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Arsenic extraction from aqueous solution: Electrochemical oxidation combined with ultrafiltration membranes and water-soluble polymers

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ABSTRACT

This study shows that the combination of the liquid-phase polymer based retention technique with the electrocatalytic oxidation of arsenic(III) to arsenic(V) is an effective process to remove hazardous As(III) species from aqueous solution.

The solution of arsenite and water-soluble polymers at 20:1 polymer:As(III) molar ratio (As(III) 7.5×10^{-4} M, water-soluble polymer 15×10^{-3} M) was submitted to electrocatalytic oxidation using (carbon/polymer/Pt) nanocomposite modified electrode at +0.7 V vs. Ag/AgCl and water-soluble polymer as a support electrolyte and extracting agent.

After the exhaustive oxidation of As(III) to As(V), the arsenic was placed in the ultrafitration cell and the retention capacity of the water-soluble polymer was studied at different pH. At basic pH, the arsenic retention reached was between 70% and 100%, and the maximum for water-soluble polymer was obtained with chloride as a counter ion: 100% for P(ClDDA), 94% for P(ClAPTA) and 70% for P(SAETA) at $Z = 10$.

The enrichment method shows the maximum retention capacity for arsenate anions in aqueous solutions at pH 9. The type of anion exchanger was an important factor in the maximum retention capacity of arsenate.

1. Introduction

Arsenic is a high toxic pollutant at low concentration levels and produces serious environmental problems in several countries [1]. The maximum permissible concentration accepted by the World Health Organization (WHO) for arsenic in drinking water is 10 μg L^{-1} [2]. Arsenic in water normally occurs in the oxidation states + 3 (arsenite) and + 5 (arsenate). However, the forms, concentrations, and relative ratios of both As(V) and As(III) in water vary significantly, depending on changes in input sources, such as the pH and oxidation potential [3–5]. Arsenate is less toxic than arsenite, but more abundant and more mobile in natural surface waters, whereas arsenite is found mostly in anaerobic environments such as groundwater [6].

Several methods are used to remove traces of arsenic from water including ion exchange resins, adsorption using especially modified chelating compounds, chemical precipitation, coagulation, and membrane processes used in reverse osmosis, among others [7–9]. However, as mentioned, the redox- and pH-controlled diversity of arsenic species in water results in complex selectivity issues that have yet to be fully addressed.

As(III) removal is more difficult than As(V) removal. The presence of As(III) in aqueous solution usually exhibits a neutral charge and is more difficult to remove from solution, and therefore is usually oxidized to As(V) prior to removal [9,10]. Oxidation is a previously required step to transform As(III) species in more easily removable As(V) species [11,12].

Even when oxidation in the presence of air or pure oxygen is slow, the oxidation rate can be increased by the use of ozone, chlorine, hypochlorite, chlorine dioxide, or H_2O_2. The oxidation of As(III) is also possible in the presence of manganese oxide-coated sands or by advanced oxidation processes [12].

The electrochemical oxidation of arsenite combined with adsorption [11] or membrane ultrafiltration procedures [13,14] have recently emerged as efficient strategies to remove arsenic from contaminated aqueous solutions.

The technique called *liquid-phase polymer-based retention* (LPR) is based on the separation of metal ions that is bound to soluble extracting polymers from other free metal ions species according to their size differences [15,16]. The great advantage of the LPR method is that it can be performed in homogeneous media [16], thus largely avoiding the phenomenon of mass transfer or diffusion that occurs in heterogeneous methods. 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). In ideal cases,

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this system may be considered a steady-state mixed flow reactor [15].

The present research studies arsenite extraction in two steps. The first step is the electrocatalytical oxidation of As(III) that can be quantitatively applied in the treatment of polluted water, by using carbon/polymer-catalysts electrode materials in presence of water-soluble polymer as support. It is also possible to control *in situ* the advancement of the electrocatalytic process, i.e., to be able to follow the conversion of As(III) to As(V) into the electrochemical cell. This is based on the relationship between the As(III) concentration and the catalytic current recorded at the nanocomposite film-modified electrode.

The second step is to study the efficiency of the extraction of As(V) species produced previously by electrocatalytic oxidation (EO) of As(III) solutions, using the same water-soluble polymer as the supporting electrolyte in the electrochemical cell and as extracting of arsenic species in ultrafiltration. Arsenic-specific extracting water-soluble polymeric reagents, with $(R)_4N^+X^-$ groups, and ultrafiltration membranes were combined in order to selectively separate arsenic species from other charged or neutral substrates in water [17,18]. Finally, the maximum retention capacity of arsenate by these polymers was determined.

2. Materials and methods

2.1. Synthesis of water-soluble polymers

In this research, the water-soluble polymers were prepared in the same conditions by free radical polymerization. The following monomers were used for the free-radical polymerization: [3-(methacryloylamino)propyl]trimethylammonium chloride solution (ClAPTA) (75 wt.% in water; Aldrich, St. Louis, MO), [2-(acryloyloxy)ethyl]trimethylammonium methyl sulfate (SAETA) (80 wt.% in water; Aldrich) and commercial poly(diallyl dimethyl ammonium) chloride, P(ClDDA), (20 wt.% solution in water, Aldrich).

