Adsorption behavior and mechanism of arsenate at Fe–Mn binary oxide/water interface

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ABSTRACT

Preliminary study revealed that a prepared Fe–Mn binary oxide adsorbent with a Fe:Mn molar ratio of 3:1 was more effective for As(V) removal than pure amorphous FeOOH, which was unanticipated. In this paper, the As(V) adsorption capacities of Fe–Mn binary oxide and amorphous FeOOH were compared in detail. Furthermore, the adsorption behaviors as well as adsorption mechanism of As(V) at the Fe–Mn binary oxide/water interface were investigated. The higher uptake of As(V) by the Fe–Mn binary oxide may be due to its higher surface area (265 cm^2/g) and pore volume (0.47 cm^3/g) than those of amorphous FeOOH. The As(V) adsorption process on the Fe–Mn binary oxide is endothermic and the increase of temperature is favoring its adsorption. A slight increase in the As(V) adsorption was observed with increasing ionic strength of the solution, which indicated that As(V) anions might form inner-sphere surface complexes at the oxide/water interface. The Zeta potential along with FTIR analysis confirmed further the formation of inner-sphere surface complexes between As(V) anions and the surface of Fe–Mn binary oxide. In addition, the influences of coexisting ions such as phosphate, bicarbonate, silicate, sulfate, chloride, calcium and magnesium which are generally present in groundwater on As(V) adsorption were examined. Among the tested anions, chloride and sulfate had no significant effect on As(V) removal, silicate decreased obviously the As(V) removal, while phosphate caused the greatest percentage decrease in As(V) adsorption. On the contrary, the presence of cations of Ca^{2+} and Mg^{2+} enhanced the adsorption of As(V).

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1. Introduction

Arsenic is a well-known highly toxic and carcinogenic element. Its contamination in aqueous system has been a serious concern throughout the world. Elevated concentrations of arsenic are found in the groundwater of many regions of countries around the world, such as Argentina, Bangladesh, Canada, Chile, China, India, Japan, Mongolia, Poland, Thailand, the United States, and Vietnam [1–4]. Arsenic is introduced into aquatic environment from both natural and manmade sources. Typically, however, arsenic occurrence in groundwater is caused by the weathering and dissolution of arsenic-bearing rocks, minerals, and ores [2]. Ingesting arsenic-containing water is extremely detrimental to human health. To protect public health, a much more stringent limit of concentration of 10 $\mu g/L$ provided by World Health Organization (WHO) has been adopted as the drinking water standard by many countries.

Several methods such as precipitation, coprecipitation, ion-exchange, adsorption, ultra filtration, and reverse osmosis are available to remove arsenic from water, among them adsorption

process is proved to be cost-effective and simple to perform. Numerous materials [5] from natural ones to the specially designed have already been proposed for the adsorption of arsenic from water. The results of many studies [6–8] reveal that iron (hydr)oxides are promising sorbent materials because they have strong affinities towards inorganic arsenic species and high selectivity to arsenic in the sorption process. In addition, they are low cost and easily available. Therefore, much more researches are recently focused on removing arsenic with iron (hydr)oxides or iron-based materials as adsorbents. Dixit and Hering [7] have observed that amorphous iron hydroxide, goethite, and magnetite have high arsenic adsorption capacities. Zhang et al. [9] developed a Fe–Ce bimetal oxide adsorbent for arsenic removal. This adsorbent exhibited a significantly higher arsenate capacity than the individual Ce and Fe oxides (CeO_2 and Fe_3O_4) prepared by the same procedure. Mishra and Farrell [10] evaluated the arsenic removal using mixed valent iron oxides as adsorbents.

