



Article

Removal of Arsenic from Wastewater by Using Nano Fe_3O_4 /Zinc Organic Frameworks

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Abstract: Efficient removal of arsenic in wastewater is of fundamental importance due to the increasingly severe arsenic pollution. In this study, a new composite adsorbent (Fe_3O_4 @ZIF-8) for As(V) removal from wastewater was synthesized by encapsulating magnetic Fe_3O_4 nanoparticles into metal organic frameworks. In order to evaluate the feasibility of Fe_3O_4 @ZIF-8 as an adsorbent for As(V) removal, the adsorption properties of Fe_3O_4 @ZIF-8 were systematically explored by studying the effects of dosage, pH, adsorption isotherm, kinetics, and thermodynamics. Additionally, the characterization of Fe_3O_4 @ZIF-8 before and after adsorption was analyzed thoroughly using various tests including SEM-EDS, XPS, BET, XRD, TG, FTIR, and the properties and arsenic removal mechanism of the Fe_3O_4 @ZIF-8 were further studied. The results showed that the Fe_3O_4 @ZIF-8 has a specific surface area of $316 \text{ m}^2/\text{g}$ and has excellent adsorption performance. At 25°C , the initial concentration of arsenic was 46.916 mg/L , and pH 3 was the optimum condition for the Fe_3O_4 @ZIF-8 to adsorb arsenic. When the dosage of the Fe_3O_4 @ZIF-8 was 0.60 g/L , the adsorption of arsenic by the Fe_3O_4 @ZIF-8 can reach 76 mg/g , and the removal rate can reach 97.20%. The adsorption process of arsenic to the Fe_3O_4 @ZIF-8 can be well described by the Langmuir isotherm model and the second-order kinetic equation. At pH 3 and temperature 298 K, the maximum adsorption capacity of arsenic by the Fe_3O_4 @ZIF-8 was 116.114 mg/g . Through the analysis of thermodynamic parameters, it is proved that the adsorption process of arsenic by the Fe_3O_4 @ZIF-8 is a spontaneous endothermic reaction. The Fe_3O_4 @ZIF-8 has broad prospects for removing As(V) pollution in wastewater, because of its strong adsorption capacity, good water stability, and easy preparation.

Keywords: Fe_3O_4 @ZIF-8; As(V); nano Fe_3O_4 ; adsorption properties



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1. Introduction

Human survival and development are inseparable from water resources. With the continuous expansion of human productivity and the continuous development of the manufacturing industry, the demand for mineral resources continues to increase, and the generated pollutants enter the water body, resulting in more and more serious water pollution [1]. Arsenic is a non-metallic element, which widely exists in nature [2]. At present, hundreds of arsenic minerals have been found. Arsenic and its compounds are used in pesticides, herbicides, insecticides, and various alloys [3,4]. In 2017, the World Health Organization's International Agency for Research on Cancer placed arsenic and inorganic arsenic compounds on the list of Class I carcinogens [5]. In 2019, arsenic and arsenic compounds were included in the "List of Toxic and Harmful Water Pollutants (First Batch)" by the Ministry of Ecology and Environment. The sources of arsenic pollution in water bodies are wastewater, waste gas and industrial waste discharged from industrial production, various organic arsenic pesticides used in agricultural production to avoid

the impact of insect pests on crops, and the natural environment accompanied by volcanic eruptions and rock weathering and diffusion [6]. Arsenic-containing substances and arsenic can denature proteins and enzymes in cells, and cause cell damage by increasing reactive oxygen species in cells [7]. Studies have shown that the prevalence of arsenic poisoning is as high as 133‰ in groups who drink water with an arsenic content of 0.3 mg/L for a long time, and among patients with chronic arsenic poisoning, the cancer rate is as high as 15% [8]. In the World Health Organization's "Water Quality Standards for Drinking Water", the index value of arsenic is 0.01 mg/L. Arsenic pollution in water will not only cause serious harm to the human body, but also harm the normal growth of plants, affecting the operation of internal water and chlorophyll [9]. Therefore, arsenic pollution in water has become an urgent problem to be solved. The arsenic removal technologies reported in the literature include oxidation, coagulation/filtration, ion exchange, membrane method, biological method, electro-flocculation, and adsorption method [10,11]. The adsorption method has simple steps and is more feasible for practical application [12,13]. MOF (Metal-organic framework) materials can effectively provide tunable porosity [14], stable pore structure [15], geometry, chemical function [16], structural uniformity, and ultra-high surface area [17].

MOFs are adsorbents composed of porous crystalline materials with ultra-high surface area and highly ordered structures composed of organic ligands and metal ions linked in a three-dimensional lattice, which are promising in the fabrication of various attractive new compounds [18]. It was reported that the first MOF material for the removal of arsenic contamination from water was Fe-BTC. Fe-BTC, consisting of iron nodes and 1,3,5 trimesic acid groups, was synthesized by a facile solvothermal method and used as an adsorbent to adsorb As(V) in the pH range of 2–10. At pH 4; the adsorption capacity of Fe-BTC was 12.3 mg/g, which was more than six times that of Fe₂O₃ nanoparticles [19]. By infrared measurement analysis, a new Fe-OAs group in the infrared band appeared at 824 cm⁻¹, which confirmed the adsorption of As(V). In addition, by transmission electron microscopy, it was confirmed that the adsorption of As(V) occurred at the interior of the MOFs and interacts with the Fe nodes of the framework. Although the adsorption capacity is not strong, this is a landmark discovery in the research on arsenic removal by MOFs, which indicates that MOFs materials have great potential for arsenic capture. Moreover, the researchers also conducted studies on the removal of arsenic by classical MOFs. The reported adsorption capacity of ZIF-8 for arsenic at low equilibrium concentration (9.8 µg/L) was 76.5 mg/g. The study of the adsorption mechanism showed that the adsorption was due to the dissociative adsorption of water, which produced a large number of external active sites (Zn-OH) and formed an inner spherical complex with arsenate [20]. Due to its potential for arsenic adsorption, the research on the adsorption capacity of arsenic in wastewater provides a data basis for the treatment of arsenic pollution in wastewater.

The main objectives of this study were to: (1) synthesize a new composite adsorbent (Fe₃O₄@ZIF-8) by encapsulating magnetic Fe₃O₄ nanoparticles into metal organic frameworks for As(V) removal from wastewater, (2) evaluate the feasibility of Fe₃O₄@ZIF-8 as an adsorbent for As(V) removal by studying the effects of dose, pH, adsorption isotherm, kinetics, and thermodynamics, (3) analyze the characterization of Fe₃O₄@ZIF-8 before and after adsorption thoroughly using various tests including SEM-EDS, XPS, BET, XRD, TG, FTIR, and (4) study the properties and arsenic removal mechanism of the Fe₃O₄@ZIF-8.

2. Experimental Section

2.1. Chemicals

Arsenic standard solution (Beijing, China) was purchased from Beijing Northern Weiye Metrology Technology Research Institute. NH₄OH (Tianjin, China) was purchased from Tianjin Damao Chemical Reagent Factory. FeCl₃·6H₂O and CH₃OH (Tianjin, China) were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. In addition, FeCl₂·4H₂O (Shanghai, China), 2-methylimidazole (C₄H₆N₂, Shanghai, China) were purchased from Shanghai McLean Biochemical Technology Co., Ltd. Zn(NO₃)₂·6H₂O, and HNO₃ (Guangzhou,

China) were purchased from Guangzhou Chemical Reagent Factory. Deionized water is used throughout this study. The conductivity of H₂O was less than 2 µs/cm. As(V) stock solution was prepared with 1001 µg/mL As(V) standard solution (H₃AsO₄, Beijing). The inductively coupled plasma atomic emission spectroscope (ICP-AES) was used to measure the As(V) concentration in the aqueous solutions.

2.2. Synthesis of Adsorbents

2.2.1. Synthesis of Magnetic Fe₃O₄ Nanoparticles

Magnetic Fe₃O₄ nanoparticles were synthesized using a modified iron (II) and iron (III) co-precipitation method as described in the literature [21]. FeCl₂·4H₂O (10 mmol) and FeCl₃·6H₂O (10 mmol) were gradually poured into 30 mL deionized water and mixed by mechanical stirring, the solution was heated to 60 °C for 30 min in the ultrasonic cleaner. Then 40.00 mL of 3.50 mol/L ammonia solution was introduced into the mixed iron(II)/iron(III) solution with continuous stirring at 60 °C for 30 min. After the reaction was completed, the produced mixture was filtered and washed with deionized water until neutral and finally dried at 60 °C under the vacuum for 12 h to obtain Fe₃O₄ nanoparticles.

2.2.2. Synthesis of Fe₃O₄@ZIF-8

The preparation of Fe₃O₄@ZIF-8 was improved according to reference [22]. Weighed 3.30 g of 2-methylimidazole and 0.10 g of magnetic nanometer Fe₃O₄, dissolved in 70.00 mL of methanol. The mixture was ultrasonicated for 15 min, 1.50 g of Zn(NO₃)₂·6H₂O was weighed and dissolved in 70.00 mL of methanol, which was slowly added dropwise to the above-mentioned sonicated solution, mechanically stirred for 24 h, and then centrifuged. The obtained solid was washed with methanol at least three times, and then vacuum-dried at 80 °C for 12 h.

3. Results and Discussion

3.1. Adsorption Experiments

3.1.1. Effect of Adsorbent Dosage

Prepared 46.916 mg/L As(V) solution, added 25 mL to several centrifuge tubes, and added Fe₃O₄@ZIF-8 adsorbent 5, 10, 15, 20, 25, 30, 35 mg respectively, at pH 3, temperature was 25 °C shook in a shaker for 24 h. The adsorption capacity and removal rate of As(V) by Fe₃O₄@ZIF-8 with the dosage of adsorbent are shown in Figure 1.

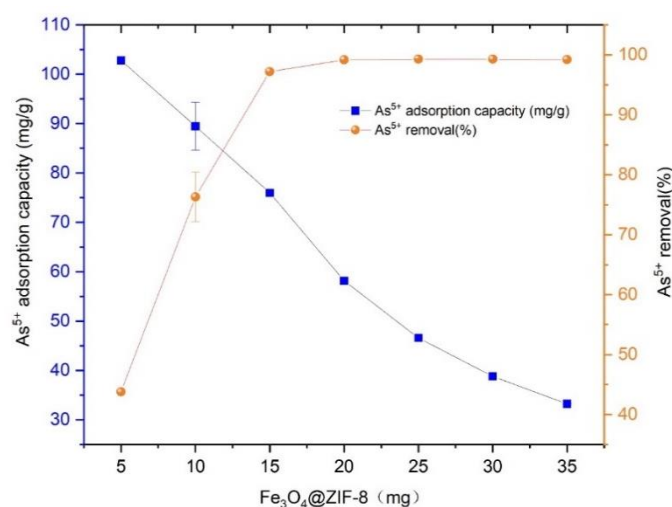


Figure 1. The adsorption effect of adsorbent dose.

As illustrated in Figure 1, the equilibrium adsorption capacity of Fe₃O₄@ZIF-8 for As(V) shows decreasing trend with the dosage. It was because that the increase in the dosage of Fe₃O₄@ZIF-8, that the number of adsorption sites in water also increased, but

the adsorption sites on the surface of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ had not reached saturation. Therefore, although the amount of adsorbed As(V) increased, the degree of saturation decreased, and $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ the equilibrium adsorption capacity of As(V) decreased.

It can be seen in Figure 1 that when the dosage of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ was 10 mg, the removal rate of As(V) reached 76.29%. When the dosage of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ was increased to 15 mg, the removal rate of As(V) reached 97.20%. When the dosage of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ was 20–35 mg, the removal rate of As(V) reached more than 99%, and the removal was basically complete. Continue to increase the dosage of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ to As(V) the removal rate did not improve much. Therefore, from the perspective of economy and resource saving, the optimal dosage of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ in this experiment is 15 mg/25 mL, which is 0.6 g/L.

3.1.2. Effect of pH

Prepared 25 mg/L As(V) solution, adjusted the pH from 2 to 11 by NaOH solution and HNO_3 solution, pipetted 25 mL into several centrifuge tubes, and dosage of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ adsorbent was 10 mg. Shook on a shaker for 24 h at 25 °C. The adsorption capacity and removal rate of As(V) by $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ are shown in Figure 2.

