Synthesis of MIL-88(Fe) and NH_2-MIL-88(Fe) using PEG under ambient pressure for methylene blue adsorption

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ABSTRACT

The MIL-88(Fe) and NH_2-MIL-88(Fe) materials were successfully synthesized using a solvothermal method using polyethylene glycol (PEG) as the solvent at ambient pressure conditions. The synthesized materials were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), and Brunauer-Emmett-Teller (BET) techniques. The materials exhibited a needle-like crystal morphology with lengths ranging from 0.5 μm to 2 μm and widths from 0.3 μm to 0.5 μm. XRD patterns of both materials revealed similar diffraction peaks, with major peaks at 9° and 10°, and additional peaks at 16°, 18°, and 20°. The BET-specific surface areas were determined to be 257 m^2/g for MIL-88(Fe) and 105 m^2/g for NH_2-MIL-88(Fe). Both materials demonstrated the ability to remove over 70% of a 10 ppm methylene blue (MB) solution after 120 minutes of adsorption.

Keywords: MIL-88(Fe); NH_2-MIL-88(Fe); Polyetylen glycol; MOF.

1. INTRODUCTION

In recent years, metal-organic frameworks (MOFs) have garnered significant attention due to their unique porous structure, high specific surface area, and tunable chemical properties, opening up extensive potential applications in adsorption, catalysis, sensing, and environmental remediation [1]. Among these, MIL-88(Fe) and its functionalized variant, NH_2-MIL-88(Fe), stand out owing to their structural flexibility, characterized by the "breathing effect," along with excellent chemical stability and strong interactions with guest molecules [2, 3]. With their superior properties, such as high porosity and surface modifiability, MIL-88(Fe) and NH_2-MIL-88(Fe) exhibit promising potential for applications in wastewater treatment, gas storage (H_2, CO_2), and the development of highly sensitive electrochemical sensors for detecting organic compounds like ethanol or heavy metals in the environment [4, 5].

These materials are commonly synthesized using methods such as hydrothermal, microwave, or ultrasonic techniques [6, 7]. Among these, the hydrothermal method, employing organic solvent at high temperatures (100 - 200 °C) and elevated pressures over extended periods (12 - 24 hours), is the most widely used [8, 9]. However, greener synthetic approaches have been explored, utilizing environmentally friendly solvents combined with ambient pressure conditions and shorter reaction times to minimize the use of hazardous chemicals and energy consumption.

Polyethylene glycol (PEG), a water-soluble polymer with a high boiling point (above 250 °C), serves as an effective reaction solvent that can withstand elevated temperatures without rapid evaporation. Compared to toxic organic solvents such as DMF (N, N-dimethylformamide) or DMSO, PEG is less toxic, biodegradable, and well-suited for green synthesis methods [10, 11]. Additionally, PEG can be recycled or recovered post-reaction due to its high boiling point, reducing costs and environmental impact. Furthermore, the -OH groups at the ends of PEG chains can form hydrogen bonds with functional groups of ligands, facilitating the self-assembly process in MOF structures.

2. EXPERIMENT

2.1. Chemicals, equipment

Chemicals: Iron(III)chloride $FeCl_3.6H_2O$; terephthalic acid (H_2BDC), 2-Aminoterephthalic acid (NH_2-H_2BDC) and polyethylene glycol (M_w = 400) were purchased from Macklin. Distilled water, ethanol, and methylene blue were purchased from Xilong.

2.2. Synthesis of materials

Synthesis of MIL-88(Fe): 6,7 mmol of H_2BDC was dissolved in 50 mL of PEG with stirring and heating until fully dissolved to obtain solution 1. Separately, 10 mmol of $FeCl_3 \cdot 6H_2O$ was dissolved in 50 mL of distilled water to obtain solution 2. Solution 1 was heated to 90 °C, and solution 2 was slowly added to solution 1 under continuous stirring for 15 minutes. The resulting material was filtered, washed three times with ethanol and distilled water, and dried at 100 °C.

