Synthesis and Characterization of Poly(hydroxamic acid)–Poly(amidoxime) Chelating Ligands from Polymer-Grafted Acacia Cellulose

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ABSTRACT: Graft copolymerization of methyl acrylate (MA) and acrylonitrile (AN) onto acacia cellulose was carried out using free radical initiating process in which ceric ammonium nitrate (CAN) was used as an initiator. The optimum grafting yield was determined by the certain amount of acacia cellulose (AGU), mineral acid (H_2SO_4), CAN, MA, and AN at 0.062, 0.120, 0.016, 0.397, and 0.550 mol L^{-1}, respectively. The poly(methyl acrylate-*co*-acrylonitrile)-grafted acacia cellulose was obtained at 55°C after 2-h stirring, and purified acrylic polymer-grafted cellulose was characterized by FTIR and TG analysis. Therein, the ester and nitrile functional groups of the grafted copolymers were reacted with hydroxylamine solution for conversion into the hydroxamic acid and amidoxime ligands. The chelating behavior of the prepared ligands toward some metal ions was investigated using batch technique. The metal ions sorption capacities of the ligands were pH dependent, and the sorption capacity toward the metal ions was in the following order: $Zn^{2+} > Fe^{3+} > Cr^{3+} > Cu^{2+} > Ni^{2+}$. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4443–4451, 2012

Key words: acacia cellulose; chelating ligands; poly(hydroxamic acid); poly(amidoxime); free radical grafting; metal ions sorption

INTRODUCTION

Cellulose is the most abundant low-cost and renewable naturally occurring biopolymer with its various significant applications of its derivatives in paper, fiber, and paint industries. Graft copolymerization is a useful technique for modifying the properties of the synthetic and natural polymers. Graft copolymers are finding their applications in the development of selective permeable membranes and outstanding sorption agents.[1] Graft copolymerization has been carried out by different techniques including irradiation with ultraviolet light, plasma ion beams, gamma rays, atoms-transfer radical polymerization, and ceric(IV) ion initiating methods.[2,3] The ceric(IV) ion initiation method involves the formation of radicals on cellulose by the abstraction of hydrogen from cellulose structure and hydroxyl group bringing to the oxidation of ceric ions with cellulosic chain ends containing glycol or hemiacetal linkages leading to C—C bond cleavage (C_2 and C_3) in the cellulosic backbone polymer.[4–7] This method offers great advantages in the formation of radicals on the cellulose through a single electron transfer technique to promote the grafting of monomers onto the cellulose.[8] Graft copolymerization gives advantages on modifying physical and chemical properties of the cellulose, which gives different structural characteristics in cellulose after introduction of monomers to cellulose leading to improvement of mechanical properties in comparison with the conventional cellulose.[9]

On the other way, the appropriate selected monomers grafted onto cellulose can modify the chemical properties such as thermal stability and resistance,[10] hydrophilic or hydrophobic character,[11] ion exchange capabilities, and resistance to chemical and biological attack.[12] However, the grafting yield is influenced by several parameters such as temperature, type and concentration of initiator and monomers applied, and also reaction period. Various methods such as chemical precipitation or coagulation, electrolytic reduction, membrane technology,

ion exchange, and absorption have been used in the removal of heavy metal ions from the waste water even at the trace level.[8,13]

The most widely applied method in metal ions removal from waste water is increasing the pH of the effluent, thus converting the soluble metal ions into an insoluble form of metals. While ion exchange is the second most widely used method in removing heavy metal ions from aqueous media.[14] Thus, ion exchange ligands bearing hydroxamic acid and amidoxime functional groups have long been interest to remove metal ions from various sources.[15] The amidoxime chelating ligands were synthesized from the acrylonitrile (AN) incorporating into wood saw dust and used in Cu^{2+} and Ni^{2+} removal from water.[16] A poly(amidoxime) chelating resin from the poly (acrylonitrile) (PAN)-grafted sago starch was synthesized and resin exhibited good absorption on copper.[17] Another approach consists of the introduction of amidoxime groups into cellulose by reacting PAN-grafted carboxymethylcellulose with hydroxylamine.[18]

For this study, we have been extracted cellulose from the acacia trees, which are available in Borneo island named Sabah. An effort has been made to study the grafting of methyl acrylate (MA) and AN onto acacia cellulose under various experimental conditions, and characteristic grafting parameters have been determined. Consequently, the novel poly(hydroxamic acid)–poly(amidoxime) chelating ligands were synthesized from the poly(methyl acrylate-*co*-acrylonitrile)-grafted acacia cellulose (PMA-*co*-PAN-graft cellulose), and these ligands were studied to the metal ions extraction from water media.

