

Synthesis and Characterization of New Water-Soluble Metal–Polymer Complex and Its Application for Arsenite Retention

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Received 20 October 2007; accepted 31 August 2008

DOI 10.1002/app.29322

Published online 3 December 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: New water-soluble metal–polymers of poly (acrylic acid)s (AA) with different amounts of tin (3, 5, 10, and 20 wt %) were synthesized and characterized. The materials were characterized by ^1H NMR and FTIR spectroscopy, X-ray diffraction (XRD), specific area by isotherm of CO_2 , and thermogravimetry-differential scanning calorimetry (TG-DSC). The synthesized material is crystalline and shows an average crystal size 90–130 nm and has a high thermal stability ($>200^\circ\text{C}$). Texturally, they are complexes of small specific area, which decreases when the crystal size increases with the tin content. Presumably, the Sn(II) ions coordinate through 2–4 carboxylate groups by a conventionally bidentate structure; however, they are not symmetric. Studies have been dedicated to support of tin in polymers to increase its efficiency in eliminating pollutants. The tin-metal salt

is added to the poly(AA) matrix to increase its ability to remove As(III) from an aqueous solution. The liquid-phase polymer-based retention technique is applied to retain and separate contaminants from water. The analysis of As(III) and As(V) species was made by combining liquid high-resolution chromatographic coupled to hydride generation absorption atomic spectrophotometer (HPLC-HG-AAS). All indicated that As(III) was the predominant species bound to the polymer complex for the pH range 4–8. The polymers containing 10 and 20 wt % Sn presented the highest retention of 70 and 90% As(III), respectively. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2720–2730, 2009

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

INTRODUCTION

Because of the presence of pollutants in water, adequate materials and methods to remove them need to be found.¹ Environmental decontamination requires the implementation of materials that have low operating costs and that are stable over the time, potentially useful, and appropriate to the specific conditions in each region.

New systems, called nanomaterials,^{2,3} based on inorganic oxides or hybrid (inorganic and organic) materials have been studied. In general, polymers containing metals have emerged as a new generation of material with tremendous potential fields. Several preparation methods⁴ that modify morphology and distribution particle size in the formation of nanostructured materials have been reported.

Numerous studies of metal–polymer complex synthesis were investigated.^{5,6} Poly(acrylic acid) (AA),

poly(4-vinyl pyridine), poly(ethyleneimine), pendant-type polymer–metal complexes have been studied considering constant rates of formation, the effect of polymer ligand configuration, the metal's characteristics, the degree of crosslinking, and the environmental effect of the polymer in a chemical reaction.

The assembly of negatively charged nanoparticles layers on adsorbed polycationic polymers films such as poly(ethyleneimine) or poly(diallyl dimethyl ammonium chloride) (PDDA) has been reported.⁷ A new polymeric anion exchanger⁸ contains a high concentration of nondiffusible, positively charged quaternary ammonium functional groups, on which hydrated iron(II) oxide were dispersed, nanoparticles.

It is well established that submicron or nanoscale hydrated iron(II) oxide particles exhibit high sorption affinity toward both arsenates and arsenites. Studies have also been dedicated to support of iron oxide particles in polymeric resins, much improving the material's efficiency in eliminating contaminants.^{9,10} New techniques¹⁰ of Fe^{+3} and Fe^{+2} impregnation on macroporous polymeric support to improve the specific area have been applied. Among these, adsorption with impregnated resins and metal-loaded chelating resins have been studied.¹¹

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Contract grant sponsor: FONDECYT; contract grant number: 3050057.

Contract grant sponsor: CIPA.

The advantages include an easy preparation, large binding energy, good stability, high preconcentration factor, mechanical stability, and good reproducibility.

The importance of metallic oxides in removing arsenic from media has been published.^{12–14} The adsorption properties of these materials were measured. Arsenic fixation is highly influenced by the metallic oxides' specific surface and crystallinity. Amorphous iron oxides have the highest surface area per unit mass in comparison with crystalline forms of iron(III) oxides (namely, goethite, hematite, and magnetite¹⁵). Novel composite adsorbents that consist of magnetite and porous resin beads^{16,17} have been recently applied to eliminate arsenate from water.

The crystalline structures of Mn oxides¹⁸ are of environmental interest because of their adsorption and oxidation capabilities. The most likely As(V)-MnO₂ complex¹⁹ is a bidentate, binuclear corner-sharing (bridged) complex occurring at MnO₂ crystallites edges and interlayer domains. In the As(III)-treated MnO₂ crystallite, reductive dissolution of the MnO₂ solid during the oxidation of As(III) caused an increase in As(V) adsorption when compared with As(V)-treated MnO₂. This suggested that As(III) oxidation caused a surface alteration, creating fresh reaction sites for As(V) on MnO₂ surfaces.

Water-soluble polymers are commercially available^{20–22} or can be synthesized by different routes.

The objective of this article is to find a synthetic methodology route and to evaluate the physico-chemical properties of the water-soluble polymers that have tin [Sn(II)] incorporated at the backbone.

Furthermore, the application of these water-soluble tin polymers in conjunction with the liquid-phase polymer-based retention (LPR) technique to separate arsenite anions from water is performed.

EXPERIMENTAL PART

Reagents

Poly(AA) (Aldrich, Milwaukee, WI) was 35 wt % solution in water, M_w 100,000. Tin chloride hydrated salt, SnCl₂ × 2H₂O, 99 % (Merck, Stuttgart, Germany). As(III) (1000 mg/L) of a NaAsO₂ solution (Merck,p.a) was used.

Preparation of metal-polymer compounds

Poly(AA) 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 % of the metal with respect to the polymer. The pH is adjusted with NaOH solution. The presence of white precipitate of Sn(OH)₂ was not observed for 3, 5, and 10 wt % tin samples. The solution gives a light-

yellow color or remains colorless, depending on the amount of water. This result suggests that the presence of poly(AA) would avoid oxidation and precipitate formation; however, the hydrolysis of tin salt was not discarded. The reaction is maintained at 30–35°C under shaking for 24 h.

The polymer-tin products are water soluble and are subsequently lyophilized. Samples with 10 and 20 wt % tin were reproducible under the same synthesis conditions. Furthermore, a sample with the mole ratio poly(AA) : tin (1 : 1) was prepared using the same procedure as previously described. On the other hand, a mixture of tin salt and poly(AA) was also prepared at pH 6 (10 wt % of tin) *in situ* in the ultrafiltration cell. As a result, short contact times between the tin salt and polymer were used before the arsenite solution was added.

Moreover, the 10 and 20 wt % tin from SnCl₂·2H₂O is put in the ultrafiltration cell, and 0.1M NaOH was added to 20 mL. At pH >2, the solution began to precipitate a white milk aspect attributed to Sn(OH)₂.

