Synthesis of Poly(hydroxamic acid) Ligand from Polymer Grafted Khaya Cellulose for Transition Metals Extraction

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Abstract: A cellulose-graft-poly(methyl acrylate) was synthesized by free radical initiating process and the ester functional groups were converted into the hydroxamic acid ligand. The intermediate and final products are characterized by FT-IR, FE-SEM, HR-TEM and XPS technique. The pH of the solution acts as a key factor in achieving optical color signals of metal-complexation. The reflectance spectra of the $[Cu-ligand]^{n+}$ complex was found to be a highest absorbance at 99.8 % at pH 6 and it was increased upon increasing of Cu^{2+} ion concentrations and a broad peak at 700 nm was observed which indicated the charge transfer (π-π transition) metals-Cu complex. The adsorption capacity of copper was found to be superior (336 mg g^{-1}) rather than other transition metals such as Fe^{3+}, Co^{3+}, Cr^{3+}, Ni^{2+}, Mn^{2+} and Zn^{2+} were 310, 295, 288, 250, 248 and 225 mg g^{-1}, respectively at pH 6. The experimental data of all metal ions fitted significantly with the pseudo-second-order rate equation. The transition metal ions sorption onto ligand were well fitted with the Langmuir isotherm model ($R^2 > 0.99$), which suggested that the cellulose-based adsorbent known as poly(hydroxamic acid) ligand surface is homogenous and monolayer. The reusability of the poly(hydroxamic acid) ligand was checked by the sorption/desorption process up to ten cycles without any significant loss in its original sensing and removal performances.

Keywords: Adsorption, Khaya cellulose, Poly(hydroxamic acid), Transition metals, Extraction

Introduction

The availability of fresh water for human utilization has substantially decreased because of global warming, climate change, sea level rise and human activities. But, to increase the volume of pure water is indisputable and to meet this point various water treatment technologies have been proposed and used at laboratories as well as field levels. Besides, there is yet a need for new technologies for wastewater treatment to come across the current regulatory limit of various metal ions discharge into the water-bodies. The aqueous wastes from many industrial effluents like metal plating, mining, tanneries, chloro-alkali, radiator manufacturing, smelting, alloy industries and storage battery industries are observed to be polluted with toxic metal ions in a remarkable amount [1]. Concerning these serious issues, scientists have been taken a lot of steps to prevent the environmental pollution. For example, toxic metal ions have been separated by the methods like precipitation, adsorption, ion exchange and reverse osmosis processes [1]. In some cases, wastewater treatment by precipitation has been followed by adsorption onto activated carbons to remove metal ions at highest level [2]. Though, it appears to be quite successful in treating industrial effluents, chemical coagulation often brings out secondary pollution due to added chemical substances [2]. Toxic metal precipitation also produces intractable sludge that must be treated often with high disposing cost [2,3]. Thus it is crucial to develop a new method which can meet

the green sustainable technique to remove the toxic metals form the industrial effluents without producing other toxic substances.

Currently scientists are interested for green sustainable and renewable resources. Looking into low cost environmental friendly and renewable resources as well as sustainable processes cellulose could be the most satisfactory material due to its advantages like large abundance in nature, low-density, bio-renewability, universal availability, low cost and interesting mechanical properties. The cellulose backbone can be chemically modify and some suitable chelating ligand can be incorporated onto the cellulose surface and the chemically remodeled cellulose can efficiently adsorb toxic metal ions [4]. The skeleton of cellulose could be adjusted with chelating or metals binding functional groups by means of attaching and changing of primary or secondary hydroxyl groups present in glucose units. It is an attractive as well as economical method to graft selected monomers to cellulose backbone through direct coupling and following functionalization of the grafted copolymer chain with accepted chelating components. The grafted copolymer is identified as the side chains covalently attached to the main chain of the cellulose skeleton in ionic or free radical initiating process [5,6]. Ceric ion (Ce^{4+}) having greater efficiency in grafting has strong impact on the initiator, which generates highly reactive free radicals at different sites on the cellulose backbone [6]. Nevertheless, the long term uses of natural polymers in the adsorption processes suffer severely form their biodegrading property [6]. Although cellulose have good chemical stability as well as mechanical strength, these properties could be

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further enhanced by means of implanting polymers onto cellulose and their subsequent conversion into known chelating ligands to produce metal ions complexes, a critical step in chelating process [7].

In this study, we drew out pure white cellulose from the khaya fibre using conventional method and chemically modified by grafting it with methyl acrylate applying free radical initiation method. The grafting of methyl acrylate onto khaya cellulose under different experimental conditions and distinctive feature of grafting parameters were estimated. The percentage of grafting attained for the cellulose graft polymer for further modification was performed. The methyl acrylate group was subsequently altered to hydroxamic acid group and thus a new poly(hydroxamic acid) chelating ligand was prepared. Moreover, we applied this new poly(hydroxamic acid) chelating ligand from the khaya cellulose-graft-poly (methyl acrylate) (PMA) for transition metal ions removal from aqueous media.

Experimental

Materials

Raw khaya (mahogany) wood dust is obtained from local saw mill at Kuantan city, Pahang, Malaysia. Khaya raw dust (100 g) was treated with 17 % NaOH (800 m*l*) and boiled for 8 h, filtered and washed with distilled water. The obtained product was then boiled with glacial acetic acid (800 m*l*) for 2 h, filtered and washed with distilled water. The resulted dark colour cellulose was bleached with hydrogen peroxide (300 m*l*) and 7 % NaOH (500 m*l*), washed with distilled water (500 m*l*) repeatedly and dried in oven at 50 °C. Methyl acrylate monomer purchased from Aldrich and monomer was passed through columns filled with chromatographic grade activated alumina to remove inhibitors. Other chemicals such as ceric ammonium nitrate (CAN) (Sigma-Aldrich), methanol (Merck), sulphuric acid (Lab Scan), metal salts and other analytical grade reagents were used without purification.

Graft Copolymerization

Exactly 3.0 g of khaya cellulose was added into 300 m*l* distilled water. The reactions were carried out in 1 *l* three-neck round bottom flask fixed with stirrer and condenser in thermostat water bath. The N_2 gas was purged into the flask to remove oxygen during the grafting process. The mixture was heated to 55 °C with stirring and 1.1 m*l* of diluted sulphuric acid (50 %) was added to the mixture. After 5 min, 1.10 g of CAN (10 m*l* solution) was added and the reaction mixture was stirred under N_2 gas. After 20 min, 10 m*l* methyl acrylate purified monomer was added into the cellulose suspension and stirred for 4 h under nitrogen. The mixture was cold at room temperature during which time the polymeric cellulose was precipitated out from the reaction mixture and washed several times with aqueous methanol (methanol: water: 4:1). The product was finally oven dried at

50 °C to obtain a constant weight [7].

Determination of Grafting Fractions

The grafting product was weighed and the homopolymer was extracted using Soxhlet purification with acetone for 12 h. The purified grafted copolymer was dried at 50 °C to get a constant weight and the percentage of grafting (Gp) was determined using equation (1):

$$\text{Grafting percentage (Gp)} = \frac{W_2}{W_1} \times 100 \qquad (1)$$

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

Synthesis of Poly(hydroxamic acid) Ligand

Hydroxylamine solution was prepared by 12.0 g of hydroxylamine hydrochloride ($NH_2OH.HCl$) dissolved in 300 m*l* of aqueous methanol (methanol:water; 4:1). About 50 % of NaOH solution was added in cold condition and the resulting NaCl was removed using filtration. The pH of the reaction was adjusted to pH 11 by adding of NaOH solution and the ratio of methanol to water was maintained at 4:1 (v/v). Then poly(methyl acrylate) grafted khaya cellulose (5.0 g) was placed into a two-neck round bottom flask fixed with a stirrer, condenser and thermostat water bath [7,8]. The prepared hydroxylamine solution was then added to the flask and the reaction was carried out at 70 °C for 6 h. After completion of reaction, the chelating polymeric ligand was separated from hydroxylamine solution by filtration followed by washing with aqueous methanol (methanol: water; 4:1). The ligand was treated with 200 m*l* of 0.1 M methanolic HCl solution for 5 min to convert into H-form of ligand. The ligand was filtered and washed several times with methanol and dried at 50 °C to get a constant weight.

