Behaviour of Polymeric Resins Bearing Various Phosphorus Containing Ligands towards Metal Ions from Aqueous Solutions

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Abstract: Polymeric resins with phosphonate esters are synthesized via Michaelis-Becker reaction, characterized and used in the removal of Cu(II) from aqueous solutions. It is found that phosphonate phenyl is able to absorb as 0.037 mmolCu/mmol phosphonate phenyl.

Keywords: phosphonates, styrene-divinylbenzene microbeads, removal of metal ions

1. Introduction

The development of crosslinked polymers and copolymers of styrene and divinylbenzene with a well-defined porous structure and monodisperse size has received great interest [1,2]. Many low molecular chelating compounds with phosphorus have been attached to polymer surfaces in order to form functional ligands, e.g. by copolymerization of suitable monomers; by immobilization of a pre-formed ligands; by chemical modification of groups originally present on the polymer surface [3].

The chemical modification was chosen in this study as the synthesis method in order to introduce specific ligands into the polymeric structure with the aim of producing chelating resins containing phosphonate functional groups able of metal ion separations from various waste-waters. In literature the synthesis of polymers functionalized with phosphonic acid groups [4,5] and phosphonate groups [6-8] is mentioned.

Interest in obtaining grafted polymers has increased lately due to the large fields of possible applications: ion exchangers [8,9] catalysts [10], antibacterial agents [3,11] and reagents in fine organic synthesis [12].

In this work we describe the chemical preparation, in multiphase systems, of phosphonates grafted on styrene-divinylbenzene copolymer and their characterization by thermogravimetric analysis.

The aim of this work was to asses the possibility of application of chelating resins obtained by functionalization of styrene-divinylbenzene copolymers with phosphonate groups in copper separation and preconcentration. Atomic absorption spectrometry is nowadays the most common method for trace metal determination in various materials.

2. Experimental

Synthesis of phosphonates grafted on insoluble macromolecular supports

The synthesis of the phosphonates grafted on a macroporous styrene-7% divinylbenzene copolymer-support was performed by the method previously described [6,7]. In a 250 ml round bottom flask fitted with stirrer, reflux condenser and thermometer, a 5 g sample of styrene-7%divinylbenzene copolymer and 100 ml dioxane were added. The mixture was then maintained under stirring for 2 hours at room temperature for swelling of the copolymer beads. Then, dialkyl/arylphosphite and natrium carbonate were added, in order to achieve a molar ratio chloromethyl groups:diphosphite:natrium carbonate = 1:1.5:1.5 and 0.05% tetramethylammonium iodide catalyst, respectively. The mixture was kept under stirring for 24 hour at a reaction temperature of 30 ^{o}C. The polymer beads separated by filtration, were washed with hydrochloric acid 0.1 N (3x20 ml), ethanol (3x20 ml), 1,2-dichloromethane (3x20 ml) and ethyl ether (3x20 ml), and dried under 2kPa vaccum at 50 ^{o}C for 24 h.

Sorption of Cu^{2+} from aqueous solution on phosphonates grafted styrene-divinylbenzene copolymer [13-15]

Cu^{2+} ion separation from aqueous solutions was performed by a batch technique at room temperature. 0.5 grams of of styrene-7%divinylbenzene copolymer functionalized with phosphonate pendant groups were added to a volume solution containing 100 mg Cu(lI) in 0.1 N HNO$_3$ and maintained under mechanical stirring for 7 hours. The residual Cu(II) content in solution was

determined on samples (1 mL) taken from the mixture as follows: at 10 min. interval in the first hour, at 15 min. interval in the second hour and at 30 min. interval in the last 5 hours. Each sample was diluted (ratio 1:25) and the concentration of Cu(II) was determined by atomic adsorption spectroscopy on SpectrA 110 coupled with GTA-110 at wavelength $\lambda= 324{,}8$ nm (Cu^{2+}).

