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Preparation and Characterization of New Metal-organic Frameworks Materials and Its Removal Performance of Sulfonamides in Water

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Abstract. In the present study, MIL-101(Fe) and its four derivatives were prepared by solvothermal synthesis. Taking six iron-based Metal-organic Frameworks (MOFs) materials including MIL-101 series derivatives, MIL-102(Fe), and Fe-Hetero as the research objects, their structural characteristics and the removal performance of sulfadioxine in water were systematically explored. The characteristic structure was observed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results show that all six materials have certain scavenging capabilities against sulfadioxine, among which MIL-102(Fe) performs the best, providing a new material selection and theoretical basis for the treatment of sulfonamides in water.

Keywords: metal-organic framework, organic pollutants, sulfonamides, sulfadoxine, MIL-101(Fe) derivatives, MIL-102(Fe), Fe-Hetero

1. Introduction

Water is a fundamental resource for maintaining the stability of ecosystems and the sustainable development of human society. However, with the expansion of the global population, the acceleration of industrialization, and the intensive development of modern agriculture, water pollution has become a key challenge restricting global ecological security and public health. Among them, organic pollutants in water, due to their generally high toxicity and difficulty in degradation, pose a threat to the ecological environment and human health. Among them, the pollution caused by the abuse of antibiotics and the emergence of drug-resistant bacteria have become serious global problems. As the world's largest producer and user of antibiotics, China has an annual production of over 200000 tons [1]. Due to insufficient emission control during the production process, unreasonable use in the medical field, and abuse in the livestock industry, more than 10000 tons of antibiotics are produced in their original form or as metabolites every year. It enters water and soil systems through industrial wastewater, domestic sewage, aquaculture wastewater and agricultural non-point source pollution, etc. These residual antibiotics not only continue to accumulate in the water environment, accelerating the lateral transfer of drug-resistant genes and the spread of drug-resistant bacteria, but also disrupt the balance of the microbial

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community in the water body, leading to a decline in the self-purification capacity of the ecosystem, posing a dual threat to human health and the ecological environment.

Sulfonamides (SAs), as a type of synthetic antibacterial drugs with a long history of application and wide range of use, are widely used in human clinical treatment and the prevention and control of livestock and poultry diseases. Their detection rate and residue levels in various water bodies remain high. The sulfonamide group (-SO2-NH -) and para-amino group (-NH2 -) contained in the molecular structure of this type of drug are its core functional sites, which determine its chemical stability and biological activity. Its chemical structure is similar to that of para-aminobenzoic acid (PABA). Its antibacterial mechanism mainly involves competing with PABA and binding to dihydropterylate synthase, thereby interfering with the synthesis of folic acid, preventing bacteria from synthesizing biological macromolecules such as DNA and RNA, ultimately hindering the normal growth and reproduction of bacteria [2], and disrupting the microecological balance of water bodies. This in turn triggers the risk of the spread of antibiotic resistance. On the other hand, such drugs have a significant bioaccumulation effect. They not only inhibit the growth and reproduction of aquatic organisms but may also be transmitted to the human body through the food chain, causing health problems such as allergies [3]. Among the numerous sulfonamides, sulfadioxin, due to its extremely long half-life and excellent chemical stability, is more prone to long-term accumulation in water environments. The removal efficiency of conventional water treatment technologies for it is generally low, making it difficult to meet the current water environmental quality standards for the control of emerging pollutants. Moreover, the characteristic of sulfadioxin is that after entering the bloodstream, its concentration can remain at an effective level for a long time, and its metabolic rate in the body is slow [4]. Therefore, the development of efficient, stable and environmentally friendly sulfonamides removal technologies has become an urgent need to ensure water body safety.

At present, traditional water treatment technologies include physical sedimentation and activated sludge process, etc. However, they all have limited removal efficiency for sulfonamides and are difficult to meet the strict water quality standards. However, advanced oxidation and membrane separation technologies have problems such as high cost and secondary pollution [5]. Against this backdrop, metal-organic frameworks (MOFs), as a novel type of porous material, have demonstrated unique advantages in environmental governance fields such as pollutant adsorption, catalytic degradation, and sensing detection, thanks to their high specific surface area, controllable pore structure, abundant active sites, and good structural designability [6], thus becoming a hot research direction in the intersection of materials science and environmental engineering at present. Among them, the MIL series, due to the use of highly stable carboxylic acid ligands coordinated with metal ions, has excellent stability and high porosity, and performs outstandingly in the adsorption and catalytic removal of water pollutants. In particular, MIL-101 is regarded as having the largest specific surface area among the porous materials discovered so far [7]. Among them, MIL-101(Fe) is formed by the coordination of Fe^{3+} and terephthalic acid. It not only inherits the high stability advantage of the MIL series materials, but also features low cost of synthetic raw materials, simple preparation process, rich Fe-based active sites and recyclability. Its application potential in the field of organic pollutant removal has received extensive attention.

