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Preparation and evaluation of a novel Fe–Mn binary oxide adsorbent for effective arsenite removal

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ABSTRACT

Arsenite (As(III)) is more toxic and more difficult to remove from water than arsenate (As(V)). As there is no simple treatment for the efficient removal of As(III), an oxidation step is always necessary to achieve higher removal. However, this leads to a complicated operation and is not cost-effective. To overcome these disadvantage, a novel Fe–Mn binary oxide material which combined the oxidation property of manganese dioxide and the high adsorption features to As(V) of iron oxides, were developed from low cost materials using a simultaneous oxidation and coprecipitation method. The adsorbent was characterized by BET surface areas measurement, powder XRD, SEM, and XPS. The results showed that prepared Fe–Mn binary oxide with a high surface area ($265 \text{ m}^2 \text{ g}^{-1}$) was amorphous. Iron and manganese existed mainly in the oxidation state +III and IV, respectively. Laboratory experiments were carried out to investigate adsorption kinetics, adsorption capacity of the adsorbent and the effect of solution pH values on arsenic removal. Batch experimental results showed that the adsorbent could completely oxidize As(III) to As(V) and was effective for both As(V) and As(III) removal, particularly the As(III). The maximal adsorption capacities of As(V) and As(III) were 0.93 mmol g^{-1} and 1.77 mmol g^{-1} , respectively. The results compare favorably with those obtained using other adsorbent. The effects of anions such as SO_4^{2-} , PO_4^{3-} , SiO_3^{2-} , CO_3^{2-} and humic acid (HA), which possibly exist in natural water, on As(III) removal were also investigated. The results indicated that phosphate was the greatest competitor with arsenic for adsorptive sites on the adsorbent. The presence of sulfate and HA had no significant effect on arsenic removal. The high uptake capability of the Fe–Mn binary oxide makes it potentially attractive adsorbent for the removal of As(III) from aqueous solution.

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1. Introduction

Arsenic, a relatively scarce but ubiquitous element, is of serious concern due to its toxicity and carcinogenicity. Long-term uptake of arsenic contaminated water can lead to cancer of the liver, lung, kidney, bladder, and skin (Roberts et al., 2004). Noncancer effects include cardiovascular and cerebrovascular disease, diabetes mellitus, and adverse

reproductive outcomes (Brown and Ross, 2002). In order to minimize these health risks, the World Health Organization (WHO) has set a guideline limit of $10 \mu\text{g L}^{-1}$ in drinking water (Holm, 2002), and this new limit has become effective from January 2006 for drinking systems in the United States.

In natural water, arsenic is primarily present in inorganic forms and exists in two predominant species, arsenate (As(V))

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and arsenite (As(III)). As(V) is the major arsenic species in well-oxygenated water (Ferguson and Gavis, 1972), whereas As(III) is the dominant arsenic in groundwater (Smedley and Kinniburgh, 2002). As(III) is much more toxic (Ferguson and Gavis, 1972), more soluble, and more mobile than As(V). Although the conversion of As(III) to As(V) in oxygenated water is thermodynamically favored, the rate of the transformation may take days, weeks, or months depending on specific conditions (Edwards, 1994). Unfortunately, elevated concentrations of arsenic are found in the groundwater of many regions around the world, such as Argentina, Bangladesh, India, Mongolia, Thailand, and Taiwan, where a majority of groundwater is contaminated with arsenic at levels from 100 to over 2000 µg/L (Ferguson and Gavis, 1972). Many different methods such as precipitation, coprecipitation, iron-exchange, adsorption, ultra filtration, and reverse osmosis have been used for arsenic removal, and adsorption process is considered to be one of the most promising technologies because the system can be simple to operate and cost-effective (Jang et al., 2006). However, all this elimination techniques are effective for As(V), but fail in case of As(III) (Frank and Clifford, 1986; Jekel, 1994; Driehaus et al., 1994). To achieve higher arsenic removal, a pretreatment for As(III) oxidation is therefore usually involved, followed by coprecipitation/adsorption of the As(V) formed onto metal oxyhydroxides. Many oxidants or oxidant-generating systems have been tested for the oxidation of As(III) for example, O₂ and/or ozone (Kim and Nriagu, 2000), chlorine (Frank and Clifford, 1986), hydrogen peroxide (Pettine et al., 1999), manganese oxides (Driehaus et al., 1994; Oscarson et al., 1981; Stumm and Morgan, 1981; Scott and Morgan, 1995; Nesbitt et al., 1998), UV/iron systems (Hug et al., 2001), and TiO₂/UV systems (Bissen et al., 2001). Due to their high oxidation potentials, ozone and hydrogen peroxide are not feasible for a specific oxidation of As(III), but result in side reactions with natural organic matter. UV radiation oxidizing As(III) requires a high energy input, which may not be cost-effective for small water treatment plant. The drawback in use of chlorine is that it will react with natural organic matter to form chlorinated by-products, which are believed to have health concern effects. However, manganese dioxide was emphasized by Oscarson et al. and others (Oscarson et al., 1981; Stumm and Morgan, 1981) as an effective oxidizing agent of As(III). In addition, the oxidation potential of MnO₂ is relative low and fit for specific oxidation of As(III). Manganese dioxide can also be used as adsorbent for removal arsenic, but its adsorption capacity is low (Lenoble et al., 2004) and this limits its application.

