Poly(ethylenimine) Coated onto Silica Gels: Adsorption Capacity Toward Lead and Mercury

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ABSTRACT: A series of poly(ethylenimines) (PEI) coated onto silica gels has been tested for the ability to complex lead and mercury in aqueous solutions. The study of the kinetics of metal uptake revealed that all sorbents exhibit a fast rate of sorption. The saturation capacities of the different systems were evaluated according to the Langmuir equation. The influence of different parameters like pH, textural characteristics of silica, and amount of coated polymer were discussed. Finally, cycles of stripping and sorption for lead metal were investigated in column system to evaluate the long-term stability of the sorption properties. One striking result was that crosslinking PEI onto silica prevents the desorption of PEI and greatly improves the sorption capacity. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 899–906, 1999

Key words: lead; mercury; sorption; poly(ethylenimine)-coated silica; regeneration

INTRODUCTION

Today, silica gels are one of the most preferred solid supports for chromatography uses. For example, in our laboratory, we have synthesized new packings for chromatography applications consisting of silica coated with functionalized polyamines.¹⁻⁴ This association silica/polymer can also be employed as a chelating ion exchange system. Polymers like polyamines coat efficiently such silica gel, and among these polyamines, poly-(ethylenimine) has very good chelating properties toward many metals ions. We have previously described the mechanism of complexation between metal ions and homopolymers of amino acids,⁵⁻⁷ and also the chelating properties of organic crosslinked resins bearing amino groups.^{8,9} Among the main drawbacks of pure organic macroporous resins in pollutant removing are as follows: (1) many sorption sites are buried inside

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the resin matrix, especially when the resin is prepared by polymerization of a prefunctionnalized monomer; and (2) they consist of a hydrophobic matrix and thus exhibit bad swelling properties in aqueous media.

Polymer coated onto porous silica can be an alternative. On one side, silica offers good enough stability to solvents and pressure to be used in column systems, wide scales of porous volume, specific area, and available sizes. On the other side, the polymer coated onto silica gives the specificity, the accessibility, and the swelling properties of these sorbents, and finally, allows a faster achievement of equilibrium sorption.

The aim of this work was to evaluate the chelating properties toward some metals ions, like Pb and Hg (current pollutants in many countries), of polyethylenimine/porous silica composite systems. We tried to correlate their physicochemical structure, studied in details in a previous paper,¹⁰ and their sorption properties. Finally, these results should help in the choice of the better system for a given application.

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| | Average Pore Radius (Å) for Bare Silica | Particle Size (µm) and Shape | Specific Area (m²/g) | Porous Volume (mL/g) | Polymer Concentration For Coating (%) | Specific Area (m²/g) | Porous Volume (mL/g) | Coat | ed PEI Γ |
|----------------------------|--------------------------------------------------|------------------------------------|----------------------------|----------------------------|---------------------------------------------|----------------------------|----------------------------|--------|-------------|
| Sorbent: Silica/Polymer | | | For Bar | e Silica | | For Coated Silica | | (mg/g) | (mg/m^2) |
| Nu100/PEIA | 100 | 30 Spherical | 303 | 1.0 | 5 | 186 | 0.8 | 149 | 0.80 |
| Nu100/PEIB | 100 | 30 Spherical | 303 | 1.0 | 0.5 | 243 | — | 36 | 0.15 |
| Nu1000/PEIA | 1000 | 30 Spherical | 43 | 0.9 | 5 | 35 | 0.8 | 38 | 1.10 |
| Nu1000/PEIB | 1000 | 30 Spherical | 43 | 0.9 | 0.5 | 35 | — | 26 | 0.75 |
| Po300/PEIA | 300 | 50 Spherical | 80 | 1.7 | 5 | 64 | — | 71 | 1.10 |
| Po300/PEIB | 300 | 50 Spherical | 80 | 1.7 | 2.5 | 64 | — | 56 | 0.88 |
| Da150/PEIA | 150 | 35–70 Irregular | 273 | 0.94 | 5 | 186 | — | 141 | 0.76 |
| Da150/PEIB | 150 | 35–70 Irregular | 273 | 0.94 | 2.5 | 207 | _ | 96 | 0.46 |

Table I Physicochemical Characteristics of Sorbents

Nu, Nucleosil; Po, Polygoprep; Da, Davisil.