The experimental procedure for the synthesis of P(ClAPTA) and P(SAETA) by free radical polymerization was as follows: approximately five grams of each monomer and 1 mol% ammonium persulfate (AP, Aldrich), used as an initiator, 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 product was dissolved in water, purified with ultrafiltration membranes, and fractionated by ultrafiltration membranes with different molar mass cut-offs (MMCO) range (10,000, 30,000, 50,000, and 100,000 Da). Polymerization yield in mass over a fraction above than 100,000 g mol^{-1} were 99% for P(ClAPTA) and 77% for P(SAETA). The structures of the different polymers used in this study are summarized in Fig. 1.

2.2. FT-IR and ^1H NMR spectroscopy

The characterization of water-soluble polymers P(ClAPTA) and P(SAETA) was carried out by FT-IR and ^1H NMR spectroscopy. Fourier transformed-infrared spectroscopy was performed with a 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 with a multinuclear Bruker AC 250 spectrometer at 250 MHz at room temperature using D_2O as the solvent.

2.3. Electrochemical oxidation of As(III) to As(V)

The possibility of using water-soluble polymers as supporting electrolytes in the electrochemical process was evaluated. At first, conductivity measurements were performed in aqueous solutions containing increasing concentrations of different polymers used in this study. As expected, both the concentration and molecular weight of polymers significantly influence solution conductivity [14]. Increasing polymer size and concentration simultaneously diminished the conductivity values but all the investigated polymers can overall be regarded as efficient electrolytes whose conductivity values fall in the range of commonly used aqueous electrolytes.

The efficiency of electro-oxidation of As(III) to As(V) was evaluated using the carbon/polymer/Pt nanocomposites-modified electrodes previously synthesized and reported [19]. The polymer films were grown by oxidative polymerization on carbon felt (RVC 2000, 65 mg cm^{-3}, from Le Carbone Lorraine) electrodes (20 mm × 20 mm × 4 mm) using a polymerization charge of 5 Coulomb. This led to the deposition onto the carbon felt of a polymeric material containing about 8–9 μmol of ammonium groups (polymerization yield 35–40%). The precipitation of platinum metal in the polymer was performed by electroreduction at–0.2 V vs. Ag|AgCl in 10^{-4} M K_2PtCl_4; a charge of 5 Coulomb was passed, which corresponds to deposition of 5 mg of platinum. Glassy carbon electrodes (3 mm diameter) were also previously modified in order to obtain the sensor nanocomposite material for As(III) monitoring by anodic oxidation [19].

All electrochemical experiments were carried out using an EGG PAR model 273 potentiostat equipped with an *x*–*y* recorder. A standard three-electrode cell was used for analytical experiments. Potentials are referred to the Ag|AgCl in 3 M KCl reference electrode in aqueous electrolyte.

The electrocatalytic oxidation of As(III) to As(V) at carbon felt modified macroelectrodes was tested in solutions containing a water-soluble polymers, P(ClAPTA), P(SAETA), and P(ClDDA), as supporting electrolyte, which are able to com-

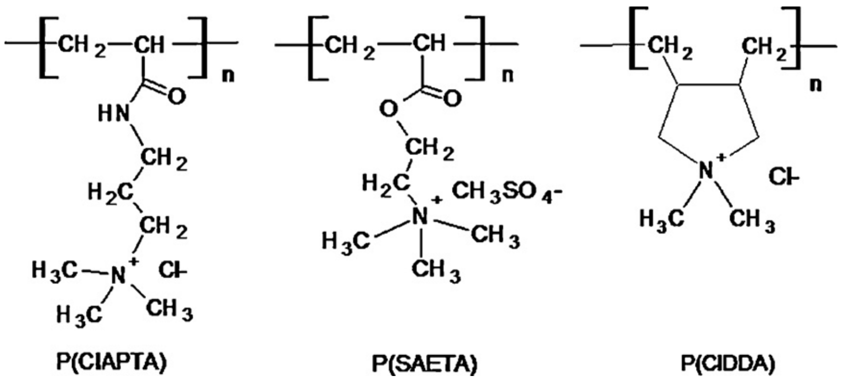

Fig. 1. Structures of the water-soluble polymers: poly[3-(acryloylamino)propyl]trimethylammonium chloride, P(ClAPTA), poly[2-(acryloyloxy)ethyl]trimethylammonium methyl sufate, P(SAETA) and poly(diallyl dimethyl ammonium) chloride, P(ClDDA).

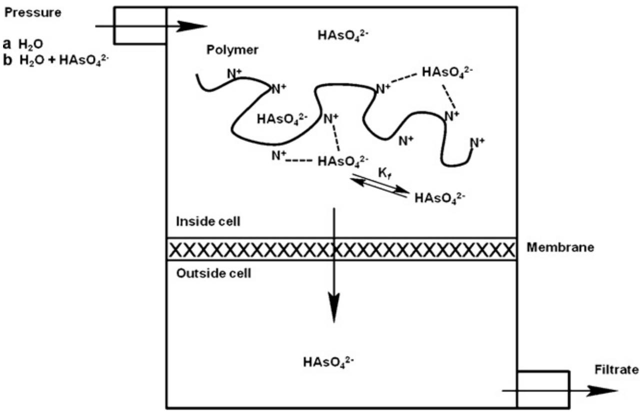

Fig. 2. General procedure of arsenate extraction using LPR technique at pH 8. The different experiments, (a) washing method, (b) enrichment method.

plex As(V) oxy-anionic species. Several electrolyses were carried out in different experimental conditions, at a 20:1 polymer:As(III) molar ratio (As(III) 7.5×10^{-4} M, water-soluble polymer 15×10^{-3} M).

