Efficient adsorptive removal of Congo red from aqueous solution by synthesized zeolitic imidazolate framework-8

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ABSTRACT
Dyes exposure in aquatic environment creates risks to human health and biota due to their intrinsic toxic mutagenic and carcinogenic characteristics. In this work, a metal-organic frameworks material, zeolitic imidazolate framework-8 (ZIF-8), was synthesized through hydrothermal reaction for the adsorptive removal of harmful Congo red (CR) from aqueous solution. Results showed that the maximum adsorption capacity of CR onto ZIF-8 was ultrahigh as 1250 mg g\(^{-1}\). Adsorption behaviors can be successfully fitted by the pseudo-second order kinetic model and the Langmuir isotherm equation. Solution conditions (pH condition and the co-exist anions) may influence the adsorption behaviors. The adsorption performance at various temperatures indicated the process was a spontaneous and endothermic adsorption reaction. The enhanced adsorption capacity was determined due to large surface area of ZIF-8 and the strong interactions between surface groups of ZIF-8 and CR molecules including the electrostatic interaction between external active sites Zn–OH on ZIF-8 and –SO\(_3\) or –N=N– sites in CR molecule, and the \(\pi\)–\(\pi\) interaction.

1. Introduction
Nowadays, dyes and pigments are widely used in chemical industries, which may enter ecosystems (e.g. aquatic, soils) during dyes production and subsequent application processes.[1] The occurrence of dyes may lead to severe water pollution problems.[2] Dyes exposure in aquatic environment creates risks to human health and biota due to their intrinsic toxic, mutagenic and carcinogenic characteristics.[2] Among various dye species, Congo red (CR) is a typical benzidine-based azo dye and mainly exists in the effluent of textile, paper, printing industries, etc.[3] After entering natural environment, CR can be metabolized to benzidine, a well-known human carcinogen, which may be a cause for human allergic diseases. Due to its high chemical stability and low biodegradability, conventional biological processes was found to be ineffective to decolorize and degrade CR wastewater treatment. Some physical-chemical techniques have been investigated for CR removal from aquatic systems, for example, sonophotocatalysis, photolysis, coagulation/flocculation and adsorption.[4–7] In all previous studies, adsorption is regarded as a competitive one due to its simplicity, low cost and effectiveness and until now, various adsorbent materials have been examined for CR removal, including activated carbon, clay materials, modified biosorbents and synthetic materials.[8–12] Metal-organic frameworks (MOFs) represent a class of porous crystalline frameworks, and consist of metal ions (or clusters) and organic ligands.[13] Due to its admirable properties (e.g. ultrahigh surface area, tunable pore structure and surface charge), MOFs have attracted worldwide concerns and been applied in various fields, for example, gas separation/recycle, catalysis, adsorbents and energy storage.[14–17] Nowadays, adsorption and removing of various hazardous compounds from aquatic solution using MOFs are receiving increasing attention with the target pollutant to be both inorganic and organic. Adsorption mechanisms between pollutants and MOFs involve hydrophobic interactions, electrostatic enhancement and \(\pi\)–\(\pi\) interactions.[18] Previous studies have reported that MOFs are promising in some dyes capture in aquatic system due to their high porosities, relatively heterogeneous surface and strong electrostatic interactions.[19,20] However, there are only two studies investigating the adsorptive removal of CR from aquatic solution using different MOFs. Moradi et al. synthesized MIL-100(Fe) (an iron based MOF) which successfully achieved the adsorption capacity of 714 mg g\(^{-1}\) for CR.[11] Khanjani and Morsali synthesized MOF-5 coating on silk fiber which could totally adsorb and remove 50 mg L\(^{-1}\) CR by adding 2 mg adsorbent into 50 mL dye solution.[21]
Zeolitic imidazolate frameworks (ZIFs) are a set of MOF materials with excellent chemical and thermal stabilities that are topologically isomorphic with zeolites and contain functionalized organic links and a high density of transition metal ions.[22,23] Among different ZIFs reported, zeolitic imidazolate framework-8 (ZIF-8) targeting to a series of materials has a sodalite-related zeolite type structure containing narrow six-membered-ring pore windows and contains explored Zn$^{2+}$– N$^-$ linkers and Zn and N$^-$ extremities on the surface.[22]

