



Preparation and characterization of irradiated carboxymethyl sago starch-acid hydrogel and its application as metal scavenger in aqueous solution



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ABSTRACT

Carboxymethyl sago starch-acid hydrogel was prepared via irradiation technique to remove divalent metal ions (Pb, Cu and Cd) from their aqueous solution. The hydrogel was characterized by using Fourier Transform Infrared (FT-IR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The removal of these metal ions was analyzed by using inductively coupled plasma-optic emission spectra (ICP-OES) to study the amount of metal uptake by the hydrogel. Parameters of study include effect of pH, amount of sample, contact time, initial concentration of metal solution and reaction temperature. FTIR spectroscopy shows the CMSS hydrogel absorption peaks at 1741 cm^{-1} , 1605 cm^{-1} and 1430 cm^{-1} which indicates the substitution of carboxymethyl group of modified sago starch. The degradation temperature of CMSS hydrogel is higher compared to CMSS due to the crosslinking by electron beam radiation and formed a porous hydrogel. From the data obtained, about 93.5%, 88.4% and 85.5% of Pb, Cu and Cd ions has been respectively removed from their solution under optimum condition.

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1. Introduction

Excessive heavy metals are very toxic and carcinogenic to nature and living organism. This becomes a serious issue with the rapid development of industries such as electroplating, mining, batteries, automotive and fertilizers. Some of toxic heavy metals that particularly involve in treatment of industrial wastewater are lead (Pb), copper (Cu) and cadmium (Cd). Lead can cause the failure in kidney, liver, reproductive system, and brain function. The diseases symptoms are dizziness, headache, weakness of muscles and renal damage (Naseem & Tahir, 2001). The excessive ingestion of Cu will bring serious toxicity such as vomiting cramps or even death (Paulino et al., 2006). While, cadmium is listed as probable human carcinogen by U.S Environmental Protection Agency which chronic exposure can cause kidney dysfunction and death.

There are various methods that have been developed to remove heavy metal ions from inorganic effluent by conventional process such as chemical precipitation which metal ions will form

insoluble precipitate in the present of hydroxide, sulfide and carbonates group (Fu & Wang, 2011; Ozverdi & Erdem, 2006). Besides that, the ion-exchange resin also widely used to treat heavy metal ions because of fast kinetic and high treatment efficiency and capacity. The resin can be synthetic or natural solid and has specific ability to exchange its cations such as zeolites, sulfonic and carboxylic acid group with the metal ions (Abdelwahab, Amin, & El-Ashtoukhy, 2013; Gode & Pehlivan, 2006). In addition, the membrane filtration technology such as ultrafiltration (Landaburu-Aguirre, García, Pongrácz, & Keiski, 2009), reverse osmosis (Dialynas & Diamadopoulos, 2009), nanofiltration (Yuan, Meng, Zeng, Fang, & Shi, 2008) and electro dialysis (Kabdaşlı, Arslan, Olmez-Hanci, Arslan-Alaton, & Tünay, 2009) shows a great promise to remove metal due to high efficiency, space saving and easy operation. 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 on low cost adsorbents and natural sources for remediation of toxic metal ions.

Researchers focus on green synthesis sorbent from natural polymers which can be derived from non-living biomass such as bark, shell, algal biomass and microbial biomass such as bacteria and fungi (Apiratikul & Pavasant, 2008; Rozaini et al., 2010; Singanan & Peters, 2013; Zhang, Wang, Zhang, & Xia, 2014). In

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addition, the biomass can also be modified and applied as metal detector, drug delivery, fluorescent probing and analysis (Liang et al., 2014; Shen, Luo, Wang, & Sun, 2014). The development in polysaccharide-based sorbent such as cellulose (Goel, Kumar, Misra, & Varshney, 2015), chitosan (Negm, El-Sheikh, El-Farargy, Hefni, & Bekhit, 2015), starch (Teh, Wu, & Juan, 2014) and cyclodextrins (Cui et al., 2015) to treat the wastewater also has been widely discussed. Some of natural polymers are blended to improve the tensile strength, thermal stability and capability to absorb metal ions (Hiroki, Tran, Nagasawa, Yagi, & Tamada, 2009; Prakash & Arungalai, 2015). The abundance, biodegradability and high efficiency as sorbent are among the properties which make these natural polymers as potential biosorbent.

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. Another important use of sago starch is for production of ethanol (Abd-Aziz, 2002). Derivatization and modification normally done to improve the properties of native sago starch (Zainal, Karim, & Teng, 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.

