

Arsenite Retention Properties of Water-Soluble Metal–Polymers

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ABSTRACT: The properties of water-soluble metal–polymers to retain As(III) from aqueous solution are investigated. Poly(acrylic acid)s with different tin contents are prepared. Amounts of 3, 5, 10, and 20 wt % of tin are added to the polymer. The metal compositions are evaluated by thermogravimetry (TG-DSC) and atomic absorption spectroscopy. Structural properties are analyzed by infrared and ^1H nuclear magnetic resonance spectroscopy, and X-ray diffraction. Additionally, specific surface area was measured using CO_2 as adsorbate. Arsenic retention properties are studied using the liquid-phase polymer-based retention (LPR) technique. The polymers can bind arsenic species

from an aqueous solution in the pH range 4–8. The studies show that the retention capacity is a function of tin content and polymer concentration. At pH 8, the following mol ratios poly(AA)-Sn : As(III) are analyzed: 600 : 1, 400 : 1, 200 : 1, 100 : 1, and 20 : 1. The highest retention, 80%, is obtained with poly(AA)-Sn at 10 and 20 wt % of tin at mole ratios 400 : 1, and at nearly to 20 : 1 or 40 : 1 Sn-As(III). The highest retention is observed at pH 8 and 4. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1889–1894, 2007

Key words: water-soluble metal polymers; metal–polymer complex; membranes

INTRODUCTION

In the last few years, the development of polymers for water treatment as an environmental protection method has been investigated. Conventional methods include water-insoluble polymers, and more recently water-soluble polymers. The development of metal-chelating polymers^{1–5} continues to be a subject of paramount importance, undoubtedly because of their wide application in metal ion separation and monitoring. On the other hand, arsenic is well known for its high toxicity in water, around 0.05 ppm, the standard set by World Health Organization (WHO).⁶ Arsenic's high toxicity depends on its binding form, where organic arsenic compounds are less toxic than inorganic arsenic compounds.

Given that arsenic is a widely distributed element in the earth crust and that it is toxic to all living organisms, it presents a potentially serious environmental concern. It exists naturally in the earth's crust, rock, soil, water, air, plants, and animals. Because of mineral release of arsenic compounds, it can be found in natural surface water and groundwater. Arsenic occurs in a variety of forms and oxidation states. The main arsenic species present in natural waters are arsenate ions (oxidation state V) and arsenite ions (ox-

idation state III). Arsenic consumption would increase the risk of skin, lung, and kidney cancer.

The conventional arsenic elimination techniques from waters involve ion-exchange, precipitation, adsorption, reverse osmosis, and complexation.⁶ It is well known that the coexistence of As ions is controlled by factors such as pH, redox potential, and media solubility. The arsenic(III) species change according to thermodynamic predictions. It is reported that the As(III) form is difficult to separate from water, and it should only be possible after the oxidation step and at very low levels.⁷ Sorption studies for arsenite and arsenate have used a wide range of adsorbents, including iron and aluminum oxides, phyllosilicalites, soil organic matter, and whole soils. Both arsenite and arsenate present high affinity for iron oxides in soil and subsurface environment.⁸ As(III) oxidation is also possible in the presence of manganese oxide-coated sands or by advanced oxidation processes. Arsenic can be removed from waters by coprecipitation with $\text{Fe}(\text{OH})_3$, MnO_2 , or during water softening.⁹ The adsorption characteristics of As(V) and As(III) on titanium dioxide-loaded Amberlite XAD-7 resin have been studied,¹⁰ showing favorable As(III) adsorption in comparison with As(V) in column adsorption experiments for pH 5–10. The separation and enrichment of As(V) with composite resin beads containing magnetite crystals and the solvent extraction of As(V) with ultrafine magnetite particles have recently been investigated.^{11,12}

Although, many of the two-phase methods mentioned have been developed and successfully used,

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their application can be related to problems of heterogeneous reactions and interphase transfer. The membrane filtration methods are among the most promising enrichment technologies for several ions from solutions and their separations.^{13,14} This method is known as the liquid-phase polymer-based retention (LPR) technique.^{15,16}

Water-soluble polymers are commercially available or can be synthesized by different routes.¹⁷ Membrane filtration easily allows the separation of metal ions bound to water-soluble polymers from the non-bound metal ion.¹⁸ Applications of water-soluble polymers to the homogeneous enrichment or selective separation of various metal ions from dilute solutions have been reported. Ultrafiltration is found as the most suitable technique for LPR studies, and a vast amount of data is presently being published.^{19–25}

The aim of this paper is to obtain water-soluble polymers with tin-metal salt added to the poly(acrylic acid) matrix to increase its ability to remove As(III) from an aqueous solution.

