Polym. Bull. (2011) 67:237–249
DOI 10.1007/s00289-010-0373-z

ORIGINAL PAPER

Synthesis, characterization and evaluation of phosphorylated resins in the removal of Pb^{2+} from aqueous solutions

**Marcelo A. V. Souza · Luiz Claudio de Santa Maria ·
Marcos A. S. Costa · Wang S. Hui · Luciana C. Costa ·
Hiram C. Araujo Filho · Sandro C. Amico**

Received: 30 March 2010 / Revised: 31 July 2010 / Accepted: 19 August 2010 /

Abstract Phosphinic-derivative poly(styrene-co-divinylbenzene)-based on PS–DVB copolymers with different porosity degrees have been prepared by aromatic electrophilic substitution reaction using $PCl_3/AlCl_3$ followed by base-promoted hydrolysis. The phosphorylation reaction was analyzed by infra-red spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetry (TG/DTG). In addition, the phosphorous content of the phosphorylated copolymers was determined by spectrophotometry using the method based on sodium molybdate reactant so that the extension of that modification could be assessed. The performance of the phosphorylated resins in the extraction of Pb^{2+} from aqueous solutions in a batch system was also evaluated. The Pb^{2+} content was determined by atomic absorption spectrometry (AAS). These materials presented excellent extraction capacity under the contact time of 30 min and pH 6.

Keywords Styrene–divinylbenzene copolymers · Phosphorylated resins · Lead · Sorbents

---

M. A. V. Souza · L. C. de Santa Maria (✉) · M. A. S. Costa · L. C. Costa
Universidade do Estado do Rio de Janeiro, Instituto de Química,
Rua São Francisco Xavier 524, Maracanã, RJ 20550-013, Brazil
e-mail: lcsantamaria@terra.com.br

W. S. Hui
Departamento de Engenharia Metalúrgica e Materiais, Universidade de São Paulo,
Escola Politécnica, Avenida Prof. Mello Moraes 2463, Butantã, SP 05508-030, Brazil

H. C. Araujo Filho
Instituto Federal de Educação, Ciência e Tecnologia do Rio de Janeiro, IFRJ,
Rua Senador Furtado 121-125, Maracanã, RJ 20270-021, Brazil

S. C. Amico
LAPOL/DEMAT/PPGEM, Universidade Federal do Rio Grande do Sul,
Setor IV-Prédio 74, Campus Vale, Porto Alegre 91501-970, RS, Brazil

Introduction

Lead is a toxic metal used in construction, batteries, ammunition, protection against X-rays, and also as a component of alloys for various applications. The exposure of humans to lead is harmful in many ways, such as disruption of the biosynthesis of hemoglobin leading to anemia, increased blood pressure, kidney damage, among others [1].

Copolymers of styrene and divinylbenzene (PS–DVB) are widely used as polymeric supports for ion exchangers and chelating groups. Their main advantages include their chemical versatility and low cost. In addition, the aromatic ring of the styrene units may be modified into a wide variety of chemical structures and, therefore, the physical properties of the network can be tailored by controlling the parameters of the synthesis reaction [2].

Ion exchangers and chelating resins are very often used in the preconcentration and removal of various metal ions in aqueous solutions. Another application includes the use of such resins in hydrometallurgical processes [3, 4]. This field is receiving a growing attention since many metals are obtained from secondary sources, wastes, and rinsing water. Resins are particularly useful in metal recovery when the concentration of the targeted ion in solution is low, requiring the treatment of a large volume of solution [3].

Alexandratos and Natesan [5] have studied the development of a new kind of solid extracting phase called chelating ion-exchange resin, which consists of commercial styrene–divinylbenzene copolymers functionalized with phosphorylation agents. These resins are modified, incorporating hydrophilic groups to ensure better surface contact area with the aqueous phase. Many phosphorous based ion exchangers as well as ligand loaded resins for metal ion extraction may be found in the literature [3–10]. The efficiency of these compounds regarding metal removal depends on some important parameters, such as the porosity degree of the copolymers substrates, the type and concentration of the chelating groups, the type and charge of the target ion, and the regeneration of the ion-exchange resins and the pH of the solution. The morphological characteristics of the copolymers determine the extension of the modification reactions and consequently, the efficiency of the removal process [1, 11–14].

