High-Performance Functional Fe-MOF for Removing Aflatoxin B1 and Other Organic Pollutants

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1. Introduction

Mycotoxins are an important member of secondary metabolites produced by various fungi with high toxicity to humans and livestock.[1–3] Many states and regions have established rigorous criteria for the content of mycotoxins in foods such as aflatoxins, deoxynivalenol, ochratoxins, T-2 toxin, fumonisin, and zearalenone.[4–7] Aflatoxin B1 (AFB1) is one of the most harmful mycotoxins and has acute toxicity, carcinogenicity, teratogenicity, and mutagenicity to humans and mammals.[8–10] To address this issue, helpful strategies based on physics, chemistry, and biology have been adopted to monitor the AFB1 contamination for environment protection and food safety.[11–14] One effective approach is drawing support from high-efficiency adsorbents to achieve the rapid removal of AFB1.[15–20]

Currently, synthetic nanoparticles are utilized extensively to overcome critical environmental issues, medicine, industry, energy, and many related fields. The current state-of-the-art nanotechnology has created numerous opportunities to address the fundamental problems in these fields.[21–26] In such circumstances, nanoscale porous materials with high surface areas have drawn much attention in the scientific community during the past few years due to their good performance in mycotoxin adsorption.[27] For example, Xie and co-workers synthesized a magnetic graphene composite, which could be further used to adsorb AFB1 from contaminated oil with a removal rate of 90%.[28] Moreover, modified nano-diamond substrates reported by Gibson et al. have been demonstrated to process good capability in adsorbing AFB1 from water with uptake amounts as high as 10.34 mg g⁻¹.[29] Analogously, Liang and co-workers fabricated a functionalized nanoflower-like hydroxyl magnesium silicate and achieved a better uptake of AFB1 (27.34 mg g⁻¹) in the water system.[30] All the nanostructured materials described above are effective and provide new enlightenment for the development of other macromolecular porous materials for AFB1 treatment, such as metal-organic frameworks (MOFs).

MOFs are composed of metal ions/ion clusters as nodes and multidentate organic linkers bridged by coordination bonds, showing great potentials in multiple areas due to their
attractive properties, including facile synthesis, diverse compositions, synthetic versatility, and robustness. Moreover, high surface areas of the frameworks have made MOFs attractive scaffolds for functional adsorbent and photocatalysts in recent years. In this study, the synthesis and hydrophobic modification of MIL-101(Fe), an iron-based MOF using iron(III) chloride hexahydrate (FeCl₃·6H₂O) as the metal source and 1,4-benzene dicarboxylic acid (H₂BDC) as the linker, and its ability as a powerful AFB1 adsorbent are explored. Meanwhile, to demonstrate a potential MIL-adsorption application, we modify MIL-101(Fe) with chlorotrimethylsilane (TMCS) to develop hydrophobic adsorbents that can effectively eliminate AFB1 in oil. Notably, we establish the interaction model of AFB1 and adsorbent at the molecular level through molecular docking and computational chemistry, further clarifying the adsorption process mechanism. The adsorption studies of AFB1 by MIL-101(Fe) and TMCS-MIL will provide information about the potential of nanostructure adsorbents on AFB1 removal, which typically involves a complex system and more environmental applications where hazardous organic pollutants are encountered.

2. Results and Discussion

2.1. Synthesis and Characterization of MIL-101(Fe)

The MIL-101(Fe) composite was fabricated by a modified hydrothermal method using FeCl₃·6H₂O as the metal source and H₂BDC as the linker molecule. Scanning electron microscopy (SEM) was applied to determine the morphology of MIL-101(Fe). As shown in Figure 2A,B, the synthesized MIL-101(Fe) has typical octahedral shapes with an average diameter of 400 nm, in good consistency with the dynamic light scattering (DLS) results (Figure 2C). Besides, the powder X-ray diffraction (PXRD) pattern of the synthesized MIL-101(Fe) material was in good agreement with the previously reported crystal phase structure (Figure 2D). The peaks of MIL-101(Fe) located at 2θ = 8.9°, 9.2°, 10.7°, 18.5°, and 21.8° indicated the successful synthesis of MIL-101(Fe).

