PREPARATION AND CHARACTERIZATION OF POLY(HYDROXAMIC ACID) CHELATING RESIN FOR METAL IONS REMOVAL FROM WATER

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ABSTRACT

Graft copolymerization of methyl acrylate (MA) onto kenaf cellulose was carried out using redox method in which ammonium ferrous sulphate was used as an initiator. The poly (methyl acrylate) grafted kenaf cellulose was obtained at 55 °C after 2 hours stirring, and purified acrylic polymer-grafted cellulose was characterized by FTIR and ICP-MS analysis. There in, the ester and nitrile functional groups of the grafted copolymers were reacted with hydroxylamine solution for conversion into the hydroxamic acid ligands. The chelating behavior of the prepared ligands toward some metal ions was investigated using batch technique. The adsorptions of metal ions onto ligands were dependent on pH parameter and the amount adsorbed towards metal ions following order: $Zn^{2+} > Fe^{3+} > Cr^{3+} > Cu^{2+} > Ni^{2+}$.

ABSTRAK

Pempolimeran metil ekrilat (MA) dicangkukkan dengan selulosa kenaf melalui kaedah redoks di mana ferum ammonium sulfat telah digunakan sebagai bahan pemula. Pempolimeran dilakukan pada suhu 55 °C selama 2 jam dan dilakukan pencirian dengan menggunakan FTIR dan ICP-MS. Terdapat ester dan kumpulan nitril dalam kopolimer yang telah bercantum dan bertindak balas dengan larutan hidroksilamin untuk bertukar ke ligan asid hidrokamik. Sifat 'chelating ligands' yang bersedia terhadap beberapa ion logam telah disiasat dengan dengan menggunakan teknik 'batch'. penjerapan ion logam ke ligan bergantung kepada parameter pH dan jumlah yang terserap ke arah ion logam mengikut susunan yang berikut: $Zn^{2+} > Fe^{3+} > Cr^{3+} > Cu^{2+} > Ni^{2+}$.

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A	Alpha
σ-	Sigma bond
Π	Pi bond
q_e	Equilibrium sorption amount
C_0	Initial concentration of metal solution
C_e	Equilibrium concentration of metal
V	Volume of metal solution
L	Mass of polymeric ligands
M	Mol weight of specific metal

LIST OF ABBREVIATIONS

AA	Acrylamide
AGU	Anhydro Glucose Units
AN	Acrylonitrile
As	Arsenic
ATRP	Atom Transfer Radical Polymerization
CAN	Cerium (Iv) Ammonium Nitrate
Cd	Cadmium
Cell-PEI	Cellulose – Polyethyleneimine
Cr	Chromium
DSC	Differential Scanning Calorimetry Analysis
DTPA	Diethylenetriamine Pentaacetic Acid
EDTA	Ethylenediamine Tetraacetic Acid
FTIR	Fourier Transform Infrared Spectroscopy
Hg	Mercury
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IR	Infrared
M	Monomer
MA	Methyl Acrylate
MAam	Methacrylamide
MMA	Methyl Methacrylate
NDA	Nitrilotriacetic Acid
P	Polymer
PAA/PAAm	Poly(Acrylamide)

PAN	Poly(Acrylonitrile)
Pb	Lead
PHA	Poly(Hydroxamic Acid)
PMA	Poly(Methyl Acrylate)
TGA	Thermogravimetric Analysis.
Tl	Thallium
FAAS	flame atomic absorption spectrometry
PFR	phthalic acid-formaldehyde-resorcinol
DDTC	Diethyldithiocarbamate

