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**SORPTION STUDY OF METAL IONS BY USING
POLY(HYDROXAMIC ACID-AMIDOXIME)
CHELATING RESIN**

SHANMUGAM S/O GANESAN

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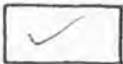
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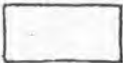
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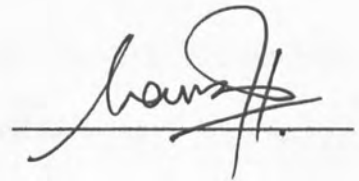
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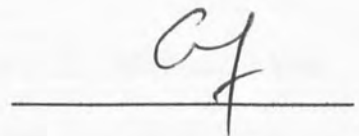
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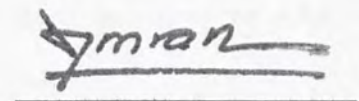
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ABSTRACT

The poly(hydroxamic acid-amidoxime) (PHA-PA) chelating resin was synthesized from poly(methyl acrylate-co-acrylonitrile) (PMA-PAN) grafted sago starch. The PMA-PAN grafted copolymer was obtained from the reaction of methyl acrylate and acrylonitrile monomers with sago starch by a free-radical initiating process in which ceric ammonium nitrate was used as an initiator. The sorption behavior of PHA-PA resin toward metal ions (Cu, Zn, Cr and Cd) was investigated in an aqueous solution at pH 3 to 6. It was found that, the sorption capacities of these metal ions were increased with increasing of pH up to 6 and the selectivity of the resin towards these metal ions were in the order $\text{Cu(II)} > \text{Cr(III)} > \text{Zn(II)} > \text{Cd(II)}$. The rate of exchange of the copper ion was very fast that is, $t_{1/2} \approx 3$ minutes.



ABSTRAK

Poly(hydroxamic acid-amidoxime) (PHA-PA) resin telah disintesis dengan menggunakan kanji sago poly(methyl acrylate-co-acrylonitrile) (PMA-PAN). Kopolimer PMA-PAN tersebut disediakan melalui tindakbalas antara monomer methyl acrylate dan acrylonitrile dengan kanji sago dengan menggunakan proses permulaan radikal bebas di mana ia menggunakan serik ammonium nitrat sebagai bahan pemula. Ciri-ciri jerapan resin PHA-PA terhadap ion-ion logam (Cu, Zn, Cr dan Cd) dikaji dalam larutan akuas pada pH 3 hingga 6. Didapati bahawa jumlah ion yang dijerap oleh resin mengalami peningkatan dengan pertambahan pH sehingga 6 dan pemilihan resin terhadap ion-ion logam ini adalah dalam susunan $\text{Cu(II)} > \text{Cr(III)} > \text{Zn(II)} > \text{Cd(II)}$. Kadar pertukaran ion logam kuprum adalah cepat iaitu, $t_{1/2} \approx 3$ minit.



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SYMBOL, ABBREVIATION AND UNIT LIST

MA	Methyl acrylate
AN	Acrylonitrile
CAN	Ceric ammonium nitrate
PMA-PAN	Poly(methyl acrylate-co-acrylonitrile)
PHA-PA	Poly(hydroxamic acid-amidoxime)
NH ₂ OH.HCl	Hydroxylamine hydrochloride solution
AAS	Atomic absorption spectrophotometer
FTIR	Fourier transform infrared spectrometer
M	Molarity
g	Gram
N ₂	Nitrogen gas
°C	Degree celsius
ml	Milliliter
L	Liter
µm	Micrometer
h	Hour
cm ⁻¹	Reciprocal centimeter
mmolg ⁻¹	Millimol per gram
mg	Milligram
mgg ⁻¹	Milligram per gram
mg ^l ⁻¹	Milligram per liter

CHAPTER 1

INTRODUCTION

1.1 Introduction

There is growing concern about the discharge of effluents and rinse water from industries and especially metal plating shops, which tend to be small enterprises dispersed throughout the country and need of simple process technology capable of recycling water and discharging toxic metals in a safe and convenient manner. There are many situations in industry where solutions containing low concentrations of metals are produced. For example, in the metal finishing industry, manufacturing of semiconductor and their components, print circuit boards, waste water released by laboratories and plants all contribute to aqueous streams requiring treatment (Goyer, 1991).

