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Study on the Adsorption Process of Antibiotics in Wastewater by Porous ZIF-8 Materials

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ABSTRACT
Antibiotics are widely used in the medical, livestock, and pharmaceutical industries. However, they have received extensive attention due to their ecological toxicity and bioaccumulation. Traditional treatment technologies are difficult to combine the characteristics of high efficiency, low cost, and convenient operation. The problem of the difficult and inefficient removal of antibiotics such as tetracyclines and sulfonamides needs to be solved urgently. The adsorption method is a commonly used industrial treatment method with simple operation and high removal efficiency. The selection of the adsorbent material is the key. ZIF-8 is a porous metal-organic framework material with a high specific surface area and stable performance. It is a potential new type of adsorbent material. This paper studies the application and performance of ZIF-8 porous material in the adsorption and purification of antibiotic wastewater. In this study, sulfanilamide and sulfamethoxazole were used as typical pollutants in antibiotic wastewater to evaluate the adsorption performance of ZIF-8. The results show that ZIF-8 exhibits high efficiency and a fast adsorption rate in the adsorption of antibiotics. In addition, the adsorption kinetic process and the isothermal adsorption curve were fitted, and the models were analyzed to further study the adsorption mechanism. This study provides a theoretical basis for the application of MOF materials in the treatment of antibiotic-containing wastewater and has guiding significance for solving the problem of antibiotic environmental pollution.

KEYWORDS
Antibiotic; Adsorption; MOF material

1 Introduction

In human medical treatment, livestock breeding, and the pharmaceutical industry, antibiotics are widely used. However, most of the active ingredients are not metabolized and instead enter surface water, groundwater, and soil environments through wastewater and animal excreta. Research indicates that the main sources of antibiotics in China's water environment include the sewage discharge from the aquaculture industry, medical institutions, and pharmaceutical enterprises (Zhen, 2018). Relevant monitoring shows that the concentrations of common sulfonamides and quinolones in most rivers or the effluent of sewage treatment plants are in the range of ng/L to μg/L. In severely polluted areas, the concentration can even reach dozens of micrograms per liter (μg/L) (Qu et al., 2024). These residual drugs not only have toxic effects on the aquatic ecosystem but also promote the spread of antibiotic resistance genes (ARGs), posing long-term threats to human health, the stability of the ecosystem, and water resource security (Uluseker et al., 2021). Therefore, researching new purification materials and processes that are highly efficient, highly selective, and easily applicable to remove antibiotics and related resistance genes from water bodies has become an urgent need in the field of environmental governance.

As the current mainstream method for treating antibiotic wastewater, traditional water treatment technologies have been widely deployed in engineering practice and commercial applications. Activated carbon adsorption, with its pore structure and good hydrophilicity, can effectively remove some organic micropollutants and is one of the commonly used physical adsorption methods at present. Biological treatment systems such as the activated sludge process and oxidation ditch have good effects on removing macromolecular organic pollutants, ammonia nitrogen, and phosphorus, and are widely used in municipal sewage and some industrial wastewaters. Advanced oxidation processes (AOPs), including ozone oxidation, UV/H_2O_2, and photocatalysis, are particularly prominent in treating refractory organic pollutants due to their strong oxidizing properties and fast degradation speed. At the same time, they have the advantages of not producing sludge, etc., and have received increasing attention in the treatment of emerging pollutants. However, these traditional technologies expose numerous limitations when dealing with antibiotic wastewater. The specific surface area of activated carbon adsorption is limited, resulting in a low adsorption capacity (for example, the adsorption capacity for tetracycline is less than 50 mg/g). The biological treatment system has little ability to remove low-concentration antibiotics and antibiotic resistance genes (ARGs), and the reaction is slow. Moreover, it may even induce the generation of resistant bacterial populations due to long-term exposure (Shen, 2019). The equipment and reagent costs of advanced oxidation processes are high, and the energy consumption is large. During actual operation, unknown intermediate products are often generated, presenting potential problems of incomplete degradation and secondary pollution (Cuerda-Correa et al., 2019). In conclusion, it is very necessary to develop a highly efficient, convenient, and low-cost treatment method.

