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Research paper

Effect of structures on the adsorption performance of Cobalt Metal Organic Framework obtained by microwave-assisted ball milling

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ABSTRACT

The Co-MOFs were efficiently and low-costly synthesized by microwave-assisted ball milling without organic solvents and the adsorption of Congo Red (CR) was studied in view of adsorption kinetic and isotherm. It's find that the formation of two different structures due to the change in the molar ratio of the raw material, which contribute to a larger difference of the adsorption. The maximum adsorption capacity of the Co-MOFs toward CR reached 4885.20 mg/g. Open active metal sites and π-π stacking interactions are thought to play an important role in the adsorption of CR onto the Co-MOFs.

1. Introduction

Metal-organic frameworks (MOFs) are crystalline porous material with regular channels or pore structure constructed by metal ions connected by various organic bridges [1,2]. It also can be called porous coordination polymer (PCP) or organic-inorganic hybrid materials [3]. Compared with zeolite and activated carbon and other conventional porous framework materials, it has their diverse compositions and structure types, low crystal density, tunable pore size, coordinatively unsaturated and high specific surface area [4–6]. It is precisely because of these advantages that makes the MOFs have potential applications in gas adsorption and separation, catalysis, drug carrier, electrical materials, adsorption and adsorptive desulfurization [7–10]. One of the kind of MOFs, Co-MOFs, which they have many potential applications such as hydrogen storage [11], supercapacitor material [12] and so on. In this study, we mainly discuss about Co-MOFs.

The original methods of synthesis of Co-MOFs have slow diffusion method and solvothermal method. The crystallization process of the diffusion process takes a long time and the reproducibility of the crystals under high temperature and high pressure is poor [13–15]. Solvothermal method [16–18] makes the temperature controllable and the quality of crystal higher, but it has the problems of long synthesis time and high energy consumption. In the past few years, some new synthesis methods involving hydro-thermal [19], microwave heating [20] and ultrasound energy method [21] have been used in the MOFs synthesis process. In this paper we mention on microwave-assisted ball milling [22–25] to synthesize Co-MOFs and its composites. This method specifically placed the ball milling machine in a microwave instrument, so the coupling of microwave and ball milling plays an important role in the synthesis process. Compared with conventional methods, the microwave-assisted ball milling has fascinated because it intensely reduces the synthesis time. In addition, organic solvents are often used in the synthesis of most metal organic framework materials such as N,N-Dimethylformamide (DMF), it is well known that DMF are inert, toxic and difficult to biodegrade in waste streams [26–28]. Yet, deionized water is used as the solvent in microwave-assisted ball milling method, which not only reduce the cost of synthesis, but also avoid the harmfulness of DMF. The most important of all is the formation of two different structures due to the change in the molar ratio of the raw material during the synthesis process.

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Nowadays, the development in science and technology give rise to the excessive pollution of water resources. Therefore, how to removal of organic pollutants from waste water efficiently has changed a heated research theme. The lots of waster water has been produced by many industries including textile, paper, leather, printing, dyestuff, plastics, plating, cosmetics and so on [29]. As one of the most important pollutants in waster water, organic dyes, not only reduce the water quality [30], but also lead to a poor health. Moreover, a lot of organic dyes are deemed to be inert, mutagenic, difficult to biodegrade, biological initiative, toxic and even carcinogenic [31–33].

Usually, there are several ways [34,35], physical, chemical and biological methods, to removal of organic from the waste water. Adsorption technology does not need too higher operational temperatures with a high cost is regarded as a more complete method [36]. The method shows many superiorities [36] including low cost, easy to operate, reusability of the absorbent, high efficiency etc.

