

# Uniform surface modification of diatomaceous earth with amorphous manganese oxide and its adsorption characteristics for lead ions



Song Li, Duanyang Li, Fei Su, Yuping Ren, Gaowu Qin\*

Key Lab for Anisotropy and Texture of Materials (MoE), Northeastern University, Shenyang 110819, China

## ARTICLE INFO

### Article history:

Received 16 April 2014

Received in revised form 27 August 2014

Accepted 30 August 2014

Available online 6 September 2014

### Keywords:

Diatomaceous earth

MnO<sub>2</sub>

Adsorption

Heavy metal ions

## ABSTRACT

A novel method to produce composite sorbent material comprising porous diatomaceous earth (DE) and surface functionalized amorphous MnO<sub>2</sub> is reported. Via a simple in situ redox reaction over the carbonized DE powders, a uniform layer of amorphous MnO<sub>2</sub> was anchored onto the DE surface. The hybrid adsorbent was characterized by X-ray diffraction, scanning electron microscopy, and infrared spectroscopy. The batch method has been employed to investigate the effects of surface coating on adsorption performance of DE. According to the equilibrium studies, the adsorption capacity of DE for adsorbing lead ions after MnO<sub>2</sub> modification increased more than six times. And the adsorption of Pb<sup>2+</sup> on the MnO<sub>2</sub> surface is based on ion-exchange mechanism. The developed strategy presents a novel opportunity to prepare composite adsorbent materials by integrating nanocrystals with porous matrix.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Water contamination by toxic metal ions is considered a major environmental problem world widely. Pb<sup>2+</sup>, for example, is a typical hazardous heavy metal ion that tends to accumulate in food chains, causing numerous diseases and disorders. Strict environmental regulations on the discharge of Pb<sup>2+</sup> ion containing water into natural environment have been setup in many countries, rising demands for technologies to remove the Pb<sup>2+</sup> ion from industrial waste water. Among the developed technologies, adsorption using various sorbent materials has attracted considerable interest due to its merits of efficiency, economy and simple operation. For the removal of highly toxic heavy metal ions from water, the main challenge is to develop novel sorbent materials with high adsorption capacity and efficiency.

Natural porous materials with high specific surface areas are generally used as sorbents for heavy metal ions. To increase the adsorption capacities, the natural materials need to be modified with transition metal oxides, which is often achieved by dispersing the porous matrix in the synthesizing solution for nanocrystals growth. Nanosorbents immobilized within porous materials such as laterite [1], carbon nanotubes [2], and diatomite [3,4] exhibited

enhanced adsorption performance for heavy metal ions. During the synthesis process, metal oxide nanocrystals nucleate and grow both inside the internal pores and in the bulk solution. In many cases, the number of nanocrystals grown in the bulk solution is yet much larger than that of grown inside the pores if the matrix was not properly treated [5] because the reagent diffusion inside the pores and channels is limited. Even some decorating particles form inside the porous matrix, they are loosely bound to the matrix surface. When the composite serves as the sorbent, especially in the dynamic adsorption process using fixed bed [6], aggregation of metal oxide nanoparticles may occur and reduce working efficiency. To overcome the problem, there is a growing demand for hybrid sorbent materials with nanocrystals uniformly anchored on the surface of porous structures.

Natural diatomaceous earth (or diatomite, DE), as the fossilized skeletal remains of aquatic unicellular algae, has a porous structure and finds many applications in adsorption of pollutants [4,7–9], drug delivery carrier [10], catalyst support [11], or template to fabricate porous materials [12]. In this work, we report the formation of MnO<sub>2</sub> layer via an *in situ* reaction onto the DE surfaces without the formation in the bulk solution. We also report the applications of this material for the removal of lead ions in the water purification field. It was found that the MnO<sub>2</sub> modification largely enhanced the adsorption capacity of DE for Pb<sup>2+</sup> ions. The adsorption kinetics, pH influence, isotherms, as well as the surface chemistry were investigated.

\* Corresponding author. Tel.: +86 24 8369 1586.  
E-mail address: [lis@atm.neu.edu.cn](mailto:lis@atm.neu.edu.cn) (G. Qin).

