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JUDUL: METAL IONS RECOVERY FROM INDUSTRIAL EFFLUENTS
(ELECTROPLATING LIQUOR) USING POLYMERIC CHELATING RESINS

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METAL IONS RECOVERY FROM INDUSTRIAL EFFLUENTS (ELECTROPLATING LIQUOR) USING POLYMERIC CHELATING RESINS

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APRIL, 2007
DECLARATION

I hereby declare that this dissertation is based on my original work, except for quotations and summaries each of which have been fully acknowledged.

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In this study, poly(hydroxamic acid) (PHA) chelating resin was synthesized using poly(methyl acrylate) (PMA)-grafted sago starch. The PMA-grafted copolymer was obtained by a free-radical initiating process in which ceric ammonium nitrate was used as an initiator. Conversion of the ester groups of the PMA-grafted copolymer into hydroxamic acid was carried out by treatment of an ester in hydroxylamine in an alkaline solution. The functional groups in the resin were characterized by using FTIR. The PHA and poly(hydroxamic acid-amidoxime) (PHA-PA) chelating resin (obtained from Lutfor et al. (2001b) previous study) were used in the study of Zn$^{2+}$ and Cr$^{3+}$ removal from industrial effluents by batch and column techniques. The percentage recovery by PHA chelating resin was the highest at 98.30% in effluent containing chromium ions by batch technique. The percentage recovery by resins in column technique was lower due to the short time contact between the resins and the effluents. The overall percentage recovery of metal ions by both resins showed that the resins were able to remove metal ions from effluents. The absorbing capacity for PHA chelating resin by batch technique was high in 20 ml of effluent containing Zn$^{2+}$ at 23.15 mmolg$^{-1}$ while the absorbing capacity for the same resin in three other effluents (2A, B and C) containing Cr$^{3+}$ were approximately the same at 15.18 mmolg$^{-1}$, 11.33 mmolg$^{-1}$ and 11.14 mmolg$^{-1}$, respectively. The absorbing capacity by column technique exhibited similar trend with batch technique indicating that the absorption capacities of both resins were dependent on the initial metal ion concentration present in the effluent and not the amount of effluent used. The recovery of the investigated metal ions from the absorbed resins was done by treating the resins in HCl 0.01M, 0.1M and 1M continuously. It was found that the cumulative percentage elution of Zn(II) from PHA-PA chelating resin was the highest at 97.2% while the percentage elution of Cr(III) from the same resin was also high at 81.6%. The cumulative percentage elution of Zn(II) and Cr(III) from PHA chelating resin was lower at 54.0% and 68.8%, respectively.
PEMULIHAN ION LOGAM DARI EFLUEN INDUSTRI (AIR BUANGAN ELEKTROPLAT) MENGGUNAKAN RESIN CHELATIN POLIMER