Adsorption is a method with simple operation and relatively low cost. Its basic principle is that pollutant molecules are captured by the surface of the adsorbent through physical or chemical actions in the water body, thereby achieving the removal of pollutants in the water. The traditional activated carbon adsorption method has limitations such as low adsorption capacity, no selectivity among different types of organic substances, and relatively complex regeneration operations. Therefore, developing new functional materials with strong adsorption capabilities is an important direction for the treatment of antibiotic wastewater (Mishra, 2024).

Metal-organic framework (MOF) materials exhibit significant advantages in the field of antibiotic adsorption, thanks to their many properties such as porosity, large specific surface area, and multiple metal sites. Research indicates that MOF materials show high adsorption capacity for various types of antibiotics in wastewater, making them particularly suitable for the environmental treatment of micropollutants (Amani et al., 2024). Among numerous classic structures, the ZIF series has become a research hotspot due to its extremely large specific surface area (BET exceeding 1500–2000 m^2/g), strong pore size fine-tuning ability, and hydrothermal and chemical stability. ZIF-8 is a typical MOF material. Experiments have proven that ZIF-8 (with the chemical formula $Zn(MeIM)_2$, where MeIM is 2-methylimidazole) is a typical representative among MOF materials, featuring a three-dimensional crystal structure, excellent thermal stability, and chemical stability. Benefiting from these structural advantages, ZIF-8 is often used as a porous carrier to construct composite adsorbents, which are widely applied to remove various pollutants in aqueous solutions and have demonstrated excellent adsorption capacity and selectivity in multiple studies (Chen et al., 2019).

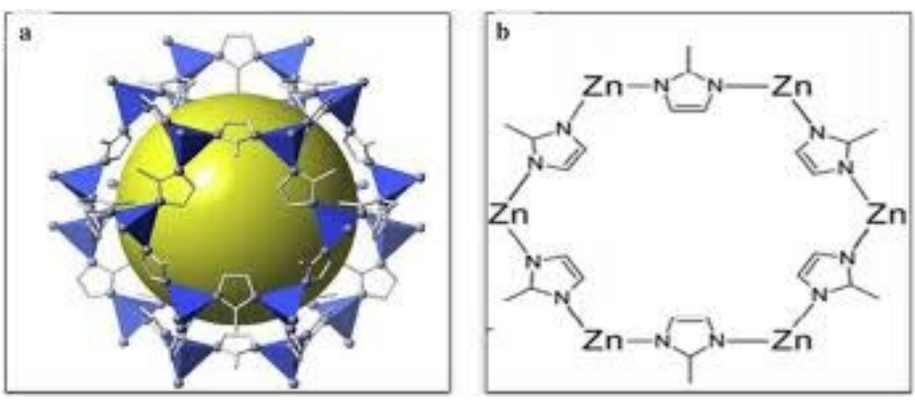

Figure 1 (a) The crystalline form of ZIF-8: Zinc is the polyhedron, nitrogen is the sphere, and carbon is the line. All the hydrogen atoms are omitted to show the crystal structure of ZIF-8 clearly. (b) The structure of the ZIF-8 framework (Kouser et al., 2022)

In response to the above problems, this paper studies the properties of MOF material based on ZIF-8 and its adsorption effect on antibiotics. In this study, physical property tests and adsorption property tests are carried out on ZIF-8 for sulfonamide antibiotics in water (sulfanilamide and sulfamethoxazole). Relevant data on adsorption capacity and dynamics analysis are obtained to explore its application potential and mechanism in removing antibiotic pollutants from water bodies.

2 Methodology

The adsorbent used in this experiment is ZIF-8 material. Sulfanilamide and sulfamethoxazole (SMX) were conducted as typical antibiotics for adsorption experiments. The main analytical instruments used include: an Ultraviolet Spectrophotometer, which is used for the preliminary detection of pollutant concentrations; and High-Performance Liquid Chromatography, which is used for qualitative and quantitative analysis of antibiotics. The experimental methods include material synthesis, physical property testing, adsorption property testing and kinetic fitting analysis. In the experiment, the standard curves of sulfonamide antibiotics sulfanilamide and sulfamethoxazole were drawn, and the adsorption properties of ZIF-8 for sulfonamide antibiotics and SMX were tested.