2.4. The LPR technique

The ability of some polymers based on ammonium salts to remove arsenate species in solution by the LPR technique has been studied [17,18].

Different modes of separations by LPR can be used for inorganic ions. The first one is the washing method (see Fig. 2a). This is a batch-like method where a liquid sample containing the polymer and the ions to be separated is placed in the ultrafiltration cell at a given pH and ionic strength. This is then washed with the reservoir water solution that may reproduce the same pH and ionic strength values. Using the washing method, several experiments at 20:1 polymer:As(V) mole ratios in the feed were studied. The different mole of the polymer in the range above 100,000 g mol^{-1} were dissolved in twice-distilled water and added together with the solution containing the minimum of 7.5×10^{-4} M of arsenate to the cell solution.

The solutions were brought to 20 mL of total volume, and the pH was adjusted to 3, 6, and 9 by adding 10^{-1} M HNO_3 or NaOH in separate experiments (by Merck). The reservoir's washing water was at the cell's same pH. The ultrafiltration experiments were performed under a total pressure of 3.5 bar at room temperature using a ultrafiltration membrane with a MMCO of 10,000 Da. 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.

The second mode is the enrichment method, analogous to a column method (see Fig. 2b). A solution containing the metal ions to be separated is passed from the reservoir through the ultrafiltration cell containing a polymer solution. Both cell and reservoir solutions may be adjusted to the same values of pH and ionic strength. The pH was controlled by a pH meter (H. Jürgen and Co.).

The enrichment method, to determine the polymer's maximum capacity, of polymer was used in aqueous solution with 4×10^{-3} M of As(V) solution and 8×10^{-4} mol of water-soluble polymers at 300 mL of total filtrate volume.

Arsenic concentration was measured in the filtrate by atomic absorption spectrometry (AAS) using a Perkin Elmer 3100 spectrometer. The amount of arsenic species retained was determined from the difference with the initial concentration.

3. Results and discussion

3.1. Characterization of water-soluble polymers

The main fractions of each polymer (above 100,000 g mol^{-1}) were characterized by Fourier transform-infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance (^{1}H NMR).

The FT-IR studies were performed in the range of 400–4000 cm^{-1} for both cases. The spectra showed the following main characteristic absorption bands (in cm^{-1}): around of 3430 cm^{-1} (N–H stretching), around 3000 cm^{-1} (C–H stretching) and of 1732 cm^{-1} (C=O stretching of the ester bond). The bending band of the quaternary ammonium groups ($-N^+(CH_3)$) is seen round 1483 cm^{-1}. In comparison with P(ClAPTA), P(SAETA) shows the distinctive asymmetric stretching (1056 cm^{-1}) and symmetric stretching (980 cm^{-1}) (S=O) bands of the tetrahedral SO_4^{2-} group (see Fig. 3).

The ^{1}H NMR spectra of 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 vinyl bond, indicated that the polymerization was achieved. The ^{1}H NMR assignments of the homopolymers were as follows. For P(ClAPTA), protons of the main chain: $\delta = 1.5$ ppm (1H), $\delta = 1.7$ ppm (2H), protons of side groups: $\delta = 2$ ppm (2H), $\delta = 3.17$ ppm (2H), $\delta = 3.3$ ppm (2H) and $\delta = 3.1$ ppm (9H) for the quaternary ammonium group. In the case of P(SAETA), protons of the main chain: $\delta = 1.8$ ppm (2H) and $\delta = 2.43$ ppm (1H). Protons of the side groups: $\delta = 3.72$ ppm (2H), $\delta = 4.5$ ppm (2H) and $\delta = 3.20$ ppm (9H) for the quaternary ammonium group. The difference between P(ClAPTA) and P(SAETA) signals correspond to $\delta = 3.69$ ppm (3H) for the $CH_3OSO_3^-$ group in the case of the last one.

3.2. Electrocatalytic oxidation of As(III) to As(V)

Efficient extraction of arsenic species can be performed by associating the liquid-phase polymer based retention (LPR) procedure, based on the As(V) adsorption properties of cationic water-soluble polymers, with the previous electrocatalytic oxidation (EO) process of As(III).

The electrocatalytic oxidation of As(III) has already been largely investigated at different platinum electrodes, including platinum wire [20–22] or disc [23] electrodes. More recently it has been especially shown that the platinum nanoparticles modified carbon electrodes results in greater arsenic sensitivity than platinum

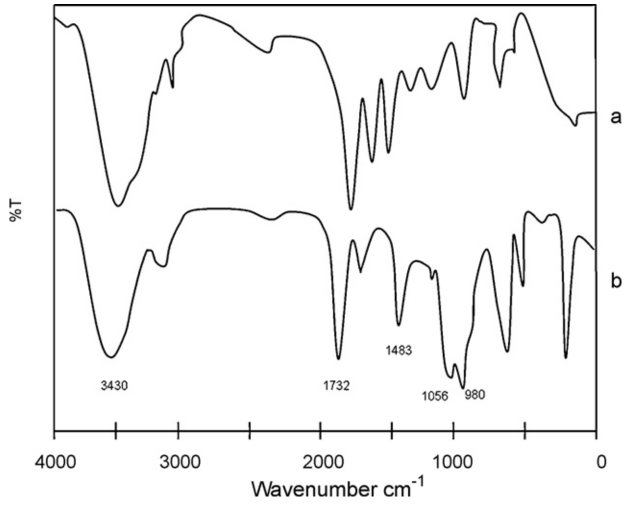

Fig. 3. Fourier transformed-infrared spectroscopy in KBr pellet of: (a) P(ClAPTA), (b) P(SAETA).

