Adsorption behavior of methyl orange onto an aluminum-based metal organic framework, MIL-68(Al)

Shi-chuan Wu, Xia You, Cao Yang and Jian-hua Cheng

ABSTRACT

MIL-68(Al), a powdered aluminum-based metal organic framework (MOF), was synthesized and used to explore its adsorption behavior toward methyl orange (MO). The adsorption isotherm, thermodynamics, kinetics, and some key operating factors as well as changes in the material’s structure were investigated. The adsorption isotherm conformed to the Langmuir isotherm model and the maximum equilibrium adsorption capacity was 341.30 mg g⁻¹. Thermodynamic data demonstrated that the adsorption process was spontaneous, endothermic and showed positive entropy. For kinetics, the process of MO adsorption onto MIL-68(Al) was more suitably described by a pseudo-second-order model. Electrostatic and hydrogen-bonding interactions contributed to dye adsorption, with electrostatic interactions considered to be the principal binding force between adsorbent and adsorbate. Furthermore, MIL-68(Al) maintained a stable structure after adsorption. From these results, MIL-68(Al) was suggested here to be a stable MOF adsorbent for removing MO from aqueous solution.

Key words | adsorption, dye, methyl orange, MIL-68(Al), MOFs, water treatment

INTRODUCTION

Currently, synthetic dyes, which are commonly used in the textile, paper, printing, leather, and plastic industries, have received great attention because of considerable discharges of dye-containing wastewater into the environment (Crini 2006). Dyes generally degrade poorly in the environment because of their anti-photolysis and oxidation resistance (Hameed & Rahman 2008; Chen et al. 2010), and even low dye-concentration wastewater is conspicuous and undesirable. Moreover, the majority of dyes have been confirmed to be toxic and carcinogenic (Crini 2006; Mittal et al. 2007; Hameed & Rahman 2008; Chen et al. 2010). For these reasons, dye removal from wastewater has become an urgent problem requiring solution.

Over the past few decades, many techniques, including chemical oxidation (Zanjanchi et al. 2011), coagulation/floculation (Zahrim et al. 2011), filtration (Nourouzi et al. 2011), and adsorption (Chan et al. 2009), have been investigated for treating dye wastewater. Among these technologies, adsorption is recognized as a superior method because it is economic, efficient, simple, and feasible (Wang et al. 2005). To date, activated carbon (Pendleton & Wu 2005), zeolite (Faki et al. 2008), fly ash (Pengthamkeerati et al. 2008), clay (Ai et al. 2011), and polymers (Ai et al. 2010) have been selected as adsorbents for dye removal from water. However, as synthetic dyes have become increasingly complex, it is increasingly necessary to exploit the novel adsorbent materials possessing superior stability and adsorption capacities.

Recently, metal organic frameworks (MOFs) have attracted much attention for their high surface areas and low crystal densities as well as the tenability of pore structure (Ferey et al. 2011; Kitagawa & Matsuda 2007; Czaja et al. 2009; Henninger et al. 2009). The application of MOFs has become an intense research topic in liquid adsorption and separation (Xie et al. 2014; Zhao et al. 2014; Tehrani & Zare-Dorabei 2016). Haque et al.’s study (Haque et al. 2010) has proven that MOF channel sizes and electrostatic effects have an important impact on methyl orange (MO) adsorption and removal from water. Haque et al. (Haque et al. 2011) found that the charged properties of the framework of MOF-235 plays a major role in the dye removal process. In addition, many other MOFs,
including MIL-100(Fe) (Huo & Yan 2012), MIL-68(In) (Jin et al. 2015), MIL-101(Fe), and MIL-101(Cr) (Tong et al. 2013), have also been applied in dye removal and exhibit excellent absorption performance. In short, MOFs have been shown to have promising potential in applications for dye wastewater treatment. However, MOF stability issues must be considered.

