The Strengthening Role of the Amino Group in Metal–Organic Framework MIL-53 (Al) for Methylene Blue and Malachite Green Dye Adsorption

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Supporting Information

ABSTRACT: In this paper, two kinds of metal–organic frameworks (MOFs), MIL-53(Al) and MIL-53(Al)-NH₂, were synthesized. Then these MOFs were used to remove methylene blue and malachite green dyes from aqueous solution. Characterizations of MOFs were carried out by X-ray powder diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared (FT-IR) spectrometry, and zeta potential. Experimental results showed that MIL-53(Al)-NH₂ can rapidly bind to the two kinds of cationic dyes from aqueous solution with high adsorption capacity. However, the adsorption capacity of MIL-53(Al) for cationic dyes is extremely low. The adsorptive selectivity of MIL-53(Al)-NH₂ to the cationic dyes resulted from the hydrogen bonding interaction between amino groups of the dyes molecule and the MIL-53(Al)-NH₂, while the extremely low adsorption capacity of MIL-53(Al) for the dyes may be main caused by the “breathing” behavior of MIL-53(Al). The factors including adsorption time, temperature, and the pH of solution that affected adsorption of the two dyes on MIL-53(Al)-NH₂ were studied. Pseudo first-order kinetic, pseudo second-order kinetic, and Weber–Morris models were used to fit the adsorption data, and the pseudo second-order kinetic model showed a better fit for the adsorption of methylene blue and malachite green than that of the pseudo first-order kinetic model. Furthermore, the internal diffusion model which represented by Weber-Morris model was involved in the step of speed control, but it was not the only speed control step, while out-diffusion also played an important role in the adsorption process. The adsorption isotherm and thermodynamics of methylene blue and malachite green on MIL-53(Al)-NH₂ were also studied. The adsorption of methylene blue and malachite green dyes on MIL-53(Al)-NH₂ can be fitted to both Langmuir and Freundlich isotherm, but the former was better than the latter. The adsorption thermodynamic experiments demonstrated that adsorption reaction was spontaneous and endothermic. Finally, according to the experimental phenomenon, the possible mechanism of adsorption was proposed. Besides, the used adsorbent can be reused for adsorptive removal through simply washing.

1. INTRODUCTION

In recent years, dye-containing wastewater has caused the environment to be deteriorated and threatened human health.1,2 Owing to the complex structures of the dye molecules, they are resistant to degradation caused by the light, heat, and oxidant in nature.3,4 Therefore, it is necessary to remove dyes from water before they were released. There are many methods to treat dye-containing wastewater, such as adsorption, flocculation, electrolysis, and biodegradation.5–8 Among them, the adsorption process has attracted more attention because of its advantage of low cost, high efficiency, and environment-friendliness. In this regard, various adsorbents, for instance, activated carbon, activated diatomite, resin, and carbon nanotubes, has been used for adsorption of dyes from aqueous solution.9,10 However, these adsorbents were often accompanied by some disadvantages, for example, low adsorption capacity, poor selectivity, complex preparation processes, and difficult to regeneration.11 However, it is important for an adsorbent to possess adsorption capacity and high selectivity to the dyes.

Metal–organic frameworks (MOFs) were new family of microporous materials, which are made up of metals (or clusters) linked to each other by organic ligands.11,12 Due to the high specific surface area and uniform and tunable pore size, MOFs have been used in many fields, such as adsorption of chemicals, storage of gas, and drug delivery.13,14 Among the numerous MOFs, aluminum(III)-based MOF (MIL-53(Al)) has attracted attention.15 It consists of AlO₄(OH)₂ octahedron and the carboxyl groups of terephthalic acid in which they are self-assembled to form a 3D framework structure with 1D diamond holes. MIL-53(Al) has specific “breathing” effect and favorable stability both in neutral and acidic solution. At present, MIL-53(Al) has been used to absorptive remove organic pollutants from water; however, most studies were conducted in a single pollutant system. Meanwhile, in order to enhance the removal of pollutants, some research groups...
introduced amino group into MIL-53(Al) and prepared MIL-53(Al)-NH₂. Though MIL-53(Al)-NH₂ has exhibited higher adsorption capacity to some organic pollutants than that of MIL-53(Al), there were few studies which involved in the selective adsorption of the cationic dyes in water. Therefore, based on the ability of −NH₂ group forming hydrogen bond with active hydrogen compound, it is necessary to study the selective adsorption of MIL-53(Al)-NH₂ for cationic dyes in water.

