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Original article

Supported carbon dots decorated with metallothionein for selective cadmium adsorption and removal

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ABSTRACT

Carbon dots are prepared and immobilized onto spherical SiO_2 through a one-step thermal oxidation and then decorated with metallothionein (MT), a protein with high affinity towards thiophilic metals. The MT-carbon dots composites are characterized by means of FT-IR, SEM and TGA, giving rise to a MT loading amount of 823 $\mu g\,g^{-1}$. The adsorption of cadmium by the composites is a fast process and follows *Langmuir* model. In comparison with native SiO_2, a 2- and 2.4-folds improvement on the static and dynamic adsorption capacity of the composites for cadmium are obtained, respectively. Moreover, the adsorption efficiency is not affected by the presence of other metals. Finally, the composites are successfully applied for the removal of cadmium in a series of environmental water samples.

1. Introduction

Known as the cause for Japan Itai-Itai disease, cadmium is among the most toxic heavy metals in surface water and soil. The total production of cadmium worldwide is estimated to be 22,300 t according to the British Geological Survey [1]. Besides natural release of cadmium through the weathering of rocks, forest fire and volcanoes, human activity accounts for almost half of the cadmium production, including manufacturing of batteries, pigments, plastic stabilizers, metal plating, and phosphate fertilizers [1,2]. Chronic accumulation of cadmium in human bodies causes the damage in kidney, liver, cardiovascular and skeletal systems, while high dosage uptake causes Itai-Itai disease or even death [3]. Cadmium is also identified as a human carcinogen [4]. Due to its detrimental effect to human health, the permissible cadmium concentration of WHO [5] and EPA [6] guidelines in drinking water is strictly restricted to below 0.003 and 0.005 mg L^{-1}, respectively.

Various physical and chemical approaches have been employed for cadmium removal, including precipitation, ion exchange, membrane separation and adsorption [1]. Among them, adsorption techniques stand out from other approaches with advantages of simplicity, favorable efficiency, and cost-effective. Conventional sorbents such as active carbon, zeolite, and metal oxides, are usually employed for the adsorption and removal of heavy metal species including cadmium. However, they always suffer from drawbacks of low capacity or limited efficiency.

Carbon based nanomaterials, including carbon nanotubes (CNTs), graphene and their derivates, are the most promising sorbents for several organic pollutants and heavy metal species owing to their large specific surface area, abundant binding sites and mechanical stability [7]. The applications of carbon based nanomaterials as heavy metal adsorbent are massively reviewed [8–14]. Metal adsorption capacity of CNTs is directly related to their total active surface acidity [10]. Oxidizing CNTs with H_2O_2, $KMnO_4$ and HNO_3 increased the adsorption capacity of cadmium mainly due to the increased oxygen-containing functional groups [15]. The preparation of graphene oxide (GO) from graphite using Hummers methods introduces more oxygen-containing groups thus generally absorbs more metal cations than non-functionalized CNTs [16]. However, for the case of GO nano-sheets, their immobilization on either magnetic core for magnetic separation [17] or solid support for on-line column packing [18] is necessary for the isolation of GO from aqueous medium. Meanwhile, the high cost of both CNTs and GO restricts their application in environmental protection [19]. Besides, neither CNTs nor GO prefers to adsorb cadmium rather than other heavy metal cations, thus functionalization procedure is necessary to improve the adsorption selectivity [19,20]. Metallothioneins (MTs) are low molecular weight (6–7 kDa) of cysteine-rich proteins that exhibit high

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capacity for metal chelation [21]. Our previous work has shown an obvious improvement on adsorption selectivity towards cadmium after surface decoration of immobilized GO with Cyanobacterium MTs [22]. The tolerance level for co-existing ions especially alkali and alkaline earth metals has been significantly improved up to 800,000 folds after MT decoration.

As the latest member in nano carbon family, carbon dots (C-dots) have attracted much attention due to their unique photoluminescence properties [23,24], but the adsorption potential has not been much exploited yet. In fact, carbon dots possess more oxygen-containing groups in comparison with its siblings, thus could potentially have higher metal adsorption capacity. Besides, unlike CNTs and graphene, the simple and economic preparation steps make the large scale production and commercialization of C-dots possible. By thermal oxidation of proper precursors on solid supports such as zeolite [25] the preparation and immobilization of C-dots could be facilitated in one step, resulting in an ideal sorbent with suitable mechanic strength and versatile binding surface for various targets.

In the present work, metallothionein isolated from rabbit liver is decorated onto the surface of supported C-dots to form a novel sorbent for the selective adsorption and removal of cadmium. The adsorption behaviors of cadmium, including the pH-dependent adsorption, the sorption capacity and selectivity, the sorption kinetics and isotherms, are investigated. This novel composite is successfully applied for the removal of cadmium in environmental waters.

