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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 were 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 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.

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Keywords

metal-organic frameworks; MIL-53(Fe); persulfate; catalytic activity; sulfate radical; chemical oxidation

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 (-N=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 H_2O_2 at room temperature [6], and $\text{SO}_4^{\cdot-}$ can be much more effective in 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 were 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 catalyst 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 Fe_3O_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, Fe_3O_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-88B [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 H_2O_2 [32], 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 also attracted a lot of attention. Up to now, 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, CH_4O , 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 (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 Cu K α ($\lambda = 0.15418$ nm) radiation, with a step size of 0.02° in two theta (2θ). 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 structures were measured using a surface area and porosity analyzer (ASAP 2020, micromeritics). Surface electronic states were analyzed via X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD, UK) with Al K α radiation operated at 1486.6 eV, 10 mA $\times$ 15 KV and 700×300 μ m. Binding energies were calibrated using C1s (284.6 eV) signal as standard. Zeta potential of the samples in ultrapure water was measured with Malvern Zetasizer Nano instrument (Malvern, UK). The amount of iron in MIL-53(Fe) was measured by atomic absorption spectrometer (Hitachi Z-2000, JP), with an extraction of MIL-53(Fe) in a boiling aqua regia solution for 1 h before detection.

2.4 Catalytic activity evaluation and analyses

Catalytic degradation of OG was conducted in a constant temperature shaker shaken at 180 rpm, 25 $^\circ$ C in a dark environment. In each experiment, MIL-53(Fe) was added into a series of 250 ml conical flasks filled with the desired concentration of OG and persulfate solution. The reaction and timer were started at the moment when MIL-53(Fe) added into the solution. The conical flasks were rotated for a required time length (for instance, 2 h, 3 h or 5 h) in the shaker throughout the experimental period. The initial pH value of the solution was adjusted using 0.05 M sulfuric acid (H $_2$ SO $_4$) or sodium hydroxide (NaOH) when needed.

At specific points in time, a certain quantity of sample was collected from the flask and mixed with pure ethanol immediately to quench the reaction. The mixed solution was then reserved for the detection of the residual content of OG and persulfate. All samples were filtrated through 0.45 μ m membrane filters prior to analysis. Samples were analyzed in duplicate within the accepted analytical error range ($\pm 5\%$), for which the average was used.

OG concentration was determined using UV-vis spectrophotometry at the wavelength of 478 nm. Persulfate anion concentration was determined by iodometry spectrophotometry at the wavelength of 352 nm. Iron ion concentration was measured by 1, 10-phenanthroline spectrophotometry at the wavelength of 510 nm. All the above detection were using Thermo Scientific Evolution 201 UV-Visible Spectrophotometers made in the USA.

2.5 EPR experiments and measurements

The measurement of free radicals was conducted as follows: Reactions was carried out in a 10 mL glass vial with PTEE-lined cap, with 9 mL Na $_2$ S $_2$ O $_8$ (PS, 32 mM) solution, 1 mL 5, 5-dimethyl-1-pyrroline N-oxide (DMPO, 88 mM) and 0.01 g MIL-53(Fe) inside. The final concentration of DMPO (used as the radical spin trap) was 8.8 mM in the reaction solutions. When sampling, the sample was taken out of the solution using a glass capillary and detected immediately by Electron Paramagnetic Resonance (EPR) apparatus.

EPR spectra of the samples were recorded at liquid nitrogen temperature with a Bruker A300 spectrometer (Switzerland), with a resonance frequency of 9.875 GHz, microwave power of 18.44 mW, modulation frequency of 100 kHz, modulation amplitude of 2.0 G, sweep width of 500 G, time constant of 81.92 ms, sweep time of 40.96 s, and receiver gain of 1.00×10^3 .

