Polym. Bull. (2010) 65:1–11
DOI 10.1007/s00289-009-0179-z

ORIGINAL PAPER

# Functional water-insoluble polymers with ability to remove arsenic(V)

**Bernabé L. Rivas · Carla Muñoz**

Received: 25 June 2009 / Revised: 10 August 2009 / Accepted: 27 September 2009 /

**Abstract** Three resins were synthesized through radical polymerization: poly[(ar-vinylbenzyl)trimethylammonium chloride] P(VBTA), poly[(ar-vinylbenzyl) trimethylammonium chloride-*co*-acryloylmorpholine] P(VBTA-*co*-AM), and poly[(2-acryloyloxy) ethyltrimethylammonium chloride-*co*-acryloylmorpholine]. The removal capacity for arsenic under different conditions was studied and compared with a commercial resin Amberlite IRA 400-Cl. The arsenic sorption capacity of the resins at the optimum pH showed the following order: Amberlite 95.5% (27.1 mg/g, 0.36 mmol/g), P(VBTA) 92.6% (16.3 mg/g, 0.22 mol/g), P(VBT-*co*-AM) 90.4% (21.5 mg/g, 0.29 mmol/g), and P(AETA-*co*-AM) 87.3% (21.7 mmg/g, 0.29 mmol/g).

**Keywords** Water-insoluble polymers · Arsenic species · Removal · Batch and column procedures

## Introduction

Arsenic is a natural element found widely in the earth's crust. It may be found in some drinking water supplies, including wells. Exposure to high levels of arsenic can cause health effects.

The real toxicity of arsenic to the human body usually comes from several ways such as, water and foods. Arsenic contamination in natural water is a worldwide problem. In water, the most common valence states of arsenic are As(V) (arsenate) which is more prevalent in aerobic surface waters and As(III) (arsenite) which is more likely to occur in aerobic ground waters [1].

---

B. L. Rivas (✉) · C. Muñoz
Polymer Department, Faculty of Chemistry, University of Concepción,
Casilla 160-C, Concepción, Chile
e-mail: brivas@udec.cl

There are trace amounts of arsenic in all living matter. Drinking water would only be the major source of exposure for people living near a source of arsenic. Arsenic may enter lakes, rivers or underground water naturally, when mineral deposits or rocks containing arsenic dissolve. Arsenic may also get into water through the discharge of industrial wastes and by the deposit of arsenic particles in dust, or dissolved in rain or snow. These arsenic particles can enter the environment through the burning of fossil fuels (especially coal), metal production (such as gold and base metal mining), agricultural use (in pesticides and feed additives), or waste burning.

Arsenic contamination of drinking water has been reported from many parts of world. In some arsenic-affected areas, substitution of drinking water source by a safe and easily available one may not be possible during part or all of the year, or may be very expensive. Arsenic removal may be a more appropriate water supply option in these situations.

Coagulation is the most common arsenic removal technology. Oxidation with chlorine or permanganate is required first. Coagulation with ferric chloride works best at pH below 8. Alum has a narrower effective range, from pH 6–8. Ion exchange resins are commercially produced synthetic materials that can remove some compounds from water. These resins only remove arsenate. Activated alumina, like ion exchange resins, is commercially available in coarse grains. Activated alumina beds usually have much longer run times than ion exchange resins, typically several tens of thousands of beds can be treated before arsenic breakthrough. Activated alumina works best in slightly acidic waters (pH 5.5–6). Membrane methods for arsenic removal include reverse osmosis and membrane nanofiltration [2–5].

Currently available membranes are more expensive than other arsenic removal options, and are more appropriate in municipal settings, where very low arsenic levels are required. Other techniques exist for arsenic removal, but are less well documented. When arsenic-rich water also contains high levels of dissolved iron, iron removal will also remove much of the arsenic. Introduction of zero-valent iron filings in three-pitcher filters to treat water in the home is showing great promise. Many new materials are being tested for arsenic removal, from low-tech iron-coated sand and greensand to specially engineered synthetic resins. In all cases, technologies should meet several basic technical criteria. The biggest challenges ahead lie, however, in applying the technologies described in poor, rural settings, and in enabling those communities to choose safe sources of water for drinking and cooking.

