Research Article

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Preparation of Zn-MOFs by microwave-assisted ball milling for removal of tetracycline hydrochloride and Congo red from wastewater

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Abstract: In this study, we prepared Zn-MOFs as an ordinary, low-cost, and efficiency method taking advantage of zinc(II) acetate monohydrate and 1,3,5-benzenetricarboxylic acid in microwave-assisted ball milling. The Zn-MOFs were measured via scanning electron microscopy, infrared spectrometry, X-ray diffraction, and thermogravimetry. We explored its use as a photocatalyst for the degradation of tetracycline hydrochloride and Congo red from aqueous solutions. The results demonstrate that the kinetic model was appropriate for the removal of organic pollutants. In general, it is feasible, inexpensive, and effective to use metal organic framework (MOF) to treat waste liquid. Therefore, our findings indicate that Zn-MOFs have broad application vista in wastewater purification.

Keywords: MOFs, MWBM, antibiotics, organic dye

1 Introduction

Antibiotics have been widely used for the treatment and prevention of bacterial infections in veterinary and human medicine, as well as in agriculture. The prevalence of their use in combination with the ineffectiveness of traditional sewage handling methods has resulted in the accumulation

of a number of antibiotics in water supplies and aquatic environments [1]. A few methods for removing antibiotics from water have been developed, including photocatalytic degradation biological treatment, advanced oxidation processes, and membrane separation [2]. Among them, photocatalytic degradation seems to be the best option, because it is environmentally friendly and cost-effective.

Since the 1990s, metal organic frameworks (MOFs) have been an intense focus on materials science research because of not only their fascinating and different structures [3,4], but also their extensive applications in energy storage [5,6], gas storage [7–9], catalysis [10,11], drug delivery [12,13], carbon dioxide capture [14,15], magnetic properties [16,17], ion exchange [18,19], and so on. A tool for the construction of lengthened porous materials was supplied by combination of organic linkers and metal ions [20,21]. Because of the sensitivity to the reaction conditions, the same reagent can produce a completely different structure under different circumstances. Different methods can be used to prepare compounds with different structures. High quality MOFs crystals can be obtained via using methods involving solvent heat or wet solution chemistry [22]. New approaches in preparation, for example, microwave [23–26], electrochemical synthesis [27,28], and mechanochemical [29,30], can greatly reduce synthesis time and increase production capabilities. Compared to traditional synthesis methods, constructing MOFs using the acoustic chemistry method is more concise, controllable, and convenient [31–34].

MOFs are usually composed of metal clusters or inorganic metal ions linked via organic ligands by coordination bonds [35,36]. Our laboratory first reported the technique of microwave-assisted ball milling (MWBM) [37–39]. The major advantages of this method are that it saves time and improves the speed of the chemical reaction [40,41]. The induction coupling of ball milling and microwaves results in the capacitance of some nanocrystalline materials produced at indoor temperatures, such as MOFs [42–44]. In this report, MOFs were synthesized using the MWBM approach, and zinc(II) acetate tetrahydrate was

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used as a source of metal ions for the preparation of MOFs. H_3BTC and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ were the raw materials and were successfully used for the reduction of the aqueous tetracycline hydrochloride and Congo red (CR).

2 Experimental

All reagents for the preparation and analysis were obtained from commercial suppliers. The ligands 1,3,5-benzenetricarboxylic acid (trimesic acid, $\text{C}_6\text{H}_3\text{O}_6$, H_3BTC , 98%), tetracycline hydrochloride, and zinc(II) acetate monohydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\geq 990\%$) were supplied by Aladdin Biological Technology Co, LTD, Shanghai, China.

We performed structural and morphological characterizations using Fourier transform infrared spectroscopy (FTIR, IRTracer-100, Shimadzu), X-ray diffraction (XRD), field emission scanning electron microscopy, and thermogravimetry (TG).

The compound was synthesized according to the method previously described [42–44], using 1,3,5-benzenetricarboxylic acid (4.994 g, 0.0238 mol), zinc(II) acetate monohydrate (3.5375 g, 0.01587 mol), a stainless steel ball (600 g), and 700 mL deionized water. After 40 min of reaction under the same conditions, the solution changed from colorless to blue until any color change ceased and acid gas was emitted. The compound was filtered and washed with water. The filtered solid was added to a beaker with ethanol and stirred for 3 h using a magnetic stirrer. The precipitate was filtered under suction and dried. The final product was collected for subsequent characterization and experiments.

