Microporous and Mesoporous Materials 193 (2014) 27–34

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

# Adsorption behavior of metal–organic frameworks for methylene blue from aqueous solution

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ARTICLE INFO

*Article history:*
Received 10 October 2013
Received in revised form 17 February 2014
Accepted 1 March 2014
Available online 13 March 2014

*Keywords:*
Metal organic frameworks
Adsorption dye wastewater
Cu-BTC
Kinetic model
Langmuir isotherm

ABSTRACT

A metal–organic frameworks (MOFs) based on copper-benzenetricarboxylates was applied to the adsorption of methylene blue (MB) from aqueous solution. Cu-BTC [BTC = 1,3,5-benzenetricarboxylate] also known as HKUST-1 is a widely studied MOF. Cu-BTC mainly possessed mesopores, high surface area and big pore volume which is benefit for the adsorption capacity. Characterization of Cu-BTC were achieved by XRD, SEM micrographs, nitrogen adsorption–desorption analysis and FT-IR spectra. The kinetics characteristic and thermodynamic parameters were also analyzed. The experimental isotherms data were analyzed using Langmuir and Freundlich isotherm equations and the results indicated that the Langmuir isotherm showed a better fit for MB adsorption. Thermodynamic parameters were calculated by the Gibbs free energy function, confirming that the adsorption process was spontaneous and accompanied by exothermic. The maximum removal has been achieved at the pH = 7.0. The possible mechanism and the adsorption behavior of the adsorption of MB onto Cu-BTC were investigated. The adsorbent Cu-BTC could be easily regenerated after washing with ethanol. The experimental results suggested that Cu-BTC materials have potential application for the wastewater treatment containing MB dye.



## 1. Introduction

Various kinds of synthetic dyes are found in effluent wastewaters from a variety of industries such as textile, leather, plastic, food processing, cosmetics, paper, printing, pharmaceutical and dye manufacturing [1]. Organic dyes released into the environment have posed a significant threat to the environment and creatures health due to the fact that it has a certain toxicity and even carcinogenic [2], which is very difficult to degrade under natural conditions. Waste water treatment is an important field of study. At present, various techniques and methods can be used to remove organic dyes from aqueous solution, such as physical, chemical, and biological methods. Adsorption is the procedure of choice, which being the widely used physicochemical method for dye removal because adsorption does not need a high operation temperature and several coloring materials can be removed simultaneously [3]. Recently, a variety of adsorbents have received much more attention for the removal of organic dyes. The use of more dye adsorbent is the granular activated carbon, active diatomaceous earth and resins. Activated carbon adsorption method is a method applied earlier, and this method is very effective for the removal of dissolved organic matter, However, it is more difficult to regenerate, and the processing cost is higher, so the application is narrow [4].

Metal–organic frameworks (MOFs), known as metal organic coordination polymers, commonly recognized as "soft" analogues of zeolites, is a new class of porous structures composed of different varieties transition metal ions (or clusters) and rigid-rod-like organic linkers. This type structure not only provides MOFs with tunable options, organic functionality, high thermal and mechanical stability, open metal sites in the skeleton, large pore sizes, and high surface areas, but also can be easily prepared in a one-pot. Metal–organic frameworks constitute an important family receiving prominence for their many potential applications in a lot of industrially important areas. To date, MOFs have exhibited numerous properties such as gas adsorption, separations, catalysis, sensors, photocatalysis and drug delivery [5–8]. Besides, the adsorptive removal of toxic compounds has also been studied using MOFs. For examples, adsorption of thiophene derivatives were carried out on MOF-5 [9] and an iron terephthalate (MOF-235) 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 [10]. The applications of

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http://dx.doi.org/10.1016/j.micromeso.2014.03.004
1387-1811/

MOF-101 (Cr) for the removal of xylenol orange (XO) from aqueous solution have also been reported [11].

Cu-BTC [$Cu_3(BTC)_2$, BTC = 1,3,5-benzenetricarboxylate], one of the most studied MOFs and often denoted as HKUST-1, first reported by Chui et al. in 1999 [12]. In the framework of this material, two octahedrally coordinated Cu atoms are connected to eight oxygen atoms of tetra-carboxylate units to form a dimeric Cu paddle wheel. Each BTC ligand holds three dimeric Cu paddle wheels to form a microporous open framework with face-centered cubic symmetry [13]. Cu-BTC was used as an example of MOFs due to its attractive features as a sorbent for the extraction of pollutants in aqueous solution, such as high surface area, uniform pore size, accessible coordinative unsaturated sites, and excellent chemical and solvent stability. As is the case with several other MOFs, most of the experimental studies so far on Cu-BTC focused on the gas adsorption. Wang et al. have studied adsorption of $N_2$, $O_2$, CO, $CO_2$, $N_2O$, $CH_4$, $C_2H_4$, $C_2H_6$, $C_{12}H_{26}$ and $H_2O$ on Cu-BTC using the constant volume method. Aprea et al. have reported volumetrically measured adsorption equilibrium of $CO_2$ on Cu-BTC in the low pressure range [14–16]. As far as we know, until now there are few reports on the kinetics of adsorption of organic dyes in Cu-BTC. Herein we described the synthesis of Cu-BTC MOFs by solvothermal reaction and then the Cu-BTC porous MOFs were applied for the absorption of methylene blue (MB) from aqueous solution. The structure formula of MB is given in Fig. 1. MB is one of the most common dying materials for wood and cotton acrylic fibers [17], and MB is a toxic dye which gives rise to some health risks in humans upon exposure such as nausea, vomiting, excessive perspiration, dyspnea, Gastritis, and so on [18,19]. Thus, it is very meaningful to remove MB dye from the wastewater.

