Selective Adsorption of Metal–Organic Framework toward Methylene Blue: Behavior and Mechanism

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ABSTRACT: In this study, Cu-BTC, a kind of metal–organic framework, was used as an adsorbent to selectively adsorb methylene blue (abbreviated as MB) from dye mixed wastewater. The synthesized Cu-BTC was characterized by scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The results indicated that the synthesized Cu-BTC have an octahedral structure, with its specific surface area at 45.16 m²/g and the pore sizes at 35–40 nm. The influence of various parameters including the initial solution pH, temperature, ionic strength, initial concentration, and contact time on MB adsorption by Cu-BTC was investigated in detail. The adsorption capacity of Cu-BTC toward MB was optimized at the pH value of 8, with a lower temperature and a higher ionic strength. The adsorption isotherm was found to fit well with the Langmuir model, and the kinetic curve was found to be in good agreement with the pseudo-second-order kinetic model. The adsorption mechanism was revealed to be the combined effects of hydrophobicity and electrostatic adsorption. The synthesized Cu-BTC adsorption material showed great potential for recovering MB from dye-mixed wastewater.

1. INTRODUCTION

The rapid growth of dyeing industries has led to the release of lots of dyes into the environment. Many of the surplus or byproduct dyes are harmful or even carcinogenic to humans, presenting a potential threat to humans and the ecosystem. Moreover, many dyes are persistent and nonbiodegradable, which bring intractable problems to wastewater remediation.1 Several technologies have been put forward to treat dyes in wastewater, such as electrochemical oxidation, membrane separation, and advanced oxidation. However, the high cost and additional chemical exhaust are the common bottlenecks faced by the above technologies.2 Adsorption is a low-cost and easy-to-practice technology, which is always used for dye separation from wastewater.3,4 However, the improper desorption methods might release dyes into water again, causing secondary pollution. Thus, it is urgent to develop efficient and selective adsorption materials for the time being.5 Recently, Fu et al.6 synthesized polydopamine and used it to selectively adsorb cationic dyes from different kinds (including acid, neutral, and cationic) of dye-mixed wastewater. Molla et al.7 used graphene oxide to selectively adsorb methylene blue (a kind of positive dye, abbreviated as MB) by utilizing the electrostatic interactions between the −NH2 group (on the surface of MB) and the oxygen functional group (on the surface of graphene oxide). Chandra and Kim8 synthesized a polypyrrole–reduced graphene oxide composite to efficiently and selectively adsorb Hg(II) from water, with the adsorption capacity at 980 mg g⁻¹.9

Metal–organic framework (MOFs) materials are attracting worldwide interest in recent years due to their large surface area and mesoporous structure. They have been widely used in gas separation, membrane permeability, electrochemical catalysis, photocatalysis, and adsorption.6 In the adsorption process, MOFs are considered as ideal materials for the removal of low-molecular-weight compounds from water. Studies have reported that MOFs showed excellent selective adsorption capacities toward different kinds of organics by surface modification.9 Qiu et al.5 synthesized acid-promoted UiO-66, which showed selective adsorption behavior to anionic dyes (methyl orange, with the adsorption capacity of 84.8 mg g⁻¹) than to cationic dyes (MB, with the adsorption capacity of 13.2 mg g⁻¹). Besides the large surface area, the zeta potential of adsorbents is a rather important factor in the process of adsorption. Yu et al.10 reported a novel adsorbent Zn-BDC-H₂O, which showed ultrahigh uptake capacities toward different-sized anionic dyes, for example, amido black 10 B (2402.82 mg g⁻¹), methyl orange (744.02 mg g⁻¹), orange II (522.83 mg g⁻¹), and direct red 80 (1496.34 mg g⁻¹).
Further analysis revealed that the main interactions between the protonated Zn-BDC-H2O and the anionic dyes were electrostatic interactions and surface adsorption, which were attributed to the oxygen and nitrogen sites decorated on the surface of Zn-MOF.

In this study, Cu-BTC (a kind of MOF) was synthesized and used as an adsorbent to specifically uptake MB from mixed-dye wastewater. The effects of adsorption conditions including the pH, temperature, and ionic strength were tested, and the adsorption isotherms and kinetic curves were studied to reveal the adsorption mechanism.

