Poly(amidoxime) from Polymer-Grafted *Khaya* Cellulose: An Excellent Medium for the Removal of Transition Metal Cations from Aqueous Solution

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A free radical chain initiation reaction was exploited to prepare poly(acrylonitrile)-grafted *Khaya* cellulose. The synthesis of the poly(amidoxime) ligand was also performed using oximation reactions. Transition metal cations formed some complexes with the polymeric ligand. The pH of the solution played an important role in the optical detection of Cu^{2+} ions. The highest absorbance (approximately 94%) of the $[Cu\text{-ligand}]^{n+}$ complex was at pH 6. The sorption quantity increased with increasing Cu^{2+} ion concentration, which was reflected by a broad peak at 600 nm that was attributed to the charge transfer (π-π transition) process. The equilibrium sorption capacity of 282 mg/g, with faster adsorption rates ($t_{1/2}$ = 8 min), suggested that copper possessed excellent adsorption capacity compared with the other cations (Fe^{3+}, Co^{3+}, Cr^{3+}, Ni^{2+}, and Zn^{2+}). The sorption data for all of the cations followed the Freundlich isotherm model, with a high coefficient of determination, reflecting a heterogeneous sorption process by the cellulose-based, poly(amidoxime) adsorbent. The feasibility for recycling of adsorbent was evaluated by the sorption/desorption study, and the results suggest that a new type adsorbent can be reused in seven cycles without any significant loss in its original sensing and removal performances.

Keywords: Khaya cellulose; Poly(amidoxime) ligand; Transition metal cations; Free radical initiation; Adsorption

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INTRODUCTION

Cellulose is the most abundantly available non-branched biopolymer, consisting of a ß-O-glucopyranose linkage between the monomers of glucose (Nada *et al*. 2007; Chowdhury *et al.* 2014). The degree of polymerization of the lignocellulosic backbone is significantly affected by the type of treatment. Vigilant selection of the reaction conditions can transform the lignocellulosic biomass into valuable forms to prepare adsorbent materials for heavy metal uptake (Chowdhury *et al.* 2016a). Because of its renewable nature, cellulose can promote the cost-effective technologies of ion exchange (Nada *et al*. 2006; Sokker *et al*. 2006) and hydrogel preparation (Kawabara *et al.* 1996; Chauhan *et al.* 2005). Furthermore, cellulose and its derivatives are widely used for metal ion absorption (Murguttim *et al.* 2000; Nada *et al.* 2003). Cellulose, after grafting, can be used as an efficient ion exchanger because of its chemical resistance and substantial hydrophilic surface area (Nada *et al.* 2007). The grafting process is comparatively easier to integrate because of the active functional groups on the backbone of a polymer chain and their absorption of metal ions. Grafting copolymerization of monomers onto cellulose, starch, and chitosan has been conducted for metal ion absorption and enzyme immobilization by Chauhan and Lai (2003). Previously, acrylamide and acrylic acid monomers have been grafted onto the cellulose backbone (Nada *et al.* 1998; Gitisudhe *et al.* 2005). Different types of functional groups, such as carboxymethyl and amines, can be incorporated with cellulose to bind metallic cations by chemical or physical adsorption (Nada and El-Wakeel 2006). Grafting acrylamide onto cellulose was investigated using ceric ammonium nitrate as the initiator, and the grafted cellulose was applied for sorption studies using Cu, Cr, Ni, and Pb ions from aqueous streams (Nada *et al.* 2007). The initiator generated radicals on the cellulose backbone that were highly reactive, and the ceric ion (Ce^{4+}) exhibited a profound effect on the initiator because of its high efficiency in grafting (Narayanan and Mahesh 2009). Subsequently, grafted copolymers have been converted into polymeric chelating ligands that can be applied to remove toxic metal ions from wastewater (Gürdag *et al.* 1997).

Pollution of aquatic streams by heavy metals causes severe environmental problems because of their toxic and carcinogenic effects (Mance 1987; Nriagu and Pacyna 1988; Liu *et al.* 2008; Chowdhury *et al.* 2016b). Heavy metals are commonly discharged into the environment from mining activities, fossil fuels, battery manufacturing, automobile emissions (Ozay *et al.* 2009), metal plating, or electric device fabrication (Denizli *et al.* 2005). To eliminate metallic cations from wastewater, numerous conventional techniques including chemical precipitation, ion exchange, reverse osmosis, membrane separation, electrochemical treatments, and solvent extraction have been extensively applied (Akkaya and Ulusoy 2008; Jang *et al.* 2008; Zhao and Mitomo 2008). Activated carbon adsorption of toxic metal ion-containing waste, followed by precipitation, improved metal ion removal considerably (Narayanan and Mahesh 2009).

Despite considerable benefits, chemical coagulation often induces secondary pollution by added chemical substances (Narayanan and Mahesh 2009), and the sludge produced incurs a high disposal cost (Narayanan and Mahesh 2009; Yong *et al.* 2012). Thus, these techniques are oftentimes costly and ineffective, particularly in removing heavy metal ions at lower concentrations (Laus and de Fávere 2011).

In this context, cellulose, starch, or chitosan are widely used to prepare adsorbents (Chen *et al.* 2008; Li *et al.* 2009; Tripathy *et al.* 2009; Liu *et al.* 2010; Zheng *et al.* 2010; Wang *et al.* 2011; Xu *et al.* 2011). These naturally occurring biomacromolecules are abundantly available, biodegradable, and environmentally friendly (Irani *et al.* 2011; Miretzky and Muñoz 2011). In this report, cellulose-based polymeric ligands were synthesized as an adsorbent material. Pure white cellulose was extracted from *Khaya* fibre using a conventional method and grafted with acrylonitrile monomers. The grafting of acrylonitrile onto *Khaya* cellulose was investigated under various experimental conditions, and the characteristics of the grafting parameters were determined. A novel poly(amidoxime) chelating ligand was synthesized from *Khaya* cellulose-graft-poly(acrylonitrile) (PAN) and tested for its ability to remove transition metal ions (Cu^{2+}, Fe^{3+}, Co^{3+}, Cr^{3+}, Ni^{2+}, and Zn^{2+}) from wastewater. This polymer ligand prepared from acrylic polymer grafted with hardwood (*Khaya*) cellulose, which is very stable in aqueous acid condition for regenerated the ligands for recycling purpose. This novel adsorbent exhibits an additional characteristic that it can be reused in seven cycles without any significant loss of removal performances.

EXPERIMENTAL

Materials

Raw *Khaya* (mahogany) wood dust was obtained from a local saw mill in Kuantan, Pahang, Malaysia. *Khaya* raw dust (100 g) was treated with 17% NaOH (800 mL) and boiled for 8 h to remove lignin and hemicellulose. The sample was filtered and washed with distilled water. The filter cake was boiled with glacial acetic acid (800 mL) for 2 h. The resultant suspension was filtered and washed with distilled water. Because the cellulose that was extracted exhibited a dark colour, it was further bleached with hydrogen peroxide (300 mL) and 7.0% NaOH (500 mL) for 4 h, washed with distilled water (500 mL) repeatedly, and dried in an oven at 50 °C. The acrylonitrile monomer (Sigma-Aldrich, Germany), was passed through a column filled with chromatography-grade activated alumina to remove inhibitors. Ceric ammonium nitrate (CAN) (Sigma-Aldrich, Germany), methanol (Merck, Germany), sulphuric acid (Lab Scan, Thailand), transition metal salts, and other analytical-grade reagents were used without modifications.

