UNIVERSITI PUTRA MALAYSIA

AMIDOXIME-MODIFIED POLY(ACRYLONITRILE) – GRAFTED CASSAVA STARCH AND ITS ADSORPTION BEHAVIOR TOWARDS COPPER(II) ION

JA'AFAR YUSUF

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By

JA'AFAR YUSUF

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Masters of Science

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DEDICATION

I dedicate this thesis to my parents, HajiaBinti Yusuf and Alhaji Yusuf Jamoh.This thesis has been written in the spirit to discover which long had energized other far reaching and greater scientists. Some of what we have come across in the following excerptions:

"He is Allah, the Creator, the Inventor of all things, theBestower of forms. To Him belong the Best Names. All that is in the heavens and the earth glorify Him. And He is the All-Mighty, the All-Wise." - Al-Quran (59:24)

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman : Abdul Halim Abdullah, PhD
Faculty : Science

The graft copolymerization of acrylonitrile onto cassava starch using sodium persulphate (SPS) and potassium persulphate (KPS) as initiators were successfully carried out. The maximum grafting efficiency (91%) and grafted yield (274%) were attained at ratio of AN:CS 3:1 within 3 hours of reaction time at 50 ℃. poly(acrylonitrile-grafted-cassava) (poly(AN-*g*-CS)) were then chemically modified with hydroxylamine hydrochloride ($NH_2OH.HCl$) to convert the nitrile groups into oxime functional groups.Due to low utilization and large availability of cassava starch (CS), an attempt was made to incorporate CS onto acrylonitrile (AN) and further chemically modified to convert the nitrile groups into amidoxime functional groups to form chelating ion exchange network based on acrylonitrile as an effective adsorbent for wastewater treatment. Thepoly(AN-*g*-CS) and amidoxime-modified poly(AN-*g*-CS) were characterized by Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), Brauner-Emmet-Teller (BET) and X-ray diffraction (XRD). The IR spectra proved that the grafting of CS onto PAN was successful and the poly(AN-*g*-CS) was successfully modified with hydroxylamine hydrochloride. It was shown that the specific surface area, pore volume and average pore diameter of CS significantly increased after grafting with AN and modification with $NH_2OH.HCl$. The influence of pH, contact time, adsorbent dosage and initial metal concentration towards adsorption of Cu(II) ions into CS, poly(AN-*g*-CS) and amidoxime-modified poly(AN-*g*-CS) onto Cu(II) ions were investigated. It was shown that the amidoxime-modified poly(AN-*g*-CS) exhibited higher adsorption capacity towards Cu(II) ions as compared to the CS and poly(AN-*g*-CS).The maximum adsorption capacities were found to be 10.12 $mg.g^{-1}$, 5.28 $mg.g^{-1}$ and 56.02 $mg.g^{-1}$ respectively for CS, poly(AN-g-CS) and amidoxime-modified poly(AN-g-CS) respectively at pH 5. The adsorption kinetic study showed that the maximum time required for Cu(II) ions to attain saturation level was 1 hour. The removal efficiency of Cu(II) ions were compared using synthetic and real wastewater containing different metal ions. The adsorption kinetic studies proved that the adsorptions were fitted with pseudo-second order. The equilibrium data were analysed by the Langmuir and

Freundlich isotherms models. It was found that the Langmuir model is the most favourable isotherm model compared to the Freundlich model.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

AMIDOXIMA POLI(AKRILONITRIL) DIUBAHSUAI - KOPOLIMER CANTUM KE ATAS SAGU UBI KAYU DAN SIFAT PENJERAPANNYA TERHADAP ION CU(II)

Oleh

JA'AFAR YUSUF

Jun 2015

Pengerusi : Abdul Halim Abdullah, PhD
Fakulti : Sains

Kopolimer cantum akrilonitril (AN) ke atas sagu ubi kayu (CS) dengan meggnatu natrium persulfat (SPS) dan kalium persulfat (KPS) sebagai pemula telah berjaya disediakan.Kecekapan cantuman maksimum (91%) dan hasil cantuman (274%) telah diperoleh pada pada nisbah AN:CS 3:1 dalam masa 3 jam tindak balas pada suhu 50 ^{o}C. Poli(akronitril-cantuman-ubi kayu) (poli(AN-*g*-CS)) kemudian telah diubahsuai secara kimia dengan hidroksilamina hidroklorida ($NH_2OH.HCl$) untuk menukarkan kumpulan nitril kepada kumpulan oxima. Poli(AN-*g*-CS) dan poli(AN-*g*-CS) diubahsuai amidoxima telah dianalisis dengan spektroskopi inframerah transformasi Fourier (FTIR), mikroskopi elektron imbasan (SEM), analisis gravimetri terma (TGA), Brauner-Emmet-Teller (BET) dan belauan sinar-X (XRD). Spektrum inframerah (IR) telah membuktikan bahawa cantuman CS kepada PAN telah berjaya dan poli(AN-*g*-CS) juga telah berjaya diubahsuai dengan hidroksilamina hidroklorida. Selain itu, luas permukaan spesifik, isi padu liang dan purata diameter liang CS juga telah dibuktikan meningkat selepas cantuman dengan AN dan pengubahsuaian dengan $NH_2OH.HCl$. Ujian keatas pengaruh pH, masa sentuhan, bilangan dos penjerap dan kepekatan logam terhadap penjerapan ion Cu(II) terhadap CS, poli(AN-*g*-CS) dan poli(AN-*g*-CS) diubahsuai amidoxima telah dilakukan. menggunakan kaedah spektroskopi penyerapan atom (AAS). Keputusan menunjukkan bahawa poli(AN-*g*-CS) diubahsuai amidoxima mempunyai kapasiti penjerapan yang lebih tinggi terhadap ion Cu(II) berbanding CS dan poli(AN-*g*-CS). Kajian kinetik penjerapan menunjukkan bahawa masa maksimumuntuk ion Cu(II) mencapai aras ketepuan adalah 1 jam. Kecekapan penyingkiran oleh ion Cu(II) telah dibandingkan dengan menggunakan larutan sisa sintetik dan larutan sisa sebenar yang mengandungi ion-ion logam yang berbeza.Kajian kinetik penjerapan menunjukkan bahawa penjerapan adalah selari dengan hukum pseudo-kedua. Data keseimbangan telah dianalisis dengan menggunakan model isoterma Langmuir dan model isoterma Freundlich. Telah dibuktikan bahawa model isoterma yang paling baik adalah model Langmuir berbanding dengan model Freundlich.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Abdul Halim Abdullah, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Siti Nurul Ain Md Jamil, PhD
Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Mohsen Nourouzi Mobarekeh
Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

BUJANG KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

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LIST OF ABBREVIATIONS

CS	Cassava starch
AN	Acrylonitrile
KPS	Potassium persulfate
SPS	Sodium persulfite
PAN	Polyacrylonitrile
Poly(AN-*g*-CS)	Polyacrylonitrile-grafted-Cassava starch
Cu	Copper
As	Arsenic
W	Watt
Cr	chromium

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Due to the alarming rate of global industrialization, introduction of poisonous substance into the environment has become a threat to both animals and plants. Thus, heavy metal ions discharge into the surrounding has caused a serious challenge to the environment as a result of their ability to transform into serious poisonous living materials (Vullo et al. 2008). Examples of such poisonous heavy metal ions that cause serious challenge to health and persistent during treatment of waste water includes copper, mercury, cadmium, zinc, lead, chromium and nickel (Fu and Wang 2011).

Sufficient amount of zinc is considered necessary and very vital for physiological activities in the human body by stabilizing several biological processes. Furthermore, when the general intake of zinc into the body is more than the required threshold level, it can cause severe stomach pains, skin rashes, vomiting, weakness of the body and anaemia (Oyaro et al. 2007). Copper being one of the most important elements in activities of the human body, if ingested more than the required amount can also lead to a serious health problems, such as; convulsion, vomiting, cramps and eventually even death (Paulino et al. 2006).

Exposition to areas with nickel concentration beyond the threshold level can cause health crisis in the lungs, liver, gastrointestinal disturbance and skin damage (Borba et al. 2006). To deal with such health issue arising from presence of high amount of heavy metal ions in our environment through wastewater, numerous investigation via scientific research have been conducted in order to find suitable technique for the treatment of such waste water. Several techniques and methods have been carried outto find the most effective method for removing heavy metal ions from industrial waste such as; filtration, chemical precipitation, ion exchange, electrode deposition, surface complexation, adsorption, and membrane processing Zhao et al. (2010) and Jamil et al. (2015). Some of the techniques have several drawbacks due to either high cost of chemicals, metal selectivity; low adsorption capacity for heavy metal ions and low potential for regeneration(Han et al. 2010).However, adsorption is regarded as one of the most vital technique due to the following factors; availability of raw materials, simplicity with ~~a~~ sufficient adsorption of heavy metal ions (Rajiv et al. 2011).

1.2 Polyacrylonitrile

Attention of many researchers has been drawn towards the use of polyacrylonitrile (PAN) for adsorption of heavy metal ions in industries due to its special features, which includes; hardness and flexibility, chemical resistance, consistency with other polar materials, permeability (Rajiv et al.2011) and the existence of nitrile functional groups along polymer chains that could be converted into another functional groups (Jamil et al. 2015). Due to the vast application of PAN in polymer industries, its performance has further been enhanced (Liu et al. 2011). PAN can be chemically modified with

various reagents such as hydroxylamine, ethylenediamine, hydrazine, thioamide and imidazoline to develop new moieties that are vital for the removal of cationic metal ions in wastewater (Haratake et al. 2006).

1.3 Cassava starch

Cassava starch, a renewable natural bi-polymer with extensive number of hydroxyl groups is considered as one the most abundant bi-polymers in the world (El-Tahlawy et al. 2007). It is a polymer consisting of two groups mainly amylose and amylopectin, often extracted from potatoes and corn. The amylopectin group of the polymer is primarily an α(1-4)-linked glucoses which are connected by β (1-6)-linkages that are in linear chains. Amylopectin has a distinctive arrangement of 45 and 75 nm chain glucose units which form two and three subgroups, respectively (Figure 1.1). A starch granule chain generally contains 12−20 glucose units having 9 nm intervals between each unit. Amylose, which is the second group in the starch polymer, contains mainly a linear chained polymer that consists of α (1-4)-linked glucose units. The amylose group constitutes up to about 20−30% of a starch polymer (Smith 2001).

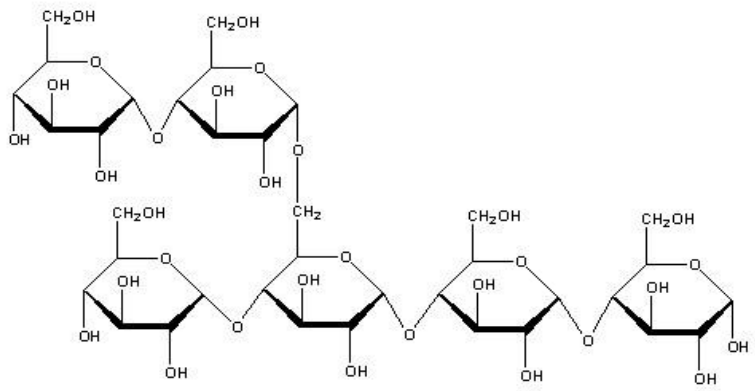

Figure 1.1: Structure of starch

Cassava starch can be used as an alternative material in solving environmental pollution issue through adsorption, due to its ability to chelate metals (Crini 2005). The hydroxyl groups of starch can form complex with heavy metal ions in the matrix, by assuming a right-handed helical conformation (Vigneshwaran et al. 2006).

1.4 Amidoxime-modified poly(AN-*g*-CS)

The use of modified polymers with oxime functional groups have been studied and proved extensively for the removal of heavy metal ions from both wastewater and industrial effluents, due to its high ability to form complex with heavy metal ions (Liu et al. 2010). As shown in Figure 1.2, poly(AN-*g*-CS) was chemically modified with hydroxylamine hydrochloride to produce amidoxime-modified poly(AN-*g*-CS).

1.5 Heavy metal ions adsorption

Discharged wastewater from the mining industries may contain heavy metal ions in which the concentration exceeds the minimum threshold level. These industries discharge toxic heavy metal ions into the streams without advanced treatment, thereby resulting in serious effect to aquatic organisms (Owlad et al. 2009).
It is indeed very challenging to overcome quantities of heavy metal ions in aqueous solutions (Rajiv et al. 2011). Hence, adsorption is considered to be as one of the most promising technique to overcome such challenge, particularly by using cheap adsorbent, such as clay materials and agricultural waste (Krestou et al. 2004). Bio-sorption materials from biological origin are also considered to be suitable for the treatment of heavy metals from various sources (Liu et al. 2010).

