Inorganica Chimica Acta 471 (2018) 203–210

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Research paper

Removal of hazardous cationic organic dyes from water using nickel-based metal-organic frameworks

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A R T I C L E I N F O

Article history:
Received 24 July 2017
Received in revised form 26 October 2017
Accepted 29 October 2017
Available online 10 November 2017

Keywords:
Nickel
Copper
MOF
Methylene blue dye
Adsorption

A B S T R A C T

The adsorption activity of a layered two-dimensional (2D) nickel-based metal-organic framework (Ni-MOF) was investigated for the removal of the harmful methylene blue dye (MB) from water. NiCu-BTC, which has high surface area, was selected as a comparable adsorbent. The morphology and structure of MOF adsorbents were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA)-differential thermal analysis (DTA), Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, nitrogen adsorption/desorption, field emission-scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). The adsorption studies of MB included kinetic and equilibrium approaches. Nanosheets of Ni-MOF showed analogous adsorption capacity (765.5 mg/g) in comparing with highly porous NiCu-BTC (798.0 mg/g). The adsorption activity of Ni-MOF may be attributed to its layered structure that facilitate the diffusion of dye species to the predominate exposed facet of (100) plane. The adsorption of dye fitted with the Langmuir isotherm and followed the pseudo-second-order kinetic model.

1. Introduction

Metal-organic frameworks (MOFs) with high surface area and well-ordered porous structure show potential activities for hydrogen storage, separation processes [1–5], catalysis [6–8], carbon dioxide capture [9,10], and abatement of hazardous materials [11,12].

The utilization of organic dyes is a significant cause of environmental pollution due to their high toxicity to aquatic life and carcinogenic influence on humans [13–17]. Methylene blue (MB) is a heterocyclic aromatic chemical compound with the molecular formula of $C_{16}H_{18}ClN_3S$, which has many uses in different fields, such as biology and chemistry. MB is considered as a common cationic industrial organic dye for wood, silk, and cotton [18]. The removal of dyes is a major task for environment protection. Several technologies are beneficial for the removal of dyes, such as physical, chemical, and biological methods [19–23].

Adsorption is regarded as one of the most competitive methods that save the processing power and give an economical cost. The adsorption process has become the most widely used technology to get rid of dyes from wastewater [17,24,25]. Recently, several works are concerned with the removal of MB using MOFs of different metals, such as iron [26–28], zinc [29,30], chromium [31], zirconium [32], aluminum [33], and copper [34–36].

In was reported that, NiCu-BTC showed high adsorption affinity towards the organic pollutants in the aqueous medium [37,38] due to the synergistic effect of both copper and nickel cations. In this work, a layered 2D Ni-MOF was successfully prepared and firstly used as an adsorbent for MB fro the aqueous solution. Simple structured Ni-MOF exhibited significant adsorption capacity in comparing with NiCu-BTC. The physical and chemical characteristics of nickel-based metal-organic frameworks were investigated in detail.

2. Experimental section

2.1. Synthesis and characterization of Ni-MOF and NiCu-BTC

The experimental details of the synthesis and characterization of the evaluated materials are listed in the Supplementary file.

2.2. Adsorption experiments

MB (1000 mg/l) was prepared as a standard stock solution. To study the adsorption isotherm, thermodynamic models, and kinet-

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https://doi.org/10.1016/j.ica.2017.10.040
0020-1693/

ics of the adsorption process, the experiments were carried out at various concentrations (20, 50, 100, 150, 200, and 300 ppm) and temperatures (30 °C, 40 °C, 50 °C, 60 °C, and 70 °C) using different amounts of Ni-MOF or NiCu-BTC (10, 25, 50, and 100 mg). The agitation times were 30, 60, 120, and 240 min and the adsorptive volume was 5 ml of these MB solutions. The pH values were adjusted to 3, 5, 7, and 10 using 0.1 M NaOH or HCl solution.

All adsorption experiments were carried out in flasks that were gently agitated on a temperature-regulated water-bath shaker at 200 rpm. At the end of every adsorption test, the suspensions were filtered via centrifugation. Then, the supernatant was obtained and determined for MB concentrations at λ_{max} = 665 nm using a UV-visible spectrophotometer. The details of the equations of the isotherm, thermodynamic models, and kinetics are listed in the Supplementary file.