3. Results and discussion

3.1 XRD Characterization of MIL-53(Fe)

Since synthesis temperature and time are important factors that can determine the crystal structure of the material, it is important to choose proper preparation conditions before using MOF as a persulfate catalyst. MIL-53(Fe) was synthesized using different temperature and time length. The powder XRD patterns are presented in Fig. 1. It can be seen from Fig. 1(a) that synthesis temperature did have great influence on the structure formation of MIL-53(Fe). The XRD peaks at 2θ of 9.3° , 12.7° , 17.6° , 18.5° and 25.5° decay in intensity as the synthesis temperature increased from 150°C to 170°C . Above 170°C , as the temperature continues to rise, it deteriorated clearly and some of them disappeared. Meanwhile, only weak characteristic peaks at 2θ of 9.3° were observed when the samples synthesized at two temperatures below 150°C . It illustrates that the temperature has a dramatic effect on coordinating capacity of the organic ligands. The frame structure can be destroyed under high temperature [38], while it cannot fully develop under low temperature because metal ions and ligands cannot coordinate successfully without an accessible dynamic situation that the reaction requires [39]. So only the diffraction pattern of the sample that was synthesized under 150°C matches well with the published data [40], that its characteristic peaks were at 2θ of 9.3° , 12.7° , 17.6° , 18.5° , 25.5° and 27.3° , demonstrating that pure MIL-53(Fe) was prepared successfully under this condition. The evaluation result of the XRD patterns of MIL-53(Fe) is shown in Fig. 1(b) as a function of the synthesis time. The diffraction patterns of the samples synthesized equal or less than 3 d were in good agreement with the literature [40], the peaks (especially at 2θ of 12.7°) gradually grew in intensity as the synthesis time elapsed, indicating that the crystallinity of MIL-53(Fe) increased when prolonging the synthesis time from 5 h to 3 d, after which, however, it deteriorated again very apparently starting on 4 d, and finally almost disappeared after 5 d, which might attribute to the variations in the number of guest molecules remaining inside the pores [41] and the structural reorganization. This phenomenon was highly in accordance with previous observations of MIL-53(Al) synthesis [42]. Thus here the highest relative crystallinity was obtained for MIL-53(Fe)-J sample.

XRD patterns of MIL-53(Fe)-A, MIL-53(Fe)-M and MIL-53(Fe)-J after activating PS were also recorded in Fig. 2(a). It can be known from the results that the crystalline structure of MIL-53(Fe) changed a lot after activation, the characteristic peaks at 2θ of around 9.3° , 12.7° , 17.6° and 25.5° all deteriorated after the reaction, while new peaks at 2θ of 28.0° were observed for both three samples. This new peaks only appeared when MIL-53(Fe) was soaking in water with pH value adjusted to less than or equal to 3.0, which may be caused by iron leach-out [43]. The recession of the characteristic peaks did not be observed in adsorption experiments, which means that it can only cause by catalysis, rather than

adsorption or soaking in the water. The variation of the patterns suggested that CUS may act as an electron donor, provide active catalytic sites for PS activation, and therefore causes the ligand dissociation and the restructuring of the framework.

3.2 OG removal by MIL-53(Fe) activated persulfate

The catalytic performance of the as-prepared MIL-53(Fe) towards PS was observed by the decolorization of OG. Fig. 3(a) shows OG removal as a function of reaction time in the MIL-53(Fe) activated persulfate system. The OG removal rates for MIL-53(Fe)-A and MIL-53(Fe)-B activated persulfate were very similar, whereas significantly smaller rates are observed for MIL-53(Fe)-C and D (at the reaction time of 60 min, OG removal rate achieved 93.7%, 92.6%, 69.2% and 45.5% in oxidation by MIL-53(Fe)-A/B/C/D activated PS, respectively). However, when using MIL-53(Fe)-M and N as the catalyst, a very fast removal rate was observed within 10min after the reaction begins, and the removal curve of OG was quite different from others (when using MIL-53(Fe)-A/B/C/D as the catalyst), which seems like homogeneous catalysis, rather than heterogeneous. This is because MIL-53(Fe)-M and N were poorly crystallized (see Fig. 1(a)) thus decomposed quickly after the reaction begins. Take MIL-53(Fe)-M for example, the total iron concentration and ferrous iron concentration formed immediately after the reaction begin was determined to be 23 mg L^{-1} and 35 mg L^{-1} , and reached a high concentration of 18.6 mg L^{-1} and 72.4 mg L^{-1} after reaction for 120 min (Fig. S3), which were much higher than that formed in MIL-53(Fe)-A. Besides, MIL-53(Fe)-M was not stable and cannot maintain a good reusability in recycling experiments, which was quite different from MIL-53(Fe)-A (Fig. S4). Thus although MIL-53(Fe)-M and N possess better catalytic capacity than A and B, they are not recommended as the catalyst for PS because of poor crystallinity, instability, and reusability. Moreover, the precursor chemical (FeCl_3 and TPA) that used to synthesize MIL-53(Fe) were tested as the catalyst to activate persulfate. Since iron content in MIL-53(Fe)-A in weight percentage was determined to be 20% via the flame atomic spectrometry, the dosage of FeCl_3 and TPA were decided to be 0.2 g L^{-1} and 0.8 g L^{-1} . From the results, it can be seen that TPA alone cannot activate persulfate, but in the presence of FeCl_3 , OG can be degraded effectively, with a removal rate of 95.2% achieved after reaction for 120 min. But since (i) the amount of leachable total iron when using MIL-53(Fe)-A (8.7 mg L^{-1} to 32.1 mg L^{-1} , Fig. S3) as a heterogeneous PS catalyst can be decreased to a large extent than using FeCl_3 (51.2 mg L^{-1} to 69.5 mg L^{-1} , Fig. S3) as a homogeneous catalyst; and (ii) MIL-53(Fe)-A showed a good reusability as a PS catalyst, which has already been demonstrated in our previous work [43]. Therefore, using MIL-53(Fe) as PS catalyst is better than using FeCl_3 .

