward oxo-anionic species with the electro-catalytic oxidation of As(III) into its more easily removable analog As(V). This process used a bulk-Pt electrode, and the products of macro electrolysis were ultrafiltered by membranes and removed as As(V) by the same organic supporting polymers.

Experimental part

Reagents

[3-(methacryloylamine)propyl)]trimethyl ammonium chloride, 50 wt% aqueous solution was obtained from Aldrich (reagent grade) and used as received. Solutions of 46 mM $NaAsO_2$ 0.1 M Na_2SO_4, 0.1 M $MgSO_4$, 0.1 M $NaNO_3$, 0.1 M $NaNO_2$, 0.1 M Na_2HPO_4, and 0.1 M $CaCl_2$ were prepared with solid reagents (Sigma) and milli-Q water by using the Millipore system.

Synthesis of polyelectrolytes

The polyelectrolyte salt, poly[3-(methacryloylamine)propyl)]trimethyl ammonium chloride P(ClMPTA) was prepared by radical polymerization using ammonium persulfate (1 mol%) as an initiator and stirring the reaction mixture at 70 °C under a nitrogen atmosphere for 24 h [13]. The polymer was fractionated through the ultrafiltration membranes, applying the different mass cut-off: 100,000, 50,000, and 30,000 Da. Fractions were then lyophilized and the main ones were found to exhibit molecular weights >100,000 Da. The resulting polymers were characterized by fourier transformed infrared (FTIR), and proton nuclear magnetic resonance (NMR H^1) spectroscopy.

Electrochemistry

Electrochemical experiments were performed using a CV-Bas 50 W potentiostat/galvanostat (Basinc, West Lafayette, IN). Standard three-electrode cells were used for analytical and electrolysis experiments with the AglAgCl in 3 M KCl as the reference electrode and a platinum wire as the counter electrode. The counter electrode was isolated from the working compartment by a glass frit. A platinum disk electrode (3 mm in diameter) polished with 1-μm diamond paste was used for analytical experiments. Preparative-scale electrolyses of the As(III) to As(V) species were performed in air, at room temperature and under constant stirring at 800 rpm on a platinum gauze electrode with a large area.

In a typical experiment, the electrolysis cell was charged with 20 ml of solution containing a cationic polymer, and used as the supporting electrolyte and extracting material, with As(III) at a 20:1 mol ratio. Also, binary mixtures of sulfate, phosphate, nitrate, or nitrite with As(III), at a mol ratio anion:As(III) (1:1), (2.5:1), and (25:1) were made. The applied potential to achieve the oxidation of As(III) on platinum was 0.9 V.

LPR-procedure

The LPR equipment and procedure have already been described [19]. Before carrying out the ultra-filtration process to remove the complexed As(V) species from the electrolyzed solution, the pH was adjusted to 8 with NaOH and maintained by stirring for about 0.5 h. Several experiments were conducted using the washing method, which is a batch-like method where a liquid sample containing the polymer and the metal ions to be separated is placed in the ultrafiltration cell at a given pH and ionic strength. Then, the polymer is washed with a water solution contained in a reservoir to reproduce the same pH and ionic strength values so that conditions may be found at which the ions of interest are retained and other species are removed.

The resulting solutions of bulk electrolysis were introduced in the ultrafiltration cell, wherein the volume was adjusted to 20 ml. The samples were then ultrafiltered and washed with water from the reservoir at the same pH. 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. The total volume in the cell was kept constant during this process and 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, and a blank assay was also performed with a solution of polymer and As(III) 20:1 molar ratio, which had not previously been electrochemically oxidized. The results of the As(V) uptake are systematically presented as the retention percentage R(%) versus the filtration factor Z(volume of filtrate/volume of the cell).

The total Arsenic concentration was measured in the filtrate by atomic absorption spectrometry (AAS) using a Perkin Elmer 3100 spectrometer and the amount retained was determined by its difference with the initial concentration. The filtrate solutions were analyzed for nitrite and phosphate content by UV–vis spectrophotometer, with the NO_2^- content being measured by the diazotization and coupling method. The sulfanilamide and *N*-(I)-ethylenediamine dichloride formed a pink-colored azo product, which was measured by Vis-spectroscopy at $\lambda = 541$ nm; and the phosphate was measured by formation of phosphomolybdate complex of blue color, at $\lambda = 890$ nm.

