



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

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## ABSTRACT

The chelating ion-exchange resin containing amidoxime functional group was prepared from polyacrylonitrile (PAN) grafted kenaf fiber. The PAN grafted copolymer was obtained by free radical initiating process using ammonium ferrous sulfate as an initiator. Conversion of nitrile groups of the PAN grafted copolymers into the amidoxime was carried out by treatment with hydroxylamine under alkaline solution. Thus, the ester and nitrile groups of the PAN were converted into the amidoxime groups. The identification of amidoxime group was performed by qualitative and FT-IR analysis. An investigation was done on the chelating behavior of the prepared resin towards a series of metal ions and the binding of some transition metal ions such as copper, iron, zinc, chromium and nickel at pH 5. The rate of exchange of nickel and copper is very fast, where the adsorption capacities of metal ions by the resin were pH dependent and the rate of exchange was  $t_{1/2} < 9$  min.

## ABSTRAK

Resin 'chelating ion-exchange' yang mengandungi amidoksim sebagai kumpulan berfungsi disediakan daripada poliakrilonitril (PAN) dan dicangkukkan pada gentian kenaf. kopolimer ini diperolehi daripada radikal bebas dengan menggunakan ammonium ferus sulfat sebagai bahan pemula. Proses penukaran kumpulan nitril kopolimer PAN yang dicangkukkan pada amidoksim. Proses ini dijalankan dengan rawatan hidroksilamin di dalam larutan alkali. Justeru itu, kumpulan ester dan nitrile dalam PAN telah ditukarkan kepada kumpulan amidoksim. Pencirian amidoksim telah dilakukan dengan menggunakan FT-IR. Kajian telah dijalankan ke atas sifat resin pengkelat terhadap ion logam dan pencantuman beberapa logam peralihan seperti tembaga, besi, zink, kromium dan nikel pada pH 5. Kadar penukaran nikel dan tembaga adalah sangat cepat, dengan kapasiti pencerapan ion logam oleh resin bergantung kepada pH dan kadar penukaran adalah  $t_{1/2} < 9$  minit.

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**LIST OF SYMBOLS**

$\rho$	Density
$m_1$	molar mass
$V_1$	Volume
%	Percentage
$G_p$	Percentage of grafting
$t$	time
min	minute
ppm	part per million
g	gram
L	liter
mL	milliliter
T	temperature
:	Ratio
mg	milligram
mmol	millimol
°C	Degree Celsius
M	molality
h	hour
cm	centimeter

## **LIST OF ABBREVIATIONS**

AAS	Atomic absorption spectroscopy
AN	acrylonitrile
DMF	Dimethylformamide
FTIR	Fourier transforms spectroscopy
IR	Infrared
PAN	Poly(acrylonitrile)

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 BACKGROUND**

##### **1.1.1 Kenaf Fiber**

Kenaf fiber constitutes the most abundant and renewable polymer resource available worldwide. It is also very inexpensive compare to other cellulose materials. On the other hand, kenaf bast fiber (KBF) has recently been gaining a lot of attention as biomass-based filler, and it is well known as a cellulosic source with ecological and economical advantages, abundant, exhibiting low density, no abrasiveness during processing, high-specific mechanical properties, biodegradability and cheap pricing (Liu et al., 2005; Ochi, 2008; Aziz and Ansell, 2004). It has been reported that KBF has a significantly high ability to accumulate carbon dioxide. Its photosynthesis speed is at least three times higher than that of usual plants, and it can absorb carbon dioxide 1.4 times that of its own weight (Nishino, 2004; Nishino et al., 2003). KBF has been mainly used for textiles and paper before, and recently composites of KBF and plastics have been studied owing to its promising properties (Liu et al., 2005; Pan et al., 2007; Nishino et al., 2003).

In term of material science, kenaf is lignocellulosics fiber which has ion-exchange capacity and general adsorptive characteristics, which are derived from their constituent polymers and structure. The polymers include extractive, cellulose, hemicelluloses, pectin, lignin and protein. These are adsorbents for a wide range of solutes, particularly divalent metal cations (Laszlo and Dintzis, 1994). In this study, the ion exchange fact act as vital method for extraction and separation chemistry

and the use of lignocellulosic fiber (kenaf fiber) in graft copolymers as a renewable source to obtaining ion exchange resin.

