

# Preparation and characterization of poly(amidoxime) chelating resin from polyacrylonitrile grafted sago starch

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## Abstract

The preparation of a chelating ion-exchange resin containing amidoxime functional group was carried out by polyacrylonitrile (PAN) grafted sago starch. The PAN grafted copolymer was obtained by free-radical initiating process using ceric ammonium nitrate as an initiator. Conversion of nitrile groups of the grafted copolymer into the amidoxime was carried out by treatment with hydroxylamine under alkaline solution. The chelating poly(amidoxime) resin was characterized by FT-IR spectra, TG and DSC analyses. The chelating behavior of the prepared resin was carried out by using some metal ions. A significant binding property of metal ions by the chelating resin was observed and the maximum copper capacity was  $3.0 \text{ mmol g}^{-1}$  at pH 6. The sorption capacities of metal ions by the resin were pH-dependent, and its selectivity towards these metal ions is in the following order:  $\text{Cu}^{2+} > \text{Fe}^{3+} > \text{As}^{3+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+} > \text{Pb}^{2+}$ . The rate of exchange was rapid, i.e.  $t_{1/2} < 9 \text{ min}$ , based on the exchange of copper ion. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Chelating resin; Poly(amidoxime) resin; Acrylonitrile; Sago starch; Binding capacity

## 1. Introduction

A number of articles have been published describing the synthesis of macroreticular resins containing amidoxime groups, because of their use in the extraction of uranium from sea water [1–4]. All articles describing the synthesis of a sorbent with an amidoxime group, mostly involve the incorporation of a nitrile group into a polymer matrix, followed by the conversion of the nitrile group into an amidoxime group by treatment with an alkaline solution of hydroxylamine. Egawa et al. [5] prepared a macroreticular chelating resin containing amidoxime by reacting acrylonitrile–divinyl benzene copolymer beads with hydroxylamine. Kobuke et al. [6]

synthesized a polyacrylo amidoxime resin from various copolymers of acrylonitrile and cross-linking agents. Another approach consists of the introduction of amidoxime groups into cellulose by the reaction of cyanoethylcellulose and acrylonitrile grafted cellulose with hydroxylamine [7]. Ref. [8] pertains to the extraction of metals from dilute solutions by poly(amidoxime) derived from fibrous homopolymers and copolymers of acrylonitrile. Divinylbenzene cross-linked poly(acryloamidoxime) resins were successfully applied to the determination of trace metals in natural waters [9,10].

Most of the work is centralized on uranium extraction in sea water by poly(amidoxime) resin. There are very few articles published on transition metal uptake by poly(amidoxime) resin. This may first be introduced to the preparation of poly(amidoxime) chelating resin from polyacrylonitrile (PAN) grafted sago starch. In this study, the PAN grafted copolymer was used as the

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cheapest starting material for poly(amidoxime) resin preparation, and we examine the binding properties of some metal ions with the resin.

## 2. Experimental

### 2.1. Materials and methods

Sago starch was purchased from Tepung Sago Co. Ltd. (Malaysia). To remove the inhibitor, acrylonitrile (Fluka) monomer was passed through the column, which was filled with chromatographic grade activated alumina. The monomer was stored at  $-10^{\circ}\text{C}$ . Ceric ammonium nitrate (BDH), hydroxylamine hydrochloride (Fluka), methanol (Beaker) and other chemicals used were of analytical reagent grade.

### 2.2. Graft copolymerization procedure

The starch slurry was prepared from 10.0 g of sago starch and 400 ml distilled water in a 1 l three-neck flask, which was equipped with a mechanical stirrer, condenser and thermostat water bath. Starch slurry was preheated at  $80^{\circ}\text{C}$  for about 30 min and was purged with  $\text{N}_2$  gas. After it was gelatinized, the contents of the flask was then cooled to  $50^{\circ}\text{C}$  and 8.0 ml diluted sulfuric acid ( $\text{H}_2\text{SO}_4:\text{H}_2\text{O}/1:1$ ) was added to the reaction mixture. After 5 min, 40 ml of 0.1 M of ceric ammonium nitrate solution was added, and another 10 min later, 24.0 ml of acrylonitrile monomer was added to the mixture. The reaction was carried out for 90 min and after completion of the reaction, the flask was cooled under running tap water. The grafted product was poured into 1 l methanol for precipitation. The copolymer was washed several times with methanol:water (4:1) and dried at  $50^{\circ}\text{C}$  to a constant weight [11].

