

Adsorption Behavior of Heavy Metal Ions on Cellulose Graft Copolymers

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Synopsis

The adsorption behavior of cadmium, copper and lead ions on holocellulosic materials containing various levels of polyacrylonitrile and poly(acrylic acid) grafts was examined. The amount of metal ions adsorbed per gram of the modified cellulosic substrate depended on the metal ion type, the nature and level of the incorporated graft polymer. In all cases grafting increased the metal ion-binding capacity of the cellulosic materials (by up to 50% for Cu (II) ions). The influence of temperature and initial metal ions concentration on the sorption behavior of the metal ions on the composite materials was investigated.

INTRODUCTION

The effects of incorporated polyacrylonitrile and of poly(acrylic acid) grafts on the water absorption and mechanical properties of cellulosic materials have been reported by several workers.¹⁻⁶ Cellulosic materials with grafts containing nitrile or carboxyl groups would be expected to interact and remove metal ions from aqueous solution. Although the removal of heavy metal ions from solution using cellulosic materials⁷⁻⁹ and polyelectrolytes¹⁰⁻¹³ have been reported, information on the sorption behavior of metal ions on cellulose/polyelectrolyte composites is scanty. In this communication, the binding of cadmium, copper, and lead ions with graft copolymers of polyacrylonitrile and of poly(acrylic acid) and cellulosic materials is reported.

EXPERIMENTAL

Preparation of the Graft Copolymers

The experimental procedures for the purification of acrylonitrile and acrylic and monomers, the preparation of the holocellulosic materials and the graft copolymers were reported in details in a previous communication.⁶

SORPTION

Equilibrium sorption of the metal ions by the modified and unmodified cellulosic materials was studied using a range of metal ion concentration (50–500 mg/L) at a constant metal ion-substrate contact period (40 min). In

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a typical experiment, a 1–2 g samples of the graft cellulosic substrate was shaken with 100 mL of a metal ion solution whose concentration had previously been determined. At the end of the contact period, the mixture was filtered (the initial 15 mL of the filtrate was discarded), and the final concentration of the metal ion in the filtrate was determined chelatometrically. The difference between the initial and final metal ion concentration was reported as the amount of metal ion bound by the substrate [after corrections have been made for the amount of metal ion in the volume of solution retained (absorbed) by the substrate]. The influence of temperature on the levels of metal ions uptake was investigated between 0°C and 45°C.

DESORPTION

To measure desorption, samples of the air-dried cellulosic adsorbent with the adsorbed metal ions were shaken with 100 mL of dilute (1% v/v) nitric acid for 40 mins. The mixture was filtered and the metal ion content of the filtrate was determined chelatometrically. The amount of metal ions recovered was reported as percentage of the amount of metal ions adsorbed.

RESULTS AND DISCUSSION

The variation of the amount of metal ions adsorbed with graft level for polyacrylonitrile graft copolymers are shown in Figure 1. The results show that although the amount of metal ions removed from solution is $\text{Pb(II)} > \text{Cd(II)} > \text{Cu(II)}$ (i.e., in the order of decreasing ionic radii), the proportion of the metal ions adsorbed due to the incorporated graft is highest for Cu(II) ions. Actually, the increase in the uptake of metal ions due to the incorporated polyacrylonitrile graft is 5% for Pb(II), 14% for Cd(II), and 53% for Cu(II) ions. The interaction of copper ions with polyelectrolytes has been reported by several workers.^{10,11} The results from these studies show that one copper ion is involved in chelation with two carboxylate (possibly adjacent) groups. This intramolecular association through Cu(II) ions causes configurational changes leading to the formation of copper polyelectrolyte complexes. It would be expected that for slightly bigger ions, such as Pb(II) and Cd(II), the requirements for polyelectrolyte-metal ion interaction could be different and that these metal ions would form complexes with the polyelectrolyte less readily than Cu(II) ions. The enhanced metal ion binding of the cellulosic substrate brought about by the incorporation of polyacrylonitrile grafts can be explained in terms of the presence of nitrile groups on the grafts which provide additional binding sites for the metal ions. Besides, the enhanced swelling of the substrate by the metal ions solution brought about by the interposition of the grafts⁶ would lead to increased uptake of metal ions. The levels of metal ions uptake generally increase with initial metal ion concentration (Fig. 2) but the proportion of the metal ion removed from solution decreases.