Characterization

UV-vis spectrometry was recorded in Lambda 35-Perkin Elmer; scanning range: 200–600 nm. By quantitative analysis, it 0.01M SnCl₂ at pH 2.4 was prepared. Additionally, this solution was adjusted at pH 8 with 1M NaOH, clearly observing the presence of the white precipitate of Sn(OH)₂. Before spectrometry measurements, the samples were filtered with 0.45-μm filter. The blank was twice-distilled water.

On the other hand, the poly(AA) with SnCl₂·2H₂O (theoretical 10 wt % tin in polymer) were placed in 20 mL of water. The solutions were adjusted at different pH: 2, 4, 6, and 8, and kept under stirring for 24 h. Then, they were filtered with 0.45-μm filter. The blank was a poly(AA) solution in the same concentration of the prepared samples. The volume and concentrations of poly(AA) and tin salt were adjusted to a mole ratio metal-polymer : As(III) (400 : 1) or Sn : As(III) (20 : 1) in the hypothetical case that As(III) remained in solution. Accordingly, the same conditions are maintained with respect to the arsenic species retention reaction.

The Fourier transformed infrared (FTIR) spectra were recorded with a Magna Nicolet 550 and Nexus Nicolet spectrometers. By quantitative analysis, 1 mg of the sample per 100 mg KBr was employed. A total of 128 accumulative scans were applied in the range 1300–1750 cm⁻¹.

The NMR spectra were recorded with a multinuclear Bruker AC 250 spectrometer at 250 MHz at room temperature and D₂O as solvent.

X-ray diffractions were performed in Rigaku diffractometer using an N filter and Cu Kα, (λ = 1.5418 Å)

radiation, 40 kV and 2 mA. Operating conditions were continuous scanning at the rate 10°/min and for the range $2\theta = 0^\circ\text{--}90^\circ$.

The thermal behavior under N₂ was studied with a thermogravimetric analyzer using a TGA 625 from Polymer Laboratories. The heating rate was 10°C/min; the sample weight was 0.5–3.0 mg.

The total arsenic concentration was measured in the filtrate by atomic absorption spectrometry (AAS) using a Perkin Elmer 3100 spectrometer. The amount retained was determined by its difference with the initial concentration. Tin contents in samples were evaluated in the same equipment. The samples were dissolved in 10% HCl solution. The pH was controlled by a pH meter (H. Jürgen and Co).

Specific area measurements were made in Micromeritic Gemini model 2379 and adsorption volumetric system with a pressure transducer MKS Baratron 170 M. Outgassing: 100 mg of sample was maintained under N₂ flow at 60°C during 4 h. The essays were performed with CO₂ as adsorbate at 0°C. Assays provide a data series of adsorbed volume in (cc/g) versus equilibrium pressure. A saturation pressure of 26,412 mmHg was used for CO₂.

LPR technique procedure

By washing method, x mmol (where $x = 0.2, 1, 2, 4$, and 6) of the poly(AA)-Sn, (10 and 20 wt % Sn) with molecular weight higher than 100,000 g/mol are dissolved in twice-distilled water, and the solution containing 0.01 mmol of As(III) was added to the cell solution. The solutions are brought to 20 mL of total volume and the pH was adjusted by adding 0.1M NaOH or 0.1M HCl. The washing water in the reservoir was at the same pH value of the cell. Furthermore, the minimum contact time of metal–polymer with arsenic was tested for 15 min, 1 h, 2 h up to 24 h before ultrafiltration. The minimum time to obtain the maximum retention was 2.5 h; however, 24 h was taken to ensure the retention. Filtration runs were performed under a total pressure of 3.5 bar by using a ultrafiltration membrane with an exclusion rating of 10,000 g/mol. The total volume in the cell was kept constant. Fractions of 20 mL were collected by filtration, and the arsenic concentration was analyzed. Similarly, the metal–polymer samples prepared *in situ* are kept in contact with arsenic solution at pH 8, during 3.5 and 24 h before ultrafiltration. Also, the white precipitate of Sn(OH)₂ was studied by the washing method. It was placed in contact with As(III) in mole ratio Sn : As(III) (20 : 1) at pH 4 and 8 with stirring during 24 h, prior to ultrafiltration.

The enrichment method to determine maximum retention capacity was also applied. The experimental conditions used were as follows: a 0.5 mM solu-

tion of NaAsO₂ [37.5 mg/L As(III)] with 4 mmol of poly(AA)-Sn (10 wt % tin) in 20 mL of cell, at 300 mL of total filtrate volume. One blank run, without polymer, was also performed.

The determination of As(III) and As(V) was carried out online, using a liquid high-performance chromatography system (HPLC) (Merck-Hitachi, model L7000) coupled to an AAS (Perkin Elmer, Analyst 100 model). The chromatographic separation of As(III) and As(V) was performed in ion pair modality on a column RP-C18, 60 mm x 4 mm according to conditions previously reported.²³ Eluted species from chromatographic column are derivatized to arsenic hydride (AsH₃) with NaBH₄ (0.8% p/v) in acidic media (10 % HCl) in a flow injection system and determined online by AAS.

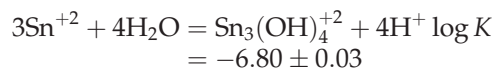
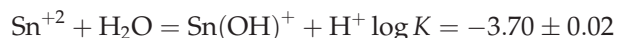
RESULTS AND DISCUSSION

General aspects on formation of tin-soluble complexes

A polymer–metal complex is defined as being composed of a polymer and bounded metal ions, and it represents an attempt to give inorganic functions to an organic polymer.⁶ The metallic salt of tin was synthesized with a polyanion containing carboxylate groups as poly(AA). When the polymer ligand was mixed directly with the metal ion, the resulting precursor principally depends on the characteristics and number coordination of the metallic salt, the ligand dissociation degree, and consequently on the media's pH, ionic strength, solvent composition, and temperature.

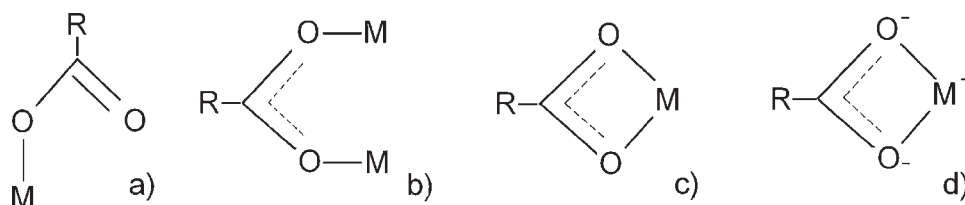
When the precursor tin(II) chloride salt is in aqueous solution, the Sn²⁺ cations suffer hydrolysis at low pH values.²⁴ Hydrolysis improves in the presence of anions that can precipitate.

The hydrolysis of tin in aqueous solution yields the following reactions in presence of 3M NaClO₄:



The hydrolysis products are SnOH⁺, Sn₂(OH)⁺² predominantly trimer species, and Sn₃(OH)₄⁺²²⁵ because Sn⁺² tends to polymerize forming polynuclear species.

