Removal of Berberine from Wastewater by MIL-101(Fe): Performance and Mechanism

Juan Li, Liangjie Wang, Yongqiang Liu, Ping Zeng,* Yan Wang, and Yizhang Zhang

ABSTRACT: The water contamination from pharmaceuticals and personal care products (PPCPs) has attracted worldwide attention in recent years because of its threat to public health. Berberine is a typical anti-inflammatory medicine and berberine wastewater is difficult to be treated due to its high toxicity, poor biodegradability, and high acidity. Metal−organic frameworks would be a good choice to remove berberine from wastewater due to its advantages of high specific surface area, ultrahigh porosity, and structural and functional tunability. In this study, MIL-101(Fe) was synthesized and used for the removal of berberine from water. Experimental results indicated that MIL-101(Fe) showed promising characteristics when berberine was adsorbed in acidic wastewater. The high concentration of chloride in berberine wastewater could promote the adsorption of berberine by MIL-101(Fe). Fitting of batch equilibrium data showed that MIL-101(Fe) had a maximum adsorption capacity of 163.93 mg/g for berberine removal at pH 7, and the berberine sorption on MIL-101(Fe) followed the pseudo-second-order model. Furthermore, the associate mechanism for berberine removal was proposed by characterizing the material and theoretical calculation. The X-ray power diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) analysis showed that no chemical reaction occurred during the adsorption of berberine by MIL-101(Fe). Also, the theoretical calculation results indicated that π−π interactions may play the main role in the adsorption of berberine onto MIL-101(Fe). The findings of this study suggest that MIL-101(Fe) is a promising sorbent for berberine removal from wastewater.

1. INTRODUCTION

The contamination of water by pharmaceuticals and personal care products (PPCPs) has attracted worldwide attention in recent years because of its threat to public health.1 Berberine is an anti-inflammatory medicine with broad-spectrum antibiotic activity and pharmacological effects.2 Berberine can be used to treat cancer, diabetes, and liver disease,3 and the demand for berberine is increasing in recent years.4 Berberine is originally isolated from a variety of Chinese herbs, but nowadays it is mainly produced by chemical synthesis.5 During the chemical synthesis of berberine, a large amount of wastewater would be produced, which usually contains a high concentration of residual berberine. At present, the berberine wastewater is mainly discharged into the traditional sewage treatment plants directly for treatment.6 However, the conventional biological treatment system was usually inefficient for the treatment of berberine wastewater because it is usually highly acidic containing a high concentration of berberine and organics with antibacterial characteristics.7,8 Because of the adverse effects of berberine,7,9 efficient treatment methods are urgently needed to treat this berberine wastewater.

Many methods have been used for the removal of berberine, including Fenton oxidation,9 electrochemistry method,10 electrocoagulation,11 biodegradation,12 and adsorption method.13 Among these, the adsorption method is a promising technology for the removal of berberine from water due to its simple operation, high removal efficiency, and low cost.13 The adsorbents used for berberine removal mainly include mesoporous carbon,14 resin,5,15 and some minerals.16,17 However, because of the high acidity and complex composition of berberine wastewater, the capacities of these materials for berberine is usually low, which limits the application of these adsorbents in berberine wastewater treatment. Thus, it is necessary and important to develop efficient adsorbents for berberine removal.

Metal−organic frameworks (MOFs) are an emerging class of porous materials, which are constructed from metal ions and organic ligands.18 MOFs have the advantages of ultrahigh porosity, good chemical stability, high thermal stability, and tunable structure and function.19,20 Thus, the potential application of MOFs has gained more and more attention from the researchers. At present, MOFs have been widely used
in gas storage, toxic gas removal, separation, photocatalysis, chemical sensors, and so on. In recent years, some water-stable MOFs have been used for the removal of pollutants from wastewater, including removal of organic dyes, heavy metal ions, and pharmaceuticals and personal care products from water. The possible mechanisms for adsorptive removal of pollutants over MOFs mainly include electrostatic adsorption, acid–base reaction, π–π complexation, and hydrogen bond. Previous studies have shown that berberine is mainly removed through hydrogen-bonding formation with berberine acting as a H acceptor, while it is reported that MOFs could be good H donors. Thus, MOFs might be promising materials for berberine removal. However, the use of MOFs for berberine removal has not been reported.

