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Investigation of Metal Ion Removal Selectivity Properties of the Modified Polyacrylamide Hydrogels Prepared by Transamidation and Hofmann Reactions

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Modified crosslinked polyacrylamides having different functional groups prepared by transamidation reaction in aqueous and non-aqueous medium and by Hofmann reaction were used as chelating agents for removal of Cu(II), Cd(II) and Pb(II) ions from aqueous solutions at different pH values. Under non-competitive conditions, polymers adsorbed different amounts of metal ions, depending on their functional groups and swelling abilities. The metal ion adsorption capacities of polymers changed between 0.11–1.71 mmol/g polymer. Under competitive conditions, while the polymers having mainly secondary amine groups were highly selective for Cu(II) ions (99.4%), those having mainly secondary amide and carboxylate groups have shown high selectivity towards Pb(II) ions (99.5%). The selectivity towards Cu(II) ion decreased and Pb(II) ion selectivity increased by the decrease of the pH of the solutions. The high initial adsorption rate (< 10 min) suggests that the adsorption occurs mainly on the polymer surface. A regeneration procedure by treatment with dilute HCl solution showed that the modified polymers could be used several times without loss of their adsorption capacities.

Keywords adsorption, hydrogel, modified polyacrylamide, chelating agent, selectivity

Introduction

Metal ions are essential raw materials for numerous areas of application such as the machine industry, chemical industry, and the electronic and plating industry (1). Among these, the potential sources of copper include metal cleaning baths, wood pulp production and the fertilizer industry, etc. (2), while cadmium is highly corrosion-resistant and is used as a protective coating for iron, steel and copper. Lead is also used mainly in hydrometallurgical processes (3). The presence of these heavy metals in the environment has been of great concern because of their toxic nature and other adverse effects

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on many life forms. Excessive intake of copper results in an accumulation in the liver. It is also toxic to aquatic organisms even at very small concentrations (2). Lead is a general metabolic poison and enzyme inhibitor (4). It can cause mental retardation and further brain damage especially in children. Cadmium can also cause diseases such as hypertension, renal and breast cancers, and kidney diseases (5).

Thus, since the industrial use of these heavy metal ions is unavoidable, their removal from water sources has been considered an obligation, as indicated by the increase in efforts of removal technology development. Ion-exchange, reverse osmosis, adsorption, complexation and precipitation are known methods and have been used for this purpose (6–8). Among these, the selective and quantitative separation of metal ions from aqueous solutions by chelating agent has been extensively investigated due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness (9–11). The selective adsorption of heavy metal ions by a chelating ligand depends on the macromolecular characteristics such as extent of crosslinking, the hydrophilic/hydrophobic balance of the macromolecular matrix, as well as the structure of the attached ligand function and the stability constants of the resulting polymer metal complex (12–14). The conventional chelating ligands suffer mainly from two shortcomings, namely; slow metal ion uptake and lack of selectivity towards a particular metal ion. Furthermore, desorption of metal ions and reusability of ligand are important criteria (11).

The present article describes the removal of heavy metal ions such as Cu(II), Cd(II) and Pb(II) under competitive and non-competitive conditions by modified crosslinked polyacrylamides (MCP) having different functional groups. The effect of pH on selective adsorption of metal ions, the adsorption rates and the effect of their swelling behavior on these rates and the regeneration properties of polymers were investigated.

Experimental

Materials and Instruments

Acrylamide (AAM) and N,N'-methylenebisacrylamide (NMBA) monomers and all of the other reagents used were "analytical grade". Linear polyacrylamide (LPAAM) had a viscosity average molecular weight of 2.3×10^6 (\bar{M}_v) (American Cyanamid). Crosslinked polyacrylamide (CPAAM) was prepared in our laboratory as described below. Technical grade NaOCl ~5.0% (w/w) was used for the Hofmann reaction. Bi-distilled water and distilled water were used for polymerization and modification reactions, respectively. $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, used for the preparation of the solutions in the adsorption studies, were Merck "analytical grade" reagents. Cu(II), Cd(II) and Pb(II) ions determinations were carried out by atomic absorption spectrometry, using a Varian Spectro AA 220-FS atomic absorption spectrometer.

