

Adsorption of Copper(II) and Chromium(III) Ions onto Amidoximated Cellulose

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Received 12 February 1999; accepted 21 June 1999

ABSTRACT: Chemical modification of cellulose powder is performed by successive reactions with acrylonitrile in an alkaline medium followed by aqueous hydroxylamine to prepare amidoximated cellulose. Due to complexation, the amidoxime groups immobilize heavy cations from buffered solutions at various pH values. The capacity of adsorption for Cu(II) and Cr(III) ions is related to the amount of amidoxime groups in the support and to the metal concentration of the polluted solution. The formation of a 1/1 complex is proved by the adsorption limit values. Desorption of the cations is possible by treatment with a stronger complexing agent such as ethylenediaminetetraacetic acid. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1624–1631, 2000

Key words: cellulose; amidoxime; heavy metals; depollution

INTRODUCTION

The removal of toxic and polluting metal ions from industrial effluents, water supplies, as well as mine waters is an important challenge to avoid one of the major causes of water and soil pollution. Various methods^{1–3} are proposed to remove heavy metal ions from industrial effluents using ion-exchange, reverse osmosis, and electro dialysis techniques, which are efficient but expensive. Chemical precipitation can be envisaged, but the generation of precipitated bulky hydroxides and colloidal particles is often a major disadvantage.

The search for an effective and economic method of removing toxic heavy metal ions requires the consideration of unconventional materials and processes that might have potential in this field. For example, many agricultural by-

products are able, eventually, after chemical treatment, to recover metal ions by adsorption: peanut skin,⁴ cotton,⁵ onion skin,⁶ wood saw,⁷ rice hulls,⁸ maize stalks,⁹ starch,¹⁰ barks,¹¹ jute fibers,¹² bamboo pulp,¹³ etc. Recently, reports have described the use of cellulose modified by a complexing group involving an amine function (aminoalkyl,¹⁴ 2,2'-diaminodiethylamine¹⁵) or an anionic moiety (phosphate,¹⁶ thiolate,¹⁷ carboxy,¹⁸ carboxymethyl¹⁹).

The purpose of the present work consisted of introducing amidoxime groups into cellulose and evaluating the influence of reaction parameters on the content of amidoxime in the modified cellulose. The adsorption on the resultant amidoxime cellulose (Am-Cell) was examined at different pH values with copper(II) ions as a reference and further adapted to chromium(III), for which little is available in the literature concerning its immobilization onto cellulosic material. The capacity of adsorption was compared to the amount of modified groups present in the cellu-

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Journal of Applied Polymer Science, Vol. 75, 1624–1631 (2000)
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Table I Volumic Composition of the Buffered Metal Solutions Following Clark and Lubs²⁰

Adjusted pH Value	Metal Solution (mL)	Potassium Hydrogen Phthalate 0.2M (mL)	HCl 0.2M (mL)	NaOH 0.2M (mL)	Deionized Water
3	50	50	20.32		
4	50	50		0.4	Completion to 200 mL
5	50	50		23.85	
6	50	50		45.45	

lose and to the concentration of metal ions. The use of such supports in the elimination of heavy cations is expected to be efficient in the range of concentrations of about $10^{-2}M$. The desorption of these cations by the sodium salt of ethylenediaminetetracetic acid (EDTA) and the recycling of the support are tested concerning the potential use of these materials as cation exchangers.

