

## Synthesis of polymeric chelating ligands from sago starch for metal removal from electroplating wastewater

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Polymeric chelating ligands containing hydroxamic acid and amidoxime ligands have been synthesized from poly(methyl acrylate-co-acrylonitrile) grafted sago starch. Batch adsorption has been performed to identify the binding property of metal ions. Maximum sorption capacity of copper is found to be  $2.80 \text{ mmol g}^{-1}$ , however other transition metals has good sorption capacity with this ligands. The rate of exchange of some metals is found to be fast, i.e.  $t_{1/2} \approx 6 \text{ min}$  (average). Three types of wastewater containing chromium, zinc, nickel, copper, and iron have been used in this study. The metal recovery is found to be high, and more than 99% of the metals could be removed from the metal plating wastewater. Polymeric chelating ligands could be used to remove the metals from wastewater.

**Keywords:** Adsorption, Chelating ligands, Electroplating wastewater, Metal, Sago starch

Excessive metal release into the environment is a major concern worldwide. Substantial environmental, public health and economic impacts are evident due to the toxic metals entering the environment. According to environmental regulations on permissible discharge levels of various metals, new technologies and waste treatment procedures are necessary to meet the current regulatory limits<sup>1</sup>.

Some contaminants are short-lived in the environment and consequently affect only the immediate areas for a short time, while others persist for decades. Long-lived chemical contaminants may remain at the area of release or may be transported to other locations. Other chemicals leach into the groundwater or adjacent streams, rivers, and lakes and are transported away from the site of disposal. Various metals that are commonly used in industrial processes are toxic and insoluble. Among the greatest threats to health are the presence of high levels of toxic metals such as arsenic, cadmium, lead, mercury, and silver in drinking water. Maximum limits for each are established by the EPA primary drinking water regulations. Toxic metals are associated with nerve damage, birth defects, mental retardation, certain cancers, and increased susceptibility to disease.

Contamination is caused by the heavy metals in aqueous wastes from various industries, such as metal

plating, mining operations, tanneries, chloro alkali, radiator manufacturing, smelting, alloy and storage Battery industries<sup>2</sup>. Heavy metals do not degrade easily into harmless end products<sup>3</sup> and due to their high toxicity the heavy metal-containing industrial wastewaters must be treated before being discharged into the environment. Several measures are taken to prevent environment pollution, such as precipitation, adsorption, ion-exchange and reverse osmosis to remove heavy metals<sup>4</sup>. 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 polyelectrolyte's to stimulate coagulation. Several researchers have reported that electro-coagulation could be used to remove heavy metals from solutions<sup>5,6</sup>. Besides these, aluminium salt is used to remove colloidal matter such as gelatinous hydroxides. 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 cost<sup>1</sup>.

Recently, a chromatographically useful packing material was prepared by the adsoption of Alizarin

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Red-S on cation exchanger stannic silicate for selective separation of cadmium and lead from some transition metal ions<sup>7</sup>. The copper is removed from the bleed stream of the electroplating unit using a laboratory-scale electrolytic cell<sup>8</sup>. A hydrometallurgical process was adopted at the laboratory scale for the recovery of copper from the copper electroplating second rinse bath solution containing 2.5 gL<sup>-1</sup> copper by solvent extraction route<sup>9</sup>. In addition, the process of heavy metals recovery and getting purified water from electroplating effluent for industrial reuse is also developed<sup>10</sup>. Agrawal *et al.*<sup>11</sup> reviewed the various aspects on iron recovery from waste pickle liquor and copper recovery from copper electroplating/electro-refining units by solvent extraction methods. With the development of a newer variety of solvents, the extraction of copper has become quite feasible and easy. However, iron recovery by solvent extraction remains a difficult job because 100% stripping of the loaded iron is quite difficult although there are several good extractants for iron.

