

# Synthesis and Characterization of Phosphonate Ester/Phosphonic Acid Grafted Styrene–Divinylbenzene Copolymer Microbeads and Their Utility in Adsorption of Divalent Metal Ions in Aqueous Solutions

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In this paper the preparation and characterization of some chelating resins, phosphonate grafted on polystyrene–divinylbenzene supports, are reported. The resins were prepared by an Arbuzov-type reaction between chloromethyl polystyrene–divinylbenzene copolymers and triethylphosphite, yielding the phosphonate ester copolymer (resin A). This can be hydrolyzed by HCl to yield the phosphonate/phosphonic acid copolymer (resin B). The phosphonate resins A and B were characterized by determination of the phosphorus content, infrared spectrometry, and thermal analysis. The total sorption capacity of the phosphonate ester functionalized resin (A) and phosphonate/phosphonic acid functionalized resin (B) for divalent metal ions such as Ca<sup>2+</sup>, Cu<sup>2+</sup>, and Ni<sup>2+</sup> was studied in aqueous solutions. Resin A retains ~3.25 mg of Ca<sup>2+</sup>/g of copolymer and 2.75 mg of Cu<sup>2+</sup>/g of copolymer, but retains no Ni<sup>2+</sup> at pH 1. On the other hand, resin B retains 8.46 mg of Ca<sup>2+</sup>/g of copolymer, 7.17 mg of Cu<sup>2+</sup>/g of copolymer, and no Ni<sup>2+</sup> at pH 1. Efficient Ni<sup>2+</sup> retention was observed at pH 7 only for the phosphonate/phosphonic acid functionalized resin (B) at the level of 19 mg of Ni<sup>2+</sup>/g of polymer B. Polymer A was incapable of retaining Ni<sup>2+</sup> at pH 7.

## Introduction

The presence of heavy metal ions in the environment is a major concern due to their toxicity to many life forms. Treatment of wastewaters containing heavy metal ions requires concentration of the metals into a smaller volume followed by recovery or secure disposal. Heavy-metal ions can be removed by adsorption on solid carriers. Nonspecific sorbents, such as activated carbon, metal oxides, silica, and ion-exchange resins have been used in the past.<sup>1</sup> Specific sorbents consist of a ligand (e.g., ion-exchange material or chelating agent) which interacts with the metal ions specifically, and a carrier matrix which may be an inorganic material (e.g., aluminum oxide, silica, or glass) or polymer microbeads (e.g., polystyrene, cellulose, poly(maleic anhydride), or poly(methyl methacrylate)).<sup>2–6</sup>

Copper is an essential element for mammals, plants, and lower forms of organisms. However, high levels of copper can be a toxic threat. Many preconcentration procedures for copper determination have been developed, and they involve different analytical techniques and several materials.<sup>7–9</sup>

Although not recognized until the 1970s, nickel plays numerous roles in biology. In fact, the urease enzyme contains nickel. The NiFe-hydrogenases contain nickel in addition to iron–sulfur clusters. A nickel coenzyme is present in the methyl coenzyme M reductase which powers methanogenic archaea. Exposure to nickel metal and soluble compounds should not exceed 0.05 mg/cm<sup>3</sup> in nickel equivalents per 40-h work week. Nickel sulfide fumes and dust are believed to be carcinogenic, and various other nickel compounds may be as well.<sup>10,11</sup>

As carrier matrixes, polymer microbeads have attracted the most attention because they may be easily produced in a wide

variety of compositions, and modified into specific sorbents, by introducing a variety of ligands. Chelating ion exchange polymers containing functional groups such as iminodiacetate, bipyridine, ketophosphonic acid, phosphonoacetic acid, phosphonic acid, aminothiophosphonate, etc., are well-known. These resins can selectively remove toxic transition-metal and alkaline-earth metal cations. They find diverse applications in the purification of drinking water. Resins containing phosphonic groups have been synthesized and reported in the literature<sup>12,13</sup> and used for ecotoxic metals recovery. Resins with  $\alpha$ -aminoalkylphosphonic groups have been synthesized as well by the addition of diethylphosphonate followed by hydrolysis<sup>14,15</sup> or by adding phosphorous acid on the corresponding polyimines. They have been used for the preliminary evaluation of the sorption capacity toward the Ca<sup>2+</sup> and Co<sup>2+</sup> ions. It was demonstrated that the polymers grafted on  $\alpha$ -aminoalkylphosphonic functional groups have better chelating properties than the commercial Duolite ES 467 resins.

Phosphonate/phosphonic acid grafted on styrene–divinylbenzene copolymers are a class of widely used resins in preconcentration procedures, because of their attractive physical and chemical properties such as porosity, high surface area, durability, and purity.<sup>16</sup> The sorbents are based on organic polymeric materials with chemically bound functional groups which can form chelate complexes with metal ions.

In this context, the purpose of this study was to synthesize phosphonate ester and phosphonate/phosphonic acid functionalized on styrene–divinylbenzene copolymers (7% DVB) and to determine the sorption capacity of Cu<sup>2+</sup>, Ca<sup>2+</sup>, and Ni<sup>2+</sup> from aqueous solutions.