Crosslinking is a process where the polymers are linked together in a network. It can be formed by physical, chemical (Kim & Lim, 1999; Singha & Guleria, 2014) or irradiation interaction (Pant et al., 2010). Furthermore, irradiation technique has an advantage over other crosslinking techniques in which the modification and sterilization can be achieved in a single step, as well as no crosslinking agent is needed. 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 period of reaction time. The main objective of the present paper was to evaluate the potential of CMSS-acid hydrogel as a metal scavenger for removal of Pb (II), Cu (II) and Cd (II) ions from aqueous solution. The factors that influence the metal uptake, sorption kinetic study and essential isotherm model of CMSS-acid hydrogel toward the studied metal ions were also discussed.

2. Experimental

2.1. Materials

Sago starch was supplied by Rumbia Biotech, Malaysia. It was used as received without further purification. Solvents such as isopropanol, methanol, absolute ethanol were purchased from System ChemAR (Malaysia), sodium monochloroacetate acid from Merck (Darmstadt, Germany), sodium hydroxide from R&M chemicals (Essex, UK), acetic acid and nitric acid from J.T Baker (Center Valley, PA, USA). In addition, lactic acid, hydrochloric acid and metal standard solutions of copper, lead and cadmium were obtained from Fisher Chemicals (Loughborough, UK). Distilled and deionized water were used throughout the experiment.

2.2. Preparation of CMSS

The carboxymethylation of sago starch was carried out according to the method published by Zainuddin (2003). 600.00 g of sago

starch powder was slurred in 9 L of isopropanol in a 10 L covered reactor flask equipped with stirrer and reflux condenser. While stirring, 20% w/v of sodium hydroxide was added to prepare basic environment for etherification process. Stirring was continued for 1 h and the temperature was increased to 55.00 °C. After that, sodium monochloroacetic acid (SMCA) was added and the mixture was stirred for 3 h. The molar ratio of SMCA to starch (AGU) was 1:1.34. Then, the mixture was allowed to cool to room temperature. The CMSS powder was washed with methanol for three times and neutralized with acetic acid glacial followed by absolute ethanol. Finally, CMSS was then filtered and dried in oven at 60.00 °C for 24 h.

2.3. Preparation of CMSS-acid hydrogel

CMSS-acid hydrogel was prepared by dissolving the CMSS (60% w/v) in 0.6 M lactic acid. This sample was then transferred into plastic mold and sealed in plastic bag. Irradiation was carried out by using electron beam radiation EPS 3000 (2 MeV, 10 mA) conducted at Malaysian Nuclear Agency, Dengkil.

2.4. Characterization on CMSS hydrogel

The structure of CMSS-acid hydrogel was characterized by FTIR spectrometer (100 Series Perkin Elmer) with Universal Attenuated Total Reflectance (UTAR) technique. About 3 mg of sample on diamond holder was irradiated with infrared in the range of 4000–280 cm⁻¹. In addition, the morphology of the swollen hydrogel was characterized using FEI, Quanta 400 scanning electron microscopy. The hydrogels were soaked in distilled water and then were freeze dried to remove the water molecule before coated with gold. The thermal stability of CMSS-acid hydrogel was examined using Perkin Elmer TGA 7. The samples were heated from 35.00 to 600.00 °C with the rate of 5 °C/min in the flow of inert nitrogen gas.

2.5. Sorption procedure

The sorption experiments were carried out in centrifuge tube containing desired amount of hydrogel and 25 mL metal ion solution at desired concentration and pH (adjusted with 1.0 M hydrochloric acid and 1.0 M sodium hydroxide). After spinning (125 rpm) for certain time, the supernatant was separated from the solution and residual concentration of metal ions was analyzed by ICP-OES (Perkin Elmer Optima 2100 DV). All the results were performed triplicate and the data recorded as a mean. The amount of metal uptake was calculated by using the following equation

$$\% \text{ metal uptake} = \frac{V_i - V_f}{V_i} \times 100 \quad (1)$$

where V_i is the initial reading of metal ion (ppm) before adding sample and V_f is the reading for filtrate solution (ppm).

3. Results and discussion

3.1. FT-IR analysis

Fourier Transform Infrared (FTIR) spectroscopy has been used to analyze the functional group of sago starch, CMSS and CMSS hydrogel. The FTIR spectra of the samples are shown in Fig. 1. The sago starch absorption peak showed the O–H stretching at 3343 cm⁻¹. The absorption peaks at 2952 cm⁻¹ and 1662 cm⁻¹ show the C–H stretching and tightly bound water present in the starch molecule. Besides that, the –CH₂ symmetrical absorption peak appeared at 1362 cm⁻¹. Broad absorption peak in the range of 1100–990 cm⁻¹

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