Different synthesizing methods can be used to produce ZIF-8 materials using solvothermal, microwave-assisted, sonochemical, mecanochemical, dry-gel, and microfluidic methods.[24] The gained ZIF-8 may possess varied physical-chemical properties resulted from different synthesized method.[25] As reported, it is a potential candidate for adsorption/separation applications. Earlier investigations have demonstrated that ZIF-8 has a high performance in gas storage and can effectively separate organic molecules in aquatic solution.[16,26] In contrast, to date, only Fan et al. [16] reported the dye molecule adsorption onto ZIF-8, who found that the uptake capacity of ZIF-8 synthesized from surfactant mediated method for rhodamine B (a cationic dye) was very low and the external adsorption between ZIF-8 and rhodamine B molecules was negligible. The low adsorption capacity is attributed to the larger molecule size of rhodamine B than the pore aperture size of ZIF-8 (3.4 Å), and to the weak specific interaction between functional groups of ZIF-8 and rhodamine B molecule.[27,28]

Current study aims to examine the ZIF-8 nanoparticles synthesized through hydrothermal reaction for adsorption of anionic CR molecules from aquatic solution. The adsorption was studied by conducting batch kinetic and equilibrium experiments. Adsorption kinetics, adsorption isotherms and thermodynamics of CR onto synthesized ZIF-8 were thus systematically investigated. Furthermore, the effects of pH and competition anions were analyzed and the adsorption mechanism was characterized.

## 2. Materials and methods

### 2.1. Experimental material preparation

The synthesis of ZIF-8 was performed using ZnCl$_2$ as metal source, C$_6$H$_{12}$N$_2$ as organic linker, methanol as solvent and CHNaO$_2$ as inducing agent. Firstly, the ZnCl$_2$ (548 mg), CHNaO$_2$ (283 mg) and C$_6$H$_{12}$N$_2$ (667 mg) were dissolved in methanol (50 mL) together and dispersed using ultrasonic. The synthesis solution was filled in Teflon lined stainless steel autoclave and heated at 393 K for 5 h. The mixture was cooled to room temperature. Then, the precipitated white powder of ZIF-8 was collected after centrifugation (4000 rpm, 20 min) and washed with methanol for three times. The ZIF-8 sample was oven dried at 80 °C prior to using. Commonly used adsorbent zeolite (diameter <0.42 mm) and granular activated carbon (diameter <1 mm) were selected as references in CR removal experiments, which were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China).

The CR was purchased from Aladdin Industrial Co. (Shanghai, China). The molecular structure and selective physical properties of CR were shown in Supplementary materials (Figure S1 and Table S1). The CR stock solution was prepared with ultrapure water, and the desired concentrations of the experimental solutions were obtained through successive dilutions. The concentration of CR was determined by using a UV–visible spectrophotometer at maximum absorbance of 496.5 nm (Shimadzu UV spectrophotometer, UV-1800).

### 2.2. Adsorption procedure

For conducting the sorption experiment, 5 mg ZIF-8 was added into 20 mL CR solutions with different initial concentrations (25 mL glass vials). Vials were shaken (230 rpm, 30 °C) for certain time intervals. After that, the suspension was centrifuged (12000 rpm, 5 min) and filtered with 0.45 μm membrane prior to determination of the CR concentration.

For studying the batch adsorption equilibrium and the time effect on the adsorption of CR onto ZIF-8, every 5 mg of adsorbent was added into a series of 20 mL CR solution (80–250 mg L$^{-1}$). Samples were collected at certain time intervals. Relatively long adsorption duration (24 h) was set in preliminary experiments.

