



Synthesis of ordered mesoporous iron manganese bimetal oxides for arsenic removal from aqueous solutions



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ABSTRACT

A novel ordered mesoporous iron manganese bimetal oxides (OMIM) was synthesized via the hard template approach. The obtained OMIM sample showed excellent performance for the arsenic removal due to its large surface area and pore volume. pH affected the removal efficiency of As(III) and As(V) significantly, and the highest removal occurred in acidic solutions for both arsenic species. The adsorption isotherms were well-described by Freundlich model, and the calculated adsorption capacities of As(III) and As(V) were 67.89 and 93.54 mg/g, respectively. The adsorption kinetics fitted a pseudo-second order model, and intra-particle diffusion was not the only rate-limiting step in the adsorption process. Samples were characterized using SEM-EDS, TEM, XRD and XPS, and the redox states and yields of the arsenic species in aqueous solutions after the reaction of As(III)/As(V) with OMIM were also investigated by HPLC-ICP-MS. The results showed that the changed valence of Mn in OMIM favored As(III) removal and the mechanisms removal of both As(III) and As(V) were complex. In addition, to remove As(III) in aqueous solutions, OMIM plays a dual function as an efficient oxidant of As(III) due to its MnO₂ content and subsequently as an excellent adsorbent for As(V).

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1. Introduction

Arsenic is one of the most toxic and carcinogenic chemical elements, and arsenic contamination is considered to be one of the most serious environmental problems [1]. Typically, widespread occurrence of arsenic contamination of groundwater is caused by a range of anthropogenic activities, including combustion of fossil fuels, mining activity and the use of arsenic in agriculture [2,3]. Soluble arsenic exists in two predominant inorganic species: arsenite and arsenate [4], which depend significantly on redox and pH conditions [5]. Further research investigating the removal of As(III) from groundwater is still required due to the compound's higher toxicity, solubility, mobility and the increased difficulty of removing it compared to As(V) [6–8]. Ingesting arsenic-contaminated water is extremely detrimental to human healthy, even at low concentrations. To address this problem, the World Health Organization (WHO) has set a maximum guideline concentration limit of 10 ppb for arsenic in drinking water, which has subsequently been adopted by the United States, the European Union and China [9,10].

Adsorption is considered to be one of the most promising technologies for arsenic remediation because it is simple to operate, versatile and cost-effective compared with other conventional methods such as coagulation, reverse osmosis and biological treatment [11–13]. Among these potential adsorbents, iron (hydr)oxides and iron-containing substances have been widely focused on for arsenic species removal due to their strong affinity and high selectivity for inorganic arsenic species in sorption processes [2]. Moreover, iron oxides are environmentally friendly materials and do not cause secondary pollution during wastewater treatment processes. However, their small surface area and low adsorption capacity are serious drawbacks limiting the use of these adsorbents. Recent studies have shown that ordered mesoporous materials with uniform and adjustable mesopores, high surface area and large pore volume, are promising candidates for adsorption and separation applications [14,15]. Moreover, the stable and interconnected frameworks of their materials could be easily modified and functionalized without any change in mesostructure [16,17], which could further tailor their adsorption performance. Therefore, these ordered mesoporous materials are considered to be ideal hard template materials.

Compared with common metal oxides or bimetal oxides, mesoporous metal oxides have high surface area and uniform pore size, geometries and compositions [18], which are advantageous for

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removing many kinds of pollutants from contaminated water. In addition, mesoporous metal oxides prepared via hard template are more effective than those prepared by soft template [18], because the hydrolysis and polymerization of these metal alkoxides during soft template synthesis is usually more difficult to control; furthermore, materials obtained from soft templates exhibit poorer structural ordering and lower thermal stability after removing the soft surfactant template compared with those prepared using hard template [19]. Some mesoporous metal oxides have been synthesized through the hard template approach [19–24], which was introduced by Ryoo et al. [25] these materials are often used as heterogeneous catalysts due to their excellent characteristics, such as high activity, thermal stability and electrical conductivity [26,27]. However, the mesoporous metal oxides obtained from the hard template method have quite limited applications in adsorption, and the correlation between material properties and adsorption performance is not yet well understood [28].

In the present study, a novel ordered mesoporous iron manganese bimetal oxides (OMIM) was successfully synthesized through the hard template approach and used as an adsorbent to remove arsenic species from aqueous solutions. The obtained material displayed large surface area and pore volume. The effect of the solution pH, adsorption capacity and adsorption kinetics of As(III) and As(V) was investigated. Characterization and analysis results were performed by SEM-EDS, TEM, XRD and XPS before and after adsorption. Based on the results of analysis, possible mechanisms were proposed based on a combination of the results derived from the fitting of data to different theoretical adsorption models.

2. Experimental

2.1. Materials

All reagents were analytical grade and were used without further purification. As(V) stock solution was prepared with $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma–Aldrich) and ultrapure water ($18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$, Millipore), and different As(III) solutions were freshly prepared using NaAsO_2 (Sigma–Aldrich) to minimize the possible oxidation.