## Experimental Section

**Reagents.** Triethylphosphite (Fluka), chloromethyl styrene–divinylbenzene copolymer (S–7% DVB, Victoria Romania),

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**Table 1. Properties of Chloromethyl Styrene–Divinylbenzene Copolymer (S–7% DVB) Used as Source**

property	
specific surface area ( $S$ ), m <sup>2</sup> /g	30
porous volume ( $V_p$ ), cm <sup>3</sup> /g	0.450
mean particle radius ( $R_m$ ), Å	170
% Cl <sup>a</sup>	17.86
$G_F$ , <sup>b</sup> mmol of Cl/g of copolymer	5.038
$x^c$	0.640
$r^d$	0.07

<sup>a</sup> Total chlorine content. <sup>b</sup> Functionalization degree. <sup>c</sup> Fraction of styrene (S) units bearing pendant  $-\text{CH}_2\text{Cl}$  groups. <sup>d</sup> Fraction of divinylbenzene (DVB) units.

hydrochloric acid concentrated solutions (Merck), 1,2-dichloromethane (Chimopar), ethanol (Chimopar), ethyl ether (Chimopar),  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Merck),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Merck),  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (Aldrich), and nitric acid (Merck) were from commercial sources and were used as received. Solutions used in the experiments were prepared by direct dilution with, or by direct solid dissolution in deionized water. The main properties of the chloromethyl styrene–divinylbenzene copolymer used as starting materials are presented in Table 1.

**Synthesis of Phosphonates Grafted on Insoluble Macromolecular Supports.** A sample of chloromethyl styrene–divinylbenzene copolymer (5 g) and 50 mL of triethylphosphite were added to a 250 mL round-bottom flask fitted with a reflux condenser, mechanical stirrer, and thermometer. The mixture was maintained under stirring for 24 h at the triethylphosphite reflux temperature. The polymer beads separated by filtration were washed with ethanol ( $3 \times 20$  mL), 1,2-dichloromethane ( $3 \times 20$  mL), and ethyl ether ( $3 \times 20$  mL), and dried under 2 kPa vacuum at 50 °C for 24 h. The phosphonate grafted on macromolecular supports (~5 g of resin) was hydrolyzed with hydrochloric acid 37% (~75 mL), with a reflux period of 15 h.

**Determination of Phosphorus Content.**<sup>5,6</sup> The phosphorus content of the polymer-supported phosphonates was obtained by adsorption in water of  $\text{P}_2\text{O}_5$  obtained from a sample of the final product precisely weighed and burnt out in an oxygen atmosphere. The solution obtained was titrated with a 0.005 M aqueous solution of  $\text{Ce}^{3+}$  in the presence of Eriochrome Black T as indicator.

**Procedure for Determination of Divalent Metals ( $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$ ) in Aqueous Solutions.** Preconcentration of  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  in water was performed by a batch technique at room temperature. (a) A 0.5 g sample of phosphonates grafted on S–DVB copolymer was mixed with a 160 mL sample volume containing 100 mg of  $\text{Cu}^{2+}$ /L (100 mg of  $\text{Ca}^{2+}$ /L) in 0.1 N  $\text{HNO}_3$ . (b) Samples (1 mL) were withdrawn from the reaction mixture maintained under mechanical stirring during 7 h in the following time intervals: from 10 to 10 min in the first hour, from 15 to 15 min in the second hour, and from 30 to 30 min in the last 5 h. (c) Each sample was diluted 25 times, and the concentration was determined.

The concentrations ( $C_c$ ) of  $\text{Cu}^{2+}$  (mg/L) and  $\text{Ca}^{2+}$  (mL/L) were determined by atomic absorption spectroscopy on a Varian SpectraAA 110 at wavelengths  $\lambda = 324.8$  nm ( $\text{Cu}^{2+}$ ) and  $\lambda = 422.7$  nm ( $\text{Ca}^{2+}$ ).

The  $C_f$  was calculated using the equation

$$C_f = 25C_c \quad (\text{mg/L}) \quad (1)$$

The amount of  $\text{Cu}^{2+}$  sorbed,  $q$  (mg/g of resin), was calculated as follows:

$$q = (C_{f,0} - C_{f,t})V(10^{-3})/G \quad (\text{mg/g}) \quad (2)$$

where  $C_{f,0}$  and  $C_{f,t}$  are the initial and equilibrium  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  concentrations in the solution at 0 and  $t$  times (mg/L),  $V$  is the volume of the solution (mL), and  $G$  is the mass of the resin sample (g).

Determination of Ni(II) was carried out by following the well-established heptoxime method.<sup>17</sup>

## Results and Discussion

The polymer-analogous Arbuzov reaction is presented in Scheme 1.

**Characterization of Phosphonate Resins.** Some general remarks concerning the analysis of the IR spectra (see Figure 1) are as follows:

(a) The formation of the phosphonate groups,  $-\text{P}(\text{O})(\text{OR})_2$ , was confirmed by the appearance of an intense absorption band at  $1245 \text{ cm}^{-1}$  associated with the  $\text{P}=\text{O}$  stretch (Figure 1a).

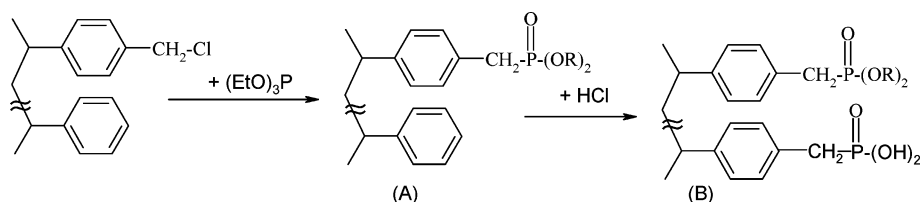
(b) The characteristic  $\text{P}-\text{OH}$  band appears at  $2350 \text{ cm}^{-1}$  (substantially reduced in the spectrum of resin A, Figure 1a), and a medium-intensity band at  $1600 \text{ cm}^{-1}$  is assigned to the  $-\text{P}(\text{O})(\text{OH})$  group (Figure 1b).