ABSTRAK

Dalam kajian ini, resin chelatin poli(hidrosamik asid) disintesis dari kanji(metil acrylate) (PMA) yang diperolehi melalui tindakbalas radikel bebas dimana cerik ammonium nitrat digunakan sebagai bahan pemula. Kumpulan ester dalam ko-kopolimer PMA tersebut ditukar kepada hidrosamik asid oleh rawatan hidroksilamin dalam keadaan alkali. Pencirian kumpulan berfungsi dalam resin tersebut dijalankan dengan menggunakan FTIR. Resin chelatin PHA dan poli(hidrosamik asid-amidosim) (diperolehi dari kajian lepas Lutfor et al. (2001b)) digunakan dalam kajian penyingkiran ion logam (Zn²⁺ dan Cr³⁺) dari efluen industri melalui teknik berkumpulan (“batch”) dan teknik pemisahan (“column”). Peratus pemulihan ion logam oleh resin chelatin PHA dalam efluen yang mengandungi ion kromium melalui teknik berkumpulan adalah paling tinggi pada 98.30%. Peratus pemulihan ion logam melalui teknik pemisahan adalah kurang berbanding dengan teknik berkumpulan. Ini adalah disebabkan oleh jangka masa retensi di antara resin dengan efluen adalah pendek. Peratus pemulihan ion logam dari efluen secara keseluruhannya menunjukkan bahawa resin chelatin berkeupayaan untuk menyingkiran ion-ion logam dari efluen. Keupayaan penyerapan resin PHA dalam 20 ml efluen (Zn²⁺) ialah 23.15 mmolg⁻¹ manakala dalam efluen lain yang mengandungi Cr³⁺ (A, B dan C) masing-masing ialah 15.18 mmolg⁻¹, 11.33 mmolg⁻¹ dan 11.14 mmolg⁻¹. Ini menunjukkan keupayaan penyerapan adalah bergantung kepada kepekatan ion logam yang hadir dalam efluen, dan bukananya amaun efluen yang digunakan. Pemulihan ion-ion logam dari resin chelatin dilakukan melalui perawatan resin dengan kepekatan HCl yang berlainan (0.01M, 0.1M dan 1M). Peratus pemulihan kumulatif Zn²⁺ dari resin chelatin PHA-PA adalah paling tinggi pada 97.2% manakala peratus pemulihan Cr³⁺ dari resin yang sama ialah pada 81.6%. Peratus pemulihan kumulatif bagi pemulihan Zn²⁺ dan Cr³⁺ dari resin chelatin PHA pula adalah lebih rendah pada 54.0% dan 68.8%, masing-masing.
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<table>
<thead>
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<th>Symbol</th>
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<td>°C</td>
<td>Degree celsius</td>
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<tr>
<td>2H4ABA</td>
<td>2-hydroxy-4-acryloyloxybenzaldehyde</td>
</tr>
<tr>
<td>AAS</td>
<td>Atomic absorption spectrophotometer</td>
</tr>
<tr>
<td>C4RAHA</td>
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<td>CAN</td>
<td>Ceric ammonium nitrate</td>
</tr>
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<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectrometer</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>GMA-IDA</td>
<td>Glycidyl methacrylate-iminodiacetic acid</td>
</tr>
<tr>
<td>IDA</td>
<td>Iminodiacetic acid</td>
</tr>
<tr>
<td>M</td>
<td>Molarity</td>
</tr>
<tr>
<td>mg</td>
<td>Milligram</td>
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<tr>
<td>mgg⁻¹</td>
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</tr>
<tr>
<td>ml</td>
<td>Milliliter</td>
</tr>
<tr>
<td>ml min⁻¹</td>
<td>Milliliter per minute</td>
</tr>
<tr>
<td>μm</td>
<td>Micrometer</td>
</tr>
<tr>
<td>mmolg⁻¹</td>
<td>Millimole per gram</td>
</tr>
<tr>
<td>moll⁻¹</td>
<td>Mole per liter</td>
</tr>
<tr>
<td>MPGI</td>
<td>Magnetic Fe₃O₄-glycidyl methacrylate-iminodiacetic acid styrene-divinyl benzene resin</td>
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<td>NH₂OH.HCl</td>
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<td>PHA</td>
<td>Poly(hydroxamic acid)</td>
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<tr>
<td>POP</td>
<td>Persistent organic pollutants</td>
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<tr>
<td>PSME-EDA</td>
<td>Poly(2-hydroxyethylmarcaptomethylstyrene – diethanolamine)</td>
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<tr>
<td>ppb</td>
<td>Parts per billion</td>
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CHAPTER 1

