SYNTHESIS AND CHARACTERIZATION OF CROSSLINKED CARBOXYMETHYL SAGO STARCH/CITRIC ACID HYDROGEL AND ITS ABSORPTION PROPERTIES FOR Pb(II), Cu(II), Ni(II) AND Zn(II) IONS IN AQUEOUS SOLUTIONS

By

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

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Heavy metal pollution is a serious environmental issue being faced around the world. To overcome this problem, sorption procedure was chosen as an effective method to remove heavy metal in wastewater treatment. Carboxymethyl sago starch (CMSS), a modified biopolymer gains much attention because of it is low cost and environmental friendly. Moreover, it possesses functional groups such hydroxyl and carboxyl, which give advantage for crosslinking reaction to form water-insoluble hydrogel. The main objective of this study was to synthesize CMSS hydrogels by crosslinking with citric acid and then applied as metal sorbent to overcome excessive heavy metal pollution. In preparation of CMSS/CA hydrogel, the effect of concentration of CMSS, concentration of citric acid, curing time and temperature on gel content were studied. The optimum conditions for preparation of CMSS/CA hydrogel were; 60% w/v of CMSS, 10% w/w of citric acid, 48 hours of curing time at 50°C curing temperature. The CMSS/CA hydrogel was characterized by Fourier-transform infrared (FT-IR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and X-ray diffraction (XRD). The absorption band at 1726 cm^{-1} observed in the FT-IR spectrum of CMSS/CA hydrogel indicated the carboxylic acid and ester bonds formed from the reaction of citric acid with hydroxyl group of CMSS. Besides, the crosslinkages in the CMSS/CA hydrogel increased the thermal stability of CMSS and the presence of various size of pores also can be seen from the SEM micrograph. The removal of heavy metal lead (II), copper (II), zinc (II) and nickel (II) ions from aqueous solution was analysed using inductively coupled plasma optic emission spectrometry (ICP-OES). The effects of pH metal solution, reaction time, initial concentration metal ions and reaction temperature on the sorption capacity and removal percentage were investigated. From the results, the sorption capacity of Pb^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} onto CMSS/CA hydrogel were 64.48, 36.56, 16.21, 18.45 mg/g, respectively. Meanwhile, the removal percentage of Pb^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} from aqueous solution were 91.97, 56.43, 34.30, 40.08%, respectively. All heavy metal ion sorption followed pseudo-second order kinetic model and the isotherm data followed Langmuir model. The thermodynamic studies revealed that sorption process of Pb^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} were spontaneous and exothermic in nature. The heavy metal removal experiment demonstrated that CMSS/CA hydrogel has high selectivity for Pb^{2+} in both non-competitive and competitive conditions. The electropositivity of Pb^{2+} made it more selective than Cu^{2+}, Ni^{2+} and Zn^{2+} due to the ability of Pb^{2+} to donate electron and interact with active site of CMSS/CA hydrogel. The desorption percentage of Pb^{2+} from CMSS/CA hydrogel was 91.86% indicated that the metal ions were able to leach from the hydrogel efficiently and also an appropriate method to dispose sorbent in safer condition. In conclusion, this study showed that the CMSS/CA hydrogel has a potential to be used as a heavy metal sorbent that can beneficially reduce the heavy metal pollution.

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

SINTESIS DAN PENCIRIAN HIDROGEL KARBOKSIMETIL KANJI SAGU/ASID SITRIK RANGKAI SILANG DAN SIFAT PENYERAPANNYA TERHADAP ION Pb(II), Cu(II), Ni(II) DAN Zn(II) DARI LARUTAN AKUEUS

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Pencemaran logam berat merupakan isu alam sekitar yang serius yang dihadapi di seluruh dunia. Untuk mengatasi masalah ini, prosedur penyerapan dipilih sebagai kaedah yang berkesan untuk membuang logam berat dalam rawatan air sisa. Karboksimetil kanji sagu (CMSS), biopolimer yang diubah suai menarik banyak perhatian kerana ia adalah kos rendah dan mesra alam. Selain itu, ia mempunyai kumpulan berfungsi seperti hidroksil dan karboksil, yang memberi kelebihan untuk tindak balas ikatan silang untuk membentuk hidrogel yang tidak larut air. Objektif utama kajian ini adalah untuk mensintesis hidrogel CMSS melalui rangkai silang dengan asid sitrik dan kemudian digunakan sebagai sorben logam untuk mengatasi pencemaran logam berat yang berlebihan. Dalam penyediaan hidrogel CMSS/CA, kesan kepekatan CMSS, kepekatan asid sitrik, masa pengawetan dan suhu pada kandungan gel telah disiasat. Keadaan optimum untuk penyediaan CMSS/CA hidrogel adalah; 60% w/v CMSS, 10% w/ w asid sitrik, 48 jam tempoh tindak balas pada 50°C suhu tindak balas. Hidrogel CMSS/CA dicirikan oleh transformasi fourier inframerah (FT-IR), pengimbasan mikroskop elektron (SEM), analisis termogravimetrik (TGA) dan belauan sinar-X (XRD). Jalur penyerapan pada 1726 cm^{-1} yang diperhatikan dalam spektrum FT-IR hidrogel CMSS/CA menunjukkan asid karboksilik dan juga ikatan ester yang terbentuk daripada tindak balas asid sitrik dengan kumpulan hidroksil CMSS. Selain itu, jaringan rangkai silang dalam hidrogel CMSS/CA meningkatkan kestabilan haba CMSS dan kehadiran pelbagai saiz liang juga dapat dilihat daripada mikrograf SEM. Penyingkiran ion logam berat plumbum (II), tembaga (II), nikel (II) dan zink (II) dari larutan akueus dianalisis dengan menggunakan Plasma Gandingan Induktif-Spektrometri Pancaran Optik (ICP-OES). Kesan pH larutan logam, masa tindak balas, kepekatan awal ion logam dan suhu tindak balas ke atas kapasiti penyerapan dan peratusan penyingkiran telah disiasat. Daripada keputusan, kapasiti penyerapan Pb^{2+}, Cu^{2+}, Ni^{2+} dan Zn^{2+} ke hidrogel CMSS/CA masing-masing ialah 64.48, 36.56, 16.21 dan 18.45 mg/g. Sementara itu, peratusan penyingkiran Pb^{2+}, Cu^{2+}, Ni^{2+} dan Zn^{2+} dari larutan akueus masing-masing adalah 91.97, 56.43, 34.30 dan 40.08%. Semua penyerapan ion logam berat mengikuti model kinetik urutan pseudo-kedua dan data isoterma mengikuti model Langmuir. Kajian termodinamik mendedahkan bahawa proses penyerapan Pb^{2+}, Cu^{2+}, Ni^{2+} dan Zn^{2+} bersifat

spontan dan eksotermik. Eksperimen penyingkiran logam berat menunjukkan hidrogel CMSS/CA mempunyai daya pilihan yang tinggi terhadap Pb^{2+} dalam keadaan tidak kompetitif dan kompetitif. Keelektropositiviti Pb^{2+} menjadikannya lebih selektif daripada Cu^{2+}, Ni^{2+} dan Zn^{2+} kerana keupayaan Pb^{2+} untuk menderma elektron dan berinteraksi dengan tapak aktif hidrogel CMSS/CA. Peratusan penyaherapan Pb^{2+} dari hidrogel CMSS/CA adalah 91.86% menunjukkan bahawa ion logam dapat larut lesap dari hidrogel dengan berkesan dan juga kaedah yang sesuai untuk membuang sorben dalam keadaan yang lebih selamat. Kesimpulannya, kajian ini menunjukkan bahawa hidrogel CMSS/CA mempunyai potensi untuk digunakan sebagai sorben logam berat yang boleh mengurangkan pencemaran logam berat.