### 2.3. Preparation of chelating resin containing amidoxime groups

The preparation of resin containing amidoxime group is based on the treatment of nitrile with hydroxylamine [1,6].

#### 2.3.1. Preparation of hydroxylamine ( $\text{NH}_2\text{OH}$ ) solution

About 42.1 g of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) was dissolved in 300 ml methanolic solution (methanol:water/5:1). The  $\text{HCl}$  of  $\text{NH}_2\text{OH}$  was neutralized by  $\text{NaOH}$  solution and the precipitate of  $\text{NaCl}$  was removed by filtration. The pH of the reaction solution was adjusted to pH 10 by adding  $\text{NaOH}$  solution. The reaction medium was maintained as methanol to water ratio 5:1.

About 20.0 g of grafted copolymer was placed into the two-neck flask, which was equipped with a me-

chanical stirrer, condenser and thermostat water bath. Then the above-prepared hydroxylamine solution was added to the flask, and the reaction was carried out at  $70^{\circ}\text{C}$  and 2 h duration. After completion of the reaction, the resin was separated from solution by filtration and washed several times with methanolic solution (methanol:water/4:1). Then, the resin was treated with 200 ml of methanolic 0.1 M  $\text{HCl}$  solution for at least 5 min. Finally, the resin was filtered and washed several times with methanolic solution (methanol-water/4:1), and then dried at  $50^{\circ}\text{C}$  to a constant weight.

### 2.4. Resin characterization

#### 2.4.1. Qualitative test of amidoxime functional group

About 0.2 g of wet resin was shaken with vanadium (V) ion in dilute hydrochloric acid solution and a purple colored complex on the resin beads was observed.

#### 2.4.2. Hydrolysis of poly(amidoxime) resin

About 1.0 g of the resin was placed into a 100 ml flask, and 50 ml of 1 M  $\text{HCl}$  was added to the flask. The flask was fitted with a condenser and immersed in a thermostat water bath. The hydrolysis was carried out at  $90^{\circ}\text{C}$  and the reaction period was 30, 60 and 120 min. After completion of the hydrolysis period, the product was washed thoroughly with methanol-water solution and dried at  $50^{\circ}\text{C}$  to a constant weight.

#### 2.4.3. FT-IR analysis

Infrared spectra of polymer samples with  $\text{KBr}$  pellets were obtained from FT-IR spectrometer (Perkin-Elmer, 1725).

#### 2.4.4. Swelling study of the resin

Exactly 0.5 g of dry resin was soaked in distilled water for 12 h and filtered under slightly reduced pressure. The filtration was continued for exactly 0.5 min after the disappearance of the surface water. The swollen resin was then pressed lightly between filter papers to remove surface water and the resin was rapidly weighed [12].

#### 2.4.5. Cation exchange capacity

A sample (about 5.0 g) of the ion exchanger was completely converted to the  $\text{H}^+$  form by treatment with excess methanolic solution of 0.1 M  $\text{HCl}$  in a conical flask by batch equilibration. The resin was then washed with methanol-water to remove sorbed  $\text{HCl}$ , until the washing solution became free of  $\text{Cl}^-$  and the resin was dried at  $50^{\circ}\text{C}$  to a constant weight. Exactly 0.2 g of the  $\text{H}^+$  form of resin was weighed into a 250 ml Erlenmeyer flask, and 25 ml of standard 0.1 M  $\text{NaOH}$  solution was added to a flask with a stopper and was shaken

for about 4 h. After shaking, 10 ml aliquots of the supernatant solution was back-titrated to the phenolphthalein end point with standard 0.1 M HCl solution [13,14].