Table 1
Charge applied, peak current of As(III) remnant, pH and time measured during the advancement of the electrolysis of 7.5×10^{-4} M of As(III) to As(V) at the preparative scale using C|poly1-$\mathrm{Pt^0}$ carbon felt modified working macroelectrode (E = +0.7 V vs. Ag/AgCl). Retention percentage (R%) of As(V) previously electro-oxidized.

Water-soluble polymer	Total charge applied (C)	Peak current (μA)	pH during electrolysis	Total time of electrolysis (min)
P(ClDDA)				
	0	4.2	9.8	0
	1.6	2.68	7	20
	2.6	1.65	5.8	40
	4.3	0.12	5.6	60
P(ClAPTA)				
	0	7.04	9.2	0
	1	5.66	6.1	20
	2	4.02	4.9	40
	3	2.62	4.2	60
	4.3	1.37	3.9	120
P(SAETA)				
	0	16.2	3.3	0
	2.2	10.1	3.2	20
	3.2	7.12	3.1	42
	4.3	3.25	3	52

macroelectrodes [24]. The As(III) to As(V) conversion is likely electrocatalyzed by the formation of platinum hydroxide on the electrode surface [22,23]:

$$\mathrm{Pt(OH)} + \mathrm{As(OH)_3} \leftrightarrows \mathrm{Pt(OH)As(OH)_3} + \mathrm{H^+} + \mathrm{e^-} \tag{1}$$

$$\mathrm{Pt(OH)As(OH)_3} \rightarrow \mathrm{Pt} + \mathrm{OAs(OH)_3} \tag{2}$$

Thus, there is a clear need for stable electrode materials affording better electrocatalytic oxidation properties toward arsenite anions in solution. Noble metals and metal oxides can be used for this purpose especially in the form of particles of nanometer size, particularly as electrode materials formed from the dispersion of nanoparticles in functionalized polymer matrices [19].

The electrocatalytic oxidation of As(III) at preparative scale using carbon felt modified macroelectrodes (carbon/polymer/Pt) was tested in solutions containing as supporting electrolyte a water-soluble polymer able to complex As(V) oxy-anionic species. In a typical experiment, a solution of arsenite and cationic polymer at a 20:1 polymer:As(III) molar ratio (As(III) 7.5×10^{-4} M, polymer 15×10^{-3} M) was submitted to electrocatalytic oxidation. The solution of As(III) was electrolyzed at +0.7 V vs. Ag/AgCl until the complete conversion of As(III) to As(V) was achieved. The progress of the oxidation of As(III) to As(V) was checked *in situ* using an analytical modified electrode of the same material (carbon/polymer/Pt).

The electrolysis was conducted in a one-compartment cell, without separator between the working modified electrode and the auxiliary electrode (a platinum basket). During the electrolysis, the solution was stirred at 1000 rpm. The pH was measured at each point of electrolysis (see Table 1). The theoretical charge for the complete oxidation was 4.3 Coulombs, calculated according to Coulomb law (Q = number electrons × 96,500 × As(III) concentration).

The solution's pH was above 9 before the oxidation using P(ClDDA) and P(ClAPTA) and around 3 for P(SAETA). At the end of oxidation, the pH decreased to acidic for all the cases due the oxidation processes correspond to acidic catalysis. However, when P(ClDDA) was used, the pH did not decrease below 5 in the course of the electrolysis, probably because P(ClDDA) gives buffer properties towards As(III) oxidation in comparison with the other polymers. Moreover, the protons generated were subsequently reduced to hydrogen at the Pt-basket counter electrode. As expected, the use of a Pt counter electrode (i.e., a Pt-basket set around the working electrode) improved the system due to the good catalytic activity of platinum for proton reduction.