Considering these results obtained above, 150°C was chosen as the optimal synthesis temperature because the sample was fully crystallized in this case, and can maintain higher catalytic capacity as well. So MIL-53(Fe)-E~L were synthesized at 150°C using different time lengths. The catalytic capacity of A, E, F, G to L differ greatly from each other, with the catalytic abilities gradually declining with the increase of synthesis time. The samples using 5 hours synthesis time exhibits the strongest catalytic activity for PS. Fig.3 (b) presents the removal rates of OG as a function of time for oxidation by PS alone, MIL-53(Fe)-A/G alone, and PS activated by MIL-53(Fe)-A/E/F/G/H/I/J/K/L. Results

indicate that persulfate alone exhibited a relatively low reactivity towards OG, while the presence of MIL-53(Fe) could obviously promote the removal of OG. For example, at the reaction time of 120 min, the removal rates of OG were approximately 1%, 40%, 52%, 59%, 61%, 65%, 74%, 81%, 94% and 98% in PS alone and PS activated by MIL-53(Fe)-L/K/J/I/H/G/F/E/A, respectively. The adsorption of OG by MIL-53(Fe)-A or MIL-53(Fe)-J alone after 120 min contributed only approximately 3% removal of OG. And similar weak adsorption behavior was also observed in the case of MIL-53(Fe)-E/F/G/H/I (Fig. S1). These results indicate that the enhanced removal of OG in the MIL-53(Fe)/PS system was mainly due to catalytic persulfate oxidation rather than adsorption.

In order to better understand the weak adsorption capacity of MIL-53(Fe) towards OG, zeta potential of MIL-53(Fe) was measured to analyze the electrostatic interactions between the catalyst and OG. The results from Fig. S2 show that the isoelectric point of MIL-53(Fe)-A/J were at 10.4 and 10.2, respectively. And the quantity of electric charge of MIL-53(Fe)-A/J were determined to be around 4 to 12 mV, and hence there is a weak electrostatic interaction between positively charged MIL-53(Fe) and OG anions. Theoretically speaking, that interaction was helpful for the adsorption of OG anions, but a weak adsorption behavior still observed. This may due to the following factors: (i) The BET surface area (show later in Table 1) and pore size of MIL-53(Fe) ($V = 904\sim 1593 \text{ \AA}^3$, $x = 15.96\sim 21.13 \text{ \AA}$, $y = 7.61\sim 14.39 \text{ \AA}$ [44]) is relatively small and not sufficient for OG (with a molecular size of $13.08 \times 7.53 \times 4.98 \text{ \AA}$ [45]) to enter in the inner space; (ii) both the adsorbate and adsorbent have benzene rings, and thus π - π stacking (between the benzene rings of OG and MIL-53(Fe)) on MIL-53(Fe) lead to a weak adsorptive attraction [46] and (iii) Since there is no Lewis base group on OG, the CUS of MIL-53(Fe) cannot act as an active species to bind OG. Huo et al. reported that the adsorption on CUS of MIL-100(Fe) towards malachite green (MG) dye molecule was attributed to an interaction between the Lewis base $\text{-N(CH}_3)_2$ on MG and the Lewis acid CUS of MIL-100(Fe), and the interaction occurred because water molecules can be substituted by the Lewis base group [47].

3.3 SEM, BET and XPS characterization of MIL-53(Fe)

To explain the causes of different catalytic activities shown in the above experiments, SEM images of MIL-53(Fe) were collected, and BET surface areas were determined. From SEM, the morphologies and particle sizes of MIL-53(Fe) can be observed. As is seen in Fig. 4, the as-synthesized MIL-53(Fe)-A consists of collapsed octahedron crystals with a non-uniform diameter from 80–500 nm, which is consistent with a previous report [48] and the calculated values from XRD pattern showed in Fig. 1. According to the Debye-Scherrer formula, the average grain size of MIL-53(Fe)-A was calculated to be 94 nm, others were 116, 97, 79 and 90 nm for MIL-53(Fe)-E/F/H/J. Although the octahedron of similar shape and size like MIL-53(Fe)-A can still be seen in MIL-53(Fe)-E/F/H/J, the morphology of them have obvious changes, the amount of octahedron decrease and a large number of irregularly shaped crystals are observed. As the synthesis time increases, the octahedron particles gradually disappear, implying that they tend to aggregate and re-combine to transform into larger particles. With the great changes of morphology, the active catalytic sites, Fe CUS, were more unordered and unevenly distributed and thus weakening the catalytic properties of MIL-53(Fe).