On the other hand, among a variety of available materials for arsenic removal, iron (hydr)oxides including amorphous hydrous ferric oxide, poorly crystalline hydrous ferric oxide (ferrihydrite), goethite and akaganéite (Pierce and Moore, 1982; Driehaus et al., 1998; Dixit and Hering, 2003) are well-known for their ability to removal arsenic from aqueous system and low cost.

Conceivably, a Fe–Mn binary composite that combines the oxidation property of manganese dioxide and the high adsorption features to As(V) of iron oxides, will be able to oxidize As(III) and have high adsorption capacity for As(V) simultaneously. Two natural Fe–Mn-mineral materials

(Chakravarty et al., 2002; Deschamps et al., 2005) whose main components are Fe₂O₃ and MnO₂, have been investigated for As(III) and As(V) removal from water and both of them are more effective for As(III) removal than that of As(V). However, their adsorption capacities for both As(III) and As(V) are very low. Besides, synthetic Fe oxide-coated MnO₂ (Oscarson et al., 1983) has also been studied for the oxidation and sorption of As(III), but its As(III) adsorption capacity was lower than that of pure Fe oxide since MnO₂ was coated by Fe oxide and could hardly oxide As(III).

To our best knowledge, no research results on the Fe–Mn binary oxide prepared by coprecipitation for arsenic removal have been reported in the literature. Therefore, the main objectives of this research were to: (1) to prepare a Fe–Mn binary oxide adsorbent by oxidation and coprecipitation from environmentally friendly and low cost raw materials for effective arsenic removal; (2) to characterize the adsorbent with a variety of techniques; and finally (3) to evaluate its arsenic adsorption capacities and to examine the influence of co-existing anions on As(III) removal.

2. Materials and methods

2.1. Materials

All chemicals were analytical grade and were purchased from Beijing Chemical Co. (Beijing, China). The As(III) and As(V) stock solutions were prepared with deionized water using NaAsO₂ and NaHAsO₄ · 7H₂O, respectively. Arsenic working solutions were freshly prepared by diluting arsenic solutions with deionized water. The concentrations of arsenic species were always given as elemental arsenic concentration in this study.

2.2. Adsorbent preparation

The Fe–Mn binary oxide adsorbent was prepared according to the following procedure: Potassium permanganate (KMnO₄, 0.015 mol) and iron(II) sulfate heptahydrate (FeSO₄ · 7H₂O, 0.045 mol) were dissolved in 200 ml of deionized water, respectively. Under vigorous magnetic-stirring, the FeSO₄ solution was slowly added into the KMnO₄ solution, and 5 M NaOH solution was simultaneously added to keep the solution pH in the range of 7 and 8. After addition, the formed suspension was continuously stirred for 1 h, aged at room temperature for 12 h and then washed repeatedly with deionized water. The suspension was filtrated and dried at 105 °C for 4 h. The dry material was crushed and stored in a desiccator for use.

