

Adsorption of Lead and Copper on Modified Polyacrylonitrile Bead

T. GODJEVARGOVA,¹ A. SIMEONOVA,² A. DIMOV¹

¹ University "Prof. Dr. A. Zlatarov," 8010 Bourgas, Bulgaria

² Technical University, 9000 Varna, Bulgaria

Received 21 September 1999; accepted 27 February 2000

ABSTRACT: Porous sorbents were prepared from copolymer of acrylonitrile-methylmethacrylate-2-acrylamidomethylpropensulfonic acid and copolymer of acrylonitrile with vinylimidazol. The sorbent obtained from the former copolymer was modified with hydroxylamine, sodium hydroxide, and hydrazinehydrochloride under optimal conditions to obtain amidooxyme, carboxylic, and hydrazide groups. These functional groups introduced in the modified sorbent and the imidazol group in the sorbent of acrylonitrile and vinylimidazol showed high ability to form complexes with heavy metals. The adsorption properties of the porous chelate-forming sorbents obtained were studied with Pb(II) and Cu(II) ions. The order of the polymer sorbents toward sorption of Pb(II) and Cu(II) ions was determined. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 283–288, 2001

Key words: acrylonitrile copolymer; porous sorbents; chemical modification; adsorption; heavy metals

INTRODUCTION

Polymer sorbents containing certain functional groups, capable of forming complexes with metal ions, are widely used as complex-forming sorbents. The possibility to modify the polymer sorbents, to bind additional functional groups, broadens the spectrum of their applications.

The preparation of modified acrylonitrile (AN) copolymers in granules has been reported in several articles. Some of the authors suggest a preliminary modification of the AN copolymer by partial hydrolysis followed by formation of the granules.¹ The sorbents prepared by this method contain significant amounts of carboxylic and amide groups but the granules obtained swell, so they are not suitable for use as sorbents.

Other authors performed surface modification of AN copolymer granules with acid or hydroxide.² The modified granules obtained were found to be hard but not porous.

The preparation of porous granules from AN copolymer has been reported previously.³ It is accomplished by mixing polymer solution with suspended mineral oil and coagulation in cool mineral oil. The granules obtained are modified with a halogenizing agent and hydroxide. The sorbent obtained has excellent characteristics, but the technique is rather complicated.

It is well known that sorbents containing hydrazide, amidooxyme, and carboxylic groups have high complex-forming capability.^{4–6} The AN copolymers are suitable for binding these groups, which makes them good complex-forming sorbents for heavy metal ions.

The aim of the present work was to prepare modified porous granules of AN copolymer with

Correspondence to: T. Godjevargova.

Journal of Applied Polymer Science, Vol. 79, 283–288 (2001)
© 2000 John Wiley & Sons, Inc.

complex-forming capability and to study the sorption of Pb^{2+} and Cu^{2+} ions.

EXPERIMENTAL

Materials

Polymer sorbents were obtained from two AN copolymers: 1. Copolymer of AN (90.6%), methylmethacrylate (MMA) (8.1%), and 2-acrylamidomethylpropensulfonic acid (AMPSA) (1.4%), products of Neftochim Co. (Bouzgas, Bulgaria); 2. Copolymer of AN (74.6%) and vinylimidazol (Vi) (25.4%) obtained in the chemical laboratory of the Shoumen Pedagogical University.

Dimethylformamide, lithium nitrate, and glycerin (Fluka Chemie AG, Buchs, Switzerland) were also used for the preparation of the polymer sorbents.

Model solutions for the study of sorption were prepared from $\text{Pb}(\text{NO}_3)_2$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Fluka Chemie AG, Switzerland). All reagents were reagent grade.

Preparation of Porous Sorbent from AN Copolymer

Porous sorbents of AN copolymer were prepared by solution of 15% copolymer of AN-MMA-AMPSA or AN-Vi in dimethylformamide at 60°C under continuous stirring in water bath. Then, 1% LiNO_3 and 3% glycerin were added to the polymer solution. The homogenized mixture was pipetted at constant volume rate into distilled water. The granules obtained are porous and have approximately the same size and shape. They were washed thoroughly with distilled water and then kept in 30% solution of glycerin for 3 h. Finally, the granules were dried at 60°C to constant weight.

Measurement of Porous Structure

Specific surface areas, pore volume, and pore radius of AN copolymer sorbent were determined on a Carlo Erba mercury porosimeter (Italy, model 1520).

