

# Research progress on degradation of organic pollutants based on metal–organic frameworks materials

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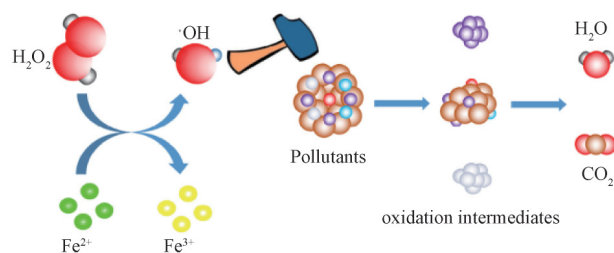
**Abstract.** As an advanced oxidation process, Fenton oxidation has attracted much attention because its reactants and products are green and pollution - free. The traditional Fenton oxidation method has some problems, such as high PH requirement and low utilization rate of hydrogen peroxide. Over the past few years, the advancements in application research of Metal-Organic Frameworks (MOFs) have presented innovative and effective ideas for addressing the aforementioned issues. This paper presents the recent advancements in Fenton oxidation technique utilizing Fenton-based materials. Based on literature analysis, it can be seen that Fe-based MOFs were initially used for catalytic reaction and the research shows that the catalytic activity of Fe-based MOFs can be increased by increasing the number of unsaturated Fe metal sites. And the doping of other metals into Fe-based MOF or dual ligand Fe-based MOFs can play a role in changing the structure and increasing the unsaturated metal sites which can further expand the direct application of MOFs in the Fenton oxidation method. However, due to the limited types of iron-based MOFs, non-iron-based MOFs materials and indirect use of MOFs have been reported in the indirect use of MOFs, catalytic active substances can be compounded into MOFs materials through in-situ growth, forming a synergistic effect to improve the efficiency of degradation by means of carbonization or pyrolysis of MOFs, MOFs derived materials can be obtained.

## 1. Introduction

At present, the main pollutants contained in the daily sewage discharge of human beings are chemical products, pesticides, dyes, drugs and personal care products. These pollutants from human activities cannot be completely removed by sewage treatment plants due to their high stability to sunlight, biodegradation and temperature, so they are called persistent organic pollutants. These persistent organic pollutants can be detected in lakes, oceans, and even everyday drinking water [1]. At present, biological treatment methods are widely used, but this method takes a long time and occupies a large area, and the biodegradation effect of some toxic pollutants is not good. However, advanced oxidation methods such as Fenton oxidation (AOPs) have remarkable mineralization effects on organic matter. They have been widely developed and applied to direct mineralization of organic pollutants [2].

Among the advanced oxidation techniques, Fenton oxidation approach boasts a diverse range of applications, formidable resistance to interference, effortless operation, and rapid degradation and mineralization rates. Its incomparable advantages make it popular [3]. The active substance hydroxyl radical ( $\cdot\text{OH}$ ) with high oxidation potential is generated by the catalytic reaction of Fe(II)

and  $\text{H}_2\text{O}_2$  in the Fenton oxidation system [4]. The reaction mechanism is shown in Figure 1. Hydroxyl radical is a green oxidizing agent with high reduction site and strong oxidation ability [5].



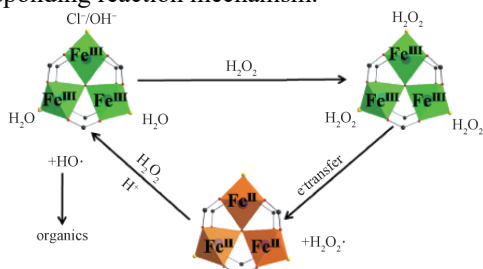
**Figure 1.** Principle of Fenton oxidation process

MOFs are supramolecular structures created through the coordination of metal ions with organic ligands. It exhibits extremely high surface area and porosity as well as high strength and desirable chemical activity [6]. In addition, MOFs-related composite materials can be derived by various preparation methods, which greatly expands its application range. In this paper, the latest research based on MOFs materials and their derivatives is briefly summarized and analyzed.

