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METAL ION REMOVAL BY MODIFIED POLYACRYLONITRILE SORBENT PRELIMINARILY CONVERTED INTO AN INNER SALT

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METAL ION REMOVAL BY MODIFIED POLYACRYLONITRILE SORBENT PRELIMINARILY CONVERTED INTO AN INNER SALT

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ABSTRACT

Metal ion removal from acidic solutions with a high electrolyte concentration was completed through a modified polyacrylonitrile sorbent. The effects of the initial ion concentration, pH, the ionic strength, and anionic influence on the sorption behavior of the modified polymer were investigated. The distribution coefficient values for metal ions of various initial concentrations at 0.1 mol/L ionic strength increased in the following order: $Mg^{2+} < Co^{2+} < Ni^{2+} < Zn^{2+} < Cd^{2+} < Cu^{2+} < Pb^{2+}$. The change of the ionic strength of the solution exerts a slight influence on the removal of copper, lead, and cadmium ions from aqueous solutions. Competition sorption studies were conducted at pH 4, ionic strength 0.5 mol/L, and with competing metal ions added at equivalent initial concentrations in the 2-component systems. Complete elution of metal ions from a loaded modified polymer was achieved with a nitric acid solution (pH 1.0–1.5) or by a subsequent treatment with 3% NH_4OH solution. The modified polymer has a high selectivity toward lead and copper ions and could be used to remove and separate different amounts of these elements from metal-bearing solutions and industrial wastewater with a high electrolyte concentration.

Key Words: Complexing polymer; Heavy metal ions; Sorption; Distribution coefficient

INTRODUCTION

The toxic nature of heavy metal ions, even at trace levels in natural waters, has been a public health problem during the past few decades. These metal ions are of a special concern because they are nondegradable toxic pollutants that interfere with the metabolism of living environmental systems (1). Waters polluted with heavy metal ions cannot self-purify and can preserve their toxicity for an indefinite time. To solve this problem, industrial waters must be treated to remove the toxic metal ions before they can be disposed into the sewerage. The most important technologies for toxic ion removal are chemical precipitation, ion exchange, and sorption. However, many metal-bearing wastes contain substances, such as complexing agents, that decrease the effectiveness of the precipitation processes, leading to relatively high metal concentrations in the effluent (2). The recovery of metals from hydrometallurgical liquors, spent electroplating baths, and metal finishing wastewater is becoming of increasing environmental, technological, and economic interest (3,4). Sorption of heavy metals on inorganic sorbents and carboxyl cation exchangers is not effective at pH values less than 5 (5). The increase of pH in such cases is often an expensive means for treating heavy metal–laden acidic industrial wastewater.

The growing problem of heavy metal contamination of natural waters has stimulated a search for new selective ion-exchange resins and adsorbents that show ion exchange and complexing properties of different metal ions under acidic conditions (6,7). The new resins and adsorbents permit a high degree of purification of industrial wastewater to be reached and some valuable metals to be utilized. Chelating sorbents have received increasing attention as adsorbents for selective removal of dissolved heavy metals from contaminated water/wastewater in preference to nontoxic competing ions, such as Ca^{2+}, Mg^{2+}, and Na^{+} (4,8,9). Adsorption through chelators can be more effective and economical. The use of chelators for adsorption also provides a potential for removal, recovery, and recycling of metals from industrial wastewater.

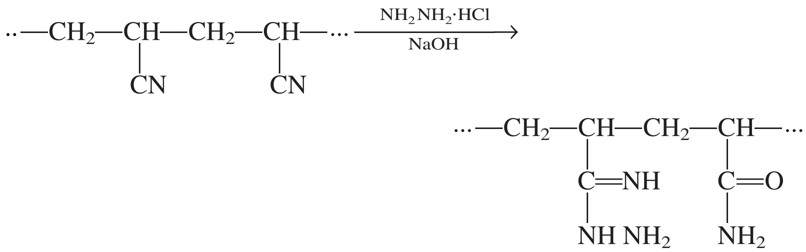
The acrylonitrile polymers and their fibrous materials can be successfully used as a polymer matrix for obtaining complexing sorbents (10). New functional groups can be introduced into acrylonitrile polymers by polymer analogous transformations of relatively reactive nitril groups. The three-dimensional spatial structure of these polymers that ensures the necessary stability in alkaline hydrolysis is created by treatment with hydrazine hydrate (11). Different ion exchange and complexing sorbents have been obtained by chemical modification of the acrylonitrile copolymer functional groups (12,13). The acid-base and complexing properties of modified polyacrylonitrile sorbent have been investigated (14).

