Structural Evolution of Mn-Substituted FeOOH and Its Adsorption Mechanism for U(VI): Effect of the Mole Ratio of Mn/(Fe + Mn)

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Abstract: Mn-substituted FeOOH with different Mn/(Mn + Fe) molar ratios are synthesized, and characterized using FESEM, XRD, FTIR, ICP-OES, BET, Zeta potential, TG-DSC, XPS, and VSM. The results show that the actual doping amounts of Mn are 0%, 3.05%, 6.13%, 9.04%, 12.70%, and 15.14%, respectively. The substitution of Mn promotes the transformation of goethite from FeOOH to MnFeO4, resulting in a saturation magnetization intensity of up to 14.90 emu/g for G-Mn15%, laying a theoretical foundation for magnetic recovery. The specific surface area of Mn-substituted FeOOH increases from 57.15 m2/g to 315.26 m2/g with an increasing Mn substitution amount. Combined with the abundant oxygen-containing functional groups such as -OH, Fe-O, and Mn-O on the surface, sufficient active sites are provided for the efficient adsorption of U(VI). The TG-DSC analysis results indicate that the substitution of Mn improves the thermal stability of goethite. In addition, XPS analysis results indicate that the substitution of Mn leads to the conversion of Fe3+ to Fe2+ in goethite, and the conversion of Mn2+ to Mn4+ replaces Fe3+ in the structure of goethite. Fe-O and Mn-O coordinate participate in the adsorption and reduction process of U(VI). The batch experiment results show that the substitution of Mn promotes the adsorption performance of goethite for U(VI). When T = 303 K, pH = 4.0, m/V = 0.5 g/L, and I = 0.01 mol/L NaCl, the maximum adsorption capacity of G-Mn15% for U(VI) is 79.24 mg/g, indicating the potential value of Mn substitution for goethite in the treatment of uranium-containing wastewater.

Keywords: Mn-substituted FeOOH; U(VI); XPS analysis; adsorption mechanism

1. Introduction

The excessive consumption of fossil fuels has caused an energy crisis and hindered social and economic development [1]. Vigorously developing nuclear energy is an effective solution to meet the growing energy demand. Nuclear energy is an emerging clean energy source with ultra-high energy density and zero carbon emissions, and is expected to become a substitute for traditional fossil fuels [2]. Uranium (U(VI)), as the main raw material of the nuclear fuel cycle, plays a crucial role in the nuclear industry [3]. However, in recent years, the rapid popularization of nuclear energy utilization has led to the continuous release of uranium-containing nuclear waste into the environment [4]. Due to the radioactive and chemical toxicity of uranium, as well as the high migration rate of soluble U(VI) in water, the remediation of uranium pollution caused by mine tailings and residual
nuclear facilities has always been a global environmental challenge [5]. For a long time, researchers have been striving to remove uranium from various sources of pollution by developing various methods such as co-precipitation, ion exchange, membrane separation, electrocatalysis, photocatalysis, and adsorption, while continuously reducing costs [6–8]. Among them, adsorption has been widely used due to its efficiency, affordability, and convenience [9–11]. As an alternative, converting soluble U(VI) into insoluble U(IV) through reduction can provide an effective way to isolate U(VI) in the environment [12,13]. If adsorption and reduction can be coordinated with U(VI), it will greatly improve the removal rate of U(VI), reduce its mobility, and thus achieve the goal of reducing the damage of U(VI) to the ecological environment.

Goethite is widely distributed in nature and is a stable hydrated iron oxide [14,15]. The surface of goethite is rich in adsorption sites, and the water environment further increases the surface-active sites, which is mainly attributed to the highly surface specific configuration of goethite on molecular structural planes such as (100), (010), (110), and (021) [16]. According to previous reports, goethite has good adsorption effects on various heavy metals, inorganic anions, and radioactive elements in the environment [17–20]. Therefore, using goethite to adsorb heavy metals in wastewater is currently a research hotspot and has great advantages and potential. However, natural goethite rarely exists in pure phase form, and most of it is replaced by homomorphic metal ions such as Mn(III), Al(III), and Pb(II) with ionic radii close to Fe(III) [21,22]. Mn is widely distributed in sediment and soil, with the same valence as iron, and its ion radius (0.0645 nm) is similar to that of iron (0.0645 nm) [23,24]. Therefore, in recent years, the physicochemical properties of manganese-doped goethite and its adsorption of heavy metals and organic pollutants have been widely studied. Li et al. [25] investigated the adsorption performance and mechanism of Mn-doped FeOOH on heavy metals. The results showed that Mn doping increased the specific surface area of goethite, and the adsorption capacity of Mn-doped FeOOH on Cd(II), Ni(II), and Pb(II) increased by 18%, 17%, and 40% compared to FeOOH, respectively. The research results of Cruz et al. [26] show that when the Mn substitution amount is 17%, the maximum specific surface area of Mn/Fe composites is 286 m²/g, accompanied by the maximum removal rate of As(V). The research results of Liu et al. [27] indicate that Mn doping of goethite affects its surface reactivity and reducing ability, alters the recrystallization mechanism catalyzed by dissolved Fe(II), and thus affects the adsorption of arsenic. Research has shown that when manganese ions enter the structure of goethite, the crystal structure and physicochemical properties of goethite undergo corresponding changes, which also affect the adsorption performance and mechanism of goethite towards target pollutants. Therefore, this article explores the structural evolution of Mn-substituted FeOOH and its adsorption and mechanism towards U(VI).