In recent years, research on the use of MOFs materials in the removal of antibiotic pollutants in water has been continuously deepened. Existing studies have confirmed that MOFs can selectively adsorb sulfonamides through coordination, electrostatic attraction and ion exchange. However, the existing MOFs materials still face many bottlenecks in practical applications. For instance, the adsorption and removal of pollutants in water environments are affected by multiple factors. There is relatively little research on the recycling and reuse of MOFs, resulting in secondary pollution or

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waste of resources. The adsorption selectivity for sulfonamides is not high, and its long-term operational performance needs to be improved [8]. In addition, the research on the structure-activity relationship between the structure of MOFs materials and the clearance performance of sulfonamides still needs to be deepened. All these issues will restrict its large-scale application in the field of water treatment.

Based on the above research background and existing problems, this study takes sulfadioxine, a typical refractory sulfonamide in water, was taken as the target pollutant. MIL-101(Fe) and its derivatives were prepared by the solvothermal method. Furthermore, two iron-based MOFs materials, MIL-102(Fe) and Fe-Hetero, were selected for comparison. Through characterization and performance testing, Systematically analyze its clearance mechanism of sulfadioxin. Through this research, not only can the application research of MOFs materials in the field of water treatment be enriched, but also theoretical basis and technical support can be provided for the removal of organic pollutants such as sulfonamides in actual water bodies. It has important theoretical value and practical significance for promoting the innovative development of water environment governance technology.

2. Experimental section

2.1. Reagents and instruments

Iron(III) chloride (FeCl3), terephthalic acid (H2bdc), N,N-dimethylformamide (DMF), sulfadioxin (purity ≥98%), MIL-102 (Fe), Fe-Hetero

Polytetrafluoroethylene-lined stainless-steel reactor, muffle furnaces, X-ray diffractometer (XRD), transmission electron microscope (TEM), UV-Vis spectrophotometer

2.2. Preparation of MIL-101(Fe)

Accurately weigh 397mg (2.45mmol) of anhydrous ferric chloride (FeCl3, purity ≥99%) and 206mg (1.24mmol) of terephthalic acid (H2bdc, purity ≥98%), and place them in a clean and dry 50mL polytetrafluoroethylene-lined stainless-steel reactor. Add 15mL of N, N-dimethylformamide (DMF, purity ≥99.5%), seal the reaction vessel and place it on a magnetic stirrer to stir for 30 minutes to ensure that the reactants are fully dissolved. Place the reaction vessel in the oven and heat it at 110℃ for 20 hours. After cooling, filter the brown solid obtained from the reaction. Wash the crude product twice with 10mL of anhydrous ethanol. During the washing process, gently stir to remove the residual DMF and unreacted raw materials. After vacuum filtration again, transfer the solid to a centrifuge tube and centrifuge for 5 minutes. Discard the supernatant to obtain the brownish-yellow MIL-101(Fe) powder.

The preparation process of MIL-101 series derivatives (MIL-101-1, MIL-101-2, MIL-101-3, MIL-101-4) was carried out in accordance with the above basic process of MIL-101(Fe), and derivative samples with different structural characteristics were obtained by fine-tuning the reaction parameters.

2.3. Sulfonamides clearance performance experiment

Take 31 mg of sulfadioxin and place it in a 10mL volumetric flask. Add 400μL of acetonitrile, then make up to the mark with deionized water and shake to prepare the sulfadioxin standard stock solution. 10% (5mg) of MIL-101(Fe), MIL-101 series derivatives, MIL-102(Fe) and Fe-Hetero

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samples were added respectively, and then placed under a 20W ultraviolet-visible light source for photocatalytic degradation experiments.

After the reaction is completed, each reaction solution is placed in a high-speed centrifuge. After treatment, the supernatant is taken and placed in a gas chromatography-mass spectrometry (GC-MS) instrument. By detecting whether the characteristic peak of the sulfonamide group ($m/z \approx 108$) exists in the chromatogram and the change in peak area, the residual amount of sulfadioxin is quantitatively analyzed, thereby further determining the clear efficiency of different materials for sulfadioxin.