EXPERIMENT

Materials and methods

Acacia cellulose was extracted from acacia wood bark obtained from Physics Laboratory at University Malaysia Sabah. Acacia wood bark was crushed in small size (3-cm long and 0.1-cm diameter average) and dried at 50°C. In this study, primary target is the synthesis of hydroxamic acid–amidoxime ligands from α-cellulose[19]; therefore, this wood (5.0 g) was heated with glacial acetic acid (20 mL) at 105°C with slow stirring and treated with 17% NaOH (10 mL) for 1 h. The acacia cellulose was bleached with hydrogen peroxide (20 mL) and washed with the mixture of hydrogen peroxide (5 mL) and distilled water (95 mL). Finally, the cellulose is washed with acetic acid (2 mL) and distilled water (20 mL) and oven dried at 50°C before use. Both MA and AN monomers were purchased from Fluka, and each monomer was passed through the columns filled with chromatographic-grade activated alumina to remove the inhibitor. The monomers were freshly purified before use for grafting reaction. Others chemicals such as ceric ammonium nitrate (CAN, Sigma-Aldrich), methanol (Merck), sulfuric acid (Lab Scan), metal salts, and other analytical grade reagents were used with out further purification.

Graft copolymerization

The reactions were carried out in 250-mL three-necked round-bottomed flask equipped 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 cellulose slurry was prepared by stirring 0.500 g of acacia cellulose in 25 mL distilled water for overnight. Then, the slurry was heated to 55°C and diluted sulfuric acid (H_2SO_4 : $H_2O = 1 : 4$) was added to the mixture. After 5-min stirring, the required amount of 0.1M CAN solution was added, and the reaction mixture was mixed homogenously. After 30-min stirring, the required amount of MA and AN monomers was dispersed in the cellulose suspension and stirred for specific periods under nitrogen. When the reaction was completed, the mixture was cooled under running tap water. Then, it was precipitated in excess amount of methanol and washed several times with methanolic solution (methanol : water = 4 : 1). The product was finally oven dried at 50°C to a constant weight.

Determination of grafting fractions

The crude product as PMA-*co*-PAN-graft cellulose was weighed and extracted the homopolymers using Soxhlet purification with acetone for 24 h. The purified copolymer product was then dried at 50°C to a constant weight. The percentage of grafting (Gp) was determined using the following equation:

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

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

Determination of the percentage grafting fractions for each monomer in the final graft copolymer was carried out based on the nitrogen content of the grafted samples determined by using LECO elemental analyzer.[20] Percentage grafting of PAN onto acacia cellulose (Gpf) was calculated according to the following equations:

$$\text{Grafting fraction (Gpf)} = \%N\left(\frac{W_2 \times 53}{W_1 \times 14}\right),$$

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

percentage of grafting fraction for poly(methyl acrylate) (PMA) onto acacia cellulose (Gpf') was determined by the following formula:

$$Gpf' = Gp - Gpf.$$

Synthesis of poly(hydroxamic acid)–poly(amidoxime) ligands

About 50,000 g of hydroxylamine hydrochloride ($NH_2OH.HCl$) was dissolved in 500 mL of methanolic solution (methanol : water = 4 : 1). The HCl of NH_2OH was neutralized by NaOH solution, and the precipitate of NaCl was removed using filtration. The pH of the reaction was adjusted to pH 11 using NaOH solutions. The ratio of methanol to water was maintained at 4 : 1 (v/v).[15,17]

About 25,000 g of poly(methyl acrylate-co-acrylonitrile)-grafted acacia cellulose was placed into a two-necked round-bottomed flask equipped with a stirrer, condenser, and thermostat water bath. The prepared hydroxylamine solution was then added to the flask, and the reaction was carried out at 70°C for 4 h. After completion of reaction, the chelating ligands were separated from hydroxylamine solution by filtration followed by washing with methanolic solution (methanol : water = 4 : 1). Then, the ligands were treated with 100 mL of methanolic 0.1M HCl solution for about 5 min for conversion into H-form ligands. The ligands was filtered and washed several time with methanolic solution (methanol : water = 4 : 1) and dried at 50°C to a constant weight.

Extraction of metal ions by batch technique

The metal ion binding capacity was measured by a batch equilibration technique with varying pH solution ranging from pH 2 to 6. Exactly 0.3000 g of dried ligands was placed into a series of clean polyethylene bottles and the ligands were equilibrated with 20 mL of distilled water for 30 min. Ten milliliters of 0.1M sodium acetate buffer solution at pH 2–6 was added to each bottle for 10 min. Exactly 20 mL of 0.1M metal ion solution was added to each bottle and shaken for 12 h by a rotary shaker. After equilibration, 5 mL of the supernatant solution was collected for the metal ion determination by AAS (Perkin-Elmer 4100), and the initial and final readings of the metal ion concentration were recorded.

Extraction of metal ions at lower concentration

Metal ions extraction study was carried out by a batch technique using 10 and 50 ppm solutions at pH ranging 2–6. Exactly 0.3000 g of dried ligands was added to the 50 mL of sodium acetate buffer solution containing either 50 or 10 ppm each metal ions, and mixtures were shaken for 12 h. Analysis was carried out according to the section "Extraction of Metal Ions by Batch Technique."