There are several materials used as adsorbents like zeolite [37], molecular sieve [38], rice husk [39], activated carbon [40] and clay [41]. However, there are some small flaws that affect their application. For instance, zeolite and activated carbon necessitate high temperature and cost in the adsorption. Compared to zeolite and activated carbon, the strong point of MOFs mentioned above make the adsorption process low cost and easy to operate. For example, Enamul Haque et al. synthesized MOF-235 and found that the adsorption capacities of MOF-235 for anionic dye methyl orange (MO) and cationic dye methylene blue (MB) are much higher than those of an activated carbon [8]. Li-Na Jin et al. reporter the maximum adsorption capacity of the MIL-68(In) nano-rods synthesized by solvothermal method toward Congo red reached 1204 mg/g [42]. But, there have been a bit reports on Co-MOFs for the removal of organic dyes from the waste water, especially the impact on the structural aspects. So, in this paper, effect of structures on the adsorption performance of Co-MOFs was studied.

2. Experimental

2.1. Chemicals and materials

1,3,5-Benzentricarboxylic acid (98%) and the Cobalt(II) acetate tetrahydrate (≧99.5%) were purchased from Aladdin biological technology Co., LTD, Shanghai, China. Congo red, CR was purchased from Aladdin biological technology Co., LTD, Shanghai, China. In this study, all the materials were used without further purification.

2.2. Preparation of the Co-MOFs

1,3,5-Trimesic acid and Cobalt acetate tetrahydrate with different molar ratio (2:1, 1.5:1, 1:1, 1:1.5, and 1:2, the total weight of the two materials were 10 g), stainless steel ball (700 g) and 700 ml deionized water were put into a tetrafluoroethylene milling pot (diameter 140 mm, high 90 mm, volume 1.38 L). The microwave oven and stir milling were turned on simultaneously and the stirring speed was 200 r/min. The precursor solution was synthesized various time (15 min, 30 min, 60 min) later, the synthesized pink Co-MOFs solid was filtered and washed with absolute ethanol several times. Finally, the product was dried in vacuum at 90 °C for 8 h.

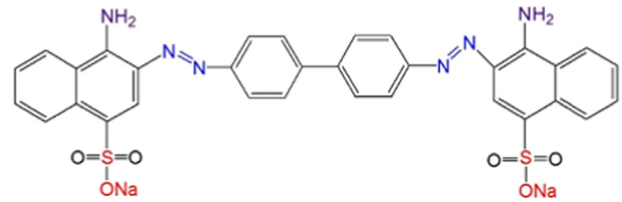

Fig. 1. The structure of Congo red.

2.3. Adsorption measurements

In order to characterize the adsorption capacity of the synthesized Co-MOFs, measurements on adsorption of Congo Red (CR) chosen as a model pollutant to evaluate the adsorption capacity of the Co-MOFs. The structure of CR is showed in Fig. 1.

Before adsorption, the adsorbents were dried in vacuum 2 h. After that an exact amount of the adsorbents (20 mg) were added into the aqueous CR solutions (100 ml) having fixed CR concentrations from 20 ppm to 300 ppm. Then the solutions containing the adsorbents (Co-MOFs) were stirred on a magnetic stirrer at 298 K for a fixed time (0.5–12 h). After adsorption, the solution was separated from the adsorbents with a syringe filter (PTFE, hydrophobic, 0.45 um). The absorbance values of the solutions were analyzed by ultraviolet spectrometer (UV-2550 220 V Shimadzu instruments (Suzhou) Co., Ltd.) at 495.5 nm. Then, the adsorbed amount of CR, q_t (mg g^{-1}), at equilibrium can be calculated from Eq. (1):

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

where C_0 and C_t (mg L^{-1}) are the concentrations of CR solutions at initial and time = t, respectively. V(L) is the volume of the CR solution and W (g) is the weight of the adsorbents (Co-MOFs).

3. Results and discussions

3.1. Characterization of the prepared Co-MOFs

Under the microwave-assisted ball milling process [43], Co would like lose two electrons from its s orbital, and trimesic acid is deionized to form a π_3^5 negative ion in aqueous solutions. Then, trimesic acid anion can provide electrons to the metal ions and release acetic acid molecules, which react with the metal ions in a proportion. The specific reaction mechanism of Co-MOFs can be described as follows: