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Ultrasound-assisted synthesis of Zinc(II)-based metal organic framework nanoparticles in the presence of modulator for adsorption enhancement of 2, 4-dichlorophenol and amoxicillin

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ABSTRACT

In this study, under a sonochemical method, a 3D, porous Zn(II)-based metal-organic framework $[Zn(TDC)(4\text{-}BPMH)]_n{\cdot}n(H_2O)$ is produced, which is called compound 1. To this end, the dicarboxylate linker of TDC, (2,5-thiophene dicarboxylic acid) and the pillar spacer of 4-BPMH, (N,N-bis-pyridin-4-ylmethylene-hydrazine) were employed. Moreover, variations in the morphology and growth of the micro/nanoparticles of compound 1 were investigated in terms of the effect of temperature, ultrasound irradiation power, sonication time, initial reagent concentrations, and pyridine concentration as a modulator. DFT model was used to examine the sonication effect on the distribution of the pore sizes. Moreover, the preparation method effect on the porosity and removal of two sample pollutants (i.e., 2,4-dichlorophenol (24-DCP) and amoxicillin (AMX)) from wastewater was studied.

1. Introduction

It has been a considerable challenge to remove pharmaceutical pollutions from water resources [1,2]. Clearly, antibiotics have frequently been utilized in both human and veterinary medicine. These materials have gradually entered aquatic environments, and hence bacteria have obtained further resistance towards antibiotics even when their concentrations are low [3,4]. In this regard, great importance has been attached to the deletion of the antibiotic pollutions from wastewater. The most widely-used antibiotic, i.e., AMX, is excreted without bodily consumption (with a percentage of about 80–90%) due to its poor metabolism in the living organisms [5–8]. On the other hand, chlorophenols, which are widely applied for the synthesis of drugs, dyes, fungicides, and pesticides, are toxic pollutants and hard to eliminate from water resources as cited in the US EPA Clean Water Act [9,10]. The chlorophenol pollutants have created many problems since they cause toxicity and are perhaps carcinogenic materials. As an example, 24-DCP has often been observed to be a persistent pollutant, which is present in numerous industrial effluents, since it is largely employed in the preparation of different herbicides, insecticides, preservatives, disinfectants, antiseptics, etc. [11–13]. Unfortunately, since chlorophenols are biotoxic and have a stable molecular structure, they cannot be efficiently destroyed using conventional treatment processes [14]. As a result, a more efficient and viable approach need to be developed for a better elimination of these contaminations from water resources.

One important and recently-enhanced class of the inorganic materials is related to the metal-organic frameworks (MOFs). Owing to their high and tunable porosity, different pore architectures and compositions, pore functionality, open metal sites, etc., MOFs are observed to be better than the other porous materials [15–17]. In recent years, adsorption of a large number of pollutants via MOFs has been extensively explored [18,19]. As recorded in the literature, nanostructured MOFs demonstrate singular morphology and size-dependent characteristics such as considerable availability of the active sites in the porous structure and capability of functionalizing the surface area [20–22]. In this regard, different physical and chemical methods have recently been applied for the synthesis of the MOFs nanostructures [23].

As a safe technique, the ultrasound-assisted preparation, possessing advantages such as short reaction time under ambient pressure and at room temperature, considerable reaction yield, and high quality of the final products, has been in the focus of scholarly attention [24,25]. Some other advantages of the ultrasonic illumination are its eco-friendliness, cost-efficiency, and proper controllability for the preparation of the nanostructures with improved surficial area. Through the contact of the liquids with a high-intensity source of the ultrasound illumination, an acoustic cavitation occurs by means of the shock waves in the medium [26,27]. High pressure (up to 1000 atm) and temperature (up to 5000 K) localized spots are thus formed by the creation of the bubbles and their consequent intense collapsing in the liquids [28].

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A proper approach for provision of nanomaterial, particularly MOF, with optimal shape and size is to use the modulating synthesis technique [29]. When the modulating synthesis technique is combined with sonochemistry, the growth of the crystals can be directed towards particular structural size and shape [30–32]. In this context, the synthesis procedures show a better reproducibility, and resultantly the products' crystallinity and sometimes the size, the shape, and the degree of agglomeration/aggregation of the crystals are enhanced [33–36]. The modulating molecules are assumed to dramatically influence the nucleation and growth of crystals through competition with linker molecules for metal sites coordination over MOFs [37].

The present study has elaborated upon the modulated synthesis of the micro/nanoparticles of compound 1 with excellent features for the elimination of 24-DCP and AMX pollutants from wastewater, compared to the bulk structures. In order to increase the micro/nanoparticles quality and to have a better adsorption capability, dissimilar precursor concentrations, temperature and time of sonication, power of illumination, as well as the impact of the concentration of the pyridine as modulator reagent were considered.

2. Experimental

2.1. Materials and physical techniques

All of the considered solvents and reagents were commercially supplied from the market, and then they were utilized without any subsequent purifications. From Sigma-Aldrich, zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), and TDC were purchased. The ligand of 4-BPMH was provided in compliance with the procedure outlined in the literature [38]. Under an ultrasonic bath SONICA-2200 EP having a 30-kHz frequency, the ultrasonic preparation was performed. A Philips X'pert diffractometer having monochromated Cu-K_α radiation ($\lambda = 1.54056$ Å) was used to do the powder X-ray diffraction (PXRD) analyses. Furthermore, a gold-coated field emission scanning electron microscope (FE-SEM) (Mira TESCAN) was applied to characterize the shape of the samples. Using a PL-STA 1500 device with a 10 °C min^{-1} rate under a static argon atmosphere, measurements of the thermal behavior were carried out. A Shimadzu UV 2100 UV–Visible spectrometer was used to investigate the UV–Vis absorption spectrums. The infrared spectra were recorded on a nicolet fourier transform IR, nicolet 100 spectrometer in the range 400–4000 cm^{-1} using the KBr disk.