All of the technologies for arsenic removal rely on a few basic chemical processes, which are summarized below:

- Oxidation/reduction: reactions that reduce (add electrons to) or oxidize (remove electrons from) chemicals, altering their chemical form. These reactions do not remove arsenic from solution, but are often used to optimize other processes.
- Precipitation: causing dissolved arsenic to form a low-solubility solid mineral, such as calcium arsenate. This solid can then be removed through sedimentation and filtration. When coagulants are added and form flocs, other dissolved

compounds such as arsenic can become insoluble and form solids, this is known as co-precipitation. The solids formed may remain suspended, and require removal through solid/liquid separation processes, typically coagulation and filtration.

- Adsorption and ion exchange: various solid materials, including iron and aluminum hydroxide flocs, have a strong affinity for dissolved arsenic. Arsenic is strongly attracted to sorption sites on the surfaces of these solids, and is effectively removed from solution. Ion exchange can be considered as a special form of adsorption, though it is often considered separately. Ion exchange involves the reversible displacement of an ion adsorbed onto a solid surface by a dissolved ion. Other forms of adsorption involve stronger bonds, and are less easily reversed [6].
- Solid/liquid separation: precipitation, co-precipitation, adsorption, and ion exchange, all transfer the contaminant from the dissolved to a solid phase. In some cases the solid is large and fixed (e.g. grains of ion exchange resin), and no solid/liquid separation is required. If the solids are formed in situ (through precipitation or coagulation) they must be separated from the water. Gravity settling (also called sedimentation) can accomplish some of this, but filtration is more effective. Most commonly, sand filters are used for this purpose.
- Physical exclusion: some synthetic membranes are permeable to certain dissolved compounds but exclude others. These membranes can act as a molecular filter to remove dissolved arsenic, along with many other dissolved and particulate compounds.
- Biological removal processes: bacteria can play an important role in catalyzing many of the above processes. Relatively little is known about the potential for biological removal of arsenic from water.
- Boiling does not remove arsenic from water.

Inorganic arsenic acts as oxo-anion in an aqueous solution: 3+ and 5+ are the predominant oxidation states of the element. The conjugate acid of As(III) and As(V) are expressed as $H_3AsO_3$ and $H_3AsO_4$, respectively. A trivalent arsenic anion ($H_2AsO_3^-$) has been favorably extracted to an organic phase using dithiocarbamantes, dithiols, or inorganic acid of high concentration, whereas these reagents showed rather poor extractability for pentavalent arsenic. Therefore, arsenic(V) is often reduced to arsenic(III) or converted to heteropolyacids or the catechol complex, prior to extraction [7].

On the other hand, $H_2AsO_4^-$ was preferably adsorbed onto a wide variety of solid inorganic materials and, hence, has been comprehensively used to separate arsenic from dilute solutions. Especially, hydrous metal oxides of iron(III), zirconium(IV), titanium (IV), aluminum(III), and rare earth elements(III), etc. have been examined as selective adsorbents of arsenic(V) ion. However, since hydrous metal oxides are generally obtained as fine powders or gel, their handling is often difficult.

Ion exchange and chelating polymers have attracted more interest, due to their applications in waste water treatment, metal recovery from diluted solution as protective coating on metal surfaces or as a priming layer, coating on paper, fiber and fabrics, selective binding of enzymes [8–12]. The study of polymeric ligands and their metal complexes are very useful in metal separation, as a catalyst and bio-inorganic chemistry [13]. In a polymeric ligand or polychelates, the function of a ligand is often only a small portion of three dimensional polymer support; hence, it is subjected to a number of structural variables compared to a low molecular weight ligand. This indicates a definite dependence on the complexing abilities of the insoluble polymeric ligands and physicochemical properties of the derived polychelates [14, 15].

Few other anion exchangers have been reported recently for the removal of arsenate/arsenite ions from water. Bhaumik et al. [16, 17] have reported the layered double hydroxide (LDH) Mg–Al hydrotalcite. The exchange reaction was very simple and the efficiency of the process remained almost the same in many cycles. This efficiency of arsenic removal from contaminated ground water has been drastically improved by treatment with a small amount of dilute aqueous $H_2O_2$ to oxidize As(III) to As(V) under acid pH condition followed by its exchange with hydrotalcite.

This research group also reported the arsenic removal properties of mesoporous poly(triallylamine) which carry positively charged nitrogen atoms in the mesoporous framework. It is reflected in its high anion exchange efficiency (92.9%) from aqueous solutions.

