Insights into the novel application of Fe-MOFs in ultrasound-assisted heterogeneous Fenton system: Efficiency, kinetics and mechanism

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\textbf{Abstract}

In this work, as a new strategy, ultrasound/H\textsubscript{2}O\textsubscript{2}/MOF system was firstly applied by environmental-benign Fe-MOFs (MIL-53, MIL-88B and MIL-101) for tetracycline hydrochloride removal. The synthetic Fe-MOFs were characterized by XRD, FTIR, SEM, XPS, \textit{N\textsubscript{2}} sorption-desorption isotherms and CO-FTIR. MIL-88B demonstrated the best catalytic performance because of its highest amount of Lewis acid sites. Influencing factors, contrast experiment, and corresponding dynamics were carried out to obtain the best experimental conditions and reaction system. Under optimal conditions ([Tetracycline hydrochloride] = 10 mg/L, [MIL-88B] = 0.3 g/L, [H\textsubscript{2}O\textsubscript{2}] = 44 mM, [ultrasound power] = 60 W, and pH = 5.0), the-first-order kinetic rate constant \(k\) was calculated to be 0.226 min\(^{-1}\), higher than the simple combination of the ultrasound system (0.004) and MIL-88B/H\textsubscript{2}O\textsubscript{2} system (0.163), indicating the importance of synergistic effect between ultrasound and Fenton reaction. EPR test and quenching experiment proved that -OH is mainly responsible for tetracycline hydrochloride removal. The major reaction path is the adsorption and decomposition of H\textsubscript{2}O\textsubscript{2} by coordinative unsaturated iron sites on Fe-MOF, but it is not the only path. The direct decomposition of H\textsubscript{2}O\textsubscript{2} and the cavitation effect caused by ultrasound also contribute to the generation of \(-\text{OH}\).

1. Introduction

Nowadays, the worldwide usage of antibiotics has posed an increasing threat to the aquatic environment since some of them are persistent and stable [1]. As a widely used therapeutic medicine, tetracycline hydrochloride (TC-HCl) is frequently detected in water, which poses a serious threat to aquatic life and human beings through the food chain and bioaccumulation [2]. The conventional water treatment processes are not effective to remove antibiotics since they are refractory to biodegradation [3]. Therefore, searching for new effective and environmentally benign treatment strategies has become an urgent topic over the world.

Fenton and Fenton-like reactions, exhibiting excellent characteristics of the low energy input and strong oxidation capability, have captured tremendous attentions in antibiotics removal [4,5]. Nevertheless, the strict and narrow pH range (pH 2.8–3.5), the loss of the catalyst and Fenton iron sludge hamper its further application to some extent. In order to improve the applicability of the traditional Fenton process, solid iron-based catalysts such as Fe\textsubscript{3}O\textsubscript{4}, FeOCl, MnFe\textsubscript{2}O\textsubscript{4} and α-Fe\textsubscript{2}O\textsubscript{3} have been developed in heterogeneous Fenton-like processes [6–9]. Among various solid catalysts, Fe-MOFs, containing iron ions or clusters and organic ligands, show great potential in heterogeneous Fenton-like reaction [5,10]. Fe is non-toxic and abundant in crustal minerals. The synthesis of Fe-based MOFs is cheaper and easier than many other MOFs [11,12]. Moreover, the tunable porosity, large surface areas and wide distribution of single iron sites endow Fe-based MOFs with abundant exposed active sites, which are significant for the adsorption of H\textsubscript{2}O\textsubscript{2} and the formation of -OH in the heterogeneous Fenton-like reactions [10]. It has been proved that -OH radicals are mainly responsible for pollutant removal in Fe-MOFs heterogeneous Fenton-like systems. The generation rate of -OH is related to two key points: the interaction of H\textsubscript{2}O\textsubscript{2} with the active sites and the reduction rate of Fe(III) to Fe(II) [10]. Fe-MOFs have abundant exposed active sites, which make their catalytic performance better than traditional heterogeneous catalysts. However, the common mass transfer rate and the single generation path of -OH limit the reaction rate. New technology need to be explored to accelerate
pollutant removal efficiency.

