



Short communication

## Adsorptive removal of methyl orange and methylene blue from aqueous solution with a metal-organic framework material, iron terephthalate (MOF-235)

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## ABSTRACT

An iron terephthalate (MOF-235), one of the metal-organic frameworks (MOFs), has been used for the removal of harmful dyes (anionic dye methyl orange (MO) and cationic dye methylene blue (MB)) from contaminated water *via* adsorption. The adsorption capacities of MOF-235 are much higher than those of an activated carbon. The performance of MOF-235 having high adsorption capacity is remarkable because the MOF-235 does not adsorb nitrogen at liquid nitrogen temperature. Based on this study, MOFs, even if they do not adsorb gases, can be suggested as potential adsorbents to remove harmful materials in the liquid phase. Adsorption of MO and MB at various temperatures shows that the adsorption is a spontaneous and endothermic process and that the entropy increases (the driving force of the adsorption) with adsorption of MO and MB.

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## 1. Introduction

Recently, considerable amount of waste water with color has been generated from many industries including textile, leather, paper, printing, dyestuff, plastic and so on [1]. Removal of dye materials from contaminated water is very important because water quality is highly influenced by color [1] and even a small amount of dye is highly visible and undesirable. Moreover, many dyes are considered to be toxic and even carcinogenic [1–3].

It is difficult to degrade dye materials because they are very stable to light and oxidation reactions [3]. For the removal of dye materials from contaminated water, several methods such as physical, chemical and biological methods have been investigated [1,3]. Among the proposed methods, removal of dyes by adsorption technologies is regarded as one of the competitive methods because of high efficiency, economic feasibility and simplicity of design/operation [3,4]. Moreover, adsorption of dyes on inorganic supports like silica is important to produce pigments [5,6].

Methyl orange (MO) is one of the well-known acidic/anionic dyes, and has been widely used in textile, printing, paper, food and pharmaceutical industries and research laboratories [2]. Methylene blue (MB) is one of the most common dye materials for wood, silk and cotton [4]. The structures of MO and MB are shown in Scheme 1 and the removal of MO and MB from water is very important due

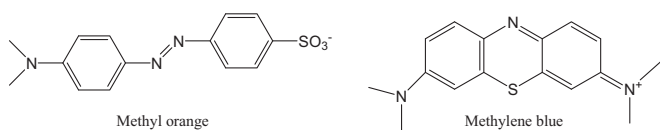
to their toxicity [2–4]. MO and MB for the reasons stated above were selected in this study as a representative acidic (anionic) dye and basic (cationic) dye, respectively. Several adsorbents such as activated carbon [7,8], alginate bead [9], cellulose-based wastes [10], diaminoethane sporopollenin [11] have been studied for the removal of both MO and MB dyes.

Metal-organic frameworks (MOFs) are crystalline materials which are well known for their various applications [12–19]. The particular interest in MOF materials is due to the easy tunability of their pore size and shape from a micro to a meso scale by changing the connectivity of the inorganic moiety and the nature of organic linkers [12–14]. MOFs are especially interesting in the field of adsorption, separation and storage of gases and vapors [15,18,20]. The removal of hazardous materials such as sulfur-containing materials has also been studied using MOFs [21,22].

However, so far, there has been little report of the use of MOFs in the removal of dye materials. Very recently, we have suggested [23] the potential applications of MOFs for the adsorptive removal of MO. Especially MOFs having a positive charge such as protonated ethylenediamine-grafted Cr-terephthalate (MIL-101) show high adsorption capacity, rapid uptake and ready regeneration for the MO [23].

In this work, we report the results of the adsorption of not only an anionic dye (MO) but also a cationic dye (MB) over a MOF called MOF-235 [24] because removal of both cationic and anionic dyes are not readily achieved simultaneously [9] and the adsorption can be understood with a comparison of the two adsorbates. MOF-235,  $[\text{Fe}_3\text{O}(\text{terephthalate})_3(\text{DMF})_3][\text{FeCl}_4]$  (DMF stands

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Scheme 1.

for *N,N*-dimethylformide), is readily available at low temperature and composed of non-toxic  $\text{Fe}_3\text{O}$  clusters [24]. The MOF-235 frameworks have positive charge (+1 per formula unit), which is balanced with  $[\text{FeCl}_4]^-$  ion [24]. The adsorptive removal of MO and MB is interesting because both anionic and cationic dyes are adsorbed in liquid phase even though MOF-235 is regarded as a nonporous material as nitrogen is hardly adsorbed over the MOF-235 at low temperature.