The variation of the amount of metal ions adsorbed with poly(acrylic acid) grafts is shown in Table 1. As with the cellulose-polyacrylonitrile graft copolymers, the amount of metal ions removed from solution is $\text{Pb(II)} > \text{Cd(II)} > \text{Cu(II)}$; but the increase in the uptake of metal ions due to the incorporated grafts is $\text{Cu(II)} > \text{Cd(II)} > \text{Pb(II)}$. The amount of metal ions removed from

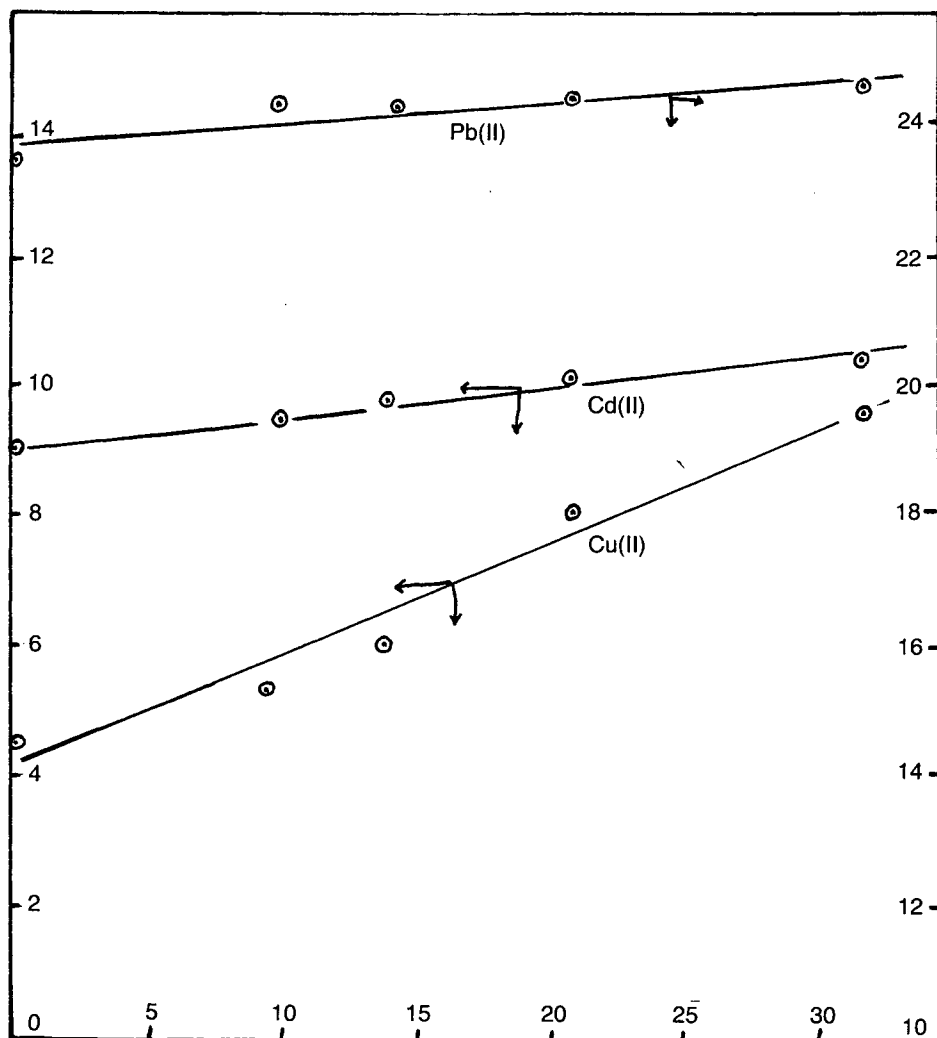


Fig. 1. Equilibrium sorption by cellulose-polyacrylonitrile graft copolymers of metal ions from 100 mL of 500 mg/L solutions 29°C. ord. amount of metal ions adsorbed/(mg/g); absc. Graft Level (%).

solution by cellulose-poly(acrylic acid) graft copolymers is relatively higher than for cellulose-polyacrylonitrile graft copolymers. The difference between the hydration energies of carboxylate and nitrile groups, and between the ease of formation of carboxylate-metal ion and nitrile-metal-ion bonds would explain the higher levels of metal ion uptake by the cellulose-poly(acrylic acid) graft copolymers.