At present, most of the researchers for adsorption on MOFs are about comparing cationic and anionic dyes adsorption. The studies of adsorbing various cationic dyes from solution on MOFs are less reported. Methylene blue (MB) and malachite green (MG) are the typical representatives of cationic dyes, and their chemical structures were shown in Figure 1. MB was widely used to dye wood and polyamide fiber. However, MB is a toxic chemical and can produce health risks, such as nausea, vomiting, excessive perspiration, dyspnea, and gastritis when organisms exposure it for a long time. Malachite green (MG) was also extensively applied in various industries, for example, aquaculture, fish hatchery, and antifungal therapy of animal husbandry. MG has also been proved to be a dangerous substance with high toxicity and can induce cancer, abnormality, and respiratory disease. Thus, it is very meaningful to remove MB and MG dyes from aqueous solution.

In this study, based on preparation of MIL-53(Al) and MIL-53(Al)-NH₂, the two adsorbents were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). The selective adsorption of MIL-53(Al)-NH₂ for MG and MB was studied to compare with MIL-53(Al)-NH₂, which were synthesized by a hydrothermal method reported in the literature. First, Al(NO₃)₃·9H₂O (1.125 g) and NH₂-BDC (0.56 g) were dissolved in deionized water (20 mL) and DMF (80 mL), respectively, and the two separate solutions were mixed together quickly into a 200 mL Teflon-lined steel autoclave. Then, the autoclave was placed in an oven at 150 °C for 24 h. After the reaction, the white or yellow solid product was isolated by filtration. The samples were immersed in DMF and boiled for 8 h to remove the remaining water molecules or unreacted ligands trapped in the pores. Finally, all the products were separated by filtration and washed with acetone. The resulting white solid was dried overnight in a vacuum oven at 30 °C, for the further applied. The MIL-53(Al) was synthesized by a hydrothermal method as described in ref 24, in which terephthalic acid, Al(NO₃)₃·9H₂O, and deionized water were used in the process of preparation.

2.2. Preparation of MIL-53(Al)-NH₂ and MIL-53 (Al). The sorbents used in this study were metal–organic framework MIL-53(Al)-NH₂ and MIL-53(Al), which were synthesized by a hydrothermal method reported in the literature. First, Al(NO₃)₃·9H₂O (1.125 g) and NH₂-BDC (0.56 g) were dissolved in deionized water (20 mL) and DMF (80 mL), respectively, and the two separate solutions were mixed together quickly into a 200 mL Teflon-lined steel autoclave. Then, the autoclave was placed in an oven at 150 °C for 24 h. After the reaction, the white or yellow solid product was isolated by filtration. The samples were immersed in DMF and boiled for 8 h to remove the remaining water molecules or unreacted ligands trapped in the pores. Finally, all the products were separated by filtration and washed with acetone. The resulting white solid was dried overnight in a vacuum oven at 30 °C, for the further applied. The MIL-53(Al) was synthesized by a hydrothermal method as described in ref 24, in which terephthalic acid, Al(NO₃)₃·9H₂O, and deionized water were used in the process of preparation.

2.3. Adsorption Experiments. An aqueous stock solution of MB or MG (5 mg L⁻¹) was prepared by dissolving MB or MG in deionized water (relatively high concentration was used for adapting to high adsorption capacity of MIL-53(Al)-NH₂). Before adsorption, the adsorbents were dried overnight under vacuum at 100 °C and were kept in a desiccator. In the absorption kinetics experiment, an exact amount of the adsorbents (10 mg) was put in the aqueous MB or MG dye solutions (100 mL). The dye solutions containing the adsorbents were mixed well with stirring in HZQ-QS oscillator at 160 rpm. After adsorption for a predetermined time, the solution was separated from the adsorbents with a syringe filter (PTFE, hydrophobic, 0.45 μm), and the dye concentration was calculated. To get the adsorption isotherm, 10 mg of adsorbents were added into different concentration solutions of MB or MG dye (100 mL) at 288, 298, and 308 K. Then, the maximum adsorption capacity was calculated using the Langmuir adsorption isotherm after adsorption equilibrium. To determine the adsorption capacity at various pH, the pH of the dye solutions was adjusted with 0.1 M HCl or 0.1 M NaOH aqueous solution. At the end of the experiment, adsorbents were recycled by washing thoroughly with methanol and 60% acetonitrile solution and stirring by magnetic stirring.

