Selective adsorption of a cationic dye by UiO-66-NH$_2$

Fatemeh Varmini, Faranak Manteghi*

Department of Chemistry, Iran University of Science and Technology, Teran, Iran

*f_manteghi@iust.ac.ir

Abstract

Zirconium (IV)-based MOF, UiO-66-NH$_2$ has been successfully prepared by a facile solvothermal method. They exhibit small size and large surface area with the ability of selective adsorption of cationic dyes from aqueous solution. This adsorption selectivity is due to the favorable electrostatic interactions between the adsorbents and cationic dyes. Furthermore, owing to the individual micropore structure of UiO-66-NH$_2$ and its more negative zeta potential resulted from the charge balance for the protonation of –NH$_2$, UiO-66-NH$_2$ displays much higher adsorption capacity for cationic dyes and lower adsorption capacity for anionic dyes than UiO-66.

Keywords: UiO-66-NH$_2$, Selective adsorption

1. Introduction

In recent years, dyes are widely used in textile, paper and printing industries, so the treatment of dye-containing wastewater is one of the most crucial problems to be solved [1,2]. Owing to the complex aromatic molecular structures, dyes are generally stable to light, heat and oxidizing agents [3]. The dye-containing wastewater causes damage to the environment and dramatically threatens human health [4]. There are many methods to treat dye containing wastewater including adsorption, flocculation, electrolysis and biodegradation. Among them, adsorption has the advantages of low cost, high efficiency and environment friendly. Therefore, adsorption has been extensively investigated to decontaminate the dye-containing wastewater. In this context, a tremendous amount of work has been done on finding an adsorbent, which can effectively remove dyes from water and can be easily separated from solution.

Metal organic frameworks (MOFs) are a class of advanced porous, crystalline materials synthesized from organic linkers and transition metal ions (or clusters) [5]. These materials are receiving increasing scientific attention for variety of applications owing to their ease of synthesis, high surface area, high porosity, high thermal and mechanical stability, tunable structural and functional properties, etc. [5,6]. The MOFs have been extensively investigated as an adsorbent for the treatment of polluted water [7,8]. However, most of these materials are unstable in water and subject to degradation through ligands displacement or hydrolysis [8]. Among the reported MOFs, UiO-66-NH$_2$ (UiO=University of Oslo) exhibit high stability in water and has excellent sorption properties [8,9]

MOFs generally have microporous structure, whereas most of the dye molecules are too big to be able to enter the inside micropores of MOFs, and as a result, dye molecules will most possibly adsorb on the external surface of MOFs rather than small gas molecules absorbed in the inside micropores of MOFs. Therefore, the surface properties of MOFs may exert a great influence on the adsorption of dye molecules.

Through changing the organic ligand from benzene-1,4-dicarboxylic acid to NH$_2$ substituted derivative, 2-aminobenzene-1,4-dicarboxylic acid, we can modulate the electrostatic interaction, as well as the

corresponding adsorption selectivity and the adsorption capacity of MOFs for various dyes via protonation of –NH$_2$. In this work, we have synthetized UiO-66-NH$_2$ and studied adsorption properties for a cationic dye in aqueous solutions. Owing to the favorable electrostatic interactions for cationic dyes, UiO-66-NH$_2$ displays much higher adsorption performance for cationic dyes than for anionic dyes [1].

2. Experimental

2.1. Materials

In this study, zirconium tetrachloride, 2-aminobenzene-1,4-dicarboxylic acid, N,N-dimethyl formamide (DMF), and chloroform were purchased from Merck Co., and used to prepare the samples.

2.2. Preparation of UiO-66-NH$_2$

Synthesis of UiO-66-NH$_2$ was performed by dissolving 0.363 mmol ZrCl$_4$ and 0.363 mmol 2-aminobenzene-1,4-dicarboxylic acid in 544 mmol DMF with ultrasonic vibration. The as-obtained mixture was transferred to a Teflon-lined autoclave and then maintained at 393 K for 24 h. After this time, the solution was cooled in air to room temperature and the resulting solid was filtered, repeatedly washed with CHCl$_3$ and dried at room temperature.