Kinetics study by batch technique

The rate of exchange of copper in the acetate buffer at pH 6 was determined by 0.3000 g of ligand beads in 10 and 50 ppm of metal solution for various time intervals such as 2, 5, 10, 20, 30, 60, and 120 min, and the copper concentrations were estimated by inductively-coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elmer, Optima 5300 DV, USA). The residual metal concentration was determined with replicated experiment and deduct from initial (50 and 10 ppm) metal ions concentration.

FTIR analysis

Acacia cellulose sample, grafted polymer, and the synthesized chelating ligands were characterized by infrared (IR) spectra using FTIR Spectrometer (Perkin-Elmer).

Thermogravimetry analysis

Thermogravimetry analysis (TGA) was performed by Perkin-Elmer Thermal Analyzer (Model 6). The TGA was carried out in N_2 atmosphere from room temperature to 700°C at a heating rate of 10°C min^{-1} with N_2 flow rate at 20 mL min^{-1}. The thermograms of acacia cellulose, grafted cellulose, and synthesized chelating ligands were obtained.

RESULTS AND DISCUSSION

FTIR analysis

The FTIR spectrum of acacia cellulose showed absorption bands at 3401 and 1450 cm^{-1} for the O—H stretching and bending modes, respectively [Fig. 1(a)]. Others absorption bands showed at 2888 and 1074 cm^{-1} for the C—H and C—O stretching modes, respectively [Fig. 1(a)]. The IR spectrum of purified grafted cellulose showed that new absorption band at 2242 cm^{-1} belongs to CN stretching of AN. In addition, a new absorption at 1732 cm^{-1} corresponds to the C=O stretching of acrylate and 1448 cm^{-1} due to C—H bending mode, respectively [Fig. 1(b)]. The poly(hydroxamic acid)–poly(amidoxime) ligands showed that new absorption bands at 1653, 1564, and 1110 cm^{-1} correspond to the C=O, N—H, and N—O stretching modes, respectively [Fig. 1(c)]. It was observed that the CN band for 2242 cm^{-1} and C=O band for 1732 were disappeared, and the new absorption band for hydroxamic acid and amidoxime groups was appeared, which is the confirmation
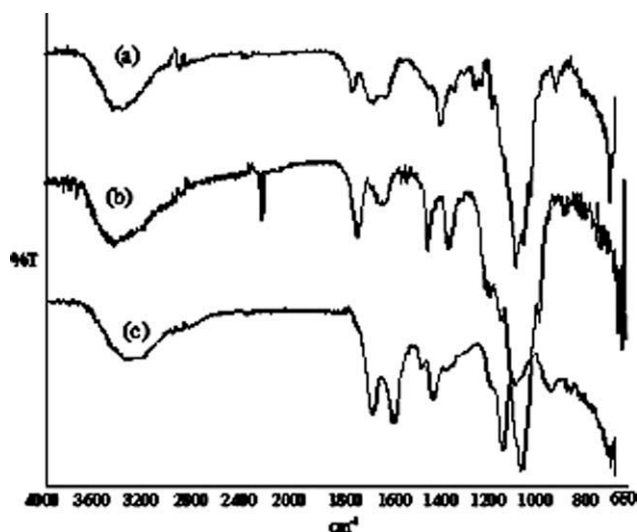
Figure 1 FTIR spectra of (a) acacia cellulose, (b) poly (methyl acrylate)–poly(acrylonitrile)-grafted acacia cellulose, and (c) poly(hydroxamic acid)–poly(amidoxime) chelating ligands.

of successful synthesis of ligands from cellulose-grafted copolymers [Fig. 1(c)].

Reaction mechanism

Literature survey reveals that many reports are available regarding the mechanism of acrylic monomers grafted with starch or cellulose materials.[21–23] In this study, acacia cellulose is grafted with MA and AN using free radical chain mechanism, which involved the ceric ion as an initiator (Scheme 1). In initiation step, the ceric(IV) ion forms a complex with the cellulose molecules via oxidation reaction. The hydrogen atom is oxidized by the reduction of Ce^{4+} ion to Ce^{3+} ion. Consequently, the bond cleavage of the glycol group of cellulose at C_2–C_3 position occurs forming keto-alcohols free radical. We have abbreviated the cellulose structure as Cell. The cellulose free radical could initiate grafting by the addition of double bond to acrylic monomers. This results in the formation of a covalent bond between acrylic monomers and cellulose to form radical for propagation reaction. The termination of the growing polymer chain involved in cellulose–monomer molecules results in combination of grafting or homopolymer formation. However, two types of monomers are involved in this reaction, and possible mechanisms are shown in Scheme 1 although alternative mechanisms are possible for termination reaction.[21,22]
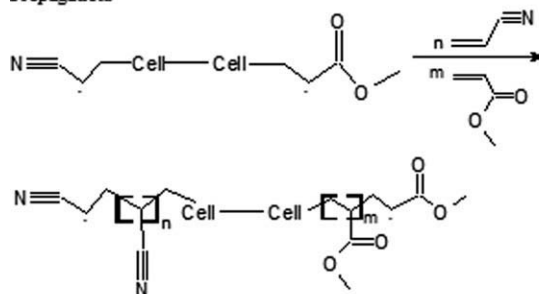
Effect of temperature