The heavy metal removal below the regulatory standards is crucial; thus a limited number of studies have been reported on high efficient absorbents. Therefore, the need for an effective methodology to overcome this drawback is essential to treat industrial effluents. For this reason, the ligands having multiple binding sites look to be a possible answer to heavy metal remediation and wastewater treatment. Therefore, the novel bidentate chelating ligands have been developed for the safe and effective removal of heavy metals from industrial wastewaters. Starch allows it to twist and bend in the direction out of the plane, so that the molecule is moderately flexible. Chemical reactivity is largely a function of the high donor reactivity of the OH groups, which may covalently attach to the functional groups capable to bind heavy metal ions. In particular, two main approaches have been tried in the conversion of starch into compounds capable of adsorbing heavy metal ions from aqueous solutions. The first of these methods involves a direct modification of the starch backbone with the introduction of chelating or metal binding functionalities producing a range of heavy metal adsorbents. Alternative approaches have focused on grafting of selected monomers onto the starch backbone either directly introducing metal binding capability or with subsequent functionalization of these grafted polymer chains with known chelating moieties<sup>12,13</sup>.

Heavy metal removal from the effluent with acceptable concentrations is the aim of this study. Therefore, a chelating ligands poly(hydroxamic acid) and poly(amidoxime) (PHA-PA) ligands have been synthesized from poly(methyl acrylate-co-acrylonitrile) grafted sago starch. The chelating behaviour of the prepared ligands with a series of heavy metals is investigated using batch techniques. In addition, heavy metals are removed from wastewaters by these ligands using column technique.

### Experimental Procedure

Poly(methyl acrylate-co-acrylonitrile) grafted sago starch (PMA-co-PAN) was prepared according to the procedure described earlier<sup>12</sup>. Commercially available metal sulfates or nitrates of analytical reagent grade (Sigma-Aldrich, Malaysia) were used in this study. The metal standard solution (1000 mgL<sup>-1</sup>) was obtained from Perkin-Elmer (Malaysia) and working standard solutions were used according to appropriate dilution. Metal measurement was performed with an inductively-coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elmer, Optima 5300 DV, USA). Three types of plating wastewaters were collected from BI-PMB Waste Management Sendirian Berhad, Shah Alam, Kuala Lumpur (Malaysia), namely chromium plating wastewater (Cr-wastewater), cyanide process wastewater (CN-wastewater) and acid/alkali (H/OH-wastewater). All wastewaters were adjusted to pH 4 using HCl (0.10 mol L<sup>-1</sup>) or NaOH solution (0.10 mol L<sup>-1</sup>) and analyzed by ICP-OES (Table 1). The polymeric ligand is allowed to swell at higher pH >5 and for this reason substantial pressure is needed for passing the wastewater through the column. For reducing the swelling of ligands, the wastewaters

Table 1—Metal concentrations in the wastewater test at pH 4

Metal ions	Metal ions concentrations, mg L <sup>-1</sup>		
	Cr-wastewater	CN-wastewater	H/OH-wastewater
Cu	2.30	6.16	0.62
Co	0.079	0.188	0.06
Cr	27.43	2.05	0.24
Mn	0.10	0.40	0.07
Fe	1.90	9.65	0.87
Ni	6.12	33.2	2.97
Zn	4.79	44.4	4.81
Pb	0.11	0.11	0.025
Cd	0.24	0.07	0.07

were kept at pH 4 due to easy pass into a column for proper extraction study using column technique.

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

To prepare hydroxylamine solution ( $\text{NH}_2\text{OH}$ ), 42 g hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) was dissolved in 300 mL methanolic solution (methanol : water 5 : 1). The HCl was neutralized by NaOH solution and the precipitated NaCl was removed by filtration. The reaction solution was adjusted to pH 12 by addition of NaOH (50%) solution. The reaction medium was maintained at a methanol-water ratio of 5 : 1.

The preparation was carried out in a 1 L double neck flask fitted with a condenser and immersed in a thermostat water bath. About 20 g of PMA-co-PAN grafted sago starch was placed in the flask and the hydroxylamine solution was added to the flask. The reaction was carried out at 70°C for 2 h. After completing the reaction, the resin was separated from solution by filtration and washed several times with methanolic solution. The resin was treated with 200 mL of methanolic HCl solution ( $0.2 \text{ mol L}^{-1}$ ) for 5 min. Finally, the resin was filtered and washed several times with 100 mL methanolic solution and then dried in an oven at 50 °C to a constant weight.