The percentage removal (%) and uptake amount, $q$ (mg g$^{-1}$), were calculated using Equations (1) and (2), respectively:

$$\text{Percentage removal} (%) = \left( \frac{C_i - C_f}{C_i} \right) \times 100$$

$$q = \left( C_i - C_f \right) \times \frac{V}{m}$$

where $C_i$ is initial concentration of CR (mg L$^{-1}$); $C_f$ is equilibrium concentration of CR (mg L$^{-1}$); $V$ is solution volume (mL); and $m$ is the weight of ZIF-8 (mg).

### 2.3. Adsorption kinetics of CR adsorption

To determine the adsorption kinetic, 5 mg ZIF-8 was added into a series of CR solutions (20 mL) with the same initial concentrations. The CR concentrations left in different vials were detected after shaking in predetermined time intervals. The kinetic characteristics of adsorption process were described by pseudo first-order rate equation (Equation (3)) and binuclear pseudo-second order equation described below (Equation (4)).[29,30]

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
\[ \frac{t}{q_t} = 1/(k_1 q_e^2) + \frac{t}{q_e} \]  
where \( t \) is the contact time (min); \( k_1 \) is the first order adsorption rate constant (min\(^{-1}\)); \( k_2 \) is the second order adsorption rate constant (g mg\(^{-1}\) min\(^{-1}\)); \( q_e \) and \( q_t \) is the uptake amount at equilibrium and time \( t \), respectively (mg g\(^{-1}\)).

### 2.4. Adsorption isotherm of CR adsorption

To conduct the adsorption isotherm experiment, 5 mg ZIF-8 was added into CR solutions (20 mL) with different initial concentrations (120–1046 mg L\(^{-1}\), pH 7.8, 30 °C, 700 min). Langmuir isotherm (Equation (5)) and Freundlich isotherm (Equation (7)) were selected for analyzing adsorption isotherm.[31,32] Langmuir isotherm is valid for monolayer adsorption on a surface owning to finite identical sites and Freundlich isotherm assumes the adsorption of dye molecule occurs on a heterogeneous surface by multilayer adsorption.[33]

\[
\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \tag{5}
\]

where \( q_e \) is the uptake amount of CR at equilibrium (mg g\(^{-1}\)); \( C_e \) is the equilibrium concentration of CR (mg L\(^{-1}\)); \( Q_m \) and \( b \) are the Langmuir constants related to maximum adsorption capacity and rate of adsorption, respectively. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor (\( R_L \)):

\[
R_L = \frac{1}{1 + bC_0} \tag{6}
\]

where \( C_0 \) is the highest CR concentration (mg L\(^{-1}\)). The value of \( R_L \) indicates the type of the isotherm to be either unfavorable (\( R_L > 1 \)), linear (\( R_L = 1 \)), favorable (\( 0 < R_L < 1 \)) or irreversible (\( R_L = 0 \)). The Freundlich isotherm was described as

\[
\ln q_e = \ln K_f + (1/n) \ln C_e \tag{7}
\]

where \( K_f \) and \( 1/n \) are Freundlich equilibrium constants indicative of adsorption capacity and adsorption intensity respectively. Value of \( n > 1 \) represents a favorable adsorption condition. \( 1/n \) and \( K_f \) were obtained by plotting \( \ln q_e \) against \( \ln C_e \).