Liu et al. (Xie et al. 2014; Han et al. 2015) have reported that MIL-68(Al) possesses great water stability. Thus, it is considered as a good candidate for wastewater treatment applications. MIL-68(Al), first synthesized by Férey’s group, is constructed from the infinite chains of corner-sharing AlO4(OH)2 octahedral structures linked via the terephthalate ligands. These materials possess three-dimensional networks with triangular and hexagonal channels, with opening diameters of 6.0–6.4 Å and 16–17 Å (Barthelet et al. 2004; Yang et al. 2012), respectively. Meanwhile, MO, a well-known azo/anionic dye, was chosen here as a model adsorbate. According to a literature survey, there have been no reports to date regarding MIL-68(Al) use in MO adsorption, the solution was separated using 0.22 μm membrane filters (Millipore Corp.). The resulting purple solid was then washed three times with 50 mL of DMF at RT to remove residual reactants, producing a mauve, solid, powder product. For later use, the product was activated by quadruple extraction with 50 mL of methanol to remove organics inside the substrate’s pores and then the product calcined under 573 K for 5 h.

Characterization of the MIL-68(Al)

MOF products were analyzed by X-ray diffraction (XRD) on an Empyrean Multi-Purpose Research X-ray diffractometer XRD (PANalytical B.V., The Netherlands) using Cu-Kα radiation. Fourier transform-infrared (FT-IR) spectra were obtained in a Thermo-Nicolet spectrometer (CCR-1; Thermo Nicolet Corp., Madison, WI, USA). Data from nitrogen adsorption-desorption isotherms and Brunauer-Emmett-Teller (BET) surface areas were assessed in a surface characterization analyzer from Micromeritics 3Flex (Micromeritics Instrument Corp., Norcross, GA, USA) at 77 K. Before analyses, samples were degassed at 423 K under vacuum for 12 h. Zeta potentials were measured with a Zetasizer Nano ZS90 (Malvern Instruments Ltd, Worcestershire, UK) at 298 K. Data from X-ray photoelectron spectroscopy (XPS) spectra were obtained using an ESCALAB250Xi spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) with an Al Kα source (1,361 eV). The internal reference was the C 1s line at 284.6 eV. Sample morphologies were observed on a scanning electron microscope (SEM; Carl Zeiss Microscopy, GmbH, Jena, Germany).

Adsorption batch experiments

During all experiments, the adsorbent dosage (m = 20 mg), MO volume (C0 = 100 mL), flask volume (250 mL), and shaking speed (150 rpm) were held constant. Dye concentration (C0 = 1–100 mg L−1), pH (pH = 2–11), temperature (T = 298–308 K), and reaction time (t = 0–720 min) were designated according to experimental requirements. After adsorption, the solution was separated using 0.22 μm membrane filters (Millipore Corp.). Thereafter, dye concentrations were calculated using a UV-Vis standard calibration curve (Figure S1, Supplementary material, available with the online version of this paper) for A464 with a decreased to 0.0350 A464. The resulting purple solid was then washed three times with 50 mL of DMF at RT to remove residual reactants, producing a mauve, solid, powder product. For later use, the product was activated by quadruple extraction with 50 mL of methanol to remove organics inside the substrate’s pores and then the product calcined under 573 K for 5 h.

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Materials and methods

Materials

Aluminum chloride hexahydrate (AlCl3·6H2O, 99.9%), terephthalic acid (H2BDC, 98%), and calconcarboxylic acid (98%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd (Shanghai, China). MO (99%), methanol (99%), hydrochloric acid (37%), and sodium hydroxide (98%) were obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China). All chemical reagents were analytical grade. Deionized water (18.2 MΩ cm) was produced from a water purification system (EMD Millipore Corp., Merck KGaA, Darmstadt, Germany) and used in all experiments.

