Carboxymethyl cellulose fiber as a fast binding and biodegradable adsorbent of heavy metals

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Wei Wei [a], Sok Kim [a], Myung-Hee Song [a], John Kwame Bediako [a], Yeoung-Sang Yun [a,b,*]

[a] Division of Semiconductor and Chemical Engineering, Chonbuk National University, Jeonbuk 561-756, Republic of Korea
[b] Department of Bioprocess Engineering, Chonbuk National University, Jeonbuk 561-756, Republic of Korea

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ABSTRACT

In this study, a fast kinetic sorbent, epichlorohydrin cross-linked carboxymethyl cellulose fiber (ECMCF), was developed by using a simple synthetic method. SEM images showed that the ECMCF has a thin fibrous shape (20–90 μm of diameter) with a rough and porous surface, which is beneficial for the purpose of sorption. Cadmium metal ion (Cd(II)) was chosen as a model divalent heavy metal and the sorption performance of ECMCF was evaluated by batch and column experiments. The result of pH edge revealed that pH 6.0 was the best condition for Cd(II) sorption. The maximum uptake of Cd(II) by ECMCF was 150.60 ± 10.47 mg/g, which was comparable and higher than previously reported sorbents. Batch kinetic study showed that the ECMCF had a fast binding rate of Cd(II) within 2 min. Even in the column study, the ECMCF had a better breakthrough curve than two typical commercial ion exchange resins, Amberlite IRC 86 and Amberlite IR 120H, which were used as comparative sorbents.

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1. Introduction

Toxic heavy metal pollution is a serious problem in the environment and to human health. It widely exists in rivers and waterways [1]. Cadmium is a typical toxic heavy metal that not only causes choking, abdominal pain, anemia, renal dysfunction and diarrhea, but also has been listed as a carcinogen by the US Environmental Protection Agency [2]. Cadmium ions have little tendency to hydrolyze at pH less than 8, but at pH greater than 11, all cadmium ions exist as a hydroxo-complexes. Due to its high toxicity and non-degradable nature, the metal ion has gained wide public attention [3]. The drinking water guideline value recommended by the World Health Organization is 0.003 mg Cd/L [4]. Thus it is very important to develop effective methods for the removal of cadmium from wastewater before it enters into the natural environment. In this perspective, various technologies including chemical precipitation, chemical cementation, membrane filtration, electrolysis, sorption and biological methods have been employed in recent decades to remove cadmium from aqueous solutions [5–10]. Among the different methods, sorption is one of the most recommended treatment processes because of its simplicity, flexibility, and high efficiency in industrial applications [11,12]. The key point of sorption technology is to find a cost-effective and high performance sorbent.

The traditional sorbents applied in the removal of cadmium mainly include zeolites, clays, activated carbons, biomass and polymeric materials [12]. However, many of them suffer from low sorption capacities and difficult solid–liquid separation problems. A good sorbent should not only possess large surface area, but also need to exhibit rapid kinetics toward target metals in order to remove a high amount of metals in a short time, especially when the sorbent is employed in scaled-up industrial wastewater treatment. For rapid kinetics, the size of sorbents needs to be reduced, because size reduction generally leads to a fast removal rate of the metals [13]. Thin fiber-type sorbents have large surface area and are able to quickly bind metal ions. A thin sorbent fiber that is long enough can be used in a flow-through column without severe pressure drops or column clogging problems, allowing easier hydrodynamic transfer [13].

Carboxymethyl cellulose (CMC) is an ionic polysaccharide and rich in carboxyl groups, which can be used as binding sites for metal cations. Because CMC is regarded to be cheap, abundant, and biodegradable, it can be an attractive starting material to prepare sorbents [14]. Therefore, CMC-based adsorbents for metal ions and dyes have attracted wide interest in recent years [15–19].

In this study, CMC was used as a raw material to prepare a fiber form of cadmium-removal adsorbent using a simple fiber-spinning method. Sorption capacity of the developed fiber was first evaluated by batch sorption experiments. In order to confirm the fast binding property of the fiber, a continuous sorption system i.e., flow-through column, was operated and the performance was compared with

* Corresponding author: Tel.: +82 63 270 2308; fax: +82 63 270 2306.
E-mail address: ysyun@chonbuk.ac.kr, ysyun@jbnu.ac.kr (Y.-S. Yun).

two typical commercial ion exchange resins of Amberlite IRC 86 and Amberlite IR 120H.

2. Materials and methods

2.1. Materials

Cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$, 98.0%) was purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan). Amberlite IRC 86 (gel polyacrylic copolymer, H-form, beads and active group: carboxylic acid group), Amberlite IR 120H (gel styrene–divinylbenzene, H-form, beads and active group: sulfonic acid group), epichlorohydrin (ECH) and carboxymethyl cellulose sodium salt (molecular weight: 700 kDa, DS: 6.5–8.5 carboxymethyl groups per 10 anhydroglucose units, and theoretical amount of negative charge: 3.2 mmol/g) were all purchased from Sigma-Aldrich LLC. (Yongin, Korea). All other chemicals were of analytical grades, and purified water supplied by Direct-Q deionized water equipment was used throughout.

