

Highly Pb(II)-selective resin based on crosslinked poly(acrylamido glycolic acid) copolymer

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SUMMARY

The crosslinked poly(acrylamido glycolic acid) (180-250 μm) was used in the adsorption/desorption studies. Adsorption rate, capacity of the resin for the selected metal ions, i.e. Cd(II), Zn(II), Hg(II), Pb(II), and Cr(III) were investigated in aqueous media. At different pH values (1.0-5.0) very high adsorption was observed for Pb(II) at pH 3 and 5. The adsorption equilibrium was rapidly achieved in about 5-10 min. However, when the Pb(II) ions competed with Cd(II) (in the case of the adsorption from their binary mixture) the amount of adsorption for Pb(II) decreased. Desorption of Pb(II) was studied by using 1-4M HNO_3 and 1-4M HClO_4 . High desorption ratios (more than 90%) were achieved in all cases. Adsorption/desorption cycles showed the possibility of repeated use of this resin.

INTRODUCTION

The presence of heavy-metal ions in the environment is one of the major concerns due to their toxicity to many life forms. Therefore, the need to reduce the amount of heavy-metal ions particularly in waste-water streams of hydrometallurgical and other industries and the subsequent re-use of these metal ions. In particular the search for metal ion-specific resins has been increased (1-15). Since such a wide range of materials and methods of synthesis are possible, it is not surprising that the exchangers physical form may vary from rock-hard material to soft gel. The desirable properties of these materials are the high capacity for the metal of interest, high selectivity, fast kinetics, and high mechanical strength and toughness of the particles. In this paper we report the sorption capacity of a crosslinked poly(acrylamido glycolic acid) resin toward Cd(II), Hg(II), Pb(II), Zn(II), and Cr(III) ions in aqueous media at different pH values. The sorption isotherms, and equilibrium time studies for Pb(II) were also carried out. The possibility of recycling, i.e. desorption of the metal ions, was also investigated.

EXPERIMENTAL PART

Reagents: Acrylamido glycolic acid (AGA) (Aldrich), ammonium peroxydisulfate (APS), N,N'-methylene bis acrylamide (MBA) (Aldrich) and all the metal salts (Merck) were used as received.

Synthesis of the adsorbent: The starting crosslinked resin CAGA was prepared by aqueous radical polymerization using, a mixture of acrylamido glycolic acid (AGA), (0.012 mol, ammonium peroxydisulfate) (APS) (0.5 mol%, 13.7 mg) and N,N'-methylene bis acrylamide (MBA) (6 mol%, 111 mg) at 70°C during 24 h (13). Yield 97%.

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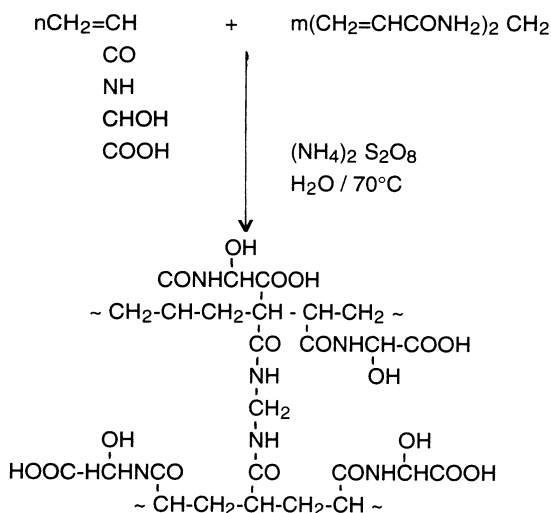
Batch metal-uptake and stripping experiments: The CAGA resin (100 mg) was treated with Cd(II), Hg(II), Zn(II), Pb(II), and Cr(III) salt solutions in aqueous media and stirring for 2 hours at 20°C. The concentration of metal ion in the remaining layer was determined by atomic absorption, and the adsorption capacity was evaluated from the difference between the initial and the final concentrations in the aqueous phase. The resin-metal complex was repeatedly washed with water and then dried under vacuum.