### 2.5. Thermodynamic of CR adsorption

Five mg ZIF-8 was added into CR solutions (20 mL) with an initial concentration of 640 mg L\(^{-1}\) at different temperatures (293, 303 and 313 K). Thermodynamic parameters of standard Gibbs free energy (\( \Delta G^* \)), standard enthalpy (\( \Delta H^* \)) and standard entropy (\( \Delta S^* \)) were determined. The amounts of \( \Delta H^* \) and \( \Delta S^* \) could be calculated from the slope and intercept of the straight line obtained by plotting \( \ln K_f \) against \( 1/T \) using Equations (8)–(10).[34]

\[
\ln K_f = \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \tag{8}
\]

where \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the absolute temperature of the aqueous solution (K). \( K_f \) is the distribution coefficient, which is mass-weighted partition coefficient between solid phase and liquid supernatant phase (mL g\(^{-1}\)) reflecting the selectivity for objective pollutant, calculated according to the formula:

\[
K_f = \frac{C_0 - C_t}{C_t} \times \frac{V}{M} \tag{9}
\]

where \( C_0 \) and \( C_t \) are the concentrations of CR at contact time of 0 (initial concentration) and \( t \), respectively (mg L\(^{-1}\)). \( V \) is the volume of solution (mL) and \( M \) is the mass of adsorbent used (g).

After obtaining \( \Delta H^* \) and \( \Delta S^* \) values of the adsorption, \( \Delta G^* \) of each temperature was calculated as follows:

\[
\Delta G^* = \Delta H^* - T \Delta S^* \tag{10}
\]

### 2.6. Conditional adsorption experiments

To analyze the effect of solution pH on the adsorption, the pH of CR solution was adjusted with 0.1 M HCl and NaOH to get the final pH of 4, 6, 8 and 12 (initial CR concentration, 625 mg L\(^{-1}\), 30 °C). The effects of competition ions on the adsorption were evaluated by addition of 0.02 M NaCl, Na\(_2\)SO\(_4\), NaHCO\(_3\) and Na\(_2\)C\(_2\)O\(_4\) to the aqueous solution (initial CR concentration, 583 mg L\(^{-1}\), 30 °C). For studying the effect of CR adsorption on the zeta potential variation of ZIF-8, every 5 mg adsorbent was put into 20 mL CR solution at various initial concentrations of 0, 40, 80 and 100 mg L\(^{-1}\) (pH 7.8, 30 °C). After 700 min, the total amount of CR in solution was transferred onto ZIF-8 with adsorption amount of 0, 160, 320, 400 mg g\(^{-1}\), respectively. The final zeta potentials of ZIF-8 loaded with different amount of CR were measured with Zeta Potential Analyzer (Malvern Zetasizer Nano ZS). Furthermore, the UV–vis spectra of CR solution after adsorption for different time intervals (initial CR concentration, 120 mg L\(^{-1}\), 30 °C) were also determined by UV spectrophotometer (Shimadzu, UV-1800). In order to investigate the regeneration of the adsorbent, CR-loaded ZIF-8 was washed with 0.05 mol L\(^{-1}\) NaOH after the adsorption (pH 4, \( C_0 = 400 \) mg L\(^{-1}\), 6 h, 30 °C) and was shaken with another 20 mL 0.05 mol L\(^{-1}\) NaOH for 4 h. After that, the desorbed ZIF-8 was washed with deionized water and was dried at 60 °C for the next adsorption test. The adsorption-desorption cycle was repeated for three times.

### 2.7. Characteristics analysis of adsorbents

The morphology of the samples (before and after adsorption) were measured with a scanning electron microscopic (SU8010, Hitachi, Japan). A thin Pt film was loaded...
profiles of the CR removal with ZIF-8 at various initial CR concentrations. It was clear that the adsorption rate was initially fast and then gradually decreased to reach equilibrium.

Two kinetic models, pseudo-first order model and pseudo-second order model were selected to study the adsorption kinetic of CR onto ZIF-8. Obviously, Pseudo-second order model (Figure 2(b)) could fit the experimental results better than pseudo-first order model (Figure 2(a)). Table 1 showed the kinetic parameters for different initial concentrations of CR obtained utilizing two adsorption kinetic models. The pseudo-second order model generated a high degree of fitting ($R^2 > 0.9918$). The rate constants, $k_2$ for pseudo-second order decreased with the increase of initial concentration of CR (80–200 mg L$^{-1}$). This phenomenon is probably due to the lower competition for the adsorption sites at lower initial concentration of CR.[8] Similarly, the competition for the surface active sites will be stronger at higher initial concentration and the adsorption rates were consequently decreased.[36] The pseudo-second order model is based on the assumption that the rate-limiting factor in the adsorption was determined by chemisorption. Thus, the CR adsorption process onto synthesized ZIF-8 was a chemisorption rather than physical sorption.

