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Removal of Arsenate from Aqueous Solution by Manganese and Iron (hydr)oxides Coated Resin

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A composite adsorbent MIR, manganese and iron (hydr)oxides coated resin, was prepared by coating manganese and iron (hydr)oxides onto the weak basic anion exchange resin D301. The effects of solution pH, contact time, ionic strength, and coexisting ions on arsenate removal with MIR were investigated in batch experiments. The results showed that As(V) can be effectively removed in a wide pH range of 4 ∼ 9. The presence of coexisting anions such as Cl^-, NO_3^-, SO_4^{2-}, and F^- had no noticeable effect on arsenate removal efficiency. However, HCO_3^- and PO_4^{3-} were found to interfere with the arsenate removal significantly. Arsenate adsorption efficiency decreased with the increment of ion strength of the solution. The adsorption isotherm could be well described by the Freundlich model. A pseudo second-order kinetics was able to provide a realistic description of the adsorption kinetics.

Keywords anion exchange resin; arsenic; iron (hydr)oxides; manganese (hydr)oxides; removal

INTRODUCTION

Inorganic arsenic a kind of endocrine disruption chemicals (EDCs) (1), has been classified as one of the most carcinogenic chemical elements by the International Agency for Research on Cancer (IARC) and the United States Environmental Protection Agency (USEPA) (2,3). In order to reduce its health risk, the maximum contaminant level (MCL) of arsenic in drinking water has been lowered to 10 μg/L in Europe and USA (4).

Arsenic contamination has been found to exist within the shallow zones of groundwater of many countries like Argentina, Bangladesh, India, Mexico, Thailand, China, Canada, USA, etc (5). In some areas of China, such as Shanxi, Xinjiang, and Ningxia, arsenic concentration in polluted groundwater was observed to range between 200 and 2000 μg/L (6). Therefore, the remediation of contaminated groundwater by arsenic has emerged as a major global concern.

So far, numerous technologies for arsenic removal have been developed. Among these, co-precipitation and coagulation process with lime, aluminum, and ferric salts have been conventionally employed for the removal of arsenic (7–8). However, these methods are limited by the solubility of arsenic. Furthermore, they require the addition of large amounts of chemicals and result in the management of wet bulky sludge. Polymeric anion exchangers prefer sulfate to arsenate, the arsenic removal capacity is greatly reduced in the presence of high concentrations of competing sulfate ions. Reverse osmosis (RO) is possible, but its application is usually encumbered by problems of the fouling of membranes and high operating pressure. Adsorption technique is now receiving increasing attention for arsenic removal because of its simplicity, potential of regeneration, and sludge free operation. In recent years, many effective absorbents such as activated red mud (9), zeolite (10), manganese dioxide (11), iron hydroxide and oxides (12), Ce(VI)-doped iron oxide (13), zero-valent iron (14), granular titanium oxide (15), and biomass materials (16) have been developed and applied for both As(III) and As(V) removal from water solutions. Among them, manganese (hydr)oxide and iron (hydr)oxides are widely studied and employed for the remediation of arsenic contaminated water (17,18,19) because of their stable chemical properties, high surface areas, and the ability to exhibit strong affinity for arsenic by means of ion exchange, specific adsorption to surface hydroxyl groups and co-precipitation. However, these oxides are usually in colloidal forms and not convenient for practical column process. This situation in recent years has led to a growing interest in the syntheses and application of composite adsorbents by forming an oxide surface loading on another solid. A number of composite adsorbents of this type (20–25) such as iron oxide-coated sand, pedogenic Fe–Mn nodules, and iron-coated GAC have been tried in

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the laboratory and/or field-scale testing for the removal of trace arsenic. These adsorbents showed more future promise because of high removal efficiency and convenience for practical column process.

The objective of this study is to synthesize a high efficient composite adsorbent for the removal of As(V) from aqueous solution and avoid the disadvantage of the colloidal form of the adsorbent. By using a polymer resin as the supporting material, an efficient composite adsorbent MIR (manganese and iron (hydr)oxides coated resin) was prepared and applied for the removal of arsenate in aqueous solution. The effects of various experimental parameters on the adsorption process were investigated.