Preparation of MIL-68(Al)

MIL-68(Al) was synthesized and activated on the basis of an open BASF patent (Schubert et al. 2013). Terephthalic acid (5.0 g, 30 mmol), AlCl3·6H2O (4.88 g, 20 mmol) and calconcarboxylic acid (3.5 g, 7.5 mmol) were added to a 500 mL glass flask and dissolved in 300 mL of dimethylformamide (DMF; 248.0 g, 3,891 mmol) and the mixture was heated at 403 K with stirring for 18 h. Next, the mixture was cooled gradually to room temperature (RT) and filtered. The resulting purple solid was then washed three times with 50 mL of DMF at RT to remove residual reactants, producing a mauve, solid, powder product. For later use, the product was activated by quadruple extraction with 50 mL of methanol to remove organics inside the substrate’s pores and then the product calcined under 573 K for 5 h.

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Hach DR 5000 UV-Vis spectrophotometer (Hach Co., CO, USA), and dye concentrations \(>15 \text{ mg L}^{-1}\) diluted before analysis. Final results were determined by the average of triplicate parallel experiments. Dilute solutions of NaOH and HCl were used to adjust MO solution pHs.

The equilibrium adsorption amounts for MO, \(q_e\) (mg g\(^{-1}\)), were calculated from Equation (1):

\[
q_e = \frac{(C_o - C_e)V}{M}
\]

where \(C_o\) and \(C_e\) (mg g\(^{-1}\)) are the MO concentrations in the initial and equilibrium states, respectively; \(V\) (L) is the dye solution volume; and \(M\) (g) is the mass of MIL-68 (Al) used.

Adsorption isotherms were analyzed using the Langmuir isotherm model (Mittal et al. 2010), expressed as Equation (2):

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}
\]

in which \(q_m\) is the maximum adsorption capacity (mg g\(^{-1}\)) with the highest dye concentration used in the experiment and \(K_L\) is the Langmuir constant (L mg\(^{-1}\)) associated with the adsorption rate.

The Langmuir adsorption isotherm was used to calculate the maximum adsorption capacity (Ho & McKay 1999; Hameed & Rahman 2008), pseudo-first-order or pseudo-second-order kinetic equations were used to calculate adsorption rate constants (Wang et al. 2006; Lin & Juang 2009), and the thermodynamic parameters, such as \(\Delta G\), \(\Delta S\), and \(\Delta H\), obtained by thermodynamic equations.

**Adsorption kinetics**

For kinetic experiments, dye solutions were withdrawn at the particular time intervals and MO amounts adsorbed at a desired time \(t\), \(q_t\) (mg g\(^{-1}\)), were calculated based on Equation (3):

\[
q_t = \frac{(C_o - C_i)V}{M}
\]

where \(C_i\) is the residual concentrations in the liquid phase of MO at time \(t\) (min).

Kinetic data were analyzed using pseudo-first- and pseudo-second-order models (Ho & McKay 1999), expressed as Equations (4) and (5).

Pseudo-first-order model,

\[
\ln(q_e - q_t) = \ln(q_e) - k_1t
\]

where \(q_e\) and \(q_t\) (mg g\(^{-1}\)) are the equilibrium adsorption capacity and a particular time adsorption capacity, respectively, and \(k_1\) (min\(^{-1}\)) represents the first-order kinetic constant and \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) is the second-order kinetic constant.

Relative deviation, \(\Delta q\) (%), was used to measure the applicability of different kinetic models, expressed in Equation (6):

\[
\Delta q(\%) = \frac{q_{e,\text{exp}} - q_{e,\text{cal}}}{q_{e,\text{exp}}} \times 100\%
\]

**Adsorption thermodynamics**

For adsorption thermodynamics, \(\Delta G\) (kJ mol\(^{-1}\)), \(\Delta H\) (kJ mol\(^{-1}\)), and \(\Delta S\) (J mol\(^{-1}\) K\(^{-1}\)) were employed to investigate the adsorption behavior of MO onto MIL-68 (Al). The above parameters were calculated based on Equations (7)–(9):

\[
K_c = \frac{C_o}{C_e}
\]

\[
\Delta G = -RT \ln K_c
\]

\[
\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
\]

where \(K_c\) is the distribution coefficient; \(C_o\) (mg L\(^{-1}\)) is the MO amount absorbed per mass of MIL-68 (Al); \(T\) (K) is the solution temperature, and \(R\) (8.314 J mol\(^{-1}\) K\(^{-1}\)) is the universal gas constant.