Table II shows the amounts of adsorbed metal ions recoverable with dilute nitric acid. The results indicate that as the amount of metal ions bound by the substrate increased, the amount of desorbed metal ions increased, but the fraction of the metal ion desorbed decreased. Desorption, like adsorption is an equilibrium process representing a partition of the adsorbed metal ions between the solid cellulosic substrate and the continuous aqueous phase.

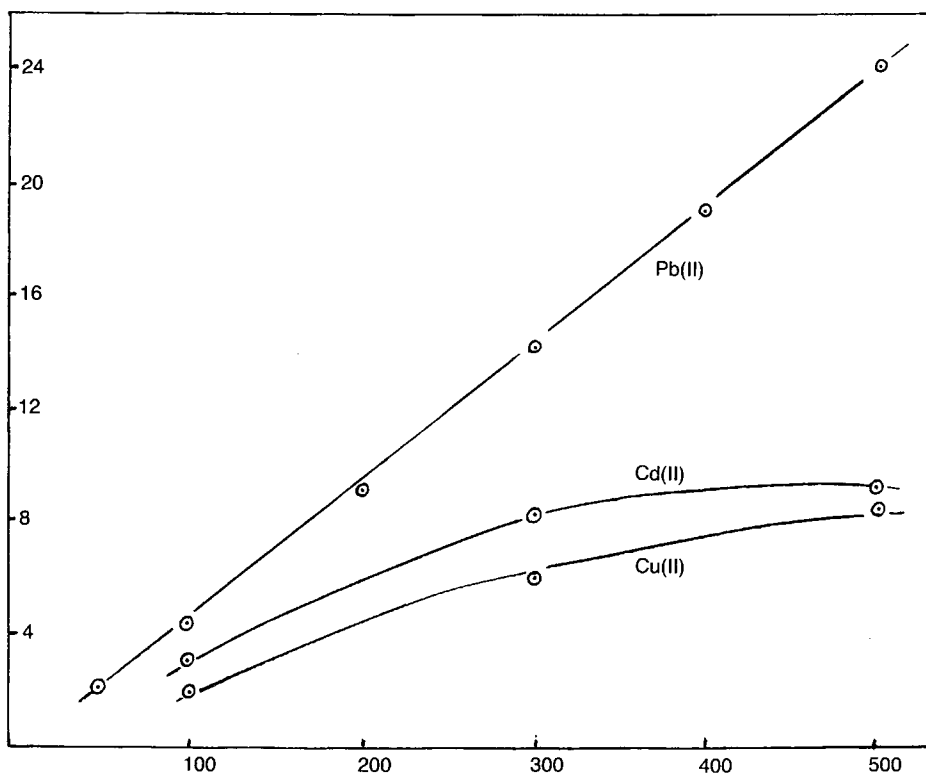


Fig. 2. Variation of the level of uptake of metal ions with initial metal ions concentration using cellulose-polyacrylonitrile graft copolymer at 9.6% graft level. ord. amount of metal ion adsorbed (mg/g); absc. initial metal ion concentration (mg/L).

TABLE I
Uptake of Metal Ions by Cellulose-Polyacrylic Acid Graft Copolymers Using 100 mL of 500 mg/L Metal Ions Solutions at 29°C

Graft level (%)	Amount of metal ions adsorbed (mg/g)		
	Cd(II)	Cu(II)	Pb(II)
0	9.1	6.2	23.4
12.3	9.5	10.1	23.9
25.6	10.0	14.4	23.8

Salts used $\text{Cd}(\text{SO}_4)$, CuCl_2 , $\text{Pb}(\text{NO}_3)_2$.