The grafting behavior of methyl acrylate (MA) and acrylonitrile (AN) onto acacia cellulose was studied by three reaction temperatures 45, 55, and 65°C at

constant concentration of sulfuric acid, CAN, MA, and AN were 0.120, 0.016, 0.397, and 0.550 mol L^{-1}, respectively, as shown in Table I. In this study, the grafting yield (Gp) was observed to increase up to 55°C. The maximum Gp obtained 413% at 55°C (Table I), which was presumably the optimum condition of the grafting of acacia cellulose. Increase of temperature would advantage in swelling of cellulose to a larger extent, increased in solubility and diffusion of monomers to the grafting site, enhancing the rate of initiation and propagation and also easier decomposition on initiating redox system. Therefore, percent grafting was attained highest at temperature of 55°C. However, on further increasing the temperature beyond 55°C, the Gp was decreased.
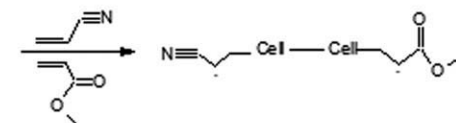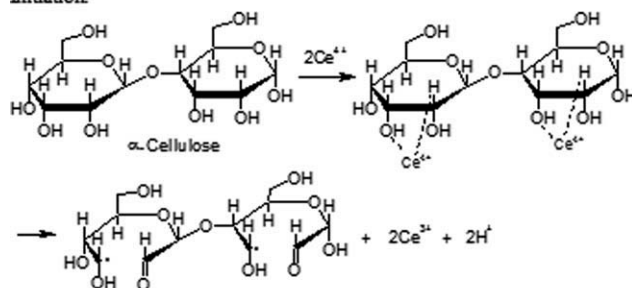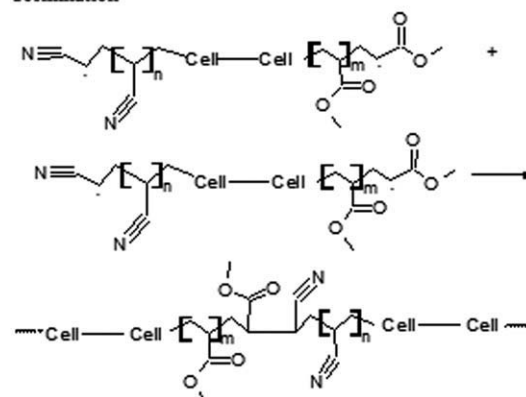

Scheme 1 Graft copolymerization of acacia cellulose with methyl acrylate and acrylonitrile.

TABLE I
Effect of Reaction Conditions on the Percentages of Grafting (Gp)[a]

Effect of temperature Temperature		Effect of acid Acid		Effect of reaction period Reaction period		Effect of initiator Initiator		Effect of monomer MA + AN	
(°C)	GP	(mol L^{-1})	GP	h	GP	(mol L^{-1})	GP	(mol L^{-1})	GP
45	318	0.048	385	1	370	0.012	385	0.221 + 0.305	336
55	413	0.120	413	2	413	0.016	444	0.309 + 0.427	405
65	312	0.168	383	3	403	0.020	413	0.397 + 0.550	503
				4	370	0.024	423	0.486 + 1.493	553

[a] Acacia cellulose (AGU, 0.062 mol L^{-1}).

This might due to the thermoresponsive reversible phase transition of grafted polymeric chains from hydrophilic state to hydrophobic state, which affected the diffusion of MA and AN molecules to reach the active sites of acacia cellulose and resulting in homopolymers formation.[1] Besides, increase of temperature beyond the optimization would also lead to increase of the termination rate and resulted in limitation of grafting process.

Effect of reaction period

The effect of reaction period on the percentage of grafting (Gp) was investigated from 1 to 4 h. The trend of Gp increased from 1 to 2 h, where the maximum Gp was observed at 413% (Table I). Thereafter, slightly decreased till 4 h probably due to experimental error, because increasing the reaction time more than 2 h caused the reaction rate usually level off. This leaving off can be ascribed to the depletion in monomer and initiator, as well as the shortage of available grafting sites as the reaction proceeds. Therefore, the Gp increased with increasing reaction time to 2 h. This increase in graft after particular time is considered to be a detrimental effect.[24]