Preparation of Modified Polyacrylamides

Free radical polymerization of AAM (50 g) and NMBA (0.5 g) in aqueous media was carried out with a $\text{K}_2\text{S}_2\text{O}_8$ (0.15 g) and KHSO_3 (0.15 g) initiator couple at 50°C, to give crosslinked polyacrylamide (CPAAM). The details of the preparation were given elsewhere (15). The polymer was purified by disintegrating the suspension in methanol by a blender, filtering, washing again by methanol and drying under vacuum. This cross-linked polyacrylamide in white powder form was used for the modification reactions.

Transamidation Reactions in Aqueous and Nonaqueous Media

Aminofunctionalized crosslinked polyacrylamides with ethylenediamine (EDA) and diethylenetetramine (DETA) were obtained by the transamidation reaction of CPAAM in aqueous media, as described previously (15). In brief, the transamidation reaction was carried out at 90°C for 9 h by adding EDA or DETA (36% (w/w) aqueous solution) to CPAAM previously swollen in water at a ratio(*r*) of 1 : 12 (*r* = the molar ratio of AAm units to amine compound). The resulting gels were suspended in methanol, disintegrated by a blender, filtered and washed with distilled water to remove unreacted amine compounds and then washed with methanol and dried under vacuum to give white fine powders. Transamidation reaction products obtained in aqueous media with EDA and DETA are named as TA1 and TA2, respectively.

Transamidation reaction products of LPAAM in nonaqueous media were obtained by the reaction of amine compounds (EDA, DETA), as described previously (15). A predetermined amount of amine compound (EDA or DETA) to provide *r* = 1 : 12 was loaded to a round-bottom flask and LPAAM was added while stirring. After reaction at 90°C for 9 h, the mixture was poured into methanol and filtered, then washed with methanol and dried under vacuum to give white or yellowish colored powders. Transamidation reaction products in nonaqueous media obtained with EDA and DETA are named as TN1 and TN2, respectively.

Hofmann Reaction

The Hofmann reaction products were obtained by the reaction of NaOCl/NaOH and CPAAM in the presence of amine compounds (EDA or DETA), as described previously (15). The amine compound (*r* = 1 : 12) was added to the CPAAM previously swollen in water and stirred for 30 min at 20°C and a NaOCl/NaOH solution (1 : 0.323 mole) which was prepared at 5°C was added to provide the molar ratio of AAm:NaOCl = 1 : 1. After the reaction was continued at 20°C for 2 h, the product was disintegrated in isopropyl alcohol in a blender, filtered and washed with distilled water. The gels were washed with isopropyl alcohol again and dried under vacuum to give white fine powders. The Hofmann reaction products prepared with EDA and DETA are named as H1 and H2, respectively.

Metal Ion Adsorption Studies

Non-competitive Adsorption. The polymers (50 mg) were added to the stirred solution (25 ml) at ambient temperature containing the single metal ion (0.01574 mol/l Cu(II), Cd(II) or Pb(II)) which was acidified to pH = 4.5 by HNO₃ to avoid the precipitation of Pb(II) ions (16). The change in the amount of residual metal ion in the solution was followed by atomic absorption spectrometry (AAS) up to 1 h. The amount of metal ions adsorbed, *Q*, (mmol/g) was calculated by the following equation:

$$Q = (C_0 - C)V/m,$$

where *C*₀ and *C* are the concentration of the metal ions in the initial solution and after adsorption, respectively (mmol/ml); *V* is the volume of the solution added (ml) and *m* is the amount of the polymer used (g).

Competitive Adsorption. The above mentioned procedure and conditions were applied, but the solution contained all three ions. A second set of experiments were run at pH = 3.0, as well as at pH = 4.5. The effect of preliminary swelling of polymer with water was followed by repeating the experiment at pH = 4.5 with swollen TN1 polymer.

Regeneration Studies. Two of the polymers (TN1 and TN2) after metal adsorption and filtration were stirred for 1 h at ambient temperature in 0.1 N HCl, and the amount of desorbed metals in solution was determined with atomic absorption spectrometry. The acid-treated polymers were neutralized with 0.1 N NaOH, washed with distilled water and were used for further adsorption experiments. The regeneration procedure was repeated for 3 cycles.