Ultrasound (US) has been developed into an attractive method for organic pollutant removal since 1990 because of its special advantages of safety, cleanness, no secondary pollutants and high penetrability [13]. The “hot spot” theory and “sonoluminescence” phenomenon caused by ultrasonic cavitation lead to the formation of oxygen radicals and the degradation of recalcitrant organic compounds [14–16]. However, US itself has the disadvantages of expensive equipment and large energy input, which seriously limits its application in the actual water treatment process. Accordingly, combining US with other energy sources (i.e. ultraviolet/visible irradiation), catalyst, and chemical additives can improve the scavenging efficiency of oxygen radicals and reduce the amount of oxidizer added (Eqs. (1)–(3), “” denotes the ultrasonic irradiation);

\[
\begin{align}
H_2O(\text{aq}) + \text{US} &\rightarrow \text{OH} + \cdot H \\
O_2(\text{aq}) + \text{US} &\rightarrow 2\text{H}_2\text{O} + 4\cdot \text{OH} \\
2\cdot \text{OH} + \cdot H &\rightarrow 2\text{H}_2\text{O} \\
2\cdot \text{OH} &\rightarrow \text{H}_2\text{O}_2
\end{align}
\]

2) US can promote the decomposition of \(H_2O_2\) to generate \(\cdot OH\) [20]; 3) US can also accelerate the mass transfer and the reduction rate of Fe (III) to Fe(II) [21]. As heterogeneous Fenton materials, Fe-MOFs reasonably have higher catalytic efficiency in ultrasound/Fenton system. However, most previously reported literature used US as a synthesis method of Fe-MOF, and no research used it as an assistant method for removing organic pollutant in water by Fe-MOF based heterogeneous Fenton system.

In this work, the US/Fenton catalytic performance of MIL-Fe-MOFs was firstly explored to remove tetracycline hydrochloride. The removal performance of different Fe-MOFs, the influential factors, the system contrast experiments, the kinetic and the mechanism analysis were conducted. This work will open up a new perspective for the application of Fe-based MOF materials, reveal the attractive potential of ultrasonic technology for pollutant removal, and provide a valuable direction in the field of water treatment.

2. Experimental

2.1. Materials

All solvents and reagents were obtained from commercial sources without any purification. Ferric chloride hexahydrate (FeCl₃·6H₂O), terephthalic acid (H₂BDC) and sodium hydroxide (NaOH) were obtained from Aladdin, China. Dimethylformamide (DMF) was supplied by Titan, China. Hydrogen peroxide (H₂O₂, 30%) was purchased from Lingfeng Chemical Reagent Co., LTD, China. Terti-butanol (TBA, ≥99%) and phosphoric acid (H₃PO₄) were provided by Kelong Chemical Reagent Factory, China. Deionized water was used during the whole experiment.

2.2. Synthesis of Fe-MOFs

MIL-88B was synthesized by the solvothermal method described in previous publication with some modifications [22]. Briefly, 2.703 g FeCl₃·6H₂O, 1.16 g H₂BDC, 4.0 mL NaOH (2 M) and 50 mL DMF were mixed and stirred at room temperature to form a clear solution. The mixed solution was then transferred into a Teflon-lined reactor and kept at 100 °C for 12 h. After cooling, the precipitate was collected by centrifugation. Impurities of the precipitate were removed by repeated washing with DMF (50 mL) and ethanol (50 mL). Finally, the product was dried at 110 °C in vacuum, and ground manually into powder. The synthesis processes of two other Fe-MOFs (MIL-53 and 101) were described in detail in the Text S1.

2.3. Characterization

The surface morphology of the obtained products was observed by scanning electron microscopy (SEM, FEI Inspect F50, USA). The crystal structure was characterized by an X-ray diffractometer (XRD, Smartlab 9, Japan) with a current intensity of 150 mA over the 20 scanning range of 5-40. Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR spectrometer (PerkinElmer, USA). X-ray photoelectron spectroscopy (XPS) patterns were received with a spectrometer (ThermoFisher Scientific K-Alpha, USA). Brunauer-Emmett-Teller (BET) method was used to measure the specific surface area (SSA) and porosity by N₂ adsorption at 77 K (ASAP 2460, Micromeritics, USA). The coordinatively unsaturated ions in catalysts were tested by CO adsorption infrared spectra (CO-FTIR, VERTEX 70, Germany), and the method was described in Text S2. The concentration of Tetracycline hydrochloride was obtained from a UV–Vis spectrometer (TU-1900, PERSEE, China) at the wavelength of 357 nm. The mineralization degree of contaminants were analysed by a Total Organic Carbon analyser (TOC, multi N/C-3100, Germany). The iron ions leached of the withdrawn solution were measured with inductively coupled plasma optical emission spectroscopy (ICP, Perkin Elmer Optima 5300DV, USA). The ROS generated in the US/Fenton system was investigated with EPR technique (Bruker A320, Germany). Cyclic voltammetry curves were recorded on an electrochemical work station (CV, CHI760e, China), the experimental condition was shown in the Text S3.