2.2. Preparation of the sorbents

In order to obtain stable fiber, the ECMCF was synthesized by two-step crosslinking. In the experiment, a 2% (w/v) CMC solution was prepared by directly mixing 5 g of NaOH and 2 g of CMC with 100 mL of deionized water. Then, 5 mL of ECH was added under stirring for 30 min and the mixture was extruded through a stainless steel spinneret (0.14 mm in diameter) into a methanol solution. The resulting fibers were again cross-linked with 20 mL of ECH in 100 mL of alkaline alcohol solution for 24 h at 45 °C. The products were washed with methanol and deionized water to remove ECH residues until the washed out water was neutral. Finally, the fibers were freeze-dried and subsequently labeled as ECMCF. To confirm the necessity of ECH crosslinking for making CMC fiber, pure CMC fiber (PCMCF) without ECH crosslinking was also prepared. The preparation procedure was as follows. Just as in the initial step of preparing the ECMCF, 5 g of NaOH and 2 g CMC were mixed in 100 mL deionized water in order to prepare 2% (w/v) CMC solution, which was spun into the methanol solution using the same nozzle used in preparing the ECMCF. Next, the obtained PCMCF was washed with methanol and then freeze-dried.

Because the ECMCF was Na-form according to the preparation process, it was necessary to change the H-form of Amberlite IRC86 and Amberlite IR 120H to Na-form resins in order to make an equitable comparison. The treatments of these two commercial resins were the same, and the procedure is as follows. Measured amounts of resins were soaked in 5% (w/v) NaCl solution and stirred for 24 h while controlling the pH to around 7 using 1 mol/L NaOH solution. Finally, the resulting Na-form resins were washed with deionized water until the washed water was neutral, and then they were freeze-dried.

2.3. Water-stability test of PCMCF and ECMCF

The purpose of the water-stability test of PCMCF and ECMCF was to investigate the effect of ECH for the preparation of CMC fiber. Certain amounts of PCMCF and ECMCF were put in two glass bottles, and water was added to each bottle separately. The fibers were examined and images were taken at set times of 0 min, 2 h, and 12 h in order to observe any change over time.

2.4. Characterization of PCMCF and ECMCF

FTIR spectra of PCMCF and ECMCF were performed using a Nicolet 8700 spectrometer (Thermo-Fusions Co., USA) and the test samples were prepared by the KBr-disk method. The morphologies of PCMCF and ECMCF were examined with scanning electron microscopy (SEM, JSM-6000, JEOL, Japan). Before analyzing, samples were coated in an Auto Fine Coater fitted with an Au target.

2.5. Batch sorption studies

For sorption experiments, 0.03 g of sorbent was brought into contact with 30 mL of Cd(II) solution in a 50 mL falcon tube. 1000 mg/L of Cd(II) solution was prepared as a stock solution for the further dilution. The pH values of the solutions were adjusted in the range of 2–7 using 1 M HNO_3 and 1 M NaOH solutions. All tubes were agitated in a shaker at 160 rpm and 25 ± 2 °C. Sorption isotherm experiments were conducted with solutions of different initial concentrations of Cd(II) in the range of 0–800 mg/L and the solution pH values were kept within 6 ± 0.1 throughout the sorption period by adjusting with 0.1 M HNO_3 or 0.1 M NaOH solution at appropriate time intervals. In the kinetic experiments, the sorption process was the same as the sorption experiments and the samples were collected at desired time intervals. Cd(II) concentrations of all samples were analyzed by an inductively coupled plasma spectrometer (ICP-7500, Shimadzu, Japan) after appropriate dilution.

The Cd(II) uptake was calculated from the following equation:

$$q = \frac{C_i V_i - C_f V_f}{M} \tag{1}$$

where q is the uptake of Cd(II) (mg/g), C_i and C_f are the initial and final Cd(II) concentrations in the solution (mg/L), V_i and V_f are the initial and final (initial plus added HNO_3 or NaOH solutions) solution volumes, respectively, and M is the dry weight of the sorbents used in Cd(II) sorption (g).

2.6. Column sorption studies

The column system which was purchased from Omnifit Ltd. (USA) contained a vertical borosilicate glass column of 1-cm internal diameter and 10-cm length. The column was packed with 3 mL of sorbents, and 285 mg/L of Cd(II) solution with an initial pH of 6 was pumped upward through the column using a peristaltic pump at a flow rate of 8 mL/min at 25 ± 2 °C. Excurrent samples were collected regularly from the column outlet to determine the residual Cd(II) concentration. Operation of the column was stopped when equilibrium was achieved between the inlet and outlet Cd(II) concentrations. The samples of Cd(II) concentration collected from the column were also analyzed using an ICP-7500.

3. Results and discussion

3.1. Water-stability test of PCMCF and ECMCF

In order to evaluate the effect of ECH for the synthesis of CMC fiber, the water-stability tests of PCMCF and ECMCF were investigated. The physical changes of PCMCF and ECMCF in water were observed, as shown in Fig. 1. The results showed that the fibrous form of both PCMCF and ECMCF could be seen clearly before adding water. However, the appearance change of PCMCF was obvious compared to the ECMCF when the water was injected. The visibility of PCMCF became less clear following the addition of water. Most of the fibers were dissolved after 2 h and were completely soluble after 12 h. In contrast, the ECMCF was almost stabilized without any changes of the appearance during the testing time. This indicated that CMC was successfully cross-linked with ECH. Moreover, some researchers also reported that ECH can be used as a good crosslinker to react with the hydroxyl groups of polysaccharides [14]. Therefore, ECH was required to give stability to the CMC fiber, without affecting the active carboxyl groups.

3.2. FTIR analyses

As stated, cross-linking was required to give mechanical strength to the prepared fiber without adversely affecting its metal binding