Chinese Industry and Technology of Eco-environment
2025, VOL. 6, NO. 4, 73-78
DOI: 10.47297/wspciateWSP2633-772X12.20250604

Research on the Adsorption and Purification Process of Marine Emerging Pollutants Using ZIF-8 Metal-Organic Framework (MOF) Materials

Hongyi Zhu

Shanghai Starriver Bilingual School, Shanghai, 201108, China

ABSTRACT

Emerging marine pollutants pose a severe threat to global marine ecosystems due to their high toxicity, environmental persistence, bioaccumulation potential, and long-range transport capabilities. Adsorption is an effective method for their removal, characterized by high purification efficiency and simple equipment operation. ZIF-8, as a novel adsorbent, features a high specific surface area, good thermal and chemical stability, and tunable pore size. This study investigates the application and performance of ZIF-8 metal-organic framework (MOF) materials in the adsorption and purification of emerging marine pollutants. Through nitrogen adsorption-desorption tests and adsorption experiments, the physical properties of the material were thoroughly analyzed. Rhodamine B was used as a model for recalcitrant organic pollutants, and antibiotics were selected as representatives of emerging pollutants to evaluate the adsorption performance of ZIF-8 on typical marine pollutants. The results indicate that ZIF-8 exhibits high efficiency and rapid adsorption rates for Rhodamine B. Additionally, ZIF-8 maintains high adsorption efficiency over extended periods. This study provides a theoretical basis for the application of MOF materials in the treatment of emerging marine pollutants and offers innovative ideas and effective solutions for addressing marine environmental pollution.

KEYWORDS

Marine pollutants; Adsorption; Adsorption isotherm

1 Introduction

Emerging marine pollutants, such as organophosphate flame retardants (OPFRs), perfluoroalkyl substances (PFAS), pharmaceutical residues, and microplastics, have posed a severe threat to global marine ecosystems [1]. These pollutants are of particular concern due to their high toxicity, environmental persistence, bioaccumulation potential, and long-range transport capabilities. They primarily enter the marine environment through terrestrial discharges (e. g., industrial wastewater and agricultural runoff) and atmospheric deposition, forming enrichment hotspots in estuaries and coastal areas. Studies have confirmed that microplastics can accumulate in marine organisms through the food chain, and perfluoroalkyl substances (PFAS) are widely detected in seafood, posing potential threats to human health [2]. Although international conventions (such as the Stockholm Convention) have regulated the emissions of some traditional pollutants, there is still a significant gap in the regulation of emerging pollutants. Their combined effects and long-term ecological risks are not yet fully understood, especially in vulnerable areas such as the Arctic, where pollutant concentrations are still rising [3]. Therefore, pollution control is urgently needed.

Currently, various treatment technologies have been developed for emerging pollutants, especially recalcitrant organic pollutants, including chemical oxidation processes, physicochemical methods, and biological methods. Chemical oxidation processes degrade organic pollutants by generating highly oxidative free radicals. Fenton oxidation technology activates hydrogen peroxide (H_2O_2) to produce hydroxyl radicals (·OH), which have strong oxidizing power and effectively degrade organic pollutants [4]. Ozone oxidation technology degrades pollutants through the direct oxidation of ozone and the generation of hydroxyl radicals [5]. Sulfate radical-based advanced oxidation processes generate sulfate radicals by activating persulfate [6]. Although oxidation methods have strong oxidizing capabilities, it is difficult to maintain the stability of the catalyst, some activation methods require specific equipment, and the operating costs of the technology are high. Physicochemical methods separate or transform pollutants through physical or chemical means. Membrane separation technology uses separation membranes with different pore sizes to retain pollutants, but it cannot decompose pollutants, and the membrane materials are prone to fouling and clogging [7]. Biological methods degrade organic pollutants through microbial metabolism. Activated sludge is commonly applied through the construction of artificial wetlands [8]. The biofilm method has high efficiency and selectivity in treating recalcitrant organic pollutants. Immobilized microorganism technology performs well in treating wastewater containing phenols, chlorophenols, and phenolic compounds [9]. However, biological methods are sensitive to changes in water quality, have long sludge acclimatization periods, unstable operation, and microbial activity may be inhibited when treating high-concentration pollutants. Adsorption, as a type of physicochemical method, uses porous solid adsorbents to adsorb pollutants, retaining pollutant components on the solid surface through molecular forces or chemical bonds, thereby achieving separation. This method has high purification efficiency, can recover useful components, has simple equipment operation, and is easy to automate [10]. Common adsorbents include activated carbon, silica gel, activated alumina, and zeolite, which have porous structures and large specific surface areas. The selection of adsorbents needs to consider their performance requirements, such as large specific surface area, suitable pore structure and surface structure, strong adsorption capacity, ease of manufacture, easy regeneration, good mechanical strength, chemical and thermal stability, and low cost and availability. Traditional adsorbents (such as activated carbon) are usually non-selective and can adsorb a variety of pollutants, which can easily become saturated, limiting their effectiveness in treating complex water matrices (such as industrial wastewater containing multiple pollutants). Therefore, it is particularly important to find a new type of adsorbent.