Results and Discussion

Properties of Modified Crosslinked Polyacrylamides (MCPs)

Crosslinked polyacrylamides can be prepared from their monomers with a different amount of crosslinking agents (12, 17, 18). CPAAM with a high equilibrium degree of swelling (3280%), in comparison with those reported previously (12, 18), was prepared by using a low amount of crosslinking NMBA, and by solution polymerization of the monomers in water. The MCPs obtained from this polymer by the above mentioned modification reactions had a high equilibrium degree of swelling (EDS) and amine values (AV), as seen from Table 1.

The details of characterization (FTIR and chemical analysis) of these MCPs were discussed in a previous paper (15). The polymers had different functional groups such as primary and secondary amine, secondary amide, carboxylate and unreacted amide groups depending on the applied modification reaction and the amine compound used. For example, the polymers had primary amide, primary amine and secondary amide groups when EDA was used in transamidation reaction in non-aqueous media. When the reaction was repeated with DETA, secondary amine groups were present in addition to these groups.

Table 1

The adsorption capacities (Q), amine values (AV) and equilibrium swelling degrees (EDS) of MCPs under noncompetitive conditions at pH = 4.5

Polymer	Q (mmol/g)			AV (mmol/g)	EDS (%)
	Cu(II)	Cd(II)	Pb(II)		
CPAAM	2.7×10^{-2}	1.1×10^{-2}	1.3×10^{-2}	—	3280
TA1	1.71	0.56	1.22	2.46	17900
TA2	1.45	0.47	0.70	2.19	8750
TN1	0.73	0.11	0.91	3.09	3950
TN2	0.71	0.22	0.42	3.22	2900
H1	1.71	0.81	0.50	1.86	18400
H2	1.56	0.12	0.28	1.33	11200

The amount of secondary amine groups increased with a corresponding decrease in primary amine groups due to the crosslinking reactions. In the case of transamidation reaction products obtained in aqueous media, the carboxylate groups were also present in addition to these functional groups, due to a simultaneous hydrolysis reaction (15).

Hofmann reaction products had bisubstituted urea, primary amine and secondary amide groups when EDA was used in the reaction. But, in contrast with the transamidation reaction products, $-NH$ groups of primary amide in acrylamide units did not disappear during the reaction. On the contrary, $-NH_2$ groups of bonded amine compounds were converted into secondary amide groups, so the amount of these groups in Hofmann products was higher than those of transamidation reaction products. When DETA was used, secondary amine groups were present in addition to these functional groups.

Metal Ion Adsorption Studies

Non-Competitive Conditions. Heavy metal ion adsorption capacities of MCPs in the single metal ion solutions were determined with a batch equilibrium technique at $pH = 4.5$, since lead hydroxide precipitates at $pH > 4.5$ at the employed concentration.

Unmodified crosslinked polyacrylamide has a very low metal ion adsorption capacity, as seen from Table 1. As expected, the MCPs were effective and the heavy metal ion adsorption capacities of polymers depended mainly upon their AV and EDS. TA2, TN1 and TN2 polymers indicate that EDS is the controlling parameter, since they show low metal adsorption capacity, despite their high AV. Also, the low pH may have contributed to lower adsorption capacities of these polymers (11). The Cu(II) ion adsorption capacities of all polymers (except for TN1) were higher than the other metal ions. The Cu(II) ions have a smaller size than the other ions, which facilitates diffusion into the polymer. On the other hand, Cd(II) ion adsorption capacities of polymers generally were lower than their Pb(II) ion adsorption capacities, although the Cd(II) ion is smaller than the Pb(II) ion. The effect of the functional group on selectivity is clearly observed for example for TN1, where the secondary amide groups in the polymer increased the Pb(II) ion adsorption capacity. The highest Cu(II) and Cd(II) ion adsorption capacities were observed for both TA1 and H1 polymer, respectively. The TA1 polymer also had the highest Pb(II) ion removal capacity among all the MCPs.