## 2. Experimental

MOF-235 was synthesized under autogeneous pressure according to the reported method [24]. An exact amount of terephthalic acid (0.205 g, 1.23 mmol; Sigma–Aldrich, 98%) was mixed with 60 mL of DMF (DC Chem., 99%). Then the mixture was stirred for 10 min till a clear solution was formed. After that  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.200 g, 0.738 mmol; Duksan, 99.7%) was added into the solution and stirred for 5 min. The reactant mixture of 30 mL and 30 mL of ethanol (DC Chem., 96%) were loaded into a Teflon-lined autoclave, sealed and placed in a preheated electric oven (80 °C) for 1 day. Orange powder of MOF-235 was collected by centrifugation and was washed with a DMF/ethanol mixture at least three times. Then the product was dried overnight at 150 °C to remove DMF and then stored in a glass vial. Activated carbon was purchased from Duksan (granule, size: 2–3 mm).

An aqueous stock solution of MO or MB (1000 ppm) was prepared by dissolving MO ( $\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$ , MW: 327.34, Daejung) or MB ( $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ , MW: 373.9, Sigma–Aldrich) in deionized water. Aqueous solutions with different concentration of MO or MB (5–200 ppm) were prepared by successive dilution of the stock solution with water. The MO or MB concentrations were determined using an absorbance (at 464 and 665 nm, respectively) of the solutions after getting the UV spectra of the solution with a spectrophotometer (Shimadzu UV spectrophotometer, UV-1800). The calibration curve was obtained from the spectra of the standard solutions (5–50 ppm) at a specific pH (usually 5.6).

Before adsorption, the adsorbents were dried overnight under vacuum at 100 °C and were kept in a desiccator. An exact amount

of the adsorbents (~5 mg) was put in the aqueous dye solutions (50 mL) having fixed dye concentrations from 20 ppm to 200 ppm. The dye solutions containing the adsorbents were mixed well with magnetic stirring and maintained for a fixed time (10 min to 12 h) at 25 °C. After adsorption for a pre-determined time, the solution was separated from the adsorbents with a syringe filter (PTFE, hydrophobic, 0.5  $\mu\text{m}$ ), and the dye concentration was calculated, after dilution (if necessary), with an absorbance. The adsorption rate constant was calculated using pseudo-second or pseudo-first order reaction kinetics [25–27] and the maximum adsorption capacity was calculated using the Langmuir adsorption isotherm [25,28] after adsorption for 12 h. To get the thermodynamic parameters of adsorption such as  $\Delta G$  (free energy change),  $\Delta H$  (enthalpy change) and  $\Delta S$  (entropy change) the adsorption was further carried out at 35 and 45 °C. To determine the adsorption capacity at various pHs, the pH of the dye solutions was adjusted with 0.1 M HCl or 0.1 M NaOH aqueous solution.

## 3. Results and discussion

The XRD pattern in Supporting Fig. S1 shows that the synthesized material has the MOF-235 structure [24]. The SEM image (Supporting Fig. S1) and nitrogen adsorption isotherm (Supporting Fig. S2) illustrate that the MOF-235 has homogeneous morphology and adsorbs little nitrogen compared with activated carbon.

As shown in Fig. 1a, the adsorbed quantity of MO and MB over MOF-235 is much higher than those over an activated carbon. The amount of adsorbed dyes slightly increases with the initial concentrations (Supporting Fig. S3), showing the favorable adsorption at high dye concentration. To compare the adsorption kinetics precisely, the changes of adsorbed amount with time are treated with the versatile pseudo-second-order kinetic model [25–27]:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (1)$$

or

$$\frac{t}{q_1} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where  $q_e$ : amount adsorbed at equilibrium (mg/g);  $q_t$ : amount adsorbed at time  $t$  (mg/g);  $t$ : adsorption time (h).

Therefore, the second order kinetic constant ( $k_2$ ) can be calculated by  $k_2 = \text{slope}^2 / \text{intercept}$  when the  $t/q_t$  is plotted against  $t$ .

