

Preparation of Aminoalkyl Celluloses and Their Adsorption and Desorption of Heavy Metal Ions

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SYNOPSIS

Aminoalkyl celluloses (AmACs) were prepared from 6-chlorodeoxycellulose and aliphatic diamines $H_2N(CH_2)_mNH_2$ ($m = 2, 4, 6, 8$). Their adsorption and desorption of divalent heavy metal ions such as Cu^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} and their mixtures were also investigated in detail.

Adsorption of metal ions on AmACs was remarkably affected by the pH of the solution, the metal ion and its initial concentration, and also the number of methylene units in the diamines. No adsorption of metal ions occurred on AmACs in strongly acidic solutions. However, metal ions were adsorbed rapidly on AmACs from weakly acidic solutions and the amount of adsorption increased with increasing pH. The effectiveness of AmACs as adsorbents decreased with increasing length of the methylene moiety, and AmAC from ethylenediamine ($m = 2$) was most effective. The adsorption of metal ions on AmACs was in the order $Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$. Accordingly, their behavior followed the Irving-Williams series and Cu^{2+} ions were preferentially adsorbed from solutions containing metal ion mixtures. The adsorbed ions were easily desorbed from the AmACs by stirring in 0.1 M HCl.

INTRODUCTION

Cellulose is most abundant among renewable natural polymers and has three reactive hydroxyl groups in every constituent anhydroglucose unit. Therefore, cellulose is a very promising raw material for the preparation of various functional polymers.

Chlorodeoxycellulose (CDC) has wide applications as an intermediate for various cellulose derivatives. Tashiro and Shimura¹ have synthesized several sulfur- and nitrogen-containing cellulose derivatives by the reactions of CDC with various nucleophilic reagents. They have also examined the ability of these cellulose derivatives to adsorb mercuric ions in aqueous solutions.

In this article, a series of aminoalkyl celluloses (AmACs) were prepared from 6-chlorodeoxycellulose (6-CDC) using ethylenediamine, tetramethylenediamine, hexamethylenediamine, and octame-

thylenediamine as diamines, and their adsorption and desorption behavior was examined in detail for various transition metal ions from aqueous solutions.

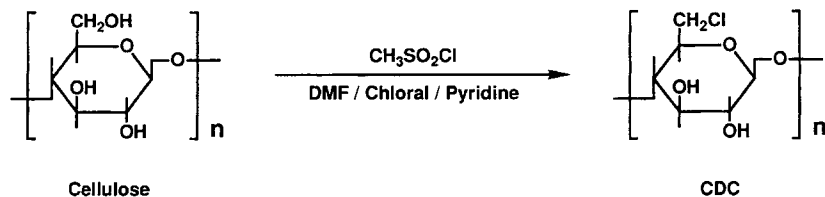
EXPERIMENTAL

Materials

Bleached sulfite pulp was used as cellulose material. Reagent grade anhydrous chloral, diamines, and methanesulfonyl chloride were used as purchased. Dimethylformamide (DMF), pyridine, and other aprotic solvents were purified by conventional methods.

Preparation of 6-CDC

Chlorination of cellulose with methanesulfonyl chloride was performed in a homogeneous system using a mixture of chloral and DMF, which was re-



Scheme I

ported to be a solvent for cellulose (Scheme I).² Ten grams of sulfite pulp were pretreated by the water activation-solvent exchange method using DMF as solvent. Activated cellulose was dispersed in 260 mL of DMF with stirring. To the solution were added 120 mL of chloral and then 110 mL of pyridine, which accelerates the rate of dissolution of cellulose.³ The mixture was stirred for 2 h at room temperature to give a yellow viscous solution, which was diluted with 500 mL of DMF. While the temperature of the solution was raised and maintained at a predetermined temperature, 100 mL of methanesulfonyl chloride was added to the solution over the course of 1 h. After the addition was complete, stirring was further continued for 4 h at that temperature. Then the solution was cooled to room temperature and poured into a large volume of MeOH/water mixture (1 : 1 by volume) with vigorous agitation. The precipitate was filtered, washed with MeOH, and treated with a 5 L of 5% aqueous sodium carbonate solution. The product was again washed thoroughly with water and MeOH and then dried. The degree of substitution (DS) was obtained from the chlorine content as determined by the micro combustion method.⁴