EXPERIMENTAL

Materials

Different types of porous silica were chosen. Nucleosil ones (from Macherey Nagel) were chosen for their relative structural homogeneity, Polygoprep (Macherey Nagel) and Davisil (Aldrich) for their lower cost. These gels also differed by their textural parameters, especially their porous volume and surface area (Table I).

The poly(ethylenimine) (PEI) sample was a commercial branched polymer (Aldrich) with values of 25, 50, and 25 for primary, secondary, and tertiary amine distributions respectively. Its average molecular weight ($\bar{M}_w = 768,000 \pm 36,000$ g/mole) was determined by capillary viscosimetry using the Mark–Houwink relationship.¹¹

PEI-coated silica were prepared using a procedure previously described.¹² On the basis of previous studies,¹⁰ the polymer concentration in the solution used for coating was varied in order to obtain, for each kind of silica, two different samples with low and high rate of coverage by PEI (referred to respectively as PEIA and PEIB in Table I). The quantities of polymer adsorbed were determined from thermogravimetric analysis in an air atmosphere using a Shimadzu Thermoanalyser TGA51. This method was found more convenient than the elemental analysis of nitrogen and also allowed the determination of water.

Specific areas were measured using BET isotherms (Apparatus Quantasorb Junior).¹³

In order to strengthen the fastening of PEI onto silica (for column tests), the polymer was crosslinked according to two different methods previously described in the literature: (1) with epichlorhydrin¹⁴ and (2) with glutaraldehyde.¹⁵

The physicochemical characteristics of these sorbents are summarized in Table I.

Metals solutions were prepared from $Pb(NO_3)_2$ and $HgCl_2$ salts purchased from Prolabo. To adjust pH, nitric acid, chlorhydric acid, and tris(hydroxymethyl)aminomethane solutions were used.

Adsorption Tests

Adsorption tests were performed by batch or column techniques. All glasses were previously washed with nitric acid then rinsed with water. For batch tests, 90 mg of sorbent were shaken with 30 mL of a solution of metal ion at a known concentration. After the test, the solid-liquid separation was carried out by centrifugation. For column tests, 100 mL of metal solution were passed through 250 mg of sorbent enclosed in the column at a flow rate of 5 mL/mn. The sorbent in the column was always extensively washed with water before a test and between each cycle. The concentration of metal ion in the liquid phase was determined by atomic absorption (2380 Perkin Elmer) and Inductively Coupled Plasma spectrophotometry (3510 ICP Varian) for Pb and Hg, respectively.

To evaluate and compare the saturation capacities of the different adsorbents, the metal adsorption isotherms were analyzed using Langmuir model written as

$$\left| egin{array}{c} rac{C_e}{q_e} = rac{C_e}{q_s} + rac{1}{K\!\cdot\!q_s}
ight.$$

in which q_e is the adsorbed metal amount (mg/g), C_e the sample concentration at the equilibrium (µg/mL), q_s the capacity at saturation (mg/g), and K the adsorption coefficient (mL/µg)

RESULTS AND DISCUSSION

As expected, the coating process decreases the specific area of all the silica. For a given concentration of the polymer solution (5%), the rate of decrease depends on the nature of the silica. It is all the greater as the silica is more porous and ranges from 40 to 20%. In addition, the decrease of the surface area increases with the polymer concentration used, mainly for highly porous materials as Nu100 and Da150.

Kinetics and equilibrium sorption studies were performed using batch methods and only on Nucleosil silica, because of its good textural homogeneity. Further studies (essentially columns tests) were mainly undertaken with Polygoprep and Davisil silica.



Figure 1 Adsorption kinetics of Pb in relation to the type of sorbent (90 mg of sorbent /30 mL of 100 ppm lead solution).



