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Liquid-Phase Polymer-Based Retention of Chromate and Arsenate Oxy-Anions

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Summary: The retention of chromate and arsenate anions was studied by liquid-phase polymer based retention (LPR) technique by washing and enrichment methods. The extracting agents were water-soluble cationic polymers (WSCPs) containing quaternary ammonium salts with chloride or methylsufate counterions. Through to washing method, the Cr(VI) and As(V) removal experiments were carried out at different pH (3, 6, 9) using WSCPs. The results showed highest retention capacity of Cr(VI) and As(V) at pH 9. The retention capacity in both cases was optimum for polymers containing chloride counterions. The decrease in the arsenic retention ability of the WSCPs is likely due to an increase in the ionic strength of solution by the presence of different concentrations of Na_2SO_4 or NaCl. The study of polymer:anion ratio showed the optimum molar ratio as 10:1 and 20:1 for efficient chromium and arsenic removal respectively. The maximum retention capacity (MRC) was determined by the enrichment method. It was between 79 to 165 mg ion retained/g polymer.The FT-IR spectra of polymer-anion were compared after and before to the maximum retention capacity showing differences due to the presence of Cr(VI) ions.The retention-elution process shows that the elution process of the arsenate ions from polymers can be performed when the polymer-arsenate was in contact with the acid solution from the reservoir.

Keywords: maximum retention capacity; pollutant; ultrafiltration membranes; water-soluble cationic polymer

Introduction

Chromium and arsenic are a very toxic chemical species associated to serious problems of environmental pollution as well as several diseases.

Chromium species are mainly present in wastewater from different industries such as metal plating, paints and pigments, leather tanning, textile dyeing, and printing inks and also in additives for wood preservation among others.[1–3] On the other hand, the high arsenic concentrations in the environment are coming from natural sources and human activities such as waste chemicals, the smelting of arsenic bearing minerals, the burning of fossil fuels, and the application of arsenic compounds in many products.[4]

In aqueous solution, chromium and arsenic species are present forming mainly oxy-anions depending on the pH. The chromium species exist mainly with hexavalent and trivalent oxidation states (Cr(VI) and Cr(III) respectively).[3] The arsenic species present in water are mainly arsenate, As(V), and arsenite, As(III).[4–6]

The World Health Organization (WHO) recommends the maximum concentration of chromium (VI) at the level of $50\,\mu g\,L^{-1}$,[7,8] and for arsenic of $10\,\mu g\,L^{-1}$ in drinking water.[9,10]

Several alternative methods have been reported for the removal of chromium and arsenic including chemical precipitation-coagulation, ion-exchange, membrane filtra-

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tion, adsorption, and biological processes, among others.[11–17] However, many of these processes are not widely used due to their disadvantages such as incomplete toxic species removal, requirements for expensive equipment and monitoring systems, or generation of toxic sludge or other waste products that require disposal.[14] Still, the complete extraction of these toxic species from drinking water, wastewaters, and industrial effluents in order to reach acceptable levels still represents a true challenge.

Recent investigations show the possibility to remove chromium or arsenic oxy-anion species using a hybrid method of membrane separation called polymer enhanced ultrafiltration.[18–29] This method is also known as liquid-phase polymer-based retention (LPR). The LPR technique involves the simultaneous use of ultrafiltration membranes and functional water-soluble polymers to separate and concentrate low molecular weight species in aqueous solution. These low molecular weight species interact with the functional groups of water-soluble polymers forming a new macromolecular species with a size larger than the pore diameter of the membrane and therefore are retained.[23,30,31]

In LPR, two kinds of experiments can be identified: a) washing method, which is an elution method based in the continuous diafiltration by addition of solvent at constant volume and b) enrichment method, which is a concentration method based in the continuous diafiltration by addition of solvent and metal ions at constant volume. This method is used to determine the maximum retention capacity of the water-soluble polymer.

In the present study the removal of chromate and arsenate oxy-anions is analyzed by LPR technique using water-soluble cationic polymers (WSCPs) through washing and enrichment methods. The extracting agents are polymers containing quaternary ammounium salts such as poly[3-(acryloylamino)propyl]trimethylammonium chloride, P(ClAPTA), poly(ar-vinyl benzyl) trimethylammonium chloride, P(ClVBTA), poly[2-(acryloyloxy) ethyl] trimethylammonium chloride, P(ClAETA), and poly[2-(acryloyloxy) ethyl] trimethylammonium methylsufate, P(SAETA). These polymers were synthesized and fractionated through of membranes with different cut-off.

Using the washing method the removal of chromium (VI) and arsenic (V) was performed at pH 3, 6, and 9 with P(ClAPTA), P(ClVBTA), P(ClAETA) and P(SAETA) with molecular weight above 100,000 g mol^{-1}. The blank experiment without WSCP was done previously at same pHs. The interference of other ions, such as NaCl and Na_2SO_4 in solution, using the washing method at constant ionic strength was analyzed for arsenic removal. The effect of counterion and optimum molar ratio of polymer: anion for efficient separation were also determined.

Through to enrichment experiments the maximum retention capacity (MRC) was determined for Cr(VI) and As(V).

The FT-IR spectra of polymer and polymer-chromate were compared after and before to the MRC.

The retention-elution process of arsenate was performed changing the pH of the solution from basic to acid in two cycles.

