POLY(AMIDOXIME) CHELATING RESIN USED FOR RECOVERY OF ZINC AND CADMIUM METAL IONS

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DECLARATION

I declare that this dissertation is the result of my own independent work, except where otherwise stated.

09 FEBUARY 2003

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ABSTRACT

The polyacrylonitrile grafted starch was obtained from the acrylonitrile monomer with sago starch and grafting reaction was carried out by free radical initiating process. The purpose of this research was to study of poly(amidoxime) resin used for recovery metal ions and rate of metal ions study. For metal ions sorption capacity, it was measured by the batch equilibration with varying pH solutions (pH 3-6). It was found that metal ions uptake by resin was increased with increasing pH up to 6.The sorption capacity of Zn^{2+} and Cd^{2+} metal ions by resin were pH dependent. The sorption capacities for zinc metal ions are higher than cadmium metal ions sorption capacities. The resin selectivity toward both these metal ions is $Zn^{2+} > Cd^{2+}$. From the kinetic exchange for zinc metal ion, it was found that the rate of sorption capacity for zinc metal ion is rapid at $t_{1/2} < 10$.

ABSTRAK

Polyacrylonitrile daripada kanji yang diproses dipeolehi daripada tindak balas diantara monomer acrylonitrile dengan kanji sago melalui proses pembentukan radikal bebas.. Tujuan utama kajian ini adalah untuk mendapatkan data-data mengenai bagaimana resin poly(amidoxime) yang digunakan untuk mendapatkan ion ion logam serta kajian tentang kadar jerapan ion logam. Untuk kapasiti jerapan ion logam, penggiraan adalah melibatkan keseimbangan pada pH yang berlainan (pH 3-6) oleh setiap larutan logam pada kepekatan yang berbeza. Didapati bahawa jumlah ion yang diserap oleh resin poly(amidoxime) mengalami peningkatan dengan pertambahan pH. Daripada keputusan ujian AAS pula, didapati bahawa jerapan ion logam zink adalah lebih tinggi berbanding kapasiti jerapan ion logam kadmium iaitu $Zn^{2+} > Cd^{2+}$. Daripada tindak balas yang berlaku untuk perubahan kinetik ion logam zink dan kadmium, didapati bahawa kapasiti jerapan adalah terpantas untuk ion logam zink a pada selang masa $t_{1/2} < 10$.

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ABBREVIATIONS, SYMBOL, FORMULA AND UNIT LIST

AGU	Sago Starch
AN	Acrylonitrile
CAN	Ceric Ammonium Nitrate
EGF	Epidermal Growth Factor
g	gram
GSH	Intracellular Glutathione
HRI	Heme-Regulated eukaryotic Inition
HSAC	High Surface Area Cathod
L	liter
MA	Methyl Acrylate
mg	milligram
mg/L	Concentration
ml	milliliter
MT	Metallothioneins
NRK	Normal Rat Kidney Fibroblast
NTA	Nitrilotriacetic Acid
PAN	Polyacrylinotrile
ppm	Part per million
RDA	Recommended Dietary Allowance
RO	Reverse Osmosis
%	Percentage

CHAPTER 1

INTRODUCTION

1.1 RESIN FROM POLYACRYLONITRILE (PAN)

The preparation of 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 (Lutfor *et al* 2000). Conversation of nitrile groups of the grafted copolymer into the amidoxime was carried out by treatment with hydroxylamine under alkaline solution (Lutfor *et al* 2000). The chelating behavior of the prepared resin was carried out by using some metal ions. The sorption capacities of metal ions by the resin were pH dependent.

The resin containing Amidoxime group was used in the extraction of uranium from seawater. A number of articles have been described the synthesis of a sorbent with an Amidoxime group. This involved the incorporation of a nitrile group into a polymer matrix followed by the conversation of the nitrile group into an Amidoxime group. This procedure were treatment with an alkaline solution of hydroxylamine.(Egawa *et al*).

This study may the first introduced to the preparation of poly(amidoxime) chelating resin from polyacrylonitrile (PAN) grafted sago starch. The PAN grafted copolymer was used as the cheapest starting materials for poly(amidoxime) resin preparation. The preparation of resin containing an amidoxime group is based on the treatment of nitrile with hydroxylamine. From the analysis of an amidoxime functional group, a purple colored complex was observed.

The objective of this study is to investigate the multistage ion exchange process of chelating resin. Stage wise mass balance equations are developed that allow determination of optimum allocation of ion exchange resins among the adsorption stages. To verify the theoretical developments, experimental tests are also conducted to examine the heavy metal removal efficiencies. The theoretical mass balance equations developed in this work can be of significant value to practical design of the multistage ion exchange process.

1.2 OBJECTIVE

- Sorption study of zinc and cadmium metal ions using Poly(amidoxime) resin.

- Rate of metal ions sorption study.