Figure 2 Adsorption kinetics of Hg in relation to the type of sorbent (90 mg of sorbent /30 mL of 100 ppm mercury solution).

Kinetics

Kinetic curves were realized at pH 6. The sorption capacities are expressed in terms of weight of metal adsorbed per unit weight of sorbent (q_e) . Figures 1 and 2 give results for Pb and Hg, respectively.

For Pb, the equilibrium is reached in less than one hour for Nu100 and Nu1000 sorbents (Fig. 1). The process is faster with Hg for the two sorbents (about 10–15 min). All systems are convenient for future column tests.

Batch Tests

In Table II are summarized the sorption capacities for Pb and Hg in relation with the nature of the sorbent and the polymer content (Γ). It was checked that the bare silicas are unable to adsorb the two metal ions.

Lead

When considering the amount of metal adsorbed per unit weight of sorbent (qe), the sorbent efficiency decreases in the order Nu100/PEIA > Nu1000/PEIA > Nu100/PEIB > Nu1000PEIB. This is also the decreasing order of polymer content. But when the amount of metal is expressed with regard to the amount of polymer (q_e^*) , the more porous sorbents are also the more effective and the order of decreasing efficiency becomes Nu1000/PEIA >Nu1000PEIB Nu100/PEIB > Nu100/PEIA. For example, Nu100/PEIB and Nu1000/PEIA have the same quantity of polymer per gram of sorbent, but the latter is the more efficient despite the higher specific area of the former. It is evident that two main factors govern the adsorption phenomenon: (1) the number of

| Sorbent | Metal | $\begin{array}{c} q_e \\ (\mathrm{mg/g}) \\ (q_0 \ = \ 33.3 \ \mathrm{mg/g}) \end{array}$ | q_e^* (mg/g PEI) |
|-----------------------------------|------------|-------------------------------------------------------------------------------------------|-----------------------|
| Bare Nu100 and Nu1000 | Pb and Hg | 0 | 0 |
| Nu100/PEIA | Pb | 30 | 200 |
| $\Gamma = 149 \text{ mg/g}$ | $_{ m Hg}$ | 26 | 177 |
| Nu100/PEIB | Pb | 10 | 274 |
| $\Gamma = 36 \text{ mg/g}$ | Hg | 20 | 559 |
| Nu1000/PEIA | Pb | 17 | 447 |
| $\Gamma = 38 \text{ mg/g}$ | Hg | 28 | 750 |
| Nu1000/PEIB $\Gamma = 26 mg/g$ | Pb | 9 | 346 |

Table II Sorbent Capacities for Pb and Hg at the Equilibrium for Batch Tests

 q_0 (mg/g) is the initial quantity of metal in solution per weight of sorbent (i.e., maximum value available for sorption).

coordination sites, in this case amino groups, and (2) the accessibility of these sites to the metal ion.

In a previous paper,¹⁰ it was shown that branched PEI does not cover the whole silica surface but forms some aggregates or entanglements. So the metal diffusion to amine groups is better in macropores of 1000 Å than in mesopores of 100 Å.

Mercury

In this case, q_e is about the same whatever the sorbent is. This can probably be explained by the fact that, for a metal concentration of 100 ppm, the equilibrium sorption capacity for Nu100/PEIA is far from reached (as shown in Fig. 4).

From the q_e^* values, the same conclusions as for lead may be drawn. The more porous sorbents are the better ones for adsorption.

Except for Nu100/PEIA (see above), mercury is more adsorbed than lead in any case.

Sorption Isotherms

A contact time of 2 h and a pH 6 were chosen as experimental conditions for the determination of the isotherms reported in Figure 3 and Figure 4 for lead and mercury, respectively.⁷

The equilibrium sorption data in Figure 3 and Figure 4 were fitted to the Langmuir isotherm, yielding correlation coefficients better for lead than for mercury. Values of the saturation capacity q_s are given in Table III.Data show, like the kinetics results, that PEI sorbents are more efficient for mercury than for lead. Theoretical arguments¹⁶ and experimental results in the literature^{17–19} already showed that polyamines adsorb mercury more strongly than lead. It is well known that lead complexes essentially by an ionic process whereas mercury uses a "covalent process." At pH 6 mercury is in the HgCl₂ form and thus is less affected by ionic repulsion toward nitrogen sorption sites. For these reasons, we found a ratio of N/metal greater for Pb (nearly 5) than for Hg



Figure 3 Lead adsorption isotherms for two sorbents.