2.3. Adsorbent characterization

The specific surface area was measured by nitrogen adsorption using the BET method with a Micromeritics ASAP 2000 surface area analyzer. The point of zero charge (PZC) was estimated using the common intersection point (CIP) method. It was determined by potentiometric titration of the Fe–Mn binary oxide with 0.05 M NaOH and 0.05 M HNO₃ in a background NaNO₃ electrolyte solution

at three ionic strengths (0.001, 0.01 and 0.1M) (Parks and de Bruyn, 1962). The obtained PZC value was 5.9. Particle size of the adsorbent was determined by a Mastersizer 2000 (Malvern Co.). The particle shapes were observed using a scanning electron microscope (SEM) with an EDAX KEVEX level 4 (Hitachi S-3500N). X-ray diffraction (XRD) analysis was carried out on a D/Max-3A diffractometer using Ni-filtered copper $K\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) data were collected on an ESCA-Lab-220i-XL spectrometer with monochromatic Al $K\alpha$ radiation (1486.6eV).

2.4. Batch adsorption tests

The rate of arsenic adsorption is an important factor for arsenic removal. Batch experiment was performed to determine the reaction time to reach adsorption equilibrium. Defined amount of As(III) stock solution was added in a 500-ml glass vessel containing 400ml 0.01M NaNO_3 solution, to make 133 μM of As(III) concentration. After the solution pH was adjusted to 6.9 by adding 0.1M HCl and NaOH, Fe–Mn binary oxide was added to obtain a 0.2 g L^{-1} suspension. The suspension was mixed with a magnetic stirrer, and the pH was maintained at 6.9 throughout the experiment by addition of the acid and base solutions. Approximately 5 ml aliquots were taken from the suspension at the following intervals: 0.083, 0.167, 0.25, 0.5, 0.67, 1, 2, 3.5, 6, 10, 16 and 24 h of reaction. The samples were filtered through a 0.45 μm membrane filter. Total As in the filtered solution was determined using an inductively coupled plasma atomic emission spectroscopy (ICP-OES). Speciation of As(III) in the solution samples was performed with a hydride generation-atomic fluorescence spectroscopy (HG-AFS). The soluble As(V) concentration was calculated from the difference between the total soluble arsenic and the soluble As(III) concentrations.

Adsorption tests were performed in 150 ml glass vessels to evaluate arsenic removal capability. The effect of solution pH values on arsenic removal and isotherms for As(III) and As(V) were determined in batch adsorption experiments. Experiments to determine the effect of solution pH values on arsenic removal were performed by adding 10 mg of the adsorbent sample into the vessel, containing 50 ml of 0.133 mM arsenic solution. The pH of the solutions was adjusted every 4 h with HCl and NaOH to designated values in the range of 4–10 during shaking process. The equilibrium pH was measured and the supernatant was filtered through a 0.45 μm membrane after the solutions were mixed for 24 h. As(III) and As(V) adsorption isotherms were determined at the equilibrium pH values of 5.0 ± 0.1 . Initial arsenic concentrations were varied from 6.67×10^{-3} to 6.67×10^{-1} mM. In order to test the effects of co-existing anions, anions concentrations ranged from 0.1 to 10 mM. Ionic strength was adjusted to 0.01 M with NaNO_3 . All batch experiments were carried out at $25 \pm 1^\circ\text{C}$ with an adsorbent content of 200 mg L^{-1} and all the suspensions were shaken on an orbit shaker at 140 rpm for 24 h. The quantity of adsorbed arsenic was calculated by the difference of the initial and residual amounts of arsenic in solution divided by the weight of the adsorbent.