INTRODUCTION

1.1 Overview

Today, in most industrial fields, many of its operations release wastewater or effluents which are heavily contaminated with heavy metals into the environment. These operations are such as metal plating, tanning and also mining (Atiaa et al., 2005a). Other operations such as metallurgical, chemical manufacturing and battery manufacturing industries also contribute in the release of wastewater to the environment. The heavily contaminated wastewater is one of the major factors which cause the decline in environmental quality. According to Young et al. (1973), these wastewaters also cause exponential growth in the phytoplankton’s population. Apart from that, heavy metals in the contaminated wastewaters are not biodegradable. Industrial effluents, in any form, therefore, need to be controlled in order to protect human health and the environment. This is due to the fact that industrial effluents and sewage water has a high potential in carrying chemical pollutants such as heavy metals and persistent organic pollutants (POPs) (Jones & Alcock, 1997).
Many methods have been developed throughout the years for heavy metal removal from aqueous solution. Those methods include the use of conventional activated sludge treatment (Cosgrove & Oliver, 1974), the use of biosorption column using immobilized Mucor rouxii biomass or microbial cells as absorbents (Viraraghavan & Yan, 2001) and precipitation of metal sulfides with sodium sulfide on the surface of bentonite (Banfalvi, 2006). Other methods also include the electroflotation technique via the electrogeneration of gas bubbles (hydrogen and oxygen) at the electrodes with a variety of pH (Khelifa et al., 2005) and Diebold & Jenke (1984) treated the acid mine wastewater by using the electroprecipitation method. Among all the methods that have been developed, the use of chelating resin in the removal of toxic metal ions from both environment and sewage waters is one of the most promising methods. This is because chelating resins are generally efficient in the removal and recovery of heavy metal ions due to their physical and chemical stabilities (Garg et al., 1999).

Chelating resins can generally be prepared by a two-step synthesis (Garg et al., 1999). The first step is the insertion of an appropriate functional group on the surface of the prepared polymer and the second step is the immobilization of ligand by condensation or coupling reaction. In other words, chelating resins can be prepared by anchoring a functional group to a polymeric backbone and this functionally group has generally been found to exhibit greater selectivity towards some metal ions than usual cation and anion exchange resins. The design and preparation of each chelating resins depends much on the stability of the basic macromolecular network and also its ability to add on the desired chelating functional group. These groups contain two or more electron donor atoms that are able to form bonds with selected single metal atoms.
Therefore, the desired chelating functional groups are known to work specifically towards selected metal ions (Kirchner & Winston, 1978).

The preparation, characteristics and the applications of chelating resins have been widely studied by many scientists around the world. These chelating resins include those with different amine, thio and amine-mercaptan functionalities which were synthesized through the polymerization of glycidyl methacrylate (Atiaa et al., 2005b). Lutfor et al. (2000a) had also synthesized poly(hydroxamic acid) chelating resin from poly(methyl acrylate)-grafted sago starch and poly(amidoxime) chelating resin from polyacrylonitrile grafted sago starch. The chelating behaviors of these synthesized resins towards metal ions are usually investigated using the batch technique (Lutfor et al., 2001a).

Chelating resins with different functional groups have long been of interest in the removal of specific metal ions from water. According to Vernon & Eccles (1976), they can be used for the extraction of toxic metals in the environment and sewage waters. Chen et al. (2006) investigated the removal of Ni(II) from synthetic electroplating wastewater using a strong-acid resin in fixed beds. Dogutan et al. (2003), on the other hand, prepared a new melamine based polymeric sequestering resin so that the pre-concentration, separation and the sequestering action of the hexavalent chromium from wastewater can be investigated. These heavy metal ions are such as Cd(II), Co(II), Ni(II), Zn(II), Cu(II) and Zr(IV). Elothmani et al. (2005) used the polydiphenylamine resin in the removal of metal ions from aqueous solutions. Battacharyya et al. (2006), on the other hand, found that stable chelating resins can
also be employed for the water purification as the resins reveal sorption ability towards toxic metal ions and exhibits no affinity to alkali or alkaline earth metal ions.

1.2 Research Objectives

The objectives of this research are:-

i. To prepare poly(hydroxamic acid) chelating resin from poly(methyl acrylate)-grafted sago starch.

ii. To employ the poly(hydroxamic acid) and poly(hydroxamic acid-amidoxime) chelating resin (obtained from Lutfor et al. (2001b) previous study) in the absorption and recovery of metal ions from industrial effluents.

iii. To evaluate the absorbing capacity for each resin towards selected metal ions and its percentage recovery of metal ions.