The most of works that describe the development of phosphorylated resins deals with the suitable conditions to phosphorylation reaction, complexation capacity, and the selectivity of the products through several metal ions. The influence study of the morphological copolymers characteristics on complexation capacity has not been sufficiently studied in these works. However, the porous structure and swelling capacity of the polymer influence the process of reagent diffusion and consequently the extent of the modifications reactions for introducing phosphoryl groups in this matrix, as well as the accessibility of those introduced groups by metal ions [15]. Thus, this article addresses synthesis, characterization, and evaluation of different sorbents based on styrene–divinylbenzene copolymers containing phosphoryl group, with different degrees of porosity, for the removal of Pb^{2+} from aqueous solution.

Experimental part

Chemicals

Commercial styrene (S) was donated by Petroflex *Indústria e Comércio S.A.* (Rio de Janeiro, Brazil) and commercial divinylbenzene (DVB) by Nitriflex *Indústria e Comércio S.A.* (Rio de janeiro, Brazil). Commercial 2-hydroxyethylcellulose was purchased from Union Carbide (New Jersey, USA). Toluene and phosphorus trichloride were purchased from Merck (Rio de Janeiro, Brazil) and aluminum chloride from Proquimios (São Paulo, Brazil). Other reactants and solvents were purchased from Vetec Química Fina Ltda. (Rio de Janeiro, Brazil).

Preparation of PS–DVB copolymers

Copolymers of styrene and divinylbenzene were obtained via free radical suspension polymerization. The organic phase was prepared by mixing 46 mL of styrene, 14 mL of divinylbenzene, and 1.21 g of benzoyl peroxide (initiator). The aqueous phase was prepared by mixing 0.96 g of gelatin and 50 mL of deionized water at 50 °C for 30 min and then adding 0.48 g of 2-hydroxyethylcellulose and 200 mL of deionized water, which was left overnight. Finally, 19.2 g of sodium chloride was dissolved into this aqueous phase.

In order to prepare the PS–DVB copolymer of low porosity, called (RM-l), the organic phase was diluted in 42 mL of toluene and 18 mL of *n*-heptane. For the copolymer of medium porosity, called RM-m, the organic phase was diluted in 36 mL of *n*-heptane and 24 mL of toluene. Finally, for the preparation of highly porous copolymer, called RM-h, 6 mL of toluene and 54 mL of *n*-heptane were used.

Each respective organic phase was transferred to a reactor (500 mL), which was attached to a reflux condenser. The system was kept under reflux and mechanical stirring for 24 h at 85 °C in an oil bath. The copolymer was washed with 3 L of deionized water at 70 °C. The beads were thoroughly extracted with acetone under reflux for 24 h in a Soxhlet apparatus and dried in an oven at 60 °C for 24 h [1].

Phosphorylation of PS–DVB copolymers

The phosphorylation reaction was conducted with 4.5 g of the RM-h copolymer and 90 mL of 1,2-dichloroethane in a 500-mL reactor equipped with a reflux condenser. The beads were left for 30 min to swell. Besides, 41.04 g of $AlCl_3$ and 18 mL of PCl_3 (molar ratio $P/Al = 1/1.5$) were added to the reactor. The reactor was immersed in an oil bath, the temperature was raised until 60 °C and the reaction was conducted for 15 h. After that, 90 mL of tetrahydrofuran was added to the reactor. Then, 300 mL of cold NaOH 3 mol L^{-1} aqueous solution was slowly added to the system, using an ice bath. After this treatment, the modified beads were thoroughly washed with hot distilled water, then followed by washing with a HCl 3 mol L^{-1} solution and then hot distilled water, and finally with 180 mL of acetone [1].

Determination of total phosphorus

The polymer resin (50 mg), 1.5 g of catalyst (prepared with 14.35 g of K_2SO_4 and 2.5 g of Se), and 4 mL of concentrated sulfuric acid were placed into a Kjeldahl tube. The digestion of the sample was carried out on a hotplate. After cooling the tube, the digested sample was transferred to a 250 mL volumetric flask. The sample was neutralized with NaOH (2 mol L^{-1}) until pH 7 and the flask was filled up with deionized water. Next, 25 mL samples of this solution were transferred into tubes and 5 mL of sodium molybdate (12.5 g sodium molybdate dihydrate/500 mL sulfuric acid—5 mol L^{-1}) and 2 mL of hydrazine solution (1.5 g hydrazine sulfate/1 L water) were added. Thus, the exact final volume after the reagents addition was 32 mL. The tubes were immersed in boiling water for 30 min. After cooling to room temperature, the absorbance at 830 nm was evaluated [16].

Materials characterization

The apparent density of the synthesized copolymers was determined using 10 ± 0.1 mL test tubes. A 10-mL volume of the dry sample was placed into the test tube, which was then weighed. The amount of copolymer was evaluated using the mass of the empty test tube as discussed in reference [17].

