SYNTHESIS AND CHARACTERISATION OF POLY(HYDROXAMIC ACID AND AMIDOXIME) GRAFTED SAGO STARCH CHEATING RESIN FOR EXTRACTION OF SOME METAL IONS

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ABSTRACT

SYJTHESIS AND CHARACTERISATION OF POLY(HYDROXAMIC ACID AND AMIDOXIME) GRAFTED SAGO STARCH CHELATING RESIN FOR EXTRACTION OF SOME METAL IONS

Sago starch (AGU, anhydro glucose unit) was used to prepared a poly(hydroxamic acid-amidoxime) chelating resin. Methyl acrylate (MA) and acrylonitrile (AN) were firstly graft copolymerized onto sago starch by using a free radical initiating process in which ceric ammonium nitrate was used as an initiator. The percentage of grafting was significantly dependent upon the concentration of mineral acid (H_2SO_4), ceric ammonium nitrate (CAN), MA, AN, as well as the reaction temperature and period. The highest yield was obtained when the concentrations of H_2SO_4, CAN, AN and MA were used at 0.7090 mol/L, 4×10^{-3} mol/L, 0.6016 mol/L and 0.4392 mol/L, respectively. The optimum temperature and reaction period were 50 °C and 90 min, respectively. The conversion of ester and nitrile groups of the poly(methyl acrylate-co-acrylonitrile) (PMA-co-AN) grafted AGU into hydroxamic acid and amidoxime functional groups was then prepared via treatment of hydroxylamine under alkaline solution. The optimum poly(hydroxamic acid-amidoxime) (PHA-PA) chelating resin was obtained when concentration of hydroxylamine hydrochloride was used at 0.8634 mol/L; reaction temperature at 75 °C; 2 hours of reaction period; while the varying pH value was pH 13. The optimization of the PHA-PA chelating resin was evaluated by measured the sorption capacity of the resin towards copper metal ion with batch method. The PMA-co-AN grafted AGU and PHA-PA were characterized by FT-IR spectroscopy. The chelating behavior of the prepared resin towards cadmium, chromium, copper and zinc metal ions were investigated by using batch method. The binding capacities of the optimum chelating resin towards these metal ions were observed and it exhibited high sorption capacity for copper which observed at 3.576 mmol/g, at pH 6 after 24 hours of reaction period. The maximum binding capacities of the optimum chelating resin towards cadmium, chromium and zinc metal ions were observed at 1.585 mmol/g, 1.658 mmol/g and 1.817 mmol/g, respectively; at pH 6 after 24 hours of reaction period. The optimum resin obtained also showed that it was capable to form a chelate complex when reacted with metal ions in trace level.

ABSTRAK

Tepung sago (AGU, anhydro glucose unit), telah digunakan untuk penyediaan chelating resin yang bernama poly(hydroxamic acid-amidoxime). Sebagai langkah pertama, kedua-dua monomer yang bernama metil acrylate (MA) dan acrylonitrile (AN) telah digunakan untuk bergabung ke atas tepung sago dengan menggunakan proses pencantuman radikal bebas di mana ceric ammonium nitrate bermain peranan sebagai initiator. Dengan jelasnya, peratus pencantuman antara tepung sago dengan kedua-dua monomer ini adalah bergantung kepada kepekatan acid mineral (H_2SO_4), ceric ammonium nitrate (CAN), MA, AN, bersama dengan suhu dan tempoh yang digunakan semasa tindak balas dijalankan. Hasil optimum di antara pencantuman tepung sago dengan monomer telah diperolehi semasa kepekatan H_2SO_4, CAN, MA, dan AN yang digunakan pada 0.7090 mol/L, 4 × 10^{3} mol/L, 0.6016 mol/L and 0.4392 mol/L, masing-masing pada tindak balas sedemikian. Suhu dan tempoh optimum dalam tindak balas Ini telah tercapai pada 50 °C apabila dibiarkan bertindak balas dalam tempoh 90 min. Pertukaran antara kumpulan ester dan nitrile dalam poly(methyl acrylate-co-acrylonitrile) (PMA-co-AN) cantuman AGU kepada kumpulan berfungsi hydroxamic acid dan amidoxime telah disediakan dengan menggunakan rawatan hydroxylamine di dalam keadaan beralkali. Poly(hydroxamic acid-amidoxime) (PHA-PA) chelating resin yang optimum telah diperolehi apabila hydroxylamine hydrochloride dengan kepekatan 0.8634 mol/L telah digunakan; 75 °C suhu tindak balas bersama dengan 2 jam masa tindak balas dalam keadaan pH 13 semasa reaksi tersebut dijalankan. PHA-PA chelating resin yang optimum telah dinilai berdasarkan muatan penyerapan antara resin dengan ion logam kuprum dengan menggunakan kaedah kelompok. Ciri-ciri PMA-co-AN cantuman tepung sago dan PHA-PA yang optimum telah dikaji dengan menggunakan spektro FT-IR. Tindak balas antara chelating resin yang optimum terhadap ion logam cadmium, kromium, kuprum dan zink telah dikaji dengan menggunakan kaedah kelompok. Muatan dari segi ikatan antara chelating resin yang optimum dengan ion-ion logam yang digunakan telah dikaji dan didapati bahawa muatan penyerapan terhadap kuprum adalah yang tertinggi; di mana 3.576 mmol/g telah diserap pada nilai pH 6 selepas bertindak balas selama 24 jam. Muatan dari segi ikatan antara chelating resin yang optimum terhadap ion kadmium, ion kromium dan ion zink juga telah dikaji dan mencatatkan nilai penyerapan pada 1.585 mmol/g, 1.658 mmol/g and 1.817 mmol/g masing-masing pada nilai pH 6 selepas bertindak balas selama 24 jam. Resin yang disediakan juga menunjukkan bahawa ia dapat membentukan komplex dalam keadaan kelat apabila bertindak balas dengan ion-ion logam yang kepekatan sangat rendah.