## 2. Experimental

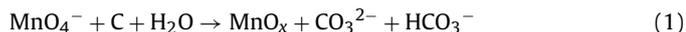
The diatomaceous earth (DE) used in this work was obtained from Changbai, China. The experimental procedure for functionalizing diatomaceous earth with nano-MnO<sub>2</sub> consists of two steps: (i) formation of carbon layers on the pore surface of DE, and (ii) growth of MnO<sub>2</sub> in the DE pores to replace the carbon layer. Typically, 100 mL of glucose solution (5 wt%) containing 20.0 g of DE powders was agitated for 2 h at room temperature. The DE slurry collected by filtration was calcined at 600 °C for 2 h in nitrogen gas to coat a carbon layer on the surface of DE powders. Subsequently, 1.0 g of carbon covered DE powders was dispersed into 100 mL of KMnO<sub>4</sub> solution (0.38 mol L<sup>-1</sup>) under agitation. The resulting suspension was microwave heated for 10 min. The microwave power was set as 700 W. After naturally cooled to room temperature, the product was collected and washed with deionized water for several cycles.

X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert Pro X-ray powder diffractometer using copper K $\alpha$  radiation. Scanning electron microscopy (SEM) was carried out using a JEOL 6510A scanning electron microscope at an accelerating voltage of 15 kV. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3000 analyzer. Prior the measurements, the samples were degassed in vacuum at 200 °C for 4 h. Fourier transform infrared spectra (FTIR) were recorded on a spectrometer. Samples were dried at 120 °C for 10 h before the FTIR measurement.

Adsorption for Pb<sup>2+</sup> ion was measured *via* batch mode adsorption experiments which were conducted using typically 0.1 g of adsorbent with 100 mL of aqueous solution containing Pb<sup>2+</sup> ions of scheduled concentration at a constant temperature. For kinetic study, samples were taken and then filtered to separate the adsorbent from the solution at time intervals. The residual heavy metals in the solution were determined with an inductively coupled plasma-mass spectrometer. To evaluate the effect of pH on adsorption, 0.1 M NaOH or 0.1 M HCl solutions were used to adjust the pH of the Pb<sup>2+</sup> solution. No buffer was added during the adsorption measurement. The pH value of the solution was monitored using a pH meter. The amount of adsorbed Pb<sup>2+</sup> ion per unit mass of adsorbent was calculated from  $q = (C_0 - C_t)/m$ , where  $C_0$  and  $C_t$  are the concentrations of Pb(II) in the solution before and after adsorption, respectively.

## 3. Results and discussion

A two-step method was adopted to synthesize the hybrid adsorbent MnO<sub>2</sub>@DE. Firstly, The DE powders were coated by a carbon layer through thermal-carbonization of adsorbed glucose which has been successfully applied to produce carbon encapsulated core-shell materials [13,14]. After the carbon-coated diatomaceous earth (C@DE) was dispersed in KMnO<sub>4</sub> solution, MnO<sub>2</sub> grew on the surface of C@DE as a result of the following redox reaction: [15]



The reaction is slow because atomic diffusion across the interface is difficult so that hours are generally required to exhaust the carbon. However, under the microwave irradiation, the redox reaction is accelerated and the formation of MnO<sub>2</sub> stops naturally when the carbon layer is used up. Fig. 1(a) shows the XRD spectra of DE powders before and after surface modification with carbon and manganese oxide. From the results, the raw DE powders are mainly composed of amorphous silica and the sharp peaks at 20.8° and 26.7° which can be assigned to crystalline quartz are characteristic of bio-silica [16]. Some other small peaks may be due to the impurity phases in the DE minerals. For samples prepared in the KMnO<sub>4</sub> solution, no obvious peak related to Mn was found. After