Though these adsorbents have relatively high adsorption capacities towards arsenate, they are not so effective for arsenite removal. Therefore, it is necessary to develop new adsorbents which are of low-cost and can effectively remove both arsenate and arsenite simultaneously. Recently, a novel Fe–Mn binary oxide adsorbent (with a Fe:Mn molar ratio of 3:1) has been synthesized by a

simple and low cost method in our laboratory [11]. This adsorbent is aimed at enhancing arsenite removal since the present manganese dioxide could effectively oxidize arsenite to arsenate. Experimental results show that it is very effective for arsenite removal. It is expected that the presence of manganese dioxide will lower its arsenate removal efficiency because manganese dioxide has very low adsorption capacity to arsenate. However, preliminary result indicates the uptake of arsenate by this Fe–Mn binary oxide is higher than that by pure iron oxide. Thus, it is necessary to investigate the adsorption behaviors and mechanism of arsenate on this adsorbent.

The adsorption mechanism of arsenic on iron (hydr)oxides has also been investigated by a number of researchers using EXAFS and IR spectroscopic techniques and shows that arsenic forms binuclear bidentate as well as monodentae complexes on the iron oxide surface [12–15]. In addition to spectroscopic techniques, isoelectric point determinations have been used to verify specific or nonspecific adsorption of adsorbate ions on solid surfaces. Hingston et al. [16] observed a shift of isoelectric point of goethite with specifically adsorbed anions to lower value.

The main objectives of this research were (1) to compare the adsorption performance of arsenate on pure iron oxide and Fe–Mn binary oxide; (2) to study the kinetics and equilibrium of the adsorption of arsenate on the Fe–Mn binary oxide; and finally (3) to investigate arsenate adsorption mechanism.

2. Materials and methods

2.1. Materials

All chemicals used were analytical grade and were purchased from Beijing Chemical Co. (Beijing, China). The As(V) stock solution was prepared with deionized water using $NaHAsO_4 \cdot 7H_2O$. 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. Adsorbents preparation

The Fe–Mn binary oxide with a Fe:Mn molar ratio of 3:1 was prepared according to the procedure published previously [11]. Potassium permanganate ($KMnO_4$, 0.015 mol) and iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, 0.045 mol) were dissolved in 200 mL of deionized water, respectively. Under vigorous magnetic-stirring, the $FeSO_4$ solution was slowly added into the $KMnO_4$ 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 hour and then washed repeatedly with deionized water until no SO_4^{2-} was detected. The suspension was filtrated and dried at 105 °C for 4 h. The dry material was crushed and stored in a desiccator for use. The pure amorphous FeOOH adsorbent was synthesized using the following method: contacting 0.5 M $FeCl_3$ with 1 M NaOH, aging the formed suspension for 4 h and drying at 105 °C for 24 h. The prepared Fe–Mn binary oxide has been well characterized elsewhere.

2.3. Batch adsorption tests

The kinetics experiments were conducted in batch mode. Defined amount of As(V) stock solution was added in a 1000–mL glass vessel containing 750 mL 0.01 M $NaNO_3$ solution, to make 10 mg/L or 20 mg/L of As(V) concentration. After the solution pH was adjusted to 6.9 by adding 0.1 M HCl and/or NaOH, 0.15 g of Fe–Mn binary oxide was added to obtain a 0.2 g/L suspension. The suspension was mixed with a magnetic stirrer, and the pH was

maintained at 6.9 throughout the experiment by addition of the dilute acid and/or base solutions. Approximately 5 mL aliquots were taken from the suspension at the following intervals: 0.083, 0.167, 0.25, 0.333, 0.67, 1, 1.5, 2, 4, 7, 11 and 22 h of reaction. The samples were filtered through a 0.45 μm membrane filter. The concentration of arsenate in the filtered solution was determined using an inductively coupled plasma atomic emission spectroscopy (ICP–OES).