Chemical Modification of the Sorbent from Copolymer AN-MMA-AMPSA

Chemical Modification with Sodium Hydroxide

The porous sorbent swelled in 5% solution of dimethylformamide for 30 min at room temperature. Then it was immersed in 20% NaOH solu-

tion for 30 min at 60°C. The modified sorbent was washed thoroughly with distilled water.

Chemical Modification with Hydroxylamine

The porous sorbent swelled in 5% solution of dimethylformamide for 30 min at room temperature. The swollen granules were immersed in 10% solution of hydroxylamine for 120 min at 40°C.

Chemical Modification with NaOH and Hydroxylamine

The porous sorbent swelled in 5% solution of dimethylformamide for 30 min at room temperature. Then they were immersed in a mixture (1:1) of 15% solution of NaOH and 15% solution of hydroxylamine for 50 min at 60°C.

Chemical Modification with Hydrazinehydrochloride

The granular sorbent swelled in 10% solution of dimethylformamide for 1 h. Then it was modified with 75% solution of hydrazinehydrochloride at 75°C for 120 min.

Chemical Modification with NaOH and Hydrazinehydrochloride

The granular sorbent swelled in 10% solution of dimethylformamide for 1 h. Then it was immersed in a mixture of 15% NaOH and 15% hydrazinechloride in a 4:1 ratio for 45 min at 60°C.

Adsorption Characteristics

Adsorption Isotherms

AN copolymer sorbent (1 g) and 50 cm³ solution of $\text{Pb}(\text{NO}_3)_2$ or $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in concentrations from 0.005 to 2.0 g/L were stirred with a magnetic stirrer at 25°C for 2 h at pH 3. The amounts of metal ions adsorbed on the sorbent were determined by chelatometric titration of metal ions in the supernatant.⁷

Determination of Adsorption Kinetics

AN copolymer sorbent (1 g) and 50 cm³ solution of $\text{Pb}(\text{NO}_3)_2$ or $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (2.0 g/L) were stirred with a magnetic stirrer at 25°C and pH 3 for 2 h. The concentration of Pb^{2+} or Cu^{2+} ions was monitored at certain intervals by chelatometric titration in the supernatant.

Table I Active Groups' Content in Polymer Sorbents

No.	Copolymers	Amide-, Amidooxyme Groups (mg eq/g)	Carboxylic Groups (mg eq/g)	Imidazol Groups (mg eq/g)
1	AMCAPAN	0.54	0.43	—
2	IMPAN	—	—	0.92
3	AMPAN	0.80	—	—
4	CAPAN	0.20	0.58	—
5	HYCAPAN	0.20	0.23	—
6	HYPAN	0.28	—	—

Determination of pH Optimum for Adsorption

AN copolymer sorbent (1 g) and 50 cm³ solution of Pb(NO₃)₂ or CuSO₄ · 5H₂O (2.0 g/L) were stirred at 25°C and pH from 1 to 5 for 2 h. The concentration of Pb²⁺ or Cu²⁺ ions was measured at certain intervals.

RESULTS AND DISCUSSION

Two types of AN copolymers were used for the preparation of polymer sorbents: ternary copolymer of AN, MMA, and AMPSA, and binary copolymer of AN and Vi. Polymer granules were obtained by the method described in the Experimental section. Glycerin and sodium hydroxide provided the porous structure of the sorbents. The granules were from 0.5 to 1 mm in diameter, specific area was 10 m²/g, pore volume was 3 × 10⁻³ m³/g, and average pore radius was 1000 Å.

Five types of sorbents were prepared from the ternary copolymer of AN, MMA and AMPSA:

AMPAN—by treating the sorbent with 10% hydroxylamine to produce amidooxyme groups.

CAPAN—sorbent treated with 20% NaOH to introduce carboxylic and amide groups.

AMCAPAN—treatment with 15% hydroxylamine and 15% NaOH to produce amidooxyme and carboxylic groups.

HYPAN—treatment with 15% hydrazinehydrochloride to form hydrazide groups.

HYCAPAN—treatment with 15% NaOH and 15% hydrazinehydrochloride to introduce hydrazide and carboxylic groups.

The optimal conditions for each modification were determined experimentally.

The sixth sorbent (IMPAN) was prepared from copolymer of AN and Vi without additional modification. Vi introduced imidazol groups which are proved to form complexes with heavy metals.

The modifications performed with hydroxylamine and hydrazinehydrochloride created three-dimensional structures, which gave good mechanical strength to the polymer granules.⁸ The mechanical stability of the porous granules is one of their major advantages compared with fibrous sorbents.

