

A NEW PHOTOCATALYST FOR THE DEGRADATION OF TNT BY METAL ORGANIC FRAMEWORK NH₂-MIL-88B(Fe)

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Abstract: NH₂-MIL-88B (Fe), (MIL = Materials of Institute Lavoisier) a mesoporous metal-organic framework (MOF) with high surface area was synthesized. The structural characteristics of NH₂-MIL-88B(Fe) have exhibited an advantageous application potentialities in gas storage, separation and heterogeneous catalysis. This MOF is usually obtained by the hydrothermal synthesis in a Teflon-lined autoclave at high temperature (>150°C) under static conditions. However, this method exhibits several disadvantages such as high temperature, high pressure, long reaction time, and relatively low MOF yield. In this study, NH₂-MIL-88B(Fe) has been successfully synthesized by using reflux method at low-temperature. Structure and properties of materials have been characterized by using: XRD, IR, SEM, TGA. The study has showed that NH₂-MIL-88B(Fe) is as catalysts and the solution of trinitrotoluene (TNT) 50 ppm was decolorized after an hour under simulated sun-light radiation.

Keywords: Metal-organic frameworks (MOFs), NH₂-MIL-88B(Fe), Reflux method, Photocatalyst.

I. INTRODUCTION

Metal-organic frameworks (MOFs) are crystalline porous materials that consist of metal-carboxylate units, metal ions and organic linkers. These metal ions are coordinated to form the rigid organic molecules with one, two or three-dimensional structures that can make the very porous framework [1-3]. The special interest in MOF materials is due to the easy tunability of their pore size and shape from a micro to a mesoscale by changing the connectivity of the inorganic moiety and the nature of organic linkers. MOFs are well known for their various applications in adsorption and gas store [4], separation [5], catalysis [6], drug delivery [7], and for photocatalysis [8-10]. MOFs exhibit comparative advantages over to traditional catalysts because of their desirable topology and high surface area that allow for accommodation of guest molecules [1]. Additionally, the HOMO-LUMO gap can easily be tuned through modification of the inorganic or organic units of the molecule during its synthesis [3].

2,4,6-trinitrotoluene (TNT) is one of the most common toxic pollutant present in wastewater generated from ammunitions plants. Due to its potential carcinogenic characteristics, TNT present in water bodies represents a risk for human health and aquatic life [11]. Wastewater containing TNT can be treated by adsorption on activated carbon or advanced oxidation processes (AOPs) [12]. Besides, these photo induced techniques, semiconductor photocatalyst has been proven to be more effective in degradation of nitroaromatic compounds. Among various semiconductors, nano TiO₂ was a widely used as photocatalyst, due to its chemical inertness, photostability and non-toxicity. However, these processes have limitations associated with the regeneration and ultimate disposal of the contaminated catalysts. Besides, TiO₂ is only photoactive under UV light irradiation due to its wide band gap energy (3.2 eV: anatase).

In this study, a new method for synthesis of photocatalytic material based on NH₂-MIL-88B(Fe) at low temperature (80°C) and atmospheric pressure by reaction of iron(III) chloride hexahydrate (FeCl₃.6H₂O) and 2-aminoterephthalic acid (H₂N-BDC) under reflux condition like in [13] has been presented. Due to the synthesis conducted with agitation, the obtained NH₂-MIL-88B(Fe) has exhibited high yield and large specific surface area, accompanied with low synthesis temperature and short synthesis time. This method could be applied for MOF synthesis in large scale. Its photocatalytic activity was also investigated over the degradation of TNT using visible light irradiation. This is the first time, TNT has been treated by this MOF photocatalyst.

II. EXPERIMENTS

2.1. Materials

All chemicals used such as iron(III) chloride hexahydrate (FeCl₃.6H₂O), 2-aminoterephthalic acid (H₂N-BDC), dimethylformamide (DMF), ethanol (C₂H₅OH) are chemicals with analytical purity grade prepared in de-ionized water.

2.2. Synthesis method

NH₂-MIL-88B(Fe) was prepared at low-temperature in atmospheric pressure. Taken FeCl₃.6H₂O (0.72 g), H₂N-BDC (0.24 g) and an additional amounts of DMF (28 mL) were mixed and charged into a three-neck round bottom flask equipped with a magnetic stirrer with 300 rpm for 8 hrs under reflux condenser at 80°C. The reaction product was purified three times with a extraction solvent including de-ionized water (350 mL) and ethanol (350 mL) at 70°C for 24 hrs, finally dried in a vacuum desiccator at 150°C for 10 hrs.