#### 2.4.6. Sorption of metal ions by batch technique

Metal ion binding capacity was measured by the batch equilibration technique with varying pH solutions (pH 2–6). For the batch technique, the resin (100–200  $\mu\text{m}$  size) was dried at 50°C to a constant weight. Exactly 0.2 g of dry resin was placed into a series of 100 ml clean polyethylene bottles, and the resins were allowed to equilibrate with 25 ml distilled water for at least 10 min. After adding 20 ml of 0.1 M sodium acetate buffer at various pHs, 20 ml of 0.1 M metal ion solution was added to each bottle 10 min later. The mixture was shaken for about 24 h by a rotary shaker. After equilibration was completed, 5 ml supernatant solution was collected for metal ion determination. The initial and final amounts of metal ion concentration was determined by AAS (GBC-903).

#### 2.4.7. Kinetic exchange

The rate of exchange of copper in acetate buffer at pH 4 was determined by 0.15 g of resin beads into contact with 10 ml of 0.1 M copper solution for various time intervals, and copper ion was determined as described above. The time required for 50% exchange ( $t_{1/2}$ ) was calculated from the plot of copper capacity ( $\text{mmol g}^{-1}$ ) vs. time [15].

#### 2.4.8. Sorption of metal ion with HCl

Exactly 0.15 g of resin was placed into the polyethylene bottle. Ten ml of various concentration of HCl solutions ranging from 1.0 M to 0.001 M and 10 ml of 0.1 M metal ion solution were added to each mixture. Shaking the mixture for about 24 h the metal ion was analyzed as above.

analyses were carried out in a  $\text{N}_2$  atmosphere from room temperature to 1000°C at a heating rate of 10°C  $\text{min}^{-1}$  with a  $\text{N}_2$  flow rate of 50  $\text{ml min}^{-1}$ . Primary thermograms were obtained by plotting percent residual weight against temperature.

#### 2.4.10. Differential scanning calorimetry analysis

Differential scanning calorimetry (DSC) experiments were carried out by Polymer Laboratories (PL-DSC) at a  $\text{N}_2$  flow rate of 50  $\text{ml min}^{-1}$ . The DSC thermograms were obtained from the PAN grafted sago starch and poly(amidoxime) resin, which were packed into Al pans, and heated at a rate of 10°C  $\text{min}^{-1}$ .

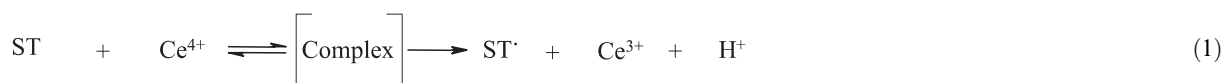
### 3. Results and discussion

#### 3.1. Grafted copolymer

The polyacrylonitrile grafted sago starch was obtained from the acrylonitrile monomer with sago starch and the grafting reaction was carried out by free-radical initiating process. The optimum yield of the PAN grafted copolymer was obtained at the concentration of ceric ammonium nitrate, acrylonitrile, sago starch (expressed as anhydroglucose unit) and sulfuric acid of  $9.52 \times 10^{-3}$ , 0.506, 0.146, and 0.190  $\text{mol l}^{-1}$ , respectively. The reaction temperature and period was 50°C and 90 min, respectively.

The mechanism of graft copolymerization of the vinyl monomer onto starch macromolecules was proposed by Ceresa [16]. Here, the reaction of acrylonitrile monomer with sago starch initiated by ceric ion takes place in three steps as follows:

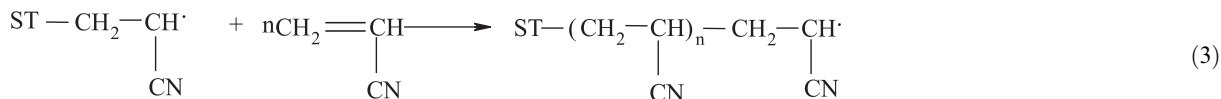
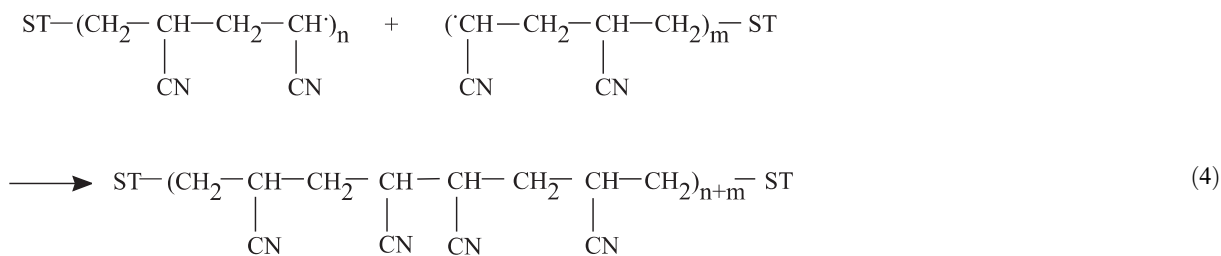
##### Initiation



#### 2.4.9. Thermogravimetry analysis

Thermogravimetry (TG) experiments were performed by DuPont Thermal Analyzer (Model-990). The

where ST and  $\text{ST}^{\cdot}$  is the sago starch and free radical of sago starch, respectively.

*Propagation**Termination*

(PAN grafted sago starch)

*3.2. Poly(amidoxime) resin*

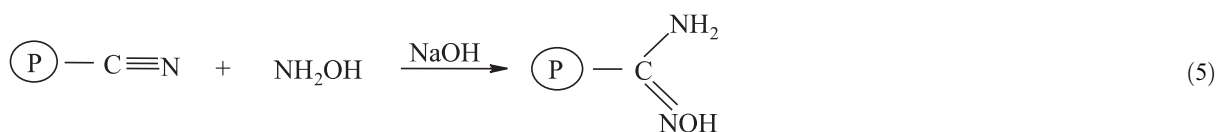
The conversion of nitrile to amidoxime was carried out by the treatment of hydroxylamine in an alkaline medium. Experimental parameters such as grafted copolymer–hydroxylamine ratio, 1:1; reaction period, 2 h; temperature, 70°C; reaction medium methanol–water ratio, 5:1; pH, 10 of the reaction medium were determined.

According to Egawa et al. [2], the reaction mechanism of polyacrylonitrile with hydroxylamine to convert poly(amidoxime) is shown as follows:

where P is the backbone polymer.

*3.3. Qualitative test of amidoxime functional groups*

Several methods have been employed for confirmation of amidoxime groups in the resin [17]. Many metal ions bind with amidoxime to produce a visual color in the resin bead. Therefore, the presence of amidoxime groups in the resin was confirmed by vanadium ion test in the formation of a purple complex.



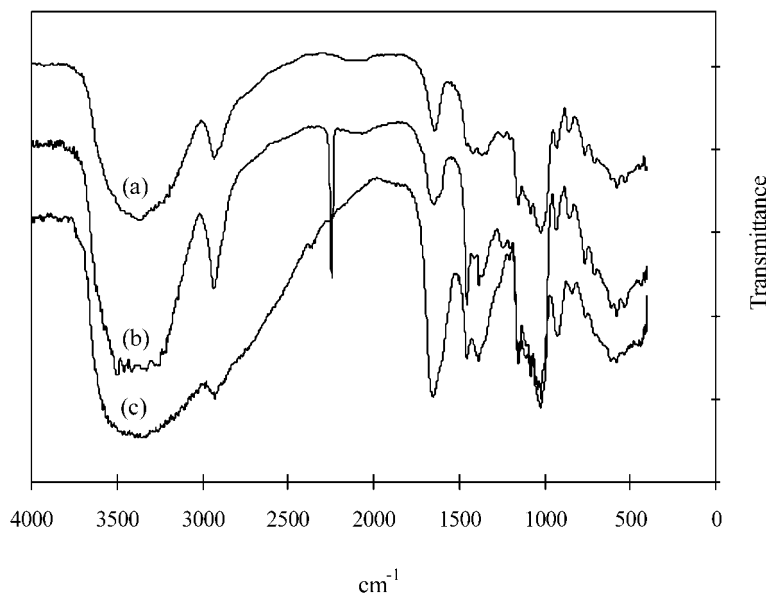


Fig. 1. FT-IR spectra of (a) sago starch; (b) polyacrylonitrile grafted sago starch and; (c) poly(amidoxime) resin.