These polynuclear oxy-hydroxy complex types frequently present a composition near to 3SnO × H₂O. The X-ray diffraction studies showed a polyhedral group Sn₆O₈ that forms a pseudocubic structure.²⁶ This structure contains Sn₆O₄(OH)₄ units as octahedron. The hydrate oxide is amphoteric and is



Scheme 1 (a) Unidentate, (b) bidentate, (c) chelating bidentate, and (d) ionic interactions.

dissolved in alkaline media. It has been proposed that the polynuclear complex $\text{Sn}_6\text{O}_8\text{H}_4$ can form SnO in the media at higher pH.^{24,26}

When the polymer ligand surrounds, the metal complex constitutes an electrostatic or hydrophobic domain in aqueous solution.⁶ This polymer domain governs the metal complex's chemical reactivity. This phenomenon can be described as an "environmental effect of polymer" in a chemical reaction. One effect is the conformational change of the ligand chain. The conformation of the polymer complex is closely related to the strength of its electronegativity domain and the reaction rate. The effects of the polymer chain on reactivity are understood not only in terms of static chemical environment but also as dynamic effects that vary with the solution conditions, such as pH, ionic strength, solvent composition, and temperature.

Polymers and copolymers of AA and its derivatives are widely used as macroligands.²⁰ The chelating process of a metal ion by a polymer may be preceded by long-range attractive interactions. Once the metal ion condenses on the polymer surface, it is site-fixed by the polymer ligands as shown in Scheme 1.²⁷

The structures (a–c) admit a degree of covalency. The structure (d) is purely ionic. Depending on the pH value, the organic molecule's behavior, indicates that the ionized poly(AA) may form complexes with D_{2h} or D_{4h} (dimers) symmetry. At a lower pH, the poly(AA) is not dissociated, and the dissociation degree depends on cationic alternating environment. It is known that organic integral polycations produce changes in the critical pH due to poly(AA) types. At higher critical pH values, the poly(AA) chain has a drawn shape because of the electrostatic repulsion of charged carboxylate groups. Thus, metal ions are binding with either one or two neighbor groups. At pH 4.6, according to Tsuchida and Abe,²⁸ the macromolecular globule contracts and the metal ions are able to coordinate with 2–4 carboxylic acid groups at $pK_a = 5.6$. In the case of poly(AA), the accepted mechanism for this polymer–metal ion interaction can be described as follows: positively charged tin polynuclear species [i.e., $\text{Sn}(\text{OH})^+$] or tin hydrate hydroxy can coexist at a moderately acid pH. This form is adequate to achieve the complexation reac-

tion of tin salt with poly(acrylate) anion at pH 5–6. The binding is predicted by the oxygen of carboxylate group of polyanion with tin as shown in Scheme 1, as suggested by others authors.²⁷ Nevertheless, it is not discarded that insoluble species may coexist in solution without matrix binding. The experimental evidence provided here indicates that all poly(AA) is bound to tin, considering the mole ratio (1 : 1) of poly(AA) : $\text{Sn}(\text{II})$.

Characterization

UV–vis spectrometry was used to demonstrate the presence of complexes and compounds in the dissolution of tin chloride. It would show water-soluble tin species that were present during the solid formation. Figure 1(a) shows that SnCl_2 at pH 2.4 maintains two absorption zones for soluble Sn^{+2} species, at 290 nm and 215 nm. When, the pH is increased to

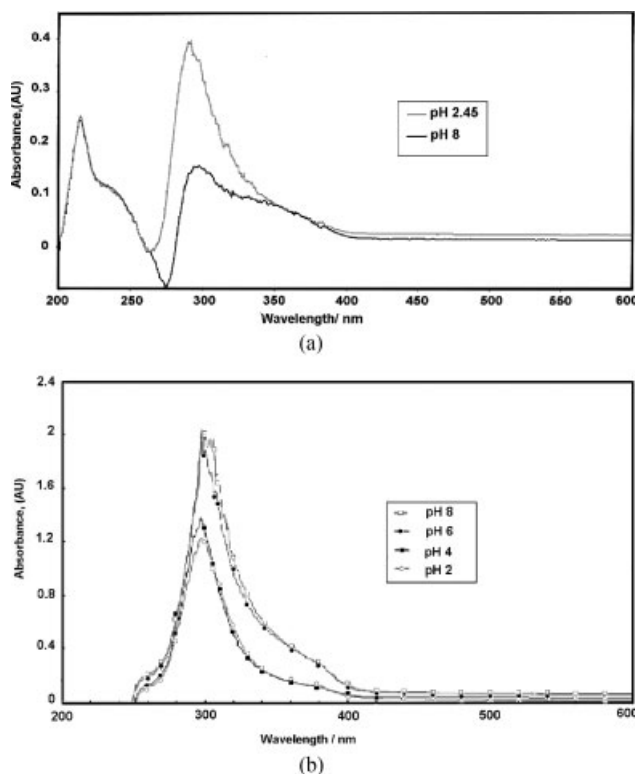


Figure 1 UV–vis spectra: (a) SnCl_2 at pH 2.4 and 8; (b) poly(AA)– $\text{Sn}(\text{II})$ (10 wt % tin) for pH 2, 4, 6, and 8.

pH 8, the filtrated waters showed a decrease in absorbance intensity and a displacement from 290 to 297 nm of the absorption band. The band at 215 nm maintains constant absorbance. Comparing the experimental results with data from literature,²⁵ the authors reported (1) a predominant soluble specie that absorbs at 290 nm and another that absorbs at 263 nm because of the aqueous Sn^{+2} , and (2) the formation of polynuclear cationic hydrolyzed species $\text{Sn}(\text{OH})^+$, $\text{Sn}_2(\text{OH})_2^{+2}$, $\text{Sn}_3(\text{OH})_4^{+2}$ are evidenced by new absorption bands at 224 or 236 nm.

Figure 1(b) presents the UV-vis spectra for poly(AA)-Sn(II) (theoretical 10 wt %) for pH range 2–8. The quantity of soluble Sn^{+2} species present at 297 nm, measured in UA, increased notably because of the presence of poly(AA) in the media. In contrast with the aqueous media, the band at 224 nm did not appear, and the increase in pH from 2 to 8 increased the UA for the band at 297 nm.