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AGU - Anhydro glucose unit

PHA-PA - Poly(hydroxamic acid-amidoxime) chelating resin

PHA - Poly(hydroxamic acid) chelating resin

PA - Poly(amidoxime) chelating resin

MA - Methyl acrylate

AN - Acrylonitrile

PMA - Poly(metyl acrylate)

PAN - Poly(acrylonitrile)

PMA-co-AN - Poly(methyl acrylate-co-acrylonitrile)

CAN - Ceric ammonium nitrate

M - Molarity

mmol/g - Milimol per gram resin

mg/L - Milligram per liter

mol/L - Mol per liter

mg/g - Sorption of metal ions in milligram by per gram resin

cm - Centimeter

mL - Milliliter

g - Gram

% - Percentage

°C - Degree Celsius

min - Minute

h - Hour

ppm - Part per million

CHAPTER 1

INTRODUCTION

1.1 Chelating Resins

Many methods have been developed in recent years for heavy metal removal from aqueous solution. Various approaches such as chemical precipitation, reverse osmosis, membrane separation, evaporation and electrochemical treatment techniques have been developed for the removal and recovery of the metal ions from industrial wastewater (Zohuriaan-Mehr *et al.*, 2004 and Ramnani & Sabharwal, 2006). Among those separation techniques, many scientists concentrated on the use of chelating resin in the removal of toxic metal ions from both wastewater and sewage water (Chen *et al.*, 2006). Indeed, chelating resins are effective for removal of metal ions due to their stability and its capacity for metal binding, the metal binding strength and selectivity (Hosseini *et al.*, 2006).

Generally, chelating resins can be prepared by two step synthesis technique (Garg *et al.*, 1999). The synthesis technique consists of the insertion of an appropriate functional group (monomer) onto the surface of the polymer and followed by the immobilization of ligand of particular suitable by virtues of a condensation or coupling reaction (Garg *et al.*, 1999). In other words, chelating resins can be prepared by anchoring the active site (functional group) to a solid support in a polymer matrix (polymer backbone) and this active site has normally been found to exhibit greater selectivity towards some metal ions (Pramanik *et al.*, 2004). Therefore, the design and preparation of a chelating resin depends on the stability of the basic macromolecular network with its ability to add on the desired chelating functional group, which suits to the specific metal ions is capable to extract a complex variety of metal ions from various sources (Varadharaj *et al.*, 1996).

In recent years, the preparation, characterization and applications of chelating resin gained the attention of many researchers because these chelating ion-exchange resins with different functionalities have potential applications in the selective removal of metal ions from industrial waste solutions (Atia *et al.*, 2005a). For example, Atia and coworkers have synthesized glycidyl methacrylate-divinylbenzene (GMA/DVB) resin bearing iminoacetate function for the removal of Zn^{2+}, Cd^{2+}, Pb^{2+}, Mg^{2+}, and Ca^{2+} (Atia *et al.*, 2005a). At the same year, they also prepared a chelating resin with amine-mercaptan groups for the recovery of Hg(II) (Atia *et al.*, 2005b). A dithizone-anchored poly(vinylpyridine) resin was synthesized for the preconcentration and separation of palladium(II) and platinum(IV) (Shah & Devi, 1997). Lutfor *et al.* (2000a) had synthesized poly(hydroxamic acid) chelating resin from poly(methyl acrylate)-grafted sago starch for the binding of copper, iron, cobalt and cadmium. In addition, Lutfor and his research group (2000f) had also prepared a poly(amidoxime) chelating resin from poly(acrylonitrile) grafted sago starch for the recovery of various metal cations such as Cu^{2+}, Fe^{3+}, As^{3+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+} and Pb^{2+}.

