

## Synthesis of Polyamidoxime Chelating Ligand from Polymer-Grafted Corn-Cob Cellulose for Metal Extraction

Md Lutfor Rahman, Nik Rohani Nik Mustapa, Mashitah Mohd Yusoff

Faculty of Industrial Sciences and Technology, University Malaysia Pahang, Gambang 26300, Kuantan, Pahang, Malaysia

Correspondence to: M. L. Rahman (E-mail: lutfor73@gmail.com)

**ABSTRACT:** A conventional free-radical initiating process was used to prepare graft copolymers from acrylonitrile (AN) with corn-cob cellulose with ceric ammonium nitrate (CAN) as an initiator. The optimum grafting was achieved with corn-cob cellulose (anhydroglucose unit, AGU), mineral acid ( $H_2SO_4$ ), CAN, and AN at concentrations of 0.133, 0.081, 0.0145, and 1.056 mol/L, respectively. Furthermore, the nitrile functional groups of the grafted copolymers were converted to amidoxime ligands with hydroxylamine under basic conditions of pH 11 with 4 h of stirring at 70°C. The purified acrylic polymer-grafted cellulose and polyamidoxime ligand were characterized by Fourier transform infrared spectroscopy and field emission scanning electron microscopy analysis. The ligand showed an excellent copper binding capacity (4.14 mmol/g) with a faster rate of adsorption (average exchange rate = 7 min), and it showed a good adsorption capacity for other metal ions as well. The metal-ion adsorption capacities of the ligand were pH-dependent in the following order:  $Cu^{2+} > Co^{2+} > Mn^{2+} > Cr^{3+} > Fe^{3+} > Zn^{2+} > Ni^{2+}$ . The metal-ion removal efficiency was very high; up to 99% was removed from the aqueous media at a low concentration. These new polymeric chelating ligands could be used to remove aforementioned toxic metal ions from industrial wastewater. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40833.

**KEYWORDS:** adsorption; cellulose and other wood products; grafting; resins

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### INTRODUCTION

Cellulose can be modified by the introduction of chelating/metal-binding functionalities in the cellulose backbone for the adsorption of toxic metal ions in various media. The chelating functional groups can be attached to the primary or secondary hydroxyl groups of cellulose through a variety of chemical reactions, including esterification, etherification, halogenation, and oxidation. An alternative method is the grafting of desired monomers to the cellulose backbone by either the direct introduction of a metal-binding ligand or the subsequent functionalization of these grafted polymer chains with known chelating moieties. The graft copolymerization reactions can be initiated by free-radical or ionic chemical groups.<sup>1,2</sup> Radical formation can occur on either the cellulose backbone or the monomer to be grafted; this induces homopolymerization of the monomer. Therefore, initiators creating radicals at various sites on the cellulose backbone are the choice for desired graft copolymerizations.<sup>3</sup> A number of redox-type initiators have been reported, however; ceric ion ( $Ce^{4+}$ ) has great importance because of its higher grafting efficiency. A serious disadvantage of natural polymers or biopolymers for long-term applications is the adsorption processes because of their biodegradable character. However, cellulose materials have been modified as grafted

copolymers that exhibit good chemical stability and mechanical strength and subsequent modification into known chelating ligands; this facilitates complex formation with a wide range of metal ions.

The wastewater treatment procedures are necessary to adapt with new technologies to meet the current regulatory limit on permissible discharge levels of various metals into the environmental. The contamination by toxic metal ions occur from the aqueous wastes of many industries, such as the metal plating industry, mining operations, tanneries, chloro alkali manufacturing, radiator manufacturing, smelting, alloy industries, and storage battery industries.<sup>4</sup> Various techniques have also been used for toxic-metal-ion removal, including precipitation, adsorption, ion exchange, and reverse osmosis for the prevention of environmental pollution.<sup>5</sup> So far, precipitation is the most applicable and is considered to be economical, but chemical coagulation induces secondary pollution caused by added chemical substances.<sup>6</sup> Toxic metal precipitation usually produces an intractable sludge that must be treated, and its disposal is often costly. To overcome this drawback, an effective treatment is essential for industrial effluents.

