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PREPARATION AND CHARACTERIZATION OF POLY(HYDROXAMIC ACID) CHELATING RESIN

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THIS DISSERTATION IS WRITTEN TO FULFILL PART OF THE REQUIREMENT TO OBTAIN A BACHELOR DEGREE IN SCIENCE WITH HONOURS

HS07 INDUSTRIAL CHEMISTRY
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2005

DECLARATION

I declare that this is my own work with the exception that all short forms that sources for each of them are mentioned.

30 March 2005

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(PROF MADYA DR. AMRAN AHMED) ____________________

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ABSTRACT

A resin containing the hydroxamic acid functional group was synthesized from poly(methyl acrylate)-PMA grafted sago starch. The conversion of ester groups of the grafted copolymer into hydroxamic acid was carried out by treatment of the polyester with hydroxylamine in an alkaline solution. The characterization of the poly(hydroxamic acid) chelating resin was performed by FTIR analysis. The hydroxamic acid functional group was identified by infrared spectroscopy. The sorption of the prepared resin toward some metal ions was investigated by a batch technique. The binding capacity of copper was maximum at pH 6 and the capacity was 2.244 mmol/g. The rate of exchange of the copper ion was, $t_{1/2}$ = 7 minutes. It was also observed that the metal ion sorption capacities of the resin were pH dependent and its selectivity toward the metal ions is in the following order: $Cu^{2+} > Pb^{2+} > Cd^{2+}$.

PENYEDIAAN DAN PENCIRIAN RESIN POLY(HYDROXAMIC ASID)

ABSTRAK

Polimer yang mengandungi kumpulan berfungsi asid hidroxamic yang dibuat dalam kajian ini adalah dihasilkan daripada poly(methyl acrylate)-PMA. Pertukaran kumpulan berfungsi dalam PMA kepada asid hidroxamic terjadi akibat daripada tindakbalas antara polyester dengan hidroxylamine di dalam larutan yang beralkali. Pencirian poly(hydroxamic acid) dibuat dengan menggunakan kaedah analisis FTIR. Kumpulan berfungsi bagi asid hidroxamic dikenalpasti melalui spektroskopi inframerah. Kadar jerapan bagi poly(hydroxamic acid) terhadap beberapa ion logam dikenalpasti dengan menggunakan teknik 'batch'. Dalam kaedah ini, ion kuprum menunjukkan jerapan maksimum pada pH 6 dengan kapasiti sebanyak 2.244mmol/g. Masa yang diperlukan untuk kadar 50% perubahan ion kuprum, $t_{1/2}$ adalah 7 minit. Selain itu, dapat juga diperhatikan bahawa kadar jerapan ion logam terhadap poly(hidroxamic acid)-PHA adalah bergantung kepada nilai pH larutan dan daripada kajian ini dapat diperhatikan kecenderungan PHA terhadap ion logam adalah dalam susunan berikut: $Cu^{2+} > Pb^{2+} > Cd^{2+}$.

LIST OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

C	celcius
cm	centimeter
g	gram
L	liter
mg	miligram
M	molarity
mL	milliliter
ppm	part per million
%	percentage

CHAPTER 1

INTRODUCTION

1.1 Introduction

Resin is an insoluble polymeric matrix containing labile ions capable of exchanging with ions in the surrounding medium. Ion exchange resins are classified as cation exchangers, which have positively charged mobile ions available for exchange, and anion exchangers, whose exchangeable ions are negatively charged. Both anion and cation resins are produced from the same basic organic polymers. They differ in the ionizable group attached to the hydrocarbon network. It is this functional group that determines the chemical behavior of the resin. Resins can be broadly classified as strong or weak acid cation exchangers or strong or weak base anion exchangers (Abe *et al.*, 1991).

Chelating resins behave similarly to weak acid cation resins but exhibit a high degree of selectivity for heavy metal cations. Chelating resins have special functional groups that contain two or more electron donor atoms that can form coordinate bonds to a single metal atom. Chelating resins contain specially oriented ionic and non-ionic groups that selectivity captures specific ions from complex mixtures. Chelating resins are used to remove specific metal ions and extract a complex of metal ions from various sources, to recover heavy metal from aqueous media and also to extract microelements from a complex solution. A characteristic feature of the chelating resin is the preservation of their high selectivity with respect to individual ions in the presence of large quantities of other ions. The apparent selectivity for a given metal depends upon concentration, the presence of other species, and pH. The affinity of the resin for a given metal can be increased or decreased by adjusting the pH. To obtain the desired pH, buffer solutions are preferably used (Lutfor *et al.*, 2000).