The degree of swelling (DS) in 1,2-dichloroethane of the synthesized copolymers was determined using a graduated cylinder (10 ± 0.1 mL), which was filled with about 3 mL of dry copolymer. The solvent was added up to the 10-mL grading and 24 h later the final volume was read. The DS was calculated according to Eq. 1:

$$\mathrm{DS}\ (\%) = (V_\mathrm{f} - V_\mathrm{i})/V_\mathrm{i} \tag{1}$$

where: V_i = volume of the dry copolymer (mL) and V_f = volume of the copolymer after swelling for 24 h (mL) .

Thermal analysis of the unmodified and the phosphorated copolymers was conducted in a TA Instruments (mod. 2050) thermogravimeter from room temperature to 750 °C, at a heating rate of 20 °C min^{-1}, under inert atmosphere (nitrogen) and using open alumina crucibles. Each sample weighed around 20 mg and a gas flow rate of 90 mL min^{-1} was used. The copolymers were also characterized by infrared spectroscopy (FTIR—Perkin-Elmer Spectro One) using KBr pellets.

Shape and surface texture of the particles were monitored with a Philips XL-30 scanning electron microscope operating at 20 keV. The samples were spread on a conductive tape and submitted to gold sputtering prior to analysis. A secondary electron detector, a backscattered electron detector, and an EDS X-ray detector were coupled to the SEM. The set-up conditions used were able to produce good resolution images with minor polymer degradation due to radiation. ASAP area analyzer via nitrogen adsorption (Micromeritcs, ASAP 2010 apparatus) was used to estimate specific surface area, pore diameter, and pore volume.

Pb^{2+} removal from aqueous solutions by phosphorylated cross-linked resins

Influence of pH on the Pb^{2+} removal: A pre-set amount (0.2 g) of phosphorylated resin was added into small beakers with lids. Then, 10 mL of a 50-ppm $Pb(NO_3)_2$ solution was added to the flasks and the pH was adjusted to 3 (using HNO_3—0.1 mol L^{-1}). The flasks were agitated for 10 min on a shaker and the solutions were used for the determination of lead by atomic absorption spectrometry. This procedure was repeated for pH 5 and 6 [18]. Basic solutions were not used due to the undesirable precipitation of lead (II) hydroxide.

Influence of extraction time on the Pb^{2+} removal: a pre-set amount (0.2 g) of phosphorylated resin was added into small beakers with lids containing 10 mL of a 10 ppm $Pb(NO_3)_2$ solution. The pH was adjusted as described above. The solutions were stirred for 1, 15, and 30 min and then the supernatant was collected for the determination of lead by atomic absorption spectrometry. All Pb^{2+} removal evaluations were performed in duplicate.

Results and discussion

In order to prepare three copolymers with varied porosity degrees, the copolymerization of styrene and DVB was carried out using mixtures of toluene and *n*-heptane, a solvating and a non-solvating solvent, respectively, for polystyrene chains, as pore forming agent in different proportions [19]. The apparent density, specific surface area, pore volume, and degree of swelling results obtained for the synthesized (PS–DVB) copolymers are shown in Table 1.

As shown in Table 1, the increase of the *n*-heptane proportion on diluent mixture provoked a slight increase on porosity degree of the copolymers, as can be seen by the values of surface area and apparent density. The copolymer RM-l (30% of *n*-heptane) presented low surface area and unmeasurable pore volume by nitrogen adsorption, whereas the copolymer RM-h (90% of *n*-heptane) showed a surface area of 58 m^2/g and a pore volume of 0.3 cm^3/g. These results are confirmed by the

Table 1 Physico-chemical characterizations of copolymers

Copolymers	Tol/Hep[a]	d_{ap}^{b} (g cm^{-3})	S^{c} (m^2 g^{-1})	V_{fp}^{d} (cm^3 g^{-1})	SD[e] (%)	P^{f} (%)
RM-l	70/30	0.64	0.3	<0.1	167	9.1
RM-m	40/60	0.58	<0.1	<0.1	133	10.0
RM-h	10/90	0.46	58	0.3	93	12.2

[a] Tol/hep: toluene/*n*-heptane ratio in the diluent mixture

[b] Apparent density

[c] Specific surface area

[d] Average pore volume

[e] Swelling degree in 1,2-dichloroethane

[f] Phosphorus incorporated

swelling degree for those copolymers in 1,2-dichloroethane. It is possible to observe that the increase on *n*-heptane content caused a decrease on swelling capacity in this solvent, which can be explained considering that 1,2-dichloethane is a solvating

