



# Ferrocene-modified iron-based metal-organic frameworks as an enhanced catalyst for activating oxone to degrade pollutants in water

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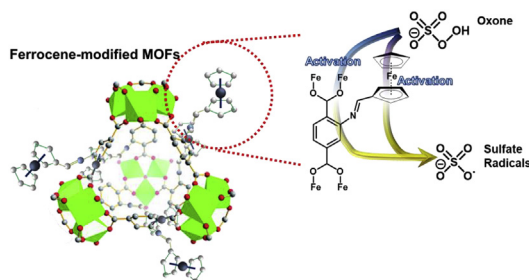
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## HIGHLIGHTS

- Ferrocene (Fc) is grafted on MIL-101 to form Fc-modified MIL-101 (Fc-MIL).
- Fc-MIL outperforms MIL-101 and Co<sub>3</sub>O<sub>4</sub> for activating Oxone to degrade amaranth.
- $E_a$  of amaranth degradation by Fc-MIL-activated Oxone is lower than reported values.
- Fc-MIL is also re-used to activate Oxone for amaranth degradation over many cycles.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Ferrocene (Fc) has been regarded as a useful catalyst for activating Oxone to generate sulfate radicals (SR) in degradation of organic pollutants. Nevertheless, direct usage of Fc molecules in aqueous solutions may lead to difficult recovery and aggregation. While a few attempts have immobilized Fc on several substrates, these substrates exhibit very low surface areas/porosities and, especially, do not offer significantly additional contributions to catalytic activities. In this study, a Fe-containing metal organic frameworks (MOFs), MIL-101, is particularly selected for the first time as a support to immobilize Fc chemically. Through the Schiff base reaction, ferrocenecarboxaldehyde can react with amine-functionalized MIL-101 (namely, MIL-101-NH<sub>2</sub>) to form Fc-modified MIL-101 (Fc-MIL). As Fc-MIL consists of both Fe from MIL-101 and Fc and also exhibits high surface areas, it appears as a promising catalyst for activating Oxone. Catalytic activities for Oxone activation by Fc-MIL are studied using batch-type experiments of amaranth dye degradation. Fc-MIL shows higher catalytic activities than its precursor MIL-101-NH<sub>2</sub> owing to the modification of Fc, which equips with MIL-101 with more catalytic sites for activating Oxone. Besides, Fc-MIL also outperforms the benchmark catalyst of Oxone activation, Co<sub>3</sub>O<sub>4</sub>, to degrade amaranth. In comparison to the other reported catalysts, Fc-MIL shows the much smaller activation energy for amaranth degradation, proving its advantage over other catalysts. The synthesis technique proposed here can be also employed to develop other Fc-modified MOFs for other environmental catalysis applications.

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## 1. Introduction

Oxone (potassium peroxymonosulfate) has been increasingly employed as an easily-accessible, low-cost and environmentally-friendly oxidant for producing sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) (SR) to degrade organic pollutants in wastewater treatments (Hu and Long, 2016). Nevertheless, since the spontaneous self-decomposition of Oxone is very slow, Oxone requires “activation” in order to generate SR efficiently.

To date, even though numerous techniques have been proposed for Oxone activation, usage of metal catalysts for activating Oxone is validated as the most promising technique (Anipsitakis et al., 2005). While several transition metals are proven to activate Oxone (e.g., Co, Mn, Cu, Fe and Ru) (Oh et al., 2016), Fe appears to be an even more attractive catalyst among these metals as it is by mass the most common element on earth and exhibits a wide range of oxidation states, making it a promising catalyst for various applications.

Nonetheless, direct usage of homogeneous Fe ions for activating Oxone would be difficult for recovery, leading to secondary aqueous pollution. Therefore, many studies have proposed heterogeneous Fe-containing materials, such as iron oxides, and iron complexes (Ji et al., 2013). Among these Fe-based materials, a special Fe-containing compound, ferrocene (Fc), recently receives increasing attention for catalytic applications (Ye et al., 2014a; Ye et al., 2014b; Lin et al., 2017a; Lin et al., 2017b; Lin and Lin, 2017; Lin et al., 2017c; Andrew et al., 2017). Fc, comprised of two cyclopentadienyl rings bound on opposite sides of a central Fe, can exhibit excellent redox reversible properties (Wang et al., 2013); Fc is validated as a highly stable and non-toxic compound. As a result, Fc has developed as a catalyst to activate numerous oxidants for oxidation reactions, including wastewater treatments (Ye et al., 2014a; Lin et al., 2017d).

However, Fc molecules are nanoscale and direct usage of Fc in aqueous solutions could also lead to difficult recovery and aggregation (Lin et al., 2017d). Thus, a few attempts have been made to graft Fc to substrates via chemical bonding to anchor and distribute Fc.