3.2. Adsorption isotherms of CR onto ZIF-8

The adsorption isotherm of CR adsorption onto ZIF-8 was showed in Figure 3(a). Langmuir and Freundlich isotherms were widely used in describing adsorption organic pollutants onto porous materials. In current study, Freundlich isotherm was failed in fitting adsorption data during the whole experimental period. According to experiences of previous studies on adsorption of pollutants onto ZIF-8, the Langmuir isotherm model was selected to explain how adsorption takes place for CR onto ZIF-8.[27,37] In Langmuir fitting (Figure 3(b)), results of high degree of linear fitting between $C_e/Q_e$ vs. $C_e$.
observed by Reddy et al., who employed jujube seeds to adsorb CR from aqueous solution.[40] The positive value of $\Delta S^0$ indicated an increase in disorder of solid-liquid interface of material during adsorption of dye.[9] The negative values of $\Delta G^0$ and the positive values of $\Delta H^0$ revealed that the adsorption process of CR onto the ZIF-8 surface was a spontaneous and endothermic adsorption reaction.

### 3.4. Characteristics of ZIF-8 before and after adsorption

The XRD analysis was performed for ZIF-8 samples before and after adsorption (Figure 4(a)). All characteristics peaks were highly consistent with the simulated pattern of ZIF-8 and published patterns for synthesized ZIF-8 in previous studies.[37,41] The crystallized structure of ZIF-8 was stable after the adsorption by comparing XRD patterns for original and CR loaded ZIF-8. The FTIR spectra illustrated in Figure 4(b) showed some variations. The peak at 420 cm$^{-1}$ assigned to Zn–N mode in ZIF-8 which could generate Zn–OH and N–H groups.[42] Therefore, the broad peak at 3440 in spectra of CR loaded ZIF-8 is ascribed to the vibration of N–H and OH groups.[38]

### Table 1. Kinetic parameters for adsorption of CR dye using ZIF 8.

| Parameter | First-order kinetic model | Second-order kinetic model |
|-----------|--------------------------|---------------------------|
| Initial $C_{aw}$ (mg L$^{-1}$) | $q_{eexp}$ (mg g$^{-1}$) | $k_1$ (min$^{-1}$) | $q_{ecal}$ (mg g$^{-1}$) | $R^2$ | $k_2$ (min$^{-1}$) | $q_{ecal}$ (mg g$^{-1}$) | $R^2$ |
| 80 | 367.0 | 0.0306 | 292.5 | 0.9120 | 2.51 $\times$ 10$^{-4}$ | 370.4 | 0.9992 |
| 120 | 512.0 | 0.0313 | 612.0 | 0.9320 | 1.06 $\times$ 10$^{-4}$ | 526.3 | 0.9990 |
| 160 | 638.0 | 0.0157 | 538.0 | 0.9272 | 0.52 $\times$ 10$^{-4}$ | 666.0 | 0.9982 |
| 200 | 798.0 | 0.0122 | 837.0 | 0.9464 | 0.15 $\times$ 10$^{-4}$ | 909.0 | 0.9918 |
| 250 | 994.0 | 0.0067 | 875.0 | 0.9841 | 0.10 $\times$ 10$^{-4}$ | 1111.0 | 0.9936 |

Notes: $k_1$, first order adsorption rate constant (min$^{-1}$); $q_{eexp}$, experimental uptake amount at equilibrium; $q_{ecal}$, calculated uptake amount at equilibrium; $k_2$, second order adsorption rate constant (g mg$^{-1}$ min$^{-1}$).