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## 2. Direct application of MOFs

In the past decade, the application of Fe-based MOFs in heterogeneous Fenton reactions has increased rapidly due to their high efficiency of  $\cdot\text{OH}$  formation [7]. As early as several years ago, some researchers have found that there is an open Fe site in the Fe-based MOF material MIL-88B-Fe, which has an unsaturated property [8]. On the basis of previous studies, Quan [9] used the chemical composition of MIL-88B-Fe as  $\text{Fe}_3\text{O}[\text{C}_6\text{H}_4(\text{CO}_2)_2]_3\text{X}\cdot n\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}^-$  or  $\text{OH}^-$ ). Yang [10] synthesized a series of iron-based MOFs to degrade tetracycline hydrochloride. Compared with the original MIL-53-Fe, the performance of L-MIL-53 (Fe, Mn) is significantly enhanced. The figure illustrates the activation of  $\text{H}_2\text{O}_2$  by MIL88B-Fe and its corresponding reaction mechanism.



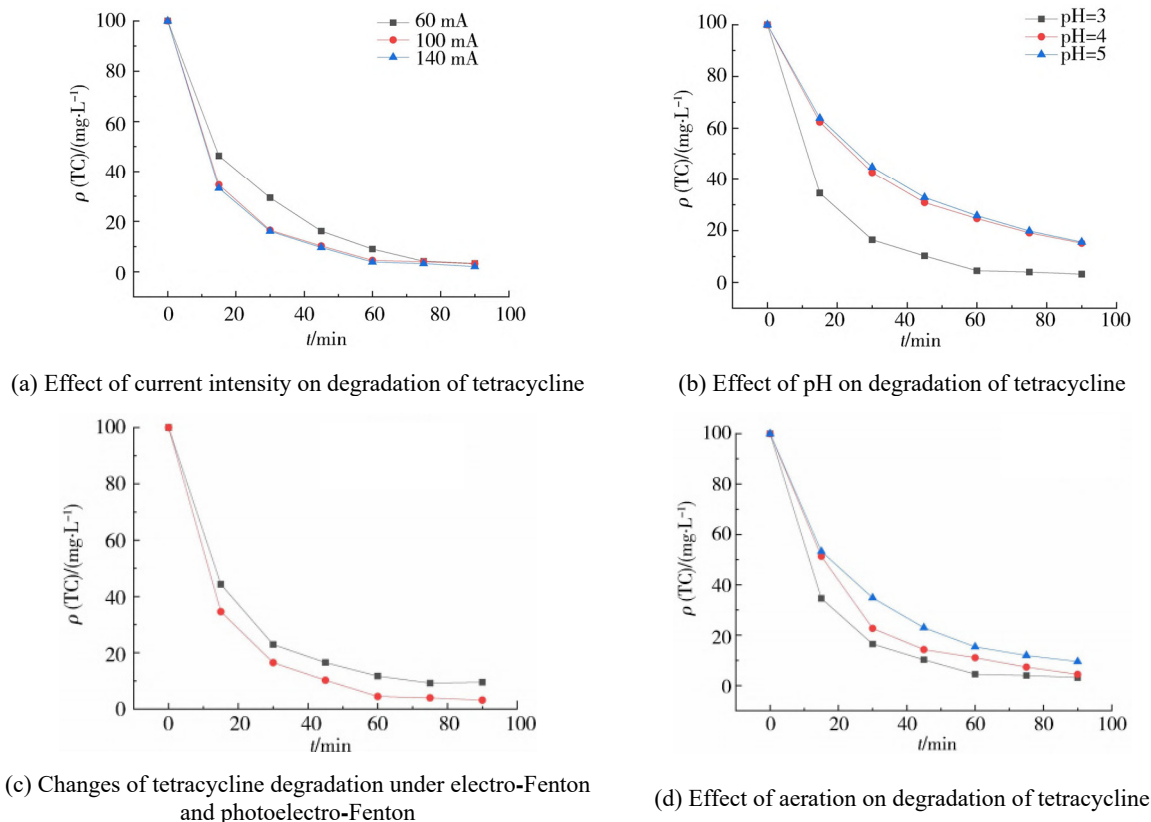
**Figure 2.** Reaction mechanism of activation

