

Article

Study on the Adsorption Properties of Iron Tailings for GO

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Abstract: Iron tailings can be used as adsorbents to effectively remove graphene oxide (GO) in aqueous solutions. Experimental data show that pH, iron tailing quality, GO concentration and temperature have significant effects on the removal of GO, the adsorption of the tail involves a single layer adsorbed Langmuir model with exothermic reaction, and it compliance with the proposed dynamics model meets the requirements, the adsorption process is a spontaneous physical adsorption process. Combining scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) to analyze the iron tail according to the mechanisms of ore adsorption of GO, it was concluded that iron tailings might be a very promising material to effectively remove GO in aqueous solutions. The results of this research provide key information for the transportation and potential fate of GO in the natural environment.

Keywords: iron tailings; GO; adsorption; kinetic; isotherm



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1. Introduction

In recent years, graphene has strong application prospects in many scientific fields due to its unique electrical, optical, mechanical and other properties and has received extensive attention from many scholars [1–4]. Graphene oxide (GO) is a derivative of graphene, it is usually synthesized from pure graphite powder by modified Hummers method [5]. It is easy to manufacture, low in cost, rich in oxygen-containing functional groups, has a high specific surface area [6], and is easily dispersed stably in solvents [7]. The oxidized graphene has super-high strength and toughness and has a significant enhancement effect on cement soil, ceramics and other polymers, and it has become a new material studied by many scholars [8,9].

GO is a kind of nano-material with finer particles that can easily enter biological cell tissues. With the gradual expansion of application fields, GO gradually diffuses and spreads in water, air, soil and other media. Some documents have shown that GO itself has certain toxicity, which easily produces toxic and side effects on cell tissues. The higher the concentration, the stronger the toxicity [10,11]. The toxicity of GO itself limits its promotion and application. Therefore, we are constantly looking for a material with low toxicity and good compatibility to adsorption GO to reduce its impact on the safety of environmental biological cells. The adsorption of GO through adsorbents to form flocs is an effective way to control the dispersion of GO toxicity [12].

In recent years, the exploitation of a large number of mineral resources will inevitably produce too much solid waste, and these tailings are waste after beneficiation. By the end of 2017, the tailings stock has reached 8 billion tons, of which iron tailings account for 1/3 of the total [13]. The massive discharge of iron tailings takes up a large number of land resources and is also prone to safety hazards. According to statistics, as of the end of 2015, the comprehensive utilization rate of iron tailings in China was only 28.9%, which was far behind the 60% in Western developed countries [14]. Therefore, the resource utilization of solid waste is the focus of future research [15–17].

Iron tailings are continuously polished into fine sands in the process of beneficiation. Compared with general adsorbent materials, iron tailings have a larger specific surface area, and there are articles showing that the surface of the tailings' sand particles has stronger chemical adsorption activity [18]. Therefore, the promotion and application of iron tailings as adsorbent materials has important strategic significance for the sustainable development of our country's mining industry. At present, there are few research articles on the interaction between iron tailing sand and GO in aqueous solutions. Therefore, this article uses iron tailing sand as an adsorbent material to conduct an adsorption test on GO in aqueous solution, make full use of a large number of idle iron tail mines to adsorb leaks in the nature world, avoiding GO to generate harm by water circulating into human cells through water.

2. Experimental Section

2.1. Materials

The adsorbate GO solution used throughout this experiment is 100 mL brown-yellow aqueous solution with a concentration of 2 mg/mL a purity of 98%, a lamella diameter of 0.2–10 μm , and a thickness of about 1 nm. NaOH and HCl are domestic analytical grades without further purification. The adsorbent iron tailings were taken from Zhuji Lizhu Iron Mine, Shaoxing, and then dried and sifted through 1 mm standard sieve. Deionized water is prepared by UPW-R15 ultra-pure water machine.

2.2. Test Instrument

We used a pH meter (FE28) to measure the pH of the solution. We used a constant temperature shaker (THZ-100B, Yiheng, Shanghai, China) to control the temperature during the test. We used an ultraviolet–visible (UV) spectrophotometer (UV75N, yoke, Shanghai, China) to measure the absorbance of the solution after equilibrium. The SEM image was obtained by a JSM-6360LV scanning electron microscope (JEOL, Beijing, China). A transmission electron microscope (TEM) (JEM-2100F, JEOL, Beijing, China) and atomic force microscope (AFM) (SPA400, Bruker, Massachusetts, MA, USA) were used to further observe the microstructure of the sample. The XRD patterns of the samples were measured by Empyrean X-ray diffract graph. The FT-IR test instrument was a NEXUS FT-IR spectrometer (Thermo Nicolet Corporation, Madison, WI, USA). The XPS test instrument was an Escalab 250XI, Thermo Scientific (Thermo Fisher Scientific, Waltham, MA, USA).

2.3. Adsorption Experiment

This study mainly studied the adsorption of GO by iron tailings in different solution pH (5, 6, 7, 8, 9, 10), the mass of iron tailings (30 mg, 40 mg, 50 mg, 60 mg, 70 mg) and the adsorption effect of GO at initial concentrations (40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L) and temperatures (298.15 K, 303.15 K, 313.15 K) and the corresponding adsorption isotherm model, adsorption thermodynamic model and adsorption kinetic model were obtained by fitting the test data.

2.4. Analytical Method

All the experiments were carried out in polyethylene tubes at 25 ± 0.1 °C by a batch technique. Iron tailings were selected as the adsorbent in the static experiments. The desired pH of the suspensions in each tube was adjusted within the range of 5.0 to 10.0 by adding negligible volumes of 0.10 or 0.05 mol/L HCl or NaOH. Meanwhile, the UV–vis spectrophotometer (UV75N) was employed to monitor the coagulation of GO and iron tailings by testing the absorbance at a wavelength of 201 nm. All the experimental data were the average of duplicate determinations, and the relative errors were about 5%. From the blank tests, the coagulation of GO on the polyethylene tube wall was negligible. According to the initial concentration C_0 (mg/L) and equilibrium concentration C_e (mg/L) of GO, the adsorption amount Q_e (mg/g), adsorption rate R (%) and constant distribution coefficient K_d were calculated by Equations (1)–(3). V (mL) and m (g) are the volume of GO and the

mass of iron tailings. The test results are the average of three parallel tests, and the relative error was less than 5%.

$$Q_e = \frac{(C_o - C_e) \times V}{m} \quad (1)$$

$$R = \frac{C_o - C_e}{C_o} \times 100\% \quad (2)$$

$$K_d = \frac{Q_e}{C_e} \quad (3)$$

3. Results and Discussion

3.1. Characterization of Material

3.1.1. SEM and TEM

Microscopic morphology is a method of determining whether the adsorption occurs by comparing the topography before and after adsorption. In this study, SEM and TEM were used to characterize the microstructure of GO, iron tailings, and GO/iron tailings, and the obtained images are shown in Figure 1. The SEM and TEM images of GO are shown in Figure 1a,d. It can be seen from the figure that GO showed a relatively uniform, layered structure distribution with slight wrinkles on the surface of the structure. The SEM image, Figure 1b, of the iron tailings shows a needle-like structure with disordered arrangement and no obvious agglomerated layered structure. The SEM image, Figure 1c, of the GO/iron tailings adsorption mixture after the iron tailings adsorbed GO shows a certain irregular layered structure, the surface of the structure is rough and uneven, and there is obvious accumulation, which indicates that GO is attached to the surface of the iron tailings. In addition, in the GO/iron tailings TEM image, Figure 1e, there is an obvious agglomeration phenomenon. The agglomerated nanoparticles were formed by crystal aggregates in iron tailing sand particles [19,20]. At the same time, in the batch test, the iron tailing sand also showed good adsorption, with GO adsorbed on the surface of the particles to form flocs and suspended at the bottom of the solution. The changes of the solution before and after adsorption are shown in Figure 1f, g, which are consistent with the results of the SEM and TEM experiments, indicating that the iron tailings had a good effect on the adsorption of GO.

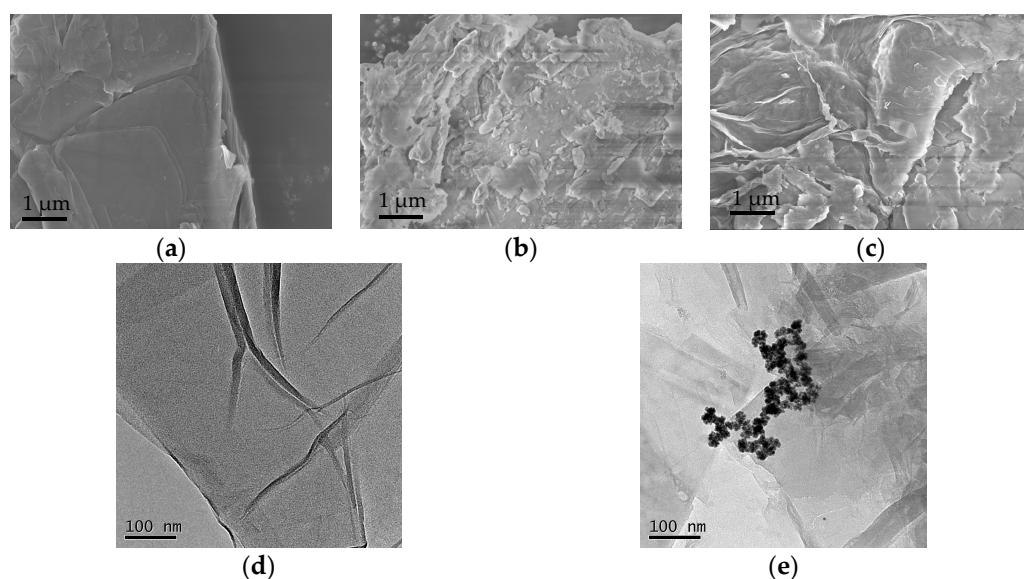


Figure 1. Cont.

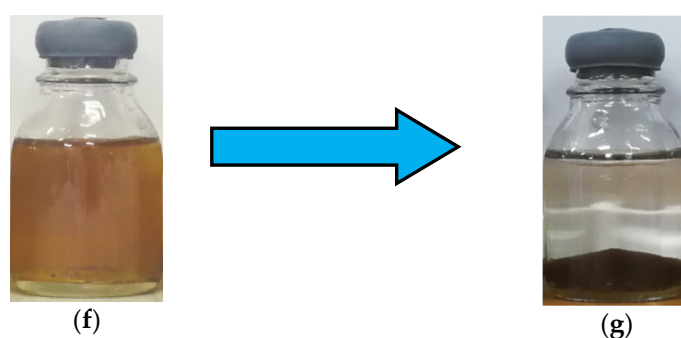


Figure 1. SEM (a) and TEM (d) of GO; SEM (b) of iron tailings; SEM (c) and TEM (e) of GO/iron tailings; solution image before adsorption (f); solution image after adsorption (g).

3.1.2. XRD and AFM

X-ray diffraction technology has become the most basic, most important structural test [21]. In order to further reveal the adsorption mechanism of iron tailings to GO, the Cu target $K\alpha$ was used as the radiation power source, and the characteristic diffraction peaks of GO/iron tailings, GO and iron Tailings were compared by XRD. The X-ray diffraction spectrum is shown in Figure 2. It was found from the XRD spectrum that the characteristic diffraction peaks of GO/iron tailings were included in the characteristic diffraction peaks of GO and iron tailings, no new diffraction peaks appeared, and the intensity of the diffraction peaks is lower than that of GO and iron tailings [22]. The compound GO/iron tailings had small particle size and low crystallinity, which indicated that GO was adsorbed on the surface of iron tailing particles. In order to further confirm that GO was adsorbed on the surface of iron tailing sand, the AFM test results of GO and GO/iron tailings are shown in Figure 3. The results showed that the maximum lamellar thickness of GO was about 1 nm, while the maximum thickness of GO/iron tailings was about 2.02 nm, and its height increased significantly [23].