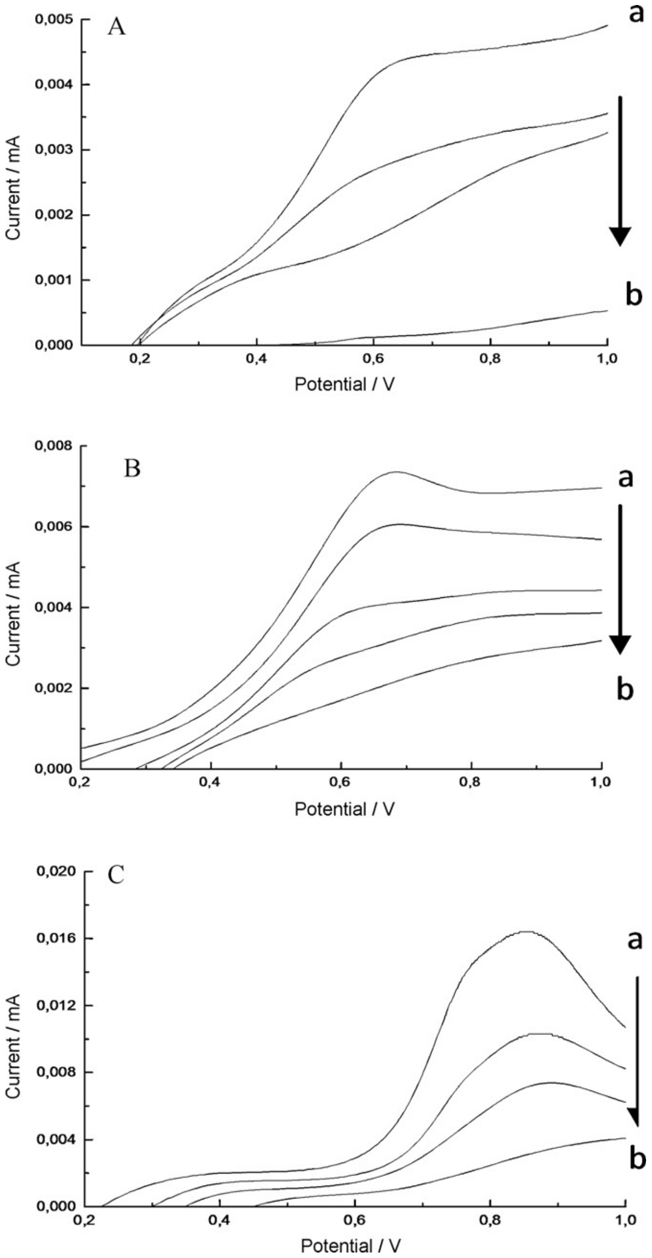

Fig. 4. Exhaustive oxidation experiments of 7.5×10^{-4} M of As(III) at a carbon/polymer/Pt carbon felt modified macroelectrode, using (A) P(ClDDA), (B) P(ClAPTA) and (C) P(SAETA) as supporting polyelectrolyte. The anodic voltammetry shows the advancement of electrolyses (carried out at E = +0.7 V vs. Ag/AgCl), monitored *in situ* by recording at a carbon/polymer/Pt analytical modified electrode. The decrease of the anodic CV peak corresponding to the remnant As(III) species.

The progress of the oxidation of As(III) to As(V) was monitored *in situ* using an analytical modified electrode (glassy carbon/polymer/Pt) [19] as an amperometric sensor to determine the remaining arsenite (see Fig. 4A–C). Compared to our previous work [13] performed in bulk platinum electrodes, the use of a (carbon/polymer/Pt) modified electrode allows catalytic oxidation of As(III) at a lower potential.

The use of these kinds of water-soluble polymers as a support electrolyte for the arsenite electrochemical oxidations was tested. These polymers show excellent behavior in both, for exhaustive oxidation and for analytical measurements. Using (A) P(ClDDA), the (B) P(ClAPTA) containing $\mathrm{Cl^-}$ counter ion shows the oxidation potential between +0.6 V and +0.7 V (see Fig. 4A and B). On the other hand, the use of P(SAETA) as a support in the electrochemical process increases the current response of arsenite measurements at +0.8 V (see Fig. 4C). The counter ion Cl^- on the water-soluble polymer was important factor in order to obtain a lower oxidation potential during the electrolysis, it was due to better charge transport by this class of support water-soluble polymers. All the investigated polymers can overall be regarded as efficient electrolytes whose conductivity values fall in the range of commonly used aqueous electrolytes [14].

The results showed a complete conversion of As(III) to As(V), reaching the theoretical charge calculated for the process under these conditions. The exhaustive oxidation of the As(III) solution was completed in less than 2 h (see Table 1).

3.3. Removal of arsenic by LPR technique

In order to determine the polymer's retention capacity of arsenic ions from solution using the ultrafiltration technique, two factors need to be defined: (1) Retention (*R*) and (2) Filtration factor (*Z*). Retention is the fraction of ions remaining in the cell, according to the expression:

$$R = \frac{M^{c}}{M^{init}} \tag{3}$$

where M^c correspond to the absolute amount of ions that are retained in the cell and M^{init} is the absolute amount of ions at the start of the experiment.

The filtration factor (*Z*) is the ratio between the total volume of permeate and the volume of retentate:

$$Z = \frac{V_f}{V_o} \tag{4}$$

Depending on the experimental data, a graph (retention profile) in which *R* is represented as a function of *Z* can be drawn. Using the LPR technique, different separation types can be performed. In the washing method, the solution containing the arsenic ionic species and the polymer is placed into the cell with an ion solution and is ultrafiltrated by eluting with pure solvent. This method is similar to diafiltration or the batch method. In the enrichment method, the polymer solution is placed inside the cell and ultrafiltrated, creating a flow of liquid with an ion through the cell [15].

The main advantages are that it is also possible to obtain selectivity towards oxy-arsenic ions in solution and the technique has the capacity of water-soluble polymer regeneration as well as a low cost.

The first arsenic retention experiment was done in order to compare the removal capacity of As(V) and As(III) at pH 9 and a polymer:arsenic (20:1) molar ratio using the LPR technique-washing method in separate experiments.

The results show the high affinity of the polymer to interact and remove As(V) species and the non-retention of As(III) species. This can be explained by the speciation of As(III) in aqueous media. Different As(III) species are present in solution [4], according to the pH: $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-}, with $pK_{a1} = 9.2$, $pK_{a2} = 12.1$ and $pK_{a3} = 13.4$. Therefore, at pH 9, the As(III) species are in equilibrium between the non-dissociated salt and the mono arsenic oxy-anion. On the other hand, As(V) species coexist in an aqueous medium according to the pH: $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}; pK_{a1}: 2.2; pK_{a2}: 7.0 and pK_{a3}: 11.5.