The amount of Cu(II) sorbed, q (mg/g), was calculated as follow:

$$q = (C_{f,0} - C_{f,t}) \times V \times 10^{-3} / G \ \ (mg/g) \quad (1)$$

where: $C_{f,0}$ −, $C_{f,t}$ – are initial and the equilibrium Cu(II) concentration (mg/L) in the solution at 0 and t times; V – is the volume of the solution (mL), G- is the mass of resin sample (g).
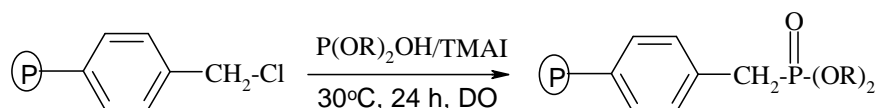
Characterization

Determination of the chlorine content: A sample of the final reaction product, precisely weighted, was burnt out in an oxygen atmosphere; the gases were absorbed in an aqueous solution of H_2O_2 (0.15 %,W) and the chloride ion was quantitatively determined by potentiometric titration with an aqueous solution of $AgNO_3$ 0.05M [16].

Scanning electron microscopy (SEM) with a Philips XL-20 microscope, the thermal analysis of samples was performed with TG 209 (Netzsch) in nitrogen atmosphere with a neat rate of 5 K/min in range $20^{o}C$ to $600^{o}C$, the quantitative analysis of metal ions was carried out by atomic adsorption spectroscopy on Varian SpectrAA 110 coupled with GTA-110.

3. Results and Discussion

Phosphonates grafted on a "gel-type" styrene-7%divinylbenzene copolymer are presented in Scheme 1.
The products of the polymer-analogous reactions were clearly confirmed as phosphonates by the following observations resulted from the analysis of the IR spectra:
- the decrease in the intensity of the chloromethyl absorption band, δCH_2Cl at 1430 cm^{-1} suggests that a polymer-analogous reaction of the chloromethyl groups of the initial copolymer took place;
- the appearance of the absorption band at 1210 cm^{-1} was associated with the valence vibration of P=O bond, respectively the apparition of the absorption band at 1050 cm^{-1} was attributed to the valence vibration of P-O-C bond.

Scheme 1. Preparation of the polymer-grafted phosphonates

The chlorine content in the functionalized copolymers was used in order to determine their functionalization degrees and yields of the polymer-analogous reactions.
The fraction of the repetitive units functionalized with phosphonate groups, was determined by accepting the statistical structure of the repetitive unit of the final copolymer presented in Figure 1.
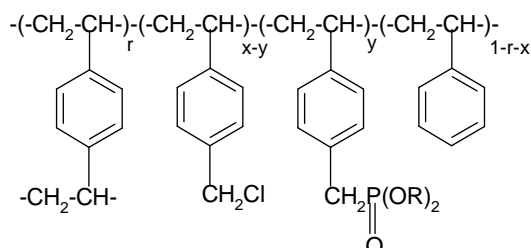

Figure 1. Design of statistical structure of the repetitive unit of the functionalized copolymer

Using the notations:
x – fraction of styrene units bearing pendant $-CH_2Cl$ groups (Fi); y – fraction of styrene units bearing pendant $-CH_2P(O)(OR)_2$ groups (Ff); 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; %Clf –chlorine percentage in the final copolymer; A_{Cl} – atomic weight of chlorine; M_S – molecular weight of the repetitive unit of the styrene; M_{DVB} – molecular weight of the repetitive unit of the divinylbenzene; M_{SFi} – molecular weight of the repetitive unit of the styrene functionalized unit Fi groups; M_{SFf} – molecular weight of the repetitive unit of the styrene functionalized with Ff groups; G_F – functionalization degree; η_F – functionalization yield.

The fraction of styrene units bearing phosphonate groups, obtained by polymer-analogous reactions was calculated from the chlorine content in the final products:

$$\%Cl_f = \frac{(x-y) \cdot A_{Cl}}{M_{mf}} \cdot 100 \quad (1)$$

where:
$$M_{mf} = M_{mi} + y(M_{SFf} - M_{SFi}) \quad (2)$$
$$M_{mi} = r \cdot M_{DVB} + x \cdot M_{SF}CH_2Cl + (1-r-x) \cdot M_S \quad (3)$$

The fraction of the styrene units bearing pendant phosphonate groups was calculated with the equation (4):

$$y = \frac{100 \cdot x \cdot A_{Cl} - \%Cl_f \cdot M_{mi}}{100 \cdot A_{Cl} + \%Cl_f \cdot (M_{SFf} - M_{SFi})} \quad (4)$$

The yields of functionalization are relatively high (see Table 1), ranging from 37 to 75%, ensuring a sufficient concentration of active centers per unit mass of the copolymer and being well suited for application in environmental separations. The functionalization yields are directly correlated with the texture and porosimetric properties of the starting chlorometylated copolymers.