2.4. Evaluation of degradation performance

Tetracycline hydrochloride (TC-HCl, 10 mg/L) was chosen as the targeted pollutant to evaluate the US/Fenton performance of the as-prepared catalysts. Adsorption is a precondition for the degradation of TC-HCl. Firstly, the suspension containing 0.2 g/L of catalysts and 50 mL of TC-HCl solution was stirred vigorously in the dark for 30 min to achieve the adsorption−desorption equilibrium. Then, 44 mM of H₂O₂ was added into the above solution, followed by ultrasonic treatment using an ultrasonic cleaner (KHS200DE, 40 Khz ± 10%). Approximately 4 mL of the suspension was extracted with a syringe at a regular interval, and solid particles were removed by filtration with a 0.22 μm membrane. The data was recorded to calculate the removal efficiency. Comparing experiment was conducted by using MIL-53, MIL-88B, MIL-101 and α-Fe₂O₃ in US/Fenton system. Influencing factors experiments were investigated by changing the reaction conditions such as US power, catalyst dosage, H₂O₂ concentration and pH value. Quenching experiments and EPR test were conducted to ascertain the main reactive oxidation species (ROS) that responsible for the degradation of TC-HCl, TBA and N₂ were used as quenchers. H₂PO₄ was added into the solution during the US/Fenton process to explore the mechanism.

3. Results and discussion

3.1. Structure of Fe-MOFs

As shown in Fig. 1a, XRD characterization was carried out to obtain the crystal structure of MIL-88B, MIL-53 and MIL-101. The peak at ~10° may be related to the different topologies and crystal structure of all Fe-MOFs. All particles displayed well-defined diffraction peaks, which matches well with the simulated ones reported in the previous literatures [22,23], demonstrating the successful synthesis of the Fe-MOFs. The typical diffraction peaks of (002), (101), (103), (202), and (211) planes can be observed in XRD patterns, indicating the well-development of MIL-88B [10]. The molecular structures and functional groups were determined by FT-IR spectroscopy. According to Fig. 1b,
the structural vibrations of all MOFs are similar, and it can be reasonably concluded that they are all composed of trivalent metal centre and carboxylate bridging ligands. The peaks located at around 1655, 1599, 1390, 749 and 547 cm\(^{-1}\) are ascribed to the C–O stretching vibration of free carboxylic groups, the C–O asymmetric vibrations of carboxyl groups, the C–O symmetric vibrations of carboxyl groups [10,24,25], the C–H bending vibrations in benzene and stretching vibration of Fe–O, respectively.

The morphology images of the synthesized Fe-MOFs were displayed in Fig. 2. MIL-53 particles (Fig. 2a, b) have a smooth surface but irregular octahedron-like structure, with a size between 150 nm and 700 nm, which can also been seen in others’ work [26,27]. MIL-88B is a spindle-shaped crystal with an average size of 700 nm in length and 200 nm in diameter (Fig. 2c, d). SEM images of MIL-101 show favourable dispersibility and regular octahedron morphology, with an average diameter of 750 nm. The images of MIL-88B and 101 are also consistent with the observation previously reported [28].

In order to further detect the elemental composition and electronic structure of Fe-MOFs, XPS analysis was performed. As can be seen from Fig. 3a, C, O, and Fe elements were detected in all the Fe-MOFs. In the high resolution XPS spectrum of C 1s shown in Fig. 3b, two peaks located at around 284.8 eV and 288.8 eV are assigned to the C–C–C and C–O components of H\(_2\)BDC in Fe-MOFs [29]. In Fig. 3c, the high resolution XPS spectrum of O 1s could be fitted into two peaks at binding energy around 532.2 eV and 531.6 eV, corresponding to the oxygen components on the carboxylate groups of the H\(_2\)BDC linkers and the Fe-O bond, respectively [30]. Two peaks centered at around 725.6 eV and 711.8 eV could be assigned to the Fe 2p\(_{3/2}\) and Fe 2p\(_{1/2}\), respectively. The separation of these two peaks is calculated to be 13.8 eV, which is very similar to the characteristic of \(\alpha\)-Fe\(_2\)O\(_3\). The fitted peaks located at 727.0, 725.3, 712.4 and 711.2 eV are normally ascribed to the Fe (III) cation, and another peak located at 717.6 eV is the shakeup satellite of Fe (III), which indicates that Fe (III) is the predominant form of iron state in MIL-88B [31,32].