#### 3.4. Analysis of FT-IR spectra

For the study of FT-IR spectra of sago starch, the characteristic absorption bands of starch at 3402 and 1639 cm<sup>-1</sup> due to O–H stretching and bending modes, respectively are shown in Fig. 1(a). In addition, ab-

sorption bands of starch appeared at 2930 and 1024 cm<sup>-1</sup> due to the C–H stretching and bending modes, respectively. FT-IR spectrum of polyacrylonitrile grafted sago starch are presented in Fig. 1(b). The characteristic absorption of polyacrylonitrile at 2245 cm<sup>-1</sup> due to C≡N stretching modes in addition to same absorption

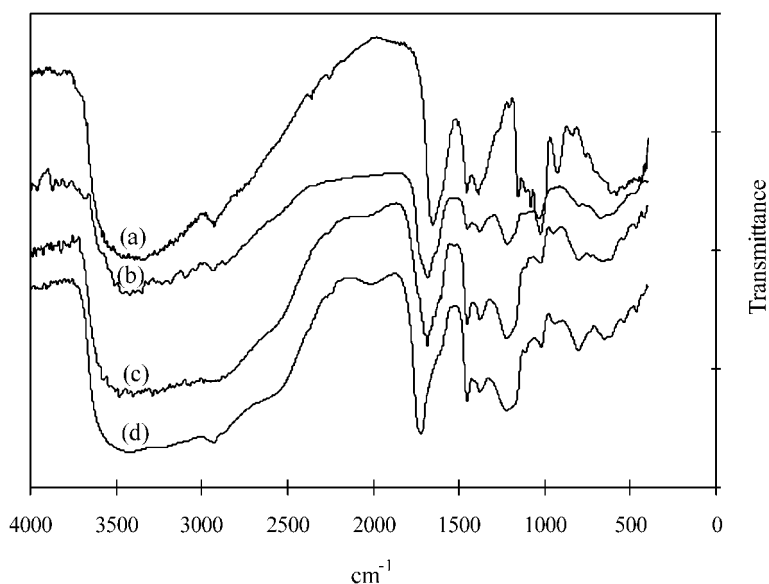


Fig. 2. FT-IR spectra of (a) poly(amidoxime) resin; (b) 30 min hydrolysis of resin; (c) 60 min hydrolysis of resin and; (d) 120 min hydrolysis of resin.