#### Sorption of metals by batch technique

Exactly 300 mg of the ligands (PHA-PA) (dry basis, 100-200  $\mu\text{m}$  size) was placed into a series of 100 mL polyethylene bottles and the contents were allowed to equilibrate with 20 mL distilled water for 30 min. Then 20 mL of  $0.1 \text{ mol L}^{-1}$  sodium acetate buffer solution, at differing pH ( $0.10 \text{ mol L}^{-1}$  of sodium acetate solution, pH adjusted by acetic acid) was added. Ten minute later 20 mL of  $0.1 \text{ M}$  metal ion solution was added to each bottle. The mixtures were shaken for 12 h using a rotary shaker. After equilibrium was attained, 5 mL supernatant was collected for determination of the concentration of each metal by ICP-OES (Perkin Elmer Optima 5300 DV). The amount of metal ion uptake was determined from the difference in concentrations at the beginning and end of the batch test. All experiments were carried out with duplicate for appropriate absorption capacity. The amount of metal sorption in the sample was calculated using the following equation:

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

where  $q_e$  is the equilibrium sorption amount ( $\text{mmol g}^{-1}$ );  $C_o$ , the initial concentration of metal solution ( $\text{mgL}^{-1}$ );  $C_e$ , the equilibrium concentration of metal ( $\text{mgL}^{-1}$ );  $V$ , the volume of metal solution (L);  $L$ , the mass of the polymeric ligands (g); and  $M$ , 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 0.3000 g of ligand beads in 20 mL of  $0.1 \text{ M}$  metal solution for various time intervals, such as 2, 5, 10, 20, 30 and 60 min, and the metal concentrations were estimated by ICP. The residual metal concentration was determined with replicated experiment and the sorption amount was calculated according to the following equation:

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

#### Extraction of metals by column technique

For the column operation, slurry of PHA-PA ligands (5.0 g) was made with buffer at pH 4 and was packed in glass columns (200 mm long  $\times$  20 mm i.d.). To prevent air entrapment, the column was first filled with buffer (pH 4) solution. Next, the slurry of ligands was introduced carefully into each column, which was then slowly allowed to settle down by displacing the heel of the buffer solution. Metal ion solutions of specific wastewater (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 the replicated experiment to ensure appropriate percent extraction of metal ions from wastewaters. The breakthrough curves were determined from these experiments.

## Results and Discussion

Hydroxamic acid is used in a wide variety of ways as reagents in organic and inorganic analysis. It contains the bidentate groups, which meets all the requirements necessary for the formation of metal complexes. Complexes are usually formed via substitution of a hydrogen atom of hydroxylamine by a metal cation and ring closure via carbonyl oxygen atom<sup>13</sup>. It has been observed that complex formation requires the hydroxylamine oxygen to be unsubstituted, although the nitrogen may bear a substituent. The hydroxamate anion is a bidentate ligand and forms a complex, in which the metal ion is

bound with both the oxygen by chelation<sup>14</sup>. The formation of metal chelates via this mechanism for a long time constitutes the basis of a wide variety of analytical methods. Because of the non-ionic nature of such a metal complexes (or inner complexes), they can be extracted in all cases from aqueous solutions or suspensions with the aid of solvents immiscible with water, such as benzene, chloroform, carbon tetrachloride, higher alcohols, or dichlorobenzene; separation processes involving solvent extraction are based on this feature<sup>15</sup>. In this study, we have used polymeric backbone attached to the carbon atom of ligands, therefore, complex formation of metals and polymeric ligands are insoluble in aqueous media. Most of hydroxamic acids complexes with transition metal salts are highly coloured. Amidoximes exist predominantly in the hydroxyimino-form which is stabilized by intra-molecular hydrogen bond<sup>16,17</sup>. Amidoxime may coordinate as a non-ionic group, but they generally undergo the metal-assisted hydroxyl proton dissociation upon coordination. The latter type of coordination<sup>18</sup> is expected for metal ions at pH 6. However, amidoxime coordination system is analogy with hydroxamic acid system as well<sup>14</sup>.