Metal-organic frameworks (MOFs) are a new type of porous material that have attracted attention for their high specific surface area, good thermal stability, chemical stability, and tunable pore size. Through material design and structural regulation, the pore size of MOFs can be precisely controlled to achieve selective adsorption of pollutants of specific sizes. ZIF-8 (Zeolitic Imidazolate Framework-8), as a typical MOF material, has received widespread attention for its convenient synthesis method. The specific surface area of ZIF-8 can reach 1000-2000 m^2/g, with high porosity, providing a large number of adsorption sites. It maintains structural stability over a wide temperature range (up to 500 °C) and has good tolerance to acidic and alkaline environments. ZIF-8 exhibits excellent adsorption capacity for a variety of organic pollutants (such as benzalkonium chloride and p-aminobenzenesulfonic acid), with an adsorption capacity of up to 0.05 g/g, and the adsorption process fits the pseudo-second-order kinetic model, indicating that its adsorption is mainly achieved through chemical bonding [11]. In addition, ZIF-8 can effectively degrade organic pollutants under visible light irradiation, with conversion rates of toluene and acetaldehyde reaching 72.7% and 70.74%, respectively [12]. Under low-temperature and high-pressure conditions, ZIF-8 has a CO_2 adsorption capacity of up to 2.079 mmol/g, and the adsorption process fits the pseudo-first-order kinetic model, indicating that its adsorption is mainly achieved through physical adsorption, with good regeneration performance.

In summary, ZIF-8 materials, with their high specific surface area, excellent thermal stability, and chemical stability, show significant advantages in treating recalcitrant organic pollutants. This study synthesizes ZIF-8 metal-organic framework adsorbent materials and conducts in-depth analysis of their physical properties. Rhodamine B is used as a model for recalcitrant organic pollutants, and antibiotics are selected as representatives of emerging pollutants to evaluate the adsorption performance of ZIF-8 on typical marine pollutants. The aim is to explore the application potential of ZIF-8 in treating emerging marine pollutants and to provide innovative ideas and effective solutions for addressing marine environmental pollution.

2 Experimental method

This study prepared ZIF-8 metal-organic framework materials via the solvent method and used them as adsorbents. Rhodamine B, as a typical representative of recalcitrant organic pollutants, and sulfonamide, as a typical representative of antibiotics, were selected for pollutant adsorption experiments to investigate the adsorption and purification process of emerging marine pollutants by ZIF-8 adsorbents. The physical properties of the materials, such as specific surface area and pore size, were characterized and analyzed through nitrogen adsorption-desorption experiments using the BET method.

In this experiment, Rhodamine B was used as a typical representative of recalcitrant organic pollutants to test the adsorption process of the MOF material and to conduct kinetic analysis. The concentration of the pollutant was measured using spectrophotometry. Through full-spectrum scanning of absorbance, it was found that Rhodamine B has a maximum absorption peak at a wavelength of 554 nm. Therefore, the absorbance was tested at $\lambda = 554$ nm to establish a linear relationship between absorbance and concentration, as shown in Figure 1. The linear equation is $A=0.1673C + 0.0148$, with $R^2=0.9955$, indicating a good linear relationship within the range of 0-5 mg/L.