EXPERIMENTAL

Reagents

Poly(acrylic acid), (AA), (Aldrich), 35 wt % solution in water, M_w 100,000. Tin chloride hydrated salt, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 99% (Merck). (1000 ppm of As(III) of a $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ solution (Merck) was used.

Preparation of metal–polymers

Poly(acrylic acid) is dissolved in 50 mL of water. The tin chloride solution is added to the vessel reaction in adequate amounts to achieve 3, 5, 10, and 20 wt % percent of the metal over polymer. The pH is adjusted at 6. The reaction is maintained at 35°C under shaking for 24 h. The products are soluble in water, and are subsequently lyophilized. Different samples are characterized by Fourier transformed infrared (FTIR) and ^1H NMR spectroscopy, and TG-DSC.

Procedure

By washing method, x mmol (where $x = 0.2, 1, 2, 4,$ and 6) of the poly(AA)-Sn, with weight molecular over 100,000 g mol^{-1} , are dissolved in twice-distilled water, and the solution containing 0.01 mmol of As(III) is added to the cell solution. The solutions are brought to 20 mL of total volume and the pH is adjusted by adding 0.1M NaOH or 0.1M HNO_3 . The washing water in the reservoir is at the same pH value of the cell. Filtration runs are performed under a total pressure of 3.5 bar by using a ultrafiltration membrane with an exclusion rating of 10,000 g mol^{-1} . The total volume in the cell is kept constant. Fractions

of 20 mL are collected by filtration, and the metal ion concentration is analyzed.

Measurements

Total arsenic concentration is measured in the filtrate by atomic absorption spectrometry using a Perkin–Elmer 3100 spectrometer. The amount retained is determined from the difference with the initial concentration. The pH is controlled by a pH meter (H. Jürgen and Co).

The FTIR spectra are recorded with a Magna Nicolet 550 and Nexus Nicolet spectrometers. Nevertheless, it is difficult to quantitatively monitor a polymer material because the polymer material is barely ground, and therefore a given quality sample with different particle sizes strongly affects the IR spectrum profile. In the present work, there is no control of particle size. Only the fraction obtained with a membrane with a defined molecular mass cut off, MMCO, is considered. Consequently, by quantitative analysis, 1 mg of the sample per 100 mg KBr is employed. The NMR spectra are recorded with a multi-nuclear Bruker AC 250 spectrometer at 250 MHz, room temperature, and D_2O as solvent.

The thermal behavior under N_2 is studied with a thermogravimetric analyzer using a TGA 625 from Polymer Laboratories. The heating rate is $10^\circ\text{C min}^{-1}$. Weight of samples: 0.5–3 mg.

Specific area of polymers in solid state are measured in Micromeritic Gemini model 2379 and adsorption volumetric system with a pressure transducer MKS Baratron 170 M. During 2 h, 100 mg of sample is maintained under N_2 flow at 60°C. The essays are performed using CO_2 as adsorbate at 0°C.

RESULTS AND DISCUSSION

Synthesis and characterization of water-soluble metal polymers

Polymers and copolymers of acrylic acid and its derivatives are widely used as macroligands.¹⁷ The chelating process of a metal ion by a polymer may be preceded by long-range attractive interactions. Once the metal ion is condensed on the polymer surface, it is site-fixed by the polymer ligands.