For instance,  $\text{g-C}_3\text{N}_4$  and chitosan have been successfully demonstrated as supports for immobilizing Fc via chemically reacting ferrocenecarboxaldehyde (Fc-CHO) with amine groups of  $\text{g-C}_3\text{N}_4$ /chitosan for oxidation applications (Ye et al., 2014a; Lin et al., 2017b). However, these substrates exhibited extremely low surface areas and porosities (Ye et al., 2014a; Lin et al., 2017b), making the resulting composites less advantageous. Besides, some of these substrates themselves were merely supports, exhibiting no additional catalytic activities. Therefore, a high-surface-area and porous substrate, which can also contain catalytic functionalities, would be a promising support for immobilizing Fc. To this end, here we propose, for the first time, to employ metal organic frameworks (MOFs) as an intriguing substrate to immobilizing Fc because MOFs can exhibit high surface areas and porosities. MOFs can be also comprised of transition metals as nodes to exhibit catalytic activities for various applications, including wastewater treatments (Andrew Lin and Chen, 2015; Andrew Lin et al., 2015; Azhar et al., 2018a, 2018b; Liang et al., 2017, 2018). Especially, several Fe-based MOFs are also developed as catalysts for activating oxidants for oxidizing reactions (Andrew Lin and Chen, 2015; Andrew Lin et al., 2015). For instance, Fe-MIL-88A has been used to activate persulfate for obtaining SR as  $\text{Fe}^{3+}$  of MIL-88A can catalyze decomposition of persulfate (Andrew Lin et al., 2015). Besides, Fe-MIL-88B is also used as a catalyst for Fenton reaction to degrade pollutants owing to its inclusion of Fe (He et al., 2018).

In particular, MIL-101 is selected because it is a very common Fe-containing MOF and exhibits high surface areas and porosities. Moreover, MIL-101 can be easily functionalized with primary amine

groups, which are required in order to chemically bind Fc-CHO via the Schiff base reaction. The resulting Fc-modified MIL-101 (Fc-MIL) consists of Fe moieties from MIL-101 and Fc, and also exhibit high surface areas/porosities, making it a promising catalyst for activating Oxone.

Fc-MIL for activating Oxone is evaluated by batch-type degradation experiments of a toxic azo dye, amaranth. Catalytic activities of Fc-MIL are studied through investigating amaranth degradation by Fc-MIL-activated Oxone under various conditions and the mechanism of amaranth degradation is determined by evaluating effects of radical scavengers and Electron Paramagnetic Resonance (EPR) spectroscopic analysis. Reusability of Fc-MIL for Oxone activation is also studied for long-term Oxone activation.

## 2. Experimental

### 2.1. Preparation and characterization of Fc-MIL

Fc-modified MIL-101 was prepared according the scheme shown in Fig. 1 via the Schiff base reaction by reacting Fc-CHO with  $\text{NH}_2$  groups of amine-functionalized MIL-101- $\text{NH}_2$  in ethanol at  $100^\circ\text{C}$ . MIL-101- $\text{NH}_2$  as first prepared using  $\text{FeCl}_3$  and 2-aminoterephthalic acid solvothermally. The detailed preparation and characterization of Fc-MIL is described in the supporting information (please see Text S1).

### 2.2. Oxone activation by Fc-MIL for amaranth degradation

To evaluate catalytic activities of Fc-MIL for Oxone activation, degradation of amaranth dye was employed as a model test. The detailed batch-type amaranth degradation experiment using Fc-MIL-activated Oxone can be found in the supporting information (please see Text S2).

## 3. Results and discussion

### 3.1. Characterization of Fc-MIL

As Fc-MIL was prepared via the modification of MIL-101- $\text{NH}_2$ , the morphology of MIL-101- $\text{NH}_2$  was first characterized as shown in Fig. 2(a). The as-synthesized MIL-101- $\text{NH}_2$  exhibited a shape of hexagonal microrod and such a special shape of MIL-101- $\text{NH}_2$  had been also reported in the literature (Zhang et al., 2016). After Fc-modification, the resulting Fc-modified MIL-101 also exhibited a very similar morphology of hexagonal microrod as displayed in Fig. 2(b). This indicates that the Fc-modification did not alter the morphology and the framed structure of MIL-101. Fig. 3(a) further reveals EDS results of MIL-101- $\text{NH}_2$  and the resulting Fc-MIL for determining chemical compositions. As MIL-101- $\text{NH}_2$  consisted of Fe and aminoterephthalic acid, significant signals of Fe and O can be detected (the N signal was typically less easily detected in EDS). Similarly, Fc-MIL also exhibited strong signals of Fe and O; however the signal of Fe in Fc-MIL seemed even larger, suggesting that Fc-MIL contained a higher fraction of Fe and Fc seemed to be grafted on MIL-101.

Furthermore, the crystalline structure of MIL-101- $\text{NH}_2$  and Fc-MIL were also investigated as shown in Fig. 3(b). Before the Fc-modification, the XRD pattern of the as-synthesized MIL-101- $\text{NH}_2$  was identical to the typically-reported XRD pattern of MIL-101 in the literature (Kim et al., 2016), confirming that MIL-101 had been successfully synthesized. After the Fc-modification, the XRD pattern of Fc-MIL was very similar to that of MIL-101 and no additional significant signals were observed. This validates that the Fc-modification did not change the crystalline structure of MIL-101. Besides, as Fc was chemically bound to MIL-101 instead of being

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