2. Experimental

2.1. Instrumentation

A GGX-200 atomic absorption spectrometer (Beijing Hai-Guang Instrument Co. Ltd, Beijing, China) with deuterium background correction is employed. A cadmium hollow cathode lamp (General Research Institute for non-ferrous metals, Beijing, China) is used as light source at a wavelength of 228.8 nm and operated at 5 mA, with a 0.4 nm slit width. Pyrolytically coated graphite tubes are used. Peak area (integrated absorbance) values are adopted for quantification. The GFAAS temperature program for the detection of cadmium is given herein (ramp/holding time): drying at 100 °C (15 s/10 s), pyrolysis at 350 °C (15 s/10 s), atomization at 1900 °C (1 s/3 s), and cleaning at 2100 °C (1 s/3 s).

A FIAlab 3000 sequential injection system (FIAlab Instruments Inc., Medina, WA, USA) equipped with a 24,000-step syringe pump (Cavro, Sunnyvale, CA, USA, with a 2.5 mL syringe) and a 6-port selection valve is employed for fluidic delivery and sample processing.

2.2. Chemicals

Unless otherwise specified, all the chemicals used in the present study are analytical reagent grade obtained from the Sinopharm Chemical Reagent Co. (Shanghai, China). Metallothionein (MT) isolated from rabbit liver is purchased from Yuanye Bio-Technology Co. Ltd (Shanghai, China). Spherical SiO_2 particles (75–150 μm in diameter, Makall Group, Qingdao, China) are dried at 120 °C for 2 h before use.

A stock solution of cadmium (1000 mg L^{-1}) is prepared by dissolving appropriate amount of cadmium pellet in 1.0 mol L^{-1} HNO_3. Working standards of various concentrations are prepared by serial dilution of the stock solution. pH value of the sample solution is adjusted to pH 6.0 by using 0.1 mol L^{-1} HNO_3 and/or 0.1 mol L^{-1} NaOH. Deionized (DI) water (18.2 MΩ cm) is used throughout.

2.3. One-step preparation of supported C-dots

One-step preparation of supported C-dots is achieved by thermal oxidization of the homogeneous mixture of SiO_2 spherical particles and the precursor to C-dots, as illustrated in Fig. 1A.

The preparation of precursor to C-dots: Briefly, 2 g of $H_2N(CH_2)_{10}COOH$ is dissolved in 25 mL of DI water, followed by the addition of 0.45 g NaOH. 25 mL of citric acid (8% (m/v)) is then added slowly under vigorous stirring. Thereafter, the white precipitate is collected, washed and dried at room temperature for 24 h and followed by further drying at 85 °C for 2 h. The dried

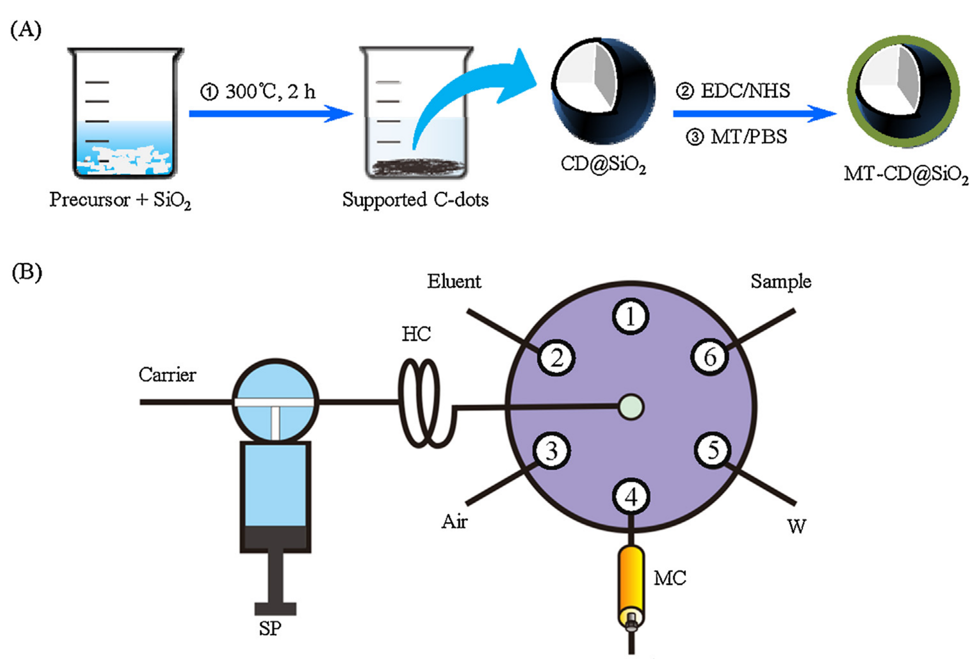

Fig. 1. (A) Scheme of the fabrication of supported C-dots decorated by MT. (B) Flow manifold of the sequential injection system for conducting on-line adsorption of cadmium by MT-CD@SiO_2. SP, syringe pump; HC, holding coil; W, waste; C, microcolumn.