2.2. Synthesis of $[Zn(TDC)(4\text{-}BPMH)]_n{\cdot}n(H_2O)$as single crystal

Following the same procedure under the diffusion technique, the single crystals of $[Zn(TDC)(4\text{-}BPMH)]_n{\cdot}n(H_2O)$ were synthesized [39].

2.3. Synthesis of $[Zn(TDC)(4\text{-}BPMH)]_n{\cdot}n(H_2O)$ micro/nanoparticles by a sonochemical process

The micro/nanoparticles of compound 1 were ultrasonically synthesized under atmospheric pressure using an ultrasonic bath with dissimilar irradiation powers (30, 40, and 60 W) for 30, 60, 45, 90, and 120 min through various precursor concentrations at the temperatures of 25, 50, and 75 °C. After that, as represented in Table 1, impact of the concentration of pyridine as modulator on the samples' morphology was explored. The produced powder was centrifuged and isolated, and then it was washed with ethanol 3 times and finally dried in the air so as to be characterized.

2.4. Adsorption equilibrium studies

In order to assess the absorption behavior of the synthesized samples, amoxicillin (AMX, $C_{16}H_{19}N_3O_5S$) and 2,4-Dichlorophenol (24-DCP, $Cl_2C_6H_3OH$) were taken into account as two sample pollutions.

Table 1
Experimental details for synthesis of micro/nanoparticles of compound 1.

Samples name	Temperature (°C)	Time (min)	Concentration [Zn $(CH_3COO)_2{\cdot}2H_2O$]/[*TDC*]/[*4-BPMH*] (M)	Power (W)	Modulator (Pyridine)
1	25	60	[0.05]/[0.05]/[0.05]	30	–
2	50	60	[0.05]/[0.05]/[0.05]	30	–
3	75	60	[0.05]/[0.05]/[0.05]	30	–
4	50	30	[0.05]/[0.05]/[0.05]	30	–
5	50	45	[0.05]/[0.05]/[0.05]]	30	–
6	50	90	[0.05]/[0.05]/[0.05]]	30	–
7	50	120	[0.05]/[0.05]/[0.05]]	30	–
8	50	90	[0.025]/[0.025]/[0.025]	30	–
9	50	90	[0.0125]/[0.0125]/[0.0125]	30	–
10	50	90	[0.025]/[0.025]/[0.025]	40	–
11	50	90	[0.025]/[0.025]/[0.025]	60	–
12	50	90	[0.025]/[0.025]/[0.025]	30	1 mL
13	50	90	[0.025]/[0.025]/[0.025]	30	2 mL
14	50	90	[0.025]/[0.025]/[0.025]	30	3 ML

These pollutants were dissolved in deionized water, so that an aqueous stock solution can be provided for the pollutants. In order to arrive at the most proper pollutant concentrations in the suggested solution, the aqueous stock solution was diluted with water. The adsorption capability was then examined via stirring the aqueous solution in a cylinder-shaped quartz reactor which involved around 100 mL of 50 ppm pollutants in the aqueous solution, where 40 mg samples were used. Sonication of the suspension was subsequently carried out for 10 min. At defined times, from the reaction suspension, samples were taken to be analyzed. For further analysis of the samples, they were promptly centrifuged and removed at 5000 rpm for a time period of 6 min. In this context, by the application of a UV–Vis spectrophotometer (Shimadzu UV 2100), AMX and 24-DCP adsorptions were studied at 237 and 284 nm, respectively. Using a calibration curve, the concentrations of the AMX and 24-DCP pollutants in different samples were measured at λ_{max} = 237 and 284 nm, respectively. In this way, the pollutants' removal rate in percent can be calculated in various time intervals. The percentage of the pollutant removal can be formulated as follows:

$$\%Removal = \frac{(C_i - C_t)}{C_i} \times 100 \quad (1)$$

In the above formula, C_i shows the initial pollutant concentration while C_t stands for the pollutant concentrations at a specified time.

3. Results and discussion

However, the micro/nanoparticles of compound 1 were produced using similar solvents under ultrasound illumination at ambient temperature merely in a few minutes or a few hours. Different preparation routes of the $[Zn(TDC)(4\text{-}BPMH)]_n{\cdot}n(H_2O)$ are summarized in Fig. 1.

The scanning electron microscopy (SEM) was utilized to characterize the shape and the size of the synthesized micro/nanoparticles of compound 1 in the presence of ultrasonic irradiation. In this context, five factors were examined: temperature of sonication, time of sonication, precursor concentrations, power of sonication, and nucleation management in the presence of the modulator of pyridine. These factors were observed to affect considerably the shape and the size of the suggested micro/nanoparticles. In nearly all of our samples, the main structural shape was in the form of nanoplates. As reported in the literature, the morphology and size of the nanostructures is influenced by temperature [40]. As shown in Fig. 2a and b, under the circumstances

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