Other adsorption tests were performed in 150 mL glass vessels. The effect of ionic strength of the solution on arsenate removal and As(V) adsorption isotherms were determined in batch tests. Experiments to determine the effect of ionic strength on arsenate removal were performed by adding 10 mg of the adsorbent sample into the vessel, containing 50 mL of 10 mg/L arsenic solution. The pH of the solutions was adjusted every four hours with dilute HCl or/and NaOH solution 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. Adsorption isotherms of As(V) by pure amorphous FeOOH and Fe–Mn binary oxide were determined at the equilibrium pH values of 6.9 ± 0.1. Initial arsenic concentrations were varied from 5 mg/L to 50 mg/L. The influence of temperature on arsenate adsorption on the Fe–Mn binary oxide was carried out at pH 5.5 ± 0.1. In order to test the effects of coexisting ions on As(V) removal, ions concentrations ranged from 0.1 mM to 10 mM. Ionic strength of the solution was adjusted to 0.01 M with $NaNO_3$. All batch experiments except for the test examining the effect of temperature on arsenate adsorption were carried out at 25 ± 1 °C with an adsorbent content of 200 mg/L 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.

2.4. Analytical methods

As(V) concentrations were determined using an inductively coupled plasma atomic emission spectroscopy (ICP–OES) (SCIEX PerkinElmer 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. All samples were analyzed within 24 h of collection.

2.5. Characterization

Specific surface area, pore volume, and pore size distribution were measured by nitrogen adsorption–desorption isotherm using the BET method with a Micromeritics ASAP 2000 surface area analyzer. X-ray diffraction (XRD) analysis was carried out on a D/Max-3A diffractometer using Ni-filtered copper Kα 1 radiation for crystalline phase identification.

FTIR spectra were collected on a Nicolet 5700 FTIR spectrophotometer (Nicolet Co., USA) using transmission model. Samples for FTIR determination were ground with spectral grade KBr in an agate mortar. IR spectra of arsenate adsorbed on Fe–Mn binary oxide were obtained as dry samples in KBr pellets corresponding to 5 mg of sample in approximately 200 mg of spectral grade KBr. All IR measurements were carried out at room temperature.

A Zeta potential analyzer (zetasizer 2000, Malvern, UK) was used to analyze the Zeta potential of Fe–Mn binary oxide particles before and after arsenate adsorption. The content of the Fe–Mn binary oxide in the solution is about 200 mg/L and As(V) concentration is 10 mg/L. 0.01 M $NaNO_3$ was used as background electrolyte to maintain an approximately constant ionic strength. After adsorption equilibrium, 20 mL of oxide suspension was transferred to a sample tube. Zeta potential of the suspensions was then measured by electrokinetic analysis.

Table 1
BET specific surface area and porosity measurements of amorphous FeOOH and Fe–Mn binary oxide.

Adsorbent	Specific surface area (m^2/g)	Average pore diameter (Å)	Average pore volume (cm^3/g)
Amorphous FeOOH	247	40	0.25
Fe–Mn binary oxide (3:1)	265	71	0.47

3. Results and discussion

3.1. Adsorbent characterization

The specific surface area and pore volume of Fe–Mn binary oxide and pure amorphous FeOOH were determined by the surface area analyzer. The data are listed in Table 1. The BET surface area of pure amorphous FeOOH is 247 m^2/g. This is in agreement to the results obtained by other researchers. For an example, Crosby et al. [17] reported that the surface area of amorphous FeOOH aged for 2 h to 12 days was 159–234 m^2/g. The Fe–Mn binary oxide has a high specific surface area of 265 m^2/g with a pore volume of 0.47 cm^3/g and the Fe oxide and Mn oxide of the Fe–Mn binary composite exist mainly in amorphous form [11]. The XRD pattern of pure iron (hydr)oxide adsorbent (not presented in this paper) showed that no obvious crystalline peak was detected, indicating its amorphous structure.

