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Ferrum-Based Metal Organic Framework for Methyl Orange Removal from Aqueous Solution

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Abstract

Metal organic framework materials (MOFs) are a classic three-dimensional porous crystalline materials formed by the assembly of metal ions or metal clusters and organic ligands. They have large specific surface areas, uniform pore size distributions, unsaturated metal active sites, and many other advantages. The introduction of other functional materials through functional group modification or doping can give MOFs more excellent performance, which is of great significance for improving the ability of a single MOFs material to remove pollutants in water. In this paper, MIL-53(Fe) and Br-MIL-53 (Fe) were synthesized to adsorb methyl orange from organic dyes. The results show that Br-modified MIL-53(Fe) exhibits higher adsorption performance than the original MIL-53(Fe). The effect of time, pH value, temperature, and dosage on adsorption performance of Br-MIL-53(Fe) have been studied. Moreover, it is also found that the MOF material is a highly efficient adsorption material that can be expected to be used to remove methyl orange from dye wastewater.

Keywords

Metal organic framework; Composite material; methyl orange; adsorption.

1. INTRODUCTION

Metal-Organic Framworks (MOFs) are different from other traditional porous materials due to their high porosity and thermal stability. The three-dimensional MOFs are crystalline assemblies of inorganic metal ions and organic ligands. They have a flexible structure. By selecting different structural units, a clear pore size, surface area and function can be defined. The special properties of MOFs materials have attracted the interest of many researchers. To date, more than 20,000 different MOF structures have been reported and studied [1].Compared with traditional zeolite-type materials, MOFs have many advantages. One is that zeolite-related materials need to form a certain organic or inorganic template, and for MOFs materials, the solvent is the main template molecule [2]. The second is that compared with materials based on a small amount of cations, most metal cations can be formed with MOF synthesis.

In addition, MOF has many applications in the environment, including gas adsorption, separation of chemicals, drug delivery, removal of pollutants in the water environment, photocatalytic applications, etc. Based on the potential applications of MOF in various fields, we know that MOF is a promising material because of their huge porosity, which leads to the selective adsorption of certain specific guest molecules with specific functional groups. Central metal coordination unsaturation sites, functionalized modified and supported active materials have been successfully used for some other interactions between adsorbates and MOF materials. MOF is superior to other porous adsorbents and can effectively remove harmful compounds. In

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various interactions, acid-base, π complexes, H bonds and coordination with open metal sites play important roles in adsorption. Wu et al. [3] synthesized a rod-shaped metal organic framework (MOF-5) nanomaterial by a solvothermal method and applied it to effectively adsorb U (VI) from an aqueous solution. Huynh et al. [4] synthesized a metal-organic framework and iron-doped MIL-101 (Fe-MIL-101) using a hydrothermal method. Compared with single MIL-101, the introduction of iron into MIL-101 significantly improved the adsorption capacity of Pb (II).The ZIF-67 synthesized by Park et al.[5] is to dissolve anhydrous cobalt nitrate and 2-methylimidazole in anhydrous methanol, then mix the two solutions and let stand for 24 h to crystallize ZIF-67 Crystal. However, the yield is low and the time required for synthesis is long, which is not suitable for industrial development. Li Ling et al.[6] used the layer-by-layer self-assembly method to use HKUST-1 as a template, and Fe_3O_4@MOFs was synthesized by circulating Fe_3O_4 and organic ligands on HKUST-1, and Fe3O4@MOFs/GO was synthesized by the same method. Abdol et al. [7] ultrasonically synthesized a metal organic framework of cadmium terephthalate, MOF-2(Cd), Cd-TPA, as an adsorbent at room temperature for efficient ultrasonic-assisted removal of lead and copper in aqueous solutions.

At present, the environmental pollution caused by industrial wastewater in China is serious. New treatment methods, especially the use of new materials to adsorb harmful substances, reduce the environmental pollution of industrial wastewater is very important. At present, dye wastewater is the most difficult to solve in the harmful industrial wastewater. The characteristics of dye wastewater are deep color, high toxicity, and difficult to degrade [8].