Synthesis of NH_2-MIL-88(Fe): The procedure was identical to that for MIL-88(Fe), except that 6,7 mmol of NH_2-H_2BDC was dissolved in 50 mL of PEG to prepare solution 1.

2.3. Characterization of material properties

The synthesized materials were evaluated for structure by X-ray diffraction at Hanoi University of Science and Technology, and infrared absorption spectroscopy (FT-IR) analysis method at Institute of Chemistry - Materials. The morphology of the material was observed by scanning electron microscopy (SEM) and measuring the BET surface area at the Institute of Chemistry, Vietnam Academy of Science and Technology.

2.4. Evaluation of organic compound removal capacity

The synthesized materials were tested for their ability to adsorb methyl blue (MB) from an initial concentration of 10 ppm. A material/solution ratio of 1 g/L (1 g of material per liter of MB solution) was used, and the samples were placed on a shaker (frequency 150 times/min) in a dark chamber during the adsorption process. The residual MB concentration in the solution was measured after 30, 60, 90, and 120 minutes using UV-Vis spectroscopy at a wavelength of 671 nm.

3. RESULT AND DISCUSSION

3.1. Material property characterization

The MIL-88(Fe) and NH2-MIL-88(Fe) framework materials are shown in figure 1

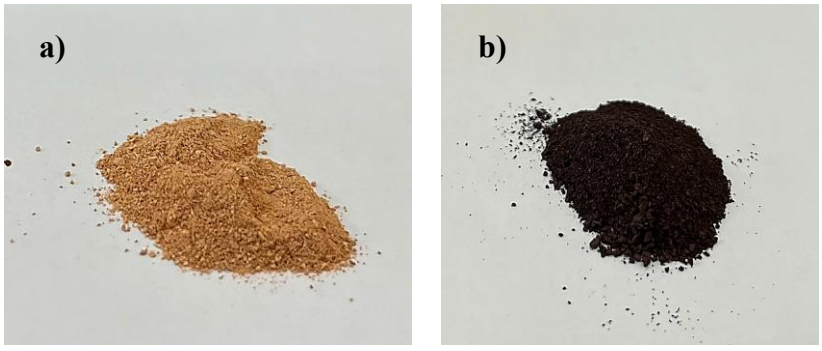

Figure 1. *Photographs of the synthesized materials: (a) MIL-88(Fe) and (b) NH_2-MIL-88(Fe).*

The uniform coloration of the materials indicates that the synthesis via the solvothermal method with PEG achieved high purity and homogeneity. The formation of the material can be explained by a mechanism involving solvent diffusion and temperature. Organic ligands dissolved in PEG diffuse into the aqueous phase, where they react with iron salts to form MOF materials. Due to the low solubility of organic molecules in water, this diffusion promotes supersaturation and facilitates crystallization, resulting in materials with improved crystallinity. MIL-88(Fe) exhibits a light

brown color, while NH_2-MIL-88(Fe) appears darker brown. This difference is attributed to the presence of the -NH_2 functional group in NH_2-MIL-88(Fe), which enhances light absorption in the visible region, resulting in a darker hue.

The synthesized materials were examined using scanning electron microscopy (SEM). The images reveal that the materials exhibit good crystallinity, comparable to those synthesized via hydrothermal methods at high temperatures and pressures [12, 13]. At 30,000x magnification, both MIL-88(Fe) and NH_2-MIL-88(Fe) display a needle-like crystal morphology, with lengths ranging from 0.5 μm to 2 μm and widths from 0.3 μm to 0.5 μm, consistent with the flexible structure (breathing effect) characteristic of the MIL-88 series (figure 2). The similarity in morphology between the two materials indicates that the addition of the -NH_2 group does not significantly alter the fundamental structure.