In this study, cellulose was extracted from corn-cob fibers, and we purified it for subsequent chemical modification by a



**Figure 1.** Physical appearance of the (a) corn cob, (b) corn-cob cellulose, (c) PAN-grafted corn-cob cellulose, and (d) polyamidoxime ligand. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

free-radical initiation method. The grafting of acrylonitrile (AN) onto corn-cob cellulose under various experimental conditions was performed to determine the optimum grafting parameters. A new polyamidoxime chelating ligand was synthesized from the corn-cob cellulose-*graft*-polyacrylonitrile (PAN), and this ligand was used for the metal-ion extraction from aqueous media.

## EXPERIMENTAL

### Materials and Methods

Corn cobs were obtained from Gambang Market, Pahang, Malaysia. To extract pure cellulose, the corn cobs [see image in Figure 1(a)] were cut to small sizes and washed with distilled water. The corn cob (100 g) was boiled with 10% NaOH (500 mL) for 2 h and washed with distilled water. The resulting product was boiled in glacial acetic acid (500 mL) for 1 h and washed with distilled water. The obtained corn-cob cellulose was bleached with hydrogen peroxide (300 mL) and 5% NaOH (300 mL). The cellulose was washed with distilled water (500 mL) several times and then methanol (500 mL) and oven dried at 50°C [see the physical appearance of corn-cob cellulose in Figure 1(b)]. AN monomer purchased from Aldrich, and the monomer was passed through columns filled with chromatographic-grade activated alumina to remove the inhibitor. Others chemicals, including ceric ammonium nitrate (CAN; Sigma-Aldrich), methanol (Merck), sulfuric acid (Lab Scan),

metal salts, and other analytical-grade reagents, were used without further purification.

### Graft Copolymerization

We prepared a cellulose slurry by stirring 6.00 g of corn-cob cellulose in 150 mL of distilled water overnight. The reaction was performed in a 250-mL, three-necked, round-bottomed flask fitted with a stirrer, condenser, and thermostated water bath. The N<sub>2</sub> gas was purged into the flask to remove oxygen during the grafting reaction. The reaction was maintained at 55°C, and 2.17 mL of diluted sulfuric acid (H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O = 1:1) was added to the mixture. After 5 min, 2.00 g of CAN in a 10-mL solution was added, and the reaction mixture was stirred under N<sub>2</sub> gas. After 20 min, 14 mL of the purified AN monomer was added to the cellulose suspension and stirred for 1 h period under nitrogen. When the reaction was completed, the mixture was cooled under running tap water. The product was precipitated out in an excess amount of methanol (500 mL) and washed several times with a methanolic solution (methanol/water = 4:1). The product was finally oven-dried at 50°C to obtain a constant weight.<sup>7</sup>

### Determination of the Grafting Fraction ( $G_f$ )

For the purpose of removing the homopolymer as PAN, the crude grafting product was purified with Soxhlet extraction method with dimethylformamide for 12 h. The purified grafted copolymer (cellulose-*graft*-PAN) was dried at 50°C to a constant weight [see the physical appearance of the graft copolymer in

Figure 1(c)]. The percentage grafting ( $G_p$ ) was determined with the following equation:

$$G_p = \frac{W_2}{W_1} \times 100 \quad (1)$$

where  $W_1$  is the weight of the parent polymer and  $W_2$  is the weight of the grafted polymer.

The  $G_p$  fractions for each monomer in the final graft copolymer was determined on the basis of the nitrogen content of the grafted samples determined with a Vario Marco Cube Elemental analyzer.  $G_p$  fractions of PAN onto corn-cob cellulose was calculated according to the following equation:<sup>8</sup>

$$G_f = \%N \left( \frac{W_2 \times 53}{W_1 \times 14} \right) \quad (2)$$

where 53 is the molecular weight of the repeating unit of PAN and 14 is the atomic mass of nitrogen.