Competitive Conditions. The selectivity properties of a chelating agent are important in practice, such as preconcentration and recovery of heavy metal ions from wastes. Certainly, many factors such as the adsorption capacity, swelling ability, the functional groups in polymer, adsorption rate and pH of the feed metal ion solution can effect the employment of a polymeric ligand. To investigate their selectivity properties under competitive conditions, the MCPs were added to the ternary mixture of Cu(II), Cd(II) and Pb(II) ions at $pH = 4.5$ and 3.0 . The adsorption capacities of the polymers at different pH are given in Figures 1 and 2.

The percentages given on top of the bars in figures are selectivities calculated from the adsorption ratios.

In adsorption experiments, similar to non-competitive conditions, CPAAM had very low metal ion adsorption capacity (1.6×10^{-3} mmol/g) and has no practical use. But, all MCPs had high adsorption capacities and showed selectivity (Figure 1). For example, TA1 polymer modified with EDA adsorbed the Pb(II) ions rather than Cu(II) ions at $pH = 4.5$ (Cu(II) = 0.41 (mmol/g), Pb(II) = 1.12 (mmol/g)) in contrast with non-competitive conditions. This is due to the presence of secondary amide and carboxylate groups in polymer,

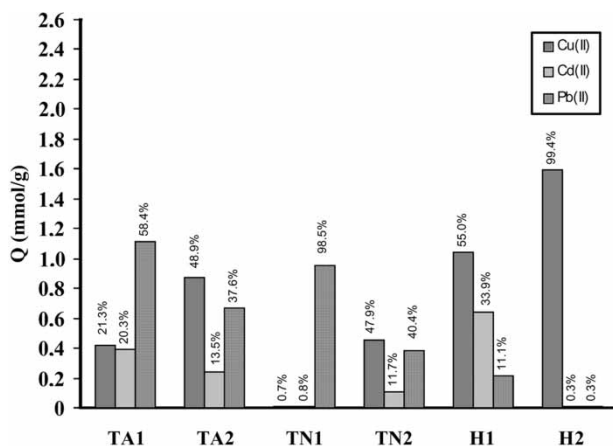


Figure 1. The adsorption capacities and selectivity (%) of MCPs under competitive conditions at pH = 4.5. (Total capacity: TA1 = 1.92, TA2 = 1.78, TN1 = 0.97, TN2 = 0.94, H1 = 1.89, H2 = 1.60 mmol/g).

which, coupled with the lack of secondary amine groups, induced the selectivity towards Pb(II) ions. At pH = 3.0, this tendency is stronger and the amount of adsorbed Pb(II) ion increased to 2.3 mmol/g with a selectivity of 79.6% (Figure 2.). The amount of Cu(II) ions adsorbed by all the polymers decreased at pH = 3.0 (15), probably since more sites for Pb(II) ion adsorption were free. Also, pH = 4.5 may be high enough for the beginning of shell formation of lead hydroxide complex, preventing further diffusion into the polymer matrix. In the case of the TA2 polymer, which was modified with DETA, an increase in Cu(II) ion capacity at pH = 4.5 is due to the presence of secondary amine

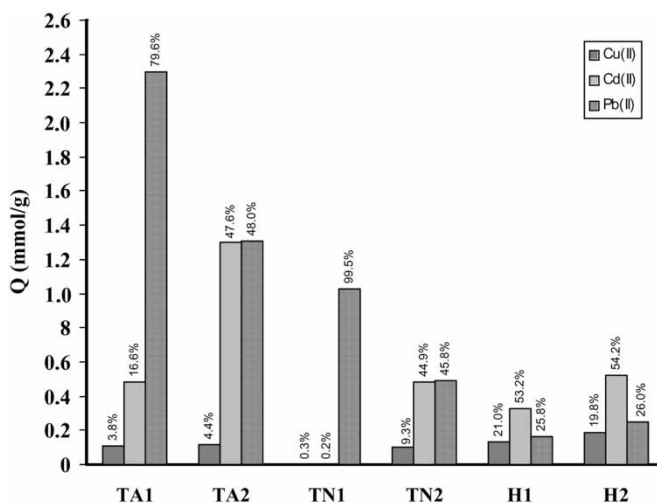


Figure 2. The adsorption capacities and selectivity (%) of MCPs under competitive conditions at pH = 3.0. (Total capacity: TA1 = 2.89, TA2 = 2.73, TN1 = 1.03, TN2 = 1.07, H1 = 0.62, H2 = 0.96 mmol/g).

groups in polymer (Cu(II) = 0.87 mmol/g, Pb(II) = 0.67 mmol/g), as seen from Figure 1. Also, at pH = 3.0, the Pb(II) ion adsorption capacity of TA2 polymer is higher as expected, but Cd(II) ions seems to be competing for the same sites.

