Adsorption of Heavy Metal Ions from Aqueous Solutions by Porous Polyacrylonitrile Beads

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ABSTRACT: The adsorption of Cu(II), Ni(II), Zn(II), and Pb(II) from aqueous solutions on acrylonitrile copolymer sorbents was studied. We prepared five types of sorbents from polyacrylonitrile by varying its concentration in the initial polymer solution and the composition of the coagulation bath, aiming to achieve a different porous structure. The specific area, pore volume, and pore radius of the sorbents were determined on a porosimeter. The porous structure was studied by scanning electron microscopy. Modification of sorbents with sodium hydroxide and hydroxylamine was carried out to form amidooxyme and carboxylic groups with proven complex-forming properties toward heavy metal ions. The optimal pH of the sorption of metal ions was found. The adsorption kinetics were investigated. The order of polymer sorbents toward the sorption of Pb(II), Cu(II), Ni(II), and Zn(II) ions, and the order of heavy metal uptake were determined for all types of sorbents. The effectiveness of heavy metal desorption and the coefficient of recovery of sorption ability were determined. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 3036–3044, 2002; DOI 10.1002/app.2334

Key words: acrylonitrile copolymer; porous beads; chemical modification; adsorption; heavy metal ions; desorption

INTRODUCTION

Sorption of metals is one method for the purification of industrial effluents. For that purpose, different materials, such as ion-exchange fibers and resins, have been used. In recent years, the utilization of chelate sorbents to form strong complexes with heavy metal ions has been considered to be more perspective.[1]

Considerably active nitrile groups present in acrylonitrile (AN) copolymers allow additional functional groups to be introduced by special polymer reactions. Many authors have reported on different modifications of polyacrylonitrile (PAN) fibers to obtain cathionite, anionite, and ampholyte.[2] Some authors have carried out surface modifications of PAN with NaOH to obtain a significant number of carboxylic groups.[3] Others have applied modification with hydroxylamine to form amidooxyme groups.[4] Several articles[5,6] have been devoted to PAN modifications with NaOH and hydrazinhydrate, which resulted in three-dimensional structure and good mechanical strength of the sorbent.

Methods for the preparation of AN copolymer beads have been described in several patents. Stoy[7] reported on nonporous spherical PAN beads formed by a process in which the polymer solution was dispersed in a liquid medium that was not a solvent for the polymeric material. Processes for

Table I   Porosity Characteristics of Modified Polymer Sorbents Prepared from AN Copolymer

Characteristic	CAPAN (18 wt %)	AMCAPAN1 (9 wt %)	AMCAPAN2 (7 wt %)	AMCAPAN3 (18 wt %)	AMCAPAN4 (9 wt %)
Specific area (m^2/g)	7.61	19.9	21.9	11.1	3.8
Pore volume (cm^3/g)	0.013	0.019	0.021	0.021	0.0076
Maximum pore distribution (Å)	20–100	30–100	30–100	20–80	30–100
Pore average size (Å)	67.5	36.2	37.8	75.7	78.2
Micropores (< 20 Å)	No	No	No	No	No

the production of porous PAN beads have also been patented[8] where the beads were made from an AN polymer solution by a thermally induced phase-separation process.

In a previous study,[9] we prepared porous PAN beads with defined porosity and then made six types of chemically modified sorbents. We proved that the modified PAN sorbent with NaOH and NH_2OH (AMCAPAN) had the best sorption characteristics. The aim of this study was to prepare AN copolymer chelate sorbents (AMCAPAN) with a different porosity and study their adsorption of Cu, Ni, Zn, and Pb from aqueous solutions.

EXPERIMENTAL

Materials

Polymer sorbents were obtained from AN copolymer. AN (90.6%), methyl methacrylate (8.1%), and 2-acrylamido-methylpropensylfonic acid (1.4%) were obtained from Neftochim Co. (Bourgas, Bulgaria). Dimethylformamide (DMF), lithium nitrate, and glycerin (Fluka Chemie AG, Buchs, Switzerland) were also used for the preparation of polymer sorbents.

The modification of AN copolymer beads was carried out with aqueous solutions of sodium hydroxide and hydroxylamine (Fluka Chemie AG).

Model solutions with certain concentrations of heavy metal ions were prepared from $Pb(CH_3COO)_2 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$, $NiCl_2 \cdot 6H_2O$, and $Zn(NO_3)_2$ (Fluka Chemie AG). All reagents were analytical grade.