Preparation of AmAC

AmAC was prepared by the modification of Vigo's method⁵ for the reaction of cellulose with aliphatic monoamines (Scheme II). A mixture of 0.1 g of 6-CDC, 10 mL of solvent and prescribed amount of diamines was stirred at predetermined temperature. After the completion of reaction, the homogeneous solution was dropped into 500 mL of a MeOH/acetone mixture (1 : 1 by volume) with agitation and

the precipitate was filtered, washed with a MeOH/acetone mixture (1 : 1 by volume), and dried. The nitrogen content of the products was determined with a Perkin-Elmer 240C Elemental Analyzer. The DS was calculated from the nitrogen and chlorine contents.

Adsorption of Metal Ions

Aqueous solutions containing prescribed concentrations of metal ions were prepared from metal chlorides such as manganese(II) chloride, cobalt(II) chloride, nickel(II) chloride, and copper(II) chloride. The pH of the solutions was adjusted with Clark-Lubs' buffer solutions.⁶ AmAC powder (0.1 g) was put into a glass bottle containing 50 mL of the metal chloride solution. The mixture was gently stirred for a predetermined time, the adsorbent was filtered off, and the amount of metal ions remaining in an aliquot of the filtrate was determined by atomic absorption analysis.

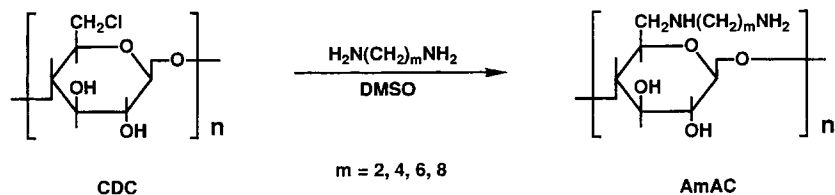
Desorption of Metal Ions

AmAC (0.1 g) with adsorbed metal ions was stirred in 10 mL of 0.1 M hydrochloric acid for 2 h at room temperature and then filtered. The metal ions in the filtrate were determined by atomic absorption analysis.

RESULTS AND DISCUSSION

6-Chlorodeoxycellulose

The chlorine content increased abruptly at the initial stage of reaction, which occurred within 1 h both



Scheme II

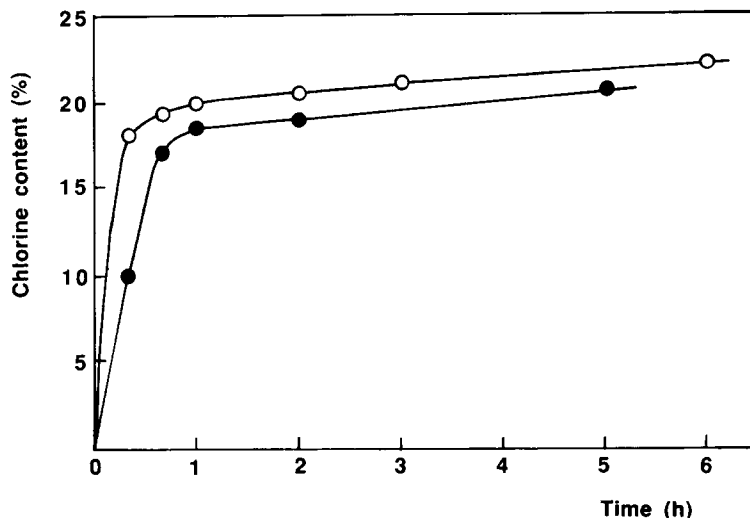


Figure 1 The effect of temperature on the chlorination of cellulose with methanesulfonyl chloride in a mixture of chloral and DMF: (○) 100°C; (●) 75°C. Reaction conditions: cellulose, 1 g; methanesulfonyl chloride, 10 mL; chloral, 12 mL; DMF, 76 mL; pyridine, 11 mL.