Recyclability: The Pb(II)-complexed CAGA resin (100 mg) was added to an aqueous solution of HNO₃ (1-4 M) and HClO₄ (1-4 M) and stirred for 1 h, and then the polymer was filtered and washed with water. Pb(II) was determined in the filtrate by atomic absorption.

Measurements: Atomic absorption spectroscopy was performed with a Perkin Elmer 3100 atomic absorption spectrometer. Infrared spectra were obtained on a FTIR 550 Magna Nicolet spectrophotometer. Thermal stabilities under N₂ of the resins were evaluated by thermogravimetric analysis with a Polymer Laboratories STA-625 thermogravimetric analyzer.

RESULTS AND DISCUSSION

The crosslinked poly(acrylamido glycolic acid) resin was obtained by aqueous radical polymerization. It was selected due to the presence of three potential groups, amide, alcohol, and carboxylic groups to interact with the metal ions.



This material was completely insoluble in water. The yield was 97%. Immediately after the synthesis the size of the particles was higher than 1000 μm (83%). Subsequently it was crushed and the fraction between 250 and 180 μm was used to investigate the metal ion sorption properties. All the FTIR spectra show the

characteristic absorption bands at 1764 cm^{-1} ($\nu_{\text{C=O}}$, carboxylic group), 1659 cm^{-1} ($\nu_{\text{C=O}}$, amide), and 1093 cm^{-1} ($\nu_{\text{C-O}}$, alcohol group).

Batch metal-uptake and stripping studies: The metal-ion capacities of the CAGA resin were determined under non-competitive conditions at several pH values of aqueous solutions of Cd(II), Hg(II) (chloride salts) and Pb(II), Zn(II), and Cr(III) (nitrate salts). The uptake results are given in Table 1.

Table 1. pH effect on the sorption (%) of the di- and trivalent metal ions. 100 mg of resin with 10 ml of an aqueous solution containing 1000 ppm.

| Metal ion | Initial pH | | | |
|-----------|------------|-----|------|------|
| | 1 | 2 | 3 | 5 |
| Cd(II) | 0.0 | a) | 46.9 | 9.6 |
| Hg(II) | 0.0 | 7.0 | a) | a) |
| Pb(II) | 3.4 | a) | 97.6 | 98.0 |
| Zn(II) | 0.0 | a) | 32.0 | a) |
| Cr(III) | 0.0 | a) | 28.9 | 33.9 |

a) It was not carried out.

The behavior of CAGA resin showed that the uptake of Pb(II) increases rapidly with increasing pH up to 98% at pH 5. At pH 1 and 2 there is not interaction between the resin and the metal ions. At pH 5 the resin shows higher capacity for Pb(II) than for the other metal ions.

The maximum capacity of load for Pb(II) was determined after three contacts of 1.0 g of the resin with 50 mL of an aqueous solution (1 g/L in Pb) for each time. It was 123 mg/g of dry resin which correspond to 82% of the initial concentration solution.

Freed CAGA resin was suspended at 25°C for 1 h at pH 5 in an aqueous solution containing equal amounts (0.5 g/L) of Pb(II) and Cd(II). The sorption was determined by observing the concentration of two metal ions in the aqueous phase by atomic absorption spectroscopy. The sorption selectivity defined by percent adsorption of Pb(II) in total adsorbed metal ions (Pb(II) + Cd(II)) was 70% which is an adequate value that would allow to separate both metal ions.

The time dependence of adsorption of Pb(II) at pH 5.0 at 25°C shows that the adsorption occurs rapidly and the equilibrium after approximately 5 min is achieved (see Fig. 1).

The CAGA resin concentration dependence of sorption of Pb(II) at pH 5 shows that up to an initial concentration of 2 g/L, the sorption of Pb(II) was higher than 91% ($>8.9\text{ mmol/L}$), therefore it decreases strongly for an initial concentration of 4.0 g/L (19.3 mmol of Pb(II) to only 51.5% (9.9 mmol/L). That means that at these concentrations all or the majority of the ligand groups are occupied by the metal ions (see Fig. 2).