Fig. 1b shows the plots of the pseudo-second-order kinetics of the MO and MB adsorption over the MOF-235 and activated carbon at initial dye concentration ( $C_i$ ) of 30 ppm. The calculated kinetic

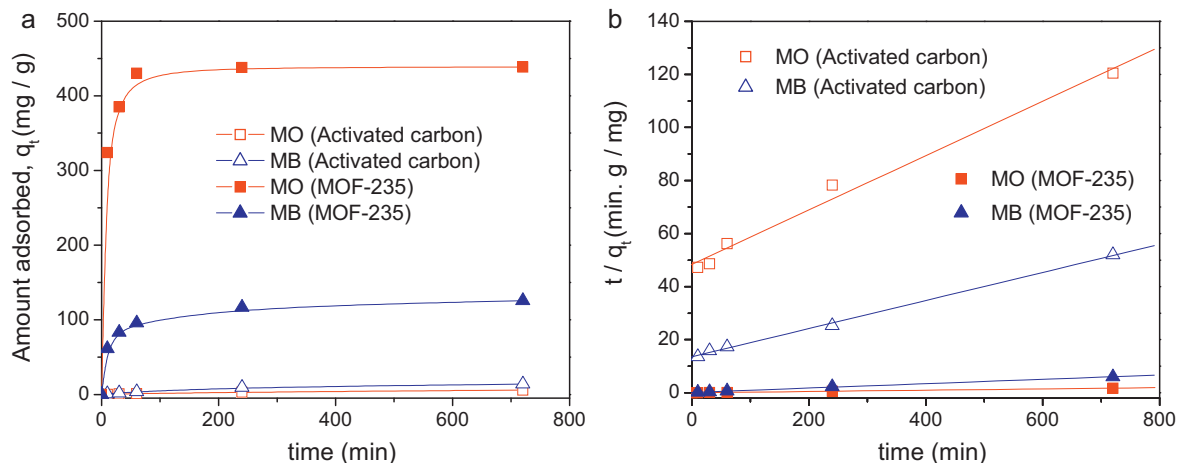


Fig. 1. (a) Effect of contact time on the MO and MB adsorption over MOF-235 and activated carbon; and (b) plots of pseudo-second-order kinetics of MO and MB adsorption over MOF-235 and activated carbon ( $C_i$ : 30 ppm).

**Table 1**

The pseudo-second-order kinetic constants ( $k_2$ ) with correlation coefficients ( $R^2$ ) at various initial MO and MB concentrations and the maximum adsorption capacities ( $Q_0$ ) of MOF-235 and activated carbon.

Adsorbents	Dyes	Pseudo-second-order kinetics constants $k_2$ (g/(mg min))						Adsorption capacity, $Q_0$ (mg/g)
		20 ppm		30 ppm		40 ppm		
		$k_2$	$R^2$	$k_2$	$R^2$	$k_2$	$R^2$	
MOF-235	MO	$7.67 \times 10^{-4}$	0.999	$8.79 \times 10^{-4}$	0.998	$9.10 \times 10^{-4}$	0.998	477
	MB	$9.58 \times 10^{-5}$	0.995	$1.67 \times 10^{-4}$	0.993	$2.18 \times 10^{-4}$	0.998	187
Activated carbon	MO	$1.95 \times 10^{-4}$	0.994	$2.17 \times 10^{-4}$	0.987	$2.34 \times 10^{-4}$	0.981	11.2
	MB	$9.71 \times 10^{-5}$	0.997	$1.14 \times 10^{-4}$	0.979	$1.48 \times 10^{-4}$	0.972	26.0

constants ( $k_2$ ) and correlation coefficients ( $R^2$ ) are shown in Table 1 for  $C_i = 20, 30$  and  $40$  ppm. The adsorption kinetic constants for MO adsorption over MOF-235 are larger than the constants over activated carbon. However, the kinetic constants for MB over MOF-235 are nearly similar to those over activated carbon. Interestingly, the kinetic constants for MO over MOF-235 are smaller than those over MIL-101s [23] even though the adsorption capacities ( $Q_0$ ) over MOF-235 are larger than those over MIL-101s [23]. The kinetic constants over MOF-235 and activated carbon increase slightly with increasing the initial dye concentrations, showing rapid adsorption in the presence of dyes in high concentration, similar to previous reports [25,29–31]. The adsorption data were also analyzed using the pseudo-first-order kinetic model [25], and the results of kinetics (Supporting Table S1) are in accordance with the results of pseudo-second-order kinetic model.

The adsorption isotherms were obtained after adsorption for 12 h, and the results are compared in Fig. 2a. The amount of adsorbed dyes over MOF-235 is higher than that over activated carbon for the experimental conditions, suggesting the efficiency of the MOF-235. As shown in Fig. 2b, the adsorption isotherms have been plotted to follow the Langmuir equation [25,28]:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \quad (3)$$

where  $C_e$ : equilibrium concentration of adsorbate (mg/L);  $q_e$ : the amount of adsorbate adsorbed (mg/g);  $Q_0$ : Langmuir constant (maximum adsorption capacity) (mg/g);  $b$ : Langmuir constant (L/mg or L/mol).