Experimental Part

Preparation of WSCPs

The P(ClAPTA), P(ClVBTA), P(ClAETA) and P(SAETA) were prepared by free-radical polymerization. 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 hours.[22,28]

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

The polymers were dissolved in water and purified by ultrafiltration membranes of poly(ethersulfone) with different molar mass cut-offs (MMCO) range (10,000, 30,000, 50,000, and 100,000 Da). The maximum yield (95%) obtained in mass over a fraction above than 100,000 g mol^{-1}.[22,28] The WSCP structures are in the Figure 1.

Fourier Transform-Infrared (FT-IR) Spectroscopy

The characterization of polymers and polymer-chromate was carried out by FT-IR spectroscopy. FT-IR was performed with a Magna Nicolet 550 and Nexus Nicolet spectrometers. For quantitative analysis 1mg of the sample per 100 mg of KBr was employed.

LPR Technique

In this study, two different modes of LPR were used to remove chromium (VI) and arsenic (V) oxy-anions. The first one is the washing method (see Figure 2a), which is a batch-like procedure wherein washing is performed with water at constant pH. Before carrying out ultrafiltration the pH of the solution was adjusted to 3, 6, and 9 by adding 10^{-1} M HNO_3 or NaOH in separate experiments (Merck). The pH was controlled by a pH-meter (H. Jürgen and Co.). A solution of 300 mg L^{-1} of $K_2Cr_2O_7$ (Merck) and $Na_2HAsO_4.7H_2O$ (Merck) were used. The mixture polymer-anion was stirred at room temperature, and then placed in the ultrafiltration cell (Amicon). The solution was introduced to the ultrafiltration cell and washed with reservoir water at the same pH. The ultrafiltration was carried out under a total pressure of

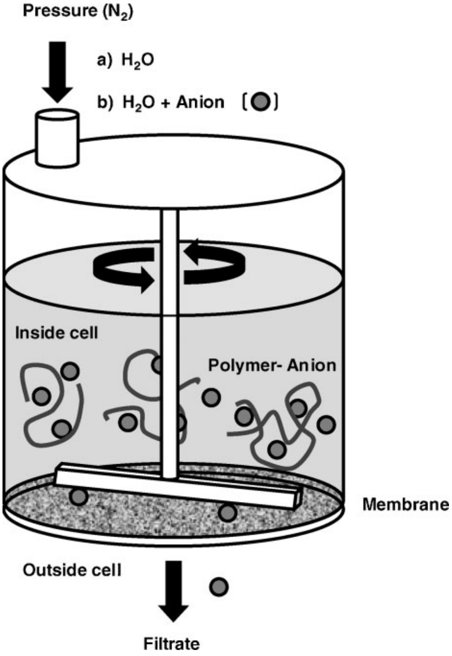

Figure 2.
Procedure of oxy-anions removal using LPR technique. The different experiments: a) washing method, b) enrichment method.

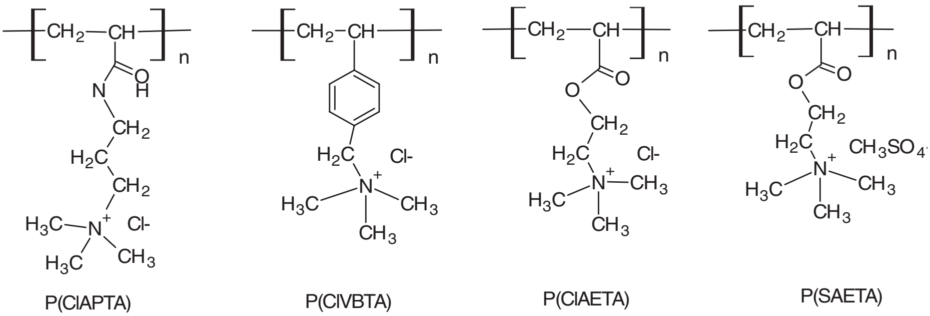

Figure 1.
Structures of WSCP: poly[3-(acryloylamine) propyl] trimethyl ammoniumchloride, P(ClAPTA), poly(ar-vinyl benzyl) trimethylammonium chloride, P(ClVBTA), poly[2-(acryloyloxy) ethyl] trimethylammonium chloride, P(ClAETA), poly[2-(acryloyloxy) ethyl] trimethylammonium methyl sufate, P(SAETA).

1 bar using a ultrafiltration membrane with molecular mass cut-off, (MMCO), 10,000 Da. Total cell volume was kept constant during the filtration process. All the experiments, in the case of pH studies, were performed with a solution of polymer and Cr(VI) or As(V) (20:1 polymer:anion mole ratio) using 30 mg L^{-1} of Cr(VI) or As(V). Chromium and arsenic concentration were measured in the filtrate by atomic absorption spectrometry (AAS) using a Perkin Elmer 3100 spectrometer. Results of the Cr(VI) or As(V) uptake are systematically presented as the percentage of retention R (%) versus the filtration factor Z (volume of filtrate/volume of the cell).

The second ultrafiltration mode is the enrichment method, analogous to a column method (see Figure 2b). A solution containing the toxic oxy-anions to be separated is passed from the reservoir through the ultrafiltration cell containing a WSCP solution. Both cell and reservoir solutions may be adjusted to the same values of pH and ionic strength.

The enrichment method, to determine the MRC of WSCP, was performed passing a solution of 2.5×10^{-3} M of Cr(VI) (131 mg L^{-1}) from the reservoir to the cell containing 2.5×10^{-4} mol of WSCP and collected 150 mL of total filtrate volume. In the case of arsenic, 4×10^{-3} M of As(V) solution and 8×10^{-4} mol of WSCP were used and collected 300 mL of total filtrate volume.

