UNIVERSITI PUTRA MALAYSIA

REMOVAL OF Pb2+, Cu2+ AND Cd2+ IONS FROM AQUEOUS SOLUTION BY CARBOXYMETHYL SAGO STARCH AND CARBOXYMETHYL SAGO STARCH/CHITOSAN HYDROGELS

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By

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

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

REMOVAL OF Pb^{2+}, Cu^{2+} and Cd^{2+} IONS FROM AQEOUS SOLUTION BY CARBOXYMETHYL SAGO STARCH AND CARBOXYMETHYL SAGO STARCH/CHITOSAN HYDROGELS

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September 2015

Chair : Norhazlin binti Zainuddin, PhD

Faculty : Science

Modified polysaccharides such as starch and cellulose play important role in the polymer research because they are from natural resources and biodegradable. The main objective of this study was to prepare the hydrogels from modified sago starch and chitosan which were then applied as metal scavenger for lead (Pb), copper (Cu) and cadmium (Cd). In this study, carboxymethyl sago starch (CMSS) and chitosan were dissolved in L (+)-lactic acid (LA) and cross-linked by using electron beam (EB) irradiation. The highest gel content of hydrogel was obtained from 60% (w/v) of CMSS in 0.6 M of LA at 20 kGy EB irradiation. Similar composition as CMSS hydrogel has been used for CMSS/chitosan (CMSS/Chi) hydrogel with the addition of 4% (w/v) of chitosan which showed high metal uptake. Then, both CMSS and CMSS/Chi hydrogels were structurally and morphologically characterized by Fourier Transform Infrared (FT-IR) and Scanning Electron Microscopy (SEM). The hydrogels (<300 µm) were dispersed in aqueous solution of divalent metal ions (Pb, Cu and Cd, 100 ppm) and the hydrogels-metal complex was filtered and examined using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). The study on removal metal ions was carried out under non-competitive and competitive condition, either one metal ion stand in a solution or mixed up together. Under non-competitive condition, the removal of heavy metal was about 93.54%, 88.42% and 85.45% of Pb, Cu and Cd ions respectively by CMSS hydrogel. While in CMSS/Chi about 92.80%, 62.00% and 70.20% of Pb, Cu and Cd ions, respectively were removed from the aqueous solution. The amount of metal removed by CMSS/Chi hydrogel was lower compared to CMSS hydrogel due to the fewer amounts of active sites available to bind with metal ions. The interaction between CMSS and chitosan in CMSS/Chi hydrogel can be seen from FTIR spectrum at wavenumber of 1727 cm^{-1} and 1604 cm^{-1} is due to hydrogen and ionic bonding, thus reduce the amount of

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metal uptake. Meanwhile, the Pb ions uptake by both CMSS and CMSS/Chi hydrogels are quite similar due to high molecular weight and radius which caused less attraction towards nucleus and easily be bonded to active binding site of hydrogels. All the metal uptake achieved equilibrium within 1 hour reaction time and showed the pseudo second order reaction in kinetic study. Except the reaction between CMSS hydrogel and Pb ion, the isotherm study showed the reaction was followed the Freundlich isotherm model. In addition, under competitive condition, CMSS/Chi hydrogel showed high selectivity towards Pb ion compared to Cu and Cd ions. This probably due to small pore size of CMSS/Chi hydrogel as shown by SEM micrograph which have the ability to entrap the large Pb ions and hindered the active site from in contact with Cu and Cd ions. In conclusion, these results supported the role of both CMSS and CMSS/Chi hydrogels as metal scavenger for Pb, Cu and Cd ions.

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

PENYINGKIRAN ION Pb^{2+}, Cu^{2+} DAN Cd^{2+} DARIPADA LARUTAN AKUEUS OLEH HIDROGEL KARBOKSIMETIL KANJI SAGU DAN KARBOKSIMETIL KANJI SAGU/KITOSAN