Results and discussion

Electro-oxidation of As(III) to As(V) at the preparative scale, followed by removal of Arsenic by LPR technique

Electro-catalytic oxidation and As(III) detection have been widely investigated at different platinum electrodes [24]. The authors have previously reported [13] the typical cyclic voltammetry responses at a platinum disk electrode upon addition of As(III) to a 0.1 M Na_2SO_4 or P(ClMPTA) solution (scan rate 10 mV s^{-1}), where, the pH enhanced to 9 and 10. In the presence of As(III), the large peak observed around 0.7 V in the positive potential scan was attributed to the oxidation of As(III) to As(V). In the studied concentration range (0–3 mM), the peak height increased linearly with the concentration of As(III), whose oxidation was electrocatalyzed by surface oxides [8, 24]. The small anodic peaks at *ca* 0.2–0.3 V were attributed to the oxidation of bulk As(0) and As(0) adatoms, [24] formed by cathodic deposition. In previous studies [12, 13], it was also focused on the removal of As(III), by releasing the anions from aqueous solutions by coupling off-line electro-oxidation and polymer assisted liquid phase retention techniques (EO-LPR). The efficiency of this novel coupled procedure was due to the straightforward electro-catalytic oxidation of As(III) into its more easily removable analog As(V) as well as to the selective adsorption properties of cationic water-soluble polymers toward As(V) oxo-anionic species.

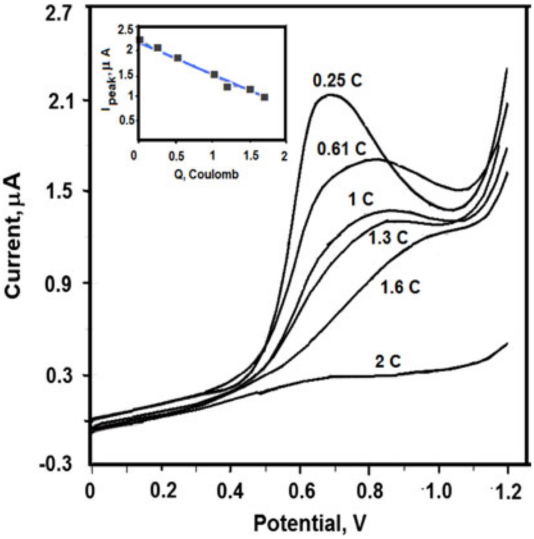
The cyclic voltammeter in a bulk Pt electrode (ø = 1.5 or 5 mm) showed two oxidation potentials: one at 0.35–0.4 V for the transformation of As(0) to As(III) and the second at 0.7–0.9 V for the oxidation of As(III) to As(V). In the electrolysis studies at a controlled potentials (0.8 and 0.9 V), these were applied close to the highest current peak of the oxidation of As(III) to As(V), because a lower potential (i.e., 0.7 V) resulted in a much longer electrolysis time, and a much higher potential (e.g., 1 V) produced oxidation of organic matter and higher energetic costs. Thus, bulk electro-oxidation of As(III) to As(V) was performed at a Pt-gauze electrode with a supporting electrolyte P(ClMPTA) at 0.9 V in a pure mixture P(ClMPTA):As(III) (20:1) mol ratio, using 0.5 mmol/L As(III). The theoretical charges were calculated, considering two equivalents of electrons passing from As(III) to As(V) for 0.5 mmol/L As(III): $Q_{\text{total}} = 2 \times 5 \times 10^{-4}$ (20/1000) $\times$ 96.500 = 1.93 coulomb, and for 0.13 mmol/L As(III), $Q_{\text{total}} = 2 \times 1.33 \times 10^{-4}$ (20/1000) $\times$ 96.500 = 0.52 coulomb. During electrolysis, the arsenite was constantly oxidized into arsenate for each charge applied, and this process was monitored by identifying the drop in peak current in the cyclic voltammeter diagram, as shown in Fig. 1. An analytic electrode (ø = 1 or 1.5 mm) using the linear sweep stripping voltammeter (10 mV/sec, 1 µA/V (0–1.2 V), time deposition 600 s was utilized. The assays were performed several times, which confirmed the obtained results, with the electrolysis being complete and the LPR-P presenting the maximum retention as arsenate.