EXPERIMENTAL

Materials

Cellulose powder (60–65% crystalline) was supplied by Sigma (Sigma-Aldrich Chimie Sarl, St. Quentin Fallavier, France). Acrylonitrile (Aldrich), hydroxylamine (Fluka Chimie, St. Quentin Fallavier, France), EDTA (Merck, Darmstadt, Germany), potassium hydrogen phthalate (Prolabo, Fontenay-sous-Bois, France), and the salts of copper ($CuCl_2 \cdot 2H_2O$, Prolabo) and of chromium ($CrCl_3$ in aqueous solution, Aldrich) were used without further purification. Aqueous solutions containing these ions at various concentrations (10^{-2} – $10^{-1}M$), were prepared from metal salts and controlled by titration with a standard

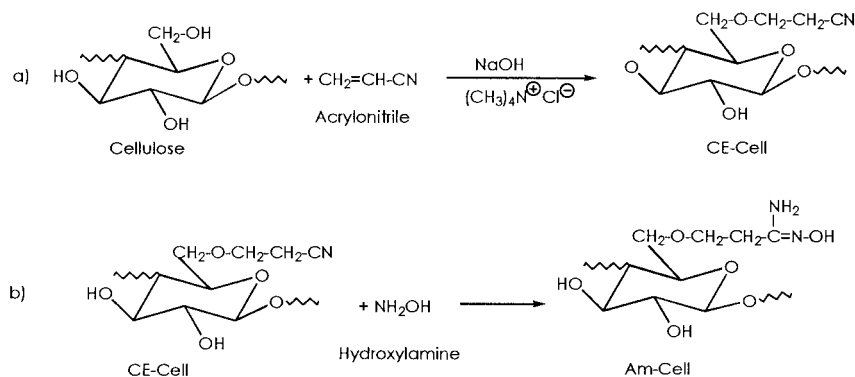
EDTA solution and by atomic absorption. The pH of the solutions was adjusted with Clark–Lubs buffer solutions²⁰ at four values according to indications given in Table I.

Preparation of Cyanoethyl Cellulose

Cyanoethyl cellulose (CE-Cell) is prepared under alkaline conditions by cyanoethylation of cellulose with acrylonitrile (AN) [Fig. 1(a)], as described previously.²¹ When the reaction is complete, the mixture is treated with 30 mL of isopropanol in order to dissolve and then eliminate the unreacted AN.¹⁴ The mixture is then poured into water and the resulting CE-Cell is filtered and dried under reduced pressure at 25°C. The degree of substitution (DS) of CE-Cell is obtained by the elemental nitrogen analysis (% N_1) using relation (1):

$$DS = \frac{M_{glup}N_1}{100M_N - M_{AN}N_1} \quad (1)$$

where M_{glup} is the molecular weight of the glucopyranose unit (162 g); M_N , the atomic weight of nitrogen (14 g); and M_{AN} , the molecular weight of AN (53 g).


Figure 1 (a) Cyanoethylation of cellulose; (b) amidoximation of CE-Cell.

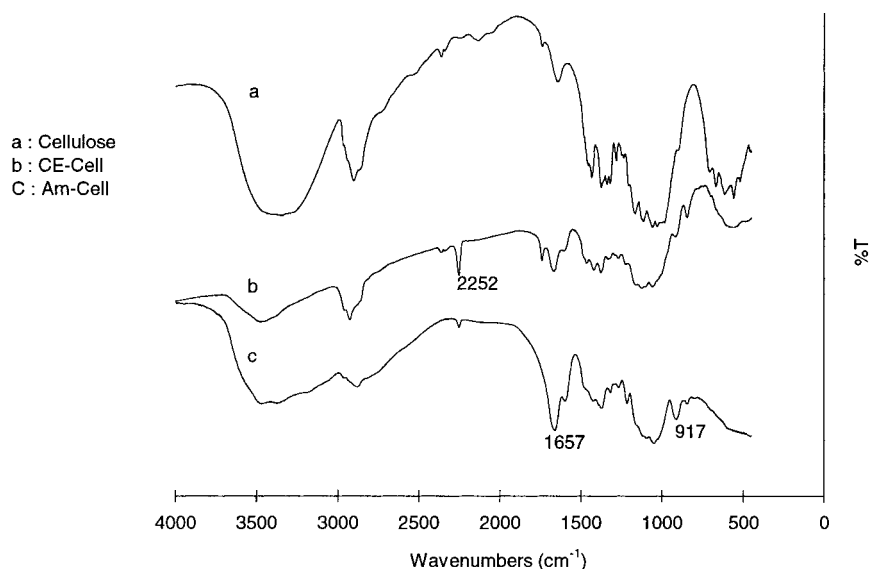


Figure 2 IR spectra of (a) untreated cellulose, (b) CE-Cell, and (c) Am-Cell.