MATERIALS AND METHODS

Materials

All reagents used were of analytical grade. Solutions were prepared with double-distilled water (DDW). All glassware were cleaned by soaking in 10% HNO_3 and rinsed three times with DDW. The arsenate stock solution (1000 mg/L) was prepared from sodium heptahydrate salt $Na_2HAsO_4 \cdot 7H_2O$ (Fluka, purity >98.5%). $KMnO_4$ and $FeSO_4 \cdot 7H_2O$ were used for the loading process. The pH was adjusted using 0.1 mol/L HCl and 0.1 mol/L NaOH solutions. In order to maintain a relatively constant ionic strength, all artificial As(V) solutions, except ionic strength effect experiment, contained 0.1 mol/L $NaNO_3$ as background electrolyte.

The polymer resin, D301 (Shanghai Resin Co. Ltd, China), is a weakly basic, macroporous anion exchange resin, and its main properties are given in Table 1. For the experiments, the resin was pretreated with 0.05 mol/L sulfuric acid and then with 0.05 mol/L sodium hydroxide to remove impurities from its synthesis process. After extensive rinsing with DDW, the anion exchanger resin was applied for the further experiments.

Preparation of Manganese and Iron (hydr)oxides Coated Resin (MIR)

MIR, manganese, and iron (hydr)oxides coated resin, was prepared according to the following method: The amount of 1 g D301 resin was dipped in solution of 0.05 mol/L $KMnO_4$. After shaking for 10 min, the same volume of 0.05 mol/L $FeSO_4$ was added into the mixture, then continuously shaken at 25°C for 2.5 h and aged for 12 h. The prepared absorbent was washed thoroughly with DDW and air-dried at $T \leq 60°C$ for 1 hr before further studies.

TABLE 1
Characteristics of D301 ion exchange resin

Polymer matrix	Styrene-DVB
Functional group	di-methyl-ammonium
Ionic form	Cl^-
Exchange capacity	$\geq 1.4\,mmol\ mL^{-1}$
Operating temperature	$\leq 100°C$
Effective size	$0.40 \sim 0.70\,mm$

Zero Point Charge of MIR

The pH of zero point charge (pHzpc) was determined according to the reported method (25). To a series of 125 ml polyethylene bottle that contained 40 ml of 0.01 mol/L $NaNO_3$, different volumes of either 0.1 mol/L HCl or 0.1 mol/L NaOH were added so as to obtain wide ranging pH $2 \sim 10$. The total volume of the solution in each bottle was made up to 50 ml by 0.01 mol/L $NaNO_3$. After 2 h of equilibration, the pH values were measured and designated as initial pH or pH_i. A known amount of absorbent was added in each bottle which was then flushed with nitrogen gas for 3–5 min and stoppered securely. After 72 h of equilibration at room temperature with intermittent shaking, the pH values of the supernatant liquid in each bottle was noted and designated as final pH or pH_f. The difference between pH_i and $pH_f(\Delta pH)$ was plotted against pH_i. The pHzpc value for an adsorbent was at the pH value where curve intersects ($\Delta pH = 0$). At this pH, the absorbent does not induce the release of either H^+ or OH^- ion in solution, and the surface does not undergo or acquire any charge through acid-base dissociation.

Adsorption Experiments

The effect of pH on arsenate removal by MIR was conducted by shaking 0.1 g of MIR with 100 mL of solution containing different initial As(V) concentration of either 1 mg/L or 10 mg/L for 24 h at temperature of $25 \pm 1°C$.

Isotherm studies were conducted by reacting 100 mL of solution containing different initial As(V) concentration between 0.50 to 2.50 mg/L with 0.1 g of MIR of known effective size range at pH 5.0 at temperature of $25 \pm 1°C$.

The adsorption kinetics was carried out by shaking 0.1 g of MIR with 100 mL of different initial As(V) concentration of either 1 mg/L or 10 mg/L at different time intervals at a temperature of $25 \pm 1°C$. The solution pH was maintained constantly at 5.0.

The effect of the ionic strength on the arsenate removal by MIR was performed by shaking 0.1 g of MIR with 100 mL of initial As(V) concentration of 10 mg/L, and with electrolyte concentration range of $0 \sim 0.25$ mol/L $NaNO_3$ at pH 5.0 and temperature of $25 \pm 1°C$.