In wastewater treatment processes the sorbents are usually used in the presence of big quantities of various ions. Therefore, the primary investigation presented here regards the possibility of metal ion removal from acidic solutions with a high electrolyte concentration through the use of a modified polyacrylonitrile sorbent that had been preliminarily converted into an inner salt.

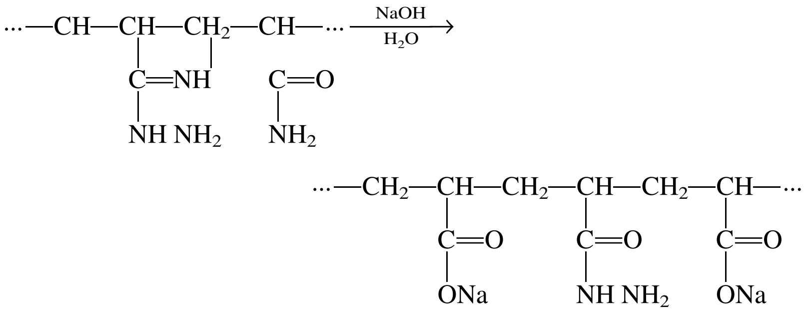
MATERIALS AND METHODS

Preparation and Characterization of Modified Sorbent

The modified sorbent was obtained from a triple copolymer of acrylonitrile (88.45%), methylmethacrylate (6.47%), and sodium vinylsulfonate (5.08%) with molecular weight 5.1×10^4. Its nitrogen and sulfur contents were 22.82% and 1.25% respectively. The nitrogen content in the copolymer was determined by the method of Keldal. The content of sulfur (from sulfonic groups) was determined by weight analysis after preliminary treatment of the polymer with concentrated nitric acid and 70% perchloric acid in a weight ratio of 6:4 (15). The density of the copolymer was 1.18 g/cm^3. The modification of the polymer was accomplished by treatment with 4% NaOH and 4% $NH_2NH_2{\cdot}HCl$ in a ratio of 4 to 1 at a contact time of 3 hours, at 97°C, and under continuous agitation. The correlation between the solid and the liquid phases was 1:50. For the removal of the 2 reagents, the obtained product was repeatedly washed with distilled water. The modified polymer was obtained in the following way:



$$\cdots-\mathrm{CH_2}-\underset{\begin{array}{c}|\\\mathrm{CN}\end{array}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\begin{array}{c}|\\\mathrm{CN}\end{array}}{\mathrm{CH}}-\cdots\xrightarrow[\mathrm{NaOH}]{\mathrm{NH_2NH_2{\cdot}HCl}}\cdots-\mathrm{CH_2}-\underset{\begin{array}{c}|\\\mathrm{C{=}NH}\\|\\\mathrm{NH\,NH_2}\end{array}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\begin{array}{c}|\\\mathrm{C{=}O}\\|\\\mathrm{NH_2}\end{array}}{\mathrm{CH}}-\cdots$$



The modified sorbent preliminarily treated with 2 mol hydrochloric acid solution was converted into an inner salt by washing with boiling distilled water until the filtrate was at pH 5.5 and no chloride ions were present in the wash waters. The sorbent showed acidic properties: Ion exchange capacity with regard to 0.1 mol/L NaOH was 6.30 ±0.03 mmol/g; it also showed alkaline properties: Ion exchange capacity with regard to 0.1 mol/L HNO_3 was 0.88 ±0.03 mmol/g. The characteristic dissociation constant of the carboxyl groups was 4.57×10^{-5} ($pK = 4.39$) at ionic strength $\mu = 1$. The nitrogen content in the modified polymer converted into an inner salt was 4.70% and the sulfur content was 0.14%. The specific surface area (31.6 m^2/g) of the material was measured by the Brunauer, Emmett, and Teller (BET) method through the use of a Quantasorb model QS-7 surface analyzer. The pore volume (0.652 cm^3/g) and the average pore radius (28.7 nm) of the modified sorbent were determined by a MOD Carbo-Erba mercury porosimeter. The sorbent was obtained in spherical beads with sizes varying from 0.3 to 0.5 mm.