Methods

Characterization

Changes in the morphology of *Khaya* cellulose, PAN-grafted cellulose, poly(amidoxime) ligand, and poly(amidoxime) ligand after the adsorption of Cu^{2+} cations were observed using a scanning electron microscope (SEM; JEOL JSM-7800F, UK). All five samples were placed over black carbon tape before capturing the image. The high resolution transmission electron microscopic images (HR-TEM) of the poly(amidoxime) ligand after adsorption of Cu^{2+} cations were taken using a Hitachi HR-TEM instrument (HT-7700, Hitachi, Japan). Changes in the chemical functional groups of the ligand were verified using infrared spectroscopy. The Fourier transform infrared (FT-IR) spectra of *Khaya* cellulose, poly(acrylonitrile)-grafted *Khaya* cellulose, and poly(amidoxime) chelating ligand were recorded using a spectrometer (PerkinElmer, Waltham, MA, USA). The FT-IR spectra were recorded in the range of 500 to 4000 cm^{-1}.

Graft copolymerization

The grafting process was carried out in a 1.0-L, three-neck round bottom flask fitted with a magnetic stirrer and condenser. The flask was placed in a thermostat-controlled water bath using N_2 gas flow with constant stirring. About 3.0 g of extracted *Khaya* cellulose was added to 300 mL of distilled water. The reaction mixture was heated to 55 °C, and then 1.1 mL of sulphuric acid (50%) was added. After 5 min, 0.90 g of CAN (10 mL solution) was added, and the reaction was maintained for 20 min. A total of 12 mL of purified acrylonitrile was added to the cellulose suspension and stirred for 4 h. After the reaction was complete, the mixture was cooled, and methanol was added to precipitate the product. The product was filtered and washed several times with a mixture of methanol and water (4:1 v/v). The product was oven-dried at 50 °C to obtain a constant weight (Yong *et al.* 2012).

Grafting fractions determination

The grafted product was weighed, and the homo-polymer was purified using a

Soxhlet extractor with dimethylformaldehyde (DMF) DMF for 12 h. The purified, grafted copolymer was dried at 50 °C to a constant weight. The grafting percentage (*Gp*) was calculated using Eq. 1,

$$Gp(\%) = \frac{W_2}{W_1} \times 100 \tag{1}$$

where W_1 is the weight of parent polymer (cellulose) and W_2 is the weight of the grafted polymer, poly(acrylonitrile).

Synthesis of poly(amidoxime) ligand

Twenty grams of hydroxylamine hydrochloride (NH_2OH HCl) was dissolved in 500 mL of a methanol/water (4:1) mixture. Approximately 50% of NaOH was added to the cold solution, which was filtered to remove NaCl precipitates. The pH was adjusted to 11 by the addition of NaOH. Thus, the prepared hydroxylamine solution was added to the flask containing poly(acrylonitrile)-grafted *Khaya* cellulose (9.0 g), and the reaction was maintained at 70 °C for 6 h (Lutfor *et al.* 2001; Yong *et al.* 2012). After the reaction was run to completion, the mixture was filtered to separate out the chelated polymeric ligand and washed with methanol/water (4:1) solution. The ligand was treated with 100 mL of 0.1 M HCl in methanolic solution for 5 min. Finally, the ligand was filtered and washed several times with methanol and dried at 50 °C until a constant weight was observed.

Optical sensing of copper (II) ion

Preliminary screening studies showed that there were higher removal efficiencies of Cu^{2+} cations than other transition metal cations (Zn^{2+}, Ni^{+2}, Co^{3+}, Cr^{3+}, and Fe^{3+}). Thus, the optical sensing capacity of the prepared ligand was confirmed using Cu^{2+} ions. Briefly, 150 mg of polymer ligand was added to each of the 10 mL buffer solutions within the pH range of 2 to 9 (0.1 M sodium acetate with acetic acid). Cu^{2+} (5.0 mg/L) was added to each of the solutions, which were placed in a controlled shaker machine (SI-600, Lab Companion, Europe). The shaking process was conducted at 30 °C for 2 h at a constant agitation speed of 180 rpm to ensure good colour separation. To optimize the colour, 150 mg of polymeric ligand was immersed in 10 mL of acetate buffer at pH 6, and 10 mL of Cu^{2+} ion solution (5, 10, or 20 mg/L) concentration was added. The mixture was maintained in a shaker machine for 2 h for good colour separation. A blank was also taken for comparison and detection, following the same procedure (Awual *et al.* 2013; Awual *et al.* 2014). After equilibration was reached, the ligand was separated by filtration and dried at 50 °C for 2 h. The optical colour assessment and absorbance were measured by solid-state UV-Vis nuclear infrared resonance (NIR) spectroscopy (UV-2600, Shimadzu, Japan).

Batch adsorption

First, 150 mg of polymeric ligand was immersed in 10 mL of the individual 0.1 M metal ion solutions (Cu^{2+}, Fe^{3+}, Co^{3+}, Cr^{3+}, Ni^{2+}, and Zn^{2+}). Next, 10 mL of sodium acetate buffer (pH 3 to 6) was added and maintained in a shaker machine for 2 h at 180 rpm. After equilibration was reached, the ligand was separated by filtration, and the residual metal ion concentrations were determination by inductively coupled plasma optical emission spectrometry, ICP-OES (Optima 8300, PerkinElmer, Waltham, MA, USA). The initial and final readings (after adsorption) of the metal ion concentrations were calculated according to Eq. 2 (Chowdhury *et al.* 2012a,b, 2015),

$$q_e = \frac{(C_0 - C_e)V}{L} \tag{2}$$

where q_e is the equilibrium adsorption amount (mg·g^{-1}), C_0 is the initial concentration of the metal solution (mg/L), C_e is the equilibrium concentration of the metal solution after adsorption (mg/ L), V is the volume of the metal solution (L), and L is the mass of polymeric ligand (g). The initial and final level (after adsorption) of the metals solutions were analysed by ICP-OES and calculated using Eq. 2.

For the isotherm experiments, batch adsorption experiments (Cu^{2+}, Fe^{3+}, Co^{3+}, Cr^{3+}, and Ni^{2+}) were performed using the traditional bottle-point method at 30 °C in a shaker machine, at the above mentioned conditions, with an initial concentration of metal ions ranging from 5 to 1300 mg/L. The initial and final metal solutions were analysed by ICP-MS, according to Eq. 2.

Kinetic study

The sorption kinetics study was carried out as follows. First, 150 mg of ligand was immersed into 10 mL of each metal ion solution (0.1 M), and 10 mL of acetate buffer was added to the shaking bath (maintained at pH 6), with a speed of 180 rpm at various time intervals (2, 5, 10, 20, 30, 60, and 120 min).

The metal ion concentrations were estimated by ICP-OES (Optima 8300, Perkin Elmer, Waltham, MA, USA).

RESULTS AND DISCUSSION

Characterization

The infrared spectrum of *Khaya* cellulose is illustrated in Fig. 1a. Absorption bands at 3432, 2924, and 1162 cm^{-1} were attributed to O-H, C-H, and C-O stretching vibrations, respectively. The characteristic bands observed at 1636, 1423, and 1371 cm^{-1} were assigned to the bending mode of absorbed water (Chuan *et al*. 2006), CH_2 symmetric bending, and O-H bending, respectively. A strong band was observed at 1050 cm^{-1} as a result of C-O-C pyranose ring skeletal vibration.