The overall objective of the current study is to explore the possibility of removing berberine from water by MOFs. MIL-101(Fe) was synthesized and used for berberine removal in this study. The effect of temperature, adsorbent dosage, solution pH, and chloride on the material’s properties for berberine adsorption was examined. The capacity and the kinetics of the material for berberine removal were studied by conducting batch experiments. Also, the associated mechanism for berberine removal by the material was proposed together with experimental results and theoretical calculations.

2. RESULTS AND DISCUSSION

2.1. Effect of Temperature and Adsorbent Dosage on the Adsorption of Berberine by MIL-101(Fe)

The influence of temperature on berberine removal was studied under the temperature of 298, 308, and 318 K, as shown in Figure 1a. The results showed that the removal of berberine increased with the increase of temperature. When the temperature increased from 298 to 308 K, the adsorption amount of berberine increased from 61.55 to 82.03 mg/g. Further increasing the temperature to 318 K could increase the adsorption amount of berberine to 103.38 mg/g. However, considering the energy consumption of temperature increase, this study mainly focused on the removal of berberine at room temperature.

Furthermore, the thermodynamic parameters including the standard Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated for the adsorption of berberine on MIL-101(Fe) according to the method reported in the previous study. As shown in Table 1, the Gibbs free energy changes were positive at 298 and 308 K, indicating that the adsorption process is not spontaneous for the adsorption of berberine on MIL-101(Fe). While the Gibbs free energy change was negative at 318 K, which indicates that the adsorption process is spontaneous under 318 K. Also, ΔH° and ΔS° were positive for the adsorption of berberine on MIL-101(Fe), indicating that the adsorption process was endothermic.

The effect of the dosage of MIL-101(Fe) on the adsorption of berberine was also studied, as shown in Figure 1b. It can be seen that the adsorption amount of berberine for per unit of adsorbent decreased with the increase of adsorbent dosage. However, the concentration of removed berberine increased with the increase of adsorbent dosage. When the dosage of MIL-101(Fe) increased from 0.2 to 1 g/L, the removed berberine concentration increased from 21.68 to 61.55 mg/L. However, when the dosage of MIL-101(Fe) was higher than 1.0 g/L, further increase in the adsorbent dosage resulted in less increase in berberine adsorption. Especially, when the MIL-101(Fe) dosage increased from 2 to 3 g/L, the removal of berberine increased from 80.07 to 86.27 mg/L.

2.2. Effect of pH on the Adsorption of Berberine by MIL-101(Fe)

The pH of the solution is usually very important for the adsorption of organics. In this study, the influence of the initial pH on berberine removal by MIL-101(Fe) was conducted at pH from 4 to 10, as shown in Figure 2. As illustrated, the initial pH did not have much influence on the removal of berberine by MIL-101(Fe). The adsorption amount of berberine was almost the same at the initial pH from 4 to 10. This result is different from that of other studies. Shan et al. found that the initial pH had a great influence on the removal of berberine by resin H103. This is because the adsorption of berberine onto resin is highly dependent on the size of berberine in the solution. Berberine molecules dissociate into R and Cl− when the pH is lower than 7.0 but form R−OH2+ ions when the pH is higher than 7.0.
The initial pH did not have much influence on the adsorption of berberine by resin H103. In this study, the pH of the solution was less than 5.3. Similarly, the adsorption capacity of berberine by resin H103 for berberine decreased obviously when the pH was lower than 5.3. Therefore, the initial pH had a great influence on the adsorption of berberine by MIL-101(Fe). In this study, the pH of the solution decreased rapidly after the addition of MIL-101(Fe), as shown in Figure 2. The pH of the solution decreased rapidly after the addition of MIL-101(Fe) due to the strong acidity of the material. Therefore, the initial pH did not have much influence on the removal of berberine by MIL-101(Fe).