### Synthesis of the Polyamidoxime Ligand

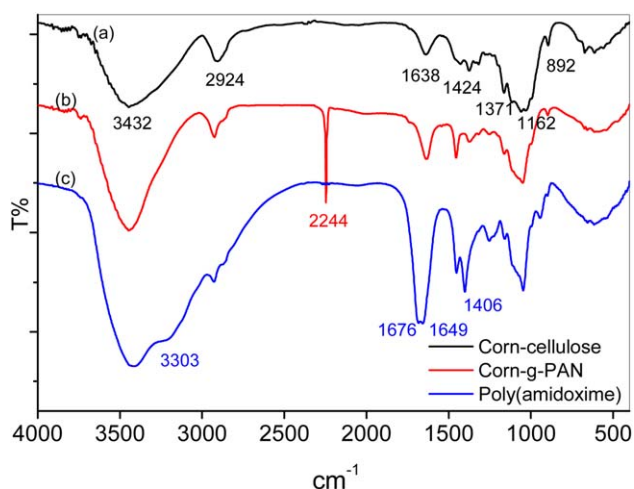
Exactly 20 g of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) was dissolved in 500 mL of methanolic solution (methanol/water = 4:1). The solution of  $\text{NH}_2\text{OH}$  was prepared according to our earlier study.<sup>8</sup> A 1-L, two-necked, round-bottomed flask was fitted with a stirrer, condenser, and thermostated water bath. Exactly 10 g of corn-cob cellulose-graft-PAN was added to the flask with a hydroxylamine solution, and the reaction was maintained at 70°C for 4 h. Therein, the hydroxylamine solution was decanted, and the polyamidoxime ligand was washed with a methanolic solution (methanol/water = 4:1). Then, the product was treated with 100 mL of methanolic solution having 0.1M HCl for about 5 min to convert the ligand into its hydrogen form.<sup>8,9</sup> The ligand was washed several times with a methanolic solution (methanol/water = 4:1) and dried at 50°C to a constant weight [see physical appearance of ligand in Figure 1(d)].

### Adsorption of the Metal Ions by the Batch Technique

A batch equilibration technique was used to determine the metal-ion binding capacity with various solutions with pHs ranging from 3 to 6. Exactly 0.1500 g of dried ligand was transferred into a series of plastic bottles, and equilibration of the ligand was performed with 10 mL of distilled water for 2 h. Then, 5 mL of a 0.1M sodium acetate buffer solution (pH 3–6) was added to each bottle for 1 h. Exactly 5 mL of a 0.1M metal-ion solution was added, and the mixture was shaken for 12 h with a mechanical shaker. After equilibration, 1 mL of the supernatant solution was pipetted out and diluted with distilled water for metal-ion determination by atomic absorption spectroscopy (PerkinElmer AAnalyst-800). The initial and final readings of the metal-ion concentration were calculated according to eq. (3):

$$q_e = \frac{(C_0 - C_e)V}{L} \times \frac{1}{M} \quad (3)$$

where  $q_e$  is the equilibrium adsorption amount (mmol/g),  $C_0$  is the initial concentration of the metal solution (mg/L),  $C_e$  is the equilibrium concentration of metal (mg/L),  $V$  is the volume of metal solution (L),  $L$  is the mass of the polymeric ligand (g), and  $M$  is the molecular weight of the specific metal.



**Figure 2.** FTIR spectra of the (a) corn-cob cellulose, (b) PAN-grafted corn-cob cellulose, and (c) polyamidoxime chelating ligand. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Adsorption of the Metal Ions at Lower Concentrations

A batch technique was used for metal-ion extraction with 10-ppm solutions at pH 6. Exactly 0.1500 g of dried ligand was added to 10 mL of water, 5 mL of a sodium acetate buffer solution, and 5 mL of 10 ppm each metal ions and shaken for 12 h. The metal-ion concentrations in the initial and final solutions were analyzed by inductively coupled plasma mass spectrometry (ICPMS) (Agilent 7500 series), and analysis was carried out according to eq. (3).

### Adsorption Kinetic Study

The adsorption rate of metal ions in the acetate buffer at pH 6 was determined by 0.1500 g of ligand in a 50-ppm metal solution for various time intervals, including 2, 5, 10, 20, 30, 60, and 90 min, and the metal-ion concentrations were estimated by atomic absorption spectroscopy. The residual metal concentration was determined with replicated experiments, and the final value deducted from the initial metal-ion concentration (50 ppm) was calculated according to eq. (4):

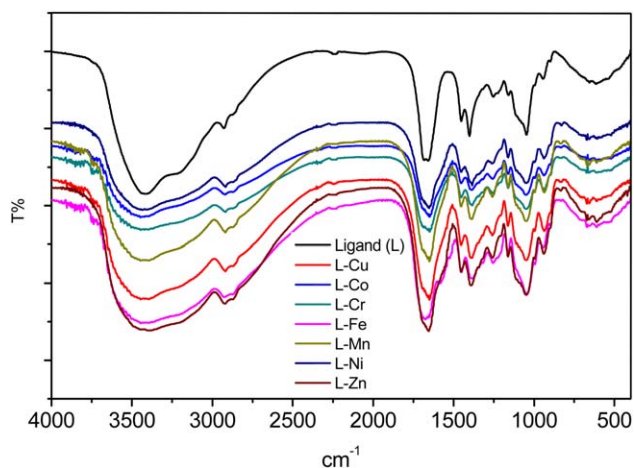
$$q_t = \frac{(C_0 - C_t)V}{L} \times \frac{1}{M} \quad (4)$$

where  $q_t$  is the adsorption amount at time  $t$  (mmol/g) and  $C_t$  is the metal concentration at time  $t$  (mg/L).