The effect of various competing anions such as $Cl^-, NO_3^-, SO_4^{2-}, F^-, HCO_3^{2-}, PO_4^{3-}$ on arsenate removal by MIR was also investigated. The initial concentration of As(V) was fixed at 10 mg/L and the adsorbent dosage was 1 g/L. Adsorption was conducted at pH 5.0 at temperature of $25 \pm 1°C$ for 24 h.

Analysis Methods

The determination of Fe and Mn concentration was performed using Perkin-Elmer Optima 2000DV ICP spectrometer.

Arsenic concentration was determined by hydride generation atomic fluorescence spectrophotometry (HG-AFS) (AFS-230E, Beijing, Haiguang Corporation). The arsenic detection limit of AFS-230E was 0.1 μg/L, and the analytical regression coefficient $\gamma^2 > 0.9990$.

The FT-IR spectra of MI (mixed manganese and iron (hydr)oxides, prepared by a similar procedure as MIR except without D301 present) and MIR were recorded in KBr media and performed by Bruker Tensor 27 Spectrometer.

RESULTS AND DISCUSSION

Characterization of MIR

The FTIR spectra for MI and MIR were shown in Fig. 1. The oxide coated on the surface of weak basic anion exchange resin D301 was the same as that prepared by the similar procedure as MI without resin D301 present. The band at wave number around 3550–3200 cm^{-1} represented H-O-H stretching vibration, and that at 1641 cm^{-1} represented H-O-H bending vibration of the water molecule (26). The symmetric stretching of Fe-O was indicated by a band at 615 cm^{-1} and the characteristic vibration of γ(Mn-O) was indicated by the band range of 440–490 cm^{-1} (27). A strong band at 1130 cm^{-1} and 1050 cm^{-1}, which corresponded to the bending vibration of hydroxyl group (M–OH) (28). From the above FTIR analysis, it could be speculated that, on the surface of MIR, there existed Mn oxide, Fe oxide, and a great deal of hydroxyl groups.

The pHzpc of MIR was shown in Fig. 2. The pHzpc was observed at pH 4.6. Below the pHzpc, the surface charge of MIR will be positive and above the pHzpc the surface charge of MIR will be negative.

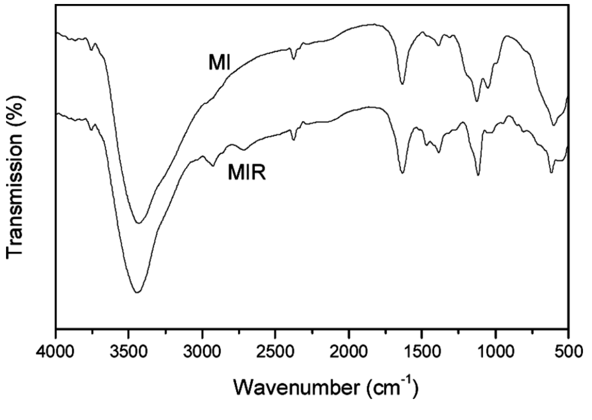

FIG. 1. FTIR spectra for MI and MIR (MI, mixture of Mn oxide and Fe oxide; MIR: Mn and Fe (hydr)oxide coated D301Resin).

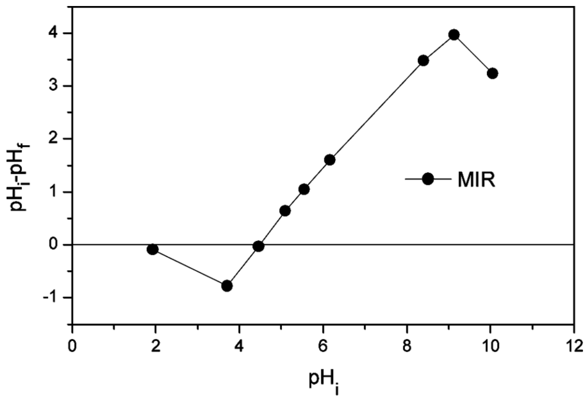

FIG. 2. Change in pH of MIR as a function of pHi.

Effect of pH on Arsenate Adsorption

The solution pH is generally known to play a very important role in adsorption process. It affects species distribution of arsenic in solution and the surface charge of the absorbent.