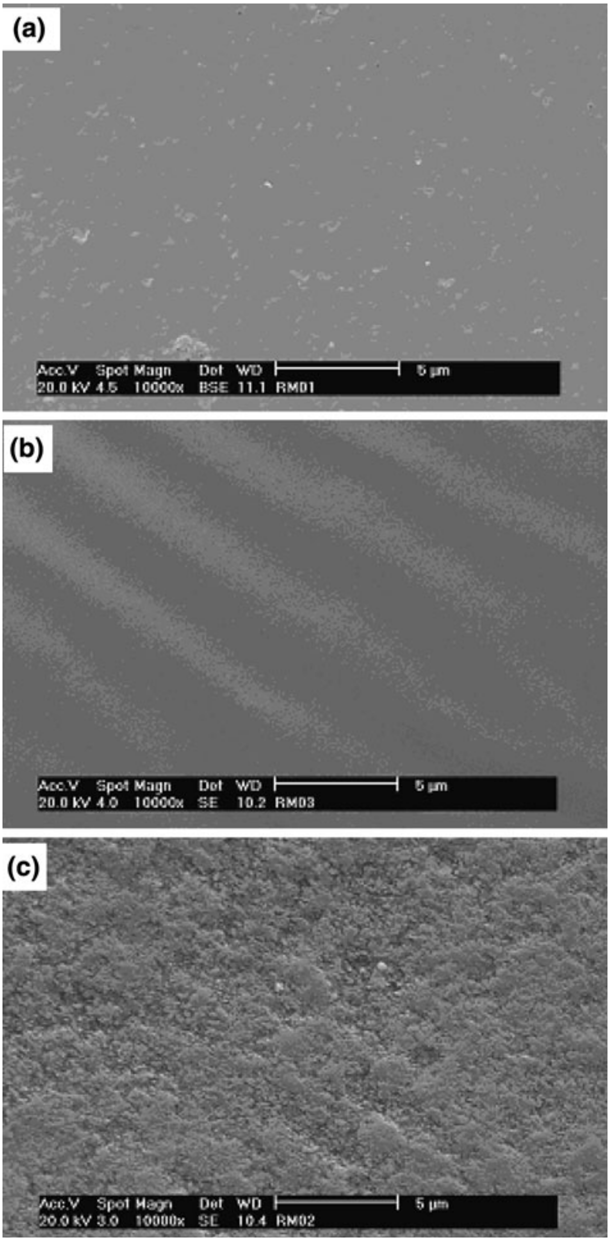

Fig. 1 SEM micrographs: **a** low porosity copolymer (RM-l), **b** medium porosity copolymer (RM-m), and **c** high porosity copolymer (RM-h) (Magnification: ×10,000)

solvent for polystyrene chains and the copolymer RM-l presents a higher content of collapsed mass [20]. The swelling capacity of copolymer beads in a solvating solvent is a result of three contributions: filling of fixed pores, collapsed pores expansion, and internuclear chains swelling [20]. Materials with a lower porosity present a high swelling capacity in solvating solvents than the porous ones because those structures possess higher content of collapsed mass. The expansion of the collapsed mass effectively contributes to the enhancement of the swelling degree.

Scanning electron microscopy was used to evaluate texture, roughness, and physical integrity of the copolymers pearls (Fig. 1a–c). A slight difference in porosity between the synthesized copolymers can be noticed from this figure. The copolymers RM-m and RM-h presented a more heterogeneous surface than the copolymer RM-l indicating that these materials possess a more porous structure.

The copolymers beads RM-l, RM-m, and RM-h with different porosity degrees were reacted with PCl_3 in presence of $AlCl_3$ in order to introduce phosphoryl groups on aromatic rings (Fig. 2). The modification of the copolymers was confirmed by FTIR bands related to P–OH (1040–910 cm^{-1}), P=O ($\sim$1,150 cm^{-1}), and P–H ($\sim$2,350 cm^{-1}) which are characteristics of the phosphoryl group (Fig. 3). In addition, it can be easily seen that the modified copolymers became hydrophilic because of the widening of the bands in the 2,200 to 3,600 cm^{-1} region, which can be attributed to water absorption by the phosphoryl groups [21].