In particular, berberine wastewater is usually highly acidic with pH in the range from 0.06 to 1.2.9-37 However, the adsorbents used to remove berberine in the current studies are usually less effective in removing berberine under acidic conditions. For example, the adsorption capacity of polymeric resin H103 for berberine decreased obviously when the pH was less than 5.3.38 Similarly, the adsorption capacity of berberine on ZSM-5 molecular sieves reached the maximum at pH 8 and decreased with the decrease in pH.39,40 However, MIL-101(Fe) synthesized in this study is suitable for the removal of berberine under acidic conditions, which is favorable for its practical application.

2.3. Effect of Chloride on the Removal of Berberine by MIL-101(Fe). Because berberine wastewater usually contains high concentrations of chloride (Cl\(^-\)) in the range from 6555 to 12670 mg/L,49,40 it is necessary to investigate the influence of chloride on the adsorption of berberine by MIL-101(Fe). The removal of berberine by MIL-101(Fe) in the presence of chloride was examined at different concentrations, as shown in Figure 3. It can be seen that Cl\(^-\) had little effect on the adsorption of berberine at low concentrations. However, it was found that chloride could promote berberine removal by MIL-101(Fe) when the concentration of chloride was more than 50 mM (2922 mg/L). This result indicated that the presence of chloride was advantageous for the adsorption of berberine from berberine wastewater by MIL-101(Fe). This might be because berberine molecules dissociate into R\(^+\) and Cl\(^-\) under reaction conditions. The presence of high concentrations of Cl\(^-\) may lead to the formation of neutral berberine molecules, which is favorable for the adsorption of berberine.43 Thus, the high concentration of chloride in berberine wastewater could promote the adsorption of berberine by MIL-101(Fe), which is beneficial for the application of MIL-101(Fe) in berberine wastewater treatment.

2.4. Isothermal Adsorption of Berberine by MIL-101(Fe). Adsorption isotherm of berberine by MIL-101(Fe) at pH 7 is shown in Figure 4. It can be seen that the adsorption of berberine increased with the increase of berberine concentration. To further analyze the adsorption behavior of berberine on MIL-101(Fe), Langmuir isotherm model, Freundlich isotherm model, and Temkin isotherm model were used to analyze the batch adsorption results. The fitting parameters of Langmuir, Freundlich, and Temkin isotherm were listed in Table 2. The fitting results showed that the Langmuir equation was better to analyze the isotherm data than the Freundlich equation or the Temkin equation. The correlation coefficients from the Langmuir equation were higher than 0.99. Based on the fitting of the Langmuir equation, the synthesized material had a maximum capacity of 163.93 mg/g for berberine, which is higher than those of the previously reported adsorbents (Table 3). These results demonstrate that MIL-101(Fe) has good prospects for the removal of berberine from water.

2.5. Kinetics of Berberine Removal by MIL-101(Fe). Kinetics of berberine adsorption by MIL-101(Fe) was examined at pH 7, as shown in Figure 5. It can be seen that the berberine was adsorbed by MIL-101(Fe) quickly in the first 30 min, and the concentration of berberine decreased fast. The adsorption of berberine by MIL-101(Fe) reached an equilibrium in about 6 h. At the beginning of the reaction, MIL-101(Fe) contained a lot of adsorption sites on the surface of the material and the berberine in the solution can be adsorbed quickly. However, the reaction sites on the surface of the material were consumed gradually with the increase in the reaction time, and the decrease in the concentration of berberine in the solution resulted in a slower reaction rate. Further, the typical kinetic models including intraparticle diffusion, pseudo-first-order and pseudo-second-order models were used to fit the experimental results and analyze the adsorption kinetics of berberine on MIL-101(Fe). The kinetic parameters and coefficients of the three models are shown in Table 4. It can be seen that the correlation coefficient of the pseudo-second-order model is greater than 0.99, which is much higher than that of the two other models. Thus, the experimental data can be fitted well to the pseudo-second-order kinetic model rather than to the intraparticle diffusion equation or the pseudo-first-order equation. This indicated that the rate-limiting step for the adsorption of berberine on MIL-101(Fe) may be a chemisorption process.
2.6. Characterization of MIL-101(Fe) before and after Adsorption. To observe the changes in the material before and after the adsorption of berberine, scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) analysis were conducted. The morphologies of the MIL-101(Fe) before and after the adsorption of berberine were observed by SEM, as shown in Figure 6. The synthesized MIL-101(Fe) had typical octahedral shapes before the adsorption of berberine, which is in accordance with the previous reports.\(^4^1\) The morphology of the material changed obviously after the adsorption of berberine, as presented in Figure 6b. After the reaction with berberine, the octahedron shape of MIL-101(Fe) was depressed. This result indicated that the metal site of MIL-101(Fe) may not participate in the reaction with berberine.