3.2. Adsorption isotherms

Preliminary study revealed that the prepared Fe–Mn binary oxide adsorbent was more effective for arsenate removal than pure amorphous FeOOH. To further compare their As(V) adsorption capacities, adsorption isotherms for 25 °C were obtained at pH 6.9 ± 0.1 by varying the initial concentration of As(V) (5–50 mg/L). The adsorption isotherms thus obtained are demonstrated in Fig. 1a. As can be seen from the figure, the Fe–Mn binary oxide has a much higher adsorption capacity of As(V) than that of pure amorphous FeOOH. The higher uptake of As(V) by the Fe–Mn binary oxide is unexpected because manganese dioxide has very low adsorption capacity to arsenate and its presence in the adsorbent should lower the arsenate removal efficiency. The specific surface area and pore volume of these two adsorbents might account for this result. Generally, adsorbent with a high specific surface area has a high adsorption capacity. The specific surface area of the Fe–Mn binary oxide (265 m^2/g) is higher than that of amorphous FeOOH (247 m^2/g). Furthermore, the pore volume of the Fe–Mn binary oxide (0.47 cm^3/g) is remarkably larger than that of amorphous FeOOH (0.25 cm^3/g). It is possible that the high specific area and pore volume enhance the As(V) adsorption performance of Fe–Mn binary oxide. The Fe–Mn binary oxide has high potential to be used as adsorbent for arsenic removal, considering its high adsorption capacities towards both arsenate and arsenite [11].

Data from the adsorption isotherms were modeled using Freundlich and Langmuir isotherm models (only Freundlich type provided in Fig. 1a). It was found that both Freundlich and Langmuir models were suitable for describing the adsorption behavior of arsenate on amorphous FeOOH. However, for the Fe–Mn binary oxide, Freundlich model fitted the data better. This is perhaps due to the heterogeneity of the adsorbent surface with the presence of manganese dioxide. The Freundlich isotherm describes adsorption where the adsorbent has a heterogeneous surface with adsorption sites that have different energies of adsorption. The energy of adsorption varies as a function of the surface coverage and is represented by the Freundlich constant K_F (L/g) in Eq. (1).

$$Q_e = K_F C_e^{1/n} \tag{1}$$

where Q_e is the quantity of solute (arsenate) adsorbed per unit mass of adsorbent, C_e is the concentration of solute in the solution at
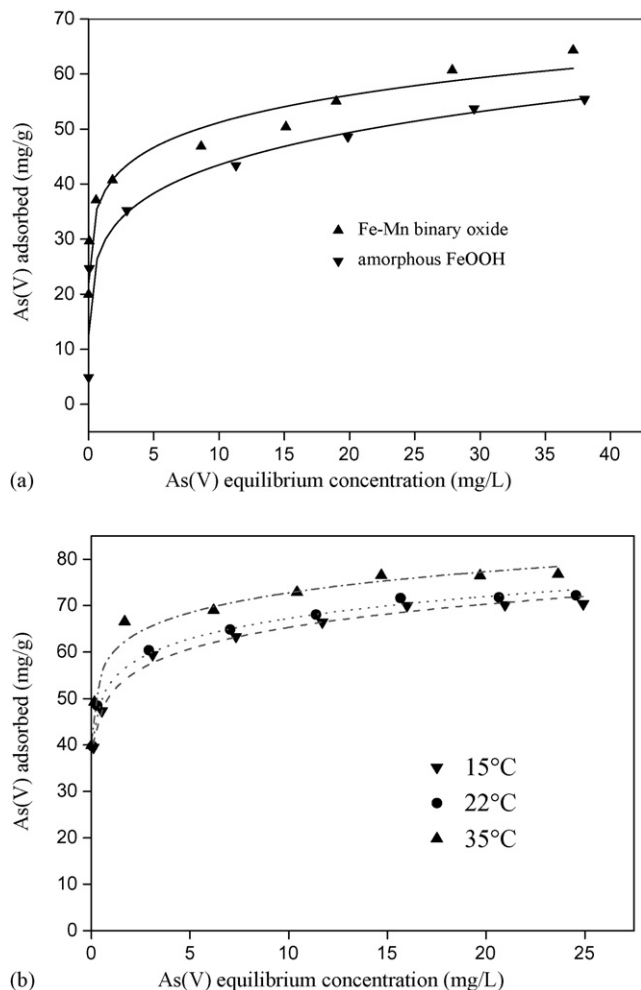