Sorption Studies

All chemicals were of an analytical grade. The salts were copper, lead, zinc, cadmium, cobalt, nickel, and magnesium nitrates. The stock solutions (0.25 mol/L) of the test species were made by dilution with double-distilled water. The initial pH of the solutions was adjusted with 0.05 mol/L HNO_3 and 0.05 mol/L NaOH respectively. The addition of different sodium nitrate quantities into the solution changed the ionic strength. Batch mode sorption studies were carried out to determine the sorption of metal ions on the modified sorbent that was preliminarily converted into an inner salt. Samples of the modified sorbent (0.1 g by dry weight) were equilibrated with 100 mL aqueous solution of metal ions at varying concentrations, pH values, and ionic strengths in different glass bottles. As preliminarily established, 7 days were needed to reach equilibrium in the system sorbent–metal ion solution. The samples were centrifuged at 5000 rpm for 15 minutes. The concentration of the metal cations in single adsorbate systems was determined titrimetrically by ethylenediaminetetraceticacid (disodium salt). The metal ion concentration in competition experiments was determined by atomic absorption. All experiments were repeated and the average values are presented. The maximum deviation was 4%.

Distribution coefficient values (K_d) for the investigated metal ions at various initial solution concentrations were calculated using bath experiment data as follows:

$$K_{d(i)} = \frac{q_{e(i)}}{C_{e(i)}} \tag{1}$$

where $q_{e(i)}$ is the amount of metal ion sorbed at equilibrium (mol/g), and $C_{e(i)}$ is the equilibrium concentration of metal ion in solution (mol/mL).

The competitive effect of metal ions was interpreted through the use of the selectivity coefficient. This coefficient is a measure of the relative selectivity between 2 competing solutes and is equal to the ratio of their distribution coefficients between the exchanger phase and the aqueous phase:

$$D_{A/B} = \frac{K_{d(A)}}{K_{d(B)}} \tag{2}$$

Desorption Studies

After sorption experiments, the metal-laden sorbent, separated by filtration, was gently washed with distilled water to remove any unadsorbed metal ions. The spent samples (0.5 g) were agitated with 50 mL of acidified water adjusted to different pH values with diluted HNO_3. The desorbed metal ions were estimated by analyzing the acid solutions as before. The percentage desorption was determined.

RESULTS AND DISCUSSION

Sorption Isotherms

The dependence of equilibrium concentration of lead, copper, zinc, cadmium, cobalt, nickel, and magnesium ions on sorption capacity at 22°C and polymer-solution ratio 1 g/L to 0.1 mol/L ionic strength was investigated. Isotherm experiments for lead and copper ions were performed at initial pH 4.10, while others were conducted at pH 5. Sorption isotherms (Fig. 1) reveal that metal uptake increased with increased metal concentration. The curves for Cu^{2+}, Cd^{2+}, and Pb^{2+} show a very steep increase in the amount of metal ion initially sorbed. The curves for Ni^{2+} and Mg^{2+} reflect a gradual increase in the amount sorbed and show ion saturation at higher solution concentrations.

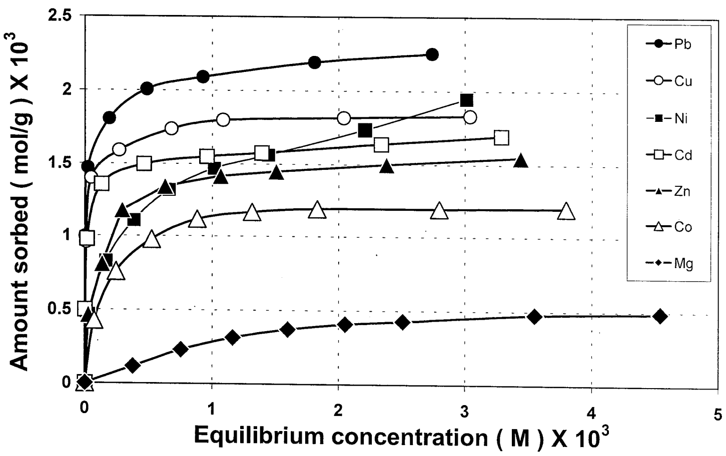


Figure 1. Sorption isotherms for metal ions at initial pH 4.10 (Pb^{2+} and Cu^{2+}) and pH 5 (other ions) at 0.1 mol/L ionic strength.