The XRD spectra of the material before and after the adsorption of berberine are shown in Figure 7. The XRD spectra of the synthesized MIL-101(Fe) were well in agreement with the previously reported data,\(^4^2\) which indicated that MIL-101(Fe) was successfully synthesized in this study. After the adsorption of berberine, the XRD spectra of the material changed. However, the typical main diffraction peaks did not change. Shown in Figure 8 are the FTIR spectra of MIL-101(Fe) before and after the adsorption of berberine at pH 7 for 12 h. The FTIR spectra of the synthesized material confirmed the successful synthesis of MIL-101(Fe).\(^4^3\) The bands in the region of 1600−1400 cm\(^{-1}\) represent the asymmetrical and symmetrical stretchings of O−C−O, which are the typical characteristic peaks of MIL-101.\(^4^4\) The peaks at 590 and 790 cm\(^{-1}\) can be attributed to the vibration of Fe−O\(^{4+}\),\(^4^5\) and C−H bending vibrations of the benzene,\(^4^6\) respectively. After the adsorption of berberine, the main peaks of the FTIR spectra for the material weakened, while the

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c03422)

**Table 2. Langmuir, Freundlich, and Temkin Parameters for the Adsorption of Berberine on MIL-101(Fe)**

<table>
<thead>
<tr>
<th>adsorbents</th>
<th>conditions</th>
<th>(Q_{\text{max}}) (mg/g)</th>
<th>(K_L)</th>
<th>(R^2)</th>
<th>(K_F)</th>
<th>(R^2)</th>
<th>(B)</th>
<th>(K_T)</th>
<th>(R^2)</th>
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<td>163.93</td>
<td>0.0044</td>
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<td>10.11</td>
<td>12</td>
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<td>10.11</td>
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<td>MIL-101(Fe)</td>
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<td>163.93</td>
<td>this work</td>
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**Table 3. Comparison of Maximum Berberine Adsorption Capacities of Various Adsorbents**

<table>
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<th>adsorbents</th>
<th>conditions</th>
<th>(Q_{\text{max}}) (mg/g)</th>
<th>reference</th>
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<td>molecularly imprinted polymer AD-10</td>
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<td>58</td>
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<tr>
<td>berberine hydrochloride imprinted polymers</td>
<td>298 K, 5 h</td>
<td>10.11</td>
<td>12</td>
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<td>macroporous resin AB-8</td>
<td>303 K, 28 h</td>
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<tr>
<td>macroporous resin HPD300</td>
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<td>117.8</td>
<td>59</td>
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<tr>
<td>MIL-101(Fe)</td>
<td>298 K, 12 h</td>
<td>163.93</td>
<td>this work</td>
</tr>
</tbody>
</table>
position of the main peaks did not change, indicating no changes in the chemical bond.

Furthermore, to analyze the surface chemistry of MIL-101(Fe) before and after the adsorption of berberine, XPS was conducted, as shown in Figure 9. Figure 9a shows the full-survey spectrum of MIL-101(Fe), in which the signals of Fe, C, and O could be detected. Before the adsorption, the XPS spectra of Fe 2p showed two peaks at 711.80 and 725.60, which can be assigned to Fe$^{3+}$. Because that the Fe species in MIL-101 was Fe$^{3+}$, the presence of Fe$^{3+}$ validated the formation of MIL-101(Fe) with Fe as the metal site. After the adsorption, the XPS spectra of Fe 2p consist of two subpeaks at 711.47 and 725.31, which were also attributed from Fe$^{3+}$. This result indicated that Fe, as the metal site of the material, did

Table 4. Kinetic Parameters and Coefficients of the Intraparticle Diffusion, Pseudo-First-Order, and Pseudo-Second-Order Model for the Adsorption of Berberine on MIL-101(Fe)