1.3 Scope of Study

This study focuses mainly on the absorption and recovery of metal ions from industrial effluents. Two different polymeric chelating resins were used in this study. They are the poly(hydroxamic acid) (PHA) and poly(hydroxamic acid-amidoxime) (PHA-PA) chelating resin. The PHA chelating resin was prepared from poly(methyl acrylate)-grafted sago starch by the graft copolymerization technique. Sago starch was grafted with methyl acrylate monomers by utilizing ceric ammonium nitrate (CAN) as an initiator. The PHA chelating resin was synthesized by the conversion of ester groups in the poly(methyl acrylate)-grafted copolymer to PHA chelating resin.
Characterization of functional groups in the new material synthesized was performed by using the FTIR spectroscopy. The metal sorption abilities for both resins were tested by using industrial effluents containing zinc and chromium ions. The absorption of metal ions from effluent was determined by using the batch and column technique. Both chelating resin’s absorbent capacity towards metal ions and its recovery of metal ions were evaluated. For this reason, the atomic absorption spectrophotometer (AAS) was used to determine the initial and final concentration of metal ions in each sample.
2.1 Chelating Resins

In the analysis of trace metal ions determination in wastewater, the direct determination with various instrumental methods is not possible because of its limited sensitivity. Therefore, the separation and preconcentration of metal ions in the sample is very important to be able to determine the metal ion concentration in a sample. Various methods are used for the separation and preconcentration of the metal ions. Those methods are such as the liquid-liquid extraction, precipitation technique, freezing-based concentration methods, carbon adsorption, distillation, sublimation, evaporation and also the use of ion-exchange resins (Garg et al., 1999). There are several types of ion-exchange resins. They are such as cation exchangers, anion exchangers and chelating resins. In recent years, the use of chelating resins has increased drastically (Kantipuly et al., 1990). These chelating resins can be synthesized by various methods and can be widely applied in many aspects.
In general, chelating resins are a group of materials having complexing or chelating groups on their surfaces. For example, the Chelex 100 is based on the chemical modification of a resin surface with iminodiacetic acid groups (Schmuckler, 1965). According to Garg et al. (1999), there are several advantages for the use of chelating resins over conventional methods during the extraction of metal ions. These includes:-

i. Selective determination of metal ions will be possible by using a chelating resin having a ligand possessing high selectivity to the targeted metal ion;

ii. It is free from difficult phase separation, which is caused by the mutual solubility between water and organic solvent layers;

iii. The chelating resin method is an economical method since it uses only a small amount of ligand and extraction solvent and this also increases the sensitivity of the system;

iv. Trace metal ions at as low as parts per billion (ppb) can be determined because the targeted ion is enriched on the solid phase;

v. The concentration of metal ion can be visibly estimated from the color intensity of the solid phase if the metal complex formed possess adsorption in the visible wavelength region;

vi. Use of carcinogenic organic solvents is avoided and thus the technique is eco-friendly to nature.
Today, there are many types of chelating resins available. These chelating resins are mainly used to absorb metal ions from aqueous media. According to Sengupta et al. (1991), chelating resins can remove trace amounts of metal cations from the background of very high concentrations of competing alkaline and alkaline earth metal ions at an acidic pH level. Chelating resins can be prepared from various sources of different materials. In other words, various chelating resins are obtained from various monomers. A few examples of chelating resins are such as poly(hydroxamic acid) and poly(hydroxamic acid-amidoxime) chelating resin. The two chelating resins mentioned were used for this study. Apart from that, there are many other types of chelating resins which can be synthesized and be applied in several aspects.