The adsorption experiments were conducted in a thermostatic water bath. A 100 mL solution of Rhodamine B with a

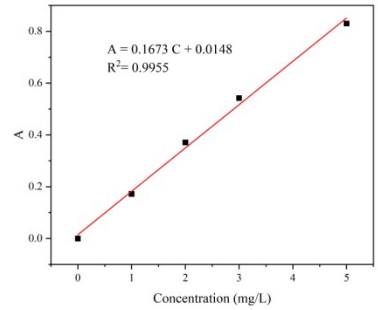

Figure 1 Calibration curve obtained from spectrophotometric analysis

certain concentration was prepared, and 0.1 g of the adsorbent was added. The mixture was continuously stirred mechanically at a speed of 500 rpm. Samples were taken at regular intervals to determine the concentration of the solution, and the removal rate and adsorption capacity were calculated using the following formulas. Solutions with different concentrations were prepared for isothermal adsorption tests. Each solution was stirred at a constant temperature for 3 hours until adsorption equilibrium was reached. The concentrations of the solutions before and after adsorption were measured to obtain the relationship between adsorption capacity and initial concentration. Data from the isothermal adsorption experiments were fitted using different models.

$$\text{Adsorption efficiency } (\%)=(C_0-C_t)/C_0\times100\% \quad (1)$$

$$\text{Adsorption amount } Q_e=(C_0-C_t)\times V/m \quad (2)$$

where C_0 is the initial concentration of rhodamine B, C_t is the concentration of Rhodamine B 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 Surface area and pore size analysis of zif-8 material

The BET specific surface area and porosity of the ZIF-8 microporous material were determined using nitrogen adsorption-desorption experiments. As shown in Figure 2, the nitrogen adsorption-desorption isotherm of ZIF-8 corresponds to Type IV isotherms, with a rapid increase in nitrogen uptake at low pressures, indicating the presence of microporosity. At higher relative pressures (P/P_0), a distinct hysteresis loop is observed, which indicates the existence of mesoporous structures. The hysteresis loop conforms to the H3 type, and the absence of a clear saturation plateau suggests an irregular pore structure.

The average pore size of ZIF-8 was measured to be 3.46 nm. The size of the mesopores in the material was estimated using the Barrett-Joyner-Halenda (BJH) method, with a mesopore diameter of 5.1 nm. The pore size distribution is shown in Figure 3. According to the test results, the specific surface area of the material is 1853.95 m^2/g, the total pore volume is 1.65 cm^3/g, and the micropore volume is 0.27 cm^3/g. The results indicate that the material has a relatively rich pore structure, with a specific surface area exceeding that of general carbon materials (<1500 m^2/g). Moreover, the enhanced pore volume of the MOF plays an important role in the adsorption and mass transfer of large molecular-sized organic pollutants within the MOF channels.

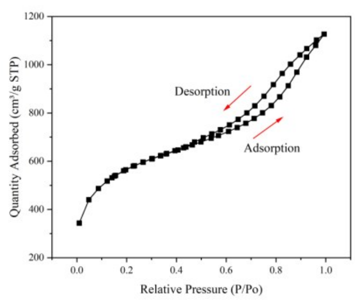

Figure 2 Nitrogen adsorption-desorption isotherms of ZIF-8

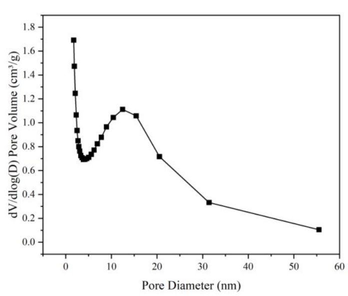

Figure 3 Pore size distribution of ZIF-8

3.2 Adsorption performance and kinetics analysis

To evaluate the effect of the adsorbent on removal efficiency, adsorption-performance curves were measured (Figure

4). Within the first 0–40 min, the adsorption capacity of ZIF-8 for Rhodamine B increases sharply with time, indicating that Rhodamine B rapidly reaches the active sites on the ZIF-8 surface and undergoes efficient adsorption. After 40 min, the adsorption rate gradually decreases; adsorption continues but is limited by the decreasing substrate concentration, slowing the process until saturation is approached at 70 min. Beyond 70 min, the adsorption capacity remains essentially constant, confirming that the MOF material has reached saturation with Rhodamine B. Under these conditions, the final removal efficiency reaches 97.98%.