3.2. Degradation performance

Degradation performance of different Fe-MOFs and \(\alpha\)-Fe\(_2\)O\(_3\) was investigated by examining the removal efficiency of TC-HCl by US/Fenton system. MIL-88B exhibited the highest removal efficiency to TC-
HCl, followed by MIL-101 and MIL-53, which are all higher than that of α-Fe₂O₃.

In order to explore the adsorption behavior of different Fe-MOFs, BET technical was performed and the results were summarized in Fig. S1 and Table 1. It can be deduced that all the materials have mesoporous features in their microstructures as they all show a tape-IV hysteresis loop in the obtained isotherms (Fig. S1). According to the Table 1, MIL-53 and MIL-101 have the similar SSAs and average pore diameters, explaining that there is no obvious difference in adsorption efficiency (24.7% for MIL-101 and 25% for MIL-53). Interestingly, compared with others, the SSA of MIL-88B is much smaller, the average pore size is much larger, but its adsorption efficiency is similar with other two MOFs, indicating average pore diameter plays a more important role in the adsorption process than SSA, which is similar to Tan’s conclusion [33].

According to the degradation stage shown in Fig. 4 a, MIL-88B exhibited the highest removal efficiency, wherein 83.3% of TC-HCl was eliminated within only 7 min. In order to better understand the degradation kinetics, the pseudo-first-order model was applied to simulate the experimental data (Eq. (4)):

\[ \ln \left( \frac{C_0}{C_t} \right) = -kt \]  

where \( C_t \) and \( C_0 \) are the TC-HCl concentration at time t and the initial concentration, respectively, and k is the rate constant. From the result shown in Fig. 4b, the US/Fenton process can be divided into two stages: 0–3 min (\( k_1 \)) and 3–7 min (\( k_2 \)). The k value was calculated according to the time scale (Eq. (5)):

\[ k = \left( \frac{3}{7} \right) k_1 + \left( \frac{4}{7} \right) k_2 \]  

The values of k and \( R^2 \) for two stages of different catalysts are shown in Table S1. It is obvious that MIL-88B has the highest k value of 0.216 min\(^{-1}\), while the apparent rate constant of MIL-101 and MIL-53 are 0.206 min\(^{-1}\) and 0.193 min\(^{-1}\), respectively. They are all higher than that of α-Fe₂O₃ (0.056 min\(^{-1}\)). Generally, the unsaturated coordination sites of metals are responsible for the catalytic performance [22,34]. To further explore the reason that MIL-88B exhibited better US/Fenton performance than other two MOFs, cyclic voltammetry (CV) and CO adsorption infrared analysis (CO-FTIR) were carried out. As shown in Fig. 5 a, all Fe-MOFs have a similar onset potential (\( 0.3 \) V vs Ag/AgCl) but different current density. As the working electrode, MIL-101 has the maximum current density, which indicates that Fe(III) could be more easily reduced in MIL-101. However, it is worth mentioning that MIL-88B exhibits a lower current density than MIL-101, which seems inconsistent with the US/Fenton performance. The result indicates that the catalytic activity does not depend greatly on the redox property. Additionally, Fe-MOFs show a peak intensity sequence of MIL-88B > MIL-101 > MIL-53 at 2172–2179 cm\(^{-1}\) in Fig. 5 (b), proving that MIL-88B has the highest amount of Lewis acid sites, which represents the most coordinated unsaturated sites in the structure of MIL-88B [10]. The results of CO-FTIR analysis are consistent with the experimental phenomenon, thus inferring that the number of coordinated unsaturated sites is the main factor that responsible for the TC-HCl degradation.