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LIST OF ABBREVIATIONS

AGU	Anhydroglucose unit
C_e	Equilibrium concentration
CMC	Carboxymethyl cellulose
CMC/GO	Carboxymethyl cellulose/graphene oxide
CMC-AA	Carboxymethyl cellulose/acrylic acid
CMS	Carboxymethyl starch
CMS/MMT	Carboxymethyl starch/montmorillonite
CMSS	Carboxymethyl sago starch
CMSS/CA	Carboxymethyl sago starch/citric acid
CMSS/MAA	Carboxymethyl sago starch/methacrylic acid
DCA	Dichloroacetic acid
DS	Degree of substitution
ECMCF	Epichlorohydrin carboxymethyl cellulose fiber
EPI	Epichlorohydrin
FTIR	Fourier Transform Infrared
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometer
k_1	Pseudo-first order rate
k_2	Pseudo-second order rate
K_a	Adsorption equilibrium constant
K_F	Freundlich constant
K_L	Langmuir constant
MB	Methylene blue
MCCS	Modified cellulose corn stalk
m-CVP	Magnetic carboxymethyl starch-g-polyvinyl-imidazole
PBS	Phosphate buffer solution

PEG	Polyethylene glycol
PEGDE	Polyethylene glycol diglycidyl ether
PEUF	Polymer-enhanced ultrafiltration
PS	Porous starch
PSC	Porous starch citrate
PSX	Porous starch xanthate
q_e	Sorption capacity at equilibrium
q_m	Maximum sorption capacity
q_t	Sorption capacity at time
SDS	Sodium n-dodecyl sulfate
SEM	Scanning Electron Microscopy
SMCA	Sodium monochloroacetate
SNC	Starch nanocrystal
STMP	Sodium trimetaphosphate
STPP	Sodium tripolyphosphate
TGA	Thermo Gravimetric Analysis
UV	Ultraviolet
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background Study

Natural polymer such as polysaccharides (chitosan, cellulose and starch), polyamides, polynucleotides and their derivatives are examples of renewable sources that become a highlight in polymer industries because worldwide emphasized more on sustainable materials rather than petroleum based polymer. It is called natural polymer because the polymer can be found in natural environment. Among several alternatives sources, starch draws innumerable attention as natural occurring polymer and environmentally friendly energy sources. It is second most abundance storage biopolymer, origin from crops like corn, rice, wheat, potato, tapioca and sago (Cheng and Ou, 2009). They are biodegradability, abundancy, biocompatibility and economical material to be developed for various industries such food packaging, tissue engineering, drug delivery and also industrial wastewater treatment.

Sago starch, isolated from sago palm (Ahmad et al.,1999) played important role as a promising raw material. In general, native sago starch has limited utilization in wider commercial type of applications unless the physio-chemical and physico-chemical properties are modified by several techniques. Carboxymethyl sago starch (CMSS) is one of sago starch derivative with carboxymethyl functional group on the starch backbones. Through carboxymethylation, a method of chemical modification, the instability of native sago starch under variety kinds of pressure, shear and temperature can be altered. CMSS have been constantly used as natural polymer in hydrogel synthesis due to advantages of low rates of retrogradation, increase thermal stability and hydrophilic functional group. Despite favourable key structure of carboxylic COO^- groups that can bind to divalent metal ions, CMSS has low mechanical strength and instability in the gel form. Chemically crosslinked hydrogel is crucial in order to form permanent gel with high porosity which play prominent roles to enhance pollutant sorption (Benhalima et al., 2017). Eco-friendly crosslinker such as citric acid preferably used rather than intrinsic toxic of common crosslinkers such as epichlorohydrin, phosphorous chloride or formaldehyde that may give potential risks to environment.

Thus, in this research, carboxymethyl sago starch/citric acid (CMSS/CA) hydrogel was synthesized from CMSS by using citric acid as crosslinker. Sago starch and citric acid were considered to be excellent natural material to be used in application of heavy metal removal because of its biodegradable and renewable compared to synthetic polymer which may create secondary pollution. The main goal of this study was to demonstrate that CMSS/CA hydrogel with hydrophilic groups can sorb heavy metal ion from aqueous solution.