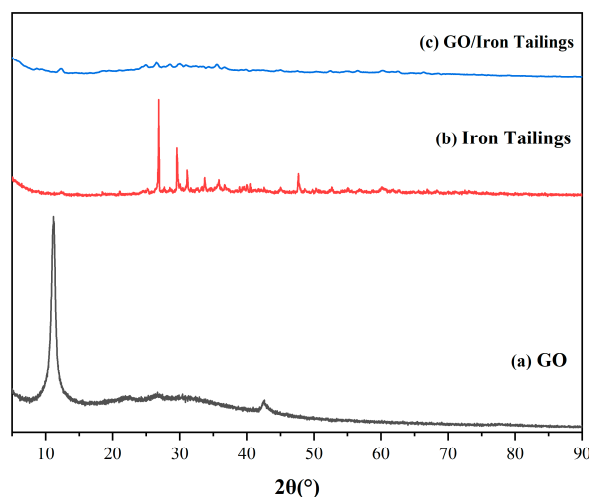


Figure 2. XRD image of GO (a), iron tailings (b), GO/iron tailings (c).

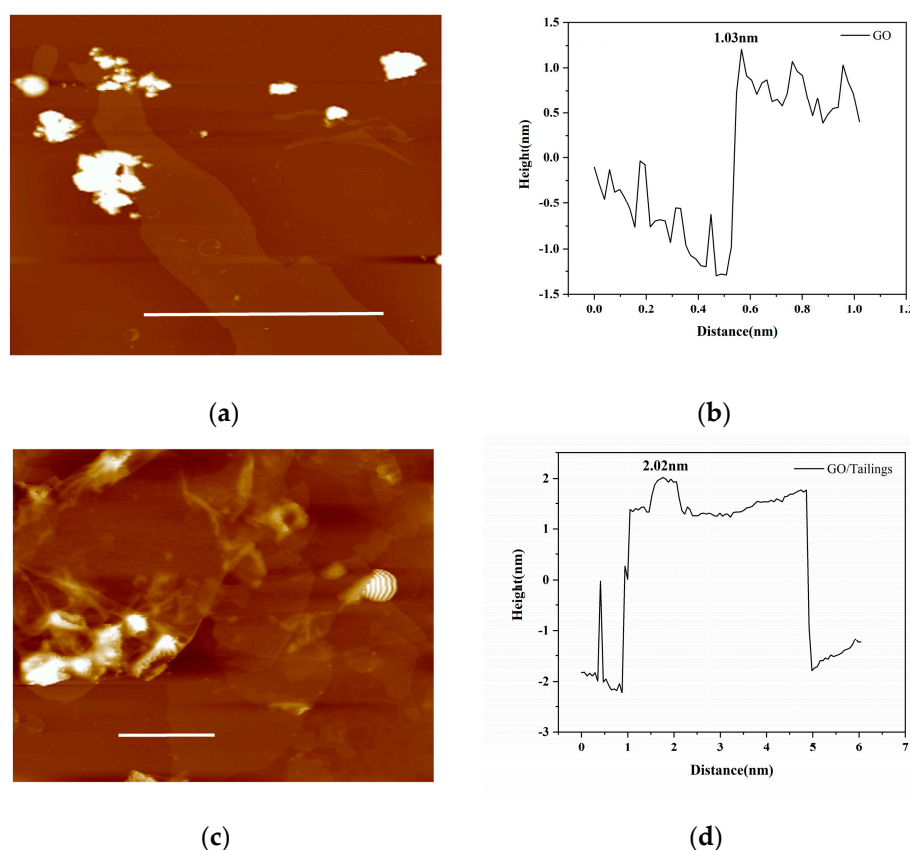


Figure 3. (a,b) is the AFM image of GO; (c,d) is the AFM image of GO/iron tailings.

3.1.3. FT-IR

The FT-IR spectra are very helpful to characterize surface functional groups. Figure 4 shows the FT-IR spectra of GO, iron tailings and GO/iron tailings. First, it was found that the spectra of iron tailings and GO/iron tailings were similar, but the absorption peaks corresponding to different functional groups were different. Among them, the bands at 3450 cm^{-1} approximately were assigned to O–H stretching and bending vibrations [24]. The peaks at 1570 cm^{-1} were associated with the C=C stretching vibrations [25]. The deformation peak of C–OH is reflected through the peaks at 1400 cm^{-1} , and the peak at 1000 cm^{-1} can be ascribed to the tensile vibration of C–O [26]. Compared with the FT-IR spectrum of iron tailings, GO/iron tailings have stronger absorption peak intensities at 3450 cm^{-1} and 1570 cm^{-1} and weaker absorption peaks at 1400 cm^{-1} and 1000 cm^{-1} . The intensity of the absorption peak indicates that there is a coordination reaction or ion exchange between GO and iron tailings, which may be the reason why iron tailings have an adsorption effect on GO [27]. The characteristic peaks of GO at 2920 cm^{-1} and 2850 cm^{-1} produced C–H stretching vibrations, but they disappeared on the GO/iron tailings spectrum. Compared with GO and iron tailings, the FT-IR spectrum of GO/iron tailings neither produced new absorption peaks nor shifted the original peaks, indicating that the adsorption of iron tailings to GO was not chemical adsorption but physical adsorption [28].