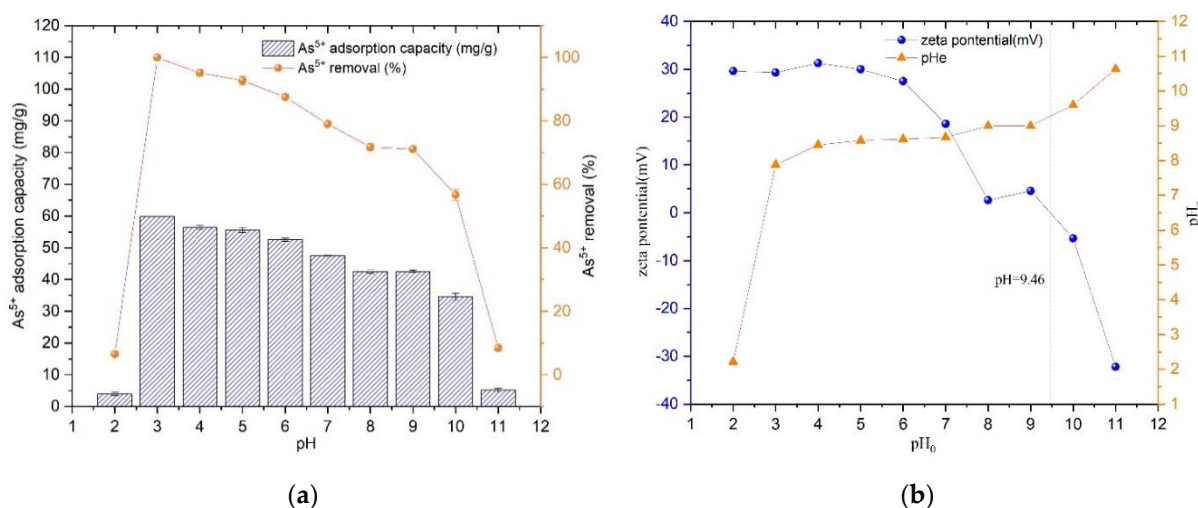


Figure 2. (a) The adsorption effect of pH; (b) Isoelectric point of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$.

From Figure 2a, it can be found that the adsorption amount of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ reached the maximum when $\text{pH} = 3.0$, and the removal rate of As(V) was the largest; when $\text{pH} < 3.0$, the adsorption of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ decreased rapidly. The amount of As(V) adsorption by $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ decreased gradually with the increase of pH when $\text{pH} > 3.0$. When $\text{pH} > 9.0$, the adsorption capacity and removal rate of As(V) decreased rapidly. This phenomenon can be explained by Figure 2b. The experimentally measured isoelectric point of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ was 9.46. Therefore, when $\text{pH} < 9.46$, the surface of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ was positively charged. According to the literature, when $\text{pH} < 2$, As(V) mainly exists in the form of H_3AsO_4 in water. When pH is 2–7, As(V) mainly exists in the form of H_2AsO_4^- . When $\text{pH} > 7$, As(V) It mainly exists in the form of H_2AsO_4^- [23,24]. Combined with the experimental data, it can be seen that when $\text{pH} = 2$, the content of H_3AsO_4 was relatively high, which was not conducive to the adsorption of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$. When $\text{pH} = 3$ –9, the positive charge of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ decreased with the increase of pH and adsorption capacity for H_2AsO_4^- and HAsO_4^{2-} decreased. When $\text{pH} > 9.46$, the positive charge on the surface of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ changed to negative charge, which repelled each other with HAsO_4^- , so the adsorption amount and removal rate of As(V) reduced rapidly.

3.1.3. Adsorption Isotherm

Prepared 25 mL of As(V) solution with an initial concentration of 40–120 mg/L and $\text{pH} = 3$ and added 10 mg of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ adsorbent. Shook for 24 h on a shaker at 25 °C,

35 °C and 45 °C. The obtained adsorption isotherms are shown in Figure 3. At different temperatures, the adsorption isotherms of Fe₃O₄@ZIF-8 for As(V) were fitted by Langmuir and Freundlich models as shown in Figure 3. From the data in Table 1, it can be seen that the Langmuir adsorption isotherm equation was more suitable for describing the adsorption process of As(V) by Fe₃O₄@ZIF-8, and the calculated correlation coefficient was higher than that of the Freundlich adsorption isotherm equation.

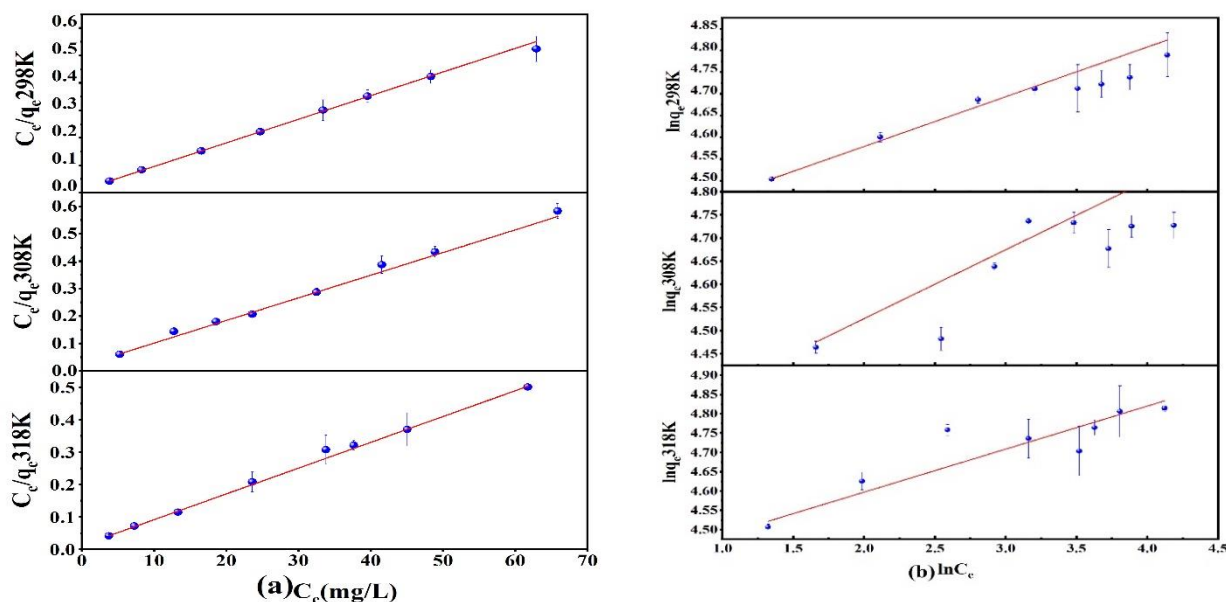


Figure 3. (a) Langmuir adsorption isotherm model; (b) Freundlich adsorption isotherm model.

Table 1. The kinetic parameters for adsorbing As(V) by Fe₃O₄@ZIF-8.

Temperature (K)	Langmuir Equation				Freundlich Equation		
	$q_{\max}$ (mg/g)	K_L (L/mg)	R^2	R_L	K_f (L/mg)	n	R^2
298	116.114	0.907	0.9996	0.009	77.493	8.740	0.9846
308	120.919	0.445	0.9876	0.018	68.601	6.722	0.7088
318	125.628	0.690	0.9995	0.012	79.365	8.976	0.9158

This indicated that the adsorption of As(V) by Fe₃O₄@ZIF-8 was monolayer adsorption. Moreover, the R_L value was between 0 and 1, which meant that the adsorption was easy to proceed. When the reaction temperature was 318 K, the maximum adsorption capacity of Fe₃O₄@ZIF-8 simulated by the Langmuir adsorption isotherm model was 125.628 mg/g. It can be found that Fe₃O₄@ZIF-8 has a good adsorption effect on As(V).