2.3. Characterization

- X-ray diffraction (XRD) measurements were conducted using standard powder diffraction analysis procedures.
- SEM images were performed to identify the morphologies and particle size distribution of the crystals.
- Functional groups were determined by FT-IR spectra.
- The thermal stability of NH₂-MIL-88B(Fe) was investigated by thermal gravimetric analysis (TGA).

2.4. Photocatalytic reaction

The photocatalytic activity of the NH₂-MIL-88B(Fe) was tested by degradation of TNT. 50 mg of catalyst was added in 100 mL TNT solution (concentration of 50 ppm) with 0.5 mL of H₂O₂ solution 30%, pH = 7, stirring for 60 min in the dark to reach adsorption-desorption balance stage. The photocatalytic degradation started under the irradiating with simulated sun-light (sunlight simulation lamp, 15 W, 4-6% UV, 340-315 nm wavelength), for each 15 min, taking 2 mL solution, centrifuging to get TNT left. The TNT concentrations left were analyzed by HPLC method [10]. The other two series of experiments such as the samples involving only TNT or TNT plus H₂O₂ were carried out to comprising.

III. RESULTS AND DISCUSSION

3.1. Structure and components of NH₂-MIL-88B(Fe)

Morphologies of MOF that have been identified by SEM micrographs. NH₂-MIL-88B (Fe) micro-sized crystals produced from an aqueous reaction mixture of FeCl₃.6H₂O and H₂N-BDC resulted in the morphology of bipyramidal hexagonal prism, and size of 10 μm in length and 2 μm in width.

Composition and structure of the material were analyzed by X-ray diffraction (XRD), SEM and infrared spectroscopy, the results are shown in Fig 1 and Fig 2.

Samples showed good crystallinity. Fig 1 showed that the peak was very sharp. Characteristic peaks of the NH₂-MIL-88B(Fe) are $2\theta = 8,9^\circ; 10^\circ; 17,8^\circ, 27,72^\circ$ respectively.

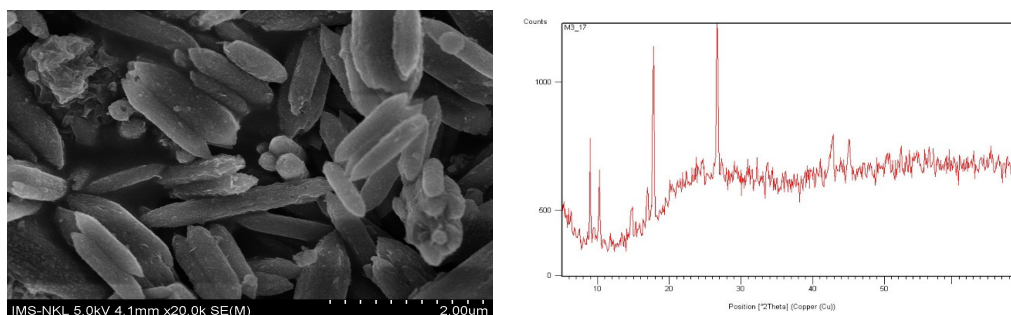


Fig 1. SEM images and XRD pattern of NH₂-MIL-88B(Fe).

The FT-IR spectrum of NH₂-MIL-88B(Fe) (left fig 2) is similar to the previous results in [8]. The two bands at 1578 cm⁻¹ and 1422 cm⁻¹ are corresponding to the symmetric and asymmetric C-O stretching vibrations of carboxylates, thus indicates the presence of 2-aminoterephthalic acid anions. Band at 3334 cm⁻¹ corresponds to the asymmetrical and symmetrical stretching of the amine moieties in 2-aminoterephthalic acid. Band at 1336 cm⁻¹ indicates the C-N stretching absorption distinctive of aromatic amines (2-aminoterephthalic acid).