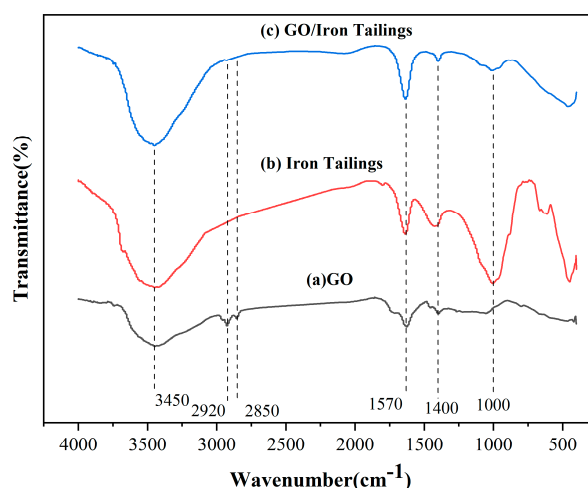


Figure 4. FT-IR of GO (a), iron tailings (b) and GO/iron tailings (c).

3.1.4. XPS

Regarding the XPS energy spectrum analysis of GO and GO/iron tailings, the results are shown in Figures 5 and 6. GO only had two energy peaks of O 1s and C 1s at 531.97 eV and 285.97 eV. In addition to the O 1s and C 1s energy peaks of GO/iron tailings, energy peaks such as Mg 1s, Ca 2p, Al 2p and Si 2p also appeared, but the energy peak intensity of C 1s was significantly lower than that of GO C 1s. Therefore, the C 1s area in the XPS spectrum of GO was further analyzed, and the C1 spectral deconvolution could be divided into three components [29]. The binding energies were 284.79 eV, 286.80 eV, and 288.10 eV, respectively, corresponding to the C–C/C=C, C–O, C=O structure [26,30]. The shape and position of the C1s peak of the GO/iron tailings compound after the iron tailings adsorbed GO changed significantly, the relative intensity of the C–C/C=C energy peak increased and the relative intensity of the C–O and C=O energy peaks decreased, and their positions moved to 284.78 eV, 286.66 eV and 288.52 eV, respectively. This was consistent with the results of FT-IR, which provided direct evidence for the change of oxygen-containing functional groups in the process of iron tailings adsorbing GO.

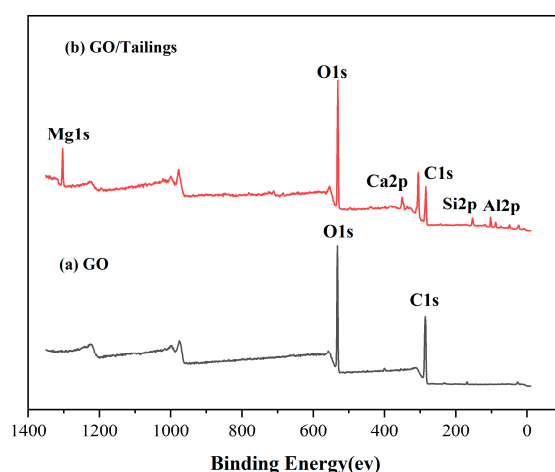


Figure 5. XPS spectra of GO (a) and GO/iron tailings (b).

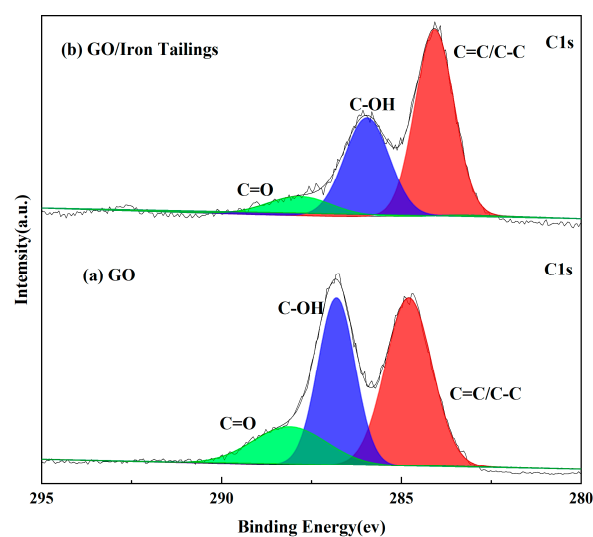


Figure 6. The high C1s deconvolution of GO (a) and GO/iron tailings (b).

3.2. Effect of pH

pH is an important factor affecting the adsorption of anions and cations at the solid–liquid interface. When the mass of iron tailing sand was 50 mg, and the initial content of GO was 60 mg/L, in order to explore the influence of pH change on the adsorption of GO by iron tailing sand, the pH value of the solution was adjusted to 5–10, Test temperature is 303.15 K.

The changes in GO adsorption capacity Q_e , adsorption rate R and distribution coefficient K_d of iron tailings at different pH values are shown in Figure 7. As can be seen from the figure, the adsorption rate of GO by iron tailings was more than 70% in the range of pH 5–10. The adsorption effect was the best at pH = 7, and the adsorption rate was 90%, which indicated that iron tailings, as an adsorbent, could effectively adsorb GO in the solution. In addition, the change in pH had a great influence on the adsorption of GO by iron tailings. With the increase in PH value, the adsorption capacity Q_e , adsorption rate R and distribution coefficient K_d reached the maximum at pH = 7, which were 53.95 mg/g, 89.92% and 8.92 respectively, showing a trend of increasing at first and then decreasing.

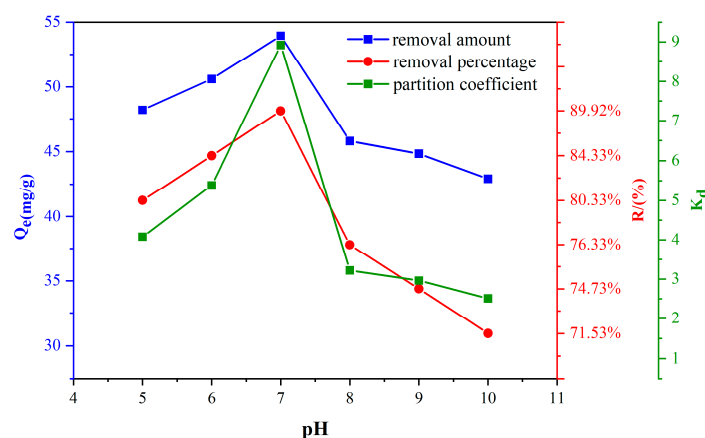


Figure 7. Effect of pH on adsorption of GO by iron tailings.