Figure 4 Mercury adsorption isotherms for two sorbents.

| | | q_s | | q_s^* | Molar | Corrln Coeff. |
|---------------|---------------------------|------------|---------------------------------------------|-------------------|------------------|------------------|
| Metal/Sorbent | | mg/g | mmole/g | mmole metal/g PEI | Ratio N/metal | |
| Lead | Nu100/PEIA | 127 | 0.60 | 4.0 | 5.9 | 0.99 |
| 7.6 | Nu1000/PEIA | 38 | 0.18 | 4.7 | 5.0 | 0.98 |
| Mercury | Nu100/PEIA Nu1000/PEIA | 310 100 | $\begin{array}{c} 1.54 \\ 0.50 \end{array}$ | 10.3 13.2 | 2.3 1.8 | 0.87 0.94 |

Table III Saturation Capacities Evaluated from Langmuir Isotherms

(nearly 2). Rather surprisingly, the N/metal molar ratio for mercury is close to that reported for the same complex in homogeneous water solutions,¹¹ despite the restrictions due to the solid surface and probable chain entanglements. The influence of chain entanglements is reflected in the slight increase of the N/metal molar ratio when going from Nu1000/PEIA to Nu100/PEIA.

Contribution of Chemical and Textural Parameters to Adsorption

Influence of pH

The influence of pH on the sorption capacity was studied under batch conditions for two sorbents with high polymer coverage (PEIA) (Fig. 5).

The tests were limited to the range pH 2–9 because of precipitation of $Pb(OH)_2$ in basic medium. At any pH, the two bare silicas do not adsorb at all. At strongly acidic pH, both sorbents under study do not adsorb. This can be explained by the fact that, at this pH, most of amine functions are protonated.²⁰ Then cationic repulsion can occur between Pb ionic species (such as Pb²⁺ itself and PbNO₃⁺) and protonated PEI units. In mildly acidic pH 4–6, sorbents are effective for decontamination. The curves pass through a maximum. In fact, two opposite factors govern adsorp



Figure 5 Influence of pH on Pb adsorption for two sorbents.

tion: (1) the swelling capacity and the diffusion inside the polymer layer of the sorbent, which is better when the amine groups are protonated inducing PEI extension, and also when the sorbent contains less PEI; (2) the availability of the nitrogen doublet for the dative bond, which is effective only when amine groups are deprotonated. Such a pH effect is characteristic of metal complexation by basic polymers. A low pH increases the swelling factor, but introduces a very pronounced effect of competition between lead and H^+ species.

Influence of Chemical and Textural Properties of the Sorbent

Several types of silica coated with different amounts of PEI were chosen for these studies. The aim was to evaluate the influence of their porosity and of the amount of coated PEI. Tests were undertaken in batch systems at pH 6. Results are gathered in Table IV.

This study shows that lead adsorption is governed by three factors. It is high when

- 1. the amount of chelating agent Γ is high. It is obvious that lead adsorption is dependent on the amount of coated PEI. Nu100/ PEIA is three times more efficient than Nu100/PEIB. But for a given silica, there is no linear relationship between PEI amount (Γ) and lead adsorption (q_e^*) because of (2).
- 2. the accessibility of PEI units increases. It occurs when PEI is in a relatively low quantity and also when it is coated in pores of large diameter. In fact, a part of the PEI is ineffective when the PEI quantity is too great and especially when pores are smaller, probably because of entanglements inside the pores. The higher efficiency obtained with Nu100B compared to Nu100A shows that, in micropores, the ac-

