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Selective adsorption of cationic dyes from aqueous solution by polyoxometalate-based metal–organic framework composite

Xiaoxia Liu, Wenpeng Gong, Jing Luo, Chentao Zou, Yun Yang, Shuijin Yang*

Hubei Collaborative Innovation Center for Rare Metal Chemistry, Hubei Key Laboratory of Pollutant Analysis & Reuse Technology, College of Chemistry and Chemical Engineering, Hubei Normal University, Cihu Road No. 11, Huangshi 435002, China

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ABSTRACT

A novel environmental friendly adsorbent $H_6P_2W_{18}O_{62}$/MOF-5 was synthesized by a simple one-step reaction under solvothermal conditions and characterized by XRD, FTIR, thermogravimetric analyses (TGA) and N_2 adsorption–desorption isotherms. The removal rate of $H_6P_2W_{18}O_{62}$/MOF-5 was quite greater (85%) than that of MOF-5 (almost zero), showing that the adsorption performance of porous MOF-5 can be improved through the modification of $H_6P_2W_{18}O_{62}$. Further study revealed that $H_6P_2W_{18}O_{62}$/MOF-5 exhibited a fast adsorption rate and selective adsorption ability towards the cationic dyes in aqueous solution. The removal rate was up to 97% for cationic dyes methylene blue (MB) and 68% for rhodamine B(Rhb) within 10 min. However, anionicdye methyl orange(MO) can only reach to 10%. The influences including initial concentration, contact time, initial solution pH and temperature of MB adsorption onto $H_6P_2W_{18}O_{62}$/MOF-5 were investigated in detail. The kinetic study indicated that the adsorption of MB onto $H_6P_2W_{18}O_{62}$/MOF-5 followed the pseudo second-order model well. The isotherm obtained from experimental data fitted the Langmuir model, yielding maximum adsorption capacity of 51.81 mg/g. The thermodynamic parameters analysis illustrated that the MB adsorption onto $H_6P_2W_{18}O_{62}$ immobilized MOF-5 was spontaneous and endothermic process. Besides, these results implied that designing a novel material polyoxometalate-based metal–organic frameworks is great potential for removing cationic organic pollutants and even extended to improve other specific application.

1. Introduction

With the rapid industrial development, the pollution of water is becoming more and more serious resulting in the shortage in water supply [1]. Dyes are color organic compounds and widely used in the synthesis, textile, cosmetic, leather, printing, paper, food and other industries [2–4]. So far, more than 7×10^5 t year^{-1} and 10,000 different types of dyes are produced all over the world. To be sure, 10% to 15% of the dye is discharged due to washing operations and incomplete exhaustion of coloring materials during the dyeing process [5], which poses a significant threat to environment and human health because of their toxicity, potential mutagenicity, and even carcinogenicity without reasonably processing [6–8]. Moreover, the discharge of the dyes without treatment into the rivers is easily noticed since dyes are highly visible, which is commonly harmful to aquatic life [9,10]. Therefore, it is necessary to find appropriate treatment strategies for efficient removal of dyes from waste-water system before their discharge.

So far, there are many techniques which have been reported on the effective elimination of hazardous substances from aqueous solutions such as biological methods, physical, chemical, electrocoagulation, photocatalytic degradation, oxidation and so on [11–15]. Among the proposed techniques, adsorption is the procedure of choice and can reach good results as it is highly efficient, inexpensive and simple in operation [16–18]. This has encouraged the exploration of adsorbents with abundant availability and good economy. Nowadays a huge amount of low cost adsorbents are investigated including the common adsorbents, products of industrial or agricultural origin such as activated carbon [19], carbon nanotubes [20], activated slag, sugarcane, wood dust, fruit peel [21], tea waste ash, rice husk [22], metal–organic frameworks(MOFs) [23,24] and so on. However, there is still a great need to explore some kinds of new and low cost adsorbents with high adsorption capacity, even high selectivity and short contact time towards specific dyes [25].

Recently, the adsorbents with a high selectivity towards targeted dyes have attracted more and more researchers' interests due

* Corresponding author. Tel.: +86 0714 6515602.
E-mail address: yangshuijin@163.com (S. Yang).

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to their huge potentiality in the controlled separation of dye mixtures and chemicals during treating industrial wastewater, as well as making sensors for the detection and identification of certain types of dyes [26]. MOFs fabricated by metal ions or metallic clusters connected through organic ligands by strong bonds are a new class of porous crystalline organic-inorganic hybrid materials [27]. Compared with conventional inorganic porous materials, MOFs have some unique features such as ultrahigh porosity, incredibly large BET surface area, multiple coordination sites, big pore volume and structural adaptivity, which brings many various potential applications such as gas separation and storage, sensors, energy storage, pollutant removal, catalysis, drug delivery and so on [28,29]. So many researches have been aimed at designing new MOFs structures and studying their various applications during the past two decades [30]. However, MOFs also exhibit several weak points such as the relative low stability in solution and brittleness or lack of flexibility hampering their realistic applications. It is necessary to introduce a new functionality for enhancing their realistic properties.

Wells–Dawson acids $H_6P_2W_{18}O_{62}$, one of the polyoxometalate (POM), possesses controllable shape and size, remarkable stability both in the solid state and in solution [31], oxo-enriched and highly negatively charged surfaces. These properties make them suitable to be used in selective adsorption and separation towards cationic dyes due to exerting a stronger electrostatic attraction to cationic dyes than anionic dyes [32]. However, $H_6P_2W_{18}O_{62}$ with feasible dissolution in water or polar organic liquids and relatively low surface area (<10 $m^2\,g^{-1}$) also limits its applications by preventing the accessibility to the active sites. In recent years, POM-based MOFs composite has been explored and used in the fields of various catalytic reactions such as the hydrolysis of esters [33], Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate [34], and so on. Nevertheless, POM-based inorganic-organic hybrid material may also be a reasonable choice as a new type of adsorbent for removing cationic dyes. Recently, there have been two reports involved in the use of POM@MOFs composite as adsorbent in Wang's group and Sun's group [35,36]. Besides, POM-based materials in the adsorption application have not been still investigated up to now.

