Competitive Removal of Heavy Metal Ions by Cellulose Graft Copolymers

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ABSTRACT: The effect of composition of graft chains of four types cellulose graft copolymers on the competitive removal of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions from aqueous solution was investigated. The copolymers used were (1) cellulose-g-polyacrylic acid (cellulose-g-pAA) with grafting percentages of 7, 18, and 30%; (2) cellulose-g-p(AA–NMBA) prepared by grafting of AA onto cellulose in the presence of crosslinking agent of N,N'-methylene bisacrylamide (NMBA); (3) cellulose-g-p(AA–AASO$_3$H) prepared by grafting of a monomer mixture of acrylic acid (AA) and 2-acrylamido-2-methyl propane sulphonic acid (AASO$_3$H) containing 10% (in mole) AASO$_3$H; and (4) cellulose-g-pAASO$_3$H obtained by grafting of AASO$_3$H onto cellulose. The concentrations of ions which were kept constant at 4 mmol/L in an aqueous solution of pH 4.5 were equal. Metal ion removal capacities and removal percentages of the copolymers was determined. Metal ion removal capacity of cellulose-g-pAA did not change with the increase in grafting percentages of the copolymer and determined to be 0.27 mmol metal ion/ $g_{copolymer}$. Although the metal removal rate of cellulose-g-p(AA–NMBA) copolymer was lower than that of cellulose-g-pAA, removal capacities of both copolymers were the same which was equal to 0.24 mmol metal ion/$g_{copolymer}$. Cellulose did not remove any ion under the same conditions. In addition, cellulose-g-pAASO$_3$H removed practically no ion from the aqueous solution (0.02 mmol metal ion/$g_{copolymer}$). The presence of AASO$_3$H in the graft chains of cellulose-g-p(AA–AASO$_3$H) created a synergistic effect with respect to metal removal and led to a slight increase in metal ion adsorption capability in comparison to that of cellulose-g-pAA. All types of cellulose copolymers were found to be selective for the removal of Pb^{2+} over Cu^{2+} and Cd^{2+}. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2034–2039, 2003

Key words: cellulose; graft copolymers; adsorption; functionalization of polymers; metal removal

INTRODUCTION

Cellulose is cheap, renewable, biodegradable, and the most abundant organic raw material in the world. It is modified by graft copolymerization of vinyl monomers. Depending on the chemical structure of the monomer grafted onto cellulose, graft copolymers gain new properties such as hydrophilic or hydrophobic character, improved elasticity, absorption of basic dyes,[1] water absorption,[2] ion-exchange capability,[3–4] and heat resistance.[5–8] During recent years, removal of heavy metal ions, both from waste water and natural waters, has gained importance to solve and minimize the industrial and ecological waste problems. Cellulose graft copolymers having ion-exchange property find applications for removal of heavy metal ions from aqueous solutions.[9–16] Similarly, natural polymers like vinyl grafted starch and chitin copolymers are also used in the removal of metal ions.[17–24]

Waly et al.[9] compared the capabilities of dye and heavy metal removal of three types cellulose copolymers based ion exchangers prepared by grafting of (1) glycidyl methacrylate (GMA), followed by aminization with ethylene diamine; (2) dimethyl aminoethyl methacrylate (DMAEMA), followed by quaternization; and (3) acrylic acid (AA) onto cotton fabric. Among the copolymers, pAA–cotton copolymer was the most active one with respect to removal of heavy metal ions, i.e., Co^{2+} and Cu^{2+} ions and was very effective for removal of the basic dye. Beker et al.[10] reported a promising ion exchanger resin for noncompetitive removal of metal ions, prepared by esterification of hydroxyethyl cellulose with phthalyl chloride. Bıçak et al.[11] have grafted acrylamide onto cotton cellulose and showed that the graft copolymer was a very efficient selective sorbent for removal of Hg^{2+} ions from aqueous solutions. Okieimen[12] used cellulose-g-pAA copolymers as the sorbent for single removal of Cd^{2+} and Cu^{2+} ions from aqueous solutions and reported a maximum metal ion binding capacity of 14 mg of Cd^{2+}/g for the cellulose-g-pAA with 12.3% pAA grafts. In the study of adsorption of Cu^{2+} ions on polystyrene-, poly(styrene-co-acrylonitrile)-, poly(styrene-co-methacrylic acid)-grafted cellulose, Chauhan[13] observed that graft copolymers synthesized by