As shown in Fig. 3 for 1 mg/L of initial As(V) concentration, the removal of arsenate was found to be nearly complete (100%) in the wide pH range of 2∼9. For 10 mg/L of initial concentration As(V), the removal efficiency of arsenate decreased with increasing pH. The removal efficiency of arsenate by MIR was reduced from 96.1 to 67.5 as pH shifted from 2 to 10 under the As(V) concentration of 10 mg/L. Figure 3 showed that the removal rate is more sensitive to pH for a higher concentration of arsenate. The reason may be related to the surface characteristics of the adsorbent. Based on the value of pHzpc, we can know the surface charge of MIR is negative when pH > 4.6, and As(V) mainly exists as a monovalent ($H_2AsO_4^-$) or divalent ($HAsO_4^{2-}$) anions. So

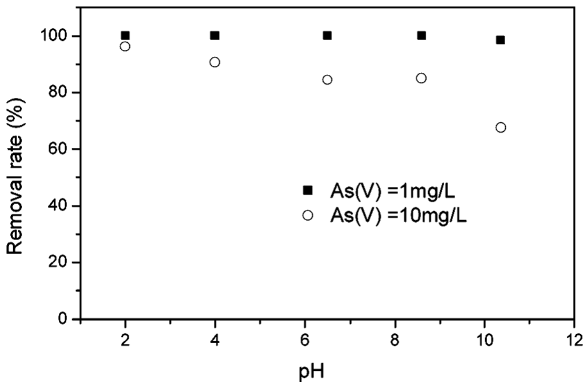

FIG. 3. Effect of pH on As(V) removal by MIR, with reaction conditions: initial As(V) concentration is 1 mg/L and 10 mg/L, separately, adsorbent dosage = 1 g/L, the volume of solution = 100 ml, ionic strength = 0.1 mol/L $NaNO_3$, temperature = 25°C.

it is unfavorable for the removal of As(V) when pH value was high. When the initial concentration of As(V) is 1 mg/L, the adsorption capacity of MIR is high enough so that we hardly observe the negative impact on the As(V) removal rate caused by the pH change. While the initial concentration of As(v) increase to 10 mg/L or higher, pH effect began to appear more obviously.

The final pH in the presence and absence of arsenate was also studied. It was observed that the final pH in the presence of As(V) was slightly higher than that in the absence of As(V). This slight difference in pH may be attributed to the adsorptions reactions in which OH^- was replaced with arsenate anions (29).

$$XOH + H_2AsO_4^- \rightarrow XH_2AsO_4 + OH^-$$

This type of adsorption which takes place by ligand exchange mechanism is generally indicated as specific adsorption. So it could be deduced that specific adsorption of As(V) took place in the adsorption process of As(V) by MIR.

We also investigated the total re-dissolved iron and manganese. As shown in Fig. 4, below pH 4, the dissolution of iron and manganese in aqueous phase was significant. Above pH 4, concentrations of ferric ions and manganese ions in solution were almost constant, which indicated the absorbent MIR is stable in this pH range.

According to above results, further experiments were performed at the solution pH of 5.0.

Adsorption Isotherm

The Langmuir and Freundlich isotherm models were used to describe the equilibrium adsorption results. The Langmuir isotherm assumes a monolayer surface coverage limiting the adsorption due to the surface saturation, while the Freundlich isotherm model is an empirical model (30).

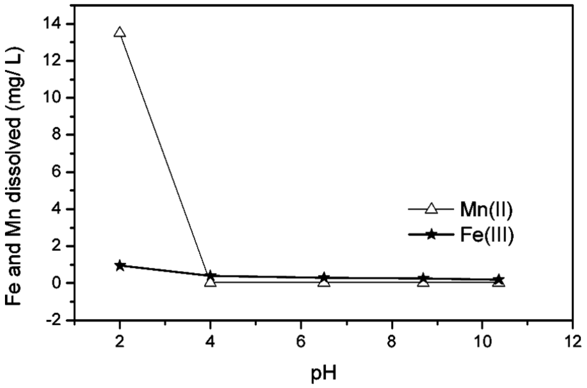

FIG. 4. Dissolution of iron and manganese from MIR in different pH values, with reaction conditions: sorbent concentration = 1 g/L, the volume of solution = 100 ml, ionic strength = 0.1 mol/L $NaNO_3$, temperature = 25°C, contact time = 24 h.