The α-glycosidic linkages between the glucose units of cellulose were confirmed by a sharp peak at 890 cm^{-1}, which corresponded to the glycosidic C_1-H deformation, with ring vibration and OH bending (Chuan *et al*. 2006). A new absorption band at 2244 cm^{-1} appeared for poly(acrylonitrile)-grafted *Khaya* cellulose, which was assigned to the -CN stretching of acrylonitrile in cellulose (Fig. 1b). This reflected that the graft copolymerization of *Khaya* cellulose had successfully taken place. The band at 2244 cm^{-1}, attributed to CN stretching of acrylonitrile, disappeared, and new stretching bands appeared at 3306 cm^{-1} and 1409 cm^{-1} for N-H bending modes, confirming the formation of the amidoxime group in the poly(amidoxime) ligand (Fig. 1c). Furthermore, the absorption bands at 1646 and 1648 cm^{-1}, corresponding to C=N stretching vibrations, reflected the presence of amidoxime functional groups.

In addition, a shoulder peak, observed at 3306 cm^{-1}, was attributed to both N-H and -OH stretching vibrations. The peak at 1409 cm^{-1} in the poly(amidoxime) ligand (Fig. 1c) showed -OH bending vibration. Thus, the results obtained from the infrared studies confirmed the formation of targeted amidoxime ligand on the poly(acrylonitrile)-grafted

Khaya cellulose.

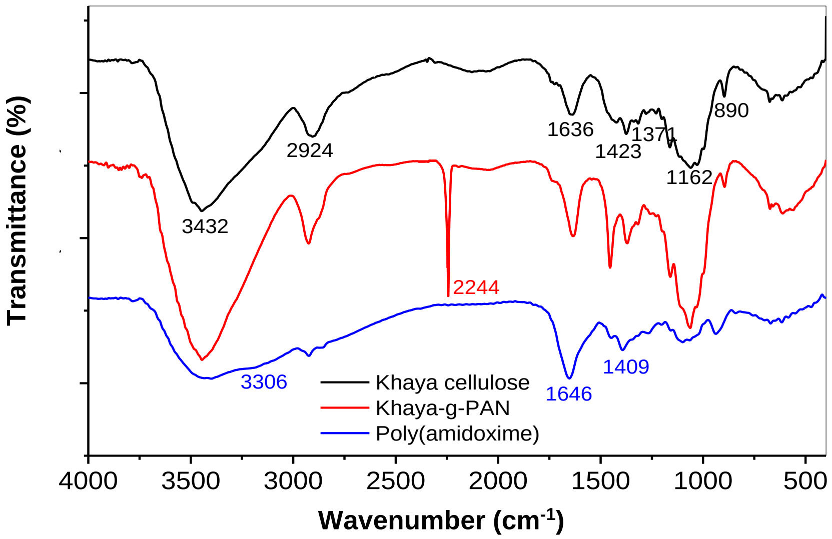

Fig. 1. Fourier transform infrared spectra of (a) *Khaya* cellulose, (b) poly(acrylonitrile)-grafted *Khaya* cellulose, and (c) poly(amidoxime)-chelated ligand

Khaya cellulose exhibited well-shaped, timber-like morphologies without impurities (Fig. 2a). The SEM micrographs of poly(acrylonitrile)-grafted *Khaya* cellulose (Fig. 2b) showed a rough surface surrounding the timber, which confirmed PAN grafting onto the surface of *Khaya* cellulose. The PAN-grafted *Khaya* cellulose surface was enlarged (Fig. 2c). Compared to the PAN-grafted surface, the poly(amidoxime) ligand contained distinct spherical particles with smaller diameters (Fig. 2d). After adsorption, the SEM micrograph showed spherical beads with a compact surface (Fig. 2e). This result provided primary evidence of adsorption by the polymeric ligand from the *Khaya* cellulose material. The HR-TEM was measured, and the nano-scale micrograph (Fig. 3f) showed agglomerate of copper ions (5 nm average size) distributed over the surface.

Graft Copolymerization

Grafting of acrylic monomers with starch or cellulose has been reported where the mechanism of grafting is free radical initiation reactions (Hall and Llewellyn 1956; Agrawal 1979). Recently, an alternative reaction pathway of cellulose units, with primarily -OH groups, has been proposed (O'Connell *et al.* 2006). In this mechanism, metal ions generate free radicals with the oxygen atoms from cellulose molecules, which consequently react with vinyl or acrylic monomers (O'Connell *et al.* 2006). The graft copolymerization of acrylonitrile onto *Khaya* cellulose is presented in Fig. 4.

Isothermal nitrogen adsorption–desorption method can be applied for the analysis of textural properties of the synthesized poly(hydroxamic) acid ligand. The pure poly(hydroxamic) acid ligand shows a typical isotherm of type II with H3 hysteresis loop (Fig. 3). A slow rise in adsorption at relative pressures of 0.5 to 0.9 and a rapid increase in adsorption at relative pressures of 0.9 to 0.99 corresponded to the capillary nitrogen condensation in the polymer ligand (Fig. 3). The BET surface areas, pore volumes, and average pore diameters were 110.5 m^{2}g^{-1}, 0.55 cm^3 g^{-1}, and 10.5 nm, respectively. It was found that the surface area of this polymer ligand is less than the reported materials.

However, the polymer ligand is quite eligible to perform as a promising adsorbent due to it's the high density of functional groups with ligand-metals complexation system.