The pH measurements for each charge applied in the electrolysis are shown in Fig. 2. The electrode detected the Arsenic species, which predominated or were acting due to pH changes. Neutral and anionic forms of Arsenic adsorb and react on the electrode surface, and the drop in pH's solution indicating OH^- consumption or neutralization, may have been due to the effect of the acidic electro-catalyst, according with a mechanism of oxidation of As(III) on the Pt electrode, similar to those proposed in previous works [25, 26]. The Pt electrode generates H^+, even on oxide-free or -covered surfaces, and the transfer of H^+ into solution was probable.

$$\text{PtOH} \rightarrow \text{PtO} + \text{H}^+ + \text{e}^-$$

Oxidation of As(III) could take place through the transfer of the hydroxyl radical formed on the Pt surface as [26]:

Fig. 1 Linear sweep voltammetry (LSV) of Pt electrodes (ø = 1.5 mm) in P(ClMPTA) solution after each charge applied at controlled potential 0.9 V. Conditions: (10 mV/sec, 1 µA/V, (0–1.2 V), time deposition 600 s. *Inset* the peak current (I_{peak}, µA) versus charge applied (Q, C)

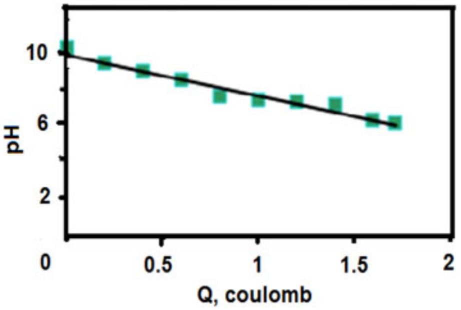


$$As(OH)_3 + PtOH \rightarrow Pt + OAs(OH)_3 + H^+ + e^-$$

The decay of pH during the electrolysis confirmed that P(ClMPTA) only performed the function of a supporting electrolyte, thereby facilitating the charge transference without acting, at this stage, as a removal agent of the transformed As(V). The negligible retention of either As(III) or As(V) by the poly quaternary ammonium salt at acidic pH made the two-stage treatment: electro-oxidation followed by the recovery of Arsenic at basic pH.

Electrolysis on the Pt electrode generated a catalytic current, which was evaluated by the maximum intensity of the current peak and then subtracted from the background of the polyelectrolyte. Figure 3 shows a linear drop occurring in the catalytic current for each charge applied when a constant potential of 0.9 V was used. The catalytic current intensity was adjustable in order to measure the As(III) concentration, by corresponding the initial concentration of 0.5 mM, with the maximum value of peak current in the voltamperogramm when the charge applied is zero. Furthermore, the consecutive charges applied decreased both the amount of As(III) remaining in solution and the catalytic current intensity. The correlation is

Fig. 2 pH measurement versus charge applied during the electrolysis (at 0.9 V) in PClMPTA solution



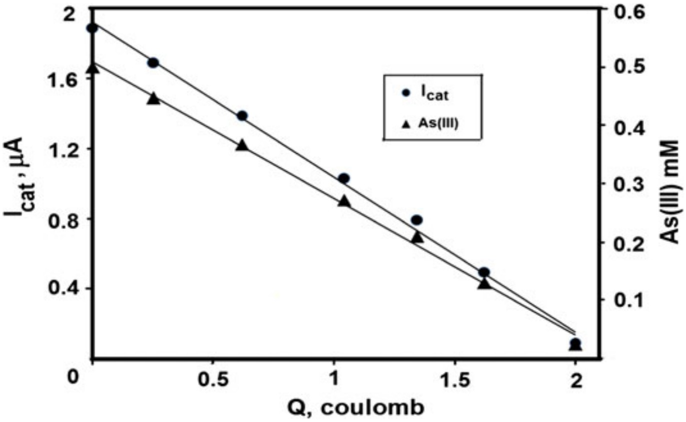


Fig. 3 Catalytic current calculated (I_{cat}, µA) and molar As(III) concentration versus charge applied (*Q*, *C*) during electrolysis at controlled potential of 0.9 V

presented in Fig. 3, where the curve's slope was used to evaluate the kinetic rate constant as As(III) disappeared. In addition, 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).

The LPR technique is a special type of ionic–exchange and differs from the conventional method using a resin as exchanger ionic, because the exchange is completely produced in a homogenous media, at pH 6–8 (near drink or tap-water), where the poly quaternary ammonium salt show high saturation capacity (i.e., 117 mg/g). On the other hand, it is known [16] a resin polymeric anion exchangers prefer sulfate over arsenate, greatly reducing their removal capacity. The previous studies [27] with this LPR system, using high concentrations of As(V), of nearly 0.5 mmol/L, and different polyquaternary ammonium salts, showed that the decrease in arsenate retention in the presence of sulfate with mol ratio sulfate: arsenate (1:1) in both bi-distilled and drinking water was less than 10%. In addition, it is probable that anionic exchanger selectivity would be enhanced when used in a soluble form because the diffusion limitations are diminished and Arsenic easily permeates at binding sites.