Effect of acid concentration

The acacia cellulose graft copolymerization process was strongly dependent on the pH of the grafting medium. In this study, concentration of sulfuric acid was investigated in cellulose-grafted polymer production. The optimum percentage of grafting (Gp) was achieved at 0.120 mol L^{-1} of sulfuric acid showing the yield of 413% (Table I). The explanation of increasing behavior with an acid in the grafting medium assists the grafting by causing intercrystalline and intracrystalline swelling of cellulose and also acting as a catalyst in hydrolysis of cellulose leading to an improvement in monomer accessibility. On the other hand, the experiment showed that the homopolymer formation was also enhanced in the presence of acid. A higher concentration of acid, however, may cause degradation of backbone chains of

cellulose as well as graft chains. Moreover, high acid concentration causes an oxidation of the formed free radicals, which decrease the rate of initiation with an increase of the homopolymer.[24]

Effect of initiator concentration

The graft copolymerization of MA and AN onto cellulose also studied at different amount of ceric (IV) ammonium nitrate ranging from 0.012 to 0.024 mol L^{-1} with other parameter kept constant. The Gp was increased from 0.012 to 0.016 mol L^{-1} of CAN. The optimum condition was achieved at 0.016 mol L^{-1} of CAN and Gp was 444%. Gp is decreased beyond 0.016 mol L^{-1} of CAN (Table I). The increasing trends in grafting up to 0.016 mol L^{-1} of CAN have been attributed to the formation of active ceric(IV) ions in the presence of an acid. The ceric(IV) ions were consumed in the formation of active sites onto cellulose, which is apparent from the increasing trend in the cellulose grafting. The decreasing trend in grafting at higher concentration of CAN (>0.016 mol L^{-1}) has been due to the decrease in ratio of an acid to CAN, hence a hydrated form of ceric(IV) ions was produced, which were not able to produce active sites onto the cellulose backbone. This has resulted in an appreciable decrease in graft conversion. The percent increase in homopolymer at high concentration of CAN is an indication that hydrated ceric(IV) ions participate preferably in the formation of homopolymer than in the formation of graft polymer.[22]

Effect of monomers concentration

It has been discussed that the initiation of graft copolymerization by means of redox couple involves reaction between initiator, cellulose, and monomers in a complex formation. Efficiency of this formation will evidently be dependent on the amount of the monomers added in the system. The larger amount of the monomers added, the more favored will be the formation of the complex that triggers the grafting reaction.

TABLE II
Percentage of Grafting Fractions on Graft Copolymerization[a]

Monomers concentration MA : AN (mol L^{-1})	Total grafting %	Nitrogen %	% Grafting fractions	
			PMA	PAN
0.221 : 0.305	336	2.50	304	32
0.309 : 0.427	405	2.80	363	42
0.397 : 0.550	503	3.00	446	57
0.486 : 1.493	553	3.20	486	67

[a] Acacia cellulose (AGU, 0.062 mol L^{-1}), 55°C, acid 0.120 mol L^{-1}, period 2 h, and CAN 0.016 mol L^{-1}.

In this study, as a consequence, increasing the amount of monomers would increase the percent of grafting. The percent of grafting of MA and AN onto cellulose was increased up to concentration 0.486 mol L^{-1} of MA and 1.493 mol L^{-1} of AN and Gp was achieved to 553% (Table I). Beyond the concentration of 0.486 mol L^{-1} MA and 1.493 mol L^{-1} AN, the percent grafting was not increased due to the formation of homopolymers in the product. The decreasing trend in graft yield at high concentration of MA and AN (>0.486 mol L^{-1} of MA and 1.493 mol L^{-1} of AN) has been attributed to the increase in viscosity of the medium, which has retarded the rate of diffusion of monomers molecules onto the cellulose surface, hence the graft yield has decreased. The steric hindrance created by grafted chains is another factor, which caused the retardation in rate of graft copolymerization at high concentration of monomers.[22] At high concentration of monomer, the rate of grafting decreased, monomer molecules were consumed more in the formation of homopolymer than in the formation of grafted chains, and the percentage of homopolymer continued to increase beyond 0.486 mol L^{-1} of MA and 1.493 mol L^{-1} of AN.

The effect of MA and AN monomers on grafting onto acacia cellulose and the percentage of grafting fractions of pure PMA and PAN are shown in Table II. The grafting fractions for both monomers are increased with increasing monomers concentration (Table II). The percentage of grafting fraction for MA is higher (486%) than AN (67%) at optimum conditions. The lower fraction of grafting with AN suggests that AN has a low affinity to attach to the acacia cellulose in comparison to MA. However, we have used these optimum parameters for the preparation of grafting product, which is further converted into hydroxamic acid and amidoxime ligands. Hence, we also anticipated that hydroxamic acid group having high proportion than amidoxime group due to grafting product containing higher fraction of PMA than PAN polymer.