2.4. Material characterization

2.4.1. XRD analysis

Place the MIL-101 series derivative samples in a vacuum drying oven (50-80℃) for 4-8 hours to thoroughly remove the adsorbed moisture and synthetic residual solvents, and avoid solvent interference with the diffraction peaks. After drying, the sample is placed in a mortar and ground into fine powder to prevent the diffraction peaks from broadening due to overly large particles. Take 50mg of the ground sample and spread it evenly in the XRD dedicated sample slot. Gently press and level it with a glass plate to ensure that the sample surface is flat and fills the sample slot. Turn on the XRD instrument and preheat it for 30 minutes. After the instrument stabilizes, place the loaded sample slot into the XRD sample stage, close the protective door of the instrument, and then start the scanning. Set the scanning parameters and compare the obtained experimental XRD patterns with the JCPDS standard card. If the positions and relative intensities of the characteristic diffraction peaks in the patterns are consistent with those on the standard card, it indicates that the material has been successfully synthesized. If additional diffraction peaks appear in the spectrum, it indicates that there are impurities in the material. The higher the intensity of the impurity diffraction peaks, the lower the purity of the sample.

2.4.2. TEM analysis

The microscopic morphology and crystal structure of MIL-101 series derivatives were characterized by TEM. Take 5mg of the sample and place it in a 10mL centrifuge tube. Add 5mL of anhydrous ethanol and shake to ensure uniform dispersion of the sample particles and avoid agglomeration that may affect the observation results. Then, use a pipette to draw 10μL of the dispersion and slowly add it to the surface of the copper mesh. Place it on a clean filter paper and let it dry naturally. After the copper mesh is completely dry, it is placed in the TEM sample chamber for observation. Bright-field TEM images and high-resolution TEM images are collected to analyze the morphological features, crystal lattice fringes and particle size distribution of the samples.

3. Results and discussion

3.1. Morphological and structural characterization

The XRD characterization results show that the diffraction patterns of the four MIL-101 series derivatives all present characteristic diffraction peaks, which have a good matching degree with the standard patterns, and there is no obvious interference of miscellaneous peaks, proving that the four derivatives have all been successfully synthesized. Among them, the XRD pattern of MIL-101-1 is highly consistent with the standard pattern (Figure 1a), and no additional impurity peaks appear,

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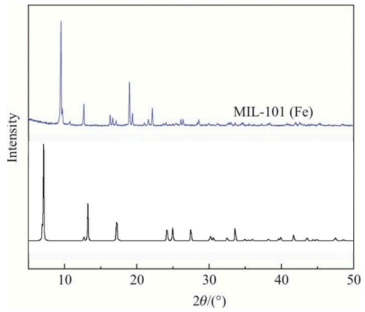
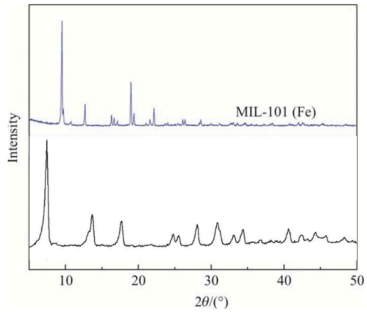
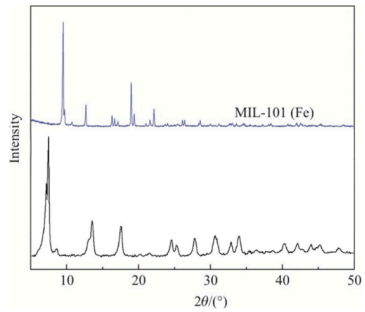
indicating that the crystal structure of the material is regular and the purity is relatively high. As shown in Figure 1b, MIL-101-2 retains the main characteristic diffraction peaks of MIL-101, but the intensity of some peaks is slightly weakened, the peak shape is slightly broadened, and there may be a small amount of lattice distortion or grain refinement. The characteristic diffraction peaks of MIL-101-3 in Figure 1c are consistent with the standard pattern, with sharp and symmetrical peak shapes and no broadening phenomenon, indicating that the crystallinity of the material is optimal. The characteristic diffraction peaks of MIL-101-4 are basically consistent with the peak positions of the standard spectra, but the peak shapes are significantly broadened, indicating that the orderness of the crystal structure of the material is greatly reduced and the integrity of the skeleton is somewhat damaged.