The retention capacity of the polyelectrolyte is in direct relation with the anion exchange of the counter ion corresponding to quaternary ammonium of polyelectrolyte because in these systems the electrostatic interactions are predominant. The literature suggests that the anionic exchange prefers more divalent ions than monovalent ions for the same conditions [17]. This can be confirmed by the high retention capacity of As(V) species and the non-retention of As(III) species using the water-soluble polyelectrolyte at pH 9 with the LPR technique [19].

3.4. The effect of pH on As(V) retention

After consumption of the charge required for the exhaustive oxidation of As(III) to As(V), the pH of the electrolyzed solution was adjusted to 3, 6, and 9 with HNO_3 or NaOH. Then the resulting solution (polymer:As(V) of 20:1 mole ratio) was assayed with the LPR-technique by the washing method and the arsenic concentration in the filtrate was determined by atomic absorption spectrometry. In these experimental conditions, at basic pH, the arsenic retention achieved was between 70% and 100%, and was maximum for polyelectrolytes with chloride as a counter ion: 100% for P(ClDDA) (see Fig. 5A), 94% for P(ClAPTA) (see Fig. 5B), and 70% for P(SAETA) (see Fig. 5C) at $Z = 10$. However, at pH 3, the species of monovalent arsenate prevail and the clearance is below 5%.

In general, As(V) is more easily retained at a pH between 6 and 9 than 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 polymer's functional group should be a parameter to control ion exchange selectivity. At pH 6, the monovalent ($H_2AsO_4^-$) and divalent ($HAsO_4^{2-}$) oxy-arsenic species exist in equilibrium. The retention capacity of the polymer is due to the presence of a positively charged quaternary ammonium group. These interactions are produced through the anion exchange between counter ion of quaternary ammonium salt and the arsenate anions. This can be corroborated by the higher retention capacity of the polymers at basic pH because divalent As(V) species are predominant.

This behavior is similar to the previous results obtained in the study of the influence of the counter ion in the arsenate retention [18]. Finally, we checked that arsenic recovery was 0% for a solution containing water-soluble polymer and As(III) in a 20:1 mol ratio that has not been submitted to electrolysis (see Fig. 5 curve (■)).

The permeate flux was different for each experiment at 3.5 bar of pressure and pH 9 showing almost the same permeate flux for polymers with chloride counter ion such as P(ClDDA) and P(ClAPTA) ($0.5\,mL\,min^{-1}$) and lower for P(SAETA) ($0.4\,mL\,min^{-1}$). Moreover, the permeate flux also depends on the pH, showing higher permeate flux for experiments at acid pH and lower at basic pH. For example, P(ClDDA) presented permeate flux of 0.8, 0.6 and $0.5\,mL\,min^{-1}$ for pH 3, 6 and 9, respectively.

The results confirm that the combination of the LPR with the electrocatalytic oxidation of arsenic at a polymer–platinum nanocomposite film modified electrode might be a useful technique for arsenic removal from contaminated solutions.

3.5. Maximum retention capacity of arsenate through the enrichment method

The maximum retention capacity (*C*) of arsenate by the water-soluble polymer was determined by the enrichment method. This method consists in adding the maximum concentration of the arsenate anion to the polymer solution so that the polymer can bind in order to reach saturation. The maximum retention (enrichment method) is defined as:

$$C = \frac{M\,V}{\mathrm{Pm}} \tag{5}$$

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. The maximum retention capacity of arsenate C was calculated in the total volume of filtrate (300 mL). Assuming a quantitative retention of As(V), the