## RESULTS

### Fourier Transform Infrared (FTIR) Analysis

The corn-cob cellulose sample, purified grafted polymer, and synthesized chelating ligand were characterized by IR spectroscopy with a FTIR spectrometer (PerkinElmer 670). The IR spectrum of corn-cob cellulose showed the absorption bands at 3432 and 2924  $\text{cm}^{-1}$  for O—H and C—H stretching, respectively [Figure 2(a)]. A broad band at 1638  $\text{cm}^{-1}$  was attributed to the bending mode of the absorbed water, and a small peak at 1424  $\text{cm}^{-1}$  belonged to  $\text{CH}_2$  symmetric bending.<sup>10</sup> A small peak at 1371 and a broad band at 1162  $\text{cm}^{-1}$  showed C—O stretching. The C—O—C pyranose ring skeletal vibration gave a strong band at 1062  $\text{cm}^{-1}$ . A small sharp peak at 892  $\text{cm}^{-1}$  corresponded to the glycosidic  $\text{C}_1$ —H deformation with ring



**Figure 3.** FTIR spectra of the polyamidoxime ligand (top black line), and the metal–ligand complexes are shown in various color lines. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

vibration contributions and OH bending; this was characteristic of  $\alpha$ -glycosidic linkages between the glucose molecule in cellulose.<sup>10</sup>

The IR spectrum of the purified grafted cellulose (corn cob-g-PAN) exhibited a new absorption band at  $2244\text{ cm}^{-1}$ , which was attributed to the CN stretching of nitrile [Figure 2(b)] and other bands retained from corn-cob cellulose ( $3432, 2922, 1638, 1424, 1371, 1162, \text{ and } 892\text{ cm}^{-1}$ ). The amidoxime functional group from the polyamidoxime new absorption bands at  $1676$  and  $1649\text{ cm}^{-1}$  corresponded to the C=N stretching and N–H bending modes, respectively [Figure 1(c)]. In addition, a shoulder created at  $3303\text{ cm}^{-1}$  for N–H and OH stretching bands and  $1406\text{ cm}^{-1}$  for OH bending mode appeared [Figure 2(c)]. Clear evidence for the CN band at  $2244\text{ cm}^{-1}$  disappeared, and a new absorption band for the amidoxime group appeared; this confirmed the successful production of the amidoxime ligand from the corn-cob cellulose grafted copolymers.

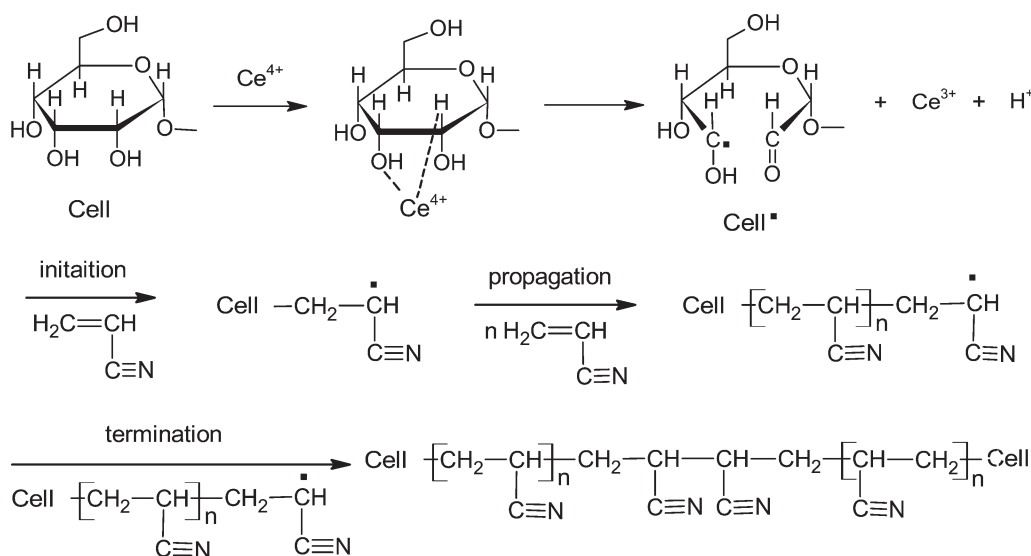
The IR spectra of the polyamidoxime ligand and the other metal–ligand complexes are shown in Figure 3. We clearly observed that the bands at  $3400\text{ cm}^{-1}$  for OH and  $3304\text{ cm}^{-1}$  for N–H stretching mode were affected for the metal–ligand complex. In addition, the bands  $1676$  and  $1649\text{ cm}^{-1}$  of the C=N stretching and N–H bending modes were also affected because of the metal–ligand complex ring formation; this was strong evidence that the adsorption occurred with metal ions on the polymeric ligand.