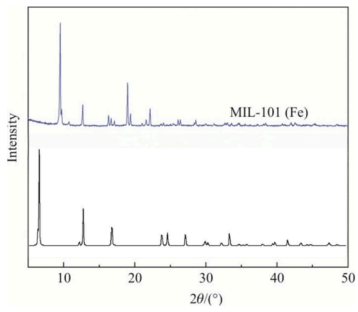
(a) XRD pattern of MIL-101-1



(b) XRD pattern of MIL-101-2



(c) XRD pattern of MIL-101-3



(d) XRD pattern of MIL-101-4

Figure 1. A figure containing four parts

MIL-101(Fe) has an octahedral structure with a diameter of approximately 500nm [9], and the TEM results of MIL-101-1 basically conform to (Figure 2a-c). In Figure 2d-f, the surface of MIL-101-2 particles is slightly rough, and slight irregular protrusions can be seen locally. Some particles have a weak tendency of agglomeration. The particle profile of MIL-101-3 is relatively clear, the crystal structure is dense, and the particle dispersion is good, which directly confirms the high crystallinity characteristic shown by XRD (Figure 2g-i). The TEM image of MIL-101-4 does not show a typical octahedral structure (Figure 2j-l), which conforms to the conjecture that the integrity of the skeleton in the XRD pattern has been somewhat damaged. This structural change may lead to the inability to form a regular polyhedral shape during the crystal growth process.

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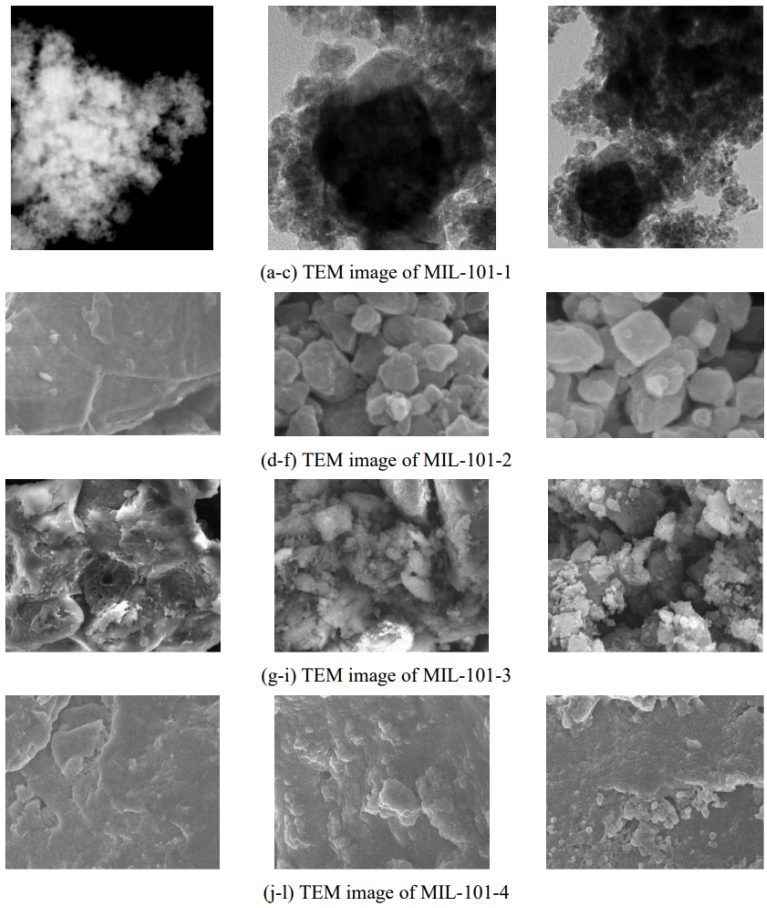

Figure 2. A figure containing twelve parts

3.2. Sulfonamides clearance performance experiment

The experimental results of sulfadioxin clearance performance show that the MIL-101 series materials all have a certain clearance ability for sulfadioxin, but there are differences in clearance efficiency. Mil-101-3 has a higher clearance efficiency than other MIL-101 derivatives due to its high crystallinity and sufficient exposure of active sites. Compared with all the materials in the MIL-101 series, MIL-102(Fe) demonstrates superior cleaning performance, which is closely related to its larger specific surface area and more diverse functional groups. It was found through gas chromatography-mass spectrometry that after the samples with higher removal efficiency were treated, the intensity of the characteristic peak of the sulfonamide group in the system was significantly weakened, indicating that the molecular structure of sulfadioxin was destroyed and effective degradation was achieved.

Based on the characterization results and the analysis of the removal performance data, the removal efficiency of sulfadioxin by MOFs materials is closely related to the crystallinity, microstructure, specific surface area and the number of active sites of the materials. The higher the crystallinity and the better the particle dispersion, the more conducive it is to the contact between pollutant molecules and the active sites of the material. The rich pore structure and functional groups can enhance the material's adsorption and catalytic degradation ability of sulfadioxin.