Fig. 1. Adsorption isotherms of As(V) (a) on amorphous FeOOH and Fe–Mn binary oxide in a 200 mg/L suspension at pH 6.9 ± 0.1 and 25 ± 1 °C, using the Freundlich model and (b) on Fe–Mn binary oxide at different temperatures in a 200 mg/L suspension at pH 5.5 ± 0.1, using the Freundlich model.

equilibrium, K_F is roughly an indicator of the adsorption capacity and n is the heterogeneity factor which has a lower value for more heterogeneous surfaces.

The effect of three different temperatures (15 °C, 22 °C, 35 °C) on arsenate adsorption was examined at pH 5.5 ± 0.1 and was presented in Fig. 1b. The adsorption isotherms were fitted by Freundlich model. The values of K_F and $1/n$ at different temperature are listed in Table 2. It was found that the adsorption capacity increased with increasing temperature which indicates that the adsorption

Table 2
Freundlich isotherm calculations.

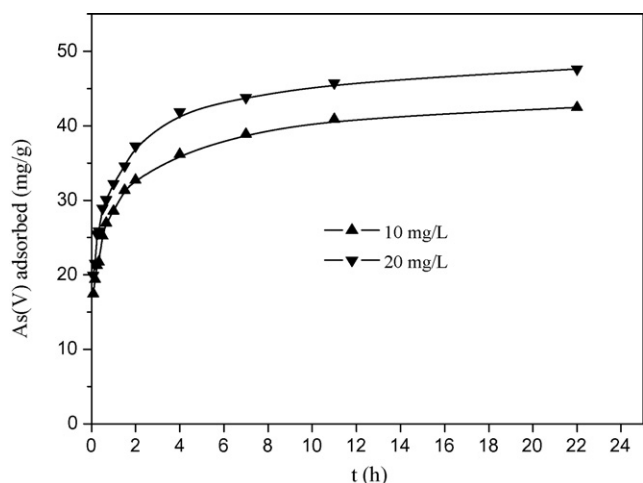|	Fe–Mn binary oxide + As(V)		
	R	K_F	$1/n$
15 °C	0.9908	51.15	0.106
22 °C	0.9942	53.72	0.097
35 °C	0.9804	59.53	0.087

Fig. 2. Adsorption kinetics of arsenate on Fe–Mn binary oxide adsorbent in a 200 mg/L suspension at pH 6.9 ± 0.1 and two initial arsenic concentrations (10 mg/L and 20 mg/L).

process is endothermic in nature. Therefore, the increase of temperature is favoring the arsenate removal by this adsorbent.

3.3. Adsorption kinetics

The adsorption kinetics of arsenate on the Fe–Mn binary oxide is illustrated in Fig. 2. The adsorption process could be divided into two steps, a quick step and a slow one. In the first step, the adsorption rate was fast, and over 80% of the equilibrium adsorption capacity was achieved within 3 h. In the subsequent step, the adsorption was slow. After 11 h, over 96% of the maximum adsorption had taken place, thus 24 h was an adequate time for equilibration to occur. Adsorption solely due to electrostatic processes is usually very rapid, in the order of seconds [6]. The adsorption of arsenate by the Fe–Mn binary oxide is on the order of hours, which may indicate a specific adsorption occurring between the arsenate species and the surface of the adsorbent.

3.4. Influence of ionic strength on arsenate adsorption

The effect of ionic strength of solution on the adsorption process of arsenate on the Fe–Mn binary oxide adsorbent is shown in Fig. 3.
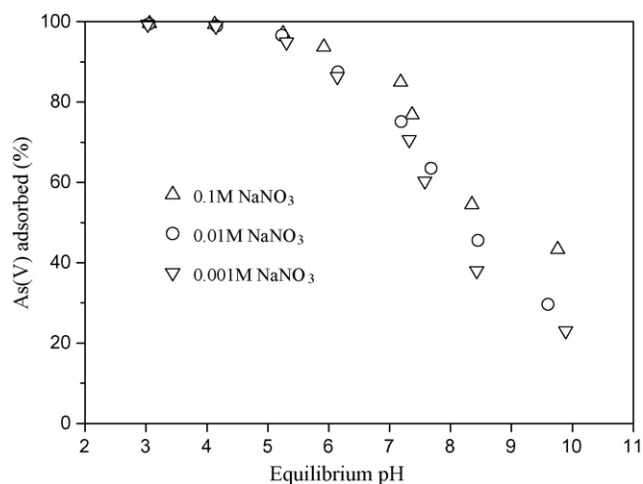
NaNO$_3$ was adopted as electrolyte in this investigation. It was found that the increase in ionic strength from 0.001 M to 0.1 M led to a shift in the position of the pH edge towards the alkaline region, and also enhanced the adsorption of arsenate in this pH range (7–10). A similar phenomenon was observed by Deliyanni and coworkers [18] when they studied the adsorption of As(V) on akaganéite. Anions that adsorb by outer-sphere association are strongly sensitive to ionic strength and the adsorption of these anions is suppressed by competition with weakly adsorbing anions such as NO$_3^-$ since electrolytes also form outer-sphere complexes through electrostatic forces. Conversely, anions that adsorb by inner-sphere association either show little sensitivity to ionic strength or respond to higher ionic strength with greater adsorption [19]. The results of this experiment suggest that arsenate anions may form inner-sphere surface complexes at the water/oxide interface.

Thus, the promoted arsenate adsorption in alkaline pH range, with increasing ionic strength, could be explained as follows. The adsorption of As(V) in an inner-sphere complexation manner increases the net negative charge of solid surfaces. A necessary consequence of surface negative charge buildup is the co-adsorption of cations. The increase of NaNO$_3$ concentration in the solution can provide more Na$^+$ cations, which are available to compensate the surface negative charge generated by specific adsorption of As(V). This favored the As(V) anions adsorption and resulted in a greater adsorption.

3.5. Zeta potential and FTIR measurements

Specific adsorption of anions makes the surface of oxides more negatively charged, which results in a shift of the isoelectric point of adsorbent to a lower pH value [20,21]. A lower isoelectric point of the system should be therefore observed, if arsenate was specifically adsorbed on the Fe–Mn binary oxide. The zeta potentials of the Fe–Mn binary oxide suspensions before and after arsenate adsorption were measured and presented in Fig. 4. The Fe–Mn binary oxide was found to have an isoelectric point of about 6.0. As predicted, this value decreased to about 4.5 when arsenic anions were adsorbed. It is clear that the presence of arsenate anions makes the adsorbent surface more negatively charged. Specific adsorption rather than a purely electrostatic interaction could be deduced from the drop of isoelectric point at the aqueous arsenate/Fe–Mn binary oxide interface.
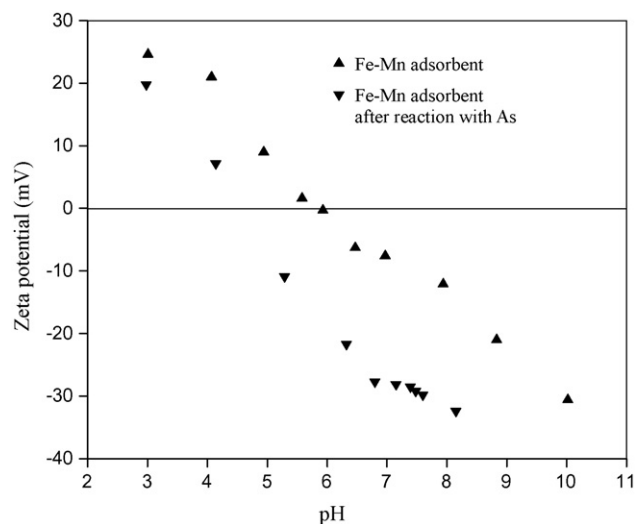