3.1.4. Kinetic Study

A 250 mL of As(V) solution with a concentration of 30 and 50 mg/L and a pH of 3 was prepared. Then, 0.1 g of Fe₃O₄@ZIF-8 adsorbent was added and shaken at 25 °C in a constant temperature shaker. The fitted kinetic equation of As(V) adsorption by Fe₃O₄@ZIF-8 is shown in Figure 4.

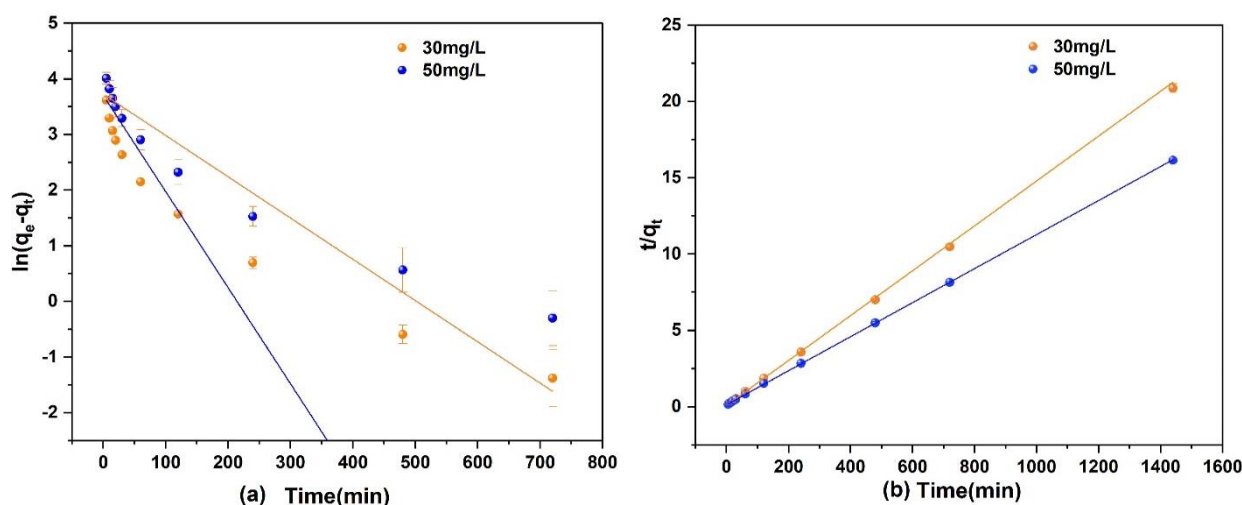


Figure 4. (a) Pseudo-first order model; (b) Pseudo-second order model.

It can be seen in Figure 4 that the fitting effect of the second-order kinetic equation for the adsorption of As(V) to Fe₃O₄@ZIF-8 was obviously better than that of the first-order kinetic model. From the data in Table 2, the correlation coefficient R^2 of the second-order kinetic model was much larger than that of the first-order kinetic model, and both were higher than 0.999. Under different concentrations of As(V) solution, the equilibrium adsorption capacity of Fe₃O₄@ZIF-8 calculated by the second-order kinetic model was basically consistent with actual adsorption capacity. Therefore, the adsorption process of As(V) by Fe₃O₄@ZIF-8 satisfies the second-order kinetic model. This means that the adsorption of As(V) by Fe₃O₄@ZIF-8 is mainly a chemical adsorption process.

Table 2. Parameters of kinetic models for As(V) onto Fe₃O₄@ZIF-8.

C_0 (mg/L)	q_e (mg/g)	Quasi-First-Order Dynamics Equation			Quasi-Second-Order Dynamics Equation		
		q_e	K_1	R^2	q_e	$K_2 \cdot 10^{-3}$	R^2
30	69.010	40.600	0.0173	0.9138	68.027	2.272	0.9992
50	89.186	41.558	0.0074	0.8584	89.686	0.919	0.9999

3.1.5. Thermodynamic Studies

The thermodynamic parameters of Fe₃O₄@ZIF-8 adsorption of As(V) at temperatures of 298 K, 308 K, and 318 K were calculated by formula, as shown in Table 3.

Table 3. Parameters of thermodynamic for the adsorption of As(V) by Fe₃O₄@ZIF-8.

Temperature (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol)
298	−3.73	40.41	0.318
308	−4.03	40.41	0.318
318	−4.16	40.41	0.318

It can be seen in Table 3 that the standard Gibbs free energy ΔG^0 of Fe₃O₄@ZIF-8 adsorbing As(V) is less than 0 at different temperatures, which indicates that Fe₃O₄@ZIF-8 adsorbing As(V) is a spontaneous reaction, and with the increase of temperature, the absolute value of ΔG^0 increases, which indicates that the increase of temperature plays a role in promoting the adsorption reaction. In addition, the standard enthalpy changes ΔH^0 during the adsorption of As(V) by Fe₃O₄@ZIF-8 is greater than 0, indicating that the reaction is an endothermic reaction. The standard entropy change of Fe₃O₄@ZIF-8 adsorption of As(V) at different temperatures is $\Delta S^0 > 0$, which indicates that the system disorder

becomes larger after the adsorption reaction, which is an entropy-driven process. The above data can prove that the adsorption process of As(V) by $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ is a spontaneous endothermic reaction.

3.2. Characterization

3.2.1. Scanning Electron Microscopy (SEM)

From a–c in Figure 5, it can be seen that the prepared $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ has irregular columnar, spherical and cubic structure particles with rough surfaces. It can be seen from the figure that the particles were adhered to each other and stacked to form many channels, and this agglomeration phenomenon provided more adsorption sites for $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ to adsorb arsenic. From the SEM image, it can be known that the particle size of the prepared $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ was about 100 nm. It can be seen from pictures d–f in Figure 5 that the prepared Fe_3O_4 was a nanomaterial, which was approximately spherical particles, and the particles adhere to each other and agglomerate together. The particle size of the prepared magnetic nano Fe_3O_4 was much smaller than that of the $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ material.