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \qquad (1)$$

$$q_e = K \cdot C_e^{1/n} \qquad (2)$$

where C_e is the equilibrium concentration of solute (mg/L), q_e is the amount adsorbed at equilibrium concentration (mg/g), Q_0 is the theoretical maximum adsorption capacity (mg/g), b is a constant related to adsorption energy (L/mg). K is the Freundlich constants denoting the adsorption capacity of the adsorbent $[(mg/g)(L/mg)^{1/n}]$, and n is the adsorption intensity parameter.

The isotherm parameters and correlation coefficients of both Langmuir and Freundlich models were shown in Table 2. It indicated that the Freundlich isotherm model fitted to the experimental data better. The Freundlich plots for the adsorption of As(V) onto MIR were shown in Fig. 5.

Adsorption Kinetics

The adsorption kinetics describes the absorbate removal rate which in turn governs the residence time in the interface of adsorbent-solution. It is one of the important characteristics in defining the efficiency of adsorption process.

As shown in Fig. 6, the adsorption was rapid in the first 30 min and then slowed down gradually as the reaction approached equilibrium. Such adsorption characteristic was observed in the process of arsenate and arsenite adsorption on other materials (7,8,17,18). It was speculated that adsorption of arsenate anions on MIR consists of two stages: a rapid initial stage and subsequent slow stage. Within the first 30 min, most of arsenate anions reached the adsorption sites of MIR by diffusion, the rest of the arsenate was slowly adsorbed by MIR in the following 24 h. For initial As(V) concentration of 1 mg/L, the equilibrium was attained within 3 h, for initial As(V) concentration of 10 mg/L, the necessary time to reach this equilibrium was about 9 h.

TABLE 2
Isotherm parameters and correlation coefficients of both Langmuir and Freundlich models for As(V) adsorption onto MIR

Langmuir			Freundlich		
Q_0 mg/g	b L/mg	R^2	K $(mg/g)(L/mg)^{1/n}$	n	R^2
128.21	0.005	0.806	1.63	1.42	0.984

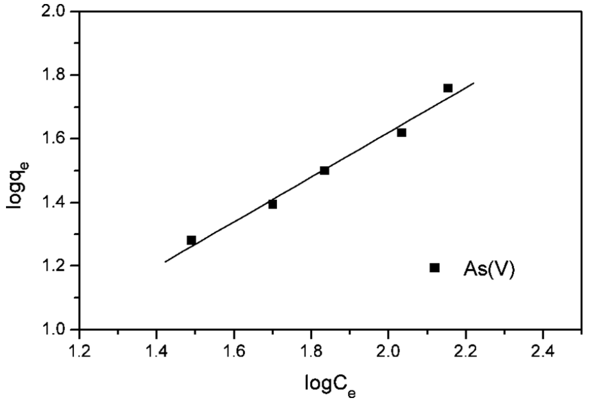

FIG. 5. Freundlich isotherm for As(V) adsorption onto MIR, with reaction conditions: pH = 5.0, adsorbent dosage = 1 g/L, the volume of solution = 100 ml, ionic strength = 0.1 mol/L NaNO$_3$, temperature = 25°C.

The pseudo second-order kinetic model was used to describe the arsenate adsorption by MIR. The rate equation can be expressed as follows (31):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where q_e and q_t are the amounts of arsenate adsorbed at equilibrium (mg/g) and at time t, respectively. k_2 is the pseudo second-order rate constant of adsorption (g/mg.min).

By linear plots of t/q_t *vs.* t according to the experimental kinetic data, two straight lines were obtained, indicating that the process followed a pseudo second-order kinetics (Fig. 7). The rate equation were found to be $t/q_t = 1.89\,t + 43.351$ ($R^2 = 0.9996$) and $t/q_t = 0.2085\,t + 15.079$ ($R^2 = 0.9925$) at the initial arsenic concentration 1 and 10 mg/L, respectively. The rate constants calculated from their intercepts were 8.24×10^{-2} (As = 1 mg/L) and 2.88×10^{-3} g/mg/min (As = 10 mg/L).