For example, a new metal chelating polymer derived from nickel (II) and copper (II) polymer complexes was synthesized (Kannan et al., 1996). The new metal chelating polymer was synthesized beginning from the preparation of 2-hydroxy-4-acryloyloxybenzaldehyde (2H4ABA) from acryloyl chloride and 2,4-dihydroxybenzaldehyde. The 2H4ABA was polymerized in 2-butanol at 65 °C using the benzoyl peroxide as initiator as shown in Figure 2.1.
The polychelates was obtained in $N,N$-dimethylformamide solution of poly(2H4ABA) with aqueous solution of Cu$^{2+}$ or Ni$^{2+}$ ions. The polymers and polychelates obtained from the study were characterized by elemental analysis and spectral studies. From both the elemental analysis and spectral studies, Kannan et al. (1996) have suggested that the metals are coordinated through the oxygen of the aldehyde group and oxygen of the phenolic-hydroxide group. From the study, the Cu(II)-polychelates was found to be more stable than the Ni(II)-polychelates. It was also confirmed that the chelation of metal ions may possibly occur between two groups from different polymeric chains as shown in Figure 2.2. The thermal properties of polymer-metal complexes and their catalytic activity were also discussed.
Donia et al. (2005), on the other hand, have successfully prepared a chelating resin with amine-mercaptan groups by using the methyl thiirane methacrylate (II) as an intermediate. The resin obtained from the study showed high durability towards mineral acids and alkalis. In the study, the recovery of mercury (II) was investigated by both batch and column methods. The newly synthesized chelating resin’s uptake capacity towards Hg(II) reached 3.10 mmol g⁻¹. Apart from that, the nature of interaction between the metal ion and the resin was found to be dependent upon the acidity of the medium as well as the type of the conjugate anion. The interaction between the metal ion and the resin was explained via the complex formation or ion exchange mechanism. Donia et al. (2005) have also found that the Hg(II) could be selectively separated from Ca(II), Mg(II), Pb(II), Cd(II), Cu(II) and Zn(II) at pH 2.7. Finally, the elution process of Hg(II) was tested using hydrochloric acid (HCl), nitric acid (HNO₃) and sulphuric acid (H₂SO₄) with different concentrations. HNO₃ and H₂SO₄ gave a high elution ratio (>90%) whereas HCl showed a low elution ratio (≈32%).

Figure 2.2 Possible coordination of (a) Cu(II)-polychelates and (b) Ni(II)-polychelates (Source: Kannan et al., 1996)
Chelating resins containing macroreticular with thiol functional groups were found to be able to remove mercury (II) from water (Ratto et al., 2000). In the study, a detailed experimental and theoretical analysis of the adsorption process of mercury by Duolite GT-73 chelating resin was done. The Duolite GT-73 chelating resin is a macroreticular chelating resin containing thiol (S-H) functional groups. This resin was proven to have very high adsorption efficiency, reaching 30-40% of its weight and its efficiency decreases as the pH decreases due to the competition between two ions, H⁺ and Hg²⁺.

In another study of the mercury (II) adsorption by chelating resin, poly(2-hydroxyethylmercaptomethylstyrene) (PSME) and diethanolamine (EDA) was used as starting materials for the synthesis of a novel chelating resin containing sulfur, nitrogen and oxygen atoms (Qu et al., 2006). The adsorption capacity of the poly(2-hydroxyethylmercaptomethylstyrene – diethanolamine) (PSME-EDA) resin for Hg²⁺ ion was investigated. It was found that the adsorption capacity of the PSME-EDA for the Hg²⁺ ion could reach to about 1.1 mmol g⁻¹ at 25 °C when the initial Hg²⁺ metal ion concentration was at 0.02 mol l⁻¹. Some factors affecting the adsorption such as temperature, reaction time and ion concentration were also studied. From the study, it was concluded that the increasing of temperature was beneficial to the adsorption process and the adsorption mechanism of PSME-EDA resin for mercury (II) was confirmed by X-ray photoelectron spectroscopy.

Then, another type of chelating containing a stable thiol group was synthesized using polystyrene as the starting material (Joseph & Pillai, 1987). It was found that the resin is stable towards concentrated HCl, HNO₃ 0.1M and NaOH 0.1M. The resin also
REFERENCES