The main reason for the above phenomenon was that when the $\text{pH} < 7$ of the solution, the anion groups of GO produced protonation and weak negative charges under the actions of acidity, which caused electrostatic repulsion with metal ions such as Fe, Mg, Al and the metal oxides in iron tailings, thus inhibiting the adsorption of GO by iron tailings. With the increase in pH, the deprotonation of the anionic group of GO was strengthened [31] such

that the electrostatic adsorption of carboxyl, hydroxyl and other anionic groups with metal cations on the surface of iron tailing sand particles was enhanced, and the adsorption of iron tailings to GO was improved. When the solution pH > 7, OH⁻ competed with carboxyl, hydroxyl and other anionic groups for the active adsorption sites on the surface of iron tailing particles [32], and thus the adsorption of iron tailings to GO was reduced.

3.3. Mass Effect of Iron Tailings

In order to explore the effect of the mass of iron tailings on the adsorption of the GO solution, iron tailings of different masses (30 mg, 40 mg, 50 mg, 60 mg, 70 mg) were added to the GO solution with an initial content of 60 mg/L, and the adsorption experiments were carried out at 303.15 K and pH = 7. The test results are shown in Figure 8.

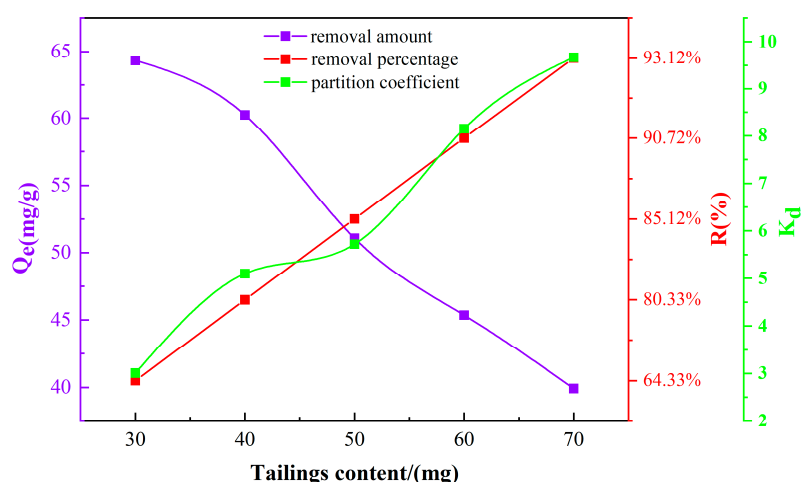


Figure 8. Effects of iron tailings' mass on the adsorption of GO.

The adsorption capacity Q_e decreased with the increase in iron tailing content, while the adsorption rate R and distribution coefficient K_d increased with the increase in iron tailing content. The main reason was that the total number of effective adsorption sites on the surface of iron tailings increased with the increase of the quality of iron tailings, thus increasing the total adsorption rate and distribution coefficient. However, with the increase in the mass of iron tailings, the number of particles per unit volume increased, and collision agglomeration easily occurred, resulting in a decrease in the number of effective active adsorption sites per unit mass of iron tailings and thus reducing the adsorption capacity of iron tailings per unit mass [33]. Therefore, for the consideration of economy, the optimal content was when the mass of iron tailings was 50 mg.

3.4. Effect of GO Content

In order to explore the adsorption effect of iron tailings on different initial contents of GO, when $T = 303.15$ K, pH = 7, and iron tailing sand mass was 50 mg, the initial content (40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L) GO solutions were subjected to adsorption tests, and the test results are shown in Figure 9.

The adsorption capacity Q_e increased with the increase of the initial content of GO, while the adsorption rate R and the distribution coefficient K_d increased at first and then decreased with the increase of the initial content of GO. When the initial content of GO was 60 mg/L, the adsorption rate R and distribution coefficient K_d reached their maximums, which were 85.92% and 6.1%, respectively. The main reason was that when the initial content of GO was low, there were a large number of idle active adsorption sites on the surface of iron tailings that could not be effectively used to adsorb GO, resulting in low adsorption capacity and adsorption rate. When the initial content of GO is large, the contact chance between the unit volume of GO and the active point on the surface of iron tailings decreases, so that the adsorption rate of GO by iron tailings decreases.

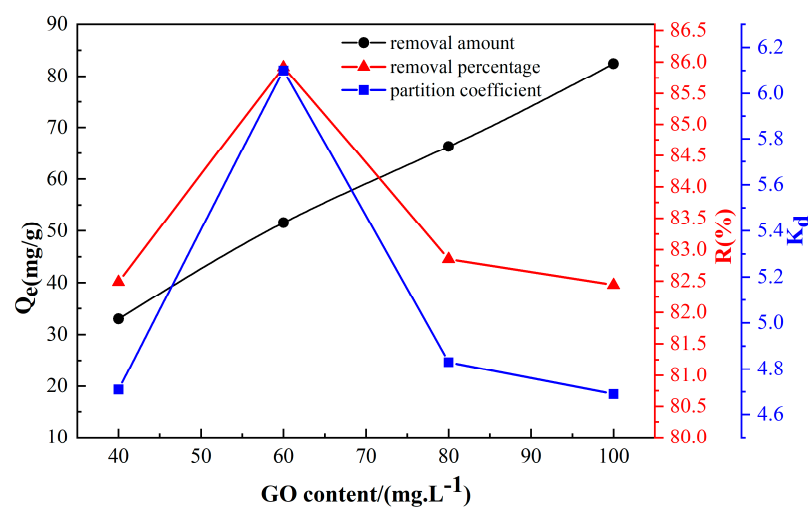


Figure 9. Effects of GO content on the adsorption of GO by iron tailings.