2.3. Adsorption experiments

20 milligrams of UiO-66-NH$_2$ were added into 50 mL dye solution containing 20 mg/L dye with continuous stirring in a dark place. Samples were taken at a certain time and were filtrated. The absorbance of filtrate was tested using a UV spectrophotometer.

3. Results and Discussion

In the structure of the metal-organic framework, the most important analysis to confirm the synthesis of the desired phases is the pattern of X-ray diffraction (XRD). The pattern of the sample was determined in the range of 2θ=4–50°, given in Fig. 1. The UiO-66-NH$_2$ pattern synthesized by the solvothermal method has been reported to have unique crystalline phases according to the computational model and synthesized sample, which is confirmed for the synthesis of the desired compound.
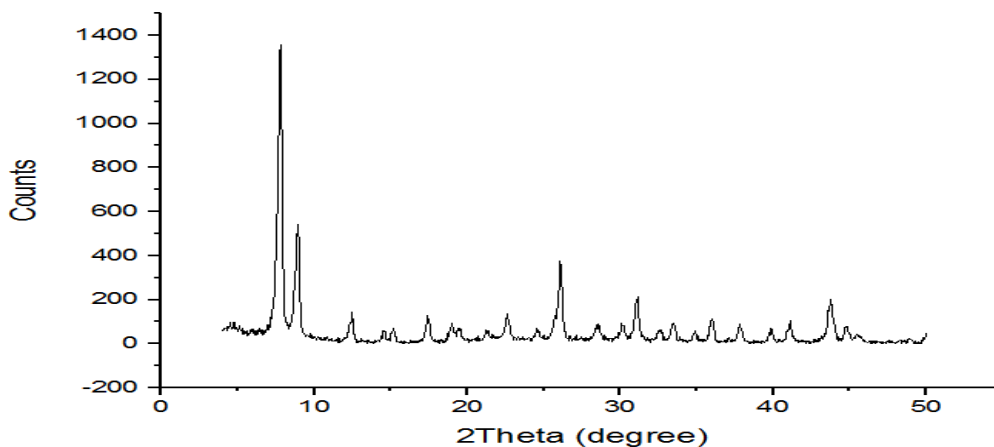

Fig. 1. The XRD pattern of UiO-66-NH$_2$.

Fig. 2 is the FT-IR spectra of sample. In the spectrum of UiO-66-NH$_2$, new peaks appeared at 3461 cm^{-1} and 3361 cm^{-1}, respectively, corresponding to the symmetric and asymmetric vibration peak of –NH$_2$. The peak at 1621 cm^{-1} corresponds to the N–H bending vibration. The peaks at 1482 cm^{-1} and 1382 cm^{-1} can be attributed to the N–H bending vibration and C–N stretching vibration, respectively.
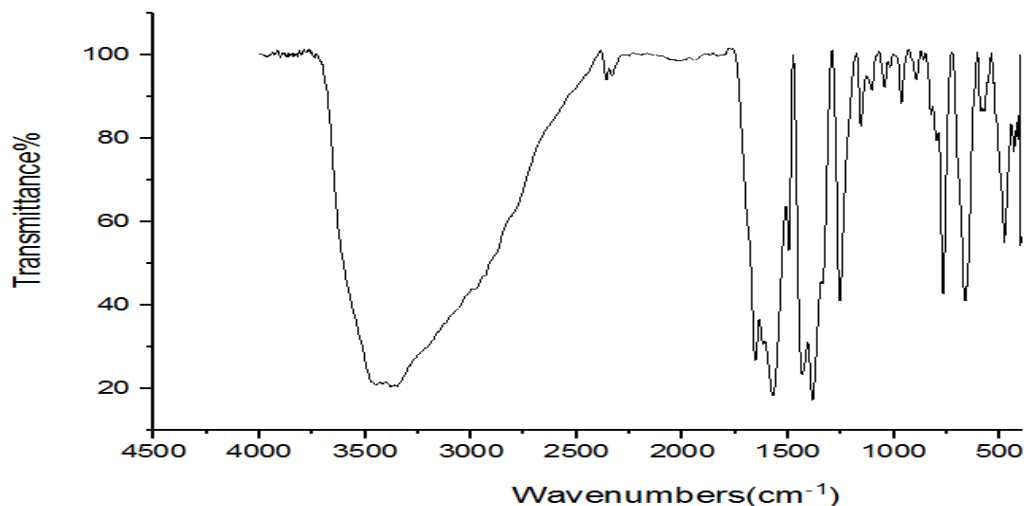