Optical Sensing of Copper Ion

For a typical optical copper ion sensing, 150 mg of the polymeric ligand was immersed into 10 m*l* of buffer solution which is adjusted to appropriate pH from 2-9 (0.1 M sodium acetate with acetic acid). Then copper ion solution concentration of 5 mg l^{-1} was added to each pH solution with shaking in a temperature controlled shaker machine (Lab companion, SI-600) at 30 °C for 2 h at a constant agitation speed of 180 rpm to achieve good colour separation. In case of colour optimization, 150 mg of the polymeric ligand was also immersed into 10 m*l* of acetate buffer at pH 6 and metal ions solution (10 m*l* of metal ion) concentration of 5 and 10 mg l^{-1} was added at constant volume (20 m*l*) with shaking in a similar manner for 2 h at a constant agitation speed of 180 rpm to achieve good colour separation. A blank solution was also prepared following the same procedure for comparison of colour formation and detection [22,23]. After equilibration, the solid ligand was separated using filtration and dried at 50 °C for 2 h. The optical colour assessment and absorbance

were measured by solid state UV-vis NIR spectrophotometer (UV-2600 Shimadzu).

Batch Adsorption

In case of removal experiments, transition metal ions (Cu^{2+}, Fe^{3+}, Co^{3+}, Mn^{2+}, Cr^{3+}, Ni^{2+} and Zn^{2+}), exactly 150 mg of the polymeric ligand was also immersed into metal ion (single metal) solution of 10 ml (0.1 M) to appropriate pH (3-6) using sodium acetate buffer (10 ml) and shaking for 2 h with speed of 180 rpm. After equilibration, the ligand was separated by filtration and metal ions concentration was determined by ICP-OES (Perkin Elmer, Optima 8300). The initial and final readings (after adsorption) of the metal ion concentration were calculated according to equation (2).

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

Here, q_e is the equilibrium adsorption amount (mg g^{-1}), C_0 is the initial concentration of metal solution (mg l^{-1}), C_e is the equilibrium concentration of metal (mg l^{-1}) after adsorption, V is the volume of metal solution (L), L is the mass of polymeric ligand (g).

In case of trace level of metal ions removal experiment, 5 ml of 10 ppm metal ions (single metal) solution at pH 6 (sodium acetate buffer) was used with 150 mg of dried ligand, shaking for 2 h with speed of 180 rpm. The initial metals solution and final solution (after adsorption) was analysed by ICP-MS (Agilent 7500 series) and analysis was carried out according to equation (3).

In case of isotherm experiments, batch adsorption experiments (Cu^{2+}, Fe^{3+}, Co^{3+}, Cr^{3+} and Ni^{2+}) were performed using the traditional bottle-point method with constant temperature at 30 ^{o}C and 180 rpm agitation by shaker machine (Lab companion, SI-600). The poly(hydroxymich acid) ligand (150 mg) were equilibrated with 20 ml (5-1500 ppm) aqueous solutions of metal ions (single metal) for 2 h. The initial metals solution and final solution (after adsorption) was analysed by ICP-MS (Agilent 7500 series) and analysis was carried out according to equation (2).

Kinetic Study

Sorption kinetic study was carried out with 150 mg of ligand immersed into 10 ml of 0.1 M metal ion (single metal) and 10 ml of acetate buffer at pH 6, shaking with speed of 180 rpm at various time intervals such as 2, 5, 10, 20, 30, 60 and 120 min, and the metal ions concentrations were estimated by ICP-OES. The residual metal concentration was determined using the final concentration (after adsorption) is deducted from initial metal ions concentration, as calculated by equation (3):

$$q_t = \frac{(C_0 - C_t)V}{L} \qquad (3)$$

Here, q_t is the adsorption amount at time t (mg g^{-1}), C_0 is the

initial concentration of metal solution (mg l^{-1}) and C_t (mg l^{-1}) is metal concentration at time t.

Results

FT-IR Analysis

IR spectra are taken by FT-IR Spectrometer (Perkin-Elmer) and characterized the khaya cellulose, grafted cellulose copolymer and the synthesized chelating ligand. Khaya cellulose showed adsorption bands at 3433 and 2917 cm^{-1} at IR spectrum, which were referred to O-H and C-H stretching respectively (Figure 1(a)). Due to the bending mode of the absorbed water a band at 1627 cm^{-1} was found [11]. A smaller band at 1421 cm^{-1} was observed for the CH_2 symmetric bending. The absorbance at 1370 and 1163 cm^{-1} originated from the O-H bending and C-O stretching, respectively. The C-O-C pyranose ring skeletal vibration produced a strong band at 1061 cm^{-1}. A small sharp peak at 891 cm^{-1} corresponded to the glycosidic C_1-H deformation with ring vibration contribution and OH bending, which is characteristic of α-glycosidic linkages between glucose units in cellulose [11]. The IR spectrum of purified poly(methyl acrylate) grafted cellulose (khaya-g-PMA) showed new absorption band at 1741 cm^{-1} and 827 cm^{-1} due to C=O and CH_3 stretching, respectively of methyl acrylate (Figure 1(b)) and other bands retained from khaya cellulose (3433, 2917, 1627, 1421, 1370, 1163, 1061 and 891 cm^{-1}). The hydroxamic acid functional group from poly(hydroxamic acid) ligand showed new absorption bands at 1682 and 1651 cm^{-1} corresponding to the C=O stretching and N-H bending modes, respectively (Figure 1(c)). In addition, a new broad band at 3188 cm^{-1} for N-H stretching and 1400 cm^{-1} for OH bending was observed (Figure 1(c)). Furthermore, the band at 1741 cm^{-1} for C=O disappeared and the new absorption stretching bands for
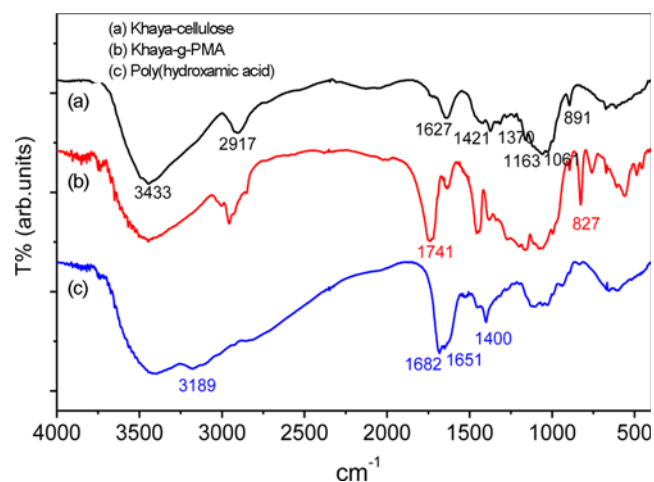

Figure 1. FTIR spectra of (a) khaya cellulose, (b) poly(methyl acrylate) grafted khaya cellulose (120 % grafting copolymer), and (c) poly(hydroxamic acid) chelating ligand.

hydroxamic acid group appeared at 3189, 1682, 1651 and 1400 cm^{-1}. These spectral data confirmed the of successful synthesis of hydroxamic acid ligand from poly(methyl acrylate) grafted khaya cellulose.