The thermogravimetry (TG) and derivatives (DTG) curves for RM-l, RM-m, and RM-h copolymers and their phosphorilate derivatives are showed in Figs. 4 and 5. Similar thermal degradation curves can be seen for all unmodified copolymers. In the same way, the DTG curves for the three copolymers were similar, presenting only one thermal decomposition stage, with the peak thermal decomposition temperature around 439 °C. Comparing the Figs. 4 and 5, it is possible to observe that the chemical modification of the copolymers was successful. The modified copolymers presented three degradation steps (at approximately 100, 200, and 400 °C) and three DTG peaks related to those weight-loss stages. The first thermal decomposition step at 100 °C can be associated to residual water into the polymers. The second thermal decomposition stage around 200 °C is due to the degradation of phosphoryl groups and the last thermal decomposition stage around 400 °C can be attributed to the degradation of the carbon chains of the copolymers. In addition, the weight loss by thermal decomposition of the unmodified copolymers was almost 100%, leaving almost no residue, while the degradation of the phosphorylated resins was around 60%, with 35–40% of residue.

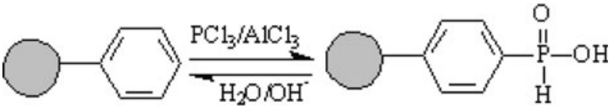

Fig. 2 Reaction of copolymers S–DVB with PCl_3 in presence of $AlCl_3$ [7]

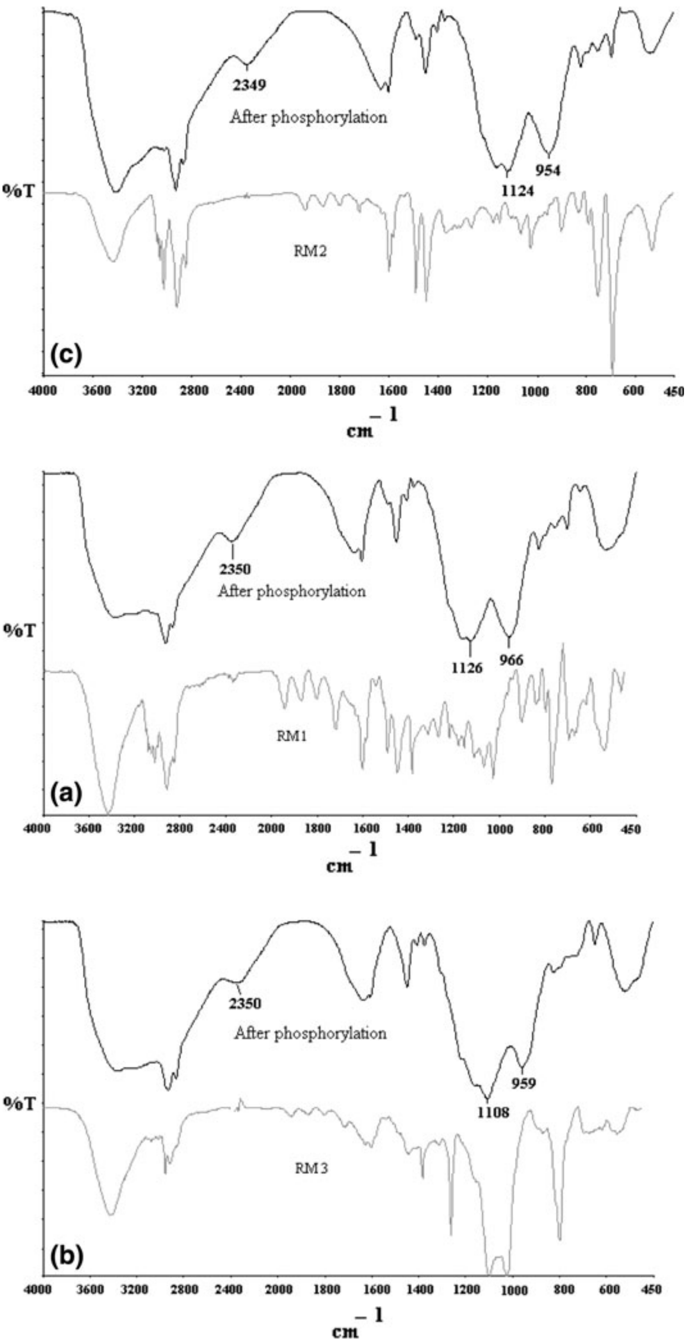

Fig. 3 FTIR spectra of the (PS–DVB) copolymers before and after phosphorylation: **a** low porosity (RM-l), **b** medium porosity (RM-m), and **c** high porosity (RM-h)