at 75°C and at 100°C. Subsequently the increase in chlorine content was very slow, and the degree of chlorination did not increase very much above 20% even after 20 h of reaction (Fig. 1). A sample of CDC with DS of 1.0 (chlorine content 19.6%) was obtained after about 5 h of reaction at 75°C, and after about 1 h at 100°C.

In the chlorination of cellulose with methanesulfonyl chloride in DMF, it has been reported that the chlorination occurs exclusively at the primary OH groups of the C-6 position. The secondary OH groups at the C-2 and C-3 positions react very slowly.⁷ Therefore, it is assumed that the chlorination also occurs predominantly at the C-6 position in this reaction system.

The chlorodeoxycelluloses obtained were insoluble in solvents irrespective of chlorine content, but were swollen on heating in polar aprotic solvents such as DMF, DMAc, NMP and DMSO.

Aminoalkyl Cellulose

The results of the reaction of 6-CDC (DS = 1.0) with ethylenediamine in a variety of solvents are shown in Table I. The reaction mixtures were initially nonhomogeneous irrespective of solvent. After a few minutes of reaction, however, they became homogeneous and the reaction proceeded in a homogeneous manner with the exceptions of reactions in THF and butanol. The reactivity of 6-CDC toward diamines was somewhat affected by the polarity of

the solvent. Products with higher substitution were obtained with DMSO and DMF.

Because DMSO was found to be most suitable as a solvent, the reaction conditions were examined in detail in DMSO solution (Table II). The products with higher DS were obtained by reacting at higher temperature for longer duration in the presence of an excess amount of diamine. A maximum DS of 0.78 was attained for ethylenediamine under very severe conditions in which a large excess of diamine was used without solvent. However, the yield decreased remarkably due to partial degradation of cellulose chains, and to the solubilization of the re-

Table I Reaction of CDC with Ethylenediamine in Various Solvents^a

Solvent	Temperature (°C)	Product	
		Yield (g)	DS ^b
DMF	100	0.035	0.25
NMP	100	0.066	0.18
DMAc	100	0.070	0.18
DMSO	100	0.052	0.30
THF	70	0.082	0.20
BuOH	100	0.082	0.14

^a Reaction conditions: CDC (DS 1.08), 0.1 g; molar ratio of diamine to Cl of CDC, 3 (mol/mol); solvent, 10 mL; reaction time, 6 h.

^b Degree of substitution of diamine.

Table II Reaction of CDC with Ethylenediamine in DMSO^a

DS ^b	Temperature (°C)	Time (h)	Diamine/CDC ^c (mol/mol)	Product	
				Yield (g)	DS ^d
0.79	100	3	1	0.085	0.13
0.99	100	3	1	0.082	0.13
0.99	100	3	3	0.089	0.24
1.08	120	3	3	0.085	0.34
1.08	120	24	25	0.083	0.48
1.08	120	24	100 ^e	0.042	0.78

^a Reaction conditions: CDC, 0.1 g; DMSO, 10 mL.

^b Degree of substitution of Cl in CDC.

^c Molar ratio of diamine to Cl of CDC.

^d Degree of substitution of diamine.

^e No solvent was used.

sulting low molecular weight fraction in a MeOH/acetone mixture when the reaction mixture was dropped into a MeOH/acetone mixture after the reaction.

The reaction of 6-CDC with other diamines was carried out under the conditions which resulted in

highly substituted products with ethylenediamine (Table III).

These reactions may be accompanied by intra- and intermolecular crosslinking. However, crosslinking occurred scarcely at all because of the high solubility of the highly substituted products in water.