Therefore, the  $Q_0$  can be obtained from the reciprocal of the slope of a plot of  $C_e/q_e$  against  $C_e$ . The  $Q_0$  values that are determined from Fig. 2b are summarized in Table 1. The  $Q_0$  of MO over MOF-235 is larger than that over activated carbon by around 43 times. For the case of MB, the  $Q_0$  over MOF-235 is larger than activated carbon by about 7 times. The  $Q_0$  values for MO and MB are generally

**Table 2**

The maximum adsorption capacity and thermodynamic parameters of MO and MB adsorption over MOF-235 at different temperatures.

Dyes	Temp. (°C)	$Q_0$ (mg/g)	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol/K)
MO	25	477	-31.1	99.6	441
	35	448	-35.9		
	45	501	-41.0		
MB	25	187	-26.2	63.1	300
	35	230	-29.5		
	45	252	-32.2		

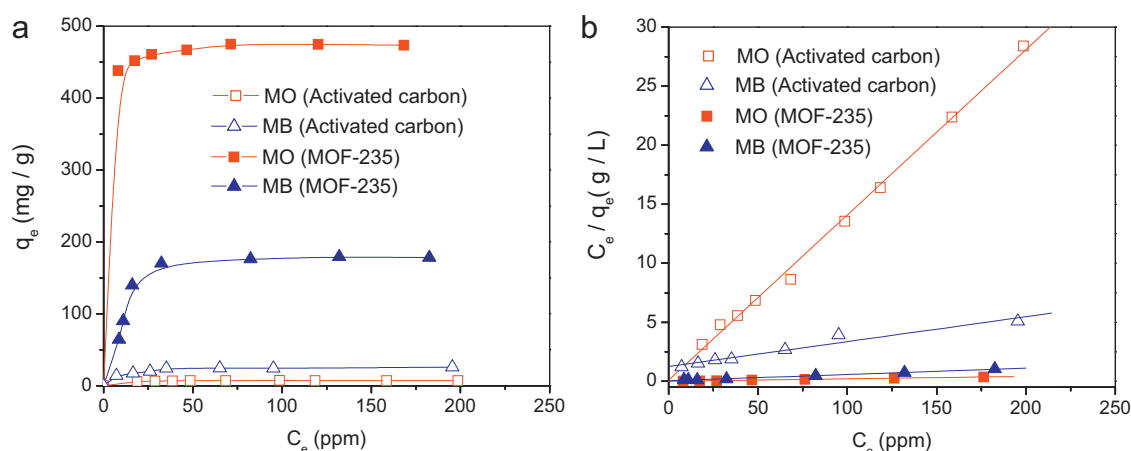
larger than those over other adsorbents like activated carbon [7], cellulose-based wastes [10] and magnetic cellulose bead [8], which is important for simultaneous adsorption.

To shed light on the dyes adsorption over MOF-235, the adsorption free energy, enthalpy and entropy change were calculated from the adsorption of MO and MB over MOF-235 at various temperatures. Supporting Figs. S4 and S5 show the adsorption isotherms and their Langmuir plots at the temperature of 25, 35 and 45 °C. The adsorption capacity increases with increasing adsorption temperature, suggesting an endothermic adsorption similar to previous results [23,32].

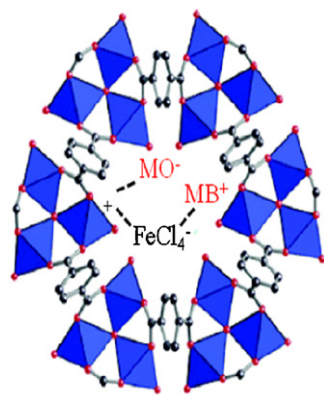
The Gibbs free energy change  $\Delta G$  can be calculated by the following Eq. (5) [7,27,33,34]:

$$\Delta G = -RT \ln b \quad (\text{where } R \text{ is gas constant}) \quad (4)$$

The Langmuir constant  $b$  (dimension: L/mol) can be obtained from the slope/intercept of the Langmuir plot of Fig. 2b. The negative free energy change ( $\Delta G$ ) shown in Table 2 suggests spontaneous adsorption under the experimental conditions.