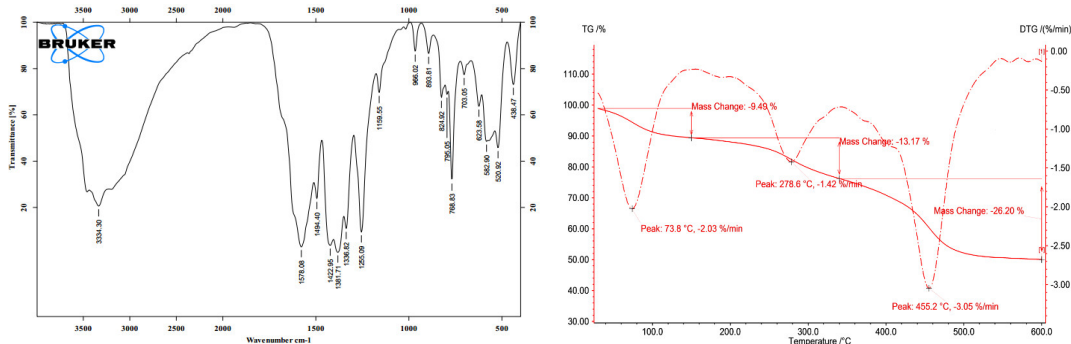


Fig 2. IR pattern and thermogravimetric analyses of NH₂-MIL-88B(Fe).

3.2. Thermogravimetric analysis of NH₂-MIL-88B(Fe)

The TGA curve of NH₂-MIL-88B(Fe) shows two steps of weight loss between 25 and 600°C (right fig 2). The first one (≈ 9.5 wt.%) in a temperature range from

25 to 120°C, is attributed to the desorption of the free water molecules inside the pores. The second weight loss (≈ 13 wt.%) in the temperature range from 120 to 320°C is related to the decomposition of NH₂-BDC to produce iron oxide. This clearly indicates that the overall thermal stability of the current NH₂-MIL-88B(Fe) sample is similar to that of the samples synthesized by other methods in [8].

3.3. Adsorption and photocatalytic activity of NH₂-MIL-88B(Fe)

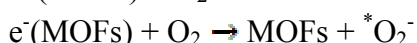
3.3.1. Efficiency adsorption of NH₂-MIL-88B(Fe)

The experiment was carried out in the dark. The TNT concentration left are shown in Table 1. The results showed that TNT concentrations decreased by increasing adsorption time, for 60 min, can decrease from 50 to 8.54 ppm. This proves that TNT has been adsorbed from solution onto Fe-MOF material.

3.3.2. Photocatalytic efficiency of NH₂-MIL-88B(Fe)

The experiments were carried out as suggested in previous item (2.4). The experimental data showed that in the sample involving MOFs, TNT, the photodegradation efficiency of TNT is higher than others. This photodegradation of TNT might be explained as following.

The main proposed pathways of TNT photodegradation by MOFs under visible light irradiation are shown, presented in [9, 10]. It was considered that the initial process of photocatalysis was the generation of electron-hole pairs in the MOFs. After absorption of energy equals to or greater than the band gap of the MOFs, the electrons (e⁻) were excited from the valence band (VB) and entered into the conduction band (CB), leaving the holes (h⁺) in the VB. The electrons and holes migrated to the surface of the MOFs, then electrons reducing the oxygen (O₂) to form oxygen radicals (*O₂⁻), holes oxidizing the hydroxyl (H₂O) to hydroxyl radicals (*OH). Hydroxyl radicals (*OH) and oxygen radicals (*O₂⁻) were capable of decomposing TNT effectively.



The results of TNT concentration remaining after experiment are shown in table 1.

The results in table 1 show that photocatalytic reaction is fast. After an hour of treatment, TNT is metabolized 99%. With the second loop, the reaction is similar.

Table 1. TNT concentration left after treatment by NH₂-MIL-88B(Fe) (ppm) versus time.

Time (min)	0	15	30	45	60
TNT adsorption	50	20.18	10.95	9.62	8.54
TNT Photochemical	50	49.50	49.11	48.75	48.18
TNT Photochemical with H ₂ O ₂	50	48.98	47.84	46.69	45.22
TNT Photocatalysis with MOFs	50	13.53	2.52	1.08	0.52

IV. CONCLUSIONS

NH₂-MIL-88B(Fe) material was synthesized at low temperature (80°C) and atmospheric pressure for 8 h. The material has the particle size of 10 μm in length and 2 μm in width and is crystalline in structure. It has high potentiality for applications in adsorption and photocatalysis to treat of TNT from solution.