Some scholars [9] have found that the use of UVA-LED as UV light source synergistic process with electric Fenton can promote tetracycline degradation more effectively than electric Fenton alone. During the treatment time of 180 min, the tetracycline in the

simulated wastewater was degraded and mineralized continuously. As shown in Figure 3.

Since then, a series of iron-based MOFs have been synthesized by a research group as a Fenton-like catalyst to degrade tetracycline hydrochloride, and it has been proved for the first time that visible light can accelerate the light-based Fenton system based on iron and oxygen heteroclusters in the frame. Among these iron-based MOFs, MIL-101 has the highest activity, due to its high specific surface area and pore volume, and has the most coordinated unsaturated iron position. The effective pH range of MIL-101 can reach 10.2, which has good reusability and stability. Solve the influence of pH limitations on the application range of Fenton oxidation method.

In photocatalytic applications, due to the high recombination tendency of the electron-hole pairs generated by Fe-MOFs, its photocatalytic activity is low. Therefore, the research team used a simple one-pot solvothermal method to reduce the crystallization time. Successfully synthesized LMIL-53. This is mainly due to the synergy between heterogeneous metal nodes to enhance the electron-rich Fe check point and Mn check point formed by the nanyl, which can increase the specific surface area and promote visible light absorption and the separation and transportation of carriers in the low crystalline state. In addition, the increase of the check point of metal coordination unsaturation activity is beneficial to the activation of  $\text{H}_2\text{O}_2$ . In addition, the optical Fenton system has good stability and reusability, showing good application prospects.



**Figure 3.** Influence factor curve of tetracycline degradation

### 3. Indirect application of MOFs

Due to the limitation of the types and properties of Fe-based MOFs, the direct application of MOFs in Fenton oxidation is still limited. It can be indirectly applied to Fenton catalysis by introducing or transforming into a catalytic active substance in various ways. MOFs materials are limited by the types and properties of Fe-based MOFs, and the research on direct application in the Fenton oxidation process is still relatively limited. The introduction of catalytic active substances or conversion into catalytic active substances through in-situ growth, loading and carbonization can be indirectly applied to

direct Fenton, light Fenton and electric Fenton. MOFs materials and MOFs derivative materials can further expand the application range of MOFs materials in Fenton oxidation

#### 3.1 Composite MOFs material

Composite MOFs materials can be grown in situ by adding catalytically active substances or co-catalytic substances to MOFs precursors. MOFs is synthesized, and catalytic material with changed activity is obtained directly. After 45 minutes experiment, the removal rates of TMX reached 50% and 96%, respectively. The potential reaction mechanism is illustrated in Figure 4.

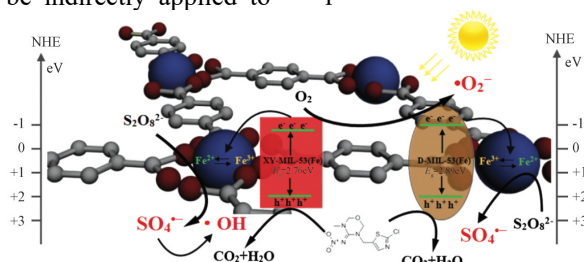


Figure 4. Potential reaction mechanism

Zhou [7] successfully constructed g-C<sub>3</sub>N<sub>4</sub>/NH<sub>2</sub>-MIL-100-Fe octahedral heterojunction photocatalyst by solvothermal loading ultra-thin mesoporous g-C<sub>3</sub>N<sub>4</sub>(U-g-C<sub>3</sub>N<sub>4</sub>) onto the ferritic organic skeleton NH<sub>2</sub>-Fe-MOFs. The loaded ultrathin mesoporous g-C<sub>3</sub>N<sub>4</sub> sheet structure has more active check points to produce more H<sub>2</sub>O<sub>2</sub>. It is beneficial to the production of hydrogen peroxide and significantly promotes the generation of hydroxyl radicals.