These assignments are based on literature vibrational studies on phosphonate materials.<sup>18</sup>

The thermal behavior of the copolymer samples studied by thermogravimetric analysis shows a characteristic “two-step” weight loss (see Figure 2). In the first step (22–200 °C) the constant weight loss (~8%) was attributed to the partial degradation of styrene and impurities such as dialkylphosphates. In the second step (300–450 °C) the weight loss (~50%) was attributed to the depolymerization of polystyrene chains and the degradation of styrene oligomers and impurities such as dialkylphosphates and degradation of  $\text{P}-\text{C}$  bonds of the pendant groups. From the analysis of experimental data was observed that the stability of the copolymer is influenced by the nature of the pendant groups of phosphonate type.

The phosphorus content in the functionalized copolymers was used in order to determine their functionalization degrees. The fraction of the repetitive units functionalized with phosphonate groups was determined by accepting the statistical structure of the repeat unit of the initial copolymer (I) and final copolymer (F), presented in Figure 3.

The following notations are used for the calculation of phosphorus content.

**Scheme 1. Preparation of the Polymer-Grafted Phosphonates ( $\text{R} = -\text{C}_2\text{H}_5$ )**

**Table 2. Characteristics of the Phosphonates Grafted on Styrene–7% Divinylbenzene Copolymers (Resin A) Obtained by Polymer-Analogous Arbuzov Reaction**

phosphite	<i>P</i> (%)	<i>y</i> <sup>a</sup>	<i>G</i> <sub>F</sub> , <sup>b</sup> mmol/g	<i>M</i> <sub>mf</sub> <sup>c</sup>
(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P	6.16	0.34	1.98	170.96

<sup>a</sup>  $y = (\%P)M_{mi}/[100n_P A_P - (\%P)(M_{SF_i} - M_{SF_i})]$ ;  $M_{mi} = rM_{DVB} + xM_{SF_i} + (1 - r - x)M_S$ . <sup>b</sup>  $G_F = y/M_{mf}$ . <sup>c</sup>  $M_{mf} = rM_{DVB} + (x - y)M_{SF_i} + yM_{SF_i} + (1 - r - x)M_S$ .<sup>5,6</sup>

**Table 3. Characteristics of the Bifunctional Phosphonate Ester/Phosphonic Acid Grafted on Styrene–7% Divinylbenzene Copolymers (Resin B)**

group	<i>P</i> (%)	<i>z</i>	<i>y</i> – <i>z</i>	<i>G</i> <sub>F1</sub> , mmol of phosphonic acid/g	<i>G</i> <sub>F2</sub> , mmol of phosphonate/g	<i>M</i> <sub>mf</sub>
P(O)(OH) <sub>2</sub>	3.19	0.18	0.16	1.16	1.03	155.30

$F_i = -CH_2P(O)(OR)_2$  groups  
 $F_f = -CH_2P(O)(OH)_2$  groups  
 $x - y =$  fraction of styrene units bearing pendant  $-CH_2Cl$  groups  
 $y =$  fraction of styrene units bearing pendant  $-CH_2P(O)(OR)_2$  groups (see I)  
 $y - z =$  fraction of styrene units bearing pendant  $-CH_2P(O)(OR)_2$  groups (see F)  
 $z =$  fraction of styrene units bearing pendant  $-CH_2P(O)(OH)_2$  groups (see F)  
 $M_{mi} =$  average molecular weight of the repetitive unit of the initial copolymer  
 $M_{mf} =$  average molecular weight of the repetitive unit of the final copolymer  
 $\%P =$  phosphorus percentage in the final copolymer  
 $A_P =$  atomic weight of phosphorus  
 $M_S =$  molecular weight of the repetitive unit of the styrene  
 $M_{DVB} =$  molecular weight of the repetitive unit of the divinylbenzene  
 $M_{SF_i} =$  molecular weight of the repetitive unit of the styrene functionalized with  $F_i$  groups  
 $M_{SF_f} =$  molecular weight of the repetitive unit of the styrene functionalized with  $F_f$  groups  
 Expressing the percent of *P* as eq 3:

$$\%P = \frac{(y - z)A_P}{M_{mf}} \times 100 \quad (3)$$

The fraction of the styrene units bearing pendant  $-P(O)(OH)_2$  groups can be calculated with eq 4:

$$z = \frac{100yA_P - (\%P)M_{mi}}{100A_P + \%P(M_{SF_f} - M_{SF_i})} \quad (4)$$

where

$$M_{mi} = rM_{DVB} + (x - y)M_{SFCH_2Cl} + yM_{SF_i} + (1 - r - x)M_S \quad (5)$$

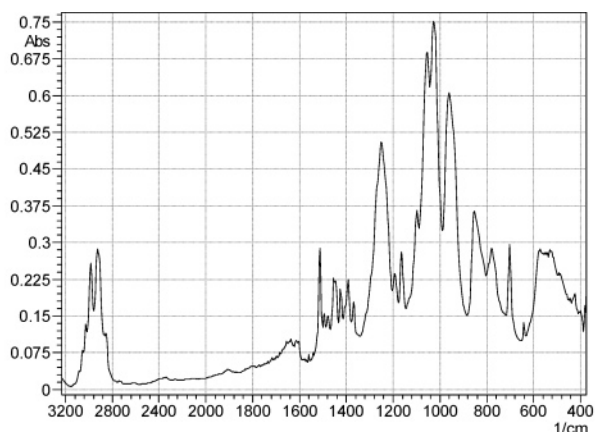
On this basis, the functionalization degrees with  $-P(O)(OH)_2$  and  $-P(O)(OR)_2$  groups were calculated with eqs 6 and 7:

$$G_{F_1} = \frac{z}{M_{mf}} \quad (\text{mmol of } -P(O)(OH)_2 \text{ groups/g of copolymers}) \quad (6)$$