3. Results and discussion

3.1. Characterization of the prepared materials

The chemical composition of the digested NiCu-BTC sample using A.A. showed that the MOF sample was composed of about 52 wt% copper and 48 wt% nickel. The thermogravimetric analysis (TGA) profiles showed two weight loss steps for Ni-MOF and NiCu-BTC (Fig. 1). The first weight losses completed at 200 °C (~6 wt%) and 125 °C (~11 wt%) corresponded to the loss of physisorbed water molecules in the pores of Ni-MOF and NiCu-BTC, respectively. The second weight losses of Ni-MOF (~52 wt%) and NiCu-BTC (~33 wt%) were associated with endothermic peaks at 486 °C and 280 °C, respectively. The second may refer to the complete decomposition of the structure. The prepared Ni-MOF showed thermal stability for temperatures higher than those in recently published works [39,40].

The X-ray diffraction (XRD) patterns of Ni-MOF and NiCu-BTC (Fig. 2) were agreement with previous published works [37–40] and confirmed the successful synthesis under the mild solvothermal method. XRD pattern of Ni-MOF showed that the (100) plane can be considered as the largest exposed facet [39]. The crystallite size of NiCu-BTC was calculated from the full width at half-maximum (FWHM) of diffraction peaks at 2θ = 6.7°, 9.5° and 11.7°, which corresponded to the (0 0 2), (0 2 2) and (2 2 2) crystallographic planes of fcc using the Scherrer formula [41]. The calculated mean crystallite size was ~111 nm, which is close to the previously published values for Cu-BTC [42–45]. This result might indicate that no deformation had been happen in the Cu-BTC crystallites due to the embedding of nickel cation.

The Fourier transform infrared (FTIR) and Raman spectra of both samples showed the characteristic bands of carboxylate groups and benzene carboxylate presented in the structure. The details of the FTIR and Raman spectra of both samples are listed in the Supplementary file (Figs. S1 and S2).

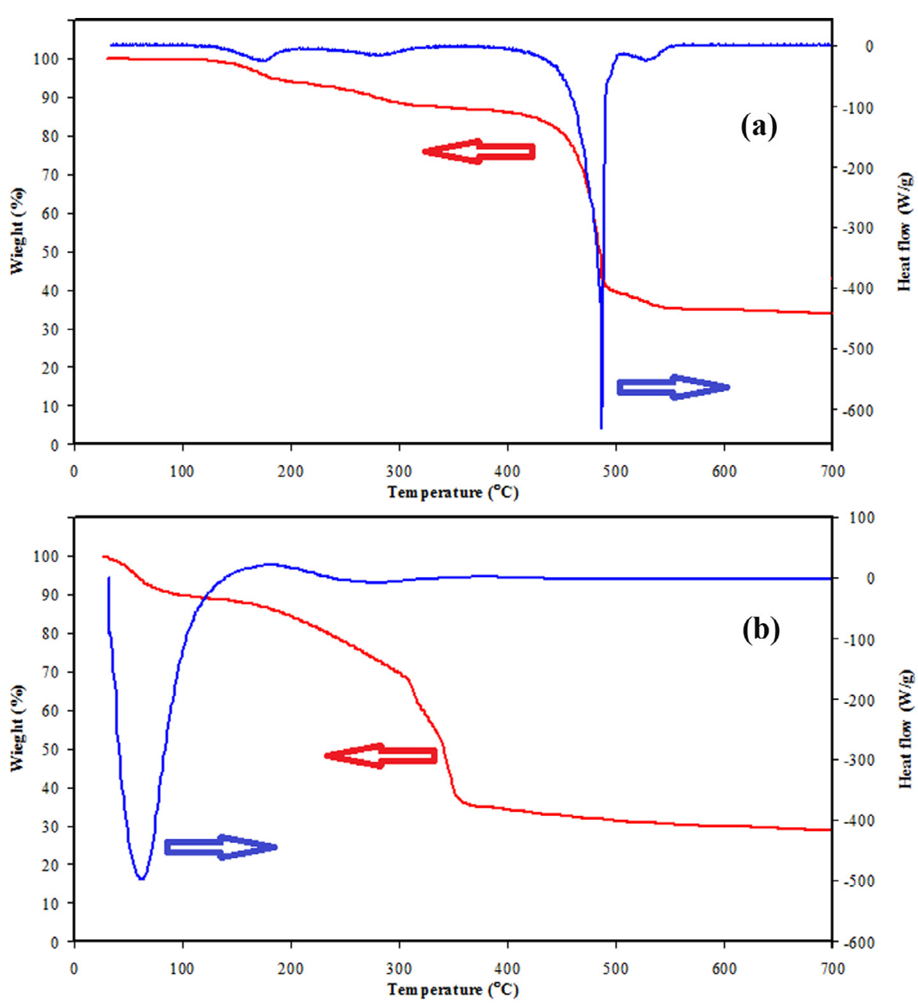

Fig. 1. TGA (red line) and differential thermal analysis (DTA; blue line) curves of as-synthesized (a) Ni-MOF and (b) NiCu-BTC. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)