Fig. 2. FT-IR spectra of the starting UiO-66-NH$_2$

We initiated our studies using a solution of the cationic dye Methylene Blue (MB). Fig. 3 displays the UV–vis spectrum of the MB solution collected each 80 min during MB adsorption on UiO-66-NH$_2$. The absorbance in the UV–vis spectrum of MB was rapidly reduced in 300 min, indicating that MB molecules were efficiently adsorbed by UiO-66-NH$_2$. The dye removal efficiency of this dye was summarized in Table 1.
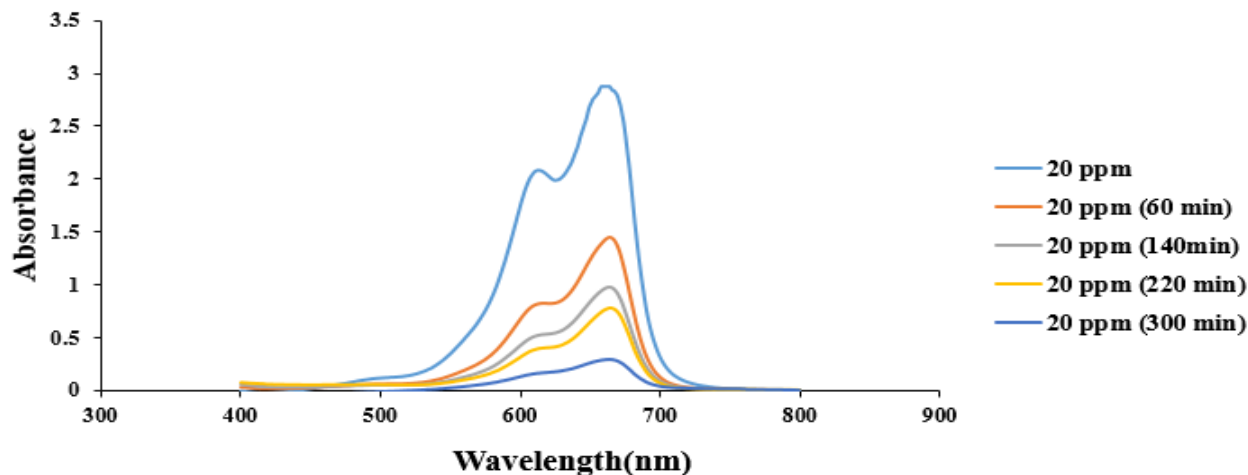

Fig. 3. Time evolution of the UV–vis spectrum collected during MO adsorption on UiO-66-NH$_2$.

Table 1: The dye removal efficiency of UiO-66-NH$_2$.

Dye removal efficiency	Cationic Methylene Blue
60 min	49.54%
140 min	65.84%
220 min	72.66%

300 min	89.76%

4. Conclusion

 UiO-66-NH$_2$ with small size and large surface area was successfully synthetized by a facile solvothermal method, and can remove a cationic dye from solution more effectively than for anionic dyes. Possible reason for the selective adsorption of cationic dyes is due to the electrostatic attraction between the adsorbents and cationic dyes. UiO-66-NH$_2$ shows higher adsorption capacity for cationic dyes and lower adsorption capacity for anionic dyes.

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