Chemosphere 214 (2019) 738–742

Contents lists available at ScienceDirect

Chemosphere

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

A biomimetic SiO_2@chitosan composite as highly-efficient adsorbent for removing heavy metal ions in drinking water

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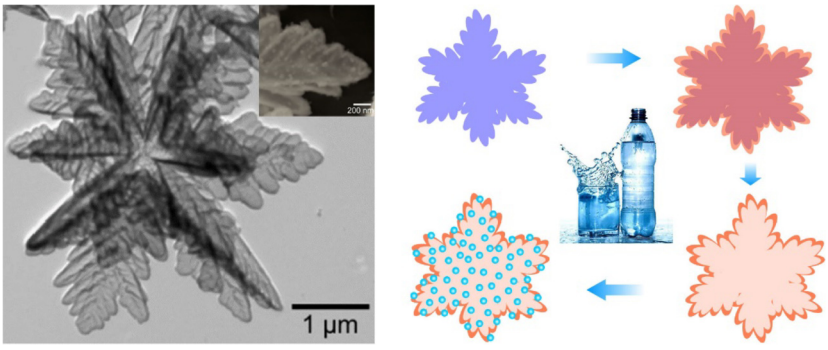
HIGHLIGHTS

- A unique biomimetic SiO_2@chitosan composite adsorbent is prepared.
- Leaf-like SiO_2@chitosan shows high adsorption performance toward As(V) and Hg(II).
- Agglomeration and loss of adsorbents are reduced by biomimetic structure.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 July 2018
Received in revised form
19 September 2018
Accepted 29 September 2018
Available online 2 October 2018

Handling Editor: T.S. Galloway

Keywords:
Adsorbents
Composite
Adsorption
Heavy metal ion
Drinking water

ABSTRACT

Highly efficient adsorbents for drinking water purification are demanded since the contaminants are generally in a low concentration which makes it difficult for conventional adsorbents. Herein, we present a novel biomimetic SiO_2@chitosan composite as adsorbent with a high adsorption capability towards heavy metal ions including As(V) and Hg(II). The hollow leaf-like SiO_2 scaffold within the adsorbent has a stable chemical property; while on the surface SiO_2, the chitosan nanoparticle provide a large amount of active sites such as amino and hydroxyl groups for adsorbing heavy metal ions. The special SiO_2 structure also prevents the agglomeration and loss of chitosan, which enables the efficient contact between the functional groups of chitosan and heavy metal ions. The SiO_2@chitosan composite exhibits maximum adsorption capacities of 204.1 and 198.6 mg g^{-1} towards Hg(II) and As(V), respectively. In addition, the removal efficiency reaches over 60% within 2 min. The adsorption performance enables the presented biomimetic adsorbent suitable for adsorbing low-concentration heavy metal ions, especially possessing a promising potential for drinking water purification.

1. Introduction

Contaminants in drinking water are mainly in the form of micro-pollution with a low concentration, which is different from the

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https://doi.org/10.1016/j.chemosphere.2018.09.172
0045-6535/

industrial pollution containing a high concentration of toxic substances (Kokkinos et al., 2018; El-Moselhy et al., 2017; Al-Qodah and Al-Shannag, 2017). Among many contaminants, inorganic micro-pollutants mainly include heavy metal ions such as Pb(II), As(III), Hg(II), Cu(II), and Cr(V) which are highly harmful to human body. The sources of heavy metal ions in drinking water are extensive including industrial production and dissolution of heavy metals in natural materials (Sener et al., 2017). The purification process is commonly complicated, high-cost, and time-consuming. Therefore, how to efficiently remove the low-concentration heavy metal ions from drinking water resource remains a great challenge. Among many purification approaches, adsorption strategy using adsorbents is currently one of the most attractive one (Onur et al., 2018; Ko et al., 2018). However, because of the low concentration of heavy metal ions in the drinking water, it is difficult to achieve deep adsorption. Since that, emerging adsorbents with a highly-efficient adsorption performance are desired.

Chitosan (CS), which is obtained from deacetylation of chitin, is widely existed in shells of crustacean shrimps and crabs, carapace of insects, cell walls of fungals and plants. CS has a good biocompatibility and biodegradability, and is broadly used in pharmaceutical, chemical, papermaking and environmental protection industries (Wu et al., 2018; Mittal et al., 2016). The solubility of CS is related to the degree of deacetylation, relative molecular mass, and viscosity. It contains a large number of functional groups including $-NH_2$ and $-OH$, which enables a good adsorption capacity towards heavy metal ions. Researchers have reported many methods to modify CS such as introducing a cross-linking reaction to stabilize chitosan (Zhang et al., 2018; Taghizadeh and Hassanpour, 2017; Ngwabebhoh et al., 2016; El-Salam et al., 2017). In addition to the complex operation, the quantity of functional groups decreases, which reduces the adsorption capacity of CS.