Figure 3. (a) Adsorption isotherm of CR onto ZIF-8; (b) adsorption isotherm of CR onto ZIF-8 fitted by Langmuir isotherm equation.

Note: Adsorbent dosage 0.4 g L$^{-1}$, 30 $^\circ$C.
Sorption occurred since the molecule size of Rhodamine B at 13.4 Å was larger than the aperture size of ZIF-8 at 3.4 Å. However, they further found that the adsorption capacity was very low although the SSA of the synthesized ZIF-8 was as high as 1256 m² g⁻¹. In this study, the molecular size of CR is 26.6 Å (Table S1, Supplementary materials) which is much larger than the Rhodamine B molecule, and thus the CR could not enter the pores in ZIF-8 structure.[45] The adsorption of large CR molecule depends on the external surface area of the ZIF-8 and the average primary particle size of ZIF-8 was around 0.93 μm (Figure S3).[46] The large adsorption capacity may be attributed to the strong adsorption of CR on the surface of ZIF-8, where surface chemical interactions (e.g. through functional groups) between ZIF-8 and CR could not be negligible for the adsorption process. Our result was also consistent with a previous study from Tanaka et al. who found the adsorption capacities of Rhodamine B onto monocrystal and polycrystal ZIF-8 could reach 9.0 and 8.8 μmol g⁻¹, respectively mainly through the

Table 2. Thermodynamic parameters for the adsorption of CR on ZIF-8 at different temperatures.

| Temperature (K) | K_d (mL g⁻¹) | ΔG (kJ mol⁻¹) | ΔH (kJ mol⁻¹) | ΔS (kJ K⁻¹ mol⁻¹) |
|----------------|--------------|--------------|--------------|------------------|
| 293            | 3071.8       | −19.263      | 33.77        | 0.181            |
| 303            | 4012.8       | −21.073      |              |                  |
| 313            | 7479.8       | −22.883      |              |                  |

Notes: K_d, the distribution coefficient; ΔG°, standard Gibbs free energy; ΔH°, standard enthalpy; ΔS°, standard entropy.

Figure 4. (a) XRD pattern of pristine ZIF-8 and CR loaded ZIF-8; (b) FTIR spectra of pristine ZIF-8 and CR loaded ZIF-8; (c) SEM micrographs of pristine ZIF-8; (d) SEM micrograph of CR loaded ZIF-8.

The intense peak at 619 nm in spectra of CR and ZIF-8 after adsorption is assigned to –SO₃⁻.[43] Furthermore, the variation peak at 1060 also assigned to S=S stretching vibrations in CR could still be observed in spectra of CR-loaded ZIF-8 but it shifted to some higher wave numbers (1060–1120 cm⁻¹).[44] Variations above indicated the successful interaction of –SO₃⁻ in CR onto Zn–OH sites of ZIF-8 by ion exchange. The bond at 1590 cm⁻¹ attributed to C=C in benzene in CR structure diminishes in ZIF-8 after adsorption could be related to the π–π interaction between benzene rings of CR and the aromatic imidazole rings of ZIF-8.[12]

The SEM images visually displayed a crystalline structure of the ZIF-8 and the alterations between original and CR-loaded ZIF-8 (Figure 4 (c) and (d)), showing that the ZIF-8 was coated with dye molecules after the adsorption process. The dye molecules seem to have formed a film covering the ZIF-8 particles and porosity in aggregates. Fan et al. [16] found that it was unable for Rhodamine B to enter the pores in ZIF-8 and just surface
In the UV–vis spectra of CR solutions (Figure 5(b)), a main peak at around 496 nm is corresponding to chromophore structure next to the azo agent. Peaks located at 347 and 235 nm were assigned to the naphthalene and benzoic rings, respectively. There was no obvious horizontal shift for these peaks during the whole adsorption period. The spectra also prove high solvent stability of ZIF-8 structure after dispersed in water during the adsorption process, which agrees with the results of XRD patterns. Figure 5(b) also reveals that the removal rate of CR using ZIF-8 is extremely high because the color of 120 mg L⁻¹ CR solution is almost colorless after adsorption for 150 min. Various anions coexist with CR in wastewater, and some common anions (Cl⁻, SO₄²⁻, HCO₃⁻, and C₂O₄²⁻) were selected to analyze their effects on the removal efficiency (Figure 5(c)), showing that coexisting mono or di-valent anions have no significant effects on the adsorption capacities.

3.5. Conditional adsorption properties

ZIF-8 contains different functional groups which possess different charges. The zeta potential of ZIF-8 remained positive at pH below around 10 and varied to negative at higher pH values was found in previous studies.[26,27] The changes of electricity properties of ZIF-8 were detected before and after adsorption by analyzing its zeta potential. It should be noted that the adsorbed CR anions brought negative zeta potential onto ZIF-8 (Figure 5(a)). The linear fitting between adsorbed amount of CR and the variation in zeta potential of ZIF-8 (Zeta_{final} - Zeta_{original}) was satisfied ($R^2 = 0.9556$). This proves that the adsorption occurs between the negatively charged sites in dye anions and positively charged sites of ZIF-8. Besides, the $\pi-\pi$ interactions between benzene or naphthalene rings of CR with the aromatic imidazole rings of ZIF-8 should also be considered for the adsorption of CR onto ZIF-8.[27,42]

Figure 5. (a) The effect of the amount of adsorbed CR on the changes in zeta potential of ZIF-8 (pH 7.8); (b) UV–vis detection for CR removal efficiency at different time (initial concentration, 120 mg L⁻¹); (c) Effect of competition anions on the adsorption capacities; (d) Effect of initial pH on the adsorption.

In the UV–vis spectra of CR solutions (Figure 5(b)), a main peak at around 496 nm is corresponding to chromophore structure next to the azo agent. Peaks located at 347 and 235 nm were assigned to the naphthalene and benzoic rings, respectively. There was no obvious horizontal shift for these peaks during the whole adsorption period. The spectra also prove high solvent stability of ZIF-8 structure after dispersed in water during the adsorption process, which agrees with the results of XRD patterns. Figure 5(b) also reveals that the removal rate of CR using ZIF-8 is extremely high because the color of 120 mg L⁻¹ CR solution is almost colorless after adsorption for 150 min. Various anions coexist with CR in wastewater, and some common anions (Cl⁻, SO₄²⁻, HCO₃⁻, and C₂O₄²⁻) were selected to analyze their effects on the removal efficiency (Figure 5(c)), showing that coexisting mono or di-valent anions have no significant effects on the adsorption capacities.

As an acidic dye, CR contains negatively charged sulfonated group, and pH may play an important role in the active sites on ZIF-8 and in the dye speciation during the adsorption process. The adsorption efficiency of CR on ZIF-8 decreased with the increase of pH (Figure 5(d)).
The CR concentration almost decreased to zero after 60 min following ZIF-8 addition, while the final CR concentrations were 55.7 and 47.0 mg L\(^{-1}\) when adding zeolite and activated carbon as the sorbents, respectively. The SSA of ZIF-8 at 1256 m\(^2\) g\(^{-1}\) was much higher than zeolite and activated carbon (57 and 372 m\(^2\) g\(^{-1}\), respectively, Table S2). And also, the pore volume for ZIF-8 at 0.6 cm\(^3\) g\(^{-1}\) was larger than those for zeolite and activated carbon (0.14 and 0.37 cm\(^3\) g\(^{-1}\), respectively). Generally, a larger SSA and pore volume are favorable for the adsorption process between adsorbent and CR in solution.[9] For the three adsorbents, the adsorption processes increased rapidly at the initial stages. This trend could be attributed to the large vacant surface sites for interaction between different adsorbents and CR molecule.[36]

