EXTRACTION AND SEPARATION OF HEAVY METAL IONS BY USING POLY (HYDROXAMIC ACID) CHELATING RESIN

G.KUBANESWARY A/P GENGARAJU

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KUBANESWARY GENGARAJU
HS2004-2160

PERPUSTAKAAN
UNIVERSITI MALAYSIA SABAH

APRIL, 2007
NAME: G. Kubaneswary d/o Gengaraju
TITLE: Extraction and separation of heavy metal ions using poly(hydroxamic acid) chelating resin.

VERIFICATION

DR. MD. LUTFOR RAHMAN

ASSOC. PROF. DR. MARCUS JOPONY

MR. MOH PAK YAN

DEAN

APRIL, 2007
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ABSTRACT

Poly(hydroxamic acid) (PHA) chelating resin was synthesized utilizing poly(methylacrylate) (PMA) grafted sago. The PMA grafted copolymer was obtained by free radical initiating process where ceric ammonium nitrate was used as an initiator. Ester group of PMA were converted to hydroxamic acid groups by treatment of hydroxylamine under alkaline solution. The PHA resin was characterized using FT-IR spectra to determine the functional groups of the ligand. The prepared resin was used to separate heavy metal pairs (Cu-Cd, Cu-Zn, Zn-Cr and Cu-Cr). The separation was done by column technique with HCl as an eluent. It is found that Zn and Cd ions were eluted using 0.001M, 0.01M and 0.1M HCl. Whereas, Cu ion was eluted with 0.1M and 0.5M HCl. Finally Cr ion was eluted with 0.5M and 1.0M HCl. The selectivity of the resin toward the metal ions used was in the following order: Cr$^{3+}$ > Cu$^{2+}$ > Zn$^{2+}$ > Cd$^{2+}$. The rate of exchange of copper, cadmium and chromium ion was rapid where the $t_{1/2}$ ≈ 6, 5 and 4 min, respectively and the swelling of the resin was 40.382 g water g$^{-1}$. 
PENGASINGAN ION LOGAM BERAT DENGAN MENGGUNAKAN POLY(HYDROXAMIC ACID) RESIN

ABSTRAK

Poly(hydroxamic acid) (PHA) resin telah disediakan daripada kanji sago poly(methyl acrylate). Tindak balas dilakukan melalui proses permulaan radikal bebas dengan menggunakan ceric ammonium nitrat sebagai pemula. Penukaran kumpulan ester kopolimer kanji sago poly (methyl acrylate) kepada hidroxamic dilakukan dengan merawat ia dengan hidroksilamin dalam larutan beralkali. Kumpulan berfungsi resin telah dikenalpasti dengan menggunakan spektroskopi Fourier Transform Infrared (FTIR). Resin yang telah disediakan digunakan untuk pengekstrakkan pasangan ion logam berat (Cu-Cd, Cu-Zn, Zn-Cr, dan Cu-Cr). Pengekstrakkan dijalankan dengan menggunakan teknik turus dengan asid HCl. Didapati bahawa ion zink dan cadmium dapat disingkirkan daripada resin dengan menggunakan kepekatan HCl sebanyak 0.001M, 0.01M dan 0.1M. Ion kuprum boleh disingkirkan dengan menggunakan 0.1M dan 0.5M HCl. Manakala ion kromium pula dapat disingkirkan dengan menggunakan 0.5M dan 1.0M HCl. Siri keselektifan resin terhadap ion logam adalah Cr\(^{3+}\) > Cu\(^{2+}\) > Zn\(^{2+}\) > Cd\(^{2+}\). Didapati kadar penukaran ion dengan resin adalah cepat bagi ion kuprum, cadmium dan kromium dimana setengah hayat bagi ion-ion ini adalah 6, 5 dan 4 minit masing-masing. Kadar penyerapan air oleh resin adalah 40.382 g air g\(^{-1}\).
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<td>Ceric ammonium nitrate</td>
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</tr>
<tr>
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INTRODUCTION