The S_{BET} and Total pore volume of MIL-53(Fe)-A were determined to be $88.64 \text{ m}^2 \text{ g}^{-1}$ and $0.1206 \text{ cm}^3 \text{ g}^{-1}$ (Table 1), respectively. As a comparison, the reported BET surface areas and pore sizes of MIL-53 from other literature were also provided in Table 1. It can be seen that MIL-53(Fe) synthesized by different conditions possesses a quite different BET surface areas [26, 49–51]. The BET surface area and total pore volume of MIL-53(Fe)-E/F/G/H/I/J decrease dramatically compared to MIL-53(Fe)-A, verifying that MIL-53(Fe) with the morphology of small octahedrons possess larger BET surface area. It is the aggregation of the octahedron and the generation of the larger irregular shaped particles that causes the obvious decrease of its BET surface area. And the lower surface area observed indicates that the anhydrous form of MIL-53(Fe) exhibits closed pores with almost no accessible porosity to nitrogen gas at 77 K [52]. The adsorption average pore width (4V/A by BET) exhibited a pore size centered about 3.03–16.00 nm. Another point that needs attention is that the decrease of BET surface area is not the only reason that causes the reduction of the catalytic capacity of MIL-53(Fe). Because compared with MIL-53(Fe)-A, the S_{BET} of MIL-53(Fe)-E decrease sharply, its catalytic activity only decreased slightly (Fig. 2(b)), and the catalytic activities of MIL-53(Fe)-H/I/J were very close to each other. Thus, there must be other factors that determine the catalytic activity of this material.

In order to further explain the differences of catalytic activities between the as-prepared MIL-53(Fe) materials, XPS spectra were recorded to analysis the elementary composition and element valence. Results showed that MIL-53(Fe) contained only C, Fe and O. The relative mass percentages of C, Fe, and O were approximately 68%, 11%, and 21%, respectively. The relative content of N was too low to quantify, this means that DMF (the only source of N) was sufficiently removed from MIL-53(Fe) during the elution process, which was attributed to the ligand dissociation between iron and DMF (because iron cations coordinated with DMF in the process of synthesis), followed by the exposure of iron coordinative unsaturated metal center [53]. This means iron CUS was successfully formed, and hence can provide the feasible site for activating persulfate. Full scan spectra and curve fitting for C, Fe, and O were conducted to quantitate the contribution of each valence state. The survey spectrums with the fitting results of C 1s, Fe 2p and O 1s spectra of MIL-53(Fe)-A and MIL-53(Fe)-G are displayed in Fig. 5 where the original data are shown as dots, and the calculated fit is plotted in a line-style. Fe 2p spectrum is composed of a doublet structure due to multiples splitting ($\text{Fe } 2p_{3/2}$ and $\text{Fe } 2p_{1/2}$). The $\text{Fe } 2p_{3/2}$ spectrum (Fig. 5 (c)) can be classified into three major peaks (named Fe-1, Fe-2, and Fe-3) with binding energies at 709.4, 711.3 and 713.9, represent Fe(II), Fe(III) and Fe(II) as suggested in previously studies, respectively [54]. Fig. 5 (d) shows the detail spectra of the O 1s. Each spectrum can be fitted with five components (named O-1, O-2, O-3, O-4, and O-5). Based on the results reported in another study [55], these five components can be assigned to different chemical compounds: Fe_3O_4 , FeOOH , $\text{HOCC}_6\text{H}_4\text{COOH}$, $\text{C=O/H}_2\text{O}$ and $\text{HOCC}_6\text{H}_4\text{COOH}$, respectively. The peak fitting results of both Fe 2p and O 1s all indicate that the major existent states of Fe are Fe(II) and Fe(III). In addition, based on our analysis data, it can be seen that the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ relative content ratio decreased from 1.76 (MIL-53(Fe)-A) to 0.87 (MIL-53(Fe)-G) when prolonging the synthesis time from 5 h to 72 h, which reveals that Fe^{II} CUS decreased during this process. These findings suggest that the increase of $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$

relative amount ratio at the node of framework unit could enhance the catalytic activity of the MIL-53(Fe) catalyst.