In the retention-elution process, the enrichment method and washing method were alternately used. In both cases, a blank experiment (in the absence of the WSCP) is included in order to evaluate the interaction of the membrane with toxic anions.

Results and Discussion

Removal of Cr(VI) and As(V) by LPR Washing Method

Two values need to be defined for determine the retention capacity of Cr(VI) or As(V) oxy-anions from solution: (1) Retention (R) and (2) Filtration factor (Z).

Retention is the fraction of toxic oxy-anions remaining in the cell according to the expression:

$$R = [\mathrm{Anion_{cell}}]/[\mathrm{Anion_{init}}] \qquad (1)$$

where [Anion $_{\mathrm{cell}}$] corresponds to the absolute amount of oxy-anions that are retained in the cell and [Anion $_{\mathrm{init}}$] is the absolute amount of oxy-anions at the start of the experiment.

The filtration factor (Z) is the ratio between the total volume of permeates (V_p) and the volume of retentate (V_{cell}):

$$Z = V_p/V_{\mathrm{cell}} \qquad (2)$$

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

Effect of pH on Cr(VI) and As(V) Removal

Chromium (VI) and arsenic (V) normally exists in the anionic form in aqueous environments. Chromium is mainly present in water as $Cr_2O_7^{2-}$, $HCrO_4^-$ or CrO_4^{2-} forms depending on the pH and concentration. At pH value below 1 the predominant species is chromic acid (H_2CrO_4). In acidic media with pH value of 2–4 Cr(VI) exists mostly in the form of dichromate ($Cr_2O_7^{2-}$) ions. At pH between 4 and 6 $Cr_2O_7^{2-}$ and $HCrO_4^-$ ions exist in equilibrium, and under alkaline conditions (pH 8) it exists predominantly as chromate anion (CrO_4^{2-}).[22,32] On the other hand, As(V) species coexist in an aqueous medium as oxy-anion 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 respectively.[26]

The removal experiments of chromate and arsenate were performed in function of pH by washing method. The pH was previously adjusted to 3, 6, and 9 in both the LPR cell and the water reservoir. Then the resulting solution polymer:anion of 20:1 mole ratio was carried out with the LPR-technique by the washing method. In these experimental conditions, at pH 9, the retention of Cr(VI) (see Figure 3) and As(V) (see Figure 4) was maximum for all the WSCP studied.[22,23]

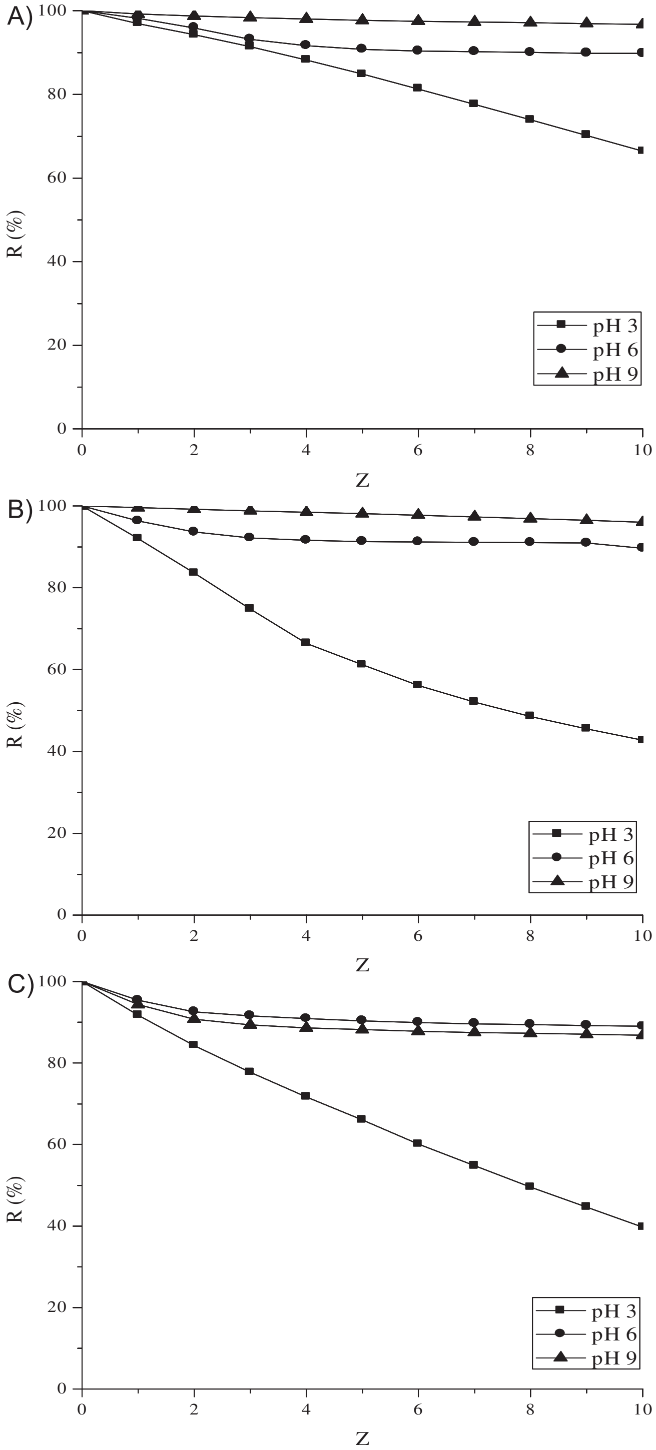

Figure 3.