Polymeric chelating resins in water treatment for human consumption and industrial uses and as well as environmental protection is of prime importance. Chelating resins are prepared by anchoring a functional group to a polymeric backbone and generally this functional group has been found to exhibit greater selectivity towards some metal ions than usual cation and anion exchange resins. The design of such chelating resins depend on the stability of the basic macromolecular network and



its ability to add on the desired chelating functional group, which suits the specific metal ions (Winston and Kirchner, 1978). Because the alkali and alkaline earth metals occur in high concentration in natural waters, a desirable property of metal chelating ligands having useful in environmental or commercial application would be the ability to bind the heavier transition elements in the presence of calcium, magnesium and sodium (Lutfor *et al.*, 2000).

There are many types of chelating resins have been reported for binding of metal ions. In this sequences, poly(hydroxamic acid) and poly(amidoxime) are well known chelating resins whose bind the wide metal ions in presence of alkali metal ions. The poly(hydroxamic acid) resin seems to have potential to form complexes with a wide range of metals. It has been found to be an effective chelating ligand with metal ions such as Cu^{2+} , Fe^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} and Zn^{2+} (Lutfor *et al.*, 2001). Poly(hydroxamic acid) resins have been synthesized by various methods. The general method used is the reaction of an ester with hydroxylamine. The chemical properties of poly(hydroxamic acid) resin are greatly dependent on the functional groups in the polymer matrix (Vernon and Wan Yunus, 1981).

On the other hand, a macroreticular resins containing amidoxime groups that are used in the extraction of uranium from seawater has been studied by Egawa *et al.* (1993). The synthesis of a sorbent with an amidoxime group mostly involves 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 (Lutfor *et al.*, 2000).



1.2 Research Objectives

- a. To carry out graft copolymerization of methyl acrylate and acrylonitrile onto sago starch.
- b. To prepare poly(hydroxamic acid-amidoxime) chelating resin from vinyl polymer grafted sago starch.
- c. To study the sorption behavior of the chelating resin towards a series of metal ions such as copper, zinc, chromium and cadmium at various pH (3-6).

1.3 Scope of Study

The project focuses only on the preparation of poly(hydroxamic acid-amidoxime) chelating resin by using methyl acrylate and acrylonitrile as a monomer. Further on, fourier transform infrared spectrometer has been used to determine the functional groups of the prepared resins. Other than that, the project focuses on the evaluation of sorption study of the chelating resin towards a series of metal ions at various pH. For that reason atomic absorption spectrophotometer has been used to determine the initial and final concentration of the metal ions.



CHAPTER 2

LITERATURE REVIEW

2.1 The Metals and Its Properties

Copper is malleable like gold and silver. It can be bent and shaped without cracking, when either hot or cold. Copper also is ductile, that is, it can be drawn out into thin wire. Copper is an excellent conductor of heat and electricity making it an important metal in cookware, refrigerators and radiators. Copper is resistant to corrosion, that is, it will not rust. If the air around it often is damp, it will change from its usual reddish orange color to reddish-brown. Copper's color is a unique softly reflective brown red to deep brick red. Exposure to oxygen causes copper to tarnish and turn a teal green. The melting point of copper is 1083.4 °C. Liquid copper form boils at 2567 °C (Yaws, 1999).

Copper is an element and appears often in nature in compounds that form minerals such as Malachite- CuCO_3 or $\text{Cu}(\text{OH})_2$, a green semi-precious stone and Azurite- 2CuCO_3 or $\text{Cu}(\text{OH})_2$, a blue crystal and the basic carbonate of copper. Copper is easily mixed with other metals to form alloys such as bronze and brass (Yaws1999). It is present in the environment in different valence states and in different complexes.