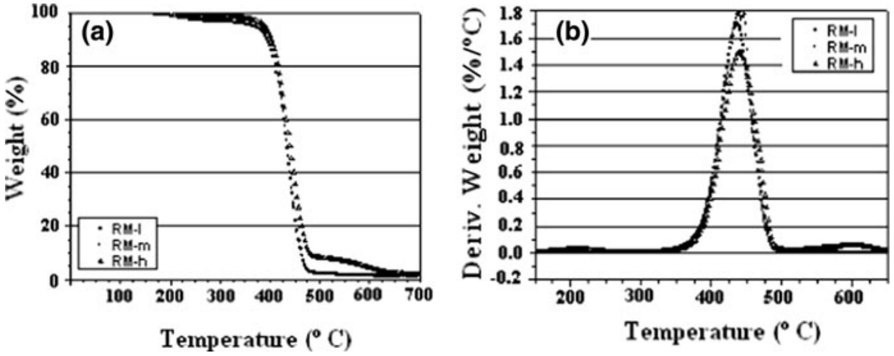

Fig. 4 Curves of TG (**a**) and DTG (**b**) of the PS–DVB unmodified copolymers

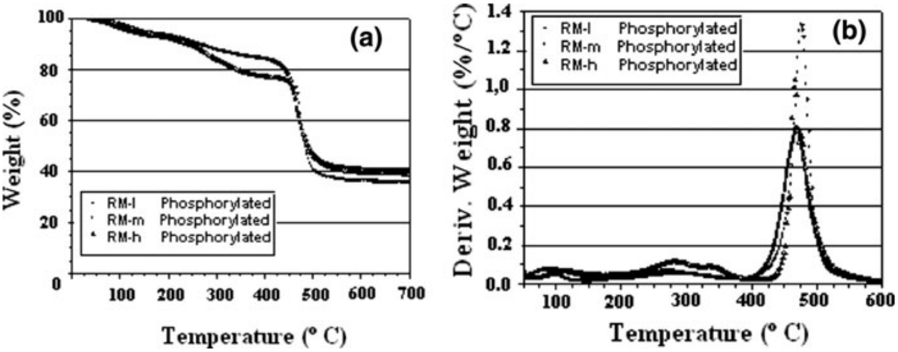

Fig. 5 TG (**a**) and DTG (**b**) curves of the phosphorylated PS–DVB copolymers

The content of total phosphorus incorporated into the phosphorylated resins was determined by spectrophotometry. The phosphorylated copolymers RM-l, RM-m, and RM-h have shown a *%P* content of 9.1, 10.0, and 12.2, respectively (Table 1). Thus, the degree of porosity showed an influence on the phosphorus incorporation, which may be explained by an easier diffusion of the phosphorylating reactants into the network structure brought by the higher porosity. The swelling capacity in 1,2 dichloroethane not influenced the phosphorous content incorporated into copolymers. Although the copolymer RM-h has presented a lower swelling capacity in 1,2-dichloroethane, this material presented higher phosphorous content. The copolymer RM-h presented higher surface area (Table 1). Probably, the higher content of the pores in this material permitted the reactants to reach the more internal network structure, consequently the reaction was more complete for this copolymer [20].

Figure 6 shows SEM micrographs of the unmodified PS–DVB copolymer (RM-h) and the respective phosphorylated resin. After phosphorylation, morphological changes can be noticed on the surface of the resin, such as the appearance of scales and alveoli, confirming the chemical modification of the material.

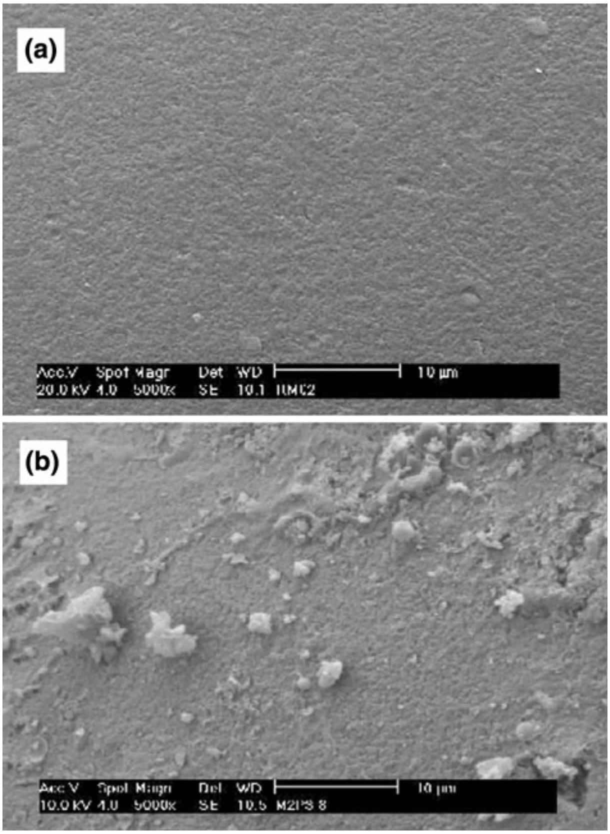

Fig. 6 SEM micrographs of the unmodified high porosity PS–DVB copolymer (**a**) and the corresponding phosphorylated resin (**b**)