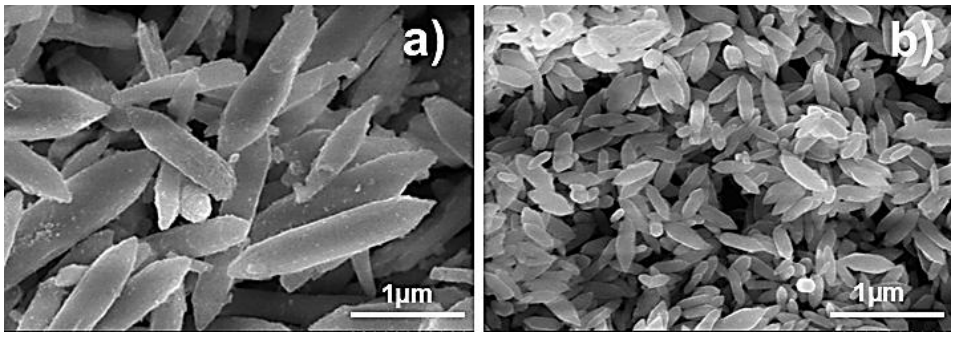

Figure 2. *SEM images of the materials at 30,000x magnification: a) MIL-88(Fe); b) NH_2-MIL-88(Fe).*

The crystals of both materials show uniform size and shape distribution, indicating well-controlled synthesis conditions with minimal formation of impurities or unwanted crystals. The NH_2-MIL-88(Fe) particles exhibit a slightly rougher surface compared to MIL-88(Fe), possibly due to the influence of the -NH_2 group on the crystallization process. The elongated, needle-like shape may enhance surface contact area, contributing to improved adsorption or catalytic performance, particularly when combined with high porosity.

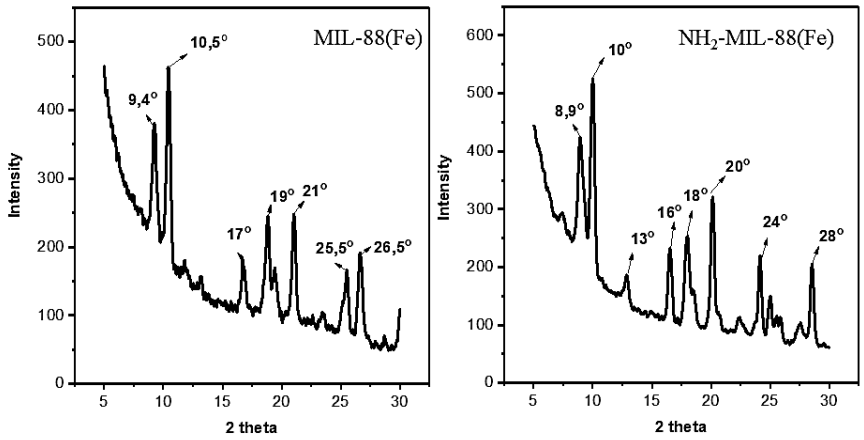

Figure 3. *XRD patterns of the materials.*

Both XRD patterns of MIL-88(Fe) and NH_2-MIL-88(Fe) display sharp diffraction peaks, confirming their well-defined crystalline structures, which are typical of the MIL-88 MOF series (figure 3). The presence of major peaks at 2θ angles of 8-10° and secondary peaks at 13-28° is characteristic of the flexible structure (breathing effect) of MIL-88(Fe) [14]. The high intensity and

narrow width of these peaks indicate that the solvothermal synthesis with PEG produced crystals with high purity and uniform size, minimizing the presence of amorphous phases or impurities.

MIL-88(Fe) exhibits major diffraction peaks at 8.9°, 10°, 13°, 17°, 19°, 20°, 24°, 25.5°, and 26.5° consistent with previously reported data for MIL-88(Fe). NH_2-MIL-88(Fe) shows similar peaks at 9.4°, 10.5°, 13°, 17°, 19°, 21°, 25°, and 28°, with a slight shift in 2θ angles (e.g 9.4° vs 8.9°, 10.5° vs 10°) [15]. This shift may result from changes in unit cell dimensions due to the presence of the -NH_2 group, which could increase interatomic distances or alter packing density.

Both FT-IR spectra of MIL-88(Fe) and NH_2-MIL-88(Fe) exhibit absorption bands in the 400-4000 cm^{-1} range, reflecting the presence of organic functional groups and metal-organic linkages consistent with Fe^{3+}-based MOFs with dicarboxylate ligands. The sharp and distinct peaks indicate high-quality synthesis with minimal organic impurities or unwanted phases (figure 4).