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Pengubahsuaian polisakarida seperti kanji dan selulosa memainkan peranan penting dalam penyelidikan polimer kerana mereka berasal dari sumber alam dan terlupus secara semula jadi. Objektif utama kajian ini adalah untuk menyediakan hidrogel dari kanji sagu terubahsuai dan kitosan dan kemudiannya digunakan sebagai perangkap logam untuk plumbum (Pb), kuprum (Cu) dan kadmium (Cd). Dalam kajian ini, karboksimetil kanji sagu (CMSS) dan kitosan telah dilarutkan dalam L (+) - asid laktik (LA) dan di sambung silang dengan menggunakan sinaran alur elektron (EB). Kandungan gel tertinggi bagi hidrogel CMSS telah diperolehi daripada 60% (w/v) CMSS dalam 0.6 M LA pada 20 kGy sinaran EB. Komposisi yang sama seperti hidrogel CMSS telah digunakan untuk hidrogel CMSS/kitosan (CMSS/Chi) dengan tambahan 4% (w/v) kitosan yang telah menunjukkan pengambilan logam yang tinggi. Kemudian, kedua-dua hidrogel CMSS dan CMSS/Chi telah dicirikan secara struktur dan morfologi oleh Fourier Transform Infrared (FT-IR) dan Pengimbas Mikroskopi Elektron (SEM). Hidrogel (<300 μm) telah disebarkan dalam larutan akueus ion logam dwi-valens (Pb, Cu dan Cd, 100 ppm) dan kompleks hidrogel-logam telah ditapis dan dikaji menggunakan Pasangan Induktif Plasma-Optik Pelepasan Spektrometer (ICP-OES). Kajian ke atas penyingkiran ion logam ini dijalankan di bawah keadaan tidak kompetitif dan kompetitif, iaitu sama ada satu logam ion dalam suatu larutan atau bercampur bersama-sama. Dalam keadaan tidak kompetitif, hidrogel CMSS menyingkirkan logam berat kira-kira 93.54%, 88.42% dan 85.45% daripada Pb, Cu dan Cd ion masing-masing. Manakala CMSS/Chi kira-kira 92.80%, 62.00% dan 70.20% daripada Pb, Cu dan Cd ion masing-masing telah disingkirkan daripada larutan akues. Jumlah logam disingkirkan oleh hidrogel CMSS/Chi adalah lebih

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rendah berbanding dengan hidrogel CMSS kerana jumlah tapak aktif tersedia yang lebih sedikit bagi mengikat ion logam. Interaksi di antara CMSS dan kitosan dalam hidrogel CMSS/Chi boleh dilihat daripada FTIR spectrum pada nombor gelombang 1727 cm^{-1} dan 1604 cm^{-1} disebabkan ikatan hydrogen dan ion, dengan itu mengurangkan jumlah pengambilan ion logam. Sementara itu, pengambilan ion Pb oleh kedua-dua hidrogel CMSS dan CMSS/Chi adalah sama kerana berat molekul dan saiz jejari yang tinggi menyebabkan kurang daya tarikan ke arah nukleus dan mudah terikat ke tapak pengikat aktif hidrogel. Semua pengambilan logam itu mencapai keseimbangan dalam masa 1 jam tindak balas dan menunjukkan tindak balas tertib kedua dalam kajian kinetik. Kajian isoterma menunjukkan tindak balas mengikuti model isoterma Freundlich bagi semua hidrogel kecuali hidrogel CMSS dengan ion Pb. Di samping itu, dalam keadaan yang kompetitif, hidrogel CMSS/Chi menunjukkan pemilihan yang tinggi terhadap Pb ion berbanding Cu dan Cd ion. Ini mungkin disebabkan oleh saiz liang kecil hidrogel CMSS/Chi seperti yang ditunjukkan oleh SEM mikrograf mampu untuk memerangkap ion Pb yang besar dan menghalang tapak aktif ini dari berinteraksi dengan Cu dan Cd ion. Kesimpulannya, keputusan kajian ini menyokong peranan kedua-dua hidrogel CMSS dan CMSS/Chi sebagai perangkap logam untuk Pb, Cu dan Cd ion.

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I certify that a Thesis Examination Committee has met on 23rd September 2015 to conduct the final examination of Sri Norleha binti Basri on her thesis entitled "Removal of Pb^{2+}, Cu^{2+} and Cd^{2+} Ions From Aqueous Solution by Carboxymethyl Sago Starch and Craboxymethyl Sago Starch/Chitosan Hydrogels" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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LIST OF ABBREVIATIONS

AAc/AG	Acrylic acid/sodium alginate
AGU	Anhydrose Glucose Unit
CMC	Carboxymethyl cellulose
CMC/MMT	Carboxymethyl cellulose/clay
CMCS	Carboxymethyl corn starch
CMCts	Carboxymethyl chitosan
CMSS	Carboxymethyl sago starch
CMSS/Chi	Carboxymethyl sago starch/ chitosan
CTS-g-PAA	Chitosan grafted polyacrylic acid
DS	Degree substitution
DTG	Diffrential Thermal Gravimetric
FTIR	Fourier Transform Infrared
ICP	Inductively Coupled Plasma
K_1	First order rate
K_2	Second order rate
K_F	Freundlich constant
K_L	Langmuir constant
LA	Lactic acid
NIPam	N-isopropylacrylamide
q	Sorption capacity
R^2	Correlation coefficient
SEM	Scanning Electron Microscopy
SMCA	Sodium monochloro acetic acid
TGA	Thermal Gravimetric Analysis
XRD	X-ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Natural polymers such as cellulose, starch and chitosan have interesting characteristics which are biodegradable, low cost and non-toxic. Thus, they receive a lot of attention from the researchers in reducing amount of synthetic petroleum-based polymer and chemical waste. Starch and cellulose are produced in most green plant as an energy store and a main component in cell wall, while chitosan is produced after deacetylation of chitin originated from crustacean shell such as crab and shrimp. In polymer technology, modification and derivatization of these natural polymers are important to improve some properties such as biocompatibility, absorbing efficiency, and to provide specific functional group for specific application.