Preparation of Porous Sorbents from AN Copolymer

Sorbent PAN1 and PAN2: First Method

AN copolymer (9 g for PAN1 and 7 g for PAN2) was dissolved in 100 mL of DMF and homoge-

nized in a water bath at 60°C under continuous stirring. Then, 1 g of $LiNO_3$ and 3 g of glycerin were added to the polymer solution. The mixture was pipetted into 20 wt % aqueous DMF, whereby particles of porous structure were obtained.

Sorbent PAN3 and PAN4: Second Method

AN polymer (18 g for PAN3 and 9 g for PAN4) was dissolved in 100 mL of DMF and homogenized in a water bath at 60°C under continuous stirring. We then obtained porous sorbents of AN copolymer by adding 1 g of $LiNO_3$ and 3 g of glycerin to the polymer solution and pipetting the homogenized mixture at constant volume rate into distilled water.

All granules obtained were washed thoroughly with distilled water and then kept in a 30% solution of glycerin for 3 h. Finally, the granules were dried at 60°C to a constant weight.

Measurement of Porous Structure

Specific surface area, pore volume, and pore radius of AN copolymer sorbents were determined on a Autosort-3B (Quantachrome Corp.). The porous structure was studied with a scanning electron microscope (type S44 Cam Scan, Electron Optics Ltd., England).

Chemical Modification of Sorbents PAN1, PAN2, PAN3, and PAN4

Chemical Modification with NaOH

Sorbent PAN3 was swelled in a 5 wt % aqueous solution of DMF for 30 min at room temperature. Then, it was immersed in a 20% NaOH solution for 30 min at 60°C. The modified sorbent, called CAPAN, was washed thoroughly with distilled water.

Chemical Modification with NaOH and Hydroxylamine

PAN1, PAN2, PAN3, and PAN4 sorbents were swelled in a 5 wt % aqueous solution of DMF for
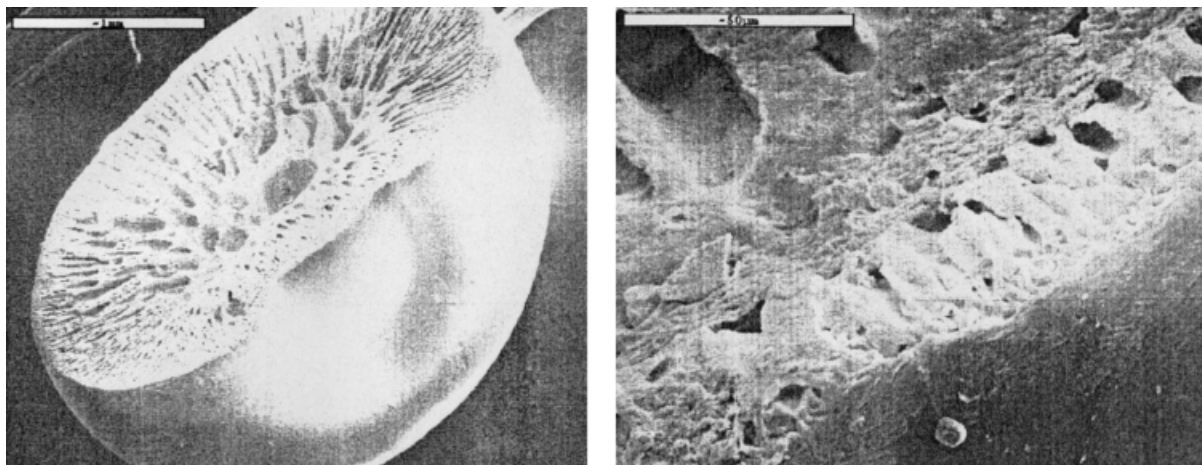
Figure 1 SEM photographs of PAN granules (CAPAN).

30 min at room temperature. Then, they were immersed in a mixture (1:1) of 15 wt % aqueous solution of NaOH and 15% aqueous solution of hydroxylamine for 50 min at 60°C. The polyampholites obtained (AMCAPAN1, AMCAPAN2, AMCAPAN3, and AMCAPAN4) were thoroughly washed with distilled water.