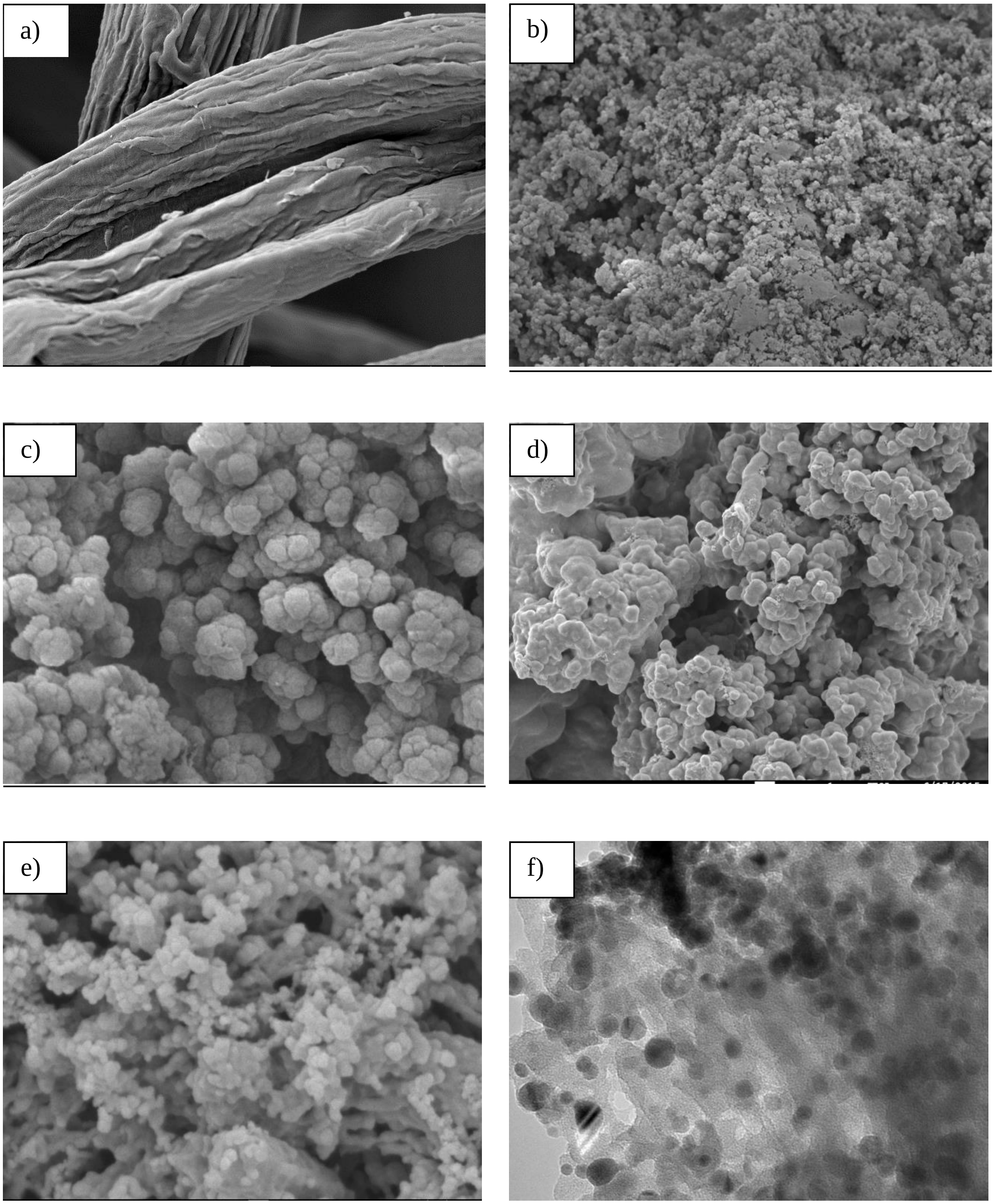

Fig. 2. Field emission scanning electron microscopic (FE-SEM) images of (a) *Khaya* cellulose, (b) PAN-grafted cellulose, (c) an enlarged view of PAN-grafted cellulose, (d) poly(amidoxime) ligand, (e) poly(amidoxime) ligand after adsorption of Cu^{2+}, and a (f) HR-TEM micrograph of the poly(amidoxime) ligand after adsorption of Cu^{2+}

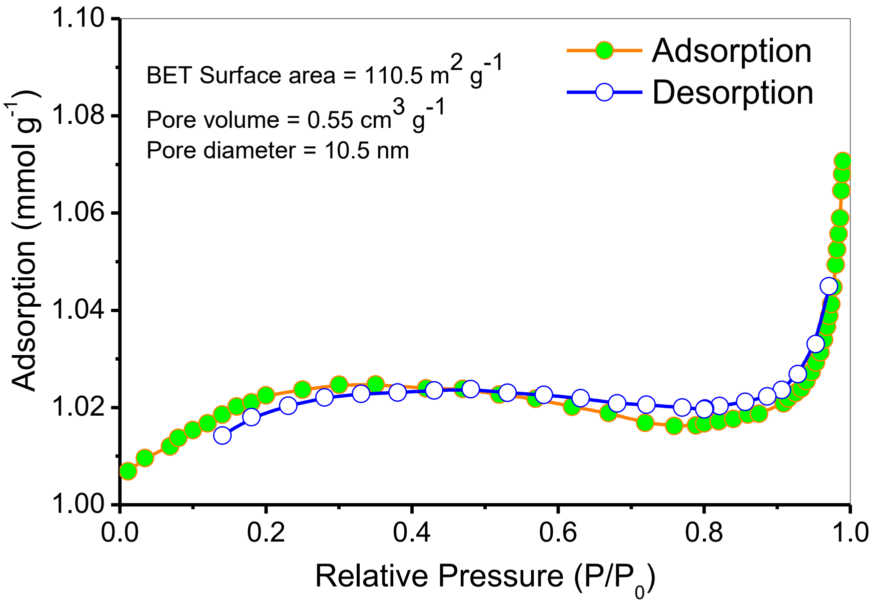

Fig. 3. Nitrogen adsorption–desorption isotherms of poly(hydroxamic acid) ligand

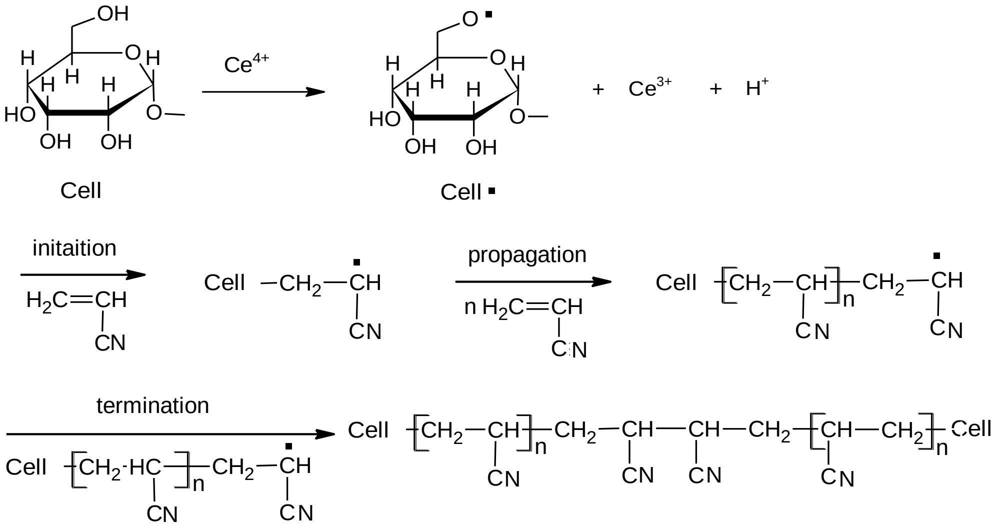

Fig. 4. Graft copolymerization of acrylonitrile onto *Khaya* cellulose (Cell • is a glucose unit of cellulose)

In the present study, the Ce^{4+} ion was used as an initiator for free radical chain reactions of *Khaya* cellulose grafting with acrylonitrile. The -OH groups on the glucose units of cellulose react with ceric (IV) ions to form complexes. The hydrogen atoms are oxidized by the reduction of Ce^{4+} to Ce^{3+} ion, thus, generating free radicals of cellulose units that undergo addition reactions with acrylonitrile, inducing the initiation reaction of grafting. Thus, free radicals that propagate the reactions are generated. The termination reaction of the growing polymer chain of the cellulose-monomer results in the combination of grafting (Fig. 4) (Lutfor *et al.* 2014).

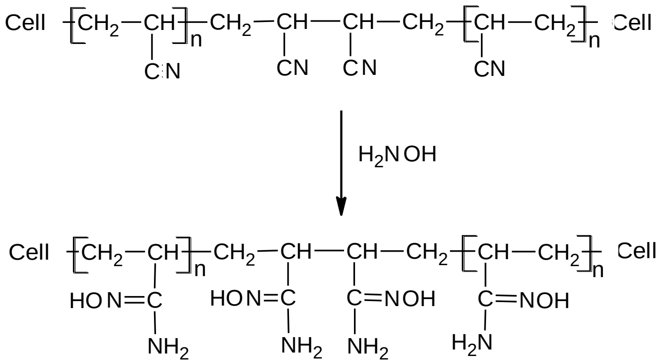

Fig. 5. *Khaya* cellulose-g-PAN conversion into the poly(amidoxime) ligand

Poly(amidoxime) Ligand Formation

The graft copolymerization of *Khaya* cellulose with acrylonitrile by free radical polymerization yielded the *Khaya* cellulose-graft-poly(acrylonitrile) copolymer. A grafted copolymer was synthesized, containing a reactive nitrile group. This nitrile group reacted with hydroxylamine to form the polymeric chelating ligand, consisting of poly(amidoxime) functional groups, by Beckmann- or Lossen-type rearrangement (Fig. 5). Optimization of the amidoximation process was conducted according to previous work (Lutfor *et al.* 2014). The optimized reaction was obtained at 70 °C for 4 h, with a pH of 11 and a methanol to water ratio of 4:1. The optimized reaction parameters for concentration of the cellulose (AGU), mineral acid (H_2SO_4), ceric ammonium nitrate (CAN), and acrylonitrile (AN) were obtained at 0.040, 0.032, 0.0035 and 0.805 mol L^{-1}, respectively. The ligand was treated with a 0.1 M HCl solution to obtain the H-form of the ligand. Physical and chemical properties of the poly(amidoxime) ligand are summarized in Table 1.

