Chemical Engineering Journal 229 (2013) 217–224

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Chitosan supported on porous glass beads as a new green adsorbent for heavy metal recovery

Chun Shen, Yujun Wang *, Jianhong Xu, Guangsheng Luo *

State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

HIGHLIGHTS

- A new green adsorbent-chitosan supported on porous glass beads has been synthesized.
- The loading amount of chitosan ranges from 5.22 wt.% to 12.07 wt.%.
- Capacities for Cu^{2+}, Pb^{2+}, Ag^{+}, and Cd^{2+} are 7.27, 8.84, 5.15, and 4.29 m mol/g, respectively.
- This adsorbent reached 100% recovery after 5 cycles showing good regeneration performance.

ARTICLE INFO

Article history:
Received 18 April 2013
Accepted 1 June 2013
Available online 13 June 2013

Keywords:
Chitosan
Porous glass beads
Heavy metal adsorption
Recyclable support

ABSTRACT

This paper presents a new green adsorbent-chitosan supported on porous glass beads and its heavy metal adsorption properties. The adsorbent was characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Thermo Gravimetric Analyzer (TGA), and BET analysis. The adsorption properties and capacities to several kinds of heavy metal ions were determined, different from pure chitosan pellets, the as-prepared adsorbent showed fast kinetic, high adsorption capacities, and good regeneration performance. When the content of chitosan was lower than 12.07 wt.%, more than 90% of lead ions were adsorbed within 90 min with an initial concentration of 100 mg/L at 303 K. Chitosan supported on porous glass beads showed high adsorption abilities for heavy metal ions with capacities achieving up to 2.47, 7.27, 8.84, 5.15, and 4.29 m mol/g for Ni^{2+}, Cu^{2+}, Pb^{2+}, Ag^{+}, and Cd^{2+}, respectively. This adsorbent could be regenerated easily by dilute ammonia solution, showing 100% recovery after five cycles. The prepared porous glass beads supported with chitosan exhibit high mechanical strength, large specific surface area, and no obvious swelling in water, offering possibilities for future practical use.

1. Introduction

During the past few years, significant research efforts have been dedicated to the environmental contamination with heavy metal ions because of their high toxicity and non-biodegradability [1]. Many techniques have been developed for heavy metal ions removal, such as chemical precipitation, filtration, electrochemical treatment, ion exchange, liquid–liquid extraction, adsorption, chemical oxidation or reduction, and evaporation recovery [2–8].

Among these methods, adsorption is one of the most effective, economical and widely used methods for heavy metals removal in wastewater [9–11]. Studies have been carried out to develop more effective and cheaper adsorbents, which are abundant in nature and widely available. Chitosan has great potential for heavy metal adsorption based on its several advantages, such as non-toxicity, biocompatibility, biodegradability, and advantageous presence of hydroxyl, amino active functional groups on the backbone chain [12–25].

However, as an adsorbent, chitosan still presents some disadvantages. Weak mechanical properties, low surface area and poor chemical resistance have limited its wide applications in industry. Moreover, chitosan powder or flake swells in water and forms colloidal suspension causing difficulties in separation and making it unsuitable for use in an adsorption column [15,16]. Although the hydroxyl and amino groups are the main reason for adsorption of heavy metal ions, these active groups are not available when they are in a gel or in their nature forms [26]. Several attempts have been made to modify the structure of chitosan chemically, and the adsorption performance was evaluated through the adsorption for heavy metal ions. Li [13] and Monier [27] investigated the adsorption of heavy metal ions on magnetic chitosan. In Li's work [13], magnetic amination chitosan beads were used as the adsorbent for Cu (II), Zn (II) and Cr (VI) from aqueous solution. They

* Corresponding authors. Tel.: +86 10 62783870; fax: +86 10 62770304.
E-mail addresses: wangyujun@mail.tsinghua.edu.cn (Y. Wang), gsluo@tsinghua.edu.cn (G. Luo).

1385-8947/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.06.003

found that metal ion adsorption on the surface of magnetic chitosan included multilayer physical and chemical adsorption. The chemical adsorption played a decisive role. The capacities for Cu (II), Zn (II) and Cr (VI) ions are 3.20, 1.54 and 4.81 m mol/g, respectively. The kinetic and thermaldynamic parameters of the adsorption were estimated in Monier's work [27]. They noted that the adsorption process is exothermic and followed the Langmuir model. The maximum adsorption capacities for Hg (II), Cd (II) and Zn (II) were 0.67, 1.07 and 0.80 m mol/g, respectively. Sarkar et al. [15] investigated the effectiveness of surfactant (sodium dodecyl sulfate) modified chitosan beads for adsorption of Cu (II), Ni (II) and Zn (II). The resultant beads showed high capacities with values of 3.46, 3.84 and 3.55 m mol/g, respectively. The adsorption of metal ions on dithiocarbamated chitosan was reported by Khan [28]. Chitosan hydrogel beads were modified by etherization reaction with the etherification agent of chloroacetic acid in Yan's work [29]. The modified adsorbent showed enhanced adsorption capacity for Cu (II) and high selectivity for Cu (II) in the presence of Pb (II) and Mg (II). Although a lot of studies have been put in on the enhancement of adsorption capacity of chitosan through chemical modification, using various chemicals, the adsorption capacity decreased after the cross-linking. Hasan et al. [26] pointed out that adsorption capacity for Cr (VI) enhanced by dispersing chitosan on an inert substrate. It is assumed that the active group became more readily available.

