Efficient Adsorption of the Cd(II) and As(V) Using Novel Adsorbent Ferrihydrite/Manganese Dioxide Composites

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ABSTRACT: Ferrihydrite/manganese dioxide composites (FH−M) were synthesized from ferrihydrite (FH) and manganese compounds by ex situ synthesis and characterized using X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy in the present work. The influences of experimental parameters such as the solution pH value and initial concentration of adsorbate on the adsorption uptake of Cd(II)/As(V) was systematically investigated. The adsorption kinetics was analyzed by fitting quasi-first-order and quasi-second-order kinetic equations. The results showed that with increase in the pH value, the adsorption rate of Cd(II) is increased, while that of As(V) is increased first and then decreased. For the kinetic adsorption process, the adsorption performance of FH−M to As(V) was better than that to Cd(II). The quasi-second-order kinetic equation and Freundlich equation were more suitable to describe the adsorption of Cd(II)/As(V). The ligand exchange of Cd(II)/As(V) with the −OH in the composites was confirmed by analyzing the characterization results of X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. The high adsorption ability of the FH−M makes it a potentially attractive adsorbent for the removal to Cd(II) and As(V) with a good application prospect.

1. INTRODUCTION

At present, heavy-metal contamination was developed as a global environmental issue that has attracted great attention from all over the world. Due to their enrichment, heavy metals in the natural environment are difficult to degrade. Cadmium (Cd), one of the heavy-metal elements, is highly toxic and available scarcely in nature, but the development of human activities, such as mineral mining, fuel combustion, and sewage discharge, has broken its equilibrium state and caused Cd in the environment to exceed the standard level. More importantly, Cd is easily absorbed by plants, and its harm to humans at the end of the food chain should not be ignored due to its enrichment.1−5 Due to the toxicity and certain properties of arsenic (As), similar to those of heavy-metal elements, As is generally classified as a heavy-metal element. As is a trace element in nature; however, human activities such as fertilization and smelting have resulted in a serious As contamination, which is already threatening human health.6−8 Exposure of humans to increased levels of As makes them highly susceptible to cancer, diabetes, and neurological problems.9 There are many methods for removing heavy metals, such as chemical precipitation,10 electrochemical treatment,11 ion exchange,12 redox,13 adsorption,14 flotation,15 and membrane separation.16 The above methods have their own advantages, and their shortcomings are worth mentioning.17,18 Chemical precipitation and ion exchange are prone to secondary pollution. Electrochemical methods, redox methods, flotation methods, and membrane separation methods have high cost problems. In contrast, the use of adsorption to remove heavy metals is simple and relatively inexpensive. Therefore, the adsorption method is a heavy metal treatment method worthy of promotion.18 The key to the treatment of heavy metals by adsorption is the performance of the adsorbent.

The content of iron (Fe) are relatively plentiful in soils, and they exist predominantly in the form of oxides, hydroxides, and oxyhydroxides in natural environments.19 Owing to its large surface area, high surface activity, and strong adsorption capacity, ferrihydrite (FH) with an amorphous structure serves as an important adsorbent in the environment and can control the migration and conversion of many heavy metals including Cd and As. FH adsors heavy metals by the ligand exchange reaction or complexation reaction.20−24 Actually, the influence of some heavy metals on the environment depends on their
chemical form, which is determined by their valence state. Manganese oxides with catalytic and redox capabilities can oxidize As(III) to As(V) to reduce their toxicity. Due to the rich structural defects on the surface of manganese oxide, it has a high surface activity, which results in manganese oxide having a high adsorption affinity to Cd(II). Therefore, manganese oxide plays an extremely important role in controlling the migration and conversion of pollutants in the environment.

Combining the advantages of FH in the adsorption and those of manganese oxide in the conversion of some heavy metals such as Cd and As is a good idea or route to solve the environment problem of pollution by heavy metals. However, there is little work on this subject so far. Therefore, in the present work, ferrhydrite/manganese dioxide composites (FH–M) have been prepared for the first time by the ex situ synthesis method. Then, the microstructure of the synthesized FH and FH–M as well the adsorption properties of this composites on Cd(II)/As(V) was investigated. Focusing on the kinetic adsorption and isothermal adsorption, we intensively discuss the adsorption performance of the synthesized FH–M composites for Cd(II)/As(V). The application prospect of the FH–M composite adsorbent and the development of Cd(II)/As(V) removal in wastewater is pointed out in the end.