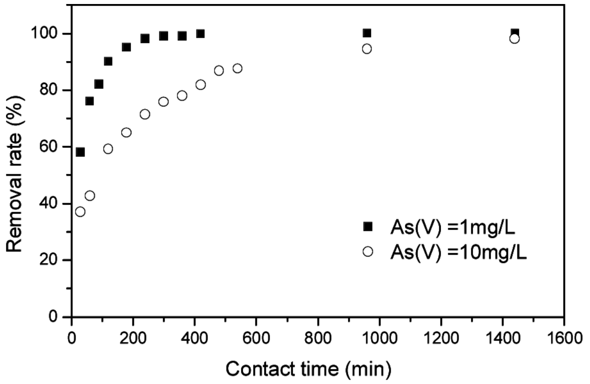

FIG. 6. Effect of contact time on As(V) removal by MIR, with reaction conditions: initial As(V) concentration is 1 mg/L and 10 mg/L, respectively, pH = 5.0, adsorbent dosage = 1 g/L, the volume of solution = 100 ml, ionic strength = 0.1 mol/L NaNO$_3$, temperature = 25°C.

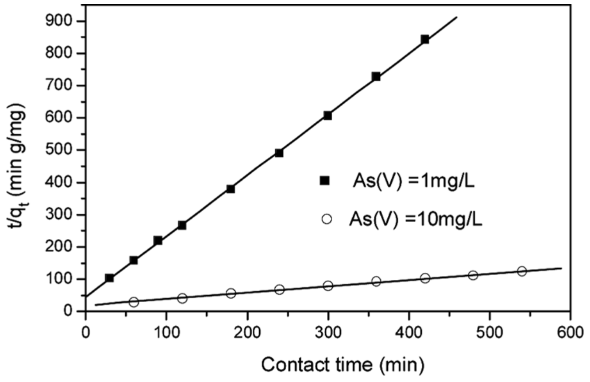

FIG. 7. The pseudo second-order rate kinetics for As(V) removal by MIR, with reaction conditions: initial As(V) concentration is 1 mg/L and 10 mg/L, respectively, solution pH = 5.0, adsorbent dosage = 1 g/L, the volume of solution = 100 ml, ionic strength = 0.1 mol/L NaNO$_3$, temperature = 25°C, contact time = 7 h.

Effect of Ionic Strength

The effect of ionic strength on cation and anion adsorption onto metal oxides provides important information of the relative bonding affinity of these ions for surface sites as well as the type of adsorption substance (32). In general, if the adsorption between the adsorbate and the surface sites is caused by relatively strong chemical bonds such as ion and covalent bonds, the adsorption is identified as "specific" adsorption. In "specific" adsorption, the "inner-sphere" type complexes are concurrently formed and the changing of ionic strength was found to show little effect on adsorption. While the adsorption between the adsorbate and the surface sites results from the weaker Coulomb attraction or Van der Waals bond, the adsorption is identified as "non-specific" adsorption. The adsorption substance formed during this process is named as "outer-sphere" type complexes and the amount absorbed is reduced with increasing ionic strength. Decreased adsorption with increasing ionic strength of inert background electrolytes has been taken as evidence of non-specific adsorption (33).

As shown in Fig. 8, The adsorption rate of arsenate by MIR decreased obviously with increasing ionic strength. The changing of ionic strength between 0 mol/L NaNO$_3$ and 0.25 mol/L NaNO$_3$ resulted in the decrease of the arsenate removal efficiency from 91% to 81.9%. So it was speculated that the arsenate is non-specifically adsorbed as an outer-sphere complex on the surface of MIR.