The purposes of this article are to (1) characterize the physicochemical properties of Mn-substituted FeOOH by FESEM, XRD, BET, FT-IR, TG-DSC, ICP-OES, VSM, XPS, and zeta potential; (2) discuss the influence of molar ratios of Mn on U(VI) adsorption on Mn-substituted FeOOH under various environmental conditions; (3) investigate the adsorption mechanism between Mn-substituted FeOOH and U(VI) based on XPS analysis.

2. Materials and Methods

2.1. Chemicals

In this study, Iron nitrate, manganese nitrate, potassium hydroxide, sodium hydroxide, uranyl nitrate were acquired from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Hydrochloric acid and nitric acid were acquired from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals were in an analytical state or of superior purity and employed without any further purification. Ultrapure water was used in all experiments.
2.2. Preparation of Mn-Substituted FeOOH

The preparation method of Mn-substituted FeOOH is as follows [22]: Firstly, we prepared 1 mol/L of Fe(NO₃)₃·9H₂O solution and 0.5 mol/L of Mn(NO₃)₂·4H₂O solution, and mixed them according to the Mn/(Mn + Fe) molar ratios of 3%, 6%, 9%, 12%, and 15%, respectively. Then, 45 mL of 5 mol/L KOH solution was added to the above mixture gradually. Finally, an appropriate amount of ultrapure water was added to the beaker to achieve an OH⁻ concentration of 0.3 mol/L. The mixture was aged in a 60 °C oven for 15 days. After aging was completed, the suspension was centrifuged and the collected solid was washed five times with ultrapure water, and then dried at 60 °C. To remove minerals with poor crystallization, the dried solid was mixed with dilute HCl and left under dark conditions at 25 °C for 4 h. The material was then washed with ultrapure water six times and freeze dried for later use. The obtained solids were sequentially recorded as Goethite, G-Mn3%, G-Mn6%, G-Mn9%, G-Mn12%, and G-Mn15% based on the molar ratio of Mn (for example, Goethite represents synthetic goethite; G-Mn3% represents a molar ratio of 3% for Mn; et al.). After digestion and dilution, the actual molar ratio of Mn was identified by ICP OES as 0%, 3.05%, 6.13%, 9.04%, 12.70% and 15.14%.

2.3. Characterization

The phase composition of Mn-substituted FeOOH was tested by a SmartLabSE diffractometer. The surface functional groups of Mn-substituted FeOOH were measured using a Tristar 3020 FTIR spectrometer at room temperature. The N₂ adsorption–desorption curves were tested using a VERTEX80 surface area and pore size analyzer. FESEM measurements were performed on a Thermo Scientific ESCALAB Xi+ microscope with an energy dispersive X-ray facility. The zeta potentials of Mn-substituted FeOOH were measured by a Marvin Zetasizernan. The valence states of elements such as Fe and Mn were tested by a Thermo Scientific ESCALAB Xi+ diffractometer. The magnetic characteristics of Mn-substituted FeOOH were tested using a LakeShore7404 Vibrating Sample Magnetometer (VSM). The Mn molar ratios in synthetic materials were identified using a 5110 ICP OES instrument. The thermal stability of Mn-substituted FeOOH was determined using a NETZSCH STA449F5 thermogravimetric analyzer (TG-DSC).

2.4. Adsorption Experiments

U(VI) adsorption on Mn-substituted FeOOH was investigated using batch experiments at T = 15 ± 2 °C, with the solid–liquid ratio of 0.5 g/L, using HNO₃/NaOH solution to adjust pH as 2-11. The centrifuge tubes were shaken on an oscillator with a constant speed for 24 h. After reaction, the supernatant and solid were separated by a high-speed centrifuge with 11,000 rpm for 8 min, and then poured into a syringe and filtered through a 0.22-µm membrane. Then, the concentration of U(VI) in the supernatant was measured using a UV-vis spectrophotometer.

The amount of U(VI) adsorbed on the Mn-substituted FeOOH was computed using the following equations:

\[
\text{Sorption(\%)} = \frac{(C_0 - C_e)}{C_0} \times 100\% \\
\text{Kd} = \frac{(C_0 - C_e)}{C_e} \times \frac{V}{m}
\]  

where \(C_0\) (mg/L) is the initial concentration of U(VI), \(C_e\) (mg/L) is the equilibrium concentration of U(VI), \(m\) (g) is the mass of the Mn-substituted FeOOH, and \(V\) (mL) is the volume of the suspension.
3. Results

3.1. Characterization

Figure 1 shows the FESEM of Mn-substituted FeOOH, accompanied by energy dispersive spectroscopy patterns (EDS). As shown in Figure 1A, the image of goethite exhibits short rod-shaped and scaly morphology, hundreds of nano-meters in length. The microscopic morphology of G-Mn6% shown in Figure 1C presents a difference with increasing Mn substitution for Fe; smaller particles are observed on the rod-like structure. An additional Mn element with 6.21% is observed in Figure 1D compared with Figure 1B, which illustrates that the smaller particles on the surface of G-Mn6% belong to manganese. In addition, with the increasing substitution of Mn for Fe, more particles appear on the surface of G-Mn15% (Figure 1E), and the EDS results in Figure 1F further confirm that the particles are mainly manganese. The mapping of Mn-substituted FeOOH is shown in Figure 2, which focuses on the distribution of Fe, O, and Mn elements. No obvious trace of Mn element was found on the surface of goethite; however, the distribution of Mn on the surface of G-Mn15% is abnormally concentrated compared with G-Mn6%. The result implies that Mn substitution affects the crystallization of goethite, while the particle size of goethite decreases [27].