Table III Reaction of CDC with Various Diamines^a

m	DS ^b	Temperature (°C)	Time (h)	Diamine/CDC ^c (mol/mol)	Product	
					Yield (g)	DS ^d
4	0.99	100	3	1	0.093	0.15
	0.99	100	3	3	0.084	0.25
	1.08	80	24	10	0.054	0.43
	1.08	120	24	25	0.084	0.50
	1.08	120	24	100 ^e	0.037	1.01
6	0.99	100	3	1	0.090	0.18
	0.99	100	3	3	0.099	0.29
	1.08	80	24	10	0.089	0.47
	1.08	120	24	25	0.092	0.60
	1.08	120	24	100 ^e	0.054	1.06
8	0.99	100	3	1	0.090	0.18
	0.99	100	3	3	0.079	0.29
	1.08	100	24	5	0.079	0.59
	1.08	120	24	25	0.098	0.61
	1.08	120	24	100 ^e	0.038	1.04

^a Reaction conditions: CDC, 0.1 g; DMSO, 10 mL.

^b Degree of substitution of Cl in CDC.

^c Molar ratio of diamine to Cl of CDC.

^d Degree of substitution of diamine.

^e No solvent was used.

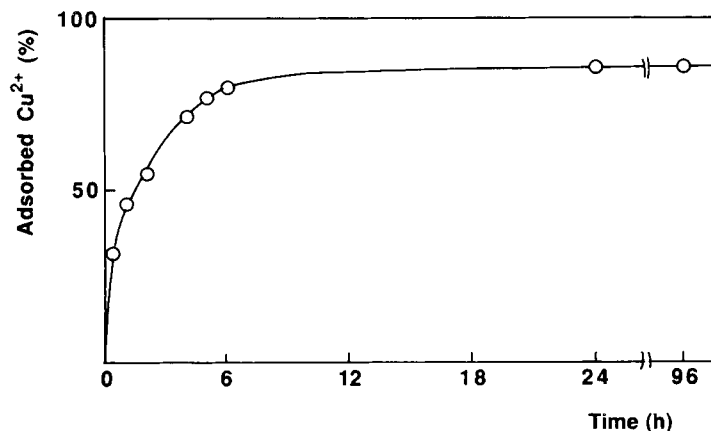


Figure 2 The adsorption of Cu^{2+} ions vs. time in the adsorption of Cu^{2+} ions on aminoethyl cellulose. Adsorption conditions: AmAC (DS 0.34), 0.1 g; CuCl_2 solution (1 mmol/L), 50 mL; pH, 5.28.

ADSORPTION OF METAL IONS

For the measurement of adsorption, AmACs with DS of less than 0.4 were used, because highly substituted AmACs were remarkably swollen and partly soluble in water.

As AmACs become highly swollen gels in water, the adsorption of metal ions onto AmACs from solution occurred very rapidly and approached a constant value within 6 h of immersion. From an 1 mmol/L Cu^{2+} solution, 89% of metal ions were adsorbed on the AmAC from ethylenediamine after 24 h of immersion at room temperature (Fig. 2). This rapid attainment of equilibrium is attributed to the hydrophilicity of the main chain and the pendant coordination sites.

Each of the pendant groups of AmACs has two coordination sites because they are prepared from aliphatic diamines with amino groups at both ends. Usually, chelate compounds are much more stable than the corresponding single-site ligands. Accordingly, it is supposed that the two nitrogen atoms derived from aliphatic diamines have a tendency to form chelate rings with metal ions, rather than each nitrogen atom coordinates with metal ions independently.

With this in mind, the effect of the methylene chain length of AmACs on the adsorption of Cu^{2+} ions was examined while the pH of the solution was varied. In strongly acidic solutions, AmACs were highly swollen because of protonation of their amino groups, and did not adsorb heavy metal ions irrespective of the number of methylene units in the diamine moieties. However, in weakly acidic solutions, the adsorption of metal ions decreased with

the increasing number of methylene units in the AmACs, and the AmAC from ethylenediamine was most effective as adsorbent (Fig. 3).