The amounts of functional groups introduced are presented in Table I. They were determined quantitatively by residual titration in a heterogeneous medium.⁹ IMPAN sorbent has the highest amount of imidazol groups and the sorbent modified with NaOH and hydroxylamine (AMCAPAN) has the highest amount of amidooxyme and carboxylic groups. The lowest concentration of functional groups showed HYPAN. AMCAPAN, CAPAN, and HYCAPAN are polyampholytes.

The functional groups introduced not only ionize but possess electron donor properties provided by the carboxylic oxygen and nitrogen atom of the amidooxyme and amide groups.

The sorption characteristics of the six sorbents were studied with Cu²⁺ and Pb²⁺. The experi-

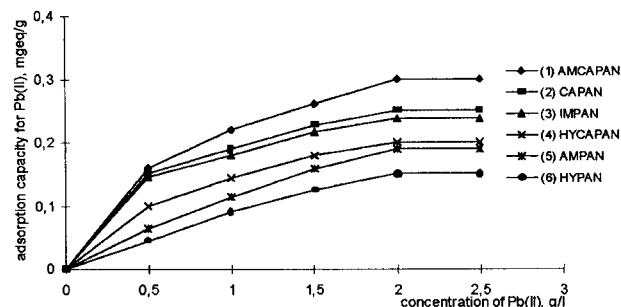


Figure 1 Sorption isotherm of Pb(II) ions on polymer sorbents.

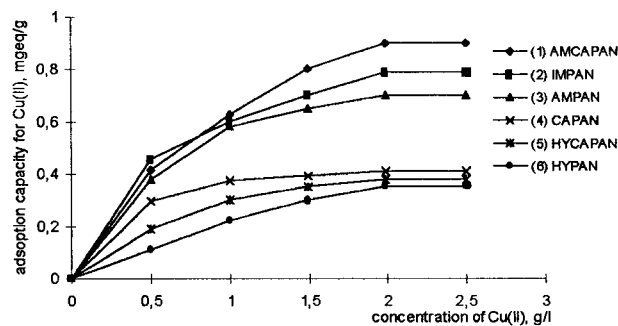


Figure 2 Sorption isotherm of Cu(II) ions on polymer sorbents.

ments were performed under static conditions with model solutions of lead nitrate and copper sulfate. Cu^{2+} and Pb^{2+} concentrations were determined complexometrically.

The sorption isotherm was studied to establish the optimal equilibrium concentration of Cu^{2+} and Pb^{2+} at which the sorption is most effective (Figs. 1 and 2).

It can be seen that saturation for all the sorbents occurred at 2 g/L concentration of Cu^{2+} and Pb^{2+} in equilibrium solutions, therefore our further studies were performed with these initial concentrations.

The sorbents were arranged in the following order according to their equilibrium sorption capacity for Pb^{2+} : AMCAPAN > CAPAN > IMPAN > HYCAPAN > AMPAN > HYPAN with maximum adsorption capacity of 0.29 mg eq/g.

With Cu^{2+} ions, the polymer sorbents reach maximum adsorption capacity of 0.90 mg eq/g for AMCAPAN and can be arranged in the following order: AMCAPAN > IMPAN > AMPAN > CAPAN > HYCAPAN > HYPAN.

The comparison of Figures 1 and 2 shows that in all the cases, Cu^{2+} ions are sorbed to a higher extent than Pb^{2+} .

Table II Effect of pH on Adsorption Capacity for Pb^{2+} (mg eq/g)

Sorbent	pH = 5	pH = 4	pH = 3	pH = 2
AMCAPAN	0.24	0.26	0.29	0.25
CAPAN	0.22	0.25	0.26	0.19
IMPAN	0.18	0.22	0.24	0.19
HYCAPAN	0.16	0.19	0.21	0.18
AMPAN	0.16	0.20	0.20	0.17
HYPAN	0.15	0.17	0.19	0.14

Table III Effect of pH on Adsorption Capacity for Cu^{2+} (mg eq/g)

Sorbent	pH = 5	pH = 4	pH = 3	pH = 2
AMCAPAN	0.60	0.82	0.90	0.73
IMPAN	0.57	0.80	0.86	0.65
AMPAN	0.40	0.76	0.77	0.65
CAPAN	0.38	0.46	0.51	0.42
HYCAPAN	0.41	0.43	0.47	0.35
HYPAN	0.26	0.33	0.37	0.29

The optimal pH for sorption of Cu^{2+} and Pb^{2+} was studied with the sorbents obtained under static conditions, constant temperature, 60-min contact time, and different pH of the solutions used.