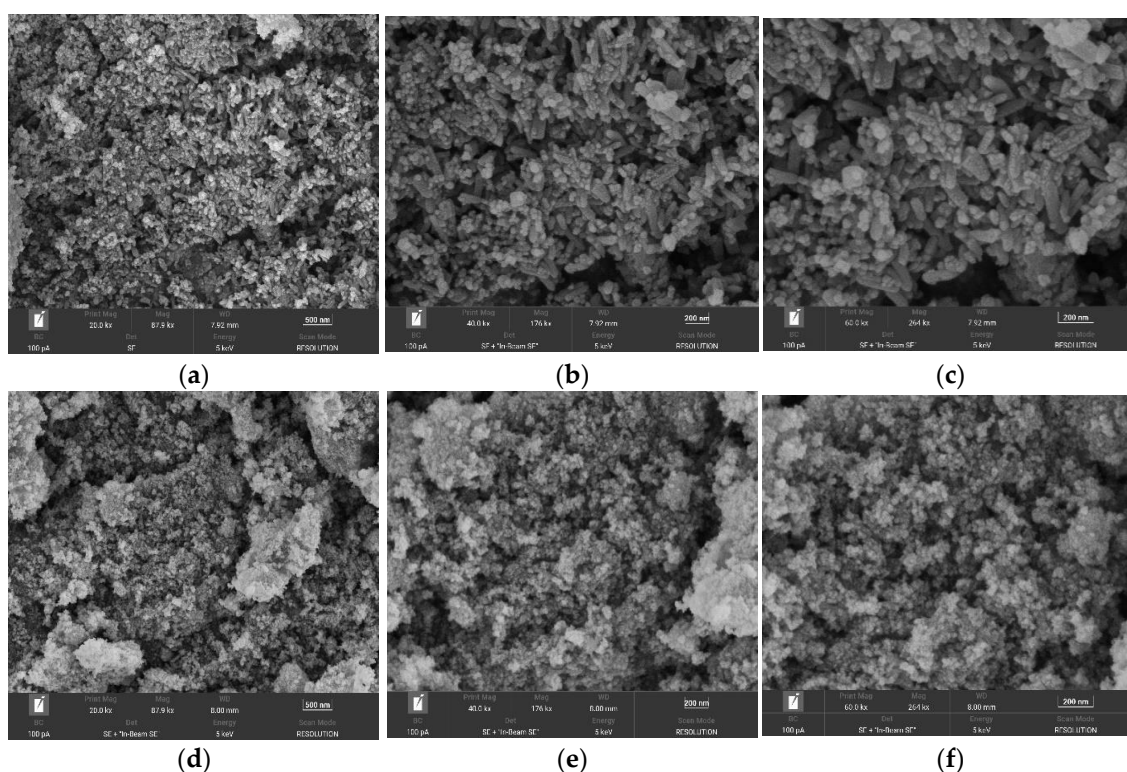


Figure 5. (a–c) SEM of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$; (d–f) SEM of Fe_3O_4 .

From Figure 6, it can be seen that the $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ particle gap after adsorption of arsenic is reduced, which indicates that the arsenic in the water is adsorbed to the surface of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$, thus filling the pores.

It can be seen from Figure 6 that the $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ particle agglomeration phenomenon after adsorption is more obvious, which reflects the strong adsorption capacity of the material. The particle shape of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ after adsorption was changed and the particle size became smaller than that before adsorption.

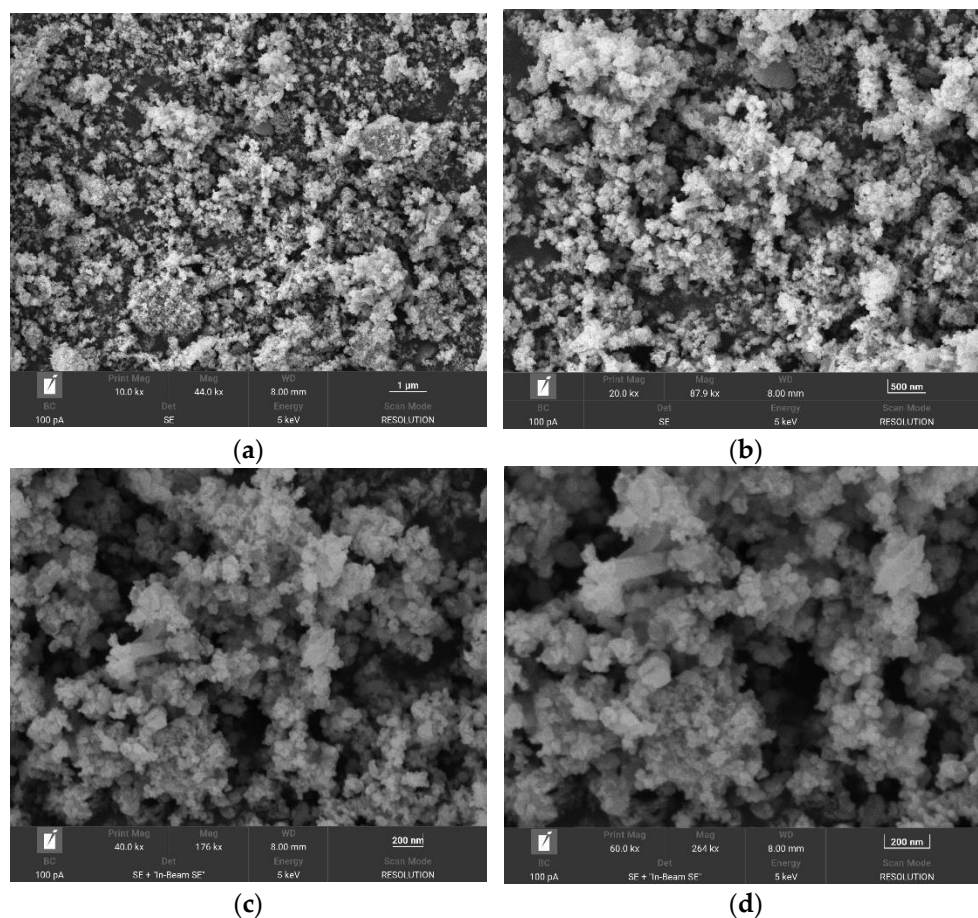


Figure 6. SEM of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ after adsorption. (a–d) show the effects of 10,000 times, 20,000 times, 40,000 times and 60,000 times magnification respectively.

3.2.2. EDS Analysis

The EDS analysis of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ before and after arsenic adsorption are shown in Figure 7 and Table 4. Through EDS analysis of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$, we can find that As element was not detected in $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ before adsorption, while As element was detected in $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ after adsorption. This proved that $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ has adsorption capacity for arsenic. The $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ before adsorption detected C, N, O, Fe and Zn elements, which were consistent with the elemental composition of the $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ material, which proved that the metal-organic framework composite was successfully synthesized [25].