2. METHODS

2.1. Synthesis of Cu-BTC. The synthesis methods of Cu-BTC were adopted from Yan et al.11 First, three solutions were prepared. Solution 1: 1.74 g of Cu(NO3)2·3H2O was added to 8 mL of deionized water, followed by ultrasonication for about 20 min until it dissolved completely. Solution 2: 0.293 g of ZnO powder and 8 mL of deionized water were added and ultrasonicated subsequently for 10 min to get ZnO nanocolloids. Solution 3: 0.84 g of trimesic acid was dissolved in 16 mL of ethanol. Then, in a beaker containing 16 mL of N,N-dimethylformamide, under continuous stirring, solution 1, solution 2, and solution 3 were added in sequence. After 1 min, the appeared blue particles were filtered and washed with ethanol more than three times and then dried in a vacuum for 6 h. Next, the Cu-BTC powder was obtained after annealing at 600 °C under a N2 atmosphere for 2 h.

2.2. Material Characterization. The synthesized Cu-BTC particles (before and after adsorption) were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The XRD patterns of Cu-BTC were obtained using Co Kα radiation at the scanning rate of 0.01 s−1, with 2θ ranged from 5 to 30. In the FT-IR test, the spectra of materials were obtained in the wavelength range from 4000 to 400 cm−1 at the resolution of 4 cm−1 by the conventional KBr disk tablet method. The analysis of XPS was performed using C 1s (284.6 eV) as the calibrated binding energy. The specific surface area and the distribution of pores of Cu-BTC were calculated using a multistation extended surface and porosity analyzer (ASAP 2460, Micromeritics Instrument Corp., U.S.A).

2.3. Test for Selective Adsorption toward MB. The adsorption of Cu-BTC was tested in mixed-dye wastewater. The mixed-dye wastewater was prepared with methyl orange, rhodamine B, and MB, and the concentration of all solutions was 100 mg·L−1. Adsorption was tested by adding 200 mg of Cu-BTC particles in 100 mL of mixed-dye wastewater (pH = 7), which was adsorbed for 24 h under strong agitation with the rotation rate of 150 rpm and the temperature of 25 °C. After 24 h, the supernatant solution was tested by an absorption photometer after centrifugation (8000 rpm for 5 min) at the wavelength of 450 nm (for methyl orange), 554 nm (for rhodamine B), or 665 nm (for MB).

The removal rate was calculated as follows:

\[ R = \frac{C_0 - C_e}{C_0} \times 100\% \]

The adsorption capacity was calculated as follows:

\[ Q_e = \frac{(C_0 - C_e)}{m} \times V \]

where \( R \) is the removal rate, \( Q_e \) is the equilibrium absorption capacity, mg·g−1; \( C_0 \) is the initial concentration, mg·L−1; \( C_e \) is the final concentration, mg·L−1; \( V \) is the volume of wastewater, L; \( m \) is the weight of the adsorbent, g.

2.4. Effects of Initial Conditions. Before the test, a batch of samples was prepared through the addition of 40 mg of Cu-BTC adsorbents in 20 mL of aqueous solution, whose concentration of MB was 100 mg·L−1 in all samples.

2.4.1. Effects of pH. In the test, the pH of the samples was adjusted from 2 to 10 using HCl or NaOH aqueous solution. The samples were oscillated at 25 °C for 24 h, with the rotation rate at 150 rpm. After being adsorbed for 24 h, the solution was centrifuged, and the adsorption ability of the MB solution was tested.

2.4.2. Effects of Temperature. In this test, the prepared samples were set at different temperatures (288, 298, and 308 K). The samples were oscillated for 24 h, with the rotation rate at 150 rpm. After being adsorbed for 24 h, the solution was centrifuged, and the adsorption ability of the MB solution was tested.

2.4.3. Effects of Ionic Strength. In the test, different weights of sodium chloride were added to adjust concentration of the above mixture to 0, 0.01, 0.05, and 0.1 mol·L−1, respectively. The samples were oscillated for 24 h at a proper degree and pH condition, with the rotation rate at 150 rpm. After being adsorbed for 24 h, the solution was centrifuged, and the absorbency of the MB solution was tested.