Adsorption Performance Test: Prepare standard solutions of the target sulfonamide antibiotics (sulfanilamide and SMX) at a certain concentration as the initial pollutant solutions. Dilute them with deionized water to ensure that the concentration is suitable for subsequent analysis. Then accurately weigh amount of ZIF-8 material and add it to 50 mL of the antibiotic standard solution. Place it in a constant-temperature oscillator and oscillate at 400 rpm for a certain period of time to investigate the effect of adsorption time on performance. Use a High-Performance Liquid Chromatography to measure the residual antibiotic concentration in the filtrate. Record the absorption peak area and calculate the corresponding concentration. Compare it with the initial concentration to evaluate the removal efficiency.

Evaluation Indicators of Adsorption Performance: The key points for evaluating adsorption performance mainly include the removal efficiency and the adsorption capacity. The residual concentration is calculated by converting the

absorbance value measured by high-performance liquid chromatography through the standard curve, to calculate the removal rate of antibiotics in water by ZIF-8. The adsorption capacity reflects the maximum removal capacity of the material for a unit mass of pollutants and is a key parameter for evaluating the adsorption performance. Their calculation formula is as follows. Through the above indicators, the adsorption capacity and application potential of ZIF-8 for specific antibiotics can be comprehensively analyzed.

Adsorption efficiency (%)=$(C_0-C_t)/C_0\times100\%$（Formula 1）

Adsorption amount $Q_e=(C_0-C_t)\times V/m$（Formula 2）

Here, C_0 represents the initial concentration of the sulfonamide antibiotics, C_t denotes the concentration of the antibiotics at a certain time, V is the volume of the solution, and m is the mass of the adsorbent.

3 Results and discussion

3.1 Physical properties of adsorption materials

In this study, the ZIF-8 metal-organic framework material was prepared by the solvent method and used as an adsorbent for adsorption experiments. BET tests were carried out, and the specific surface area and porosity of the material were determined through N_2 adsorption-desorption experiments. The experimental results showed that the specific surface area of the material was 1853.95 m^2/g, the total pore volume was 1.65 cm^3/g, and the average pore diameter was 3.46 nm. The results indicated that this material had a relatively rich pore structure. Its specific surface area exceeded that of the commonly used adsorbent activated carbon (about 500–1500 m^2/g), and it could also increase the pore volume of the MOF. This played an important role in the adsorption and mass transfer of organic pollutants with large molecular sizes in the MOF channels.

3.2 Establishment of the adsorption testing procedure

In this experiment, sulfonamide antibiotics were used as the research object to test the adsorption process of MOF materials on them and conduct kinetic analysis. The concentration of pollutants was measured by high-performance liquid chromatography. Different substances have different retention times under the testing conditions, and qualitative analysis is carried out based on this. Under these testing conditions, the retention times of sulfanilamide and sulfamethoxazole are 2.916 min and 8.462 min, respectively, and the qualitative results are shown in Figure 2.

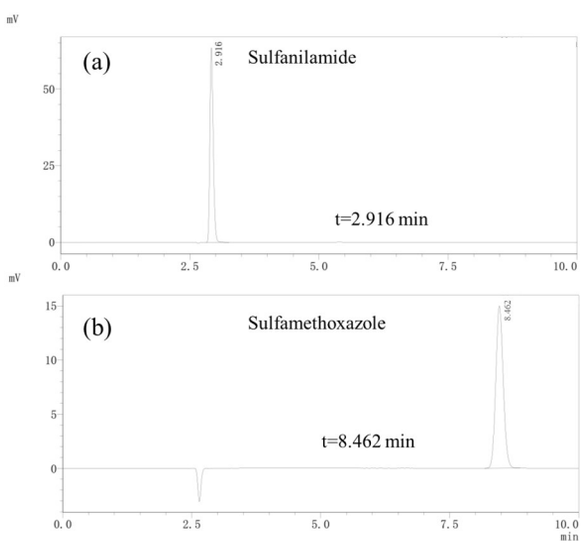

Figure 2 Qualitative results of (a) sulfanilamide and (b) sulfamethoxazole tested by high-performance liquid chromatography

Under qualitative conditions, prepare test solutions with different concentrations and conduct high-performance liquid chromatography (HPLC) determinations. Establish the linear relationship between peak area and concentration and then carry out quantitative analysis. The standard curve is shown in Figure 3. The linear equations of sulfanilamide and sulfamethoxazole are y=28244.3257x-1215.6 (R^2=0.9999) and y=15020.802x-249.907 (R^2=0.9999), respectively, showing good linear relationships within the ranges of 0-20 mg/L and 0-10 mg/L, respectively.

