



Synthesis of Poly(hydroxamic Acid)-Poly(amidoxime) Chelating Ligands for Removal of Metals from Industrial Wastewater

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Abstract: Synthesis of poly(hydroxamic acid)-poly(amidoxime) chelating ligands were carried out from poly(methyl acrylate-co-acrylonitrile) grafted sago starch and hydroxylamine in alkaline medium. The binding property of metal ions was performed and maximum sorption capacity of the copper was 3.20 mmol/g and the rate of exchange of some metals was faster, *i.e.* $t_{1/2} \approx 7$ min (average). Two types of wastewater containing chromium, zinc, nickel, copper and iron, *etc.* were used and the heavy metal recovery was found to be highly efficient, about 99% of the metals could be removed from the metal plating wastewater.

Keywords: Absorption, Heavy metals, Plating wastewater, Polymeric chelating ligands

Introduction

Environmental contamination with heavy metals has been a potential threat to humans and animals and such metals do not undergo biodegradation. Removal of heavy metals from waste streams employs various technologies, which are often either expensive or inefficient, especially when very low residual concentrations in the wastewater. Heavy metals contamination in aqueous wastes from various industries, such as metal plating, mining operations, tanneries, chloro alkali, radiator manufacturing, smelting, alloy and storage battery industries¹. Heavy metals do not degrade easily into harmless end products and due to their high toxicity heavy metal-containing industrial wastewaters must be treated before being discharged into the environment².

Several measures are taken to prevent environment pollution, such as precipitation, adsorption and ion exchange and reverse osmosis to remove heavy metals³. At present precipitation is the most applicable of the current techniques available and is also considered to be the most economical. Chemical coagulation occurs by adding lime to raise the pH, thus

inducing precipitation, followed by the addition of activated silica or polyelectrolytes to stimulate coagulation. Several researchers have reported that electro-coagulation could be used to remove heavy metals from solutions^{4,5}.

In some cases, wastewater treatment by precipitation may be followed by adsorption onto activated carbon to remove the metals at the highest level. Although known to be quite effective in treating industrial effluents, chemical coagulation induces secondary pollution due to the addition of chemicals. Heavy metal precipitation also produces intractable sludge that must be treated and disposed of often at high cost⁶. Therefore the need for an effective methodology to overcome this drawback is essential to treat industrial effluents.

Heavy metal removal from the effluent with acceptable concentrations is the aim of this study. Therefore, a polymeric chelating ligand containing hydroxamic acid and amidoxime ligands was synthesized from poly(methyl acrylate-co-acrylonitrile) grafted sago starch. The chelating behavior of the prepared ligands in response to a series of heavy metals was investigated using batch techniques. In addition, heavy metals were removed from wastewaters by these ligands carried out using column technique.

Experimental

The poly(methyl acrylate-co-acrylonitrile) grafted sago starch (PMA-co-PAN) were prepared according to the procedure described in an earlier paper⁷. Commercial available metal sulfate/ nitrate of analytical reagent grade were used in this study. The standard solution of metals (1000 mg/L) was obtained from Perkin Elmer.

Two types of plating wastewaters were collected from BI-PMB Waste Management Sdn. Bhd, Shah Alam, Kuala Lumpur (Malaysia): chromium plating wastewater (Cr-wastewater) and cyanide process wastewater (CN-wastewater). Both wastewaters were adjusted to pH 4 using acid/alkali (HCl/ NaOH) solutions and analyzed by ICP-OES (Perkin Elmer Optima 5300 DV). All metal ions concentrations were presented in Table 1.

Table 1. Heavy metal concentration in the wastewater test at pH 4

Metal Ions	Concentration of metal ions, mg/ L	
	Cr-wastewater	CN-wastewater
Cu	2.301 (± 0.05)	6.156 (± 0.25)
Co	0.079 (± 0.15)	0.188 (± 0.06)
Cr	27.43 (± 0.08)	2.051 (± 0.16)
Mn	0.103 (± 0.04)	0.396 (± 0.08)
Fe	1.901 (± 0.09)	9.651 (± 0.25)
Ni	6.123 (± 0.18)	33.16 (± 0.48)
Zn	4.793 (± 0.24)	44.44 (± 0.55)
Pb	0.110 (± 0.02)	0.106 (± 0.04)
Cd	0.242 (± 0.07)	0.068 (± 0.03)