2. RESULTS AND DISCUSSION

2.1. Microstructure of Ferrhydrite and Ferrhydrite/Manganese Dioxide Composites. The phase composition and surface morphology of the synthesized samples are analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD patterns of MnO₂, FH and FH–M samples are shown in Figure 1. It shown that the FH sample has no obvious diffraction peak, only two broad characteristic peaks at 2θ of 35° and 62°, which means that the sample has low crystallinity. This result is consistent with the standard XRD pattern of FH reported by Schwertmann and Cornell. Therefore, the synthesized product is proved to be FH. The synthesized FH has a large specific surface area (292.632 m²·g⁻¹), which is measured by the BET-N₂ adsorption method, consistent with the results reported by Schwertmann and Cornell. It shown that MnO₂ has only two characteristic peaks at 2θ of 37° and 65°, the FH–M has two characteristic peaks at 2θ of 36° and 64°. The positions of the two diffraction peaks of FH and MnO₂ are very close, and the degree of crystallization of the synthesized FH as well MnO₂ is so low that the intensity of these peak is low and the width is broad. This explains why the diffraction patterns are similar before and after compounding in Figure 1, the position of the diffraction peak does not change significantly, and no new diffraction peak appears. This indicated that the combination of FH and manganese dioxide did not destroy the original crystal structure of the FH, and no new crystal form appeared.

The SEM images and energy-dispersive X-ray spectrum (EDS) of the prepared FH and FH–M samples are shown in Figure 2. One can see that the size and shape of FH particles vary in the SEM images of Figure 2a, which can be due to the small size of the FH particles and the presence of agglomeration. From the EDS spectrum of FH exhibited in Figure 2b,c, it shown that the main elements are O and Fe, which is consistent with the constituent elements of FH. The scanning electron microscopy image of a manganese dioxide hydrated iron ore composite is shown in Figure 2d. Compared to Figure 2a, the particles of the composite surface shown in Figure 2h (high-power SEM image of composite material) were relatively regular and uniform. The main elements in the EDS spectrum of FH–M are O, Fe, and Mn (in Figure 2e–g). In summary, manganese dioxide is indeed adsorbed on the surface of the FH.

2.2. Chemical Composition of Ferrhydrite/Manganese Dioxide Composites before Adsorption. Figure 3 shows the X-ray photoelectron spectra (XPS) of the prepared FH–M and those of O 1s, Fe 2p, and Mn 2p electron binding energies. The surface of the FH–M contains Fe, Mn, and O elements (in Figure 3a), which is consistent with the previous XRD and SEM-EDS test analysis results. The binding energies at 725.9 and 712.4 eV in the Fe 2p spectrum (in Figure 3b) correspond to Fe 2p₁/₂ and Fe 2p₃/₂ of Fe(III) in FH, respectively. The “satellite peak” present at 719.4 eV is exactly the same as the characteristic peak of Fe(III) in Fe₂O₃. This is also consistent with the chemical formula (5Fe₂O₃·9H₂O) added to FH by Schwertmann and Cornell. The binding energies at 654.8 and 642.2 eV in the Mn 2p spectrum (Figure 3c) correspond to Mn 2p₁/₂ and Mn 2p₃/₂ of Mn(IV) in MnO₂, respectively. There is no satellite characteristic of MnO₂ in the Mn 2p spectrum. The “satellite peak” present at 645.6 eV is consistent with MnO with satellite characteristics, which may be reduced by Fe(III) to Mn(II) during the recombination process. The binding energies at 530.2, 531.6, and 533.3 eV in the O 1s spectrum (in Figure 3d) correspond to O in FM–O (FM represents Fe or Mn), FM–OH, and H₂O, respectively.