gamma irradiation initiation adsorbed three times more than graft copolymers obtained by using the persulphate redox initiator. Although the grafting of vinyl monomers improved the metal ion sorption behavior of cellulose, there was no correlation between the grafting percentages and Cu^{2+} ion retention capacities of the copolymers. Gerente et al.[25] investigated the sorption mechanism of Cu^{2+}, Ni^{2+}, and Pb^{2+} ions on sugarbeet pulp and reported that the fixation percentages of Pb^{2+} and Cu^{2+} ions by ion exchange mechanism are 75 and 95, respectively. The rest of these ions were removed by adsorption. Adsorption of Ni^{2+} ion onto sugarbeet pulp occurred only by ion exchange.

Studies of heavy metal ion removal reported in the literature can be classified into two groups: competitive adsorption and noncompetitive or single adsorption. In the first method, the solution made to come into contact with adsorbent contains all the ions to be removed and all the metal ions are adsorbed simultaneously with varying degrees of success depending on their affinities for the functional groups of the adsorbent. Noncompetitive adsorption is used to describe the behavior of metal ion removal from aqueous solution containing only one type of metal. The amount of metal removed by noncompetitive adsorption is about twice of that can be achieved by competitive adsorption.[26] Khalil and Farag[23] observed different adsorption values in the treatment of poly(acrylamide)-g-starch copolymer with the solutions of copper acetate, chloride, or sulphate. This was due to dependence of adsorption of any metal ion on the gegen ion. Thus, all metal salts used in the present study were metal acetate.

The aim of this work was to investigate the effects of composition of graft chains of cellulose graft copolymers on competitive removal of heavy metal ions, i.e., Pb^{2+}, Cu^{2+}, and Cd^{2+}. Competitive metal ion removal was aimed by cellulose graft copolymers because both the natural and waste water rarely contain a single metal, in contrast, a mixture of these heavy metal salts.

EXPERIMENTAL

Materials

N,N'-methylene bisacrylamide (NMBA), 2-acrylamido 2-methylpropane sulphonic acid ($AASO_3H$), ceric ammonium nitrate (CAN), nitric acid, dioxane, acetone (Merck, Darmstadt, Germany), and cellulose (Sigma, St. Louis, MO) were used as received. AA monomer was distilled under vacuum and stored at $-8°C$ until it was used. Bidistilled and vacuum-degassed water was employed in copolymerization reactions. Nitrogen was purified by passing it through a freshly prepared alkaline pyrogallol solution.

The functional group contents of four main types of cellulose graft copolymers employed for the removal of heavy metal ions from the aqueous solution, which were prepared in our previous work,[27] and grafting conditions were given in detail in Table I. These copolymers are:

Cellulose-g-pAA copolymers containing various amounts of –COOH groups (0.6–3.4 mmol –COOH group/$g_{copolymer}$) due to varying grafting percentages of AA onto cellulose.

Cellulose-g-p(AA–NMBA) copolymer prepared by grafting of AA onto cellulose in the presence of crosslinking agent of NMBA, contains 3.8 mmol –COOH group per gram of copolymer.

Cellulose-g-pAASO₃H copolymer with –SO₃H group contents of 0.53 mmol/$g_{copolymer}$ which

TABLE I
Functional Group Contents of Cellulose Graft Copolymers[a]

Cellulose copolymer	Grafting percentage (%)	Functional group content (mmol/$g_{copolymer}$)		
		—COOH	—SO₃H	—COOH+—SO₃H
Cellulose-g-pAA	7	0.9		
Cellulose-g-pAA	18	2.1		
Cellulose-g-pAA	30	3.2		
Grafting conditions: AA : 0.85M; CAN/HNO₃: 4×10^{-3} M/2.5 $\times 10^{-3}M$; 30°C; 3 h.				
Cellulose-g-pAA		3.4		
Cellulose-g-p(AA–NMBA)		3.8		
Grafting conditions: AA: 0.85M/(AA+NMBA): 0.85M containing 0.05 mol % NMBA of AA; CAN/HNO₃: $2 \times 10^{-3}M$/17.5 $\times 10^{-3}M$;5°C; 5.5 h.				
Cellulose-g-pAA	4.5	0.6		
Cellulose-g-pAASO₃H	5		0.53	
Cellulose-g-p(AA–AASO₃H)	0.71[b]			0.71
Grafting conditions: AA: 0.85M/AASO₃H: 0.85M/(AA+AASO₃H): 0.85M containing 10 mol % of AASO₃H, CAN/HNO₃: 4×10^{-3} M/7.5 $\times 10^{-3}M$; 30°C, 3 h.				

[a] Copolymers were prepared in our previous work.[27]
[b] GP value of cellulose-g-p (AA-AASO₃H) copolymer was given in mmol/$g_{copolymer}$ since the sum of —SO₃ and —COOH groups can be determined by titration method.

was prepared by the grafting of AASO₃H onto cellulose.

Cellulose-g-p(AA–AASO₃H) copolymer prepared by the grafting of the mixture of AA and AASO₃H containing 10 mol % AASO₃H onto cellulose contains functional groups of –SO₃H and –COOH and the sum of these groups is 0.71 mmol/g of copolymer.

Copper acetate, lead acetate, and cadmium acetate were of high purity chemicals (Merck). Distilled water was used to prepare the metal ion solution for the removal experiments.

Preparation of cellulose graft copolymers

Since the grafting procedure of AA, AASO₃H, and NMBA monomers onto cellulose was described in detail in our previous work,[27] it will only be summarized below.

Four grams of cellulose was dispersed in 320 mL of $2.5 \times 10^{-3}M$ HNO₃ solution in a three necked flask, kept in a constant-temperature water-bath at 30°C (or 5°C) for the grafting of AA onto cellulose in the presence of crosslinking agent of NMBA to obtain cellulose-g-p(AA–NMBA) copolymer. In order to remove the dissolved oxygen, nitrogen purging was carried out for 30 min under continuous and constant stirring. Then, CAN (initiator) and monomer(s) (AA; AA + AASO₃H; or AA + NMBA) were added into the reaction mixture depending on the copolymer aimed to prepare, respectively. The grafting reaction was carried out in an N₂ atmosphere. After the desired reaction time, the grafting reaction was stopped by addition of hydroquinone. The graft copolymer and homopolymer mixture was separated from the reaction medium by acetone addition. The mixture was filtered and precipitated product was washed with acetone, then dried. Dried homopolymer and graft copolymer mixture was subjected to extraction with dioxane in a Soxhlet apparatus for 40 h to remove the homopolymer.

Grafting percentage (GP) determination[28]

The grafting percentages of copolymers were determined by a titration method based on the neutralization of carboxyl groups of pAA graft chains in the copolymer. The graft copolymer in a 0.1N NaBr solution was titrated with a solution of 0.1N NaOH in the presence of phenolphthalein indicator and GP was calculated from the following equation:

$$GP(\%) = \frac{\text{weight of grafted polymer (g)}}{\text{weight of cellulose (g)}} \times 100$$

Removal of metal ions

Stock solution containing Cd^{2+}, Cu^{2+}, and Pb^{2+} ions all together was prepared by dissolving metal acetate salts in distilled water. The concentration of each ion was equal at 4 mmol/L. pH of stock solution was adjusted to 4.5 by using diluted HNO₃ solution. Cellulose graft copolymer (0.5 g) was added in a given amount of stock solution (50 mL) and the mixture was stirred by a magnetic stirrer. The amount of residual metal ions in the aliquots of withdrawn solution was followed by atomic absorption spectrophotometer (Varian Spectro AA 220-FS) up to 5 h. The amount of metal ion removed per gram of copolymer was determined by taking the difference between initial and final concentrations of ion in the solution.