This article describes the potential application of polymers containing ammonium groups and chloride as counterion to remove efficiently arsenic(V).

## Experimental part

### Reagents

(Ar-vinylbenzyl)trimethylammonium chloride (VBTA, 99%, Aldrich); (acryloyloxy)ethyltrimetilammonium chloride (AETA, 80%, Aldrich), 4-acryloylmorpholine (AM, Aldrich), Amberlite IRA-400-Cl (Aldrich) was utilized as obtained. N,N′-methylene-bis-acrylamide (MBA, 99%, Aldrich) and ammonium peroxide disulfate (AP, Fluka) were used as obtained as cross-linking and initiator reagents, respectively.

For adsorption studies, the metal salt used was $Na_2HAsO_4$. Metal salt was purchased from Merck. The analytical grade $HNO_3$, $H_2SO_4$, $HClO_4$, and HCl were purchased from Fisher.

### Synthesis of the resin

The synthesis of the resin poly1(ar-vinylbenzyl)trimethylammonium chloride] P(VBTA) was performed in a polymerization flask as follows: 3 g ($1.4 \times 10^{-2}$ mol) of (ar-vinylbenzyl)trimethylammonium chloride was mixed with 0.0436 g ($2.8 \times 10^{-4}$ mol) of MBA and 0.0162 g ($7.1 \times 10^{-5}$ mol) of PSA. The system was kept under $N_2$ at 70 °C for 4 h. Then, the resin was filtered and washed with distilled water and dried up to constant weight at 40 °C.

The other resins, P(VBTA-*co*-AM) and P(AETA-*co*-AM), were synthesized in a similar form to P(VBTA), but using an equimole quantity of two different monomers. The copolymerization yield are the following: P(VTA) 89%, P(AETA-*co*-AM) 81%, and P(VAETA-*co*-AM) 78%.

### Removal of arsenic by batch and column equilibrium procedures

To determine the arsenic retention capacity of the resins, first a batch equilibrium procedure was applied of the synthesized and commercial adsorbents. All experiments were performed in a flask mounted on a shaker. The adsorption equilibrium experiments were carried out to study the effects of pH. 0.05 g of dried resin and 5 mL of metal ion solution were shaken for 1 h at 20 °C. After shaking, the resin samples were filtered and washed with water at the same pH. The metal ions concentrations in the filtrate were determined by atomic absorption spectroscopy (AAS).

In the regeneration experiments, $HNO_3$, $H_2SO_4$, HCl, and $HClO_4$ at two concentrations were studied as potential stripping reagents by using the batch method. A 0.05 g of resin-loaded with As(V) ions were eluted with 5 mL of eluent for 1 h.

For the column experiments, 0.1 g of resin was placed into a column with 15 cm length and 1 cm diameter. In all runs, a 10 mL metal salt solution passed through the column. The fractions were collected and analyzed for the metal ion concentration.