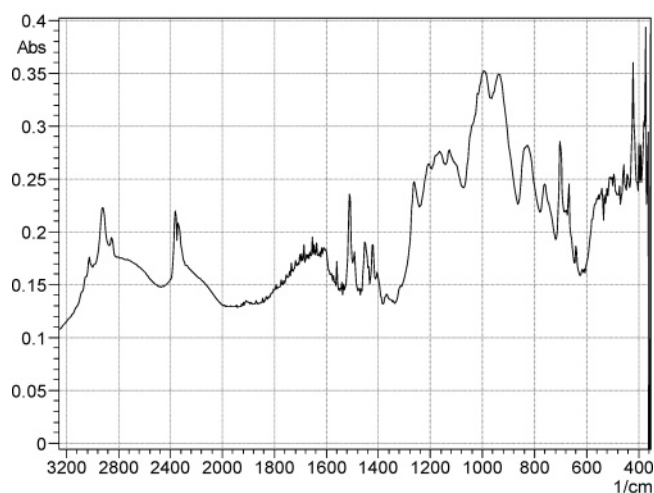
$$G_{F_2} = \frac{y - z}{M_{mf}} \quad (\text{mmol of } -P(O)(OR)_2 \text{ groups/g of copolymers}) \quad (7)$$

where

$$M_{mf} = M_{mi} + z(M_{SF_f} - M_{SF_i}) \quad (8)$$



(a)



(b)

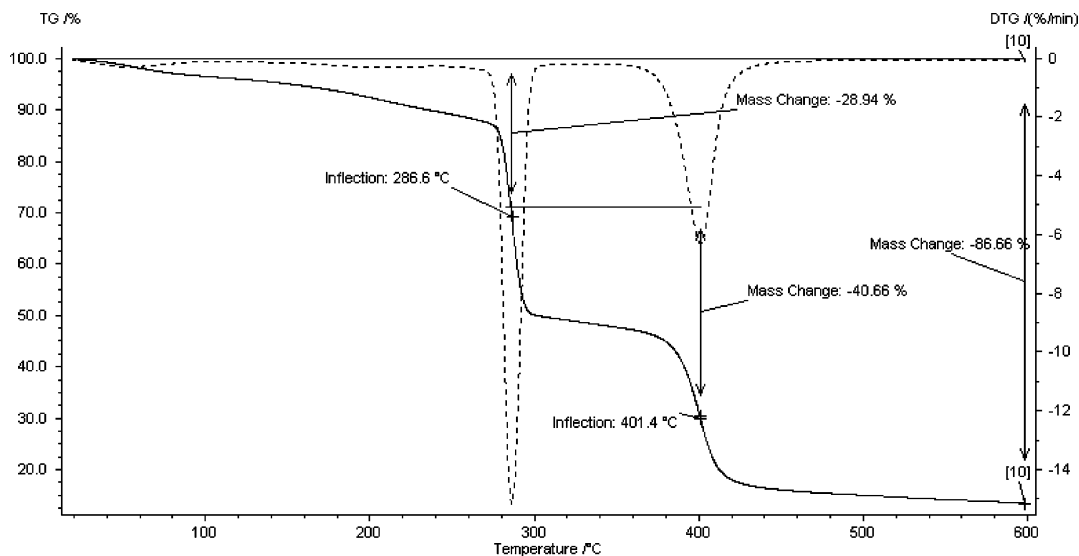
**Figure 1.** IR spectra of polymer-supported diethylphosphonates (resin A (a)) and phosphonate/phosphonic acid (resin B (b)).

The main characteristics of the copolymer functionalized with phosphonate groups are presented in Tables 2 and 3.

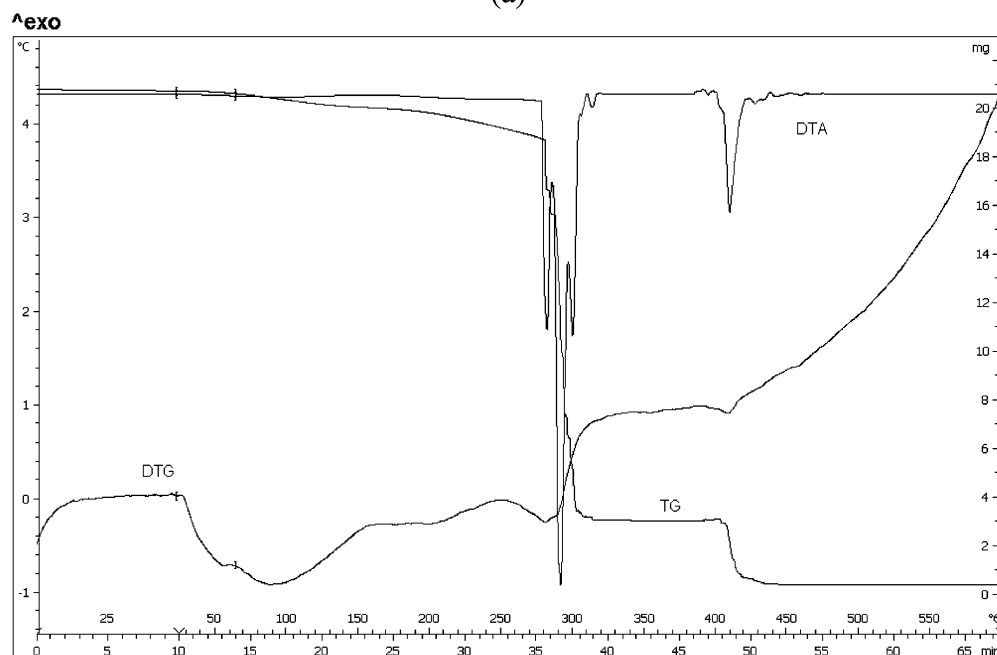
The calculated functionalization degrees found by the analysis above can be explained by the hypothesis that, in spite of extensive swelling of the starting copolymer, some reactive chloromethyl groups are embedded into the micropores of the copolymer “pearls” and could not be accessed by the bulky functionalization agent. Therefore, the functionalization degrees are correlated directly with texture and porosimetric properties of the starting chloromethyl copolymers.