### **1.1.2 Poly(acrylonitrile) Grafted Fiber**

A process in which side chain grafts are covalently attached to a main chain of a polymer backbone to form branched copolymer is called graft copolymerization. Usually the active sites initiating polymerization reactions would be free radical or ionic chemical groups (Nasef and Sayed, 2004). High energy radiation, photochemical and chemical initiation techniques is used to initiate the backbone cellulose polymer for grafting (Bhattacharya and Misra, 2004). Initiation methods producing free radicals have received the greatest attention due to their practicality. The cellulose backbone and the monomer to be grafted is the location for the radical formation for the initiation reaction. The slower procedure is generated homopolymerization of the monomer. Hence, initiators creating radicals at various sites on the cellulose backbone is preferred (Gurdag et al., 1997). The chemical initiation method has been extensively used due to higher graft yields (Shukla and Athalye, 1994). A redox-type initiators such as iron ion ( $\text{Fe}^{2+}$ ), has great importance because of its high grafting efficiency. Natural polymers are biodegradable and it is a disadvantage for long term application in adsorption processes because adsorbent needs recycling for cost efficient use. Kenaf fiber shows good chemical stability and mechanical strength, thus, kenaf fiber can be fictionalization as grafted polymers and subsequent modification into known chelating ligands.

### **1.1.3 Chelating Ion Exchangers**

Chelating adsorbents, also selected as chelate resins and chelating ion exchangers, have been known for a long time. The chelating ion exchangers have been synthesized for selective properties with respect to individual ions or groups. Certain groups of atoms able of selectivity interacting with the elements are introduced into polymer matrices. However, the adsorptive properties of adsorbents obtained at the early stages of investigation in this field proved to be worse than

could have been expected. They had insufficient selectivity and adsorptive capacity and a slow adsorption rate.

After known more information regarding to synthesis of chelating adsorbents. Certain progress has been made in the field of polymeric matrices synthesis and numerous chelating adsorbents with various chemically active groups fixed on different matrices are known today. The most widely known chelating adsorbents are based on polymeric organic matrices. In addition, chelating adsorbents are assumed to form chelate rings in the adsorbent phase during the adsorption of metals. The coordination properties of adsorbents and the possibility of a chelate ring being formed in the phase of adsorbents are radically affected by the nature of chemically active groups in the adsorbents. Chelate rings can be formed with the participation of donor atoms situated in one unit of polymeric matrix and nearby complexing groups in the neighboring units of polymeric adsorbent. The term frequently used is “chelate resins”, which seems to be too narrow since today, along with the traditional resin-type polymeric matrices, matrices of various other types and structures are used, e.g. cellulose, fibers, etc. The term “chelating sorbents” or “ion exchangers”, appears to be more correct (Myasoedova and Savvin, 1986).

#### **1.1.4 Poly(amidoxime) Chelating Resin**

Conventional water-softening is depending on an ion-exchange resin in which hardness ions are exchanged for by sodium ions. Water softening is the reduction of the concentration of calcium, magnesium, and other ions in hard water. 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 would be the ability to bind the heavier transition, rare earth, and main group metal ions in the presence of calcium, magnesium, sodium and potassium.

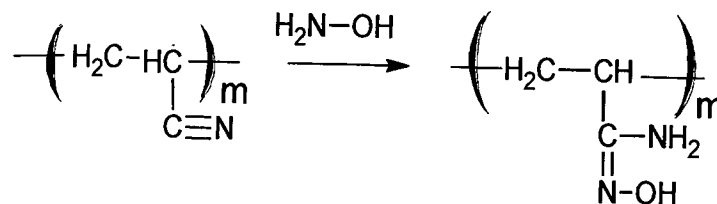
There are number of papers have been published about macroreticular resins with amidoxime groups and its comprehensive descriptions of synthesis were appeared in their reports (Egawa et al. 1987, 1992, 1993). Most part of papers were

involved the incorporation of a nitrile group into a polymer matrix, followed by the conversion of the nitrile group into an amidoxime group by treatment with a solution of hydroxylamine. In order to improve both the stability of swelling and free movement of the functional groups, amidoxime-groups containing fibrous adsorbents (Omichi et al., 1985) for metal ions were synthesized by high-energy radiation-induced grafting of acrylonitrile followed by amidoximation of cyano groups with hydroxylamine.