Polymeric chelating resins are able to bind heavier transition, lanthanide and actinide metal ions in the presence of calcium, magnesium, sodium, and potassium. Poly(hydroxamic acid) chelating resin has potential commercial importance with the knowledge that hydroxamic groups are able to form complexes with wide range of metal ions. This resin exhibits high affinity for copper, iron, chromium, nickel, and uranium. It is used for separation of some transition metal ions from their binary mixture. Poly(hydroxamic acid) resin can be synthesized by various methods and for various purposes. Some of the methods are (1)from copoly(acrylamide divinylbenzene) by treatment with hydroxylamine hydrochloride in the presence of potassium hydroxide, (2)from acrylhydroxamic acid with divinylbenzene by free radical solution polymerization, and (3)from poly(methyl acrylate) and hydroxylamine in an alkaline medium. The preparation using the poly(methyl acrylate) grafted copolymer is said to be efficient, cost effective with simple work (Lutfor *et al.*, 2000). Much attention has been given to the synthesis of these chelating resins and application to immobilization of enzymes, as well as applications in medicine, agriculture and etc (Lutfor *et al.*, 2000).

1.2 Objectives of the Study

1. To prepare poly(hydroxamic acid) chelating resin.
2. To characterize the resin such as identification of functional group with Fourier-Transform Infrared (FTIR) analysis, sorption of metal ion, kinetic exchange, swelling study, and cation-exchange capacity.

CHAPTER 2

LITERATURE REVIEW

2.1 Starch

White, odorless, and tasteless is the main characteristic of a starch. It is made up of glucose repeat units. It plays a vital role in the biochemistry of both plants and animals and has important commercial uses. In green plants starch is produced by photosynthesis. It is stored most abundantly in tubers, roots, seeds, and fruits. The plant source can usually be identified by microscopic examination of the starch grains. Starch is one of the major nutrients in the human diet. Its presence in foods and other substances can be detected by the blue-black color produced when iodine solution is added to a sample of the material to be tested. By treatment with hot water, starch granules have been shown to consist of at least two components, known as amylopectin and amylose. Amylopectin is a branched glucose polymer and amylase is a linear glucose polymer (Stanley *et al.*, 1992).

A highly fraction of starch, amylopectin, occurs in nature in semi-crystalline form. This observation stands in sharp distinction to the behavior of other branched polymers. The highly ordered nature of the starch granule results from the non-random nature of the branching and the non-random distribution of the linear regions.

Starch is widely used for sizing paper and textiles, for stiffening laundered fabrics, and in the manufacture of food products (Stanley *et al.*, 1992).