2.2. Combination of Toxin and Adsorbent

Thermogravimetric analysis (TGA) curves showed the weight loss of MIL-101(Fe) (Figure 3A). Subsequently, we verified the combination of toxin and adsorbent by Fourier-transform infrared spectroscopy (FT-IR) and transmission electron microscopy (TEM). First, FT-IR was carried out to illustrate the difference before and after the adsorption of AFB1 at pH 7 for 12 h and confirmed the successful synthesis of MIL-101(Fe) material. The infrared absorption bands at 1658–1396 cm⁻¹ represent the typical characteristic peaks of MIL-101(Fe). The bands at 1396 and 1583 cm⁻¹ can be ascribed to the stretching vibration of the carboxyl group of MIL-101(Fe). The bands at 1018 and 752 cm⁻¹ could be attributed to the C–H bending vibrations of the benzene ring. FT-IR analysis was conducted to identify changes in the chemical structure of the MIL-101(Fe) upon adsorbing AFB1. From Figure 3B, typical bands in the FT-IR spectra of MIL-101(Fe) are also observed in AFB1-adsorbed MIL-101(Fe) with decreased intensity, which indicates no changes in the chemical bonds. Compared to the material's
Figure 2. A, B) SEM images of MIL-101(Fe); C) Hydrodynamic diameters distribution of MIL-101(Fe) based on DLS; D) PXRD pattern of MIL-101(Fe).

Figure 3. A) TGA curves of MIL-101(Fe); B) FT-IR spectra of MIL-101(Fe) before and after the adsorption of AFB1; TEM images of MIL-101(Fe) C) before and D) after adsorption of AFB1.
morphology displayed in Figure 3C, one can find that AFB1 was attached to the material (Figure 3D). After adsorbing the toxins, the MIL-101(Fe) particles still maintained the octahedron shape, indicating that the metal site of MIL-101(Fe) did not participate in the reaction with AFB1 molecules.

2.3. Effects of Temperature, Adsorbent Dosage, Time, and Cycling on the Adsorption

The adsorption effect was represented by AFB1 removal rate ($R$), which was calculated according to Equation (1)

$$R = \frac{C_0 - C}{C_0} \times 100\%$$

where $C_0$ and $C$ are respiration concentrations of AFB1 solutions before and after adsorption. The values of $C_0$ and $C$ can be calculated according to the linear equation given in Figure S1, Supporting Information.

As in Figure 4A, the influence of temperature on AFB1 removal was studied at 273, 288, 303, 318, and 333 K, respectively. The removal rate of AFB1 increased with elevated temperature and reached 89.5%. However, considering the practical application and energy consumption, our current research mainly focused on the detoxification of AFB1 at room temperature.

The variation of the adsorption effect of AFB1 with adsorbent dosage is displayed in Figure 4B. The removal rate of AFB1 was promoted by increasing the adsorbent dosage from 0.4 to 1.25 mg mL$^{-1}$ (based on the oil volume) and tended to be stable after that. The maximum removal rate of 89.4% was attained at the adsorbent dosage of 1.25 mg mL$^{-1}$. It is worth mentioning that the adsorption of MIL-101(Fe) toward AFB1 is an almost instantaneous process due to the excellent dispersion of the material in water. The primary adsorption process was completed rapidly from 0 to 5 min and then slowly reached the highest removal rate at ~25 min (Figure 4C). To determine the maximum loading amount of AFB1, we conducted the cycle adsorption experiment. As shown in Figure 4D, the adsorption capacity of MIL-101(Fe) on AFB1 reached saturation after eight cycles and achieved 96 mg g$^{-1}$, which is significantly higher than other nano-adsorbents when they accomplish the same adsorption capacity to the best of our knowledge.[27–30]

