



## Research Paper

# Synthesis of iron-based metal-organic framework MIL-53 as an efficient catalyst to activate persulfate for the degradation of Orange G in aqueous solution



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## ABSTRACT

A series of MIL-53(Fe) materials was synthesized using a solvothermal method under different temperature and time conditions and were used as catalysts to activate persulfate and degrade Orange G (OG). Influences of the above conditions on the crystal structure and catalytic behavior were investigated. Degradation of OG under different conditions was evaluated, and the possible activation mechanism was speculated. The results indicate that high synthesis temperature (larger than 170 °C) leads to poor crystallinity and low catalytic activity, while MIL-53(Fe) cannot fully develop at low temperature (100 or 120 °C). The extension of synthesis time from 5 h to 3 d can increase the crystallinity of the samples, but weakened the catalytic activity, which was caused by the reduction of BET surface area and the amount of Fe (II)-coordinative unsaturated sites. Among all the samples, MIL-53(Fe)-A possesses the best crystal structure and catalytic activity. In optimal conditions, OG solution can be totally decolorized after degradation for 90 min, and a removal rate of 74% for COD was attained after 120 min. The initial solution pH had great influence on OG degradation, with the greatest removal in acidic pH environment. ESR spectra showed that sulfate radical ( $\text{SO}_4^{\cdot-}$ ), hydroxyl radical ( $\text{OH}\cdot$ ), persulfate radical ( $\text{S}_2\text{O}_8^{\cdot-}$ ), and superoxide radical ( $\text{O}_2^{\cdot-}$ ) exist in this system under acidic conditions. Furthermore, with the increase of pH, the relative amount of  $\text{O}_2^{\cdot-}$  increases while that of  $\text{OH}\cdot$  and  $\text{SO}_4^{\cdot-}$  decreases, resulting in a reduced oxidizing capacity of the system.

## 1. Introduction

Azo dyes, the largest and most versatile class of synthetic dyes, have been widely and frequently used in various industries including textile, leather, paper, printing, plastic, food, pharmaceutical and cosmetic [1,2]. A relatively high amount of azo dyes are released into wastewater effluents annually during the manufacturing or processing operations, leads to contamination of the environment. Since azo dye molecules are characterized by the presence of one or more azo bonds ( $-\text{N}=\text{N}-$ ) connected with aromatic rings and auxochromes, most of them are stable and recalcitrant, and thus cannot be easily removed by conventional wastewater treatment methods [3]. These compounds are toxic, mutagenic, carcinogenic and non-biodegradable, and will pose a long-term risk to the ecosystem and human health [4].

Advanced oxidation processes (AOPs) making use of in-situ formed

highly reactive radicals have emerged as useful methods for treating most toxic and bio-refractory organic pollutants in wastewater. Several AOP processes have been employed to degrade and mineralize azo dyes in wastewater, such as Fenton, Fenton-like, photocatalysis, ultrasonic catalysis, electrochemical catalysis, and persulfate oxidation. Among them, persulfate (PS) is the latest investigated oxidant and has been used to treat numerous types of contaminants, especially in terms of in-situ chemical oxidation (ISCO) for soil and groundwater remediation [5]. PS is a strong oxidant ( $E^0 = 2.01 \text{ V}$ ) and can generate the stronger oxidative sulfate radical ( $\text{SO}_4^{\cdot-}$ ,  $E^0 = 2.5\text{--}3.1 \text{ V}$ ) via activation under certain conditions. Compared to photo, ultrasonic and electrochemical catalysis, there is no need to use external energies in support of PS oxidation processes, which greatly reduces treatment costs. Compared to Fenton or Fenton-like processes, PS is much more stable than  $\text{H}_2\text{O}_2$  at room temperature [6], and  $\text{SO}_4^{\cdot-}$  can be much more effective in

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contaminant degradation than  $\text{OH}\cdot$  due to longer half-life period, higher stability and lower reactivity with natural organic materials present in water [7,8].