Desorption of Pb(II) ions was studied with HNO_3 and HClO_4 at pH 5.0. The resin (100 mg) carrying the Pb(II) ions was placed in the desorption medium and stirred for 1 h at 25°C . The final metal ion concentration was determined by AAS. The desorption ratio was calculated from the amount of Pb(II) ions adsorbed on the resin

and the final metal ions concentration in the desorption medium, by using the following expression:

$$\text{Desorption ratio} = \frac{(\text{Amount of Pb(II) desorbed to the elution medium})}{(\text{Amount of Pb(II) adsorbed on the resin})}$$

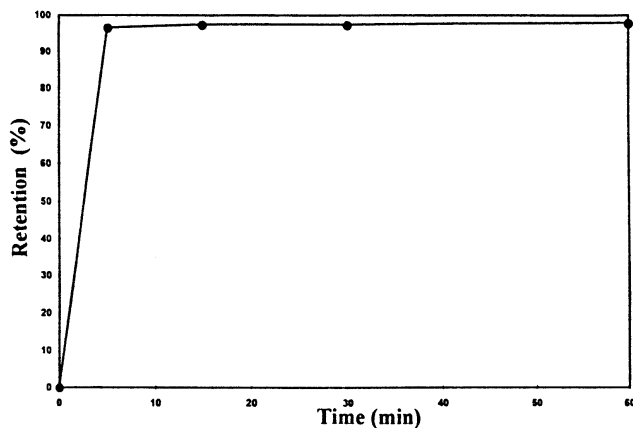


Figure 1. Time dependence of adsorption equilibrium for Pb(II) ions. CAGA resin: 100 mg; metal ion: 1 g/L. Temperature: 25°C, pH = 5.0.

Recoveries or desorption ratios were very high, up to 98.6%, for 1M HNO₃. There is not an important effect of the eluent concentration (see Table 2).

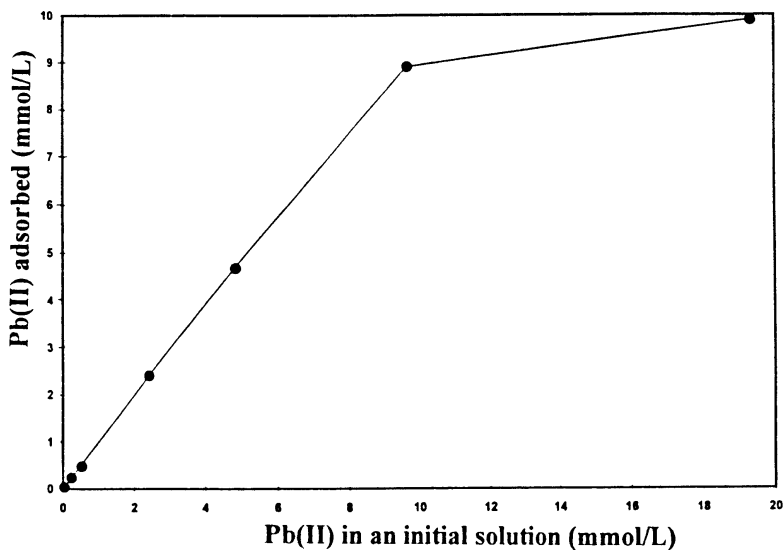


Figure 2. CAGA resin concentration dependence of sorption of Pb(II) ions. CAGA 100 mg. Metal ion: 10 mL of an aqueous solution of different concentrations. pH: 5, time: 1 h, temperature: 25°C.

Table 2. Desorption of Pb(II) from CAGA resin by HNO₃ and HClO₄.

| Eluent | Concentration (M) | Desorption (%) |
|-------------------|-------------------|----------------|
| HNO ₃ | 1 | 98.6 |
| HNO ₃ | 2 | 96.8 |
| HNO ₃ | 3 | 96.8 |
| HNO ₃ | 4 | 96.8 |
| HClO ₄ | 1 | 94.0 |
| HClO ₄ | 2 | 94.0 |
| HClO ₄ | 3 | 94.0 |
| HClO ₄ | 4 | 97.0 |

In order to obtain the reusability of the CAGA resin, the adsorption-desorption cycle was repeated four times by using the same sorbent. Table 3 shows these data.

