UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF NEW CHELATING RESINS CONTAINING THIOUREA AS THE FUNCTIONAL GROUP

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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October 2002

Chairman: **Sidik bin Silong, Ph.D.**

Faculty: **Science and Environmental Studies**

A series of chelating resins, derived from a macroreticular styrene-divinylbenzene (2%) copolymer beads grafted with various spacer from propylene groups $(-CH_2-CH_2-CH_2)_n$ (n=1, 2, 4) and containing thiourea as chelating function, have been synthesized in a four-step reaction sequence. The steps began by the reaction of diethyl malonate with a spacer (ethylene groups), followed with the attachment of the arm group to the polymer. The polymer was then hydrolyzed and converted to its polychloride acid derivatives and followed by the attachment of the thiourea functional group to produce the new chelating resins.

The reaction of diethyl malonate with the spacer has been monitored by using nuclear magnetic resonance analysis. Meanwhile, the presence of all the functional

groups has been deduced by infrared spectroscopy. Due to the insolubility of the backbone resin, the presence or absence of certain bands expected for particular functional groups in their infrared spectra was used to monitor the success of the grafting process. The C, H, N and S elemental analyses data were used to estimate the degree of conversion in each and every step of the reactions and the surface morphology was studied by using scanning electron microscopy.

The complexation behavior of these resins was investigated towards Hg(II), Cu(II) and Pb(II) ions in aqueous solutions by the batch equilibration technique. The influence of pH on adsorption capacity was also examined. The adsorption values for metal ions' intake followed the order Hg(II) > Cu(II) > Pb(II). Polymers can be regenerated by washing with the mixture solution of hydrochloric acid and an aqueous solution of thiourea by using the column method.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN RESIN PENGKELAT BARU YANG MENGANDUNGI KUMPULAN BERFUNGSI TIOUREA

Oleh

MOHD SHABERI BIN MOHD AMIN

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Satu siri resin pengkelatan diterbitkan dari manik-manik rangkaian makro ko-polimer stirena-divinilbenzena (2 %) yang tercangkuk dengan bahagian lengan mengandungi kumpulan berfungsi tiourea menerusi beberapa peruang propilena (-CH_2-CH_2-CH_2)$_n$ (n = 1, 2, 4), telah disediakan melalui empat langkah tindak balas. Dimulai dengan tindak balas dietilmalanot dengan peruang (kumpulan etilena) yang kemudiannya dirangkaikan kepada polimer. Seterusnya polimer terubahsuai itu dihidrolisis dan ditukarkan menjadi asid poliklorida terbitan, serta diikuti dengan memasukkan kumpulan berfungsi tiourea bagi mendapatkan resin pengkelat baru.

Tindak balas diantara dietilmalanot dengan peruang telah ditentukan menggunakan analisis resonan magnetik nuklear. Manakala kehadiran semua

kumpulan berfungsi ditentukan melalui spektroskopi infra-merah kerana ketidak larutan rangka asas resin. Kejayaan setiap langkah tindak balas penyangkukan ditentukan berdasarkan kepada kehadiran atau ketidakhadiran jalur-jalur serapan tertentu bagi kumpulan-kumpulan berfungsi berkaitan. Analisis unsur C, H, N dan S dilakukan bagi menganggarkan kadar pengubahan bagi setiap langkah tindak balas, manakala morfologi permukaan dikaji menggunakan mikroskopi pengimbasan elektron.

Pembentukan komplek resin ini terhadap ion-ion Hg(II), Cu(II) dan Pb(II) telah dikaji dalam larutan akuas menggunakan teknik keseimbangan pukal. Kesan pH terhadap kapasiti penjerapan resin juga dikaji. Nilai jerapan resin ini terhadap ion logam adalah mengikut urutan Hg(II) > Cu(II) > Pb(II). Polimer ini boleh dijana semula selepas dibilas menggunakan campuran larutan asid hidroklorida dan larutan akuas tiourea melalui keadah turus.