The sorption data were fitted with the Langmuir adsorption equation. Langmuir adsorption parameters were obtained based on the equation:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \tag{3}$$

where C_e is the equilibrium concentration of divalent cations in the solution (mol/L); q_e is the equilibrium sorption capacity (mol/g); Q_0 is the Langmuir constant related to the maximum sorption (mol/g); and b is the sorption constant related to the binding energy between the cations and the exchanger sites of the modified polymer. Table 1 presents the Langmuir constants Q_0 and b for these systems. The obtained sorption affinity sequence in the presented work was Pb^{2+}

Table 1. Langmuir Constants for Metal Ion Sorption on Modified Polymer

Metal Ions	$Q_0 \times 10^3$ (mol/g)	$b \times 10^{-4}$ (L/mol)	Correlation Coefficient R^2
Pb^{2+}	2.247	3.272	0.999
Ni^{2+}	2.026	0.343	0.985
Cu^{2+}	1.806	6.085	0.999
Cd^{2+}	1.682	2.185	0.998
Zn^{2+}	1.558	0.961	0.998
Co^{2+}	1.246	0.776	0.999
Mg^{2+}	0.606	0.084	0.987

Table 2. Distribution Coefficients (K_d) for Metal Ions at Various Initial Solution Concentrations

Metal Ions	Initial Concentration of Metal Ions, $C_0 \times 10^{-3}$ (mol/L)							
	0.5	1.0	1.5	2.0	2.5	3.0	4.0	5.0
Pb^{2+}	5.18×10^6	4.56×10^5	6.99×10^4	9.47×10^3	4.13×10^3	2.23×10^3	1.21×10^3	8.21×10^2
Cu^{2+}	1.45×10^5	8.81×10^4	2.29×10^4	4.69×10^3	2.26×10^3	1.65×10^3	8.91×10^2	5.87×10^2
Cd^{2+}	6.58×10^5	6.29×10^4	1.05×10^4	3.27×10^3	1.57×10^3	1.13×10^3	6.92×10^2	5.16×10^2
Zn^{2+}	1.69×10^4	4.51×10^3	4.05×10^3	2.14×10^3	1.30×10^3	9.62×10^2	6.55×10^2	4.33×10^2
Ni^{2+}	1.61×10^4	5.02×10^3	2.88×10^3	1.99×10^3	1.45×10^3	1.06×10^3	7.92×10^2	6.47×10^2
Co^{2+}	5.82×10^3	3.11×10^3	1.86×10^3	1.27×10^3	8.96×10^2	6.34×10^2	4.26×10^2	3.16×10^2
Mg^{2+}	3.08×10^2	3.05×10^2	2.69×10^2	2.32×10^2	1.99×10^2	1.76×10^2	1.27×10^2	1.01×10^2

$> Ni^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Mg^{2+}$. The sorption (binding) constant for copper ions was bigger than those for other metal ions. This phenomenon is not rare for the binding of copper ions in carboxyl sites (16). However, the maximum amount of copper ions sorbed was lower than that of lead and nickel ions. This result probably indicates that not each ionogenic site is available for copper ion binding. The lead ions have the highest sorption capacity and also a relatively high binding constant.

The distribution coefficient values (K_d) for the investigated heavy metal ions at various initial solution concentrations at 0.1 mol/L ionic strength were calculated and the results are shown in Table 2. The distribution coefficients show that the modified polymer was more selective for Pb^{2+} than it was for Cu^{2+} and Cd^{2+} and much more selective than for Zn^{2+}, Ni^{2+}, Co^{2+}, and Mg^{2+}. The K_d values for all metal cations decreased when the initial solution concentration was increased. The modified polymer could be used for the removal of lead, copper, and cadmium ions from water solutions at initial concentrations less than 1×10^{-3} mol/L in acidic medium. The sorbent exhibited selective properties toward Pb^{2+}, Cu^{2+}, and Cd^{2+} ions in acidic conditions at 0.1 mol/L ionic strength. These metal ions may have been concentrated on the sorbent in the presence of alkaline earth elements, and zinc, nickel, and cobalt ions in the solution.