Adsorption is a commonly used method in wastewater treatment, so it is very important to develop efficient, economical, environmentally friendly, and recyclable adsorption materials. MOFs materials have been gradually used as adsorbents for the removal of pollutants in wastewater due to their high specific surface area, highly ordered porosity, adjustable pore size, and functional modification, etc., and have shown good results [9]. The topological structure of MOFs materials is special. The characteristics of unsaturated metal sites make them have higher reactivity and selectivity, and they have advantages in applications in the field of catalysis [10].

Doping MOFs with other functional materials can not only maintain the original properties and functions of MOFs, but also improve the porosity, specific surface area, and morphology of MOFs. It also has new specific functional characteristics. The synergistic effect can give it better performance [11]. At present, the materials commonly used to dope with MOFs are metal oxides, metal ions, graphene, magnetic microspheres, polyoxometalates, polymers, carbon materials, fibers, etc [12].

Dye wastewater has seriously threatened the environment and human health. Methyl orange is a typical representative of hard-to-degrade compounds in dye wastewater, and it has a strong irritation to the eyes and skin. Based on the characteristics of large specific surface area and porosity of MOFs, Br-MIL-53 (Fe) was synthesized as an adsorbent, and the research on its adsorption of methyl orange solution was conducted.

2. EXPERIMENTAL PART

2.1. Main Reagents and Instruments

Experimental reagents: methyl orange, N, N-dimethylformamide and terephthalic acid were purchased from Aladdin Reagent Factory; ferric chloride hexahydrate was purchased from Xilong Chemical Co., Ltd. The experimental reagents were of analytical grade.

Experimental equipment: Collecting constant temperature heating magnetic stirrer (DF-101S, Zhengzhou Kefeng Instrument Equipment Co., Ltd.); Vacuum drying box (XMTD-8222, Changshu Zhongsheng Medical Instrument Co., Ltd.); Desktop high-speed refrigerated centrifuge TGL-20M, Shanghai Anting Scientific Instrument Factory); UV-visible

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spectrophotometer (Lambda 800, PerkinElmer, USA). Hydrothermal synthesis reactor 100ML (Xi'an Hongchen Instrument Factory)

2.2. Preparation of Composite Materials

Preparation of MIL-53(Fe) material was synthesized by hydrothermal synthesis method [13]. 3.881g of $FeCl_3.6H_2O$ and 2.37g of H_2BDC were dissolved in 40mL of DMF. The mixed solution was transferred to a polytetrafluoroethylene-lined reaction kettle, and placed in a dry box at 150°C for a constant temperature reaction for 16 hours. After the reaction kettle was cooled to room temperature, the obtained sample was centrifuged, washed repeatedly with DMF, absolute ethanol, and deionized water, and then baked in a drying box at 150°C for 24 hours to obtain iron-based metal organic framework material MIL-53(Fe).

The method of Br-MIL-53(Fe) material is similar to that of MIL-53(Fe). 3.881g of $FeCl_3.6H_2O$ and 3.071g of Br-H_2BDC were dissolved in 40mL of DMF. The mixed solution was transferred to a polytetrafluoroethylene-lined reaction kettle, and placed in a dry box at 150°C for a constant temperature reaction for 16 hours. After the reaction kettle was cooled to room temperature, the obtained sample was centrifuged, washed repeatedly with DMF, absolute ethanol, and deionized water, and then baked in a drying box at 150°C for 24 hours to obtain iron-based metal organic framework material Br-MIL-53(Fe).

2.3. Adsorption Experiment

Take a certain amount of MOFs material Br-MIL-53(Fe) and add it to a stoppered milled triangle bottle containing 50 mL of 30 mg/L methyl orange solution, put it in a dual-function water bath constant temperature shaker, and shake at a constant temperature for a certain time After centrifugation, the supernatant was taken out. After high-speed centrifugation, the absorbance was measured with a spectrophotometer at a wavelength of 465.2nm, and the equilibrium concentration Ce after adsorption was calculated according to the standard curve of Congo red content. Then, according to the formulas (1) and (2), the removal rate and adsorption amount of the adsorbent were calculated.

$$Q_t = \frac{(C_i - C_t)V}{m} \tag{1}$$

$$E = \frac{(C_i - C_t)}{C_i} \times 100\% \tag{2}$$

In the middle:Qt—Adsorption at time t (mg/g);

Ci—Initial concentration of methyl orange (mg/L);

Ct—methyl orange concentration at time t (mg/L);

V—Volume of methyl orange added (L);

m—Quality of added materials (g);

E—Removal rate of methyl orange.

