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Removal of Arsenic from Wastewater by Using Nano Fe$_3$O$_4$/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$_3$O$_4$@ZIF-8) for As(V) removal from wastewater was synthesized by encapsulating magnetic Fe$_3$O$_4$ nanoparticles into metal organic frameworks. In order to evaluate the feasibility of Fe$_3$O$_4$@ZIF-8 as an adsorbent for As(V) removal, the adsorption properties of Fe$_3$O$_4$@ZIF-8 were systematically explored by studying the effects of dosage, pH, adsorption isotherm, kinetics, and thermodynamics. Additionally, the characterization of Fe$_3$O$_4$@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$_3$O$_4$@ZIF-8 were further studied. The results showed that the Fe$_3$O$_4$@ZIF-8 has a specific surface area of 316 m$^2$/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$_3$O$_4$@ZIF-8 to adsorb arsenic. When the dosage of the Fe$_3$O$_4$@ZIF-8 was 0.60 g/L, the adsorption of arsenic by the Fe$_3$O$_4$@ZIF-8 can reach 76 mg/g, and the removal rate can reach 97.20%. The adsorption process of arsenic to the Fe$_3$O$_4$@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$_3$O$_4$@ZIF-8 was 116.144 mg/g. Through the analysis of thermodynamic parameters, it is proved that the adsorption process of arsenic by the Fe$_3$O$_4$@ZIF-8 is a spontaneous endothermic reaction. The Fe$_3$O$_4$@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$_3$O$_4$@ZIF-8; As(V); nano Fe$_3$O$_4$; adsorption properties

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 Fe\(_2\)O\(_3\) 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 (Fe\(_3\)O\(_4\)@ZIF-8) by encapsulating magnetic Fe\(_3\)O\(_4\) nanoparticles into metal organic frameworks for As(V) removal from wastewater, (2) evaluate the feasibility of Fe\(_3\)O\(_4\)@ZIF-8 as an adsorbent for As(V) removal by studying the effects of dos-age, pH, adsorption isotherm, kinetics, and thermodynamics, (3) analyze the characterization of Fe\(_3\)O\(_4\)@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 Fe\(_3\)O\(_4\)@ZIF-8.

2. Experimental Section

2.1. Chemicals

Arsenic standard solution (Beijing, China) was purchased from Beijing Northern Weiye Metrology Technology Research Institute. NH\(_4\)OH (Tianjin, China) was purchased from Tianjin Damao Chemical Reagent Factory. FeCl\(_3\)-6H\(_2\)O and CH\(_3\)OH (Tianjin, China) were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. In addition, FeCl\(_2\)-4H\(_2\)O (Shanghai, China), 2-methy imidazole (C\(_4\)H\(_6\)N\(_2\), Shanghai, China) were purchased from Shanghai McLean Biochemical Technology Co., Ltd. Zn(NO\(_3\))\(_2\)-6H\(_2\)O, and HNO\(_3\) (Guangzhou,
China) were purchased from Guangzhou Chemical Reagent Factory. Deionized water is used throughout this study. The conductivity of H$_2$O was less than 2 µs/cm. As(V) stock solution was prepared with 1001 µg/mL As(V) standard solution (H$_3$AsO$_4$, Beijing). The inductively coupled plasma atomic emission spectrocope (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 Fe$_3$O$_4$ Nanoparticles

Magnetic Fe$_3$O$_4$ nanoparticles were synthesized using a modified iron (II) and iron (III) co-precipitation method as described in the literature [21]. FeCl$_2$·4H$_2$O (10 mmol) and FeCl$_3$·6H$_2$O (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 Fe$_3$O$_4$ nanoparticles.

2.2.2. Synthesis of Fe$_3$O$_4$@ZIF-8

The preparation of Fe$_3$O$_4$@ZIF-8 was improved according to reference [22]. Weighed 3.30 g of 2-methy imidazole and 0.10 g of magnetic nanometer Fe$_3$O$_4$, dissolved in 70.00 mL of methanol. The mixture was ultrasonicated for 15 min, 1.50 g of Zn(NO$_3$)$_2$·6H$_2$O 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 Fe$_3$O$_4$@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 Fe$_3$O$_4$@ZIF-8 with the dosage of adsorbent are shown in Figure 1.

![Figure 1](image_url)

**Figure 1.** The adsorption effect of adsorbent dose.

As illustrated in Figure 1, the equilibrium adsorption capacity of Fe$_3$O$_4$@ZIF-8 for As(V) shows decreasing trend with the dosage. It was because that the increase in the dosage of Fe$_3$O$_4$@ZIF-8, that the number of adsorption sites in water also increased, but...
the adsorption sites on the surface of Fe₃O₄@ZIF-8 had not reached saturation. Therefore, although the amount of adsorbed As(V) increased, the degree of saturation decreased, and Fe₃O₄@ZIF-8 the equilibrium adsorption capacity of As(V) decreased.

It can be seen in Figure 1 that when the dosage of Fe₃O₄@ZIF-8 was 10 mg, the removal rate of As(V) reached 76.29%. When the dosage of Fe₃O₄@ZIF-8 was increased to 15 mg, the removal rate of As(V) reached 97.20%. When the dosage of Fe₃O₄@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 Fe₃O₄@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 Fe₃O₄@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 HNO₃ solution, pipetted 25 mL into several centrifuge tubes, and dosage of Fe₃O₄@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 Fe₃O₄@ZIF-8 are shown in Figure 2.

![Figure 2](image)

(a) The adsorption effect of pH; (b) Isoelectric point of Fe₃O₄@ZIF-8.

From Figure 2a, it can be found that the adsorption amount of Fe₃O₄@ZIF-8 reached the maximum when pH = 3.0, and the removal rate of As(V) was the largest; when pH < 3.0, the adsorption of Fe₃O₄@ZIF-8 decreased rapidly. The amount of As(V) adsorption by Fe₃O₄@ZIF-8 decreased gradually with the increase of pH when pH > 3.0. When 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 Fe₃O₄@ZIF-8 was 9.46. Therefore, when pH < 9.46, the surface of Fe₃O₄@ZIF-8 was positively charged. According to the literature, when pH < 2, As(V) mainly exists in the form of H₃AsO₄ in water. When pH is 2–7, As(V) mainly exists in the form of H₂AsO₄⁻. When pH > 7, As(V) is mainly exists in the form of H₂AsO₄⁻ [23,24]. Combined with the experimental data, it can be seen that when pH = 2, the content of H₃AsO₄ was relatively high, which was not conducive to the adsorption of Fe₃O₄@ZIF-8. When pH = 3–9, the positive charge of Fe₃O₄@ZIF-8 decreased with the increase of pH and adsorption capacity for H₂AsO₄⁻ and HAsO₄²⁻ decreased. When pH > 9.46, the positive charge on the surface of Fe₃O₄@ZIF-8 changed to negative charge, which repelled each other with HAsO₄, 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 pH = 3 and added 10 mg of Fe₃O₄@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 Fe$_3$O$_4$@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 Fe$_3$O$_4$@ZIF-8, and the calculated correlation coefficient was higher than that of the Freundlich adsorption isotherm equation.

![Figure 3](image_url)

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

**Table 1.** The kinetic parameters for adsorbing As(V) by Fe$_3$O$_4$@ZIF-8.

| Temperature (K) | q$_{\text{max}}$ (mg/g) | K$_L$ (L/mg) | R$^2$ | R$_L$ | K$_F$ (L/mg) | n | R$^2$ |
|----------------|--------------------------|--------------|-------|-------|--------------|---|-------|
| 298            | 116.114                  | 0.907        | 0.996 | 0.009 | 77.493       | 8.740 | 0.9646 |
| 308            | 120.919                  | 0.445        | 0.987 | 0.018 | 68.601       | 6.722 | 0.7088 |
| 318            | 125.628                  | 0.690        | 0.995 | 0.012 | 79.365       | 8.976 | 0.9158 |