The form of copper affects its solubility; therefore, the copper forms present in water will be different from those found in food. In rivers, copper is generally adsorbed to insoluble particles or complex with inorganic ligands. In drinking water, copper is generally free in solution (Goyer, 1991).

Copper release into water occurs from weathering of soil, industrial discharge, sewage-treatment plants and antifouling paints. The concentrations of copper in drinking water can be greatly increased during the distribution of drinking water. Many pipes and plumbing fixtures contain copper, which can leach into the drinking water. Characteristics of the water that can increase the leaching of copper include low pH, high temperature and reduced hardness (Goyer, 1991).

Zinc has a melting point of 419.58 °C, boiling point of 907 °C and specific gravity of 7.133 (25 °C). Zinc is a lustrous blue-white metal. It is brittle at low temperatures, but becomes malleable at 100-150 °C. It is a fair electrical conductor. Zinc burns in air at high red heat, evolving white clouds of zinc oxide (Yaws, 1999).

The primary ores of zinc are sphalerite or blende (zinc sulfide), smithsonite (zinc carbonate), calamine (zinc silicate) and franklinite (zinc, iron and manganese oxides). Zinc is used to form numerous alloys, including brass, bronze, nickel silver, soft solder, spring brass and aluminum solder. Zinc is used to make die castings for use in the electrical, automotive and hardware industries. Zinc is used to galvanize other metals to prevent corrosion. Zinc oxide is used in paints, rubbers, cosmetics, plastics, inks, soap, batteries, pharmaceuticals and many other products. Zinc most

commonly enters the water supply from deterioration of galvanized iron and dezincification of brass. Zinc in water also may result from industrial waste pollution (Goyer, 1991).

Taking too much zinc into the body through water can affect health. If large doses of zinc are taken by mouth even for a short time, stomach cramps, nausea and vomiting may occur. Ingesting high levels of zinc for several months may cause anemia, damage the pancreas and decrease levels of high-density lipoprotein (HDL) cholesterol (Goyer, 1991).

Chromium has a melting point of 1857 ± 20 °C, boiling point of 2672 °C and specific gravity of 7.18 to 7.20 (20 °C). The metal is a lustrous steel-gray colour, which takes a high polish. It is hard and resistant to corrosion. Chromium has a high melting point, stable crystalline structure and moderate thermal expansion. All chromium compounds are colored (Yaws, 1999).

Chromium compounds are toxic. The principal ore of chromium is chromite (FeCr_2O_4). The metal may be produced by reducing its oxide with aluminum. Chromium is used to harden steel. It is a component of stainless steel and many other alloys. The metal is commonly used for plating to produce a shiny, hard surface that is resistant to corrosion. Chromium is used as a catalyst. It is added to glass to produce an emerald green colour. Chromium compounds are important as pigments, mordants and oxidizing agents (Goyer, 1991).



It occurs in several forms or oxidation states. The two most common are chromium(VI) and chromium(III). The form depends on pH. Natural sources of water contain very low concentrations of chromium. Most chromium releases to water from industrial organic chemical industries. In humans, the toxicity of chromium may be expressed as skin lesions or rashes and kidney and liver damage (Goyer, 1991).

Cadmium has a melting point of 320.9 °C, boiling point of 765 °C, specific gravity of 8.65 (20 °C), and a valence of 2. Cadmium is a blue-white metal soft enough to be easily cut with a knife (Yaws, 1999). Cadmium is used in alloys with low melting points. It is a component of bearing alloys to give them a low coefficient of friction and resistance to fatigue. Most cadmium is used for electroplating. It is also used for many types of solder, for NiCd batteries, and to control atomic fission reactions. Cadmium compounds are used for black and white television phosphors and in the green and blue phosphors for color television tubes. Cadmium salts have wide application. Cadmium sulfide is used as a yellow pigment. Cadmium and its compounds are toxic (Goyer, 1991).