Effect of pH on Metal Ion Sorption

The influence of pH on the removal of metal ions from aqueous solutions at concentration 5×10^{-3} mol/L and 0.1 mol/L ionic strength was investigated (Fig. 2). The data regarding pH effects showed that the sorption of all metal ions was markedly influenced by the solution pH. The experimental data obtained show an increase of the metal ion uptake at pH values higher than 2.5–3.0. The carboxyl cation exchange resins adsorbed metal ions only as a result of ion exchange at pH > 5. The dissociation of carboxyl groups began at pH ≥ 3 (17). The salt form of amino groups does not show coordination properties during interac-

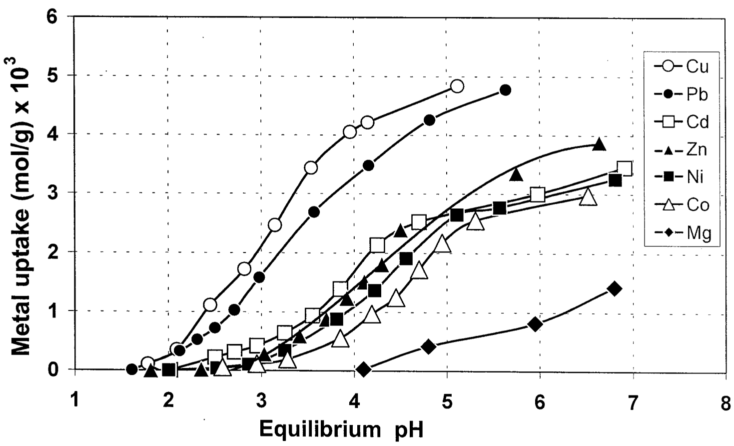
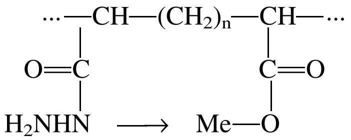


Figure 2. Effect of pH on metal ions sorption by the modified polymer at initial concentration 5 × 10^{-3} mol/L and 0.1 mol/L ionic strength.

tion with the metal cations because the N—H bond is more stable than the N—Me bond (18). Therefore, one can suppose that the sorption of the metal ions is realized by a simultaneous formation of ionic and coordination bonds in which carboxyl and nitrogen-containing functional groups (> N—NH$_2$, —NH—NH—, —NH—NH$_2$) of the modified polymer take part. The complex formed in the polymer phase is expected to have the following general formula:



$$\begin{array}{ccccc}
\cdots- & \mathrm{CH} & -(\mathrm{CH_2})_n- & \mathrm{CH} & -\cdots \\
 & | & & | & \\
\mathrm{O=} & \mathrm{C} & & \mathrm{C} & \mathrm{=O} \\
 & | & & | & \\
\mathrm{H_2NH} & \mathrm{N} & \longrightarrow\ \mathrm{Me-} & \mathrm{O} &
\end{array}$$

With the increased pH of the equilibrium solution the concentration of coordination active (deprotonated) ionogenic groups was enhanced. Their electron donor properties and the degree of polymer swelling in water solution changed too.

According to the concept of hard and soft acids and bases, the functional groups in the chelating polymer materials usually act as bases: Oxygen-containing functional groups are hard, and functional groups with a basic nitrogen atom have an intermediate character (19). While copper, nickel, lead, zinc, and cobalt act as an intermediate type of acid (1), the modified polymer with oxygen- and nitrogen-containing functional groups can be used to remove these metal ions from the water solution. Also, one can use nitrogen- and sulfur-containing functional groups for removal of soft acids, such as cadmium.

The removal of metal ions depends not only on the degree of deprotonation of the functional groups but also on the stability of the polymer complex, the concentration, and the state of the polymer in the solution. The stability of the obtained complexes in the polymer phase probably depends on the three-dimensional position of the ligand groups in the sorbent, the flexibility of the polymer chain, and the possibility for ligand group participation in the formation of complexes with a respective stereochemistry. By potentiometric titration, the stability of the complexes formed between carboxyl groups of modified polymer and different cations was found to increase in the following order: $Ni^{2+} < Cd^{2+} < Co^{2+} < Zn^{2+} < Pb^{2+} < Cu^{2+}$ (14).

The comparison between the obtained experimental results with the results given by other authors confirms the rule that the stronger the complex formed in the polymer phase the lower the values of pH at which the metal begins to adsorb (17). The sodium ions (from the background electrolyte) do not form complexes with the functional groups of the modified sorbent. The alkali-earth metals form stable complexes in neutral and alkaline medium.

The pH regions in which a rapid increase in metal ion sorption at an initial concentration of 5×10^{-3} mol/L was found were 2.5–4.0 for copper ions, 2.5–4.5 for lead ions, 3.5–5.0 for zinc and cadmium ions, and 4.0–5.5 for nickel and cobalt ions. Because the functional groups of sorbent contain oxygen and nitrogen atoms with undivided electron pairs, the recovery of metal ions with free orbitals from water solutions could be carried out by forming ionic, coordination, or a simultaneous realization of both kinds of bonds.