Preparation of Am-Cell

CE-Cell is treated either by an aqueous solution of hydroxylamine at a known concentration or by an aqueous solution of hydroxylamine hydrochloride, whose pH is adjusted to between 9 and 10 by adding sodium carbonate²² [Fig. 1(b)]. After treatment at a constant temperature (from 60 to 80°C) for a given time (from 30 min to 3 h), the modified cellulose is filtered, washed with deionized water, and dried under a vacuum. The values of the degree of substitution (DS') in amidoxime groups are obtained from the elemental nitrogen analysis (% N₂) using relation (2):

$$DS' = \frac{(N_2 - N_1)(M_{glup} + M_{AN}DS)}{100M_N - M_{NH_2OH}(N_2 - N_1)} \quad (2)$$

where M_{NH_2OH} is the molecular weight of hydroxylamine (33 g).

DS' is generally lower than is DS, indicating that only a part of the cyano groups in CE-Cell are transformed to amidoxime. The amidoxime content, C_A , in mmol/g, is a more pertinent parameter than is DS' and it can be determined by two methods: First, it is provided by relation (3):

$$C_A = \frac{N_2 - N_1}{M_N} \times 10 \quad (3)$$

Second, it can be obtained by the HCl adsorption method²¹: Am-Cell, 0.1 g, is treated with 100 mL of

a 0.01M aqueous hydrochloric acid solution at 25°C for 24 h and the sample is filtered off. An aliquot of the filtrate is titrated with a 0.01M aqueous sodium hydroxide solution. Infrared spectra of CE-Cell and Am-Cell in KBr pellets were obtained on a 1760-X Perkin-Elmer FTIR instrument.

Metal-Ion Batch Adsorption and Desorption

Am-Cell powder (0.1 g) is added to 10 mL of the buffered metal chloride solution. The mixture is stirred for 24 h at 25°C in a closed vessel. The amount of remaining metal ions is determined by spectrometric titration, performed on an Uvikon 941+ spectrometer at the maximum absorption wavelength of the corresponding metal-phthalate complex. The path length is 1 cm.

Am-Cell (0.1 g) containing adsorbed metal ions is stirred with 10 mL of a standard EDTA solution and then filtered off. The remaining ions in the

Table II Evolution of the DS of CE-Cell with the Reaction Conditions at 25°C

Reaction Time (min)	TMAC ^a /Cellulose (w/w)	N ₁ (wt %)	DS
60	0	3.59	0.48
30	1/30	5.37	0.78
60	1/30	9.84	1.81
120	1/30	10.15	1.91

^a TMAC: tetramethylammonium chloride.

Table III Influence of Selected Reaction Parameters in the Preparation of Am-Cell from CE-Cell with Different DS

CE-Cell		Reaction				C_A	
N_1 (wt %)	DS	Temperature (°C)	Time (min)	Concentration of NH_2OH (%)	N_2 (wt %)	From N_2	From HCl Titration
2.07	0.26	70	60	4.75	3.36	0.94	
		70	60	10	4.03	1.4	
9.84	1.81	80	30	10	11.49	0.60	0.58
		80	60	10	12.58	1.17	1.19
		80	120	10	13.31	2.47	2.5
		80	180	10	15.26	3.76	3.8
2.78	0.34	60	60	10	3.10	0.23	
		70	60	10	4.56	1.28	
		80	60	10	5.17	1.68	

filtrate are determined by spectrometric titration for Cu(II) ions and by atomic absorption for Cr(III) ions. Atomic absorption is performed on a AA 3110 Perkin–Elmer instrument.