**Fig. 2.** (a) Adsorption isotherms for MO and MB adsorption over MOF-235 and activated carbon; (b) Langmuir plots of the isotherms of (a).



Scheme 2.

The enthalpy change  $\Delta H$  can be obtained by using the van't Hoff equation [33,34]:

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

The calculated  $\Delta H$  values, obtained from the ( $-\text{slope} \times R$ ) of the van't Hoff plot (Supporting Fig. S6), are 99.6 and 63.1 kJ/mol for MO and MB adsorption, respectively, confirming endothermic adsorption in accord with the increasing adsorption capacity associated with increasing adsorption temperature (Supporting Figs. S4 and S5). The endothermic adsorptions may be due to a stronger interaction between pre-adsorbed water and the adsorbent than the interaction between MO or MB and the adsorbent.

The entropy change  $\Delta S$  can be obtained from the ( $\text{intercept} \times R$ ) of the van't Hoff plot (Supporting Fig. S6), and the obtained entropy change  $\Delta S$  is 441 and 300 J/(molK) for MO and MB, respectively. The positive  $\Delta S$  means the increased randomness with adsorption of MO or MB probably because the number of desorbed water molecule is larger than that of the adsorbed MO or MB molecule (dyes are very bulky compared with water; therefore several water molecules may be desorbed by adsorption of a dye molecule). Therefore, the driving force for the dyes adsorption (negative  $\Delta G$ ) on MOF-235 is due to an entropy effect (large positive  $\Delta S$ ) rather than an enthalpy change ( $\Delta H$  is positive).

The adsorption of a dye usually is highly dependent on the pH of the solution [2,7]. MO and MB adsorption at various pH values was measured after equilibration with MOF-235. As shown in Supporting Fig. S7, the amounts of adsorbed MO decrease with increasing the pH of the MO solution, which is quite similar to previous reports [2,7,23]. The decrease of adsorbed MO with increasing pH might be due to the fact that the density of positive charge of the adsorbent decreases with increasing pH (see below). On the contrary, the adsorbed MB increases with increasing pH, similar to previously reported results [4,7,35]. The increase of adsorbed MB with increasing pH might be due to the fact that the concentration of negative charge of the adsorbent increases with increasing pH (see below).

Even though a more detailed study is necessary to clearly understand the mechanism of MO or MB adsorption on MOF-235, the adsorption may be explained with an electrostatic interaction between the dyes and adsorbents (as proposed in Scheme 2). MO and MB usually exist in negative and positive forms, respectively; therefore, there will be an electrostatic interaction with an adsorbent having a positive (frameworks) and negative charge (charge-balancing anion), respectively. The surface charge of MOF-235 decreases with pH as shown in Supporting Fig. S8. Therefore, the change of adsorption capacities of MO and MB with pH may be explained with the increased negative charge of the adsorbent in a high pH condition. A similar adsorption mechanism *via* elec-

trostatic interaction has been reported [23,34]. However, other mechanism like  $\pi$ - $\pi$  interaction [9] between benzene rings of MOF-235 and dyes cannot be ruled out.

It is quite remarkable that MOF-235 readily adsorbs MO and MB in liquid phase because the MOF-235 has little porosity as confirmed with nitrogen adsorption (Supporting Fig. S2). MOFs are different to inorganic porous materials because of flexible frameworks [12,13]. In some cases MOFs may change their structures with strong interaction with adsorbates [36,37]. At this moment, it is not clear whether the MOF-235 changes its framework or not with the adsorption of dyes. However, the high adsorption capacity may suggest a strong interaction between the dyes and MOF-235 structure.

#### 4. Conclusion

Representative dyes (anionic MO and cationic MB) in contaminated water can be efficiently removed with a MOF-type material. MOF-235, an iron terephthalate, can adsorb very large amount of both MO and MB *via* a specific interaction like electrostatic interaction between the dyes and the adsorbent. The adsorption of MO or MB over MOF-235 at various temperatures shows that the adsorption is spontaneous and endothermic and the randomness increases probably with desorption of pre-adsorbed water. The driving force of MO or MB adsorption over MOF-235 is mainly due to an entropy effect rather than an enthalpy change. It is remarkable that the MOF-235 readily adsorbs both cationic and anionic dyes in liquid phase even though the MOF-235 hardly adsorbs nitrogen. From this study, it can be suggested that MOF-type materials, even if they do not adsorb gases, may be applied in the adsorptive-removal of dye materials in the liquid phase.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.09.035.

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