Tetracycline hydrochloride and CR were chosen as model contaminants to evaluate the degradation ability of the Zn(II)-MOFs. Tetracycline hydrochloride and CR were used as the raw materials and were dissolved in a 250 mL beaker at room temperature ($\sim 25^\circ\text{C}$). The degradation of tetracycline hydrochloride and CR was tested in a beaker containing 55, 30, or 15 ppm of the aqueous tetracycline hydrochloride solution with 100 mg and 50 mg MOFs under the action of a Xe lamp or nature light on a magnetic stirrer. The absorbance at 358 nm [45] and 495 nm was monitored by UV-visible spectrophotometer (UV-2550, 220 V, Shimadzu Instruments [Suzhou] Co, Ltd) from the reaction suspension every 30–60 min, respectively. In this way, the removal rate of tetracycline hydrochloride and CR could be obtained at different time intervals. The amount of degraded tetracycline hydrochloride and CR were calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m}, \quad (1)$$

where C_0 , C_e , V , and m are the initial concentrations of the solution (ppm), equilibrium concentrations of the solution (ppm), the volume of the solution (L), and the mass of the Zn-MOFs (g), respectively.

3 Results and discussion

MWBM is a way of preparing MOFs that is fast and does not require organic solvents, and a simple reaction mechanism for this process has been provided elsewhere [42]. Briefly, under the combined effects of microwave and ball milling, anionic H_3BTC is formed easily in an aqueous environment via ionization. The H_3BTC anions then attack metal cations of the salt to form coordination compounds [46]. As compared to the other methods shown in Figure 1, synthesis of Zn-MOFs and MIL-101-Cr [46], MIL-53(Fe) [47], MIL-125(Ti) [48], MIL-68(In) [49], and HUT-091 [50] are compared as shown in Figure 1, and Zn-MOFs are superior to other MOFs materials.

As shown in Figure 2, the Fourier transform infrared spectroscopy spectrum showed the characteristic peaks of the MOFs at $1,556$ and $1,371\text{ cm}^{-1}$. Because of the existence of carboxyl, no peak appears at $1,710\text{ cm}^{-1}$ where a strong carbonyl peak would be expected. This is primarily because of extended conjugate π -bonds that are created from the carboxylate formed from carboxyl anion, thus making the two oxygen atoms equivalent. Therefore, the density of the electron cloud between atoms is distributed symmetrically.

Figure 1: Comparison of the preparation time of MOFs.

Figure 2: IR of Zn-MOFs.

The XRD characterization of the materials is shown in Figure 3. The XRD pattern shows that there is no wide absorption peak, which proves that the crystallization of the materials is very good.

The morphology of the Zn-MOFs was observed by SEM, as exhibited in Figure 4. The result showed the unusual morphology of the Zn-MOF particles and also revealed MOF crystals with high dispersibility. At present, the molecular interaction of the organic ligand is weakened or even vanished, and the deprotonation of the organic ligand was enhanced, which promoted the growth of crystal in aqueous solution.

As shown in Figure 5, thermogravimetrics analysis demonstrated that the TG curve exhibits three different stages: the first is a mass loss (17.8%) stage between 20°C and 176°C that could also be put down to evaporation of the solvent water molecules from the sample; the second

Figure 3: XRD of Zn-MOFs.

between 176°C and 421°C is mainly caused by the solvent because of oxidation of Zn^{2+} which accounted for 53% of the loss [42]; the third stage starts at 421°C, at which temperature the structure and the organic linker of the Zn-MOFs are destroyed, indicating that the thermal stability of the Zn-MOFs is 421°C. The quality of this loss is stable at 421°C and then completed at 800°C. The residue was 48.05% of the initial mass. Most often the reaction of organic ligands and metal ions via a common synthesis procedure yields MOFs with more stable structures [51].

Figure 6 shows that the BET surface area was $85 \text{ m}^2/\text{g}$. The average particle size was 706 nm, indicating a mesoporous material.