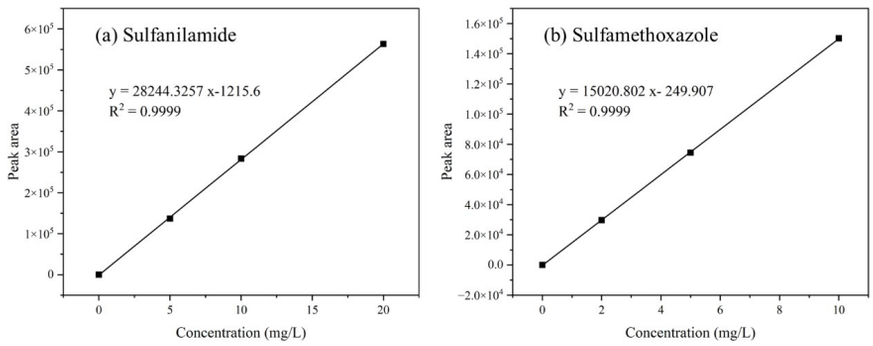

Figure 3 The linear curves of (a) sulfonamide and (b) sulfamethoxazole

3.3 Analysis of adsorption performance and adsorption kinetics

In order to study the influence of adsorption materials on the removal rate of sulfonamide antibiotics, adsorption performance tests were carried out. Solutions of sulfanilamide and sulfamethoxazole with a certain initial concentration were placed in a constant-temperature oscillator and stirred evenly. Samples were taken at regular intervals to measure the remaining content of the analytes in the solution, so as to calculate the change process of the adsorption capacity over time. The results are shown in Figure 4. As can be seen from the figure, within 0 20 min, with the increase of the reaction time, the adsorption capacities of ZIF-8 for sulfanilamide and sulfamethoxazole increased rapidly. In this stage, the antibiotic analytes could quickly reach the adsorption active sites on the surface of the adsorption material, thus enabling efficient adsorption. After 20 minutes, the adsorption rate gradually decreased. During this process, the adsorption process continued, but was limited by the substrate concentration, and the adsorption process slowed down until the adsorption equilibrium was basically reached. The experiment showed that the saturated adsorption capacity of ZIF-8 for sulfanilamide reached 149.44 mg/g, and the saturated adsorption capacity for sulfamethoxazole could reach 362.93 mg/g. Under the same conditions, it had a higher adsorption capacity for sulfamethoxazole.

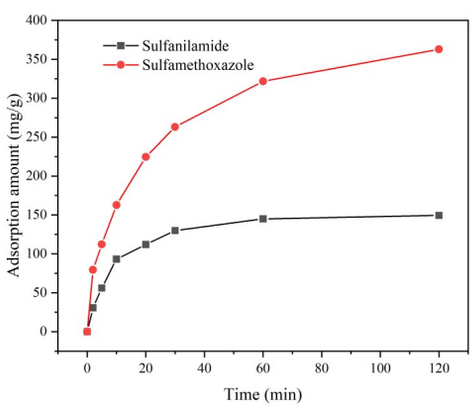

Figure 4 Adsorption performance curve

On this basis, an adsorption kinetic analysis of the adsorption process is carried out to further explore the adsorption behavior of the material, elaborate on the rate-controlling step of the adsorption reaction. The kinetic experimental data are fitted using the pseudo-first-order kinetic model (Formula 3) and the pseudo-second-order kinetic model (Formula 4). The model fitting formulas are as follows.

$$\ln(qe - qt) = \ln qe - k1t \quad \text{(Formula 3)}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad \text{(Formula 4)}$$

Among them, q_t is the adsorption amount (mg/g) at a certain moment, q_e is the equilibrium adsorption amount, t is the adsorption time, and k_1 and k_2 are the equilibrium rate constants of the pseudo-first order and pseudo-second-order kinetic models, respectively.