(1) Effect of reaction time on adsorption effect

To 100 mL of a 30 mg/L methyl orange simulation solution, add a certain mass of MIL-53 (Fe) or Br-MIL-53 (Fe) metal-organic framework adsorbent, and shake at 25 oC in a constant temperature water bath for 10 minutes. , 20, 30, 60, 90, 120, 180, 240min. Sampling, filtration and separation, transfer a certain amount of filtrate for dilution, and then measure the

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absorbance of methyl orange with a UV spectrophotometer, and calculate the adsorption amount to get the best reaction time.

(2) Effect of pH on adsorption effect

Transfer 100mL of a 30 mg/L methyl orange simulation solution into a conical flask, adjust the $Cr6^{+}$ or methyl orange solution to a different pH value with 0.1 mol/L HCl or NaOH solution, and add a certain amount of MIL-53 (Fe) or Br-MIL-53 (Fe) metal-organic framework adsorbent, sampled after shaking at 25 oC in a constant temperature water bath for 3 hours, filtered and separated, and a certain amount of filtrate was diluted for determination with a UV spectrophotometer to measure $Cr6^{+}$ Or methyl orange absorbance and calculate the amount of adsorption to determine the optimal pH.

(3) The effect of the dosage on the adsorption effect

Transfer 100mL of methyl orange simulation solution with a concentration of 30mg / L into an Erlenmeyer flask, adjust the methyl orange solution to the optimal pH value, and add different qualities of MIL-53 (Fe) or Br-MIL-53 (Fe) Metal-organic framework adsorbent, sampled after shaking at 25 ° C in a constant temperature water bath for 3 hours, filtered and separated, removed a certain amount of filtrate for dilution, and measured the absorbance of methyl orange with an ultraviolet spectrophotometer, and calculated the adsorption amount to determine Optimal dosage.

(4) Effect of temperature on adsorption effect

Transfer 100 mL of a methyl orange simulation solution with a concentration of 30 mg/L, adjust the methyl orange solution to the optimal pH value, and add MIL-53 (Fe) or Br-MIL-53 (Fe) at the optimal dosage. The metal-organic framework adsorbent was shaken in a constant temperature water bath for 3 hours under different temperature conditions, and then filtered and separated. A certain amount of filtrate was removed and diluted. The absorbance of methyl orange was measured with an ultraviolet spectrophotometer, and the adsorption amount was calculated and the temperature was analyzed. Effect on the adsorption of methyl orange by the adsorbent.

(5) Adsorbent regeneration experiment

MIL-53 (Fe) or Br-MIL-53 (Fe) metal-organic framework adsorbents were used to adsorb methyl orange solution to study the recycling performance of the adsorbents. The adsorbed saturated adsorbent was washed three times with deionized water, added to 100 mL of a 0.05 mol/L NaOH solution, and sonicated for 30 min. This process was repeated twice, and then washed with deionized water multiple times until neutral. The adsorbent is dried in a blast drying box, and the dried adsorbent can be subjected to repeated adsorption experiments.