This indicated that the adsorption of As(V) by Fe$_3$O$_4$@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 Fe$_3$O$_4$@ZIF-8 simulated by the Langmuir adsorption isotherm model was 125.628 mg/g. It can be found that Fe$_3$O$_4$@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 Fe$_3$O$_4$@ZIF-8 adsorbent was added and shaken at 25 °C in a constant temperature shaker. The fitted kinetic equation of As(V) adsorption by Fe$_3$O$_4$@ZIF-8 is shown in Figure 4.
It can be seen in Figure 4 that the fitting effect of the second-order kinetic equation for the adsorption of As(V) to Fe$_3$O$_4$@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 Fe$_3$O$_4$@ZIF-8 calculated by the second-order kinetic model was basically consistent with actual adsorption capacity. Therefore, the adsorption process of As(V) by Fe$_3$O$_4$@ZIF-8 satisfies the second-order kinetic model. This means that the adsorption of As(V) by Fe$_3$O$_4$@ZIF-8 is mainly a chemical adsorption process.

![Figure 4. (a) Pseudo-first order model; (b) Pseudo-second order model.](image)

| 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 Fe$_3$O$_4$@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 Fe$_3$O$_4$@ZIF-8.](table)

| Temperature (K) | $\Delta G^0$ (kJ/mol) | $\Delta H^0$ (kJ/mol) | $\Delta S^0$ (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 $\Delta G^0$ of Fe$_3$O$_4$@ZIF-8 adsorbing As(V) is less than 0 at different temperatures, which indicates that Fe$_3$O$_4$@ZIF-8 adsorbing As(V) is a spontaneous reaction, and with the increase of temperature, the absolute value of $\Delta G^0$ increases, which indicates that the increase of temperature plays a role in promoting the adsorption reaction. In addition, the standard enthalpy change $\Delta H^0$ during the adsorption of As(V) by Fe$_3$O$_4$@ZIF-8 is greater than 0, indicating that the reaction is an endothermic reaction. The standard entropy change of Fe$_3$O$_4$@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 Fe$_3$O$_4$@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 Fe$_3$O$_4$@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 Fe$_3$O$_4$@ZIF-8 to adsorb arsenic. From the SEM image, it can be known that the particle size of the prepared Fe$_3$O$_4$@ZIF-8 was about 100 nm. It can be seen from pictures d–f in Figure 5 that the prepared Fe$_3$O$_4$ 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$_3$O$_4$ was much smaller than that of the Fe$_3$O$_4$@ZIF-8 material.
3.2.2. EDS Analysis

The EDS analysis of Fe₃O₄@ZIF-8 before and after arsenic adsorption are shown in Figure 7 and Table 4. Through EDS analysis of Fe₃O₄@ZIF-8, we can find that As element was not detected in Fe₃O₄@ZIF-8 before adsorption, while As element was detected in Fe₃O₄@ZIF-8 after adsorption. This proved that Fe₃O₄@ZIF-8 has adsorption capacity for arsenic. The Fe₃O₄@ZIF-8 before adsorption detected C, N, O, Fe and Zn elements, which were consistent with the elemental composition of the Fe₃O₄@ZIF-8 material, which proved that the metal-organic framework composite was successfully synthesized [25].
was relatively successful. Comparing the XRD patterns of Fe₃O₄ indicates the successful preparation of magnetic nano Fe₃O₄.