2.5. Analytical methods

Total arsenic (As(III) + As(V)) concentrations were determined using an ICP-OES (SCIEX Perkin Elmer Elan mode 5000). Prior to analysis, the aqueous samples were acidified with concentrated HCl in an amount of 1%, and stored in acid-washed glass vessels. As(III) analysis was conducted using a spectroscopy equipment (AF-610A, Beijing Ruili Analytical Instrument Co., Ltd. China) on the basis of HG-AFS. All samples were analyzed within 24 h of collection.

3. Results and discussion

3.1. Characterization of Fe–Mn binary oxide adsorbent

3.1.1. Particle size and BET surface area

The medium mass particle size of the powdered adsorbent was 26 μm . Solute adsorption depends on the surface area, and other characteristics of the porous adsorbent. Previous studies (Cornell and Schwertmann, 1983) show that the surface areas of both natural and synthetic iron oxides were around 6.4–320 $\text{m}^2 \text{g}^{-1}$, higher for amorphous FeOOH , and lower for goethite and hematite, mostly depending on prepared method, aging time and drying means. In this study, the BET surface area of Fe–Mn binary oxide adsorbent was 265 $\text{m}^2 \text{g}^{-1}$, which was relatively high since the adsorbent had been dried at 105°C for 4 h.

3.1.2. X-ray diffraction

The XRD pattern of Fe–Mn binary adsorbent showed that no obvious crystalline peak was detected, indicating that both the Fe oxide and Mn oxide of the Fe–Mn binary composite exist mainly in amorphous form, which may be responsible for the high surface area. The surface characteristics of Fe oxide was mainly determined by its crystalline phase. Generally, amorphous iron has a very high surface area and a large number of surface active sites. The surface area and active sites decrease greatly with the increase of crystallinity. Amorphous iron (hydr) oxides are known to gradually transfer to crystalline iron(III) oxides (Deng and Stumm, 1994). But it appeared that it did not take place for our samples, and even the preparation procedure involved drying at 105°C for 4 h. This suggested that the formation of crystalline iron(III) oxides and Mn oxide was blocked by the co-existing of them during the synthesis process of Fe–Mn binary adsorbent.

3.1.3. Scanning electron microscopy

The morphology and surface elements distribution of Fe–Mn adsorbent were studied by a SEM combined to an EDAX KEVEX level 4. The image obtained for the Fe–Mn adsorbent showed that the material was constituted by many aggregated small particles (Fig. 1a), which led to a rough surface and the presence of porous structure. The EDS analysis (Fig. 1b) revealed that Fe and Mn were evenly distributed on the surface and the Fe/Mn molar ratio on the surface was about 2.86, a little lower than that of bulk, which was in the range of 2.93–3.02.

Fig. 1 – SEM micrograph ($\times 10000$) (a) and EDS surface analysis (b) of Fe–Mn binary oxide.

3.1.4. X-ray photoelectron spectroscopy

XPS was used to examine the oxidation states of the iron and manganese in the Fe–Mn binary oxide system. The results of Fe 2p and Mn 2p electron binding energies are shown in Fig. 2. The Fe $2P_{1/2}$ and $2P_{3/2}$ peak positions (724.8 and 711.1 eV) and shape are characteristic of Fe(III) (Glisenti, 2000), while the binding energies at 653.3 and 642.0 eV are assigned to the Mn $2P_{1/2}$ and Mn $2P_{3/2}$ transitions of Mn^{4+} , respectively. The results suggested that the iron and manganese in the synthesized sample were in the oxidation states +III and +IV, respectively.

3.2. Kinetics of arsenite removal by the Fe–Mn binary oxide adsorbent

Kinetic experiments were performed to determine the rate of As(III) removal from the water by the adsorbent. Fig. 3 shows the kinetics of arsenite removal and change in concentration of arsenic species in the aqueous phase with time. The initial As(III) concentration was $133 \mu M$ and the solution pH value was controlled at around 6.9 by adding dilute NaOH solution

Fig. 2 – XPS spectra of Fe–Mn binary oxide: (a) Fe2p and (b) Mn2p.