The data presented in Fig. 2 show that the modified polymer could be used for concentration or removal of copper and lead ions from water at pH 2.5–3.5. Lead or copper ions may be removed selectively from a mixture containing zinc, cadmium, nickel, cobalt, and magnesium ions through a careful adjustment of the pH and other reaction conditions. Complete removal of copper ions was established after treatment of a model solution containing Cu^{2+} and Cd^{2+} ions with the sorbent at pH 3.

The dependence of equilibrium concentration of zinc ions on the sorption capacity at pH 2.02, 2.92, 4.06, and 5.02, created and maintained by universal buffers (H_3PO_4, CH_3COOH, H_3BO_3), was investigated. The final pH of buffered solution (after contact with modified polymer) remained close to the initial pH of the metal solution. Preliminary sorption studies were conducted with zinc ion solution (2.5×10^{-3} mol/L) at initial pH 5.02 in buffered and unbuffered systems. The metal uptake increased 26% more by buffering the system than it was in an unbuffered system ($pH_{final} = 4.5$). The increased metal removal is due to the neutralization of the hydrogen ions released during deprotonation of the functional groups, breaking of inner salt bonds in the modified polymer, and metal uptake. The obtained values of Langmuir constants at different pH values are given in Table 3. At pH = 1, the hydrolysis of sorbent nitrogen-containing groups becomes

Table 3. Langmuir Constants for the Sorption of Zinc Ions at Different pH Values

pH	$Q_0 \times 10^3$ (mol/g)	$b \times 10^{-4}$ (L/mol)	R^2
2.01	0.202	0.440	0.967
2.92	0.257	0.616	0.986
4.06	1.245	0.883	0.961
5.02	1.760	82.332	0.999

practically impossible. Therefore, under acidic conditions ($\mathrm{pH} \leq 2$) the metal removal capacities of chelating polymers are essentially lost because of the formidable competition with hydrogen ions (10). At such low pH, the sorption of metal ions on weak alkaline groups can be accomplished only by the ion exchange mechanism. At the experimental conditions, zinc ions could be removed as anion complexes formed with the components of a universal buffer (acetate, phosphate), but zinc does not form stable complexes with these anions. The very low sorption capacity established at the studied pH values could also be connected with the relatively small amount of nitrogen-containing groups in the polymer compared with the amount of acidic groups. At pH values of approximately 2.5–3.0, the investigated ions can form comparatively stable complexes in the polymer phase. The concentration of deprotonated ionogenic groups in the modified polymer increases with the increase of solution pH. Thus, a possibility for realization of ionic, coordination, or simultaneous formation of 2 kinds of bonds is created, and the values of the Langmuir constants increase (Table 3).

Ionic Strength Effect

The heavy metal sorption from industrial wastewater is usually carried out in the presence of various ingredients. Ionic strength is one of the functions for expressing the total amount of coexistent ions. The acid-base and electron-donor properties of sorbent, the flexibility of the polymer chains, and the degree of polymer swelling in water depends on the ionic strength of the solution. The effect of changed electrolyte concentration (in this case $NaNO_3$) on the sorption behavior toward metal ion removal was studied in a model solution of metal ions with an initial concentration of 5×10^{-3} mol/L at pH 4.20 (Fig. 3). The nitrate was the only anion in the system. Nitrate is an extremely poor ligand; therefore, any significant complexation between divalent cations and nitrate ions can be ruled out (9). Thus, the change of the polymer sorption capacity as a result of recharging the metal ions and also the complexation with the anti-ions of the nitrogen-containing groups can be neglected.

The ionic strength effect on the removal of metal ions could be connected with the type of the formed surface complexes (their relative strength) and with the screening of the protonated coordination groups of the modified sorbent by small electrolyte ions. As the figure shows, the smallest change of copper, lead, and cadmium ions sorbed on the polymer was found with the solution ionic strength increases of up to 2 mol/L. The ionic strength change of the solution exerts the strongest influence on the removal of magnesium, nickel, cobalt, and zinc ions. The results obtained are in good agreement with the calculated values (Table 1) for the Langmuir constant *b*, which is related to the binding energy between the cations and the functional groups of the modified polymer. The experimental results show that as the forming complexes between the metal ions and the ionogenic polymer groups become increasingly stable, the negative influence of the increased ionic strength becomes weaker. The screening effect of the small ions on the ionic dissociated carboxyl groups cannot be compensated with the increase of the electron-donor properties of the deprotonated nitrogen-containing groups. The modified sorbent probably does not contain equal quantities of both types of ionogenic groups.

