Colloids and Surfaces A: Physicochem. Eng. Aspects 502 (2016) 34–43

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Preparation and evaluation of adipic acid dihydrazide cross-linked carboxymethyl chitosan microspheres for copper ion adsorption

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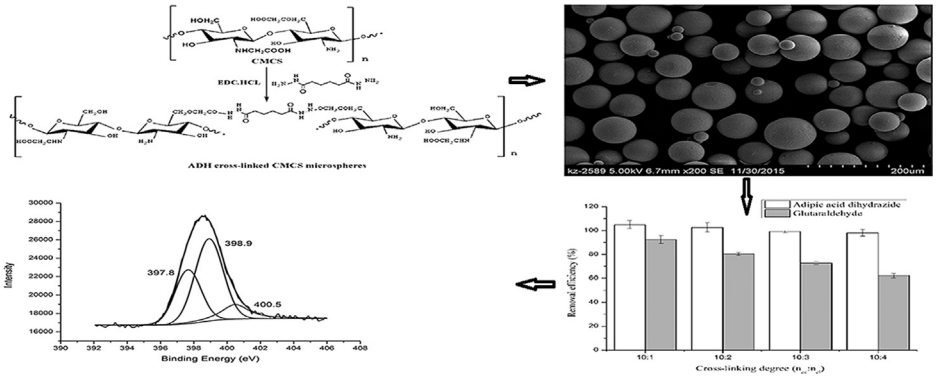
HIGHLIGHTS

- ADH was used to cross-link CMCS microspheres instead of traditional crosslinkers.
- XPS technique was performed to investigate the Cu^{2+} adsorption mechanism.
- The adsorbed Cu^{2+} mainly interacted with N and O atoms existing in ADH and CMCS.
- ADH in microspheres was able to supply extra adsorption sites for Cu^{2+} removal.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 January 2016
Received in revised form 24 April 2016
Accepted 1 May 2016
Available online 4 May 2016

Keywords:
Carboxymethyl chitosan
Adipic acid dihydrazide
Microsphere
Copper ion
Adsorption mechanism

ABSTRACT

Adipic acid dihydrazide (ADH) was used to cross-link carboxymethyl chitosan (CMCS) microspheres for Cu^{2+} removal from aqueous solution. SEM, FTIR, XPS and BET techniques were performed to characterize the ADH cross-linked CMCS (ADH-CMCS) microspheres. The effects on adsorption capacities of pH value, adsorption time, and initial Cu^{2+} concentration were investigated. The adsorption experiments demonstrated ADH-CMCS microspheres had high adsorption capacity for Cu^{2+} removal. Furthermore, in order to investigate the effect of ADH in ADH-CMCS microspheres on Cu^{2+} adsorption, cross-linking experiments and XPS tests were carried out to reveal the adsorption mechanism. The results suggested that ADH in ADH-CMCS microspheres had a compensation action on its consumption of binding sites for Cu^{2+} adsorption. The XPS etching results showed cross-linking reaction occurred mainly on the surfaces of the microspheres. The kinetics of Cu^{2+} adsorption on ADH-CMCS microspheres complied with the pseudo-second-order model, indicating a chemical reaction process. The adsorption data analysis using three different adsorption isotherm models indicated that ADH-CMCS microspheres were of heterogeneity surfaces. Moreover, the ADH-CMCS microspheres still exhibited good adsorption performances after the fifth adsorption-desorption cycle.

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http://dx.doi.org/10.1016/j.colsurfa.2016.05.003
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1. Introduction

Heavy metals discharged into environment are able to cause health hazard by reason of their toxicity and bioaccumulation in organisms [1]. Copper (Cu) is one of the most common heavy metal pollutants for its widespread application in industrial activities, such as metal plating, mining, metallurgy, alloy, and electronic goods manufacturing [2]. Excessive Cu can cause brain, skin, pancreas and heart diseases, although it is an essential element for human health at low concentration [3]. In order to protect human health and environment from the hazard of Cu, EPA (U.S Environmental Protection Agency) stipulates the maximum concentration of Cu is 1.3 mg/L in national primary drinking water [4]. Therefore, it is quite necessary to remove the excessive Cu from the contaminated drinking water.

Many technologies have been developed to remove heavy metals from the contaminated water, including chemical precipitation, chemical oxidation/reduction, coprecipitation, ion-exchange, flocculation, reverse osmosis, electrodialysis, electroplating and adsorption [5–9]. Among such technologies, adsorption is one of the most attractive methods to remove heavy metals from aqueous solution due to its high efficiency and easy operation [10]. Playing a key role in adsorption process, adsorbents such as activated carbon, activated alumina, zeolites, chitosan and its derivatives have been extensively investigated in water treatment [11].