Retention profile of Cr(VI) using (A) P(ClVBTA), (B) P(ClAPTA) and (C) P(SAETA), at different pHs, with 2×10^{-4} mol absolute polymer and 1×10^{-5} mol absolute Cr(VI).

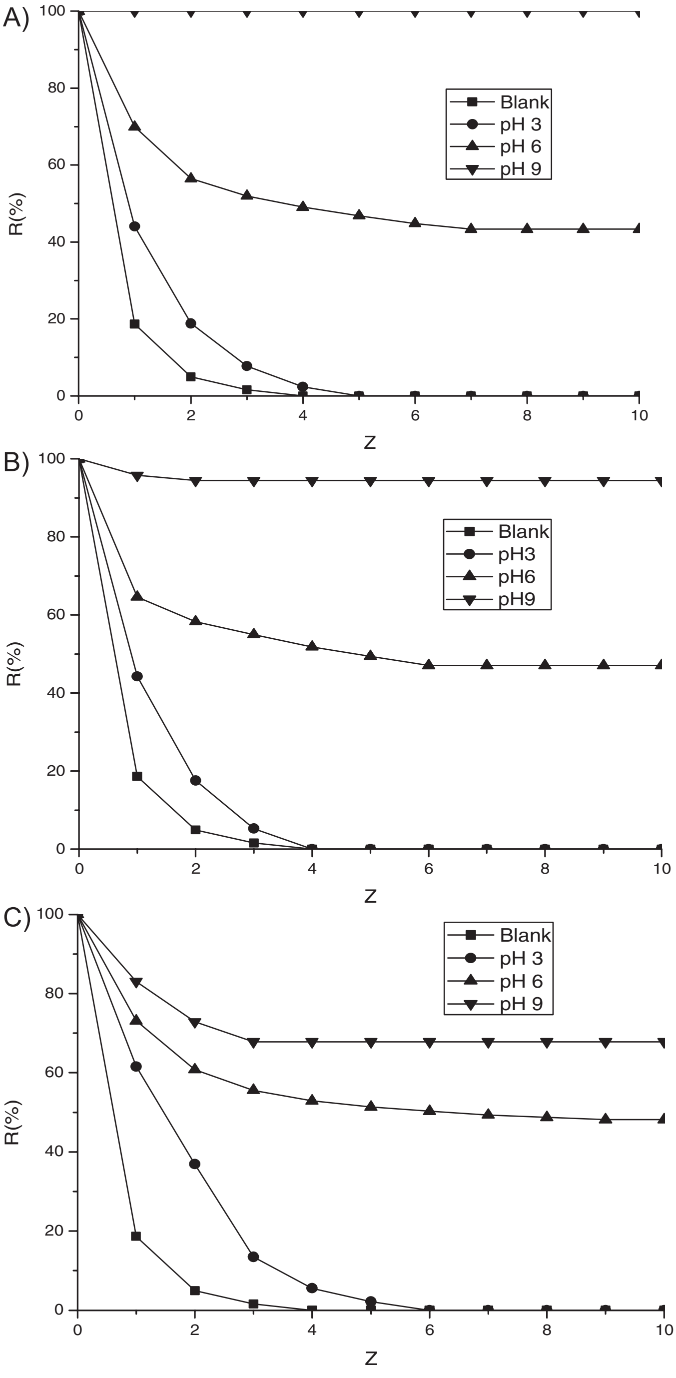

Figure 4.
Retention profile of As(V) using using (A) P(ClVBTA), (B) P(ClAPTA) and (C) P(SAETA), at different pHs, with 2×10^{-4} mol absolute polymer and 1×10^{-5} mol absolute As(V).

The retention capacity of these oxy-anions by the WSCP is mainly due to the presence of a positively charged quaternary ammonium group of the polymer. The polarity of the functional group is assumed to be a parameter to control the selectivity of ion exchange. The interactions are produced mainly through the anion exchange between counterion of the polymer and the chromium or arsenic anion species, preferably with divalent charge. This can be corroborated by the higher retention capacity of the polymers at pH 9 because divalent CrO_4^{2-} or $HAsO_4^{2-}$ species are predominant. The chromium and arsenic removal decreased at pH 6 because $Cr_2O_7^{2-}$ and $HCrO_4^-$ or $HAsO_4^{2-}$ and $H_2AsO_4^-$ ions exist in equilibrium. The retention of chromium and arsenic was low at pH 3 compared to basic pH in both cases. However, the removal of chromium (VI) by LPR technique using the washing method with WSCP was suitable in a wide range of pH.[22]

On the other hand, we checked the chromium recovery in blank experiments, without WSCP (blank), to determine the influence of the regenerated cellulose membrane for the chromium retention. In order to compare with the WSCP the same experimental conditions were used; 5.71×10^{-6} mol absolute Cr(VI) in 10 mL of solution and 1bar of pressure. The results showed that the membrane interact with chromium oxy- anions, preferably at pH basic than acid (see Figure 5), for a wide range of Z. However, these interactions were finally weak because at $Z = 10$ the removal of chromium below to 10% at pH 9.[22] We can consider depreciable the influence of the membrane for chromium removal in our experimental conditions.