Table 1. Physical and Chemical Properties of Poly(amidoxime) Ligand

Percentage of grafting (Gp)	135
Swelling capacity (%)	10
Average exchange rate ($t_{1/2}$ min)	8
Highest adsorption capacity Cu^{2+} (mg/g)	236.4

Optical Detection of Cu^{2+} Ions

Effect of solution pH

The pH of the solution played an important role in the selective optical detection of metal ions (Awual *et al.* 2013, 2014). The effect of solution pH was more pronounced when the ligand was used for sensing the Cu^{2+} ions. Thus, a wide range of pH was used for examining the reflectance spectra of the [Cu-ligand]$^{n+}$ complex. The adsorption process of Cu^{2+} ions by the prepared poly(amidoxime) ligand was sufficient to achieve good color separation (or signal) between Cu^{2+} ion-containing samples and the blank solution (Fig. 6). The ligand exhibited a strong optical color intensity and signal response for Cu^{2+} ions, with the highest absorbance of 94% at pH 6. Thus, the ligand had high functionality and affinity towards Cu^{2+} ions at pH 6. This result confirms that pH played a key role in the selectivity of targeted metal ions by ligand-supported adsorbent materials (Awual *et al.* 2013; Awual *et al*. 2014).

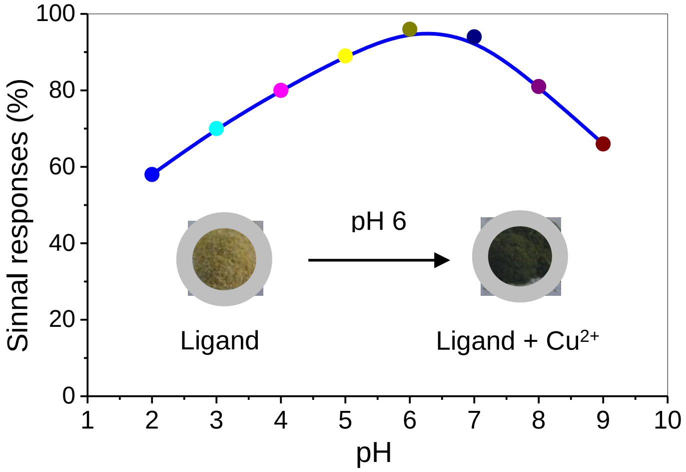

Fig. 6. Effect of solution pH on Cu^{2+} ion sensing by the poly(amidoxime) ligand with different pH solutions. Experimental conditions: 5 mg/L Cu^{2+}, 30 °C, 20 mL volume, and 2 h

Visual inspection of the Cu^{2+} ions showed that the adsorbent poly(amidoxime) ligand exhibited excellent physical and textural properties. The reflectance spectra of Cu^{2+} ions at different concentration levels are presented in the Fig. 7. As the Cu^{2+} ion concentration increased from 0 to 10 ppm, the reflectance also increased under the same experimental conditions. The poly(amidoxime) ligand in the blank solution (0 ppm Cu^{2+} ions) did not show any peak near 600 nm. A broad peak at 680 nm was observed when the poly(amidoxime) ligand absorbed Cu^{2+} ions from the solution. The formation of this new peak was attributed to the formation of a ligand charge transfer (π–π transition) complex, when Cu^{2+} ions were added to the ligand. This method is advantageous for the sensitive determination in ultra-trace concentrations of Cu^{2+} cations without sophisticated instruments (Awual *et al.* 2013; 2014).

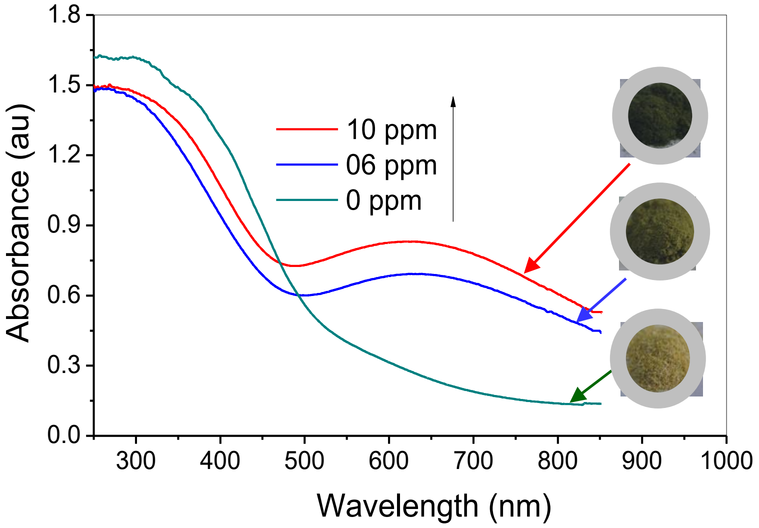

Fig. 7. The reflectance spectra for colour optimization with increasing concentrations of Cu(II) ions at pH 6

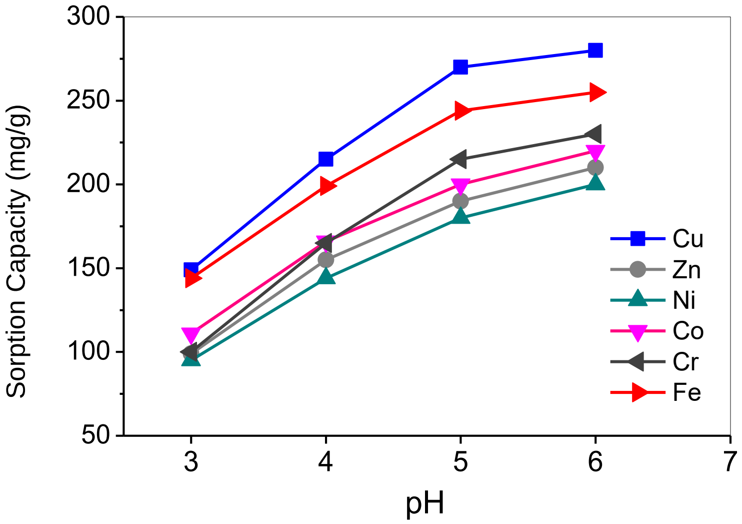

Fig. 8. Metal ion adsorption capacity by the ligand as a function of pH. Experimental conditions: 150 mg of dried ligand, 10 mL of 0.1 M sodium acetate buffer solution, pH 3 to 6, and 10 mL of 0.1 M metal ion solution, shaken for 2 h

Effect of pH on the removal of various transition metal ions

The effect of pH on the adsorption behavior of various metal ions by the poly(amidoxime) ligand was evaluated over a pH range of 3 to 6 (Fig. 8). A sodium acetate buffer solution was used to maintain the solution pH. The binding capacities of Cu^{2+}, Fe^{3+}, Cr^{3+}, Co^{3+}, Zn^{2+}, and Ni^{2+} were 282, 254, 229, 221, 211, and 202 mg/g, respectively, at pH 6. The adsorption capacity of the synthesized ligand towards the metal ions followed this order: $Cu^{2+} > Fe^{3+} > Cr^{3+} > Co^{3+} > Zn^{2+} > Ni^{2+}$. Hence, the ligand exhibited a clearly higher affinity towards the Cu^{2+} ion; however, the adsorption of iron, cobalt, and chromium by the ligand at pH 6 was also satisfactory. The trend in the curve showed that the adsorption of the metal ions increased with increasing pH. Thus, the synthesized *Khaya* cellulose-based poly(amidoxime) ligand functioned as an adsorbent, forming complexes with the metal ions that prompted their subsequent removal from wastewater (Lutfor *et al*. 2001; Yong *et al*. 2012; Awual *et al.* 2013; Lutfor *et al.* 2014).

