

Metal ions binding by chelating ligands from new polymer bearing amidoxime functional groups[†]

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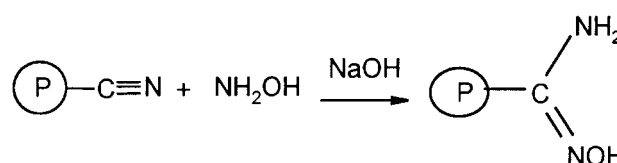
A new polymer bearing amidoxime chelating resin was prepared from polyacrylonitrile (PAN) grafted sago starch and the significant binding capacity of metal ions by the resin was observed with a rapid sorption rate.

Chelating polymer materials are mainly used in analytical, industrial and radiochemical laboratories, but only to a limited extent in solving environmental problems. Metal pollution of the environment presents a unique problem, since metals are not subjected to biodegradation. The chelating resins containing amidoxime groups have been playing a vital role in environmental monitoring of toxic trace metals. The amidoxime chelating resins can be used for extraction of toxic metals in the environment and sewage waters. The possibility of uranium recovery from seawater has been studied in many countries, a particularly high number of publications come from Japanese scientists, which contain the synthesis of macroreticular resins bearing amidoxime groups, because of their use in extraction of uranium from seawater.^{1–4} Most of these papers involve the incorporation of a nitrile group into a polymer matrix, followed by the conversion of the nitrile group into an amidoxime group using the alkaline solution of hydroxylamine. Egawa *et al.*⁵ prepared a macroreticular chelating resin containing amidoxime by reacting acrylonitrile-divinyl benzene copolymer with hydroxylamine. Kubota and Shigehisa⁶ proposed a new route in which amidoxime groups were prepared by the reaction of cyanoethylcellulose and acrylonitrile grafted cellulose with hydroxylamine. Fetscher⁷ described the extraction of metals from dilute solutions by poly(amidoxime) resin derived from fibrous homopolymers and copolymers of acrylonitrile. Divinylbenzene cross-linked poly(acryloamidoxime) resins were obtained and successfully used in the determination of trace metals in natural waters.^{8,9}

Most of the work centralised on the uranium extraction in sea water by poly(amidoxime) resin. There are very few articles published for transition metal uptake by poly(amidoxime) resin. This may first be introduced by the preparation of poly(amidoxime) chelating resin from polyacrylonitrile (PAN) grafted sago starch. In this report, the PAN grafted copolymer was used as a cheapest starting material to obtain the poly(amidoxime) resin and the binding property of the chelating resin was examined with a series of metal ions.

The PAN grafted sago starch was prepared from acrylonitrile monomer and sago starch using the free radical initiating process according to the reaction mechanism suggested by Ceresa.¹⁰ The grafting procedure was described elsewhere.¹¹ The optimum yield of PAN grafted copolymer at the concentration of ceric ammonium nitrate, acrylonitrile, sago starch (AGU, anhydroglucose unit) and sulfuric acid were 9.52×10^{-3} , 0.506, 0.146 and 0.190 mol/l respectively, as well the reaction temperature and period were 50°C and 90 min, respectively. The conversion of the nitrile group into amidoxime was carried out by the treatment of hydroxylamine in an alkaline medium. According to the mechanism suggested

by Schouteden,¹² the reaction of PAN with hydroxylamine is shown in Scheme 1, where P is the backbone polymer.



Scheme 1

The amidoxime functional group was identified by IR spectroscopy (Perkin-Elmer 1725). The characteristic absorption band of nitrile (PAN) was observed at 2245 cm^{-1} due to $\text{C}\equiv\text{N}$ stretching modes in addition to the same absorption bands of sago starch¹¹ as shown in Fig. 1a. To obtain a poly(amidoxime) resin, the amidoxime group was inserted to the PAN grafted copolymer, the $\text{C}\equiv\text{N}$ band of 2245 cm^{-1} disappeared and formed a new band of amidoxime at 1652 cm^{-1} and amide II band of N–H at 1568 cm^{-1} respectively, as shown in Fig. 1b. This result suggested that the nitrile groups of PAN grafted copolymer were converted into amidoxime groups.

