Using Fe–Mn binary oxide three-dimensional nanostructure to remove arsenic from aqueous systems
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ABSTRACT
Fe–Mn binary oxide flower-like three-dimensional nanostructure synthesized from a hydrothermal procedure was used to remove arsenic (As) from aqueous solution. The samples were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier-transform infrared spectrometry (FTIR). SEM images revealed that the Fe–Mn binary oxide was dispersed as flower-like spheres with a diameter of 500 – 800 nm and the width of the petals was 20 – 30 nm. Sorption of the As to the Fe–Mn binary oxide reached equilibrium in less than 180 s, which is much faster than pure MnO2 and amorphous iron manganese binary oxide. The adsorption isotherm agreed well with the Freundlich adsorption model with adsorption capacities of 26.5 mg/g, when the equilibrium concentration was 34.5 mg/L. The effect of temperature revealed that the adsorption of As was exothermic, and the adsorption decreased with increasing temperature from 20 °C to 70 °C. The removal percentage of As by Fe–Mn binary oxide reached 100% from aqueous solution at pH 4.0 – 6.0. The Fe–Mn binary oxide nano-flowers are a potential highly efficient nanomaterial for removal of As from water.

Key words | adsorption, arsenic, Fe–Mn binary oxide, interface, nanostructure

INTRODUCTION
Arsenic (As) is a metalloid, and is well known as one of the most toxic metals in the environment (Mandal & Suzuki 2002; Ravenscroft et al. 2009; Singh et al. 2015). Surveys report that more than 150 million people around the world have suffered from a variety of adverse health effects, including dermal changes, respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic and carcinogenic effects, and even interference with the immune system due to chronic exposure to As (Mandal & Suzuki 2002; Smedley & Kinniburgh 2002; Duker et al. 2005; Ravenscroft et al. 2009; Singh et al. 2015). In particular, over 200,000 people die from various diseases caused by As poisoning each year in Bangladesh (Alkorta et al. 2004). Thus, it is a very important and challenging task for us to reduce the health risk of As in the environment, especially in water systems. Nowadays, the authorities have had to implement strict regulations concerning As contaminated water, for example, the World Health Organization (WHO) and the US Environmental Protection Agency (USEPA) have revised the guideline values for As in drinking water down from 0.05 to 0.01 mg/L (USEPA 2000; WHO 2011). Moreover, a lot of scientists have tried their best to develop effective technologies such as precipitation, oxidation, membrane separation, ion exchange, and adsorption to remove As from water (Dambies 2004; Garelick et al. 2005; Mohan & Pittman 2007; Cassano et al. 2010; Ren et al. 2011; Lin et al. 2012; Singh et al. 2015).

Among the above-mentioned technologies, adsorption has been deemed to be the best available technology for As removal due to its advantages of being technically simple, and having excellent regeneration potential and sludge free operation properties (Dambies 2004). Thousands of As adsorbents e.g., activated carbon, agricultural...
products, oxides, and biosorbents have been employed to remove As from drinking water (Mohan & Pittman 2007). Among all these As adsorbents, the iron oxides like ferrihydrite, goethite, and amorphous ferric oxide are the most common adsorbents for As contaminants. However, iron oxides are not stable in aqueous solutions with high concentrations of acid. Moreover, among all the fractions of As that occur naturally in water, as the removal of As(III) is less effective relative to As(V), it is necessary to convert As(III) into As(V) prior to adsorption in order to achieve a greater removal of As. Some studies have emphasized that manganese dioxide (MnO₂) is a common and efficient oxidizing agent for As(III) because the low adsorption capacity of MnO₂ is mainly attributed to its negative zeta potential, and low surface-to-volume ratio (Oscarson et al. 1985; Li et al. 2010). However, its adsorption capacity is low (Lenoble et al. 2004; Deschamps et al. 2005; Li et al. 2010), which limits its application. To overcome this disadvantage, iron manganese binary oxide has been developed as a novel As adsorbent, and the amorphous Fe–Mn binary oxide with high adsorption capacity for As using the co-precipitation method has been fabricated (Zhang et al. 2007a, 2009). The amorphous Fe–Mn binary oxide has a high surface-to-volume ratio, however, slow removal kinetics have been found. In order to enhance the surface-to-volume ratio, the adsorbents are usually prepared as nanoparticles because this produces small particle sizes with high capacity. Recent studies suggest that many nanosized metal oxides remove As from water systems effectively and thoroughly (Mohan & Pittman 2007; Hua et al. 2012). However, it is difficult to separate the nanoparticles from the aqueous system after adsorption has occurred. Usually, there are three methods to overcome this defect. First, magnetism is added into the adsorbent, for example by modifying the magnetic Fe₃O₄ with some functional group to capture the adsorbates (Peng et al. 2012; Yang et al. 2013). Second, the nanoparticles are loaded on a substrate such as active carbon (Zhu et al. 2009), montmorillonite (Masih et al. 2007), a molecular sieve (Yoshitake et al. 2003) and a polymer (Cumbal et al. 2005). Third, a large three-dimensional nanostructure is fabricated. These structures combine a large volume and surface area such as the urchin-like FeOOH (Wang et al. 2012), and the nanoﬁber TiO₂ (Yang et al. 2008).