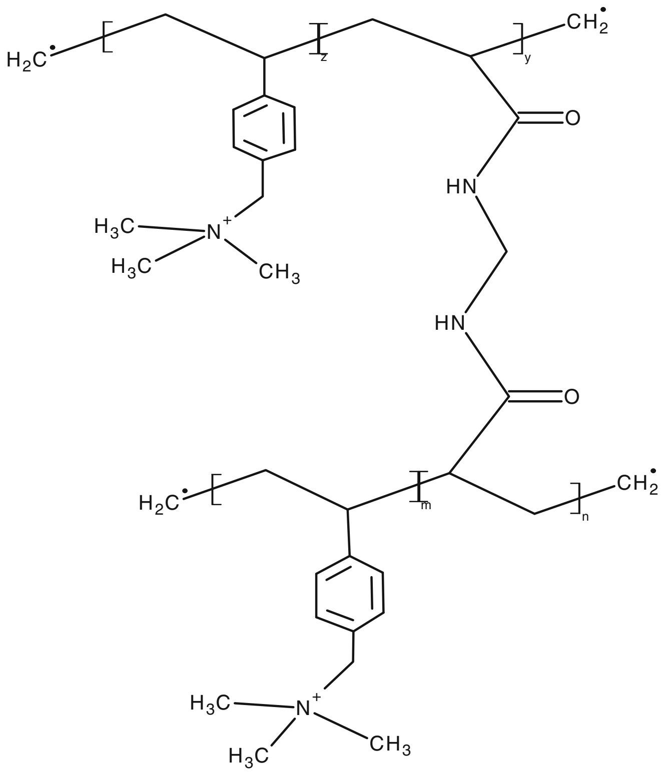
### Measurements

A Julabo air-batch shaker was used for shaking the solution at a desired temperature. The pH was measured with a digital pH meter Inolab, WTW, level 1. The equipment used for the determination metal ions was an atomic absorption spectrometer Unicam Solaar 5 M series. The FTIR spectra of the samples were recorded with a Magna Nicolet 550 spectrophotometer. The thermograms of the loaded and unloaded resins were recorded on an STA-625 thermoanalyzer. Approximately 5 mg of the dry sample was heated at a heating rate of 20 °C/min under a dynamic nitrogen atmosphere.

## Results and discussion

The synthesis of the resins was carried out by homo- and copolymerization. AP was used as an initiator and MBA as a cross-linking reagent, respectively (see Schemes 1, 2, and 3). The copolymerization yield for the three resins was higher 75%.

FT IR spectra show the most characteristic absorption bands (in $cm^{-1}$): P(VBTA) Ar–C–H st (3023), $N^+R$ (1447), Ar–C–H $\delta$ (889), P(VBTA-*co*-AM) $N^+R$ (1447), Ar–C–H st (2911), P(AETA-*co*-AM) $N^+R$ (1471), –N–C = O (1737), $N^+R$ (1471). C–O (1112).



**Scheme 1** P(VBTA)

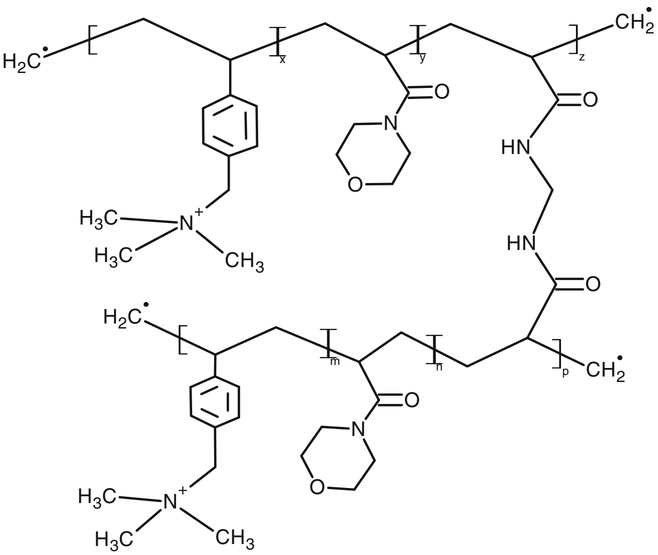
The synthesized resins have quaternary ammonium groups as a potential ion exchange/complexing groups which are able of interact with the metal ion and produce the retention (see Schemes 1, 2, and 3).

## Arsenic removal properties

The affinity between the resin's active groups and the ions is studied by batch and column equilibrium procedures, using a resin–metal ion relationship in mol between functional group on the resin and metal ion, 20:1. This ratio ensures the metal ion's access to ligand sites.

## Effect of the pH on the removal

The pH was varied between 4 and 8. The ligand groups and the metal ions form change with the pH; therefore, the retention behavior is dependent of this parameter. The highest retention behavior was observed at pH 8 for Amberlite 95.5% (0.362 mmol/g), P(VBTA) 92.6% (0.213 mmol/g), P(AETA-co-AM) 87.3%