X-ray reflections of Mn-substituted FeOOH are show in Figure 3. As shown in Figure 3A, the reflections at 2θ = 21.06, 33.13, 34.71, 36.47, 39.80, 41.14, 53.06, 58.91, and 61.17° observed in the XRD patterns of Goethite, G-Mn3%, and G-Mn6% are identified as the crystal planes of (101), (301), (210), (111), (211), (401), (212), (601), and (020) of FeOOH [13,26,28] compared with the standard reference pattern [ICSD-071809]. The only difference among them is that the diffraction peak intensity of FeOOH decreases with the increasing Mn substitution amount, which probably inhibits the growth of FeOOH crystals along the b-axis direction [23]. However, when the substitution amount of Mn increases to 9%, the phase composition of G-Mn9% gradually transforms from FeOOH to MnFe$_2$O$_4$ ([ICSD-024497]), and the diffraction peak intensity of MnFe$_2$O$_4$ is positively correlated with the substitution range of Mn. To further analyze the effect of Mn substitution on XRD diffraction peaks, the magnification of selected XRD patterns between 30 and 40 degree is shown in Figure 3B. The reflections for FeOOH are shifted to the higher angle and broadened with increasing Mn substitution, which is probably caused by crystal disorder, or smaller crystal size [21,29]. XRD analysis demonstrates that the influence of Mn substitution on the crystal structure of FeOOH is closely related to its amount, and a high proportion of Mn substitution (Mn/(Mn + Fe) = 0.09-0.15) inhibits the growth of goethite crystals along the b-axis direction, leading to the formation of a large amount of MnFe$_2$O$_4$. 
Figure 1. The FESEM and EDS of Mn-substituted FeOOH. (A) Goethite; (B) EDS of Goethite; (C) G-Mn6%; (D) EDS of G-Mn6%; (E) G-Mn15%; (F) EDS of G-Mn15%.

Figure 2. Mapping of Mn-substituted FeOOH. (A) Goethite; (B) G-Mn6%; (C) G-Mn15%.
Figure 3. (A) XRD patterns of Mn-substituted FeOOH (G-Goethite; M-MnFe₂O₄); (B) Partial enlarged image of XRD; (C) FTIR of Mn-substituted FeOOH; (D) Hysteresis loop of Mn-substituted FeOOH; (E) TG-DSC of Goethite; (F) TG-DSC of G-Mn6%; (G) TG-DSC of G-Mn15%.

The FT-IR spectra for Mn-substituted FeOOH are shown in Figure 3C. The peak that appears at ~3450 cm⁻¹ belongs to -OH stretching vibration of the adsorbed water [30,31]. The peaks present at 893 and 797 cm⁻¹ are attributed to in-plane bending (δOH) and out-of-plane bending (γOH), respectively [26]. The peaks at 639 cm⁻¹ correspond to Fe-O/Mn-O lattice vibrations [24,32]. The FTIR analysis results indicate that the substitution of Mn increases the oxygen-containing functional groups on the surface of goethite, such as Mn-O, providing more abundant active sites for uranium attachment.

The hysteresis loop of Mn-substituted FeOOH is shown in Figure 3D. It is reasonable that goethite has almost no magnetism, while the saturation magnetization strengths of
G-Mn6% and G-Mn15% are 10.66 and 14.90 emu/g, respectively. With such high saturated magnetizations, the samples can be easily recovered from aqueous solution using an external magnetic field. Combining the analysis results of XRD and FTIR, the hysteresis loop results confirm that MnFeO$_4$ has strong magnetism, providing good magnetic properties for solid–liquid separation.

Figure 3E–G show the TG/DSC curves of Mn-substituted FeOOH under nitrogen atmosphere conditions. Figure 3E shows the thermogravimetric diagram of Goethite, with a calcination temperature range of 30–600 °C and a sample weight of 14.00 mg. The total weight loss of Goethite is 14.23%, and the TG curve of Goethite has three stages of weight loss. In the first stage, there is a weight loss of 0.10% at room temperature of around 30 °C, which should be attributed to the removal of physically adsorbed water relying solely on van der Waals forces [33,34]. In the second stage, the temperature increases from room temperature to around 203 °C, resulting in a mass loss of 1.80%, which should be attributed to the removal of the second type of adsorbed water through hydrogen bonding [34,35]. Based on the DSC curve, Goethite undergoes an exothermic reaction during pyrolysis, with a clear peak appearing at 109.15 °C. In the third stage, the temperature increases from 203 °C to around 600 °C, resulting in a mass loss of 12.33%. A sharp peak appears at around 266.91 °C, which may be attributed to the removal of hydroxyl groups during the phase transition of goethite by heat treatment [20,36]. Comparing the TG/DSC spectra of Goethite, G-Mn6% and G-Mn12%, two peaks can be observed in both graphs. As the amount of Mn substitution increases, the pyrolysis temperature increases from 267.88 °C to 275.07 °C and 282.25 °C. The mass loss rate of the sample decreases from 14.23% to 12.79% and 10.34%, respectively, indicating that the substitution of manganese effectively improves the thermal stability of goethite.