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

1.1.1 Softwood of Cellulose

Cellulose is one of many polymers found in nature (Simon et al., 2011). Wood, paper, and cotton all contain cellulose. It occurs in almost pure form in cotton fiber and in combination with other materials, such as lignin and hemicelluloses, in wood, plant leaves and stalks, etc. The principle and main routes of direct modification of the cellulose for the preparation of adsorbent materials are esterification, etherification, acetyl formation, hydrolysis, oxidative degradation, and thermal degradation. For industrial use, cellulose is mainly used to produce paperboard and paper. Converting cellulose from energy crops into bio-fuels such as cellulosic ethanol is under investigation as an alternative fuel source. The efficient conversion of inexpensive cellulosic materials into fuel ethanol is expected to be the needed breakthrough in producing affordable and renewable liquid fuel (Ye Sun and Jiayang Cheng, 2002). To break down cellulosic biomass into fermentable reducing-sugars, enzymatic hydrolysis is considered the most promising vehicle. However, cellulosic bio-mass is more difficult and more expensive to convert into ethanol than corn grain based on current technologies; one of the main obstacles is the poor enzymatic hydrolysis of cellulose. To make cellulose susceptible to hydrolysis, a pretreatment process is needed to remove lignin, reduce the cellulose crystallinity, and increase the cellulose porosity (Galbe and Zacchi, 2002).

X-ray diffraction can showed significant differences in monoclinic angle of two groups of hardwoods and softwoods. These differences were reduced by chemical treatments (hydrolysis and delignification). Electron reflection showed little difference. From these observations it is concluded that the structural variations of cellulose crystals between hardwoods and softwoods are preferable to non-crystalline substances such as amorphous cellulose, polyposis and lignin which may have some connections with cellulose crystals in the cell walls.

Softwoods are the dominant lignocelluloses feedstock for bioconversion in the Northern hemisphere and are viewed as a potential source of fermentable carbohydrate for fuel-ethanol production in Canada, Sweden and US. In British Columbia, an estimated 2.2 million tons of surplus wood residues are generated per year. Conversion of these residues into fuel ethanol and other commodity chemicals provides an attractive opportunity for more sustainable development of forest resources.

A primary techno-economic challenge in all lignocelluloses to ethanol bioconversion processes is overcoming the recalcitrance of the cellulose fraction to enzymatic hydrolysis. Cellulose is intrinsically resistant to enzyme attack and is further protected by the surrounding matrix of lignin and hemicelluloses in lingo-cellulose. Softwood lignocelluloses are considered particularly recalcitrant for hydrolysis owing to the amount and nature of the lignin component. Steam explosion is one of the most intensively studied pretreatment methods for bioconversion of softwood materials. The steam explosion process uses high temperature and pressure, followed by sudden release, to separate individual fibers within the wood. Meanwhile, most of hemicelluloses is hydrolyzed and removed during steam explosion, contributing to the improved susceptibility of the substrate. However, the steam-explosion process does not result in net delignification: the lignin content after steam explosion is actually increased due to the removal of hemicelluloses.

1.1.2 Ion Exchange Resins

Ion exchange resins bearing chelating functional groups have long been of interest for removing metals from water. The design of chelating ligands depends on the stability of the basic macromolecular network and its ability to add on the desired chelating functional groups. Because the alkali and alkaline earth metals occur in relatively high concentrations in natural waters, a desirable property of metal chelating ligands having useful environmental or commercial application is their ability to bind heavier elements selectively. They should be able to bind the heavier transition, rare earth, and main group metal ions in the presence of high concentration of calcium, magnesium, sodium and potassium. The different ion exchange resins consist of different polymers and different ligands covalently bound to the polymers. Ion exchange resins are useful because of the insolubility of the resin phase. After contact with the ion containing solution, the resin can be separated by filtration. Ion exchange resins have been used in water softening, removal of toxic metals from water in the environment, wastewater treatment, hydrometallurgy, sensors, chromatography and bio-molecular separations. They have also been used as catalysts, both in place of homogeneous catalysts such as sulfuric acid and to immobilize metallic catalysts.

$$[\text{Polymer}] - X^{+} A^{-} + B^{-} \rightarrow [\text{Polymer}] - X^{+} B^{-} + A^{-}$$

Anion exchange resin

$$[\text{Polymer}] - Y^{-} C^{+} + D^{+} \rightarrow [\text{Polymer}] - Y^{-} D^{+} + C^{+}$$

Cation exchange resin

Scheme 1.1: Exchange of ions between an insoluble (polymer) phase and a solution phase.

