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Removal of copper(II) from aqueous solution in fixed-bed column by carboxylic acid functionalized deacetylated konjac glucomannan

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ABSTRACT

Carboxylic acid functionalized deacetylated konjac glucomannan (CADKGM) with regular cylinder shape was thermoplastically prepared by a single screw extruder. Thermoplastic deacetylated konjac glucomannan (TDKGM) using for preparation of CADKGM adsorbent showed good rheological processing properties with equilibrium torque of 13.1 N m and plasticizing time of 26 s at 160 °C, which was close to high density polyethylene (HDPE). The scanning electron micrograph results showed that CADKGM was porous inside the structure of the adsorbent. The removal of copper by CADKGM was studied in fixed-bed column. A comprehensive study was conducted to determine the breakthrough curves with varying bed heights, flow rates and initial concentrations. The breakthrough data gave a good fit to Thomas model. The consecutive adsorption–desorption cycles were applied to investigate the reusability of CADKGM. The adsorbed copper ions on CADKGM were easily desorbed by 0.01 mol L^{-1} HCl solution with desorption efficiency of 98%. The column capacity of CADKGM was not affected by an increase of reusable time.

1. Introduction

Agricultural field irrigated with heavy metal contaminated water causes a serious public health problem since many heavy metals can concentrate and accumulate in human body through food chain (Nayek, Gupta, & Saha, 2010; Wei & Yang, 2010; Wu, Tseng, & Juang, 2010). It is well acknowledged that toxic heavy metal ions are among the most poisonous pollutants in wastewater, which cannot be biodegraded or destroyed by any treatment process (Li, Wang, Allinson, Li, & Xiong, 2009; Liu, Yang, et al., 2009; Lu, Wang, Lei, Huang, & Zhai, 2009; Peng, Song, Yuan, Cui, & Qiu, 2009; Shi, Shao, Li, Shao, & Du, 2009; Sunarso & Ismadji, 2009). Copper ions are commonly found in industrial effluents such as mining, electroplating and battery manufacturing drainage. Copper is an essential element and plays an essential role in the human diet. However, acute doses can cause health problem such as nausea, vomiting and abdominal pain. Long-term exposure to higher than 0.5 mg L^{-1} of copper in natural water may cause liver damage. Moreover, copper in the dissolved form is potentially very toxic to aquatic plants and animals. From the environmental and public health point of view, it is important to effectively remove copper ions from the industry wastewaters before discharging. Many treatment processes, including chemical precipitation, ion-exchange, coagulation-flocculation, membrane filtration and adsorption, are used to remove heavy metal ions of polluted water (Babel & Kurniawan, 2003; El Samrani, Lartiges, & Villieras, 2008; Matlock, Howerton, & Atwood, 2002; Pehlivan & Altun, 2007; Sang, Gu, Sun, Li, & Liang, 2008). Among the treatment processes, the biosorption process using natural materials or waste products as adsorbents to remove heavy metal ions from wastewater is one of the most popular and effective processes (Bailey, Olin, Bricka, & Adrian, 1999; Demirbas, 2008; Farooq, Kozinski, Khan, & Athar, 2010; Sud, Mahajan, & Kaur, 2008; Vijayaraghavan & Yun, 2008; Wan Ngah, Teong, & Hanafiah, 2011; Wang & Chen, 2009). Compared with conventional treatment methods, the advantages of biosorption process lie in its low-cost and high removal efficiency. The concentration of heavy metal ions can be reduced to very low levels after the wastewater is treated by biosorption process.

In order to improve adsorption capacity of biosorbents, chemical modification is widely used (Wu, Kang, et al., 2010), including a direct chemical modified method and grafting of functional group chains on matrix biopolymer (O'Connell, Birkinshaw, & O'Dwyer, 2008). Modified biosorbents would be of great importance and be hoped for removal of heavy metal ions from wastewater in actual application. However, related literatures concerning concrete steps of applying modified biosorbents to practice are seldom found. The major reason is that many kinds of modified biosorbents are hard to be prepared or processed on a large scale. Moreover, many kinds of modified biosorbents have poor mechanical strength with high water absorbency, which cannot meet the industrial application requirements.

It was reported in our previous study that chemical modified konjac glucomannan by grafting hydrophobic monomers onto its backbone could be processed by thermoplastic extrusion (Xu, Luo,

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Lin, Zhuo, & Liang, 2009). It was further reported in a batch adsorption study that carboxylic acid functionalized deacetylated konjac glucomannan as a weak acid cation adsorbent showed relatively high adsorption capacity for removal of copper ion and lead ion from aqueous solution (Liu, Luo, Lin, Liang, & Chen, 2009). In order to prepare and process konjac glucomannan based adsorbent with relatively high mechanical strength on a large scale, carboxylic acid functionalized deacetylated konjac glucomannan (CADKGM) with regular cylinder shape was thermoplastically extruded and prepared by single screw extruder with subsequent chemical activation by sodium hydroxide. The main objective of this study was to investigate the copper ions removal efficiency and adsorption capacity of CADKGM adsorbent in fixed-bed column. Effects of various parameters on breakthrough curves were conducted. Thomas model was applied to fit the results obtained from the column study.