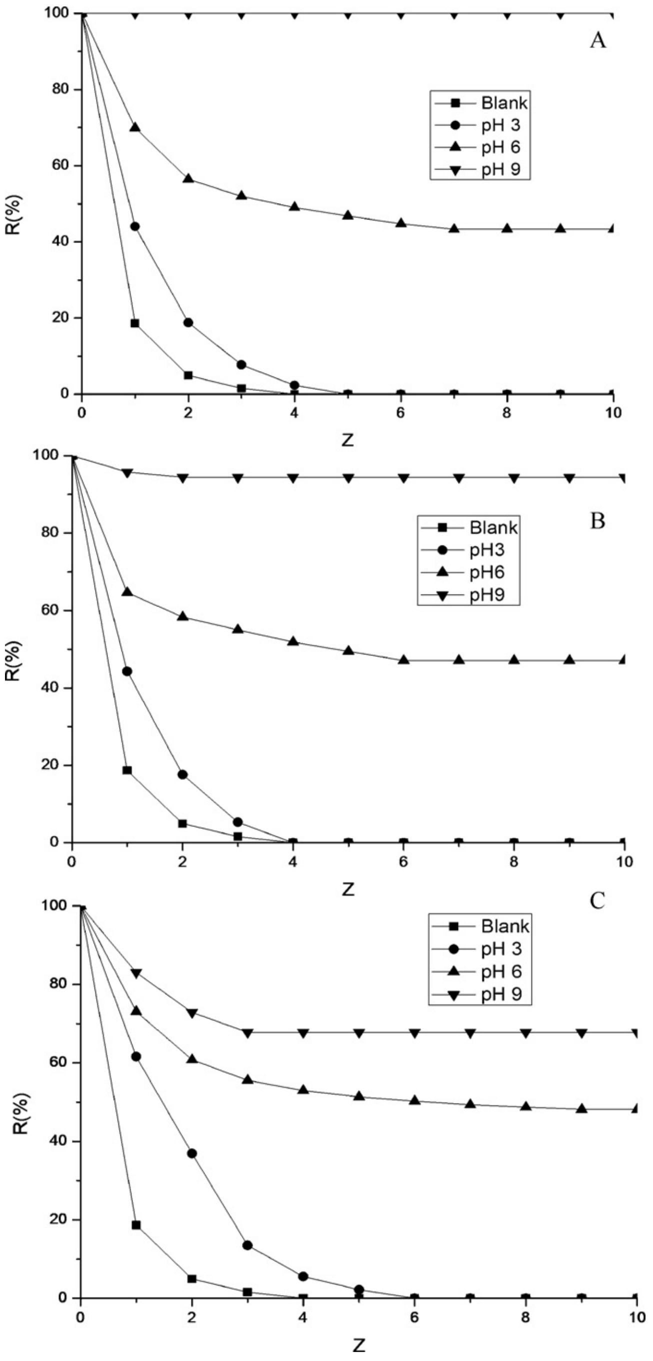

Fig. 5. Retention profile of As(III) after exhaustive oxidation of the solution and without oxidation (blank; ■) using (A) P(ClDDA), (B) P(ClAPTA), (C) P(SAETA) as a extracting agent, at different pH, with 2×10^{-4} mol absolute polymer and 1×10^{-5} mol absolute As(V) ion.

enrichment factor E is a measurement of the binding capacity of the polymer and it is determined as follows:

$$E = \frac{PC}{M} \tag{6}$$

where P is the concentration of polymer ($\mathrm{g\,L^{-1}}$). As 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. From the difference in the slopes, the amounts of arsenate ions bound to the polymer and free in solution as well as the maximum retention capacity can be easily calculated (see Fig. 6).

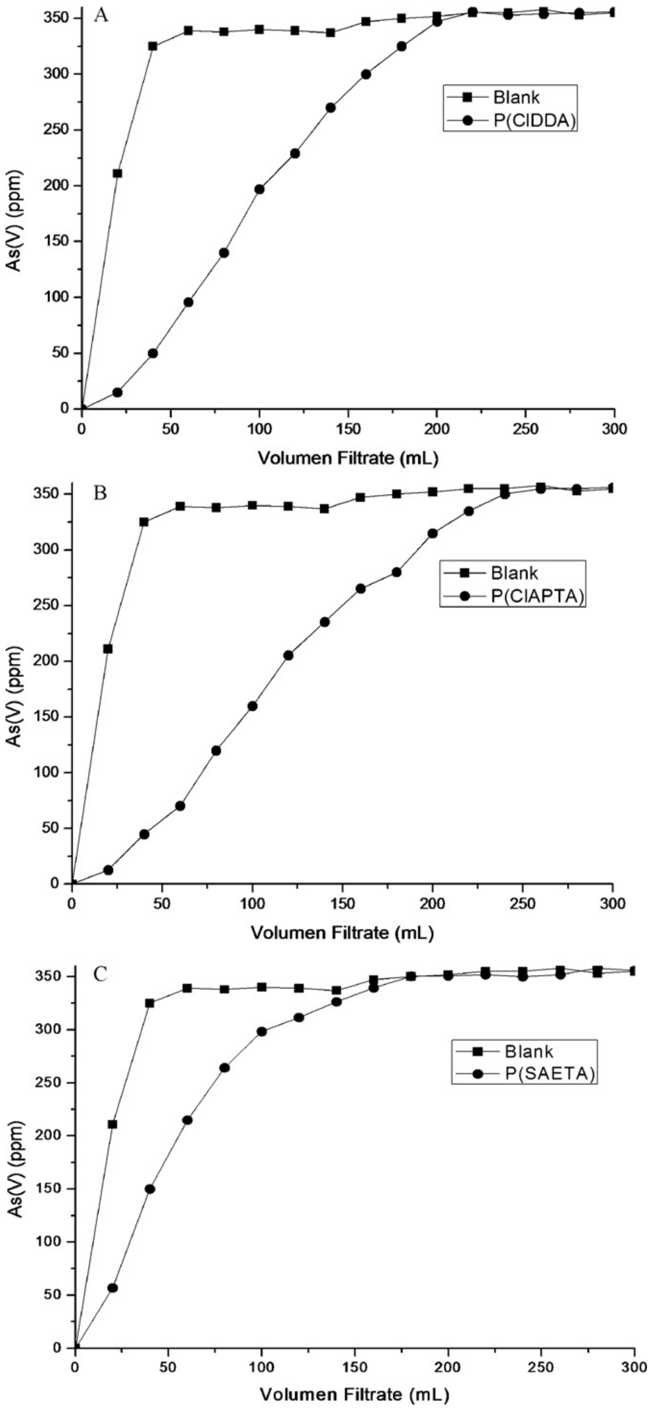

Fig. 6. Maximum retention capacity of arsenate using (A) P(ClDDA), (B) P(ClAPTA), (C) P(SAETA) as a extracting agent at pH 9. Mole ratio of 8×10^{-4} mol of polymer and 4×10^{-3} mol of As(V). The blank (■) is the experiment without polymer.