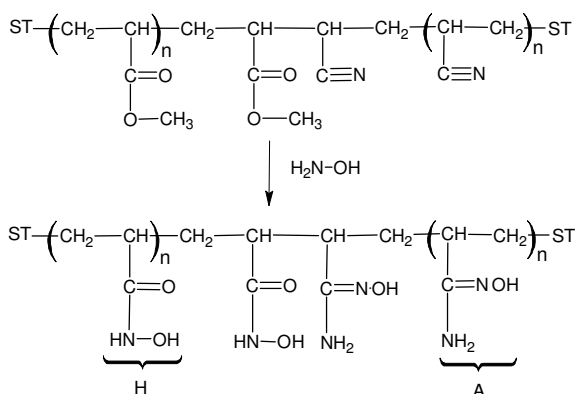
Preparation of poly(hydroxamic acid)-poly(amidoxime) chelating ligands

Preparation of hydroxylamine solution (NH₂OH)

About 21.00 g of hydroxylamine hydrochloride (NH₂OH.HCl) was dissolved in 150 mL methanolic solution (methanol: water / 5: 1). The HCl was neutralized by NaOH solution and the precipitated NaCl was removed by filtration. The pH of the reaction solution was adjusted to pH 12 by addition of NaOH solution. The reaction medium was maintain at a methanol to water ratio of 5: 1.

A double neck flask 500 mL size was fitted with a condenser and immerse in a thermostat water bath. About 10.00 g of PMA-co-PAN grafted sago starch was placed in the flask and the hydroxylamine solution is added to the flask. The reaction was carried out at 70 °C for 2 h. The products were separated from solution by filtration and washed several times with methanolic solution (methanol: water/ 5: 1). The ligands were treated with 100 mL of methanolic HCl solution (0.2 M) for 5 min and washed several times with methanolic solution (methanol : water/ 5 : 1). The product was dried in oven at 50 °C to a constant weight and screening the ligands bead approximate size 100-200 µm.

The structure of PMA-co-PAN grafted sago at upper and the structure of poly(hydroxamic acid)-poly(amidoxime) ligands at lower (ST is the sago starch, H hydroxamic acid and A amidoxime ligand) is shown in Scheme 1.



Scheme 1. Reagents and conditions: PMA-co-PAN grafted copolymer and hydroxylamine ratio, 1: 1; pH 12, temperature 72 °C, reaction period 2 h. 0.2 M metal solution for complex.

Sorption of metals by batch technique

The dry ligands exactly 0.2000 g were allowed to equilibrate with 20 mL distilled water for 30 min and 10 mL of 0.1 M sodium acetate buffer solution was added at differing pH, About 20 minutes later 10 mL of 0.1 M metal ion solution was added and the mixtures were shaken for 6 h using a rotary shaker. The amount of metal ion uptake was determined from the difference in concentrations at the beginning and end of the batch test. All experiment was carried out in replicated for appropriate absorption capacity. The amount of metal sorption in the sample was calculated using Equation 1.

$$q_e = \frac{(C_0 - C_e)V}{L} \times \frac{1}{M} \quad (1)$$

Where q_e is the equilibrium sorption amount (mmol/g), C_0 is the initial concentration of metal solution (mg/L), C_e is the equilibrium concentration of metal (mg/L), V is the volume of metal solution (L), L is mass of the polymeric ligands (g) and M is the mol weight of the specific metal.

Sorption kinetics by batch technique

The rate of exchange of heavy metals in the acetate buffer at pH 6 was determined by 0.2000 g of ligand beads in 10 mL of 0.1 M metal solution for various time intervals such as 2, 5, 10, 20, 30 and 60 minutes. The residual metal concentration was determined by ICP and the sorption amount was calculated according to Equation 2.

$$q_t = \frac{(C_0 - C_t)V}{L} \times \frac{1}{M} \quad (2)$$

Where q_t is the sorption amount at time t (mmol/g), C_0 is the initial concentration of metal solution (mg/L), C_t (mg/L) is metal concentration at time t , V is the volume of metal solution (L), L is the mass of polymeric ligands (g) and M is the mol weight of the specific metal.