Effect of Anions

The anions for the investigation were chosen according to the anion compositions of common industrial wastewater. Table 4 shows the results of the batch equilibrium tests in which copper concentration (6.8×10^{-4} mol/L) and the pH

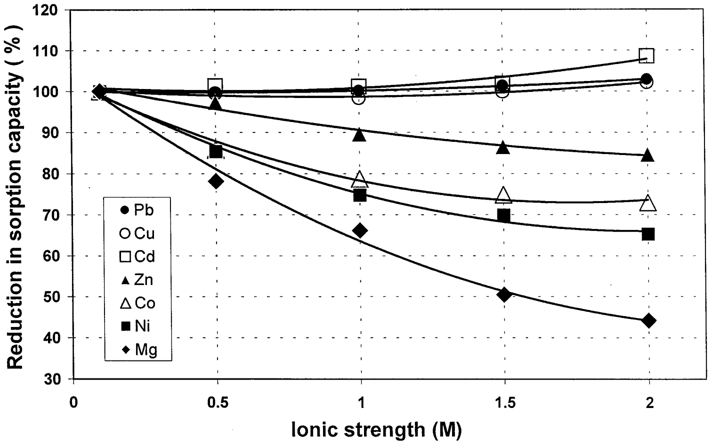


Figure 3. Effect of ionic strength on the metal ion sorption at initial concentration 5×10^{-3} mol/L and pH 4.20.

(3.3–3.4) were kept constant. The ionic strength dependence of sorbent solution was 0.25 g/L. The increased ionic strength of up to 1 mol/L sodium nitrate, up to 0.5 mol/L sodium chloride, and up to 0.1 mol/L sodium sulfate did not affect the sorption of copper ions. Because sodium salts were used, the observed changes in the system polymer solution could only depend on the anion type. The anions could influence the extent of ion association in the aqueous solutions, the type of ion formations created, and their stabilities. Results in Table 4 clearly indicate that the increased ionic strength (up to 1 mol/L) at acidic pH markedly decreases dissolved heavy-metal uptake in sodium chloride and sodium sulfate solutions by the modified polymer. This effect restricts the application of the sorbent to the treatment of relatively diluted solutions. The sorption ability of the investigated polymer for copper ions was negligibly affected by the presence of large amounts of sodium nitrate. Similar observations (not presented here) were also made for cadmium removal.

Sorption from 2-Component Solutions

Industrial wastewater always contains different metal ions that can compete with the target element for sorption sites. As the modified polymer has a high Langmuir constant *b* for copper, lead, and cadmium, these elements were chosen for studying sorption from 2-component solutions. Among the other heavy metals investigated in the present work, lead had the highest uptake and could have the greatest effect on the removal of metal ions. Competition sorption studies were conducted at pH 4, 0.5 mol/L ionic strength, and with competing metals added at equivalent initial concentrations (approximately 1×10^{-3} mol/L) in solution. The total metal concentration was below the sorbent saturation limit.

Table 4. Effect of Anions on the Sorption of Copper Ions

	Copper Ions Sorbed (%) in the Presence of		
Concentration of Anions (mol/L)	Nitrate Ions	Chloride Ions	Sulfate Ions
1.4×10^{-3}	100.00	100.00	100.00
1.0×10^{-2}	100.06	99.26	99.94
5.0×10^{-2}	99.92	99.67	99.62
1.0×10^{-1}	100.09	99.23	98.72
5.0×10^{-1}	99.25	98.86	82.16
1.0	99.85	76.54	63.45

Not all percentages add to 100% due to rounding errors.