3.4 Influence of MIL-53(Fe) dosage, PS concentration and OG initial concentration on OG removal

In this section, MIL-53(Fe)-A was used to activate persulfate and degrade OG. Batch experiments were conducted as below to obtain the optimal catalytic and degradative conditions. The influence of persulfate concentration (range from 2 mM to 32 mM, corresponding to 10:1 to 160:1 of PS/OG molar ratio) on OG decolorization rate was detected while maintaining OG initial concentration and MIL-53(Fe)-A dosage at 0.2 mmol L⁻¹ and 1 g L⁻¹ at an ambient pH. Fig. 6 shows the time-dependent OG concentration profiles measured at 25 °C under different persulfate initial concentrations. Kinetic constants are listed in Table 2. The OG decolorization was well fit by the first-order reaction model ($R^2 > 0.99$), and the decolorization process can be described by one stage. It clearly shows that the value of k increased with the increasing of persulfate concentration. The apparent rate constants of OG degradation (k)/10⁻² were 0.05, 0.77, 1.67, 2.63, 3.33 and 4.56 min⁻¹ at the initial PS concentration of 2, 16, 20, 24, 28 and 32 mM, respectively. These indicate that increase of initial persulfate concentration can accelerate the degradation reaction of OG by MIL-53(Fe)-A catalyzed persulfate, due to the generation of more SO₄^{•-} in the system. However, minimal additional degradation occurs after 90 min when PS initial concentration was 32 mM, indicating that PS was in excess. So PS/OG molar ratio of 32 was the best choice to degrade OG within the shortest time.

Fig. 7(a) shows the OG degradation curve over the reaction time when using different MIL-53(Fe)-A dosage. PS used in this experiment was 24 mM, equivalent to 120:1 of PS/OG molar ratio. From the results, it is clear that the optimal catalyst dosage is 0.5 to 1.0 g L⁻¹, whereas OG removal rate decreased when catalyst dosage was below 0.3 g L⁻¹ and increased slightly only when the dosage was 1.5 or 2.0 g L⁻¹. This may be due to the excessive available CUS for persulfate activation, which resulted in the waste of CUS as the active catalytic site.

The 32 mM PS dosage may cause an overdose of residual SO₄²⁻ in solution, and thus the effect of different initial OG concentration was tested as shown in Fig. 7(b). Results show that MIL-53(Fe) activated PS system was suitable for higher OG initial concentration to 0.5 mM. Although the degradation rate decreases, OG can still be fully removed after 180 min. In this situation, PS/OG molar ratio was 64:1.

PS consumption during the reaction process was monitored, as depicted in Fig. 8. After 120 min, the conversion rate of PS achieved 22.6%, the depletion of PS verified that the addition of MIL-53(Fe) promoted the decomposition of PS and the generation of free radicals, making it possible that OG can be degraded through oxidation. Fig. 8 also shows the removal of COD in this system as a function of time. As expected, COD removal rate was about 55% after reaction for 1 h and reached 74% after 2 h. Therefore, it is possible to degrade OG efficiently when using this system.

3.5 Free radical quenching experiment using molecular probes

In order to gain insight into the degradation mechanism, scavenging experiments were conducted. Ethanol (EtOH), tert butyl alcohol (TBA) and nitrobenzene (NB) are three commonly used candidates for free radicals quenching experiments. This is because EtOH is regarded as scavengers of both $\text{SO}_4^{\cdot-}$ ($k = (1.6\text{--}7.7) \times 10^7$) and $\text{OH}^{\cdot}$ ($k = (1.2\text{--}2.8) \times 10^9$), while TBA and NB are considered as the scavenger of only $\text{OH}^{\cdot}$ ($k_1 = (3.8\text{--}7.6) \times 10^8$ and $k_2 = (3.0\text{--}3.9) \times 10^9$) (rather than $\text{SO}_4^{\cdot-}$) [56]. Both TBA and NB are good scavengers to identify $\text{SO}_4^{\cdot-}$. As expected, at the reaction time of 90 min, the removal rates of OG decreased to 55.3%, 42.8% and only 17.8% in the presence of NB, TBA and EtOH, respectively (Fig. 9). All the fitting results of kinetic constants (k) decreased to some extent after adding the scavenger (Table S1). It is evident that the presence of EtOH resulted in a significant decrease on OG removal, which indicates that free radical oxidative reactions were vital to the degradation of OG. The addition of TBA and NB slowed down the degradation rate to a certain degree, but OG was still able to be completely removed after 300 min of reaction. Since $\text{OH}^{\cdot}$ can be completely consumed by TBA and NB, leaving $\text{SO}_4^{\cdot-}$ remaining, this strongly indicates that both $\text{SO}_4^{\cdot-}$ and $\text{OH}^{\cdot}$ were involved in this oxidation process.

3.6 The role of pH in the removal of OG by MIL-53(Fe)/PS and the generation of free radicals

Since solution pH has a significant effect on the oxidation of organic pollutants, the removal rate of OG was measured in the initial pH range of 2.5–7 within 300 min as shown in Fig. 10. The pH value of 2.5 represents the situation without adjustment. Results indicate that OG removal ratio decreased rapidly as water pH increased to 3, and tend to be extremely slow when initial pH was above 4, implying that MIL-53(Fe) activated PS system was most applicable in the acidic environment. It is because pH higher than 4 led to the precipitation of surface $\equiv\text{Fe}^{3+}$ ions to form oxyhydroxides (see following equations (1) to (4)) [57], and thus have low efficiency for activating persulfate to form sulfate radicals.