FE-SEM and HR-TEM Analysis

The SEM micrograph of the khaya cellulose measured with JEOL (JSM-7800F) revealed timber like morphologies (Figure 2(a)), whereas the SEM micrograph of the poly(methyl
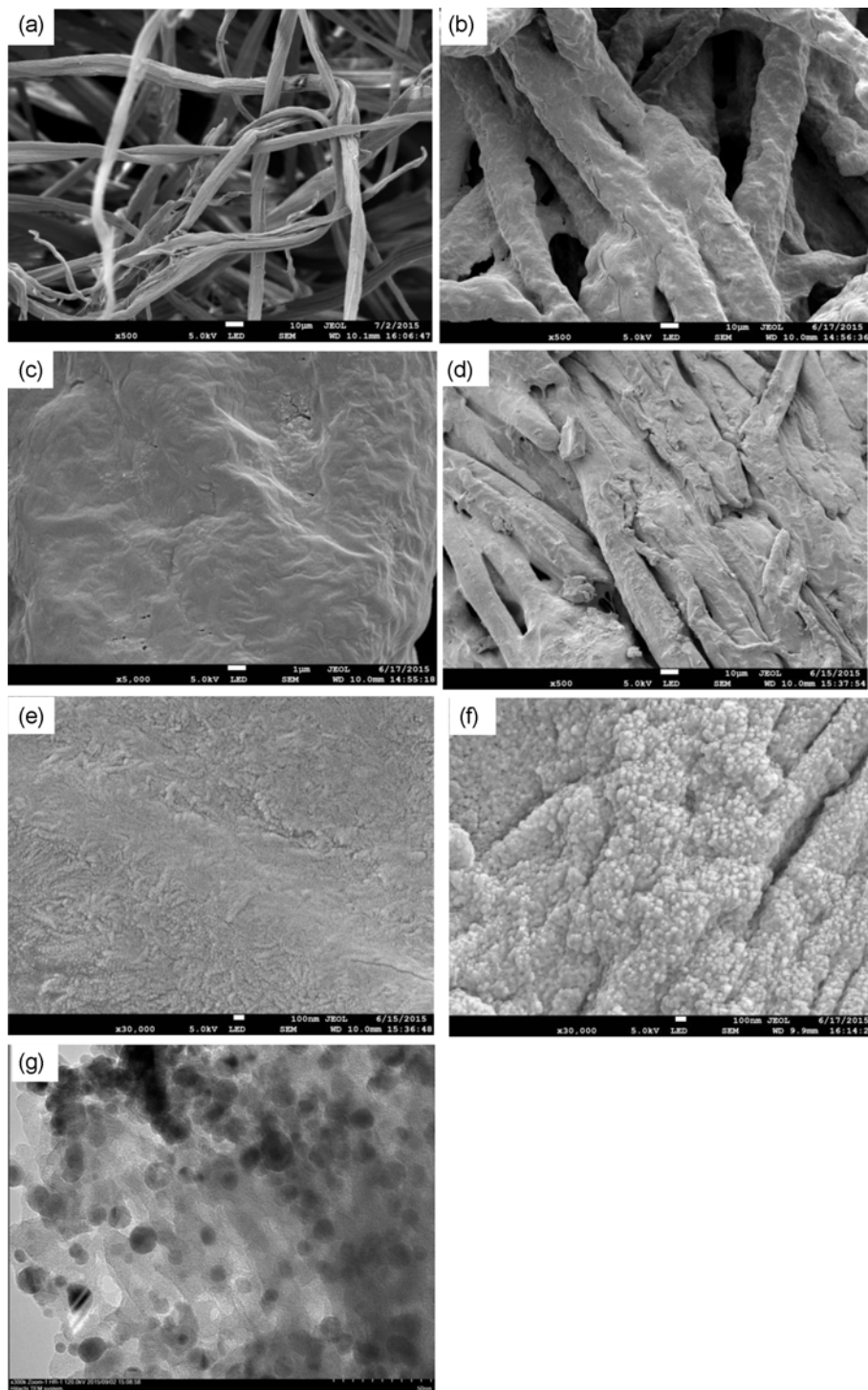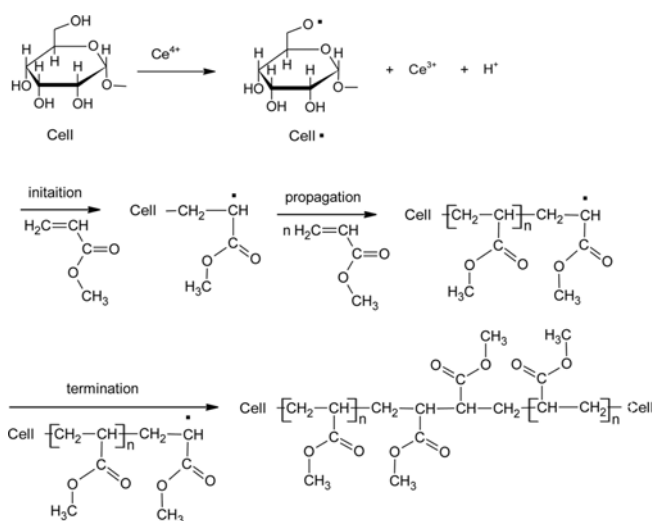

Figure 2. FE-SEM micrographs of (a) khaya cellulose, (b) PMA grafted cellulose (120 % grafting copolymer), (c) enlarge view of PMA grafted cellulose, (d) poly(hydroxamic acid) ligand, (e) enlarge view of poly(hydroxamic acid) ligand (f) poly(hydroxamic acid) ligand after adsorption of Cu^{2+}, and (g) HR-TEM micrographs of poly(hydroxamic acid) ligand after adsorption of Cu^{2+}.

acrylate) grafted khaya cellulose showed that distinguishable grafting occurred on the surface of timber like cellulosic structure having unsmooth and thick layer surrounding the stick due to PMA grafting (Figure 2(b)). The enlarge view of poly(methyl acrylate) grafted khaya cellulose showed unsmooth surface (Figure 2(c)). The poly(hydroxamic acid) ligand showed also unsmooth surface (Figure 2(d)). The enlarge view of poly(hydroxamic acid) ligand shows sandy surface (Figure 2(e)), which is quite more smooth morphologies compare to grafting copolymer (Figure 2(c)). The poly (hydroxamic acid) ligand after adsorption with copper(II) metal ion exhibited small spherical bead (Figure 2(f)). On the other hand, nanoscale micrograph (Figure 2(g)) of HR-TEM measured with Hitachi instrument (HT-7700) displayed scattered Cu^{2+} complex (average 5 nm size) which is a strong proof to the adsorption occurred by the polymeric ligands.

Reaction Mechanism

Several studies are accessible on the mechanism of grafting reaction of acrylic monomers with starch or cellulose materials using free radical initiation method [12,13]. An alternative mechanism has been suggested in current studies for the grafting of cellulose units having primary hydroxyl groups in which metal ions creates a free radical on the oxygen atom which undergo polymerization reaction with vinyl or acrylic monomers [14]. In this report, khaya cellulose is grafted with methyl acrylate using free radical chain reaction with the ceric ion as initiator (Scheme 1). The ceric (IV) ion form a complex with the OH groups of glucose units in the khaya cellulose and the hydrogen atom is oxidized by the reduction of Ce^{4+} ion to Ce^{3+} ion. Then the cellulose free radicals induced the initiation of grafting by the addition of double bond in methyl acrylate (acrylonitrile)

monomer. This generates (results in) the radical formation for propagation reaction. Scheme 1 showing the termination reaction of the developing polymer chain of the cellulose-monomer molecules produces in the combination of grafting though termination by disproportionation is also possible [15].
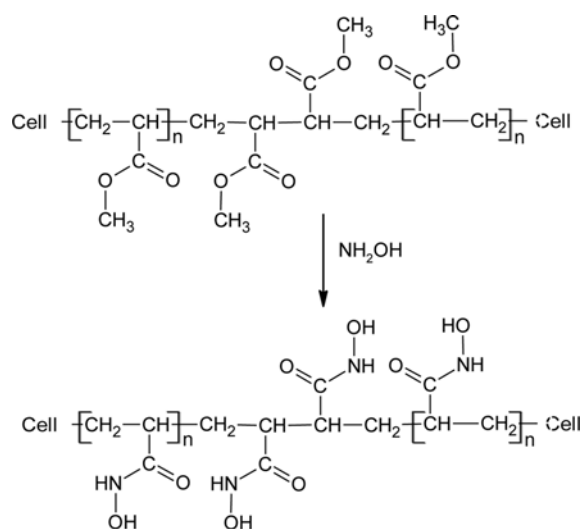
Poly(hydroxamic acid) Ligand

As described earlier, the khaya cellulose-g-poly(methyl acrylate) copolymer was prepared from the reaction between khaya cellulose and methyl acrylate monomer applying free radical polymerization process. The optimum reaction conditions of graft copolymerization were observed to be 0.036, 0.041, 0.006 and 0.602 mol l^{1} for cellulose (AGU), mineral acid (H_2SO_4), ceric ammonium nitrate (CAN) and methyl acrylate (MA), respectively. Subsequently, the grafted copolymer having acrylate group was reacted with hydroxyl-amine for conversion of polymeric chelating ligand known as the poly(hydroxamic acid) functional groups (Scheme 2). The conversion of ligand was reached to maximum 98 %. Therefore, the hydroxamic acid functional group would take part in increasing the special binding properties with metal ions.