CHAPTER 2

LITERATURE REVIEW

2.1 REMOVAL OF HEAVY METAL FROM AQUEOUS SOLUTION

Removal of heavy metals from aqueous solution is necessary because of frequent appearance of these heavy metals in wastewaters from many industries, including electroplating, metal finishing, metallurgical, tannery, chemical manufacturing, mining and battery manufacturing industries. This problem has received considerable amount of attention in recent years due primarily to concern that marine animals can readily adsorb those heavy metals in wastewater and directly enter the human food chains, thus presenting a high health risk to consumers. Hence, removal of heavy metals from industrial wastewater is of practical interest.

Many physicochemical methods have been developed for heavy metal removal from aqueous solution, including chemical coagulation, adsorption, extraction, and ion exchange and membrane separation process. Among these methods, ion exchange is a highly popular one and has been widely practiced in industrial wastewater treatment process. The chelating resin employed in the ion exchange processes in general is non-selective and has affinity for alkaline earth, alkali and heavy metals. Improvement of the resin selectivity for heavy metal involves introducing specialty functional groups onto the polymer matrix of the ion exchange resin. The operation of ion exchange for heavy metal removal is usually carried out in a batch vessel or packed column. The batch ion exchange process in a single vessel offers the advantages of high operating flexibility. However, a single-stage ion exchange process seldom achieves the desired level of heavy metal removal. As an alternative, a multistage ion exchange process is more desirable, leading to either enhanced heavy metal efficiency or saving of significant amount of ion exchange resin.

2.2 TOXIC HEAVY METAL

Addition of toxic heavy metal ions (Cd^{2+}, Hg^{2+}, and Pb^{2+}) to hemin-supplemented rabbit reticulocyte lysate brings about the activation of the heme-regulated eukaryotic initiation factor 2 alpha kinase (HRI) and the inhibition of protein chain initiation. In this report we examined the effects of monothiol and dithiol compounds metal ion-chelating agents and metallothioneins (MT) on metal ion-induced inhibition of protein synthesis.The dithiol compounds dithiothreitol and 2,3-dimercaptopropane sulfonic acid prevented and relieved the inhibition of protein synthesis caused by Cd^{2+} and Hg^{2+} in hemin-supplemented lysates but the monothiol compounds 2-mercaptoethanol, cysteamine, D-(-)penicillamine and glutathione had no effect.

The inhibition of protein synthesis caused by Cd^{2+} was reversed by the addition of excess EDTA but not by the addition of excess nitrilotriacetic acid. Toxic heavy metal ions inhibited the capacity of hemin-supplemented lysate to reduce disulfide bonds. Addition of excess EDTA to Cd^{2+} inhibited lysates restored the capacity of the lysate to reduce disulfide bonds and inhibited the phosphorylation of eukaryotic initiation factor eIF-2. MTs and their apoproteins (apoMTs) inhibited the activation of HRI and protected protein synthesis from inhibition by Cd^{2+}, Hg^{2+}, and Pb^{2+}. Addition of apoMTs to heavy metal ion-inhibited lysates restored the capacity of lysates to reduce disulfide bonds.

The restoration of the lysates thioredoxin/thioredoxin reductase activity was accompanied by the inactivation of HRI and the resumption of protein synthesis, indicating that apoMTs can detoxify metal ions already bound to proteins. Several observations presented in this report suggest that the binding of metal ions to the alpha-domain of MT is responsible for the ability of MT to sequester bound metal in a non-toxic form. Addition of glucose 6-phosphate or NADPH had no effect on protein synthesis in metal ion-inhibited lysates and NADPH concentrations in Cd^{2+} inhibited and hemin-supplemented control lysates were equivalent. The data suggest that the metal ions cause the inhibition of protein synthesis by binding to vicinal sulfhydryl groups present in some critical proteins, possibly the dithiols present in the active site of thioredoxin and thioredoxin reductase, which leads to the activation of HRI. (Matts 1991).

2.3 ZINC AND ZINC COMPOUNDS

Zinc is one of the most common elements in the earth's crust. It is founds in air, soil and water and is present in all foods. Pure zinc is a bluish-white shiny metal.

Zinc is an essential element in people diet. Too little zinc can cause health problems, but too much zinc is harmful. The US Recommended Dietary Allowance (U.S RDA) for zinc is 5 to 15 milligrams a day for humans. Not enough zinc is one's diet can result in a loss of appetite, a decreased sense of taste and smell, slow wound healing and skin sores, or a damaged immune system. Young men who don't get enough zinc may poorly developed sex organs and slow growth. If a pregnant woman doesn't get enough zinc, her baby may experience growth retardation.

Too much zinc however, cans damage to humans health. Harmful health effects generally begin at level from 10 to 15 times the US RDA (in 100 to 250 mg/day range). Eating a large amounts of zinc even for a short time, can course a stomach cramps, nausea and vomiting. For longer period, it can cause anemia, pancreas damage and lower levels of high-density lipoprotein cholesterol.