RESULTS AND DISCUSSION

Characterization of CE-Cell

The prepared CE-Cell, in white powder form, is characterized by infrared spectroscopy. By comparison with the pure cellulose [Fig. 2(a)], a sharp peak appears [Fig. 2(b)] at 2252 cm^{-1} , corresponding to the stretching of the $C\equiv N$ bond.

To obtain higher DS values, two reaction parameters (duration and presence of tetramethylammonium chloride) were modified. Table II indicates that a reaction time limited to 1 h is generally sufficient. The presence of the quaternary ammonium salt appears necessary to improve the dispersion of the alkali within the cellulose matrix and to enhance the activity of the cellulose ions formed.⁹

Characterization of Am-Cell

Am-Cell is a white powder and its IR spectrum [Fig. 2(c)] displays two new absorption peaks at 1657 and 917 cm^{-1} , corresponding to the stretch-

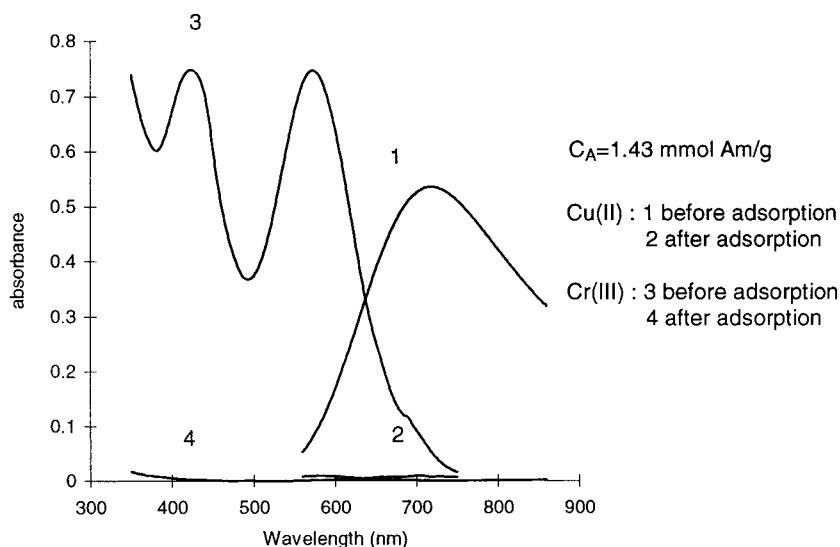


Figure 3 Adsorption spectra of metal ions complexed by phthalate at pH 6. Initial concentration of metal ions: $10^{-2}M$.

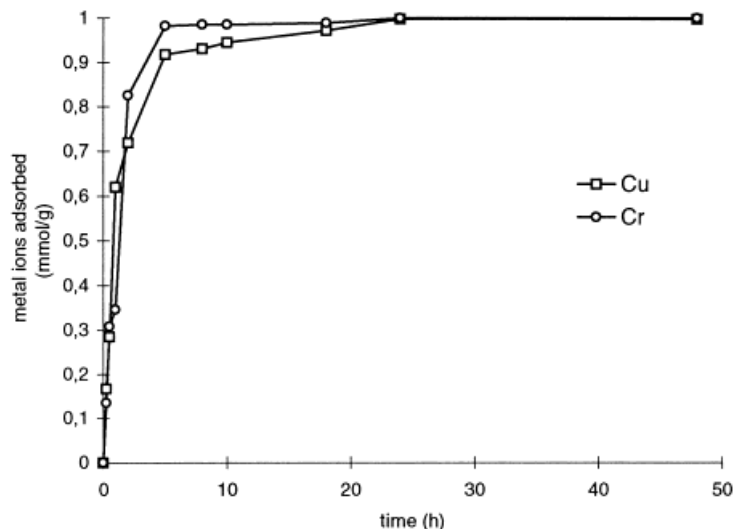


Figure 4 Effect of contact time on the adsorbed quantity of metal ions. Initial concentration of metal ions: $10^{-2}M$.

ing vibration of C=N and N—OH bonds, respectively. A high decrease in absorbance at 2252 cm^{-1} is observed simultaneously. The titration of the amino groups by the HCl adsorption method is in good agreement with the nitrogen determination (Table III).