### Reaction Mechanism

The mechanism of grafting reactions for acrylic monomers with starch/cellulose materials with a free-radical initiation method is well known.<sup>11,12</sup> In this study, corn-cob cellulose was grafted with AN with a free-radical chain reaction in which ceric ion acted as the initiator (Scheme 1). The ceric(IV) ion formed a complex with the glucose units in the corn-cob cellulose, and the hydrogen atom was oxidized by the reduction of the  $\text{Ce}^{4+}$  ion to the  $\text{Ce}^{3+}$  ion.<sup>7</sup> Bond cleavage occurred on the glycol group of cellulose at the  $\text{C}_2$ – $\text{C}_3$  position and formed keto alcohol free radicals.<sup>8</sup> Therein, the cellulosic free radicals induced the initiation of the grafting reaction by the addition of the double bond of the AN monomer; this, thereby, resulted in the radical formation of the propagation reaction. The termination reaction of the growing polymer chain of the cellulose–monomer molecules produced in combination with the grafting reaction is shown in Scheme 7, although termination by disproportionation was also possible.<sup>13,14</sup>

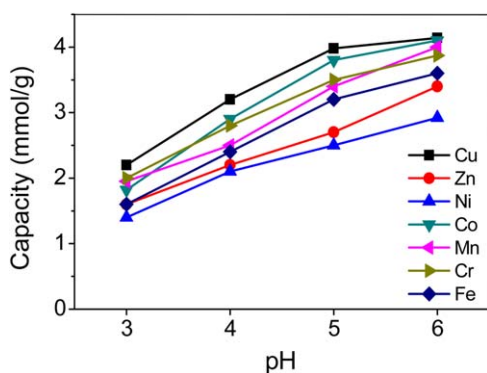
### Polyamidoxime Ligand

The corn-cob cellulose was grafted with the AN monomer with free-radical polymerization to form the cellulose-*graft*-PAN copolymer. The optimum reaction conditions of graft copolymerization were found to be for cellulose (anhydroglucose unit, AGU), mineral acid ( $\text{H}_2\text{SO}_4$ ), CAN, and AN at  $0.133, 0.081, 0.0145, \text{ and } 1.056\text{ mol/L}$ , respectively. The optimum reaction period and temperature for grafting were found to be  $50^\circ\text{C}$  and  $1\text{ h}$ , respectively. Subsequently, the copolymer was reacted with hydroxylamine for



**Scheme 1.** Graft copolymerization of AN onto corn-cob cellulose.





**Figure 5.** Metal-ion adsorption capacity by the ligand as a function of the pH. Other conditions: 0.1500 g of dried ligand, 10 mL of distilled water, 5 mL of 0.1M sodium acetate buffer solution at pH 3–6, 5 mL of 0.1M metal-ion solution, and shaking time = 12 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