The maximum retention capacity (C) and enrichment factor (E) for all the polymers are summarized in Table 2. The highest retention capacity was found for polymers with counter ion $\mathrm{Cl^-}$, such as P(ClDDA) and P(ClAPTA) (see Fig. 6A and B), compared to P(SAETA) (see Fig. 6C) that contain $\mathrm{CH_3OSO_3^-}$. The nature of counter ion was a more important factor for the maximum retention of arsenate ions than the position of the quaternary nitrogen with respect to polymer chain, showing almost the same behavior for P(ClAPTA) and P(ClDDA) in all the experiments.

The interaction between the polymer and arsenate was not purely electrostatic, presumably because of the formation of a cova-

Table 2
Maximum retention capacity of arsenate and enrichment factor of water-soluble polymers.

Polymer	Maximum retention capacity (*C*), mg As(V)/g polymer	Enrichment factor (*E*)
P(ClAPTA)	380	7.5
P(ClDDA)	369	9.4
P(SAETA)	79	2.5

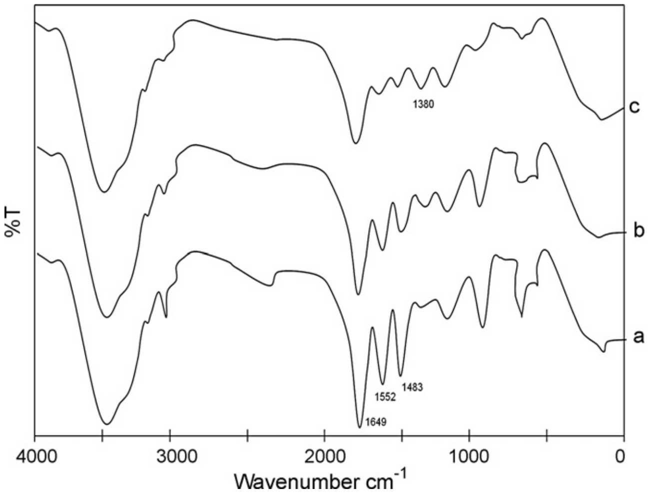

Fig. 7. FT-IR spectra (KBr) of (a) poly[(3-acryloylamine) propyl]trimethylammonium chloride P(ClAPTA), (b) P(ClAPTA) with arsenate at pH 4, (c) P(ClAPTA),with arsenate at pH 8.

lent bond between a partially movable functional group on the polymeric network and one on the oppositely charged arsenate anion. This pairing may be explained by the water structure induced by ion pairing, where the larger and more polarizable ions disrupt the local water structure and associate more easily with a given quaternary ammonium ion [25].

The FT-IR spectra of P(ClAPTA) before and after the maximum retention capacity of the polymer with As(V) are shown in Fig. 7. In the high region of the spectra, only the vibrations of a functional group corresponding to P(ClAPTA) could be identified. Some modifications were observed in the spectra in the 1700–1300 cm^{-1} range. The band intensity at 1649 cm^{-1}, corresponding to the C=O stretching vibration, was taken as a reference. Following the addition of arsenate at different pH, a marked decrease in band intensity at 1552 cm^{-1} [coupling of ν(C–N) and δ(N–H)] and 1482 cm^{-1} by δ(–N$^+$(CH$_3$)] was observed, along with the appearance of a new band at 1380 cm^{-1} from arsenate groups corresponding to ν(As=O) [26,27].

The fact that the band intensity at 1380 cm^{-1} depends on the pH clearly supports that there is an interaction between the polymer and the arsenate oxy-anions. The intensity of this band at pH 4 was lower than at pH 8, indicating a weaker interaction with arsenate anions at lower pH. The band at 845 cm^{-1} was assigned to the ν(As–O) stretching vibration. At lower frequencies, the region of 200–500 cm^{-1}, deformation modes showed one strong band at 369 cm^{-1} by δ(As–O).

4. Conclusions

This study showed that the combination of the liquid phase polymer based technique with the electrocatalytical oxidation of As(III) to As(V) retention is an effective process to remove the hazardous As(III) species from aqueous solution.

We have also shown the capability of the nanocomposite electrode materials (carbon/polymer/Pt) to carry out bulk electrocatalytic oxidation of arsenite solutions at a lower potential in the presence of a water-soluble poly(quaternary ammonium) salts acting as supporting electrolyte and also as agent to remove As(V) species. The results showed a complete conversion of As(III) to As(V), reaching the theoretical charge calculated for the process under these conditions. The exhaustive oxidation of the As(III) solution was completed in less than 2 h. These are decisive advantages in their application since they do not require the addition of other reagents such as salts in the medium of homogeneous electrocatalytic processes.

The highest retention capacity of the polymers was at basic pH. After the electrochemical oxidation, all the polymers remove more efficiently arsenate ions at pH 9 than in the range of pH 6–3. At basic pH, arsenic retention achieved was between 70% and 100%, reaching its maximum for polyelectrolytes with chloride as a counter ion: 100% for P(ClDDA), 94% for P(ClAPTA) and 70% for P(SAETA) at *Z* = 10.

The enrichment method shows the maximum retention capacity for arsenate anions in aqueous solutions at pH 9. The type of anion exchanger was an important factor in the maximum retention capacity of arsenate.

Future work will focus on the development of a on line LPR-electrocatalysis process, where electrolysis is carried out directly inside the LPR cell or in a separated cell inserted in the fluid circuit and connected to the reservoir of the LPR equipment. In this context, the use of a flow cell equipped with a porous carbon felt-modified electrode with a nanocomposite material is as an attractive approach.

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