According to multi-point BET analysis, the specific surface area of goethite is 57.15 m$^2$/g, and Mn substitution increases the specific surface area of the sample. The specific surfaces of G-Mn3%, G-Mn6%, G-Mn9%, G-Mn12%, and G-Mn15% are 69.40, 83.11, 99.37, 120.97, and 315.26 m$^2$/g, respectively, which may be attributed to the rough surface and high dispersion of the sample [27]. In addition, after Mn substitution, the total pore volume of the sample shows an increasing trend, with the average pore size slightly decreased. The specific parameters are shown in Table 1 and Figure 4. The BET results indicate that as the amount of Mn substitution increases, the growth trend of the specific surface area of goethite is positively correlated, providing active sites for U(VI) adsorption and laying a theoretical foundation for efficient U(VI) removal.

Table 1. The selective parameters of Mn-substituted FeOOH.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Actual Mn Molar Ratio</th>
<th>S$_{BET}$ (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>0%</td>
<td>57.15</td>
<td>0.073</td>
<td>5.30</td>
</tr>
<tr>
<td>G-Mn3%</td>
<td>3.05%</td>
<td>69.40</td>
<td>0.079</td>
<td>4.15</td>
</tr>
<tr>
<td>G-Mn6%</td>
<td>6.13%</td>
<td>83.11</td>
<td>0.082</td>
<td>3.97</td>
</tr>
<tr>
<td>G-Mn9%</td>
<td>9.04%</td>
<td>99.37</td>
<td>0.10</td>
<td>3.52</td>
</tr>
<tr>
<td>G-Mn12%</td>
<td>12.70%</td>
<td>120.97</td>
<td>0.11</td>
<td>3.69</td>
</tr>
<tr>
<td>G-Mn15%</td>
<td>15.14%</td>
<td>315.26</td>
<td>0.30</td>
<td>3.69</td>
</tr>
</tbody>
</table>
3.2. Adsorption Kinetics

Figure 5A displays the effect of the reaction time of U(VI) adsorption on Mn-substituted FeOOH. The equilibrium time is one of the most important parameters for economical wastewater treatment plant applications [26,37]. The reaction conditions for adsorption kinetics are as follows: solid–liquid ratio of 0.5 g/L, U(VI) initial concentration of 20 mg/L, pH = 4.0, reaction times of 5 min, 10 min, 30 min, 1 h, 2 h, 4 h, 8 h, and 24 h, respectively. Within the first 30 min of the reaction, the adsorption rate of U(VI) by Mn-substituted FeOOH rapidly increases. From 30 min to 4 h, the removal rate slowly increased until adsorption saturation. The above results are attributed to the fact that there are more active sites on the surface of the adsorbent during the rapid increase stage of adsorption. As time goes on, the active sites on Mn-substituted FeOOH become saturated, and the removal rate increases slowly as the U(VI) concentration in the solution decreases. On the other hand, the removal rate of U(VI) by Mn-substituted FeOOH (88.67%–100%) is much higher than that of Goethite (34.05%), and the removal rate has increased by 54.62–65.95 percentage points. Based on the previous characterization results, it can be concluded that the substitution of Mn introduces more active sites on the surface of the adsorbent, enhancing the affinity between the adsorbent and U(VI).

To further explore the adsorption mechanism of U(VI) on Mn-substituted FeOOH, the pseudo-first-order and pseudo-second-order kinetic models are used to fit the adsorption kinetic (Figure 5B). Their linear forms are shown in Equations (3) and (4), respectively [38].

\[
\ln (Q_e - Q_t) = \ln (Q_e) - K_1 \times t \\
(3)
\]
\[
t/Q_t = 1/(K_2 \times Q_e^2) + t/Q_e \\
(4)
\]

where \(Q_t\) (mg/g) and \(Q_e\) (mg/g) are the adsorption concentration of U(VI) at equilibrium time and time \(t\), respectively [39]. \(K_1\) and \(K_2\) are the adsorption rate constants (g/(mg·min)) [40]. The detailed parameters are listed in Table 2. The adsorption kinetics of U(VI) on Mn-substituted FeOOH are well simulated by pseudo-second-order kinetic model \((R^2 > 0.9706)\) compared to pseudo-first-order kinetic model \((R^2 < 0.9852)\).
Figure 5. (A) Adsorption kinetics of U(VI) on Mn-substituted FeOOH; (B) pseudo-second-order kinetic model; (C) Effect of pH and ionic strength on adsorption of U(VI) on Goethite; (D) Effect of pH and ionic strength on adsorption of U(VI) on G-Mn15%; (E) Zeta potential of Mn-substituted FeOOH; (F) Ion distribution diagram of U(VI) in solutions with different pH values. C_U(VI) = 20 mg/L, m/V = 0.5 g/L, I = 0.001–0.1 mol/L NaCl, T = 288 K, pH = 2.0–11.0, t = 24 h.
3.3. Effect of pH and Ionic Strength