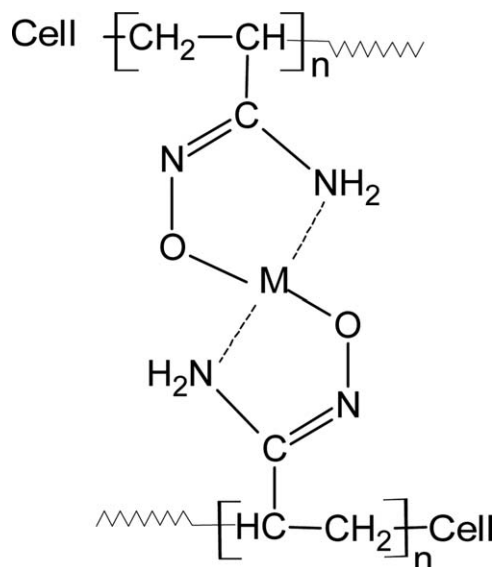
ions with the chelating ligand. The batch adsorption process was performed in a sodium acetate buffer solution at pH values ranging from 3 to 6. We observed that the metal-ion adsorption capacities for the selected metal ions were observed to increase the pH from 3 to 6. The chelating ligand showed a higher affinity toward some metal ions, including copper, cobalt, manganese, and chromium, compared to iron, nickel, and zinc (Figure 5). The binding capacities of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$  at pH 6 are given in Table II. We found that the metal-ion uptake by the ligand was pH-dependent. The adsorption capacity of the synthesized chelating ligands toward the metal ions was in the following order:  $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Cr}^{3+} > \text{Fe}^{3+} > \text{Ni}^{2+} > \text{Zn}^{2+}$ .

The complex formation of the amidoxime group with the metal ions resulted in a highly colored chelating ligand after batch equilibration with the metal ions. The color detection was mainly observed from the resin after absorption with some colored transition-metal ions. The amidoximate anions were bidentate ligands that trapped the metal ions and formed five-member ring complexes. The metal ions were bound to both

**Table II.** Adsorption of the Cellulose, Cellulose-g-Copolymer, and Polyamidoxime Ligand<sup>a</sup>

Metal ion	Adsorption capacity (mg/g)		
	Corn-cob cellulose	Cellulose-g-copolymer	Polyamidoxime ligand
Cr	8.15	1.54	215.26
Mn	0.88	0.07	225.24
Fe	8.25	0.03	223.38
Co	0.04	0.09	228.07
Ni	1.11	0.13	211.29
Cu	2.40	1.01	216.05
Zn	8.63	2.67	190.99

<sup>a</sup>0.1500 g of sample, 10 mL of distilled water, 5 mL of 0.1M sodium acetate buffer solution at pH 6, 5 mL of 0.1M metal-ion solution, and shaking time = 12 h.



**Figure 6.** Polymeric ligands with metal ions.

oxygen atoms and the amine group; the chelate complex is shown in Figure 6.

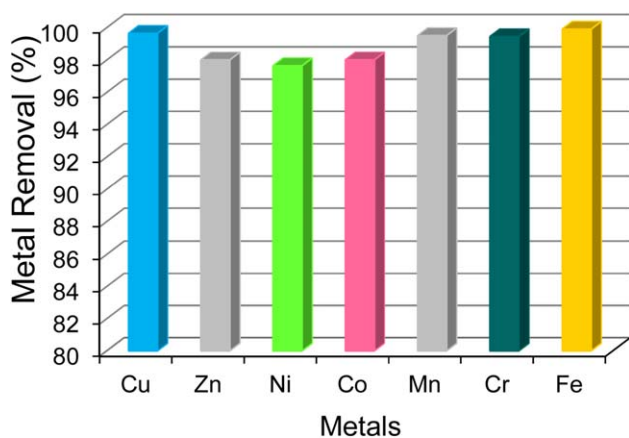
The binding properties of the cellulose, cellulose-*graft*-copolymer, and polyamidoxime ligand are listed in Table II. For comparison purposes, adsorption studies were carried out with metal ions at pH 6. It was found that metal-ion uptake by the ligand was excellent, whereas the corn-cob cellulose and cellulose-*graft*-copolymer showed a very negligible binding affinity to all of the metal ions (Table II). We also observed that the binding capacity with the cellulose grafting copolymer was lower than that of the corn-cob cellulose because the nitrile groups with the grafting materials were hydrophobic, and this gave more hindrance to the adsorption affinity.