Poly(hydroxamic acid)-poly(amidoxime) (PHA-PA) chelating ligands were synthesized from poly(methyl acrylate-co-acrylonitrile) grafted sago starch under alkaline solution. Physical and chemical properties of the ligands are presented in Table 2, percentage of grafting is 110, PMA and PAN concentrations are 58 %, sago starch concentration is 42% and particle size around 100 – 200  $\mu\text{m}$ . The structures of PMA-co-PAN grafted sago starch (a) and poly(hydroxamic acid)-poly(amidoxime) ligands (b) are shown in Scheme 1 (ST is the sago starch, H, hydroxamic acid and A, amidoxime ligand).

The binding property of hydroxamic acid and amidoxime is usually bidentate<sup>19</sup>. The hydroxamic acid and amidoxime groups are a bidentate ligands, and a stable five-membered chelating ring can form between one hydroxamic group and one metal ion as

Table 2—Physical and chemical properties of the ligands

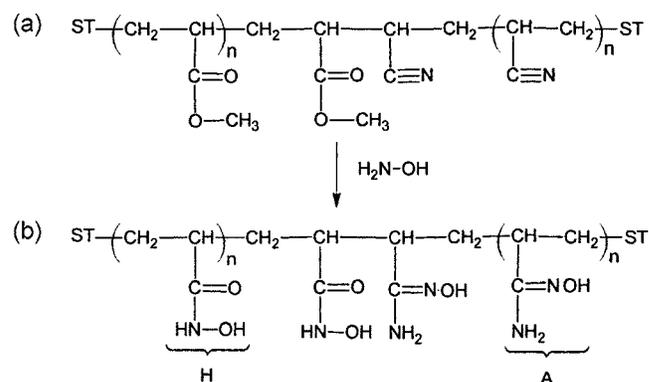
Parameter	Value
Grafting, %	110 ( $\pm 3$ )
PMA and PAN conc., %	58 ( $\pm 2$ )
Sago starch conc., %	42 ( $\pm 2$ )
Particle size, $\mu\text{m}$	100 – 200 ( $\pm 20$ )
Swelling capacity, %	15 ( $\pm 5$ )
Cation exchange capacity, $\text{mmol g}^{-1}$	6.95 ( $\pm 0.25$ )

such one amidoxime group and one metal ion can also form stable five-membered chelating ring. The possible combining mode of hydroxamic acid and amidoxime ligands with metal ions is shown in Scheme 2.

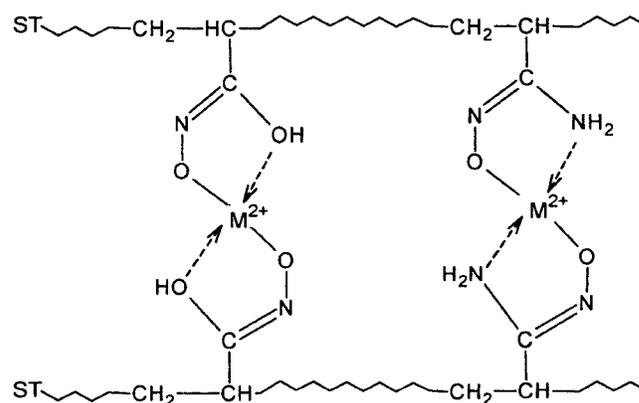
#### FTIR spectra analysis

The characteristic absorption bands are found at  $1741\text{ cm}^{-1}$  which corresponds to C=O stretching mode<sup>8</sup> for an ester and C–H stretching vibrations at  $828\text{ cm}^{-1}$  belongs to poly(methyl acrylate) grafted copolymer. In addition CN stretching mode at  $2244\text{ cm}^{-1}$  belongs to the nitrile of polyacrylonitrile grafted copolymer (Fig. 1b). All these absorption bands are absent in the ungrafted sago starch (Fig. 1a).