Carboxymethyl chitosan (CMCS), a kind of chitosan (CS) derivative, has been widely used in water treatment due to the presence of abundant amine, hydroxyl and carboxyl groups [12,13]. However, CMCS has good solubility in water, which limits its application as adsorbent in water treatment and may even cause secondary pollution to water. Various physical and chemical methods have been employed to promote the feasibility and stability of CMCS in aqueous solution and increase the resistance to biochemical and microbiological degradation [14,15]. Most of them refer to the modifications that cross-link the CMCS adsorbents with traditional crosslinkers such as methanal [16], glutaraldehyde [17] or epichlorohydrin [18]. But the adsorption capacities of the cross-linked adsorbents may significantly decrease, especially in the case of chemical reactions occur between chemical reagents and active groups (amine group, hydroxyl group and carboxyl group), because these active groups are consumed after cross-linking [19]. In addition, the potential toxicity and recontamination issue of these chemical reagents must be taken into account during the water treatment.

Compared with most of the traditional crosslinkers, adipic acid dihydrazide (ADH), a low molecular weight compound that has a hydrazide group at each end, is able to supply extra adsorption sites for heavy metals, which can maintain or even increase the adsorption capacities of the cross-linked adsorbents in theory [20]. Due to its water-soluble, odorless and low toxic properties, ADH has been used as a crosslinker in many fields, including preparing mechanical latexes films and injectable oxidized hyaluronic acid hydrogel [21,22]. The introduction of ADH enables the reaction with latexes or oxidized hyaluronic acid mentioned above, which makes the structures of the films and hydrogel stable in practical application. Similarly, CMCS contains a large number of carboxyl groups that are able to react with amino groups existing in ADH. After the reaction, the imine groups in ADH can supply extra adsorption sites for heavy metals. Nevertheless, there are few published literatures using ADH to cross-link CS and its derivatives as adsorbents to remove heavy metals from aqueous solution as yet.

In the present study, ADH cross-linked CMCS (ADH-CMCS) microspheres were prepared by inverse suspension method. In order to make a comprehensive investigation of the properties of ADH-CMCS microspheres, batches of experiments were carried out as follows. Scanning electron microscope (SEM), Fourier transform infrared (FTIR), Brunauer-Emmett-Teller (BET) and X-ray photoelectron spectroscopy (XPS) were used to characterize the ADH-CMCS microspheres. Several adsorption experiments were conducted to evaluate Cu^{2+} adsorption of the microspheres from aqueous solution at conditions of various pH values, contact time, and initial Cu^{2+} concentrations. The effect of cross-linking degree on Cu^{2+} adsorption was studied via comparing two kinds of CMCS microspheres cross-linked by different crosslinkers. XPS technique was performed to investigate the adsorption mechanism through analyzing N 1s, O 1s and Cu 2p spectra of the microspheres. Additionally, the regeneration and reusability of the microspheres were examined by adsorption-desorption tests for five times.

2. Materials and methods

2.1. Materials

CMCS (pharmaceutical grade, degree of substitution >80%, and a viscosity of 20 cps) was supplied by Nantong green god biological engineering Co., Ltd. (China). ADH was provided by Adamas reagent Co., Ltd. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCL) was provided by Shanghai source biological technology Co., Ltd. All other chemicals used in this study were of analytical grade and supplied by Sinopharm. Stock solution of 1000 mg/L was prepared by dissolving appropriate amounts of copper sulfate pentahydrate in distilled water and diluted to 1000 mL. Working solutions ranging from 10 to 400 mg/L of Cu^{2+} were prepared by diluting the stock solution. Adjustment of pH was carried out using 0.1 mol/L HCL and 0.1 mol/L NaOH.

2.2. Preparation of ADH cross-linked CMCS microspheres

Firstly, 1.0 g CMCS was dissolved in 20 mL distilled water and stirred at room temperature until becoming transparent, then viscous solution was obtained (solution A). Thereafter, 0.16 g ADH and 0.18 g EDC·HCL were added into 1 mL distilled water, respectively (solution B and C). The pH values of the above suspensions were adjusted to 4.5 using 0.1 mol/L HCL and 0.1 mol/L NaOH. The pH value of the reaction system should be strictly controlled in acidic condition. Afterwards, 1 mL Span80 was dispersed into 50 mL of liquid paraffin under the stir of electric mixer at 500 rpm (Oil phase).

Furthermore, 10 mL solution A was slowly added into the oil phase by a sterile syringe without needle under the stir of 800 rpm at 25 °C. After 20 min, solution B and C were successively added into the mixed suspension above slowly, and continually stirred for 6 h till the end of reaction. The product was separated by the 120 mesh sieve and washed with tap water repeatedly, then rinsed with distilled water and alcohol of different concentrations, and dried in hot air at 40 °C. The final ADH-CMCS microspheres were weighed. The reaction process above is shown in Scheme 1.

2.3. Characterization of ADH cross-linked CMCS microspheres

FTIR spectra were measured by Nicolet AVATAR360 instrument (FTIR, Nicolet Instrument, Thermo Company, Madison, USA) via a KBr pellet method to ensure the formation of production. The morphology and size of microspheres were obtained with JSM-840 scanning electron microscope (SEM, JEOL, Japan). Thermo ESCALAB 250XI X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, USA) was used to study the adsorption mechanism by analyzing the binding energy of nitrogen, oxygen and copper elements on CMCS and ADH-CMCS microspheres before and after Cu^{2+} adsorption. The specific surface area and pore size of ADH-CMCS microspheres were measured by NOVA 1200e BET Surface Area & Pore Size Analyzer (BET, Quantachrome Ins, USA).

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