The amidoxime group of the ligand formed complexes with the metal ions after the batch equilibrium process, yielding an intensely-coloured solution. The poly(amidoxime) ligand, with amidoximate anions, acted as a bidentate ligand. The metal ion formed a bond with oxygen atoms, and the amine group formed five-membered ring complexes, as illustrated by Fig. 9. Eigen and Tamm (1962) proposed the mechanism of chelate formation, which considers a first step, diffusion controlled, with the formation of an electrostatic ion pair between the metal and the ligand and a subsequent step where a water molecule leaves the coordination sphere and is replaced by a ligand one. The second step is slower, its rate depending on the energy of the metal-ligand bond. This mechanism is generally referred to as the Eigen–Wilkins mechanism (Eigen and Wilkins 1965). The rate-determining step is the loss of the first water molecules with the formation of the monodentate complex, while ring closure is most commonly rapid (Wilkins 1964). The second step clarifies the fundamental role played by the solvent. Indeed, in this slow step the breaking of the $M\text{-}OH_2$ bond occurs and, therefore, this stage must have many characteristics in common with the solvent exchange process in the metal coordination sphere. The variation is found for the logarithm of K_{H2O} with the number of d electrons in different metal ions (Helm and Merbach 1999). It can be clearly seen that Cr^{3+} and Co^{3+} ions are the weak, while ion Cu^{2+} are the most reactive and attains maximum sorption capacity. The rate constant is dependent on the H_2O exchange process on the number of d electrons in different cations (Beccia *et al*. 2011). In this study, identical hydroxamic acid ligand supported by copolymers is involved in chelation process and also ligand exhibit highest affinity towards d electrons of Cu^{2+} ion (Fig. 8).

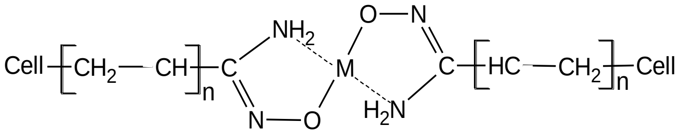

Fig. 9. Polymeric ligand with metal ions

Previously, a modified, spheroidal cellulose adsorbent was prepared through a grafting reaction with acrylonitrile and subsequent conversion into a polymeric ligand containing active carboxyl groups on its surface; the polymeric ligand efficiently bound copper ions and formed bidentate complexes (Liu *et al.* 2002). The cellulosic material was wood pulp, which was modified into the ligand form by esterification with citric acid to introduce carboxyl groups on its surface (Low *et al.* 2004). In this case, the carboxyl and hydroxyl groups of the wood surface formed bonds with the Cu^{2+} and Pb^{2+} ions, thereby initiating their removal from aqueous solution.

The modified cellulose adsorbent material consisted of functional groups belonging to group V (nitrogen) and VI (oxygen) of the periodic table, and these have tendencies to bind metallic cations and thus acts like a ligand. The modified material thus acts like a ligand, as a ligand consists of ions or molecules possessing non-bonding electron pairs that could bind metal ions. In the present study, a polymeric chelating ligand containing amidoxime functional units over modified cellulose was synthesized and used as an adsorbent of metal ions. The ligand showed the highest affinity for copper (236.4 mg/g) at pH 6. The nitrogen of amino groups consisted of a lone pair of electrons, which formed a covalent bond with metal ions, resulting in a metal complex.

Comparative Removal Percentages of Transition Metal Ions at Low Concentrations

The concentration of the metal ions was maintained at 10 ppm to ascertain the effectiveness of the poly(amidoxime) ligand. Because the metal binding by the ligand is pH dependent, metal ions were extracted at pH 6 using a sodium acetate buffer solution and the batch technique. However, the trend in metal ion adsorption at low concentrations was slightly different than at higher concentrations.

As most of the metals were bound successfully at the 10 ppm concentration level, the percentage of metal ion removal was measured instead of metal ion adsorption. At 10 ppm and pH 6, the percentage removal of Cu^{2+}, Zn^{2+} , Ni^{+2} , Co^{3+}, Cr^{3+}, and Fe^{3+} was 99.9, 97.0, 98.1, 99.2, 98.5, and 99.9%, respectively (Fig. 10). Thus, it was evident that the metal ions were removed from water at low concentrations. This data confirmed that the newly developed ligand was a good adsorbent. Because of the lower removal efficiencies of Zn^{2+} cations, equilibrium kinetics and isotherm studies were conducted for Cu^{2+}, Ni^{+2} , Co^{3+}, Cr^{3+}, and Fe^{3+} only.

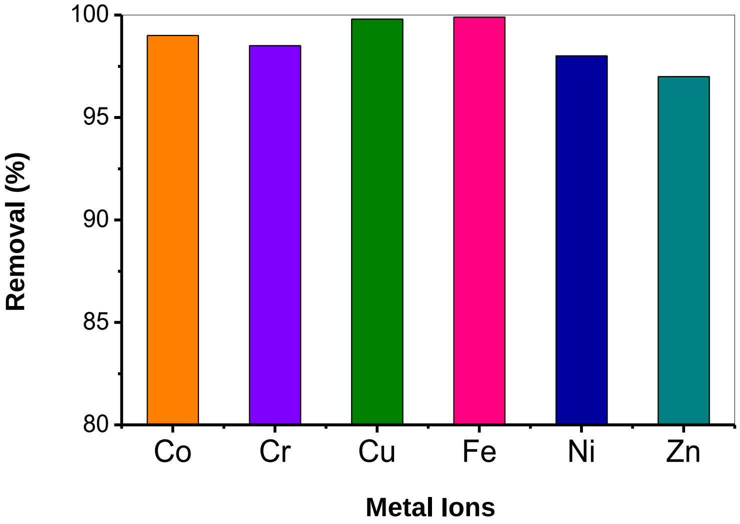

Fig. 10. Metal ion removal by the ligand at pH 6. Experimental conditions: 0.1500 g of dried ligand, 10 mL of distilled water, 5 mL of 0.1 M sodium acetate buffer, 5 mL of 10 ppm metal ion solution, shaking for 12 h

Kinetics of Adsorption

A series of batch experiments determined the equilibrium contact time between the metal ions (Cu^{2+}, Fe^{3+}, Co^{3+}, Cr^{3+}, Ni^{2+}, and Zn^{2+}) and the polymeric ligand. Various metal ions were studied in a buffer solution (pH 6) to determine the rate of adsorption. The time required for 50% exchange ($t_{1/2}$) was calculated from the plot of the metal ion adsorption capacity (mg/g) *versus* time (Fig. 11). The $t_{1/2}$ for Fe^{3+}, Cu^{2+}, Cr^{3+}, Co^{3+}, and Ni^{2+} was 7, 7.5, 8, 8, and 8.5 min, respectively; the adsorption rate of metal ions was very fast. Thus, the ligand had the advantage of achieving a faster rate of equilibrium, and hence, it was more promising to eliminate toxic metal ions using the column technique.