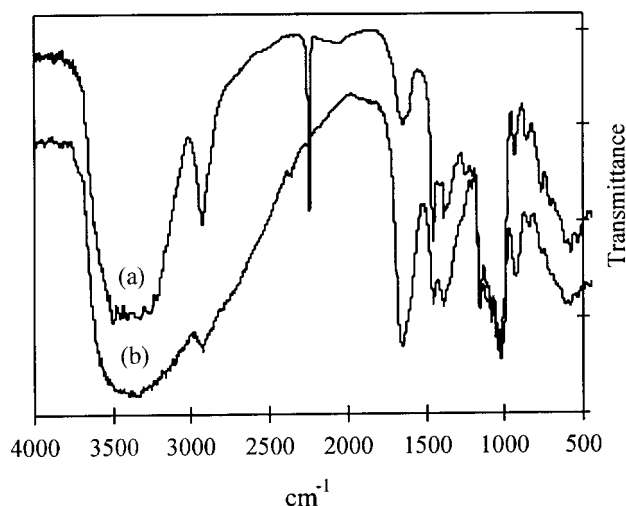


Fig. 1 FT-IR spectra of (a) polyacrylonitrile grafted sago starch and (b) poly(amidoxime) resin.

Here we present the results of the binding property of poly(amidoxime) resin with a series of metal ions. The sorption study was carried out in buffer at pH 2 to 6 and it was found that the metal ion uptake by the resin was increased with increasing of pH up to 6 (Table 1). This chelating resin exhibits high affinity for copper, iron, zirconium, zinc, uranium and lanthanum i.e. the binding capacities of Cu, Fe, Zr, Zn, U and

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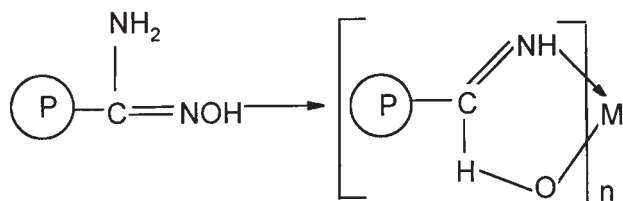
La were 3.00, 2.18, 1.99, 1.61, 1.35 and 1.28 mmol/g, respectively at pH 6. Although the binding capacity of copper is high, other metal ions also have significant sorption capacity as shown in Table 1. The sorption capacities of metal ions are pH dependent and the selectivity towards these metal ions is in the following order: $\text{Cu}^{2+} > \text{Fe}^{3+} > \text{Zr}^{3+} > \text{Zn}^{2+} > \text{U}^{6+} > \text{La}^{3+} > \text{Gd}^{3+} > \text{Nd}^{3+} > \text{Th}^{4+} > \text{As}^{3+} > \text{Ce}^{3+} > \text{Tb}^{3+} > \text{Ni}^{2+} > \text{Pr}^{3+} > \text{Dy}^{3+} > \text{Cd}^{2+} > \text{Cr}^{3+} > \text{Co}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$.

Table 1 Metal ions capacity by poly(amidoxime) resin.^a

Metal ions	Metal ions capacity (mmol/g) pH				
	2	3	4	5	6
Cu^{2+}	0.89	1.12	1.59	2.72	3.00
Fe^{3+}	0.68	0.88	1.01	1.61	2.18
Zr^{3+}	0.56	0.71	1.56	1.58	1.99
Zn^{2+}	0.55	0.88	1.18	1.33	1.61
U^{6+}	0.68	1.03	1.12	1.19	1.35
La^{3+}	0.78	0.89	0.99	1.05	1.28
Gd^{3+}	0.59	0.89	0.88	0.85	1.12
Nd^{3+}	0.39	0.65	0.76	0.91	1.07
Th^{4+}	0.31	0.52	0.83	0.82	1.01
As^{3+}	0.19	0.55	0.75	0.81	1.00
Ce^{3+}	0.52	0.61	0.75	0.92	0.97
Tb^{3+}	0.29	0.50	0.85	0.88	0.96
Ni^{2+}	0.25	0.48	0.62	0.71	0.83
Pr^{3+}	0.19	0.30	0.55	0.72	0.82
Dy^{3+}	0.40	0.53	0.58	0.61	0.72
Cd^{2+}	0.18	0.19	0.25	0.41	0.56
Cr^{3+}	0.12	0.18	0.32	0.25	0.37
Co^{2+}	0.08	0.11	0.22	0.37	0.47
Ca^{2+}	0.13	0.19	0.20	0.46	0.56
Mg^{2+}	0.14	0.21	0.22	0.29	0.41
Na^+	0.11	0.11	0.18	0.24	0.33

^a0.2000 g dry resin and 20 ml of 0.1M metal ion solution.