Since late 90s, Malaysian researchers have started studying on the utilization of sago palm (*Metroxylon sago*) products such as starch, cellulose and sago pulp waste. It is because of the abundant amount of sago production in peat swamp area in Sarawak and limited application in industries, other than food industry. The palm continually produce sucker, which turn grow into adult palm and no necessity for replanting after harvest. Sago starch is extracted from the spongy trunk or pith of the palm tree. The physicochemical properties of the sago starch are quite similar to other common starch like potato and tapioca, it has unique characteristics such as the granules range from 10 to 50 μm, have smooth surface and being gelatinized when dissolving the starch at 69.05 to 70.2 °C (Karim *et al.*, 2008).

During gelatinization process, the starch will undergo retrogradation when the amylose and amylopectin start to realign themselves and causing transformation of liquid to gel. Therefore, some modification on the sago starch will make it worth by reducing the gelatinization temperature and form a permanent gel. There are several techniques can be used to modify the natural polymers such as grafting, crosslinking, oxidation and end-capping, as well as derivatization such as etherification or esterification. The etherification of natural polymer is one of popular and cheapest technique. Usually, etherification process involves the substitution of carboxymethyl group from sodium monochloroacetic acid in alkali organic solution (Pushpamalar *et al.*, 2006; Zainuddin, 2003).

In order to reduce the additional chemical waste, the CMSS hydrogel was produced using radiation-crosslinking method. There is no need to put in the crosslinker to start the crosslinking process. Therefore, radiation method is important in producing a clean, free additives and environmentally safe product. Compared to other modification technique, ionizing radiation provides the combination of sterilization and synthesis of polymer in a single step. The CMSS forms an anionic polymer in water and acid solution under irradiation. Besides that, blending is an effective method in improving the performance of polymer material. Thus, in this

research, chitosan has been added to CMSS hydrogel as cationic segment to improve selectivity on metal uptake.

1.2 Problem Statement

Water pollution has been a major concern faces by many countries in response to aggressive economic development. Industries like electroplating, mining, energy and fuel contribute a lot in heavy metal pollution. These heavy metals are very toxic elements and not biodegradable like organic pollutant. In Malaysia, the heavy metal pollution is not only found in water resources (Shazili *et al.*, 2006; Tajam and Kamal, 2013), but also at landfill and sediment (Agamuthu and Fauziah, 2010; Ripin *et al.*, 2014). Some of toxic heavy metals that particularly involved in treatment of industrial wastewater are lead, copper, cadmium, zinc, mercury, chromium and nickel. There are various methods to remove the metal ions from water such as chemical precipitation ion exchange, adsorption, reverse osmosis, floatation, sedimentation and filtration (Barakat, 2011; Fu and Wang, 2011). Most of techniques that have been listed above is not fully effective and generates secondary effluent, consume a huge capital investment, and face with lacks of sources. As a result, intensive research and development effort has been done upon low cost adsorbents and natural sources for remediation of toxic metal ions.

1.3 Significance of the Study

In this study, our native starch from sago (*Metroxylon sago*) has been chosen for removal of heavy metal ions from aqueous solution. Sago palm is easily found in swampy area; either it is cultivated or wild stand in tropical climate of Asia (Singhal *et al.*, 2008). In Malaysia, sago palm can be found mainly in the state of Sarawak. Sago starch is commonly used as animal food, stabilizer and thickener in food industry as well as adhesive in textile, plywood and paper industries. Derivatization and modification normally done to improve the properties of native sago starch (Zainal *et al.*, 2005). Etherification of starch is one of derivatization technique where the carboxymethyl group from monochloroacetic acid substituting the hydroxyl group of starch backbone (Zainuddin, 2003). Thus, the presence of new functional group in the modified starch makes it more stable and easily soluble in water at ambient temperature. Furthermore, crosslinking by irradiation has an advantage over other crosslinking techniques such as physical and chemical. The modification and sterilization can be achieved in a single step, as well as no crosslinking agent is needed in irradiation technique. In this experiment, the etherified sago starch was dissolved in acid solution and irradiated by using electron beam irradiation. As a result, a strong hydrogel is formed in a simple technique and short reaction time. Then, the prepared hydrogel were used to remove Pb, Cu and Cd ions from its aqueous solution. The presence of chitosan in the hydrogel networks was to improve the efficiency of the hydrogel to sorb the metal ions.

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1.4 Objectives of the Study

In this study, the main objectives were:

1. To prepare and characterize carboxymethyl starch from sago palm
2. To prepare and characterize hydrogels from carboxymethyl sago starch (CMSS) and carboxymethyl sago starch/chitosan (CMSS/Chi) in lactic acid using electron beam irradiation
3. To evaluate the removal of Pb, Cd and Cu ions from its aqueous solution by hydrogels

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