The effect of pH and ionic strength on U(VI) adsorption on Mn-substituted FeOOH was investigated by the batch technique. The specific experimental conditions were as follows: pH = 3.0–11.0, solid–liquid ratio of 0.5 g/L, initial concentration of 10 mg/L, ionic strength of 0.001–0.1 mol/L NaCl, respectively. As shown in Figure 5C,D, when the pH < 3.0, the adsorption of U(VI) by Goethite is relatively low (11%–40%), while the adsorption of U(VI) by G-Mn15% remains at 29%–66%. When the pH > 4.0, both adsorbents rapidly increase the adsorption of U(VI) until it reaches 100% (complete removal of U(VI)). However, when the pH > 8.0, the adsorption of U(VI) by Goethite slightly decreases and remains around 96%, while the adsorption of U(VI) by G-Mn15% is not affected by pH and has remained as high as 100%. This result indicates that G-Mn15% has a stronger adsorption capacity for U(VI) than Goethite and is consistent with the adsorption kinetics results.

As displayed in Figure 5E, the substitution of Mn reduces the zeta potential of goethite; positively and negatively charged Goethite and G-Mn15% appear at pH < 7.44/pH > 7.44 and pH < 5.70/pH > 5.70, respectively. The ion distribution curves of U(VI) under different pH are shown in Figure 5F, when the pH < 3.0, U(VI) mainly exists as UO₂₂⁺, and U(VI) mainly exists as UO₂(OH)₂⁺, UO₂OH⁻, (UO₂)₃(OH)⁶⁺, and (UO₂)₃(OH)⁷⁺ in aqueous solutions of 3.0 < pH < 8.0. Negatively charged species dominate ([UO₂]₃(OH)⁶⁺, (UO₂)₃(OH)⁷⁺, and (UO₂)₃(OH)⁸⁺), the aqueous solution. Combining the charge distribution of Goethite and G-Mn15% with the ion distribution of U(VI), the lower adsorption of U(VI) on Goethite and G-Mn15% is owing to the electrostatic repulsion between positively charged Mn-substituted FeOOH and UO₂⁺ [41]. The increase of U(VI) adsorption on Goethite and G-Mn15% at pH 3.0–5.7 is not owing to the electrostatic interactions, which can probably be ascribed to the reduction/surface complexation of U(VI) on Mn-substituted FeOOH [13]. Additionally, the decrease of U(VI) adsorption by Goethite at pH > 8.0 is mainly assigned to the electrostatic repulsion between negatively charged Goethite and U(VI) species. The adsorption of U(VI) on G-Mn15% is not affected by pH, which may be mainly due to the high specific surface area ensuring sufficient active sites, and the substitution of Mn enhancing the affinity, reduction, or complexation ability between the Mn-substituted FeOOH and U(VI) [23,26].

In addition, the ionic strengths of different concentrations of NaCl are used to explore their effect on U(VI) adsorption on Goethite and G-Mn15%. As shown in Figure 5C,D, when the pH ranges from 2 to 6, U(VI) adsorption is greatly affected by pH, and the adsorption of U(VI) is better when the ion strength is 0.01 mol/L. Interestingly, when pH > 6, the adsorption of U(VI) is basically not affected by ion strength. Based on previous reports, it can be concluded that when pH < 6, U(VI) adsorption on the surface of Goethite and G-Mn15% is mainly influenced by outer-sphere complexation. Conversely, when pH > 6, inner-sphere complexation dominates the adsorption of U(VI) [8,42,43].

3.4. Adsorption Isotherms

Figure 6 shows the removal capacities of U(VI) on Mn-substituted FeOOH. The experimental conditions were as follows: pH = 4.0, reaction temperatures of 15 °C, 30 °C, and 45 °C, solid–liquid ratio of 0.5 g/L, reaction time of 24 h, and initial concentrations of
U(VI) are 5, 10, 15, 20, 25, 35, 45, and 55 mg/L, respectively. As shown in Figure 6A–C, the adsorption capacities of U(VI) by Mn-substituted FeOOH are positively correlated with the initial concentration and reaction temperature. This is because as the initial concentration increases, the mass transfer driving force is enhanced, and more U(VI) ions are adsorbed on the active sites of the samples [22,23]. As shown in Figure 6A–C, the adsorption capacity of U(VI) by Mn-substituted FeOOH follows the pattern: G-Mn15% > G-Mn12% > G-Mn9% > G-Mn6% > G-Mn3% > Goethite. Based on the characterization results of Mn-substituted FeOOH, Mn substitution affects the surface properties or aggregation of goethite. The presence of Mn affects the crystal growth of goethite, leading to a decrease in crystal size and an increase in specific surface area, causing an increase in U(VI) adsorption capacity. In addition, increasing the reaction temperature further enhances the adsorption rate and amount of U(VI) on Mn-substituted FeOOH. For example, the adsorption capacity of U(VI) on G-Mn15% increases from 78.20 mg/g to 82.11 mg/g and 87.60 mg/g, respectively, as the temperature increases from 15 °C to 30 °C and 45 °C, respectively.