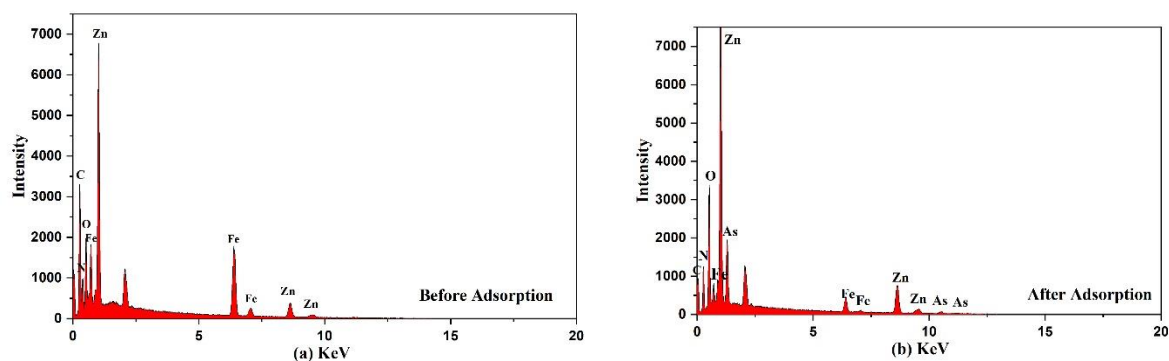


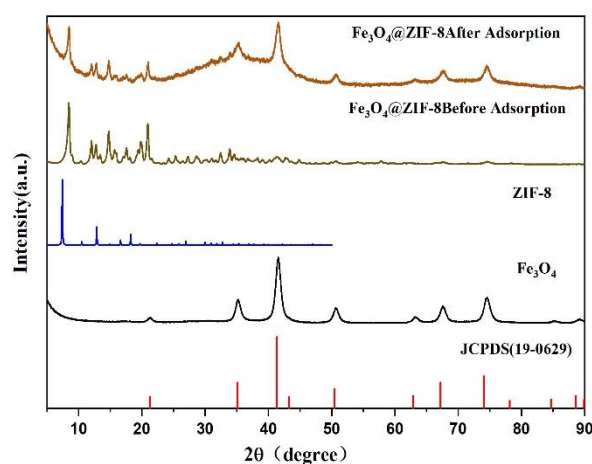
Figure 7. EDS spectra of the adsorbent (a) before (b) after adsorption.

Table 4. EDS analysis of Fe₃O₄@ZIF-8 before and after adsorption.

Element	Wt (%)		At (%)	
	Before	After	Before	After
C K	41.65	24.61	61.58	50.33
N K	19.39	0.75	24.58	1.32
O K	3.51	17.60	3.90	27.02
Fe K	6.58	6.38	2.09	2.81
Zn K	28.88	40.25	7.85	15.12
As K	0	10.39	0	3.41

3.2.3. XRD Analysis

Figure 8 was the XRD pattern of Fe₃O₄ and Fe₃O₄@ZIF-8. These include the XRD patterns of Fe₃O₄@ZIF-8 before and after adsorption, the XRD patterns of the prepared magnetic nano Fe₃O₄, the corresponding ZIF-8 standard pattern [26], and the Fe₃O₄ standard card (JCPDS 19-0629).

**Figure 8.** XRD pattern of synthesized Fe₃O₄@ZIF-8, Fe₃O₄.

Comparing the prepared magnetic nano Fe₃O₄ and Fe₃O₄ standard cards, it is found that the characteristic peak positions of the standard cards were the same, which can prove the successful preparation of magnetic nano Fe₃O₄. By comparing the standard cards of Fe₃O₄@ZIF-8, ZIF-8, and Fe₃O₄, it can be found that the characteristic peaks are basically the same as those of Fe₃O₄ and standard cards, and there were diffraction peaks consistent with the standard pattern of ZIF-8, which can prove that Fe₃O₄@ZIF-8 synthesis was relatively successful. Comparing the XRD patterns of Fe₃O₄@ZIF-8 before and after adsorption, it can be found that the position of the diffraction peak of Fe₃O₄@ZIF-8 does not change after adsorption of arsenic, and the relative intensity of the peak increases, which indicates that Fe₃O₄@ZIF-8 is adsorbing arsenic. The arsenic process did not destroy the structure and properties. Therefore, the material can exist stably in an aqueous solution.

3.2.4. Thermogravimetric Analysis (TG)

In order to evaluate the stability of Fe₃O₄@ZIF-8 material, Fe₃O₄@ZIF-8 was heated from 30 °C to 800 °C under N₂, and the stage of material weight loss was analyzed. As shown in Figure 9, it can be observed that Fe₃O₄@ZIF-8 was in a state of gradual weight loss at 30–264.5 °C, with a weight loss of 8.5%. This can be attributed to desorption of adsorbed water or solvent. At 264.5–800 °C, the weight loss rate of Fe₃O₄@ZIF-8 increased and remained in a weightless state, which may be due to the decomposition of the ligand ZIF-8. Comparing the weight loss changes of Fe₃O₄@ZIF-8 before and after adsorption, Fe₃O₄@ZIF-8 after adsorption of arsenic was heated from 30 °C to 516.5 °C, and the weight

loss was 15.2%. It was obvious from Figure 9 that Fe_3O_4 after the adsorption of arsenic, the weight loss rate of @ZIF-8 was significantly slowed down. At 800 °C, the weight loss of Fe_3O_4 @ZIF-8 before adsorption reached 66.4%, and the weight loss of Fe_3O_4 @ZIF-8 after adsorption was 36.8%. This shows that Fe_3O_4 @ZIF-8 has good thermal stability after adsorbing arsenic, and arsenic is adsorbed to the surface of Fe_3O_4 @ZIF-8, and it is not easy to desorb and decompose.

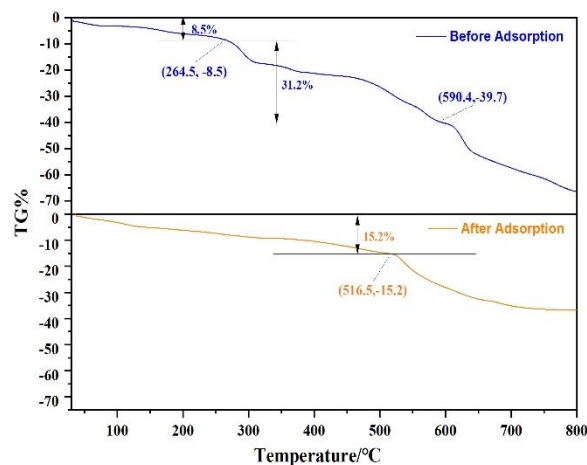


Figure 9. The TGA curve of Fe_3O_4 @ZIF-8.