Fig. 3. Effect of pH on As(V) adsorption on Fe–Mn binary oxide for different ionic strengths. Initial As(V) concentration was 10 mg/L and adsorbent content was 200 mg/L.

Fig. 4. Zeta potential of Fe–Mn binary oxide before and after reaction with As(V). As(V) concentration was 10 mg/L and adsorbent content was 200 mg/L.

More useful information about the interaction between aqueous arsenat and solid Fe–Mn binary oxide can be provided by the FTIR technique. According to Stumm [22], there are usually occurring metal hydroxyl groups on the surface of many metal oxides, which are the most abundant and active adsorption sites for adsorbate and can be detected by IR spectroscopy. IR spectroscopy has therefore been used to investigate the surface structures and the mechanism of adsorption.

The FTIR spectra of Fe–Mn binary oxide is obtained with the KBr-pressed disk technique and is shown in Fig. 5. It is noted that infrared spectra of the adsorbent was earlier given and discussed [23]. For the Fe–Mn binary oxide sample, the band at 1625 cm^{-1} was assigned to the deformation of water molecules and indicated the presence of physisorbed water on the oxides; the peak at 1384 cm^{-1} was ascribed to the vibration of NO_3^- because sodium nitrate was used to adjust the solution ion strength; three peaks at 1127, 1047 and 974 cm^{-1} are due primarily to the bending vibration of hydroxyl groups of iron (hydr)oxides (Fe–OH) vibration [24].

The vibration models associated with the stretching and bending motions of Fe–OH groups are sensitive to the presence of adsorbed anions. FTIR spectra of the Fe–Mn binary oxide after reaction with arsenic solutions containing 1–50 mg/L of As(V) at an initial pH of 6.9 for 24 h were collected and also shown in Fig. 5. It can be clearly seen that the Fe–OH bending bands (peaks at 1127, 1047 and 974 cm^{-1}) weakened gradually, while a new band, corresponding to As–O stretching vibration [24], appeared at 820 cm^{-1} and its intensity increased with the increase of As(V) concentration. This indicates that the As(V) is bound as a surface complex and not as a precipitated solid phase. The peaks at 1127, 1047 and 974 cm^{-1} were almost disappeared when the concentration of As(V) reached 50 mg/L. An increase in solution pH value was also observed after As(V) adsorption. From the FTIR analysis, it could be concluded that specific adsorption must occur at the aqueous arsenate/Fe–Mn binary oxide interface and the replacement of surface hydroxyl groups by the As(V) species is the main arsenate adsorption mechanism.

3.6. Effect of coexisting ions on arsenate adsorption

From above, the arsenate removal by the Fe–Mn binary oxide was mainly realized by forming surface complexes at the active sites on the surface of the adsorbent. Coexisting ions such as phosphate, bicarbonate, silicate, sulfate, chloride, calcium and magnesium are generally present in groundwater, and could interfere in the uptake
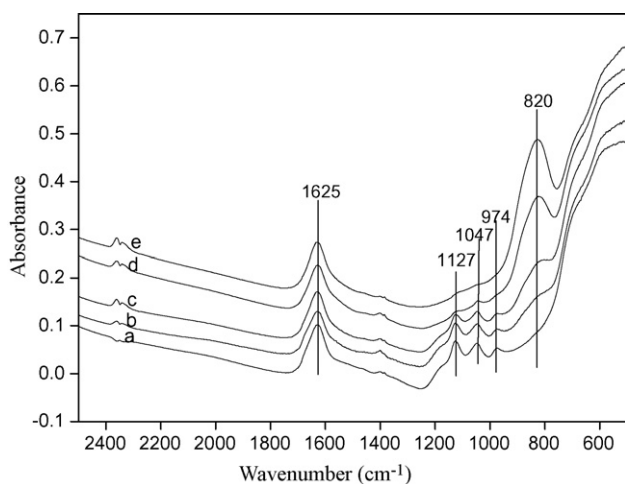
Fig. 5. FTIR spectra of Fe–Mn binary oxide (a) and after treatment in aqueous solutions of four different As(V) concentrations, (b) 1 mg/L, (c) 5 mg/L, (d) 20 mg/L and (e) 50 mg/L.