Table 3. Sorption-desorption cycles for Pb(II) ions. CAGA resin: 100 mg. Pb(II): 10 ml of an aqueous solution 1.0 g/L; pH 5, time: 1 h, temperature: 25°C.

| Cycle N ^o | Adsorption (%) | Desorption (%) |
|----------------------|----------------|----------------|
| 1 | 97.2 | 95.6 |
| 2 | 97.9 | 96.5 |
| 3 | 88.1 | 98.3 |
| 4 | 98.8 | 98.9 |

As seen here, resorption capacity of the CAGA resin for Pb(II) ions is very high and did not significantly change during the repeated adsorption-desorption cycles.

Isotherms and physico-chemical parameters of Pb(II) sorption

In order to evaluate the applicability of CAGA resin to preconcentration of metal ions, the sorption isotherms for Pb(II) was investigated at different temperatures by a batch equilibrium experiment. For this resin it is assumed that the Pb(II) sorption proceeds according to the Langmuir adsorption isotherm (16): (see Figure 3)

$$1/w = 1/(K \cdot w_s \cdot c) + 1/w_s \quad (K = k_1/k_2)$$

where w corresponds to the amount of Pb(II) adsorbed per repeating unit (mol/mol), w_s is the maximum quantity of Pb(II), K is the binding constant and c is the concentration of free Pb(II).

The binding constants K and the maximum adsorption of Pb(II), w_s were obtained from the slope and intercept of the straight line (see Table 4 and Figure 3). K is 2355 L/mol at 308 K. The maximum adsorption of Pb(II) ions was 0.309 mol/unit mol for CAGA resin at 20°C. The w_s value obtained indicates that there exists roughly one adsorption site per ca. three repeating units of the resin.

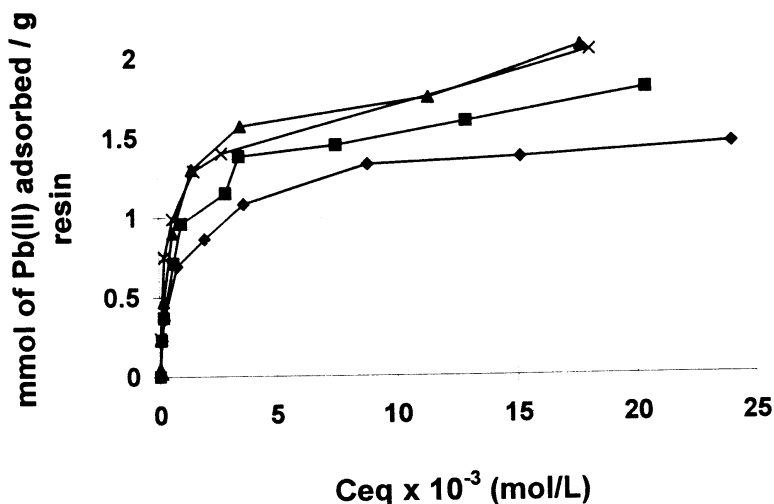


Figure 3. Adsorption of Pb(II) ions on CAGA resin at different temperatures, Pb(II) concentration: 1 g/L; time: 72 h; pH: 5; T: (▲) 293 K, (×) 298 K, (■) 308 K, and (◆) 313 K.

If ΔH is considered constant during the adsorption process in the temperature range studied, it is possible to use the following equation:

$$\frac{d \ln k}{dT} = \frac{\Delta H^\circ}{RT^2} \text{ or } \frac{d \ln k}{d(1/T)} = -\frac{\Delta H^\circ}{R}$$

where the plot $\ln k$ vs. $1/T$ yields a straight with a slope corresponding to $-\Delta H^\circ/R$ (see Figure 4). Moreover, ΔG° and ΔS° were calculated according to the following relationships:

$$\Delta G^\circ = -RT \ln K \text{ and } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The results are summarized in Table 4.

Table 4. Binding constants (K), maximum adsorption (w_s) of Pb(II), and thermodynamical parameters for the CAGA resin -Pb(II) complexes at pH 5.0.

| T (K) | w_s (mol/unit mol) | K (L/mol) | ΔG° (kJ/mol) | ΔH° (kJ/mol) | ΔS° (J/mol K) |
|----------|-------------------------|--------------|------------------------------|------------------------------|-------------------------------|
| 293 | 0.293 | 2039 | -19.9 | -3.0 | 56.4 |
| 298 | 0.240 | 5693 | | | |
| 308 | 0.228 | 2354 | | | |
| 313 | 0.205 | 2097 | | | |

These values indicate that physical and chemical adsorption processes participate in the Pb(II) sorption on the resin.