### Table 1

| Fe-MOFs | SSA (m²/g) | Average Pore Diameter (nm) | Pore Volume (cm³/g) | Adsorption efficiency (%) |
|---------|------------|----------------------------|---------------------|---------------------------|
| MIL-53  | 291.46     | 3.82                       | 0.044               | 25                        |
| MIL-88B | 42.11      | 11.40                      | 0.064               | 25.2                      |
| MIL-101 | 258.96     | 4.14                       | 0.038               | 24.7                      |

3.3. Influential factors on MIL-88B performance

Because of the best performance, MIL-88B was chosen as the catalyst
to explore the influential factors of the US/Fenton degradation of TC-HCl. The effect of US power, catalyst dosage, \( \text{H}_2\text{O}_2 \) concentration and initial pH value were investigated. The results are displayed in Fig. 6, and the corresponding kinetics are calculated in Fig. 7 and Tables S2–S5.

The US power of the US/Fenton system was first explored by changing the US power from 40 to 100 W. According to Fig. 6a, at the range of 40–80 W, increasing the US power improved the removal of TC-HCl with the rate constant increased from 0.187 to 0.219 min\(^{-1}\), which can be attributed to more cavitation bubbles formed and collapsed at higher US power, resulting in forming more \( \cdot\text{OH} \) and other radical species [35]. Microstreaming occurred during US irradiation promotes the mixing of the solid–liquid interfaces and is helpful to clean the surface of the catalyst for further surface reactions. This facilitated the exposure of the active site and speeded up the reaction between \( \text{H}_2\text{O}_2 \) and MIL-88B. In this way, more \( \cdot\text{OH} \) were generated and the pollutant degradation was promoted. Besides, turbulence can be generated by cavitation bubble collapse, which is able to enhance the mixing intensity and mass transfer rate [36,37]. However, when the US power further increased to 80 W, there was no obvious improvement (\( k_{60W} = 0.216 \text{ min}^{-1} \) and \( k_{80W} = 0.219 \text{ min}^{-1} \)), and an evident decline of removal efficiency appeared at 100 W (0.183 min\(^{-1}\)). Two possible reasons should be considered to explain this reduction: 1) Excessive bubbles are generated at a high US power, which cause the sound waves to scatter to the surrounding vessel wall. Thus the utilization efficiency of US energy is decreased, and the generation of radicals is reduced [38,39]. 2) The turbulence of solution enhances with the increasing of US power, and appropriate turbulence contributes to mass transfer [19,40]. However, when the turbulence reaches the optimal level, continuous increase will lead to shortened contact time between reactant, which is detrimental to the generation of active radicals and the degradation of pollutants. Therefore, appropriate US power contributes to the rapid degradation of pollutant, but it is important to select the appropriate US power in US-related system. In this experiment, the removal efficiency and reaction rate at 60 W were just slightly lower than that at 80 W (~1% and ~0.003 min\(^{-1}\)). While considering the high energy consumption at high US power, 60 W is more economic and cost-effective. Notably, actual power dissipated into the system were 0.013, 0.02, 0.04, and 0.07 W/ml for 40, 60, 80 and 100 W, respectively, which were obtained by calorimetric analysis according to Text. S(4). The low dissipation is due to the short reaction time.

The effect of catalyst dosage was investigated by changing the catalyst dosage from 0.2 to 0.4 g/L. As can be seen from Fig. 7b, with the catalyst dosage increasing from 0.2 to 0.3 g/L, although the removal rate did not change significantly (~83–84%), the k value increased from 0.216 to 0.226 min\(^{-1}\), indicating a faster reaction rate for 0.3 g/L. On the one hand, the mass transfer property is enhanced with the increasing of the catalyst dosage. On the other hand, more Lewis acid sites are induced into the reaction system, which increase the probability of \( \text{H}_2\text{O}_2 \) binding to the active site, thus producing more activity. Nevertheless, a decline could be seen as the catalyst dosage increased to 0.4 g/L. This can be explained for two reasons. First, excessive amount of catalysts easily leads to the aggregation phenomenon. Second, the generated \( \cdot\text{OH} \) would be quenched at excessive iron active sites [10]. Hence, 0.3 g/L should be regarded as the optimal dosage of MIL-88B.

As a good electron acceptor and the main source of \( \cdot\text{OH} \) in Fenton-
Fig. 6. Influential factors experiments: effects of US power (a), catalyst dosage (b); H$_2$O$_2$ concentration (c) and pH value (d). ([TC–HCl]= 10 mg/L, pH = 5.0, T = 287 K).

Fig. 7. The first-order dynamic model of different influential factors: effects of US power (a), catalyst dosage (b); H$_2$O$_2$ concentration (c) and pH (d). ([TC–HCl]= 10 mg/L, pH = 5.0, T = 287 K).
related system, H₂O₂ has a remarkable influence on the catalytic performance. It can be seen from Fig. 6c, degradation efficiency in the system with no H₂O₂ addition was much lower than that in any of the US/MIL-88B/H₂O₂ systems. That’s because the main source of OH⁻ is the combination of H₂O₂ and coordinative unsaturated iron sites on MIL-88B, which greatly contributes to the degradation of the TC-HCl. Although some H₂O₂ could be generated by US [16], the amount is not enough for the rapid degradation of the pollutant. The removal rate first increased and then decreased with the increase of H₂O₂ concentration, which is similar with previous literature [28]. The removal rate reached the highest at 44 mM with the rate constant of 0.226 min⁻¹, the superior catalytic performance is attributed to the increasing amount of OH⁻ derived from H₂O₂. However, as shown in Eq. (6−7), excessive H₂O₂ will act as the scavengers of ·OH, leading to a decrease in reaction rate. 44 mM was considered as the optimal H₂O₂ concentration for the subsequent experiments. For example,

\[
\begin{align*}
H_2O_2 + \cdot OH & \rightarrow H_2O + \cdot HOO \\
\cdot HOO + \cdot OH & \rightarrow H_2O + O_2
\end{align*}
\]  

(6) 

(7)

The effect of pH value of the solution on the removal of TC-HCl in US/Fenton system is also investigated. As depicted in Fig. 6d and Fig. 7d, adsorption performance had no obvious change in the range of 5−9, and more than 80% of TC-HCl was removed within 7 min under all pH values, indicating that MIL-88B is effective in a broad pH range under US/Fenton system. However, the rate constant shows a declining trend from 0.226 to 0.206, 0.208 and 0.189 min⁻¹ with the increasing of pH value, from acidic solution to alkaline solution. The higher reaction rate in acidic solution are attributed to the fact that H₂O₂ is easy to be decomposed to molecular oxygen and H₂O in alkaline solution [41]. It is worth noting that the degradation efficiency of TC-HCl is still considerable even under the condition of pH = 11, and the kinetic constant is greater than the highest kinetic constant of other literatures [10,34]. This advantage is due to the involvement of US. Although some reduction of ·OH production happened because of the decomposition of H₂O₂, the US cavitation effect compensated for this loss to some extent. It was reported that “hot spot” and “sonoluminescence” phenomenon could be caused by US cavitation effect [14−16]. On one hand, H₂O₂ could be decomposed into ·OH. On the other hand, MIL-88B could be stimulated to produce electron-hole (e⁻·h⁺) pairs. Electrons could react with O₂ to generate ·O₂⁻, while holes could react with OH⁻ or H₂O to generate ·OH. Overall, the result indicates the good function of US on the heterogeneous Fenton system and the stable catalytic performance of MIL-88B under different pH conditions.

Total Organic Carbon analyzer (TOC, multi N/C-3100, Germany) was used to measure the mineralization rate of the TC-HCl. The optimum experimental conditions were determined by the former experiments (US/Fenton system, 60 W of US power, 0.3 g/L of MIL-88B dosage and 44 mM of H₂O₂ concentration). After 30 min of adsorption and 7 min of degradation, TOC removal efficiency was 42.5%, revealing a good mineralization ability of MIL-88B in US/Fenton system.

3.4. Contrast experiments

Contrast experiments including US, US/MIL-88B, US/H₂O₂, MIL-88B/H₂O₂, US/MIL-88B/H₂O₂ were carried out to explore the best availability system for TC-HCl removal. The removal process, corresponding dynamic curves and parameters are illustrated in Fig. 8 and Table S6. Fig. S2 shows the pure removal efficiency caused by different systems (Pure %=Total %−Adsorption %). A negligible removal rate (~2.5%) is observed in the single US system, while H₂O₂ was added to the US system, the removal rate increases to ~8%, indicating that few reactive radicals could be generated by US alone, and H₂O₂ could be decomposed into ·OH under the ultrasonic cavitation (Eq.(8))). An improvement removal rate could also be obtained when combine MIL-88B with the US (12.7%), demonstrating the combination of iron-based catalyst with US can help to amplify ultrasonic effect and improve the removal efficiency. That’s attributed to that catalyst particles act as extra nucleus for cavitation bubbles, which will generate more cavitation bubbles, causing stronger cavitation effects, and leading to higher removal efficiency [43]. Additionally, because of cavitation effect, H₂O will be dissociated to ·OH and finally produce H₂O₂ (Eqs. (1)−(3)) [14−16]. ·OH have the ability to attack the target, while H₂O₂, as the initiator of the Fenton reaction, will react with Fe(II) or Fe(III) to form more ·OH (Eqs. (9) and (10)). In order to verify this explanation, EPR technique was applied to prove the role of ·OH and H₂O₂ in US/MOF system. Corresponding signal peaks can be observed in Fig. S3. Moreover, mechanical effect caused by US irradiation can promote the mass transfer and contact more sufficient between pollutants and MIL-88B or active radicals [44].