REFERENCES

- [1]. R. Macgillivray L., “*Metal-organic framework: Design and application*”, Published by John Wiley & Sons, Inc., Hoboken, New Jersey (2010).
- [2]. James, S.L., “*Metal-organic framework*”, Chem. Soc. Rev., **Vol. 32** (2003), pp. 276-288.
- [3]. O.M. Yaghi, M.O’Keeffe, N.W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, “*Reticular synthesis and the design of new materials*”, Nature, **Vol. 423** (2003), pp. 705-714.
- [4]. Rosi N. L., Eckert J., Eddaoudi M., Vodak D. T., Kim J., O’Keeffe M., Yaghi O. M., “*Hydrogen storage in microporous metal-organic frameworks*”, Science, **Vol. 300** (2003), pp. 1127-1129.
- [5]. Bae Y. S., Mulfort K. L., Frost H., Ryan P., Punnathanam S., Broadbelt L. J., Hupp J. T., Snurr R. Q., “*Separation of CO₂ from CH₄ using mixed-ligand metal-organic frameworks*”, Langmuir, **Vol. 24** (2008), pp. 8592-8598.
- [6]. Corma A., Garcia H., Xamena F. X. L., “*Engineering metal-organic frameworks for heterogeneous catalysis*”. Chem. Rev, **Vol. 110** (2010), pp. 4606-4655.
- [7]. Huxford R. C., Rocca J. D., Lin W., “*Metal-organic frameworks as potential drug carriers*”, Curr. Opin. Chem. Biol, **Vol. 14** (2010), pp. 262-268.
- [8]. D. Dimitrova, “*Iron based metal-organic frameworks as photocatalysts for chromium (VI) degradation*”, Published by University Utrecht, Netherlands, (2015).
- [9]. Katrien G. M. Laurier, Frederik Vermoortele, Rob Ameloot, Dirk E. De Vos, Johan Hofkens, Maarten B. J. Roefsaers, “*Iron(III) based metal-organic frameworks as visible light photocatalysts*”, J. Am. Soc. Chem. **Vol. 39** (2013), pp. 14488-14491.
- [10]. Chong-Chen Wang, Jian-Rong Li, Xiu-Liang Lv, Yan-Qiu Zhang, Guangsheng Guo, “*Photocatalytic organic pollutants degradation in metal-organic frameworks*”, Energy & Environmental Science, **Vol. 7** (2014), pp. 2831-2867.
- [11]. T. Urbanski, “*Chemistry and technology of explosives*”, **Vol. 1**, PWN - Polish Scientific Publishers, Warszawa (1964).
- [12]. C. Zaharia, D. Suteu, “*A preliminary modelling and optimisation study of a homogenous advanced oxidation process applied for an industrial coloured effluent*”, Journal of Environmental Protection and Ecology, **Vol. 15** (2014), pp. 1680-1689.
- [13]. Jing Shi, Shengtao Hei, Huanhuan Liu, Yanghe Fu, Fumin Zhang, Yijun Zhong, Weidong Zhu, “*Synthesis of MIL-100(Fe) at low temperature and atmospheric pressure*”, Journal of Chemistry, **Vol. 4** (2013), pp. 1-4.

TÓM TẮT

CHẤT XÚC TÁC QUANG ĐỂ XỬ LÝ TNT TRÊN CƠ SỞ
VẬT LIỆU NH₂-MIL-88B(Fe)

Vật liệu khung cơ kim (MOFs) trên cơ sở NH₂-MIL-88B(Fe) có diện tích bề mặt cao. Các đặc tính cấu trúc của NH₂-MIL-88B(Fe) đã thể hiện cho thấy vật liệu có nhiều tiềm năng ứng dụng trong hấp phụ, tách và lưu trữ khí, xúc tác dị thể... Thông thường, NH₂-MIL-88B(Fe) được tổng hợp bằng phương pháp thủy nhiệt ở nhiệt độ cao trong điều kiện tĩnh. Tuy nhiên, phương pháp này có những nhược điểm như: nhiệt độ và áp suất cao, thời gian phản ứng dài, năng suất thấp... Trong nghiên cứu này, vật liệu NH₂-MIL-88B(Fe) đã được tổng hợp thành công bằng phương pháp hồi lưu ở nhiệt độ thấp. Đặc tính, cấu trúc của vật liệu đã được xác định bằng các phương pháp: XRD, IR, SEM, TGA. Nghiên cứu phản ứng quang xúc tác khi sử dụng vật liệu NH₂-MIL-88B(Fe) cho thấy, dung dịch trinitrotoluen (TNT) 50 ppm bị xử lý sau một giờ dưới ánh sáng mô phỏng.

Từ khóa: Vật liệu khung cơ kim (MOFs), NH₂-MIL-88B(Fe), Phương pháp hồi lưu, Chất quang xúc tác.

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