Poly(AA)-Sn(II), poly(AA), and tin(II) chloride salt were studied by thermogravimetry (TG) and differential scanning calorimetry (DSC) in range 25–550°C [see Fig. 2(a–e)]. The weight loss was evaluated in each range, and the each maximum was obtained for DSC peak. $\text{SnCl}_2 \times 2\text{H}_2\text{O}$ showed an exothermic broad peak at nearly 428°C, with a 33 wt % loss, and an endothermic peak at 248°C, with 6% weight loss. The poly(AA) showed a well-defined endothermic maximum at 202°C, and small exothermic peaks at 310 and 438°C, but the higher weight loss occurred in the range 270–400°C. The poly(AA)-Sn(II) complexes showed two well-defined maxima in the range 385–480°C. In this zone, the weight loss is almost constant with tin content. It is assumed that the maximum temperature by DSC (i.e., 470–480°C) displaced to a higher temperature with respect to the pure tin salt (i.e., 428°C) represents tin anchorage sites on poly(AA) complex. The authors²⁹ have reported interesting results for TG-DSC with the evaluation of IR peaks during the thermal degradation for polyacrylate/ZnO nanocomposites. The filler load of the composite was (6.1, 14.3, and 21.1 wt % of ZnO). The main weight loss occurred between 300 and 390°C, and the DSC under nitrogen atmosphere showed a maximum temperature at 410°C, which is attributed to the decomposition of polyacrylates by surface hydroxyl groups on the ZnO surface, catalyzing the thermal degradation of polyacrylate.³⁰ After this primary weight loss, the TG curves of polyacrylate/ZnO nanocomposite films showed one additional stage of weight loss from 390 to 470°C. This indicates a change in the degradation mechanism, which must be due to a chemical interaction between the filler and the polymeric materials. The authors proposed a mechanism for the formation of the complex by the interaction of polyacrylate and zinc oxides particles. The reaction could be inter- or intra-molecular.³¹

Tin contents of dissolved poly(AA)-Sn(II) were determined by AAS. A double synthesis of 10 and 20 wt % tin samples are showed in Table I. The evaluation of tin content by AAS presented good linearity with $R^2 = 0.9916$.

FTIR spectra of poly(AA)-Sn (3, 5, 10, and 20 wt % tin) materials, in the region 400–4000 cm^{-1} are shown in Figure 3(a–d). The analysis of high zone 1400–1750 cm^{-1} shows polymer behavior in the presence of a metal (see Table II). The metal's nature is fundamental²⁷ because it is assumed that an increase of covalent M-O character leads to the higher frequency of a asymmetrical carboxyl group and an increase in the frequency separation of the two COO^- stretching bands. Thus, metal anion-carboxylate interactions increases the effect on the COO^- stretching frequency monodentate $\nu_{\text{asym}}(+)$ and $\nu_{\text{sym}}(-)$ difference as the M-O bond becomes stronger. In the bidentate bridging complex mode, the difference $\nu_{\text{asym}} - \nu_{\text{sym}}$ is recognized to be around 180 cm^{-1} for carboxylate groups.

The FTIR spectra of the sample prepared with a mole ratio poly(acrylic acid) : Sn (1 : 1) indicated the absence of $\nu(\text{C}=\text{O})$ of undissociated HCOOH at 1720 cm^{-1} with respect to pure polyacrylic acid. The presence of a strong band with a maximum at 1576 cm^{-1} of $\nu_{\text{asymm}}(\text{COO}^-)$ is discerned in the spectrum, and at 1395 cm^{-1} of the correspondent symmetric carboxylate (it is not shown in figure). Based on these results, it is possible to suggest that under these synthesis conditions, the coordination of carboxylate groups with tin (II) salts should be possible.

The spectrum of poly(AA)-Sn(II) presents symmetric stretching vibrations $\nu_{\text{sym}}(\text{COO}^-)$ at 1405 cm^{-1} and stretching asymmetric vibrations $\nu_{\text{asymm}}(\text{COO}^-)$ at 1600 cm^{-1} , maintaining some free carboxylate COO^- . The difference was detailed by applying FTIR (128 scans) to discern the asymmetric [$\nu_{\text{asim}}(\text{COO}^-)$ at 1639 cm^{-1}] and free (1576 cm^{-1}) stretching forms. The nonionized or nondissociated stretching group appears at 1720 cm^{-1} . The absorption bands at 777 cm^{-1} and 540 cm^{-1} show the presence of Sn–O. The authors^{32,33} have reported that the band at 770 cm^{-1} is $\nu_{\text{as}}(\text{Sn–O–Sn})$, while others²⁵ have reported that the absorption band at 810 cm^{-1} can correspond to flexion by Sn–O–H, and the band at 570 cm^{-1} can be associated to traction band of Sn–C.

Presumably, in one of the absorption modes, the Sn(II) ion coordinates with 2–4 carboxylate groups in a conventionally bidentate structure; however, they are not symmetric. Nakamoto²⁷ has suggested that there are four types of metal carboxylate structure as previously shown in Scheme 1. Several studies^{34–36} were carried out using salts of divalent metal chlorides and oxide metal in glass polyalkenoates, as