2.4. Effect of pH on Adsorption Efficiency and Adsorbent Architecture

The acidity and alkalinity of the solution significantly impact the material properties and cargo adsorption effect. We tested the adsorption effect of MIL-101(Fe) under gradient pH values (~2–13) of AFB1 solutions. It turns out that the percentage of removal was increased as the solution pH turned to be neutral (Figure 5A). The absorbance of the solution with a pH over 9 is lower because AFB1 can be degraded in a strongly alkaline environment (Figure 5B). However, the absorbance increases abnormally while the pH is higher than 10. Therefore, we believed that the structure of MIL-101(Fe) was also destroyed. To investigate the effect of the different pH values on MIL-101(Fe) structure, a PXRD analysis was performed under pH of 2–13 (Figure 5C). The material’s crystal structure is damaged.
somehow after the material was treated in the solution of pH 11, which indicates that the material has preferable stability in the environment of pH < 11. MIL-101(Fe) maintained its strength at pH < 7, however, the elution of AFB1 by acid can lead to poor adsorption. Moreover, the material cannot be dispersed as a suspension under high pH conditions and forms massive precipitation (Figure 5D). In summary, the MIL-101(Fe) sorbent displayed the highest adsorption effect in a neutral environment while not qualified in a strong basic environment.

2.5. Adsorption Thermodynamic, Isotherm, and Kinetics Analysis

Furthermore, the thermodynamic parameters of the adsorption process were calculated under ≈303–333 K according to the following equations.

\[
K = \frac{C_a - C}{C} \tag{2}
\]

\[
\Delta G = -RT \ln K \tag{3}
\]

\[
\Delta G = \Delta H - T \Delta S \tag{4}
\]

\[
\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{R} \cdot \frac{1}{T} \tag{5}
\]

The thermodynamic data of MIL-101(Fe) material are listed in Table 1. The results suggest the adsorption is an endothermic process (\(\Delta H > 0\)), and the \(\Delta G\) values are negative at different temperatures, proving that the adsorption is a spontaneous process.

2.6. AFB1 Adsorption Isotherm and Kinetics

The adsorption isotherms were used to describe the AFB1 adsorption behavior of MIL-101(Fe) based on Langmuir and Freundlich models. The expression of the Langmuir and Freundlich isotherms is presented by Equations (6) and (7):

\[
Q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \tag{6}
\]

\[
Q_e = K_f C_e^{1/n} \tag{7}
\]

where \(Q_e\) is the apparent adsorption capacity of adsorbent to adsorbate at adsorption equilibrium (mg g\(^{-1}\)), and \(C_e\) is the equilibrium concentration (mg L\(^{-1}\)).

The fitting parameters of the adsorption isotherm of AFB1 described by the Langmuir and Freundlich models are shown in Table 2 and Figure S2A,B, Supporting Information. The correlation coefficient (\(R^2\)) obtained by the Freundlich model was significantly higher than the Langmuir model, suggesting
better applicability of the Freundlich equation in analyzing the adsorption of AFB1. Moreover, the value of \( n > 1 \) demonstrates a more vital interaction between the AFB1 and MIL-101(Fe).

The pseudo-first-order and pseudo-second-order models were applied to analyze the adsorption kinetics and describe the adsorption of AFB1 by MIL-101(Fe). The linear models are expressed by following Equations (8) and (9):

\[
\ln Q_t = \ln Q_{ce} - \frac{K_1}{Q_{ce}} t
\]

\[
\frac{t}{Q_t} = \frac{1}{Q_{ce} K_2} + \frac{1}{K_2 Q_{ce}^2}
\]

where \( Q_c \) (mg g\(^{-1}\)) means the adsorption capacity of AFB1 per unit weight of MIL-101(Fe) at time \( t \) (min), \( K_1 \) (min\(^{-1}\)) and \( K_2 \) (g mg\(^{-1}\) min\(^{-1}\)) are the rate constants for these two models, respectively.