3.5. Adsorption Isotherm and Chemical Thermodynamics

When pH = 7 and the mass of iron tailing was 50 mg, we explored the adsorption experiment regarding iron tailings in different initial contents of GO solution (20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L) at different temperatures (298.15 K, 303.15 K, 313.15 K). The test results are shown in Figure 10a. The adsorption capacity of iron tailings for GO solutions with different initial contents decreased with increasing temperature. The higher the GO content, the more obvious the influence of temperature on the GO adsorption of iron tailings.

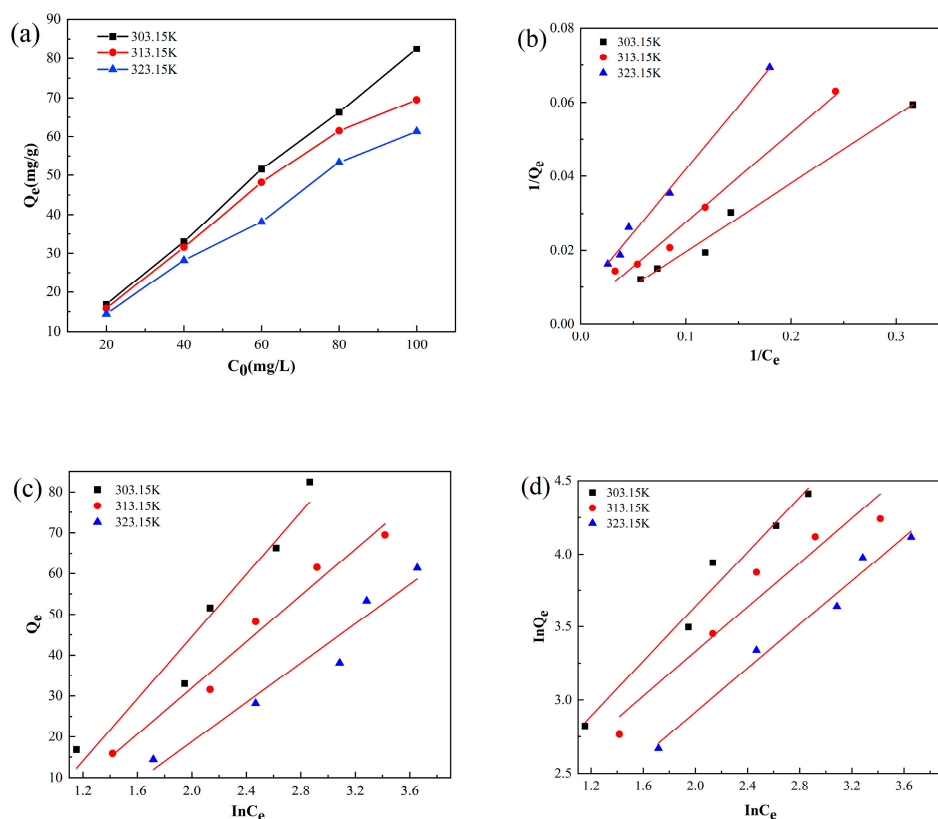


Figure 10. Iron tailing adsorption isotherm of GO (a), Langmuir (b), Freundlich (c) and Temkin (d) isotherm equation fitting curves.

The Langmuir, Freundlich and Temkin adsorption isotherm model equations were used to fit the adsorption process of iron tailings to GO, as shown in Equations (4)–(6), and the fitting results are shown in Table 1, Figure 10b–d. It can be seen from the table that the correlation coefficient R^2 fitted by the Langmuir model was greater than that of Freundlich and Temkin, indicating that the Langmuir model could more effectively describe the adsorption process of iron tailings to GO, and the adsorption process was mainly uniform, monolayer adsorption. In addition, the maximum adsorption capacity Q_{max} fitted by the Langmuir model decreased with the increase in temperature, indicating that the temperature rise was not conducive to the progress of the adsorption reaction. In addition, And the parameter n fitted by the Freundlich isotherm equation are all greater than 1, indicating that the iron tailing adsorption of GO was a “preferential” adsorption [34].

Table 1. Parameters of Langmuir, Freundlich and Temkin adsorption isotherm equations.

C_0 (mg/L)	pH	Temperature (K)	Langmuir			Freundlich			Temkin		
			Q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2	K_T (L/mg)	C	R^2
60	7	303.13 K	909.091	0.006	0.986	5.853	1.068	0.973	0.436	38.095	0.947
		313.13 K	285.714	0.015	0.987	6.095	1.313	0.939	0.418	28.334	0.976
		323.13 K	129.87	0.023	0.993	4.129	1.334	0.981	0.295	24.097	0.947

Langmuir adsorption isotherm model:

$$\frac{1}{Q_e} = \frac{1}{K_L Q_{max}} \frac{1}{C_e} + \frac{1}{Q_{max}} \quad (4)$$

Freundlich adsorption isotherm model:

$$\ln Q_e = \ln K_F + \frac{\ln C_e}{n} \quad (5)$$

Temkin adsorption isotherm model:

$$Q_e = C \ln K_T + C \ln C_e \quad (6)$$

Q_e (mg/g) is the equilibrium adsorption capacity. Q_{max} (mg/g) is the highest adsorption capacity. C_e (mg/L) is the equilibrium concentration. K_L (L/mg) is the Langmuir balance factor regarding the affinity of binding sites; K_F is the Freundlich equilibrium constant and the index n is a non-linear factor corresponding to the heterogeneous energy of the adsorption surface. The value of C (L/mg) is associated with the adsorption heat, and K_T is a Temkin equilibrium constant related to maximum binding energy.

In order to further analyze the effect of temperature on the adsorption of GO by iron tailings, thermodynamic analysis was performed on the adsorption process, and the energy change during the adsorption process was analyzed through the fitting calculation of thermodynamic parameters to determine whether the adsorption behavior was spontaneous [35].