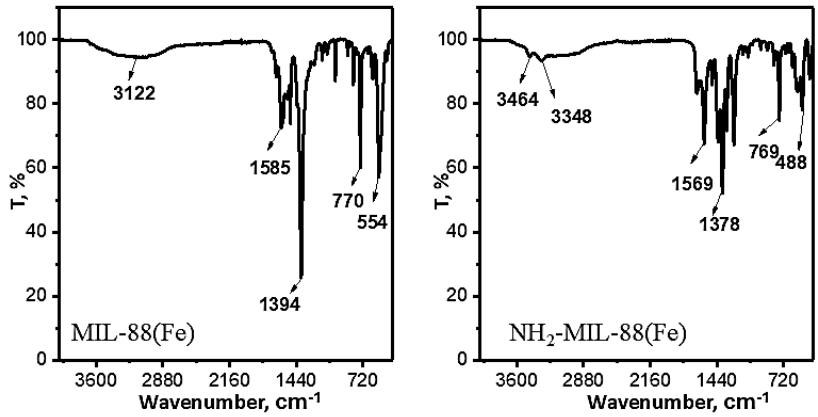

Figure 4. *FT-IR spectra of the materials.*

For MIL-88(Fe), the band at 3122 cm^{-1} corresponds to the stretching vibration of aromatic C-H bonds from the 1,4-benzenedicarboxylic acid (BDC) ligand, characteristic of the MIL-88(Fe) framework. The bands at 1585 cm^{-1} and 1394 cm^{-1} represent the asymmetric and symmetric stretching of the carboxylato (COO^-) group, indicating strong and stable bonding between Fe^{3+} and the BDC ligand. The bands at 770 cm^{-1} and 554 cm^{-1} are associated with framework deformation and Fe-O vibrations, confirming MOF formation. The 1370-1500 cm^{-1} region may include overlapping C=C aromatic vibrations from the benzene ring structure.

For NH_2-MIL-88(Fe), additional bands at 3464 cm^{-1} and 3348 cm^{-1} are characteristic of the asymmetric and symmetric stretching of the -NH_2 group, confirming successful functionalization with 2-aminoterephthalic acid. Other bands, such as those at 1569 cm^{-1} and 1378 cm^{-1} (carboxylato COO^-) and 769 cm^{-1} and 488 cm^{-1} (Fe-O vibrations), are similar to those of MIL-88(Fe), with slight shifts possibly due to the influence of the -NH_2 group.

The nitrogen adsorption-desorption isotherms of both materials are classified as Type IV according to the IUPAC classification, with both exhibiting an H3 hysteresis loop. However, MIL-88(Fe) shows a larger gap between the adsorption and desorption branches, indicating greater structural flexibility. The narrower hysteresis loop in NH_2-MIL-88(Fe) suggests that the -NH_2 group may reduce this flexibility (breathing effect).

In the low-pressure region, a rapid increase in adsorbed quantity indicates micropore filling, a hallmark of MOF materials. In the intermediate-pressure range, the nearly linear curve with a gradual increase suggests multilayer adsorption on external surfaces and within mesopores. The sharp rise in the high-pressure region is indicative of capillary condensation, characteristic of mesopores, confirming that both MIL-88(Fe) and NH_2-MIL-88(Fe) are porous materials with both micropores and mesopores (figure 5).