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I certify that an Examination Committee met on 28th October 2002 to conduct the final examination of Mohd Shaberi bin Mohd Amin on his Master of Science thesis entitled "Synthesis and Characterization of New Chelating Resins Containing Thiourea as the Functional Group" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. The members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work expect for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

MOHD SHABERI BIN MOHD AMIN

Date: 27/12/2002

TABLE OF CONTENTS

III EXPERIMENTAL

IV RESULTS AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

ppm	Part per million
DVB	Divinylbenzene
PSR	Polystyrene resin
ν	Stretching vibration
δ	Bending vibration
δ_s	Scissor vibration
δ_p	Rocking vibration
δ_τ	Twisting vibration
δ_w	Wagging vibration
C_o	Initial concentration
C	Equilibrium concentrations
W_R	Weight of dry resin
Q	Capacity
	Polymeric chain

CHAPTER I

INTRODUCTION

1.1 Heavy Metal

The problem of heavy metal contamination in waterbodies is widespread and becoming more acute, threatening an ever increasing portion of global population. Such an environmental pollution is mainly due to rapid industrialization together with the increase in modern method of agriculture especially in the developing countries.

Water pollution is mainly caused by untreated released of effluent by industries such as plating, electroplating, leather, textile and battery manufacturer. (Some of the sources where heavy metals could be found are listed in Table 1.1). Among the most common heavy metals found in industrial wastewater are Cu, Ni, Zn, Cr, Hg and Pb. Accumulation of these metal ions in trace quantity in human body cause physiological and neurological disorder. However, at a higher concentration they are very toxic and cause severe health problem, which may cause death. Therefore, heavy metal ion concentration in wastewater must be controlled and reduce to a low level.

Chemical precipitation, ion exchange, reverse osmosis, solvent extraction and ultrafiltration could achieve removal of metal ions from wastewater.

Table 1.1: Substances Present in Industrial Effluents (Lester, 1987).

Substances	Usage in Industries
Arsenic	Semi-conductors & photoconductors, agrochemical such as insecticides.
Aluminum	Construction of building and transport, aluminum foils.
Cadmium	Electroplating & coating industry pigment for paint.
Chromium	Machinery-construction industry alloys in transport & heater elements.
Copper	Electronics, plating, brass & other alloys, fertilizer, rayon manufacture.
Lead	Battery manufacture, anti-knock additions for gasoline, piping.
Mercury	Instrumentation for measurement and control, amalgam in dentistry.
Nickel	Alloys, electroplating, pigments, catalysts, electrical contacts & batteries.
Silver	Photographic products plated silverware, jewelry & battery manufacture.
Zinc	Brass & bronze alloys for galvanization, cosmetics & pharmaceuticals.

Shkinev *et al.* (1989) reported a new method for determination of trace heavy metal in water by atomic absorption spectrometry after preconcentration by liquid-phase polymer-based retention. The method has been applied to the determination of Ni, Cu, Zn, Hg and Cd in drinking and river water with poly(ethyleneimine) and its thiourea derivative as complexing polymer. The metals were determined in aqueous concentrate after a 250-fold preconcentration by 2% polymer solution at pH 7.

Zaporozhets *et al.* (1999) obtained the modified sorbents with dithizone and zinc thizonate adsorbed on the silica surface. Adsorption of heavy metal ions from aqueous solutions onto loaded silica was studied. Color scales for Ag(I), Hg(II) and Pb(II) visual test detection were developed. The modified silica gels were established to be applicable to the quantitative determination of these metal ions in buttermilk, natural, mineral and wastewater.