In the present work, we described the synthesis of Cu-BTC MOFs by solvothermal reaction, characteristics of Cu-BTC and its adsorption properties such as adsorption equilibrium, kinetics, thermodynamics, adsorption mechanism, were investigated. Remarkably, the Cu-BTC were demonstrated to exhibit significantly fast adsorption kinetics for MB dye removal. In addition, the material can be reused at least three times after washing with ethanol.

## 2. Experimental section

### 2.1. Materials

Copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), 1,3,5-benzenetricarboxylic acid ($H_3BTC$), N,N-dimethylformamide (DMF), ethanol, methylene blue (MB), were used as obtained from commercial sources and used without further purification.

### 2.2. Synthesis procedure

The Cu-BTC MOFs was synthesized by a hydrothermal method as reported by Liu et al. [20], and it was a modification of previous works by Rowsell and Yaghi [21]. Two solutions prepared separately by dissolving 1,3,5-benzenetricarboxylic acid (1.50 g) in 45 mL of a 1:1 mixture of ethanol/N,N-dimethylformamide (DMF) and copper(II)nitrate trihydrate (3.114 g) in 22.5 mL deionized water were mixed and stirred at ambient temperature for 10 min. Subsequently, they were then loaded into a Teflon-lined stainless steel autoclave of 100 mL capacity and heated at 373 K for 10 h. The resulting blue microcrystals were isolated by filtration and washed with methanol several times. The obtained products were dried under vacuum at 333 K overnight and used for further experiments.

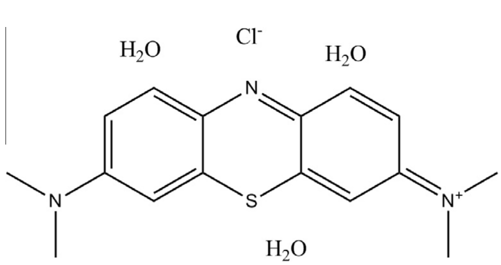


**Fig. 1.** Chemical structure of MB.

### 2.3. Adsorption experiments

Batch adsorption experiments were carried out by allowing a weighed amount of Cu-BTC to reach equilibrium with the MB solution of known concentration. To obtain the adsorption capacity, 5.0 mg of Cu-BTC was dispersed in 10 mL of MB solutions at different concentrations (from 1.0 $\mu$mol $L^{-1}$ to 10 $\mu$mol $L^{-1}$), then the solutions were stewing in a thermostatically controlled water bath and the desired time at constant temperatures of 298 K, 308 K and 318 K, respectively. At the end of the desired equilibrium period, the solution was centrifuged for 3.0 min, and Ultraviolet spectroscopy was used to analyze the residual concentrations of MB. Batch kinetic studies were identical to the adsorption experiments, and the aqueous samples were taken at prespecified time intervals. The equilibrium adsorption capacity $Q_e$ ($\mu$mol $g^{-1}$) was calculated according to Eq. (1):

$$Q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where $C_o$ and $C_e$ ($\mu$mol $L^{-1}$) were the initial and final concentrations of MB, respectively. $V$ (L) was the volume of the solution, and $m$ (g) was the mass of sorbent. The effect of pH on the removal of MB was studied by batch mode experiment. To study the effect of pH on the removal of MB from aqueous solutions, 5.0 mg of Cu-BTC was dispersed in 10 ml of solution containing MB (10 $\mu$mol $L^{-1}$), adjusted the solution pH to 2.0, 4.0, 6.0, 8.0, 10, 12 using a certain amount of dilute HCl or NaOH solution. After stewing in the thermostatic water bath for 6 h at 298 K, the supernatant fluid was obtained through the high-speed centrifuge. Ultraviolet spectroscopy was used to analyze the remanent concentrations of MB.

### 2.4. Characterization

The structure of the crystal was verified by X-ray powder diffraction (XRD). In this work, X-ray diffraction (XRD) patterns of the samples were collected on a D/max-RA X-ray diffractometer (Rigaku, Japan), with Ni-filtrated Cu-Ka radiation (40 kV, 200 mA) over the $2\theta$ range of 5.0–55° at a scanning rate of 5.0° $min^{-1}$. The shapes and morphologies of synthesized samples were characterized by scanning electron microscope. Cu-BTC MOFs surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77 K using either a Micromeritics ASAP 2420 or ASAP 2020 volumetric adsorption analyzer. Surface areas of the samples were determined by the Brunauer-Emmett-Teller (BET) method, pore size distributions and pore volumes were analyzed by the Barrett-Joyner-Halenda (BJH). Samples were degassed at 393 K for 15 h under vacuum (10–5 bar) before analysis. FT-IR spectra of the Cu-BTC samples were obtained between 4000–400 cm with a FTIR spectrometer (AVATAR 360Madison, Nicolet). A minimum of 32 scans was signal-averaged with a resolution of 2.0 $cm^{-1}$ in the 4000–400 $cm^{-1}$ ranges.

### 2.5. Regeneration experiments

The Cu-BTC MOFs (20 mg) were subjected to multiple cycles ($n$ = 4) to reduce the adsorbent cost. After completion of each cycle