The porosity normally accessible in aqueous solutions and nonswelling media falls in a broad range, and can vary from microporous dimensions of  $<20 \text{ \AA}$  through the mesoporous range of 20–500  $\text{\AA}$  to the macroporous range of  $>500 \text{ \AA}$ .<sup>19</sup>

The analysis of the statistical structure of the repetitive unit of the final copolymer revealed that 16% of the aromatic



(a)



(b)

Figure 2. Thermogravimetric curves for copolymers with diethylphosphonate (resin A (a)) and phosphonate/phosphonic acid (resin B (b)).

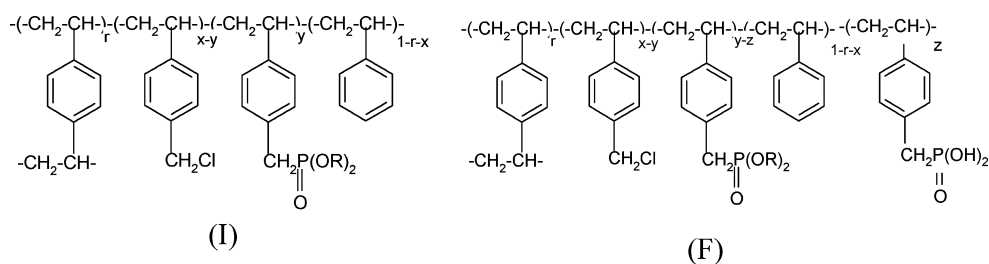


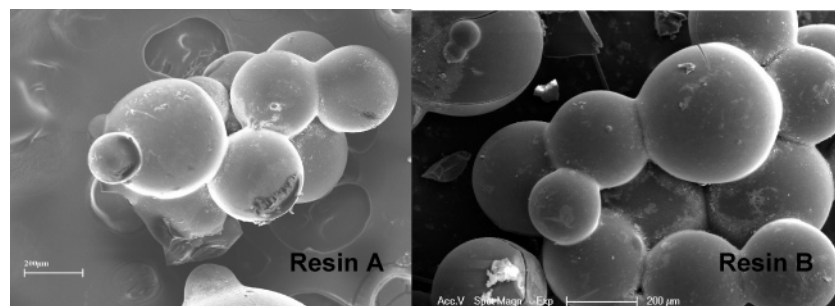
Figure 3. Statistical structure of the repeat unit of the functionalized copolymer (I, F), where R = C<sub>2</sub>H<sub>5</sub>.

rings bear phosphonate groups, 18% of the aromatic rings bear phosphonic acid, and 30% bear residual chloromethyl groups. It should be noted that in the initial copolymer 64% of the aromatic rings were functionalized with chloromethyl groups.

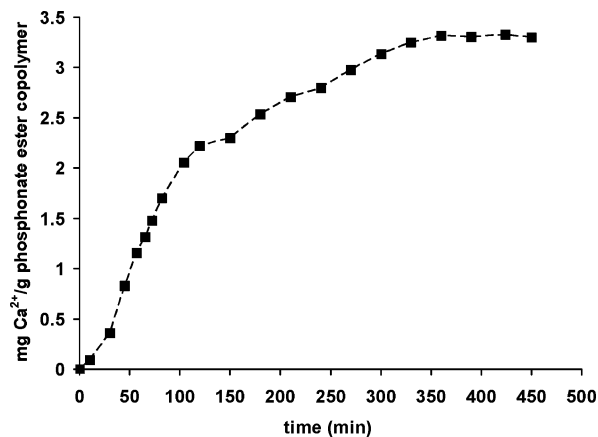
The degrees of functionalization with phosphonates and phosphonic acid groups are relatively high (Table 3), ensuring

a sufficient concentration of active centers per unit mass of the copolymer and being well-suited for application as polymer-supported sorbents in environmental separations.

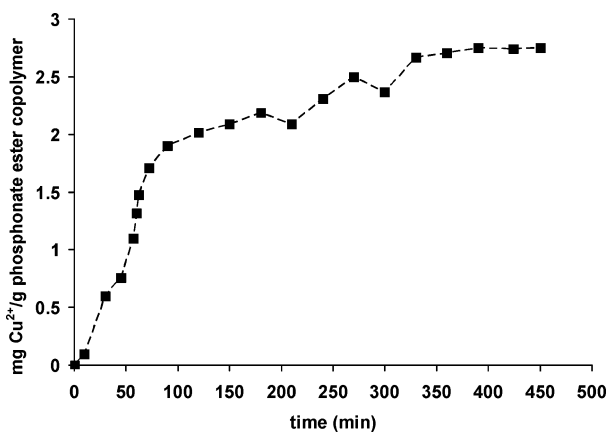
Figure 4 shows scanning electron microscopy (SEM) micrographs of phosphonate ester and phosphonate/phosphonic acid resins A and B. The images reveal that there is a range of particle size from 150 to 250  $\mu\text{m}$ .