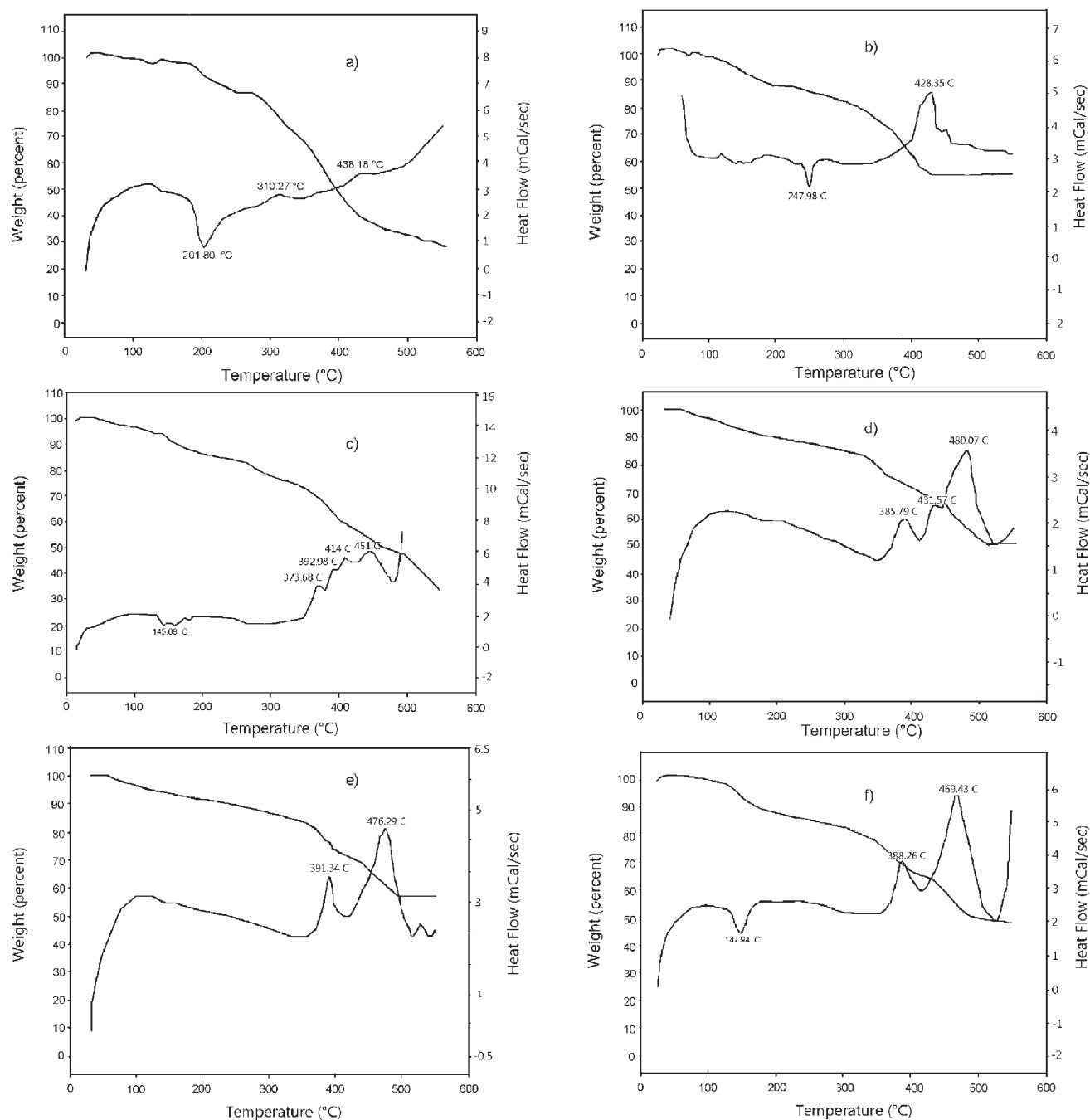


Figure 2 TG-DSC of (a) poly(acrylic acid), poly(AA), (b) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, tin chloride dehydrated salt, (c) poly(AA)-Sn, 3 wt % tin, (d) poly(AA)-Sn, 5 wt % tin, (e) poly(AA)-Sn, 10 wt % tin, and (f) poly(AA)-Sn, 20 wt % tin.

TABLE I
Tin Composition for Poly(AA)-Sn(II) Evaluated by Atomic Absorption Spectroscopy (AAS)

Theoretical tin content (wt %)	Tin content (wt %) by AAS
3	2.7
5	4.5
10	7.5
10	8.74
20	15
20	11

those of the main group elements, transition metals. The authors^{34,36} are in agreement that the absorption bands assigned to the COO^- asymmetric stretching did not correspond to the bands in the spectrum of pure poly(AA). These results would indicate that the asymmetric mode is more sensitive than the symmetric mode and that the frequencies vary from 1550 to 1620 cm^{-1} (metal chlorides)³⁴ or from 1500 to 1650 cm^{-1} (metal oxide),³⁶ depending on the coordination between the metal ion and the COO^- group; however, it moves as far as about 1634 cm^{-1}

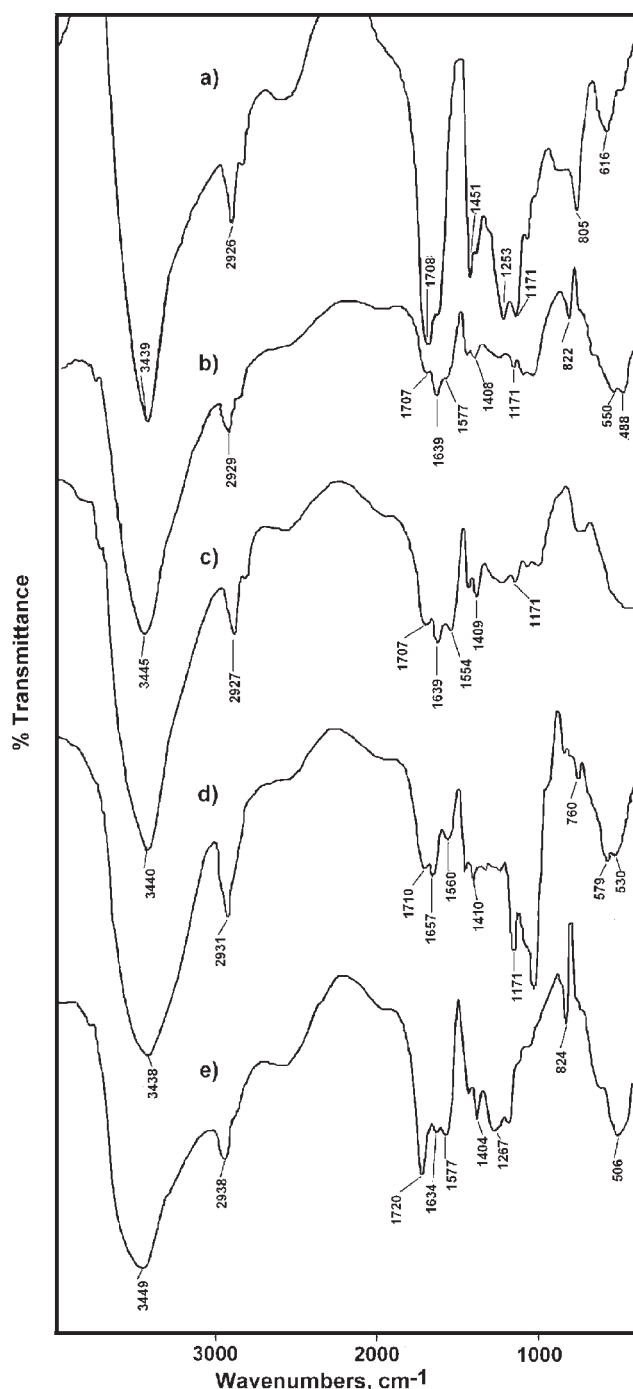


Figure 3 FTIR of (a) poly(AA)-Sn(II) (3 wt % tin), (b) poly(AA)-Sn(II) (5 wt % tin), (c) poly(AA)-Sn(II) (10 wt % tin), and (d) poly(AA)-Sn(II) (20 wt % tin).

for the fairly unusual case of the unidentate structure.³⁴ For II metal groups, two bands appear as asymmetric stretching at 1639 (strong) and 1550 (medium) cm^{-1} . The bands at 1550–1527 cm^{-1} are associated with chelating bidentate structure. Thus, two interactions seem to appear for each of the II group, both of which seem to possess some degree of covalent character.

^1H NMR spectra of poly(AA) and poly(AA)-Sn(II) shows the following signals (in ppm): at 1.67–2.00 corresponding to H^1 of (CH_2) group; at 2.4 corresponding to H^1 of (CH) group; at 7.0, the signal of OH group appears; at 4.8, the signal corresponds to the solvent protons. Apparently, signal displacement did not exist in (b) relative to the poly(AA) spectrum.

X-ray diffraction of the first series samples of poly(AA) and poly(AA)-Sn(II) are shown in Figure 4(a–e). Poly(AA) is not crystalline. It is observed that peak intensity and resolution as well as crystallinity increase with an increase of tin content. The crystal size was calculated with the Scherrer equation. $(B \cos \theta = S \lambda / D)$, where $B = \text{FWHM}$ (middle width peak), $S = 0.9$, and $\lambda = 0.154178 \text{ nm}$. The peaks used for the analysis are mainly 31.7° and 45.36° 2θ , with $I/I_0 = 100$ and 52, respectively. An increase of crystallinity with the tin content ($I/I_0 = 100$) is observed. However, the crystal size is not proportional because it drops in the range of 90–130 nm, as can be seen in Figure 5.