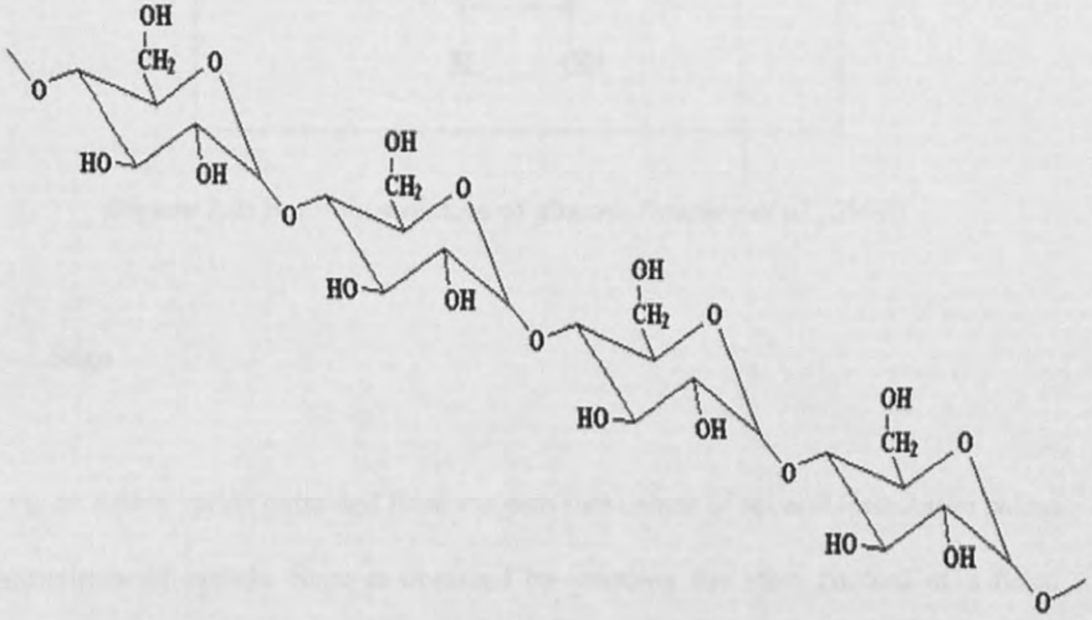

Figure 2.1: Formula structure of starch (Stanley *et al.*, 1992)

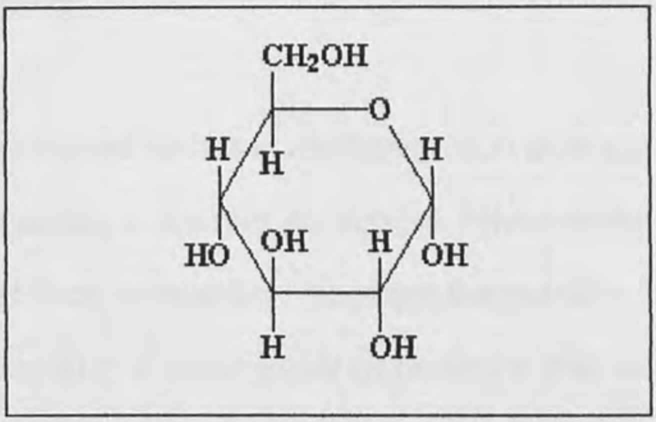

Figure 2.2: Formula structure of glucose (Stanley *et al.*, 1992)

2.2 Sago

Sago is an edible starch extracted from the pith like center of several East Asian palms or sometimes of cycads. Sago is obtained by grinding the stem content of a filled mature sago palm that is beginning to flower into powder and washing the starch free. For local used it is pulverized, but for the market it is usually sieved and then heated to form granule (Stanley *et al.*, 1992).

2.3 Polymer

Polymer means "many parts" and designates a large molecule made up of smaller repeating units or as known as monomer. A monomer is a molecule that combines with other molecules of the same or different type to form a polymer. Polymer generally have molecular weights greater than about 5000 but no firm lower limit need be defined since the meaning of the word is nearly always clear from its use. The word macromolecule is a synonym for polymer (Raymond *et al.*, 1992)

2.4 Polymerization

Polymerization is a chemical reaction in which the product molecules are able to grow indefinitely in size as long as reactants are supplied. Polymerization can occur if the monomers involved in the reaction have the proper functionalities. The functionality of a molecule is the number of sites available for bonding to other molecules under the specific conditions of the polymerization reaction (Rudin, 1999).

2.5 Graft Copolymer

Graft copolymers are formed by growing one polymer as branches on another preformed macromolecule. A supposedly linear main chain (the backbone) has attached to it polymeric side chain (the graft) of different chemical nature, in most cases distributed randomly. Interactions generally occur between backbone and grafts, resulting in a marked tendency to yield intramolecular phase separation in the bulk polymer. The interest in graft copolymers arises in part from the protection exerted by the graft on the backbone, and this specific feature has led to a number of applications as emulsifiers, surface-modifying agents, coating materials and compatibilizers in polymer blends (Rudin, 1999).

Graft copolymers in which grafts and backbone are of the same chemical nature are generally referred to as branched or comb-like polymers. They evidently do not exhibit the characteristic behavior of species involving blocks of different chemical structure nature. However, the methods of graft copolymer synthesis are generally applicable to comb-like polymers (Rudin, 1999).

2.6 Graft Copolymerization

Graft Copolymerization is the methods used to synthesize graft copolymers. It can be classified into three main categories that is 'grafting from' process, 'grafting onto' process, and 'grafting through' process (Stanley *et al.*, 1992).

2.6.1 'Grafting From' Processes

A polymer chain can have initiating sites attached to it, or functions capable of generating such sites. The polymerization of a second monomer can then be initiated from the backbone chain to yield the grafts, provided that initiation occurs by addition to the incoming monomer. The sites created on the backbone can be of free radical, anionic, cationic or Zeigler-Natta type. These methods are generally referred to as 'grafting from' processes, to stress that the backbone is made first, and that the graft are grown from it in a second polymerization process (Stanley *et al.*, 1992).