And the precipitation of surface $\equiv\text{Fe}^{2+}$ occurs (Eqn. (5) and (6)) when pH value above 6 [58]. The precipitation of $\equiv\text{Fe}^{3+}$ and $\equiv\text{Fe}^{2+}$ ions inhibited the activation of persulfate, and thus weakened the oxidative ability of this system.

To explain the decrease of oxidative capacity of MIL-53(Fe) activated persulfate system at higher pH conditions, different radicals and combinations of radicals were detected under different pH conditions using EPR, the results are shown in Fig. 11. As shown in Fig. 11(b), a typical six split lines of DMPO- SO_4^- and four split lines of DMPO-OH signals with $g = 2.011$ at symmetry centre were formed. The hyperfine splitting constants (HFSC) of DMPO radical adducts were $a_N = a_H = 14.2$ G (DMPO-OH) and $a_N = 13.1$ G, $a_H = 10.2$ G, $a_H^{\gamma 1} = 1.45$ G, $a_H^{\gamma 2} = 0.75$ G (DMPO- SO_4^-). These signal were in agreement with the literature data [59] and are characteristics for the stable adduct with $\text{OH}^\cdot$ and $\text{SO}_4^{\cdot-}$, suggesting that both $\text{SO}_4^{\cdot-}$ and $\text{OH}^\cdot$ were the predominant radical species and play an important role in OG degradation at pH 2.5, which was also verified by quenching experiment shown in Fig. 9. The formation of both DMPO- SO_4^- and DMPO-OH signal in MIL-53(Fe)/PS were much higher than that in PS alone, indicating that the concentration of $\text{SO}_4^{\cdot-}$ and $\text{OH}^\cdot$ in MIL-53(Fe)/PS was higher than that in PS, that was why PS alone cannot decolorize OG. But the intensity of DMPO-OH signal decreased obviously at pH 3, with another two different DMPO adducts appeared. On the basis of the HFSC, this spectrum can be explained as being the result of superposition of the spectra of three adducts, DMPO-OH, DMPO-OOH (the adduct of superoxide radical $\text{O}_2^{\cdot-}$ [60], a four-line spectrum with relative intensities of 1:1:1:1 and $a_N = 14.1$ G, $a_H^\beta = 11.2$ G, $a_H^\alpha = 1.3$ G) and DMPO- $\text{CH}_3^\cdot$ (the adduct of methyl radical $\text{CH}_3^\cdot$ [61], a six-line spectrum with relative intensities of 1:1:1:1:1:1 and $a_N = 15.2$ G, $a_H = 22.8$ G), respectively. This means that reactive radical species $\text{O}_2^{\cdot-}$, $\text{SO}_4^{\cdot-}$ and $\text{OH}^\cdot$ coexist at pH 3. Since there were no methanol nor DMSO (Dimethyl sulfoxide) that added into this system, the existence of $\text{CH}_3^\cdot$ may be explained by the derivation of DMPO, namely the products of DMPO decomposed by oxidation with the $\text{OH}^\cdot$ [62]. It was found that the intensity of DMPO-OH and DMPO- $\text{CH}_3^\cdot$ signal enhanced clearly at pH 5, and achieved the strongest at pH 7. Combine with earlier data in Fig. 10. It can be seen that the conversion of $\text{OH}^\cdot$ to $\text{CH}_3^\cdot$ weakened the oxidative ability of MIL-53(Fe) activated persulfate.

Based on the above data that we acquired, herein, a possible mechanism (Fig. 12) was proposed as follows. According to our previous work [43], when solution pH was 2.5, Fe^{II} CUS and Fe^{III} CUS (represent iron species that exist in the framework of MIL-53(Fe)) work as heterogeneous catalytic active site for persulfate activation, and thus generated $\text{SO}_4^{\cdot-}$ and $\text{S}_2\text{O}_8^{\cdot-}$ (Eqn (7), (8)). And Fe^{II} CUS can react with dissolved O_2 and generated reactive oxidants (ROS) $\text{O}_2^{\cdot-}$ (Eqn (9)). But $\text{O}_2^{\cdot-}$ only act as an intermediate, and thus it reacts with

H^+ and Fe^{II} CUS rapidly and finally generated $OH\cdot$ (Eqn (10) to (12), and it can also react with residual persulfate and generated $SO_4\cdot^-$ (Eqn (13)). That's why the signal of DMPO-OOH was relatively weak in this condition. In addition, iron ion (Fe^{2+} and Fe^{3+}) that existed in the solution which was caused by the leach of MIL-53(Fe)) also act as an electron donor for activating persulfate, but homogeneous reaction only provides a minor contribution to the oxidative processes (Table. S2).