1.2 Problem Statement

Water pollution arises from heavy metal pollutants continuously become a worldwide environmental issue. Developing countries like Malaysia has been exposed to heavy metal pollution from different sources including agriculture activities, industrial and domestic sewage (Kadhum et al., 2015). Industries like electroplating, mining, fertilizers, batteries, tanneries, pesticides, paper and textile (Fu and Wang, 2011) predominantly contributors to high concentration of heavy metal ions through their sewage and eventually straight to water sources. Heavy metals are inorganic contaminants that accumulated in living organisms but not biodegradable and not break down into harmless form over times. Some of heavy metals such as Pb, Cu, Ni, Zn, Cd, As, Fe and Cr listed as the most hazardous inorganic pollutants (Lim et al., 2012). As these metals could enter the food chains, its potentially risk to human health because of excessive heavy metals content lead to detrimental effect on the nature and also living organism with high toxicity and carcinogenicity.

For the purpose of protecting the nature and also human being from tremendously affected by heavy metal pollution, industries are obligated to undergo water treatment. Several conventional methods to remove heavy metal from water include chemical precipitation, ion exchange, adsorption on activated carbon, solvent extraction and membrane filtration (Fu and Wang, 2011) have been implemented in order to control and reduce the concentration of heavy metal and also environment pollution before releasing the effluents into aqua systems. However, these methods have significant defects such as consume high energy and high cost operation requirements, incomplete removal especially in low concentration of metal ions and produce large quantities of toxic sludge that unintentionally become second pollution (Barakat, 2011; Singha and Guleria, 2014). Thus, a low cost and more efficient method of removing heavy metal from aqueous solution which is also environmental friendly is needed as a promising alternative. Hence, in this study, the removal of heavy metals by CMSS/CA hydrogels act as sorbent was prepared to overcome the problems.

1.3 Significance of Study

Removing heavy metal ions from aqueous solution via sorption considered one of the choice of wastewater treatment for industries application. In this research, carboxymethyl sago starch/citric acid (CMSS/CA) hydrogel was prepared in attempt to be utilized as the sorbent for removing heavy metal ions from aqueous solution efficiently.

Native sago starch was chosen as it is one of rich source for low cost sorbent that comes from natural material. By utilizing the hydroxyl group availability in starch molecule, etherification was done to substitute it with carboxymethyl group from monochloroacetic acid (Lviii et al., 2013). Then, CMSS undergo crosslinking reaction with citric acid via esterification to build polymeric network and porous hydrogel. The highlight benefit of choosing citric acid as crosslinking agent is it has good affinity towards metal ions (Demitri et al., 2008). As a result, CMSS/CA hydrogel was formed with the presence of new functional groups within polymeric network. The new functional groups possess hydrophilic character which swelled when come in contact with aqueous solution without being dissolved. The CMSS/CA hydrogels provide active sites that have governing role in coordinate with heavy metal ions. The usage of low-cost and bio-sorbent like CMSS/CA hydrogel is crucial for industries as its bring benefit in term of operation cost and environmental friendly.

Through this research, the removal of heavy metal ions by sorbent for wastewater treatment can be achieved for a better application in industrial scale. Thus, minimizing the pollutants can create a healthy environment for us to live in.

1.4 Objectives of Study

The aim of this research was to produce hydrogel from CMSS and study its sorption properties towards heavy metal ions in aqueous solution. With the main aim of this study, the following objectives were:

1) To optimize the formation of CMSS/CA hydrogel

2) To analyse the swelling behaviour of CMSS/CA hydrogel in media of alkaline, acidic and salt solution.

3) To evaluate the sorption properties of Pb^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} in aqueous solution by CMSS/CA hydrogel.

4) To examine the selectivity of CMSS/CA hydrogel towards the removal percentage of Pb^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}.

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