Poly(hydroxamic acid)–poly(amidoxime) ligands

The grafted copolymers based on acacia cellulose were reacted with hydroxylamine for conversion of polymeric chelating ligands. Thus, PMA reacted with hydroxylamine to form hydroxamic acid, while PAN forms amidoxime groups (Scheme 2), and conversion of ligands is maximum due to % N content is 6.3 in the polymeric ligands, whereas % N content is 3.2 in the grafting product. Hence, the hydroxamic acid and amidoxime functional groups would contribute to the binding ability of the chelating ligands toward the metal ions. The methanol to water ratio is maintained at 4 : 1 to prevent the swelling of grafted copolymers during reaction for amidoximation/hydroximation.[15,17] According to the literature procedure,[15] we have optimized the amidoximation/hydroximation preparation at pH 11 using the highest copper exchange capacity for H form of ligands after treatment with HCl solution.

Sorption of metal ions by ligands

The sorption behavior of the poly(hydroxamic acid)–poly(amidoxime) chelating ligands toward the metal ions was determined by the binding of Cu^{2+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, and Cr^{3+} with the chelating ligands. The sorption process was carried out in sodium acetate buffer solution at pH ranged from 2 to 6 using the batch technique. From the result, one can conclude that the metal ions sorption capacities for the selected metal ions were observed to increase from pH 2 to 6. The chelating ligands showed higher affinity toward metal ions Zn^{2+}, Cr^{3+}, and Fe^{3+} compared to Ni^{2+} and Cu^{2+}. The binding capacities of Zn^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, and Cu^{2+} were 3.78, 2.8, 3.31, 1.2, and 2.55 mmol g^{-1}, respectively at pH 6 (Fig. 2). The metal ion of Zn^{2+} achieved highest sorption
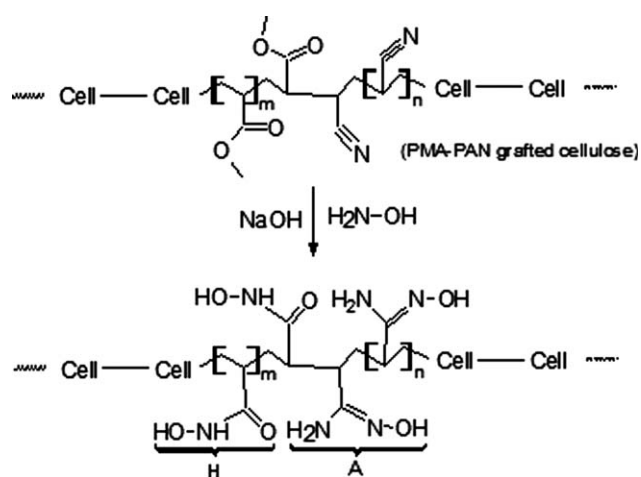
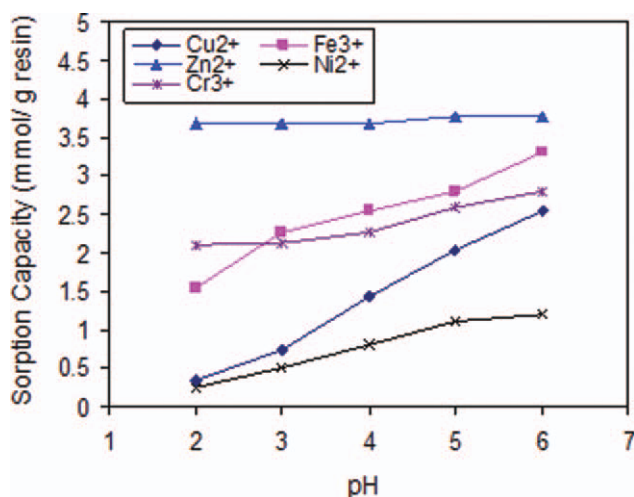**Scheme 2** Polymeric ligands with hydroxamic acid (H) and amidoxime (A).

Figure 2 Metal ions sorption capacity by the ligands as a function of pH. Other reaction condition: 553% of PMA-PAN-grafted acacia cellulose, 25.0 g; hydroxylamine hydrochloride ($NH_2OH.HCl$), 50.0 g; methanolic solution (methanol : water = 4 : 1), 500 mL; temperature, 70°C; and reaction period, 4 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

capacity when compared with the others metal ions, which also have significant sorption capacities. It was found that metal ions uptake by the ligands was pH dependent except zinc. Such discrepancy was found on the amphoteric type chelating resin, which was reported by Shah et al.,[25] and their results showed that several metal ions exchange capacity is pH dependent, while ion exchange capacity of Zn^{2+} is independent of pH in the range of pH 3.5–6.5. The sorption capacity of the synthesized chelating ligands toward the metal ions is in the following order: $Zn^{2+} > Fe^{3+} > Cr^{3+} > Cu^{2+} > Ni^{2+}$.