Chen [7] added carbon nanotubes (CNTs) with electron-rich oxygen functional groups on the surface to MIL-88B-Fe. This increased the Fe (II) content and enhanced the Fenton-like properties. At the same time, it was found that the synthesized CNT@MIL-88B-Fe (C@M) has a significantly catalytic ability for H<sub>2</sub>O<sub>2</sub> than MIL-88B-Fe.

Ahmad M. synthesized CUCs-MIL-88B-Fe catalysts with valence unsaturated (Fe<sup>II</sup> /Fe<sup>III</sup>) centers (CUC: coordination unsaturated metal center) on ultrathin Ti<sub>3</sub>C<sub>2</sub> nanosheets [8]. CUCs-MIL-88B-Fe/Ti<sub>3</sub>C<sub>2</sub> showed higher photofenton activity for degradation of phenol and sulfamethoxazole (SMX) and removal of TOC than conventional MIL-88B-Fe. CUCs-MIL-88B-Fe/Ti<sub>3</sub>C<sub>2</sub> has good stability and reusability, and low Fe leaching rate.

Preparing composite materials with MOFs and semiconductors is an effective strategy to improve charge transfer efficiency. Zhao [10] successfully used Cu<sub>2</sub>O to grow on MIL-100-Fe surface, which enhanced the deep degradation of thiamethacloprid (TCL) in collaboration with photofenton catalysis at the interface greatly.

Zhang [10] successfully synthesized Fe<sub>3</sub>O<sub>4</sub>@MIL-100-Fe hybrid composite by in-situ growth method, and verified its high photocatalytic activity. This increased catalytic activity was ascribed to the combined effect of Fe<sub>3</sub>O<sub>4</sub> and MIL-100-Fe, exhibiting synergistic action. The team believes that this high catalytic activity is due to the synergistic effect of Fe<sub>3</sub>O<sub>4</sub> and MIL-100-Fe, which enhances the charge distribution and accelerates the reduction of Nanyan. In addition, the composite material

of Fe<sub>3</sub>O<sub>4</sub> and MIL-100-Fe has excellent stability and recyclability. Moreover, the method has a low iron leaching rate and can effectively degrade lofloxacin in actual surface water. These results indicate that as an advanced oxidation technology, it may be used more and more.

#### 3.2 MOFs derived materials

MOFs materials are usually composed of metal centers and organic connectors due to their diverse composition and customizable structure. This can be used as a precursor for the preparation of various metal-long carbon composites. For the carbon matrix based on MOFs, compared with the pure carbon structure, it is beneficial to improve the charge transfer efficiency and adjust the electronic structure. So as to improve the overall catalytic activity of the electric Fenton. However, the problem that the traditional Fenton oxidation method requires a high pH range still exists. In response to this problem, Liu [6] used CMOF@PCM obtained by calcination and carbonization of MIL-88 (Fe) -NH<sub>2</sub> as the catalyst for the reaction system, and used electro-Fenton method based on the catalyst to degrade herbicide. It can play the following roles: promote the electron transfer between the graphite carbon shell layer and the Fe<sub>3</sub>O<sub>4</sub> core layer, and improve the electric Fenton reaction activity; improve the catalytic activity by reducing the lattice mismatch between the graphite carbon shell layer and the Fe<sub>3</sub>O<sub>4</sub> nucleus; immobilize the three-dimensional Sansi species in the Fe<sub>3</sub>O<sub>4</sub> nucleus, and lock the Fe atom in the Fe<sub>3</sub>C.