#### Adsorption of the Metal Ions at Lower Concentrations

The effectiveness of the ligand was investigated with adsorption at a low concentration of metal ions (10 ppm). These extraction experiments were carried out in a sodium acetate buffer solution at pH 6 with the batch technique. The metal-ion binding by the ligand were also pH-dependent; however, the trend of metal-ion adsorption was slightly different with higher concentrations. We measured the percentage of metal-ion removal instead of metal-ion adsorption because most of the metals were bound fully in the 10-ppm metal solution. The removal percentages of copper, zinc, nickel, cobalt, manganese, chromium, and iron were 99.64, 98.01, 97.64, 98.00, 99.51, 99.44, and 99.90% at pH 6 using 10 ppm metal concentration (Figure 7). Therefore, we concluded that the low concentrations of metal ions resulted in highly efficient removals of nearly 100%; therefore, this ligand had an excellent ability to remove metal ions from water media.

#### Kinetics of Adsorption

The rates of adsorption of metals were investigated in buffer solution at pH 6. The time required for 50% exchange [average exchange rate ( $t_{1/2}$ )] was calculated from the plot of the metal-ion adsorption capacity (mmol/g) versus time (Figure 8). The



**Figure 7.** Metal-ion removal by the ligand at pH 6. Other conditions: 0.1500 g of dried ligand, 10 mL of distilled water, 5 mL of 0.1M sodium acetate buffer, 5 mL of 10-ppm metal-ion solution, and shaking time = 12 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

metal-ion adsorption was very fast; that is, the  $t_{1/2}$  values for copper, iron, zinc, chromium, nickel, cobalt, and manganese were 7, 9, 10, 7, 9, 7, and 7 min, respectively. This ligand had the advantage of a faster rate of equilibrium; therefore, toxic metal-ion removal was most favorable with the column technique.

## DISCUSSION

The modified cellulose adsorbent materials had a range of functional/ligand groups of the elements in groups V (nitrogen and phosphorus) and VI (oxygen and sulfur) of the periodic table. The ion or molecule possessing a pair of nonbonding electrons, where the binding metal could be defined as a ligand. In this study, a transition-metal-ion adsorption study was performed with a polymeric chelating ligand containing an amidoxime ligand. This ligand exhibited a high affinity to copper (4.14 mmol/g) at pH 6, and the uptake of other metals, such as manganese, chromium, and iron, were excellent at pH 6. In comparison with other cellulose-based adsorbents, our prepared ligand from corn-cob cellulose showed higher adsorption properties.

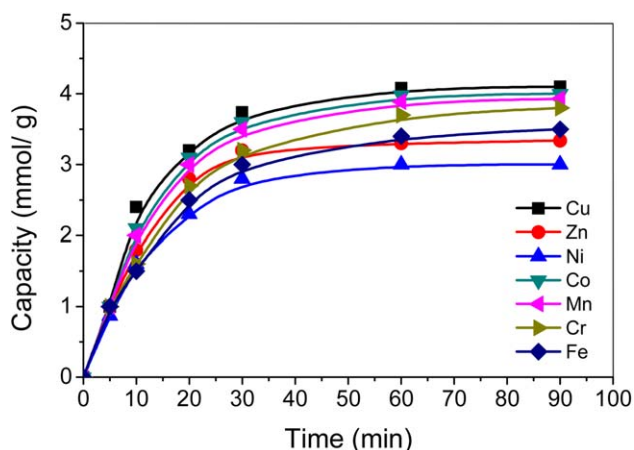
A spheroidal cellulose adsorbent was synthesized through a grafting reaction with AN, and it was converted into carboxyl groups on its surface. This modified cellulose adsorbent had carboxyl groups, which were used for the removal of Cu from aqueous solutions, with a bidentate complexation.<sup>15</sup> For example, the amidoxime group had a bidentate ligand, which lost a proton and a basic lone pair of electrons on the nitrogen to form a coordinate with the metal ions.<sup>7</sup> An imidazole was synthesized by a binding agent on a glycidyl methacrylate grafted cellulose adsorbent and imidazole having a five-membered ring containing two nitrogen atoms.<sup>16</sup> An important aspect of unsaturated nitrogen donors, such as imidazole, was the possibility of  $p$ -backbonding between it and the metal ion.<sup>17</sup>

Significant adsorption capabilities were achieved with the modified cellulose materials. Significant variations in the adsorption levels for each cationic species were observed; these depended

on the cellulose modification method, and the nature of the chelating or metal-binding ligands. The detailed mechanism of each adsorption process was difficult to recognize, but a number of fundamental interactions were conceivable, including ion exchange, complexation, coordination/chelation, electrostatic interactions, acid-base interactions, hydrogen bonding, hydrophobic interactions, physisorption, and possibly precipitation.<sup>18</sup> However, the nature of metals and the solution conditions, including pH, metal concentration, and solubility products, on the adsorption interactions were affected by the chemical and physical compositions of the modified cellulose.