The corresponding parameters and \( R^2 \) values of kinetic models are listed in Table 3 and Figure S2C,D, Supporting Information. Due to the higher \( R^2 \) (0.999), a pseudo-second-order kinetic model was chosen to describe the adsorption process of MIL-101(Fe) toward AFB1. According to the pseudo-second-order model, the maximum loading capacity for AFB1 was 30.58 mg g\(^{-1}\), which is the highest among the current studies (Table S1, Supporting Information).

### 2.7. Desorption of AFB1

The stability of MIL-101(Fe) was further assessed by the desorption experiments (Figure 6). The results show that the AFB1 removal efficiency of adsorbed MIL-101(Fe) can still be above 90% after eluting with methanol. Additionally, the toxicity desorption rate on adsorbent reached 83% with methanol elution, ensuring the efficiency of adsorbent recycling.

### 2.8. Adsorption Effect Comparison of Different Materials on AFB1 and Other Organic Pollutants

In addition to mycotoxins, organic dyes and pesticide residues generate potential health risks to both humans and animals. Here, we conducted the adsorption test of MIL-101(Fe) toward other pollutants, including three organic dyes (rhodamine B [RhB], methylene blue [MB], methyl orange [MO]) and three pesticides (acetamiprid [ACE], 2-methyl-4-chlorophenoxyacetic acid [MCPA], carbendazim [CAR]), to evaluate its universality. The standard curve for converting absorbance to concentration is given in Figure S3, Supporting Information. Additionally, we synthesized four other popular MOF materials, that is, MIL-88A, ZIF-67, ZIF-8, and UiO-66-NH\(_2\), as adsorbents for horizontal comparison of their adsorption effects. The SEM images and PXRD patterns demonstrated the successful synthesis of the above four materials (Figure S4, Supporting Information). It is worth mentioning that MIL-101(Fe) exhibited a remarkably higher adsorption effect on AFB1 than other tested materials and accomplished a good removal effect on other pollutants (Figure 7A). On the contrary, removing several contaminants by MIL-88A that possesses MIL frames with fumaric acid as ligands is negligible. Our results thus suggest that using p-phthalic acid as ligands might offer the MIL structure a significant adsorption effect. According to the heat map, it can be judged that the material maintained outstanding advantages in pollutants removal (Figure 7B).

### 2.9. Iron Ion Infusion Test

To avoid the potential health dangers caused by Fe\(^{3+}\) leached from adsorbent in water, we detected the concentration of Fe\(^{3+}\) infused from MIL-101(Fe) in suspension. After soaking for 120 min, the concentration of Fe\(^{3+}\) kept lower than 1.0 µg L\(^{-1}\) (Figure 7C,D), which is far below the limited concentration to exert its biological significance.\(^{[40]}\) The low toxicity of the MIL-101(Fe) ensures its safety and practicability as an adsorbent.

### 2.10. Hydrophobic Modification of MIL-101(Fe)

Edible seeds like peanuts or groundnuts are susceptible to being contaminated by aflatoxins. AFB1 can enter the human food chain via commonly used peanut oil during storage, transportation, processing, manufacturing, and handling due to its high
stability. It is of great practical importance to achieve the adsorption of MIL-101(Fe) toward AFB1 under the presence of hydrophobic fatty acids in actual contaminated oil. For this reason, we carried out the hydrophobic modification of MIL-101(Fe) to permit it to play an adsorbent role in oil detoxification. The PXRD spectra were conducted to identify the changes of the material structures before and after the modification by TMCS (Figure 8A); the typical prominent diffraction peaks of MIL-101(Fe) appear in both materials. Compared with the material before modification, the relative strength decreased to a certain extent, which may be related to the grating narrowing caused by the connection of TMCS to the crystal structure. The peak at 1250 cm\(^{-1}\) was caused by \(-\text{Si(CH}_3\text{)}_3\), indicating that TMCS was successfully connected to the framework without changing the material structure (Figure 8B). The surface suspension experiment confirmed that the normal MIL-101(Fe) dispersed in water quickly, while the hydrophobic TMCS-MIL-101(Fe) tends to diffuse in peanut oil (Figure 8D). Subsequently, an adsorption experiment on AFB1 in oil showed that hydrophobic TMCS-MIL-101(Fe) achieved an adsorption amount of 11.22 mg g\(^{-1}\), which is higher than 25% of isolated MIL-101(Fe) (Figure 8C). The results reflected that hydrophobic TMCS-MIL-101(Fe) exhibited an excellent decontamination effect in oil though adsorption capacity was lost due to hydrophobic modification. To further characterize the hydrophilicity of the two materials, the water contact angle was measured. Compared with the MIL-101(Fe), the water contact angle of the modified TMCS-MIL-101(Fe) increased to 85.5°, which further demonstrated that MOF successfully transformed from hydrophilic to hydrophobic (Figure 8E,F).