As mentioned, PS is capable of generating  $\text{SO}_4^{\cdot-}$  under various activation methods. Thermal, UV (Ultraviolet) and transition metals are the most common methods that are used. But the high cost of heat and light application limits the widespread use of thermal and UV methods. Among all the tested effective transition metals, iron is the most preferred because it widely exists in nature so that it is cost-effective and environmentally friendly [9]. Both homogeneous and heterogeneous iron catalysts can be used as the activator for persulfate. Ferrous ion or chelated-ferrous ion are the most common choices as homogeneous catalysts [10], but they do have some drawbacks. Sulfate radicals can be scavenged by the excess ferrous ion in solution, thus causing the accumulation of ferric ion and the generation of iron sludge [11]. Most chelating agents that are used are organic materials [12] and can cause the increase of Chemical Oxygen Demand (COD) and secondary pollution of water. Zero-valent iron (ZVI) [13], iron oxide (such as  $\text{Fe}_3\text{O}_4$  [14]) and their composites [15] or supported iron catalysts [16] are usually used as heterogeneous catalysts for persulfate. However, researchers have reported that the surface components of these catalysts (such as ZVI,  $\text{Fe}_3\text{O}_4$ ) are often not stable and readily deactivated [17] during the activation processes, which complicates maintenance of catalytic capacity as well as catalyst recycling.

Very recently, researchers have investigated the use of iron-based metal organic frameworks as persulfate catalysts and have made some progress. Metal-organic frameworks (MOFs) themselves are a relatively new and rapidly growing class of compounds. These inorganic-organic porous materials are microporous crystals comprised of metal ions linked by organic bridging ligands, which possess unique attributes, such as tailorable molecular properties, good thermal stability and uniform structured nano scale cavities [18]. These features endow them with outstanding properties and potential applications in drug delivery [19], gas storage [20], separation [21], molecular sensing [22], adsorption [23], and especially in catalysis [24].

Several kinds of MOFs have been used as catalysts in AOPs. In general, there are two ways of using MOFs themselves as AOPs catalysts. One purpose is to use them in photo catalysis because MOFs are good semiconducting materials. The organic bridging ligands of MOFs can serve as antennas to harvest light and activate the metal nodes in the fashion of a linker to a metal cluster charge transition (LCCT) under light irradiation [25], which has been verified by previous studies that some MOFs such as MIL-53(Fe) [18,26], MIL-88 B [27] and MIL-101(Fe) [28] are good photo catalysts. Another way is to use them as Fenton-like catalysts through utilizing the coordinatively unsaturated sites (CUS) (also known as open metal sites (OMS)) as the active catalytic site. Formation of CUS during the construction of MOF's occurs when metal sites are coordinated partly to the guest molecule (for example the organic solvent), rather than fully coordinated only to the organic linkers [29]. Through removing the solvent molecule bonded to metal, CUS are thus formed on the pore surface of MOFs [30]. This unique property of having CUS makes it possible to use MOFs themselves as Fenton-like catalysts, such as: using MILs (Materials of Institute Lavoisier) to activate persulfate [31] and  $\text{H}_2\text{O}_2$  [32], or ZIFs (Zeolitic Imidazole Framework) to activate peroxymonosulfate [33]. Besides the above two approaches, using MOFs as templates or precursors to prepare functional MOF-derived carbon composites such as magnetic cobalt-graphene [34] or carbonaceous nanocomposite [35] as peroxymonosulfate catalysts has also attracted a lot of attention. However, research on the application of MOFs on AOPs is still at a very early stage.

A lot of studies have shown that synthesis conditions have great influence on the structure of MOFs. The products and intermediates formed during crystal growth are dependent on the temperature, concentration, pH, synthesis time and solvent mixture [36]. This is because they change the capability of coordination of organic ligands, the

coordination mode between metal ions and organic ligands, and thus changes the skeleton units and frame structure of MOFs [37]. Developing an understanding of the influence of some of the above factors on MOFs' structure and catalytic properties is critical to their effective application. Also, observation of catalytic performance and assessment of the possibility of using MOFs as persulfate catalysts are of great interest.