Optical Detection of Metal Ions

Effect of Solution pH

The effect of solution pH is a key factor for selective optical detection of metal ions [9,10]. The pH of the solution was found to be a significant factor when using the ligand to sense transition metal ions. The reflectance spectra of the $[Cu-ligand]^{n+}$ complex was observed over a wide pH ranges from 2-9. The amount of Cu^{2+} ion adsorbed by polymeric ligand was adequate to attain good color separation (signal) between the ligand (blank) and Cu^{2+} ion-sensing sample as

Scheme 1. Graft copolymerization of methyl acrylate onto khaya cellulose (Cell · is a glucose unit of cellulose).

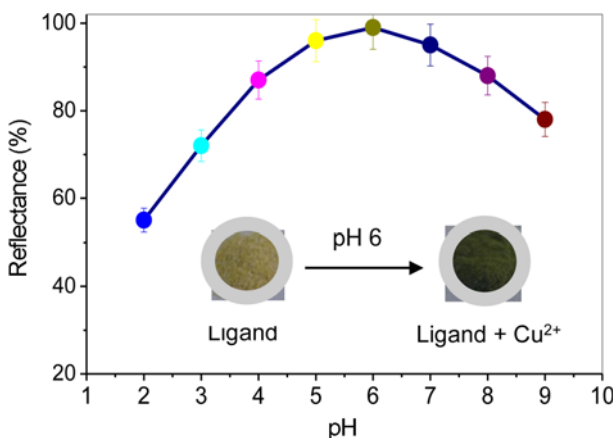**Scheme 2.** Khaya cellulose-g-PMA converted into poly(hydroxamic acid) ligand.

Figure 3. Effect of solution pH for Cu^{2+} ions sensing by polymeric ligand amount 150 mg at different pH conditions with 6 mg l^{-1} of Cu^{2+} ion at 30 °C in 20 ml volume for 2 h, 120 % grafting copolymer.

shown in Figure 3. The ligand was robust at pH 6-7 for its optical color intensity and signal response for Cu^{2+} ions in which the highest absorbance was 99.8 % at pH 6. These findings indicated that the ligand has prominent performance and affinity to Cu^{2+} ions at pH 6 using sodium acetate buffer solution (0.1 M sodium acetate solution adjusted pH by adding acetic acid).

Hence, to obtain a high sensitive response for the copper ion pH 6 was selected as optimum experimental condition in the optical sensing system. This result proved that the selective identification of target metal ions by ligand supported adsorbent at a specific pH region is the significant factor for metals ions capturing [9,10].

Color Optimization

For visual investigation of transition metal ions, the polymeric ligand (adsorbent) displayed high physical and textural properties. The reflectance spectra was increased when increasing of Cu^{2+} ion concentration from 0 to 10 ppm at other experimental conditions were fixed as shown in
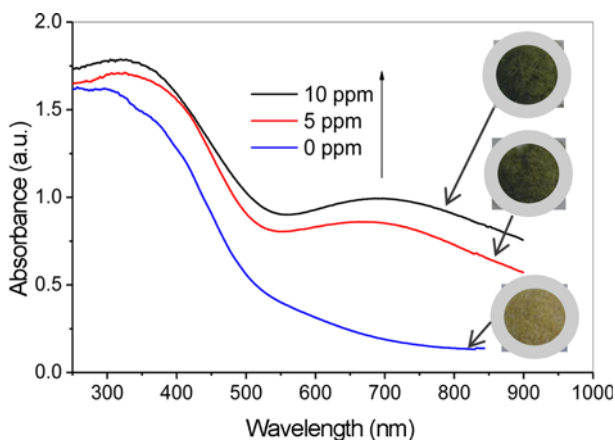

Figure 4. Colour optimization with increasing concentrations of Cu(II) ions at pH 6 with reflectance spectra.

Figure 4. In addition, a broad peak at about 702 nm was created when Cu^{2+} ion is adsorbed by ligand whereas blank polymeric ligand does not shows any peak at 702 nm. The reflectance spectra of the polymeric ligand exhibited a new peak at about 702 nm with addition of Cu^{2+} ion indicating the charge transfer (π-π transition) complex. Thus, it is obvious that the increasing of the absorbance correlates with equilibrium color formation between ligand and metal ions are sensitive in ultra-trace concentrations [9,10].

Adsorption of Metal Ions by Ligand
Effect of pH for Removal of Metal Ions

To evaluate the effect of pH on the metal ions adsorption behavior by the poly(hydroxamic acid) chelating ligand, adsorption experiment was carried out over a pH ranges from 3-6 and pH was corrected with sodium acetate buffer solution. Thus, adsorption behavior of the polymeric ligand was determined by the binding of some transition metal ions. The analytical results render the metal ions adsorption capacities of the selected metal ions were found to be increase from pH 3 to 6. The ligand has high affinity to Cu^{2+} ion in neutral pH region, even other common transition metals showed higher affinity such as iron, cobalt, manganese and chromium at pH 6. The binding capacities of Cu^{2+}, Fe^{3+}, Co^{3+}, Cr^{3+}, Ni^{2+}, Mn^{2+} and Zn^{2+} were 336, 310, 295, 288, 250, 248 and 225 mg g^{-1}, respectively at pH 6 (Figure 5). It was found that metal ions uptake by the ligand was pH-dependent. The adsorption capacity of the synthesized chelating ligand towards the metal ions was in the order of $Cu^{2+} > Fe^{3+} > Co^{3+} > Cr^{3+} > Ni^{2+} > Mn^{2+} > Zn^{2+}$. Although the khaya cellulose modified ligand is pH sensitive for target ions detection and removal, the ligand moiety of polymeric adsorbent is actively functioning to form complexes with metal ions to remove them from water [7-9,15].
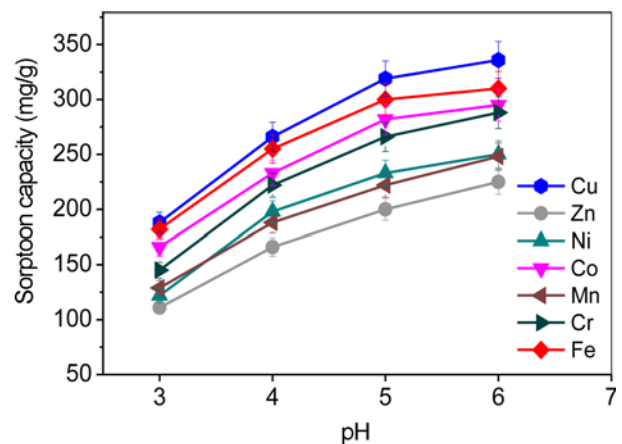

Figure 5. Metal ions adsorption capacity by the ligand as a function of pH. Reaction condition was 150 mg of dried ligand, 10 ml of 0.1 M sodium acetate buffer solution at pH 3-6, and 10 ml of 0.1 M metal ion solution shaken for 2 hours, 120 % grafting copolymer.
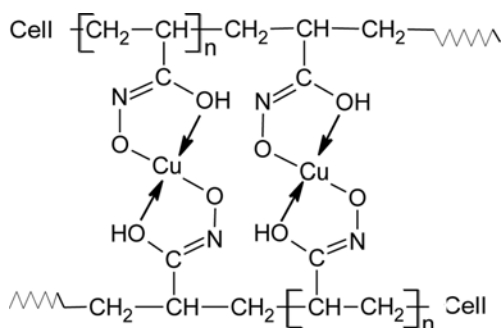
Figure 6. Polymeric ligand with metal ions.