Adsorption Characteristics

Adsorption Kinetics

The AN copolymer sorbent (1 g) was put in contact with 50 cm^3 aqueous solution of Pb(CH$_3$COO)$_2$ · 2H$_2$O, CuSO$_4$ · 5H$_2$O, NiCl$_2$ · 6H$_2$O, and Zn(NO$_3$)$_2$, and the mixture was stirred with a magnetic stirrer at 25°C and pH 3.5 for 2 h. The concentration of heavy metal ions was measured by complexometric titration[10] at certain intervals until equilibrium was reached.

pH Optimum for Sorption Uptake

The adsorption experiments were performed on a rotating shaker. The AN copolymer sorbent (1 g) was immersed in 50 cm^3 of metal-bearing solution and stirred at 25°C and pH 2–5 for 2 h. The metal uptake was calculated by the following equation:

$$a = \frac{(C_0 - C_f)V}{1000m} \text{ (mg/g)}$$

where V is the volume of the solution in the contact batch flask (mL), C_0 is the initial concentration of the metal ions (mg/L), C_f is the equilibrium
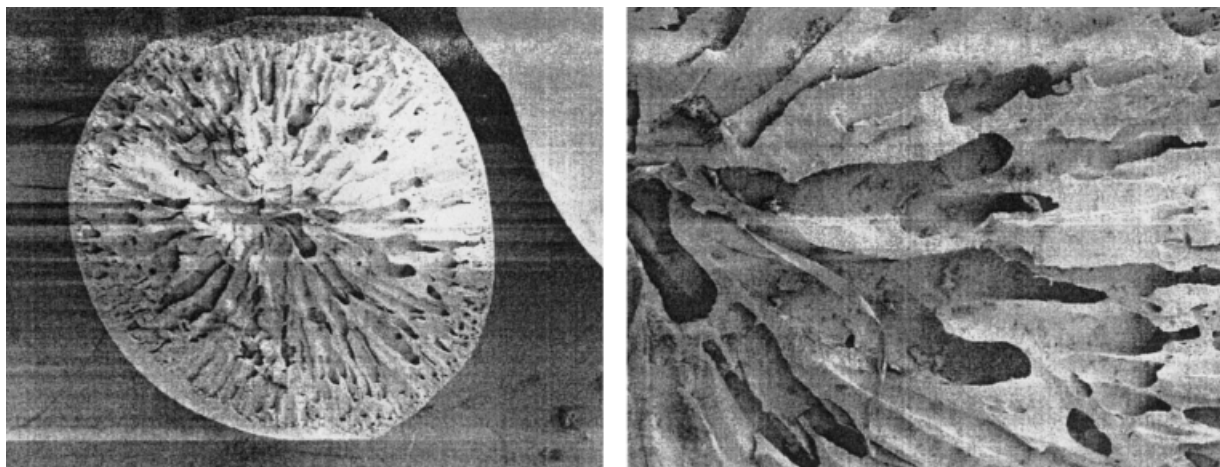
Figure 2 SEM photographs of PAN granules (AMCAPAN3).
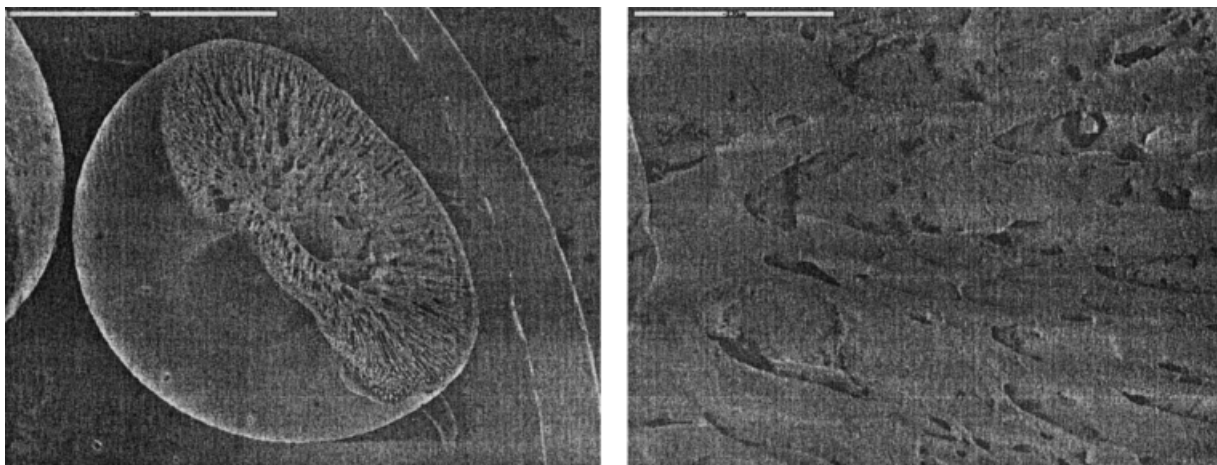
Figure 3 SEM photographs of PAN granules (AMCAPAN1).

concentration (mg/L), and m is the weight of the sorbent (g).