2.4. Characterization and analysis. The crystalline structure and composition of the MIL-53(Al)-NH₂ and MIL-53(Al) were identified, respectively, by a D/max-III X-ray diffractometer (Shimadzu, Japan) with Cu Kα X-rays as target at the scanning range of 5°–60° at the scanning speed of 6°/min. Fourier transform infrared spectroscopy (FT-IR) were taken with a Germany Bruker Company EQUINOX55, using KBr pellet pressing method at the scanning wavelength range of 400–4000 cm⁻¹. The morphologies of MIL-53(Al)-NH₂ and MIL-53 (Al) were observed with a scanning electron microscope (SEM) (model EPMA-8705QH2, Shimadzu Co., Japan). Before SEM measurement, the samples were dispersed on monocrystalline wafer and then were treated by spray-gold for 45 s. Thermogravimetric analysis of MIL-53(Al)-NH₂ was carried out using a Rigaku TG-8120, scanning from 25 to 700 °C with the heating rate 4 °C/min under the protection of nitrogen. The concentration of MB and MG were measured by spectrophotometry using a UV-1800 spectrophotometer (Shimadzu, Japan). Before adsorption measurement, the samples were dispersed on monocrystalline wafer and then were treated by spray-gold for 45 s. Thermogravimetric analysis of MIL-53(Al)-NH₂ was carried out using a Rigaku TG-8120, scanning from 25 to 700 °C with the heating rate 4 °C/min under the protection of nitrogen.
using a UV–vis spectrophotometer (Shimadzu, UV-1800) in absorbances of 663 and 619 nm, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of Adsorbents. FT-IR spectrum of MIL-53(Al)-NH₂ and MIL-53(Al) were shown in Figure 2. For MIL-53(Al), the strong absorption peak at 1690 cm⁻¹ attributed to −C=O stretching vibration; the strong absorption peaks at 1596 and 1510 cm⁻¹ might be attributed to dissymmetry stretching vibration νasym (CO₂⁻) of −(O−C−O)−; the absorption peaks at 1510 and 1416 cm⁻¹ should be attributed to symmetry stretching vibration νsym (CO₂⁻) of −(O−C−O)−; the absorption peak about 3424 cm⁻¹ might be attributed to −OH stretching vibration. In the FT-IR spectrum of MIL-53(Al)-NH₂, a series of peaks at the range of 1400–1700 cm⁻¹ were involved in carbonyl groups that coordinated with A1³⁺ and the carbonyl groups of DMF molecule which adhered to channels of the sorbent. Specifically, the absorption peaks at 1400 and 1440 cm⁻¹ should be the symmetry stretching vibration of carbonyl group; the peaks at 1500 and 1600 cm⁻¹ might be the dissymmetry stretching vibration of the carbonyl group, while the absorption peak at 1670 cm⁻¹ was the stretching vibration of carbonyl group in DMF which were trapped in the pores of adsorbent; the peaks at 3380 and 3500 cm⁻¹ were −NH₂ stretching vibration.

Figure 3 showed the XRD patterns of MIL-53(Al)-NH₂ and MIL-53(Al). It can be seen that the XRD patterns for the prepared samples are similar to that reported in literature. However, the intensities of MIL-53(Al)-NH₂ and MIL-53(Al) are different should be attributed to the volume ratio of H₂O and DMF during the preparation process. In this work, it is different that the solvents of the two adsorbents during the preparation process, resulting in the difference of intensities.

Figure 4 showed the SEM images of MIL-53(Al) and MIL-53(Al)-NH₂ samples. The morphology of as-synthesized MIL-53(Al) was consistent with the SEM image which was published in literature. In Figure 4a, it can be found that some long strips with 5 μm size of MIL-53(Al) crystals were clearly visible, and most of them were octahedral shape, which were uniformly dispersed and were not aggregation. In Figure 4b, the surface of MIL-53(Al)-NH₂ seemed much rougher than that of MIL-53(Al), and the length of MIL-53(Al)-NH₂ particle was shortened to 100 nm. Generally, in aqueous solution, the molecule interactions of ligands will wake or even disappear, and the deprotonated effect of the ligands can be enhanced so that the growths of the crystal surface were promoted. Meanwhile, the agglomerations of the nanoparticles were prevented from the dispersion effect induced by water molecules. In this case, the specific surface area was increased sharply, which made the crystal into long strips. However, for the preparation of MIL-53(Al)-NH₂, the reaction solvent was composed of a large number of DMF and a small amount of water (DMF:H₂O = 4:1), the decrease of the amount of water will decrease the deprotonation rate of the ligands, because of the ability of DMF molecule to capture the carboxyl proton is stronger than the water molecule, which promoted the nucleation rate and the crystal particle size.

