Selective Adsorption of Cationic Dyes for Stable Metal–Organic Framework ZJU-48

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ABSTRACT: A cationic metal–organic framework (MOF) ZJU-48 with one-dimensional pores of about 9.1 × 9.1 Å² has been prepared from zinc ions, adenine, and carboxyl ligands. ZJU-48 displays excellent water stability for about one week, exhibiting its potential application for adsorption and separation of dyes. Cationic and anionic dyes with similar sizes are adopted to study the adsorbing and separating properties of ZJU-48. Cationic dyes are adsorbed better than anionic dyes because of the negatively charged zeta potential of the material surface, implying its selective adsorption to cationic dyes, and it is charge-based adsorption. Meanwhile, the adsorption ability of the MOF to cationic dyes with different sizes is also investigated. We find that the adsorbed amount decreases with increase in the size of organics, indicating that it is size-based adsorption. Furthermore, the cationic dye methylene blue (MB) is employed and focused on for its suitable charge and fitting size to evaluate the maximum adsorption capacity and desorption progress of ZJU-48. The results show that the maximum loaded amount of MOF toward MB reaches 582.44 mg/g, and about 90% of loaded dyes can be released from frameworks in N,N-dimethylformamide with NaCl over 6 h, exhibiting satisfactory adsorptive property and possibility as a reusable adsorbent.

INTRODUCTION

For decades, many dyes have been widely used in many industries such as plastic, dyestuff, textile, paper, leather, printing, and so on. The colorful effluents containing toxic dyes are dumped into the water cycle, which pollute the environment. As a result, these carcinogenic dyes, which are hard to be degraded because of their stability to oxidants and light, result in severe threats to the environment and human health. Several methods such as physical, chemical, and biological methods have been applied for the removal of dyes. Many adsorbents such as activated carbon and gels are fabricated to adsorb and separate dyes. Commercially activated carbon is well-known as an ideal sorbent for the removal of color molecules, but its expensive cost limits its application. Gels are new soft materials with high effective surface area and environmental harmony, which makes them viable for dye removal and water purification. However, reuse and selectivity of the pollutant uptake of gels is still needed to be optimized. Metal–organic frameworks (MOFs), synthesized from metal centers and organic ligands, are fascinating porous crystalline materials with outstanding characteristics such as large surface areas, tunable structures, pore sizes, and modifiable surfaces. MOFs have been widely used in biomedicine, gas storage and separation, catalysis, solid-phase extraction, solid-phase microextraction, sensing, and luminescence, while only a few MOFs are explored in adsorption or separation of dye molecules. Generally, dye removal is based on the size effect and virtue of ionic selectivity. Lan et al. constructed a mesoporous MOF of about 38Å size-tunable cages and investigated that separation of large dye molecules depend on the size-exclusion effect. Zhang and co-worker synthesized a novel anionic MOF material (NENU-505) which exhibited adsorption toward cationic dyes as an alternative. NENU-505 can potentially be served as a column-chromatographic filler for the separation of dyes. The adsorption capacity of NENU-505 at room temperature was 33.5 mg/g for methylene blue (MB), and the cationic dyes can be released in N,N-dimethylformamide (DMF) with NaCl. Haque et al. obtained two typical highly porous MOFs, ED-MIL-101 and PED-MIL-101, which are used for the adsorptive removal of methyl orange (MO), and the maximum adsorption capacities.
are 160 and 194 mg/g, respectively. Many adsorption investigations reported have been carried out in the organic solvent such as DMF. However, in practical applications, most of the dyes are released into water. Therefore, it is more practical to prepare an MOF material with high water stability. More importantly, it is valid to prepare an ionic material to remove dyes based on the virtue of their ionic selectivity because many dyes are ionic dyes.

In this work, the water-stable cationic MOF ZJU-48 was fabricated from Zn(OAc)$_2$·2H$_2$O, adenine, and (E)-4,4′-(ethene-1,2-diyl) dibenzoic acid (H$_2$EDDA), and the adsorption and separation of ZJU-48 for dyes with different charges and sizes were studied. Furthermore, the maximum adsorption and desorption capacity of ZJU-48 to the normal cationic dye MB were also investigated.