Removal percentage for each ion based on its initial concentration was calculated according to following equation.

$$\text{Removal percentage (\%)} = \frac{C_i - C_f}{C_i} \times 100$$

where C_i is the initial concentrations of Pb^{2+}, Cu^{2+}, or Cd^{2+} ions in the solution (mmol metal ion/L); and C_f is the concentrations of Pb^{2+}, Cu^{2+}, or Cd^{2+} ions in the solution after adsorption (mmol metal ion/L).

Metal ion removal capacities of the copolymers were calculated according to equation below:

$$\text{Removal capacity (mmol/g}_{\text{copolymer}}) = \frac{\sum(C_i - C_f)}{m_{\text{copolymer}}}$$

where $\Sigma(C_i - C_f)$ is the sum of differences between initial and final concentrations of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions and $m_{\text{copolymer}}$ is the weight of copolymer.

Used cellulose-g-pAA copolymer was regenerated with 1M HCl for 2 h and, then it was reemployed in metal ion removal.
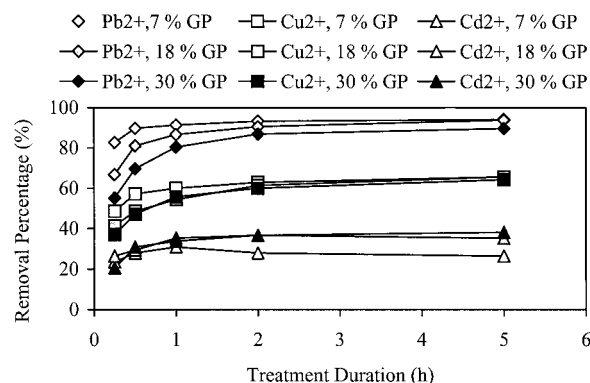

Figure 1 Competitive removal of heavy metal ions by cellulose-g-pAA copolymers with different grafting percentages at different durations.
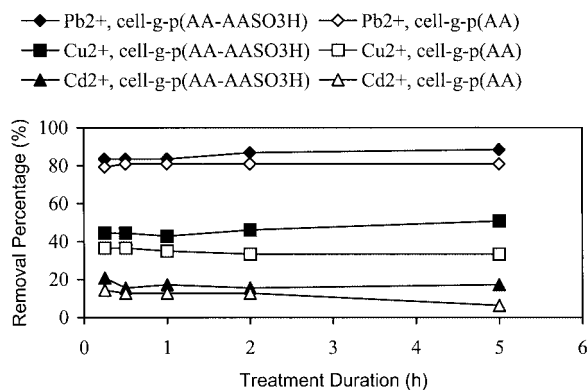
Figure 2 Competitive removal of heavy metal ions by cellulose-g-pAA and cellulose-g-p(AA–AASO$_3$H) copolymers at different durations.

RESULTS AND DISCUSSION

Grafting percentages and functional group contents of cellulose graft copolymers employed in the competitive removal of heavy metal ions in this work are presented in Table I.

Depending on the structure of adsorbent, metal ion uptake can be obtained by several mechanisms such as physical adsorption, ion exchange, and chelation with the functional groups at the surface of adsorbent. In case of cellulose-g-pAA copolymer, carboxyl groups of pAA introduced to cellulose by grafting are mainly responsible for the heavy metal removal. No metal removal was observed on the original (ungrafted) cellulose. The variations of removal percentages of metal ions on cellulose-g-pAA copolymers having different grafting percentages are illustrated in Figure 1. As it can be seen from the data in Figure 1, the removal

percentages of each ion did not increase with the increase of pAA grafting and carboxyl group contents of cellulose copolymer.