Thermogravimetric analysis of the adsorbent sample was showed in Figure 5. The thermal stability of the MIL-53(Al) from 30 to 600 °C depicts the initial weight loss at 100 °C due to the dehydration process and corresponds to the removal of water molecules. The second weight loss at 520 °C corresponds to the collapse of MIL-53(Al) framework, indicating that the MIL-53(Al) framework is thermally stable up to 520 °C. It can also be seen in Figure 5 for the MIL-53(Al)-NH₂ that a small weight loss (2–3% weight loss) was appeared below 80 °C, which also be attributed to the water molecules evaporation from surface of the sample. The first big weight loss occurred between 80 and 280 °C with 22–24% weight loss which might be the result of the releasing of DMF from the pore of adsorbents; the second big weight loss took place at around 410 °C was attributed to the destruction of the framework structure, which meant that the framework of MIL-53(Al)-NH₂ could be stable enough until 410 °C if the solvent molecules were
removed completely. As the temperature increased, the weight loss of framework structure accelerated; the reason might be the burning of 2-aminoaterephalic acids released after the collapsing.

3.2. Adsorption Kinetics for MB and MG Dyes on MIL-53(Al)-NH2. The adsorption performance of MIL-53(Al) and MIL-53(Al)-NH2 for MB and MG was studied. Figure 6 showed that the adsorbed quantities (qt) of MB and MG dyes on MIL-53(Al) and MIL-53(Al)-NH2 related to time t, which can be calculated with the following relationship:

\[ q_e = \frac{V(C_0 - C_e)}{M} \]  \hspace{1cm} (1)

\[ q_t = \frac{V(C_0 - C_t)}{M} \]  \hspace{1cm} (2)

where \( q_e \) and \( q_t \) was the amount (mg/g) of dye adsorbed on the adsorbents at equilibrium and time t, respectively. \( C_0, C_e, \) and \( C_t \) were the liquid-phase concentrations (mg/L) of dye at initial, equilibrium, and time t, respectively. V (L) and M (g) were the volume (L) of the dye solutions and the mass of the adsorbents, respectively.

As can be seen in Figure 6, the adsorption capacity of MIL-53(Al) and MIL-53(Al)-NH2 for both MB and MG increased rapidly at the first stage and then gradually slowed down and reached adsorption equilibrium with the contact time increasing. However, the \( q_e \) values of MB and MG were quite different. For MIL-53(Al)-NH2, the \( q_e \) values of MB and MG were 45.2 and 37.8 mg/g, respectively, whereas for MIL-53(Al), the \( q_e \) values only 3.6 and 2.9 mg/g, respectively. Obviously, the different results were due to the introduction of −NH2. Additionally, according to the adsorption kinetics in Figure 6, most of dyes were adsorbed within the first 50 min, which meant that the adsorption of cationic dyes on MIL-53(Al)-NH2 were effective and rapid. It is possible because the initial concentrations of dyes were big enough to provide the driving force to overcome the resistances of mass transfer between the aqueous phases and the solid phase. (The adsorption kinetics models for MB and MG dyes on MIL-53(Al)-NH2 in detail were in Supporting Information.)

3.3. Adsorption Isotherm for MB and MG on MIL-53(Al)-NH2. Figure 7a and b gave the adsorption isotherms of MB and MG on MIL-53(Al)-NH2 at 35 °C after a period of time (24 h). The adsorption capacities of MIL-53(Al)-NH2 to the dyes were considerably larger than MIL-53(Al) under the same experimental conditions, indicating that the introduction of −NH2 strengthened tremendously the adsorption capacities of MIL-53(Al)-NH2 for cationic dyes.

The Langmuir isotherm is based on the assumption that adsorption process is monolayer, and this made it possible to estimate the saturated adsorption capacity. Therefore, Langmuir isotherm was used to analyze the adsorption isotherms to further evaluate the isothermal adsorption of cationic dyes on MIL-53(Al)-NH2, and the Langmuir model was based on eq 3:

\[ \frac{C_e}{q_e} = \frac{1}{K_L q_{\text{max}}} + \frac{C_e}{q_{\text{max}}} \]  \hspace{1cm} (3)

where \( q_{\text{max}} \) (mg/g) was the maximum adsorption capacity; \( K_L \) was the Langmuir constant that was related to the adsorption binding energy. Generally, the larger the \( K_L \) value, the more favorable the adsorption process. \(^{28}\) The fitting results of Langmuir isotherm model to the adsorption data of MB and MG on MIL-53(Al)-NH2 were given in Figure 7a and b, respectively. The adsorption isotherm constants, such as \( q_{\text{max}} \) and \( K_L \), at different temperatures were listed in Table 1. It can be found that all of the \( R^2 \) values of Langmuir isotherm model were above 0.99, and the \( q_{\text{max}} \) and \( K_L \) values increased with the temperature increasing, which demonstrated that Langmuir isotherm model can explain the adsorption isotherm data and that the increased temperature benefited absorption of MB and MG.
MG on MIL-53(Al)-NH₂. In other words, the adsorption processes were endothermic reaction.