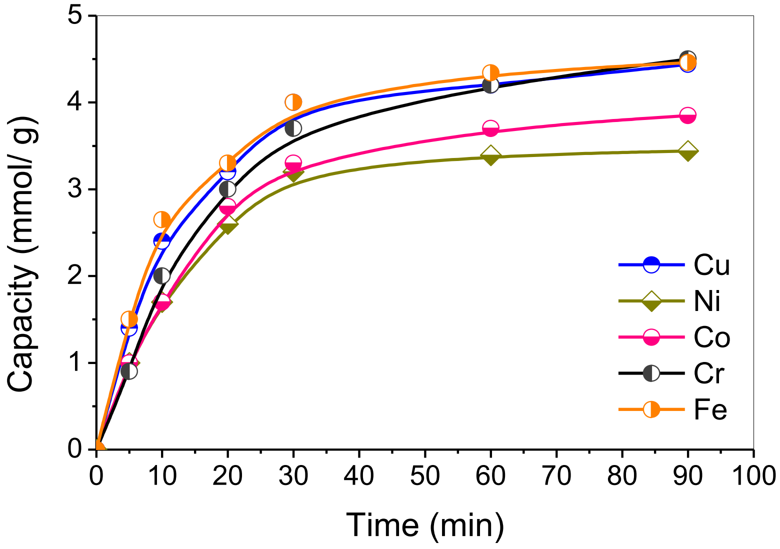

Fig. 11. Rate of exchange of metal ions ($t_{1/2}$) as a function of time (min). Experimental conditions: 0.1500 g of dried ligand, 10 mL of 0.1 M sodium acetate buffer, and 10 mL of 0.1 M metal ion solution

Sorption Isotherms

The effect of metal ion concentration on the adsorption capacity and the sorption isotherm provided useful information about metal uptake by the adsorbent. Various concentrations of Cu^{2+}, Fe^{3+}, Co^{3+}, Cr^{3+}, and Ni^{2+} were adsorbed by a cellulose-based poly(amidoxime) ligand. The initial metal ion concentration was increased from 5 to 1400 mg/L, while the ligand ratio, pH, and agitation period were kept constant. The results showed that the adsorption capacity increased with increasing ion concentration up to the maximum adsorption capacity (Fig. 12).

The equilibrium data of the adsorption from aqueous media was investigated by the Langmuir and Freundlich isotherm model (Chowdhury *et al.* 2012a, b). The Langmuir isotherm model uses the assumptions of a monolayer adsorption and a certain number of identical active sites (active sites distributed evenly on the surface of the adsorbent), assuming zero interaction between the adsorbents. The linear form of the Langmuir isotherm equation is given by Eq. 4 (Hamid *et al.* 2014),

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} \mathrm{K_L}} + \frac{1}{q_{\max}} C_e \tag{4}$$

where q_e is the adsorption capacity (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/ L), q_m represents the maximum adsorption capacity of adsorbents (mg/ g), and K_L is the Langmuir adsorption constant (L/mg).

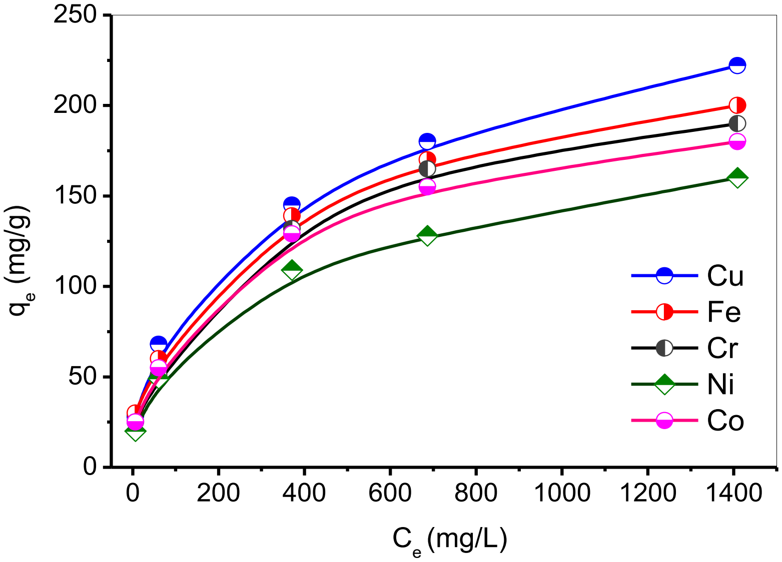

Fig. 12. Effect of the initial concentration of transition metal ions on the adsorption capacity of the polymeric ligand. Experimental conditions: initial metal ion concentration range of 5 to 1400 mg/L, sample dose of 150 mg/20 mL, solution pH of 6, 32 °C, and a contact time of 2 h

The regression of C_e/q_e against C_e was plotted according to the Langmuir sorption isotherm model (linear regression), as presented in Fig. 13. The values of q_m and K_L were calculated from the slope and the intercept of the linear plot of C_e/q_e and C_e. The calculated data for the maximum sorption capacity (q_m) and the sorption coefficient (K_L) are presented in Table 2. The R^2 values (< 0.97) suggested that the Langmuir isotherm model was less appropriate for metal ion sorption onto the ligand.

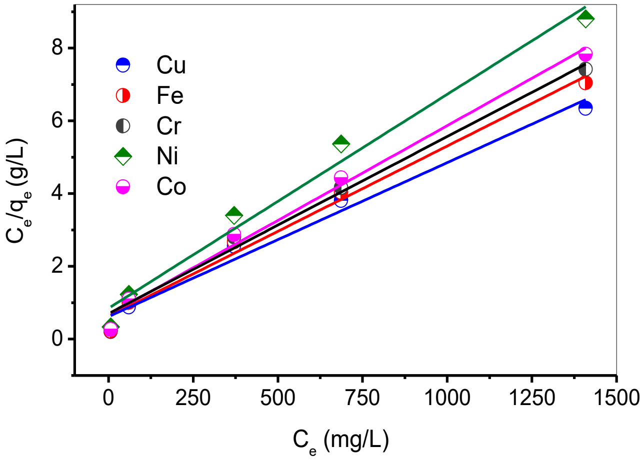

Fig. 13. Langmuir adsorption isotherms of metal ions, and the linear form of the Langmuir plot. Experimental conditions: initial metal ion concentration ranging from 5 to 1400 mg/L, sample dose of 150 mg/20 mL, solution pH of 6, 32 °C, and a contact time of 2 h

Table 2. Comparison of the Langmuir and the Freundlich Models for Transition Metal Ion Adsorption onto the Poly(Amidoxime) Ligand

Adsorbate	Langmuir				Freundlich		
	q_m (mg/g)	K_L (L/mg)	R^2		*n*	K_F (mg/g)	R^2
Cu	236.4	0.0068	0.974		2.700	13.010	0.997
Fe	213.2	0.0075	0.983		2.698	15.632	0.989
Co	191.9	0.0079	0.987		2.595	18.550	0.989
Cr	205.3	0.0069	0.983		2.491	10.456	0.983
Ni	170.0	0.0067	0.977		2.525	12.356	0.994

The Freundlich isotherm, which is best known for its suitability for quantifying adsorption on heterogeneous surfaces (Wang *et al.* 2015), is described by Eq. 5,

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{5}$$

where K_F and *n* are the adsorption capacity and the adsorption strength, respectively. Figure 14 shows a corresponding plot of the data.