2. Experimental

2.1. Materials and instruments

The following chemicals including methyl acrylate (MA), methyl methacrylate (MMA), ammonium persulfate, alcohol, sodium hydroxide, hydrochloric acid, copper sulfate used in this work were all of analytical grade and obtained from Chengdu Kelong Chemicals Company. Refined KGM flour (50–150 μm) was purchased from Mianyang Anxian Dule Company and was used without further purification. High density polyethylene (HDPE) was purchased from Shanghai Secco Petrochemical Company.

The following instruments were used in this study: torque rheometer and single screw extruder (XSS-300, Shanghai Kechuang Rubber Machinery Co., Ltd.), atomic adsorption spectrometer (AA700, PE), scanning electron micrograph (S440, Leica Cambridge Ltd.), and peristaltic pump (BT-100, Shanghai Qingpu Huxi Instrument Factory).

2.2. Preparation of DKGM

KGM flour (200.0 g) and sodium hydroxide (15.0 g) were dispersed in 960 mL alcohol/water mixture solution (400:560 v/v) in a three-necked round-bottomed flask (2000 mL) equipped with a mechanical stirrer. The reaction mixture was stirred at a temperature of 50 °C for 2 h. As a result, deacetylated konjac glucomannan (DKGM) was obtained. DKGM powder was filtered out and washed with distilled water, and then was dried at 60 °C for further graft copolymerization experiment.

2.3. Synthesis of TDKGM

A mixture of 45.0 g of dried DKGM and 1200 mL of distilled water was stirred mechanically at 25 °C for 30 min in a three-necked round-bottomed flask (2000 mL) under nitrogen atmosphere. This treatment was followed by the addition of 120 mL of MA and 80 mL of MMA. Copolymerization was carried out at 75 °C for 3 h by adding ammonium persulfate (6.85 g) into the mixed solution. After 3 h, thermoplastic deacetylated konjac glucomannan (TDKGM) was filtered out of reacted system and washed thoroughly with distilled water and then refluxed with hot water for 12 h in order to remove any homopolymers that may be attached to the surface of TDKGM powder. The copolymer sample (TDKGM) was dried to a constant weight (175.0 g) at 50 °C. The graft percentage was determined by the following equation:

$$\text{Graft}\ \ (\%) = \frac{W_g - W_o}{W_o} \times 100 \qquad (1)$$

where W_o and W_g represent the initial weight and the graft weight of DKGM, respectively. The graft percentage of TDKGM was calculated as 289%.

2.4. Thermoplastic extrusion of TDKGM

Processing of the TDKGM was performed using a single screw extruder. The applied temperature during extrusion was kept at 160 °C. The extruder speed was kept at 40 rpm in all cases. Unifilar TDKGM was extruded through nozzles with a diameter of 1.25 mm. Unifilar TDKGM was cut into short cylinder pieces with length of 5 mm by granulator.

2.5. Chemical activation of TDKGM for CADKGM adsorbent

Short cylinder pieces of TDKGM were chemically activated under alkali condition using sodium hydroxide as follows: short cylinder pieces of TDKGM (200.0 g) were immersed in 500 mL of sodium hydroxide aqueous solution with the concentration of 10 wt%. The mixture was agitated at 50 °C for 12 h. The chemically activated TDKGM was neutralized by hydrochloric acid and collected by filtration and washed with distilled water. The product of CADKGM adsorbent was then dried at 60 °C.

2.6. Fixed-bed column experiments

Fixed-bed column experiments were conducted using a column with 3.0 cm internal diameter and 30 cm length. The column was packed with short cylinder pieces of CADKGM between two supporting layers of glass wool. The column was charged with Cu^{2+} aqueous solution in the up flow mode. Temperature was maintained at 15 °C. The column studies were performed at pH 5. A Perkin-Elmer-AA700 atomic absorption instrument was used in the determination of Cu^{2+} concentration of effluent by line's calibration curve.

The adsorption–desorption cycle experiments were carried out in a column with a bed height of 14 cm. The Cu^{2+} ion solution of 50 mg L^{-1} was fed through the bed in up-flow mode at 10 mL min^{-1} flow rate. Operation of the column was stopped when the effluent Cu^{2+} ion concentration reached a constant value. The Cu-loaded CADKGM was regenerated by using 0.01 mol L^{-1} hydrochloride. Hydrochloride was fed through the bed in up-flow mode at 8 mL min^{-1} flow rate until the effluent Cu^{2+} ion concentration reached a lowest value. The regenerated CADKGM was neutralized by 0.01 mol L^{-1} sodium hydroxide until the pH value in the effluent achieved a value of 6, and then deionised water was used to wash the bed for 5 h at a flow rate of 10 mL min^{-1}. The regenerated column was employed in the next adsorption cycle to investigate the reusability of CADKGM.

2.7. Characterization of TDKGM and CADKGM

A torque rheometer (XSS-300, Shanghai Kechuang Rubber Machinery Co., Ltd.) was used to study the effect of processing temperature on rheological processing properties of TDKGM. The processing temperature was set at 120 °C, 140 °C and 160 °C. The processing speed was kept at 40 rpm in all cases. The sample of TDKGM or HDPE with amount of 45.0 g was added into in an internal mixer at setting temperature. Various processing parameters could be obtained from the torque curves.

The morphologies of TDKGM and CADKGM were investigated by SEM (S440, Leica Cambridge Ltd.). All dried samples were sputter coated with gold prior to examination.

Water absorbency of the samples was determined as follows: 1.0 g of dry sample was added into a centrifuge tube (100 mL) containing 50 mL of distilled water. The sample was allowed to swell