



Pore size and interactions effect on removal of dyes with two lead(II) metal-organic frameworks



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ABSTRACT

Two typical highly porous metal-organic framework (MOF) materials based on lead(II), [Pb(4-bpdh)(NO₃)₂(H₂O)]_n (**TMU-1**) and [Pb(4-bpdh)(NO₃)₂]_n (**TMU-2**) have 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 **TMU-1** and **TMU-2** are much higher than those of an activated carbon. Our results show that the difference between MO and MB adsorption in **TMU-1** and **TMU-2** could be related to pore size and coordinated H₂O interactions. Dye elimination has also been studied by the use of adsorption/desorption process. The delivery of dyes from compounds in methanol at room temperature was determined by UV/vis spectroscopy.

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1. Introduction

Metal-organic frameworks (MOFs), hybrid materials built up from metal clusters and organic linkers, have shown a huge potential for a wide range of applications [1]. In recent years, MOFs have set new records in terms of specific surface areas and pore volumes [2,3] and therefore are highly suitable as storage materials for small and large molecules. In the textile and food industries, the uses of organic dyes are the important sources of environmental contaminations due to their high toxicity to aquatic creatures and carcinogenic effects on humans [4,5]. There are a number of technologies available for the removal of dyestuffs, such as physical, chemical and biological methods [6–8]. Adsorption technology is regarded as one of the most competitive methods because it does not need a high operation temperature and several coloring materials can be removed simultaneously [9]. Physical adsorption, because of its low cost, high efficiency, easy handling, wide variety of adsorbents, and high stabilities toward the adsorbents, has become the mostly widely used method for eliminating dyes from wastewaters. Meanwhile, other methods, such as solvent extraction [10], sonochemistry [11], and biodegradation [12], have also demonstrated high potential for applications.

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. Methylene blue (MB) is one of the most common dyeing materials for wood, silk and cotton. The structures of MO and MB are shown in Table S1 and the removal of MO and MB from water is very important due to their toxicity [13–15]. In this work, we report the results of the adsorption of not only an anionic dye (MO) but also a cationic dye (MB) over two our reported MOFs, [Pb(4-bpdh)(NO₃)₂(H₂O)]_n (**TMU-1**) [16] and [Pb(4-bpdh)(NO₃)₂]_n (**TMU-2**) [17], because removal of both cationic and anionic dyes are not readily achieved simultaneously and the adsorption can be understood with a comparison of the two adsorbents.

2. Results and discussion

TMU-1 and **TMU-2** were obtained by the branched tube method with a thermal gradient method [16,17]. Compound **TMU-1** is a porous 3D coordination polymer with nano-size pores (1.8 × 2.1 nm). Absence of H₂O molecules in compound **TMU-2** lead to smaller pore size only (0.4 × 1.8 nm) (Fig. S1). Porous structure in **TMU-1** and **TMU-2** are suitable for adsorption of some molecules with special directional physical properties and a few examples of dye inclusion into MOFs [18,19] are known. For argument of porosity in the compounds **TMU-1** and **TMU-2** we successfully tested their porosity with MO and MB by suspending

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them in a water solution of MO and MB. The IR spectra of **TMU-1**, **TMU-2**, MO, and MB@**TMU-1** as well as **TMU-2** are shown in Fig. S2. The IR spectrum of the compound **TMU-1** shows more similarity with the IR spectra of MO@**TMU-1** and MB@**TMU-1** material, so the MO@**TMU-1**, MB@**TMU-1** and **TMU-1** have the same structures. The IR spectrums of **TMU-2** and MO@**TMU-2** and MB@**TMU-2** are shown in Fig. S2, too. The IR spectrum of these compounds also shows more similarity with the IR spectra of MO@**TMU-2** and MB@**TMU-2** material, so the MO@**TMU-2** and MB@**TMU-2** and **TMU-2** have the same structures. Fig. S3 makes a comparison between the XRD pattern of single crystal X-ray data of compound **TMU-1** and **TMU-2** with the XRD pattern of a typical sample of MO@**TMU-1**, MB@**TMU-1** and MO@**TMU-2** as well as MB@**TMU-2**. An acceptable match, with slight differences in 2θ , was observed between **TMU-1** and MO@**TMU-1** and MB@**TMU-1**, but several reflections are shifted up to 3° in 2θ . The comparison between **TMU-2** and MO and MB@**TMU-2** also has been shown an acceptable match, with slight differences in 2θ . The slight differences in the IR spectra and PXRD patterns of MO@**TMU-n** and MB@**TMU-n** with related **TMU-n** materials may suggest the loading of MO and MB into the **TMU-1** and **TMU-2** and also presence of some interactions between the **TMU-n** and dyes.

2.1. Dye adsorption

A few samples (100 mg of **TMU-1** and **TMU-2**) in a sufficient amount of water solution of MO and MB (200 ppm) have been immersed in a small sealed flask at room temperature, and observed that the dark solutions of MO and MB fade slowly to very pale yellow and blue (Figs. 1 and 2) respectively. Our observation shows that compound **TMU-2** adsorbed MO and MB molecules in a longer time (about 72 h) whereas compound **TMU-1** become

transparent in about 48 h and adsorb 100% of dye (Fig. 1). Our observation shows that this result for MB adsorption is same (Fig. 2). MO and MB adsorption in **TMU-1** occurs in shorter time in comparison with **TMU-2** that must be because of larger pore size in **TMU-1**. This phenomenon can be justified with attendance of H₂O molecules in **TMU-1** pores too, so interactions between H₂O and MO and MB molecules led to higher amount of adsorption and faster adsorb rate.