<table>
<thead>
<tr>
<th>intraparticle diffusion model ( Q_t = K_p t^{1/2} + C )</th>
<th>pseudo-first-order model ( C_t = C_0 e^{-K_1 t} )</th>
<th>pseudo-second-order model ( \frac{1}{Q} = \frac{1}{K_2 Q_e} + \frac{1}{Q_e} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_p )</td>
<td>( R^2 )</td>
<td>( K_1 ) (min$^{-1}$)</td>
</tr>
<tr>
<td>1.3049</td>
<td>0.8529</td>
<td>0.0003</td>
</tr>
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</table>

Figure 6. SEM images of MIL-101(Fe) before (a) and after (b) adsorption of berberine.
not participate in the reaction with berberine. Combined with the results of XRD and FTIR, the chemical composition of the material may not change after the adsorption of berberine.

2.7. Adsorption Mechanism. It is important to understand the plausible mechanism of the interactions between the adsorbent and adsorbate. Several adsorption mechanisms such as electrostatic interaction, acid/base complexing, $\pi-\pi$ interactions, and hydrogen bonding have been used to explain the adsorption of organics over MOFs. From the characterization results of MIL-101(Fe) before and after adsorption, it can be concluded that no obvious chemical reaction occurred between MIL-101(Fe) and berberine. To further understand the mechanism of the adsorption of berberine by MIL-101(Fe), theoretical calculations were performed to analyze the weak interactions between MIL-101(Fe) and berberine. Figure 10 shows the possible adsorption site of MIL-101(Fe) for berberine (Figure 10a–c) and the isosurface of $\delta g$ (Figure 10d). The green area in the isosurface of $\delta g$ between MIL-101(Fe) and berberine represents $\pi-\pi$ interactions, and the blue area represents hydrogen bonding. It can be seen that there is a weak hydrogen bond between MIL-101(Fe) and berberine, while $\pi-\pi$ interactions play the main role in the adsorption of berberine by MIL-101(Fe). Thus, it can be inferred that berberine is mainly adsorbed on MIL-101(Fe) through $\pi-\pi$ interactions.

3. CONCLUSIONS
MIL-101(Fe) was used for berberine removal from water in this study. As a new type of porous materials, MIL-101(Fe) showed some advantages in the removal of berberine. First, MIL-101(Fe) can be used for berberine removal under acidic conditions. Second, a high concentration of chloride could promote the removal of berberine by MIL-101(Fe). Third, MIL-101(Fe) has a high capacity for berberine with the maximum sorption capacity of 163.93 mg/g at pH 7. For the removal mechanism of berberine by MIL-101(Fe), the characterization results indicate that no chemical reaction occurred between berberine and MIL-101(Fe). Through theoretical calculation, it can be inferred that the main mechanism for the adsorption of berberine by MIL-101(Fe) can be attributed to $\pi-\pi$ interactions. The findings of this study suggest that MIL-101(Fe) is a promising sorbent for berberine removal from water. For future research, the capacity of MIL-101(Fe) for berberine can be further improved through the modification of nitrogen-containing functional groups to enhance the hydrogen-bonding reaction between adsorbent and berberine.

4. MATERIALS AND METHODS
4.1. Materials. The following reagents were used in this study: ferric chloride hexahydrate and terephthalic acid (TPA) were purchased from Shanghai Macklin Biochemical Co., Ltd. NaCl, NaNO₃, Na₂SO₄, NaHCO₃, NaOH, HCl, N,N-dimethylformamide (DMF), and ethanol were provided by Sinopharm Group, China.
4.2. Preparation of MIL-101(Fe). MIL-101(Fe) was synthesized through a hydrothermal synthesis method reported previously, with slight modifications. First, ferric chloride hexahydrate and terephthalic acid were dissolved in DMF solution in a ratio of 2:1. Then, the mixture was transferred to a Teflon-lined autoclave and put into a preheated (at 110 °C) electric oven and maintained for 20 h. The autoclave was cooled to room temperature after the reaction and a solid product was recovered by centrifugation. The product was washed with DMF and ethanol 2 times, respectively. And then, the product was vacuum-dried at 60 °C for 24 h. The prepared MIL-101(Fe) had a Brunauer−Emmett−Teller (BET) surface area of 1312 m²/g.