**RESULTS AND DISCUSSION**

**Characterization of MIL-68(Al)**

The prepared MIL-68(Al) and MIL-68(Al) + MO were characterized by FT-IR, XRD, SEM, XPS, and N\(_2\) adsorption-desorption experiments.

MIL-68 topology exhibited characteristic peaks at 2\(\theta\) = 5\(^\circ\), 10\(^\circ\), and 15\(^\circ\) in its XRD patterns. In particular, in the case of aluminum terephthalate, the structure of the
material’s corresponding porous MOF was recognized by the XRD pattern having a main reflection in the range of \(4^\circ < 2\theta < 6^\circ\) (Schubert et al. 2013). The experimental XRD pattern of MIL-68(Al) maintained a high level of agreement with the simulated version, showing successful preparation of MIL-68(Al) (Figure 1(a)). After MO adsorption, MIL-68(Al) retained original features of its diffraction peak, indicating the adsorbent did not disrupt the material’s skeletal structure. A new peak appeared and some peak intensities changed with MO adsorption relative to without. The FT-IR spectra of MIL-68(Al) and MIL-68(Al) + MO are shown in Figure 1(b). Depending on the existing literature (Barthelet et al. 2004; Zhang et al. 2012; Xie et al. 2014), peaks were assigned to various functions. The broad peak around 3,446 cm\(^{-1}\) was associated with free water O-H stretching vibrations and the peak at 3,665 cm\(^{-1}\) was classified as O-H from a \(\mu_2\)-hydrox group of MIL-68(Al). MIL-68(Al) + MO exhibited no bands in the range of 3,800–3,550 cm\(^{-1}\), which might be ascribed to the \(\mu_2\)-OH group having hydrogen-bond interactions with the MO molecules. The band around 1,120 cm\(^{-1}\) was assigned to S-O bonds from MO, confirming MO’s presence onto MIL-68 (Al) surfaces.

Information regarding specific surface areas and pore volumes of MIL-68(Al) and MIL-68(Al) + MO were determined by N\(_2\) adsorption-desorption isotherms. As shown in Figure 1(c), this is a type I isotherm, illustrating that the material channel was a microporous structure (Peng et al. 2012). The textural parameters of MIL-68(Al) are presented in Table 1. The BET surface area and total pore volume of MIL-68(Al) were 1,346 m\(^2\) g\(^{-1}\) and 0.69 m\(^3\) g\(^{-1}\), respectively. After MO adsorption, both the BET surface area and total pore volume were decreased and, more notably, decreased internal surface area and micropore volume were the main changes. Micropore size distribution curves exhibited pore size ranges from 0.6 to 1.7 nm and micropore amounts decreased significantly after MO adsorption (Figure 1(d)). All these results above revealed that micropore volume played a crucial role in this adsorption.

SEM images of MIL-68(Al) are shown in Figure 2, in which rod-like crystals with different sizes and

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**Figure 1** | (a) XRD patterns, (b) FT-IR spectrum, (c) nitrogen adsorption-desorption isotherms and (d) pore distribution of the MIL-68(Al) and MIL-68(Al) + MO.
comparatively smooth surfaces were observed. These crystals were observed stacked together in a disorderly manner to form clusters.

From adsorbent XPS, survey scans of MIL-68(Al) before and after adsorption are shown in Figure 3(a). The new adsorptions were designated as N 1s and S 2p from MO, indicating MO adsorption onto MIL-68(Al) surfaces. Two peaks emerged at 284.8 and 289.0 eV (Figure 3(b)), corresponding to the single carbons of phenyl and carboxyl, respectively (Gardella et al. 1991; Gerenser 1993; Zhu et al. 2014). In the O 1s spectrum (Figure 3(c)), one peak at 531.9 eV related to the carboxylate oxygen in the framework (Tait et al. 2008). The Al 2p spectrum (Figure 3(d)) exhibited one peak at 74.7 eV, revealing the presence of Al3+ ions in the MIL-68 AlO4(OH)2 framework (Zhang et al. 2014). After MO adsorption, the peaks of Al 2p, C 1s, and O 1s were not altered, illustrating that Al, C, and O retained their original chemical environment after adsorption. This conclusion was consistent with the XRD results.