The LPR method was operated at about pH 8. Therefore, for the different cases studied, the ions species present would mainly be: HPO_4^{2-}, SO_4^{2-}, NO_3^{-}, NO_2^{-}, and $HAsO_4^{2-}$. A systematic study of electro-oxidation coupled to Arsenic retention in a binary mixture with sulfate can be observed in Fig. 4, which shows the retention profile (R%) of the polymer versus the filtration factor (Z) at pH 8, using 0.5 or 0.13 mmol/L of As(III) for different sulfate anion concentrations. In all cases, the mol ratio P(ClMPTA):As(III) was maintained at 20:1. The competition of Arsenic with sulfate in binary equimole presented the maximum retention at the lowest As(III) concentration, and a marked reduction occurred when the mol ratio of SO_4^{2-}/As(III) was 10:1 for 0.13 mmol/L of As(III).

Factors that affected retention could be the competitive action of anionic forms ($HAsO_4{}^{2-}$ and $SO_4{}^{2-}$) on the polymers' cationic sites (ions of same charge have

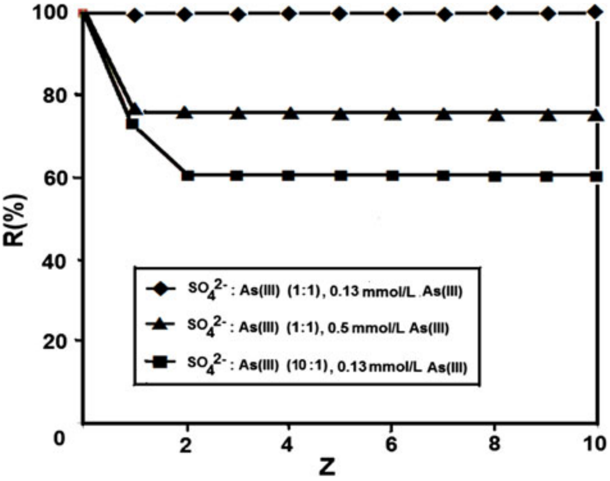


Fig. 4 Arsenic retention profile using P(ClMPTA) as supporting electrolyte and polychelatogen at pH 8, following conversion of a 20 ml solution of As(III) to As(V) by oxidation at a Pt-gauze electrode ($E_{app} = 0.9$ V), using 0.5 mmol/L of As(III) and mol ratio SO_4^{2-}:As(III) 1:1 (*filled triangle*); or 0.13 mmol/L of As(III) for different mol ratio SO_4^{2-}:As(III) 1:1 (*filled diamond*), and 10:1 (*filled square*)

the same affinity for the binding sites), and the nature of the sodium sulfate salt during the electrochemical conversion of As(III) to As(V). Shakkthivel and Singh [26], by considering the role of the surface oxides on the Pt surface, observed that the formation of PtO is dominant in Na_2SO_4 solution at lower As(III) concentrations and that the generated PtO surface is a non-conductor, thus preventing/inhibiting As(III) oxidation.

Anions commonly form species of different valences in water, with the concentration of each ion depending on the pH. Thermodynamically, phosphate species coexist as monovalent and divalent species at pH values similar to those of arsenate species, as pH is the main factor limiting Arsenic removal. For the P(V) ions, the predominant species at pH values ≤ 2.2 is H_3PO_4, with $H_2PO_4^-$ and HPO_4^{2-} existing in equal amounts at pH 7.2, but PO_4^{-3} predominating at the highest pH. In addition, since arsenate and phosphate have the same geometric disposition to form tetrahedral structures, competition for the polyelectrolyte's polycationic sites is greater. As described above, the macro electro-oxidation of 0.13 mmol/L As(III) on the Pt electrode was calculated at 0.52 coulomb. The results of the conjunction methods are shown in Fig. 5 for the retention profile of electro-oxidized Arsenic formed at pH 8, with the mol ratios HPO_4^{2-}: As(III), 1:1, 2.5:1, and 25:1. The authors suggest that the phosphate anions presented an interference in arsenate retention during the LPR assay, but this did not occur on bulk electro-oxidation.

Regardless of the amount of phosphate in aqueous media, the polycationic retention was more prone selective to the arsenate anion. Thus, for an equimolar mixture with phosphate at pH 8, the calculated retention of the electro-oxidized form was 70% for $HAsO_4^{-2}$ but only 28.4% for HPO_4^{-2}, using the UV–vis determination method for total *P*. When comparing the competition between the two divalent anionic forms together in 0.13 mmol/L of As(III) feed, the effect of phosphate in preoxidized

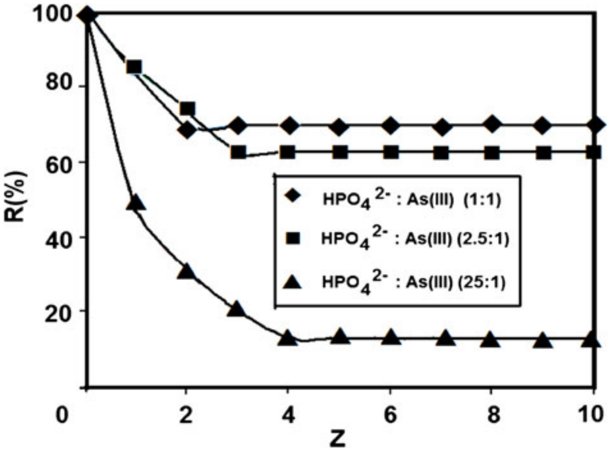


Fig. 5 Arsenic retention profile using P(ClMPTA) as supporting electrolyte and polychelatogen at pH 8, following conversion of a 20 ml solution of As(III) to As(V) by oxidation at a Pt-gauze electrode ($E_{app} = 0.9$ V), using 0.13 mmol/L of As(III) for different mol ratio HPO_4^{2-}:As(III) 1:1 (*filled diamond*), 2.5:1 (*filled square*), and 25:1 (*filled triangle*)

water was found to be higher than that exerted by sulfate on As(V) removal. While 1.3 mmol/L SO_4^{2-} decreased As(V) removal to 60% (mol ratio 10:1 with As(III), as is shown in Fig. 4), only 0.325 mmol/L of HPO_4^{2-} was required to reach the same retention profile (mol ratio 2.5:1 with As(III), see Fig. 5). Also, only a small change (<25%) was found in the typical concentration range of 0.13–0.5 mM As(III), when the equimole mixture with SO_4^{2-} was tested. However, in the typical range of 0.13–3.25 mM for a constant 0.13 mmol As(III) feed, the variation of phosphate influenced As(V) removal, resulting in a change greater than 70%.

The bulk electro-oxidation of As(III) was also assayed in the presence of monovalent anions such as nitrite and nitrate. All these experiments were realized at room temperature and basic pH, because the equilibrium of NO_2^- is unstable in aqueous acidic media and at high temperatures due to nitrous acid decomposing to NO and NO_3- [28],with nitrate ions from most metal nitrate salts or strong nitric acid being found as NO_3^- at low and high pH value. Figure 6 shows the retention profiles for both NO_2^- and the electro-oxidized form ($HAsO_4^{2-}$) when 0.13 mmol/L As(III) was assayed.

For the binary mixture, NO_2^-:As(III), at a mol ratio of 1:1, the monovalent anion exerted a slightly weaker effect on arsenate retention, with about 90% being recovered from water. However, when a mol ratio 2.5:1 was used, the arsenate retention decreased to 75%, while the nitrite retention was only 5%. As already demonstrated [19–21], P(ClMPTA) is an ion exchanger with a greater affinity for divalent than monovalent anions. Related this, the previous studies have reported [29] the retention properties for nitrites of water-soluble quaternary ammonium salt polymers using the washing method, with the effect of pH and mol ratio polycation: NO_2^- on maximum retention being analyzed specifically for P(ClMPTA). Since a mol ratio of 20:1 only retained 20% NO_2^- in a mixture of free anions and bi-distilled water, the mol ratio was increased up to 60:1 in order to obtain