2.11. Adsorption Mechanism

The dramatic enhancement of the adsorption effect inspired us to investigate the adsorption mechanism of MIL-101(Fe) from a micro-perspective. Comparing the IR spectra of MIL-101(Fe) before and after adsorption suggested that no obvious chemical reaction occurred between MIL-101(Fe) and AFB1, which indicates the adsorption should be more likely to be a physical process. To gain deeper insights into the internal interaction between AFB1 and MIL-101(Fe), molecular docking coupled with computational chemistry was utilized. Figures 9A and 10A
Figure 8. A) PXRD pattern of MIL-101(Fe); B) FT-IR spectra of MIL-101(Fe) before and after modification of TMCS; C) Removal efficiency of MIL-101(Fe) and TMCS-MIL-101(Fe) on AFB1 in peanut oil; D) Suspension experiment of MIL-101(Fe) and TMCS-MIL-101(Fe) in water and peanut oil, respectively; E) Water contact angle measurement of TMCS-MIL-101(Fe); F) Water contact angle measurement of MIL-101(Fe).

Figure 9. Interaction analysis of adsorption model-1: A) Adsorption active site displayed by molecular docking analysis; B) Investigation of electrostatic potential between interacting molecules; C) Weak interaction characterization according to the isosurface map, scatter diagram, and color map.
show two stable adsorption patterns of AFB1 by MIL-101(Fe) with binding free energies $-6.29$ and $-6.16$ kcal mol$^{-1}$, respectively. Additionally, docking results clearly showed the polar contacts from oxygen atoms on the furan ring and carbonyl group in the AFB1 to the terephthalates in MIL-101(Fe), confirmed by the two models’ charge distribution (Figures 9B and 10B). To further demonstrate the interfacial behavior of interaction, the type of force between AFB1 and terephthalates ligands was further investigated using the interaction region indicator (IRI) model based on density functional theory (DFT). In the isosurface map, as shown in Figures 9C and 10C, a weak steric effect (red area) between MIL-101(Fe) occurred, and van der Waals force (green area) plays the critical role in the adsorption of AFB1 by MIL-101(Fe). On the other hand, spikes could be seen in $\approx -0.04$ to $-0.03$ area of IRI versus sign ($\lambda$) $\rho$ scatter diagram, indicating the appearance of van der Waals force, in agreement with analysis in the isosurface map. The strength of the weak interaction between AFB1 and terephthalates was further displayed according to the IRI map on the XY dimer plane to reflect the strength and position of the force visually. Therefore, we speculate that the van der Waals force plays a significant role in promoting the adsorption process.

3. Conclusion

In summary, the MIL-101(Fe) nanocomposite exhibited a remarkably enhanced adsorption effect toward AFB1, with a 30.58 mg g$^{-1}$ loading capacity. According to the mechanism analysis, van der Waals force between toxin molecules and terephthalic acid ligands is the critical driver of the adsorption process. Testing the MIL-101(Fe) with different pH values showed its stability with pH from 2 to 10. Subsequently, we evaluated the adsorption effect of different MOFs on several pollutants and demonstrated that MIL-101(Fe) excels in organic pollutant treatment. In comparison, optimized TMCS-MIL-101(Fe) possessed excellent hydrophobicity and excelled at adsorbing AFB1 in oil, exceeding normal MIL-101(Fe) by over 25%. We expect our investigation to inspire more studies to understand the effect of MOFs on mycotoxins management and their performances in various applications.