1.1 Metal pollution

Environmental pollution is one of the critical problems faced by all living cultures worldwide in present times. Environmental and industrial problems arising from polluted waters markedly influence the relevance of the identification of trace metal ions and their species (Egawa et al., 1987). Metal pollution in the environment has become a serious and critical problem. This is due to the metals which are not biodegradable (Lutfor et al., 2000). In recent years, environmental contamination with heavy metal ions is of growing public concerns because of their tendency to bioaccumulate (Chuh et al., 2005). The effluents from the metal finishing industry are also heavily contaminated with metal. Heavy metals can enter a water supply by industrial and consumer waste or even from acidic rain. The heavy metals causing pollution are mercury, arsenic, copper, barium, cadmium, chromium, lead, zinc and so on (Chuh et al., 2005).

Toxic heavy metal ions are well known to be severely harmful to human health. These toxic metals enter the human body via water, food and air and also absorption through the skin. When there is an excessive intake of metals such as copper in
ed in the liver, which results in 
glu et al., 2003). People come 
pharmaceuticals manufacturing and 
contaminated soil. Examples of 
plutonium and beryllium (Chuh et al., 

Wastewater Treatment

...
metals from aqueous media. According to previous studies, polymeric chelating resins containing hydroxamic acid groups have ability to form complexes with a wide range of metals such as Fe$^{2+}$, Fe$^{3+}$, Cu$^{2+}$, Cr$^{3+}$, Zn$^{2+}$, Au$^{3+}$, Ag$^+$, Co$^{2+}$, Cd$^{2+}$, Ni$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, UO$^{2+}$ and V$^{5+}$ (Lee and Hong, 1995). Besides that, poly(hydroxamic acid) is utilized to produce adsorbents products such as diapers, feminine napkins and so forth (Lutfør, et al., 2001a).

There are various methods of synthesizing chelating polymer containing hydroxamic acid groups by various starting material such as starch for the adsorption of toxic heavy metal ions. (Chang, 1993).

Starch is a naturally low-cost polymer that can be highly cross linked with various cross linking agents. Chemical modification of cross linked starch with various reactive monomers yields ionomer products that can be used to remove heavy metal ions from wastewater (Chang, 1993).

Grafting has been utilized as an important technique for modifying physical and chemical properties of polymers (McDowall et al., 1984). The use of grafted sago starch gives stronger materials with enhanced water resistance. Free radical graft copolymerization method has received the greatest amount of attention due to their practicality. Modification of starch or starch derivatives are mostly by introduction of vinyl and ester monomers onto starch. Poly(hydroxamic acid) chelating resin involve the incorporation of a nitrile and ester groups into a polymer matrix, followed by the conversion of nitrile and ester groups into an hydroxamic acid groups.
1.3 Objectives of Research

The objectives of research are:

a) to carry out graft copolymerization of methyl acrylate onto sago starch.

b) to prepare poly(hydroxamic acid) resin from poly(methyl acrylate) grafted sago starch.

c) to determine metal-ion uptake by of the resins

d) to separate metal ions.

1.4 Scope of Study

Synthesis of a polymer bearing hydroxamic acid will be carried out from the cheapest starting material, sago starch. Sago starch will be grafted by methyl acrylate utilizing ceric ammonium nitrate (CAN) as an initiator. Poly(hydroxamic acid) resin will be synthesized by conversion of ester and nitrile groups of poly(methyl acrylate) to poly(hydroxamic acid) chelating resin by treatment with hydroxylamine in an alkaline solution. The functional group of the resin will be performed by FTIR spectroscopy. The separation process will be carried out. Heavy metal ions that will be used in this research is cadmium, nickel, zinc, and iron.
CHAPTER 2