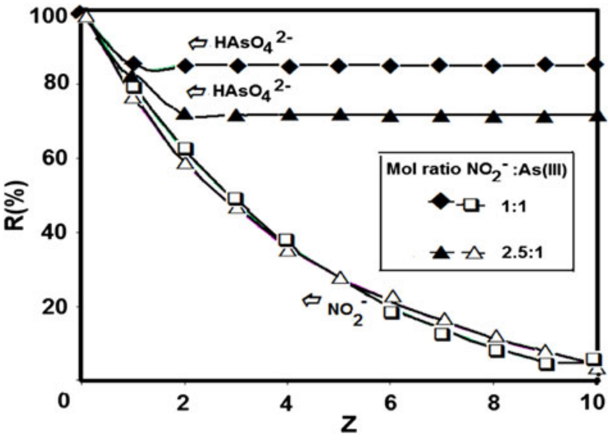


Fig. 6 Arsenic retention profile (*black points*) and nitrite retention (*white points*) using P(ClMPTA) as supporting electrolyte and polychelatogen at pH 8, following conversion of a 20 ml solution of As(III) to As(V) by oxidation at a Pt-gauze electrode ($E_{\mathrm{app}} = 0.9$ V), using 0.13 mmol/L of As(III) for different mol ratio NO_2^-:As(III) 1:1 (*filled diamond*, *open square*), 2.5:1 *filled triangle*, *open triangle*)

maximum retention. In this study the authors considered the possible oxidation of NO_2^- by Pt electrodes, although the results on nitrite determination by UV–vis showed an equilibrated mass balance in feed which was recovered or permeated in the filtrate. The lowest retention was achieved by monovalent anions, with these results also being corroborated in the literature [30], confirming that valence is the predominant variable affecting anion removal.

It is assumed that increasing ionic strength influences the ability of ions to bind the polymer, and consequently decreases the Arsenic removal in solutions with sodium nitrate or nitrate salts. This effect is attributed to a change in the value of the

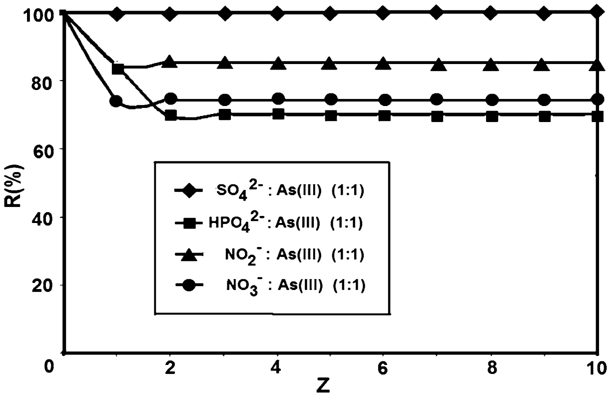


Fig. 7 Arsenic retention profile using P(ClMPTA) as supporting electrolyte and polychelatogen at pH 8, following conversion of a 20 ml solution of As(III) to As(V) by oxidation at a Pt-gauze electrode ($E_{\mathrm{app}} = 0.9$ V), using 0.13 mmol/L of As(III) for mol ratio anion:As(III) 1:1, of SO_4^{2-} (*filled diamond*), HPO_4^{2-}(*filled square*), NO_2^- (*filled triangle*), NO_3^- (*filled circle*)

dissociation constant during filtration (due to screening effects) to changes in the polymer conformation, and to competition of monovalent anions with polyvalent ones to bind the polymer [30–32].

Figure 7 shows the incidence that each monovalent and divalent anion had on the recovery of the transformed form of $HAsO_4^{2-}$ in an initial equimolar mixture with As(III) and for the unique mole ratio P(ClMPTA): As(III) 20:1 at basic pH. The interference of HPO_4^{2-} on arsenate retention was greater for SO_4^{2-}, while a similar arsenate retention profile was maintained in the presence of NO_2^- or NO_3^-. Furthermore, it showed that the presence of both monovalent and divalent co-ions lowed Arsenic retention, with this being is more pronounced for the divalent co-ion with the same molecular form, a result that may be attributed to a higher electrostatic attraction.

Conclusions

The combination of macro-electro-oxidation and liquid-phase polymer-based retention (LPR) techniques was shown to be a convenient two-step route to retain Arsenic in the presence of other anions in an aqueous solution. The quaternary ammonium groups presented important electroselectivity on retention of divalent anions at basic pH, and the macromolecule was an effective ion carrier during the electrolysis of As(III). In a solution of free anions with other salts, the electrolysis of As(III) performed with macro Pt electrodes resulted in maximum retention for As(V) by P(ClMPTA). The results demonstrated that the selectivity for $HAsO_4^{2-}$ in the presence of other anions was from 90 to 70% for equimolar binary mixtures. In general, the decrease in selectivity was in the following order: $HPO_4^{2-} > {}^-NO_3^- \cong NO_2^- > SO_4^{2-}$.

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