**Scheme 2** P(VBTA-*co*-AM)

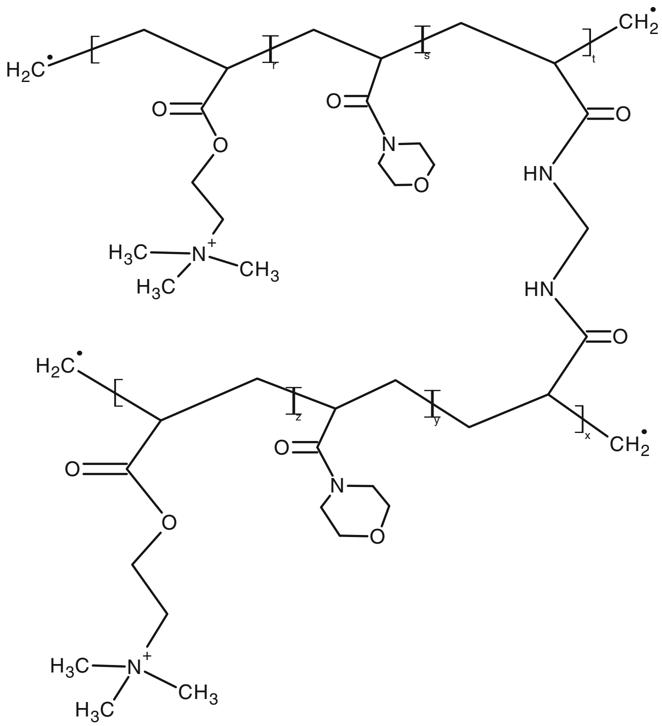
(0.289 mmol/g), and P(VBTA-*co*-AM) 90.4% (0.287 mmol/g). Therefore, these pH values were chosen for the following runs. The Fig. 1 shows experimental results obtained at pH 4, 6, and 8 by batch equilibrium procedure.

To explore the applications of the resin, the maximum adsorption capacity (MAC) needs to be determined. Based on the MAC, the maximum retention capacity (MRC) in batch and column equilibrium procedures was determined for As(V). These values are shown in Table 1.

## Resin reusability

The arsenic ions need to be absorbed but then desorbed to reuse the resin, to the elution several stripping reagent can be utilized. The resin's ion capacity should be maintained after the treatment with an eluent reagent and the metal ion adsorbent by the resin should be easily released under appropriate conditions. The batch desorption studies were carried out by first separately loading resin samples. The four stripping reagents studied (HCl, $H_2SO_4$, $HClO_4$, and $HNO_3$) at two different concentrations were selected because they should be able to displace the arsenic ion species (see Table 2).

Amberlite is a commercial resin which was included by comparison with these resins. In all cases, as the stripping concentration increases, the elution also increases. The two copolymers resins showed a higher elution behavior, and $HNO_3$ and $H_2SO_4$ were the best stripping reagent to remove arsenate species from P(VBTA-*co*-AM).



**Scheme 3** P(AETA-*co*-AM)

**Fig. 1** Effect of pH on arsenic retention capacity for the different resins

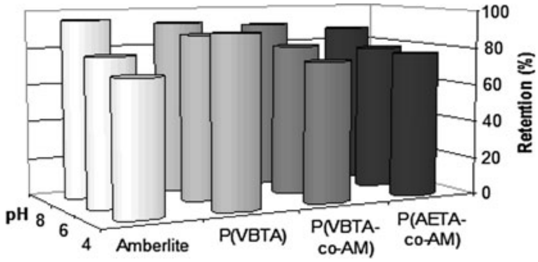


**Table 1** Maximum retention capacity of the resins for arsenic(V)

| Resin | MRC (mmol/g) |
|---|---|
| Amberlite IRA 400-Cl | 1.41 |
| P(VBTA) | 1.66 |
| P(VBTA-*co*-AM) | 1.23 |
| P(AETA-*co*-AM) | 0.93 |

**Table 2** Regeneration capacity with different stripping reagents

| Stripping reagent | Elution (%) | | | |
|---|---|---|---|---|
| | Amberlite | P(VBTA) | P(AETA-*co*-AM) | P(VBTA-*co*-AM) |
| HCl | | | | |
| 1 M | 57.7 | 50.2 | 67.1 | 64.1 |
| 2 M | – | 43.5 | 65.7 | 64.0 |
| $HNO_3$ | | | | |
| 1 M | 59.1 | 46.6 | 54.1 | 69.3 |
| 2 M | – | 53.7 | 53.9 | 63.9 |
| $H_2SO_4$ | | | | |
| 1 M | 52.8 | 55.8 | 64.8 | 70.4 |
| 2 M | – | – | 68.5 | 63.8 |
| $HClO_4$ | | | | |
| 1 M | – | 28.0 | 63.7 | 58.9 |
| 2 M | – | – | 67.1 | 59.8 |

Therefore, for resin reusability, the sorption–desorption cycle was repeated thrice with the same sorbent in batch and column processes. The results are presented in Figs. 2, 3, 4, and 5.

