Adsorptive and Photocatalytic Dye Removal from Wastewater Using Metal-Organic Frameworks

Fuhua Wei1,.*, Qinhui Ren1, Lili Yang1, Liu Wu1, Qianqian Jian1, Zhao Liang2, Ding Chen2, a

1College of chemistry and chemical Engineering, Anshun University, Guizhou Anshun 561000, PR China
2State Key Laboratory of Advanced Design and Manufacturing for Vehicle Body, College of Mechanical and Vehicle Engineering, Hunan University, Changsha 410082, PR China

*Corresponding author e-mail: wfh.1981@163.com, *chending@hnu.edu.cn

Abstract. Trimesic acid in conjunction with microwave-assisted ball milling was used to produce Fe-based metal-organic frameworks (Fe-MOFs). Fe-MOFs were then used to eliminate organic dyes from aqueous solutions. Our results indicated Fe-MOFs eliminated nearly all Methylene Blue (MB) and Methyl Orange (MO). Within 120 min of Xe or natural light exposure, Fe-MOFs were able to remove 93.11% and 91.6%, respectively, of 10 mg/L MB in a 200 mL solution. Within 300 min of Xe or natural light exposure, Fe-MOFs were able to remove 96.34% and 52.32%, respectively, of 5 mg/L MO from a 200 mL solution. Collectively, these results show that both dyes are suitable for use in the second kinetic model.

1. Introduction
Significantly increased environmental pressure from pollution, rapid urbanization, sustained economic development, and continuous growth in the global population has resulted in daily increases to the pollution in our environment [1]. Critically, the fast pace of industrialization has led to increasingly serious water pollution around the globe. These water pollutants are varied, and include herbicides and pesticides, hexavalent chromium, aromatics/organics, and dyes [2]. All of these—and more—are pollutants that require liquid disposal. Dyes have become a particular problem, given their wide application in plastics, cosmetics, rubbers, textiles, paper, food, and carpets. They are frequently found in water sources and often contaminate industrial wastewater. Given their ubiquity, the need to efficiently eliminate dyes from outlet water sources has led to several physical, biological, and chemical methods [3]. One of the most commonly used approach is using ordinary adsorbent materials that contain a range of material, including metal-organic frameworks (MOFs), silica gel, molecular sieves, activated carbon, metal hydroxides, or activated alumina. MOFs are of particular interest and are comprised of organic linkers and either metal ion or metal-oxo clusters. They have several beneficial properties, including a large, specific surface area, intricate crystalline structure, good porosity, and modifiable chemistry [2]. Given this, the use of MOFs in both adsorption and catalysis has led to increasing research interest.
Since the 1990s, MOFs have become widely investigated, not only because of their interesting chemical structure and attendant properties, but also their potential applications in areas of research like adsorption/storage in the gas phase [4], catalysis, drug delivery/biomedicines, polymerizations, magnetism [5], liquid phases, luminescence [6], and chemical separation [4]. Importantly, MOFs have been the target of recent focus as potential agents for the liquid-phase adsorption of hazardous compounds. These compounds include sulfur-and nitrogen- containing compounds [7] and separation from non-aqueous and aqueous solutions. The increased interest in MOFs has led to multiple methods for their preparation, such as microwave, ultrasonic, hydrothermal, chemical mechanical polishing, and mechanical approaches [8].

To add to this list of preparatory approaches for MOF, our laboratory now adds a microwave-assisted ball milling method. This approach was founded on a solid-liquid ball milling (MSBM) method, whereby a microwave includes a ball-milling machine [9]. The coupling induction between the ball milling process and microwaves produces nanocrystal material formation at room temperature. Thus far, this approach has yielded MOFs [10], magnetic ferrite, and metal oxidation [11]. Here, we produced MOFs using our ball milling and microwave approach using trimesic acid (H₃BTC) and Fe₂(SO₄)₃ as raw materials. We then applied our Fe-MOF product to the removal of two dyes—methyl orange and methylene blue. Removal was successful and gives further evidence to the method of MOF preparation as well as their utility in dye removal from aqueous solutions.

2. Experimental

2.1. Production process and MOFs characterization
MOFs were prepared using Trimesic acid, Fe₂(SO₄)₃ with our microwave-assisted ball milling method in aqueous solution. After 40 min of this process, the colorless liquid turned into a white solid. This solid was then filtered and cleaned using water; after filtration, the solid was washed using ethanol and dried until later characterization and experimentation [2].

2.2. Dye removal
At room temperature (approximately 10 °C), organic dyes were adsorbed into a 250 mL beaker. MOF samples (100 mg) were introduced to a 200 mL solution of organic dye (either methylene blue (MB) or methyl orange (MO)). These solutions were stirred using a magnetic stirrer and subjected to either Xe or natural light, treated every 30 min with either 10 mL of MO or MB solution. Ultraviolet spectrometry (UV-2550 220V, Shimadzu Instruments Co., Ltd., and Suzhou) was used to analyze the resulting dye concentrations at 463 nm and 664 nm, respectively. The adsorption rate is described by the equation 

\[ C(\%) = (C_0 - C_t)/C_0 \times 100 \]

where \( C_0 \) is the starting concentration and \( C_t \) is the concentration at \( t \) minutes into the reaction.