Desorption Studies

Effectiveness of Heavy Metals Desorption

Desorption of the heavy metals was carried out under static conditions (50 cm^3 of eluent and 1 g of sorbent with adsorbed metal ions for 2 h). Four eluting agents, 1N HCl, 1N HNO$_3$, 1N H$_2$SO$_4$, and 0.5N EDTA, were used. Concentration of the metal ions in the eluate was monitored until equilibrium was reached. The regenerated granules were used for the next sorption. The desorption was expressed as a percentage of the sorbents' initial uptake.

Coefficient of Recovery of Sorption Properties After Regeneration

The metal distribution coefficient between the solution and fresh sorbent (K_d) was calculated by the following equation:

$$K_d = a/C,$$

where a is the metal concentration in the sorbent (mgeq/g) and C is the metal concentration in the solution (mgeq/g).

The metal distribution coefficient between the solution and regenerated sorbent (K_{dp}) was determined by the same formula. The coefficient of the recovery of sorption properties after regeneration was calculated by the following equation:

$$K_{d'} = K_{dp}/K_d$$

RESULTS AND DISCUSSION

This study examined Cu(II), Ni(II), Zn(II), and Pb(II) ions sorption from aqueous solutions by five types of AN copolymer sorbents under static conditions.

Polymer granules were obtained by the method described in the Experimental section. All the granules obtained were porous and spherical and were approximately the same size (0.5 mm). Different porous structures were achieved by variation of the concentration of AN copolymer in DMF in the initial polymer solution (Table I) and in the composition of the coagulation bath.

Modification of PAN3 sorbent with 20 wt % sodium hydroxide was carried out to form carboxylic and amido groups. The modified sorbent was called CAPAN. Sorbents PAN1, PAN2, PAN3, and PAN4 were modified with 15 wt % NaOH and 15 wt % hydroxylamine aqueous solutions. Because amidooxyme and carboxylic groups were

Table II   Active Groups Content in Modified PAN Sorbents

Sorbents from AN Copolymer	Amidooxyme	
	Amido Groups (mgeq/g)	Carboxyl Groups (mgeq/g)
AMCAPAN2	0.68	0.53
AMCAPAN1	0.59	0.52
CAPAN	0.38	0.54
AMCAPAN4	0.40	0.15
AMCAPAN3	0.33	0.12

Table III   Effect of pH on Adsorption Capacity for Pb(II) (mgeq/g)

Sorbent	pH			
	5	4	3	2
AMCAPAN2	0.12	0.19	0.20	0.15
AMCAPAN1	0.09	0.11	0.15	0.10
CAPAN	0.09	0.13	0.14	0.11
AMCAPAN4	0.07	0.09	0.10	0.08
AMCAPAN3	0.06	0.08	0.09	0.07

Table V   Effect of pH on Adsorption Capacity for Ni(II) (mgeq/g)

Sorbent	pH			
	5	4	3	2
AMCAPAN2	0.60	0.68	0.78	0.65
AMCAPAN1	0.41	0.60	0.70	0.55
CAPAN	0.36	0.41	0.51	0.39
AMCAPAN4	0.31	0.37	0.44	0.36
AMCAPAN3	0.24	0.32	0.34	0.29

formed, the new sorbents were called AMCA-PAN1, AMCAPAN2, AMCAPAN3, and AMCA-PAN4.

It can be seen from Table I that we obtained sorbents (AMCAPAN1 and AMCAPAN2) with a higher specific area, higher pore volume, and smaller pore size by pipetting the polymer mixture into a 20 wt % solution of DMF (the first method), compared to the sorbents we obtained by pipetting into water (second method). This is probably due to the weaker surface tension on the forming polymer beads in the coagulation bath containing DMF. Granules could not be formed from polymer solutions of concentrations lower than 7 wt %, and the flakes obtained were rather soft and mechanically unstable. Better surface characteristics were observed with granules prepared from 7 and 9 wt % polymer solution by the first method (coagulation bath with a 20 wt % aqueous solution of DMF). The granules prepared with 9 wt % polymer solution, however, were harder and more stable mechanically. The increase of polymer concentration above 9 wt % (by the first method) decreased sorbents' specific area and pore size. Therefore, the optimal concentration of the polymer was assumed to be from 7 to 9 wt %.