EDS analysis of Fe₃O₄ and ZIF-8 before and after adsorption is shown in Table 4.

| Element | Wt (%) Before | Wt (%) After | At (%) Before | At (%) After |
|---------|---------------|--------------|---------------|--------------|
| C       | 41.65         | 24.61        | 61.58         | 50.33        |
| N       | 19.39         | 0.75         | 24.58         | 1.32         |
| O       | 3.51          | 17.60        | 3.90          | 27.02        |
| Fe      | 6.58          | 6.38         | 2.09          | 2.81         |
| Zn      | 28.88         | 40.25        | 7.85          | 15.12        |
| As      | 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@ZIF8 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.](image)

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\textsubscript{3}O\textsubscript{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\textsubscript{3}O\textsubscript{4}@ZIF-8 before adsorption reached 66.4%, and the weight loss of Fe\textsubscript{3}O\textsubscript{4}@ZIF-8 after adsorption was 36.8%. This shows that Fe\textsubscript{3}O\textsubscript{4}@ZIF-8 has good thermal stability after adsorbing arsenic, and arsenic is adsorbed to the surface of Fe\textsubscript{3}O\textsubscript{4}@ZIF-8, and it is not easy to desorb and decompose.

![Figure 9. The TGA curve of Fe\textsubscript{3}O\textsubscript{4}@ZIF-8.](image)

### 3.2.5. FTIR Analysis

From the infrared spectrum of magnetic nano Fe\textsubscript{3}O\textsubscript{4} in Figure 10, it can be seen that absorption bands corresponding to the carboxylate groups on the surface of Fe\textsubscript{3}O\textsubscript{4} NPs appeared at 1384.25 cm\textsuperscript{-1} and 1628.70 cm\textsuperscript{-1} [27]. At 590.88 cm\textsuperscript{-1} and the peak at 631.52 cm\textsuperscript{-1} can be attributed to the Fe-O bond of Fe\textsubscript{3}O\textsubscript{4} [28,29]. Analysis of the infrared spectrum of Fe\textsubscript{3}O\textsubscript{4}@ZIF-8 shows that the peaks at 3179.34 cm\textsuperscript{-1} and 2926.14 cm\textsuperscript{-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\textsuperscript{-1}. The absorption peak of CN bond appeared at 1143.10 cm\textsuperscript{-1} and 994.82 cm\textsuperscript{-1}, and the vibration peak of functional group in Zn-N appeared at 423.37 cm\textsuperscript{-1}. At 591.03 cm\textsuperscript{-1} and 628.44 cm\textsuperscript{-1} the peaks appearing at −1 can be assigned to Fe-O peaks [32–34]. The analysis of Fe\textsubscript{3}O\textsubscript{4}@ZIF-8 by FTIR can prove that the experiment successfully complexes Fe\textsubscript{3}O\textsubscript{4} with ZIF-8. Comparing the infrared spectrum of Fe\textsubscript{3}O\textsubscript{4}@ZIF-8 after arsenic adsorption, 3359.15 cm\textsuperscript{-1} corresponds to the stretching vibration region of O−H and N−H. A new strong band is observed near 427.90 cm\textsuperscript{-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\textsuperscript{-1}, which may be due to the formation of As-O groups [38] showing that arsenic was bound to Fe\textsubscript{3}O\textsubscript{4}@ZIF-8.

### 3.2.6. XPS Analysis

Through XPS analysis of Fe\textsubscript{3}O\textsubscript{4}@ZIF-8 before and after arsenic adsorption in Figure 11, it can be found that the full spectrum in Figure 11 of Fe\textsubscript{3}O\textsubscript{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\textsubscript{3}O\textsubscript{4}@ZIF-8 material. Fe\textsubscript{3}O\textsubscript{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.
Zn 2p3/2, before and after adsorption, move to the position with higher binding energy, suggesting adsorption.

XPS spectra of Fe3O4 demonstrated an adsorption amount of 21.27 mg/g for As (V). The maximum adsorption capacity of Fe3O4@ZIF-8 can reach 116.114 mg/g.

Figure 10. FTIR pattern of synthesized Fe3O4, Fe3O4@ZIF-8 shows that the peaks at 3179.34 cm⁻¹ and 2926.14 cm⁻¹ appear at pH 2, with a value of 3.70 mg/g for As (V).

Figure 11. XPS spectra of Fe3O4@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 2p1/2 and Zn 2p3/2, 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
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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