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 triethylphosphate, 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$^{2+}$, Cu$^{2+}$, and Ni$^{2+}$ was studied in aqueous solutions. Resin A retains ~3.25 mg of Ca$^{2+}$/g of copolymer and 2.75 mg of Cu$^{2+}$/g of copolymer, but retains no Ni$^{2+}$ at pH 1. On the other hand, resin B retains 8.46 mg of Ca$^{2+}$/g of copolymer, 7.17 mg of Cu$^{2+}$/g of copolymer, and no Ni$^{2+}$ at pH 1. Efficient Ni$^{2+}$ retention was observed at pH 7 only for the phosphonate/phosphonic acid functionalized resin (B) at the level of 19 mg of Ni$^{2+}$/g of polymer B. Polymer A was incapable of retaining Ni$^{2+}$ 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. 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)).

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.

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$^2$ in nickel equivalents per 40-h work week. Nickel sulfide fumes and dust are believed to be carcogenic, and various other nickel compounds may be as well.

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 and used for ecotoxic metals recovery. Resins with α-aminoalkylphosphonic groups have been synthesized as well by the addition of diethylphosphonate followed by hydrolysis or by adding phosphorous acid on the corresponding polyimines. They have been used for the preliminary evaluation of the sorption capacity toward the Ca$^{2+}$ and Co$^{2+}$ ions. It was demonstrated that the polymers grafted on α-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 pre-concentration procedures, because of their attractive physical and chemical properties such as porosity, high surface area, durability, and purity. 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$^{2+}$, Ca$^{2+}$, and Ni$^{2+}$ from aqueous solutions.

Experimental Section

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

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hydrochloric acid concentrated solutions (Merck), 1,2-dichloromethane (Chimopar), ethyl ether (Chimopar), Ca(NO₃)₂·4H₂O (Merck), CuSO₄·5H₂O (Merck), NiSO₄·6H₂O (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 × 20 mL), 1,2-dichloromethane (3 × 20 mL), and ethyl ether (3 × 20 mL), and dried under 2 kPa vaccum 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

The phosphorus content of the polymer-supported phosphonates was obtained by adsorption in water of P₂O₅ 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 Ce₃⁺ in the presence of Erichrome Black T as indicator.

### Procedure for Determination of Divalent Metals (Ca²⁺, Cu²⁺, and Ni²⁺) in Aqueous Solutions

Preconcentration of Cu²⁺ and Ca²⁺ 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 Cu²⁺/L (100 mg of Ca²⁺/L) in 0.1 N HNO₃. (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.

### 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, −P(O)(OR)₂, was confirmed by the appearance of an intense absorption band at 1245 cm⁻¹ associated with the P=O stretch (Figure 1a).

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

These assignments are based on literature vibrational studies on phosphonate materials.

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 P–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 determined by atomic absorption spectroscopy on a Varian SpectrAA 110 at wavelengths λ = 324.8 nm (Cu²⁺) and λ = 422.7 nm (Ca²⁺).

The Cᵣ was calculated using the equation

\[ Cᵣ = \frac{25C_c}{V(10^{-3})/G} \] (1)

The amount of Cu²⁺ sorbed, q (mg/g of resin), was calculated as follows:

\[ q = \frac{(C_{t,0} - C_{t,e})V(10^{-3})/G}{m} \] (2)

where \(C_{t,0}\) and \(C_{t,e}\) are the initial and equilibrium Cu²⁺ and Ca²⁺ 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.

### Scheme 1. Preparation of the Polymer-Grafted Phosphonates (R = −C₂H₅)

![Scheme 1. Preparation of the Polymer-Grafted Phosphonates (R = −C₂H₅)](image)
The fraction of the styrene units bearing pendant \(-\text{CH}_2\text{Cl}\) groups
\[ x-y = \text{fraction of styrene units bearing pendant \(-\text{CH}_2\text{Cl}\) groups} \]

\[ y = \text{fraction of styrene units bearing pendant \(-\text{CH}_2\text{P(O)(OH)}_2\) groups (see I)} \]

\[ y-z = \text{fraction of styrene units bearing pendant \(-\text{CH}_2\text{P(O)(OR)}_2\) groups (see F)} \]

\[ z = \text{fraction of styrene units bearing pendant \(-\text{CH}_2\text{P(O)(OH)}_2\) groups (see F)} \]

\[ M_{mi} = \text{average molecular weight of the repetitive unit of the initial copolymer} \]

\[ M_{mf} = \text{average molecular weight of the repetitive unit of the final copolymer} \]

\[ \%P = \text{phosphorus percentage in the final copolymer} \]

\[ A_P = \text{atomic weight of phosphorus} \]

\[ M_S = \text{molecular weight of the repetitive unit of the styrene} \]

\[ M_{DVB} = \text{molecular weight of the repetitive unit of the divinylbenzene} \]

\[ M_{SF_i} = \text{molecular weight of the repetitive unit of the styrene functionalized with F}_i \text{ groups} \]

\[ M_{SF_f} = \text{molecular weight of the repetitive unit of the styrene functionalized with F}_f \text{ groups} \]