3. Results and Discussion
As shown in Fig.1 and Fig.2, the structure of the Fe-MOFs was tested via SEM, FTIR, XRD, TG, N₂ adsorption-desorption. The two absorption peaks can be found at ~1650–1550 cm⁻¹ and ~1420–1300 cm⁻¹, which identify the characteristics of the carboxylate peak. The BET surface area of the Fe-MOFs was found to be 31.05 m²/g. The average pore diameter was 4.17 nm, indicating the formation of mesoporous materials. When the chemical bonds began to crack the benzene ring and carboxyl were lost and at 346 °C, the frame structure collapsed completely when the temperature reached 506 °C.

Here we tested the photocatalytic activities of Fe-MOFs on sample anionic (MO) and cationic (MB) dyes in aqueous medium. The removal capacity of Fe-MOFs for both MO and MB is shown in Figure 3. The removal rates of MOFs for MO under either Xe or natural light conditions and at 300 min were 96.34 and 52.32%, respectively. The removal rates of MOFs for MB under either Xe or natural light conditions at 120 min were 93.12 and 91.61%, respectively. As shown in Figure 3, the removal rate for MO was notably slow and approximately 64.33% of MO has been photocatalytically decomposed.
after 120 min of irradiation. Comparatively, the rate of degradation of MB was very fast after light irradiation and occurred within 10 min. A more uniform rate of degradation followed after and up to 120 min. approximately 67% of the anionic dye was degraded after 20 min, which amounted to a 30% difference when compared to that of the cationic dye at the same time point during the reaction.

To research the kinetics of MOFs removal of MO and MB removal, we next examined MO and MB binding to the Fe-MOFs using pseudo-first-order and pseudo-second-order kinetic models. Linear analysis methods were used with dye adsorption. The models used are expressed as follows [11]:

Pseudo-first order model:

\[
\ln \frac{C_i}{C_0} = k_1 t
\]  

Pseudo-second order model:

\[
\frac{dq}{dt} = k_2 (q_e - q_t)^2
\]

\[
\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}
\]

\[
q_e = \frac{(C_0 - C_e)v}{m}
\]

\[
q_t = \frac{(C_0 - C_t)v}{m}
\]  

Figure 1. SEM of Fe-MOFs

Figure 2. Structural characterization of Fe-MOFs
Where $C_0$ and $C_t$ are the initial and time $t$ concentrations of the liquid-phase dye (mg/L). $k_1$ (L/min) and $K_2$ (g/ (mg min)) are the kinetic constants of the pseudo-first and pseudo-second order models. $q_e$ and $q_t$ are the dye amounts (mg/g) adsorbed by the adsorbents at time $t$ and at equilibrium, respectively. $M$ (g) and $V$ (L) represent adsorbent quality and the volume (L) of the dye solution, respectively.

As shown in Figures 4 and 5 as well as Table 1, we established the feasibility of a pseudo-second-order model for MOF-mediated dye removal by fitting the experimental data using a least squares regression analysis (all correlation coefficients ($R^2$) were greater than 0.995). As shown in Table 1, $R^2$ of the linear equation under the effect of Xe light was larger than that under natural light conditions.

A comparison of our results with calculated $R^2$ is shown in Table 1. There is a small degree of deviation between the experimental and theoretical data. All $R^2$ for the first-order kinetic model obtained at all of our selected concentrations were notably low, which indicates that this adsorption system was not a first-order reaction. Rather, these findings indicate that the adsorption system is likely a second-order kinetic model. A similar outcome has been observed regarding the adsorption of dye RR189 on crosslinked chitosan beads [14], dye AB9 on mixed sorbents (e.g., activated clay and carbon) [15], dye BB69, and DR227 on activated clay [16].

![Figure 3. Removal rates of MO and MB by Fe-MOFs](image1)

![Figure 4. Pseudo-first-order analysis of dye adsorption over Fe-MOFs](image2)
Figure 5. Pseudo-second-order analysis of dye adsorption over Fe-MOFs

Table 1. Kinetic model parameters of the MO adsorption over Fe-MOFs

|          | pseudo-first-order | pseudo-second-order |
|----------|--------------------|---------------------|
|          | $R^2$      | $k$          | $R^2$   | $k$       |
| MO       | Xe light  | 0.96059   | -0.01043 | 0.99616   | 0.03614   |
|          | Nature light | 0.93883   | -0.00172 | 0.99662   | 0.07772   |
| MB       | Xe light  | 0.98755   | -0.01427 | 0.99702   | 0.02458   |
|          | Nature light | 0.98456   | -0.01529 | 0.99564   | 0.02414   |