In actual wastewater treatment, the original pollutant concentration is a key factor to achieve the desired degradation effect, as shown in Figure 7. When the initial concentration of CR was 50 mg L^{-1} and quality of Zn-MOFs was 100, 50, and 25 mg, the final concentration was reduced by 89.11%, 83.91%, and 22.78%, respectively. When the initial concentration of CR was 30 mg L^{-1} and quality of Zn-MOFs was 50 mg, the final concentration was reduced by 97.2%. When the initial concentration of tetracycline hydrochloride was 15, 30, and 55 mg L^{-1} , the final concentration was reduced by 70.66%, 54.37%, and 22.78%, respectively. When the initial concentration of CR was 100 mg L^{-1} and quality of Zn-MOFs was 50 mg, the final concentration was reduced by 56.14%. Increasing initial concentrations of wastewater resulted in a decreasing removal rate. Increasing quality of Zn-MOFs resulted in an increasing removal rate. Competition among tetracycline and molecules for photocatalytic sites of the catalyst is an important factor in this effect, especially because tetracycline hydrochloride and CR molecules can produce other intermediates in the photocatalytic process [52]. In addition, when the concentration of tetracycline hydrochloride is high, the path length of the photon into the tetracycline solution decreases [53]. It is also worth noting that Zn-MOFs can show high photocatalytic activity for tetracycline hydrochloride and CR degradation. The results clearly show that Zn-MOFs have great potential for tetracycline and CR degradation at relatively low concentrations.

To research the impact the amount of catalyst has on the removal of tetracycline, we studied two amounts, 50 and 100 mg of Zn-MOFs, in a 30 mg/L tetracycline hydrochloride solution. Results revealed that the larger the amount of catalyst, the higher the removal rate. However, when the amount of catalyst was doubled from 50 to 100 mg, the removal rates were 47.63% and 54.37%, respectively. To study the influence of the amount of Zn-MOF and the concentration of CR on the removal rate, we studied three amounts, 25, 50, and 100 mg, concentration

Figure 4: SEM of Zn-MOFs.

of tetracycline hydrochloride solution were 30, 50, and 100 mg L^{-1} . The results revealed that the larger the amount of catalyst, the higher the removal rate. However, when the

amount and concentration of the catalyst were different, the maximum and minimum removal rates were 97.2% and 34.9%, respectively. First, Zn-MOFs precipitate and

Figure 5: TG of Zn-MOFs.

Figure 6: N₂ adsorption-desorption isotherms of Zn-MOFs.

accumulate under addition of large number of catalyst, thus reducing the production of active substances in the photocatalytic process [54]. Second, the more the presence of catalyst, the higher the turbidity of the solution, thereby dispersing the light and reducing the effect of light passing through the solution [55]. To determine the reusability of Zn-MOFs, the used Zn-MOFs were washed in water, dried, and reused. The results showed that after three cycles, the decrease in the activity of Zn-MOFs was only 52%, which showed reasonable reusability. The results of TC removal by Zn-MOFs and Fe₃O₄@SiO₂-chitosan/GO [56], NH₂-MIL-101(Cr) [57], MIL-101(HCl) [58], ZIF-8 [59], GBCM350 activated carbon [60], and UiO-66 [61] adsorbents are compared as shown in Figure 8, and the Zn-MOFs are superior to other adsorbents.

To fully understand and study the kinetics of Zn-MOF-mediated photocatalytic degradation of tetracycline

Figure 7: The removal of Zn-MOFs: (a) CR and (b) tetracycline hydrochloride.

Figure 8: Comparison of the Zn-MOFs adsorbent with other materials on TC adsorption.

and CR, optimum conditions were analyzed. In accordance with reports in the literature, photocatalytic

Figure 9: The kinetic model of Zn-MOFs: (a) pseudo-first order and (b) pseudo-second order.

degradation of contaminants was described by kinetics model [44,62]. The equations are as follows:

$$\ln \frac{C_t}{C_0} = k_1 t, \quad (2)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}. \quad (3)$$

In these equations, C_t , C_0 , k_1 , k_2 , and t are the concentration of tetracycline at time t , the initial concentration of tetracycline, the kinetics reaction rate constant (min^{-1}), and the reaction time (min), and q_t and q_e represent the amounts (mg g^{-1}) of the adsorbents at time t and equilibrium, respectively. The results of Zn-MOFs calculations are presented in Figure 9 and Tables 1 and 2. The kinetics pseudo-first-order model was appropriate to describe the photocatalytic degradation of tetracycline hydrochloride. The pseudo-second-order model is more suitable to describe the photocatalytic degradation of Zn-MOFs for CR, the concentration, and the sample dosage, which have certain influence on the photocatalytic effect.