Effect of Polymer Counterion on Cr(VI) and As(V) Removal

The results demonstrate the influence of the counterion of the WSCP. Polymers with chloride exchanger groups, such as P(ClAPTA), P(ClAETA) and P(ClVBTA), show a higher ability to remove Cr(VI) or As(V) ions than the polymer that contains methyl sulfate as anion exchanger group, P(SAETA), at the same conditions. Polymers with chloride exchanger groups have the highest capacity to remove these oxy-anions at basic pH. The results can be attributed to the easier release of the

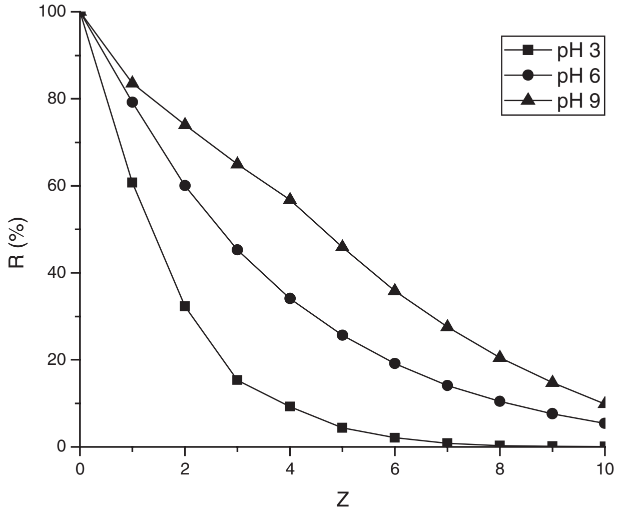

Figure 5.
Blank removal experiments without cationic hydrophilic polymers at different pH using 1×10^{-5} mol absolute Cr(VI) in 10 mL of solution and 1bar of pressure.

chloride anion in comparison with the methyl sulfate anion, which are associated with the quaternary ammonium groups (see Figure 3 and Figure 4).

The results confirm that the WSCP with chloride counterion used in conjunction with ultrafiltration membranes might be a useful technique for chromium or arsenic removal from contaminated solutions.

Optimum Polymer:Anion Molar Ratio

The removal of chromium (VI) and arsenic (V) was optimized by changing the polymer:anion ratio in moles. The influence of the concentration of polymers in the chromium and arsenic removal was studied using the washing method.

Different polymer: Cr(VI) molar ratios such as 40:1, 20:1, 10:1, and 5:1 were prepared at pH 9. The results of retention R (%) of Cr(VI) with a filtration factor of $Z = 10$ are shown in Table 1. The retention capacity was limited by the polymer concentration when 5.71×10^{-6} mol absolute Cr(VI) ($30\,\mathrm{mg\,L^{-1}}$) was used. The results indicate an optimum of 10:1 (polymer:Cr VI) molar ratio for all the polymers in order to reach the maximum chromium (VI) removal. The maximum removal in these molar ratio conditions were 100% for P(ClAPTA), 99% for P(ClVBTA), and 88% for P(SAETA). The effect of the conformational changes of cationic polymer and cannot be discarded.

The influence of the concentration of polymers P(ClAETA) and P(ClVBTA) in the arsenate removal was studied using the washing method. Different of polymer:-As(V) molar ratios such as 31:1, 20:1, 10:1, 6:1 and 3:1, were prepared at pH 9. The results of retention R (%) of As(V) with a filtration factor of $Z = 10$, P(ClVBTA) and P(ClAETA) by the washing method are presented in Table 2. The retention capacity of WSCP was determined when 10–84 $\mathrm{mg\,L^{-1}}$ arsenic concentration range was used.

The results indicate an optimum of 20:1 (polymer:arsenate) molar ratio for the complete removal of arsenate. This happened even in two range orders of magnitude: 2×10^{-4} and 7×10^{-5} mol of polymer. This is important from the point of view of application due to the high efficiency of the polymer with respect to the recovery of the toxic species, even at high concentrations.

Competitive Effect of other Monovalent and Divalent Anions on Arsenate Retention at Constant Ionic Strength

The WSCP present the highest retention of arsenate species by the LPR technique

Table 1.
Behavior of different molar ratio polymer:Cr(VI) in the removal of chromate using P(ClVBTA), P(ClAPTA), and P(SAETA) at pH 9.

Molar ratio Polymer: Cr(VI)	Mole of polymer	Mole of Cr(VI)	P(ClVBTA) R(%)	P(ClAPTA) R(%)	P(SAETA) R(%)
(40:1)	2.28×10^{-4}	5.71×10^{-6}	96	94	74
(20:1)	1.14×10^{-4}	5.71×10^{-6}	97	96	87
(10:1)	5.71×10^{-5}	5.71×10^{-6}	99	100	88
(5:1)	2.86×10^{-5}	5.71×10^{-6}	96	93	69

Table 2.
Behavior of different molar ratio polymer:As(V) in the removal of arsenate using P(ClVBTA) and P(ClAETA) at pH 9.

Molar ratio Polymer: As(V)	Mole of polymer	Mole of As(V)	P(ClVBTA) R(%)	P(ClAETA) R(%)
(31:1)	7×10^{-5}	2.25×10^{-4}	70	84
(20:1)	7×10^{-5}	3.45×10^{-6}	10	100
(20:1)	2×10^{-4}	1.00×10^{-5}	100	100
(10:1)	7×10^{-5}	6.90×10^{-6}	88	59
(6:1)	7×10^{-5}	1.12×10^{-5}	77	60
(3:1)	7×10^{-5}	2.25×10^{-5}	54	14

when no other anions are present in the solution.