TABLE 1. Characteristics of the polymer-grafted phosphonates

No.	Prod. code	Phosphite	Cl_f (%, W)	y	G_F^a (mmoles/g)	η_F^b (%)
1	Bu	$(C_4H_9O)_2POH$	4.27	0.399	1.997	62.34
2	De	$(C_{10}H_{21}O)_2POH$	7.85	0.239	1.320	37.34
3	FE	$(C_6H_5O)_2POH$	2.36	0.485	2.084	75.78
4	Bz	$(C_6H_5CH_2O)_2POH$	2.74	0.455	1.900	71.09

a. $G_F = \dfrac{y}{M_{mf}}$; b. $\eta_F = \dfrac{y}{x} \cdot 100$, x= 0.640.

Even admitting an extensive swelling of starting copolymer, we justify the functionalization degrees by the fact that some of functionalizable chloromethyl groups are placed into the micropores from the structure of copolymer pearls and it could be inaccessibly for the bulky functionalization agent, so the functionalization degrees are correlated directly with texture and porosimetric properties of the starting chloromethyl copolymers.

The presence of aryl radicals in the environment of phosphonate groups had a favorable effect on functionalization degrees and functionalization yields.

Figure 2 shows scanning electron microscopy (SEM) micrographs of phosphonate ester. The increase in the alkyl chain length of the phosphonate groups had an unfavorable effect, the best results being obtained with dibuthylphosphonate groups.
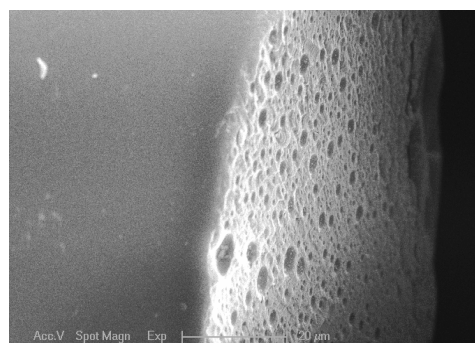

Figure 2. SEM Image of phosphonate copolymer

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.

TABLE 2. The weight loss for all synthesized polymers

Sample	Prod. Code	Weight loss (%)			T inflexion (°C)
		20-200°C	20-300°C	20-400°C	
0	S-7%DVB	3.25	14.25	23.72	427.7
1	Bu	4.70	12.99	39.57	405.0
2	De	4.74	12.27	52.87	394.7
3	FE	7.24	11.85	34.04	399.2
4	Bz	5.36	11.51	42.24	405.1

The thermogravimetric analysis indicated changes in the thermal stability of the polymers functionalized with phosphonate pendant groups in comparison with the chloromethylated styrene-divinylbenzene macromolecular support. As it can be seen in Table 2, the thermal stability is affected by the nature of the R radicals of the phosphonate groups; product 0, divinylbenyene have a better thermal stability as the copolymers. As the alkyl chains from R grows (polymers 1, 2) the molecule is more branched and the thermal stability is affected.

We investigate adsorption of copper ions from aqueous solution using grafted on styrene-7% divinylbenzene copolymers as specific sorbent. Aqueous solution containing amount of metal ions (100mg Cu/l in 0.1 N HNO_3) was treated with the sorbents at pH 1 at room temperatura.
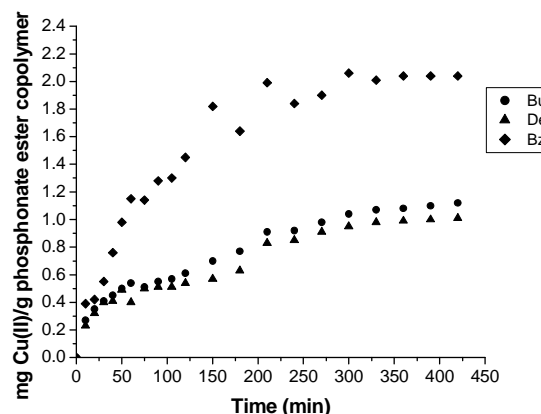

Figure 3. Specific adsorbtion capacity as a function of time, for the resins bearing phoshonate groups, at pH=1 and 25 °C.