**RESULTS AND DISCUSSION**

The porous crystals ZJU-48 with one-dimensional (1D) channels (about 9.1 × 9.1 Å$^2$) and Brunauer–Emmett–Teller surface area of 1450 m$^2$·g$^{-1}$, as shown in Figure 1, were synthesized from Zn(OAc)$_2$·2H$_2$O, adenine, and H$_2$EDDA, according to the literature. The crystal structure of the prepared MOF was measured by PXRD. As shown in Figure 2a, the experimental patterns showed that the peaks of synthesized materials matched well with the simulated ones in key positions, implying that the MOF ZJU-48 was obtained. The as-synthesized ZJU-48 had the same structure as the reported ZJU-48, and the space group was the tetragonal space group P4/n. The Zn–adenine rod chains, which were formed from Zn atoms and adenine (ad), were linked to H$_2$EDDA ligands by –COOH groups to construct three-dimensional (3D) frameworks. The water stability of materials was estimated by suspending the powder into water at room temperature for 1, 3, 5, and 7 days (Figure 2b). As the results displayed, the crystalline structures remained unchanged after water treatment, and the significant water stability of ZJU-48 was confirmed, indicating its potential application for adsorption and separation of dyes in water.

Virtue of their ionic selectivity and size effect are the generally accepted theories accounting for adsorption mechanism of adsorbents. Therefore, dyes with different potentials and shapes were employed to assess the adsorptive and separative properties of ZJU-48. As shown in Figure 3, the structure of ZJU-48 was intact after adsorption of dyes, indicating that the frameworks were not influenced by loading. The cationic dye MB and anionic dye MO with opposite potentials and similar sizes were quantitatively determined by UV–vis spectroscopy (Figure 4), which showed that the content of MB decreased quickly, and almost no dyes were left in water after 48 h at room temperature. First, more than 40% of MB was loaded onto ZJU-48 for 5 min, and then, the dyes were adsorbed gradually. After 6 h, around 30% of initial molecules remained in solutions, and almost all MB were wiped off finally. The color of aqueous MB solution turned shallow gradually, and the solution was colorless after 48 h. On the other hand, merely few of the anionic dye MO were loaded onto the frameworks in two days, and the color of MO solution was unchanged.

To evaluate the selective adsorption and separation of ZJU-48 for different charged dyes, the crystals were soaked into aqueous solution containing two kinds of dyes MB and MO (1:1). As shown in Figure 5, the cationic dye MB was adsorbed completely, while the anionic dye MO remained in solution although they were similar in size (about 4 × 5 × 14 Å$^3$), and
the green water solution turned orange which was the color of MO. According to the previous reports, ZJU-48 (Zn8O-(EDDA)4 ·(HEDDA)2·6DMF·27H2O) was a cationic framework, and it would absorb an anionic dye in theory. However, the cationic MOF adsorbed cationic dye molecules instead of anionic ones, and it showed selective adsorption for cationic dye molecules in heterogeneous water. The unexpected phenomenon was attributed to the negative surface charge of MOF (about $-15.7 \text{ mV}$) in deionized water. ZJU-48 tended to adsorb cationic dyes by electrostatic interaction and reject anionic dye, indicating that the surface charge played an important role in adsorption and separation.

To investigate the influence of the molecular structure on the adsorptive property of ZJU-48, some cationic dyes, including MB, MO, RhB, CV, and BG were adopted in the adsorption experiment (Table 1). As shown in Figure 6, ZJU-48 absorbed more than 40% of MB in first 5 min, while absorbed 12% of RhB at the same time. However, after 4 h, RhB was adsorbed slightly in the following 2 h because of its bigger molecular volume. Over time, MB and RhB were removed completely after 48 h, meanwhile, about 28% of CV

![Figure 4](image-url)

**Figure 4.** (Top) UV–vis absorption spectra of aqueous solutions of (a) MB and (b) MO with the prepared ZJU-48. (Middle) Schematic illustration of molecules used in adsorption experiments. (Bottom) Photographs of color changes of MOFs after immersion in aqueous solutions of (a) MB and (b) MO for a period of time.