Effects of pH

Solution pH had an impact on the surface charge of the adsorbent and adsorbate. Here, experiments were carried out with a constant dye concentration at 40 mg L−1 at 298 K, and the results are shown in Figure 4. The trend was quite obvious, as the MO adsorption capacity was constant except at both pH extremes. This phenomenon could be interpreted in two ways. On the one hand, the spatial structure of MIL-68(Al) was destroyed under strong acid or alkali conditions (pH ≤ 2 and ≥ 11) (Xie et al. 2014), and thus adsorption was low at pH extremes (pH = 2 or 11). On the other hand, a significantly potent attraction with pH of 4–10 was observed between MIL-68(Al) and MO, leading to a relatively large adsorption capacity. As a result, all other experiments were carried out under the optimal condition of pH 8.0.

Effects of initial MO concentration and temperature

Initial dye concentration and temperature might have affected the mass transfer process. For this work, we chose five common temperatures (288, 293, 298, 303, and 308 K) under which to conduct experiments with dye concentrations from 10 to 100 mg L−1; the obtained linear relations are shown in Figure S2 in the Supplementary material (available with the online version of this paper). Judging from the results, at a certain temperature, adsorbent capacity increased and achieved equilibrium with increased concentration. This phenomenon was attributed to changes in the driving forces and adsorption sites. As is well known, initial dye concentration can provide the reaction driving force during the adsorption process, and the higher the initial concentration, the greater the driving force becomes. In the preliminary adsorption stage, the driving force is weak, but the surface of the adsorbent supplies a large number of adsorption sites, which result in evenly increasing adsorption capacity. Along with further increases in initial concentration, the adsorption driving force increased but, owing to gradual saturation of adsorption sites, the adsorption capacity arrived at a balance by degrees. With temperature, Figure S3 (available with the online version of this paper) shows slightly increased results while the dye initial concentration ranged from 65 to 100 mg L−1. It

Table 1 | Textural parameters of MIL-68(Al) and MIL-68(Al) + MO

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ m² g⁻¹</th>
<th>$S_{INT}$ m² g⁻¹</th>
<th>$S_{EXT}$ m² g⁻¹</th>
<th>$V_{TOTAL}$ m³ g⁻¹</th>
<th>$V_{MICRO}$ m³ g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-68(Al)</td>
<td>1,346</td>
<td>1,048</td>
<td>298</td>
<td>0.69</td>
<td>0.41</td>
</tr>
<tr>
<td>MIL-68(Al) + MO</td>
<td>276</td>
<td>97</td>
<td>179</td>
<td>0.32</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Figure 2 | SEM images of MIL-68(Al).
was clear that the adsorption capacity was essentially unaffected when the dye concentration was below 60 mg L\(^{-1}\) or more than 60 mg L\(^{-1}\); with the latter, adsorption capacity increased slightly with temperature. Also, the adsorption quantity increased with temperature under constant concentration, which suggested that the adsorption between MO and MIL-68(Al) was an endothermic process.

**Effects of ionic strength**

Examination of the ionic strength on MO adsorption revealed that adsorption increased slightly with increasing NaCl or CaCl\(_2\) concentrations from 0 to 0.3 mol L\(^{-1}\) (Figure S3). In contrast, under identical concentrations, a divalent electrolyte (CaCl\(_2\)) had a more positive effect on MO adsorption than a univalent electrolyte (NaCl). However, increasing the ionic strength did not significantly influence MO adsorption onto the MIL-68(Al). This result was ascribed to antagonism between two effects. On the one hand, joining the electrolyte compressed the electric double layer thickness and weakened the electrostatic interactions between MO and MIL-68(Al) (Filius *et al.* 2000), which led to decreased adsorption quantities. On the other hand, increased ionic strength reduced the adsorbate size and thus adsorbate was taken up by adsorbent surfaces as well as entering the adsorbent channels (Greenwood & Kendall 2000; Campinas & Rosa 2006). In addition, increased ionic strength might also have caused adsorbent reunion with MO molecules (Al-Degs *et al.* 2008), resulting in increased adsorption. In the end, ionic strength showed negligible effects on MO adsorption, suggesting that these two opposite effects were offset or too weak to be detectable.