Through these methods are quite efficient in a number of cases, no accurate knowledge of the molecular structure of the graft copolymer formed is provided. The number of grafts is not accessible experimentally, and their length may fluctuate very much within a sample. Moreover, the graft copolymers often contain a fair amount of both homopolymers (Stanley *et al.*, 1992).

2.6.2 'Grafting Onto' Processes

These methods allow a structural characterization of the graft copolymers formed, as backbone chain and grafts are made separately and can be characterized individually. Knowing the molecular weight of each of them, and the overall composition of the graft copolymer, it is possible to evaluate the number of grafts per chain, and the average distance between two successive grafts along the backbone. However, the absence of ungrafted homopolymer should be checked for (Stanley *et al.*, 1992).

These 'grafting onto' reactions have gained interest as the ionic 'living' polymerization methods have become commonplace, giving access to polymers fitted with reactive sites at the chain ends. Their domain of application now extends far beyond these cases (Stanley *et al.*, 1992).

2.6.3 'Grafting Through' Processes

If the polymerization of a monomer is performed in the presence of a polymer carrying pendant unsaturations, which can participate in the process, then grafting results. However, such reactions can involve formation of links between individual molecules, if a growing site happens to incorporate unsaturations belonging to two (or more) different backbones. Consequently, the process may result in crosslinked material. Measures have to be taken to avoid gel formation if soluble species are required. In any case, these methods cannot be considered as ways of access to tailor-made graft copolymers (Stanley *et al.*, 1992).

Another type of 'grafting through' process has attracted much interest in recent years. It involves, in a first step, the synthesis of a polymer species with a terminal polymerizable unsaturation, and referred to as a macromonomer. Copolymerization of these species with a suitable comonomer allows easy access to graft copolymers. Each macromonomer molecule incorporated forms a unit carrying a graft. As the macromonomer is made separately, it can be characterized independently. The backbone chain is formed upon copolymerization of the macromonomer with a suitable comonomer, using free radical initiation, and a random distribution of the grafts can be anticipated. An alternative way is to synthesize a polymer having two functions at one chain end and to build the backbone chain by a step growth reaction with appropriate bifunctional compounds (Stanley *et al.*, 1992).

2.6.4 Other Grafting Process

Besides the three chief grafting processes described above, a number of ways of synthesizing graft copolymers have been developed which are not easy to classify unambiguously (Stanley *et al.*, 1992).

The radical sites formed on the backbone can initiate the growth of the grafts and the process can be considered as a 'grafting from' reaction, although some doubts have been expressed. Transfer reactions have also been used for grafting purpose. Some polymers exhibit rather high transfer constants, especially with respect to unstabilized radicals. If the polymerization of a monomer is carried out in the presence of such a polymer, radical sites are formed on the backbone. They can either initiate the polymerization of the monomer to build a graft, or recombine with an incoming polymeric radical. The former case is a 'grafting from' reaction, the latter 'grafting onto'. In either case homopolymer is formed simultaneously, and no real control of the process is possible (Stanley *et al.*, 1992).

Another interesting case of grafting involving transfer to polymer is on polymerizing styrene in the presence of rubber, with benzoyl peroxide (BPO) as initiator, grafting takes place. If azobis(isobutyronitrile) is used instead of BPO, no grafting is observed. This suggests that highly reactive primary radicals are responsible for attack on the rubber backbone. Free radical 'grafting from' can then occur to form the grafts. If the primary radicals are not reactive enough, polymerization takes place but no graft copolymer is formed (Stanley *et al.*, 1992).

The methods used for the synthesis of block copolymers rest on the same basic principles. The only difference is the location of the sites (or reactive functions). If they are distributed at random along the backbone, a graft copolymer will result, while if they are always located selectively at chain ends, then block copolymers are formed (Stanley *et al.*, 1992).

2.7 Kinetics of Radical Polymerization

Chain-growth polymerizations are so called because their mechanisms comprise chains of kinetic events. For successful polymerization, some agent must first initiate the sequence of reactions, and monomers must be added consecutively to a growing macromolecule. This chain of events may then be terminated by a reaction that is inherent in the system or by the action of impurities. In any case, there are at least

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