\[
H_2O_2 + \rightleftharpoons 2 \cdot OH
\]  

(8) 

\[
Fe(III) + H_2O_2 \rightarrow Fe(II) + \cdot OOH + H^+
\]  

(9) 

\[
Fe(II) + H_2O_2 \rightarrow Fe(III) + \cdot OH + OH^-
\]  

(10)

Furthermore, compared with US system, the removal rate in MOF/H₂O₂ system was higher, which is ascribed to much more ·OH generated by Fenton-like reaction (Eqs. (9) and (10)) [10]. Compared with the MOF/H₂O₂, US/MOF/H₂O₂ system exhibits the better adsorption and degradation ability for TC-HCl, and the US/MOF/H₂O₂ system exhibited the best removal efficiency among all reaction systems. Except for the reasons above mentioned, ultrasonic waves can promote the redox reaction process and improve the reaction efficiency. More experimental data and discussion will be described in our following research work.
cycling of Fe(III)/Fe(II) [21]. Note that the k value of US/MIL-88B/H$_2$O$_2$ system (0.226 min$^{-1}$) is higher than the sum of MIL-88B/H$_2$O$_2$ (0.004 min$^{-1}$) and US systems (0.163 min$^{-1}$), implying the importance of synergistic effect between US and the Fenton process. In order to prove the superiority of the US/Fenton system, the k values for other reported systems related to Fe-MOFs are summarized in Table S7.

3.5. Mechanism analysis

As known to all, ‘OH radicals play significant role in Fenton systems, but O$_2$ radicals have been demonstrated to emerge in US system, which is ascribed to the sonoluminescence phenomenon caused by ultrasonic cavitation effect [17,45,46]. Sonoluminescence is light emission due to chemiluminescence from reactive species produced during the collapse of cavitation bubbles, it has a wide range of wavelengths including ultraviolet and visible light, which could stimulate either ultraviolet or visible light-induced semiconductors to behave as photocatalysts to produce electron-hole (e$^-$-h$^+$) pairs [18,47–49]. According to the already reported literatures, MIL-88B is visible light responsive due to the existence of extensive o xo-iron (Fe-O) clusters [34,50–52], which makes it reasonable to be stimulated by sonoluminescence. Electrons in the conduction band could react with oxygen to generate O$_2^-$ (Eqs. (11) and (12)) [53]. Through the EPR spectra, the distinct characteristic peaks of ‘OH and O$_2^-$ strongly prove the existence of ‘OH and O$_2^-$ in the US/MIL-88B/H$_2$O$_2$ system (Fig. 9b). As Section 3.4 described, ‘OH could be produced through several aspects: 1) ultrasonic cavitation effect; 2) direct decomposition of H$_2$O$_2$ by US; 3) the combination of Fe(III) sites of MIL-88B with H$_2$O$_2$.

\[
\text{MIL} - 88B + \text{H}_2\text{O}_2 \rightarrow \text{e}^- + \text{h}^+ \tag{11}
\]

\[
\text{e}^- + \text{O}_2 \rightarrow \text{O}_2^- \tag{12}
\]

To further determine the radicals mainly responsible for the removal of TC-HCl, TBA and N$_2$ were added into the solution to quench ‘OH and O$_2^-$, respectively. As shown in Fig. 9b, the removal efficiency in pure US/Fenton stage decreased from 64.2% to 12.2% after adding 40 mM of TBA. O$_2$ was removed from solution by flowing N$_2$ into solution for an hour before reaction, and US/Fenton experiment was performed in N$_2$ atmosphere. The removal efficiency of TC-HCl was 74.2% after reaction, only ~8% lower than that in the solution without quenchers, indicating ‘OH and O$_2^-$ both contribute to the TC-HCl degradation, while ‘OH is the predominant reactive species.