**Figure 4.** SEM micrographs of the polymer-supported phosphonate ester (A, left) and bifunctional phosphonate/phosphonic acid (B, right).



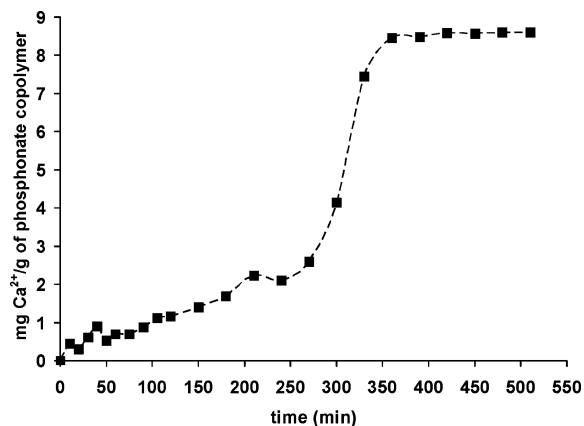
**Figure 5.**  $\text{Ca}^{2+}$  adsorbed from solution as a function of time for phosphonate resins (A) at pH 1.



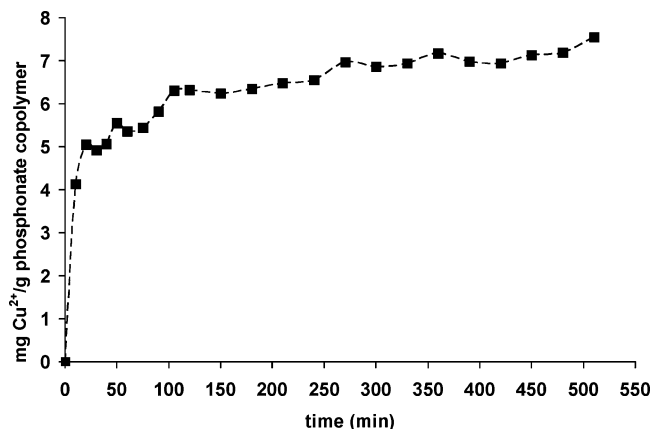
**Figure 6.**  $\text{Cu}^{2+}$  adsorbed from solution as a function of time for phosphonate resins (A) at pH 1.

We initially investigated the adsorption of  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  ions from aqueous solution using the phosphonate/phosphonic acid grafted on styrene-7% divinylbenzene copolymers as specialty sorbents. Aqueous solutions (160 mL) containing specific concentrations of metal ions (100 mg of  $\text{Cu}^{2+}/\text{L}$  in 0.1 N  $\text{HNO}_3$ , or 100 mg of  $\text{Ca}^{2+}/\text{L}$  in 0.1 N  $\text{HNO}_3$ ) were treated with the sorbents at pH 1, in a 250 mL round-bottom flask fitted with a mechanical stirrer at room temperature. Figures 5–8 show adsorption rates of  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  ions onto phosphonate/phosphonic acid grafted copolymer microspheres as a function of time.

Figures 5 and 6 (from resin A) and Figure 7 (from resin B) show high initial adsorption rates, and after 360 min fairly constant values are reached. As can be seen from Figure 8 (from resin B), high adsorption rates are observed at the beginning of adsorption, and after 250 min constant values are obtained. Adsorption of  $\text{Cu}^{2+}$  ions was faster than  $\text{Ca}^{2+}$  ions due to the



**Figure 7.**  $\text{Ca}^{2+}$  adsorbed from solution as a function of time for bifunctional phosphonate/phosphonic acid resins (B) at pH 1.



**Figure 8.**  $\text{Cu}^{2+}$  adsorbed from solution as a function of time for bifunctional phosphonate/phosphonic acid resins (B) at pH 1.

much higher affinity of bifunctional phosphonate/phosphonic acid groups for the first species (see Figures 7 and 8).

The amount of metal ions adsorbed per mass unit of copolymer (i.e., adsorption capacity) increased first with the exposure time of functionalized copolymer with phosphonate (A)/phosphonic acid (B) groups and then reached a constant value which represents saturation of the active centers (available for specific metal ions) on the microspheres.

The total adsorption capacities of the resin functionalized with phosphonate (A) and bifunctional phosphonate/phosphonic acid (B) groups were 2.75 and 7.17 mg/g for  $\text{Cu}^{2+}$ . The maximum  $\text{Ca}^{2+}$  adsorption capacity of the bifunctional phosphonate/phosphonic acid (B) groups grafted on S-DVB microspheres was about 8.46 mg/g of dry polymer, and for the resin functionalized with phosphonate (A) the maximum adsorption capacity was about 3.32 mg of  $\text{Ca}^{2+}/\text{g}$  of copolymer, which were observed at pH 1.0 and 360 min.