The stability of metal chelates depends on the ligand and the structure of chelate. When a chelate ring is formed from a multisite ligand and a metal ion, a five-membered chelate is more stable than a six- or higher-membered one due to the less skewed structure of the former.

The AmAC derived from ethylenediamine can form a stable five-membered chelate structure with metal ions, whereas the AmAC from tetramethylenediamine forms a more skewed, less stable seven-membered one or even a structure resulting from

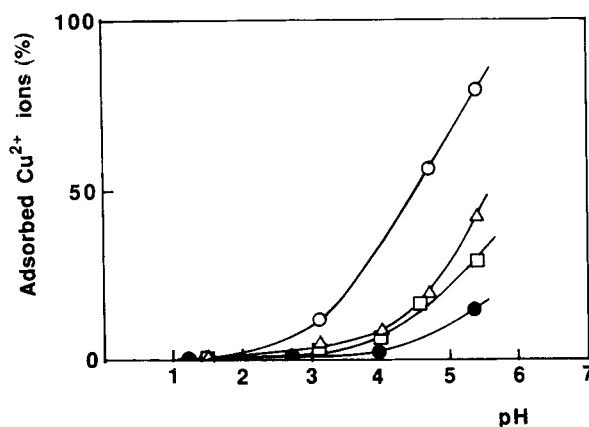


Figure 3 The effect of pH on the adsorption of Cu^{2+} ions on aminoalkyl celluloses: (○) $m = 2$; (△) $m = 4$; (□) $m = 6$; (●) $m = 8$; (m represents the number of methylene units in the diamine moiety). Adsorption conditions: AmAC (DS 0.18–0.20), 0.1 g; CuCl_2 solution (1 mmol/L), 50 mL; reaction time, 24 h.

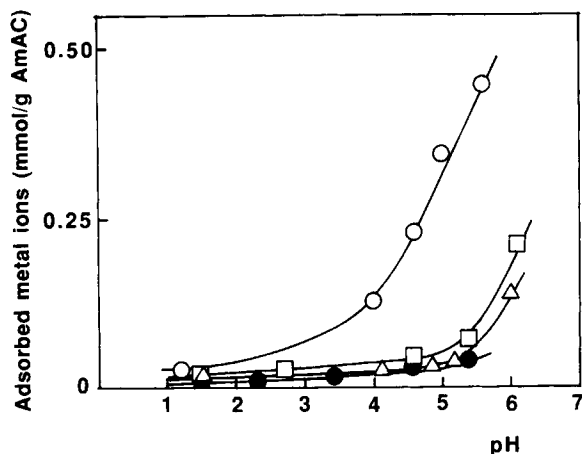


Figure 4 The effect of pH on the adsorption of various divalent metal ions on aminoethyl cellulose: (○) Cu^{2+} ; (●) Mn^{2+} ; (△) Co^{2+} ; (□) Ni^{2+} . Adsorption conditions: AmAC (DS 0.18–0.20), 0.1 g; metal chloride solution (1 mmol/L), 50 mL; reaction time, 24 h.

single-site adsorption. The high adsorption ability of the AmAC from ethylenediamine is thus explained. As the number of methylene units is increased from 4 to 8, the hydrophobicity of AmAC is increased and this in turn results in a decrease in the adsorption ability of metal ions.

The AmAC derived from ethylenediamine was the most effective AmAC for adsorbing metal ions among those studied. Various divalent metal ions were adsorbed from solution onto the AmAC derived from ethylenediamine while the pH of the solution was varied (Fig. 4).