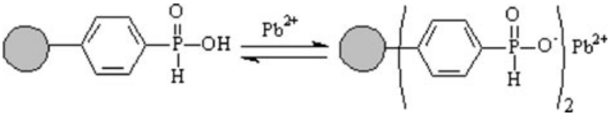

Fig. 7 Reaction of Pb^{2+} ion with phosphorylated resins [18]

The Pb^{2+} ion was removed from aqueous solutions using the phosphorylated resins synthesized as illustrated in Fig. 7 [18].

Tables 2 and 3 show the results of the influence of the pH and extraction time on the removal of Pb^{2+} from aqueous solutions. It is possible to observe that the phosphorylated copolymers presented Pb^{2+} adsorption capacity and this capacity was influenced by the pH and contact time. The highest performance regarding metal removal occurred at pH 6, the least acidic condition. The phosphoryl group gives a weak-acid character to the resin due to the P–OH acid (with moderate/poor acid character). It is possible that, by rising the pH, the acid hydroxyl can dissociate

Table 2 The influence of pH on the Pb^{2+} extraction using 0.2 g resin/50 mL (contact time: 10 min)

pH	% Removal of lead for RM-h	% Removal of lead for RM-m	% Removal of lead for RM-l
3	4.83	3.98	3.23
5	2.70	9.68	16.32
6	61.70	73.04	82.70

Table 3 The influence of contact time on the Pb^{2+} extraction using 0.2 g of resin/10 mL, at pH 6 and initial concentration of Pb^{2+} of 10 ppm

Time (min)	% Removal of lead for RM-h	% Removal of lead for RM-m	% Removal of lead for RM-l
1	47	46	68
15	68	49	99
30	97	99	99

to yield PO^-, improving the coordination with the Pb^{2+} due to an increase in electron density of the oxygen atom [22]. Metal removal increases with contact time and the maximum removal was observed for a contact time of 30 min. This was expected since a longer extraction time, allows greater diffusion of the metal ion into the polymer network. After 30 min of contact, the percentage removal has already reached nearly 100%, and therefore, no further removal will occur above that, preventing Pb^{2+} ion exchange.

Analyzing the Tables 2 and 3, it is possible to observe that, in general the increase on porosity degree provoked a decrease on complexation capacity. This behavior is opposite to the ones verified other works, which have been studied the relationship between the porous characteristics of polymer supports and the efficiency of the chelating resins produced [20, 23]. In those works, it was verified that resins derived from copolymers with higher porosity originated materials with higher capacity because the access of the metal ion to the chelating groups was favored. Probably, the introduction of phosphoryl groups into PS–DVB copolymers increased the swelling capacity in water. This can be proved analyzing the FTIR and TG/DTG data presented on Figs. 3 and 5, respectively. As the RM-l copolymer possess higher content of collapsed mass, it is possible that this copolymer had presented higher swelling degree in water than the RM-m and RM-h copolymers. It may have provided higher contact area between the Pb^{2+} ions and phosphoryl groups for that material [18].

Conclusions

Three PS–DVB copolymers with varied porosity degrees were prepared using mixtures of toluene and *n*-heptane in different proportions. It was possible to observe that the increase of the *n*-heptane proportion on diluent mixture provoked a slight increase on porosity degree of the copolymers. These materials were phosphorylated with PCl_3 and the reaction was confirmed by FTIR, SEM, and TGA.

The phosphorylated resins were effective in removing Pb^{2+} from aqueous solutions containing this metal. The highest performance regarding metal removal occurred at pH 6, the least acidic condition. Metal removal increased with contact time, reaching nearly full removal for a contact time of 30 min. The copolymer RM-l with lower porosity degree presented higher removal capacity than the copolymers RM-m and RM-h.

Acknowledgments We thank the Fundação *Coordenação de Aperfeiçoamento de Pessoal de Nível Superior* (CAPES), *Conselho Nacional de Desenvolvimento Científico e Tecnológico* (CNPq), and *Fundação Carlos Chagas de Amparo à Pesquisa do Estado do Rio de Janeiro* (FAPERJ) for financial support. We would also like to express thanks to PETROFLEX, NITRIFLEX, and METACRIL companies for reagents donation.