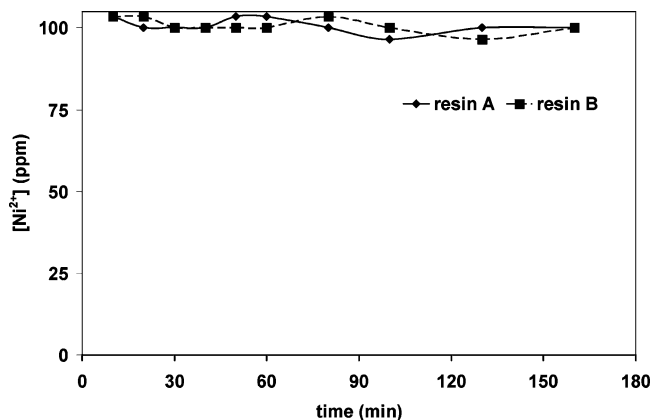


Figure 9. Ni<sup>2+</sup> adsorbed from solution as a function of time for resins A and B at pH 1.

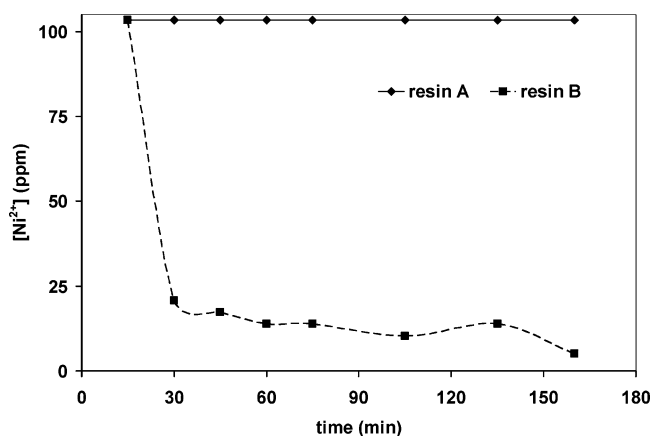


Figure 10. Ni<sup>2+</sup> adsorbed from solution as a function of time for resins A and B at pH 7.

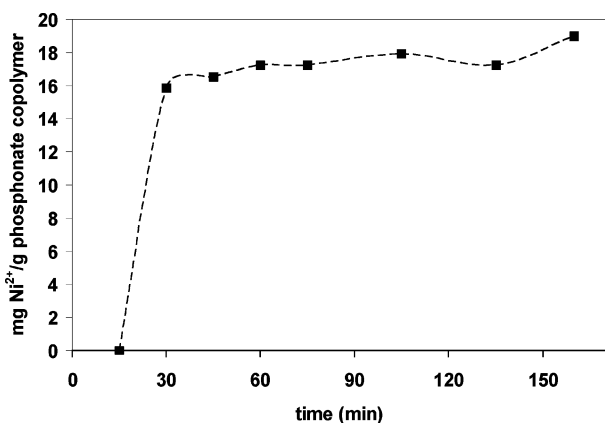
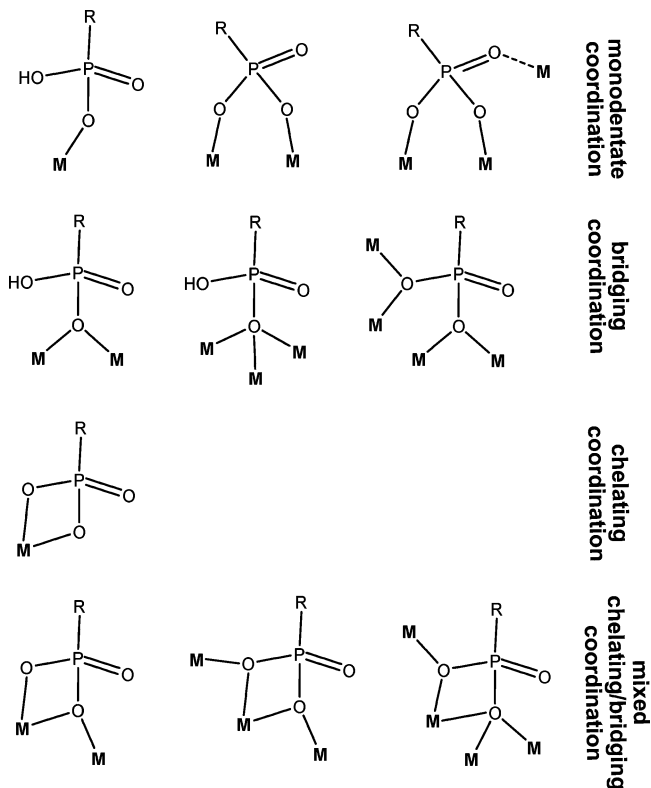


Figure 11. Ni<sup>2+</sup> adsorbed from solution as a function of time for bifunctional phosphonate/phosphonic acid resins (B) at pH 7.

The utility of resins A (phosphonate ester) and B (phosphonate) was tested for absorption of Ni<sup>2+</sup> ions from dilute aqueous solutions at pH 1 and 7. The results are shown in Figures 9–11. Resins A and B absorb no Ni<sup>2+</sup> at pH 1 (Figure 9). Efficient Ni<sup>2+</sup> absorption was observed at pH 7 (Figure 10) only for the phosphonate-functionalized resin (B) at the level of 19 mg of Ni<sup>2+</sup>/g of polymer B (Figure 11). Polymer A was incapable of absorbing Ni<sup>2+</sup> at pH 7.

The inability of both polymer supports for efficient sorption of Ni<sup>2+</sup> at pH 1 may be a result of the lower affinity of the organophosphonate/phosphonic acid pendant groups for Ni<sup>2+</sup>.<sup>20</sup> However, at pH 7 the phosphonic acid group is deprotonated, and thus, coordination to Ni<sup>2+</sup> is greatly enhanced.