1.1.3 Chelating resins

Chelating resins having a wide applicability for the selective removal of metal ions and polymeric substances with the ability to complex with metal ions are very common. These materials, which have polyelectrolyte characteristics, have a very large number of sorption sites per macromolecule and have been used to remove toxic and polluting metal ions from wastewater and mine water (Faraj et al., 2009). Chelating resin can be used to remove trace metals from water, reagents and macromolecular samples. Chelating resin has a high preference (Luthor et al., 2001). Its selectivity for divalent ions over monovalent ions is high (5,000:1) and it has a very high attraction for transition metals, even in concentrated salt solutions. The chelating polymer materials are mainly used in analytical, industrial and radiochemical laboratories.

1.1.4 Hydroxamic acid

Hydroxamic acids are versatile chelating agents forming very stable complexes with a large number of metal. Hydroxamic acids have been known for their chelation ability with heavy metals. They have been found to be effective chelating ligands with the ions such as V^{5+}, Fe^{3+}, Mo^{6+}, Ti^{4+}, Hg^{2+}, Cu^{2+}, and UO^{2}. Number of chelating polymers, containing hydroxamic acid group, have been prepared from various starting materials using different methods. Poly(hydroxamic acid) was synthesized from polyacrylamide at different conditions. Polyhydroxamic acids have found wide applications in the field of analytical chemistry (Khaled et al., 2011).

1.1.5 Effect heavy metals toxicity to health and environment

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb). Heavy metals are natural components of the Earth's crust. Heavy metal also is a member of a loosely-defined subset of elements that exhibit metallic properties. It mainly includes the transition metals, some metalloids, lanthanides and actinides. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain.

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers and groundwater.

Heavy metals in wastewater can be readily absorbed by marine animals and directly enter the human food chains, thus presenting a high health risk to consumers (Sheng et al., 2000). Small amounts of these elements are common in our environment and diet and are actually necessary for good health, but large amounts of any of them may cause acute or chronic toxicity (poisoning). Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver and other vital organs (Luthor et al., 2009). Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer.

For some heavy metals, toxic levels can be just above the background concentrations naturally found in nature. Heavy metals will not degrade into harmless end products. Thus, treatment of aqueous wastes containing soluble heavy metals

In this project, we extracted the metal ions by using batch technique. Therefore, the propose chelating ion exchange resin is the poly(amidoxime) ligands, which is applied to the removal of target metal ions such as copper, iron, chromium, zinc, cadmium, lead and arsenic.

1.2 OBJECTIVES OF THE RESEARCH

This experiment had carried out some objectives:

1. To prepare poly(methyl acrylate) grafted kenaf cellulose by chemical initiating process.

2. To synthesize a novel chelating resin containing hydroxamic acid functional groups from acrylic polymer grafted kenaf cellulose.

3. To investigate the performance of resin towards wastewater containing toxic metal ions.

1.3 SCOPE OF THE STUDY

1. The cellulose obtained from local trees and modifying the cellulose and converted to polymeric chelating ligand.

2. The polymeric chelating ligand could be used to extract metal ions from industrial waste water and it was found to be highly efficient. Thus, the polymer chelating ligand can be a suitable material as adsorbent to remove metals and save the environment.

1.4 PROBLEM STATEMENTS

Now days, our government take seriously about water pollution because it very dangerous to ourselves and animal. Heavy metal do not degrade easily into harmless end products and due to their high toxicity, industrial wastewater containing heavy metals must be treated before being discharged in the environment. A large environment, public health and economic impact are evident due to the toxic metals entering into the environment. Heavy metals contamination in aqueous wastes from many industries such as metal plating, mining operation, tanneries, chloroalkali, radiator manufacturing, smelting, alloy industries and storage batteries industries.