Effect of the Reaction Conditions on C_A

Table III shows the effects of the reaction conditions such as concentration of hydroxylamine, time, and temperature on C_A . The content in amidoxime increases with NH_2OH concentration and temperature; it also sharply increases linearly with time from the start of the reaction, then tends to a steady value after 2 h, indicating that it is not necessary to prolong the reaction time. These observations are in accordance with results previously reported.^{6,13}

Another efficient way to enhance the amidoxime content consists of treating the support twice in succession: The C_A of a given Am-Cell is thus enhanced from 0.31 to 0.93 mmol/g.

Metal-ion Adsorption

The adsorption of metal ions occurs in the presence of potassium hydrogen phthalate acting as a buffer and involves different complexes depending on the pH. First, the complexing of Cu(II) and Cr(III) ions by the phthalate ions is followed between pH 3 and 6 in order to estimate the evolution of the solution absorbance without cellulosic support. As expected, compared with the initial metal chloride solution,

the absorbance of the complex species is enhanced and presents a hypsochromic shift. At pH 6, the conditional constants and the distribution curves of the Cu(II)–phthalate²³ and Cr(III)–phthalate²⁴ systems determine the presence of the $[\text{Cu}(\text{phthal})_2]$ and $[\text{Cr}(\text{phthal})_3]$ complexes, respectively, as a major species.

Untreated cellulose and CE-Cell appear to have no affinity for copper and chromium ions in the presence of phthalate: Absorption spectra of the solutions are identical before and after a prolonged contact. On the contrary, Am-Cell (0.1 g) immersed in the same metal solutions (10 mL, $10^{-2}M$) during

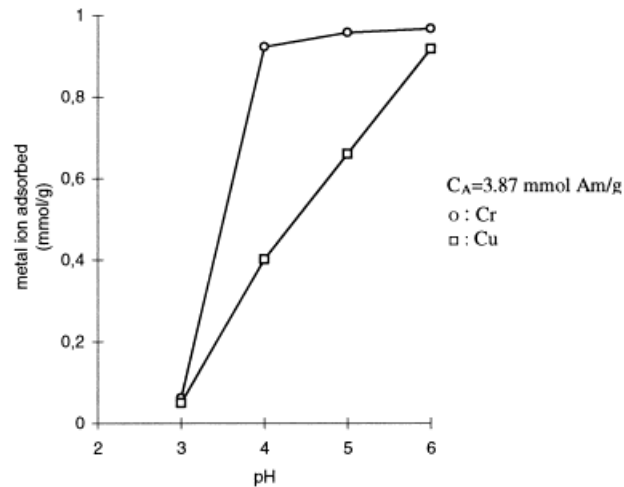


Figure 5 Effect of pH on the adsorbed amount of metal ions ($10^{-2}M$) on Am-Cell.