For transamidation reaction products in nonaqueous media, a somewhat similar behavior was observed. The TN1 polymer, which was modified with EDA, showed the high selectivity towards Pb(II) ions (98.5%) at pH = 4.5, due to the secondary amide groups in its structure. It was observed that this selectivity was even slightly higher (99.5%) at pH = 3.0. Similar to TA2, TN2 showed higher selectivity towards Cu(II) ion at pH = 4.5, which was replaced with Cd(II) ion at pH = 3.0.

The H1 polymer which was modified with EDA had higher removal capacity for Cu(II) ion than Pb(II) ion, although it had secondary amide groups (Figure 1). Also, the selectivity towards Cd(II) ions was higher compared to the other modified polyacrylamides, which may be due to the presence of bisubstituted urea groups (15) in the polymer. The H2 polymer, which is modified with DETA, was very selective to Cu(II) ions (99.4%) (Figure 1). It is quite probable that the secondary amine groups of DETA molecules, in addition to bisubstituted urea groups, induced this selectivity. The decrease in the total metal ion adsorption capacity at low pH for both H1 and H2 resulted from the significant decrease of adsorption of Cu(II) ions. It may be concluded that secondary amine groups were selective for Cu(II) ions, but secondary amide groups were effective for adsorption of Pb(II) ions. The carboxylate groups contributed to the Pb(II) ion adsorption, but under non-competitive conditions, they were also effective for Cu(II) ion adsorption.

Adsorption Rate

The adsorption rate of metal ions is quite effective on the selectivity properties of the polymeric agent and for practical use. For example, adsorption must be fast when the chelating agent is used as a filtering agent with a short period of contact with wastewater. Previously prepared various polymeric sorbents have adsorbed different metal ions from aqueous solutions with different adsorption rates. Latha et al. (18) studied ethylenediamine functionalized polyacrylamide resin for extraction for several metal ions such as Fe(III), Fe(II), Cu(II) and Ni(II) and they reported that complex forming proceeds very slowly (equilibrium time 5 h). B. Mathew and V. N. R. Pillai (12) studied the removal of different metal ions such as Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions by ethylenediamine functionalized divinylbenzene crosslinked polyacrylamides and reported that the equilibrium time of adsorption was approximately 2 h. Godjevargova et al. (19) studied adsorption of Pb(II) and Cu(II) ions on modified polyacrylonitrile bead and reported that adsorption proceeding occurs in 30 min. B. George (11) reported that the adsorption times of Co(II), Ni(II), Cu(II) and Zn(II) by glycine functionalized divinyl benzene- and NMBA-crosslinked polyacrylamides were 90 min and W. S. Wan Ngah et al. (20) studied the removal of Cu(II) ions from aqueous solution onto crosslinked chitosan beads and they found that the adsorption period changed between 60–90 min.

Similarly, to investigate this property of our polymers, MCPs were added to ternary metal ion solutions at different pH values (3.0 and 4.5) and the amounts of adsorbed metal ions were determined with time intervals. The results of TN1 polymer at pH = 4.5 are given in Figure 3. It was observed that the adsorption was very fast and the largest fraction of the adsorbed metal ion was attached to the polymer within 5 min. After this period, further adsorption was slow and a saturation level was reached for all metal ions within 20 min. This high initial rate suggests that the adsorption occurs mainly on the polymer surface, although a mechanism of intrapore diffusion was also involved in