A number of papers have been published describing about the uptake of uranium by using a chelating ligands. An amidoxime resin prepared from precursory acrylonitrile-divinylbezene copolymer was designed for the recovery of uranium from seawater (Egawa *et al.*, 1994). Zhang *et al.* (2003) had also synthesized a macroporous fibrous polymeric adsorbent containing amidoxime chelating functional group for the removal of uranium(VI) from seawater. On the other hand, Choi *et al.* (2003) also prepared a resin with amidoxime and amidoxime/carboxyl group for the investigation of adsorption of uranium ions from seawater.

However, chelating resin not only played an important role in the separation and recovery of metal ions in wastewater or seawater. For example, a cloth filter was synthesized by grafting of acrylonitrile/methacylic acid onto cotton cloth using a radiation-induced technique followed by amidoximation reaction was prepared by Othman and his research team for the adsorption of hazardous ions from radioactive waste (Othman *et al.*, 2006).

The removal of polluting metal ions from industrial effluents, water supplies and mine waters has received much attention in recent years. To avoid a negative impact towards environment, the wastewater contaminated with heavy metals from industries especially metal plating and other semi-conductor industries should be treated well before discharge into the stream. There are a few small enterprises are facing a serious problem because of the high cost for a complete and efficient waste water treatment plant. Thus, a variety of low cost adsorbent materials could be developed for their capacity to remove toxic metal ions (Ramnani & Sabharwal, 2006). Based on this situation, chelating resin which is low in cost (Han *et al.*, 2003), biodegradable (Patil *et al.*, 1995), high efficiency towards selective metal ions (Lutfor *et al.*, 2001c and Lutfor *et al.*, 2000f) and could be regenerated (Pramanik *et al.*, 2004), become more important based on their potential application in industries. As more industries are aiming zero waste discharge, waste treatment procedures may need to be revised and ion exchange technology could be applied.

1.2 Criteria for a Chelating Polymer

The lack of selectivity of the conventional ion-exchange resins has led to the development and discovery of a new class of polymers which are now known as specific and selective ion exchange chelating resins (Sahni & Reedijk, 1984).

The synthesis of a chelating ion-exchange resin can be summarized in the funtionalisation of a polymeric matrix which generally consists of an irregular, macromolecular, three-dimensional network of hydrocarbon chains (Sahni & Reedijik, 1984; Kantipuly *et al.*, 1990; Garg *et al.*, 1999). In this case, functionalisation means incorporation of chelating ligands into polymeric matrices. Alternatively, a chelating monomer can be polymerized and subsequently cross-linked to obtain a chelating ion-exchanger.

The novel chelating ion-exchange resin consists essentially of two components, a chelating group and a polymeric matrix. Thus, the properties of both components have to be considered when designing and synthesizing a chelating ion-exchange resin. Some suitable chelating group for incorporation into polymeric matrix must have properties such as (Sahni & Reedijk, 1984),

a) It should be capable of resin formation, or be capable of substitution into a polymeric matrix,

b) It should be sufficiently stable a withstand the polymerization process, and

c) It should be compact enough so that its chelating ability is not hindered by the dense polymeric matrix.

The chelating ion-exchange resins should possess mechanical stability and resistance towards acids and bases used for regeneration of resins. Such suitable chelating ligands should formed 1:1 complexes when reacted with metal ion. The selective behavior of a chelating ion-exchange resin is based on the different stabilities of the metal complexes formed by a resin at appropriate pH values and the point of maximal efficiency for the separation of a given set of metal ions can be established by variation of the pH. Based on the above idea proposed, long chain molecules like ethylenediaminediacetic acid appeared unsuitable due to the improbability that the chelate configuration occurring in aqueous solution could be maintained on a cross-linked polymer.