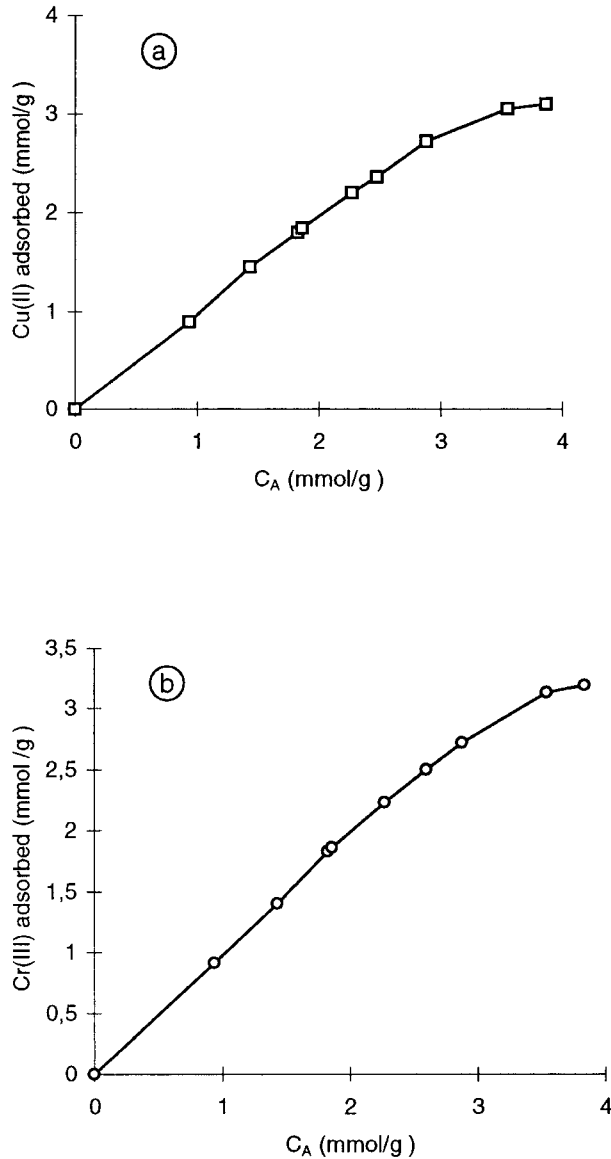


Figure 6 Variation of the quantity of metal ion adsorbed (mmol/g of support) with the content in amidoxime group C_A : (a) Cu(II); (b) Cr(III). Initial concentration of metal ion: $5.10^{-2}M$; pH 6.

24 h adsorbs almost all the heavy cations, as shown in Figure 3. This effect is attributed exclusively to the presence of amidoxime groups.

Factors Affecting the Adsorption of Metal Ions

Effect of Contact Time

Figure 4 shows that the amount of metal ions adsorbed per gram of substrate sharply increases during the first 5 h (92 and 98% of the total amount adsorbed for copper and chromium ions,

respectively); an equilibrium is reached after 24 h of immersion.

Effect of pH Value

Figure 5 shows the variation of the adsorbed amount of metal ions when the pH of the solution is adjusted at different values using buffer solutions. At pH 3, the capacity of Am-Cell is limited by the amino group protonation. However, in a weakly acidic solution, the adsorption of metal ions increases with the pH. Whatever the pH (3–6), Cr(III) ions are always more strongly adsorbed than are Cu(II) ions: In the case of pH 4, it is observed that the adsorption of Cr(III) ions is twice that of Cu(II) ions. In considering the Cu(II)