Breathing large amounts of zinc can cause a specific-term disease call metal fume fever. This is believed to an immune response affecting the lung and body temperature.
It is not known if high levels of zinc affect human reproduction or cause birth defect. Rats that were fed large amounts of zinc became infertile or had smaller babies. Irritation was

also observed on the skin of rabbits, guinea pigs and mice when exposed to some zinc compounds. Skin irritation may occur in people.

2.4 USAGE OF ZINC

Zinc has many commercial uses. It is used as coating to prevent rushes, in dry cell batteries, and mixed with other metals to make alloys like brass and bronze. Zinc and copper alloys is used to make pennies in the United States.

Zinc combines with other elements to form zinc compounds. Zinc compounds are widely used in industry to make paint, rubber, dye, wood preservatives and ointments. Commons zinc compounds found at hazardous waste sites include zinc chloride, zinc oxide, zinc sulfate and zinc sulfide.

Pollution prevention means using source reduction techniques in managing waste problems and as second preference, environmentally sounds recycling. The benefits of practicing pollution prevention include reduced operating costs, improved worker safety, reduced compliance costs, increased productivity, increased environmental protection, reduced exposure to future liability costs, continual improvement, resource conservation and enhanced public image.

Pollution prevention in a manufacturing setting generally means materials substitution, process improvement and product change or redesign. Often, pollution prevention practice involves applying one or more of these strategies in tandem. Material Substitution is the use of different materials that are less toxic or nontoxic. This may include the use of a non-zinc containing raw material or different equipment that does not require zinc. To comply with government regulations, as well as reduce operating costs, a fiberglass plant needed to replace the chromate and zinc products used for corrosion and deposit control in its cooling water treatment program. After laboratory tests demonstrated that replacement products were effective, the cooling system was treated with alternative azole and polymer based products for scale and corrosion inhibition, and other biocides for microbiological control. The process was completely automated with a computerized monitoring, feed and delivery system. Elimination of chromate and zinc brought the plant into environmental compliance. Further benefits include improved control over treatment parameters, the ability to use recycled wastewater in the cooling system, reduced water usage and less wastewater disposal.

Process improvement means to improve the operational process, thereby reducing or eliminating the need for zinc usage. This includes, for example, increasing the operating efficiency of equipment or a process, good maintenance programs and training to reduce the risk of waste generation.

Metal finishers can reduce the waste generation through techniques such as counter-current rinsing, restricting water flow, drain boards and air knives. Recovery techniques such as evaporation, reverse osmosis, ion exchange, electrodialysis and electrolytic recovery can be used to reuse or recycle the valuable metals.

Reverse osmosis (RO) recovers plating chemicals from plating rinse water by removing water molecules with a semi-permeable membrane. The membrane allows water to pass through but blocks metals and other additives.

Diluted or concentrated rinse waters are circulated past the membrane at pressures greater than aqueous osmotic pressure. This action results in the separation of water from the plating chemicals. The recovered chemicals can be returned to the plating bath for reuse and permeate, which is similar to the condensate from an evaporator, can be used as make-up water. RO units work best on dilute solutions.

The design and capacity of an RO unit is dependent on the type of chemicals in the plating solution and the drag out solution rate. Certain chemicals require specific membranes. For instance, polyamide membranes work best on zinc chloride and watts nickel baths. RO systems have a 95 percent recovery rate with some materials and with optimum membrane selection.

In electrolytic recovery, metal ions are plated out of solution electrochemically by reduction at the cathode. There are essentially two types of cathodes used for this purpose; a conventional metal cathode (electrowinning) and a high surface area cathode (HSAC). The (HSAC) cathode can effectively plate-out metals, such as gold, zinc, cadmium, copper, nickel, etc. Therefore, electrolytic recovery can be used with most plating baths. Product Change or Redesign may eliminate zinc altogether from the manufacturing process, especially where zinc is incorporated into the product.

A systematic approach to pollution prevention establishes and maintains a systematic management plan designed to continually identify and reduce environmental impacts through pollution prevention. Many facilities are incorporating pollution prevention into their quality programs or environmental management systems. The options identified and implemented often incorporate the pollution prevention techniques mentioned earlier.

2.5 CADMIUM AND CADMIUM COMPOUNDS

Cadmium is found at low concentrations in the Earth's crust, mainly as the sulfide in zinc-containing mineral deposits. Since the early twentieth century, it has been produced and used in a variety of applications in alloys and in compounds. Among the important compounds of cadmium are cadmium oxide (used in batteries, as an intermediate and catalyst and in electroplating), cadmium sulfide (used as a pigment), cadmium sulfate (used as an intermediate and in electroplating) and cadmium stearate (used as a plastics stabilizer).

Occupational exposure to cadmium and cadmium compounds occurs mainly in the form of airborne dust and fume. Occupations in which the highest potential exposures occur include cadmium production and refining, nickel-cadmium battery manufacture, cadmium pigment manufacture and formulation, cadmium alloy production, mechanical plating, zinc smelting, soldering and polyvinylchloride compounding. Although levels vary widely among the different industries, occupational exposures generally have decreased in the last two decades.

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