Besides, the adsorption isotherm can also be fitted with the Freundlich isotherm model (eq 4).28

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

where \( K_F \) indicated Freundlich constant and \( 1/n \) was the heterogeneous factor which was related with heterogeneity of the surface of absorbent. Parameter \( n \) represented the strength of the driving force of adsorption. The larger value of \( n \) meant that it was much more feasible to the adsorption. Freundlich isotherm assumed that there are monolayer and multilayer adsorption in an adsorption system. Thus, both chemical and physical adsorption should be considered when the model was used. The adsorption data of MB and MG on MIL-53(Al)-NH₂ were fitted to Freundlich isotherm model, which were given in Figure 7a and b, respectively, and the fitting curves with Langmuir model and Freundlich model for the adsorption of MB and MG.

Table 1. Adsorption Isotherm Parameters Derived from the Langmuir Model and the Freundlich Model at Different Temperatures

<table>
<thead>
<tr>
<th>dyest</th>
<th>temp.(°C)</th>
<th>( q_m (\text{mg g}^{-1}) )</th>
<th>( K_L (\text{L mg}^{-1}) )</th>
<th>( R^2 )</th>
<th>( K_F (\text{mg g}^{-1}) )</th>
<th>( n (\text{g L}^{-1}) )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB</td>
<td>15</td>
<td>167.0</td>
<td>0.5980</td>
<td>0.9906</td>
<td>57.33</td>
<td>2.479</td>
<td>0.9722</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>188.6</td>
<td>0.6680</td>
<td>0.9913</td>
<td>68.41</td>
<td>2.518</td>
<td>0.9749</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>208.3</td>
<td>0.7080</td>
<td>0.9933</td>
<td>78.32</td>
<td>2.596</td>
<td>0.9784</td>
</tr>
<tr>
<td>MG</td>
<td>15</td>
<td>141.0</td>
<td>0.2340</td>
<td>0.9774</td>
<td>30.34</td>
<td>1.272</td>
<td>0.9726</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>152.1</td>
<td>0.2850</td>
<td>0.9987</td>
<td>35.87</td>
<td>1.284</td>
<td>0.9725</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>164.9</td>
<td>0.3090</td>
<td>0.9978</td>
<td>39.65</td>
<td>1.287</td>
<td>0.9768</td>
</tr>
</tbody>
</table>

Table 2. Thermodynamic Parameters for the Adsorption of Methylene Blue and Malachite Green onto the MIL-53(Al)-NH₂

<table>
<thead>
<tr>
<th></th>
<th>( \Delta H^0 ) (kJ mol⁻¹)</th>
<th>( \Delta S^0 ) (J mol⁻¹K⁻¹)</th>
<th>( \Delta G^0 ) (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB</td>
<td>27.17</td>
<td>189.9</td>
<td>-27.51</td>
</tr>
<tr>
<td></td>
<td>-25°C</td>
<td>-29.40</td>
<td>-31.30</td>
</tr>
<tr>
<td>MG</td>
<td>13.24</td>
<td>131.1</td>
<td>-24.51</td>
</tr>
<tr>
<td></td>
<td>25°C</td>
<td>-25.82</td>
<td>-27.13</td>
</tr>
</tbody>
</table>