The influence of pH on the formation of complexes is well known. The change of pH affects the concentration of the active ionogenic groups, their electron donor properties, degree of swelling of the ionite, and mutual disposition of the ligand groups in it. The complex forming properties depend to a greater extent on the pH of the contact solution, compared with ion-exchange ones. This effect can be observed especially by the formation of the coordination bond nitrogen-metal. Therefore, the value of pH is a powerful factor determining the mechanism of sorption.¹⁰ The dependencies of sorption capacity of Cu^{2+} and Pb^{2+} ions from pH of the solution for all modifications are given in Tables II and III.

For all six sorbents, the optimal pH for the sorption of Cu^{2+} and Pb^{2+} was found to be 3.

Copper ions form strong coordination bonds with amide and amidoxime groups. This could explain the higher adsorption capacity found for Cu^{2+} ions compared with Pb^{2+} ions. Moreover, Pb^{2+} ions possess greater ion radius.

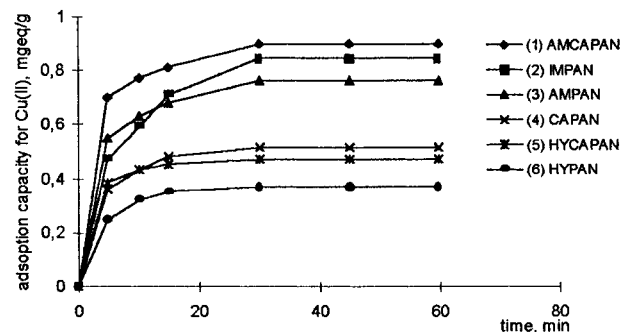


Figure 3 Kinetics of sorption of Cu(II) ions on polymer sorbents.

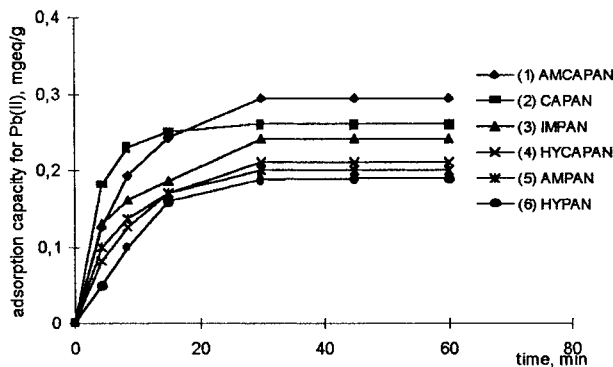


Figure 4 Kinetics of sorption of Pb(II) ions on polymer sorbents.

It is well known that, in the amide, amidoxime and hydrazide groups, the nitrogen atom provides the electron donor properties whereas in carboxylic groups—oxygen atom. Different metal ions tend to bind to different donors.¹¹ Because Cu²⁺ ions form stronger coordination bonds with nitrogen than with oxygen, this is the probable explanation for the order (mentioned above) of the sorbents according to their sorption capacity toward Cu²⁺ ions.

The lowest sorption capacity both for Cu²⁺ and Pb²⁺ ions showed the modification of AN copolymer with hydrazinehydrochloride—HYPAN. This can be explained by the lowest content of functional groups in the sorbent.

The kinetics of sorption of Cu²⁺ and Pb²⁺ ions on the sorbents at pH optimum of 3 was studied (Figs. 3 and 4). Full saturation was reached after 30 min, and the basic amount of metal ions was bound during the first 10–15 min.

The comparison of the sorption capacities of all the modified sorbents shows that the best Cu²⁺ and Pb²⁺ sorbents are AMCAPAN and IMPAN, because they had the highest amounts of functional groups.

An important characteristic of a sorbent is the possibility for its regeneration for further use.