LITERATURE REVIEW

2.1 Starch

Starch had been subject of academic as well as of industrial interest for the past few decades. Besides its low cost and availability, the biodegradability has gained even more importance in this environmentally concerned era (Lee et al., 2003). Modified and unmodified starch products are extensively used for variety of applications such as sizing agents for textiles and paper, as adhesives for corrugated and laminated paper boards and wall papers, flocculants, blinders, fabric printing aid, thickeners, and many other non-food industrial applications. Starches are readily available and renewable. Next to cellulose, starch is the most abundant carbohydrate in the world. The raw material is available in sufficient amounts and in high purity. To fulfill the various demands for the functionality in different starch products, industrially processed starch is modified enzymatically, physically or chemically. In most chemical modifications of starch, usually referred to as chemical derivation, the granule form is maintained and the hydroxyl groups are partially substituted, yielding starch ethers and esters, as well as anionic and cationic starches. Other types of chemical derivatization are oxidation, cross-linking and grafting of starches (Han et al., 2003).
Starch is a mixture of two polymers, amylase, a linear (1-4)-linked \(\alpha\)-D-glucan and amylopectin a highly branched molecule which consists of short chains of (1-4) \(-\alpha\)-D-glucose with (1-6) \(-\alpha\)-linked branches. All starches are made up of two polysaccharides. The ratio varies with the starch source but is typically 20:80 amylose to amylopectin. Starch is a high polymer composed of repeating 1,4-\(\alpha\)-D-glucopyranosyl units (often called as anhydroglucose units, or simply AGU) and is, generally, a mixture of linear and branched components as shown in Figure 2.1 (Fanta, 1996). The linear component, amylase, has a molecular weight of several hundred thousand while the molecular weight of the branched amylopectin is of the order of several million. Branching in amylopectin occurs at C-6 of the glucopyranosyl unit (Fanta, 1996). Starch occurs in living plants in the form of discrete granules, which range from about 5-40 \(\mu\) in average diameter, depending on the plant source (Patil and Fanta, 1994a). Starch granules contain regions of crystalline and if starch is slurried in water at room temperature, its solubility is negligible, even though it is a hydrophilic polymer (Fanta, 1996). Starches from different sources differ in overall structure through size distribution of the granules, shape, amylase and lipid content, distribution of chain length in amylopectin and crystalline structure.

Sago starch is isolated from sago palm \((Metroxylon\) spp.) which is better known as ‘rumbia’. Sago palm has various uses, especially in production of starch either as sago flour or sago pearl. Sago can compete economically on yield and price compared to other crops. Sago starch is cheap and some other important properties were reported such as gelatinize, its high viscosity if properly extracted and the ease with which it can be moulded (Fasihuddin \textit{et al.}, 1999). It has been assessed by
Pranamuda et al., that sago starch has bright prospects for its utilization as fermentation.

\[
\begin{align*}
\text{CH}_2\text{OH} & \\
\text{O} & \\
\text{O} & \\
\text{OH} & \\
\text{H} & \\
\text{OH} & \\
\end{align*}
\]

Source: (Fanta, 1996)

**Figure 2.1** Molecular structure of sago starch

### 2.2 Graft Copolymerization

If a polymer consists of two or more different monomers then the resulting polymer, it is called copolymer (Billmeyer, 1982). The copolymer is classified into four types depending on the sequences of monomers in the polymer backbone. They are random copolymers, regular copolymers, block copolymers and graft copolymers (Bhattacharya and Maldas, 1984). Grafting has been used as an important technique for modifying physical and chemical properties of polymers (Han et al., 2003).

A graft copolymer consists of a polymeric backbone with lateral covalently linked side chains. Both the backbone and the side chain polymers can be homopolymers or copolymers. On various polymeric backbones on which grafting are suitable monomers can be made, starch appears to be very interesting and promising (Bhattacharya and Maldas, 1984).
Among the various methods, graft copolymerization of vinyl monomers onto starch produces composites of starch with synthetic polymers. Graft copolymerization of starch and other natural macromolecules can be initiated by transition metal ions, of which $\text{Fe}^{3+}$, $\text{Cu}^{2+}$, $\text{Co}^{3+}$, $\text{V}^{3+}$, $\text{Cr}^{6+}$, and especially $\text{Ce}^{4+}$, as well as their complexes are the most commonly used initiator. Oxidized metal ions may directly oxidize starch and produce free radicals onto starch to initiate the graft copolymerization (Lutfor et al., 2000). Transition metal acetyl acetonate chelates such as $\text{Zn(acac)}_2$, $\text{Mn(acac)}_3$, $\text{Fe(acac)}_3$, and $\text{Al(acac)}_3$ was used in the graft copolymerization of cellulose with various monomers, and was found that the initiating capability of initiators was related to the monomers used (Gao et al., 1994).