**Adsorption isotherms for MO onto MIL-68(Al)**

The MO adsorption isotherms onto MIL-68(Al) were measured at pH = 8.0 with different temperatures. The Langmuir isotherm model was used to fit the experimental data, based on Equation (2) (Figure 5).
The parameters $q_m$ (maximum adsorption capacities), Langmuir constants ($K_L$), along with $R^2$ values (correlation coefficients) are presented in Table 1. Clearly, the calculated $q_m$ of MO onto MIL-68(Al) were 328.60, 330.03, 334.05, 338.98, and 341.30 mg g$^{-1}$ at 288, 293, 298, 303, and 308 K, respectively, which agreed well with the experimental results (Figure 5(b)), and the $q_m$’s were relatively high compared with those of MOF materials reported to date (Table S1, available with the online version of this paper). Here, it is worth mentioning that MIL-68(Al) has great potential for removing MO from water. MIL-100(Fe) and MOF-235 were both Fe-based MOFs; although the maximum adsorption capacities for MO were higher than that of MIL-68(Al), their adsorption quantities could be greatly influenced by pH, more specifically, the adsorption capacities decreased rapidly at a solution pH > 6. The maximum adsorption capacities of Cr-based MOFs were lower than that of MIL-68(Al), and the Cr ion is also poisonous. By contrast, MIL-68(Al) could maintain a stable adsorption quantity over a wide pH range (pH = 4–10), and the Al ion is relatively safe. As above, MIL-68(Al) could be used as a new and effective adsorbent to remove MO from water. It was also observed in Table 1 that the Langmuir isotherm fit the data well ($R^2 > 0.999$), suggesting a homogeneous and monolayer adsorption occurring in MIL-68(Al) with finite adsorption sites.

**Thermodynamics of MO adsorption onto MIL-68(Al)**

In practical applications, the energy changes in an adsorption process can be predicted according to thermodynamic parameter values. Here, MO equilibrium absorption capacity onto MIL-68(Al) was obtained from Equation (1), with $K_c$ calculated according to Equation (7) (Karagoz et al. 2008), $\Delta G$ based on Equation (8), and on the basis of Equation (9), and $\Delta H$ and $\Delta S$ calculated from the slopes and intercepts of graphs of $\ln K_c$ versus $T^{-1}$ (Figure 6). All of the thermodynamic parameter values are shown in Table 2. The adsorption $\Delta H$ for MO onto MIL-68(Al) was +5.98 kJ mol$^{-1}$, confirming that the adsorption process was an endothermic reaction; meanwhile, $\Delta H$ was also in the range of 2.1–20.9 kJ mol$^{-1}$, corresponding to physical adsorption (Belala et al. 2011). Adsorption $\Delta G$ values were $-21.89$, $-22.56$, $-22.84$, $-23.33$, and $-23.81$ kJ mol$^{-1}$ at 288, 293, 298, 303, and 308 K, respectively (Table 2). The negative $\Delta G$ values confirmed that the adsorption reaction here was spontaneous, and positive $\Delta S$ values indicated that randomness increased during the reaction process.
Kinetics for MO adsorption onto MIL-68(Al)

The influence of adsorption time versus adsorption capacity was obtained to study the kinetics of MO adsorption onto MIL-68(Al) (Figure 7). The results showed that MO adsorption capacity increased with increasing adsorption time and that adsorption capacities reached equilibrium within ∼90 min. Saturation adsorption amounts were 99.36, 195.59, 259.52, 271.78, and 289.27 mg g⁻¹/C₀ with initial MO concentrations of 20, 40, 60, 80, and 100 mg L⁻¹, respectively. Moreover, MO adsorption capacities increased significantly during the first 60 min (Figure 7), a phenomenon that might be interpreted in terms of the availability of exposed surface adsorption sites at the preliminary adsorption stage. In addition, adsorption capacities increased as MO initial concentrations increased, indicating that high MO concentrations were conducive to adsorption onto MIL-68(Al).