2.3. Effect of Initial Concentration on Adsorption Properties. The effect of the initial concentration of Cd(II)/As(V) on the adsorption of FH and FH–M is shown in Figure 4. It can be seen from Figure 4 that the removal rate of Cd(II)/As(V) decreases with the increase of initial concentration no matter before and after compound. When the initial concentration of Cd(II)/As(V) is low, the removal rate decreases very slowly. This result is because the low concentration is still within the adsorption capacity of FH and FH–M. Once the initial concentration of Cd(II)/As(V) increases to a certain value, the removal rate reduces obviously. This is due to the limited adsorption capacities of FH and FH–M. When the initial concentration of Cd(II)/As(V) gradually increases, the adsorption site is slowly occupied. However, when the initial concentration is 50 mg/L, the As removal rate can still be above 90%. It shows that FH and FH–M have good purification effect on different concentrations of arsenic-containing wastewater. In contrast, the removal rate of Cd is slightly lower. However, the removal rate to Cd(II)/As(V) by FH–M is higher than that by FH, which indicates a higher adsorption capacity of Cd(II)/As(V) by FH–M.
2.4. Effect of pH Value of Solution on Adsorption. It can be seen from Figure 5a that the adsorption rate of Cd(II) by FH and FH–M at different pH values (4–10) under the condition of initial concentration of Cd(II) of 50 mg/L, adsorption temperature of 25 °C, and adsorption time of 24 h.

The figure shows that the initial pH value has a great influence on the adsorption effect of Cd(II). The overall rule is that the adsorption rate increases with the increase of pH value. The results showed that the adsorption effect of FH–M on Cd(II) was slightly better than that of FH. At lower pH values, there is a higher concentration of H+ in the solution, and FH and FH–M will protonate due to the large amount of H+ accumulated around them, resulting in a surface that tends to be positively charged. A large amount of H+ will compete with Cd(II) for adsorption, thereby hindering the adsorption binding of Cd(II) to FH and FH–M. When the pH value increases, the H+ concentration decreases rapidly and the OH− concentration increases rapidly, causing the charge on the surface of FH and FH–M to change from positive to negative, and Cd(II) in the solution changes from the free state to the combined state after binding to OH−, which facilitates the adsorption of Cd(II) by FH and FH–M. As a composite product of MnO2 and FH, FH–M has a much higher specific surface area than that of FH, which greatly increases its exposure to Cd(II). Moreover, the adsorption performance is promoted due to the high surface energy and activity of FH–M. Therefore, the adsorption effect of FH–M is better than that of FH.

It can be seen from Figure 5b that the adsorption rate of As(V) by FH and FH–M at different pH values (4–10) under the condition of initial concentration of As(V) of 50 mg/L, adsorption temperature of 25 °C, and adsorption time of 24 h.
The initial pH value is an important factor affecting the adsorption effect of As(V). It not only affects the ionic form of As in the solution but also affects the surface charge of the adsorbent and the degree of hydroxyl dissociation. \[^{34}\] It can be seen from the figure, the adsorption rate of As(V) by FH decreases with the increase of the pH value, and the adsorption rate of As(V) by FH–M increases first and then decreases with the increase of pH value. Because the surface negative charge of FH gradually increases with the increase of the pH of the reaction system. The adsorption point is very limited, and As(V) in the reaction system generally exists in the form of arsenate \(\text{H}_2\text{AsO}_4^{2−}\), \(\text{HAsO}_4^{−}\), and \(\text{AsO}_4^{3−}\). As a result, with the increase of the concentration of \(\text{OH}^−\), the competition adsorption of \(\text{OH}^−\) and arsenate on adsorption points becomes more obvious. Therefore, the adsorption amount of As(V) in the FH gradually decreases with the increase of pH value. As for FH–M, there is a ligand exchange reaction between FH–M and As(V) anion, and this specific adsorption possesses a strong adsorption force. When the pH is low, the functional group on the surface of FH–M is mainly \(\text{Mn}−\text{OH}_2^{+}\), which is easily exchanged, so the adsorption amount is large. With the increase of pH, the group on the surface of FH–M gradually becomes \(\text{Mn}−\text{OH}\). Compared with \(\text{Mn}−\text{OH}_2^{+}\), Mn–OH does not easily exchange ligand with As(V) anion. Moreover, the increased \(\text{OH}^−\) may also compete with As(V) anions for adsorption. Therefore, the adsorption rate of As(V) by FH–M increases first and then decreases with the increase of the pH value.