Since the hydroxamic acid groups form complexes with the metal ions, a highly coloured chelating ligand was found after batch equilibration with the metal ions. The colour detection was clearly (obviously) observed from the ligand, adsorbed with some transition metal ions. The hydroximate anions are bidentate ligand trapped the metal ions and forming five-membered ring structure as shown in Figure 6. Eigen and Tamm [16] 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 [17]. 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 [18]. The second step clarifies the fundamental role played by the solvent. Indeed, in this slow step the breaking of the $M-OH_2$ 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 kH_2O with the number of d electrons in different metal ions [19]. 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 [20]. In this study, identical hydroxamic acid ligand supported by copolymers are involved in chelation process and also ligand exhibit highest affinity towards d electrons of Cu^{2+} ion (Figure 6).

Adsorption Kinetic

In comparison with the ion-exchange and hydrogen bonding reaction mechanisms, the sorption by complexation reaction mechanisms are slowing kinetic to take up target ions [9, 10]. As a result, required contact time between metal ions (Cu^{2+}, Fe^{3+}, Co^{3+}, Mn^{2+}, Cr^{3+}, Ni^{2+} and Zn^{2+}) and polymeric ligand for selected metal ions removal was estimated applying a series of batch contact time experiments. The

time depending on maximum metal ions sorption by the ligand was determined (filtrate solution analyzed by ICP-OES). Several metal ions were used to study the rate of adsorption in buffer solution at pH 6. Adsorption and efficiency of the adsorption is explained by the kinetic models for appropriate understanding of the mechanism of adsorption. The pseudo-first-order kinetic equation is widely used for the adsorption of solute from solution. The equation is given by:

$$\log(q_e - q_t) = \log q_e - \frac{k1 \times t}{2.303} \tag{4}$$

where q_t and q_e are the adsorption capacity at time t and at equilibrium (mg g^{-1}), and $k1$ is the rate constant of the pseudo-first-order adsorption process (min^{-1}). The values of q_e and $k1$ can be determined from the intercept and slope of plots of log $(q_e - q_t)$ versus t (Figure 7) and corresponding values are shown in Table 1. Although R^2 values are acceptable for all adsorbates however the experimental values of adsorption capacity (q_m exp.) shows a significant variation compared to the calculated values (q_e cal.) from the first-order plot (Table 1). These results suggest least fit of the pseudo-first-order model to the experimental data.

The pseudo-second-order model represents the adsorption rate relationship with the difference of adsorption capacities at equilibrium and at different contact times, the pseudo-second-order kinetic model can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where $k2$ is the rate constant of the pseudo-second-order sorption (g mg^{-1} min^{-1}) and q_e is the amount of metals adsorbed (mg g^{-1}) at equilibrium and q_t is the amount of the adsorption (mg g^{-1}) at any time t. The values of $k2$ and q_e can be calculated from a plot of t/q_t versus t (Figure 8) and
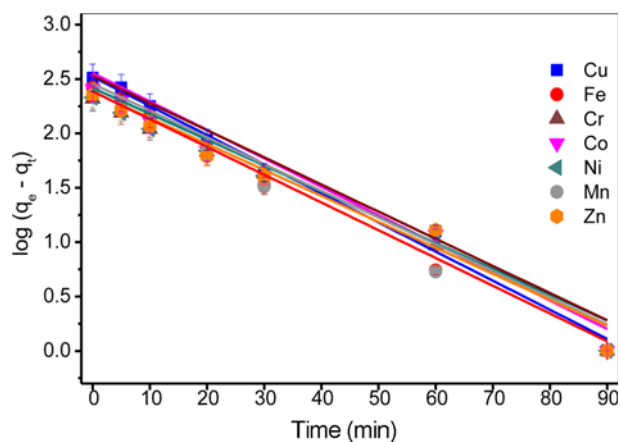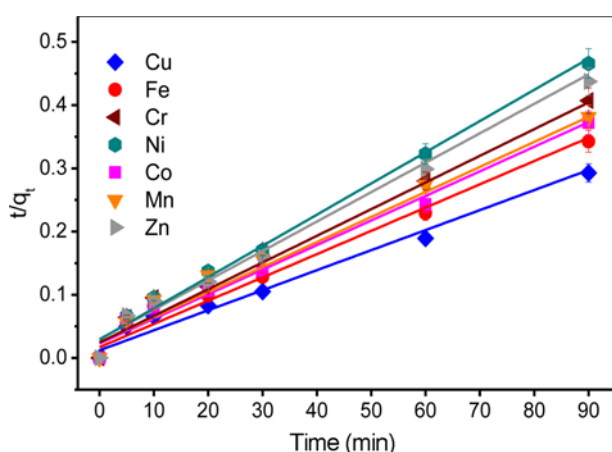

Figure 7. Kinetic plots of pseudo-first-order model for transition metals on the poly(hydroxamic) acid ligand. Other conditions: 0.1500 g of dried ligand, 10 m*l* of 0.1 M sodium acetate buffer, 10 m*l* of 0.1 M metal ion solution, 120 % grafting copolymer.

Table 1. Adsorption kinetic parameters of the pseudo-first-order model for transition metals on the poly(hydroxamic) acid ligand
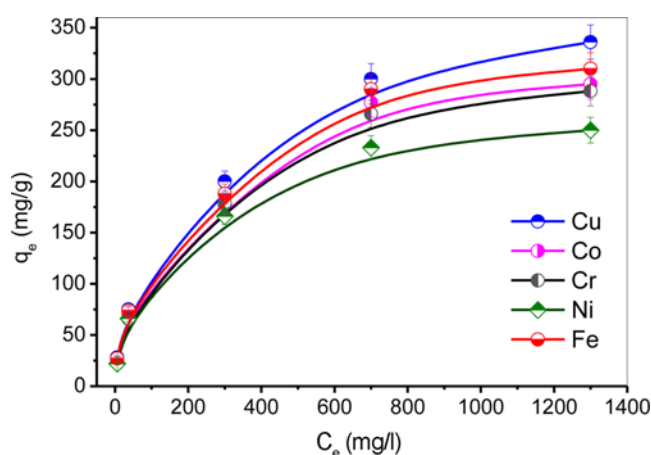
Adsorbate	Pseudo-first-order			Pseudo-second-order			Experimental q_m (mg g^{-1})
	q_e (mg g^{-1})	K_1 (min^{-1})	R^2	q_e (mg g^{-1})	K_2 (g mg^{-1} min^{-1}) $\times 10^{-3}$	R^2	
Cu	332	0.0269	0.977	335	0.0213	0.987	336
Fe	252	0.0271	0.981	286	0.0264	0.990	310
Co	253	0.0255	0.976	263	0.0256	0.991	295
Cr	215	0.0248	0.985	238	0.0324	0.992	288
Ni	216	0.0245	0.980	225	0.0298	0.997	250
Mn	220	0.0244	0.979	247	0.0334	0.985	248
Zn	219	0.0243	0.963	219	0.0277	0.993	225

Figure 8. Kinetic plots of pseudo-second-order model for transition metals on the poly(hydroxamic) acid ligand. Other conditions: 0.1500 g of dried ligand, 10 m*l* of 0.1 M sodium acetate buffer, 10 m*l* of 0.1 M metal ion solution, 120 % grafting copolymer.