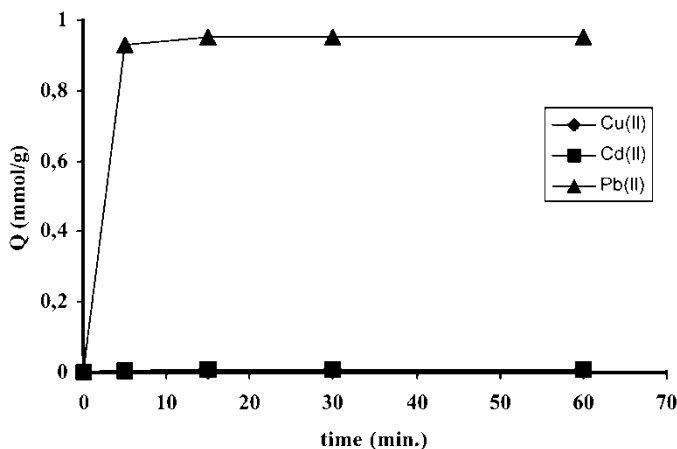


Figure 3. The adsorption rates of heavy metal ions by TN1 polymer (total metal ion ads. cap. = 0.97 mmol/g).

the adsorption, as represented by the slower adsorption rate (17) of the second stage. For the observation effect of preliminary swelling, TN1 polymer was swollen in water and added to the ternary mixture of metal ion solutions. The results given in Figure 4 show that the adsorption is again very fast and the total metal adsorption capacity is higher (1.11 mmol/g). This indicates that the intrapore diffusion was effective and smaller metal ions (Cu(II) and Cd(II)) diffuse better into the polymer matrix compared with the unswollen one. Thus, these results show that the obtained adsorption rates for removal of Cu(II), Cd(II) and Pb(II) ions are very fast compared to above mentioned applications of polymer sorbents under competitive or non-competitive conditions.

Desorption and Regeneration Studies

For practical use, the metal ion adsorbed by a polymeric agent must be desorbed easily and the agent must be used again repeatedly after regeneration. Desorption and regeneration properties of two MCPs were investigated with a batch experimental technique under

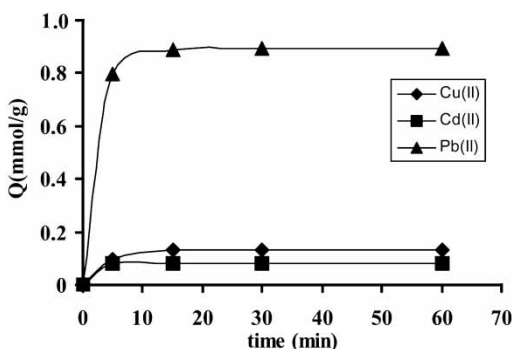


Figure 4. The adsorption rates of heavy metal ions by previously swollen TN1 polymer (total metal ion ads. cap. = 1.11 mmol/g).

Table 2
Heavy metal ions adsorption/desorption of TN1 and TN2 polymers

Cycle ^a	TN1								TN2							
	Adsorbed metal ion (mmol/g)				Desorbed metal ion (mmol/g)				Adsorbed metal ion (mmol/g)				Desorbed metal ion (mmol/g)			
	Cu(II)	Cd(II)	Pb(II)	Total	Cu(II)	Cd(II)	Pb(II)	Total	Cu(II)	Cd(II)	Pb(II)	Total	Cu(II)	Cd(II)	Pb(II)	Total
1 ^b	0.007	0.009	0.95	0.97	0.007	0.008	0.93	0.95	0.45	0.11	0.38	0.94	0.44	0.10	0.37	0.91
2	0.62	0.71	1.78	3.11	0.61	0.68	1.77	3.06	1.86	0.64	0.76	3.26	1.85	0.63	0.75	3.23
3	0.63	0.69	1.76	3.08	0.62	0.67	1.75	3.04	1.85	0.62	0.75	3.22	1.83	0.62	0.74	3.19

^aSee text for regeneration cycle.

^bAdsorption was carried out before regeneration for this cycle.