Highly colored chelating ligands were observed after batch equilibration with the metal ions due to the complexes formation of hydroxamic acid and amidoxime groups with the metal ions. The color detection was obviously observed from the resin after adsorbed Cu^{2+}, Fe^{3+}, and Cr^{3+}, whereas resin adsorbed Zn^{2+} and Ni^{2+} was hardly observed in color changing. The hydroxamate and amidoximate anions are bidentate ligands, trapped the metal ions, and formed five-membered ring complexes. The metal ions are bound to both oxygen atoms and the amine group.

Metal ions extraction at lower concentration

We have used metal ions concentrations of 10 and 50 ppm to find the effect at lower concentrations of metals by the ligands. This extraction process was carried out in sodium acetate buffer solution at pH 2–6 using the batch technique. The metal ions bind-

ing by the ligands was also pH dependent; however, the trend of metal ions sorption was different with higher concentration. We have found that the metal ions extractions were increased from pH 2 to 6. Here, we have measured as percentage of metal ions removal instead of metal ions sorption due to most of metals are bind fully at 10 and 50 ppm metal solution; therefore, sorption capacity is not applicable at lower concentration of metal ions at pH 5 and 6. The metal ions removals at pH 5–6 are highest for both 10 and 50 ppm concentration. For 50 ppm concentration, the removal of Cu^{2+}, Zn^{2+}, Cr^{3+}, Fe^{3+}, and Ni^{2+} was 98.4, 96.1, 98.1, 98.5, and 94.0%, respectively, at pH 6 (Fig. 3).

For 10 ppm metal concentration, the removal of Cu^{2+}, Zn^{2+}, Cr^{3+}, Fe^{3+}, and Ni^{2+} was 99.6, 99.5, 98.9, 98.5, and 97.3%, respectively, at pH 6 (Fig. 4). Here, we can conclude that low concentrations of metal ions could be highly efficient removals nearly 100%, and it is an excellent property of the ligands used in this study.

Kinetic study by batch technique

The study of rate of copper removal was performed using 10 and 50 ppm copper concentration at pH 6. The time required for 50% exchange ($t_{1/2}$) was calculated from the plot of the percentage of copper removal versus time (Fig. 5). The rate of copper removal under these conditions was very fast, that is, $t_{1/2}$ for Cu was 1.25 min for 10 ppm solution and $t_{1/2}$ for Cu was 1.80 min for 50 ppm solution. The copper exchange was faster rate of equilibrium;
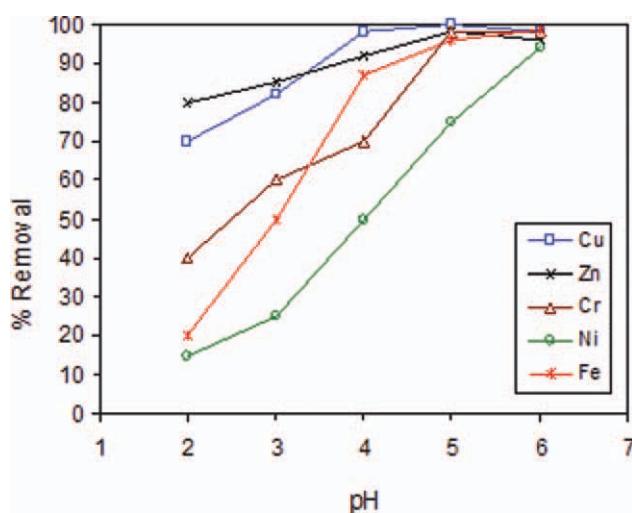

Figure 3 Metal ions (50 ppm) removal by the ligands as a function of pH. Other reaction condition: 553% of PMA-PAN-grafted acacia cellulose, 25.0 g; hydroxylamine hydrochloride ($NH_2OH.HCl$), 50.0 g; methanolic solution (methanol : water = 4 : 1), 500 mL; temperature, 70°C; and reaction period, 4 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
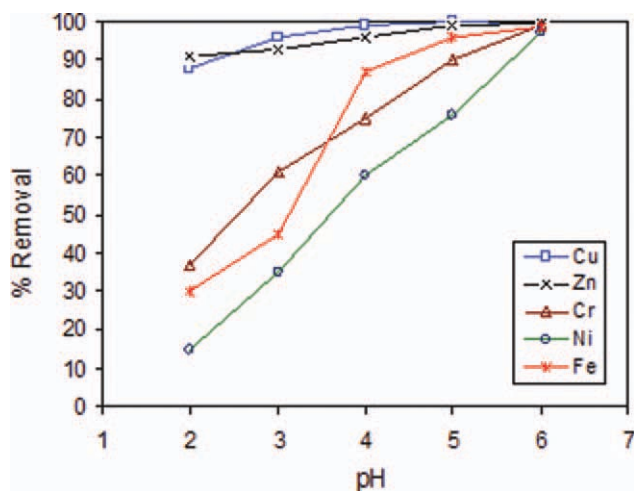
Figure 4 Metal ions (10 ppm) removal by the ligands as a function of pH. Other reaction condition: 553% of PMA-PAN-grafted acacia cellulose, 25.0 g; hydroxylamine hydrochloride ($NH_2OH.HCl$), 50.0 g; methanolic solution (methanol : water = 4 : 1), 500 mL; temperature, 70°C; and reaction period, 4 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

therefore, the column technique would be most efficient for heavy metals extraction.