In this study, the novel Fe–Mn binary oxide flower-like three-dimensional nanostructure (nanoﬂower), which combines the advantages of MnO₂ and iron oxides for the oxidation and adsorption, was prepared using the hydrothermal method. The adsorbent with the three-dimensional nanostructure could be more easily separated than the normal nanoparticle. Furthermore, this structure can maintain the required high surface-to-volume ratio to very quickly remove As in an aqueous system. The objectives of our study are to (i) synthesize the Fe–Mn binary oxide flower-like three-dimensional nanostructure and characterize it with scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier-transform infrared spectrometry (FTIR), (ii) study the removal of As(III) from aqueous solutions under different experimental conditions, including different initial pH values and dosages of the Fe–Mn binary oxide nanoﬂower, and (iii) present the adsorption kinetics as well as adsorption isotherms and analyse the possible adsorption mechanism.

MATERIALS AND METHODS

Materials

The chemicals used in this study were all of analytically pure grade and no further purification was performed prior to use. All sample solutions were prepared with deionized water. MnSO₄·H₂O, Fe (NO₃)₃·9H₂O, and K₂S₂O₈ were all purchased from Beijing Zhong Bai Chemicals Co., Ltd. An As(III) stock solution was prepared by dissolving As trioxide (As₂O₃) in 1 M hydrochloric acid. All glassware was cleaned by soaking in 15% HNO₃ before use. In all experiments, the initial pH of the solution was adjusted to a certain value by using 0.10 M HCl or 0.10 M NaOH.

Synthesis of Fe–Mn binary oxide nanoﬂowers

The method of synthesizing Fe–Mn binary oxide nanoﬂowers was modiﬁed based on a previous study (Yu et al. 2009). In a typical procedure, MnSO₄·H₂O (0.6830 g), Fe(NO₃)₃·9H₂O (1.6406 g), K₂S₂O₈ (1.0868 g) and 4 mL of concentrated sulfuric acid were mixed in 76 mL of deionized (DI) water and stirred with a magnetic stirrer for 10 min to form a homogeneous solution at room temperature. Then the solution was transferred
to a Teflon-lined stainless steel autoclave (100 mL) of 80% capacity of the total volume and loaded into an oven preheated to 110 °C for 6 h. The autoclave was allowed to cool to room temperature naturally. The precipitates were collected, washed with DI water and absolute ethanol, respectively, several times to remove impurities, and then dried at 60 °C for 8 h, cooled down in air. The pure MnO₂ and iron oxides were prepared by the above method, except that the Fe(NO₃)₃·9H₂O and MnSO₄·H₂O, respectively, were absent.

Characterization of Fe–Mn binary oxide nanoflowers

Scanning electron microscopy (SEM) was used to document surface morphologies using a H-7500 (JEM-1230HC, JPN). The crystal forms of materials were measured with a Rigaku-TTRIII X-ray diffractometer (Shimadzu X-ray, Japan). The IR-spectrum was carried out with a Perkin Elmer Spectrum 65 (USA). The zeta potential of the nanoflowers was measured at various pH values with a DELSA 440SX (USA).