2.5. Adsorption Isotherm. Adsorption isotherms are widely used to describe the adsorption process and study the adsorption mechanism, which is of great significance for optimizing the use of adsorbents. Therefore, in the actual operation, it is essential to use theoretical or empirical equations to correlate equilibrium data. Herein, four equilibrium models were studied, namely, the Langmuir isotherm model, Freundlich isotherm model, Temkin isotherm model, and D=R isotherm model.

The data obtained from the adsorption experiments were fitted with the Langmuir and Freundlich adsorption isotherm models to reveal the adsorption mechanism of MB by Cu-BTC.

In the test, 500 mL of MB solution with an initial concentration of 100 mg·L−1 was prepared, and the pH was adjusted to 8. After that, 1 g of Cu-BTC was added, and the above mixture was oscillated ultrasonically to uniformly disperse Cu-BTC. Then, the mixture was put in a thermostatic oscillator, at temperatures of 288, 298, and 308 K, and the rotation speed was set at 150 rpm. Samples were taken at 0 min, 1 min, 5 min, 10 min, 15 min, 20 min, 25 min, 30 min, 45 min, 1 h, 1.5 h, 2 h, 3 h, 4 h, 5 h, 6.5 h, 8 h, 10 h, and 24 h. The absorbance of the samples was tested after centrifugation.

2.6. Adsorption Kinetics. In order to study the control mechanism of the adsorption process, in the experiment, a pseudo-first-order kinetic model and a pseudo-second-order kinetic model were used to test the experimental data of adsorption kinetics.

The pseudo-first-order kinetic equation can be expressed by the following formula

\[ \ln(q_e - q_t) = \ln q_e - k_f t \]

The pseudo-second-order kinetic equation can be expressed by the following formula: 
\[ \frac{t}{q_t} = \frac{1}{(k_2_q_e^2)} + \frac{t}{q_e} \]

In the above formulas, \( q_e \) and \( q_t \) represent the equilibrium adsorption capacity and the adsorption capacity at time \( t \), respectively, mg g\(^{-1}\); \( t \) represents the adsorption time, min; \( k_1 \) represents the adsorption rate constant of the pseudo-first-order kinetic model, min\(^{-1}\); \( k_2 \) represents the adsorption rate constant of the pseudo-second-order kinetic model, g\( \cdot \)mg\(^{-1}\).mole\(^{-1}\).

In the test, 500 mL MB solutions were prepared with initial concentrations of 60, 80, 100, and 120 mg L\(^{-1}\). Then, the pH was adjusted to 8. After that, 1 g of Cu-BTC was added, and the above mixture was oscillated ultrasonically to make Cu-BTC uniformly disperse. Then, the mixture was put in a thermostatic oscillator, with the temperature at 298 K and the rotation speed at 150 rpm. The samples were taken at 0 min, 1 min, 5 min, 10 min, 15 min, 20 min, 25 min, 30 min, 45 min, 1 h, 1.5 h, 2 h, 3 h, 4 h, 5 h, 6.5 h, 8 h, 10 h, and 24 h. The absorbance of the samples was tested after centrifugation.

2.7. Recycling Tests. The adsorbent Cu-BTC was regenerated by washing with ethanol at a high temperature more than three times and dried in an oven at 60 °C for reuse.

3. RESULTS AND DISCUSSION

3.1. Material Characterization. The SEM image indicated that the as-prepared Cu-BTC (Figure 1a) have an octahedral structure, as previously reported.\(^\text{11}\) The particle size of Cu-BTC was obtained at 0.5–2 μm. The TEM images of Cu-BTC (Figure 1b) showed the same structure as in the SEM image, and at a high magnification, we can clearly see the lattice fringes. After the adsorption of MB, the surface of the adsorbent Cu-BTC was covered by MB molecules (Figure 1c). Furthermore, after regeneration, most of Cu-BTC was regenerated, which can be seen from Figure 1d. The specific surface area was 45.16 m\(^2\)/g, with the pore sizes focused at 35–40 nm, as analyzed by the BET method.