References

1. Teixeira VG, Coutinho FMB, Gomes AS (2004) Resinas poliméricas para separação e pré-concentração de chumbo. Quim Nova 27(5):754–762 (in Portuguese)
2. Alexandratos SD, Crick DW (1996) Polymer-supported reagents: application to separation science. Ind Eng Chem Res 35(3):635–644
3. Maheswari MA, Subramanian MS (2005) A XAD-16 3, 4-dihydroxy benzoyl methyl phosphonic acid: a selective preconcentrator for U and Th from acidic waste streams and environmental samples. React Funct Polym 62(1):105–114
4. Suresh A, Rao CVSB, Deivanayaki R, Srinivasan TG, Rao PRV (2003) Studies on the extraction behavior of octyl(phenyl)-*N*-*N*-diisobutylcarbamoylmethylphosphine oxide in polymeric adsorbent resins. Solvent Extr Ion Exch 21(3):449–463
5. Alexandratos SD, Natesan S (1999) Ion-selective polymer-supported reagents: the principle of bifunctionality. React Funct Polym 35(3):431–436
6. Hamabe Y, Hirashima Y, Izumi J, Yamabe K, Jyo A (2009) Properties of a bifunctional chelating resin containing aminomethylphosphonate and sulfonate derived from poly(ω-bromobutylstyrene-co-divinylbenzene) beads. React Funct Polym 69(11):828–835
7. Alexandratos SD, Bates ME (1988) Enhanced ionic recognition by polymer-supported reagents: synthesis and characterization of ion-exchange/precipitation resins. Macromolecules 21(10): 2905–2910
8. Matsunaga H, Ismail AA, Wakui Y, Yokoyama T (2001) Extraction of rare earth elements with 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate impregnated resins having different morphology and reagent content. React Funct Polym 49(3):189–195
9. Santa Maria LC, Souza MAV, Santos FR, Rubenich LMS, Ferreira MDJF, Sa RMR (2008) Thermogravimetric and spectrometric characterizations of poly(styrene-co-divinylbenzene) containing phosphinic and phosphonic acid groups. Polym Eng Sci 48(10):1897–1900
10. Nalwa H (2001) Advanced functional molecules and polymers. Gordon and Breach Science Publishers, Singapore
11. Jandrey AC, de Agular AP, de Agular MRMP, Santa Maria LC, Mazzei JL, Felzenszwalb I (2007) Iodine-poly(2-vinylpyridine-co-styrene-co-divinylbenzene) charge transfer complexes with antibacterial activity. Eur Polym J 43(11):4712–4718
12. Trochimczuk AW, Czerwijska S (2005) In(III) and Ga(III) sorption by polymeric resins with substituted phenylphosphinic acid ligands. React Funct Polym 63(3):215–220
13. Sahni SK, Reedijk J (1984) Coordination chemistry of chelating resins and ion-exchangers. Coord Chem Rev 59(SEP):1–139
14. Beauvais RA, Alexandratos SD (1998) Polymer-supported reagents for the selective complexation of metal ions: an overview. React Funct Polym 36(2):113–123

15. Costa PA, Teixeira VG (2010) Influence of the matrix porosity on the synthesis and adsorption behavior of dithiocarbamate styrenic resins toward zinc(II) and cadmium(II) ions. J Appl Polym Sci 116:3070–3078
16. Jeffery GH, Basset J, Mendlan J, Denney RC (2000) Vogel's textbook of quantitative chemical analysis. Person Education Limited, London, pp 427–428
17. ASTM D 1895-69 (1975) Annual Book of ASTM Philadelphia
18. Trochimczuk AW (1999) New ion-exchange/coordination resins with carboxylate and phosphate functional groups. Eur Polym J 35:1457–1464
19. Grulke EA (1999) Solubility parameter values. In: Brandrup J, Immergut EH, Grulke EA (eds) Handbook of polymers. Wiley, New Jersey, pp 675–714
20. Teixeira VG, Coutinho FMB, Petrocínio FRM, Gomes AS (2005) Determination of accessible chloromethyl groups in chloromethylated styrene-divinylbenzene copolymers. J Braz Chem Soc 16(5):951–956
21. Colthup NB, Daly LH, Wiberley SE (1964) Introduction to infrared and Raman spectroscopy. Academic Press, New York and London, pp 299–300
22. Souza MAV (2008) Synthesis, characterization and evaluation of phosphorylated resins in the removal of Pb^{2+} from aqueous solution. Masters dissertation, Post-graduate Program in Chemistry, IQ-UERJ
23. Coutinho FMB, Rezende SM, Barbosa CCR (2001) Influence of the morphological structure of macroreticular amidoxime resins on their complexation capacity. React Funct Polym 49:235–248