Figure 3 shows the influence of temperature on the uptake of Cd(II) ions. The results indicate that an increase in temperature is accompanied by a reduction in the level of metal ions uptake. The temperature dependence of the levels of metal ions uptake leads to the suggestion that preferential solubilization rather than localized binding of the metal ions is more significant in the sorption process.

TABLE II
Desorption of Bound Metal Ion from Cellulose-Poly(acrylic acid) Graft Copolymers Using 1% (v/v) Nitric Acid at 29°C

Graft Level (%)	Initial metal ion concentration (mg/100mL)	Amount of metal ion adsorbed ^a (mg)			Amount of metal ion desorbed (mg)		
		Cd(II)	Cu(II)	Pb(II)	Cd(II)	Cu(II)	Pb(II)
12.3	5.0	—	—	4.2	—	—	3.8
	10.0	3.5	2.6	9.1	1.1	0.4	5.8
	20.0	—	—	19.1	—	—	6.7
	30.0	8.4	6.2	28.4	1.4	0.7	7.9
	40.0	—	—	38.2	—	—	7.9
	50.0	9.5	10.1	47.9	1.5	1.1	8.1
25.6	5.0	—	—	4.4	—	—	4.1
	10.0	4.2	3.2	9.3	1.6	0.5	4.7
	20.0	—	—	18.9	—	—	5.1
	30.0	9.1	7.1	28.3	2.0	0.9	5.6
	40.0	—	—	38.1	—	—	6.2
	50.0	10.0	14.4	47.5	2.6	1.5	8.9

^a Amount of metal ions adsorbed from 100mL of the metal ion solutions.

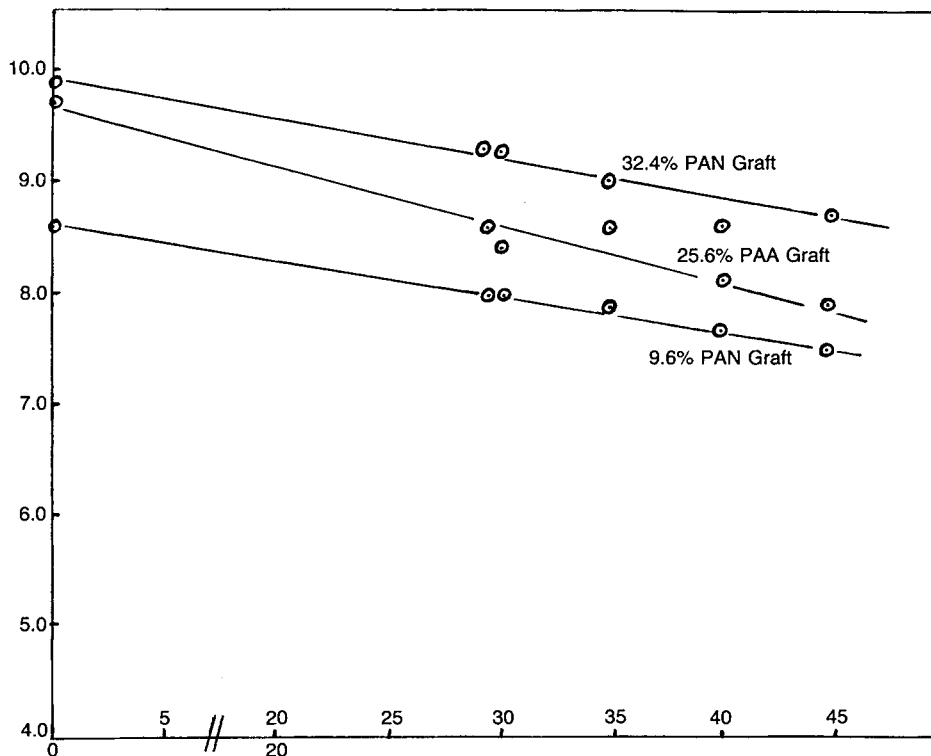


Fig. 3. Effect of temperature on the equilibrium sorption of Cd(II) ions from 300 mg/L solutions. ord. amount of Cd(II) ions adsorbed; absc. temp/°C.

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Received June 3, 1985

Accepted January 13, 1986