The experimental data are fitted by the Langmuir and Freundlich models. The linear forms of the Langmuir and Freundlich models can be described as Equations (5) and (6), respectively:

\[ \frac{C_e}{Q_m} = \frac{1}{(K_r \cdot Q_m)} + \frac{C_e}{Q_m} \]  

\[ \lg Q_e = \frac{1}{n} \lg C_e + \lg K_r \]  

where \( K_r \) (L·mg\(^{-1}\)) is a Langmuir constant, \( Q_m \) (mg·g\(^{-1}\)) is the maximum adsorption capacity at complete monolayer coverage; \( 1/n \) is the heterogeneity of the adsorption sites [10]; \( K_r \) is the equilibrium coefficient. As shown in Table 3, the adsorption of U(VI) on Mn-substituted FeOOH can be fitted well by the Langmuir model compared to the Freundlich model with \( R^2 \). The maximum adsorption capacity of U(VI) on G-Mn15% calculated from Langmuir is 88.11 mg·g\(^{-1}\) at \( T = 318 \) K and pH 4.0 (76.63 mg/g at 288 K, 79.24 mg/g at 303 K), which is higher than that of some materials in Table 4, and less than the adsorption capacity of acid/polyaniline/FeOOH and sulfonic acid-decorated FeOOH for uranium, indicating that Mn-substituted FeOOH has potential in the treatment of uranium-containing wastewater.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Sample</th>
<th>( Q_m ) (mg·g(^{-1}))</th>
<th>( K_L ) (L·mg(^{-1}))</th>
<th>( R^2 )</th>
<th>( K_F ) (mg·g(^{-1}))/(mg·L(^{-1}))</th>
<th>( 1/n )</th>
<th>( R^2 )</th>
</tr>
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<tr>
<td>288</td>
<td>Goethite</td>
<td>37.16</td>
<td>0.072</td>
<td>0.9214</td>
<td>4.37</td>
<td>0.52</td>
<td>0.9881</td>
</tr>
<tr>
<td></td>
<td>G-Mn3%</td>
<td>52.63</td>
<td>0.46</td>
<td>0.9942</td>
<td>29.42</td>
<td>0.17</td>
<td>0.9818</td>
</tr>
<tr>
<td></td>
<td>G-Mn6%</td>
<td>62.54</td>
<td>1.71</td>
<td>0.9910</td>
<td>43.35</td>
<td>0.12</td>
<td>0.8160</td>
</tr>
<tr>
<td></td>
<td>G-Mn9%</td>
<td>64.98</td>
<td>3.15</td>
<td>0.9943</td>
<td>49.18</td>
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<td>0.8287</td>
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<td>G-Mn12%</td>
<td>69.88</td>
<td>3.12</td>
<td>0.9929</td>
<td>52.40</td>
<td>0.10</td>
<td>0.8233</td>
</tr>
<tr>
<td></td>
<td>G-Mn15%</td>
<td>76.63</td>
<td>14.99</td>
<td>0.9969</td>
<td>66.53</td>
<td>0.089</td>
<td>0.7137</td>
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<tr>
<td>303</td>
<td>Goethite</td>
<td>56.56</td>
<td>0.050</td>
<td>0.8932</td>
<td>4.02</td>
<td>0.64</td>
<td>0.9917</td>
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<tr>
<td></td>
<td>G-Mn3%</td>
<td>63.53</td>
<td>0.25</td>
<td>0.8413</td>
<td>9.64</td>
<td>0.72</td>
<td>0.6199</td>
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<tr>
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<td>G-Mn6%</td>
<td>70.62</td>
<td>5.44</td>
<td>0.9976</td>
<td>49.16</td>
<td>0.16</td>
<td>0.7567</td>
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<tr>
<td></td>
<td>G-Mn9%</td>
<td>71.79</td>
<td>14.82</td>
<td>0.9947</td>
<td>67.03</td>
<td>0.14</td>
<td>0.7588</td>
</tr>
<tr>
<td></td>
<td>G-Mn12%</td>
<td>75.53</td>
<td>9.32</td>
<td>0.9973</td>
<td>61.42</td>
<td>0.095</td>
<td>0.6513</td>
</tr>
<tr>
<td></td>
<td>G-Mn15%</td>
<td>79.24</td>
<td>15.91</td>
<td>0.9947</td>
<td>67.03</td>
<td>0.14</td>
<td>0.7588</td>
</tr>
<tr>
<td>318</td>
<td>Goethite</td>
<td>67.52</td>
<td>0.046</td>
<td>0.9911</td>
<td>0.73</td>
<td>3.65</td>
<td>0.9828</td>
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<tr>
<td></td>
<td>G-Mn3%</td>
<td>70.22</td>
<td>1.11</td>
<td>0.9958</td>
<td>0.18</td>
<td>32.96</td>
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<tr>
<td></td>
<td>G-Mn6%</td>
<td>71.63</td>
<td>4.26</td>
<td>0.9978</td>
<td>0.15</td>
<td>47.53</td>
<td>0.9449</td>
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<td>G-Mn9%</td>
<td>77.76</td>
<td>10.13</td>
<td>0.9988</td>
<td>0.10</td>
<td>58.04</td>
<td>0.4848</td>
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Table 4. Comparison of adsorption capacity for U(VI) on Mn-substituted FeOOH with others.