In the weakly acidic region, a remarkable difference was observed in the adsorption of metal ions. Copper ions were strongly adsorbed on AmAC. From Figure 4, the adsorptivity of metal ions on AmACs

was in the order of $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$. This result is explained by the different stability of complexes between diamine and different metal ions.

This order of metal ions agrees well with Irving–Williams series⁸ for the stability of various ligands with nitrogen or oxygen as coordinating atoms for divalent transition metal ions.

Selective Adsorption of Metal Ions

Cu^{2+} ions were most effectively adsorbed on AmACs, especially on that prepared from ethylenediamine. Accordingly, a selective adsorption of Cu^{2+} ions is expected from a solution containing a mixture of two different metal ions.

Table IV shows the results of adsorption of metal ions on AmACs from an equimolar solution of two different metal ions. As expected, the AmAC from ethylenediamine has high adsorption ability for any metal ions and high selectivity for Cu^{2+} ions. The adsorption of coexisting metal ions from Cu^{2+} -containing solutions is suppressed compared to that from solutions containing ion mixtures without Cu^{2+} ions. The adsorption from solutions containing ion mixtures also obeys the Irving–Williams order. This selective adsorption, however, decreased with the increasing number of methylene units in diamine moieties in the AmACs.

Effect of Temperature on the Adsorption of Metal Ions

The stability constant of complexation is dependent on temperature because it is an equilibrium constant in solution. Generally, for low molecular weight complexes the stability constant becomes larger as the temperature is lowered. Therefore, the effect of temperature on adsorption of Cu^{2+} was examined

Table IV Selective Adsorption of Metal Ions on AmACs from Aqueous Solutions Containing Two Metal Ions^a

Metal Ions	Adsorbed Metal Ions (10^2 mmol/g AmAC)			
	$m^b = 2$	$m = 4$	$m = 6$	$m = 8$
$\text{Cu}^{2+} + \text{Mn}^{2+}$	22.5 + 0	3.22 + 0	2.67 + 0	1.27 + 0
$\text{Cu}^{2+} + \text{Co}^{2+}$	18.5 + 1.77	4.22 + 1.20	4.08 + 0.94	2.26 + 0.61
$\text{Cu}^{2+} + \text{Ni}^{2+}$	26.1 + 3.67	4.21 + 1.90	2.98 + 1.54	0.91 + 0.85
$\text{Mn}^{2+} + \text{Co}^{2+}$	6.85 + 6.89	3.14 + 3.27	2.53 + 2.52	1.72 + 0.18
$\text{Mn}^{2+} + \text{Ni}^{2+}$	2.01 + 8.26	1.22 + 2.14	0.96 + 1.90	0 + 1.02
$\text{Co}^{2+} + \text{Ni}^{2+}$	2.89 + 3.56	2.38 + 1.90	1.68 + 1.35	1.30 + 1.10

^a Adsorption conditions: AmAC (DS 0.18–0.20), 0.1 g; metal chloride solution (concentration of each ion; 0.5 mmol/L), 50 mL; pH, 4.8–5.0; reaction time, 24 h.

^b m is the number of methylene units in the diamine moiety.

at 20°C and at 40°C using AmAC from ethylenediamine and an initial concentration of Cu^{2+} of 0.1 to 8 mmol/L.

No difference was observed between the adsorption temperature of 20°C and that of 40°C in the lower concentration region of Cu^{2+} . However, at concentrations higher than 0.6 mmol/L higher adsorption was attained at 20°C than at 40°C (Fig. 5). Accordingly, complexes of AmACs with metal ions become more stable at lower temperatures as generally observed for low molecular weight complexes.

Desorption and Readsorption of Metal Ions

Evidently, complexation of AmACs with metal ions was inhibited in strongly acidic conditions. Therefore, the recovery of Cu^{2+} ions adsorbed on the AmAC from ethylenediamine, was examined. The Cu^{2+} ions adsorbed were easily desorbed by treating with 0.1M hydrochloric acid at room temperature for 2 h. The AmAC desorbed was effective for the readsorption of metal ions, even though the adsorption ability of AmAC decreased noticeably after several repetitions of the adsorption-desorption cycle (Fig. 6).