In order to determine the influence of other anions, different experiments in presence of divalent and monovalent anions, such as a sulfate and chloride, were performed using different concentrations of these salts at basic pH. In this study, we used the washing method at constant ionic strength adding to both the reservoir and the ultrafiltration cell concentrations in the range of 1×10^{-3} M to 1×10^{-1} M NaCl and Na_2SO_4 in separate experiments with a P(ClAETA):As(V) mole ratio of 20:1 inside of ultrafiltration cell.

The arsenate retention is found to decrease with the increasing salt concentration and the increased charge of the added anion. The decrease in the retention was due to the presence of the added salts declining in the following order $Na_2SO_4 > NaCl$.

According to the literature,[33] the order of interference in the arsenic retention is: trivalent ions > divalent ions > monovalent ions. The effect of added electrolytes on arsenic binding to the WSCP can be understood as due to the competition between arsenate and other anions for binding sites on the polymer. The affinity of anions to bind onto the polymer is similar to the behavior observed in the ion-exchange resin containing ammonium groups when removing arsenic by ion exchange process.[28] Another way of explaining the effect is that the electrical double layer is compressed around the polymer as the ionic strength increases, thus reducing the polymer's electrical potential. The divalent anions produce a greater reduction in arsenic retention than the monovalent anions because the divalent anions bind more strongly to the polymer's charged sites and also compress the electrical double layer around the polymer more effectively than the monovalent anions.[34]

It is reasonable that sulfate or chloride anions present different interference toward arsenate retention. The results prove the adsorption of the interfering ions at the same active sites on the polymer, especially in the case of sulfate, which like arsenate has a tetrahedral structure and divalent charge at basic pH. The results showed that arsenic retention decreased from 96% to 20% at $Z = 10$ when just 1×10^{-3} M of sodium sulfate was added. Moreover, arsenate retention dropped to zero when sulfate ion concentration increased to 5×10^{-3} M (see Figure 6b). On the other hand, the competition between arsenate and monovalent chloride was lower than between sulfate and arsenate. In another separate experiment, when the minimum chloride concentration was added, corresponding to 1×10^{-3} M, the arsenate retention capacity of arsenate decreased from 96% to 55% at $Z = 10$ (see Figure 6a).

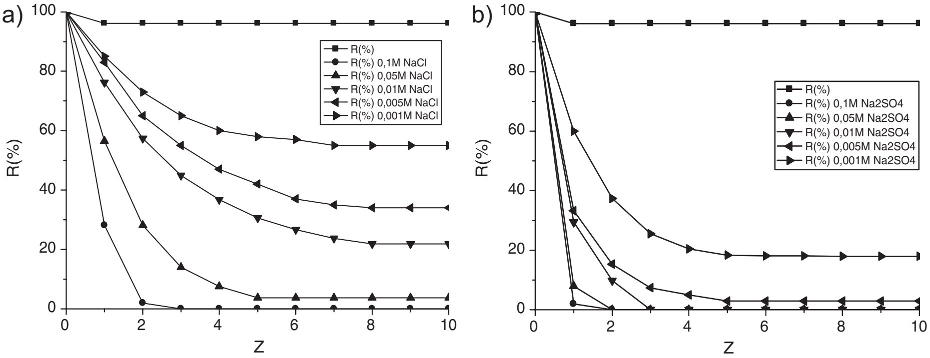

Figure 6.

Retention profile of As(V) by P(ClAETA) in presence of different concentrations of (a) NaCl and (b) Na_2SO_4 in both the reservoir and ultrafiltration cell at pH 8, using molar ratio 20:1 polymer:As(V) (3.2×10^{-4} mol:1.6×10^{-5} mol).

This behavior shows that when the concentration of chloride was increased, it was blocking the polymer active sites and the retention of arsenate was decreasing gradually. These results proved that when the ionic strength increases the retention capacity of the polymer decreases due to the competition between ions in solution. This behavior depends directly of the type and charge of ion interfering. Even at a low concentration, interfering ions block and diminish the extracting capability of the WSCP.

Maximum Retention Capacity by the Enrichment Method

The maximum retention capacity of chromium or arsenic ions by WSCP was determined through of the enrichment method. The maximum retention capacity is defined as:

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

where Pm is the amount of polymer (g), M is initial concentration of anion (mg L^{-1}), V is the volume of filtrate (volume set) containing the toxic anion (mL) that passes through the membrane. Assuming a quantitative retention, the enrichment factor (E) is a measurement of the binding capacity of the polymer and it is determined as follows:

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

where P is the concentration of polymer (g L^{-1}). As the anion-polymer interactions are processes in equilibrium, a lower slope in the rate of increase of the anion concentration in the filtrate is observed. From the difference in the slopes the amount of anions bound to the polymer and free in solution as well as the maximum retention capacity can be calculated.

The MRC and E for all the polymers are summarized in the Table 3 for chromate and Table 4 for arsenate.

The highest chromium retention capacity was found for polymers with counterion Cl^{-}, such as P(ClVBTA) (see Figure 7, curve ●) and P(ClAPTA) (see Figure 7, curve ▲), compared to P(SAETA) (see Figure 7, curve ▼) that contains $\mathrm{CH_3OSO_3^-}$. The nature of the counterion was a more important factor for the maximum retention of chromium (VI) ions.