### 2.5. Adsorption Kinetics

To investigate the mechanism of removal to Cd(II)/As(V) by FH and FH–M, its adsorption kinetics were analyzed in this section. The adsorption kinetics curve of Cd(II)/As(V) (in Figure 6) shows that the adsorption trends to Cd(II)/As(V) by FH and FH–M are identical and can be divided into two stages. The first stage is a rapid adsorption process. During the adsorption time, the adsorption rate to Cd(II)/As(V) increases linearly. After the adsorption for a period of time, the equilibrium is started, and the change of the adsorption rate tends to be stable, and then enters the slow adsorption stage. It can be seen from Figure 6 that the adsorption rate of FH–M to Cd(II)/As(V) is better than FH. The FH and FH–M enter the adsorption stationary phase after the Cd(II) adsorption increases rapidly for about 4 h, and are completely adsorbed at 8 h (in Figure 6a). The adsorption rate of the two increased significantly within 8 h, reaching 78 and 85.9% of their respective equilibrium adsorption rates, respectively. Afterward, the increased rate slowed down and the adsorption became stable. The adsorption rates at 24 h were 81.6 and 86.9%, respectively. The adsorption rate of As(V) by FH and FH–M rises rapidly within 2 h and enters the stationary phase of adsorption after 2 h (FH–M enters the stationary phase before FH) and is completely adsorbed at 8 h (in Figure 6b). The adsorption rate of the two increased significantly within 8 h, reaching 93.6 and 94.2% of their respective equilibrium adsorption amounts, respectively. Afterward, the increase rate slowed down and the adsorption became stable. The adsorption rates at 24 h were 94.5 and 94.7%, respectively. In the adsorption of Cd(II)/As(V), FH–M enters the stationary phase earlier than FH, which indicates that the stronger the mineral adsorption capacity, the shorter the time required to reach an equilibrium.

The adsorption kinetic equation is an important means to characterize the adsorption mechanism. In this study, quasi-first-order kinetic equation and quasi-second-order kinetic equation were used to fit the adsorption process of Cd(II)/As(V) by FH and FH–M, and the correlation coefficient was used to judge the fitting effect.

**Quasi-first-order kinetic equation**

\[
q_t = q_1 \left[ 1 - e^{-kt} \right]
\]

(1)

**Quasi-second-order kinetic equation**

\[
t/q_t = 1/k_2 q_e^2 + t/q_e
\]

(2)

where \(k_1\) \((\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})\) is the quasi-first-order reaction constant, \(k_2\) \((\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})\) is the quasi-second-order reaction constant, \(q_e\) \((\text{mg} \cdot \text{g}^{-1})\) is the amount of adsorption on the adsorbent at time \(t\), and \(q_t\) \((\text{mg} \cdot \text{g}^{-1})\) is the adsorption amount after adsorption.

The expressions of the dynamic equations are shown in eqs 1 and 2. The fitting results are shown in Figure 7 and Table 1.

![Figure 6. Adsorption kinetics curves of FH and FH–M for Cd(II) (a) and As(V) (b).](image)

![Figure 7. Quasi-first-order kinetic equation of FH and FH–M for Cd(II) (a) and As(V) (b). Fitting curves of quasi-second-order kinetic equation of FH and FH–M for Cd(II) (c) and As(V) (d).](image)

The results show that the quasi-first-order kinetic equation fits well to the kinetics of adsorption of Cd(II) by FH and FH–M, which indicates that the equation is more suitable for describing the kinetic adsorption process for Cd(II). The quasi-second-order kinetic equation fits well to the adsorption kinetics of FH and FH–M, and \(R^2\) is above 0.9, which confirms that the adsorption of Cd(II)/As(V) by FH and FH–M is mainly chemical adsorption.

### 2.6. Adsorption Isotherms

Freundlich model is the empirical formula for describing adsorption isotherms. \[^{35−37}\] The Langmuir model is the first theoretical adsorption
isotherm. The expression of the Freundlich model and Langmuir model are given as, respectively

\[ q_e = k_F C_e^{1/n_F} \]  \hspace{1cm} (3)

\[ q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \]  \hspace{1cm} (4)

where \( q_e \) (mg·g\(^{-1}\)) is the equilibrium adsorption amount at equilibrium concentration \( C_e \) (mg·L\(^{-1}\)), \( q_m \) (mg·g\(^{-1}\)) is the theoretical maximum adsorption amount of Cd(II), \( n_F \) is the heterogeneity factor, \( k_F \) is the Freundlich coefficient characteristic, and \( k_L \) is the Langmuir characteristic.