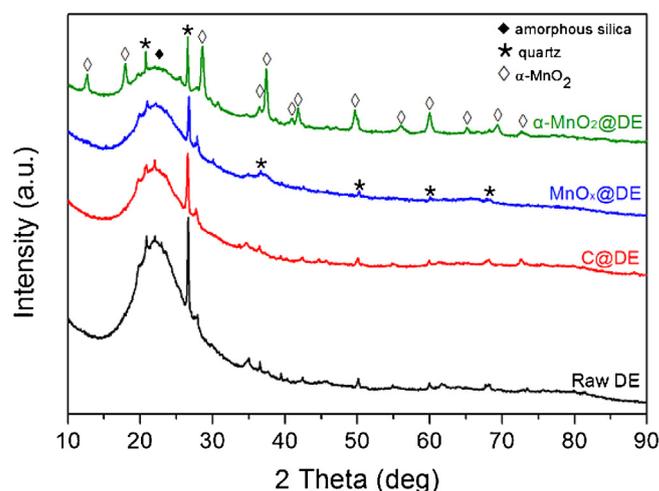


Fig. 1. XRD profiles for DE powders before and after surface modification with carbon, amorphous MnO<sub>2</sub>, and crystallized  $\alpha$ -MnO<sub>2</sub>.

calcination at 450 °C for 2 h, the peaks that can be indexed to tetragonal  $\alpha$ -MnO<sub>2</sub> (ICDD No. 44-0141) appear in the XRD spectrum, suggesting that the amorphous MnO<sub>x</sub> forms on the surface of DE after the redox reaction. To determine the oxidation state of the Mn element in the amorphous layer of MnO<sub>x</sub>@DE hybrid, X-ray photoelectron spectroscopy was performed. The survey spectrum of the studied hybrid before lead ion adsorption in Fig. 2(a) exhibits dominant peaks of Mn, Si, O, and Fe along with C(1s) peak due to the surface contamination. The peaks at 642.5 and 654.1 eV of high-resolution XPS spectrum in Fig. 2(b) agree well with reported Mn 2p in MnO<sub>2</sub> [17], which confirms that the manganese oxidation state is about 4.

The morphology of the DE powders after surface modification with amorphous MnO<sub>2</sub> was observed using SEM. As shown in Fig. 3(a), the hybrid material inherited the morphology of the raw DE powder. High-magnification SEM observation showed that a uniform layer of MnO<sub>2</sub> forms on the surface of DE. Fig. 3(b) displays the EDX mapping of MnO<sub>2</sub>@DE samples for O, Si and Mn elements. It was found that the Mn atoms have the same distribution as the Si and O elements, indicating that a thin layer of MnO<sub>2</sub> formed on the DE particles surface. When the porous DE material was functionalized with metal oxide nanocrystals using solution chemical methods, the specific surface area is generally reported to increase because the contribution of the synthesized metal oxide nanocrystals [1,4]. However, in this work, the specific surface area ( $A_s$ ) of DE powders changed little after surface modification. The measured  $A_s$  from nitrogen sorption analysis are 23.3, 26.1, and 24.1 m<sup>2</sup> g<sup>-1</sup> for raw DE, C@DE, and MnO<sub>2</sub>@DE, respectively, as indicated by their nearly identical nitrogen adsorption-desorption isothermal curves shown in Fig. 4(a). The pore size distribution plots calculated from the desorption branches of the nitrogen sorption isotherms are shown in Fig. 4(b). The maximum probabilities of pore size are around 3.8 nm for the raw and modified DE samples, and surface modification decreases probabilities as pore diameter exceeds 8 nm. It is known that the natural diatomite minerals display a bimodal porosity with small pores below 10 nm and large pores in the 100 nm scale [18]. The pore size distribution as well as the  $A_s$  characteristics reveal that the synthesized MnO<sub>2</sub> were uniformly distributed over the walls of porous DE as a result of *in situ* reaction. The formation of such structure is favorable for avoiding the aggregation problem when used as adsorbent.

FTIR spectroscopy analysis was also used to characterize the obtained samples, with an intention to get more information about the effects of surface modification on DE. As shown in Fig. 4(c), the peaks observed at 798 and 1097 cm<sup>-1</sup> were assigned to DE

Download English Version:

<https://daneshyari.com/en/article/5361044>

Download Persian Version:

<https://daneshyari.com/article/5361044>

[Daneshyari.com](https://daneshyari.com)