The X-ray diffractogram of poly(AA) showed negligible crystallinity in the zone 0° – 20° 2θ [see Fig. 4(a)]. Poly(AA)-Sn(II) complexes showed a clear spectra. The maximum intensity of diffraction for peaks was in the following order: 31.64, 45.36, and 27.32, 2θ [see Fig. 4(b–e)]. Table III shows typical diffraction patterns of 10 wt % tin.

An intensive search of diffraction pattern files³⁷ are as follows: 46-1486 and 84-2157; $\text{Sn}_6\text{O}_4(\text{OH})_4$; 14-0140 and 25-1303; $\text{Sn}_3\text{O}_2(\text{OH})_2$, with structure hydrated oxide was made. Also, SnO file: 72-2324. A comparative analysis by diffraction pattern indicates predominating 14-0140 and 46-1486 SnO· $n\text{H}_2\text{O}$ phases in the majority of samples.

Figure 6 shows the adsorbed volume as a function of relative CO_2 pressure. The measurements reached relative pressure in a small range 0–0.03 P/P_0 . This type of isotherms is assumed to be produced on heterogeneous surfaces with multiple adsorption sites. A lower range of pressure 10^{-3} characterizes the Freundlich isotherm. It is observed that the adsorbent's adsorption capacity is higher on support poly(AA) and decreases when the sample's metallic content increases. Table IV presents the results adjusting the area value by isotherm BET type model. (Transversal area CO_2 adsorbate $\sigma = 0.187 \text{ nm}^2$). It is observed that specific area decreases with tin content, seeming to indicate that tin crystal size must be increasing with tin content.

Arsenic recovery by LPR technique, and As(III) and As(V) speciation analysis

The difficulty to separate As(III) from water has been published.³⁸ As(III) removal could be possible

TABLE II
Characteristic FTIR Absorption Bands for Poly(AA)-Sn(II)

Compound	Unionized COOH, C=O		Coordinated COO ⁻ ...M ⁺		Free COO ⁻
	v (cm ⁻¹)		v (asymmetric) cm ⁻¹	v (symmetric) cm ⁻¹	
Poly(AA)-Sn(II)					
3 wt % tin	1,707		1,639	1,408	1,577
5 wt % tin	1,707		1,639	1,409	1,554
10 wt % tin	1,710		1,657	1,410	1,560
	1,724		1,641	1,404	1,558
20 wt % tin	1,720		1,634	1,404	1,577
	1,718		1,634	1,404	1,564
Poly(AA)	1,720		—	—	—

after the oxidation step as metal oxides in heterogeneous media. In this work, we analyze the direct retention of As(III) species from water by water-soluble metal-polymer complexes using the LPR technique.

Figure 7 shows the total arsenic removal by LPR technique at pH 8 for different tin contents of the poly(AA)-Sn(II) (3, 5, 10, and 20 wt %) and mole ratio poly(AA)-Sn : As(III) (400 : 1). The results demonstrated that the complexes with theoretical 10 and

20 wt % tin are able to achieve a retention in a basic medium in the theoretical mole ratio Sn : As(III) (25 : 1) or (50 : 1). Furthermore, the assays identify the arsenic species; a combination of separation by liquid chromatographic technique and detection technique by atomic absorption (HPLC-AAS) were carried out. In all cases, the analysis of As(III) and As(V), performed online, evaluated a 99 to 90 wt % of As(III) and a lower quantity (up to 10 wt %) of As(V) in the filtrate solution. In general, quantification by HPLC determined that the quantity of arsenic fed was quantitatively recovered in aqueous solution.

The differentiation analysis showed that As(III) is the main species in aqueous solution. Apparently, poly(AA)-Sn(II) did not produce the redox reaction. The reduction of As(III) to As(0)_{solid} is discarded. It is recognized that Sn in acid solution can suffer

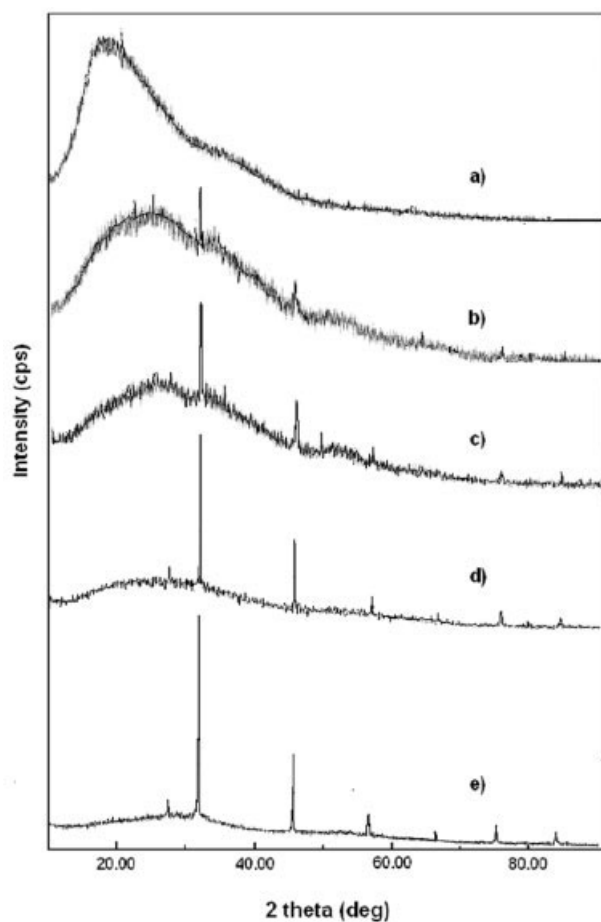


Figure 4 X-ray diffraction on (a) poly(AA), (b) poly(AA)-Sn(II) (3 wt % tin), (c) poly(AA)-Sn(II) (5 wt % tin), (d) poly(AA)-Sn(II) (10 wt % tin), and (e) poly(AA)-Sn(II) (20 wt % tin).