The adsorption isotherms of Cd(II)/As(V) on the FH and FH–M were simulated using the Langmuir and Freundlich isotherm models (Figure 8). The expressions of the Freundlich and Langmuir equations are shown in eqs 3 and 4. The fitting results are shown in Figure 9. The Langmuir and Freundlich parameters and correlation coefficients (\( R^2 \)) are concluded in Table 2. The results showed that the mechanisms of Cd(II)/As(V) adsorption onto FH and FH–M were consistent with different models. For FH and FH–M, slightly better fits were obtained using the Freundlich model than those obtained using the Langmuir model. Also, the adsorption of Cd(II)/As(V) on FH and FH–M belongs to a favorable adsorption situation \((n_F > 1)\). The Cd(II)/As(V) adsorption on FH and FH–M can be considered to be a heterogeneous surface adsorption process. Tang studied the effective removal and easy magnetic separation of arsenic(III,IV) by superparamagnetic magnesia ferrite nanoadsorbent. The results showed that the saturated adsorption capacity was 83.2 mg·g\(^{-1}\). Xu compared the adsorption behaviors of Cd from water onto Fe–Mn binary oxide. The results showed that the saturated adsorption capacity was 114.13 mg·g\(^{-1}\). The maximum adsorption capacity of Cd(II)/As(V) by FH–M was 144.82 and 180.81 mg·g\(^{-1}\), respectively.

2.7. Chemical Composition of Ferrihydrite/Manganese Dioxide Composites before and after Adsorption.

To study the morphology and elemental composition of FH–M before and after adsorption, the FH–M residue before and after adsorption of Cd(II)/As(V) was also analyzed by SEM-EDS, Fourier transform infrared (FT-IR) spectroscopy, and XPS.

The SEM images and EDS spectrum of FH–M before and after adsorption are shown in Figure 10. FH–M before the adsorption of Cd(II)/As(V) is shown in Figure 10a. The residue after the adsorption of Cd(II)/As(V) is shown in Figure 10b, and are designated as FH–M-1 and FH–M-2, respectively. The results of EDS analysis indicated that the main elements on the surface of FH–M were Fe, Mn, and O (in Figure 10b–d), the main elements on the surface of FH–M-1 after the adsorption of Cd(II) were Fe, Mn, O, and Cd (in Figure 10f–i), and the main elements on the surface of FH–M-2 after the adsorption of As(V) were Fe, Mn, O, and As (in Figure 10k–n). The appearance of the Cd(II)/As(V) element indicates that Cd(II)/As(V) in the aqueous phase has been adsorbed onto the surface of the solid phase (FH–M). It can be seen from the graphs that the three elements Fe, Mn, and O are densely distributed, while the distribution of the Cd(II)/As(V) element is significantly sparse. This may be because the amount of Cd(II)/As(V) used in this adsorption experiment is not much, resulting in a relatively less Cd(II)/As(V) actually adsorbed onto the surface of FH–M, and thus its distribution is relatively sparse.

As shown in the Figure 11, FT-IR spectrum of FH–M before and after adsorption of Cd(II)/As(V), there are characteristic absorption peaks of water and OH in FH–M (about 3300 cm\(^{-1}\)) and bending vibration absorption peaks of −OH (about 1650 cm\(^{-1}\)). The stretching vibration peak of Fe−O−Mn is about 1400 cm\(^{-1}\). Characteristic peaks appeared in the curves around 1200 cm\(^{-1}\), indicating the existence of Mn−OH, which is the difference between Mn−OH and water hydroxyl group. The absorption peak of FH is about 480 cm\(^{-1}\) in the figure. It can be seen that FH–M prepared by this method contains abundant surface groups,
which makes FH−M possess strong chemisorption activity. In the curves obtained after the adsorption of Cd(II)/As(V), about 840 cm⁻¹ absorption peaks appeared. That is, the contractive vibration absorption of Cd−O and AS−O bonds. It shows that the chemical adsorption and co-precipitation exist in the process of removing Cd(II)/As(V) from FH−M.

The XPS spectrum before and after adsorption of Cd(II)/As(V) by FH−M is shown in Figure 12a. One can see that the surface of FH−M before adsorption mainly has three elements of Fe, Mn, and O, and the presence of Cd(II)/As(V) elements was detected on the surface of the FH−M residue in the adsorption experiment, which also indicates that Cd/As in the water phase has been transferred to the surface of the solid phase (FH−M). The Cd 3d spectrum of FH−M after the adsorption of Cd(II) is shown in Figure 12b and 405.9 and 412.7 eV in the figure correspond to Cd 3d₅/₂ and Cd 3d₃/₂ of Cd(II), respectively. The As 3d spectrum of FH−M after the

| adsorbent | Freundlich | Langmuir |
|-----------|------------|----------|
|           | nᵣ | kᵣ | R² | qₘ | kₛ | R² |
| Cd(II) FH | 1.1373 | 1.95981 | 0.99654 | 137.269 | 0.01465 | 0.94908 |
| FH−M     | 1.3206 | 1.6241 | 0.99927 | 144.823 | 0.01198 | 0.93294 |
| As(V) FH  | 1.1289 | 2.1897 | 0.99902 | 165.288 | 0.01421 | 0.93733 |
| FH−M     | 1.2863 | 2.5394 | 0.99815 | 180.817 | 0.01613 | 0.94214 |