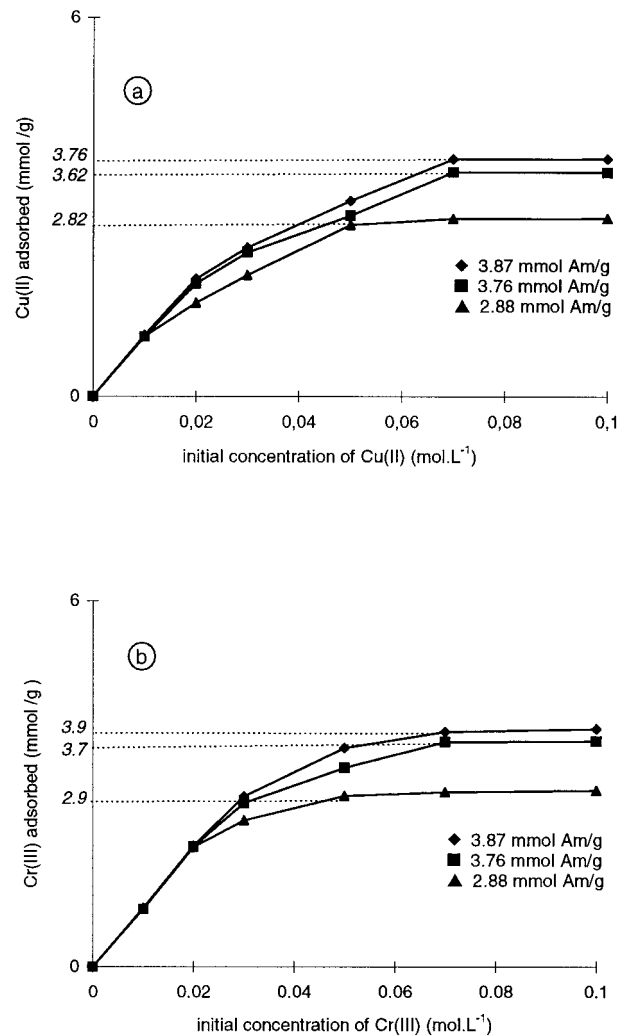


Figure 7 Variation of the quantity of metal ion adsorbed (mmol/g of support) with the initial concentration of metal ion: (a) Cu(II); (b) Cr(III).

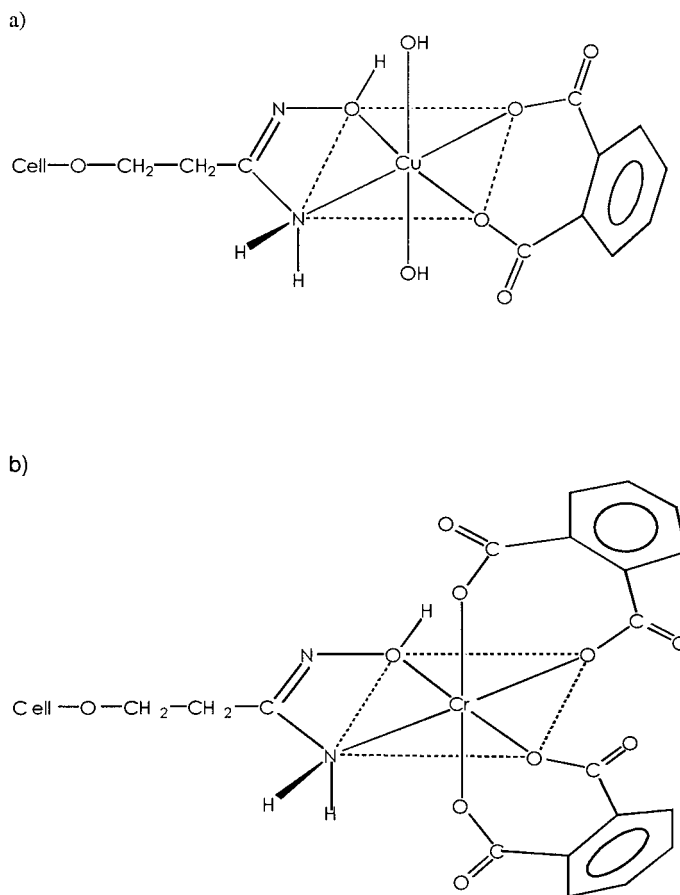


Figure 8 Octahedral complex formed among metal ion, Am-Cell, and phthalate ions: (a) Cu(II); (b) Cr(III).

and Cr(III) complex systems, the nature of the equilibria is quite different at pH 4 where the hexacoordination of Cr(III) is already completely satisfied. Under these conditions, the ternary species formed with Am-Cell is stabilized. The copper system is more labile and requires higher pH values to increase the adsorption capacity.