CONCLUSIONS

Aminoalkyl celluloses (AmACs) were prepared from chlorodeoxycellulose (CDC) and aliphatic diamines $\text{H}_2\text{N}(\text{CH}_2)_m\text{NH}_2$ ($m = 2, 4, 6, 8$).

No adsorption of metal ions occurs on AmACs from strongly acidic solutions, but metal ions are adsorbed rapidly on AmACs from weakly acidic so-

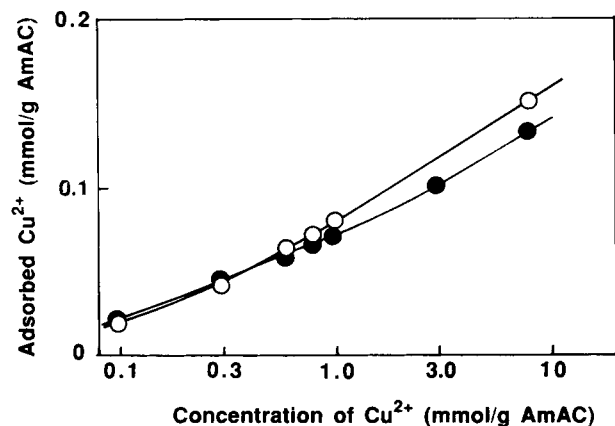


Figure 5 The effects of temperature and initial concentration of Cu^{2+} ions on the adsorption of Cu^{2+} ions on aminoethyl cellulose: (○) 20°C; (●) 40°C. Adsorption conditions: AmAC (DS 0.16), 0.1 g; CuCl_2 solution, 50 mL; pH, 5.31–5.40; reaction time, 24 h.

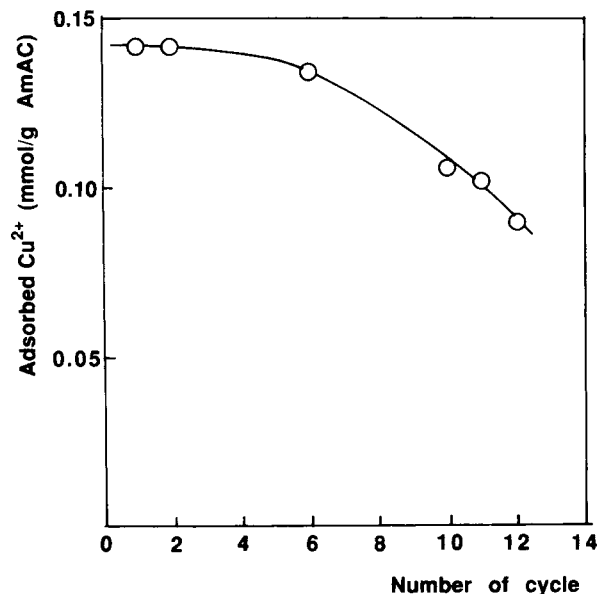


Figure 6 Adsorption-desorption cycles of Cu^{2+} ions on aminoethyl cellulose. Adsorption conditions: AmAC from ethylenediamine (DS 0.23), 0.4 g; CuCl_2 solution (3 mmol/L), 200 mL; pH, 5.31; reaction time, 24 h. Desorption conditions: AmAC (DS 0.23), 0.1 g; HCl (0.1M), 10 mL; reaction time, 2 h.

lutions and the amount of adsorption increased with increasing pH. The ability of AmACs to adsorb metal ions decreases as m increases in diamine moieties, and the AmAC from ethylenediamine ($m = 2$) is most effective. The adsorption of metal ions occurs in the order of $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$, and Cu^{2+} ions are selectively adsorbed from solutions containing two different ions. The adsorbed ions are easily recovered by stirring in 0.1M HCl.

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