The spectrum for an ester and nitrile has disappeared and a new band associated with hydroxamic acid<sup>8</sup> at  $1652\text{ cm}^{-1}$  for C=O and amide II band at  $1520\text{ cm}^{-1}$  for N–H appears (Fig. 1c). According to the literature, the signal at  $1652\text{ cm}^{-1}$  for hydroxamic acid (C=O) is overlapped and is ascribed



Scheme 1—Synthesis of poly(hydroxamic acid)-poly(amidoxime) ligands [conditions: PMA-co-PAN grafted copolymer and hydroxylamine ratio 1 : 1; pH 12, temperature  $72\text{ }^\circ\text{C}$ , reaction period 2 h]



Scheme 2—Structure of hydroxamic acid and amidoxime chelate complex with metal ions

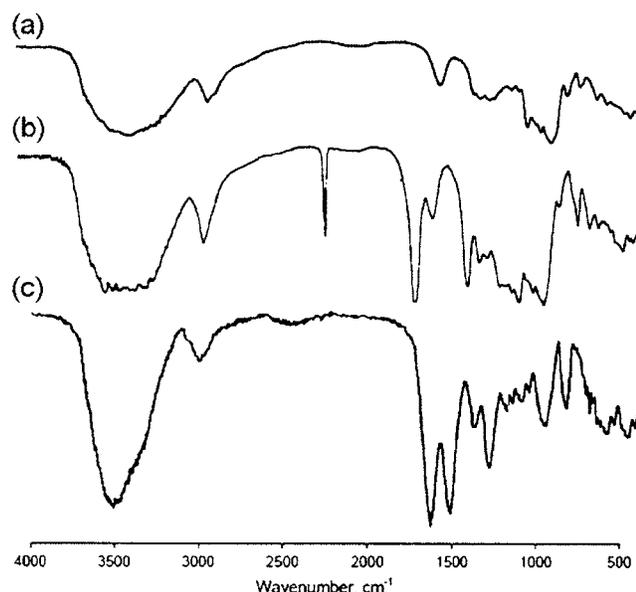


Fig. 1—FTIR spectra of (a) sago starch, (b) PMA and PAN grafted sago starch, and (c) poly(hydroxamic acid)-poly(amidoxime) ligands

to the C=N stretching vibration of the amidoxime groups. The N–O stretching mode is observed at  $920\text{ cm}^{-1}$ , which is overlapping with wagging for  $\text{NH}_2$  and N–H band. These new bands suggest that the poly(hydroxamic acid)-poly(amidoxime) chelating ligands are successfully synthesized.

The presence of hydroxamic acid and amidoxime groups on the polymeric products is confirmed by the formation of a dark violet colour with vanadium ions. The violet colour is not observed when PMA-co-PAN grafted sago starch reacted with the vanadium ions under similar conditions. It is also observed that when a  $\text{Cu}^{2+}$  solution is added to the hydrated resin, the swollen resin turned into a deep green colour, which also suggests the presence of hydroxamic acid and amidoxime groups on the polymeric ligands.

#### Swelling study

Oven-dried ligands were soaked in distilled water. The ligands were filtered under slightly reduced pressure. The swollen ligands were then pressed lightly between filter paper to remove any remaining surface water and rapidly weighed. The swelling capacity is found to be 15% (Table 2). High water regain is presumably a result of the high hydrophilicity of the hydroxamic acid groups<sup>20,21</sup>, in addition to the presence of OH group in the starch molecule. The amount of water taken up is controlled by the hydrophobic-hydrophilic balance of the polymeric matrix, the density and distribution of

chemical crosslinks and the chain entanglements. The ionizable groups are certainly hydrophilic but the acrylic polymeric backbones are very hydrophobic character, because no swelling is observed for grafted copolymers. Thus, the water tends to concentrate in molecular clusters around the ionic groups in the swollen polymer to avoid the exposed hydrophobic backbones. The first water molecules enter the polymeric the ligands to hydrate the ions and so lower the electrostatic free energy in the region of the ionic groups. The deriving force is primarily enthalpic but the ion pairs are enabled to dissociate so liberating the counter ions. Further water molecules are then entering for entropic reasons. They increase the volume available to the counter ions (osmotic pressure) and increase the configurational entropy of the polymer chains. The ultimate degree of swelling is reached when there is increase in entropy and more water enters by the elastic work. The elastic work is required to stretch the network i.e. to reduce its configurational entropy against the restraining effect of the crosslinks and the interference with the hydrogen bonding of the water<sup>22</sup>.