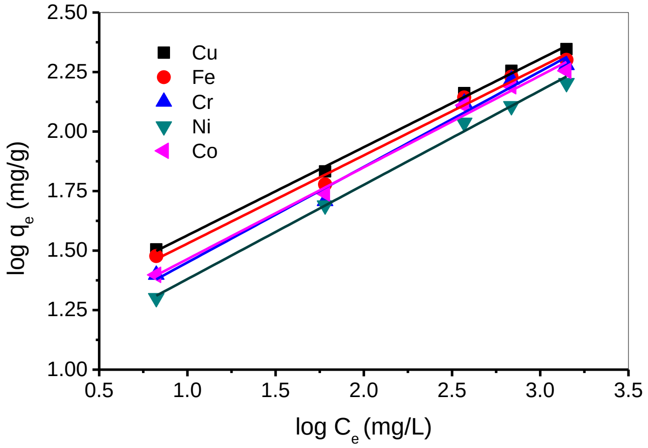

Fig. 14. Freundlich isotherms for the adsorption of metal ions. Experimental conditions: initial metal ions concentration ranging from 5 to 1400 mg/L, sample dose of 150 mg/20 mL, solution pH of 6, 32 °C, and a contact time of 2 h

The values of K_F (mg/g) and n were calculated from the intercept and the slope of the linear plot of log q_e *versus* log C_e (Fig. 14). K_F and n were calculated for all of the metal ions (Table 2). The Freundlich equation provided a better correlation coefficient ($R^2 > 0.99$), signifying a manifestation of a multilayer adsorption process for the studied transition metals.

Elution and Reusability Studies

The reuse and regeneration of the ligand is an important factor from the point of view of cost effectiveness and feasibility of the process for practical application. Hence, in the present study to ensure the reusability of the ligand, elution and regeneration of the ligand was studied by conducting the elution experiments after removal/sorption. The leaching of metal ions from the ligand is possible at acidic conditions since sorption was very low at pH 3. Thus, complete extraction of metal ions from ligand can be achieved below pH zero. Therefore, use of 2 M HCl solution provided sufficient extraction of the adsorbed Cu^{2+} ion from the adsorbent (polymeric ligand). Thereafter the adsorbent was regenerated (completely free from metal ions) by rinsing with water and buffer solution of pH 6 after every elution experiment, and the polymeric ligand was reused. The reusability was ensured by examining the sorption/elution process for seven cycles. The sorption was conducted by stirring 150 mg of ligand with 10 mL of 0.1 M Cu^{2+} solution at pH 6 for 2 h. Desorption was carried out by 2 M HCl solution with 20 mL solution. The sorption/removal and extraction efficiencies are decreased only by 8% after 7 cycles as shown in the Fig. 15. This suggests that, the synthesized polymeric ligand can be reused for removal of metal ions in many cycles without any significant loss in its content. Particularly, poly(amidoxime) ligand showed high structural ability which promotes the application of removal of Cu^{2+} ion from environmental wastewater effluents.

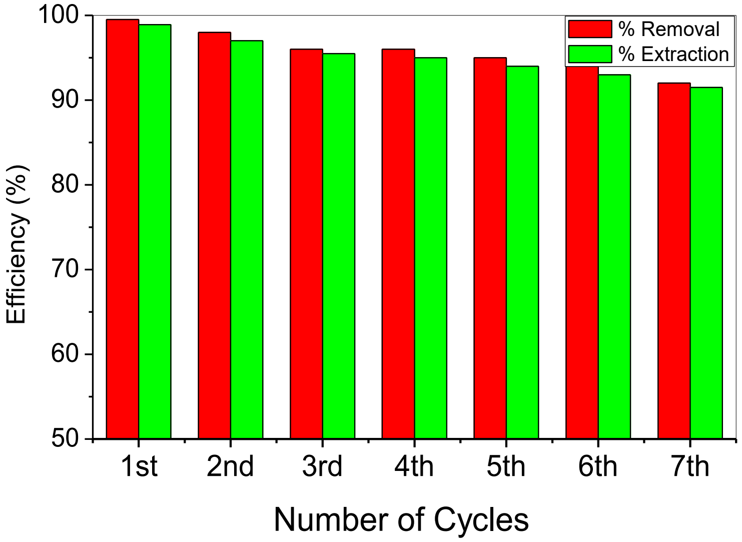

Fig. 15. Reusability studies of the ligand in several cycles of sorption/removal-extraction

It was evident that the comprehensive adsorption capacities were improved by the modified cellulose material. The extent of adsorption for cationic species varied according to the nature of the chelating agent or ligand and the overall cellulose modification method. A detailed explanation of the mechanism of the adsorption process is complicated because of the chemical and physical composition of the modified cellulose, the nature of the metal ions, and solution conditions, such as pH, metal ion concentration, and adsorbent dosage, all of which considerably affect the adsorption process. The phenomenon has been explained on the basis of various fundamental interactions, including ion exchange, complex formation, co-ordination/chelation, electrostatic interactions, acid-base interactions, hydrogen bonding, hydrophobic interactions, physi-sorption, and possibly precipitation at higher pH (Lee *et al.* 2001).

Compared with other cellulose-based adsorbents, the ligand prepared from *Khaya* cellulose demonstrated a higher adsorption capacity for Cu^{2+} cations (Table 3). Comparison of the adsorption capacities shows that the *Khaya*-based amidoxime ligand has higher adsorption efficiency for several metal ions.

Table 3. Adsorption Capacities of Cellulose-Based Materials for Metal Ions

Adsorbent Material	Modifier	Metal Ion	Adsorption Capacity (mg/g)	Reference
Cellulose	Sodium hydroxide (carboxyl)	Cu^{2+}	70.5	Liu *et al.* 2002
Cellulose	Glycidyl methacrylate	Cu^{2+}	68.5	O'Connell *et al.* 2006
Cellulose	Mercaptobenzothiozole	Hg^{2+}	204.08	Santhana *et al.* 2013
Wood pulp	Citric acid	Cu^{2+}	24.0	Low *et al.* 2004
Cellulose	Glycidylmethacrylate	Th^{4+}	96.7	Thayyath *et al.* 2011
Guar Gum	Ethylacrylate	Cd^{2+}	270.27	Vadana *et al.* 2009
Chitosan	Tripolyphosphate	Cu^{2+}	200.00	Lee *et al.* 2001
Cellulose	Poly(amidoxime) ligand	Cu^{2+}	236.4	This study

CONCLUSIONS

1. A poly(amidoxime) ligand was successfully synthesized from poly(acrylonitrile)-grafted *Khaya* cellulose.
2. The chelation behaviour of the ligand towards some transition metal ions was excellent. Its adsorption capacity for Cu, Fe, Zn, Ni, and Cr ions was pH-dependent.
3. The rate of equilibrium was very fast; therefore, the column technique would be the most efficient method for heavy metal extraction. The medium-cost of production for this *Khaya* cellulose-based poly(amidoxime) ligand makes it an excellent candidate for wastewater treatment, as metal ion removal was highly efficient.
4. According to the batch adsorption isothermal study, transition metal ion sorption onto the ligand exhibited excellent agreement with the Freundlich isotherm model, which suggested that the cellulose-based adsorbent surface was heterogeneous.
5. The utility of adsorbent was evaluated and the results suggest that a new type adsorbent can be reused in seven cycles without any significant loss in its original sensing and removal performances.

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