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4. Conclusions and prospects

In this study, MIL-101(Fe) and four derivative materials were successfully prepared by solvothermal synthesis method, laying a foundation for the systematic exploration of the structure-activity relationship between material structure and performance. Subsequently, the crystal structure of the materials was characterized by XRD technology. Through the analysis of the position and intensity of the characteristic diffraction peaks, it was confirmed that all materials presented the typical crystal structure of the MIL-101 series, with no obvious impurity peaks, indicating that the purity of the synthetic materials was relatively high. Combined with the observation by TEM, it was found that all the materials exhibited porous characteristics. Among them, the diffraction peak intensity of MIL-101-3 was the highest and the peak shape was the sharper, indicating that it had the optimal crystallinity. The regular crystal structure and porous characteristics provided a good structural basis for the adsorption of pollutants.

The study on the removal performance of sulfadioxin, a typical refractory sulfonamide in water, shows that the MIL-101 series materials all have certain removal capabilities for it. Among them, MIL-101-3 performs the best due to its high cleanliness and good pore structure adaptability. However, comparative experiments show that the overall removal efficiency of this series of materials is lower than that of MIL-102(Fe). It is speculated that the difference stems from the differences in pore size distribution, the number of surface-active sites and the coordination environment of iron active centers between the two materials. This result verified the significant influence of the structural characteristics of iron-based MOFs materials on the clearance performance of sulfonamides, providing an experimental basis for the subsequent optimization of material performance through structural modification.

This study systematically reveals the application potential of MIL-101 series iron-based MOFs materials in the treatment of water contaminated by sulfonamides, providing experimental support for the environmental application of this type of material. Based on the experimental results, subsequent research can focus on: First, by regulating the pore structure and surface functional group modification of MOFs, introducing active groups such as amino and carboxyl groups to enhance the interaction between the material and pollutants, and optimizing the pore size to improve adsorption selectivity. The second is to systematically evaluate the performance stability of the materials under different water quality conditions (such as different pH values and ionic strengths), and clarify the impact of interfering factors in the actual water body on the cleaning effect. Thirdly, it is necessary to deeply explore the recycling and regeneration mechanism of materials, and optimize the regeneration conditions through adsorption-desorption cycle experiments to reduce the actual application cost.

References

[1] Shen, S. W., Lin, Y. Z., Wang, M. N., Huang, T., & Zhu, H. J. (n.d.). Research progress on the pollution status of antibiotics in water bodies and pre-oxidation technologies. School of Municipal and Environmental Engineering, Jilin Jianzhu University, 130118.

[2] Su, M. H., Chen, Y. P., Han, X. Q., & Shi, W. B. (2025). Research progress on detection technologies for sulfonamide drug residues in aquatic products. Hebei Fisheries, 85-87.

[3] Qin, G. J. (2012). Study on migration, degradation and accumulation of sulfonamide drugs in sandy soil of Hainan [Master's thesis, Hunan Agricultural University].

[4] Wang, Y. Z., Li, Z. X., Ji, H. W., Xing, L. H., Guo, M. M., & Chang, Z. Q. (2013). Residue elimination regularity of sulfadoxine in Cynoglossus semilaevis. Chinese Fishery Quality and Standards, 3(3), 93-98.

[5] Liu, S. Y., Peng, X. T., Ma, R. R., Zeng, P., Li, J., & Zhu, X. Y. (2024). Research progress on advanced oxidation technologies based on persulfate activation for the treatment of sulfonamide drugs in water. Journal of

DOI: 10.54254/2755-2721/2026.MH30860

Environmental Engineering Technology, 14(2), 642-650.
[6] Khan, M. S., Li, Y., Li, D. S., Qiu, J., Xu, X., & Yang, H. Y. (2023). A review of metal–organic framework (MOF) materials as an effective photocatalyst for degradation of organic pollutants. Nanoscale Advances, 5, 6318-6348.
[7] Zhao, C. C., & Wu, G. R. (2019). Research progress on the application of MOFs composites in catalytic degradation of organic pollutants in water. Chemical Industry and Engineering Progress, 38(4), 1775-1784.
[8] Zou, X. Y., Chen, M., Cao, X. Q., Wang, X., Jia, R. C., Huang, Y. M., Li, G., Yan, B. Q., Wang, P., Li, L., Hu, S. G., & Lü, X. J. (2023). Application status and development trends of MOF materials in water environment pollutant removal (I). Journal of Environmental Chemical Engineering, 11(4), 109876.
[9] Huang, H., Cheng, M., Yin, J., Zhang, J., Kong, L., & Bu, X. H. (2022). MIL-101(Fe)-derived iron oxide/carbon anode for lithium-ion batteries: Derivation process study and performance optimization. Discovery: Researcher.life.