Figure 9. Effect of initial concentration of metal ions for adsorption capacity onto the polymeric ligand; experimental conditions: initial metal ions concentration range 5-1300 mg l^{-1}, sample dose 150 mg/20 m*l*, solution pH 6, temperature 32 °C, contact time 2 h, 120 % grafting copolymer.

corresponding values are also presented in Table 1. An important variation was observed between the parameters of first and second order adsorption presented in Tables 1. Nevertheless, Table 1 exhibits that the correlation coefficients for the pseudo-second-order adsorption are high and the calculated q_e values match well with the experimental values. These findings recommend that the second-order mechanism is dominant and the chemical process is nothing but the adsorption mechanism owing to the valance forces through sharing or exchanging electrons between the transition metal ions and the poly(hydroxamic) acid ligand [21,22].

Sorption Isotherms

Sorption isotherm studies were performed to determine comprehensive the metal uptake by adsorbent and the effect of metal ions concentration on the adsorption capacity. During the adsorption of transition metal ions by the cellulose-based polymeric ligand the initial concentration of metal ions was increased from 5-1300 mg l^{-1} keeping ligand dose, pH and agitation period constant. The results implied

that adsorption capacity increases with the rise of initial concentration of metal ions as well as adsorption value also gradually grew up to certain limit, referred as the maximum adsorption capacity (in Figure 9).

The Langmuir and the Freundlich isotherms are the most common isotherms models to describe and investigate the equilibrium data of adsorption from aqueous solution [21]. The Langmuir isotherm model is derived to model the assumptions of monolayer adsorption, a certain number of identical active sites, active sites distributed evenly on the surface of the adsorbent and no interaction between adsorbents [21]. The linear form of the Langmuir isotherm equations is known by the following equation (6):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{6}$$

where q_e and C_e are the adsorption capacity (mg g^{-1}) and equilibrium concentration of the adsorbate (mg l^{-1}), respectively, while q_m and K_L represent the maximum adsorption capacity
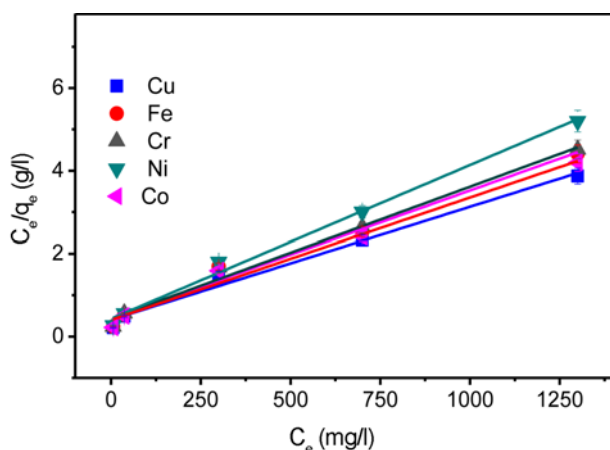
Figure 10. Langmuir adsorption isotherms of metal ions and the linear form of the Langmuir plot; experimental conditions: initial metal ions concentration range 5-1300 mg l^{-1}, sample dose 150 mg/20 ml, solution pH 6, temperature 32 °C, contact time 2 h, 120 % grafting copolymer.
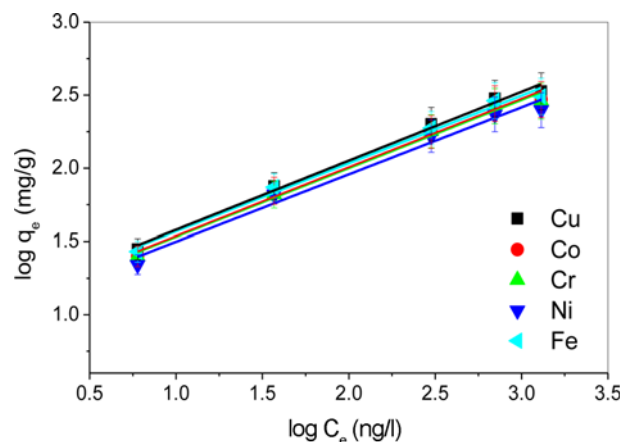

Figure 11. Freundlich isotherms for the adsorption of metal ions; experimental conditions: initial metal ions concentration range 5-1300 mg l^{-1}, sample dose 150 mg/20 ml, solution pH 6, temperature 32 °C, contact time 2 h, 120 % grafting copolymer.

of adsorbents (mg g^{-1}) and the Langmuir adsorption constant (l mg^{-1}). The data were utilized according to Langmuir sorption isotherms model (linear from) by the plot of C_e/q_e against Ce as shown in Figure 10. The values of q_m and K_L are calculated from the slope and intercept of the linear plot of C_e/q_e against C_e. The data suggested that the metal ions sorption onto ligand was well fitted with the Langmuir isotherm model as indicated by the R^2 values (>0.99). The calculated data for the maximum sorption capacity (q_m) and the sorption coefficient K_L are presented in Table 2. The value of q_m calculated from the linear plot of Langmuir isotherm corresponded to the measured q_m and also consistent with the type of metal ions e.g. copper adsorption is greater than nickel including other transition metal ions which indicate the occurrence of a monolayer adsorption by the polymeric ligand.

The Freundlich isotherm is best known as multilayer adsorption and adsorption on heterogeneous surfaces [16], which is known by the following equation (7):

$$\log q_e = \log K_F + \frac{\log C_e}{n} \qquad (7)$$

where K_F and n are the Freundlich constants, which is the adsorption capacity and the adsorption strength, respectively. K_F and n can also be calculated from the intercept and the slope of the linear plot of log q_e versus log C_e. The data were also utilized into Freundlich isotherms model by the plot of log of q_e versus C_e (Figure 11). Table 2 shows the calculated values of K_F & n as well as the experimental results of the Freundlic adsorption model with the experimental data. The Freundlich equation reveals a non-significant correlation (R^2<0.95) with the experimental data, which recommends that no multilayer adsorption was occurred.

Adsorption Mechanism of Metal Ions Sorption by Polymer Ligand

It is the bidentate hydroxamate group of poly(hydroxamic acid) ligand which has strong chelating capacity determines efficiency of copper ion adsorption. X-ray photo electron spectra (Scanning X-ray Microprobe PHI Quantera II) of polymer ligand before and after Cu^{2+} ion adsorption was investigated to interpret the sorption mechanism of Cu^{2+} ion on the polymeric ligand. The peaks at binding energies (BEs) of 284.5 eV, 399.7 eV, and 531.6 eV correspond to the C 1s, N 1s, and O 1s spectra, respectively. These peaks are

Table 2. Comparison of the Langmuir models and the Freundlich models for transition metals adsorption onto the poly(hydroxamic acid) ligand

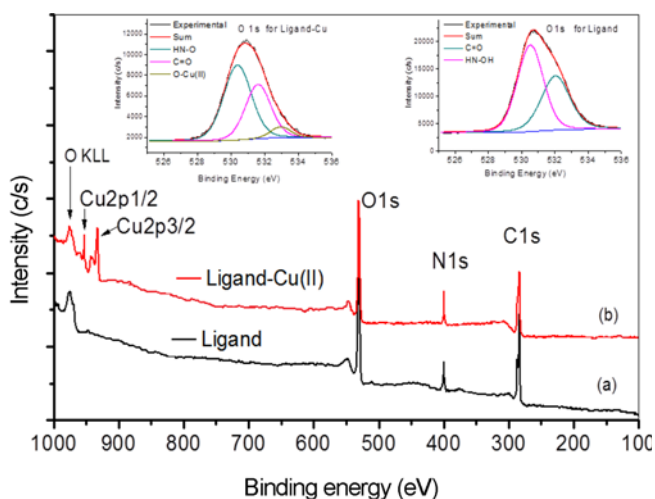| Adsorbate	Langmuir			Freundlich		
	q_m (mg g^{-1})	K_L (l m g^{-1})	R^2	n	K_F (mg g^{-1})	R^2
Cu	367.6	0.006	0.980	2.119	22.49	0.991
Fe	338.9	0.007	0.982	2.152	23.33	0.987
Co	323.6	0.007	0.980	2.130	34.70	0.986
Cr	314.4	0.007	0.980	2.137	25.89	0.988
Ni	270.2	0.008	0.991	2.178	54.80	0.976

Figure 12. Wide scan the X-ray photoelectron spectra of poly(hydroxamic) acid ligand with copper sorption (a) and poly(hydroxamic) acid ligand (b).