Cadmium is most commonly found in small quantities associated with zinc ores (e.g., sphalerite ZnS). Cadmium is obtained as a by-product during treatment of zinc, lead, and copper ores. Cadmium enters water from waste disposal and spills or leaks at hazardous waste sites and some of the cadmium dissolves in water. It doesn't break down in the environment, but can change forms. Humans can be exposed to cadmium by cadmium-contaminated water. The most serious consequence of chronic cadmium poisoning is cancer (lung and prostate). The first observed chronic effect is generally



kidney damage, manifested by excretion of excessive (low molecular weight) protein in the urine. Cadmium also is believed to cause pulmonary emphysema and bone disease (osteomalacia and osteoporosis). Cadmium may also cause anemia, teeth discoloration (Cd forms CdS) and loss of smell (anosmia) (Goyer, 1991).

2.2 Ion Exchange

Ion exchange is a process where a solid reacts with a solution. An ion exchange material is defined as an insoluble matrix containing labile ions capable of exchanging with other ions in the surrounding medium without any major physical changes taking place in its structure (Lutfor *et al.*, 2000).

2.3 Starch

Starch is the cheapest and abundant raw materials available of all natural polymers. Starch is a high polymer composed of repeating, 1,4- α -D-glucopyranosyl units (often called anhydroglucose units, AGU). It is generally a mixture of linear component amylose, which has a molecular weight of several hundred thousand and amylopectin which is of the order of several million of molecular weight. Branching in amylopectin occurs at C-6 of the glucopyranose unit. Starch occurs in living plants in the form of discrete granules. The use of sago starch in graft copolymers as a renewable source to obtaining ion exchange resin is a new technique in the study of extraction and separation chemistry (Figure 2.1) (Lutfor *et al.*, 2000).



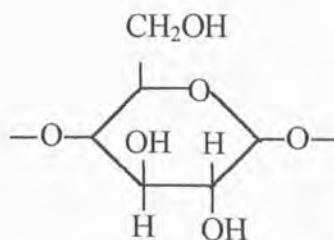


Figure 2.1 Glucopyranose unit of sago starch.

2.4 Types of Polymerization

The study of polymer science begins with understanding the methods in which these materials are synthesized. Polymerization is the formation of long, repeating organic polymer chains (Sperling, 2001). There are many forms of polymerization, and different systems exist to categorize them. Categorizations include the addition-condensation system and the chain growth-step growth system. Another form of polymerization is ring-opening polymerization, which is similar to chain polymerization (Bahadur and Sastry, 2002).

Addition polymerization describes the method where monomers are added one by one to an active site on the growing chain. Addition polymerization involves the linking together of molecules incorporating double or triple chemical bonds. These unsaturated monomers have extra, internal, bonds which are able to break and link up with other monomers to form the repeating chain (Bahadur and Sastry, 2002). Addition polymerization is involved in the manufacture of polymers such as polyethene, polypropylene and polyvinylchloride (PVC). A special case of addition polymerization leads to living polymerization (Sperling, 2001).

A condensation polymer can be defined as a polymer in which the structural unit contains fewer atoms than the monomers from which the polymer is derived. There must be an elimination of a by-product, usually water (Sperling, 2001). Condensation polymerization occurs when monomers bond together through condensation reactions. Typically these reactions can be achieved through reacting molecules incorporating alcohol, amine or carboxylic acid (or other carboxyl derivative) functional groups (Bahadur and Sastry, 2002).

The chain growth-step growth system categorizes polymers based on their mechanism. While most polymers will fall into their similar category from the addition-condensation method of categorization. Chain growth polymers are defined as polymers formed by the reaction of monomer with a reactive center. These polymers grow to high molecular weight at a very fast rate. It is important to note that the overall conversion rates between chain and step growth polymers are similar, but that high molecular weight polymers are formed in addition reactions much more quickly than with step polymerizations (Bahadur and Sastry, 2002).

Step growth polymers are defined as polymers formed by the stepwise reaction between functional groups of monomer. Most step growth polymers are also classified as condensation polymers, but not all step growth polymers like, polyurethanes formed from isocyanate and alcohol bifunctional monomers release condensates. Step growth polymers increase in molecular weight at a very slow rate at lower conversions and only reach moderately high molecular weights at very high conversion (Bahadur and Sastry, 2002).



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