#### Cation exchange capacity

The cation exchange capacity of the ligands was determined on the basis of the amount of sodium hydroxide reacting with  $\text{H}^+$  form resin. The ligands reacted with a specific amount of  $0.1\text{ mol L}^{-1}$  NaOH solution and the excess sodium hydroxide was measured by back titration up to the phenolphthalein end point with standard HCl solution. The cation exchange capacity is found to be  $6.95\text{ mmol g}^{-1}$  and the other physical and chemical properties of the ligands are presented in Table 2.

#### SEM analysis

The SEM micrographs of the poly(methyl acrylate-co-acrylonitrile) grafted sago starch show less smooth surface compared to the chelating ligands and dense morphologies with small white lumps belonging to homopolymers (Fig. 2a). The SEM micrograph of the poly(hydroxamic acid)-poly(amidoxime) chelating ligands show distinct morphologies and smoothness with variable pore sizes (Fig. 2b).

#### Sorption of metals by batch technique

The sorption behaviour of the ligands (PHA-PA) to some heavy metals was investigated, using sodium acetate buffer solution, (pH 3–7). The relative amount of metal ion taken up by the ligands steadily increases with the increase in pH up to 6. The ligands exhibit a high affinity for copper, iron, zinc, nickel, chromium,

cobalt and cadmium, but less binding capacity for lead (Fig. 3). It is found that the sorption capacities are pH dependent. Thus, these ligands can be used to remove metal ions from wastewater collected from plating industries.

**Sorption kinetic study**

The study of the sorption rate of metals was performed using a buffer solution of pH 6. The time required for 50% exchange ( $t_{1/2}$ ) was calculated from the plot of the metal sorption capacity ( $\text{mmol g}^{-1}$ ) versus time (Fig. 4). The sorption rate of metals under these conditions is found to be very fast, i.e.  $t_{1/2}$  values for Cu, Fe, Ni, Zn, Cr, Co, Cd and Pb are 4, 5, 6, 6, 7, 10, 12 and 14 min respectively. These ligands have the advantage of a faster rate of equilibrium; therefore, the column technique would be most efficient for heavy metal extraction.

**Extraction of metals by column technique**

Three types of wastewater, namely chromium wastewater, cyanide wastewater and acid/alkali

wastewater, obtained from metal plating industries contain major heavy metals like Cu, Cr, Fe, Ni and Zn (Table 1). Our prepared 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**

Heavy metals concentration was measured in wastewater from a chromium plating process and some metals, such as Cu, Ni, Cr, Fe and Zn, show higher concentrations when compared with other metals (Table 1). The chromium wastewater was adjusted to pH 4 for suitable metal extraction using the column technique. The ligands swell less at pH 4 than at pH 6; therefore, the flow rate is easily adjustable at pH 4. However, metal removal, especially Cr extraction, is 99.0% at Cr concentration of  $27.4 \text{ mg L}^{-1}$  (Fig. 5). Other heavy metals, such as