Figure 13. Reusability studies of the polymeric ligand in several cycles of sorption/removal-extraction experiments, 120 % grafting copolymer.

common in both adsorbed and unadsorbed samples (Figure 12(a) and (b)) but the appearance of two new peaks at BEs 933.0 eV and 953.2 eV as the signals of Cu2p3/2 and Cu2p1/2 (Figure 12(b)) clearly indicates the adsorption of Cu^{2+} ion. It is well reported that a sorbent produces different X-ray photoelectron spectra when it adsorb a sorbate through chemical interactions due to the change of chemical states of atoms involved in the sorption process [23,24]. Thus, oxygen atoms containing lone pair of electrons can donate their lone pair of electrons to form a coordination bond between a copper ion and an oxygen atom. As a result, the electron cloud density of the oxygen atoms is reduced and causes higher BE peaks [24]. For a detailed investigation of the interaction between metal ions and the polymer chelating ligand, the O 1s XPS spectra of the polymer ligand before and after adsorption of Cu^{2+} were analysed. The O 1s XPS spectra of the polymer ligand exhibits two peaks at BEs of 530.4 and 532.1 eV, which can be attributed to the oxygen atoms in the HN-OH and C=O species, respectively (inset of Figure 12). After the adsorption of Cu^{2+}, a new peak at BE of 533.1 eV appeared alongside the peaks of O 1s, including 530.4 and 531.8 eV for the HN-OH and C=O species, respectively (inset of Figure 12). These results are evidence that the oxygen atoms in the HN-OH and C=O species contribute to the formation of coordinate bonds between ligand and metal ions. The lone pair of electrons in the oxygen atoms of the hydroxamate group is donated to form a coordination bond between Cu^{2+} and the oxygen atoms.

Elution and Reusability Studies

From the cost effective view point, the recycling and reuses of the ligand are significant features for practical applications [9]. We have accomplished the elution experiments after removal/sorption test to assess the elution and reproduction
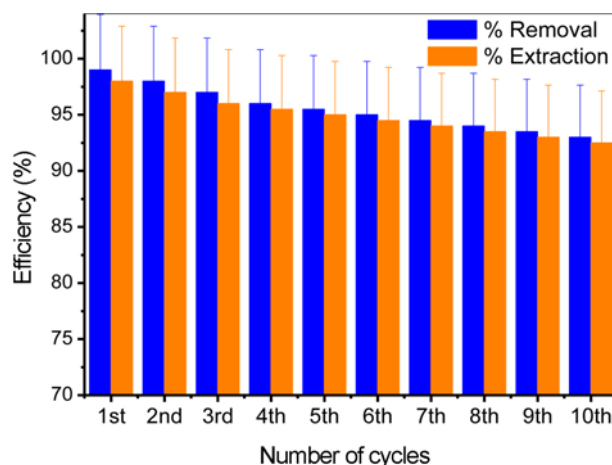
for reusability of ligand. The released of metal ions from the ligand is possible using acidic condition at pH 3. Therefore, we can use below pH zero for complete extraction of metal ions from the ligand. Thus, 2 M of HCl solution was used for sufficient to extraction of the adsorbed Cu^{2+} ion from the adsorbent. The adsorbent was regenerated into initial form after rinsing with water several times and buffer pH 6 after every elution experiments for reusability of the ligand. The reusability was examined by the sorption/elution process for 10 cycles. The sorption process was performed by stirring 150 mg of ligand with 10 m*l* of 0.1 M Cu^{2+} solution at pH 6 for 2 h. Desorption study was performed by 2 M HCl solution with 20 m*l* solution. The sorption/removal and extraction efficiencies was only about 8 % decreased after 10 cycles as depicted in Figure 13. So, the synthesized polymeric ligand could be reused in many cycles with no remarkable loss of its removal capacities. Hence, the ligand exhibits greater structural stability which encourages the applications of Cu^{2+} ion removal from environmental wastewater.

Discussion

Elements in groups V (nitrogen) and VI (oxygen) of the periodic table exist in a variety of functional or ligand groups in the modified cellulose adsorbent materials and a ligand is such chemical species(ion or molecule) which contain a pair of non-bonding electrons as well as capable of binding metals. In this work, a polymeric chelating ligand containing hydroxamic acid group as ligand was proposed to the metal ions adsorption study. This ligand showed high affinity to copper ions (326.62 mmol g^{-1}) at pH 6. Other metals like iron, chromium, manganese and cobalt uptake were also outstanding at the same pH. Our synthesized ligand from khaya cellulose exhibited higher adsorption

capacity comparative to other cellulose-based adsorbents.

Liu *et al.* [25] synthesized a spheroidal cellulose adsorbent through a grafting reaction using acrylonitrile and converted into the carboxyl groups on its surface. This modified cellulose adsorbent having carboxyl groups was used for the removal of Cu ion from aqueous solutions using a bidentate complexation. Low *et al.* [26] modified wood pulp by esterification reaction to form carboxyl groups of the citric acid and the hydroxyl groups of the wood surface and subsequent adsorption of Cu and Pb ion from aqueous solutions.

A lone pair of electrons on the nitrogen atom of amino group can be formed as coordination bond with a metal ion. For example, hydroxamic acid groups, a bidentate ligand which loses a proton and a basic lone pair of electrons on the nitrogen to form co-ordinate with the metal ion. O'Connell *et al.* [27] synthesized imidazole by a binding agent on a glycidyl methacrylate grafted cellulose adsorbent and imidazole having a five-membered ring containing two nitrogen atoms. An important aspect of unsaturated nitrogen donors such as imidazole is the possibility of p-backbonding between it and the metal ion [28].

It is distinctly demonstrated that the potential adsorption capabilities are attained with the modified cellulose materials. The notable difference in adsorption levels for each cations are found on the basis of the cellulose modification method and the nature of the chelating or metal binding ligands. The detail mechanism of each adsorption process is difficult to recognize but a number of fundamental interactions are conceivable such as ion exchange, complexation, co-ordination/chelation, electrostatic interactions, acid-base interactions and hydrogen bonding, hydrophobic interactions, physisorption and possibly precipitation [29]. However, the chemical and physical composition of the modified cellulose, the nature of the metal and solution conditions such as pH, metal concentration and solubility product issues can effects the adsorption interaction.

Cellulose was grafted with the glycidyl methacrylate, vinyl monomer by chemical initiating process and was further functionalized with thiosemicarbazide for the adsorption

of Cd^{2+} and Hg^{2+} from aqueous solutions [30,31]. Authors further extended the cellulose grafted copolymer with β-CD (cyclic oligosaccharides) and quaternary ammonium groups to build cellulose-g-GMA-β-CDN$^+$ adsorbent and the maximum adsorption capacity of Cr^{6+} reached to 61.05 mg g^{-1}. The adsorption-desorption tests of cellulose derivatives exhibited that the good reproducibility of the adsorbent and the adsorbent could be reused [31].

The mercaptobenzothiazole adsorbent synthesized from cellulose for the adsorption of Hg^{2+} showed a high adsorption capacity of 204.08 mg g^{-1} in column method [32]. Microwave-induced emulsion copolymerization was brought for ethyl acrylate and guar gum. The authors applied this copolymer sample to remove Cd^{2+} ion and demanded that the adsorbent showed high reusability and could be successfully recycled [33]. A new adsorbent was synthesized from graft copolymerization of glycidylmethacrylate onto zirconium oxide densified cellulose in the presence of N,N'-methylenebisacrylamide as cross-linker having tannin-modified poly(glycidylmethacrylate)-grafted zirconium oxide-densified cellulose [34]. For maximum adsorption pH 5.5 was observed optimum with 99.2 % removal at an initial concentration of 10 mg l^{-1} as well as maximum adsorption capacity was found to be 96.7 mg g^{-1} for absolute removal of Th^{4+} from simulated seawater. The natural biopolymer cellulose and different modifiers/chelating agents have been used to evaluate the adsorption of other metal ions such as copper, lead, nickel etc. A comparison of the adsorption capacities [25-34] shows that khaya-based hydroxamic acid ligand has high adsorption efficiency for several metal ions as shown in Table 3.