There is growing concern about the discharge of effluents and rinse water from industries and especially metal plating shops and need of simple process technology capable of recycling water and discharging toxic metals in a safe and convenient manner. There are many situations in industry where solutions containing low concentrations of metals are produced. For example, in the metal finishing industry, manufacturing of semiconductor and their components, print circuit boards, photography and printing, waste water released by laboratories, plants all contribute to aqueous streams requiring treatment. As more and more industrial organizations aim at zero waste discharge, waste treatment procedures will need to be reviewed and ion exchange technology could be applied.

There are many types of chelating ligands have been reported for binding of metal ions. Poly(amidoxime) are well known chelating ligands whose bind the wide metal ions in presence of alkali metal ions (Vernon 1982; Haron et al., 1994; Takahiro et al., 1986). Thus, The cyano groups on the poly(acrylonitrile) chains having the fiber backbone polymer is convert into poly(amidoxime) chelating resin by grafted fiber as shown in scheme 1.1.4. The chelating behavior of the prepare poly(amidoxime) resin is carry out using some metal ions and a significant binding properties of metal ions by the resin has to be observe. The adsorption capacities of metal ions by the resin were pH dependent and the rate of exchange was  $t_{1/2} < 9$  min (Lutfor et al. 2000.a; 2000.b).





**Scheme 1.1:** Preparation of poly(amidoxime). Reagents and conditions: Poly(acrylonitrile) grafted fiber,  $\text{NH}_2\text{OH}$ ,  $\text{NaOH}$ , pH 10,  $\text{MeOH}$ ,  $70^\circ\text{C}$ , 2 h

Source: Lutfor et al., (2009)

In order to overcome a number of these limitations the chelating resins, a new chelating ion exchange resin containing amidoxime functional group was synthesized from poly(acrylonitrile) grafted kenaf fiber. The poly(acrylonitrile) grafted fiber is prepared by free radical initiating process in which ammonium ferrous sulfate as an initiator. Conversion of the ester and nitrile groups of the grafted copolymer into the amidoxime groups is carried out by treatment of ester and nitrile with hydroxylamine in alkaline solution.

In this project, we were extracted the metal ions by batch technique. Therefore, the proposed chelating ion exchange resin is the poly(amidoxime) ligand, which is applied to the removal of target metal ions such as copper, iron, chromium, zinc and nickel.

## 1.2 PROBLEM STATEMENT

In recent years much attention has been focused on the use of kenaf fiber as low-cost adsorbents for the removal of heavy metal ions from contaminated waters. Spent fiber, 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 water solution. 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 water solution and protect the environment.

Immediate concerns with ligands, includes the weak non-specific 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 cation on the ligand.

### **1.3 OBJECTIVE**

- To prepare poly(acrylonitrile) grafted kenaf fiber by chemical initiating process.
- To synthesize a novel chelating resin containing amidoxime functional groups from acrylic polymer grafted kenaf fiber.
- To evaluate the binding property of chelating resin towards a transition metal ions.

### **1.4 SCOPE OF THE STUDY**

- The kenaf fiber obtained from local trees and modifying the fiber and converted to polymeric chelating ligand.
- The polymeric chelating ligand could be used to extract metal ions and it was found to be highly efficient. Thus, the polymer chelating ligand can be a suitable material as adsorbent to remove metals.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 GRAFT COPOLYMERIZATION**

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. According to 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.” A number of reviews (Stannett et al. 1984; Bhattacharyya and Maldas, 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 kenaf fiber 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. The factors affected the graft copolymerization were studied in details and the mechanism of graft reaction was proposed. And the solubility of graft copolymer and film-form properties of the graft copolymer blending with PAN in some solvents was investigated.

#### **2.2 GRAFTING INITIATED BY CHEMICAL MEANS**

Chemical means the grafting can proceed along two major paths, viz. free radical and ionic. In the chemical process, the role of initiator is very important as it determines the path of the grafting process. A number of methods have been used to initiate the backbone cellulose polymer for grafting including high energy radiation, photochemical and chemical initiation techniques (Bhattacharya and Mistra, 2004).