The rate of exchange of copper ion was determined and the time required for 50% exchange was calculated from the method described by Lee *et al.*¹³ The rate of copper exchange was rapid *i.e.* $t_{1/2} < 9$ min. Therefore, overall metal ions uptake by this resin can be achieved within a short period compared to other chelating resins.^{2,6,8} The chelate complex of the amidoxime ligand with a metal ion is presented in Scheme 2, where P is the backbone polymer and n is the oxidation state of metal (M).



Scheme 2

An extensive sorption study on poly(amidoxime) resin was undertaken for extraction of uranium from sea water by Egawa *et al.*^{1,2,5} They found that the sorption capacity of uranium is about 0.96 mmol/g. Kabay *et al.*³ reported that the sorption capacity of copper and uranium was 3.6 and 1.47 mmol/g, respectively. Vernon and Shah⁸ prepared a chelating resin bearing hydroxamic/amidoxime groups and the binding of copper

and uranium was observed to be 2.60 and 0.90 mmol/g respectively, and their kinetic study shows that the rate of sorption for copper and uranium was 12 and 13.5 min ($t_{1/2}$), respectively. However, although the overall metal ion capacities of our poly(amidoxime) resin are similar to those of other research workers, the rate of sorption is better ($t_{1/2} < 9$ min) than for other reported poly(amidoxime) resins.

In conclusion, the poly(amidoxime) chelating resin was prepared from PAN grafted sago starch and the sorption capacities of a series of metal ion were found to be high. This resin has the advantage of faster rate of equilibrium compared to earlier amidoxime resins probably due to the presence of the new backbone polymer. In future our work will be extended to the extraction of toxic metals from the environment.

Experimental

Preparation of hydroxylamine (NH_2OH) solution: About 42.10 g of hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) was dissolved in 300 ml methanolic solution (methanol: water; 5:1). The NH_2OH was neutralized by NaOH solution and the precipitate of NaCl was removed by filtration. The pH of the NH_2OH solution was adjusted to pH 10 by NaOH solution.

Preparation of the poly(amidoxime) resin: PAN grafted copolymer (20.00 g) was placed into the round bottom flask and the NH_2OH solution was added, the flask was equipped with a mechanical stirrer, condenser and water bath. The reaction was carried out at 70°C for 2 h. Then, the resulting poly(amidoxime) resin was separated by filtration and washed several times with methanolic solution for (methanol: water; 5:1). The resin was treated with 200 ml of methanolic 0.1M HCl solution for at least 5 min. Finally, the resin was filtered and washed several times with methanolic solution and dried at 50°C to a constant weight.

Metal ion binding by the resin: The metal ions binding to the resin were measured using a batch equilibration technique with varying pH of solution (pH 2 to 6). For the batch technique, the resin was dried at 50°C to constant weight. Exactly 0.2000 g of dry resin was placed into a series of 100 ml capacity polyethylene bottles and the resins were allowed to equilibrate with distilled water (25 ml). Then 0.1M sodium acetate buffer at various pH 20 ml and 0.1M metal solution 20 ml were added to each bottle. The mixture was shaken for 24 h using a rotary shaker. After equilibration, the supernatant solution 5 ml was collected for metal ion determination. The initial and final amount of metal ion concentration was determined by using AAS (GBC-903) and ICP (Perkin-1000).

Kinetic exchange: The rate of exchange of copper in sodium acetate buffer (pH 4) was determined by using 0.1500 g of resin beads with 10 ml of the 0.1 M copper solution for various time intervals. The copper ion concentration was determined as described above. The time required for 50% exchange ($t_{1/2}$) was calculated from the plot of the copper capacity (mmol/g) versus time.¹³

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