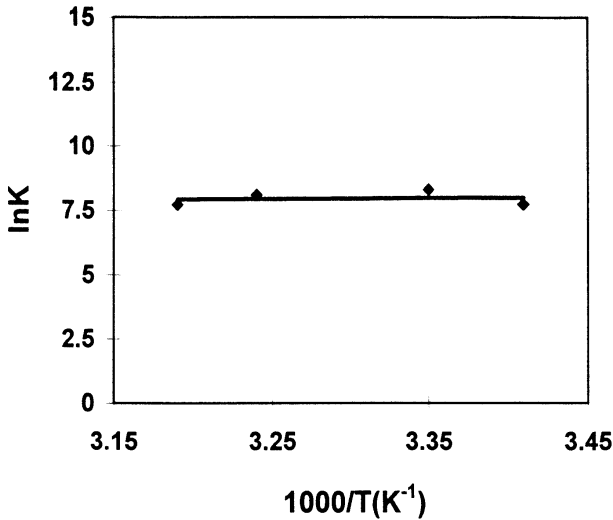


Figure 4. $\ln k$ versus $1/T$ for lead sorption of CAGA resin

Thermal stability

In order to determine the effect of Pb(II) adsorbed on the resin on thermal stability, thermogravimetric analyses were carried out. The resins were loaded with Pb(II) at pH 5.0 according to the maximum capacity (see Figure 5).

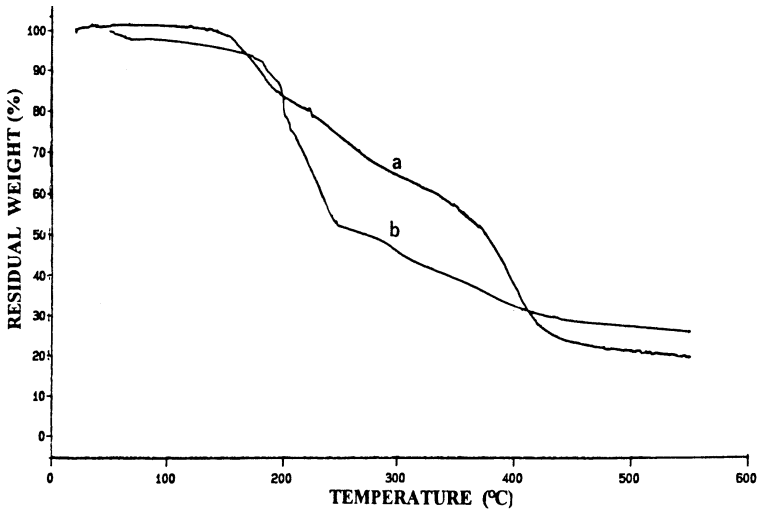


Figure 5. Thermal behavior of the unloaded resin (a) and Pb(II)-loaded resin (b) Heating rate 10°C/min, under nitrogen.

The presence of Pb(II) decreases the thermal stability in the range of 200 and 400°C. It may be attributed to probable intrapolymer-Pb(II) formation.

CONCLUSIONS

Crosslinked resins showed a high selectivity towards Pb(II) ions respect Cd(II), Hg(II), Zn(II), and Cr(III), particularly at pH 5.0. The resin contains three potential groups amide, hydroxyl, and carboxylic groups, to interact with the metal ions. According to the data the formers did not participate actively in the sorption, contributing particularly to increase the ability to adsorb water. The carboxylic groups would participate strongly in the sorption of Pb(II) ions. At pH 5.0 most of these groups remained as carboxylate groups which would coordinate with Pb(II) ions. All the ligands were found occupied with Pb(II), under non competitive conditions and decreased around 30% under binary mixture with Cd(II). The removal of Pb(II) ions with various concentrations of HNO₃ and HClO₄ was close to complete and after four adsorption/desorption cycles, the resin kept a high sorption ability to Pb(II).

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