The enthalpy change (\( \Delta H^0 \)) in Table 2 was positive, which suggested that the adsorption process was an endothermic reaction, which was consistent with the fact that adsorption capacity was increasing with increasing of temperature. Generally, in the case of without other interference factors, the adsorption is an exothermic reaction; i.e., the adsorption capacity is decreased with increased of the temperature. In this
work, the adsorption of MB and MG on MIL-53(Al)-NH₂ was an endothermic reaction ($\Delta H^\circ < 0$); the reason was due to the adsorbed water molecules on the MIL-53(Al)-NH₂ must first be desorbed before the cationic dyes were adsorbed. However, desorption was an endothermic reaction, while the adsorption is an exothermic reaction. Since the molar volume of water molecule is much smaller than that of dyes, lots of water molecules should be desorbed before a cationic dye molecule is absorbed by adsorbent. Thus, the quantity of heat absorbed by desorption of water molecules was greater than that released from the adsorption of dyes, resulting that the dye adsorption over MIL-53(Al)-NH₂ was an endothermic reaction. According to the report in literature, the $\Delta G^\circ$ of physical adsorption is usually $-20$ to $-80$ kJ mol$^{-1}$, and chemical adsorption is usually $-400$ to $-80$ kJ mol$^{-1}$. As shown in Table 2, $\Delta G^\circ$ was $-31.3$ to $-25.8$ kJ mol$^{-1}$, indicating that the adsorption was not a single physical or chemical adsorption, but there were relationship with the two types. Negative values of $\Delta G^\circ$ indicated that the adsorption process was a spontaneous and irreversible process at all the studied temperatures. The absolute values of $\Delta G^\circ$ are gradually increased with increased of the temperature, demonstrating that the higher the temperature, the much larger the spontaneous tendency on adsorption process. The total entropy change of liquid phase adsorption process is the sum of solute adsorption (along with entropy decrease, i.e., freedom decrease) and solvent desorption (resulting in entropy increase, i.e., freedom increase), which depends on the strength of interaction between solute/solvent and the surface of solid as well as the size of their volume. The $\Delta S^\circ$ values in Table 2 were positive, which indicated that the adsorption of MB and MG dyes on MIL-53(Al)-NH₂ were related with the enthalpy change and entropy change. Because the water molecules desorbed from MIL-53(Al)-NH₂ were much more than dyes molecules adsorbed on MIL-53(Al)-NH₂, the desorption of solvent made great contribution to the entropy change of system; thus, the adsorption results showed an entropy-increasing process.

**3.5. Effect of pH.** The initial pH of the dye solution was an important parameter, which controlled the adsorption process in particularly the adsorption capacity. Because of the hydrolysis of MG dye in basic solution, the influence of pH on the adsorption capacity of malachite was not evaluated further. In this work, the $q_e$ of MB adsorption at room temperature (20 °C) on the MIL-53(Al)-NH₂ at various pHs (pH 2–8) were measured after equilibration. The effect of pH on $q_e$ of MB adsorption on MIL-53(Al)-NH₂ was shown in Figure 8a. The concentration of MB dye was 5 mg L$^{-1}$. The adsorbed amounts were found to increase with increasing pH values from 2.0 to 7.0. However, when the pH values were 7.0–12, the adsorbed amounts were decreased; when the alkalinity enhanced to pH value was 12, the amount of adsorption was only 10.48 mg L$^{-1}$. The reason for above phenomenon may be, in the range of pH 2.0–7.0, a hydrogen bond controlled adsorption of MB/MG on MIL-53(Al)-NH₂. However, in low pH solution, a hydrated proton (H$_3$O$^+$) can be combined with amino groups on ligand to form $-$NH$_3^+$, which restrained the hydrogen bond interaction between MIL-53(Al)-NH₂ and dyes to some extent. In addition, hydrated proton (H$_3$O$^+$) competed with cationic MB for the AIO$_2$(OH)$_2$ sites of MIL-53(Al)-NH₂, resulting in the decrease of the adsorbed amounts. Therefore, $q_e$ following small rises. In the range of pH 7.0–12.0, although the hydrogen bond interaction between $-$NH$_2$ modified MOFs and dyes continues to play a part, the structure of MIL-53(Al)-NH₂ collapsed in alkaline solution, resulting in the dramatic decrease of the $q_e$ value.

The zeta potential of the absorbent was the one of the factors which might be an important influencing factor on the adsorption capacity. The zero point charge (pH$_{PZC}$) was defined as the point that the zeta potential on the surface of adsorbent was zero. In aqueous solutions, when pH < pH$_{PZC}$, the surface charge of a solid was positive, while it is negative when pH > pH$_{PZC}$. The pH$_{PZC}$ of MIL-53(Al) and MIL-53(Al)-NH₂ were drawn in Figure 8b. In the range of the pH experiment, the MIL-53(Al) surface carried negative charge, which should benefit the adsorption of cationic dyes on MIL-53(Al) through electrostatic interaction. But the experimental result showed that the $q_e$ of the two dyes on MIL-53(Al) is extremely low (Figure 7), which might imply that electrostatic interaction is not the major way to control the adsorption capacity of MIL-53(Al) to cationic dyes. For MIL-53(Al)-NH₂, according to the zeta potential of MIL-53(Al)-NH₂ (pH$_{PZC}$ = 10.5) (Figure 8b), when pH 2–10, the surface charge of MIL-53(Al)-NH₂ was positive. Due to MB was a positively charged cationic dye, the electrostatic repulsion between MB and MIL-53(Al)-NH₂ should make the adsorbed amounts of MB be decreased. But in fact, the $q_e$ value of MB was increasing at pH 2–7. It meant that there was the other way (such as hydrogen bond interaction) to control the adsorption of MB on MIL-53(Al)-NH₂. However, when the pH > 8.0, the zeta potential of MIL-53(Al)-NH₂ decreased, and then, the negative charge