Table 3.
Maximum retention capacity of Cr(VI) and enrichment factor of cationic water-soluble polymers.

Polymer	Maximum retention capacity (C), mg Cr(VI)/g polymer	Enrichment factor (E)
P(ClVBTA)	164	7.5
P(ClAPTA)	152	6.5
P(SAETA)	90	5.0

Table 4.
Maximum retention capacity of As(V) 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

The interaction between the polymer and chromium (VI) was not purely electrostatic presumably because of the formation of a coordination bond between a partially movable functional group on the polymeric network and one on the oppositely charged chromium 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.[22,35]

The FTIR spectra of P(ClVBTA) before and after the maximum retention capacity of the polymer with Cr(VI) are shown in Figure 8. In the high region of the spectra only the vibrations of a functional group corresponding to P(ClVBTA) could be identified. Some modifications were observed in the spectra in the 700 to 1700 cm^{-1} range. The band intensity at 1641 cm^{-1}, corresponding to the C=C of stretching vibration, was taken as a reference. Following the addition of chromium (VI) the appearance of a new band at 1380 cm^{-1} from chromate groups corresponding to $\nu(\mathrm{Cr}=\mathrm{O})$. The band at 891 cm^{-1} was assigned to the ν (Cr–O) stretching vibration.[36] The fact that the

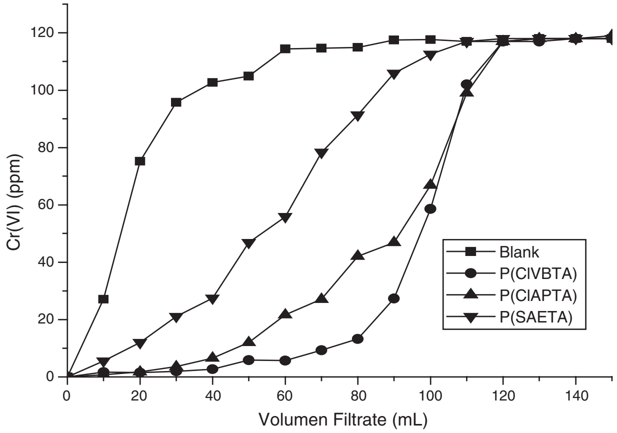

Figure 7.
Maximum retention capacity of Cr(VI) using P(ClVBTA), P(ClAPTA) and P(SAETA) as a extracting agent at pH 9. Mole ratio of 2.5×10^{-4} mol of polymer and solution of Cr(VI) 2.5×10^{-3} M. The blank (■) is the experiment without polymer at pH 9.

band intensity at 1380 cm^{-1} clearly supports that there is an interaction between the polymer and the chromium oxy-anions.

Desorbing of Arsenate: The Retention-Elution Process

In order to study the arsenate retention-elution process, the enrichment method and washing method were alternately used. In these experiments P(ClAETA) and P(SAETA), which differ only from their counter ions, were studied. The first step of the experiment was the saturation of the polymers through the enrichment method, using the conditions previously described: the enrichment method was performed

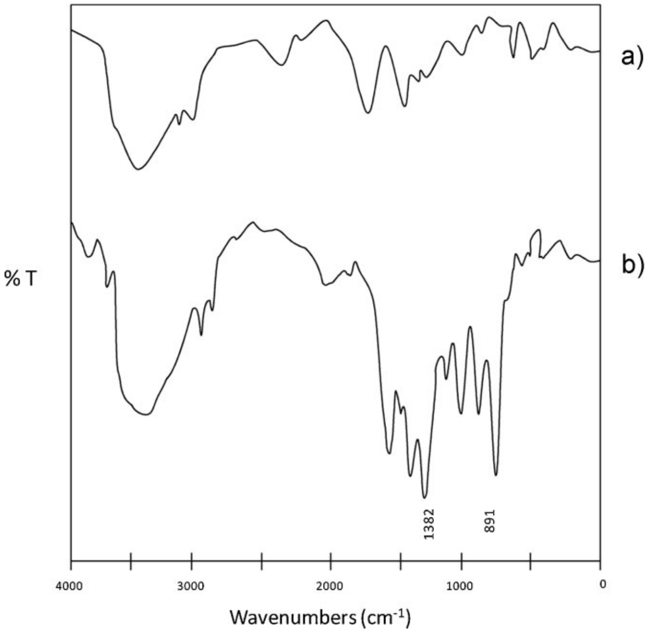

Figure 8.
FTIR spectra (KBr) of (a) P(ClVBTA), (b) P(ClVBTA)-Cr(VI) after the maximum retention capacity at pH 9.

at pH 8, using 8×10^{-4} mol of polymer into the ultrafiltration cell (20 mL) and adding a solution 4×10^{-3} M in As(V) from the reservoir. After reaching saturation, the polymer: As(V) solution was washed in the ultrafiltration cell with reservoir water buffered at pH 3, in a similar way to the washing method. It was assumed that the polymer activity can be recovered in the media's strongly acid conditions media and that this did not significantly affect the polymer's active sites because acid pH was used in the radical polymerization. The same retention-elution process was repeated twice for each polymer in order to determine the capacity of arsenate delivery and to regenerate the extracting ability of the WSCP.

Figure 9 shows the retention-elution behavior for both polymers. Figure 9(a) presents the enrichment process (MRC) reaching the same MRC obtained previously for both polymers at pH 8. The values of C were 165 mg g^{-1} for P(ClAETA) and 79 mg g^{-1} for P(SAETA), and the total filtrate volume was 300 mL.

After the charge process, the discharge process was initiated changing the pH from basic to acid using buffered solution of 1×10^{-1} M HCl. Figure 9(b) presents the discharge process of the arsenate ions from both polymers when the polymer-arsenate is in contact with acid solution (pH 3) from the reservoir. The first discharge of arsenate was effective and was carried out almost entirely in the first 100 mL of solution when a higher ion arsenate concentration is discharged from P(ClAETA) in comparison with P(SAETA) at the same volume. Both polymers discharge all the amount of arsenate at 300 mL of filtrate.

Figure 9(c) shows that the second charge process did not improve the polymers' maximum retention capacity when com-

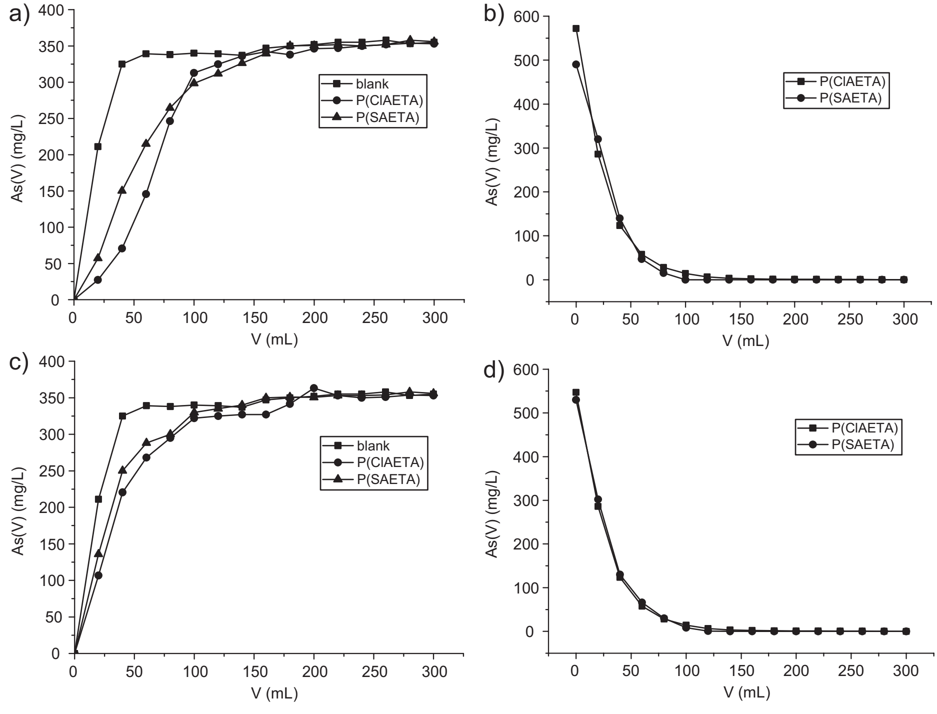

Figure 9.
Retention–elution process of arsenate ions using P(ClAETA) and P(SAETA). (a) first charge process of polymers through enrichment method at pH 8, (b) first discharge process of polymers using washing method at pH 3 with 1×10^{-1} M HCl. (c) recharge of polymers through enrichment method at pH 8, (d) second discharge process of polymers using washing method at pH 3 with 1×10^{-1} M HCl.

pared with the first charge process. P(ClAETA) lost the capacity to remove arsenate, P(SAETA) was only slightly better at the same conditions. The values of C were 83 mg g^{-1} for P(ClAETA) and 47 mg g^{-1} for P(SAETA), and the total filtrate volume was 300 mL. This result is probably due to the presence of more species in the solution when the pH was adjusted from basic to acid in the discharge process and from acid to basic in the second charge process. Finally, the second discharge process (Figure 9(d)) showed almost the same behavior in both polymers, releasing most of the arsenate ions into the filtrate in the first 100 mL in a similar manner.

Conclusion

The liquid-phase polymer- based retention (LPR) has proved to be a convenient method to significantly retain arsenate or chromate anions from solution using a polymer with quaternary ammonium groups.

The study of the pH using the washing method showed highest retention capacity of the polymers at basic pH for both toxic anions.

The polymer P(SAETA) containing bulky counterions ($CH_3OSO_3^-$), which are more hydrophobic than Cl^- ion, showed lower retention capacity. Thus, the nature of the anionic exchanger groups appears to be an important factor in the retention.

The study of polymer:anion ratio showed the optimum molar ratio as 10:1 and 20:1 for efficient chromium and arsenic removal respectively.

The decrease in the retention ability of the cationic polymer is probably due to an increase in the solution's ionic strength following the addition of Na_2SO_4, higher than that NaCl, which induced a change in polarization.

The enrichment method shows the maximum retention capacity for chromium (VI) and arsenic (V) anions between 79 to 165 mg anion retained/g polymer at pH 9.

The interaction between the polymer and chromium (VI) was not purely electrostatic. The FTIR spectra of P(ClVBTA) before and after the maximum retention capacity the polymer show differences due to presence of Cr(VI).

The retention-elution process shows that it is possible to perform the discharge process of the arsenate ions from polymers when the polymer-arsenate was in contact with acid solution from the reservoir.

In the future, this experiment should be repeated several times in order to determine until what point it is possible to use the same polymer in the retention-elution process.

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