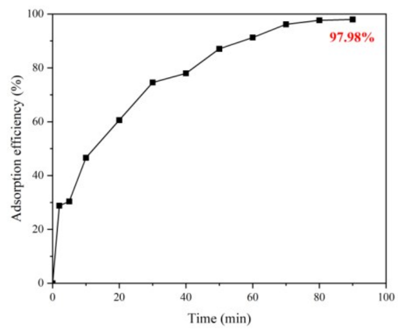

Figure 4 Adsorption performance curve

To further investigate the adsorption behavior of the material, adsorption kinetic analysis was conducted to elucidate the rate-controlling steps of the adsorption reaction. The pseudo-first-order kinetic model (Equation 3) and the pseudo-second-order kinetic model (Equation 4) were used to fit the kinetic experimental data. The model fitting equations are as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

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

Q_t represents the adsorption capacity at a given time (mg/g), q_e the equilibrium adsorption capacity, t the adsorption time, and k_1 and k_2 are the equilibrium rate constants for the pseudo-first-order and pseudo-second-order kinetic models, respectively.

The fitted curves are shown in Fig. 5, and the fitting parameters are listed in Table 1. Based on the linear fitting results and the derived kinetic parameters, the pseudo-first-order model yielded an R^2 of 0.9025, whereas the pseudo-second-order model achieved an R^2 of 0.9900. Thus, the adsorption kinetics of Rhodamine B by the adsorbent is better described by the pseudo-second-order model. Furthermore, the q_e value calculated from the pseudo-second-order model is closer to the experimentally measured value, indicating that chemisorption is likely the rate-limiting step in the adsorption process.

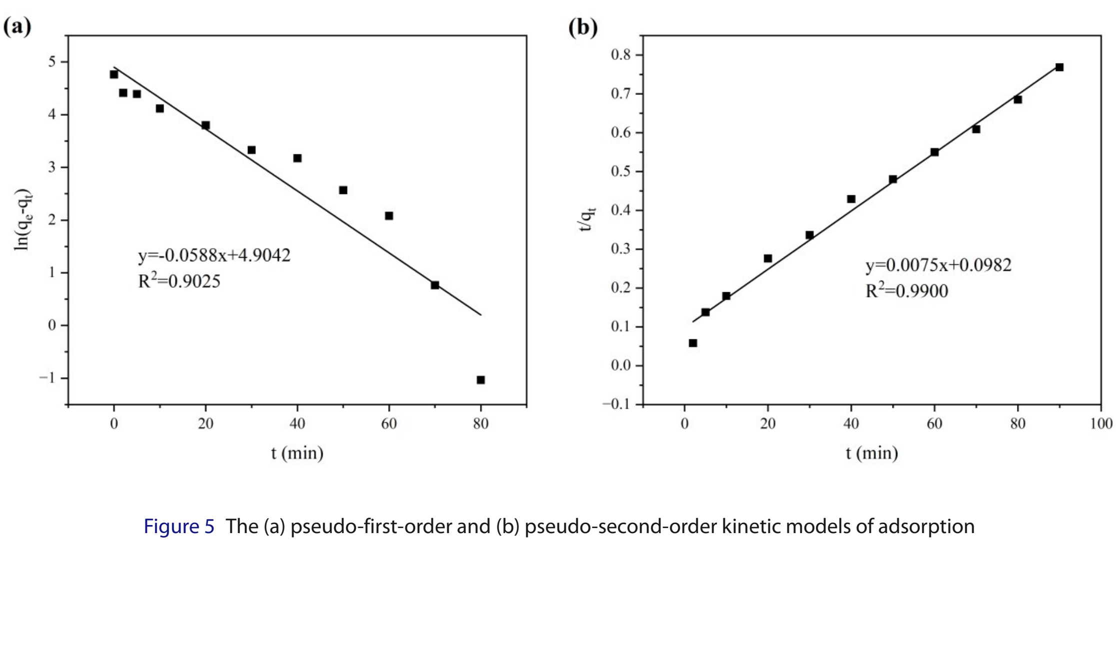

Figure 5 The (a) pseudo-first-order and (b) pseudo-second-order kinetic models of adsorption