Figure 8. (a) Effect of solution pH on the amount of adsorbed methylene blue and malachite green over MIL-53(Al)-NH₂; (b) the pH effect on the zeta potential of MIL-53(Al)-NH₂.
appeared at pH 10.5. In this case, the MIL-53(Al)-NH₂ should exhibit strong adsorption capacity to the positively charged cationic dye through electrostatic attraction. But in fact, the qₑ of MB decreased dramatically. The reason for this phenomenon was that the structure of MIL-53(Al)-NH₂ may collapse in strong basic solution and MB may be turned into other compound by hydrolysis in basic medium. Furthermore, the introduction of amino group made the pHₚₑ of MIL-53(Al)-NH₂ migrated to the basic zone (pH = 10.5). The reason for above phenomenon might be hydrated proton (H₂O⁺) entered the interior of MIL-53(Al)-NH₂ through the breathing effect. Then, the hydrated proton was captured by the amino group to form eventually the −NH₃⁺ group, resulting in positive charge inside the adsorbent. In this case, in order to neutralize excess H₂O⁺, the pHₚₑ of MIL-53(Al)-NH₂ has to be migrated the basic zone to gain −OH⁻.

3.6. Adsorption Mechanism. According to the analysis of adsorption kinetics, isotherm, and thermodynamics, it can be considered that the adsorption of MB and MG was related to the chemical action between cationic dyes and MIL-53(Al)-NH₂. In general, the variation of solution pH was related to the way of the interaction (electrostatic attraction or repulsion) between adsorbent and adsorbate. However, the predicted interaction was inconsistent with the experimental result. Therefore, there must be some other way to control the adsorption of MB and MG on MIL-53(Al)-NH₂ besides electrostatic interaction. The research indicated that the 3D framework structure of MIL-53(Al) can automatically adjust the shape and size of porous channel when it absorbed some polar molecules and hydrocarbon molecules. This adjustment was called the “breathing” effect of framework, i.e., the large pores (lp) where the guest molecules were removed turned into narrow pores (np) when they adsorbed some guest molecules, and then, the np structures turned back into lp forms as the cover degree increased. Generally, the framework structure was not destroyed in the process of transformation. According to the discussion and the zeta potential, the adsorption mechanism can be presumed as follows. The negative charge of MIL-53(Al) (Figure 8b) attracted lots of hydrated proton (H₂O⁺) onto its surface in aqueous solution. Although the kinetic diameter of H₂O⁺ may be larger than the pore of MIL-53(Al), H₂O⁺ can entered into the structure of MIL-53(Al) through the breathing effect, while the volume of MB or MG was too large to enter into the structure of MIL-53(Al), even if there was a breathing effect. Moreover, the surface negative charge of MIL-53(Al) was neutralized by H₂O⁺, which made the electrostatic interaction between cationic dyes and MIL-53(Al) weak, resulting in the qₑ of MB or MG being extremely low. For MIL-53(Al)-NH₂, due to the influence of −NH₂ in MIL-53(Al)-NH₂, the qₑ of MB or MG decreased to 55% and 57% at the second recycle time, respectively. Although the adsorption efficiency was in sharp reduction, the washing method for removal of MB and MG in the used MIL-53(Al)-NH₂ was feasible and effective. There was no obvious reduction in adsorption capacity with increasing of the recycle times. After the fourth regeneration, the adsorption capacity for MB and MG were 45% and 43% of fresh MIL-53(Al)-NH₂, respectively. Based on the possible mechanism in Figure 9, the interaction between cationic dyes and MIL-53(Al)-NH₂ was hydrogen bonding which belonged to chemical interaction. That is to say, once MB/MG is absorbed by MIL-53(Al)-NH₂, it is difficult for them to separate by simple physical washing method. More severe method was needed to break the combination between hydrogen bonding, π−π stacking interaction was much smaller in this work, which resulted in that the adsorption capacity of cationic dyes on MIL-53(Al) is extremely low. In conclusion, the possible mechanism of MB/MG adsorption on MIL-53(Al)-NH₂ may be explained by Figure 9.