A method for the determination of Cu, Zn, Fe, Ni and Cd by flame atomic absorption spectrophotometry (F-AAS) after preconcentrating on a column containing *Escherichia coli* immobilized on sepiolite has been developed by Bag *et al.* (2000). Optimum pH values, amount of adsorbent, elution solution and flow rate have been obtained for the elements studied. The effect of interfering ions on the recovery of the analytes has also been investigated. Recoveries of Cu, Zn, Fe, Ni and Cd by *E. coli* immobilized on sepiolite were 99.1 $\pm$ 0.6, 98.2 $\pm$ 0.6, 98.1 $\pm$ 0.5, 97.2 $\pm$ 0.8 and 98.2 $\pm$ 0.4 % (at 95 % confidence level), respectively. The adsorption capacity of *E. coli* immobilized on sepiolite was found to be 0.148, 0.064, 0.098, 0.134 and 0.088 mmol/g for Cu, Zn, Fe, Ni and Cd, respectively.

Tiravanti *et al.* (1997) investigated the conservative technologies to utilize natural and synthetic reactive polymers for selective metal removal, recovery and reuse. Examples refer to the treatment of industrial wastes containing silver, cadmium, mercury, chromium, iron and aluminum by different innovative processes. A precipitation process was described, namely Metals Extration by Xanthate Insolubilization and Chemical Oxidation (MEXICO), using agricultural

raw materials to prepare starch or cellulose xanthates as precipitating agents for metals.

1.2 Toxicity

1.2.1 Copper

Copper is an essential element used in process of blood formation and iron utilization, with a human daily requirement of 0.03 mg/kg for adults. The main intake is normally through the diet and water consumption. Copper occurs in aqueous solution in oxidation states of (I) and (II), but former is unstable above equilibrium concentration of 10^{-2} M and in aerated natural waters it is generally oxidized to Cu(II).

Copper is absorbed through the intestinal tract (40 to 70 %) and absorption varies with intake. Its half-life in human is 80 days and total body burden is 75 to 150 mg. Once absorbed, copper is transported in the blood and stored normally in muscle, liver and brain tissue. In cases of acute toxicity, copper is found in the brain, liver, stomach, hair roots and urine. Symptoms of acute toxicity are gastric ulcers, hemolysis, jaundice, hepatic necrosis and renal damage. Chronic toxicity in man is found infrequently but has been reported to cause "pink disease" in infant ingesting copper-contaminated water at concentrations of 0.8 mg/l. Elevated levels of copper are associated with disorders such as biliary atresia and cirrhosis in children, Hoadkin's disease, leukemia and atherosclerosis.

Microamount of copper takes part in oxidization inside the human body and is relative to some illnesses of the body, so it is important to determine microamount of copper. Ma *et al.* (1999) synthesized a new sensitive reagent based on the new long-chain saturated fatty hydrocarbon substituting group compound, *N*-undecyl-*N'*-(sodium *p*-aminobenzenesulfonate)-thiourea (UPT). According to the studies on its analytical performance, it is found that this reagent can be used to identify Cu^{2+} and determine microamounts of copper ($\varepsilon_{300.4\ nm}$ = 2.39 x 10^5 l mol^{-1} cm^{-1}) in aqueous solution. These new methods are simple and convenient and can provide satisfactory results on samples.

Ferreira *et al.* (2000) proposed a procedure for the separation and preconcentration of trace amounts of copper in natural water samples. It is based on the adsorption of copper(II) ions onto a column of Amberlite XAD-2 resin loaded with calmagite reagent. This way amounts of copper within the range from 0.0125 to 25.0 μg, in a sample volume of 25 to 250 ml, and pH from 3.7 to 10.0 was concentrated as camagite complex in a column of 0.50 g of Amberlite XAD-2 resin. Detection and determination limits of the proposed procedure for 250 ml sample volume were 0.15 and 0. 50 μg l^{-1}, respectively.

1.2.2 Lead

Lead (Pb) is one of the oldest metals known to man and, since medieval times, has been used in piping, building materials, soldering, paints, ammunition and castings. More recently, lead has been used mainly in storage batteries (35