Effect of the Amidoxime Content

Figure 6 indicates the quantity of metal ions adsorbed by various supports when the amidoxime content C_A increases. The curves show a good concordance between adsorbed ions and amidoxime sites for both types of ions, corresponding to the saturation of the support: A straight line with a slope equal to 1 is observed up to $C_A = 3$ mmol/g. At higher values, a deviation appears due to a significant decrease in free ions and perhaps to a steric hindrance for the complexed ions to attain the fixing sites. Finally, the adsorption capacity of Am-Cell is uniquely dependent on

the C_A value. The DS value of CE-Cell used to prepare Am-Cell appears to have no influence, as reported previously.¹³

Effect of the Initial Metal Concentration

At pH 6, the adsorption is affected by the initial metal concentration as shown in Figure 7. When this concentration increases, the metal-ion uptake by the substrate from the solution increases strongly and then levels off when the quantity of metal ions present in the medium is almost equal to C_A . This plateau corresponds to the saturation of the support.

All these indications allow us to estimate the structure of the complexes: A 1/1 complex is generated between each ion and the support. It seems reasonable that copper and chromium with the amidoxime group lead to an octahedral geometry as shown in Figure 8, and the two coordinating sites are the two electron pairs of nitrogen and oxygen atoms.²⁵

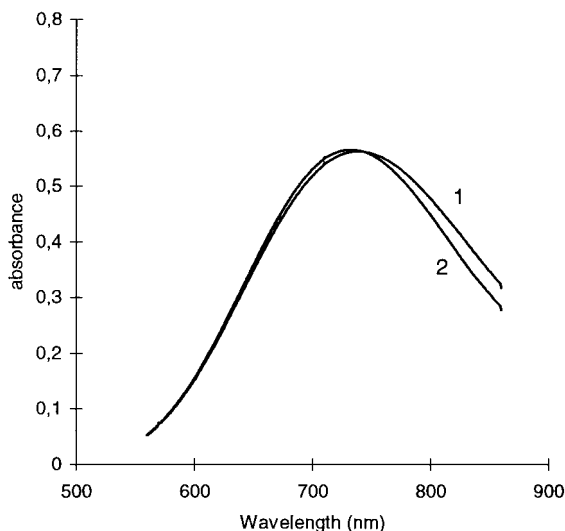


Figure 9 Absorbance of (1) Cu-EDTA solution and (2) filtrate after desorption.

Desorption and Readsorption of Metal Ions

When the adsorption is performed in the presence of EDTA, no fixation occurs onto Am-Cell due to the too high sequestering power of EDTA. Consequently, this strong ligand is able to desorb the metal ions from Am-Cell.

Cu(II) ions are easily desorbed when the support is stirred for 2–3 min at room temperature with the EDTA solution ($2 \cdot 10^{-2} M$). Figure 9 establishes the comparison between the absorbance of the initial solution containing $10^{-2} M$ Cu(II) and the absorbance of the filtrate after desorption. It is clear that all the copper ions are desorbed. The color of the support changes from green (Cu-Am-Cell) to white (Am-Cell). The renewed Am-Cell is then once again available for an eventual readsorption of copper: In a second adsorption cycle, the same efficiency is observed.

Cr(III) ions are desorbed in the same manner, but the treatment by EDTA requires 24 h. In this case, the filtrate is analyzed by atomic absorption since the color of the Cr-EDTA complex changes with time from green to violet. The amount desorbed corresponds to 90% of the adsorbed Cr(III).

CONCLUSIONS

Am-Cell is prepared by the reaction of cyano groups contained in CE-Cell with hydroxylamine. The ability of Am-Cell to adsorb metal ions increases with the concentration and tends to steady values because of the saturation of the

sites. At saturation, the Am-Cell forms a 1/1 chelate with metal ions such as Cu(II) and Cr(III). Desorption of Am-Cell is possible by the utilization of EDTA, and the regenerated support can be submitted to a new cycle.

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