Conclusion

In this study, we successfully synthesized a poly(hydroxamic acid) chelating ligand from poly(methyl acrylate) grafted khaya cellulose. Excellent chelation behaviour of this ligand towards some transition metal ions was observed. It is also found that the adsorption capacities of the ligand for Cu, Fe, Zn, Ni, Cr ions were pH-dependent. The rate of equilibrium is very fast, and the correlation coefficients for the pseudo-

Table 3. Adsorption capacities of some metal ions reported in the literature [25-34]

Adsorbent materials	Modifier	Metal ions	Adsorption capacity (mg g^{-1})
Cellulose	Sodium hydroxide (carboxyl) [25]	Cu^{2+}	70.5
Cellulose	Glycidyl methacrylate [27]	Cu^{2+}	68.5
Cellulose	Mercaptobenzothiozole [32]	Hg^{2+}	204.08
Wood pulp	Citric acid [26]	Cu^{2+}	24.0
Cellulose	β-CD and quaternary ammonium [33]	Cr^{6+}	61.05
Cellulose	Glycidylmethacrylate [34]	Th^{4+}	96.7
Guar Gum-	Ethylacrylate [33]	Cd^{2+}	270.27
Chitosan	Tripolyphosphate [29]	Cu^{2+}	200.00
Cellulose	Poy(hydroxamic acid) ligand (this study)	Cu^{2+} / Fe^{3+} / Co^{3+} / Cr^{3+} / Ni^{2+} / Mn^{2+}	336 / 310 / 295 / 288 / 250 / 248

second-order adsorption are high and the calculated adsorption values are well fitted with the experimental values. The second-order mechanism is dominant and the adsorption mechanism owing to the valance forces between the transition metal ions and the poly(hydroxamic) acid ligand. The low-cost production of khaya cellulose-based poly(hydroxamic acid) ligand can be considered as an excellent candidate for waste water treatment process since the removal of metal ions was highly efficient from water media at low concentration of metal ions. In the present work we have carried out desorption study which is useful for reusability of polymeric ligand. Real industrial effluent containing heavy metal ions would be removed by this ligand and updated results would be published in future. In agreement with the batch adsorption for isothermal study, transition metal ions sorption onto ligand was well matched with the Langmuir isotherm model indicating a homogenous and monolayer character of the cellulose based adsorbent surface. Furthermore, ten cycles sorption/desorption process assures the possibility of reusability of this new adsorbent in many cycles with no significant loss in its original removal capabilities.

Acknowledgements

References

1. E. Wilkins and Q. Yang, *J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng.*, **31**, 2111 (1996).
2. N. V. Narayanan and G. Mahesh, *J. Hazard. Mater.,* **161**, 575 (2009).
3. W. S. S. Yong, M. R. Lutfor, S. E. Arshad, N. L. Surugau, and B. Musta, *J. Appl. Polym. Sci.,* **124**, 4443 (2012).
4. S. Kamel, E. M. Hassan, and M. El-Sakhawy, *J. Appl. Polym. Sci.*, **100**, 329 (2006).
5. M. R. Lutfor, S. Silong, W. M. Z. Wan Yunus, M. Z. A. Rahman, M. Ahmad, and J. Haron, *Eur. Polym. J.*, **36**, 2105 (2000).
6. A. Bhattacharya and B. N. Misra, *Prog. Polym. Sci.*, **29**, 767 (2004).
7. G. Gurdag, M. Yasar, and M. A. Gurkaynak, *J. Appl. Polym. Sci.*, **66**, 929 (1997).
8. M. R. Lutfor, S. Silong, W. M. Z. Wan Yunus, M. Z. A. Rahman, M. Ahmad, and J. Haron, *J. Appl. Polym. Sci.*, **79**, 1256 (2001).
9. M. R. Awual, T. Yaita, S. A. El-Safty, H. Shiwaku, H. Suzuki, and Y. Okamoto, *Chem. Eng. J.,* **221**, 322 (2013).
10. M. R. Awual, M. M. R. Ismail, T. Yaita, M. A. Khaleque, and M. Ferdows, *Chem. Eng. J.,* **236**, 100 (2014).
11. F. L. Chuan, L. R. Jun, X. Feng, J. L. Jina, X. S. Jin, and C. S. Run, *J. Agric. Food Chem.*, **54**, 5742 (2006).
12. Y. K. Agrawal, *Russ. Chem. Rev.*, **48**, 948 (1979).
13. D. Hall and F. J. Llewellyn, *Acta. Cryst.*, **9**, 108 (1956).
14. D. W. O'Connell, C. Birkinshaw, and T. F. O'Dwyer, *J. Chem. Technol. Biotechnol.*, **81**, 1820 (2006).
15. M. R. Lutfor, N. N. M. Rohani, and M. M. Yusoff, *J. Appl. Polym. Sci.*, **131**, 40833 (2014).
16. M. Eigen and K. Tamm, and Z. Elektrochem, *Angew. Phys. Chem.,* **66**, 107 (1962).
17. M. Eigen and R. G. Wilkins, *Adv. Chem. Ser.,* **49**, 55 (1965).
18. R. G. Wilkins, *Inorg. Chem.,* **3**, 520 (1964).
19. L. Helm and A. E. Merbach, *Coord. Chem. Rev.*, **187**, 151 (1999).
20. M. R. Beccia, B. García, J. G. Tojal, J. M. Leal, F. Secco, and M. Tegoni, *Dalton Trans.*, **43**, 9271 (2014).
21. P. Wanga, M. Du, H. Zhu, S. Bao, T. Yang, and M. Zou, *J. Hazard. Mater.*, **286**, 533 (2015).
22. R. S. Norouzian and M. M. Lakouraj, *Synth. Met.,* **203**, 135 (2015).
23. G. A. Hope, R. Woods, G. K. Parker, A. N. Buckley, and J. McLean, *Inorg. Chim. Acta*, **365**, 65 (2011).
24. Y. Zhao, X. Wang, J. Li, and X. Wang, *Polym. Chem.* DOI: 10.1039/c5py00540j (2015).
25. M. Liu, Y. Deng, H. Zhan, and X. Zhang, *J. Appl. Polym. Sci.*, **84**, 478 (2002).
26. K. S. Low, C. K. Lee, and S. M. Mak, *Wood Sci. Tech.*, **38**, 629 (2004).
27. D. W. O'Connell, C. Birkinshaw, and T. F. O'Dwyer, *J. Appl. Polym. Sci.*, **99**, 2888 (2006).
28. D. W. O'Connell, C. Birkinshaw, and T. F. O'Dwyer, *Bioresour. Technol.*, **99**, 6709 (2008).
29. S. T. Lee, F. L. Mi, Y. J. Shen, and S. S. Shyu, *Polymer*, **42**, 1879 (2001).
30. Z. Yanmei, J. Qiang, Z. Tianwei, and A. Yoshifumi, *J. Hazard. Mater.*, **187**, 303 (2011).
31. Z. Yanmei, H. Xiaoyi, Z. Min, Z. Xiaofeng, and N. Jiangyang, *Ind. Eng. Chem. Res.*, **52**, 876 (2013).
32. K. K. A. Santhana, S. Kalidhasan, R. Vidya, and N. Rajesh, *Ind. Eng. Chem. Res.*, **52**, 11838 (2013).
33. S. Vandana, K. S. Ajit, and M. Sadhana, *Ind. Eng. Chem. Res.*, **48**, 4688 (2009).
34. T. S. Anirudhan and S. R. Rejeena, *Ind. Eng. Chem. Res.*, **50**, 13288 (2011).