Pseudo-first-order and pseudo-second-order models were used to study the adsorption kinetics according to Equations (4)–(6), respectively (Figure S4, available with the online version of this paper). The kinetic constants (k₁ and k₂, respectively), correlation coefficients (R²), normalized standard deviations (Δq), and the equilibrium adsorption capacities (qₑ, cal) are presented in Table 3. It was easy to determine that the pseudo-first-order kinetics model was unsatisfactory. Also, the equilibrium adsorption capacity (qₑ) from experiments and the calculations were inconsistent, and Δq was >50%. In contrast, the correlation coefficients of the pseudo-second-order kinetics model were high (R² > 0.999), as the experimental and calculated values of qₑ fit well and Δq was within 3%. Obviously, the influence of contact time on MO adsorption capacity onto MIL-68(Al) was more in line with the pseudo-second-order kinetic model results. Regarding the rate constant (k₂), the reaction’s speed decreased with increased initial MO concentrations. This was ascribed to competition for adsorption active sites at different concentrations; that is, the competition for active adsorption sites was lower at lower concentrations and greater at higher concentrations, thereby resulting in diverse adsorption rate constants obtained in different initial MO concentrations.

**ADSORPTION MECHANISM**

Until now, adsorption processes have been shown to include a number of different active mechanisms, including electrostatic interactions, hydrophobic interactions, π–π stacking interactions, and hydrogen-bond interactions. For a specific adsorption process, a variety of interactions might occur at the same time. The advantages of MIL-68 (Al) in MO removal were ascribed here to electrostatic
and hydrogen-bond interactions. MO usually exists in the form of a sulfate and, for this reason, the MIL-68(Al) surface, which is positively charged at certain pHs, can form a strong electrostatic interaction with oppositely charged MO (Figure 8). In addition, MIL-68(Al) has been shown to contain μ₂-OH groups in Al-O-Al units (Xie et al. 2014), which can form hydrogen bonds with MO nitrogen or oxygen atoms. Here, MO adsorption onto MIL-68(Al) led to a binding energy shift from 533.5 to 534 eV for hydroxyl groups (Figure 9) and agreed well with FT-IR results. The μ₂-OH groups were concluded to interact with MO after adsorption. Therefore, electrostatic and hydrogen-bond interactions were considered the primary adsorption mechanisms in this study.

### CONCLUSIONS

In summary, MIL-68(Al) was demonstrated to be an efficient adsorbent for MO removal from water. This material can be used over a wide pH range, maintaining high MO adsorption capacities. The maximum adsorption capacity reached 341.30 mg g⁻¹ with an MO initial concentration of 100 mg L⁻¹ at 308 K. Ionic strength and temperature had a positive effect on the adsorption process. Thermodynamic data indicated that the MO adsorption process onto
MIL-68(Al) was spontaneous, endothermic, and entropically positive. Kinetics results were found to conform to a pseudo-second-order model. Electrostatic interactions and hydrogen bonding were concluded to play a role in MO adsorption. Moreover, MIL-68(Al) maintained its original structure after MO adsorption. This study extended the scope of MIL-68(Al) characterizations and potential applications, and will be useful for employing MIL-68(Al) as a novel adsorbent for MO removal from wastewater.

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Schubert, M., Mueller, U., Marx, S. & Muller, U. 2013 Porous metal-organic framework material, useful e.g. as carrier or for producing corresponding metal oxides, comprises a bidentate organic compound (e.g. terephthalic acid), which is coordinatively bound to a metal ion (e.g. aluminum). In: BASF SE (BADI-C) MARX S (MARX-Individual) BASF SE (BADI-C) MUELLER U (MUEL-Individual) MARX S (MARX-Individual), p. 2155390-A2.