A cellulose-based adsorbent containing thiosemicarbazide was prepared for the adsorption of heavy-metal ions.<sup>19</sup> Cellulose was grafted with the vinyl monomer glycidyl methacrylate with a chemical-initiating process, in which CAN was used as the initiator. The cellulose-grafted copolymer was functionalized further with thiosemicarbazide for the adsorption of  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  from aqueous solutions.<sup>20</sup> The maximum adsorption capacities achieved for  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  were 279.33 and 505.50 mg/g, respectively. The authors extended the cellulose-grafted copolymer further with  $\beta$ -CD ( $\beta$ -cyclic oligosaccharides) and quaternary ammonium groups to build the cellulose-*g*-GMA- $\beta$ -CDN<sup>+</sup> (GMA, glycidyl methacrylate and CDN<sup>+</sup>, cyclodextrin) adsorbent and the maximum adsorption capacity of  $\text{Cr}^{6+}$  reached to 61.05 mg/g. The adsorption-desorption tests of the cellulose derivatives showed the good reproducibility of the adsorbent, and the adsorbent could be reused for a minimum of five times.<sup>20</sup>

The cellulose-based mercaptobenzothiazole was reported for the adsorption of  $\text{Hg}^{2+}$  with a high adsorption capacity of 204.08 mg/g with the column method, and potassium thiocyanate was used a valuable reagent for the desorption of  $\text{Hg}^{2+}$ .<sup>21</sup> Microwave-induced emulsion copolymerization was conducted for the acrylic monomer ethylacrylate and guar gum. The copolymer sample was used to take up the cadmium ions, and the authors claimed that the adsorbent exhibited a high



**Figure 8.** Rate of exchange of metal ions as a function of time (min). Other conditions: 0.1500 g of dried ligand, 10 mL of distilled water, 5 mL of 0.1M sodium acetate buffer, and 5 mL of 0.1M metal-ion solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

reusability and could be successfully recycled for nine cycles, in which 38% adsorption was feasible in the ninth cycle.<sup>22</sup>

A new adsorbent was synthesized from the graft copolymerization of glycidyl methacrylate onto zirconium oxide-densified cellulose in the presence of *N,N'*-methylene bisacrylamide as a crosslinker with tannin-modified poly(glycidyl methacrylate)-grafted zirconium oxide-densified cellulose.<sup>23</sup> The optimum pH for maximum adsorption was found to be 5.5 with 99.2% removal at an initial concentration of 10 mg/L. The maximum adsorption capacity was found to be 96.7 mg/g for the complete removal of Th<sup>4+</sup> from simulated seawater; this was possible with an adsorbent dosage of 3.0 g/L.

Zheng et al.<sup>24</sup> described the adsorption of cadmium ions from an aqueous solution with acrylonitrile–modified corn stalk, and the results show that acrylonitrile–modified corn stalk was an effective adsorbent for the removal of Cd<sup>2+</sup> ions and showed a maximum uptake of 12.73 mg/g compared to raw corn stalk with a maximum uptake of 3.39 mg/g. Recently, the same research group reported the corn stalk modified by graft copolymerization (AGCS–cell) with a different procedure, and the results show that AGCS–cell had a better adsorption potential for cadmium ions than the unmodified cellulose, and the adsorption capacity was 21.37 mg/g; this reflected the feasibility of using AGCS–cell as an adsorbent to remove cadmium ions.<sup>25</sup>

## CONCLUSIONS

A polyamidoxime chelating ligand was successfully synthesized from PAN-grafted corn-cob cellulose, a waste material. The polymeric ligand demonstrated an excellent adsorption capacity toward certain transition-metal ions (Cu, Co, Mn, Cr, Fe, Zn, and Ni), and this was found to be pH-dependent. The rate of adsorption equilibrium was very fast; therefore, the column technique would be useful for heavy-metal extraction. The low-cost production of the corn-cob-cellulose-based polyamidoxime ligand could be considered a promising candidate for wastewater treatment because the metal-ion removal efficiency was up to 99% from aqueous media at a low concentration of metal ions. The reusability test of the polymeric ligand was performed, and the removal of industrial effluents containing heavy metals by the ligand will also be carried out for a future publication.

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