| | | Coated | l PEI, Γ | Lead Capacity | Lead Capacity q_e^* (mg/g of PEI) | |
|-------------|-------------------------------------------|--------|-------------------|-------------------------------------|-------------------------------------------|--|
| Sorbent | Mean Porous Radius (Å) For Bare Silica | mg/g | mg/m ² | $q_e \; ({ m mg/g \ of \ sorbent})$ | | |
| Nu100/PEIA | 100 | 149 | 0.80 | 30 | 200 | |
| Nu100/PEIB | 100 | 36 | 0.15 | 10 | 278 | |
| Da/PEIA | 150 | 141 | 0.76 | 24 | 172 | |
| Da/PEIB | 150 | 96 | 0.46 | 20 | 209 | |
| Po/PEIA | 300 | 71 | 1.10 | 18 | 253 | |
| Po/PEIB | 300 | 56 | 0.88 | 17 | 303 | |
| Nu1000/PEIA | 1000 | 38 | 1.10 | 17 | 447 | |
| Nu1000/PEIB | 1000 | 26 | 0.75 | 9 | 346 | |

Table IV Lead Capacity in Relation to Chemical and Textural Parameters

cessibility is better when PEI does not cover the surface as multilayers. For macropores, the presence of multilayers of polymer is not the restrictive parameter. This is why q_e^* for sorbents with PEIB (Nu100, Da, Po) are more efficient than with PEIA, except for Nu1000 (with macropores). A recent EPR study of spin-labeled PEI adsorbed on Nu100 and Nu1000 has shown²¹ that the chain mobility decreases in the order Nu1000A > Nu100B \cong Nu1000B > Nu100A, which is also the order for q_e^* .

3. the simultaneous presence of several nitrogen atoms close to lead is favored. Statistically, this probability is greater in a pore of 100 Å than in a pore of 1000 Å. The two latter parameters may give opposite effects and explain why the efficiency (q_e^*) decreases from Nu100 to Davisil and then increases when the porosity increases from Davisil to Nu1000.

Column and Stripping Tests

Some preliminary batch tests were performed to evaluate the stripping and cycles potentialities of the above systems. The results are reported in Table V, in the case of Nu100/PEIA. These preliminary results gave important information for further investigations:

- 1. The first test induced a little desorption of PEI (12%) while the recovery with acid strongly desorbs PEI (79%).
- 2. After the first test, lead is simply rinsed out with 30 mL of nitric acid 0.1M for 90 mg of sorbent. By increasing the contact time, the % lead recovery is not improved.
- 3. In spite of the large PEI desorption, the sorbent is still efficient: q_e decreases from 30 for the first test to 25 for the second one. However, q_e^* increases strongly, in line with the decrease of the amount of PEI as previously noticed (Table II). These results show the great potentialities of these sorbents for cyclic usage. Nevertheless, it seems essential to fasten PEI onto silica, by a crosslinking reaction.

Column Tests

The cheaper sorbents were chosen for column tests: Da/PEIA and Po/PEIA. They were crosslinked in two different ways:

1. With epichlorhydrin: In this case, sorbents are marked "c₁."

| Before Test Coated PEI Γ (mg/g) | First Test q_{e_1} (mg/g of sorbent) | After Test Coated PEI, Γ (mg/g) | First Test $q_{e_1}^*$ (mg/g of PEI) | Pb Recovery in % After Acid Treatment | Second Test q_{e_2} (mg/g of sorbent) | After Test, Coated PEI, Γ (mg/g) | Second Test $q^*_{e_2}$ (mg/g of PEI) |
|---------------------------------------|----------------------------------------|---------------------------------------|--------------------------------------------|------------------------------------------------|--------------------------------------------------|----------------------------------------|---------------------------------------|
| 149 | 30 | 106 | 283 | 95 | 25 | 28 | 893 |