In an investigation of initiating systems for grafting vinyl monomers to starch, ceric ion and high-energy irradiation proved the most efficient method. In this study, the redox method with ceric salts, particularly ceric ion-alcohol systems, has been used for initiation (Reyes et al., 1966). In most chemical modifications of starch, usually referred to as chemical derivatisation, the granule form is maintained and the hydroxyl groups are partially substituted, yielding starch ethers and esters, as well as anionic and cationic starches (Han et al., 2003).

Grafting monomers onto starch is possible to attain many different properties including elasticity, sorbancy, ion exchange capabilities, and thermal resistance to microbiological attack (McDowall et al., 1984). Besides that, an important advantage of graft copolymerization is the fact that natural and synthetic components of the composite are held together by chemical bonding rather than existing merely as a physical mixture. The two dissimilar polymers, therefore, tend to be more intimately
associated, and separation of the two polymer phases cannot occur (Patil and Fanta, 1995).

### 2.2.1 Free Radical Graft Copolymerization

A number of grafting methods have been developed which may be classified into two groups: (1) crosslinking reactions of two polymer chains of different types. (2) Initiation of active sites on the polymeric backbone when the monomers can be grafted. The free radical methods have received the greatest amount of attention due to their practicality (McDowall et al., 1984). Addition or chain-reaction polymerization involves chain reaction in which the chain may be an ion or a reactive substance with one unpaired electron called a free radical (Billmeyer, 1984).

In 1937, Flory showed conclusively that radical polymerization proceeds by and requires the steps of initiation, propagation, and termination typical chain reactions in low-molecular-weight species (Billmeyer, 1984). The carbon-carbon double bond is, because of its relatively low stability, particularly susceptible to attack by free radical. In free-radical-initiated graft copolymerization, free radical produced on starch reacts with monomer to form grafted copolymer (Fanta, 1996).

**a) Initiation**

A number of initiating methods have been used to prepare graft copolymers, and these may be divided into two broad categories: initiation by chemical methods and
initiation by irradiation (Fanta, 1996). The method of choice often depends on the monomer to be copolymerized.

The use of ceric ions to initiate graft copolymerization was first suggested by Mino and Kalzetman in 1958 (McDowall et al., 1984). After initial formation of starch-ceric complex, ceric ion is reduced to cerous, a hydrogen atom is oxidized and a free radical is formed on starch, while the bond between carbon atom 2 and 3 of the glucopyranosyl unit is broken. The polymeric starch free radical so formed may then react with monomer to initiate graft copolymerization or may be lost through further reaction with ceric salt.

b) Propagation

Propagation of the growing polymer chain takes place through the addition of donor-acceptor complexes, not monomer molecules. In the presence of monomer, the starch free radical is added to the double bond of the monomer, resulting in a covalent bond between monomer and starch to create the chain reaction for propagation (Fanta, 1996). The most likely form of monomer addition is called head-to-tail addition. Alternatively, the addition may involve a head-to-head or a tail-to-tail reaction. The principal reason for the preference of head-to-tail addition lies in the greater thermodynamic stability of a free radical and perhaps also to steric inhibition of steps such as reaction.
REFERENCES


Chuh, Y.C., Chen, L.C., and Po, C.H., 2005. Adsorptions of heavy metal ions by a magnetic chelating resin containing hydroxyl and iminodiacetate groups. *Separation and Purification Technology*


resin from poly(methyl acrylate) grafted sago starch. *Journal of Applied Polymer Science* 70, 1256-1264.