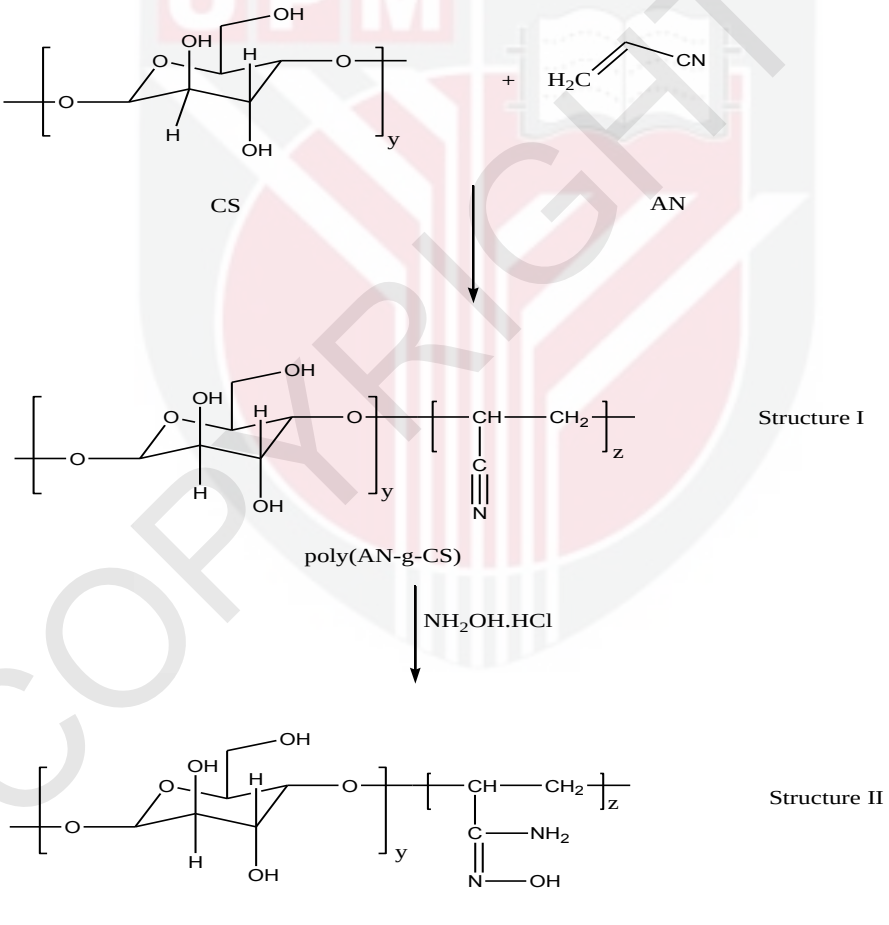

Figure 1.2 Formation of amidoxime-modified poly(AN-*g*-CS)

1.6 Problem statement

Nowadays, the issue of environmental pollution has become one of the major challenges to researchers due to the increasing number of industries in the developing nations and illegal discharge of poisonous materials to both land and sea. It is well established that heavy metal ions are present in sewages and air, therefore continue to cause serious problems to both plants and animals. Thus, it becomes imperative to find the best way for the wastewater treatment; that includes cheaper source, high availability with less or non-toxic recovery of materials production (Liu et al., 2010).

In this study, polyacrylonitrile will be incorporated with cassava starch through grafting and subsequently modified with hydroxylamine hydrochloride. Potassium persulfate (KPS) and sodium persulphate (SPS) were employed as initiators, which are believed to initiate the polymerization process (Jamil et al., 2015). It was reported that amide functional group played a vital role for heavy metal ions sorption due to higher dielectric constant and dipole moment of amide functional group (Deng et al., 2003). amidoxime are known to be bidentate ligands which will serves as an added advantage towards the complex formation of heavy metal ions (Liu et al., 2010).

1.7 Objectives of thesis

The general objective of this thesis is to synthesis poly(AN-*g*-CS) and subsequently chemical modification with hydroxylamine hydrochloride to transform the nitrile functional groups into oxime functional groups will enhance the adsorption capacity towards heavy metal ions. This will also serve as another alternative method due to its simplicity, accessibly and low cost to replace the use of expensive activated carbons.

The objectives of this thesis are as follows:

- To prepare poly(acrylonitrile-grafted-(*g*)-cassava starch) via redox method.
- To chemically modified poly(AN-*g*-CS) with hydroxylamine hydrochloride to form amidoxime-modified poly(AN-*g*-CS).
- To characterize poly(AN-*g*-CS) and amidoxime-modified poly(AN-g-CS) via FTIR, SEM, TGA, XRD and BET.
- To investigate the adsorption properties of CS, poly(AN-*g*-CS) and amidoxime-modified poly(AN-*g*-CS) towards Cu(II) ions

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