the competitive conditions mentioned above. The regeneration applications were repeated for three cycles followed by metal ion adsorption capacity determinations. No loss of capacity was observed in any of the polymers after regeneration and the adsorbed metal ions were desorbed easily. Adsorption/desorption properties of TN1 and TN2 are given in Table 2. An interesting fact is the increase in total capacity after the initial regeneration (TN1 = 3.11 mmol/g, TN2 = 3.26 mmol/g). Although such behavior was not reported previously in the literature, and a reasonable explanation would be the acid/alkaline regeneration cycle provided an ionization, which expanded the polymer matrix. The metal ion adsorption rates and selectivity properties of TN1 and TN2, after the first regeneration cycle, are given in Figures 5 and 6, respectively. It is interesting that the selectivity properties of these polymers changed. The Pb(II) ion selectivity of TN1 and TN2 was 98.5% and 40.4% at pH = 4.5, respectively (Figure 1). But, after regeneration, these selectivities towards Pb(II) ions decreased (TN1 = 57.2% and TN2 = 23.2%) and the Cu(II) ion selectivity increased (TN1 = 19.9% and TN2 = 57.1%) as seen from Figures 5 and 6. Thus, the diffusion of smaller molecules, such as Cu(II), into the expanded polymer matrix increased after regeneration. This was also confirmed by the increase of total metal ion adsorption capacities and the slight decrease in Pb(II) adsorption rate.

Conclusion

MCPs obtained from transamidation reaction in aqueous and nonaqueous media and Hofmann reaction were investigated for removal of Cu(II), Cd(II) and Pb(II) ions from aqueous solutions under competitive and non-competitive conditions. Under non-competitive conditions, polymers showed different adsorption capacities towards metal ions depending on the type and amount of their functional groups and swelling degrees. The MCPs tended to adsorb the Cu(II) ions more than the others. Depending on their functional groups and pH, under competitive adsorption conditions, changes in the selectivity properties of the polymers, were observed. The transamidation products prepared with EDA were distinctly selective towards Pb(II) ions and the Hofmann products, especially modified with DETA, were highly selective towards Cu(II) ions. Also, the selectivity

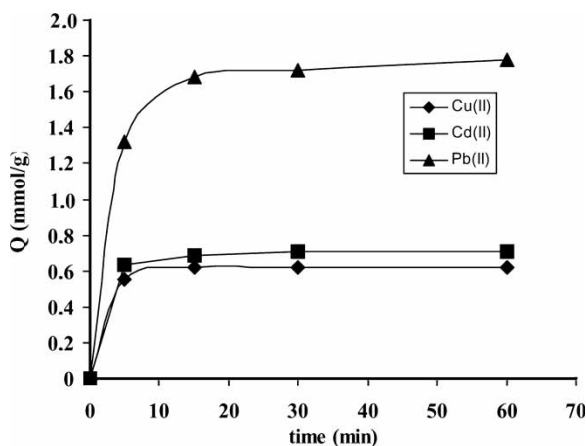


Figure 5. The adsorption rates of heavy metal ions by TN1 polymer after the first regeneration cycle (total metal ion ads. cap. = 3.11 mmol/g).

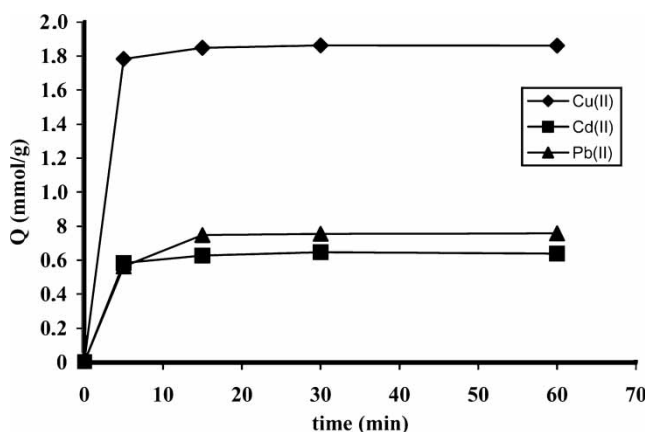


Figure 6. The adsorption rates of heavy metal ions by TN2 polymer after the first regeneration cycle (total metal ion ads. cap. = 3.26 mmol/g).

towards Pb(II) ion at pH = 3.0 increased for all polymers, while Cu(II) ion selectivity decreased for transamidation reaction products. The adsorption rates of polymers were very fast (<10 min) and preliminary swelling was effective on the increase of diffusion of small molecules into polymer and increase of adsorption capacities. The application of regeneration cycles to MCPs indicated that they could be used repeatedly without loss in capacity. After the regeneration cycle, TN1 and TN2 polymers adsorption capacities increased and their selectivity towards metal ions changed.

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