4. Conclusion
Our results indicate the successful use of a microwave-assisted ball milling to synthesis metal-organic framework. When compared with previous preparation methods, this approach is simpler and uses a cheaper catalyst. Our results indicated that Fe-MOFs effectively promoted dye degradation. However, other mechanisms that might also explain these results, like electrostatic interactions and π electrons between organic dyes and Fe-MOFs, cannot be ruled out and will need further exploration in the future. We also believe that Fe-MOFs may have open metal sites that can be occupied by Lewis bases; the basis for this hypothesis is the results seen with Xe irradiation, which was more conducive to organic dye removal than natural light. We also applied our experimental results to first- and second-order kinetic models. These results showed that Fe-MOFs removal of dyes was consistent with a second-order kinetic model. Taken together, these results show that Fe-MOFs are an effective decolorizer under both Xe and natural light irradiation and would be well-placed for wider use in the future.

Acknowledgments
This work was financially supported by the Joint Funds of Science and Technology Department of Guizhou Province with People’s Government of Anshun City and Anshun University (LH[2016]7268).

References
[1] Bao, C., Fang, C.-L. Water Resources Flows Related to Urbanization in China, Challenges and Perspectives for Water Management and Urban Development Water. Resour. Manage. 26 (2012) 531–552.
[2] Ding Chen, Peng-fei Feng, Fu-hua Wei. Preparation of Fe(III)-MOFs by microwave-assisted ball for efficiently removing organic dyes in aqueous solutions under natural light. Chemical. Engineering. Processing: Process Intensification., 135 (2019) 63–67
[3] Chen, S., Zhang, J., Zhang, C., Yue, Q., Li, Y., Li, C. Equilibrium and kinetic studies of methyl orange and methyl violet adsorption on activated carbon derived from Phragmites australis Desalination. 252 (2010) 149–156.

[4] Li, J.-R., Ma, Y., McCarthy, M.C., Sculley, J., Yu, J., Jeong, H.-K., Balbuena, P. B., Zhou, H.C. Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks Coord. Chem. Rev. 255 (2011) 1791–1823.

[5] Kurmoo, M. Magnetic metal-organic frameworks, Chem. Soc. Rev. 38 (2009) 1353–1379.

[6] Hu, Z., Deibert, B.J., Li, J. Luminescent metal-organic frameworks for chemical sensing and explosive detection Chem. Soc. Rev. 43 (2014) 5815–5840.

[7] Ahmed, I., Khan, N.A., Jhung, S.H. Graphite oxide/metal-organic framework (MIL-101), remarkable performance in the adsorptive denitrogenation of model fuels Inorg. Chem. 52 (2013) 14155–14161.

[8] Schlesinger, M., Schulze, S., Hietschold, M., Mehring, M. Evaluation of synthetic methods for microporous metal–organic frameworks exemplified by the competitive formation of [Cu2(btc)3(H2O)3] and [Cu2(btc)(OH)(H2O)] Microporous. Mesoporous Mater. 132 (2010) 121–127.

[9] Chen, D., Ai, S.Y., Liang, Z., Wei, F.H. Preparation and photocatalytic properties of zinc oxide nanoparticles by microwave-assisted ball milling Ceramics. International. 42 (2016) 3692–3696.

[10] Wei, F.H., Chen, D., Lang, Z., Zhao, S.Q., Luo, Y. Synthesis and characterization of metal–organic frameworks fabricated by microwave-assisted ball milling for adsorptive removal of Congo red from aqueous solutions RSC. Adv. 7 (2017). 46520–46528.

[11] Wei, F.H., Chen, D., Lang, Z., Zhao, S.Q., Luo, Y. Preparation of Fe-MOFs by microwave-assisted ball milling for reducing Cr(VI) in wastewater Dalton. Trans. 46 (2017) 16525–16531.

[12] Wei, F.H., Chen, D., Lang, Z., Zhao, S.Q. Comparison Study on the Adsorption Capacity of Rhodamine B, Congo Red, and Orange II on Fe-MOFs Nanomaterials. 8 (2018) 248.

[13] Zhao, Shuaiqi; Chen, Ding; Wei, Fuhua. Synthesis of graphene oxide/metal-organic frameworks hybrid materials for enhanced removal of Methylene blue in acidic and alkaline solutions., J. CHEM. TECHNOL. BIOT. 93 (2018) 698-709.

[14] Chiou, M.-S. and H.-Y. Li. Equilibrium and Kinetic Modelling of Adsorption of Reactive Dyes on Cross-Linked Chitosan Beads J. Hazard. Mater. 93 (2002) 233–248.

[15] Ho, Y.S. and C.C. Chiang. Sorption Studies of Acid Dye by Mixed Sorbents Adsorption 7 (2001) 139–147.

[16] Wu, F.-C., Tseng R.-L., and Juang R.-S. Kinetics of Color Removal by Adsorption from Water Using Activated Clay Environ. Technol. 22 (2001) 721–729.