Table V Preliminary Stripping Test for Lead and Nu100/PEIA

| | | Sorbent | | | | | | |
|-----------------------|----------------------------------------------|---------|----------------------|----------------------|--------|----------------------|----------------------|--|
| Cycle | Results | Da/PEI | Da/PEIc ₁ | Da/PEIc ₂ | Po/PEI | Po/PEIc ₁ | Po/PEIc ₂ | |
| | Coated polymer (mg/g) | 141 | 158 | 203 | 71 | 96 | 96 | |
| First | Lead adsorption q_e (mg/g of sorbent) | 20 | 15 | 15 | 15 | 8 | 12 | |
| First | Lead adsorption q_e^* (mg/g of PEI) | 142 | 95 | 74 | 212 | 84 | 125 | |
| After regeneration | Coated polymer (mg/g) | 50 | 138 | 200 | 11 | 72 | 94 | |
| Second | Lead adsorption q_e (mg/g of sorbent) | 3 | 15 | 12 | 4 | 8 | 12 | |
| Second | Lead adsorption q_e^* (mg/g of sorbent) | 60 | 109 | 60 | 364 | 112 | 128 | |
| After regeneration | Coated polymer (mg/g) | / | / | 197 | / | / | 94 | |
| Third | Lead adsorption q_e (mg/g of sorbent) | / | / | 12 | / | / | 11 | |
| Third | Lead adsorption q_e^* (mg/g of sorbent) | | | 61 | | | 117 | |

Table VI Comparison of cycle Tests for Uncrosslinked and Crosslinked Sorbents

Coated polymer means PEI alone for uncrosslinked sorbent and PEI + crosslinking agent for crosslinked sorbents.

2. With glutaraldehyde: Sorbents are marked " c_2 ." Before the first cycle, sorbents were washed with 50 mL of nitric acid (0.01*M*) then washed with water to reach pH 6. Between each cycle, lead stripping was performed using 10 mL of nitric acid 0.1*N*, then water was used to increase pH to 6. Results are summarized in Table VI.

Table VI shows that crosslinking via epichlorhydrin or glutaraldehyde increases the parameter Γ , compare to original sorbents. This proves the efficiency of these reactions.

After the first cycle of decontamination, the crosslinked sorbents are less effective than the original ones. This is due to the fact that a part of the nitrogen atoms have been involved in the reaction with the crosslinking agent and that others are deeply buried inside the network and thus are less accessible to the metal. In addition, it is difficult to compare exactly q_e expressed per weight of uncrosslinked sorbent and per weight of the crosslinked one due to the weight contribution of the crosslinker. Therefore, it seems reasonable that q_e^e does not decrease so much.

The interest and efficiency of using crosslinking reactions appears clearly after acid regeneration. The crosslinking with glutaraldehyde completely prevents the desorption of the polymer during the regeneration step, whereas a little desorption (between 10 and 20%) still occurs for sorbents crosslinked with epichlorhydrin. This can be explained by a well-known property of epichlorhydrin which is able to condense on itself. This side reaction give rise to more and less long arms between the crosslinking points.²² The presence of rather long epichlorhydrin chains was recently demonstrated in gels of cyclodextrin and epichlorhydrin.²³ The looser network so produced around silica can be slightly desorbed.

Therefore, crosslinked sorbents are always efficient and globally exhibit a constant adsorption capacity after two cycles. For the two best sorbents (Da/PEIc₂ and Po/PEIc₂), the results are equal until the third cycle. Although Po/PEI silica contains less PEI than Da/PEI, it presents an equal capacity as previously explained.

CONCLUSION

Mercury and lead metals can be removed efficiently from aqueous solutions by PEI-coated silica in the range pH 4-6. By varying the porosity of silica and the amount of coated PEI, it has been shown that the sorption capacity depends on these two parameters. These two factors take place in opposite ways: a high porosity silica contains a small PEI amount. Sorption isotherms reveal that for a same system, the capacity for mercury is higher than for lead. These capacities are close to values already published with organic adsorbents.^{18,19}

The best advantage of these silica /PEI adsorbents is their ability to show fast rate of sorption.

To improve column operations in cycles, PEI was crosslinked around silica. Crosslinking via glutaraldehyde fastened PEI more strongly than crosslinking via epichlorhydrin. After three cycles of sorption-acid regeneration-water washing, two of the systems revealed a good and constant capacity for lead.

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