<table>
<thead>
<tr>
<th>Adsorbent Sample</th>
<th>Solution Conditions</th>
<th>q_{max} (mg/g)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFeOx-TiOx</td>
<td>T = 293 K, pH = 5.0</td>
<td>66.78</td>
<td>[38]</td>
</tr>
<tr>
<td>Bacillus subtilis/FeOx</td>
<td>T = 303 K, pH = 4.0</td>
<td>20.22</td>
<td>[43]</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>T = 323 K, pH = 5.0</td>
<td>4.54</td>
<td>[40]</td>
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<tr>
<td>Humic Acid coated FeOx</td>
<td>T = 298 K, pH = 7.8</td>
<td>39.4</td>
<td>[44]</td>
</tr>
<tr>
<td>Magnetic biochar</td>
<td>T = 318 K, pH = 4.0</td>
<td>52.63</td>
<td>[45]</td>
</tr>
<tr>
<td>Montmorillonite@carbon composite</td>
<td>T = 298 K, pH = 3.95</td>
<td>20.8</td>
<td>[46]</td>
</tr>
<tr>
<td>FeOx/AC</td>
<td>T = 298 K, pH = 4.0</td>
<td>56.0</td>
<td>[47]</td>
</tr>
<tr>
<td>Acid/polyaniline/FeOOH</td>
<td>T = 298 K, pH = 8.0</td>
<td>555.8</td>
<td>[48]</td>
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<tr>
<td>Sulfonic acid-decorated FeOOH</td>
<td>T = 298 K, pH = 4.0</td>
<td>709.4</td>
<td>[49]</td>
</tr>
<tr>
<td>G-Mn15%</td>
<td>T = 303 K, pH = 4.0</td>
<td>79.24</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 6. (A–C) Adsorption isotherms of U(VI) adsorption on Mn-substituted FeOOH; (D–F) Langmuir model; (G–I) Freundlich model. C_{(VI)} = 5.0–55.0 mg/L, m/V =0.5 g/L, I = 0.01mol/L NaCl, T = 288–318 K, pH = 4.0, t = 24 h.

3.5. Mechanism Analysis

Figure 7A–E show the FESEM and mapping images of G-Mn15% adsorbed with U(VI). After U(VI) adsorption, the surface of G-Mn15% undergoes agglomeration and
stacking phenomena, becoming rough and with reduced pores. The result above can probably be attributed to the adsorption of U(VI) on G-Mn15% through surface complexation. Unlike before adsorption, the U element appeared in the mapping after adsorption (Figure 7E), confirming the successful adsorption of U(VI) on the surface of G-Mn15%. Figure 7F shows the EDS results of G-Mn15% after U(VI) adsorption with a characteristic peak of the U element, and the proportion of the U element is 0.42%, which is consistent with the mapping results. The XPS spectra of total scans, Fe 2p, Mn 2p, U 4f, and O 1s are shown in Figure 7G. The presence of the U 4f peak for Goethite, G-Mn6%, and G-Mn15% after U(VI) adsorption demonstrates that U(VI) is successfully adsorbed on Mn-substituted FeOOH. Meanwhile, the presence of the Mn 2p peak for G-Mn6%-U and G-Mn15%-U confirms the successful loading of Mn into the crystal structure of goethite. The FTIR spectra of Goethite and G-Mn15% adsorbed U(VI) are shown in Figure 7H. Compared with FTIR before U(VI) adsorption, the peaks at 1431 cm⁻¹, 903 cm⁻¹, 1645 cm⁻¹, and 3769–2969 cm⁻¹ show a weakening trend, indicating that U(VI) binds to functional groups on the surface of Mn-substituted FeOOH and mainly reacts with hydroxy-OH and uranyl ions [23]. The -OH peak at 893 cm⁻¹ and 797 cm⁻¹ is weakened, indicating the complexation reaction between Fe-OH and uranyl ions on the surface of Mn-substituted FeOOH [23]. In addition, the peak intensities at 639 cm⁻¹ and 581 cm⁻¹ weakened, indicating that Fe-O and Mn-O combined with U(VI) during the adsorption process. According to previous reports, the coordination of Mn to participate in the adsorption and reduction of U(VI).

The peak intensity of U(VI) is positively correlated with the increasing trend of Mn substitution, so as the peak area of U(VI). XPS analysis results show that Fe₂p in Goethite, G-Mn6%, and G-Mn15% after U(VI) adsorption demonstrates that U(VI) is successfully adsorbed on Mn-substituted FeOOH. Meanwhile, the presence of the Mn 2p peak for G-Mn6%-U and G-Mn15%-U confirms the successful loading of Mn into the crystal structure of goethite. The FTIR spectra of Goethite and G-Mn15% adsorbed U(VI) are shown in Figure 7H. Compared with FTIR before U(VI) adsorption, the peaks at 1431 cm⁻¹, 903 cm⁻¹, 1645 cm⁻¹, and 3769–2969 cm⁻¹ show a weakening trend, indicating that U(VI) binds to functional groups on the surface of Mn-substituted FeOOH and mainly reacts with hydroxy-OH and uranyl ions [23]. The -OH peak at 893 cm⁻¹ and 797 cm⁻¹ is weakened, indicating the complexation reaction between Fe-OH and uranyl ions on the surface of Mn-substituted FeOOH [23]. In addition, the peak intensities at 639 cm⁻¹ and 581 cm⁻¹ weakened, indicating that Fe-O and Mn-O combined with U(VI) during the adsorption process. According to previous reports, the complexation reaction between Mn-substituted FeOOH and U(VI) may result in the formation of bidentate edge shared complexes (=Fe/Mn(OH):UO₂) and bidentate angle shared complexes (=Fe/MnOH):UO₃) [30].