This result is surprising but in agreement with those obtained by Chauhan et al.[13] and Okieimen.[12] The increase of carboxyl group contents of copolymer, which can be attributed to the increase in pAA grafts, decreased the adsorption rates of the ions. It can be speculated that dense but short chain grafts or isolated but long chain grafts of the copolymer would make the ion sorption of the copolymer more difficult. But the removal capacity values of the cellulose-g-pAA copolymers with the different –COOH group contents are the same. This behavior is in good agreement with the finding of selective adsorption.[29] All the three copolymers containing different amounts of –COOH groups removed Pb^{2+} ion the most preferentially, followed by Cu^{2+} and Cd^{2+} ions. In case of Pb^{2+} ion removal, namely, the ion of the metal with higher atomic number is removed preferentially compared to those with the same valences but lower atomic number. However, this assumption is not valid for Cu^{2+} and Cd^{2+} ions removal, otherwise the reverse order of adsorption preference should have been seen.

A comparison of the adsorption percentages of each ions based on initial ion concentrations of the cellulose-g-pAA and cellulose-g-p(AA–AASO$_3$H) copolymers is shown in both Figure 2 and Table II. Both initial and equilibrium ion removal percentages of cellulose-g-p(AA–AASO$_3$H) copolymer are higher than those of cellulose-g-pAA copolymer. Although cellulose-g-pAASO$_3$H copolymer practically did not remove any ion (Table I), the presence of AASO$_3$H in the monomer mixture of AA and AASO$_3$H during

TABLE II
Competitive Heavy Metal Ion Removal Values by Cellulose Graft Copolymers

Cellulose copolymer	Treatment duration (h)	Removal percentage (%)			Removal capacity (mmol/g$_{copolymer}$)
		Pb^{2+}	Cu^{2+}	Cd^{2+}	
Cellulose-g-pAA	0.25	82.6	48.6	23.5	0.21
(GP = 7%)	5	94.2	65.7	26.5	0.26
Cellulose-g-pAA	0.25	66.7	41.4	26.5	0.19
(GP = 18%)	5	93.9	65.7	35.3	0.27
Cellulose-g-pAA	0.25	55.1	37.1	20.6	0.16
(GP = 30%)	5	89.6	64.3	38.3	0.27
Cellulose-g-pAA	0.25	87.9	61.9	34.9	0.23
(GP = 32.5%)	5	84.8	63.5	34.9	0.23
Cellulose-g-p(AA–NMBA)	0.25	23.0	27.0	20.7	0.09
(GP = 37.7%)	5	90.2	66.7	39.7	0.24
Cellulose-g-pAA	0.25	79.4	36.5	14.3	0.16
(GP = 4.5%)	5	81.0	33.3	6.3	0.16
Cellulose-g-pAASO$_3$H	0.25	6.3	7.9	7.9	0.03
(GP = 5%)	5	0	7.9	4.8	0.02
Cellulose-g-p(AA–AASO$_3$H)	0.25	83.6	44.5	20.7	0.18
Graft value: 0.71 mmol/g$_{copolymer}$	5	88.5	50.8	17.2	0.19
Regenerated cellulose-g-pAA	0.25	78.9	47.8	17.5	0.24
(GP = 32.5%)	5	91.8	66.7	25.4	0.29

grafting onto cellulose imparted the property of higher removal capability to the graft products.

The metal ion removal rate of cellulose-g-p(AA–NMBA) prepared in the presence of crosslinking agent (NMBA) during grafting of AA onto cellulose is lower than that of cellulose-g-pAA obtained without crosslinking agent (Fig. 3 and Table II). But after 5 h-contact time of graft copolymer with aqueous solution of metal salts, both copolymer samples adsorbed nearly the same amount of metal ions. The slow removal rates of cellulose-g-p(AA–NMBA) copolymers results from the crosslinked structure of the copolymer making the carboxyl functional groups to be hardly accessible by the metal ions. Thus, while the cellulose-g-pAA copolymer is selective for bulky Pb^{2+} ion after 0.25 h contact time of copolymer with aqueous metal salts solution, this selectivity became apparent for cellulose-g-p(AA–NMBA) only after 5 h-treatment duration.