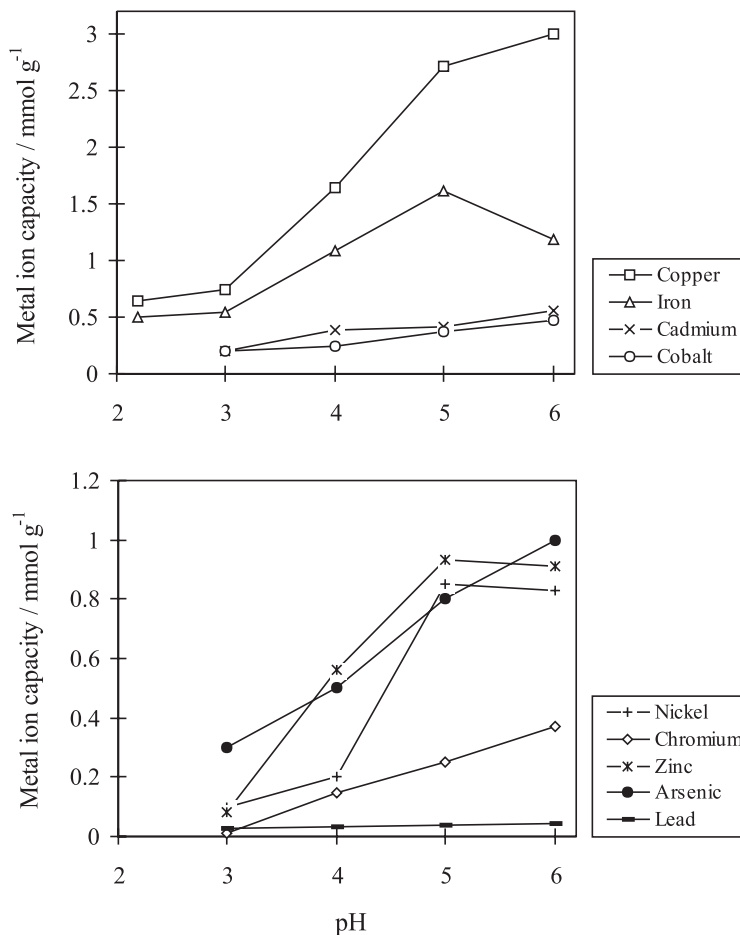


Fig. 3. Effect of pH on the sorption of metal ions by poly(amidoxime) resin. Resin, 0.165 g; shaking time, 24 h; batch technique.

bands of sago starch. After amidoxime group preparation, the  $C\equiv N$  band of  $2245\text{ cm}^{-1}$  disappeared and formed a new band of amidoxime at  $1652\text{ cm}^{-1}$ , and the amide II band of N–H at  $1568\text{ cm}^{-1}$ , respectively are shown in Fig. 1(c).

### 3.5. Proof of amidoxime by acid hydrolysis

This approach was presented by Barton and Ollis [18], and it consists in the treatment of amidoxime resin with dilute mineral acid to produce amides and prolong hydrolysis to form the corresponding carboxylic acid. The hydrolysis of amidoxime gave amides at  $1683$  and  $1689\text{ cm}^{-1}$  with a 30 and 60 min hydrolysis time, respectively, which are shown in Fig. 2(b) and (c), respectively. Finally, at prolonged hydrolysis of amidoxime gave corresponding carboxylic acid at  $1723\text{ cm}^{-1}$  in Fig. 2(d). This is a strong evidence of amidoxime formation.

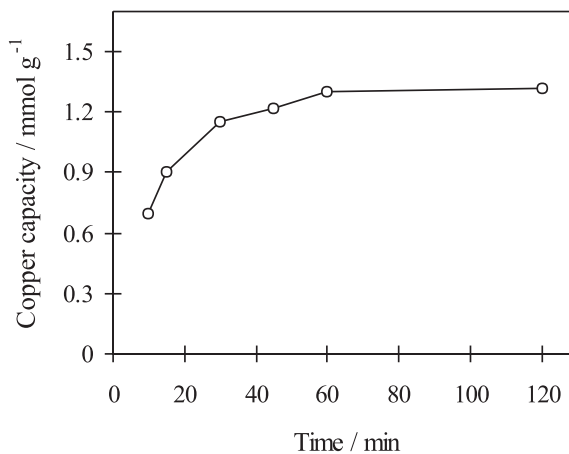
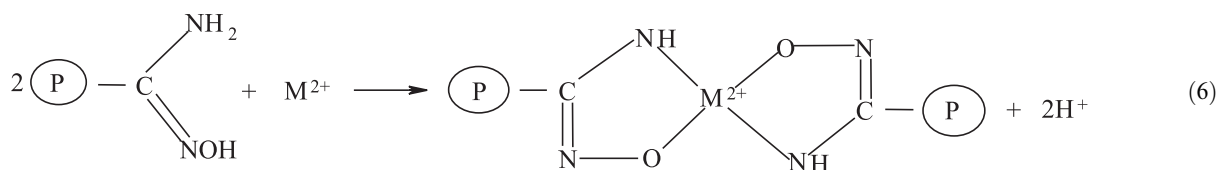


Fig. 4. Sorption rate of copper. pH 4 of 0.1 M acetate buffer; resin, 0.100 g; batch technique.