The effect of pH on As removal

The adsorption of As was measured in a batch experiment where 0.01 g sorbent and 50 mL test solution were shaken in a polythene bottle at a speed of 140 rpm for 10 min at room temperature. After 10 min, the sorbent was collected by centrifugation. The concentration of As was analyzed with an atomic fluorescence spectrometer (Jitian, China). The As removal efficiency was calculated using Equation (1):

\[
\text{Removal of arsenic (\%) = 100 \times \frac{C_0 - C_f}{C_0}}
\]

\(C_0\) and \(C_f\) are the initial and final concentrations of the As, respectively.

The influence of pH on the As removal experiment was investigated using this process, except that the pH was adjusted with 0.10 M HCl or 0.10 M NaOH to the desired pH.

Sorption capacity

The sorption capacity of the adsorbent for As was measured using the same procedure as our previous work (Peng et al. 2015), except that the initial As concentration varied between 0.05, 0.50, 1.00, 20.00 and 60.00 mg/L.

Sorption kinetics

The kinetics of metal sorption were performed as in our previous work. A weight of 0.01 g Fe–Mn binary oxide was added to the solution with 1.0 or 20.0 mg/L As, and then 1.00 mL solution was extracted to analyze the As concentration when the sorption time was 3, 5, 10, 20, 60 and 120 min. Then 0.01 g pure MnO₂ was added to the solution with 1.0 mg/L As, and the sorption kinetics were measured.

Sorption thermodynamics

The polythene bottle containing 0.01 g sorbent and 50 mL 1 mg/L As solution was shaken at a speed of 140 rpm at different temperatures (22, 30, 40, 50 and 70 °C). Then 1.00 mL solution was extracted to analyze the As concentration after sorption for 10 min.

RESULTS AND DISCUSSION

Characterization of Fe–Mn binary oxide nanoflowers

The SEM images of the as-prepared Fe–Mn binary oxide are shown in Figure 1((a)–(c)). The Fe–Mn binary oxide nanoflowers were aggregated as a sphere with a diameter of 500–800 nm, and the width of the petal was 20–30 nm. It can be seen that this nanoflower structure has a high surface-to-volume ratio.

A powder X-ray diffraction (XRD) pattern of the resulting product is shown in Figure 1(d). Some diffraction peaks in Figure 1(d) can be assigned to the tetragonal phase of α-MnO₂ (JCPDS 44-0141, \(a = 9.784, c = 2.863\) Å), and some diffraction peaks correspond to birnessite and β-MnOOH. It shows that the Fe–Mn binary oxide is a composite, and this low intensity of XRD indicates that the material is of poor crystalline nature. There is no peak corresponding to the iron oxide, implying that the iron oxide is amorphous.

The FTIR was measured and the results are shown in Figure 2. It shows the O–H stretches of the Fe–Mn binary
oxide and MnO₂ at ∼3390 cm⁻¹. The –SO₄ and H₂O were found at two spectra. The band at 1120 and 978 cm⁻¹ could be the symmetric stretch mode of –SO₄. However, the spectra of the Fe–Mn binary oxide had two extra vibration peaks at 526 and 577 cm⁻¹, corresponding to the Mn-O (Zhang et al. 2011) and Fe-O (Cao et al. 2007).

The zeta potentials of the as-prepared Fe–Mn binary oxide, MnO₂ and iron oxide were measured at varied pH values and are shown in Figure 3. The pHZC of the Fe–Mn binary oxide was 7.10, which was higher than that of pure MnO₂ (∼4.8), and lower than that of iron oxide (8.2). It is implied that the Fe–Mn binary oxide would have a high ability to adsorb As when the pH < 7.10. However, the zeta potential of the Fe–Mn binary oxide was relatively low (<2.0 mV) in an acid environment.