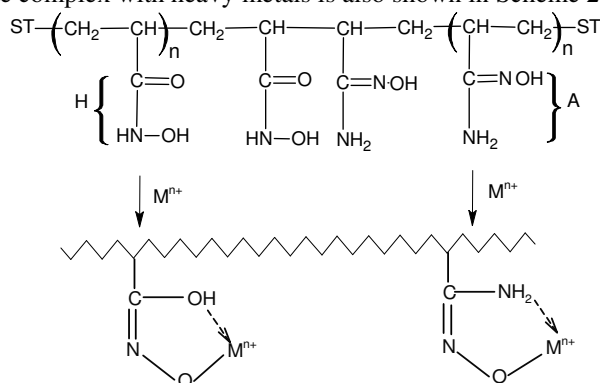
Extraction of metals by column packing technique

The slurry of PHA-PA ligands (4.0 g) was mixed with buffer at pH 4 and was packed in glass columns. Metal ion solutions of specific wastewater (*cf.* Table 1) were then allowed to percolate through each column at a flow rate of 5.0 mL/min. Samples were collected at the column outlet until the column reached saturation, followed by analysis using ICP-OES. The column operation was performed with replicated experiment to ensure appropriate percent extraction of metal ions from wastewaters.

Results and Discussion

Synthesis of poly(hydroxamic acid)-poly(amidoxime) chelating ligands

A polymeric chelating ligand containing hydroxamic acid and amidoxime ligands was synthesized from poly(methyl acrylate-co-acrylonitrile) grafted sago starch under alkaline solution. The structure of poly(hydroxamic acid)-poly(amidoxime) ligands at upper (H is the hydroxamic acid and A amidoxime ligand). The structure of the hydroxamic acid-amidoxime chelate complex with heavy metals is also shown in Scheme 2.



Scheme 2. Chelating complex of metal ions of five members ring hydroxamic acid (left) and amidoxime (right)

Sorption of metals by batch technique

A series of heavy metals was binding with the ligands (PHA-PA) using sodium acetate buffer solution from pH 3 to 6. The relative amount of metal ion taken up by the ligands steadily increased, with pH increase up to 6. The ligands exhibit a high affinity for copper (3.2 mmol/g) and other metals also have significance binding capacity such as iron, zinc, chromium, nickel, cobalt and cadmium has 2.80, 2.30, 2.10, 2.0, 1.75 and 1.57 mmol/g, respectively at pH 6, but less binding capacity for lead (Figure 1). It was found that the sorption capacities are pH dependent. The binding capacity with this ligand is the following order: $\text{Cu}^{2+} > \text{Fe}^{3+} > \text{Zn}^{2+} > \text{Cr}^{3+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$. Thus, these ligands can be used to remove metal ions from wastewater collected from plating industries.

Sorption kinetic by batch technique

The sorption rate of metals was carried out using a buffer solution at pH 6. The time required for 50% exchange ($t_{1/2}$) was calculated from the plot of the metal sorption capacity (mmol/g) vs time (Figure 2). The sorption rate of metals was very fast, *i.e.* $t_{1/2}$ for Cu, Fe, Ni, Zn, Cr, Co, Cd and Pb were 5, 5, 5, 7, 6, 8, 12 and 15 minutes, respectively. These ligands have the advantage of a faster rate of equilibrium; therefore, the column technique would be most efficient for heavy metal extraction.

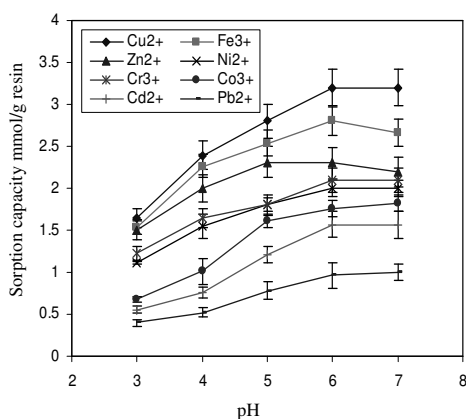


Figure 1. Heavy metals sorption capacity by the ligands as a function of pH

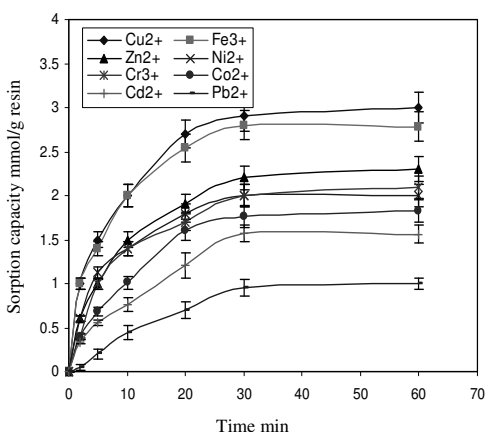


Figure 2. Rate of exchange of heavy metals by the ligands at pH 6

Extraction of metals by column technique

Two types of wastewaters such as chromium wastewater and cyanide wastewater obtained from metal plating industries having major heavy metals like Cu, Cr, Fe, Ni and Zn (*cf.* Table 1). The ligands were conditioned with buffer pH 4 and packed into the column. Each type of wastewater was poured into the column for metal recovery.