![Figure 5](image-url)

**Figure 5.** (Top) UV–vis absorption spectra of the mixed aqueous solution of MB/MO (1:1) in an adsorption experiment with the as-synthesized ZJU-48. (Bottom) Photographs of color changes of crystals after immersion in the mixed aqueous solutions for a period of time.

| Table 1. Molecular Dimensions of Dye Molecules With Different Charges Used Here |
|----------------------------------|-----------------|-----------------|
| Name    | Cationic | Anionic |
| MB      | 4.0 Å    | 4.0 Å   |
| RbB     | 6.0 Å    | 4.8 Å   |
| CV      | 12.0 Å   | 4.9 Å   |
| BG      | 13.5 Å   | 4.9 Å   |
| MO      | 16.9 Å   | 4.0 Å   |

*The colors of the atoms are: C, gray; N, blue; H, white and pink; S, yellow; Na, deep gray; O, red; and Cl, green.*
and 36% of BG remained in water because of their triangular structure and large shape. Comparing with the linear structure of MB with the size of about $4.0 \times 5.0 \times 14.2 \text{ Å}^3$, others were planar in shape and showed bigger size (Table 1), resulting in the faster rate and larger amount of adsorption for MB. Therefore, the loading was processed more slowly with the size of dye molecule increased, and the adsorption capacity was also affected by the size of adsorbed molecules, exhibiting that it was size-based adsorption.

Generally, the equilibrium adsorption capacity of the absorbent was influenced by the concentration of the dye solution. Therefore, it was vital to measure adsorption isotherms at different concentrations to assess the maximum adsorptive property of materials. Because of the suitable charge and fitting shape, the cationic dye MB was utilized. According to Figure 7a, the maximum loading amount of ZJU-48 was calculated and reached $82.44 \text{ mg/g}$, which is reported in most of the absorbents. In addition, the kinetic process and desorption capacity of MOF were estimated by the release progress of dyes MB from ZJU-48 in DMF solution with NaCl. As shown in Figure 7b, for the initial 15 min, dyes were desorbed rapidly because of the weak interaction between molecules, and then, the MB molecules were released gradually via ion exchange with NaCl. After 6 h, nearly all loaded dyes were released from the channels. In addition, the diffraction peaks of ZJU-48 after releasing MB were in accordance with the as-synthesized ZJU-48 (Figure 3), exhibiting that ZJU-48 was stable and could be reused.

**CONCLUSIONS**

In conclusion, a porous MOF ZJU-48 with 1D channels (about $9.1 \times 9.1 \text{ Å}^2$) was synthesized and showed excellent water stability. The cationic materials adsorbed cationic dyes instead of anionic ones because of their negatively charged zeta potential. Meanwhile, the adsorptive ability of MOF toward dyes decreased when the size of dyes increased, which

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Figure 6. UV–vis absorption spectra of aqueous solutions of (a) MB, (b) rhodamine B (RhB), (c) crystal violet (CV), and (d) basic green (BG) in adsorption experiments with ZJU-48.

Figure 7. (a) Absorption isotherms for MB absorption at 25 °C and (b) dye release of ZJU-48 in DMF with NaCl.
indicated that ZJU-48 can be used as an outstanding adsorbent not only for cationic dyes but also for small organics. Furthermore, the maximum adsorption capacity of the cationic small dye MB reached 582.44 mg/g, and about 90% of loaded MB could be released from frameworks over 6 h implying that ZJU-48 was an ideal adsorptive material and a reusable adsorbent.

■ METHODOLOGIES

Materials and Methods. All the chemical reagents and solvents were purchased from commercial sources and used without further purification. PXRD was carried on a Shimadzu X-ray diffractometer with Cu Kα radiation (λ = 1.542 Å) in the range of 3–50° at 293 K, and the scanning speed was 4°/min. The UV−vis absorption spectra were carried out on a UV-5500PC ultraviolet and visible spectrophotometer from Shanghai Metash Instruments Co., Ltd at room temperature.

Synthesis of ZJU-48. The fabrication of ZJU-48 was carried out, according to the literature. 0.138 mmol, 33.6 mg), adenine (0.074 mmol, 10 mg), and H2EDDA (0.113 mmol, 30 mg) were dissolved in a mixed solvent (13.5 L) at 293 K, and the scanning speed was 4°/min. The resulting solution was heated to 125 °C for 24 h. After that, ZJU-48 was obtained by filtration.

Adsorption of Dyes. The prepared ZJU-48 (10 mg) was soaked into aqueous solution of dyes (10 ppm, 10 × 10−3 L) such as MB, MO, RhB, and CV at room temperature. A UV−vis spectrophotometer was used to analyze the adsorption of ZJU-48.

Release of Dyes. The MB-encapsulated ZJU-48 (20 mg) was soaked into 30 × 10−3 L of DMF solution containing NaCl in a glass bottle. The UV−vis absorption spectra were carried out to determine the MB concentration of the extracting solution at regular intervals to investigate the desorption progress of ZJU-48.

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Notes

The authors declare no competing financial interest.

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