3.7. Regenerability of MIL-53(Al)-NH₂. In this study, the used adsorbent was regenerated with methanol and 60% acetonitrile as solvent, and the regenerated MIL-53(Al)-NH₂ was used to remove MB and MG from aqueous solution. The effect of the regeneration on cycle times was shown in Figure 10.

![Figure 9](image1.png)

**Figure 9.** Possible mechanism of methylene blue or malachite green adsorption on MIL-53(Al)-NH₂.

![Figure 10](image2.png)

**Figure 10.** Effect of recycle times of MIL-53(Al)-NH₂ on the methylene blue and malachite green adsorption capacity (room temperature, C₀ = 5 mg/L, M = 10 mg, V = 100 mL, contact time = 300 min).

It can be seen in Figure 10, in comparison with fresh MIL-53(Al)-NH₂, the qₑ of MB and MG decreased to 55% and 57% at the second recycle time, respectively. Although the adsorption efficiency was in sharp reduction, the washing method for removal of MB and MG in the used MIL-53(Al)-NH₂ was feasible and effective. There was no obvious reduction in adsorption capacity with increasing of the recycle times. After the fourth regeneration, the adsorption capacity for MB and MG were 45% and 43% of fresh MIL-53(Al)-NH₂, respectively. Based on the possible mechanism in Figure 9, the interaction between cationic dyes and MIL-53(Al)-NH₂ was hydrogen bonding which belonged to chemical interaction. That is to say, once MB/MG is absorbed by MIL-53(Al)-NH₂, it is difficult for them to separate by simple physical washing method. More severe method was needed to break the combination between...
MIL-53(Al)-NH$_2$ and dyes. According to the result of thermogravimetric analysis (Figure 5), MIL-53(Al)-NH$_2$ begins to decompose at approximately 450 °C, while the decomposition of dyes happen at 300–400 °C. Thus, the limited calefaction may be an efficient method to remove dyes from MIL-53(Al)-NH$_2$.

### 3.8. Practical Application of MIL-53(Al)-NH$_2$

Because of the widely application of MB and MG in mariculture, it is meaningful to study the adsorption of MB and MG on MIL-53(Al)-NH$_2$ in seawater. For this purpose, we used the seawater (salinity 35‰) that was purchased from Seafood Market to prepare MB (5 mg/L) and MG (5 mg/L) solution. In the batch adsorption experiment, an exact amount of the MIL-53(Al)-NH$_2$ (10 mg) was put in the MB/MG dye solution (100 mL). Then, the dye solution containing the adsorbents was mixed well with stirring for 300 min at room temperature. Finally, the amounts of MB and MG adsorbed on the MIL-53(Al)-NH$_2$ were 45.97 mg/g and 38.09 mg/g, respectively, and this was similar to the result of previous discussion, indicating that MIL-53(Al)-NH$_2$ can be used for adsorptive removal of MB and MG in mariculture water.

### 4. CONCLUSION

Prepared MIL-53(Al)-NH$_2$ can remove MB and MG in aqueous solution with a large adsorption capacity. The large adsorption capacity of cationic dyes on MIL-53(Al)-NH$_2$ might be attributed to chemical interaction, such as hydrogen bonding interaction and π−π stacking interaction. The study of adsorption kinetics demonstrated that the kinetic data fitted well with pseudo second-order kinetic model than pseudo first-order model. The adsorption isotherms were described by Langmuir and Freundlich isotherm models. Both Langmuir and Freundlich isotherm models could explain the experimental data, though the Langmuir model was better than the Freundlich model. The Gibbs free energy showed that the adsorption process was spontaneous and accompanied by endothermic process. The adsorption of MB and MG on MIL-53(Al)-NH$_2$ might be attributed to the enthalpy change and entropy change which promoted adsorption process together. Furthermore, MIL-53(Al)-NH$_2$ could be regenerated with methanol and 60% acetonitrile solution. After the fourth regeneration, MIL-53(Al)-NH$_2$ reserved certain adsorption ability. The experiment of adsorptive removal of dyes from seawater indicated that MIL-53(Al)-NH$_2$ might have potential applications. (The adsorption comparison of activated carbon and MOFs for dyes was in the Supporting Information.)

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.5b00692.

Adsorption kinetics for MB and MG on MIL-53(Al)-NH$_2$, adsorption comparison of activated carbon, and MOFs (PDF)

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### Notes

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### REFERENCES