Here, we present a novel CS-based nanocomposite adsorbent consisting of a biomimetic SiO_2 micro-/nanostructure and CS nanoparticles coating on the surface. As illustrated in Fig. 1, at first, a CdS micro/nanostructure with a biomimetic leaf-like morphology was synthesized. Then, a layer of SiO_2 was coated on the surface. After the CdS core was removed by acid, a hollow SiO_2 shell with a leaf-shaped structure was constructed. At last, on the surface of SiO_2, a CS layer was coated through a dissolution-deposition mechanism, forming a biomimetic SiO_2@CS nanocomposite. In this composite, the leaf-like structure enables the tip of each leaf contacts with each other in solution. Since that, a frame structure would be formed, resulting in a remained apace between each SiO_2@CS structure, instead of severely overlapping by tight agglomeration. It enables the sufficient exposing of adsorption sites on the composite for capturing heavy metal ions in solution. The prepared SiO_2@CS composite exhibits a high adsorption performance towards As(V) and Hg(II). The maximum adsorption capacities towards As(V) and Hg(II) are 198.6 and 204.1 mg g^{-1}, respectively, which are much exceeding many adsorbents such as iron-chitosan composite (Gupta et al., 2009), chitosan flakes (Gupta et al., 2012), cross-linked magnetic chitosan (Abou El-Reash et al., 2011), ethylenediamine-modified activated carbon (Li et al., 2009), etc.

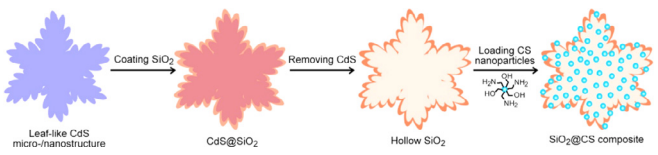

Fig. 1. Illustration for the preparation of the SiO_2@CS composite with a biomimetic leaf-like structure.

2. Experimental

2.1. Synthesis of CdS micro-/nanostructure

The biomimetic CdS micro-/nanostructure was prepared by using dimethyl sulfoxide (DMSO) as the growth template *via* a hydrothermal method. All the chemicals were purchased from purchased from Baierdi Chemical Technology Co., Ltd., and used without further purification. First, 1 mmol of $CdCl_2 \cdot 5H_2O$ and 1 mmol of thiourea ($CH_4N_2O_4S$) were dissolved in 35 mL of deionized water and stirred at room temperature to form a homogeneous solution. Then, 0.15 mL of DMSO was added to the solution, stirring was continued for 10 min until the solution was homogeneous. Finally, the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and sealed, then maintained at 170 °C for 8 h. After that, the autoclave was naturally cooled to room temperature. The orange precipitate at the bottom was collected, washed for several times with ethanol and Millipore water, and dried at 60 °C for 6 h.

2.2. Preparation of hollow leaf-like SiO_2

To achieve a hollow SiO_2 structure as the carrier of CS, 0.04 g of CdS, 40 mL of ethanol, and 8 mL of deionized water were mixed, then 2 mL of aqueous ammonia solution was added and stirred for 30 min. Subsequently, 1.6 mL of ethyl silicate solution was slowly added, and kept stirring for 2 h. The sample was collected and centrifuged. The reddish-brown precipitate was washed alternately with water and ethanol for several times, and placed in a vacuum oven at 60 °C for 6 h. Finally, the dried sample was dispersed in a diluted hydrochloric acid solution (0.2 mol L^{-1}) in a fume hood, and stirred for 15 min. The sample was centrifuged and washed with water and ethanol for several times. The product was dried in an oven at 60 °C for 6 h.

2.3. Preparation of SiO_2@CS nanocomposite

The CS particles were loaded on the obtained SiO_2 on the basis of a dissolution-deposition mechanism since the CS dissolves in acid solution and deposits in natural and alkaline surroundings. At first, 0.05 g of CS was added into 40 mL of acetic acid solution at a pH value of 3. After the CS was fully dissolved by sonication for 15 min, 0.01 g of the hollow SiO_2 was added and continuously stirred for 2 h. A certain amount of Na_2CO_3 was added to adjust the pH value of the solution to ~8. At last, the sample was centrifuged and washed for several times with water, and dried in a vacuum oven at 60 °C for 4 h.

2.4. Characterizations

The morphology, structure and composition of the samples were characterized by using scanning electron microscopy (FEI Sirion–200 field–emission scanning microscope microscope, FESEM), transmission electron microscopy (TEM) and high resolution TEM (HRTEM, JEM-2010 Microscope equipped with Oxford INCA EDX system, accelerating voltage 200 kV), photoelectron spectroscopy (XPS, ESCALab MK II, Mg Kα X-rays as excitation light source) and Philips X-ray scattering meter with Cu Kα1.5418 Å as X-ray source). The XRD peaks of this material were compared to standard JCPDS (Joint Committee on Powder Diffraction Standards) cards. Fourier transform infrared spectroscopy (FTIR) was determined by a JASCO 410 spectrometer and by KBr pelleting. The concentration of the heavy metal ion was measured on an inductively coupled plasma (ICP) atomic emission spectrometer (Jarrell-Ash model ICAP 9000).