The effect of temperature in an adsorption test can be analyzed by calculating thermodynamic parameters such as standard free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS). The calculation equations are as follows in (7), (8) and (9), and their thermodynamic fitting parameters and curves are shown in Table 2 and Figure 11. The standard free energy (ΔG) was negative at 303.15 K, 313.15 K and 323.15 K, indicating that the adsorption of GO by iron tailings was spontaneous. In addition, the absolute value of ΔG decreased with the increase in temperature at the same concentration, indicating that the increase of temperature was not conducive to the adsorption reaction. The enthalpy change ΔH was negative under different initial contents of GO, indicating that the adsorption process of GO by iron tailings was an exothermic reaction, which was consistent with the isotherm

fitting results. The entropy change ΔS was negative under different initial contents of GO, indicating that the adsorption process of GO by iron tailings tended to be orderly.

$$K_d = \frac{Q_e}{C_e} \quad (7)$$

$$\Delta G = -RT \ln(K_d) \quad (8)$$

$$\ln(K_d) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

Table 2. Parameters of thermodynamic equation.

C_0 (mg/L)	ΔG (kJ/mol)			ΔH (kJ/mol)	ΔS (J/mol·K)
	303.15 K	313.15 K	323.15 K		
20	−4.210	−3.507	−2.560	−29.860	−82.177
40	−3.905	−3.431	−2.339	−27.545	−77.660
60	−4.560	−3.663	−1.491	−50.856	−152.056
80	−3.969	−3.124	−1.860	−35.862	−104.987
100	−3.897	−2.142	−1.239	−44.342	−133.855

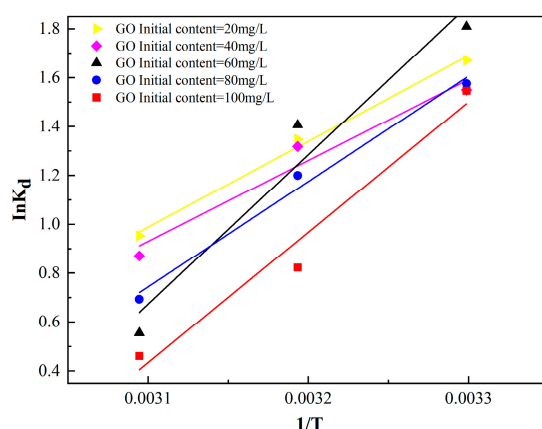


Figure 11. Thermodynamic fitting curve.

In the formula, T (K) is the absolute temperature of Kelvin, R is the standard molar gas constant (8.3145 J/mol·K) and K_d is the partition coefficient. ΔG (kJ/mol), ΔH (kJ/mol) and ΔS (J/mol·K) are thermodynamic parameters.

3.6. Adsorption Kinetics

When the temperature was 303.15 K and pH = 7, the iron tailings of 50 mg adsorbed GO solution with an initial content of 60 mg/L. The change in adsorption capacity with time is shown in Figure 12a. The adsorption capacity of iron tailings for GO per unit time gradually decreased with the increase in time, and the adsorption equilibrium was reached at 1680 min with an adsorption capacity of 51.55 mg/g. The main reason was that the number of effective adsorption sites on the surface of iron tailing particles was relatively fixed. As the reaction time increased, there were not enough active sites on the surface of iron tailing particles for adsorption, and the adsorption rate gradually decreased.

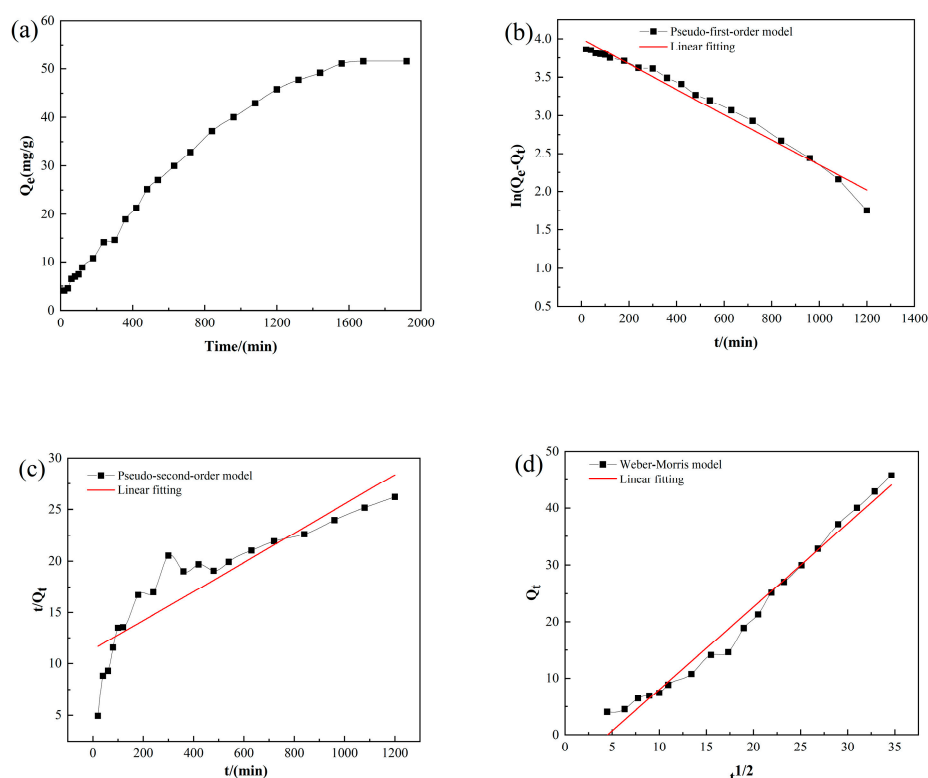


Figure 12. Relationship between adsorption capacity and time (a), fitting curve of pseudo-first order model (b), fitting curve of pseudo-second order model (c), fitting curve of Weber–Morris model (d).