3. RESULTS AND DISCUSSION

3.1. Effect of Adsorption Time on the Removal of Methyl Orange from Metal-Organic Framework Materials

The amount of methyl orange adsorbed by the adsorbent increased with time. During the 30 minutes before the adsorption, the rate of adsorption of methyl orange by the adsorbent was faster. This is due to the fact that Br-MIL-53 (Fe) There are a large number of active adsorption sites on the surface of the adsorbent, which is conducive to adsorption. With the increase of the adsorption time, the availability of the vacant adsorption sites of the adsorbent decreases. After 180 minutes, the adsorption amount basically stabilizes and reaches the adsorption equilibrium. The adsorption capacity of the composite adsorbent Br-MIL-53 (Fe) for methylene blue and methyl orange is because the composite adsorbent forms more pores and increases the specific surface area, so it exhibits more excellent adsorption performance. The final

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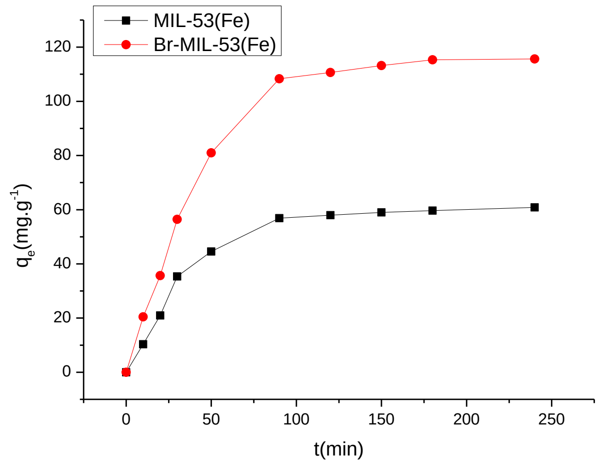
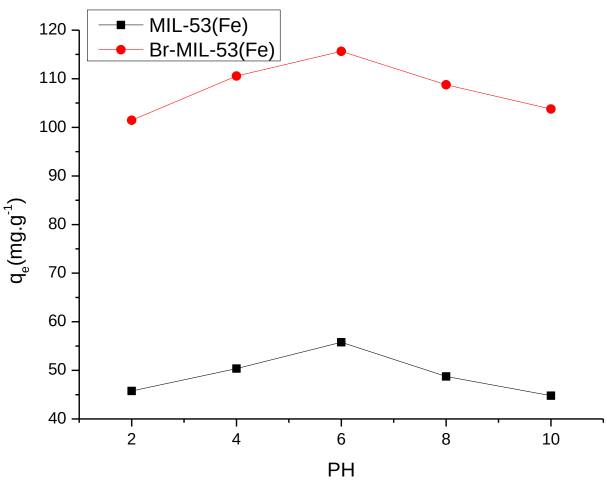
determination was 180min as the adsorption equilibrium time, and in the following experiments, 180min was used as the adsorption time to study.



(a) Effect of adsorption time

3.2. Effect of pH on the Removal of Methyl Orange from Metal-Organic Framework Materials

The adsorption effect of pH on methyl orange of Br-MIL-53 (Fe) is shown in the figure. The pH of the solution significantly affects the adsorption of the dye. Generally speaking, the interaction between adsorbent and adsorbent depends on hydrophobicity, static electricity, covalent, etc., and pH affects the surface charge of adsorbent and the degree of protonation of adsorbent. Congo red has different forms in water under different pH conditions. Br-MIL-53 (Fe) shows a good adsorption performance for methyl orange in the pH range of 2 ~ 5. The adsorption capacity of Br-MIL-53 (Fe) was the largest at pH 6.0. The color change is large, so the initial pH of Congo red solution is adjusted from 5 to 10 with hydrochloric acid and sodium hydroxide under other conditions, and the effect of pH on the removal rate of Congo red is investigated. The results showed that the removal rate did not change much from pH 5 to 6, and continued to increase the solution pH, the methyl orange removal rate gradually decreased, so the solution pH was chosen to be 6.0 in subsequent experiments.