4. Experimental Section

Preparation of MIL-101(Fe): The composite of MIL-101(Fe) was fabricated by a hydrothermal method following a previous procedure with slight modifications. First, FeCl$_3$·6H$_2$O (2.25 g), terephthalic acid (0.71 g), and DMF (50 mL) were mixed by 30 min ultrasonic processing. Then, the mixture was transferred to a hydrothermal reaction vessel. After 20 h of heating at 110 °C, the cooled powder was treated by centrifugation and purification. The product was washed with hot DMF and ethanol. Finally, the powder was vacuum dried at 60 °C for 12 h.

Preparation of TMCS-MIL-101(Fe): To obtain hydrophobic TMCS-MIL-101(Fe), MIL-101(Fe) (1.02 g) was added into toluene (100 mL). Afterward, about 200 µL of TMCS was injected into the solution quickly and mixed thoroughly. The mixed solution was stirred at 70 °C for 24 h. Then, it was strained and washed with distilled water and ethanol. The obtained solids were first dried under vacuum at 70 °C for 3 h and then dried at 110 °C for 12 h.

Generation of the Standard Concentration-Absorbance Fitting Line: The concentration of AFB1 was adjusted at 15 µg mL$^{-1}$ and preserved the solution at 4 ± 2 °C in a dark refrigerated room. Gradient diluted
the standard stock solutions using distilled water to obtain solutions with concentrations of 1.5, 2.0, 2.5, 5.0, 7.5, and 10.0 μg mL⁻¹, respectively. The solution absorbance of different concentrations was measured by an INESA-L65 ultraviolet spectrophotometer (INESA Analytical Instrument Co., Ltd, Shanghai, China) with distilled water as the control. The test was repeated three times, and the average value was taken as the absorbance value of the solution. The calculation of fitting line and variance were performed by Origin software based on the corresponding concentration and absorbance values. The preparation and data processing methods of other samples were the same as AFB1.

**Adsorption Procedure**: Immediately before the test, a suspension of a 5 mL organic pollutant solution (15 μg mL⁻¹) and adsorbent (2 mg) was ultrasonically mixed to reach the adsorption–desorption equilibrium. Subsequently, the suspension was filtered to remove the adsorbent and then determine the absorbance of the filtrate. The filtered adsorbent was added in methanol (5 mL) and mixed under ultrasonic to test the desorption degree.

Batch experiments were carried out at 298 K to investigate the adsorption of AFB1 with different initial pH. The pH value of the solution was adjusted by adding HCl or NaOH. All other experimental conditions and procedures were similar to the above experiments.

The thermodynamic study on the adsorption of AFB1 by MIL-101(Fe) was also conducted. Adsorption experiments were performed at 303, 318, 333, 348, and 363 K. Relevant thermodynamic parameters were calculated from the test data. All experiments mentioned above were repeated three times.

**Molecular Docking and Computational Chemistry**: Molecular docking was performed by Autodock 4.0 software, and visual images were generated using Autodock-vina software. Weak interaction between AFB1 and terephthalate in MIL-101(Fe) was analyzed by IRI included in the Multifit 3.7 version, and results were processed graphically by VMD 1.9.3 software. The wave function files of the complex used in the calculation were obtained with a default solvent model under the level of B3LYP/6-311G* carried out by Gaussian09 software. Because the structure file of MIL-101(Fe) was not available in the Cambridge Crystallographic Data Center (CCDC), the structure of MIL-101(Fe) was acquired by replacing the Cr atoms with Fe atom of MIL-101(Fe) from CCDC.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

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