In the photocatalytic process, hydroxyl radicals ($\cdot\text{OH}$), electrons (e^-), superoxide ions (O_2^-), and holes (h^+) as well as various active substances can be produced, and

these substances may be involved in the photodegradation of tetracycline [63]. For the sake of identification of the dominant oxidative species, the photocatalytic degradation efficiency was measured via adding H_2O_2 (2 mL) to the solution, increasing the amount of hydroxyl radical in the system to further promote the reaction. As shown in Table 1, when the concentration was 30 ppm, addition of 2 mL of hydrogen peroxide resulted in a 14% and 30% increase in the tetracycline hydrochloride removal rates of 50 mg and 100 mg catalysts, respectively. When H_2O_2 is added, the removal rate of tetracycline hydrochloride decreases as the amount of catalyst increases, which may be because of the complex interaction of various factors. Another possible cause is the inability of amodiaquine to cover all the exchangeable sites on it under the high dosage of adsorbent, leading to insufficient tetracycline hydrochloride uptake [64,65]. The detailed mechanism of Zn-MOFs adsorption on CR is consistent with Cu-MOFs [42]. Finally, the aggregation of adsorbent particles at a higher concentration results in a decrease in the surface area and an increase in the diffusion path length. We also demonstrated the existence of active substances. Among these influencing factors, h^+ plays a leading role in the removal of pollutants.

Table 1: Parameters of the process of tetracycline degradation by Zn-MOFs

Concentration and dosage	Rate equation	R^2	Removal rate (%)
55 mg/L, 100 mg	$y = -0.00106x + 0.000341$	0.99129	22.78
15 mg/L, 100 mg	$y = -0.00523 + 0.00318$	0.99496	70.66
30 mg/L, 100 mg	$y = -0.0032x + 0.01702$	0.99229	54.37
30 mg/L, 50 mg	$y = -0.00299x + 0.07416$	0.99278	47.63
30 mg/L, 100 mg + H_2O_2	$y = -0.00396x - 0.2129$	0.99405	67.8
30 mg/L, 50 mg + H_2O_2	$y = -0.00412x - 0.77061$	0.999	78.6

Table 2: Kinetic parameters for CR over Zn-MOFs

Con (mg/ L)	Qua (mg)	Pseudo-first-order kinetics		Pseudo-second-order kinetics	
		K_1 (min ⁻¹)	R^2	K_2 (g (mg min) ⁻¹)	R^2
50	100	-0.01149	0.95317	0.00942	0.98621
	50	-0.0018	0.93866	0.00987	0.9962
	25	-0.00254	0.87482	0.0048	0.99887
100	50	-0.00343	0.89493	0.0038	0.99022
30	50	-0.02116	0.94589	0.0061	0.99041

4 Conclusions

In a word, the synthesis of MOFs by MWBM is faster and simpler than other methods. These results demonstrate that this method has proven to be an effective and reliable method for synthesizing MOFs. Furthermore, ability to remove tetracycline solution from wastewater by Xe light was tested. The results showed that Zn-MOFs could effectively degrade tetracycline hydrochloride and dye. The addition of H₂O₂ into the solution promoted the photocatalytic reaction, and the degradation of tetracycline was analyzed with pseudo-first-order model. The resulting data revealed correlation coefficients of the first kinetic model all above 0.99, thus proving that the degradation of tetracycline hydrochloride and CR could be explained by the first kinetics and the second kinetics, respectively. Therefore, the application of MOFs for tetracycline hydrochloride degradation can be used in practice in the future. The results indicate that the MWBM process is an effective way for simple and fast preparation of MOFs for practical applications.

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Conflict of interest: The authors state no conflict of interest.

Data availability statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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