The characterization studies were performed to identify the metal–ligand binding. Structural studies by FTIR spectroscopy are performed in the range 400–4000 cm^{-1} and 100–600 cm^{-1} . In the FTIR spectra of poly(AA)-Sn, prepared with different tin contents, the most important absorption bands (in cm^{-1}) appear at: 3437 $\nu(\text{OH})$; 2928–2861 $\nu(\text{C—H})$ of CH_2 and CH groups; 1720 $\nu(\text{C=O})$ of carboxylic acid groups; 1567 $\nu_{\text{asym}}(\text{COO}^-)$ groups; 1407 $\nu_{\text{sym}}(\text{COO}^-)$, and so on. For pure poly(AA), the doublet at

1451–1400 cm^{-1} is observed with the maximum intensity at 1451 cm^{-1} , differing from poly(AA)-Sn where the intensity is inverted. This result suggests that the band at 1407 cm^{-1} for poly(AA)-Sn would be a symmetric carboxylate, $\nu_{\text{sym}}(\text{COO}^-)$, produced by the interaction with tin salt, which is enhanced. This result is corroborated by the enhancement of band intensity at 1612–1567 cm^{-1} attributed to $\nu_{\text{asym}}(\text{COO}^-)$. The presence of asymmetric and symmetric bands corresponding to COO^- groups on the poly(AA)-Sn samples can be used to identify the binding metal–ligand. It is remarkable that as tin content increases from 3 to 20 wt %, there is an increase of intensity of the carboxylate group band and also a displacement towards lower frequencies in this region from 1612 to 1567 cm^{-1} , respectively. It is assumed that a positive resonance effect by the carboxylate anion in the presence of tin will decrease the binding order, thus decreasing the vibrational frequency. In the zone 800–100 cm^{-1} , the gradual decrease and absence of the band at 336 cm^{-1} $\nu(\text{Sn}-\text{Cl})$ and the gradual appearance of the band at 777 cm^{-1} $\nu(\text{Sn}-\text{O})$ was observed when tin content is increased from 3 wt % up to 20 wt %, which is indicative of Sn–O bond formation. Some authors²⁶ attribute the band at 540 cm^{-1} to Sn–O bond, and the bands at 780 and 630 cm^{-1} characteristics of SnO_2 . It has been also reported²⁷ that tetragonal SnO has characteristic bands at 650, 480 cm^{-1} and the SnO_2 , a medium intensity band at 670 cm^{-1} , a shoulder at 610 cm^{-1} , and a strong band at 312 cm^{-1} .

TG-DSC is a method used for the qualitative and quantitative evaluation of tin content. The range of analysis was room temperature up to 550°C. The primary thermograms for all polymers present a typical sigmoidal shape curve. The zone used in the evaluation of tin content was 300–500°C for all the samples. In the DSC, it can be observed that the maximum decomposition temperature occurs in each step. The poly(AA) degrades in steps, showing a well-defined maximum at 205°C. The salt $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ presents a maximum at 428°C. The poly(AA)-Sn samples present two maxima defined at nearly to 390 and 480°C.

The evaluation of tin content by atomic absorption presented good linearity with $R^2 = 0.9916$. The results are summarized in Table I.

The ^1H NMR spectrum of poly(AA) and poly(AA)-Sn shows the following signals (in ppm): 1.67–2.00 corresponding to H^1 of (CH_2) group, at 2.4, H^1 of (CH) group. At higher field, 7.0 appears the signal of OH group. The signal at 4.8 ppm corresponds to the protons of solvent.

Specific surface area by CO_2 is measured on the lower relative pressure range. It is observed that the adsorbent's capacity is higher on a poly(AA) support and decreased with the tin content in the samples, indicating that the area decreases with a higher tin

TABLE I
Tin Composition for Poly(AA)-Sn Polymers by Thermogravimetry and Atomic Absorption Spectrometry

Polymer acronym	Theoretical wt % of tin	Tin composition (wt %)	
		TG-DSC	Atomic absorption
P(AA)	–	–	–
P(AA)-Sn	3	3.8	2.7
P(AA)-Sn	5	4.8	4.0
P(AA)-Sn	10	8.7	7.4
P(AA)-Sn	20	–	15

content in the samples. Surface areas are evaluated by isothermal BET CO_2 with 72 $\text{m}^2 \text{g}^{-1}$ for poly(AA) and in the order of 10 up to 20 $\text{m}^2 \text{g}^{-1}$ for poly(AA)-Sn samples.

X-ray diffraction confirmed poly(AA)-Sn sample crystallinity, resulting an amorphous poly(AA). The crystallinity increases due to the higher metal content. The poly(AA)-Sn samples clearly present a maximum I/I_0 of a tin oxide at $d_{\text{hkl}} = 2.8203 \text{ \AA}$. An average crystal size of 46–100 nm was calculated based on the peak's width at half height in the diffractogram.