The obtained fitting curve is shown in Figure 5, and the fitting parameters are listed in Table 1. From the results of linear fitting and the obtained relevant kinetic parameters, it can be seen that for sulfanilamide, the R^2 value of the pseudo-first-order kinetic model is 0.9267, while the R^2 value of the pseudo-second-order kinetic model is 0.9953. This

indicates that the adsorption kinetic process of the adsorbent material for sulfanilamide conforms more to the pseudo-second-order kinetic model, suggesting that the chemical adsorption process may be the rate-limiting step of this adsorption process. In addition, the q_e value calculated by the pseudo-second-order kinetics is closer to the experimentally measured value, reaching 157.23 mg/g. For sulfamethoxazole, the R^2 value of the pseudo-first-order kinetic model is slightly higher than that of the pseudo-second-order kinetic model, indicating that the mass transfer process is still the rate-controlling step. Its theoretical adsorption capacity can reach 332.62 mg/g.

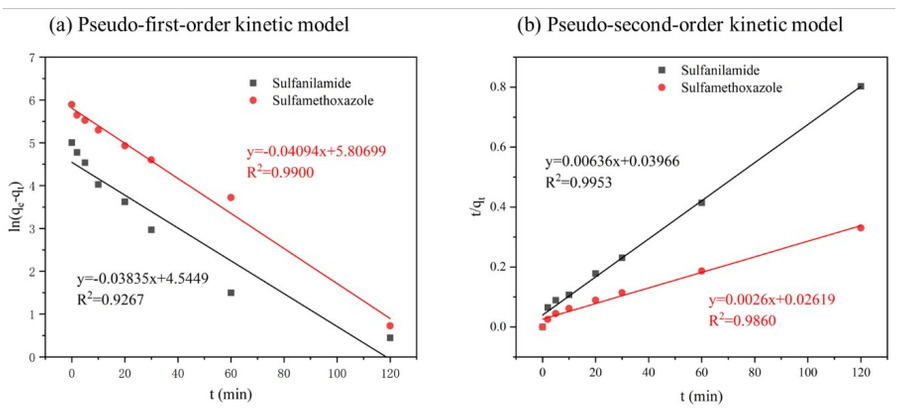

Figure 5 The (a) pseudo-first-order and (b) pseudo-second-order kinetic models of adsorption

Table 1 Fitting parameters of adsorption kinetics

Kinetic model	Parameters	Sulfanilamide	Sulfamethoxazole
PFO	q_e (mg/g)	94.15	332.62
	k_1(min^{-1})	0.03835	0.04094
	R^2	0.9267	0.9900
PSO	q_e (mg/g)	157.23	384.62
	k_2(g/(mg·min))	0.00102	0.000258
	R^2	0.9953	0.9860

3.4 Adsorption isotherm test

Taking sulfonamide as an example, further adsorption isotherm tests were carried out to analyze its adsorption performance. Figure 6 shows the effect of ZIF-8 on the equilibrium adsorption capacity of sulfonamide at different initial concentrations. It can be seen from the figure that as the initial concentration of sulfonamide increases, its equilibrium adsorption capacity continuously increases. This is because the driving force caused by the concentration gradient is enhanced, which promotes the movement of sulfonamide to the adsorption binding sites on the surface of the ZIF-8 material.

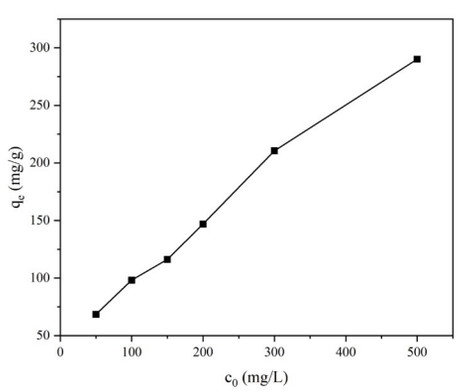

Figure 6 The influence of initial concentration on the adsorption capacity of sulfonamides

To better understand the adsorption process, the Langmuir model (Formula 5) and the Freundlich model (Formula 6) were used to fit the measured adsorption isotherm data, respectively. The fitting results and specific parameter values are shown in Figure 7 and Table 2.