**Sorption kinetics**

The sorption dynamics of As to Fe–Mn binary oxide were evaluated by adding 0.01 g as-obtained Fe–Mn binary oxide into 50 mL of a mixed solution containing 1.00 and 20.00 mg/L As (pH 4.0) at room temperature. Results (Figure 4) showed...
that sorption equilibrium was reached in ~3 min, which is the shortest equilibrium time to our knowledge, because the sorption equilibrium time of MnO₂ modified natural clinoptilolite is 48 h (Camacho et al. 2011), and that of common α-MnO₂ (Li et al. 2010) and MnO₂ coated-alumina is ~2 h (Maliyekkal et al. 2009). The data were fitted with the pseudo-second-order kinetics equation (Equation 2).

\[
\frac{t}{R_t} = \frac{1}{k_2 R_e^2} + \frac{t}{R_e}
\]  

(2)

where \(R_e\) and \(R_t\) are the removal efficiency at equilibrium and at time \(t\), respectively, And \(k_2\) is the rate constant of pseudo-second-order sorption (0.13 min⁻¹). The highest removal rate \(R_e = 100\), \(R^2 = 0.99\) occurred with 1.0 mg/L As. The removal rate of 20.00 mg/L As is as rapid as that of 1.00 mg/L. The rapid sorption kinetics are likely due to the iron oxide, because the pure α-MnO₂ nano-needles prepared with a similar method have a low adsorption rate to As, as shown in Figure 4. The As(III) sorption process of MnO₂ is divided into two parts; firstly, the As(III) is oxidized to As(V) and then it is adsorbed by the iron oxide and manganese dioxide. The iron oxide increases the adsorption rate. However, some other amorphous iron manganese binary oxides, prepared with coprecipitation, have slow adsorption kinetics. It is implied that the perfect crystalline structure of the Fe–Mn binary oxide described in this paper has a higher oxidization ability than that of an amorphous structure.

**Effect of pH**

The effect of pH on the adsorption of As ions onto Fe–Mn binary oxide is shown in Figure 5, where 10.0 mg Fe–Mn binary oxide was utilized to adsorb 1.00 and 20 mg/L As in 50 mL solution. The results showed the highest removal efficiency of As at pH 4.0, as much as 95%. At pH 2.0 the removal efficiency was 88%. At pH 8.0 the As removal efficiency was 73%, indicating that the sorption of As on the surface of the Fe–Mn binary oxide was significantly influenced by the pH. It is attributed to the fact that a change in pH of the solution results in the formation of different ionic species and different surface charge of the Fe–Mn binary oxide. The Fe–Mn binary oxide can oxidize...
the As(III) to As(V) and then adsorb As(V) on the surface of the material (Zhang et al. 2007b). When the pH is higher than the pH_{PZC} of Fe–Mn binary oxide (~7.10), the surface of the Fe–Mn binary oxide is negative and has a weak interaction with the As anion. When the solution pH is lower than the pH_{PZC} of Fe–Mn binary oxide, the surface of the Fe–Mn binary oxide is positive and has a strong interaction with the As ion, because the As acid forms as H_{2}AsO_{4} and so it increases the removal efficiency of the As at the low pH. However, when the solution pH is lower than 2, the As acid is H_{3}AsO_{4} in water and this decreases the removal efficiency.

**Effect of temperature**

The 10.00 mg Fe–Mn binary oxide was added to 50 mL solution with 1.00 mg/L As and oscillated for 5 min at different temperatures. The plot of removal efficiency as a function of temperature is shown in Figure 6. It was revealed that the removal efficiency of As decreases as the temperature increases from 20 to 70 °C. It is indicated that the removal efficiency depends on the temperature. It may be attributed to the fact that high temperature disrupts the interaction of As and Fe–Mn binary oxide.

**Thermodynamic studies**

The uptake of As by the Fe–Mn binary oxide decreases on raising the temperature confirming the exothermic nature of the adsorption step. The change in standard free energy (\(\Delta G^0\)), enthalpy (\(\Delta H^0\)) and entropy (\(\Delta S^0\)) of adsorption is calculated from the following Equation (3):

\[
\Delta G = -RT \ln K_c
\]

where \(R\) is the gas constant, \(K_c\) the equilibrium constant and \(T\) the temperature in K. The \(K_c\) value is calculated from Equation (4):

\[
K_c = \frac{C_A}{C_S}
\]

where \(C_A\) and \(C_S\) are the equilibrium concentrations of dye ions in adsorbent (mg L\(^{-1}\)) and in the solution (mg L\(^{-1}\)), respectively. Standard enthalpy (\(\Delta H\)) and entropy (\(\Delta S\)) of adsorption can be estimated from the van’t Hoff equation given in Equation (5):

\[
\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}
\]

The slope and intercept of the van’t Hoff plot is equal to \(-\Delta H/R\) and \(\Delta S/R\), respectively (Giles et al. 1960). The van’t Hoff plot for the adsorption of As onto Fe–Mn binary oxide is given in Figure 7. Thermodynamic parameters obtained are summarized in Table 1. From Table 1, the negative values of enthalpy change (\(\Delta H = -32.54\) kJ mol\(^{-1}\)) confirms the exothermic nature of the adsorption process.