Initiation methods generate free radicals have received the greatest attention due to their practicality. The radical formation for the initiation reaction can occur either on the cellulose backbone or on the monomer to be grafted. The latter procedure is generated homopolymerization of the monomer. Therefore, initiators creating radicals at various sites on the cellulose backbone are clearly preferred (Gurdag et al., 1997). The chemical initiation method has been extensively used due to higher graft yields (Shukla and Athalye, 1994). Among the various types of redox-type initiators, iron ion ( $\text{Fe}^{2+}$ ) has great importance because of its high grafting efficiency. Although various chemical initiation methods are proposed (Bhattacharyya and Maldas, 1984), the redox system constitutes the most extensively used one. Redox system generally comprises the transition metal ions, which occur in various oxidation states. Such oxidized metal ions may directly oxidize starch or its derivatives to initiate the formation of free radicals for grafting. The redox initiations can act in two ways, e.g. by direct oxidation or by chain transfer.

**Direct Oxidation:** Certain transition metal ions such as  $\text{Cr}^{6+}$ ,  $\text{V}^{5+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Co}^{3+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$  directly oxidized cellulose as a result of which free radical sites are produced. The propose mechanism for such a process has been ascribed to the intermediate formation of a metal ion and cellulose complex of chelate type. Such complex formation is not restricted to a single site of cellulose backbone. The original concept was that the primary methylol group on the starch backbone is involved in the process (Mino and Kaizerman, 1958). Later on it was believed that the secondary hydroxyl groups of the anhydroglucose unit were also involved in inducing free radical formation on the cellulose backbone. Drawing analogy with the oxidation by metaperiodate it was thought that  $\text{C}_2\text{-C}_3$  bonds were actually involved in the cleavage. In fact, electron spin resonance (ESR) studies of the system also supported the same mechanism.

Of all the transition metal ions,  $\text{Fe}^{2+}$  constitutes the most widely used initiator and the various systems that used  $\text{Fe}^{2+}$  as the initiator. Other metal ions have, however, been scarcely used in the graft copolymerization. However, the redox potential of the metal ions used constitute an important parameter in determining the grafting efficiency. The grafting efficiency is affected by the extent of

homopolymerization. If the oxidation potential of the metal ion is high, it may react as well with the monomer, which will lead to an increase in homopolymerization. Therefore to circumvent this situation, metal ions with low oxidation potential are preferred. In general one should look for a system in which the polymer is a sufficiently strong reducing agent and the oxidation potential of the metal ion is low in order that the maximum efficiency in grafting is achieved.

**Chain Transfer:** These types of redox initiators form radicals due to the reaction among themselves and the resulting radicals abstract hydrogen atoms from the cellulose substrate. Generally, hydrogen peroxide in the presence of ferrous ion constitutes a frequently used chain transfer initiator. In such a system  $\text{H}_2\text{O}_2$  reacts with the ferrous ion to produce hydroxy radicals, which abstract hydrogen atoms from the cellulose backbone leading to the formation of a free radical centres.

### **2.3 SYNTHESIS OF GRAFT COPOLYMERS BY CHEMICAL INITIATION**

A great deal of attention has been given to the  $\text{Fe}^{2+}$  electron transfer reaction discovered (Mino and Kaizerman, 1958). They had found that certain iron salts, such as the nitrate and sulfate form were very effective in a redox system. According to their discussion, the oxidation-reduction produces cerous ions and transient free radical species capable of initiating vinyl polymerization. The most important feature of the oxidation with iron ion is that it proceeds with a single electron transfer with the formation of free radicals on the reducing agent. If the reducing agent is a polymeric molecule such as polyvinyl alcohol or cellulose and the oxidation is carried out in the presence vinyl monomer, the free radical produced on the polymeric molecule (backbone) initiates polymerization to produce a graft copolymer. This method of grafting yields substantially pure graft copolymers since the free radicals are formed exclusively on the backbone.

Although in the absence of a reducing agent, iron salts do initiate the polymerization of acrylonitrile and with iron nitrate a long induction period is obtained. In the case of acrylamide, although no induction period is observed,

polymerization proceeds at a very slow rate (Mino and Kaizerman, 1958) studied a number of graft copolymers in some detail. For example, acrylamide, acrylonitrile, and methyl acrylate were grafted onto low molecular weight polyvinyl alcohol in the presence of ammonium ferrous sulfate. The graft copolymers obtained were all soluble in suitable solvents, indicating that practically no crosslinking had taken place. Their data show that the iron ion technique permits high-efficiency grafting on a large variety of polymeric backbones, both natural and synthetic. Among the effective backbones are cellulose and other polyglucosides, such as dextrans and starches.