3.2.5. FTIR Analysis

From the infrared spectrum of magnetic nano Fe_3O_4 in Figure 10, it can be seen that absorption bands corresponding to the carboxylate groups on the surface of Fe_3O_4 NPs appeared at 1384.25 cm^{-1} and 1628.70 cm^{-1} [27]. At 590.88 cm^{-1} and the peak at 631.52 cm^{-1} can be attributed to the Fe-O bond of Fe_3O_4 [28,29]. Analysis of the infrared spectrum of Fe_3O_4 @ZIF-8 shows that the peaks at 3179.34 cm^{-1} and 2926.14 cm^{-1} can correspond to the characteristic peaks of =C–O bond and C–H bond with ZIF-8 structure, respectively [30,31]. The peak of C=N bond in the imidazole ring is 1569.76 cm^{-1} . The absorption peak of CN bond appeared at 1143.10 cm^{-1} and 994.82 cm^{-1} , and the vibration peak of functional group in Zn–N appeared at 423.37 cm^{-1} . At 591.03 cm^{-1} and 628.44 cm^{-1} the peaks appearing at -1 can be assigned to Fe–O peaks [32–34]. The analysis of Fe_3O_4 @ZIF-8 by FTIR can prove that the experiment successfully complexes Fe_3O_4 with ZIF-8. Comparing the infrared spectrum of Fe_3O_4 @ZIF-8 after arsenic adsorption, 3359.15 cm^{-1} corresponds to the stretching vibration region of O–H and N–H. A new strong band is observed near 427.90 cm^{-1} , which can be attributed to the Zn–O–As vibration, which means the formation of a new inner spherical complex [35–37]. A new peak appears at 828.21 cm^{-1} , which may be due to the formation of As–O groups [38] showing that arsenic was bound to Fe_3O_4 @ZIF-8.

3.2.6. XPS Analysis

Through XPS analysis of Fe_3O_4 @ZIF-8 before and after arsenic adsorption in Figure 11, it can be found that the full spectrum in Figure 11 of Fe_3O_4 @ZIF-8 before adsorption can detect the peaks of Zn, Fe, O, N, C, which proves to be in line with the preset Chemical composition of Fe_3O_4 @ZIF-8 material. Fe_3O_4 @ZIF-8 after adsorption detected the characteristic peak of As, which proved that the material successfully combined with arsenic and had an adsorption effect.

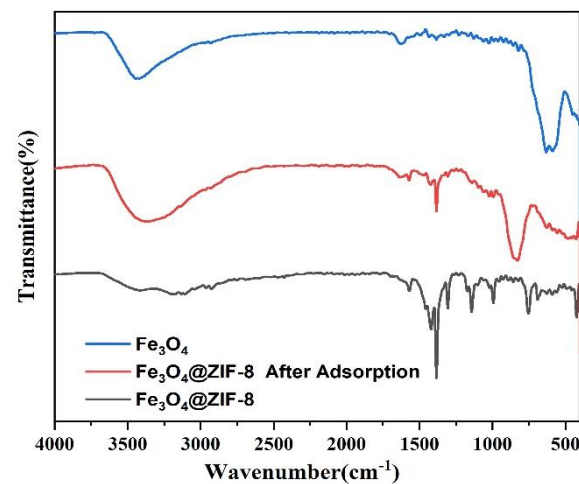


Figure 10. FTIR pattern of synthesized Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{ZIF-8}$.

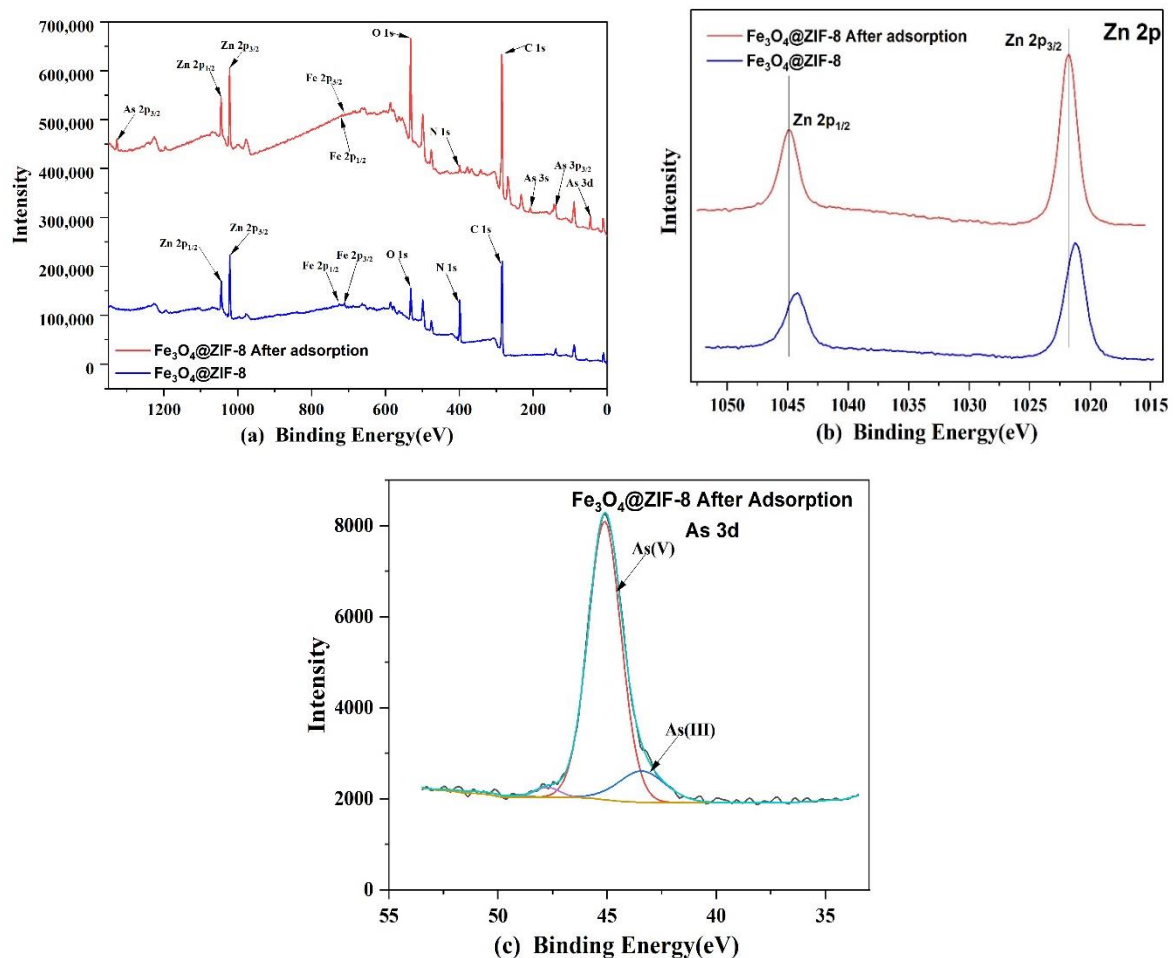


Figure 11. XPS spectra of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$: (a) Wide scan; (b) Zn 2p core level. (c) As 3d core level after adsorption.