Table 1 Fitting parameters of adsorption kinetics

Kinetic model	Parameters	Value
Pseudo-first-order kinetic model	q_e (mg/g)	134.85
	k_1(min^{-1})	0.0588
	R^2	0.9025
Pseudo-second-order kinetic model	q_e (mg/g)	133.33
	k_2(g/(mg·min))	0.0005728
	R^2	0.9900

3.3 Adsorption isotherms

Figure 6 presents the adsorption isotherms of ZIF-8 for Rhodamine B at different initial concentrations. As shown, the adsorption capacity increases rapidly with rising solution concentration and stabilizes once adsorption equilibrium is reached. To better understand the adsorption process, the Langmuir model (Equation 5) and the Freundlich model (Equation 6) were employed to fit the experimental isotherm data.

$$\text{Langmuir:}\frac{c_e}{q_e}=\frac{1}{k_L q_m}+\frac{c_e}{q_m} \quad (5)$$

$$\text{Freundlich:}lnq_e=lnk_F+\frac{1}{n}lnc_e \quad (6)$$

where C_e is the equilibrium concentration after adsorption, q_e and q_m denote the adsorption capacity at equilibrium and the maximum adsorption capacity, respectively; k_L is the Langmuir constant, and k_F and n are the Freundlich constant and exponent, respectively.

As shown by the R^2 values in Table 2 and the fitted curves in Figure 6, the Langmuir model describes the experimental isotherm more accurately, indicating that Rhodamine B adsorption on the adsorbent proceeds as a monolayer process and is essentially homogeneous. The experimentally determined maximum adsorption capacity is 278.3 mg/g, demonstrating the material ' s promising potential for wastewater treatment.

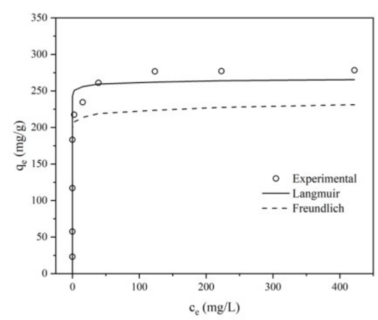

Figure 6 Adsorption isotherm data and isotherm model fitting

Table 2 Fitting results of adsorption isotherm models

Isothermal adsorption model	Parameters	Value
Langmuir	q_m (mg/g)	278.55
	K_L(L/mg)	1.1325
	R^2	0.9998
Freundlich	n	7.508
	k_F($(L/mg)^{1/n}$mg/g)	157.323
	R^2	0.8274

3.4 Adsorption performance toward other representative pollutants

In addition to refractory organic pollutants, the marine environment is also contaminated by typical emerging pollutants such as organophosphorus flame retardants, pharmaceutical residues, antibiotics, and microplastics, all of which are highly toxic and bioaccumulative. Because research on these emerging pollutants remains limited, no explicit pollution-control technical standards have yet been established. Using sulfonamide as a representative antibiotic and polyvinyl chloride (PVC) as a representative microplastic, this study examined the adsorption performance of the synthesized ZIF-8 material toward these emerging marine pollutants. The results revealed that the variations in concentration and adsorption capacity closely resemble those observed for Rhodamine B, achieving removal efficiencies above 97%. The adsorption capacity of ZIF-8 reached 452.7 mg/g for sulfonamide and 321 mg/g for PVC, demonstrating its characteristic adsorption capability toward other typical marine pollutants. Consequently, this pollution-control approach can be regarded as a universal treatment method.