The following essential requirements seem necessary for the synthesis of a chelating ion-exchange resin (Sahni & Reedijk, 1984),

a) The chelating ligand attached to a solid matrix should possess strong metal-binding properties and selectivity towards certain metal ions;

b) The chelating group should be capable of undergoing incorporation in a polymeric network and allow the process of polymerization. In turn, the chelating polymer should be resistance to strong acids and alkalis at elevated temperature;

c) The chelating ligand should preferably be multidentate, permitting formation of a 1:1 chelate with a metal ion, and the chelating ion exchanger should be monofunctional as far as possible. The occurrence of mixed functional groups such as sulfonic, carboxylic or phenolic groups should be avoided in the same resin; and

d) The chelating ion exchanger should possess good swelling properties and compatibility between polymer and the medium (generally aqueous) is essential; this can be regulated by the presence of hydrophilic groups on the polymer and by the extent of cross-linking. A higher degree of cross-linking results in increased mechanical strength, but the swelling properties of polymer are adversely affected.

There are many types of chelating ligands have been reported for binding of metal ions (Kantipuly *et al.*, 1990). Consequently, poly(hydroxamic acid) and poly(amidoxime) are well known chelating resins that bind the wide metal ions in presence of alkali metal ions. However, there are few disadvantages such as inconsistent swelling, shape and size of resin. In order to overcome a number of limitations, the chelating resins need to be modified especially the poly(hydroxamic acid) that exhibited high swelling property, which will cause negative impact for column operation. Therefore, a new chelating ion exchange resin containing hydroxamic acid with amidoxime functional group can be synthesized from poly(methyl acrylate-co-acrylonitrile) (PMA-co-AN) grafted sago starch. The PMA-co-AN grafted sago starch can be prepared by free radical initiating process in which ceric ammonium nitrate acts as an initiator. Conversion of the ester and nitrile groups of the grafted copolymer into the hydroxamic acid and amidoxime groups can be carried out via treatment with hydroxylamine in alkaline solution.

1.3 Objectives of Research

a) To carry out graft copolymerization of methyl acrylate and acrylonitrile onto sago starch by chemical initiating process,
b) To prepare a chelating resin containing hydroxamic acid and amidoxime functional groups from acrylic polymer grafted sago starch, and
c) To evaluate the binding properties of the chelating resin towards a series of metals such as cadmium, chromium, copper and zinc metal ions.

1.4 Scope of Research

This research focuses mainly on the preparation of poly(hydroxamic acid-co-amidoxime) (PHA-PA) chelating resin, followed by the recovery of cadmium, chromium, copper and zinc metal ions with the prepared chelating resin. To prepared a PHA-PA chelating resin, sago starch was grafted with methyl acrylate (MA) and acrylonitrile (AN) monomers by free radical initiating process in which ceric ammonium nitrate (CAN) acts as an initiator, followed by the conversion of ester groups in the poly(methyl acrylate-co-acrylonitrile) (PMA-co-AN) grafted copolymer to PHA-PA chelating resin. Characterization of functional groups in the new material synthesized was performed by using the FTIR spectroscopy. The metal sorption abilities resin was tested by using cadmium, chromium, copper and zinc metal ions solution respectively. The ion-exchange of PHA-PA chelating resin towards metal ions was determined by using the batch technique. The atomic absorption spectrophotometer (AAS) was used to determine the initial and final concentration of metal ions in each sample.

CHAPTER 2

LITERATURE REVIEW

2.1 Sago Starch

Sago starch has been produced from sago palm (*Metroxylon* spp.) which is better known as 'rumbia'. The main content of sago starch is a mixture of two natural polymers, amylose, a linear (1→4)-linked-α-D-glucan and amylopectin a highly branched molecule which consists of short chains of (1→4)-linked-α-D-glucose with (1→6)-α-linked branches. Commonly, chain lengths of amylose are linear and in excess of 6000 D-glucopyranose units with molecular weight between 150 000 and 600 000 Da. On the other hand, amylopectin is very branched with an average of 17-26 D-glucosyl units separating the α-(1→6) branch points with large molecular size (Ahmad *et al.*, 1999).

Starch was used for long time in the food industry for the production of vermicelli, bread, crackers, biscuits and etc (Ahmad *et al.*, 1999). However, modified and unmodified starch products are also extensively used for variety applications in other non-food industry such as sizing agents for textiles and paper, as adhesives for corrugated and laminated paper boards and wall papers, flocculants, binders, fabric printing aids, thickeners and etc (Han *et al.*, 2003). Han and his research group also reported that, the used of starch products was able to substitute with the petroleum derived polymers. A further advantage of such a substitution is the starchy portion polymer can be easily biodegradable and leading to minimal damage of the environment.

Next to cellulose, starch is the most abundant carbohydrate in the world. The raw material is available in sufficient amounts and high purity with the total annual world production is estimated to be between 25 and 45 million tons (Han *et al.*, 2003). Because of its low cost, availability and biodegradability, starch has been a subject of academic and industrial interest (Lee *et al.*, 2005). Based on the increasing demand for petroleum based products has adversely affected their cost

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