2.2. Dye elimination

The delivery of dyes from **TMU-1** and **TMU-2** performed in methanol, a nonaromatic solvent, at room temperature that was determined by UV/vis spectroscopy. The temporal evolution UV/vis spectrum for dyes in methanol solution, which shows λ_{\max} at different regions, becomes stronger by increasing the dye content (Fig. 3). Presence of H₂O molecules prevented the release of MO and MB molecules and so we expect that desorbed rate in **TMU-2** will be faster than **TMU-1** that has been shown in Fig. S4. Fig. S4 shows progress of the MO and MB release from **TMU-1** and **TMU-2** when the MOFs containing of MO and MB crystals were immersed in methanol. It seems that in **TMU-2** the pores become smaller and the MO and MB molecules are more accessible than **TMU-1**, so the delivery of MO and MB from **TMU-2** can be faster than **TMU-1** but the amount of absorbance is less. Comparison of MO and MB desorbed rate from **TMU-1** and **TMU-2** have been shown in Fig. 4. Fig. 4 shows that the regularity of dye elimination rate conforms from this relation: MO@**TMU-2** > MB@**TMU-2** > MB@**TMU-1** > MO@**TMU-1**.

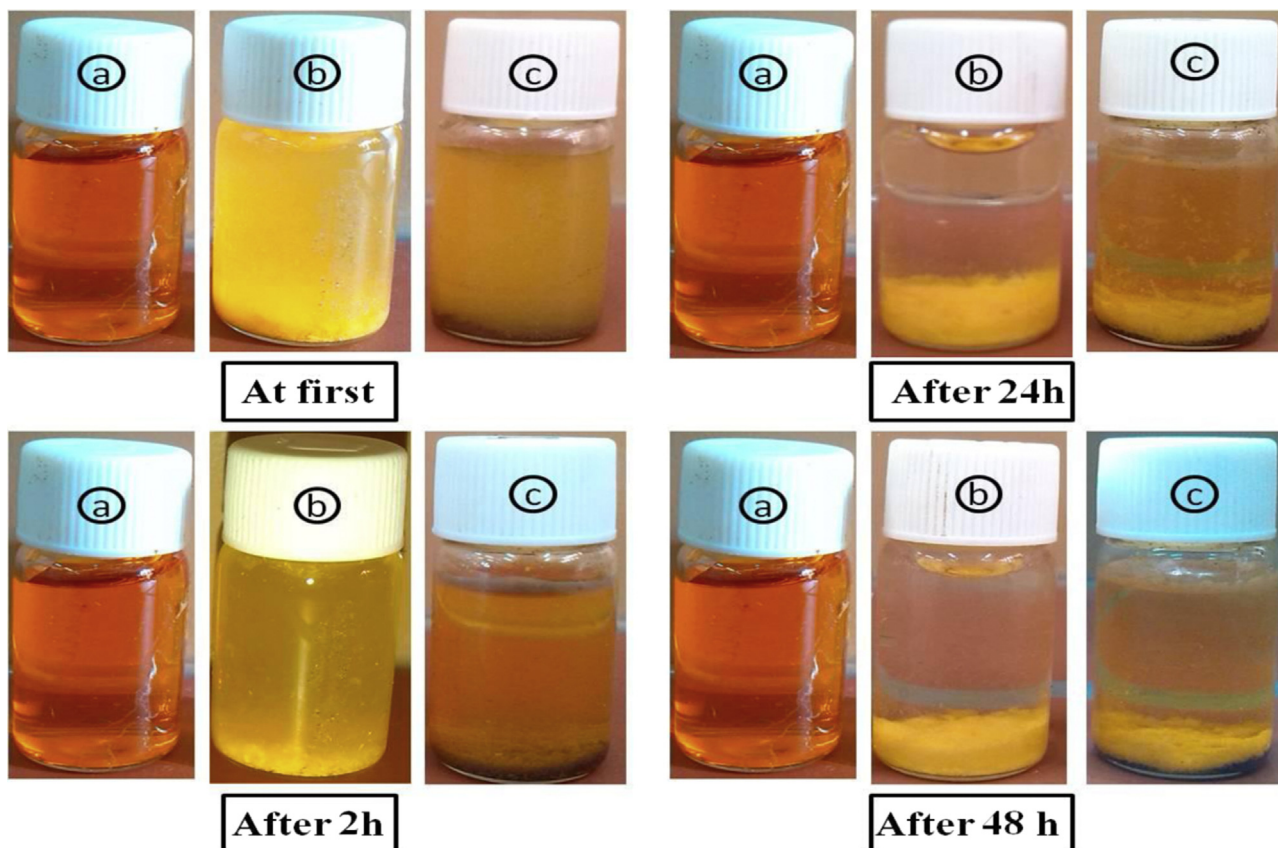


Fig. 1. Comparison of MO enrichment progress between **TMU-1** and **TMU-2**; (a) blank, (b) MO@**TMU-1** and (c) MO@**TMU-2**. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

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