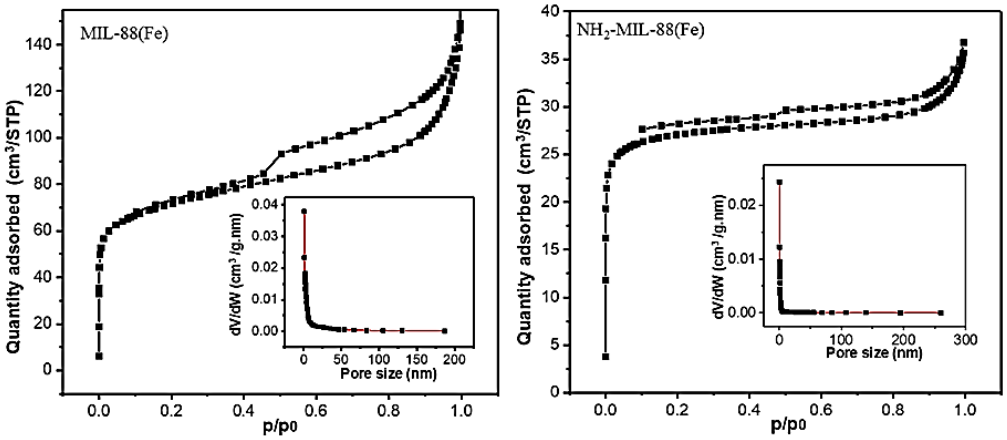

Figure 5. *Nitrogen adsorption-desorption isotherms of the materials.*

Pore size calculations for the materials are consistent, ranging from 2 nm to 4 nm. BET surface area measurements reveal that MIL-88(Fe) has a higher specific surface area of 257 m^2/g, while NH_2-MIL-88(Fe) has a lower value of 105 m^2/g, aligning with previous studies [16, 17]. The reduced surface area of NH_2-MIL-88(Fe) may be attributed to the -NH_2 group partially filling micropores or reducing pore size, thereby decreasing multilayer adsorption capacity.

3.2. Evaluation of MB removal

Both MIL-88(Fe) and NH_2-MIL-88(Fe) demonstrate MB adsorption capacity, with the MB concentration decreasing from 10 ppm to approximately 2-4 ppm after 120 minutes, indicating effective removal from the solution.

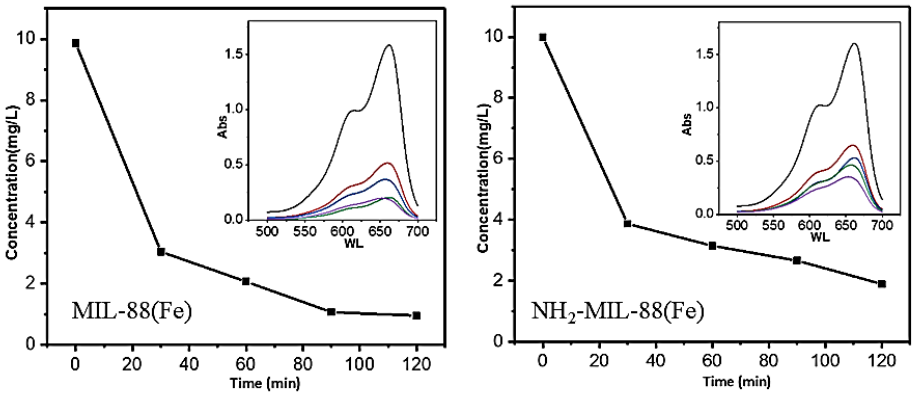

Figure 6. *MB adsorption capacity over time for the materials.*

The concentration drops most rapidly within the first 30 minutes, followed by a slower decline, reaching near-equilibrium after 90-120 minutes due to adsorption saturation. MIL-88(Fe) can remove over 80% of 10 ppm MB after 120 minutes, outperforming NH_2-MIL-88(Fe), which achieves above 70% (figure 6). This result is similar to some other publications with saturation adsorption time from 180-360 minutes [12, 18]. This aligns with the higher surface area of MIL-88(Fe). The initial rapid adsorption phase is likely driven by electrostatic interactions between Fe^{3+} (positively charged) and the -SO_3^- group of MB, combined with van der Waals forces within the pores. These results highlight the potential of both materials for treating wastewater containing toxic organic compounds.

The results calculated by the pseudo-second-order kinetic model gave qe values of the two materials from 8.1 mg/g to 9.3 mg/g. This result is also equivalent to the experimental result of 8.1

mg/g to 9 mg/g. This result is equivalent to some other publications [18]. The high correlation coefficient R^2 (R^2 = 0,9865 - 0,9909) shows that the adsorption process is consistent with the pseudo-second-order kinetic model (figure 7).