Removal heavy metal ions from wastewater need much attention and we have been focused on the use of cellulose as low cost adsorbents to remove heavy metal ions from contaminated waters. Spent cellulose, an abundantly available material that is currently disposed of as a solid waste, are potentially suitable for such applications. Besides that, most of these living plant investigated so far have limitations in terms of efficiency and their adsorption capacities for heavy metals. The limitations of some of the aforementioned technologies which include high cost, unavailability, generation of large volumes of secondary waste and poor removal efficiency has necessitated the continued search for new adsorbent materials.

The removal percentage of heavy metal is crucial. Because some heavy metal compounds still contain in waste water. In addition, the management of the heavy metal and concentrated contaminants present in the sludge is still one of the most difficult and vital problems in the field of wastewater effluent. So that, a sustainable treatment is necessary for remove heavy metal from wastewater and protect the environment.

Immediate concerns with ligands, includes the weak nonspecific binding abilities for heavy metals. The polymeric chelating ligands in the chains that lack either chain length or sufficient bonding sites may produce precipitates that are unstable over time and under certain pH conditions. For this reason, it has been the focus of our research to design and synthesize better polymeric chelating ligands, which not only bind heavy metals, but also produce stable precipitates. Stabilizing metal complexes is accomplished through interaction with metal cations on the ligand.

CHAPTER 2

LITERATURE REVIEW

2.1 Graft Copolymerization

In modern civilization, we must try to replace the natural materials with either all synthetic materials or modified natural materials. In the polymeric age, it is essential to modify the properties of a polymer according to tailor-made specifications designed for target applications. There are several means to modify polymers properties, blending, grafting and curing. Grafting is a method where in monomers are covalently bonded (modified) onto the polymer chain, whereas in curing, the polymerization of an oligomer mixture forms a coating which adheres to the substrate by physical forces. Actually, there is no time scale for the process of grafting, which can take minutes, hours or even days.

A polymer comprising molecules in which the main backbone chain of atoms has attached to it at various points side chains containing different atoms or groups from those in the main chain. The main chain may be a copolymer or may be derived from a single monomer. Graft copolymers are prepared by linking two different polymers but unlike block copolymers, structural sequence is such that one type of polymer is linked to the other through a branched structure. Based on Stannett et al., 1984, "a graft copolymer consists of a polymeric backbone with lateral covalently linked side chains, both the backbone and side chain polymers can be homopolymers or copolymers.

The formation of copolymers of various synthetic and natural polymers via graft copolymerization has been extensively studied. Various monomers such as methyl acrylate (MA) and methyl methacrylate (MMA) have been graft copolymerized with numerous polymeric backbones using various initiating systems. "A number of reviews Stannet et al., 1984; Bhattacharyya et al., 1984) were published which differ from each other in various degrees of detail. Some stressed one method of initiation while others considered different methods of initiation. However, the bulk of graft copolymerization studies owe their origin to initiation by free radical initiators. Free radicals are produced on the starch substrate and then react with the monomers to form the respective graft copolymers. Free radicals can be produced by a number of methods such as chemical method, mechanical degradation and low or higher energy irradiation technique. Our review emphasizes on the chemical initiation method.