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Table 5. Coefficients of Selectivity for the 2-Component Systems

Me_1/Me_2	D_{Me_1/Me_2}	Me_1/Me_2	D_{Me_1/Me_2}	Me_1/Me_2	D_{Me_1/Me_2}
Cu/Pb	12.15	Cu/Mg	2.84×10^4	Pb/Mg	4.23×10^4
Cu/Cd	38.76	Pb/Cd	34.56	Cd/Zn	6.72
Cu/Zn	127.89	Pb/Zn	335.66	Cd/Ni	13.50
Cu/Ni	202.35	Pb/Ni	936.11	Cd/Co	32.71
Cu/Co	516.14	Pb/Co	3020	Cd/Mg	1.61×10^4

The selectivity coefficient values for the investigated 2-component systems are shown in Table 5. The table data show that the modified polymer could be used for concentration, purification, and separation of lead and copper from other elements in water solutions. The sorption of copper was strongly influenced by the presence of lead and cadmium, and is due to the higher affinity of the modified polymer toward these metal ions. The sorbent could also be applied to the removal of copper from nickel-containing solutions ($D_{Cu/Ni} = 202$). These elements are transition-metal cations with strong Lewis-acid characteristics, and they exhibit similar properties and excellent plating characteristics for ferrous and nonferrous alloys (9). The sorption of lead decreases by approximately 11% and 9 % in the presence of equimolar concentrations of zinc and nickel respectively. The uptake of cadmium ions went down by 29.9%, 22.3%, and 14.7% in the presence of zinc, nickel, and cobalt ions in solutions. That result suggests a nonselective uptake of cadmium from water solutions in the presence of these elements. The obtained results are in accordance with the affinity sequence previously determined and show that the modified polymer has a high selectivity toward lead and copper ions. Therefore, the modified polymer could be used to separate different amounts of these elements from copper and/or lead-bearing solution with high electrolyte concentrations.

Sorbent Regeneration Studies

Economic utilization of the sorption processes for removal of toxic compounds is often tied with an inexpensive desorption of solute and regeneration of the sorbent for reuse. The metal ion desorption from the exhausted modified polymer with nitric acid solution adjusted to different pH values is presented in Table 6. The results obtained in the batch method show that the complete elution of copper, zinc, and cobalt from a loaded modified polymer was achieved at a regenerating solution of pH 1.02. The decrease of the pH in the regenerating solution increased lead and nickel recovery to 75–78% and cadmium recovery to 95–96%. Thus, Table 6 shows that the acid regeneration is quite ineffective and indicates the polymer affinity for high metal ions even under acidic conditions (pH of ap-

Table 6. Metal Ion Desorption with Nitric Acid Solution Adjusted to Different pH Values

	Metal Ion Desorbed (%)						
pH	Cu^{2+}	Pb^{2+}	Cd^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}	Mg^{2+}
4.09	N/A	N/A	0.76	N/A	1.09	0.87	10.22
3.58	0.56	0.39	3.71	0.64	4.37	4.76	38.14
3.05	1.23	0.85	10.28	12.36	20.18	26.93	73.85
2.45	16.42	7.43	21.50	40.72	42.85	74.28	100
2.05	39.74	31.14	55.32	73.25	61.34	87.45	N/A
1.50	81.35	61.95	89.45	91.58	75.77	98.23	N/A
1.02	99.96	75.48	95.67	100	78.26	100	N/A

N/A Data not available.

proximately 1.0). Subsequently, these metal ions were completely and very efficiently desorbed with 3% NH_4OH. Similar data for acid regeneration of chelating polymer XFS 4195 were reported by Sengupta and Zhu (9).

The used modified polymer can be regenerated to the original form and thus can be used many times. After 5 sorption-desorption experiments, no detectable loss was found in the complexing ability of the sorbent.

CONCLUSIONS

The removal of metal ions from acidic single and 2-component solutions with a high electrolyte concentration by modified polyacrylnitrile sorbent preliminarily converted into an inner salt was investigated. The equilibria in the polymer–metal ion solution systems were described by the Langmuir adsorption isotherms. The sorption of metal ions on the complexing polymer was strongly dependent on the equilibrium pH value of the solution. The distribution coefficient values for metal ions at various initial concentrations at 0.1 mol/L ionic strength increased in the following order: $Mg^{2+} < Co^{2+} < Ni^{2+} < Zn^{2+} < Cd^{2+} < Cu^{2+} < Pb^{2+}$. The change of the ionic strength of the solution exerts the strongest influence on the removal of Mg^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} from aqueous solutions. The following order of anion influence on the metal sorption was established: $SO_4^{2-} > Cl^- > NO_3^-$. The results show that the complete elution of metal ions from a loaded polymer was achieved with nitric acid solution (pH 1.0–1.5) or by subsequent treatment with 3% NH_4OH solution. The modified complexing sorbent has a high selectivity toward lead and copper ions at pH 2.5–3.5 and can be successfully used to remove and separate different amounts of these elements from metal-bearing solutions and industrial wastewater with a high electrolyte concentration.

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