The data obtained from the adsorption test were fitted and analyzed using the pseudo-first order kinetic model equation (Equation (10)) and the pseudo-second order kinetic model equation (Equation (11)). The fitting results are shown in Table 3 and Figure 12b,c. It can be seen from the results that the fitting correlation coefficients R^2 of the pseudo-first order and pseudo-second order kinetic model equations were 0.974 and 0.801, respectively. In addition, the equilibrium adsorption capacity fitted by the pseudo-second order kinetic model was 70.423 mg/g, while the equilibrium adsorption capacity fitted by the pseudo-first order kinetic model was 54.59 mg/g, which was closer to the actual adsorption balance of 51.55 mg/g. Therefore, the pseudo-first-order kinetic model equation is more suitable to describe the adsorption process of iron tailings to GO, indicating that the adsorption process belongs to physical adsorption, which is consistent with the test results of FT-IR.

Table 3. Parameters of pseudo-first order, pseudo-second order and Weber–Morris model.

C_0 (mg/L)	pH	Temperature (K)	Q_e (mg/g)	Pseudo-First Order Model			Pseudo-Second Order Model			Weber–Morris Model		
				Q_e	k_1	R^2	Q_e	k_2	R^2	k_{int}	C	R^2
60	7	303 K	51.55	54.59	0.0017	0.974	70.423	0.000018	0.801	1.463	−6.629	0.98

The pseudo-first order model and pseudo-second-order model are as follows:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (10)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (11)$$

In the above formula, Q_t (mg/g) and Q_e (mg/g) are the adsorption amount at adsorption time t (min) and the saturated adsorption amount at adsorption equilibrium,

respectively. k_1 (g/mg·min) and k_2 (g/mg·min) are the rate constants of the pseudo-first order and pseudo-second order models.

Solid–liquid adsorption is a complex adsorption process. In order to analyze the mechanism of particle diffusion in the adsorption process, the Weber–Morris model (Equation (12)) was used to fit the kinetic parameters, as shown in Table 3 and Figure 12d. It can be seen from the figure that Q_t and $t^{1/2}$ show a good linear relationship, and the fitted correlation coefficient R^2 is 0.98.

The Weber–Morris model is as follows:

$$Q_t = k_{int}t^{1/2} + C \quad (12)$$

k_{int} (g/mg·h^{−1/2}) is the rate constant of the intra-particle diffusion model. C is a parameter referred to the thickness of the boundary layer.

In order to further analyze the diffusion mechanism intra-particles, the whole adsorption process was divided into two stages [23]: surface adsorption stage, intra-particle diffusion and equilibrium stage [36]. As shown in Figure 13, the first stage was 0~120 min, Q_t and $t^{1/2}$ were linearly fitted, the fitting equation was $y = 0.785x$, the correlation coefficient R^2 was 0.996 and the fitting straight line passed through the origin, indicating that the intra-particles diffusion is the key step of adsorption rate in the first stage. The second stage started from 120 min to the adsorption equilibrium, the fitting equation was $y = 1.708x - 13.006$, the correlation coefficient R^2 was 0.996 and the fitted straight line failed to pass the origin, indicating that intra-particle diffusion was not a key factor in the adsorption rate in the second stage. At the same time, the intra-particle diffusion rate constant k_{int} of the second stage was 1.708 higher than the 0.785 of the first stage, and the adsorption boundary layer constant C of the second stage was -13.006 lower than the 0 of the first stage.

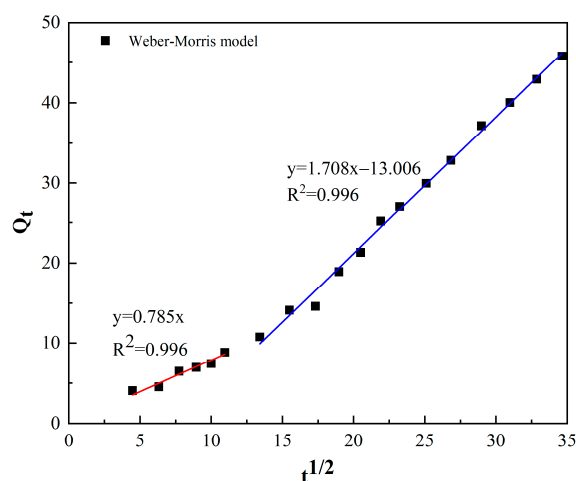


Figure 13. Weber–Morris model two-stage curve fitting.

The main reason was that at the beginning of adsorption, the membrane diffusion of particles increased the resistance of the boundary layer and decreased the diffusion rate intra-particles [37], which affected the first stage of the adsorption process. As the adsorption time increased, the diffusion rate intra-particles increased, which accelerated the second stage of the adsorption process.

4. Conclusions

By performing SEM, TEM, XRD, AFM, FT-IR, and XPS microscopic test method, it was found that there was a complex phenomenon occurring between iron tailings and GO, and there was no new substance formed in the adsorption process, which belonged to physical adsorption. The adsorption of GO by iron tailings was mainly due to the

vibration deformation and interaction of functional groups, thus revealing the adsorption mechanism of iron tailings to GO.

The results showed that iron tailings have good adsorption to GO, and the adsorption effect was the best when the mass of iron tailings was 50 mg, the content of GO was 60 mg/L and pH = 7. The equilibrium adsorption capacity was 51.55 mg/g. The adsorption isotherm of GO by iron tailings accorded with the Langmuir model, which involved monolayer adsorption, and the increase in temperature was not conducive to the adsorption reaction, and thus the adsorption process of GO by iron tailings was an exothermic reaction. The adsorption kinetics curve of GO by iron tailings accorded with the pseudo-first order kinetic model, and the adsorption process was spontaneous, which was physical adsorption. By integrating the experimental results, it was clear that iron tailings could be potentially used to elimination of GO from aqueous solutions, which could efficiently decrease the potential toxicity of GO in the natural environment.

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