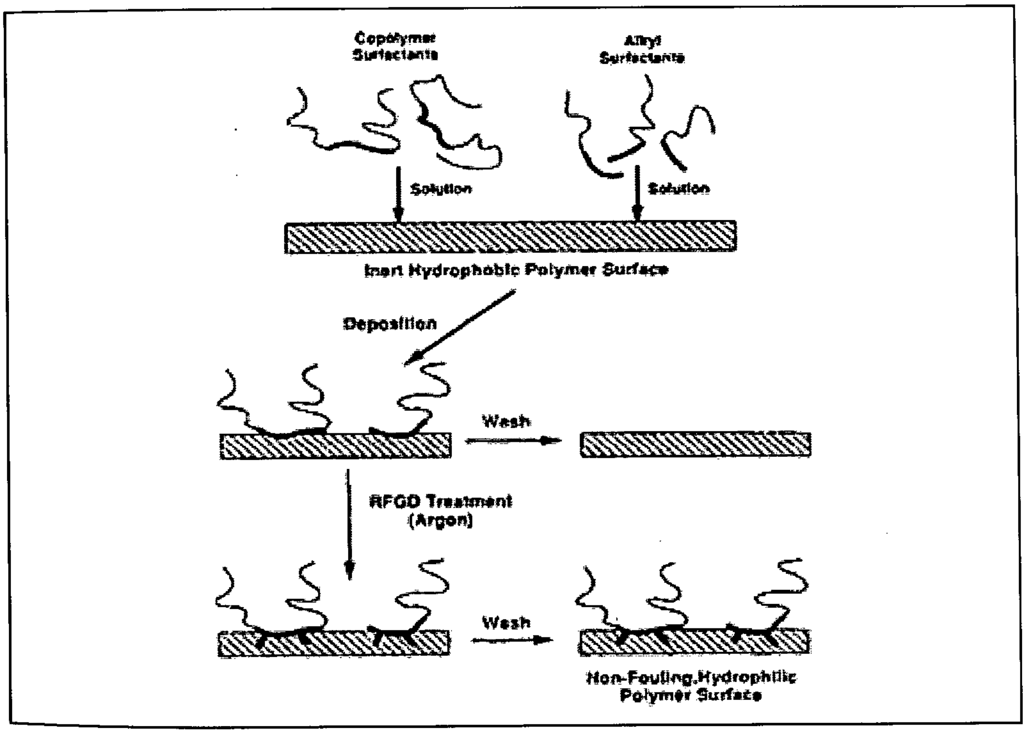

Figure 2.1: Schematic diagram of argon glow discharge treatment for the immobilization of surfactants.

Source: Stannet et al., 1984; Bhattacharyya et al., 1984

Cellulose graft copolymers is the general name given to a class of cellulose derivatives containing polymeric side chains, covalently linked to oxygen of the glycosidic unit. Since 1950, different olefins have been grafted onto cellulose and starch (Estella et al., 1998) with the aim of preparing new products having peculiar properties. Grafting processes used nowadays typically proceed under heterogeneous conditions: cellulose in the solid state is attacked by a number of chemical agents in order to undergo free-radical or ionic grafting, the free-radical methods being the most common ones. Aqueous solutions of peroxides, persulfates and redox systems (e.g. Ce^{4+} or Fe^{2+} /H_2O_2) can be used in the initiation step: however, depending on the olefin chemical nature, other suitable solvents, such as acetic acid, dimethyl sulfoxide, sulfuric acid or mixed polar solvents, may replace water. The final product, after separation from the reaction medium, is always a mixture of graft copolymer, unreacted cellulose and olefin homopolymer, the proportion among the three components depending on the processing conditions.

2.2 Grafting Initiated by Chemical Means

A method for producing polymer coatings by surface initiated polymerization from a plasma deposited coating is provided. The modification of surfaces by polymer attachment is a versatile and efficient means of controlling interfacial properties, such as surface energy (i.e. wetting behavior), permeability, bio-activity and chemical reactivity. The present invention provides a method whereby plasma deposited coating is applied to a substrate and the polymer coating formed by surface initiated polymerization is formed on the coating rather than the substrate itself. This means that the growth of the polymer using the grafting from procedure can be performed efficiently and independently of the substrate from.

Two major types of grafting methods may be considered: (i) grafting with a single monomer and (ii) grafting with a mixture of two or more monomers. The first type usually occurs in a single step. While, second step may occur with either the simultaneous or sequential use of the two monomers. There are five techniques of