The XRD results (Figure 2a) indicated that the peaks at 2θ = 6.5, 11.4, 13.3, and 18.9 were indexed to the patterns of (200), (222), (400), and (440) of Cu-BTC, respectively (MDI-JADE6).\(^\text{11,12}\)

The FT-IR spectra (Figure 2b) exhibited that there were no peaks at 2800–3200 cm\(^{-1}\), indicating the –O–H band of the substituted aromatic carboxylic acid. The peak at 1639 cm\(^{-1}\) was attributed to the stretching vibration caused by –C==O–. The peaks at 1446 and 1378 cm\(^{-1}\) were ascribed to the stretching vibrations of –C==C– in the aromatic nucleus. The peak at 1105 cm\(^{-1}\) was due to the rocking vibration of –C==C– in the aromatic nucleus. The peaks at 758 and 729 cm\(^{-1}\) were attributed to the rocking vibrations caused by ortho-substituted –C==CH– in benzene. After the adsorption of MB molecules, the materials exhibited the attenuation tendency in the peaks at 1639, 1378, and 729 cm\(^{-1}\).

The survey spectrum of Cu-BTC (Figure 2c) exhibited C 1s, O 1s, and Cu 2p in the sample. In Figure 2d, two major peaks at 934.7 and 954.6 eV were ascribed to the Cu 2p\(_{3/2}\) and Cu 2p\(_{1/2}\) binding energies, with a spin–orbit splitting of about 20.1 eV, respectively. The approximately 10 eV difference in the binding energy of the satellite peaks of 2p\(_{3/2}\) and Cu 2p\(_{1/2}\) revealed the existence of Cu\(^{2+}\).\(^\text{13}\) The spectral peaks of C 1s (Figure 2e) at 284.6 and 288.5 eV are ascribed to the C–C and C==O bonds, respectively. The spectral peak of O 1s (Figure 2f) was deconvoluted into two peaks at 531.5 and 533.5 eV binding energies, which were assigned to “O” in the C==O bond and “O” in the –C–O bond, respectively.

The material characterization results indicated that Cu-BTC was successfully synthesized with less energy consumption than the traditional solvothermal method that required a long reaction time and a high temperature.

3.2. Results of Selective Adsorption. The results of MB, RhB, and MO adsorption by Cu-BTC are exhibited in Figure 3. The results indicated that the adsorptive removal rates of MB, RhB, and MO were 94, 47, and 13%, respectively. The results indicated that Cu-BTC exhibited selective adsorption toward MB among the three mixed-dye wastewater samples, and the adsorption priority of the three dyes was of the order: MB > RhB > MO.

3.3. Effects of Conditions. 3.3.1. Effect of pH. The pH value of an aqueous solution is always considered as one of the most significant factors in adsorption. Different values of pH affect the dissociation and binding sites of the adsorbate, leading to various degrees of electrostatic charges and the ionized molecule, which was known as the zero-point charge. The effects would result in an enhanced or depressed adsorption behavior of the adsorbate.\(^\text{13}\) The test results indicated that at different conditions of initial pH (ranging from 2 to 10), the adsorption of Cu-BTC exhibited different adsorbing capacities (Figure 4). The adsorption capacity of Cu-BTC was 30–40 mg g\(^{-1}\), with the pH ranging from 3.0 to 10.0. The maximum adsorption capacity was 39.5 mg g\(^{-1}\) at pH = 8.0.

Many MOFs were used to adsorb contaminants including dyes, pharmaceuticals, and personal care products from a polluted medium. The adsorption capacities ranged from 10\(^1\) to 10\(^2\) mg g\(^{-1}\).\(^\text{14,15}\) Among the different kinds of adsorbents, MOFs always showed lower adsorption capacities but higher selectivities toward adsorbates.\(^\text{8,10}\) In this study, similar results were obtained as Cu-BTC exhibited strong affinity only toward MB among the three dyes.

3.3.2. Effect of Temperature. The influence of temperature on adsorption is another noteworthy factor because it affects the adsorption process. The results showed that the higher the temperature, the lower the equilibrium adsorption capacity was (Figure 5). According to Figure 5a, the rate of adsorption process was almost similar at ~10 min, when the temperature was changed from 288 to 308 K, indicating that the adsorption jumping behavior changed little with the change of tempera-
ature. With the temperature increased from 288 to 308 K, the adsorption capacity of Cu-BTC toward MB decreased from 41.0 to 31.3 mg g\(^{-1}\) (Figure 5b). The results indicated that the adsorption process of Cu-BTC to MB was exothermic.

3.3.3. Effect of Ionic Strength. Generally speaking, with the increase of the ionic strength, the electrostatic interactions between adsorbents and adsorbates decrease and the hydrophobic interactions increase, while the complexation does not have any obvious changes. The influence of the ionic strength (Figure 6) indicated that with the increase of the ionic strength of the aqueous solution, the equilibrium adsorption capacity of MB increased. According to the results, with the increase of the ionic strength, the electrostatic interaction between Cu-BTC and MB decreased, while the hydrophobic interactions increased. When the electrical conductivity of the solution improved from 0 to 9.36 \(\mu\)S cm\(^{-1}\), the adsorption capacity of Cu-BTC increased from 34.16 to 37.51 mg g\(^{-1}\), with an increase of about 10%. The enhanced hydrophobic interaction between Cu-BTC and MB led to a great increase of the adsorption capacity. The results indicated that the hydrophobic interaction was one of the dominant factors in the adsorption process.

3.4. Adsorption Isotherms. The data obtained from the adsorption experiments were expressed by the following isotherm models.

Langmuir isotherm model

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

Figure 2. Analysis data of Cu-BTC: (a) XRD patterns; (b) FT-IR spectra; and (c–f) XPS results: (c) Cu-BTC; (d) Cu 2p; (e) C 1s; and (f) O 1s.
In the above formulas, $C_e$ is the concentration of the adsorption equilibrium liquid, mg·L$^{-1}$; $q_m$ is the maximum adsorption amount, mg·g$^{-1}$; $K_L$ is the Langmuir adsorption equilibrium constant; $K_F$ is the Freundlich adsorption equilibrium constant; $n$ is the adsorption strength and adsorption capacity heterogeneity factor; $B$ and $\alpha_T$ are the Temkin constants, where $B = RT/b_T$; $\beta$ is the activity coefficient; and $\varepsilon$ is the Polanyi potential, where $\varepsilon = RT \ln(1 + 1/C_e)$. The fitting results are exhibited in Figure 7 and Table 1.

Obviously, the Langmuir adsorption isotherm model showed a good fit with the experimental data compared with the other isotherm models. The correlation coefficients ($R^2$) of the Langmuir model are greater than 0.99, while the correlation coefficients of other models are lower. Therefore, it was inferred that the MB adsorption was of monolayer adsorption type on the heterogeneous surface of Cu-BTC, which indicated that the adsorption process might be driven by the interaction of the active sites on the surface of Cu-BTC and MB molecules.

**3.5. Adsorption Kinetics.** Kinetic studies of any adsorption process are critical to identify the rate of the process as well as offer some valuable information on the adsorption mechanism analysis. The fitting results of the adsorption data of Cu-BTC toward MB are exhibited in Table 2 and Figure 8.

According to the results, the correlation coefficients of the pseudo-second-order kinetic models are closer to 1 (they are 0.9896, 0.9940, 0.9913, and 0.9946, respectively), and they
were much higher than those of the pseudo-first-order kinetic model. In addition, the calculated value of the $q_e$ parameter from the pseudo-second-order kinetic model exhibited great accordance with the experimental value. The results of kinetic analysis showed that the adsorption kinetics conformed with the pseudo-second-order kinetic model.

Table 1. Fitting Parameters of Different Isotherm Models

| model          | parameter data               |
|----------------|-----------------------------|
| Langmuir       | $q_m$/(mg·g$^{-1}$) 39.674  |
|                | $K_L$/(L·mg$^{-1}$) 0.241   |
|                | $R^2$ 0.9973                |
| Freundlich     | $K_F$/(L·g$^{-1}$) 73.523   |
|                | $N$ 5.089                   |
|                | $R^2$ 0.8138                |
| Temkin         | $B$ $-5.1$                 |
|                | $a_T$ $9.54 \times 10^{-6}$ |
|                | $b_T$ $-469.49$            |
|                | $R^2$ 0.6567                |
| D–R            | $q_m$/(mg·g$^{-1}$) 44.70   |
|                | $B$ $7.4 \times 10^{-7}$   |
|                | $R^2$ 0.3333                |

Table 2. Fitting Parameters of Pseudo-First-Order and Pseudo-Second-Order Kinetic Models

| $C_0$ (mg/L) | $(mg/L)$ pseudo-first-order | $(mg/L)$ pseudo-second-order | $R^2$ |
|--------------|----------------------------|----------------------------|-------|
|              | $q_e$ $(mg/g)$ $k_1$ (min$^{-1}$) | $k_2$ (g·mg·min$^{-1}$) |       |
| 60           | 1.006                      | 0.1486                     | 0.4290 |
| 80           | 2.048                      | 0.1036                     | 0.2917 |
| 100          | 1.760                      | 0.1091                     | 0.2498 |
| 120          | 2.827                      | 0.0267                     | 0.0179 |
|              | 15.748                     | 0.1117                     | 0.9896 |
|              | 25.189                     | 0.1110                     | 0.9940 |
|              | 37.736                     | 0.1170                     | 0.9913 |
|              | 45.045                     | 0.0714                     | 0.9946 |
It can be seen from Figure 8 that the adsorption rate of Cu-BTC toward MB was very fast in the first 5 min, which then reached a relatively equilibrium state after 30 min. The high adsorption rate at the beginning was attributed to the large number of accessible active sites on the surface of Cu-BTC. Then, as the adsorption process moved forward, the active sites on the surface of Cu-BTC were occupied by a large number of MB molecules, and the adsorption rate slowed down gradually until an equilibrium adsorption state was achieved. In addition, the initial concentration of MB played an important role in the adsorption of MB molecules, owing to the fact that the initial concentration of MB provided the necessary driving force to overcome the mass-transfer resistance of MB molecules moving from the aqueous phase to the surface of the solid phase (the surface of Cu-BTC).

3.6. Zeta Potential Measurements. To further reveal the adsorption mechanism, the zeta potentials of Cu-BTC, MB, RhB, and MO were tested at the pH value of 8 in the aqueous solution. The results indicated that the zeta potentials of Cu-BTC, MB, RhB, and MO were $-3.65$, $3.73$, $-2.39$, and $-2.07$, respectively (Figure 9a). The results indicated that in the adsorption process, the selective adsorption behavior of Cu-BTC toward MB was mostly due to the force of electrostatic attraction. As the zeta potentials of Cu-BTC, RhB, and MO were negative, especially for MO, the action of electrostatic repulsion prevented the migration of RhB and MO to the surface of Cu-BTC. According to Figure 9b, when the pH increased to 8, the surface charge of Cu-BTC changed slightly negative, which contributed to the attraction of MB toward the surface of Cu-BTC.

Thus, in this study, the high adsorption capacity of Cu-BTC toward MB than other dyes was mostly due to the combined effects of hydrophobicity and electrostatic attraction.

3.7. Regeneration Efficiency. Cu-BTC was studied by multiple adsorption/desorption cycles. The results are exhibited in Figure 10. After four adsorption cycles, the adsorption capacity of Cu-BTC remained 35.1 mg g$^{-1}$ (about 85% vs the initial adsorption capacity). The results indicated that Cu-BTC can be used multiple times to selectively adsorb MB from aqueous solutions.

4. CONCLUSIONS

In this study, MB was highly selectively adsorbed on the surface of Cu-BTC in mixed-dye wastewater. The results of adsorption test indicated that the adsorption isotherms fitted well with the Langmuir isotherm curve, revealing that the adsorption process of MB by Cu-BTC is mainly a monolayer adsorption. The results of adsorption kinetics indicated that the adsorption process approximates more a pseudo-second-order kinetic model. This study verified that the as-prepared Cu-BTC had good ability to remove MB from water, with the removal rate reaching 96%. It puts forward a new idea for the recycle of MB from wastewater.

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Notes
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