2.2. Synthesis of OMIM nanocomposites

Three-dimensional mesoporous silica (KIT-6) with *la3d* symmetry was used as a hard template and was synthesized according to a previous report [29]. Briefly, 6.0 g Pluronic 123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) was dissolved in a solution of 217.0 mL ultrapure water ($18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$, Millipore), then 10.3 g concentrated HCl (37%) and 6.0 g of *n*-butanol was added to the homogeneous solution at 35 °C. After vigorous stirring for 1 h, 12.9 g of TEOS (tetraethoxysilane) was added to the solution, which was then stirred for 24 h at this temperature. Subsequently, the white milky suspension was aged at 80 °C for another 24 h under static conditions. The white solid product was filtered, dried at 100 °C and finally calcined in air at 550 °C for 6 h.

The ordered mesoporous iron manganese bimetal oxides (OMIM) was synthesized as follows: 1.0 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.207 g $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, which were used as iron and manganese precursors, were dissolved in 20 mL ethanol, and 1.0 g KIT-6 was added into this homogenous solution under vigorous stirring. The melted metal nitrate automatically moved into the hard template pores because of the capillary condensation effect due to the strong interaction between metal nitrate and the inner pore surfaces of the silica. The mixture was stirred for 2 h at room temperature, and then the ethanol was evaporated at 50 °C. The obtained dry powder was heated to 300 °C and calcined at this temperature

for 6 h. The impregnation procedure was then repeated with half the amount of the metal precursors, and the precursors@silica composites were calcined at 450 °C for 6 h; the resulting sample was treated with 2 M NaOH solution to remove the silica template, centrifuged, washed several times with ultrapure water and dried at 40 °C in air, and the final obtained powder was referred to as OMIM. For comparison, Fe–Mn oxides (IM) prepared through the co-precipitation method as follows: 1.0 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.207 g $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 50 mL ultrapure water, and 5 M NaOH was added dropwise to raise the solution pH to around 10.0. The formed suspension was stirred for 2 h, aged at room temperature for 2 h, then washed several times with ultrapure water and dried at 80 °C and finally calcined in air at 450 °C for 6 h. The final obtained powder was denoted as IM.

2.3. Characterization

Scanning electron microscopy (SEM) images were collected by a field emission scanning electron microscope (SEM) (Hitachi S-4800, Hitachi, Japan) equipped with an energy dispersion X-ray spectrometer (EDS) at 200 kV. Transmission electron microscopy (TEM) images of the samples were obtained with a JEOL2010F instrument. Nitrogen adsorption/desorption isotherms were conducted with a Quantachrome Autosorb-iQ at 77 K, with degassing at 393 K prior to the measurements. The BET (Brunauer–Emmett–Teller) method was utilized to calculate the specific surface area. The pore size distribution (PSD) and pore volume (PV) were derived from the desorption branches of isotherms using the Barrett–Joyner–Halenda (BJH) model. Small-angle power X-ray diffraction (SXRD) was carried out using a Rigaku Dmax-2BR X-ray Diffractometer. A Bruker D8 Advance Powder Wide-angle X-ray Diffractometer (WXR, Germany) using a $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation source scanned from 10° to 90°, with a scanning speed of 1° min^{-1} and a step size of 0.02°. The operation voltage and current were kept at 40 kV and 40 mA, respectively. Fourier transform infrared (FT-IR) spectra of samples were recorded to monitor changes in the functional groups of the samples on a Nicolet 5700 spectrometer using KBr pellets in the range of 4000–400 cm^{-1} . The functional groups and the related oxidation states on the surface of the materials were analyzed by X-ray photoelectron spectroscopy (XPS) in a PHI 5000 Versaprobe spectrometer equipped with a rotating Al anode generating Al $\text{K}\alpha$ X-ray radiation at 1486.6 eV. The X-ray beam was monochromatized using seven crystals mounted on three Rowland circles. Samples were analyzed in the O 1s, Fe 2p and As 3d regions, which were the major elements present at the surface.

2.4. Batch experiments

Batch experiments were performed in glass bottles (50 mL) containing 40 mL As(III) or As(V) solution with the required concentrations, and the dose of OMIM was 0.2 g/L. To test the effect of pH, the mixed solutions were adjusted to desired values ranging from 3.0 to 12.0 by adding HCl or NaOH solutions. For equilibrium experiments, a series of arsenic solutions were prepared ranging from 1 to 100 mg/L; the bottles were sealed with screw caps and placed in a thermostatic shaker (200 rpm) at 25 °C for 24 h to ensure equilibrium. Samples were collected at certain time intervals in 5 mg/L and 10 mg/L arsenic solutions for the adsorption kinetics study.

To investigate the mechanism of arsenic removal by OMIM, the redox state and yield of arsenic in an aqueous solutions after the reaction of As(III)/As(V) with OMIM were investigated. The starting As(III) and As(V) solution concentration was about 1 mg/L, respectively, and the dose of OMIM was 0.2 g/L, then adjusted to the solution pH values of 3.0 by HCl.

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