In this paper, we will explore the feasibility of preparing chitosan supported on porous glass beads as an effective adsorbent for heavy metal ions in water as shown in Fig. 1. In our previous works [30,31], a subcritical water treatment method for preparing porous glass beads with an egg-shell structure has been developed. After one hour's treatment with water at 573 K, the smooth and compact surface became porous, which was covered with uniform flakes, the specific surface area reached 162.6 m^2/g. There are three possible advantages for choosing porous glass beads as the support: first, the large specific surface area would help to adsorb chitosan powders onto the outer surface of porous glass beads. Porous glass beads, as an inert substrate would lead to exposure of more-active sites for adsorption; second, porous glass beads provide mechanical support for chitosan, which may help to decrease the cross-linked degrees promoting the adsorption capacities for heavy metal ions; third, porous glass beads are reusable, cheap and environmentally friendly, offering a more efficient alternative to bulk chitosan pellets. Porous glass beads supported with chitosan layer were characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Thermo Gravimetric Analyzer (TGA), and BET analysis. The adsorption properties including kinetic (using Pb^{2+} as the model ion) and capacities to several kinds of heavy metal ions (Ni^{2+}, Cu^{2+}, Ag^{+}, Cd^{2+}, Pb^{2+}) have been determined, and regeneration performance was explored as well.

2. Experimental

2.1. Materials and chemicals

Soda-lime glass microbeads with diameters ranging from 75 μm to 150 μm and a composition of 59.7 wt.% SiO_2, 25.1 wt.% Na_2O, 9.8 wt.% MgO, and 4.9 wt.% CaO were obtained from Hebei Chiye Corporation. These beads were sieved before application, and those ranging from 95 μm to 105 μm were taken as samples. Copper sulfate, nickel nitrate, silver nitrate, lead chloride, cadmium sulfate, sodium hydroxide, acetic acid, and glutaraldehyde solution (25 wt.%) were purchased from Beijing Chemical Plant. Sinopharm Chemical Reagent Co., Ltd. (Shanghai) provided the chitosan powder (molecular weight 50,000). All the chemicals were used as received without any further treatment.

2.2. Preparation and characteristic of porous glass beads supported with chitosan coating

The porous glass beads were prepared by subcritical water treatment method, as described in our previous work [31]. First, 200 g of water and 5 g of glass beads were placed in a tank reactor with a volume of 250 cm^3. Then the reactor was gradually heated to 573 ± 0.1 K and the pressure increased from atmospheric pressure to almost 8 MPa. The subcritical state was maintained for 60 min, and the reactor was cooled to room temperature naturally. The porous glass beads were separated by filtration and washed several times with deionized water before further use.

The porous glass beads show good ion exchange ability [31,32] (modifiers contained in the porous glass, namely Na^{+}, Ca^{2+}, and Mg^{2+}, could exchange with metal ions with higher electronegativities or hydrogen ions as proven in our previous work [33]. And porous glass beads could not show the ion exchange ability after being exchanged with hydrogen ions). Since we want to study the ability of chitosan-coated nanoparticles to adsorb heavy metal ions, other impacting factors should be eliminated; especially the effect of the support. Thus all the obtained porous glass beads were treated with hydrochloric acid to replace the metal ions contained in the shell part of porous glass with hydrogen ions. In the hydroxylation experiment, 0.5 g of the prepared porous glass was added

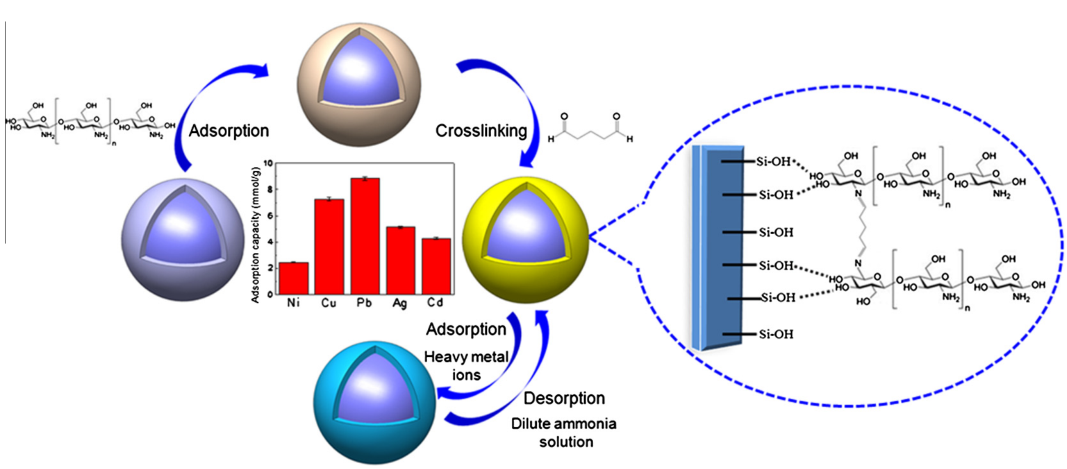

Fig. 1. Train of thought for this paper.