The Fig. 2 shows that the resin Amberlite was loaded with As(V), and the desorption was performed with 1 M $HNO_3$. The resin lost its retention capacity and desorbed capacity gradually through three cycles in the batch and column processes. The desorption in batch was smaller than in column. The Fig. 3 shows the resin P(VBTA) loaded with As(V), and the desorption was performed with 1 M $H_2SO_4$, the resin completely lost the capacity of retention and desorption in batch method, due the active site inside the resin could be destroyed when the stripping reagent is in contact with the resin in the first cycle; it does not allow the retention in the second and third cycles. In the column process, the site's destruction was produced slower than bath process, because the resin is not totally in contact at the same time with the stripper. The retained quantity in the second and third cycles was small; however, this quantity was totally desorbed. The Fig. 4 shows the resin P(VBTA-*co*-AM) was

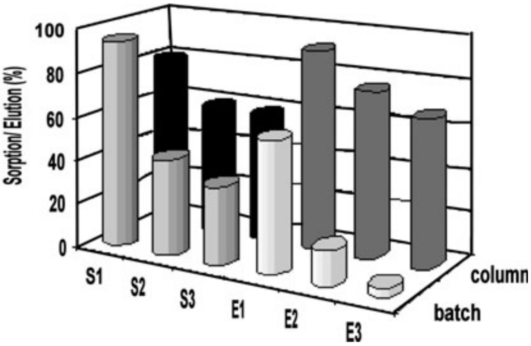


**Fig. 2** Reusability of the resin Amberlite loaded with As(V), eluent 1 M $H_2SO_4$

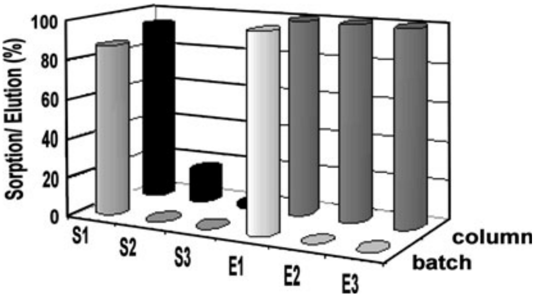


**Fig. 3** Reusability of the resin P(VBTA) loaded with As(V), eluent 1 M $H_2SO_4$. Sorption (S)–elution (E) cycles

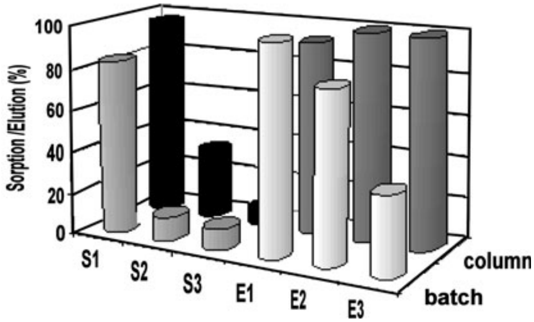


**Fig. 4** Reusability of the resin P(VBTA-*co*-AM) loaded with As(V), eluent 1 M $H_2SO_4$. Sorption (S)–elution (E) cycles

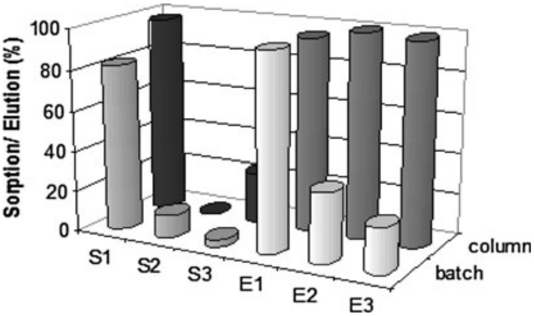


**Fig. 5** Reusability of the resin P(AETA-*co*-AM) loaded with As (V), eluent 2 M $H_2SO_4$. Sorption (S)–elution (E) cycles

loaded with As(V), and the desorption was performed with 1 M $H_2SO_4$; the resin in batch and column techniques lost its capacity of retention slowly and also its capacity of elution in a small percentage. The behavior of the resin is similar to P(VBTA), but the morpholinic group gives more stability to the active site, it produces that the retention behavior does not decrease forcedly. The Fig. 5 shows the resin P(AETA-*co*-AM) was loaded with As(V), and the desorption was performed with 2 M $H_2SO_4$. In batch process, the resin lost its capacity of retention reaching until 3.3% in batch technique and 0% in column; desorption capacity of the arsenic ions was maintained in the column and lost gradually in the batch process. Since retention is low, the stripping reagent is capable to elute all metal ions. But, there is a decreasing of active sites during the process to the interaction between the active site and the stripping reagent.