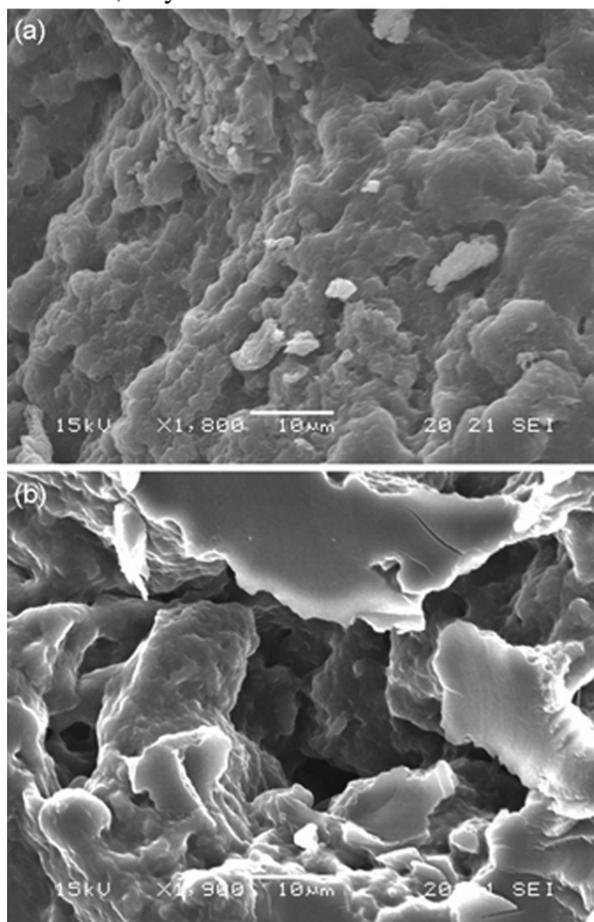


Fig. 2—SEM micrographs of PMA-co-PAN grafted sago starch (a), and PHA-PA chelating ligands (b)

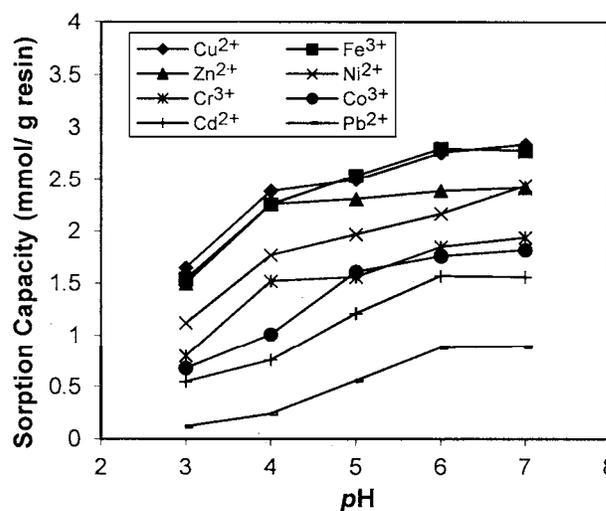


Fig. 3—Metal sorption capacity by the ligands as a function of pH

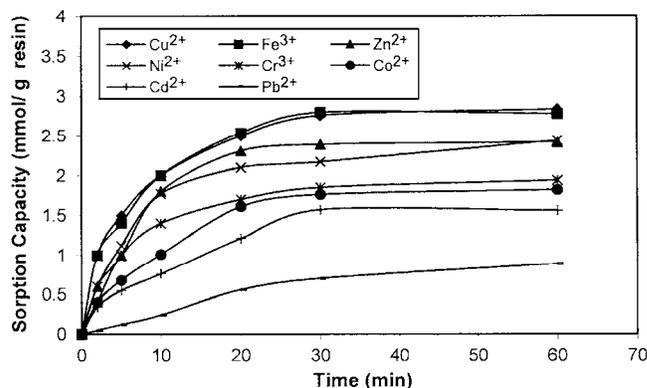


Fig. 4—Rate of exchange of metals by the ligands at pH 6

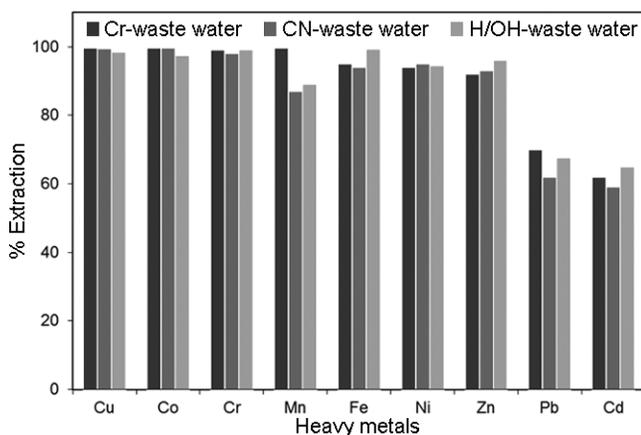


Fig. 5—Metal removal from chromium, cyanide and acid/alkali wastewaters by PHA-PA ligands [column dimensions: column bed length 20 cm, conditioned at pH 4, inner diameter 20 mm and flow rate 5 mL min<sup>-1</sup>]

Cu, Co, Mn, Fe, Ni, and Zn extraction, are 99.7, 99.6, 99.7, 95.0, 94.0 and 92.2%, respectively, from the same wastewater. Thus, Pb and Cd removal is found to be lower than the other metals; however, overall heavy metal extraction is excellent using these ligands.