## Scheme 2. Coordination, Chelating, and Bridging Modes for Metal–Phosphonate Interactions



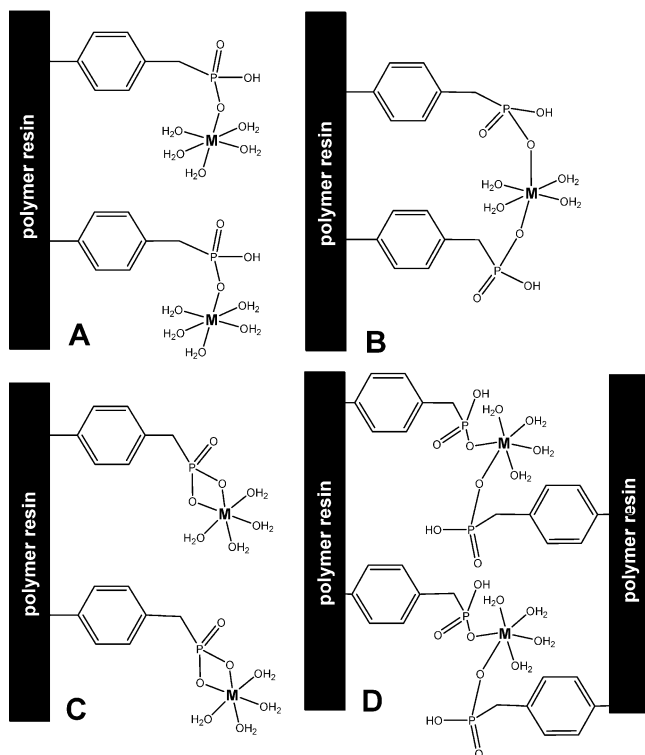
Mechanistically, adsorption of metal ions by these phosphonate-grafted copolymers is based on coordination of soluble metal ions (Cu<sup>2+</sup>, Ca<sup>2+</sup>, and Ni<sup>2+</sup> in this case). Affinity of phosphonate moieties for metal ions in aqueous solutions have been well documented in the literature.<sup>21</sup> Phosphonate groups exhibit variable affinity for various metals.<sup>22</sup> They also demonstrate a tendency to form chelate groups and bridging systems. Scheme 2 shows various coordination modes of the phosphonate moiety with a metal cation.

The number of metal–phosphonate coordination modes increases as the number of phosphonate moieties increases in the same phosphonate molecule. Due to the complication of the Fourier transform infrared spectra usually obtained for metal–phosphonate compounds, it is not possible to predict the precise mode(s) of polymer-grafted phosphonate groups with Cu<sup>2+</sup>, Ca<sup>2+</sup>, and Ni<sup>2+</sup>. However, we can propose the most probable modes, and these are shown in Scheme 3. It is worth noting that the coordination environment of the metal (most likely an octahedral coordination sphere) must be heavily hydrated due to the excess water used as solvent. Coordination scheme B seems less likely because the proximity of two phosphonate groups is necessary. Mode D cannot be excluded, as metal ions can coordinate to two different phosphonate moieties from two neighboring resin microparticles. The reduced absorption ability of resin A may be assigned to the presence of phosphonate ester groups, which have diminished coordinating capabilities compared to the “free”, deprotonated phosphonate group.

By examining Figures 5 and 7 (Ca<sup>2+</sup> absorption) and Figures 6 and 8 (Cu<sup>2+</sup> absorption), a number of important features become evident. In general, Cu<sup>2+</sup> has a greater affinity for phosphonate moieties compared to Ca<sup>2+</sup>.<sup>22</sup>

This is consistent with the fact that resin B absorbs Cu<sup>2+</sup> much faster than resin A and also has a greater final absorption capacity. Resin B absorbs ~5 mg of Cu<sup>2+</sup> within ~30 min,

### Scheme 3. Possible Mechanisms of Absorption of Metal Ions by the Phosphonate-Grafted Copolymers

 $M^{2+} = \text{Cu, Ca, Ni}$ 


whereas resin B reaches  $\sim 2.5$  mg of  $\text{Cu}^{2+}$  capacity after  $\sim 450$  min. This can be explained by the presence of ethyl phosphonate groups that have virtually no affinity for metal ions. The case of  $\text{Ca}^{2+}$  absorption requires some comment. Both resins A and B reach  $\sim 3$  mg of  $\text{Ca}^{2+}$  capacity after  $\sim 300$  min (note the difference in y-axis scale). However, resin B continues to further absorb  $\text{Ca}^{2+}$  until it reaches  $\sim 8$  mg capacity. Perhaps the low affinity of phosphonate groups for  $\text{Ca}^{2+}$  reduces the driving force for phosphonate diethyl ester hydrolysis to liberate additional phosphonate groups. Ester hydrolysis may be occurring in the  $\text{Cu}^{2+}$  case, but is likely faster than in  $\text{Ca}^{2+}$ .

### Conclusions

The proposed procedure for preparation of phosphonates grafted on S-7% DVB is simple and efficient. Copolymers styrene-divinylbenzene functionalized with phosphonate groups can retain  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  ions.  $\text{Ni}^{2+}$  can be absorbed only by resin B at pH 7. Adsorption capacity of  $\text{Cu}(\text{II})$  and  $\text{Ca}(\text{II})$  increases with the increasing of exposure time of copolymer functionalized with phosphonate/phosphonic acid groups.  $\text{Ni}^{2+}$  reaches a maximum for polymer B essentially after 30 min, reaching a 19 mg of  $\text{Ni}^{2+}$  capacity per gram of polymer B.

It is apparent that absorption performance could be improved by introducing a greater number of phosphonate groups in the polymeric resins. Such efforts are under way in our laboratories.

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