Langmuir Adsorption Model: $\frac{c_e}{q_e}=\frac{1}{k_L q_m}+\frac{c_e}{q_m}$（Formula 5）

Freundlich Adsorption Model: $\ln q_e=\ln k_F+\frac{1}{n}\ln c_e$（Formula 6）

Among them, c_e is the adsorption equilibrium concentration, q_e and q_m are the adsorption capacity at adsorption equilibrium and the maximum adsorption capacity respectively, k_L is the constant of the Langmuir adsorption model, and k_F and n are the constant and coefficient of the Freundlich adsorption model respectively.

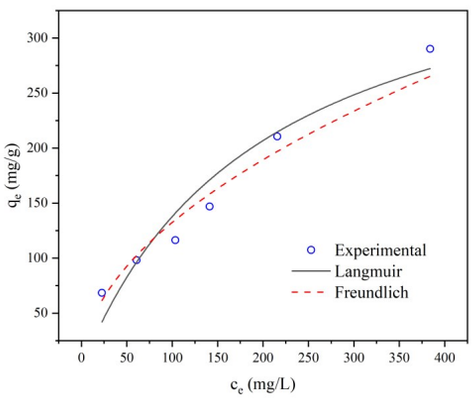

Figure 7 Adsorption isotherm test and fitting of adsorption isotherm model

Table 2 Fitting results of the isothermal adsorption model

Isothermal adsorption model	Parameters	Value
Langmuir	q_m (mg/g)	414.94
	K_L(L/mg)	0.004968
	R^2	0.8399
Freundlich	n	1.9355
	k_F((L/mg)$^{1/n}$mg/g)	12.26
	R^2	0.9611

As can be seen from the R^2 values in Table 2 and the fitting curves in Figure 6, when the adsorption experimental data of sulfonamides by ZIF-8 are fitted using the Langmuir isothermal adsorption model, the obtained determination coefficient R^2 is 0.8399. However, when the Freundlich isothermal adsorption model is used for fitting, the determination coefficient R^2 is 0.9611. This indicates that in this study, the Freundlich model is more consistent with the measured isotherm. The Freundlich model represents a chemical process of non-uniform and multi-layer adsorption, while the Langmuir model assumes that the adsorption surface is uniform and monolayer adsorption. This means that the adsorption process of sulfonamides by the adsorbent is a multi-layer adsorption process, and it tends more towards heterogeneous adsorption.

4 Results and discussion

In this study, a ZIF-8 metal-organic framework adsorbent material was synthesized and applied to the adsorption control process of typical antibiotics. The paper used sulfanilamide and sulfamethoxazole as typical antibiotics to test the adsorption performance of the adsorbent material and carried out fitting of kinetic and isothermal adsorption models. The results showed that ZIF-8 has a rich porous structure that provides active sites for adsorption. It exhibits high adsorption efficiency and adsorption capacity in the adsorption of sulfonamide antibiotics. The theoretical adsorption capacity of ZIF-8 for sulfanilamide reaches 157.23 mg/g, and for sulfamethoxazole, it can reach 332.62 mg/g. Kinetic analysis of the adsorption process showed that the adsorption process conforms better to the pseudo-second-order kinetic model and the pseudo-first-order kinetic model respectively, and the rate-controlling steps of the two adsorption processes are slightly different. Taking sulfanilamide as an example for the adsorption isotherm test, the adsorption conforms better to the Freundlich isothermal adsorption model, which belongs to a multi-layer heterogeneous adsorption process. This study provides a theoretical basis for the application of ZIF adsorbents in the treatment of antibiotic-containing wastewater and offers innovative ideas and effective methods for solving the problem of antibiotic pollution.

Since there is a wide variety of antibiotics, studying the adsorption process of broad-spectrum antibiotics also has

practical significance, which is also the focus of our next research. In addition to the adsorption process, the desorption process is also an important indicator for measuring the adsorption performance. Exploring simple and efficient regeneration methods is also a problem that must be solved for the practical application of this method.

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