Also, the hydrolysis of $SO_4\cdot^-$ happened in all solution pH thus generated $OH\cdot$ and $S_2O_8\cdot^-$ (Eqn (14) to (16)).

So It can be concluded that $\text{SO}_4^{\cdot-}$, $\text{OH}\cdot$, $\text{S}_2\text{O}_8^{\cdot-}$ coexisted when solution pH was 2.5. But it is possible that hydroperoxide ($\text{HO}_2^{\cdot-}$) generated when solution pH increase (Eqn (17)) through the hydrolysis of one persulfate molecule, then it reacted with another persulfate molecule, generated $\text{SO}_4^{\cdot-}$ and sulfate anion, with itself oxidized to superoxide ($\text{O}_2^{\cdot-}$) (Eqn (18)) [63]. This can be summarized to Eqn (19) and can explain why $\text{O}_2^{\cdot-}$, $\text{SO}_4^{\cdot-}$, and $\text{OH}\cdot$ coexisted when solution pH was above 3. But although $\text{O}_2^{\cdot-}$ formed in this condition, it can react with both $\text{SO}_4^{\cdot-}$ and $\text{OH}\cdot$, shown as Eqn (20) to (21) [64], resulted in the generation of the oxygen molecule and the reduction of effective free radicals, and thus weakened the oxidizing ability of the MIL-53(Fe) activated persulfate system.

4. Conclusions

In summary, MIL-53(Fe) was successfully synthesized by the solvothermal method under various conditions. The synthesis condition did have great influence on the structure formation of MIL-53(Fe). Among all the tested temperatures, 150 °C is optimum for the crystallization of MIL-53(Fe). MIL-53(Fe) cannot fully develop under the temperature below 150 °C. Some of the characteristic peaks of MIL-53(Fe) deteriorated clearly and even disappeared when increase the synthesis temperature from 150 °C to 220 °C, indicating a reduced crystallinity. Whereas the crystallinity of MIL-53(Fe) increased when prolonging the synthesis time from 5 h to 3 d, but the intensity of the characteristic peaks decreased very apparently starting on 4 d, and finally almost disappeared after 5 d. The various MIL-53(Fe) samples were then evaluated in the degradation of OG under ambient conditions. The best degradation result was achieved with sample MIL-53(Fe)-A. Causes for the differences between catalytic activities were investigated. As the synthesis time increase, the morphology of the MOF samples change greatly from collapsed octahedron crystals to irregularly shaped crystals and hence lead to the decrease of BET surface area (from 88.6 to a lowest 5.0 m² g⁻¹). But it was found that BET was not the only reason that changes the catalytic capacity of MIL-53(Fe). XPS results of two samples showed that the percentage

content of Fe^{II} CUS in these frameworks dropped when prolonging the synthesis time from 5 h to 72 h, which also weakened the catalytic reactivity. Batch experiments using MIL-53(Fe)-A as the catalyst to activate persulfate and degrade OG under different situations were conducted. At optimal reaction conditions, OG can be completely decolorized after 90 min, and COD removal rate achieved 74% after 120 min. But solution pH has a strong influence on the degradation of OG. This system was most applicable in acidic pH environment, which may be associated possibly with the change of iron species of the active catalytic site on the MIL-53(Fe) surface. In addition, EPR spectra and free radical quenching experiments showed that sulfate radical (SO₄^{•-}), hydroxyl radical (OH[•]), persulfate radical (S₂O₈^{•-}), as well as superoxide radical (O₂^{•-}), coexist in MIL-53(Fe) activated PS systems. With solution pH increase, the amount of each free radicals change significantly, and hence the oxidative abilities of this system altered. This work provides guidance for the application of MOF-based catalysts for activated-persulfate systems.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

XRD patterns of the MIL-53(Fe) synthesized in this work. For clarity, (a) 100, 120, 150, 170, 200, 220 °C (the same synthetic time: 5 h); (b) 5, 8, 10, 12, 24, 48, 72, 96 and 120 h (but under the same synthetic temperature: 150 °C)

Figure 2.

XRD patterns of (a) MIL-53(Fe) samples after activation PS and (b) MIL-53(Fe)-A after soaking in water with pH value adjusted to different conditions. Experimental conditions: [OG] = 0.2 mM, [PS] = 32 mM; MIL-53(Fe) dose = 1 g L⁻¹; T = 25 °C, ambient pH.

Figure 3.

OG degradation and adsorption curve in different MIL-53(Fe) activated persulfate systems.

(A) 5 h/150 °C; (B) 5 h/170 °C; (C) 5 h/200 °C; (D) 5 h/220 °C; (E) 8 h/150 °C; (F) 10 h/150 °C; (G) 12 h/150 °C; (H) 24 h/150 °C; (I) 48 h/150 °C; (J) 72 h/150 °C; (k) 96 h/150 °C; (L) 120 h/150 °C; (M) 5 h/120 °C; (N) 5 h/100 °C. Experimental conditions: [OG] = 0.2 mM, [PS] = 32 mM; MIL-53(Fe) dose = 1 g L⁻¹; FeCl₃ dose = 0.2 g L⁻¹; TPA dose = 0.8 g L⁻¹, T = 25 °C, ambient pH.