The coordinative unsaturated iron sites on Fe-MOFs can be active sites for H$_2$O$_2$ adsorption and decomposition. Phosphate is a Lewis base, and it has a stronger affinity to the metal acid sites than H$_2$O$_2$ ($pK_a$ (H$_2$O$_2$) < $pK_a$ (PO$_4^{3-}$)) [10]. To explore the role of metal acid sites and determine the reaction pathway of ‘OH formation, 100 mM phosphate was added into the US/Fenton system to inhibit the combination of coordinative unsaturated iron sites and H$_2$O$_2$. As can be seen from Fig. 5b, the degradation was severely restrained (about 5% TC-HCl was removed in US/Fenton stage), indicating that the decomposition of H$_2$O$_2$ and the formation of ‘OH mainly come from the combination of H$_2$O$_2$ with the unsaturated iron sites. In order to verify this conclusion, a comparative experiment was carried out by using magnetic agitation (MIL-88B/H$_2$O$_2$ system) instead of US. It was found that the reaction is completely restrained (Fig. 5d). This result is consistent with that in Fe-MOF/vis/H$_2$O$_2$ and Fe-MOF/H$_2$O$_2$ systems, in which the combination with coordinative unsaturated iron sites is the only reaction sites [10,34]. However, in this system, part of H$_2$O$_2$ could be decomposed to ‘OH by US directly, and cavitation effect could also contribute to degradation. Thus the pollutant can continue to be degraded if the coordinative unsaturated iron sites stop binding to H$_2$O$_2$, and the efficiency of ‘OH generation can also be improved.

Based on the above discussion, a simplified mechanism for TC-HCl removal by MIL-88B in US/Fenton system is proposed as follows: Before reaction, TC-HCl is adsorbed on the surface of MIL-88B, large pore size of catalysts and the ultrasound waves contribute to the mass transfer. As for degradation process, firstly, after adding of H$_2$O$_2$, as a Lewis alkaline, H$_2$O$_2$ quickly attaches to the active sites of Fe-MOF. Fe(III) sites on the surface of MIL-88B can react with H$_2$O$_2$ to produce ‘OH through Eqs. (9) and (10). Since US helps to promote the Fe(II)/Fe(III) cycle, this process can be enhanced. Besides, the cleaning effect caused by US makes the active sites be exposed continuously on the surface of the catalyst, thereby combining with more H$_2$O$_2$ to ensure the continuous generation of ‘OH. Secondly, the US leads to the direct cleavage of H$_2$O$_2$ into ‘OH radicals (Eq. (8)). Thirdly, the presence of solid catalysts MIL-88B enhances the cavitation effect of US, H$_2$O$_2$ can be dissociated to ‘OH, and finally H$_2$O$_2$ (Eqs. (1–3)), ‘OH radicals are able to attack TC-HCl, while as the initiator of the Fenton reaction, H$_2$O$_2$ could react with Fe(III) on the surface of MOF to form more ‘OH, which is similar with the process of Eqs. (9) and (10). Besides, ‘O$_2$ produced by sonoluminescence phenomenon also contributes to the TC-HCl removal. The introduction of US significantly improves the reaction rate of heterogeneous Fenton reaction of MIL-88B. The Schematic diagram of the proposed mechanism is shown in Fig. 10.

4. Conclusion

In summary, we report for the first time that Fe based MIL-88B possesses excellent potential in the ultrasonic-Fenton system. Its catalytic activities depend on ultrasound power, catalyst dosage, H$_2$O$_2$ concentration and initial pH value. Compared with the homogeneous Fenton reaction, the effective pH range in this system was significantly expanded. The degradation performance of ultrasound/MIL-88B/H$_2$O$_2$ system is higher than that of ultrasound and MIL-88B/H$_2$O$_2$ systems. The reaction mechanism is related to the following three aspects: 1)
ultrasound accelerates the mass transfer; 2) Ultrasound leads to the directly cleavage of H$_2$O$_2$ into -OH radicals. 3) Cavitation effect caused by ultrasound in the presence of solid catalysts produce more -OH. This work opens up a new field of view for the application of Fe-MOFs, and also presents attractive pollutant removal potential of ultrasonic technology in water treatment. More related work is worth exploring in the future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2020.105411.

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