Figure 8 shows the high-resolution scans of Fe 2p, Mn 2p, and U 4f. As shown in Figure 8A, the two peaks of Goethite at binding energies of 710.71 eV and 724.36 eV belong to Fe 2p½ and Fe 2p½, respectively [51,52]. The three peaks of Fe²⁺, Fe³⁺, and satellite peak are identified by peak deconvolution analysis of Fe 2p½ at 711.10, 713.71, and 718.80 eV, Fe 2p½ at 724.30, 726.32, and 732.31 eV respectively [32]. Compared with Goethite, the peak intensity of Fe2p in Goethite-U decreases, indicating that Fe-O is involved in the adsorption of U(VI). In addition, as the substitution amount of Mn increases, the peak intensity of Fe 2p gradually weakens, and the molar ratios of Fe²⁺/Fe³⁺ in Goethite-U, G-Mn6%-U, and G-Mn15%-U increase from 1.74 to 2.21 and 2.40, respectively, indicating that the substitution of Mn promotes the reduction process of Fe³⁺ to Fe²⁺. Figure 8B shows the high-resolution scans of Mn 2p, and the XPS spectra of Goethite and Goethite-U demonstrate the absence of the Mn element in the synthesized goethite. The two peaks of G-Mn6%-U at binding energies of 641.04 eV and 652.95 eV belong to Mn 2p½ and Mn 2p½, respectively [23,26]. The three peaks of Mn²⁺, Mn³⁺, and Mn⁴⁺ are identified by peak deconvolution analysis of Mn 2p½ at 640.58, 642.02, and 643.82 eV, Mn 2p½ at 651.88, 653.04, and 654.87 eV respectively [32,53]. As the substitution amount of Mn increases from 6% to 15%, the peak value of Mn 2p significantly increases. Through integral calculation, it is found that the molar ratio of Mn²⁺/Mn³⁺ in G-Mn6%-U and G-Mn15%-U decreases from 0.87 to 0.86, indicating that Mn²⁺ is oxidized into Mn³⁺ and replaces Fe³⁺ in the structure of goethite [23]. Figure 8C shows the high-resolution scans of U 4f, the two peaks of Goethite-U at binding energies of 381.30 eV and 392.13 eV are attributed to U 4f½ and U 4f½, respectively [52]. The two peaks of U(IV) and U(VI) are identified by peak deconvolution analysis of U 4f½ at 380.48 and 381.44 eV, U 4f½ at 391.10 and 392.44 eV, respectively [13]. The peak intensity of U(VI) is positively correlated with the increasing trend of Mn substitution, so as the peak area of U(IV), indicating that Mn substitution enhances the reduction effect on U(VI). XPS analysis results show that Fe-O and Mn-O coordinate to participate in the adsorption and reduction of U(VI). The adsorption mechanism of U(VI) on Mn-substituted FeOOH can be briefly summarized as shown in Figure 9.
Figure 7. (A–E) FESEM and Mapping of G-Mn15% after U(VI) adsorption; (F) EDS of G-Mn15% after U(VI) adsorption; (G) Total XPS spectra of survey and high-resolution scans; (H) FTIR of Goethite and G-Mn15% after U(VI) adsorption.
Figure 8. The survey and high-resolution scans of XPS spectra of U(VI) adsorption on Mn-substituted FeOOH. (A) Fe 2p; (B) Mn 2p; (C) U 4f.

Figure 9. Reaction mechanism diagram of U(VI) adsorption on Mn-substituted FeOOH.

4. Conclusions

Mn-substituted FeOOH was successfully prepared and used to adsorb U(VI) under various environmental conditions (reaction time, pH, ion strength, reaction temperature and initial U(VI) concentration). The substitution of Mn into FeOOH changed the structure, crystallinity, and morphology of goethite, and increased the surface area of the active sites. Batch experiment results demonstrated that U(VI) adsorption is highly dependent on pH values. In addition, the U(VI) adsorption performance on goethite was improved by Mn substitution, and the U(VI) adsorption process on Mn-substituted FeOOH followed the Langmuir model and pseudo-second-order model. The adsorption capacity of G-Mn15% calculated by the experiment results was 82.11 mg/g at 318 K and pH 4.0. The results of XPS analysis further verified that U(VI) adsorption/reduction on goethite is im-
proved by Mn substitution. According to FTIR analysis, the active sites for U(VI) adsorption are oxygen-containing functional groups (−OH, Fe-O and Mn-O). The results are beneficial for a deeper understanding of the structural evolution of goethite caused by Mn substitution, as well as the adsorption performance and mechanism of U(VI) on iron/manganese oxides.

Author Contributions: Conceptual design, M.L. and L.Z.; methodology, J.W.; formal analysis, L.M.; investigation, Z.P. and W.J.; data curation, X.S. and R.L.; writing—review and revision, S.D.; visualization, Y.T.; acquisition of funding, M.L. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References


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