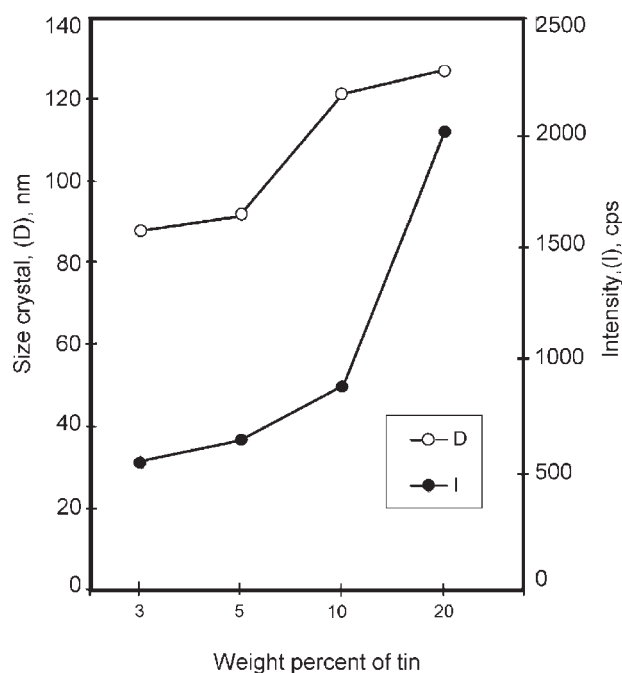


Figure 5 Maximum intensity ($I/I_0 = 100$) X-ray diffraction, size crystal, and weight percent of tin samples for poly(AA)-Sn(II) complex.

TABLE III
X-ray Pattern Diffraction of Poly(AA)-Sn(II)

d (Å)	2.8255	1.9977	3.2617	1.6285	1.4102	1.2616	1.1523
I/I_0	100	52	34	20	10	12	10

Rad. λ Cu K α 1.5406 Å, Ni filter.

hydrolysis, and hydrolyzed Sn species linked to a polymer could produce the reduction of As(III) species. Even though the As(0) species are not identified by AAS, the presence of traces of As(V) identified by HPLC-HG-AAS, during the essay, indicated that a relatively small fraction of As(III) can be oxidized in solution during the assay.

At pH 8, the sample with poly(AA)-Sn(II) 10 wt % tin using a mole ratio [poly(AA)-Sn : As(III)] (400 : 1) showed a 90 wt % of As(III) species retained. Under the same operating conditions, the poly(AA)-Sn(II) 20 wt % tin showed a similar arsenic differentiation profile with retention of nearly 80 wt % As(III). At pH 4, the poly(AA)-Sn(II) 20 wt % tin of (400 : 1) showed a retention profile in some cases of 50 up to 70 wt % As(III) (see Fig. 8).

The predominant species in solution is arsenite, which exists as neutral species HAsO_2 for a wide range of pH. Thus, a probable binding with the polymer complex is one where $\text{O}=\dot{\text{A}}\text{s}-\text{OH}$ can undergo Lewis acid-base interaction⁸ with Sn sites in the polymer, forming a monodentate complex. However, the existence of hydrolyzed species of As(III) is not discarded, depending on the media's pH value. The authors¹⁴ found $\text{As}(\text{OH})_3$ (pH = 5) and $\text{OAs}(\text{OH}_2)^-$ (pH = 10.5) when evaluating with infrared and Raman essays.

It was also determined that the equilibrium adsorption of As(III) : poly(AA)-Sn is reached after 1–2 h contact with shaking prior to ultrafiltration.

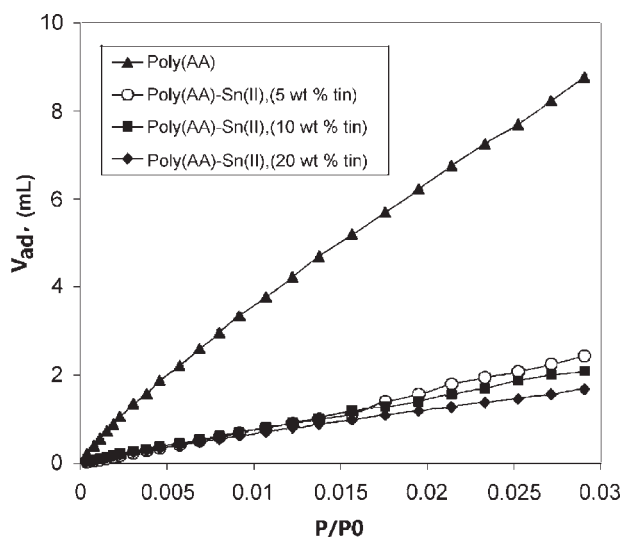


Figure 6 Isotherm adsorption CO_2 of poly(AA) and poly(AA)-Sn(II) (5, 10, and 20 wt % Sn).

The desorption of As(III) is reached decreasing the acidity at pH 3, achieving a recovery in the order of 95%.

The presence of hydrolysate of tin is not discarded completely since the arsenite retention is possible at pH 4 and 8.

We also performed a preliminary experiment considering a $\text{SnO} \cdot n\text{H}_2\text{O}$ solid, and it was observed that it maintains an acceptable performance, slightly lower than that for the metal-polymer complexes. This study is in progress to support the small quantities of $\text{SnO} \cdot \text{H}_2\text{O}$ or $\text{Sn}(\text{OH})_2$ on inorganic oxide-forming column systems. On the basis of these results, we did an experiment of aqueous $\text{Sn}(\text{OH})_2$ precipitate using the LPR technique. The $\text{Sn}(\text{OH})_2$ was used in aqueous media, and it is filtrated with arsenite solution in the mole ratio Sn : As(III) (20 : 1). It showed As(III) retention properties at pH 8 and 4 as shown in Figure 9. The tin chloride salt assay at pH < 2 in the presence of As(III) in mole ratio (Sn : As(III) (20 : 1) did not present retention. The results do not necessarily confirm that the phase $\text{Sn}(\text{OH})_2$ is formed in a water-soluble metal-polymer system or that it is the only compound responsible for the retention ability. We did not observe an insoluble chelate with metallic salt and poly(AA). This current system is a light-yellow color or colorless solution depending on the quantity of tin and water.

Additionally, the LPR technique was used to test the aqueous solution of poly(AA) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (10 wt % tin in the sample) prepared *in situ* in the ultrafiltration cell. In only few minutes at pH 5, As(III) was added in a mole relationship [polymer/tin salt : As(III)] (400 : 1) and (Sn : As(III) in nearly (20 : 1). It was performed to avoid the possible coordination of metal in the polymeric network and therefore, the effect of tin hydrolysate could be better observed if it is formed in appreciable quantity when retaining As(III). The adsorption equilibrium was 3.5 and 24 h, respectively (see Figure 9).