By the second method (coagulation bath and distilled water), the results with 9 wt % polymer solution were even worse compared to those with the 18 wt % solution. This can be explained by the higher surface tension in the water bath present during the formation of the granules. The optimal polymer concentration in this case was assumed to be 18 wt % (sorbents with much smaller pore sizes were obtained at higher concentrations).

Scanning electron microscopy (SEM) photographs taken from the samples show that sorbents prepared by the first method (AMCAPAN1) had higher specific areas and smaller pore sizes (Figs. 1–3).

Table I shows that the chemical modification also affected the porous structure. With the same initial sorbent (18 wt % polymer solution), the treatment with sodium hydroxide and hydroxylamine gave slightly larger pores and improved specific area and total pore volume compared with treatment with sodium hydroxide only.

The number of functional groups introduced was determined[11] (Table II). The highest number of functional groups was observed in AMCAPAN2 (1.21 mgeq/g) due to their higher specific area and higher degree of modification. The amido group content in CAPAN was lower due to the priority of

Table IV   Effect of pH on Adsorption Capacity for Zn(II) (mgeq/g)

Sorbent	pH			
	5	4	3	2
AMCAPAN2	0.34	0.44	0.51	0.40
AMCAPAN1	0.28	0.38	0.46	0.34
CAPAN	0.21	0.31	0.32	0.29
AMCAPAN4	0.08	0.14	0.15	0.09
AMCAPAN3	0.06	0.12	0.14	0.08

Table VI   Effect of pH on Adsorption Capacity for Cu(II) (mgeq/g)

Sorbent	pH			
	5	4	3	2
AMCAPAN2	0.85	1.07	1.15	0.96
AMCAPAN1	0.76	0.96	1.05	0.85
CAPAN	0.38	0.55	0.71	0.52
AMCAPAN4	0.35	0.44	0.49	0.41
AMCAPAN3	0.25	0.35	0.39	0.30
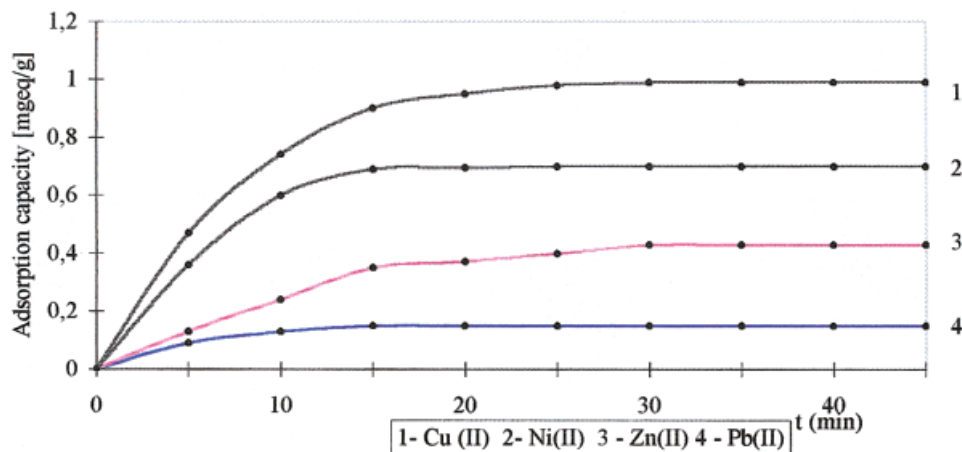
Figure 4   Kinetics of sorption of Pb(II), Zn(II), Ni(II), and Cu(II) on AMCAPAN1 at pH 3.5.

carboxylic groups introduced in the polymer structure by the sodium hydroxide treatment.

Sorption of heavy metals depends particularly on solution pH, one of the dominant parameters controlling the process. Therefore, pH influence on the sorption capacity and complex-forming properties was examined. The effect of pH on adsorption of Cu(II), Ni(II), Zn(II), and Pb (II) ions for all modifications is presented in Tables III–VI. The highest sorption with respect to all metal ions was achieved at pH 3–4.