Table 3
Effect of coexisting ions on arsenate adsorption.

Concentration	Percentage removal of As(V)						
	Cl^-	SO_4^{2-}	CO_3^{2-}	SiO_3^{2-}	PO_4^{3-}	Mg^{2+}	Ca^{2+}
0.1 mM	91.3	91.5	87.7	86.2	76.3	92.5	92.8
1 mM	90.4	90.9	81.2	76.3	55.4	94.9	95.8
10 mM	90.2	90	80.6	50.3	43.7	96.1	97.9

of arsenate by adsorbent through competitive binding or complexation. To investigate the effect of coexisting ions on the adsorption of As(V), these ions were added at three concentration levels (0.1, 1.0 and 10 mM) to arsenic solutions and the arsenic removal was studied at fixed pH of 6.9 ± 0.1. The experimental results were listed in Table 3.

It is clear that the coexisting Cl^- and SO_4^{2-} had no significant influence on As(V) removal and the presence of CO_3^{2-} decreased the removal of As(V) a little. However, the coexisting oxyanions of SiO_3^{2-} and PO_4^{3-} hindered greatly the adsorption of As(V) and the percentage of As(V) removal reduced markedly with the presence of these anions. Among all the anions, phosphate caused the greatest percentage decrease in arsenic removal at each concentration level. This high interfering effect of phosphate in the arsenate removal could be due to the strong competition for the binding sites of the adsorbent between the phosphate and arsenate. 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 ions must strongly compete with arsenate ions for adsorptive sites on the surface of Fe–Mn binary oxide. On the contrary, the presence of cations of Ca^{2+} and Mg^{2+} enhanced the adsorption of As(V). And the removal percentage increased with the increase in concentrations of these two cations. This can be explained as follows. The present cations could be adsorbed by the adsorbent and effectively compensate the surface negative charge generated by specific adsorption of As(V), which favored the As(V) anions adsorption. These results indicate that the adsorbent is promising to be used in real groundwater.

4. Conclusions

The Fe–Mn binary oxide adsorbent prepared by a simultaneous oxidation and coprecipitation method had a higher adsorption capacity towards As(V) than that of pure amorphous FeOOH. This may be due to its higher surface area (265 m^2/g) and pore volume (0.47 cm^3/g). The As(V) adsorption process on the Fe–Mn binary oxide is endothermic in nature and the increase of temperature is favoring its adsorption. The increase in ionic strength of the solution resulted in a slight increase in the As(V) adsorption, which suggested that As(V) anions might form inner-sphere surface complexes at the water/oxide interface. The Zeta potential and FTIR analysis confirmed further the formation of inner-sphere surface complexes between As(V) anions and the surface of Fe–Mn binary oxide. Among the tested anions, chloride and sulfate had no significant effect on arsenic removal, silicate reduced remarkably the As(V) removal, especially at high concentration and phosphate was the greatest competitor with arsenate for adsorptive sites on the adsorbent. On the contrary, the presence of cations of Ca^{2+} and Mg^{2+} enhanced the adsorption of As(V). The investigation of the adsorbent's application in practical water treatment is very necessary and now undergoing.

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