Table IV Degree of Elution of Pb²⁺ and Cu²⁺ Ions (%)

Sorbent	Elution of Pb ²⁺ (%)	Elution of Cu ²⁺ (%)
CAPAN	95	53
AMCAPAN	80	70
IMPAN	67	54
HYCAPAN	95	63
AMPAN	89	73
HYPAN	30	17

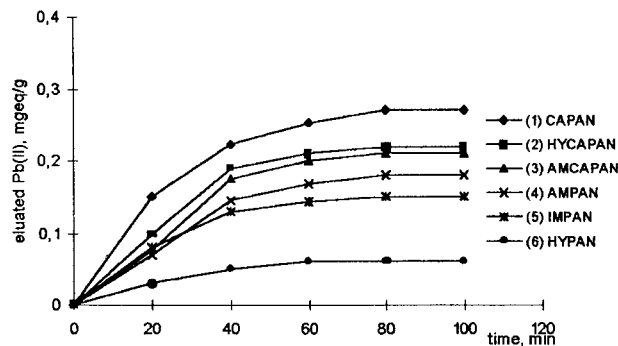


Figure 5 Elution kinetics of Pb(II) ions on polymer sorbents at pH 5.

This is why the elution of the sorbed Cu²⁺ and Pb²⁺ ions was studied. The elution was performed under static conditions with distilled water and pH ranging from 1 to 5. The best elution was achieved at pH 3 for Cu²⁺ and pH 5 for Pb²⁺. The elution degrees of Pb²⁺ and Cu²⁺ at optimal pH are presented in Table IV.

A general conclusion can be made that Pb²⁺ ions are more easily eluted than Cu²⁺ ions. This is probably attributed to the stronger coordination bonds between Cu²⁺ ions and the sorbents' functional groups.

Because the elution was performed under static conditions, full regeneration could not be achieved. Nevertheless, CAPAN and HYCAPAN regenerated almost totally from Pb²⁺ ions, which exhibits the instability of the bond Pb²⁺-functional group. The sorbent modified with hydrazinehydrochloride regenerated with the most difficulties because of the three-dimensional polymer structure and strong chelate bonds.

Figures 5 and 6 illustrate the elution kinetics for all the sorbents studied at optimal pH and static conditions. Equilibrium in the system sorbent-wa-

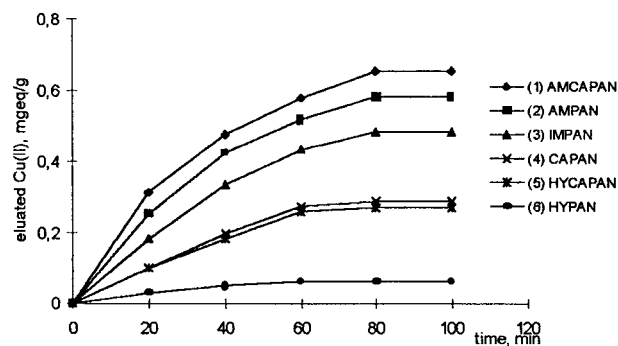


Figure 6 Elution kinetics of Cu(II) ions on polymer sorbents at pH 3.

ter solution was reached for 80 min. For full extraction of the sorbed heavy metal ions, the sorbents were subjected to elution under dynamic conditions with 0.1 n HCl and were 100% regenerated.

The study performed on the adsorption characteristics of modified AN copolymers shows that the ionites obtained, especially AMCAPAN and IMPAN, possess good adsorption characteristics and can be used successfully for extraction of heavy metal ions from water solutions.

REFERENCES

1. Stoy, M. U. S. Pat. 4,110,529, 1978.
2. Chang, L.; Anderson, L.; Ley, D. U. S. Pat. 5,194,512, 1993.
3. Rigopoulos, S. U. S. Pat. 4,143,203, 1984.
4. Myasoedova, G. I.; Savvin, S. B. Chelate Forming Sorbents [in Russian]; Nauka: Moscow, 1984.
5. Hiroaki, E.; Monaka, T.; Tsukamoto, K. Polym J 1990, 22, 120.
6. Chanda, M.; Rempel, G. Ind Eng Chem Res 1995, 34, 2574.
7. Prshibil, R. Coplexometry [in Bulgarian]; Technika: Sofia, Bulgaria, 1980.
8. Soldatov, V. S.; Sergeev, G. I.; Martsinkovich, O. V. Dokl Akad Nauk BSSR 1984, 28, 1009.
9. Dimov, K.; Sarmadjieva, V.; Pavlov, P. Laboratory Practice on Technology of Synthetic Fibres [in Bulgarian]; Technika: Sofia, Bulgaria, 1983.
10. Soldatov, V. S.; Sergeev, G. I. Zh Vses Chim Obshchestva 1990, 35, 101.
11. Saldadze, I. M.; Kopylova, D. Complex Forming Ionites; Khimiya: Moscow, 1980.