Thermogravimetry analysis

The thermal degradation of poly(hydroxamic acid)–poly(amidoxime) chelating ligands, poly(methyl acrylate-co-acrylonitrile)-grafted acacia cellulose, and acacia cellulose was performed with a heating rate of 10°C min⁻¹ at N_2 atmosphere, and the TG curve
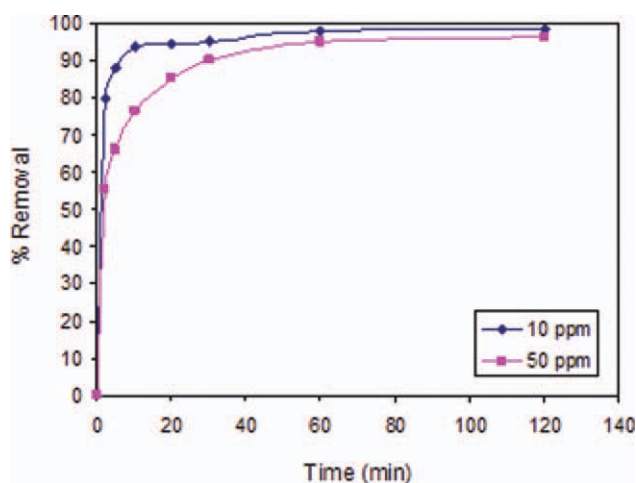

Figure 5 Rate of exchange of metal ions (10 and 50 ppm) as a function of % removal. Other reaction condition: 553% of PMA-PAN-grafted acacia cellulose, 25.0 g; hydroxylamine hydrochloride ($NH_2OH.HCl$), 50.0 g; methanolic solution (methanol : water = 4 : 1), 500 mL; temperature, 70°C; and reaction period, 4 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
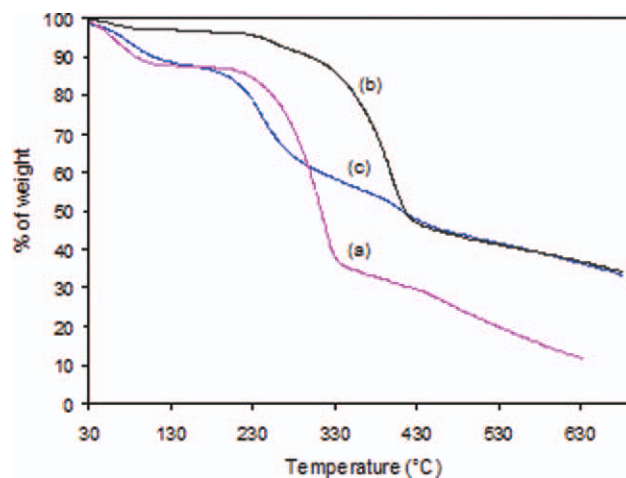
Figure 6 Thermogram of (a) acacia cellulose, (b) poly(-methyl acrylate-co-acrylonitrile)-grafted acacia cellulose, and (c) poly(hydroxamic acid)–poly(amidoxime) chelating ligands. The residual loss percentage as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is presented in Figure 6. There was moisture loss observed 12% in acacia cellulose sample [Fig. 6(a)] at 110°C and polymeric chelating ligands loss moisture 12% at 140°C [Fig. 6(c)], whereas grafting copolymer does not show moisture dehydration [Fig. 6(b)]. For cellulose materials, a sharp weight loss 66% was found at 330°C and 12% was remaining until at 700°C. The percentage weight loss of grafting copolymers and polymeric ligands was 48% at 420°C; however, initial weight loss of polymeric ligands was higher than grafting copolymers. Both copolymers and polymeric ligands are more stable than acacia cellulose and 33% weight was remaining until 700°C.

CONCLUSIONS

The chelating ligands were successfully synthesized from poly(methyl acrylate-co-acrylonitrile)-grafted acacia cellulose. The optimum yield of percent grafting was observed to be dependent on the CAN, monomers—MA and AN, acacia cellulose, mineral acid, and the reaction temperature and period. The chelation behavior of the ligands toward certain metal ions was excellent. The sorption capacities of the ligands for Cu, Fe, Zn, Ni, and Cr ions were observed to be pH dependent. The rate of equilibrium is very fast; therefore, the column technique would be most efficient for heavy metals extraction. The low-cost production of acacia cellulose-based poly(hydroxamic acid) and poly(amidoxime) ligands can be considered as an excellent candidate for waste water treatment process. The detail sorption study and metal ions removal from industrial wastewater using these ligands are now in progress and will be reported in due course.

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