Figure 4. SEM image of MIL-53(Fe) under different situations: (a) and (b) MIL-53(Fe)-A (c) MIL-53(Fe)-E (d) MIL-53(Fe)-F (e) MIL-53(Fe)-H (f) MIL-53(Fe)-J. The magnifications of picture (a) were 100 thousand, (b) to (f) were 20 thousand, respectively.

Figure 5. (a) Full scan XPS spectra of MIL-53(Fe)-A/G and its fine spectra of (b) C, (c) Fe, (d) O elements.

Figure 6.

Influence of persulfate concentration on OG decolorization. Experimental conditions: $[OG] = 0.2 \text{ mM}$, Catalyst dose = 1 g L^{-1} , $T = 25 \text{ }^{\circ}\text{C}$, ambient pH.

Figure 7.

Influence of MIL-53(Fe)-A dosage and OG initial concentration on OG decolorization.

Experimental conditions: (a) $[OG] = 0.2 \text{ mM}$, $[PS] = 24 \text{ mM}$, $T = 25 \text{ }^\circ\text{C}$, ambient pH; (b) catalyst dose = 1 g L^{-1} , $[PS] = 24 \text{ mM}$, $T = 25 \text{ }^\circ\text{C}$, ambient pH.

Figure 8.

PS consumption and COD conversion as a function of time in the system when using MIL-53(Fe)-A as the catalyst. Experimental conditions: [OG] = 0.2 mM, [PS] = 32 mM, T = 25 °C, ambient pH.

Figure 9.

Influence of radical scavenger (ethanol, TBA and NB) on OG degradation. Experimental condition: [OG] = 0.2 mM, [PS] = 32 mM, catalyst dose = 1 g L⁻¹, T = 25 °C, ambient pH. The molar ratio of Radical scavenger/OG = 500:1.

Figure 10.

Influence of initial solution pH on OG removal. Experimental condition: [OG] = 0.2 mM, [PS] = 32 mM, catalyst dosage = 1 g L⁻¹, T = 25 °C. The measurement error of pH value by the pH meter are ± 0.05 .

Figure 11.

EPR spectra of DMPO mixed with MIL-53(Fe)-A activated PS when initial solution pH adjusted to different values (a) PS + DMPO (b) MIL-53(Fe) + PS + DMPO, pH = 2.5 (c) MIL-53(Fe) + PS + DMPO, pH = 3 (d) MIL-53(Fe) + PS + DMPO, pH = 5 and (e) MIL-53(Fe) + PS + DMPO, pH = 7. Number: 1 represented the DMPO-OH adduct, 2 represented the DMPO-SO₄ adduct, 3 represented the DMPO-OOH adduct, and 4 represented the DMPO-CH₃ adduct. Experimental condition: [OG] = 0.2 mM, [PS] = 32 mM, catalyst dosage = 1 g L⁻¹, [DMPO] = 8.8 mM, t = 1 min, T = 25 °C. The measurement error of pH value by the pH meter are ± 0.05.

Figure 12.
Possible mechanism of MIL-53(Fe) activated persulfate

Table 1

Structural properties of MIL-53(Fe) prepared under different synthesis conditions

Samples name	Time (h)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{g}^{-1} \times 10^{-2}$)	Pore size (nm)	Reference No.
MIL-53(Fe)-A	5	88.64	12.06	3.03	This study
MIL-53(Fe)-E	8	7.45	2.19	8.80	This study
MIL-53(Fe)-F	10	6.80	1.82	10.73	This study
MIL-53(Fe)-G	12	6.48	1.60	11.73	This study
MIL-53(Fe)-H	24	5.13	1.60	12.45	This study
MIL-53(Fe)-I	48	5.03	1.43	12.71	This study
MIL-53(Fe)-J	72	3.59	1.41	16.00	This study
MIL-53(Fe)	—	19.10	4.80	—	[26]
MIL-53(Fe)	—	23.00	2.15	9.81	[49]
MIL-53(Fe)	—	965	—	—	[50]
MIL-53(Fe)	—	47.9	6.00	—	[51]

Table 2

The apparent rate constant of OG degradation in MIL-53(Fe) activated persulfate systems

C(PS)	k/10 ⁻² min ⁻¹	R ²
0.2 mM	0.05	0.99
16 mM	0.77	0.99
20 mM	1.67	0.99
24 mM	2.63	0.99
28 mM	3.33	0.99
32 mM	4.56	0.99