Typically, the ZIF-8 used in current study possessed better adsorption performance than other previous studied MOFs, MIL-100 (714 mg g\(^{-1}\)) and silk fibers coating MOF-5 (calculated adsorption capacity was around 1250 mg g\(^{-1}\)), even though the specific surface area (2800 m\(^2\) g\(^{-1}\)) for MIL-100 was larger than twice for ZIF-8.[11,21] It can also be revealed from Table 3 that there was no certain relationship between listed SSA of various adsorbents and the corresponding adsorption capacities. Therefore, the large adsorption capacity of CR onto the ZIF-8 was dominated both of the large SSA of the adsorbent and the chemical interactions between the surface functional groups on ZIF-8 and CR molecules including the strong electrostatic interaction between external active sites Zn–OH on ZIF-8 and –SO\(_3\) or –N=N– sites in CR molecule, and the \(\pi-\pi\) interaction.

3. Concluding remarks

ZIF-8 can be used for efficient adsorption of CR from aqueous solution. The fast adsorption kinetics, high adsorption capacity and solvent stability of ZIF-8 were observed. Although the molecular size of CR is much larger than pore aperture in ZIF-8, the ultra-high adsorption efficiency is attributed to the hydration process of ZIF-8 to form a surface hydrogen group by dissociative adsorption of water which benefits the adhesion of CR anionic species tightly to the surface of ZIF-8 as well as the \(\pi-\pi\) interaction between CR and ZIF-8. Furthermore, ZIF-8 exhibits a wide applicable pH range (4–12) and the adsorption efficiency decreases with the increase of pH.

It can be seen that, the adsorption effect still occurred when the ZIF-8 was negatively charged at pH 12 (point zero charge at pH 10). Negatively charge on the adsorbent increased following the pH increased, which does not favor the adsorption of the anionic dye due to the electrostatic repulsion.[11] This is similar to the previous finding with other adsorbents.[38]

The regeneration ability of ZIF-8 after adsorption was shown in Figure S4. It was apparent that the adsorption capacity was decreased to 44% in the second run and was further decreased to 18% in the third run. The loss of the adsorption capacity may be resulted from several reasons. Firstly, some inactive sites on ZIF-8 were occupied by some undesorbed CR molecules due to the incompletely desorption. Secondly, some minor collapse of the crystalline structure of ZIF-8 may be happened during the continued adsorption-desorption cycles.[27]

### Table 3. Comparison of maximum adsorption capacities of various adsorbents for CR.

| Adsorbent                                      | Surface area (m\(^2\) g\(^{-1}\)) | Total pore volume (cm\(^3\) g\(^{-1}\)) | \(q_m\) (mg g\(^{-1}\)) | Reference |
|------------------------------------------------|-----------------------------------|----------------------------------------|------------------------|-----------|
| Supramolecular polymer [Cu(bipy)(SO\(_4\))]\(_n\) | 2429                              |                                        |                        | [20]      |
| CoCoOH\(_2\) nanocomposite                      | 2058                              |                                        |                        | [12]      |
| ZIF-8(Zn)                                       | 1256                              | 0.6                                    | 1250                   | This study |
| MIL-100(Fe)                                     | 2800                              | 0.882                                  | 714                    | [11]      |
| Surfactant modified montmorillonite             | 358                               |                                        |                        | [38]      |
| Cellulose/Fe\(_3\)O\(_4\)/activated carbon composite | 11.87                            | 4.24\(\times\)08                      | 66                     | [10]      |
| Interconnected polypyrrole–polyaniline nanofibres | 59.7                             | 3.60\(\times\)08                      | 222                    | [7]       |
| Activated bentonites                            | 84.12                             |                                        | 7                      | [39]      |
The coexisting mono or di-valent anions have no evident effects on adsorption capacities. Therefore, ZIF-8 could be an efficient adsorbent for the removal of CR from aquatic system and is a new choice for CR removal in practical wastewater treatment.

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