Figure 10. SEM images of the FH−M before (a) and after adsorption of Cd(II) (e) and As(V) (j). EDS spectrum of FH−M before (b−d) and after adsorption of Cd(II) (f−i) and As(V) (k−n).

Figure 11. FT-IR spectrum of FH−M before and after the adsorption of Cd(II)/As(V).
adsorption of As(V) is shown in Figure 10c. The 44.9 eV in the figure is the characteristic peak of As(V).

The Fe 2p spectra of FH–M before and after the adsorption of Cd or As (a), Cd 3d spectrum after the adsorption of Cd (b), As 3d spectrum after the adsorption of As (c).

Figure 13c–e, the O 1s spectra of FH–M before and after the adsorption of Cd(II)/As(V), respectively. The peaks with binding energies around 530, 531, and 532.6 eV correspond to O in FM–O, FM–OH, and adsorbed H2O (FM stands for Fe or Mn), respectively. As shown in Figure 13c–e, the percentage of FM–OH is the highest, followed by the percentage of FM–O, and the lowest percentage of H2O. Among them, the percentage of FM–OH of FH–M after the adsorption of Cd(II)/As(V) decreased from 61.07 to 51.85 and 52.63%, respectively. Cd(II) interacts with FM–OH, and As(V) can undergo ligand exchange with FM–OH.49–54 The adsorption pathway of Cd(II) and As(V) onto FH–M is shown in Figure 14. The Mn(IV) in the synthesis process of FH–M can be reduced by Fe(III) to produce a certain amount of Mn(II). Then, some Cd(II) replaces Mn(II) in Fe–Mn–OH composites, while other Cd(II) coupling with Fe–OH and Mn–OH form a hydroxy composites. As(V) usually exists in the forms of arsenate ions (H2AsO4−, HAsO42−), and the arsenate ion acts with the hydroxyl group on the surface of FH–M by ligand exchange to form a bidentate ligand. Therefore, the reaction of FH–M with Cd(II)/As(V) consumes FM–OH, increases FM–O, and forms H2O due to its process, thereby increasing the percentage of H2O.

3. CONCLUSIONS

FH–M was synthesized by ex situ synthesis, and the microstructure as well as the adsorption properties for Cd(II)/As(V) of FH–M is investigated in this study. The changes of the elements on the surface of FH–M before and after adsorption were analyzed. The results showed that with increasing pH value, the adsorption rate of Cd(II) increased, while that of As(V) increased at first and then decreased. With increase in the initial concentration, the adsorption rate of Cd(II)/As(V) decreased. As to the kinetic adsorption process, the adsorption performance of FH–M for As(V) was better than that for Cd(II), reflected not only in the time of reaching the adsorption equilibrium but also the amount of adsorption. The quasi-first-order kinetic equation can better describe the process of adsorption of Cd(II) by FH–M with R2 at 0.94, while the quasi-second-order kinetic equation was more suitable to describe the adsorption kinetics of Cd(II)/As(V) with R2 above 0.9999. Moreover, Cd(II) was found to interact with FM–OH and As(V) can be exchanged with FM–OH (FM stands for Fe or Mn). The FH–M can be applied to the removal of Cd(II)/As(V) in a wastewater or polluted environment with a good prospect.