4.3. Characterization of Materials. The synthesized MIL-101(Fe) was characterized by Brunauer−Emmett−Teller (BET) surface area, scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). For the characterization of MIL-101(Fe) after adsorption of berberine, the material after the reaction was washed with water and ethanol two times, respectively. And then, the product was vacuum-dried at 60 °C for 24 h and used for characterization.

The specific surface area of MIL-101(Fe) was calculated by the BET equation from N₂ adsorption/desorption isotherms, which was conducted by Quadrasorb SI-MP. The morphology of the material before and after the adsorption of berberine was observed by SEM (Hitachi SU8010, Japan). The synthesized samples were also characterized by FTIR (Excalibur 3100, Varian) in the range of 400−4000 cm⁻¹ to identify the functional groups on the adsorbent surface. X-ray diffraction analysis of the samples before and after reaction with berberine was conducted using X-ray power diffraction in the range from 3 to 50°. In addition, to determine the surface chemical composition of the material before and after the adsorption of berberine, XPS (ESCALAB-MKII, VG Co., Bruker, Germany) analysis was performed.

4.4. Batch Experiments. 4.4.1. Effect of Temperature on Berberine Removal. The effect of temperature on the removal of berberine by MIL-101(Fe) was conducted. In a typical test, 20 mg of MIL-101(Fe) was mixed with 20 mL of 200 mg/L berberine solution at an initial pH of 7.0. Then, the mixture reacted in a shaking table for 12 h at temperatures of 298, 308, and 318 K, respectively. After reaching equilibrium, the mixture was filtered through a 0.22 μm syringe filter, and the concentration of berberine in the filtrate was determined using an ultraviolet−visible (UV−vis) spectrophotometer at 345 nm. The experiment was repeated three times.

4.4.2. Effect of Adsorbent Dosage on Berberine Removal. The effect of adsorbent dosage on the removal of berberine by MIL-101(Fe) was also conducted at a temperature of 298 K. The test procedures were similar to the above experiment.
except that a different adsorbent dosage was used. The experiment was also repeated three times.

4.4.3. Effect of pH on Berberine Removal. Batch experiments were carried out at 298 K to investigate the berberine adsorption as a function of the initial pH. The pH of the solution was adjusted by HCl or NaOH. All other experimental conditions and procedures were similar to the above experiments. The experiment was also repeated three times.

4.4.4. Effect of Chloride on Berberine Removal. The influence of chloride on berberine removal by MIL-101(Fe) was also studied at initial pH 7. Different levels of concentration of Cl\(^{-}\) (1, 3, 5, 10, 20, 50, 100, and 200 mM) were tested. All other experimental conditions and procedures were similar to the above experiments. The experiment was also repeated three times.

4.4.5. Adsorption Isotherms. The capacity of MIL-101(Fe) for berberine removal was examined at an initial pH of 7 by conducting the batch equilibrium experiment. The test mixture was sampled at the desired time interval with a 5 mL syringe and filtered immediately through a 0.22 μm membrane filter for an analysis of residual berberine. The experiment was also repeated three times.

4.5. Theoretical Calculations. Theoretical calculations were conducted to analyze the weak interactions between adsorbent and berberine. Multiwfn 3.7 software\(^{48}\) was used to calculate the isosurface of the \(dg\) function of the independent gradient model (IGM)\(^{50−54}\) after geometry optimization. The optimization of the molecular geometry with a default solvent model under the level of PBE1PBE/6-311G* was carried out by Gaussian software.\(^{55}\) The images of molecular structure and isosurface of the \(dg\) function were obtained by VMD software.\(^{56}\) In addition, the molecular docking was realized by AutoDockTools and Vina. Because the structure file of MIL-101(Fe) was not found in the Cambridge Crystallographic Data Center (CCDC), the structure of MIL-101(Fe) is the same as that of MIL-101(Cr),\(^{57}\) the crystal file of MIL-101(Fe) was obtained by replacing Cr of MIL-101(Cr) coming from CCDC.

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**Notes**

The authors declare no competing financial interest.