Arsenic retention properties of the water-soluble polymers

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

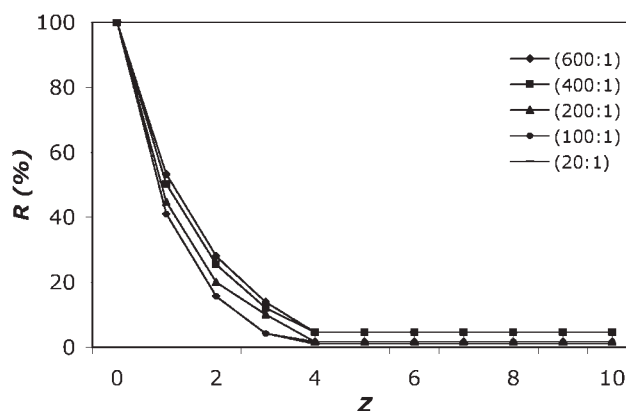


Figure 1 Retention profiles for As(III) at pH 8, using SnCl_2 -P(AA), with 3 wt % tin. Polymer: As(III) mol ratio: \blacklozenge 600 : 1, \blacksquare 400 : 1, \blacktriangle 200 : 1, \bullet 100 : 1.

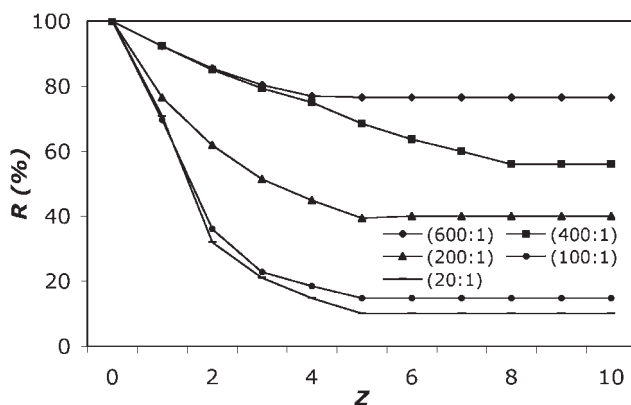


Figure 2 Retention profiles for As(III) at pH 8, using poly(AA)-Sn, with 5 wt % tin. Polymer:As(III) mol ratio: \blacklozenge 600 : 1, \blacksquare 400 : 1, \blacktriangle 200 : 1, \bullet 100 : 1, — 20 : 1.

obtained with nearly 90% of retention at a mole Sn-As(III) ratio close to 20 : 1, and a poly(AA)-Sn : As(III) ratio of 400 : 1.

The effect of the metal-polymer complex concentration is presented in Figures 1–4 for 3, 5, 10, 20 wt % of tin content, respectively. Assays with poly(AA)-Sn : As(III) mole ratios of 20 : 1, 100 : 1, 200 : 1, 400 : 1, and 600 : 1 were performed at constant pH 8. In all cases, a higher tin content improved the retention performance. At a constant tin content of 3 wt %, the retention degree is negligible. At 5, 10, and 20 wt %, the retention improved with the highest yield at 600 : 1 and 400 : 1 mol ratios. This increased concentration involves a higher number of available functional groups. However, the polymer amount does not induce an exactly proportional increase in the retention, with the optimum Sn-As(III) ratio found close to 20 : 1. Additionally, to compare the profile for samples with 5 and 10 wt % theoretical tin content at a constant poly(AA)-Sn : As(III) mol ratio, the higher retention is remarkable when the tin content is increased in 100%. These effects are well shown in

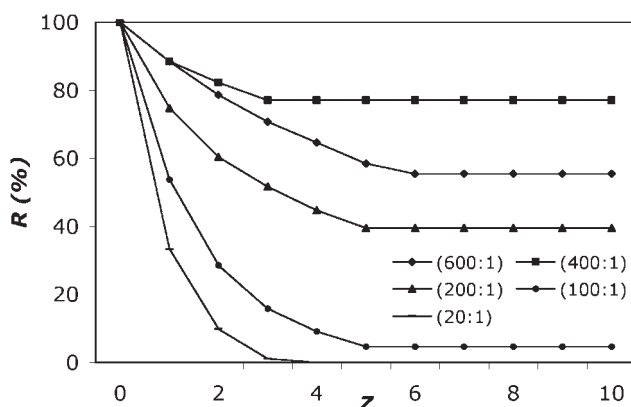


Figure 3 Retention profiles for As(III) at pH 8, using poly(AA)-Sn with 10 wt % tin. Polymer:As(III) mol ratio: \blacklozenge 600 : 1, \blacksquare 400 : 1, \blacktriangle 200 : 1, \bullet 100 : 1, — 20 : 1.

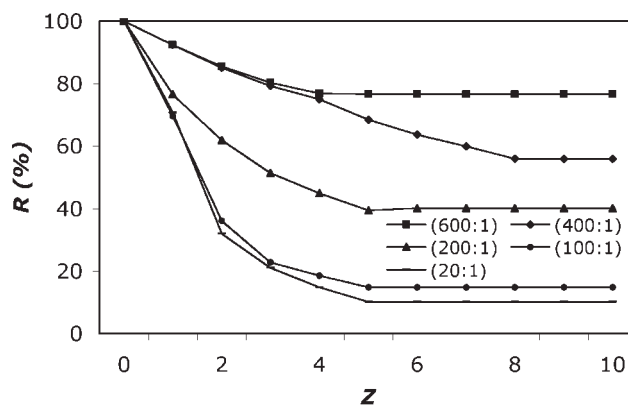


Figure 4 Retention profiles for As(III) at pH 8, using poly(AA)-Sn, with 20 wt % tin. Polymer:As(III) mol ratio: \blacklozenge 600 : 1, \blacksquare 400 : 1, \blacktriangle 200 : 1, \bullet 100 : 1, — 20 : 1.

Figure 5, with a filtration factor $Z = 10$ and a different mol ratio poly(AA)-Sn : As(III).

The retention $R = 80\%$ indicates that As(III) species are strongly bound at basic pH, such as sample 400 : 1 at 10 and 20 wt % tin content. In the second case, As(III) probably suffers a partial oxidation to As(V) due to the sample's higher tin content. However, assays in progress of speciation in solution²⁸ show that the majority remains as As(III) with traces of As(V), less than 10 wt % in the filtrate solution.

It is assumed that the functional groups' polarity should be one parameter controlling selectivity. The polymer's binding capacity is attributed to the surface metal-polymer complexes. This bond is presumably between (positively charged) tin and the oxygen of the arsenite or arsenate forming a dipole.

Dependence studies of the work's pH with the samples' tin content at constant mole ratio over arsenite solution are now presented. Depending on the pH value, ionized poly(AA) may form complexes with D_{2h} or D_{4h} (dimers) symmetry. At higher pH values, the poly(AA) chain has a drawn shape due to electrostatic repulsion of charged carboxylate groups; thus,

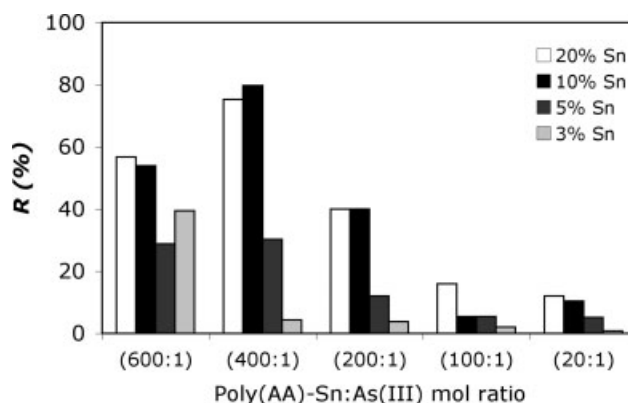


Figure 5 Retention values for As(III) at different polymer:As(III) mol ratio and tin content for $Z = 10$ and pH 8.

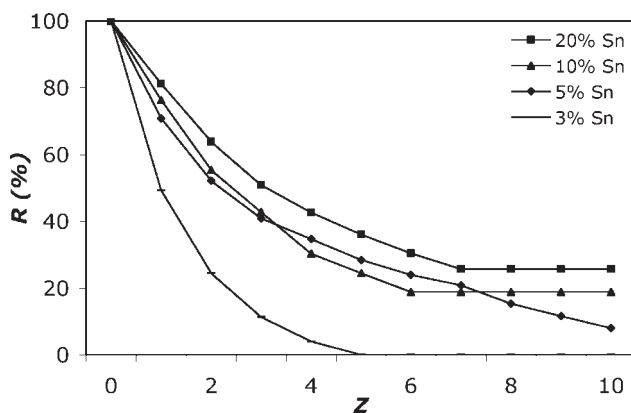


Figure 6 Retention profiles for As(III), at pH 6, at polymer-As(III) mol ratio = 400 : 1 and different tin contents.

metal ions are binding with either one or two neighbor groups. At pH 4.8, the macromolecular globule contracts and the metal ions are able to coordinate with 2–4 carboxylic acid groups.