### 3.6. Sorption of metal ion by the batch method

The binding properties of a series of metal ions i.e.  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{As}^{3+}$  and  $\text{Pb}$  with poly(amidoxime) resin were determined in buffer at pH 2–6. It was found that metal ion uptake by resin was increased with increasing pH up to 6 (Fig. 3). The copper capacity was observed to be a maximum of  $3.00 \text{ mmol g}^{-1}$  at pH 6. Sorption capacities of  $\text{Fe}^{3+}$ ,  $\text{As}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  ions were observed 1.41, 1.0, 0.93 and  $0.84 \text{ mmol g}^{-1}$ , respectively, at pH 6. Sorption capacities of Cu, Fe, Cr, Ni, Co, Zn, Cd, As, Pb ions by resin were pH-dependent, and its selectivity towards these metal ions is in the following order:  $\text{Cu}^{2+} > \text{Fe}^{3+} > \text{As}^{3+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+} > \text{Pb}^{2+}$ .

A possible chelation mechanism of amidoxime with bivalent metal ion for the the complexation is shown below.



The rate of sorption was rapid,  $t_{1/2} < 9$  min, based on the rate of sorption of copper at pH 4 is presented in Fig. 4. The physical and chemical properties of the resin are listed in Table 1.

Table 1

Physical and chemical properties of the poly(amidoxime) chelating resin

Physical or chemical properties	Parameters
% grafting	82
Polyacrylonitrile concentration, %	45
Sago starch concentration, %	55
Particle size, $\mu\text{m}$	100–200
Water regain, g water $\text{g}^{-1}$	4.5
Cation exchange capacity, $\text{mmol g}^{-1}$	4.21
Exchange rate, $t_{1/2}$ , min	<9

### 3.7. Effect of HCl on sorption capacity

The sorption capacities of the proposed resin towards the metal ion were performed in the presence of various

concentration of HCl. The capacities of resin towards  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  ions were affected in the presence of the 1.0 M HCl concentration. The copper capacity decreased gradually from 1.0 to  $0.2 \text{ mmol g}^{-1}$

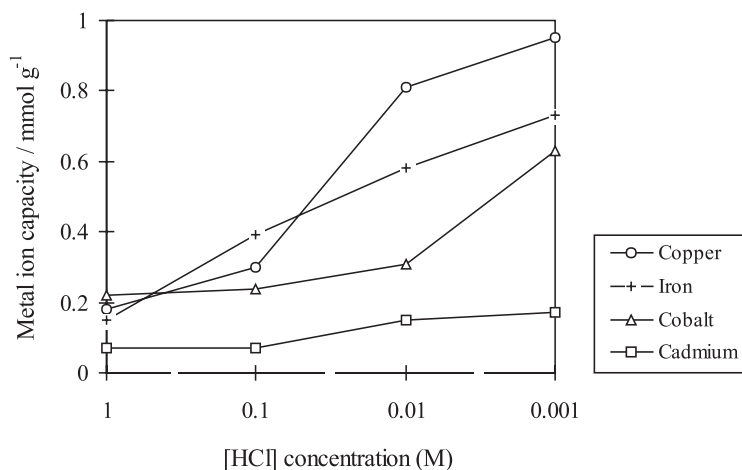


Fig. 5. Effect of HCl concentration on the sorption of metal ions by resin. Resin, 0.100 g; shaking time, 24 h; batch technique.

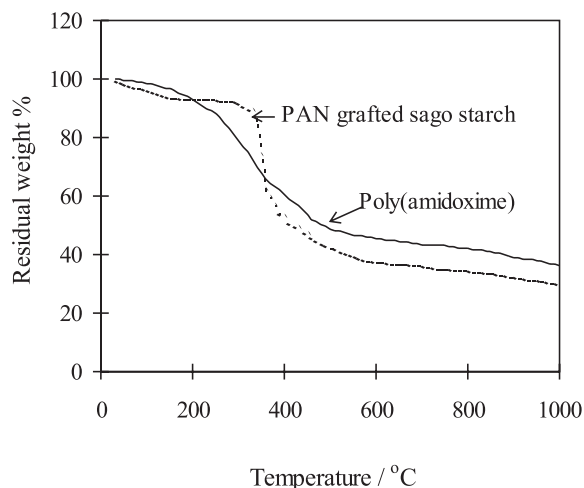


Fig. 6. Thermograms of PAN grafted sago starch and poly(amidoxime) resin.