## Conclusions

The resins were obtained by radical polymerization with a high yield, higher 72%. The resins showed a high percentage of retention to As(V). At pH 8 was observed the highest retention of As(V). From the four stripping reagents tested HCl, $HClO_4$, $H_2SO_4$, and $HNO_3$, the last two acids showed the higher capacity to remove arsenate species. In general, the resins were not capable to maintain its retention capacity and desorption through several cycles of sorption and desorption and batch, as well as, column; it is probably due the destruction or blockades of the active site during desorption reaction.

**Acknowledgments** The authors thank FONDECYT (Grant No 1070542) and “Centro de Investigación de Polímeros Avanzados”, CIPA for the financial support.

## References

1. Behpour M, Mehdi Ghoreishi S, Salehi S (2005) Solid phase extraction of arsenic by sorption on naphthalene-methyltrioctyl ammonium chloride and spectrophotometric determination. Acta Chim Slov 52:323–327
2. Rivas BL, Aguirre M, Pereira E, Moutet JC, Saint-Aman E (2007) Capability of cationic water soluble polymers in conjunction with ultrafiltration membranes to remove arsenate ions. Polym Eng Sci 47:1256–1261
3. Rivas BL, Aguirre M (2006) Retention properties of arsenate anions of water-soluble polymers by a liquid-phase polymer-based retention technique. J Appl Polym Sci 102:2677–2684
4. Rivas BL, Aguirre M (2007) Arsenite retention properties of water-soluble metal-polymers. J Appl Polym Sci 106:1889–1894
5. Rivas BL, Aguirre M, Pereira E (2007) Cationic water-soluble polymers with ability to remove arsenate through an ultrafiltration technique. J Appl Polym Sci 106:89–94
6. Wakui Y, Ndiaye SA, Matsunaga H, Yokoyama T, Akiba K (1998) Extraction of arsenic(III) with macroporous resin impregnated with bis(2-ethylhexyl)ammonium bis(2-ethylhexyl)-dithiocarbamate. Anal Sci 14:299–303
7. Wakui Y, Ebina T, Matsunaga H, Suzuki TM (2002) Solvent extraction of arsenic(V) with dispersed ultrafine magnetite particles. Anal Sci 18:793–798
8. Martinez JS, Carrel GL, Tachirret Guth RA, Althenhoff G, Litlle RD, Butler A (2001) On the regiospecificity of vanadium bromoperoxidase. J Am Chem Soc 123:3289–3294
9. Barruah B, Das S, Chakravorty A (2002) A family of vanadate esters of monoionized and diionized aromatic 1,2-diols: synthesis, structure, and redox activity. J Inorg Chem 41:4502–4508
10. Raman N, Ravichandran S (2002) Synthesis, characterization and antibacterial activity of metal complexes of N-(1-piperidinobenzyl)nicotinamide. Asian J Chem 14:1551–1555
11. Raman N, Ravichadran S, Thangaraja C (2004) Copper(II), cobalt(II), nickel(II) and zinc(II) complexes of Schiff base derived from benzyl-2,4-dinitrophenyl hydrazone with aniline. J Chem Sci 116:215–219
12. Liang Z, Na H, Jiang W, Wu Z (2002) Am Chem Soc 43(2):1184
13. Warshawasky A (1998) Polymeric ligands in hydrometallurgy. In: Streat M, Naden D (eds) Synthesis and separation using functional polymers. Wiley, New York, p 327
14. Mathew B, Pillai VNR (1994) Crosslinked polystyrene supported dithiocarbamates as metal complexing agents. Eur Polym J 30:61–65
15. Joshi JD, Patel SD, Patel GP (2007) Synthesis, characterization, thermal and ion-exchange studies of benzophenone ethane diol resin and its polychelates. J Macromol Sci A 44:65–72
16. Bhaumik A, Samanta S, Mal NK (2005) Efficient removal of arsenic from polluted ground water by using a layered double hydroxide exchanger. Indian J Chem 44A:1406–1410
17. Chandra D, Bhaumik A (2009) A new functionalized mesoporous polymer with high efficiency for the removal of pollutant anions. J Mater Chem 19:1901–1907