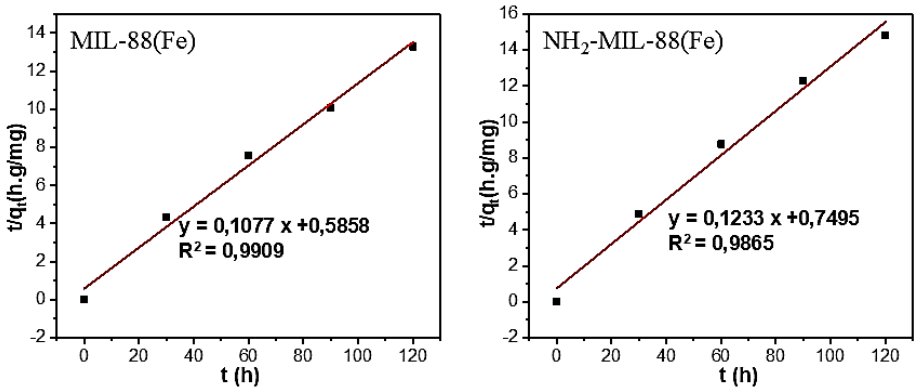

Figure 7. *Pseudo-second order adsorption kinetics.*

4. CONCLUSIONS

The MIL-88(Fe) and NH_2-MIL-88(Fe) framework materials were successfully synthesized using Fe^{3+} salts with H_2BDC and NH_2-H_2BDC ligands under ambient pressure conditions with PEG as the solvent. Material characterization results indicate high purity and good crystallinity. The measured BET surface areas were 257 m^2/g for MIL-88(Fe) and 105 m^2/g for NH_2-MIL-88(Fe), consistent with other reported methods. The successful synthesis of MIL-88(Fe) and NH_2-MIL-88(Fe) under simple reaction conditions using PEG demonstrates the potential for developing environmentally friendly MOF synthesis methods.

The evaluation of MB adsorption capacity revealed that both MIL-88(Fe) and NH_2-MIL-88(Fe) effectively adsorb MB, with MIL-88(Fe) showing superior performance due to its higher surface area. The removal efficiency reached 60-80% after 120 minutes, suggesting promising applications in wastewater treatment. Further optimization of synthesis and adsorption conditions is recommended to enhance performance.

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TÓM TẮT

Tổng hợp MIL-88(Fe) và NH_2-MIL-88(Fe) sử dụng PEG dưới áp suất thường để hấp phụ xanh metylen

Vật liệu MIL-88(Fe) và NH2-MIL-88(Fe) đã được tổng hợp thành công bằng phương pháp khuấy nhiệt với polyethylene glycol (PEG) làm dung môi trong điều kiện áp suất môi trường. Các vật liệu tổng hợp được đặc trưng bằng kính hiển vi điện tử quét (SEM), nhiễu xạ tia X (XRD), phổ hồng ngoại biến đổi Fourier (FT-IR) và các kỹ thuật Brunauer-Emmett-Teller (BET). Các vật liệu thể hiện hình thái tinh thể giống kim với chiều dài từ 0,5 µm đến 2 µm và chiều rộng từ 0,3 µm đến 0,5 µm. Các mẫu XRD của cả hai vật liệu đều cho thấy các đỉnh nhiễu xạ tương tự nhau, với các đỉnh chính ở 9° và 10°, và các đỉnh bổ sung ở 16°, 18° và 20°. Diện tích bề mặt riêng của BET được xác định là 257 m^2/g đối với MIL-88(Fe) và 105 m^2/g đối với NH2-MIL-88(Fe). Cả hai vật liệu đều có khả năng xử lý hơn 70% dung dịch xanh meylen (MB) 10 ppm sau 120 phút hấp phụ.

Từ khóa: MIL-88(Fe); NH_2-MIL-88(Fe); Polyetylen glycol; MOF.