The pHs 8, 6, and 4 are studied. Figure 6 presents the retention profile at pH 6 for the samples with 20, 10, 5, and 3 wt % tin content at mole ratio 400 : 1. The retention is lower than that at pH 8, with a maximum value of $R = 30\%$.

Figure 7 shows the retention profile at pH 4 for 20, 10, and 5 wt % of tin content. The highest retention, 80%, is found for poly(AA)-Sn with 20 wt % tin content. It is suggested that the media's conditions, in the presence of oxygen from the air and water, could produce oxidation of As(III) in filtrate solution. Nevertheless, the speciation by hydride abstraction²⁸ shows a high percent of As(III) in solution and the polymeric solution with an arsenic total quantification close to that in the feed of As(III).

Figure 8 shows the similarity in retention for the As(III) and As(V) profiles at $Z = 10$. The retention percentage as a function of tin content and different pH's shows that the best performances are found at

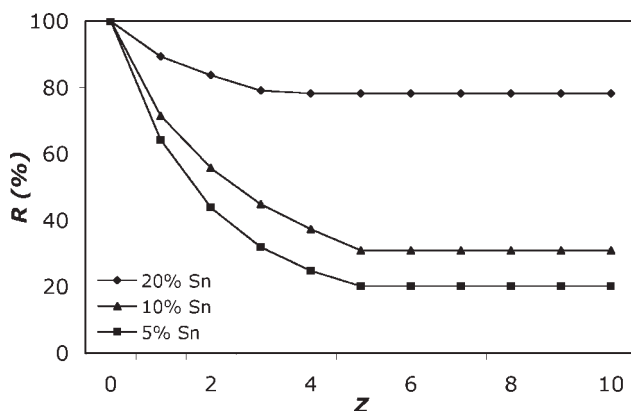


Figure 7 Retention profiles for As(III), at pH 4, at polymer: As(III) mol ratio = 400 : 1 and different tin contents.

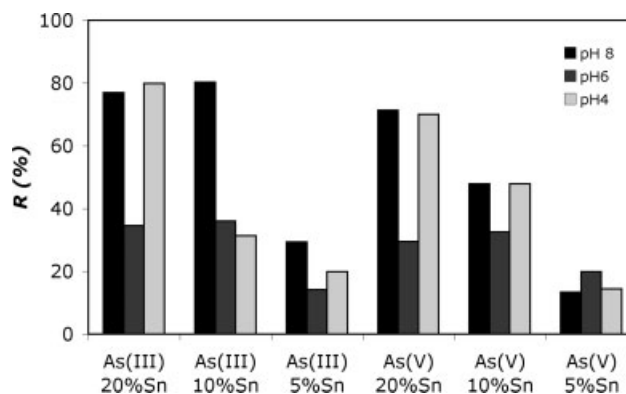


Figure 8 Retention values for As(III) and As(V) for $Z = 10$, mol ratio 400 : 1, at different pHs.

10 and 20 wt % tin content for both arsenic species with a maximum retention at pH 8 and 4.

CONCLUSIONS

The LPR technique was found to be a convenient method to remove arsenic from an aqueous solution. The polymer with all the interacting groups as surface metal-polymer complexes demonstrated an important arsenite retention ability. The arsenic anions' retention behavior depended on the pH, polymer concentrations, and tin content. The adequate Sn-As(III) mole ratio, close to 20 : 1 or 40 : 1, presented the highest yield in all cases. A good retention was found at pH 8 and 4. The probable oxidation of As(III) to As(V) could improve the retention capacity. However, the preliminary results on speciation indicate that the highest retention corresponds to the form of As(III). Additionally, the retention results with As(V) in the feed presented a similar retention behavior to values found for As(III) at $Z = 10$. Therefore, the water-soluble metal-polymer complexes prepared can recover arsenic in its two oxidation states from water.

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