Chromium wastewater

The chromium plating process wastewater was analyzed by ICP and some metals, such as Cu, Ni, Cr, Fe and Zn, showed higher concentrations (*cf.* Table 1). The chromium wastewater was adjusted to pH 4 for suitable metal extraction using the column technique and the flow rate is easily adjustable at pH 4. The metal removal, Cr extraction, was 99.0% at Cr concentration of 27.43 mg/L (Figure 3). Other heavy metals, such as Cu, Co, Mn, Fe, Ni, Zn, Pb and Cd extraction, were 99.0, 99.1, 99.6, 94.0, 94.0, 90.0, 80.2 and 88.1%, respectively. Thus overall heavy metal extraction is excellent by this ligands.

Cyanide wastewater

The cyanide wastewater was adjusted to pH 4 for metal extraction. Thus, the metal ions removal, Ni and Zn extractions, was 94.0 and 88.1%, respectively, when the concentrations of Ni and Zn were 33.16 and 44.44 mg/L, respectively (Figure 3). Although the initial concentrations of Ni and Zn were higher, better removal was found on using the ligands. The extractions of other metals like Cu, Co, Cr, Mn, Fe, Pb and Cd were 99.4, 99.6, 96.0, 95.0, 92.0, 92.1 and 93.2%, respectively. Overall, the extraction of heavy metal was very good from cyanide wastewater.

NCP (*Neurospora crassa* gene expressed in the periplasmic space) removed heavy metals from solutions containing heavy metals⁶. Three process wastewater streams such as acid/alkali, chromate and cyanide were tested and NCP was noted to be removing the heavy metals from

wastwaters at near neutral pH. Macrocyclic ligands were reported in static sorption studies to show preference for the cations of noble metals like gold, silver, platinum and palladium over other metal cations including copper, lead and cadmium⁸. Two chelating resins were synthesized incorporating imidazolylazobenzene and 1,4-bis(imidazolylazo) benzene as the functional group into the Merrifield polymer⁹. Cadmium was reported to be removed from water having the normal pH of natural water. However, no clear evidence of percent extraction of heavy metals at low concentration in wastewater using the column technique was reported.

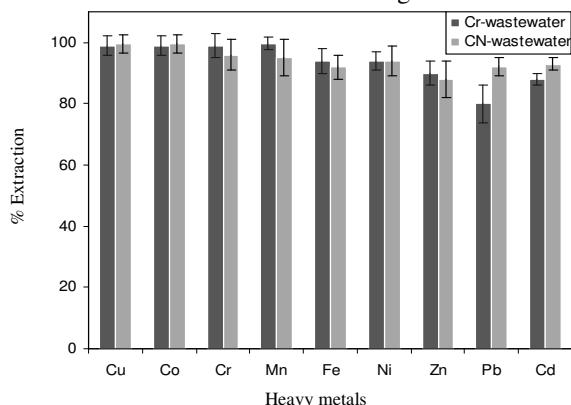


Figure 3. Heavy metal removal from chromium, cyanide and acid/alkali wastewater by PHA-PA ligands, Column condition: Column bed 20 cm, conditioned at pH 4, diameter of glass column 20 mm, flow rate 5 mL/min.

Conclusion

The binding property of some metal ions with the ligands was good at pH 6. Two types of wastewater containing heavy metals were used in the column operation and metal recovery was found highly efficient, about 99% of metals could be removed from the metal plating effluents. As high-affinity chelating polymeric ligands work in the presence of alkali metals, they are highly desirable in waste treatment. Metal removal by the PHA-PA chelating ligands system shows considerable promise in achieving this goal. Its selectivity suggests that it may be possible to recover heavy metals efficiently from wastewater. Further study is in progress to optimize metal binding and extraction performance in a column.

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