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**Figure 6** | The influence of temperature on As removal rate by Fe–Mn binary oxide.

**Figure 7** | Plot of In \(K_c\) against reciprocal temperature for As sorption onto Fe–Mn binary oxide.
The negative value of $\Delta S (\Delta S = -66.43 \text{ J mol}^{-1} \text{K}^{-1})$ reflects the affinity of the adsorbent material towards As. The spontaneity of the adsorption process is increased in the Gibbs energy of the system. The $\Delta G$ values vary over a range with the mean values showing a gradual increase from $-12.53$ to $-9.48$ (kJ mol$^{-1}$) in the temperature range of 20–70 °C.

## Sorption isotherms

The adsorption capacities of the as-obtained Fe–Mn binary oxide to As were measured individually at pH 4.0 with 10.00 mg of Fe–Mn binary oxide and varied As concentrations, and the data of the As adsorbed at equilibrium ($q_e$, mg/g) and the equilibrium As concentration ($C_e$, mg/L) were fitted to the Freundlich model (Equation 6) well.

$$q_e = K_F C_e^{1/n}$$

where $K_F$ (mg/g) and $1/n$ are the Freundlich constant and exponent, respectively. The Freundlich isotherm is empirical for heterogeneous surface energy. It assumes that the adsorption energy of an adsorbate binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied. The characteristics of the Freundlich isotherm of $K_F$ and $1/n$ were 9.89 and 0.27, respectively. The $R^2$ value for the Freundlich isotherm fitting result was 0.99. The adsorption capacity of pure MnO$_2$ and iron oxides for As were measured and the results are shown in Figure 8. All the parameters are shown in Table 2. The highest capacities of Fe–Mn binary oxide, iron oxides and pure MnO$_2$ were 26.50, 23.40 and 11.22 mg/g when the initial As concentration was 60 mg/L. The results reveal that the Fe–Mn binary oxide has a higher adsorption capacity than the other absorbents. The high adsorption capacity should correspond to the high surface-to-volume ratio of Fe–Mn binary oxide. This conclusion can be supported with the SEM and surface-to-volume ratio. The specific surface area was 123 m$^2$/g, 77 m$^2$/g, and 43 m$^2$/g for Fe–Mn binary oxide, MnO$_2$ and iron oxides, respectively.

The result of the fitted parameters indicates that the adsorption of As anions is taking place in a complicated mode. The adsorption mechanism is not monolayer chemisorption such as the Langmuir mode, because of the very low relationship between these data of the Fe–Mn binary oxide and the Langmuir model ($<0.75$). The adsorption capacity of As increased with increasing equilibrium As concentration.

## CONCLUSIONS

Flower-like three-dimensional nanostructure Fe–Mn binary oxide was prepared using a hydrothermal procedure, and its properties for removal of As from aqueous solution were investigated. SEM images revealed the Fe–Mn binary oxide...
oxide is dispersed flower-like spheres with a diameter of 500–800 nm and the width of the petals is 20–30 nm. Sorption of the As to Fe–Mn binary oxide nanoflower reached equilibrium in less than 180 seconds, and agreed well with the Freundlich adsorption model with adsorption capacities of 26.5 mg/g at an equilibrium concentration of 34.5 mg/L. The effect of temperature revealed that the adsorption of the As is exothermic, but the adsorption is decreased as temperature increases from 20–70°C. The Fe–Mn binary oxide was able to remove 100% of As in water at pH 4.0–6.0, and this adsorbent was stable in solution with low pH. The Fe–Mn binary oxide nanoflower is a potential highly efficient nanomaterial for removal of As from water.

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