Figure 8 also showed that the removal rate stabilizes at an ionic strength of 0.1 mol/L, and Fig. 3 has given the result that As(V) removal efficiency was still high above pHzpc of MIR. According to the above experimental

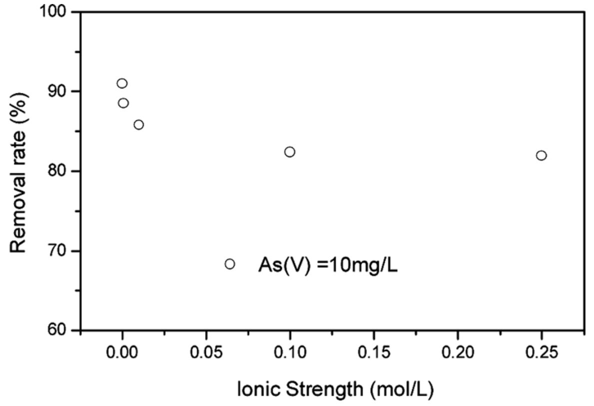

FIG. 8. Effect of ionic strength on As(V) removal of by MIR, with reaction conditions: initial As(V) concentration = 10 mg/L, solution pH = 5.0, adsorbent dosage = 1 g/L, the volume of solution = 100 ml, temperature = 25°C, contact time = 24 h.

results about the effects of pH and ionic strength, it was speculated that both specific adsorption and non-specific adsorption took place in the process of As(v) removal by MIR. The specific adsorption played a more important role than non-specific adsorption. Therefore, with the increase of ionic strength, the removal rate turned to lower slightly, but it was not so obvious. That was the reason why it was observed that the removal rate kept stable at the level of the ionic strength of about 0.1 mol/L.

Interference of Coexisting Anions on the Adsorption of As(V) on MIR

In groundwater sources, several anions might exist, which could compete with As(V) for the available adsorption sites.

The results are given in Fig. 9. It showed that the presence of anions such as Cl^- (200 mg/L), NO_3^- (200 mg/L), SO_4^{2-} (200 mg/L), and F^- (100 mg/L) has no noticeable effect on As(V) removal. However, HCO_3^- (100 mg/L) and PO_4^{3-} (100 mg/L) were found to interfere with As(V) removal significantly. The As(V) removal efficiency decreased to 64% in the presence of HCO_3^-, whereas the presence of PO_4^{3-} reduced As(V) removal rate to 43.3% under the experimental conditions. Other anions such as Cl^-, NO_3^-, and SO_4^{2-} did not interfere with the removal of As(V) under our experimental conditions.

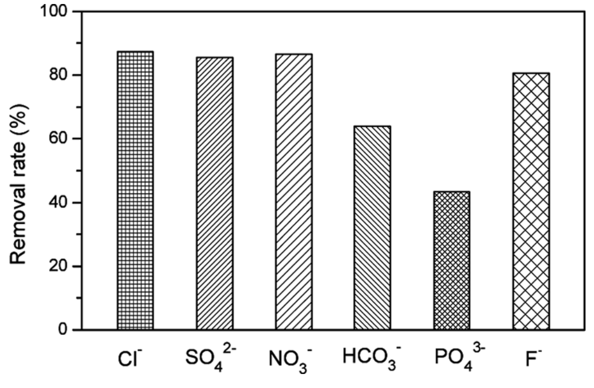

FIG. 9. Effect of coexisting anions on As(V) removal by MIR, with reaction conditions: initial As(V) concentration = 10 mg/L, solution pH = 5.0, adsorbent dosage = 1 g/L, the volume of solution = 100 ml, temperature = 25°C, contact time = 24 h.

Phosphate has a great similarity with arsenate in chemical properties and molecular structure. They are both triprotic acid with similar ionization constants (34). The suppression of arsenate adsorption by phosphate usually occurs in both natural solid and biological system. Carbonate also had a significant influence on the adsorption of As(V) in this study. These results are in accord with the previous report (35), which attributed to the displacement of adsorbed arsenic with dissolved carbonate occurs on the surface sorption site in the subsurface.

CONCLUSIONS

An efficient adsorbent MIR was developed by coating manganese (hydr)oxides and iron (hydr)oxides on weak basic anion exchange resin D301. The adsorbent MIR can be utilized as an efficient material for the removal of As(V) from aqueous solution in a wide pH range 4–9. In the case of low concentration 1 mg/L As(V), the removal efficiency can reach almost 100%. The adsorption isotherm can be well described by the Freundlich model. The adsorption process followed a pseudo second-order kinetics. Arsenate removal efficiency by MIR decreased with the increment of ion strength, and the presence of co-existing PO_4^{3-} or HCO_3^- inhibited the arsenic removal.

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