Fig. 3 – Kinetics of arsenite removal and change in concentration of arsenic species in the aqueous phase with time. Initial As(III) = $133 \mu M$; adsorbent content = 200 mg L^{-1} ; pH = 6.9.

because the adsorbent was slightly acidic. A complete depletion of As(III) from solution by oxidation or/and adsorption occurs within 16 h. The reaction between the As(III) and

the adsorbent is particularly fast during the first hour and almost 80% of the As(III) was depleted. This may be due to the fine particles of Fe–Mn binary oxide powder. The smaller particle size (26 μm) was favorable for the diffusion of arsenite molecules from bulk solution onto the active sites of the adsorbent. Then intraparticle diffusion dominated and the adsorption rate was slow. The change of As(V) concentration in solution can be explained as follows. During the initial reaction period, adsorbed As(III) was quickly oxidized to As(V) by MnO_2 of the adsorbent. As a result of the reductive dissolution of the MnO_2 , a part of the formed As(V) was detached from the surface (Nesbitt et al., 1998), resulting in an appearance of relatively high As(V) concentration in the solution. The As(V) in the solution was adsorbed by the adsorbent and reduced gradually with reaction time. Based on the results of adsorption kinetics, mixing time of 24 h was used in the other batch adsorption experiments for both As(III) and As(V).

3.3. Effect of pH on arsenic removal

The results in Fig. 4 illustrate the effects of pH on the removal of As(V) and As(III). As can be seen, the As(V) removal was evidently dependent on pH with the greatest adsorption occurring under acidic conditions and decreased with increase in solution pH. H_2AsO_4^- and HAsO_4^{2-} are dominant As(V) species in the solution under the tested pH range (4–10). Lower pH is favorable for the protonation of sorbent surface. Increased protonation is thought to increase the positively charged sites, enlarge the attraction force existing between the sorbent surface and As anions and therefore increase the amount of adsorption in the lower pH region. In higher pH region, the negatively charged sites dominate, the repulsion effect enhances, and the amount of adsorption is consequently dropped.

The same trend was observed with the As(III) species, whereas the decrease in As(III) removal was not as obvious as that of As(V) with increasing pH. Many studies also suggest

that increasing pH decreased As(V) adsorption on iron or iron-containing adsorbents (Raven et al., 1998; Jang et al., 2006), typical of anionic adsorption. Meanwhile, these studies also indicate that the effect of pH on As(III) adsorption on iron adsorbents is very different from that of As(V) since H_3AsO_3 is the dominant dissolved As(III) species at pH below 9.2. The similarity of As(III) adsorption to that of As(V) in this test suggest indirectly that initial added As(III) was oxidized into As(V) and then adsorbed by the Fe–Mn adsorbent. For the prepared adsorbent in this study, no significant decrease in As(III) removal was observed until the solution pH was increased to 7.7, indicating that the material should be effective for the majority of water supplies, which normally have a pH range of 6.5–8.5 (Gu et al., 2005).

3.4. Adsorption capacity of Fe–Mn adsorbent

The adsorption capacities of the Fe–Mn adsorbent for As(III) and As(V) were evaluated using the isotherms presented in Fig. 5. The Langmuir and Freundlich equations were employed to describe the adsorption isotherms in the figure. A maximum adsorption calculated from the Langmuir equation was used as the As(V) adsorption capacity. The adsorption constants obtained from the isotherms at certain experimental conditions are listed in Table 1.

As shown in Table 1, high regression coefficients ($R^2 > 0.98$) suggested that both Langmuir and Freundlich models were suitable for describing the adsorption behavior of As(V) by Fe–Mn adsorbent. However, the regression coefficients shown in Table 1 indicated that the Freundlich equation fitted better the As(III) experimental data. It is not surprising that Langmuir equation failed in describing the adsorption behavior As(III) because this model assumes that the sorption and desorption rates are identical. It does not include the case of an oxidation of dissolved species due to any reaction with the surface. While the As(III) removal was an sorption process coupled with redox reaction on the surface. The calculated As(V) maximum adsorption capacity is 0.93 mmol g^{-1} . Direct graphic maximal removal capacity (corresponding to the

Fig. 4 – Removal of As(III) and As(V) from aqueous solutions by the Fe–Mn adsorbent in the pH range of 4–10. Initial As(III) and As(V) concentrations are both $133 \mu\text{M}$, adsorbent content = 200 mg L^{-1} .