4 Conclusion and prospects

In this study, ZIF-8 metal-organic framework adsorbent was synthesized and applied to the control of typical emerging marine pollutants. Rhodamine B was employed as a model recalcitrant organic pollutant to evaluate the material's physical and adsorptive properties. Results show that ZIF-8 possesses a specific surface area of 1853.95 m^2/g and a hierarchical micro-/mesoporous structure that provides abundant active adsorption sites. ZIF-8 exhibits high efficiency and rapid kinetics toward Rhodamine B, achieving a final removal rate of 97.98% and maintaining elevated adsorption efficiency over extended periods. Kinetic and isotherm analyses reveal that the adsorption process follows the pseudo-second-order kinetic model and the Langmuir isotherm model, indicating monolayer adsorption. Moreover, experiments with other representative marine emerging pollutants demonstrate that ZIF-8 offers both excellent adsorption performance and broad adsorptive universality. This study furnishes a theoretical basis for the application of ZIF-8 in the treatment of emerging marine pollutants and delivers innovative strategies and effective approaches for mitigating marine environmental contamination.

In the future, ZIF-8 pore size can be further refined and architecture by altering synthesis conditions and ligand types to achieve selective adsorption of target molecules and enhanced capacity. Additionally, the regeneration of the adsorbent must be addressed. Developing simple yet efficient regeneration methods is essential for practical implementation.

References

[1] Marine Environmental Science." Advances and Thoughts on Marine Microplastics Research." Marine Environmental Science. 2023.

[2] Acta Ecologica Sinica." Research Progress on the Ecological Effects of Marine Microplastic Pollution." Acta Ecologica Sinica. 2017.

[3] "Medicine Cube." An Exclusive Interview with Professor Dai Jiayin from Shanghai Jiao Tong University: A Detailed Discussion on the" Toxicity "and" Treatment "of the Highly Concerned New Pollutant PFAS." Medicine Cube. 2023.

[4] X. Zhou, D. Xu, Y. Chen, Y. Hu, Enhanced degradation of triclosan in heterogeneous E-Fenton process with MOF-derived hierarchical Mn/ Fe@PC modified cathode, Chem. Eng. J. 384 (2020) 123324.

[5] M. Benjelloun, Y. Miyah, G.A. Evrendilek, A. El Ouali Lalami, I. Demir, B. Atmaca, S. Ssouni, S. Lairini, R. Bouslamti, Synergistic effect of coupling ozonation/ adsorption system for toxic dye efficient removal: chemometric optimization by Box Behnken response surface methodology, Desalination Water Treat. 306 (2023) 220–235.

[6] S. Li, T. Zhang, H. Zheng, X. Dong, Y.K. Leong, J.-S. Chang, Advances and challenges in the removal of organic pollutants via sulfate radical-based advanced oxidation processes by Fe-based metal-organic frameworks: a review, Sci. Total Environ. 926 (2024) 171885.

[7] J.F. Nure, T.T.I. Nkambule, The recent advances in adsorption and membrane separation and their hybrid technologies for micropollutants removal from wastewater, J. Ind. Eng. Chem. 126 (2023) 92–114.

[8] Y. Ravikumar, J. Yun, G. Zhang, H.M. Zabed, X. Qi, A review on constructed wetlands-based removal of pharmaceutical contaminants derived from non-point source pollution, Environ. Technol. Innovat. 26 (2022) 102504.

[9] Zh. Xinchu. Research progress of immobilized microbial technology in the treatment of refractory organic pollutants [J]. Energy Conservation and Environmental Protection, 2022, (09):28-29.

[10] S. Satyam, S. Patra, Innovations and challenges in adsorption-based wastewater remediation: a comprehensive review, Heliyon 10 (2024) e29573.

[11] L. Yuhong. Preparation and performance research of ZIF-8/ Polymer composites [D]. Lanzhou Jiaotong University, 2021.

[12] Zh. Yifan, W. Jiayi, W. Yi, X. Yufan, Zh. Zhiyuan, W. Keya. Comprehensive application of MOF materials in pollutant degradation [J]. Shandong Chemical Industry, 2023, 52(01):227-229.