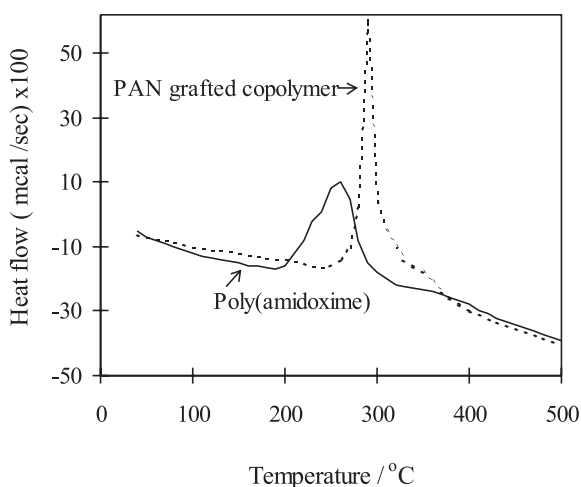


Fig. 7. DSC Thermograms of PAN grafted sago starch and poly(amidoxime) resin.

with the increase in HCl concentration from 0.001 to 1.0 M, respectively (Fig. 5). The capacity for iron was 0.73–0.15 mmol g<sup>-1</sup> from 0.001 to 1.0 M HCl, respectively. The binding of Co<sup>2+</sup> and Cd<sup>2+</sup> ions were very low at all the concentration of HCl. Therefore, the binding ability of the resin towards the metal ion in the presence of HCl reflects the instabilities of their amidoxime complexes.

### 3.8. Thermogravimetry analysis

The thermal degradation of poly(amidoxime) resin and polyacrylonitrile (PAN) grafted sago starch was performed with a heating rate of 10°C min<sup>-1</sup> in an N<sub>2</sub> atmosphere and the TG curve are presented in Fig. 6.

The main weight loss of PAN grafted sago starch and poly(amidoxime) resin occurs between the range of 290–380°C and 200–480°C, respectively. The same weight loss was found (7%) at 200°C of grafted materials and poly(amidoxime) resin. The poly(amidoxime) resin was slightly less stable than PAN grafted sago starch up to a temperature of 345°C, and again the resin was more stable than PAN grafted sago starch up to 1000°C. At the final stage, about 30% weight remain in PAN grafted sago starch, whereas 36% weight remain in poly(amidoxime) resin was observed until 1000°C.

### 3.9. Differential scanning calorimetry analysis

The DSC curves of polyacrylonitrile grafted copolymer and poly(amidoxime) resin are presented in Fig. 7. The PAN grafted copolymer material exhibited an exothermic transition at 290°C, whereas a new exothermic transition in poly(amidoxime) was observed at 260°C with a little initial moisture dehydration. The exothermic transition was shifted to the left side due to amidoximation in the grafted copolymer, which proved poly(amidoxime) resin formation.

## 4. Conclusions

The poly(amidoxime) ion exchange resin was synthesized from polyacrylonitrile grafted sago starch. The binding capacity of some metal ions by the resin was carried out by the batch technique. The sorption capacity was high for copper 3.0 mmol g<sup>-1</sup> at pH 6. The kinetic exchange rate was fast,  $t_{1/2} < 9$  min. The sorption capacities of Cu, Fe, Cr, Ni, Co, Zn, Cd, As, Pb ions by the resin were pH dependent. The proposed resin has the advantage of a faster rate of equilibrium probably due to the new backbone polymer. In future, our work will be extended to the extraction of toxic metals from environment.

## Acknowledgements

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