(Dennerberg et al., 1978) reported the preparation of cellulose-graft-poly(methyl acrylate) from corn cellulose initiated by ammonium ferrous sulfate. They also found that the grafted polymer could be extruded to give a film, which showed excellent susceptibility to fungal attack in a moist environment. The initial tensile strength of the material was excellent, however the tensile strength deteriorated rapidly after immersion in water. Tensile tests and scanning electron micrographs of the incubated samples, after being freed of mycelium, indicated substantial biodegradation of the cellulose portion of the copolymer. Therefore, they suggested the cellulose-graft-poly(methyl acrylate) could be used as a biodegradable plastic mulch.

An investigation on the graft copolymerizations of wheat cellulose with a variety of vinyl monomers were under taken as part of a research program designed (Reyes et al., (1966) to expand the industrial markets for wheat fiber and cellulose-based products. In a preliminary evaluation of initiating systems for grafting vinyl monomers to cellulose, iron ion and higher energy irradiation proved the most efficient method. The redox method with iron salts particularly, ceric ion-alcohol system has been used for initiation of polymerization and grafting of vinyl monomers. In addition, the kinetics of mechanism of the reaction was also studied. Results from model experiments designed to elucidate the mechanism of grafting to cellulose by iron salts is initiated either at the (carbon atom of the primary alcohol or at a carbon atom of the 1, 2-glycol in the glucose unit. The same mechanism could be applied to the cellulose-iron ion system. Preliminary electron spin resonance (ESR)

studies showed that the spectrum of the free radicals produced by treatment of cellulose with CAN was similar to that of irradiated starch. Both the dry CAN-treated starch powder and of irradiated starch can initiate graft copolymerization of vinyl monomers when dispersed in vinyl monomer-solvent mixtures.

An attempt was conducted (Rakesh and Ranby, 1977) to graft copolymerize of acrylonitrile onto cellulose using the pyrophosphate complex of trivalent manganese as initiator. This method was based on  $Mn^{3+}$  complex ions in aqueous solution as electron transfer agents to a substrate. Initiation of  $Mn^{3+}$  ions, complexed with pyrophosphate ions is a very specific reaction onto potato starch and cellulose substrate, which gives high grafting efficiencies (>95%) and only very small amounts of homopolymer was formed in the products. The reaction is probably an electron transfer from the substrate to the  $Mn^{3+}$  ions ( $Mn^{2+}$  ions are formed) and glycol or aldehyde groups may be involved. On the other hand, the pyrophosphate complex of  $Mn^{3+}$  ions is stable to disproportionation and exists as  $[Mn(H_2P_2O_7)_3]^{3-}$ . It can be prepared by the oxidation of  $Mn^{2+}$  ions by  $Mn^{7+}$  ions in the presence of an excess of pyrophosphate and can be conveniently used as a one-equivalent oxidant in the pH range of 1-6. Studies of low molecular weight organic compounds indicate a high specificity of attack of a manganese pyrophosphate on certain organic substrates, such as glycols, aldehydes and ketones. Polymerization of vinyl monomers in the glycol cleaving reactions of this complex has been used as evidence for the formation of free radicals. It is very specific and gives 98% grafting efficiency (only 2% homopolymer), but it could not be applied to cellulose substrates containing lignin.

Use of natural polymers such as cellulose as extends and replacements for totally synthetic polymers reduces our dependence on petrochemical derived monomers. Moreover attack by microorganism on the cellulose moiety can lead to polymer degradation. Since the poly(methyl acrylate) moiety is resistant to micro organisms (Fanta et al., 1993) explored the introduction of poly(vinyl acetate) segments by copolymerizing vinyl acetate and methyl acrylate during grafting. They expected that micro organisms would convert poly(vinyl acetate) to poly(vinyl alcohol) which degraded with cleavage of the polymer chain. The graft copolymer of methylacrylate onto potato cellulose was carried out by Mingzhu et al. (1993) and its