4. EXPERIMENTAL SECTION

4.1. Chemicals. Iron(III) nitrate nonahydrate (Fe(NO3)3·9H2O) and manganese sulfate monohydrate (MnSO4·H2O) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Sodium hydroxide (NaOH) and potassium permanganate (KMnO4) were purchased from Beijing Chemical Works. These above chemicals were analytical grade (purity > 99%). Sodium nitrate (NaNO3), cadmium nitrate tetrahydrate (Cd(NO3)2·4H2O), and sodium arsenate (AsHNa2O4) were guaranteed reagent (purity > 99.5%). Deionized water was used throughout the experiments. The standard liquid containing Cd(II) and As(V) in this experiment was prepared by cadmium nitrate tetrahydrate (Cd(NO3)2·4H2O) and sodium arsenate (AsHNa2O4).
4.2. Ferricydrate Synthesis. FH was synthesized by a developed method based on the process reported by previous literature. The general process is as follows. Forty grams of Fe(NO$_3$)$_3$·9H$_2$O was dissolved in 500 mL of deionized water. The pH of the Fe(NO$_3$)$_3$·9H$_2$O solution was adjusted to 7–8 using about 330 mL of a 1 mol/L NaOH solution. Centrifugation after stirring for about 30 min, the precipitate was repeatedly washed to remove excess electrolyte ions, dried, and ground to obtain FH.

4.3. Preparation of Ferricydrate/Manganese Dioxide Composites. The synthesized FH was added to the beaker containing KMnO$_4$ solution, and then a certain amount of MnSO$_4$·H$_2$O was added to the beaker under stirring conditions. The mass ratio of FH to MnO$_2$ is 9:1. The solution was stirred at room temperature and then aged, centrifuged for several times, and dried at 60 °C for 8 h finally. The FH–M was obtained.

4.4. Characterization. X-ray diffractometry (XRD) is performed on a TD-3500X X-ray diffractometer operating with a scanning speed of 0.5°/min from 10° to 80°. Scanning electron microscopy (SEM) is performed using a MERLIN VP compact microscope, and further energy-dispersive X-ray spectroscopy (EDS) elemental mapping is performed in the scanning SEM mode. Nitrogen sorption–desorption isotherms at 77 K are determined by means of a US Mike TRISTAR II 3020M surface area and pore size analyzer. The relative pressure ($P/P_0$) range of 0–1.0 is selected for the calculation of the Brunauer–Emmett–Teller (BET) surface areas. X-ray photoelectron spectroscopy (XPS) measurements are conducted on a Kratos AXIS Ultra DLD XPS instrument equipped with an Al Ka source at 10–9 Torr. The binding energy is corrected based on C 1s (284.8 eV). The surface functional groups of FH–M before and after adsorption were determined by Fourier transform infrared (FT-IR) spectroscopy (PerkinElmer Spectrum 100 FT-IR Spectrometer) in the wavenumber region between 4000 and 400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. Inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 5300 DV) and inductively coupled plasma mass spectrometry (ICP-MS) (ELAN DRC-e) were used to measure the content of Cd(II)/As(V) before and after adsorption.

4.5. Adsorption Performance Test. As to the effect of initial concentration of solution and adsorption isotherm on adsorption properties of FH and FH–M, the experiment was conducted in following steps. Thirty milliliters of different initial concentrations of Cd(II)/As(V) solution to be adsorbed were placed in a series of centrifugation tubes. The sample dosage was 1 g/L, and the pH was regulated by NaOH and HNO$_3$ to be around 7. Oscillations were performed at 200 rpm for 24 h at 25°C in a temperature oscillator. Then, the supernatant was centrifuged to measure the Cd(II)/As(V) content, and the adsorption amount of Cd(II)/As(V) was calculated.

As regards the effect of pH value of the solution on adsorption properties of FH and FH–M, the experiment was carried out as follows. Thirty milliliters of Cd(II)/As(V) solution to be adsorbed at an initial concentration of 50 mg/L was added to a series of centrifugation tubes. The sample dosage was 1 g/L, and the pH was regulated by NaOH and HNO$_3$ to be around 4–10. Oscillations were performed at 200 rpm in a temperature oscillator at 25°C at different time intervals. Then, the supernatant was centrifuged to measure the Cd(II)/As(V) content, and the adsorption amount of Cd(II)/As(V) was calculated.

As to the adsorption kinetics experiment, the steps were as follows. Thirty milliliters of Cd(II)/As(V) solution to be adsorbed at an initial concentration of 50 mg/L was added to a series of centrifugation tubes. The sample dosage was 1 g/L, and the pH value is regulated by NaOH and HNO$_3$ to be around 7. Oscillation was performed at 200 rpm in a temperature oscillator at 25°C and sampled at different time intervals. Then, the supernatant was centrifuged to measure the Cd(II)/As(V) content, and the adsorption amount of Cd(II)/As(V) was calculated.

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**Notes**

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