#### Cyanide wastewater

Heavy metals were in the wastewater from the cyanide plating process (Table 1) and pH was adjusted to 4 for metal extraction. Thus, the metal removal, especially for Ni and Zn extractions, is found to be 95 and 93.1% respectively, when the concentrations of Ni and Zn are 33.2 and 44.4 mg/L respectively (Fig. 5). Although the initial concentrations of Ni and Zn are higher, better removal is found on using the ligands. The extractions of other metals like Cu, Co, Cr, Mn and Fe are 99.5, 99.7, 98.0, 87.0 and 94.5% respectively. Overall, the extraction of heavy metal is good; however, Pb and Cd extractions are lower for both chromium and cyanide wastewaters as both metal ions are less capable to binding these chelating ligands.

#### Acid/Alkali wastewater

Heavy metal concentration in the acid/alkali wastewater is found to be lower than for the other two types of wastewater (Table 1). Similarly, we adjusted the pH 4 for metal extractions. The removal of metals like Cr and Fe is 99.1 and 99.2% respectively (Fig. 5). The extractions of other heavy metals, such as Cu, Co, Mn, Ni, Zn, Pb and Cd, are 98.3, 97.5, 88.8, 94.3, 96.0, 67.5 and 65.0% respectively (Fig. 5). Overall, these ligands are very good for metal removal.

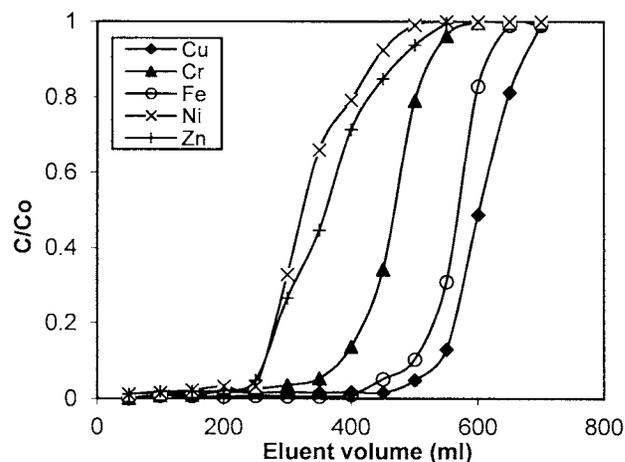


Fig. 6—Breakthrough curves of metals in Cr-wastewater [column dimensions: column bed 20 cm, conditioned at pH 4, diameter of glass column 20 mm and flow rate 5 mL min<sup>-1</sup>]

#### Breakthrough curve

In the preliminary investigation, the performance of the PHA-PA ligands was determined by the removal of some heavy metals from chromium wastewater. Five major heavy metals were used for these breakthrough curves and the results are shown in Fig. 6. The Cu and Fe concentrations in the effluents are found to be very low, within 450 and 400 mL respectively, indicating the high efficiency of the PHA-PA ligands used for Cu and Fe removal (99 and 97%). About 96% of Cr is found to have been removed from up to 350 mL of effluent. The extraction efficiency of Cr, Fe and Cu from the effluents decreases sharply thereafter, and finally, the concentration of the effluent reached the same level as that in the influent, indicating the complete exhaustion of the ligands. Thus, Ni and Zn removal is 95 and 94% respectively, within 250 mL, and the removal capacity of the ligands sharply decreases. Overall, up to 95-99.8% of heavy metals, such as Cu, Cr, Fe, Ni and Zn, could be removed from the effluents.

#### Conclusion

Three types of wastewater containing heavy metals have been used in the column operation and metal recovery is found highly efficient, where more than 99% of metals could be removed from metal plating effluents. Inorganic waste streams are characterized as having mixed metals, variable pH, organic contaminants, suspended particles, and high concentrations of nontoxic metals. As high-affinity chelating polymeric ligands work in the presence of other chemicals, they

are highly desirable in waste treatment. Metal removal by the PHA-PA chelating ligands system shows considerable promise in achieving this goal. It has high metal removal efficiency and is repeatedly re-generable. 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 by column technique at laboratory scale.

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