(b) Effect of pH

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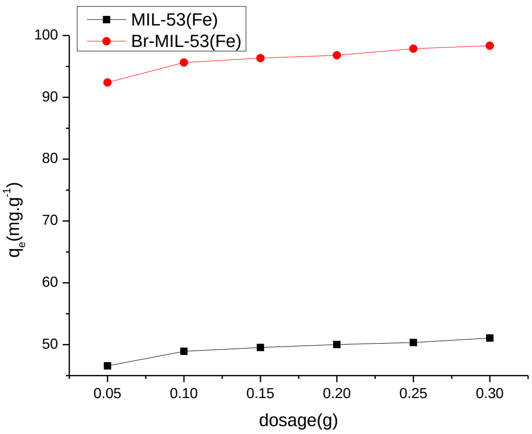
3.3. Effect of Dosage of Adsorbent on Methyl Orange Removal from Metal-Organic Framework Materials

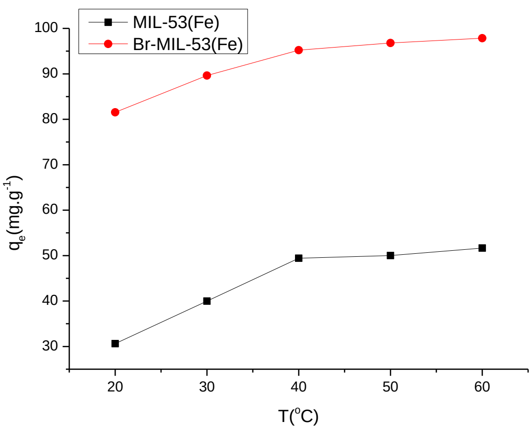
The amount of adsorbent added has a great influence on the adsorption effect. Generally speaking, increasing the amount of adsorbent added can increase the adsorption effect of Congo red. Take the 50 mg / L methyl orange solution as the adsorption target, control the temperature at 40°C, the adsorption time is 3 hours, and the dosage of the adsorbent ranges from 5 to 30 mg. Impact. The results show that with the increase of the amount of adsorbent added, the removal rate of Congo red solution by Br-MIL-53 (Fe) material is less obvious. In order to save costs, control the dosage of adsorbent to 0.1g.



(c)Effect of dosage

3.4. Effect of Temperature on the Removal of Methyl Orange from Metal-Organic Framework Materials

The mass concentration of Congo red solution was set to 50 mg / L, the adsorption time was 3 hours, the dosage of the adsorbent was 0.05 g, and the control temperature range was 20 to 60 ° C. The adsorbent Br-MIL-53 (Fe) Effect of base orange removal rate. The results show that with increasing temperature, the removal rate of Congo red by Br-MIL-53 (Fe) metal framework materials increases. When the temperature is below 40 ° C, the increase of the adsorption amount changes greatly. The degree of removal rate gradually decreases when the temperature is higher than 40 ° C. Although the removal rate increases at higher temperatures, from the perspective of energy conservation, the adsorption temperature should be 40 ° C.



(c)Effect of Temperature

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3.5. Adsorbent Desorption Regeneration

MIL-53 (Fe) and Br-MIL-53 (Fe) metal-organic framework materials adsorbed on methyl orange were used to investigate the recycling capacity of the adsorbent, and the regeneration ability could be used to test its recycling capacity. The experimental results show that after three repeated adsorption cycles, the adsorption amount of MIL-53 (Fe) adsorbent for methyl orange decreased from 170.98 mg / g to 145.65 mg / g, and the Br-MIL-53 (Fe) adsorbent pair The adsorption amount of methylene blue decreased from 222.34mg / g to 189.56mg / g, that is, after 3 times of reuse, the metal organic framework materials adsorbent of MIL-53 (Fe) and Br-MIL-53 (Fe) for methyl orange.The high adsorption capacity is still maintained, indicating that the iron-based metal organic framework material adsorbent has good regenerative and recyclable performance.

4. CONCLUSION

Functional Br-MIL-53 (Fe) was successfully synthesized by a simple solvothermal method and used to remove methyl orange from aqueous solution. The functionalized Br-MIL-53 (Fe) showed higher adsorption capacity than the original MIL-53 (Fe). The results show that the best conditions for MIL-53 (Fe) adsorption material to Congo Red are the dosage of the adsorbent is 0.05g, the pH is 6, the adsorption time is 3h, and the maximum temperature for methyl orange is 40°C. Br-MIL-53 (Fe) adsorption material is expected to be used as a highly effective adsorption material for Congo red in dye wastewater.

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