Adsorption kinetics was investigated (Figs. 4–8). Complete saturation was reached after 20

min of contact, but high sorption rates were observed during the first 15 min. Rapid metal uptake took place in all cases studied. This could be explained by the porous structure, which accelerated metal ion diffusion to the functional groups.

When the sorption capacities of all modified beads for Cu(II), Ni(II), Zn(II), and Pb(II) ions were compared, the uptake was higher for Cu(II) and significantly lower for Pb(II). This can be explained by the smaller radius of Cu(II) compared with Pb(II) and the proven strong coordination bond of copper ions with the nitrogen atom
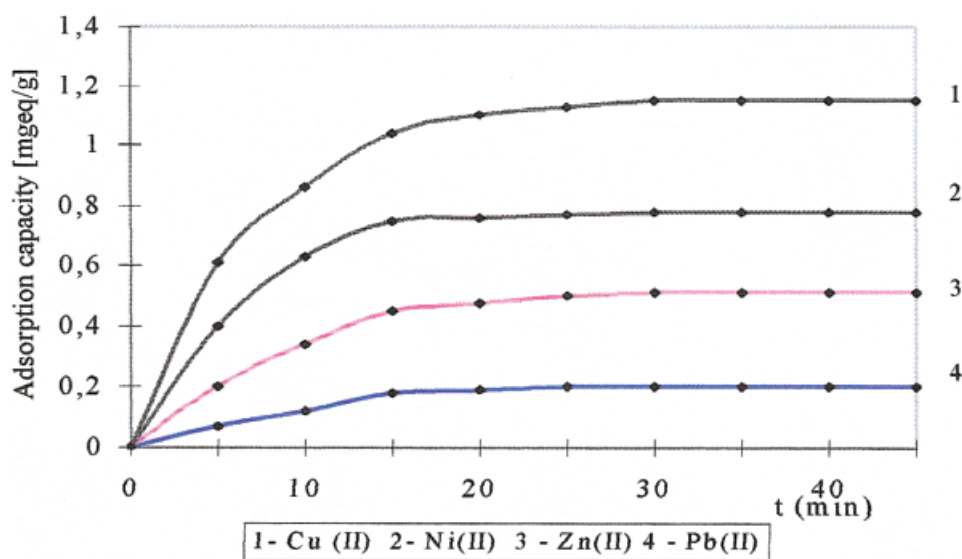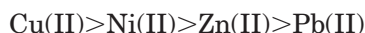

Figure 5   Kinetics of sorption of Pb(II), Zn(II), Ni(II), and Cu(II) on AMCAPAN2 at pH 3.5.
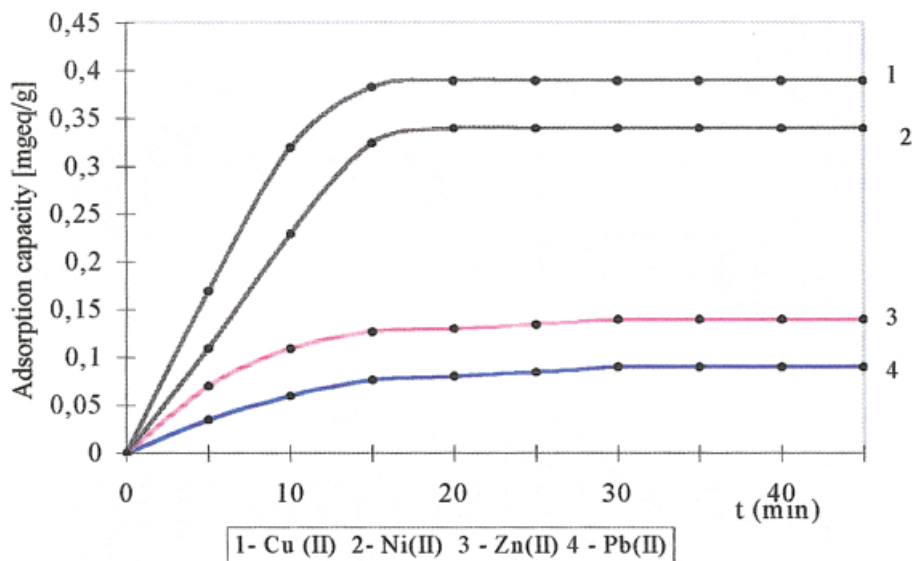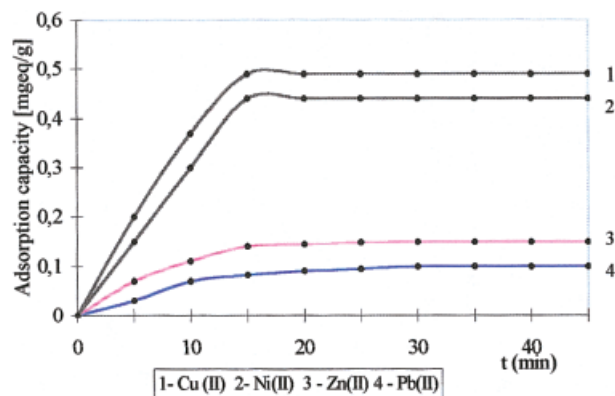
Figure 6   Kinetics of sorption of Pb(II), Zn(II), Ni(II), and Cu(II) on AMCAPAN3 at pH 3.5.

in the amidooxyme group [e.g., sorption of Cu(II) by AMCAPAN2 reached 1.15 mgeq/g]. The following order of metals uptake for all types of PAN sorbents was determined:

$$Cu(II) > Ni(II) > Zn(II) > Pb(II)$$

Sorbents AMCAPAN1 and AMCAPAN2 exhibited the best sorption characteristics with respect to all metal ions, which can be explained by the greater number of functional groups introduced in the sorbent structure and their better porosity characteristics.
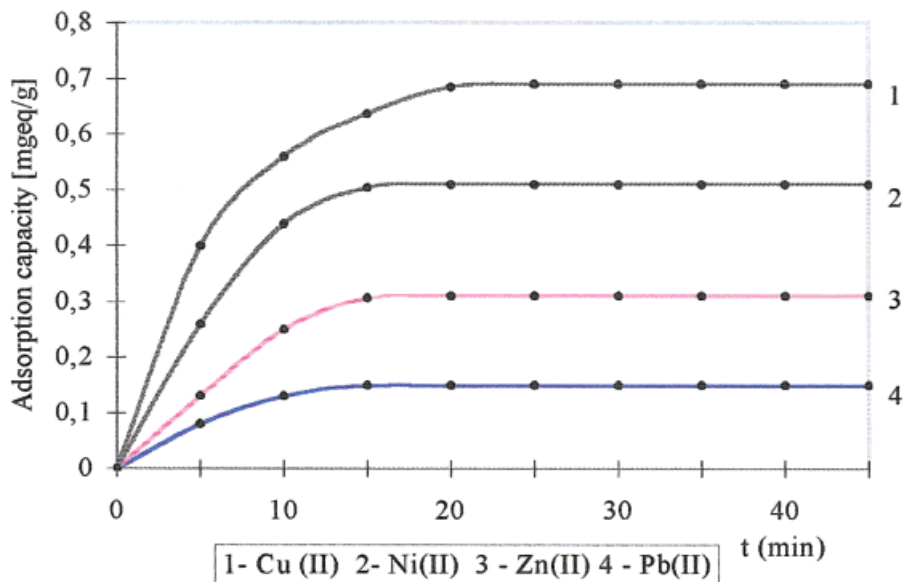

Figure 7   Kinetics of sorption of Pb(II), Zn(II), Ni(II), and Cu(II) on AMCAPAN4 at pH 3.5.

The sorbents were classified in the following order according to their sorption capacity for the heavy metal ions studied:

$$AMCAPAN2 > AMCAPAN1 > CAPAN >$$
$$AMCAPAN4 > AMCAPAN3$$

This order shows that the number of functional groups was a significant factor for the sorption characteristics. The effect of the functional groups on heavy metal sorption became obvious when the results for CAPAN, AMCAPAN4, and AMCA-PAN3 were compared. Despite AMCAPAN4 and CAPAN's poorer porosity, the number of complex-forming groups was higher, and this determined the better sorption characteristics of AMCAPAN4 and CAPAN compared to AMCAPAN3. Although AMCAPAN2 had the best sorption characteristics, it suffered partial destruction of structure during sorption because of its lower mechanical strength.

A very important property of the sorbents was their regeneration ability, which made it possible to reuse them. Two eluating agents were used: aqueous solution of HNO_3 with pH 3.5 and $1N$ H_2SO_4. The effectiveness of regeneration concerning all metal ions was determined by the comparison of metal uptake by fresh sorbents and regenerated ones. For all sorbents and both eluents, Cu(II) desorbed better than the other heavy met-

Figure 8   Kinetics of sorption of Pb(II), Zn(II), Ni(II), and Cu(II) on CAPAN at pH 3.5.

als studied. This was due to the greater copper ion uptake during sorption. Better desorption for all metals was observed with $1N$ H_2SO_4. We prepared the latter taking into account the requirements for further electrochemical separation and concentration of metals. Higher eluent concentration was not preferable because it could lead to granule shrinkage and, therefore, disturb the diffusion process.[12] Elution of Pb(II) ions with $1N$ H_2SO_4 was unsuitable because of the formation of precipitate, which made study impossible.

The kinetics of elution with aqueous solutions of HNO_3 adjusted to pH 3.5 and $1N$ H_2SO_4 were studied under static conditions. Equilibrium was reached at 70–80 min, and the full extraction of metals could not be achieved due to the static conditions. The sorption properties recovery coef-

ficient K_d' was determined (Table VII). However, complete recovery of sorption properties could not be achieved. The coefficient was higher when elution with sulfuric acid ($1N$) was carried out. With aqueous solutions of HNO_3 (pH = 3.5) and $1N$ H_2SO_4, high coefficients were achieved for all sorbents with respect to Cu(II) ions.

Detailed desorption studies of heavy metal loaded AMCAPAN1 were carried out because it had the best sorption characteristics and mechanical stability. Three eluting solutions containing a proton-exchanging agent (HCl, HNO_3, and H_2SO_4) and a complex-forming agent (EDTA) were used. The experiments confirmed results reported earlier[13,14] that maximum metal desorption can be achieved with mineral acids with concentrations of $1N$. Figure 9 shows the effectiveness of metal ion desorp-

Table VII   Coefficient of Recovery of Sorption Properties After Regeneration (K_d')

Sorbent	Cu(II)		Ni(II)		Zn(II)		Pb(II)	
	Distilled Water[a]	$1N$ H_2SO_4	Distilled Water	$1N$ H_2SO_4	Distilled Water	$1N$ H_2SO_4	Distilled Water	$1N$ H_2SO_4
AMCAPAN1	0.57	0.68	0.36	0.69	0.33	0.51	0.38	—
AMCAPAN2	0.58	0.72	0.44	0.75	0.41	0.64	0.39	—
AMCAPAN3	0.57	0.74	0.43	0.68	0.43	0.66	0.37	—
CAPAN	0.52	0.66	0.43	0.63	0.39	0.57	0.32	—
AMCAPAN4	0.58	0.68	0.43	0.75	0.39	0.59	0.39	—

[a] Aqueous solutions of HNO_3 adjusted to pH 3.5.
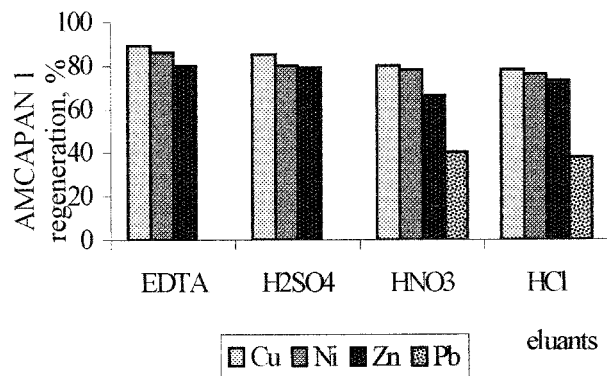
Figure 9 Effect of AMCAPAN1 regeneration with respect to Cu(II), Ni(II), Zn(II), and Pb(II).

than polymer fibers, activated carbon, and ion-exchange resins.

tion from AMCAPAN1 with $1N$ solutions of HCl, HNO_3, and H_2SO_4 and $0.5N$ EDTA. The elution of Pb II ions by H_2SO_4 and EDTA was affected because of the precipitation formed during regeneration The desorption performance of individual eluents was expressed as a percentage of sorbent's initial load. EDTA ($0.5N$) and the mineral acids ($1N$) proved to be effective eluents. The better eluent was $0.5N$ EDTA.

The results of this study show that all sorbents, especially AMCAPAN2 and AMCAPAN1, possess good sorption characteristics and are effective adsorbents for the removal of heavy metal ions from aqueous solutions. It was difficult to compare our sorbents with others described in literature because of inconsistencies in data presentation. However, from the literature reviwed,[15] our sorbents have similar absorption-capacity characteristics to polymer granules but lower capacities

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