Fig. 5 – Adsorption isotherms for As(III) and As(V) by Fe–Mn adsorbent in a 200 mg L^{-1} suspension at $\text{pH } 5.0 \pm 0.1$ at low equilibrium As solution concentrations.

isotherm plateau) gave a maximal capacity of 1.77 mmol As(III) g⁻¹. The obtained q_m values for our Fe–Mn material compare favorably with those obtained using other adsorbents (Table 2). These results suggested that Fe–Mn adsorbent was effective for both As(V) and As(III) removal. This result met the aim of developing such an adsorbent since As(III) is more toxic and more difficult to remove from water than As(V).

It should also be noted that the adsorbent had a much higher adsorption capacity for As(III) than that of As(V). If only oxidation occurred as mentioned above, maximal adsorption capacities towards As(V) and As(III) oxidized then adsorbed should be the same. Therefore, something else must occur when As(III) was oxidized to As(V). It was suggested that fresh adsorption sites for arsenic adsorption were created at the solid surface during As(III) oxidation (Deschamps et al., 2005), resulting in an increase of formed As(V) removal.

3.5. Effects of ionic strength and other water constituents on As(III) removal

Only As(III) removal was examined to be affected by ionic strength and other water constituents because As(III) could be oxidized to As(V) by the Fe–Mn adsorbent. Thus, the results from As(III) removal should be applicable to that of As(V).

The effect of ionic strength on the As(III) removal by Fe–Mn binary oxide adsorbent was illustrated in Fig. 6. It was clear that a change in ionic strength from 0.001 to 0.1 M NaNO₃ had little effect on the removal of As(III) by the adsorbent. This agrees with the fact that the dominant surface interaction between iron and As(V) is inner sphere in nature (Zeng, 2003).

When the ionic strength of the system changes, nonspecifically adsorbed ions are expected to be more sensitive to such a change than specifically adsorbed ions since electrolytes also form outer-sphere complexes through electrostatic forces.

The arsenic removal by Fe oxides was mainly realized by forming surface complexes at the active sites on the surface of Fe oxides. This is similar to that of Fe–Mn binary oxide. So the presence of those anions which can compete with arsenic anions for the adsorptive sites of adsorbent will affect the removal of arsenic. Competition of natural water constituents

Fig. 6 – Effects of ionic strength on As(III) removal. Initial As(III) concentration was 133 μM, adsorbent content = 200 mg L⁻¹.

Table 1 – Langmuir and Freundlich isotherm parameters for As(V) and As(III) adsorption on Fe–Mn adsorbent at pH 5.0 ± 0.1

As species	Langmuir model			Freundlich model		
	q_m (mmol g ⁻¹)	b (L mmol ⁻¹)	R^2	K_F (L mmol ⁻¹)	n	R^2
As(V)	0.93	6777	0.991	1.04	17.92	0.988
As(III)	1.59	187	0.801	2.00	6.87	0.970

Table 2 – Maximum arsenic adsorption capacities of some adsorbent system^a

Adsorbent	Max. As(III)	Max. As(V)	Ref.
	Adsorption capacity (mmol g ⁻¹)	Adsorption capacity (mmol g ⁻¹)	
Fe–Mn composite	1.77 (pH 5.0)	0.93 (pH 5.0)	Present study
MnO ₂	0.13	0.1	Lenoble et al. (2004)
Goethite	/	0.53 (pH 3–3.3)	Matis et al. (1997)
Al ₂ O ₃ /Fe(OH) ₃	0.12 (pH 6.6)	0.49 (pH 7.2)	Hlavay and Polyák (2005)
Fe(III)-loaded sponge	0.24 (pH 9.0)	1.83 (pH 4.5)	Muñoz et al. (2002)
Fe–Mn-mineral material	0.16 (pH 5.5)	0.09 (pH 5.5)	Deschamps et al. (2005)
TiO ₂	0.43 (pH 7.0)	0.55 (pH 7.0)	Bang et al. (2005)