The utilization efficiency of hydrogen peroxide generated by the electrosynthesis method is low, which limits the wide application of the electric Fenton method. For this reason, people have put a lot of efforts to find reasonable materials. Some people have reported a general method for preparing modified graphite electrodes for alloy-closed carbon nanomaterials. The nickel-iron alloy

closed carbon nanomaterials (NiFe@C / G) can be prepared through a simple annealed nickel-iron metal organic framework. The modified graphite electrodes have significantly improved electrocatalytic activity and stability.

Quan [6] prepared the catalyst by carbonizing Cu-doped Fe MOFs NH<sub>2</sub>-MIL-88B-Fe and used it as the cathode material for the electroFenton method. Experimental results showed that the removal rate of phenol ( $5 \times 10^{-5}$  grade) in the treated FeO<sub>x</sub>/CuN<sub>x</sub>HPC

electrofenton system was almost 100% within 90min under acidic, intermediate and even strong alkaline environment. Using MIL-101-Fe as a template, Zhou [8] prepared a new core-shell hybrid octahedron catalyst with iron base nanoparticle core (Fe/Fe<sub>3</sub>C) and graphitized porous carbon shell (Fe/Fe<sub>3</sub>C@PC) through carbonization. It was also used for catalytic degradation of sulfadimethirimidine (SMT). The application of MoFs-derived materials in the degradation of organic pollutants in electric Fenton is shown in Table 1.

**Table 1.** Application of MOFs derived materials

| S/N | Catalyst   | Anode/cathode material           | pollutant       | Time/min | pH | Clearance rate/% |
|-----|--|----------------------------------|-----------------|----------|----|------------------|
| 1   | CMOF@PCM (MIL-88 (Fe) -NH <sub>2</sub> )                             | SCE, Pt, CMOF@PCM                | diachlor        | 60       | 7  | 97               |
| 2   | FeO <sub>x</sub> /CuN <sub>x</sub> HOC (NH <sub>2</sub> -MIL-88B-Fe) | SCE, Pt, glassy carbon electrode | phenol          | 90       | 6  | 100              |
| 3   | Fe/Fe <sub>3</sub> C @PC (MIL-101-Fe)                                | Ti-RuO <sub>2</sub> , CB-CF      | sulfadimethacil | 30       | 3  | 99               |
| 4   | Mn/Fe@PC   | Pt, Mn/Fe@PC                     | triclosan       | 125      | 3  | 100              |
| 5   | CFP@PANI@MIL-101 (400) (MIL-101-Fe)                                  | BDD, CFP@PANI-101                | 4-nitrophenol   | 120      | 3  | 100              |

#### 4. Conclusion

The Fenton catalysts based on MOFs that have been reported so far have relatively good stability and high catalytic efficiency. Iron-based MOFs are an important branch of MOFs, with good stability in water, environmental protection and easy availability, and are good catalysts for Fenton oxidation. Increasing the number of unsaturated Fe metal check points of iron-based MOFs can increase their catalytic activity. The use of the second type of metal doped into the iron-based mousin or biligand Fe-based MOFs can play a role in changing the structure and increasing the check point of unsaturated metals. The direct application of MOFs in the Fenton oxidation method can be further expanded. In indirect applications, it can be grown in situ to make the catalytic active substance compound into the MOFs material to form a synergy effect to improve the degradation efficiency of the MOFs. The MOFs-derived material can be obtained by carbonization or pyrolysis of the MOFs. These composite MOFs materials and MOFs-derived materials synthesized by various synthesis and preparation methods can change their morphology, specific surface area, pore structure and conductivity through the addition and post-treatment of external active substances, thereby optimizing their catalytic performance. These synthesis methods will greatly expand the application of MOFs materials in the Fenton oxidation method. At the same time, MOFs with high charge mobility or conductivity make conductive MOFs possible, and provide opportunities for the development of such materials.

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