TABLE IV
BET Specific Area CO_2 for Poly(AA) and Poly(AA)-Sn(II)

Compound	$S_{\text{BET}(\text{CO}_2)}$ (m^2/g)
Poly(AA)	72
Poly(AA)-Sn(II) (3 wt % tin)	21
Poly(AA)-Sn(II) (5 wt % tin)	17
Poly(AA)-Sn(II) (10 wt % tin)	16
Poly(AA)-Sn(II) (20 wt % tin)	15

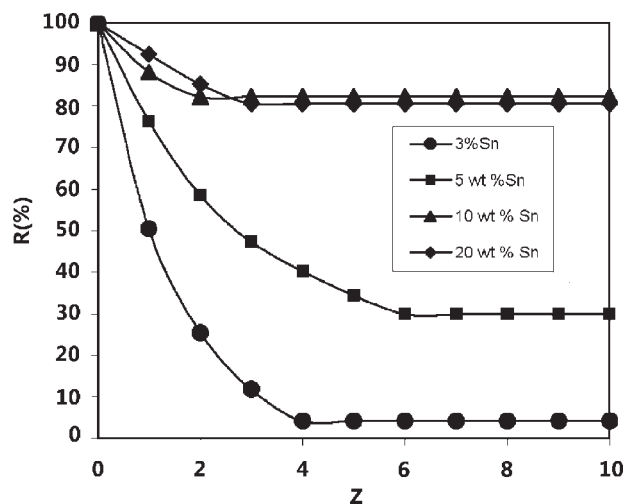


Figure 7 Retention profiles for As(III) at pH 8, using (a) \blacklozenge poly(AA)-Sn, 3 wt % tin; (b) \blacksquare poly(AA)-Sn, 5 wt % tin; (c) \blacktriangle poly(AA)-Sn, 10 wt % tin; and (d) \circ poly(AA)-Sn, 20 wt % tin.

Enrichment method

The saturation capacity of metal-polymer complex to As(III) aqueous solution was determined. Figure 10 shows the curve obtained by the poly(AA)-10 wt % Sn(II) sample (first series) and blank assays.

The maximum retention capacity is defined as follows:

$$C = MV/P_{mSn}$$

where P_{mSn} = amount of Sn of polymer (g); M = initial concentration of As(III) 37.5 (mg/L); V = filtrate

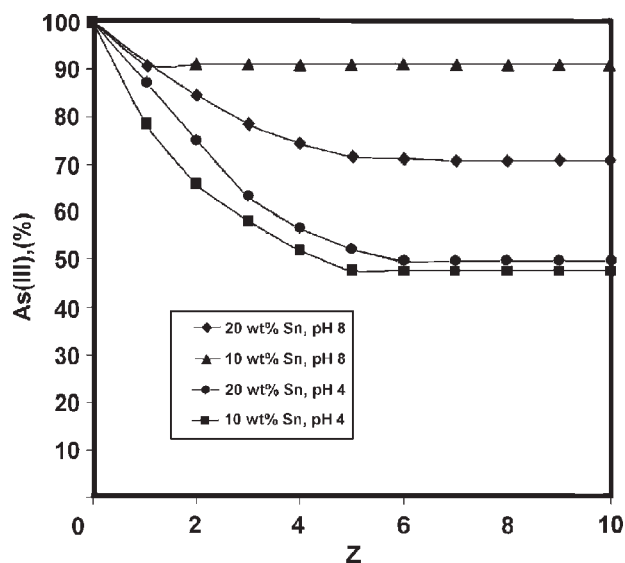


Figure 8 Species analysis, HPLC-AA in: \blacklozenge poly(AA)-Sn, 20 wt % tin; \blacktriangle poly(AA)-Sn 10 wt % tin at pH 8; and (c) \bullet poly(AA)-Sn, 20 wt % tin at pH 4.

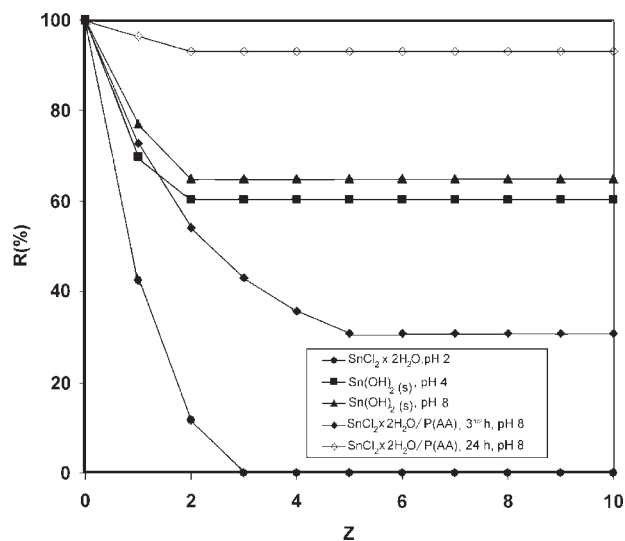


Figure 9 Retention profiles for As(III) using: \bullet SnCl_2 pH < 2; \blacksquare $\text{Sn}(\text{OH})_{2(s)}$ pH 4 and \blacktriangle pH 8; \blacklozenge SnCl_2/PAA , \blacklozenge 3.5 h, \diamond 24 h.

volume (defined volume), through of membrane-free As(III) (mL). C was calculated as 101 mg/g corresponding to the total filtrate volume of 300 mL. The maximum retention capacity is determined based on the Sn(g) mass that gives reactivity to the complex. It represents nearly 8 wt % of the polymer's active sites.

CONCLUSIONS

A single procedure to prepare metal-polymer based on tin(II) salt effectively removed arsenic as a contaminant from water. The material's characterization would indicate a coordination of the Sn(II) ion as conventionally bidentate but not symmetric with 2-4

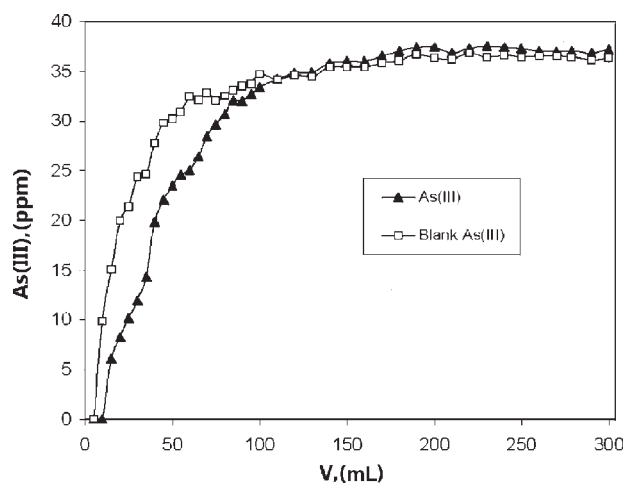


Figure 10 Arsenic(III) concentration versus filtrate volume of poly(AA)-Sn 10 wt % Sn. Polymer amount: 4 mmol. Pattern solution of As(III): 0.5 mM.

carboxylate groups. A crystalline nanomaterial mainly a phase of $\text{SnO} \cdot n\text{H}_2\text{O}$ would be a probable product of hydrolysis of Sn^{+2} . The crystallinity was increased by tin content, and the crystal size is nearly 90–130 nm. Texturally, it is characterized by a small specific area, which decreases slightly as tin content increases. This result suggests that crystal size is increasing with tin content. The polymer's thermal stability was improved in the presence of the tin salt. It is suggested that the maximum temperature peaks at 390 and 480°C exist due to the sites of Sn inserted in the poly(AA) matrix, conferring retention properties to this material.

Ultrafiltration and speciation analysis showed that the main As species retained by metal-polymers from solution is As(III). The maximum retention ability (70–90%) is found at basic pH.

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