However, the regeneration of cellulose-g-pAA copolymer with $1N$ HCl led to decrease in removal rates of metal ions, a slight increase was observed in the removal capacity values (Table II, Fig. 4). While the equilibrium Pb^{2+} ion removal percentages of the copolymer decreased from 34.9 to 25.4%, Cu^{2+} ion removal percentages remained the same even after regeneration step.

CONCLUSIONS

Although the metal ion removal rate of the cellulose-g-pAA copolymers decreased with the increase in grafting percentages of the copolymers, enhancement in the removal percentages of metal ions was observed to be proportional to the duration of treatment applied to the copolymer using aqueous solution of metal salts and reached to the same values for the copolymers with low and high graft levels.
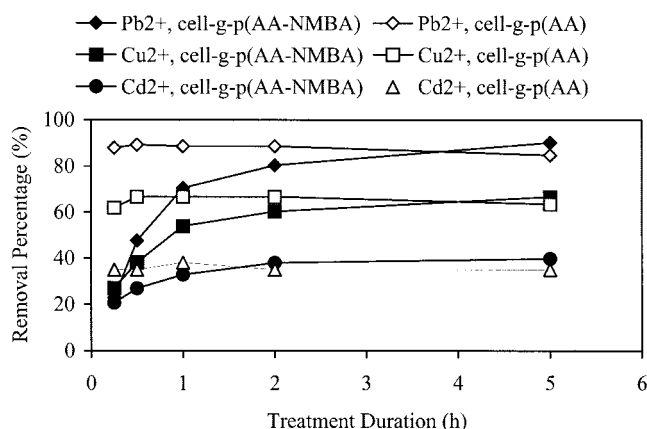

Figure 3 Competitive removal of heavy metal ions by cellulose-g-pAA and cellulose-g-p(AA–NMBA) copolymers at different durations.
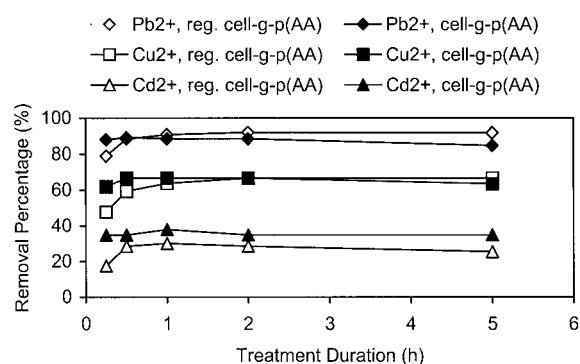

Figure 4 Comparison of competitive removal of heavy metal ions by cellulose-g-pAA and regenerated cellulose-g-pAA copolymers at different durations.

The presence of $AASO_3H$ in the p(AA–AASO$_3$H) graft chains of the copolymer created a synergistic effect for the removal of metal ions, although pAASO$_3$H-grafted cellulose removed practically no ion. The removal percentages of cellulose-g-p(AA–AASO$_3$H) copolymer were 20% higher than those of cellulose-g-pAA.

The use of a crosslinking agent of NMBA during grafting of AA onto cellulose decreased the removal rate of metal ions, since carboxyl groups of pAA grafts (possibly) hardly interacted with metal ions due to crosslinked structure of graft chains. Removal capacities of both copolymers became equal after 5 h-treatment of the copolymer with aqueous solution of metal ions.

The results obtained in this work suggest a strong interaction between Pb^{2+} ion and carboxyl groups of the graft chains of the cellulose copolymers. Removal order of the metal ions investigated over all copolymer types was the same and it followed this order: $Pb^{2+} > Cu^{2+} > Cd^{2+}$.

After the regeneration with $1N$ HCl solution, no change was observed in the removal capacity of cellulose-g-pAA, although the removal rate of metal ions decreased slightly.

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