Expressing the percent of P as eq 3:

\[ \%P = \frac{(y - z)A_P}{M_{mf}} \times 100 \]  

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

\[ z = \frac{100yA_P - (%P)M_{mi}}{100A_P + %P(M_{SF_f} - M_{SF_i})} \]  

where

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

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

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

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

where

\[ M_{mf} = M_{mi} + z(M_{SF_f} - M_{SF_i}) \]

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 \(<20\ \text{Å}\) through the mesoporous range of \(20-500\ \text{Å}\) to the macroporous range of \(>500\ \text{Å}\).

The analysis of the statistical structure of the repetitive unit of the final copolymer revealed that 16% of the aromatic...
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 μm.
We initially investigated the adsorption of Cu$^{2+}$ and 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 Cu$^{2+}$/L in 0.1 N HNO$_3$, or 100 mg of Ca$^{2+}$/L in 0.1 N 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 Cu$^{2+}$ and 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 Cu$^{2+}$ ions was faster than Ca$^{2+}$ ions due to the 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 Cu$^{2+}$. The maximum 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 Ca$^{2+}$/g of copolymer, which were observed at pH 1.0 and 360 min.
The utility of resins A (phosphonate ester) and B (phosphonate) was tested for absorption of Ni\(^{2+}\) 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\(^{2+}\) at pH 1 (Figure 9). Efficient Ni\(^{2+}\) absorption was observed at pH 7 (Figure 10) only for the phosphonate-functionalized resin (B) at the level of 19 mg of Ni\(^{2+}\)/g of polymer B (Figure 11). Polymer A was incapable of absorbing Ni\(^{2+}\) at pH 7.

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

Mechanistically, adsorption of metal ions by these phosphonate-grafted copolymers is based on coordination of soluble metal ions (Cu\(^{2+}\), Ca\(^{2+}\), and Ni\(^{2+}\) in this case). Affinity of phosphate moieties for metal ions in aqueous solutions have been well documented in the literature.\(^{21}\) Phosphonate groups exhibit variable affinity for various metals.\(^{22}\) 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 phosphate 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 phosphate groups with Cu\(^{2+}\), Ca\(^{2+}\), and Ni\(^{2+}\). 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 phosphate 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 phosphate group.

By examining Figures 5 and 7 (Ca\(^{2+}\) absorption) and Figures 6 and 8 (Cu\(^{2+}\) absorption), a number of important features become evident. In general, Cu\(^{2+}\) has a greater affinity for phosphate moieties compared to Ca\(^{2+}\).\(^{22}\)

This is consistent with the fact that resin B absorbs Cu\(^{2+}\) much faster than resin A and also has a greater final absorption capacity. Resin B absorbs \(~5\) mg of Cu\(^{2+}\) within \(~30\) min,
whereas resin B reaches ~2.5 mg of Cu\(^{2+}\) capacity after ~450 min. This can be explained by the presence of ethyl phosphate groups that have virtually no affinity for metal ions. The case of Ca\(^{2+}\) absorption requires some comment. Both resins A and B reach ~3 mg of Ca\(^{2+}\) capacity after ~300 min (note the difference in y-axis scale). However, resin B continues to further absorb Ca\(^{2+}\) until it reaches ~8 mg capacity. Perhaps the low affinity of phosphate groups for Ca\(^{2+}\) reduces the driving force for phosphate diethyl ether hydrolysis to liberate additional phosphate groups. Ester hydrolysis may be occurring in the Cu\(^{2+}\) case, but is likely faster than in Ca\(^{2+}\).

**Conclusions**

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

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

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**Literature Cited**


19. (a) Hall, P. J.; Galan, D. G.; Machado, W. R.; Mondragon, F.; Barria, E. B.; Sherrington, D. C.; Calo, J. M. Use of contrast-enhanced small-angle neutron scattering to monitor the effects of solvent swelling on the...


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