MIL-53(Fe) is an iron-based MOF. In this work, we use MIL-53(Fe) as a persulfate catalyst for the degradation of Orange G dye in simulated wastewater. All MIL-53(Fe) catalysts are post-processed under the same vacuum conditions, but the synthesis conditions differ. The purpose of this work is to (i) study the influence of synthesis conditions including crystallization time and temperature on structure and reactivity of the as-prepared MIL-53(Fe); (ii) observe the catalytic performance of MIL-53(Fe) towards persulfate and obtain the optimal activation conditions for the removal of Orange G; (iii) identify the predominant radical species in MIL-53(Fe) activated persulfate systems and illustrate the possible mechanism of activation.

## 2. Experimental

### 2.1. Chemicals

All the water used in this study was purified using a Millipore reverse osmosis (RO) system. The reagents used were purchased from the following companies: Orange G (OG, 90%) was purchased from Tokyo Chemical Industry Co., Ltd. Persulfate (PS,  $\text{Na}_2\text{S}_2\text{O}_8$ , 98%) was purchased from Aladdin Reagent Corporation. Terephthalic acid (TPA,  $\text{C}_8\text{H}_6\text{O}_4$ , 98%), dimethylformamide (DMF,  $\text{HCON}(\text{CH}_3)_2$ , 99.8%) and Potassium iodate (KI, 99.5%) were purchased from Sigma-Aldrich Corporation. Methyl alcohol (MeOH,  $\text{CH}_3\text{O}$ , 99.5%), ethanol ( $\text{C}_2\text{H}_6\text{O}$ , 99.7%), ferric chloride ( $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ , 99.0%) and sodium bicarbonate ( $\text{NaHCO}_3$ , 99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were of AR and purchased directly for use without further purification.

### 2.2. Synthesis of MIL-53(Fe)

MIL-53(Fe),  $\text{Fe}(\text{OH})[\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2]$ , was synthesized according to previous literature [40] with certain modifications. Briefly, MIL-53(Fe) was hydrothermally synthesized by a mixture of  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  (1.35 g, 5 mmol), terephthalic acid (TPA) (0.83 g, 5 mmol), and *N,N*-dimethylformamide (DMF) (25 mL) in a 100 mL Teflon autoclave placed in a fan oven. The mixture was heated at a certain temperature for the length of time required. The resulting samples were collected by filtration, washed with 150 mL MeOH and 150 mL distilled water successively. Then the samples were suspended in the fresh distilled water again and stirred overnight. Finally, the samples were vacuumed dried and heated at 170 °C for 12 h. The resulting samples were stored at room temperature in a covered glass container until needed.

MIL-53(Fe) synthesized under different temperatures for 5 h were marked as MIL-53(Fe)-N/M/A/B/C/D, representing temperatures of 100 °C, 120 °C, 150 °C, 170 °C, 200 °C, 220 °C, respectively. MIL-53(Fe) catalysts synthesized under 150 °C were marked as MIL-53(Fe)-A/E/F/G/H/I/J/K/L, representing synthesis times of 5 h, 8 h, 10 h, 12 h, 24 h (1 d), 48 h (2 d), 72 h (3 d), 96 h (4 d), 120 h (5 d), respectively.

### 2.3. Characterization of MIL-53(Fe)

Powder X-ray diffraction (PXRD) patterns were recorded with a Bruker D8 Advance X-ray Powder Diffractometer using  $\text{Cu K}\alpha$  ( $\lambda = 0.15418$  nm) radiation, with a step size of  $0.02^\circ$  in two theta ( $2\theta$ ). The morphology of samples was observed with a ZEISS Merlin field-emission scanning electron microscope (FESEM). Nitrogen physisorption isotherms were measured at 77 K for samples vacuum degassed at 393 K for 12 h before measurement. BET surface areas and porous

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