Here a new selective adsorbent $H_6P_2W_{18}O_{62}$/MOF-5 was prepared by a simple one-step solvothermal method. The adsorption of MB onto $H_6P_2W_{18}O_{62}$/MOF-5 about the effects of initial concentration, contact time, initial solution pH and temperature in the system was systematically explored. The composite exhibited a high adsorption rate and selective adsorption ability for the cationic dyes like MB compared to that of the isolated MOF-5 framework. Moreover, the adsorption isotherm, kinetic, adsorption mechanism and thermodynamic parameters of MB on the composite were thoroughly analyzed.

2. Experimental

2.1. Preparation of $H_6P_2W_{18}O_{62}$/MOF-5 adsorbents

Wells–Dawson acids $H_6P_2W_{18}O_{62}$ was prepared based on the method as in ref. [37] with some modifications. 50 g of $Na_2WO_4{\cdot}2H_2O$ (AR, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) was dissolved into 60 mL deionized water and 35 mL of phosphoric acid (H_3PO_4, 85%) was slowly added dropwise into the solution under vigorous stirring. Then the mixture was refluxed at 120 °C for 8 h. After cooling, HCl (22.5 mL, 36%) was added and the acidified aqueous solution was extracted by the same volume of ether as the solution. The heavy oily layer was collected and the ether was removed by heating gently. Finally, after drying under room temperature, heteropolyacid was obtained.

MOF-5 was prepared by a solvothermal method as in ref. [38]. $H_6P_2W_{18}O_{62}$/MOF-5 adsorbent was synthesized by the same method just like the above mention. 0.0166 g 1,4-dicarboxybenzene (H_2BDC, Tianjin Kwangfu Fine Chemical Industry Research Institute, Tianjin, China) was dissolved into 15 mL *N*,*N*-dimethylformamide (DMF) and stirred for 10 min till a homogeneous solution was formed. Then 0.149 g $Zn(NO_3)_2{\cdot}6H_2O$ and 0.05 g $H_6P_2W_{18}O_{62}$ were added into the solution with stirring continuously to form a clear mixed solution. Subsequently, the reactant mixture was loaded into a Teflon-lined stainless steel autoclave with 25 mL capacity and heated at 393 K for 21 h. The resulting white microcrystals were washed with a DMF/H_2O mixture at least five times and then dried under vacuum at 353 K overnight. Thus, $H_6P_2W_{18}O_{62}$/MOF-5 was obtained for further experiments.

2.2. Characterization

The $H_6P_2W_{18}O_{62}$, MOF-5 and $H_6P_2W_{18}O_{62}$/MOF-5 were characterized by XRD, TGA and FT-IR. X-ray powder diffraction patterns of the samples were collected on a diffractometer (Bruker Corporation) with the Cu $K\alpha$ radiation (40 kV, 40 mA) at a scanning rate of 0.02° s^{-1} and 2θ ranging from 5 to 40°. Thermogravimetric analyses (TGA) of $H_6P_2W_{18}O_{62}$/MOF-5 were performed using a thermogravimetric analyzer PERKIN ELMER at a heating rate of 5 K min^{-1} and temperature ranging from 25 °C to 800 °C in a flowing atmosphere of N_2. Functional groups of the samples were analyzed by a NICOLET 5700 FT-IR spectrometer within the wave range 4,000–500 cm^{-1}. The surface area (BET) and pore diameter of MOF-5 and $H_6P_2W_{18}O_{62}$/MOF-5 were determined from the N_2 adsorption at 77 K using a Micrometric ASAP 2020 system.

2.3. Dye adsorption experiments

In order to explore the adsorption properties and the factors influencing adsorption, batch adsorption experiments of MB (Beijing Chemical Reagent Co., Ltd, China) were conducted by using 50 mL reagent bottles with definite volume at different initial concentration under strong agitation. The solution pH was adjusted by using a certain amount of NaOH and HNO_3 solution. After adsorption, the mixture solution was centrifuged at 10000 rpm for 2 min and the concentration of residual MB was determined by using a UV–vis spectrophotometer (U-3010) at the maximum wavelength of 664 nm. The adsorption capacity q_t (mg g^{-1}) and removal rate (Removal%) were calculated according to the following equations:

$$q_t = \frac{(C_o - C_t)V}{m} \quad (1)$$

$$\text{Removal\%} = \frac{(C_o - C_t)100}{C_o} = \frac{(A_o - A_t)100}{A_o} \quad (2)$$

where C_o and C_t (mg L^{-1}) were the MB initial concentration and at time t. A_o and A_t represented the absorbance of MB before and after the adsorption. V (mL) was the volume of the MB solution and m (mg) was the mass of adsorbents.

3. Results and discussion

3.1. Characterization of the $H_6P_2W_{18}O_{62}$/MOF-5

The powder XRD patterns of MOF-5, $H_6P_2W_{18}O_{62}$ and $H_6P_2W_{18}O_{62}$/MOF-5 were shown in Fig. 1a. The characteristic diffraction peaks of MOF-5 implying the high crystallinity were consistent with the earlier reported literature well [39]. For $H_6P_2W_{18}O_{62}$, the peaks at 2θ = 7–10°, 14–19°, 24–30° matched well with Dawson structure as reported in the literature [40]. The diffraction patterns of the $H_6P_2W_{18}O_{62}$/MOF-5 composite were

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