^a pH is shown in parentheses.

with arsenic for the surface sites should mainly arise from anions, especially oxyanions, due to the anionic nature of inorganic arsenic in water (Su and Puls, 2001). Natural organic matters are not only ubiquitous in natural waters but also highly reactive toward both metals and surfaces. So its potential influences on arsenic sorption and mobility are great. Thus, four oxyanions (SO_4^{2-} , CO_3^{2-} , SiO_3^{2-} , PO_4^{3-}) whose molecular structures are similar to that of arsenic and humic acid (HA), were selected to assess the effects of co-existing anions on arsenic removal. At fixed pH of 6.9 ± 0.1 , the effects of four oxyanions at three concentration levels (0.1, 1.0 and 10 mM) were illustrated in Fig. 7.

The results in Fig. 7 showed As(III) removal was affected to a similar extent by each of four oxyanions. Phosphate caused the greatest percentage decrease in arsenic adsorption among the anions at each concentration level. The adsorbent follows the selectivity pattern phosphate > silicate > bicarbonate > sulfate. This result is in agreement with previous studies (Gu et al., 2005; Ghosh et al., 2006). This high interfering effect of phosphate in the arsenic removal can be explained by the chemical similarity between them. Phosphate element and arsenic element are located in the same main group, and the molecular structure of phosphate ion is very similar to that of arsenic ion. Thus, the present phosphate ion must compete with arsenic ion for adsorptive sites on the surface of Fe–Mn adsorbent. As shown in Fig. 6, SO_4^{2-} did not significantly affect As(III) removal. A slight

decrease in arsenic removal was observed when the sulfate concentration was as high as 10 mM, but the total removal of As(III) was still over 96%.

The data for the effect of co-existing HA on As(III) removal were listed in Table 3. It showed that the presence of HA had little effect on As(III) removal in the tested concentration range. The influence of natural organic matter on arsenic removal by hematite had been studied by Redman et al. (2002). They found that NOM dramatically delayed the attainment of sorption equilibrium and diminished the extent of sorption of both As(III) and As(V) when NOM and As were incubated together with hematite. The results indicated that the Fe–Mn adsorbent was also effective for arsenic removal when natural organic matter was present.

4. Conclusions

A novel Fe–Mn binary oxide adsorbent for effective arsenite (As(III)) removal has been prepared by a simultaneous oxidation and coprecipitation method. The prepared Fe–Mn binary oxide with a high surface area ($265 \text{ m}^2 \text{ g}^{-1}$) was amorphous and iron and manganese in this material existed mainly in the oxidation state +III and IV, respectively. The adsorbent had a high removal capacity towards both As(V) and As(III). The maximal adsorption capacities for As(V) and As(III) were 0.93 mmol g^{-1} and 1.77 mmol g^{-1} , respectively. Among the tested anions, phosphate was the greatest competitor with arsenic for adsorptive sites on the adsorbent and the As(III) removal was not significantly decreased when relatively low concentration of these anions occurred. Furthermore, ionic strength, the presence of sulfate and humic acid (HA) had no significant effect on arsenic removal. The high uptake capability of the Fe–Mn binary oxide makes it potentially attractive adsorbent for the removal of As(III) from aqueous solution.

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Fig. 7 – Effects of co-existing anions on arsenite removal at fixed initial arsenic concentration ($133 \mu\text{M}$) (pH 6.9 ± 0.1 , 200 mg L^{-1} suspension).

Table 3 – Effect of co-existing HA on arsenite removal at fixed initial arsenite concentration ($133 \mu\text{M}$) (pH 6.9 ± 0.1 , 200 mg L^{-1} suspension)

HA concentration (mg TOCL^{-1})	0 ^a	0.4	1.2	2.4	4	6.3
Arsenite removal (%)	97.1	96.9	96.9	96.5	96.4	96.2

^a Standing for no humic acid added into the arsenic solution.

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