Figure 3 show adsorption rates of Cu^{2+} ions by direct phosphonate attached copolymer microspheres as a function of time.

The total adsorption capacity of the resin functionalized with groups was 1.1 mg/g, 1.0 mg/g 4.4 mg/g and 2.0 mg/g for: Bu, De, FE and Bz which were observed at pH 1.0 and 360 min. The total adsorption capacities of the resin functionalized with phosphonate groups are lower than adsorption capacity of initial copolymer at 360min (Figure 4).

The efficiency of metal retention ability (mmoles Cu(II)/mmole phosphonate) of the functionalized polymers was found to depend on the nature of the phosphonate group, (0.037, mmolCu/mmol phosphonate phenyl), as shown in Figure 5. The efficiency was better in case of the phosphonates with aryl groups.
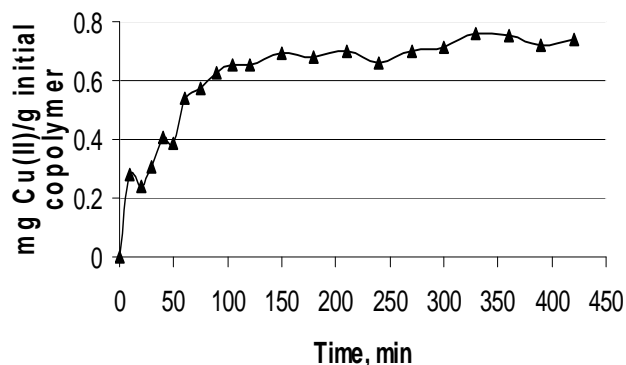

Figure 4. Specific adsorbtion capacity as a function of time, for the initial copolymer, at pH=1 and 25 °C.
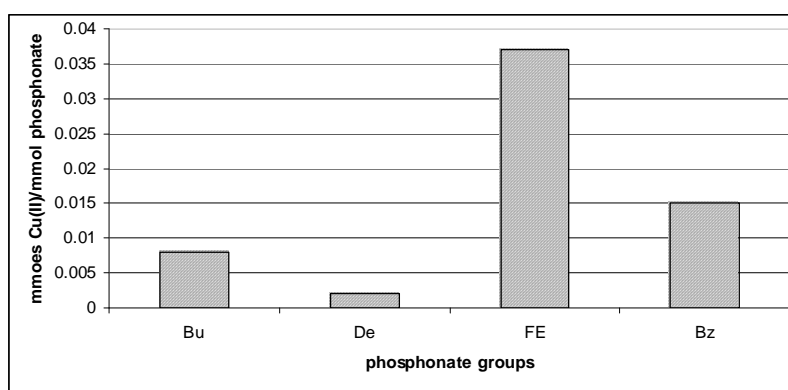

Fig. 5. Efficiency of the retention ability of the polymers bearing phosphonate pendant groups (mmoles Cu(II)/mmol phosphonate)

4. Conclusions

The chemical modification was chosen as the synthesis method, in the order to introduce phosphonate pendant groups into the polymeric structure of the support. The method is uncomplicated and reliable.

The degrees of functionalization with phosphonate groups and the reaction yields are relatively elevated, well-suited for the subsequent applications of the products. The efficiency of metal retention by the functionalized polymers was found to depend on the nature of the phosphonate group. The best results were obtained with the copolymer functionalized with phenylphosphonate groups.

The stability of the copolymers is affected by the nature of phosphonate pendant groups. The thermal stability decreases in the sequence: $(C_{10}H_{21}O)_2PO- < (C_6H_5CH_2O)_2PO- < (C_4H_9O)_2PO- < (C_6H_5O)_2PO$.

ACKNOWLEDGEMENTS

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