From Figure 11b, it can be observed that the positions of the peaks of Zn 2p_{1/2} and Zn 2p_{3/2}, before and after adsorption, move to the position with higher binding energy, which means that the electronegativity of the surrounding atoms of Zn increases, resulting in Zn element. The binding energy also increases [39–41]. By fitting the peaks of As 3d

after adsorption, it can be judged that after As(V) is adsorbed by Fe₃O₄@ZIF-8, a part of As(V) is reduced to As(III) by Fe₃O₄@ZIF-8.

3.2.7. Surface Area Analysis (BET)

The porosity and specific surface area of the prepared Fe₃O₄@ZIF-8 composites were tested by N₂ adsorption-desorption isotherms at the test temperature of 77 K. From Figure 12, it can be observed that the specific surface area of Fe₃O₄@ZIF-8 calculated by the BET method is 316.3593 m²/g, and the total pore volume measured by the single-point method is 0.224 cm³/g, and the micropore volume measured by the t-plot method is 0.097 cm³/g. The pore size is 2.83 nm, and the average mesopore size is 33.59 nm. The specific surface area of Fe₃O₄@ZIF-8 after adsorption of arsenic is 95.3942 m²/g, the measured total pore volume is 0.182 cm³/g, and the micropore volume is 0.017 cm³/g, the average pore size is 7.62 nm, and the average mesopore size is 34.35 nm. By comparison, it can be found that the specific surface area, total pore volume and micropore volume of Fe₃O₄@ZIF-8 after adsorption of arsenic are significantly reduced, indicating that arsenic is adsorbed to the surface of the material.

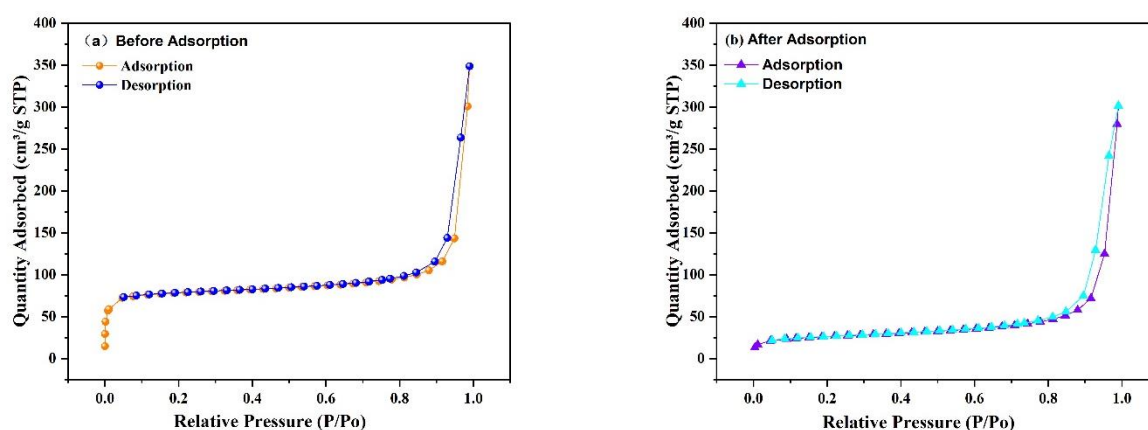


Figure 12. N₂ adsorption-desorption isotherms of Fe₃O₄@ZIF-8.

Magnetic Fe₃O₄ nanoparticles have been used for the treatment of arsenic from wastewater. Ref. [42] reported the maximum adsorption capacity of magnetite Fe₃O₄ nanoparticles occurred at pH 2, with a value of 3.70 mg/g for As (V). Due to aggregation effect, magnetic Fe₃O₄ nanoparticles are difficult to use in continuous flow systems [43]. Consequently, some researchers had encapsulated nanoparticles into metal organic frameworks to resolve above problem. Iron and 1,3,5-benzenetricarboxylic (Fe-BTC) used for As(V) removal from waters, and its adsorption capacity can reach 12.3 mg/g, more than 6 times that of iron oxide nanoparticles with a size of 50 nm [19]. Studies have shown that ZIF-8 demonstrated an adsorption amount of 60.03 mg/g [44] in comparison to that of MIL-53(Fe) (21.27 mg/g) [45]. Furthermore, the activated indium MOF (AUBM-1) was applied for As(V) removal from water and showed a high arsenic uptake capacity of 103.1 mg/g at a neutral pH. In this study, the maximum adsorption capacity of Fe₃O₄@ZIF-8 for As(V) can reach 116.114 mg/g; the result implies that the Fe₃O₄@ZIF-8 could be as a potential candidate for removing As(V) pollution in wastewater.

4. Conclusions

Characterization analysis shows that the Fe₃O₄@ZIF-8 materials prepared in this study have different shapes and small particle sizes, and the specific surface area can reach 316 m²/g. Through various characterization analyses, it can be proved that the metal-organic framework composite material was successfully prepared in the experiment; comparing the characterization results of Fe₃O₄@ZIF-8 before and after adsorption, it can be found that the material has a good adsorption effect on arsenic. At 25 °C, the

initial concentration of arsenic is 46.916 mg/L, and the initial pH is 3. When the dosage of adsorbent is 0.4 g/L, the adsorption rate at equilibrium is 76.29%. When the dosage increases to 1.0 g/L, the adsorption rate at equilibrium increases to 99.29%. However, when the dosage of adsorbent increases to 0.6 g/L, the equilibrium adsorption rate can reach 97.20%, which is not much different from the equilibrium adsorption rate when the dosage is 1.0 g/L. Therefore, from the economic benefit to the perspective of resource saving, the optimal dosage is 0.6 g/L. When the pH value is 3, the adsorption effect of Fe₃O₄@ZIF-8 on arsenic can reach the best, the adsorption amount reach 59.80 mg/g, and the removal rate is 99.93%. When pH > 3, the equilibrium adsorption capacity of Fe₃O₄@ZIF-8 to arsenic decreases with the increase of pH, and when pH > 9.46, the decreasing rate is faster. The adsorption process of Fe₃O₄@ZIF-8 for arsenic has the best fit with the Langmuir adsorption isotherm equation. When the temperature is 298 K, the maximum adsorption capacity of Fe₃O₄@ZIF-8 for arsenic can reach 116.114 mg/g. For the adsorption kinetics, the second-order kinetic equation has the best fitting result for the adsorption kinetics of arsenic on Fe₃O₄@ZIF-8, with R² > 0.999. By analyzing the fitting curve of the second-order kinetics, it can be found that the adsorption process of Fe₃O₄@ZIF-8 to arsenic-containing wastewater mainly occurs through chemical adsorption. From the analysis of thermodynamic parameters, it can be concluded that the adsorption process of Fe₃O₄@ZIF-8 to arsenic is a spontaneous endothermic reaction.

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