Metal Foam-Based Fenton-Like Process by Aeration

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Supporting Information

1. INTRODUCTION

Advanced oxidation processes (AOPs), which can generate powerful chemical oxidants, have been widely used to degrade recalcitrant pollutants.1,2 Fenton process is one of the most efficient AOPs that has been widely used in wastewater treatment because it can produce a nonselective strong oxidant, hydroxyl radical (*OH),3,4 to oxidize contaminants. Most of the organic pollutants can be easily oxidized by *OH to be smaller organics or entirely mineralized to be carbon dioxide and water.3 However, in traditional Fenton system, the storage and transportation of H2O2 combined with a large amount of iron sludge6 as the byproduct may restrict its wider application.7 To prevent the accumulation and precipitation of soluble iron, heterogeneous catalysts with low Fe dissolution, such as iron oxides,8,9 and iron-immobilized clays10 are widely used in heterogeneous Fenton systems to replace the homogeneous Fenton system.

In addition, electro-Fenton (E-Fenton) process has also drawn much attention due to its continuous H2O2 generation on anodal material and Fe2+ regeneration by direct cathodic reduction of Fe3+.11 The E-Fenton system can continuously produce H2O2 through the oxygen reduction reaction (ORR).12 subsequently, the generated H2O2 can react with dissolved Fe2+ to produce highly reactive *OH. Therefore, the key issues in Fenton system lie in the production of H2O2 and the reduction of Fe3+. In E-Fenton system, the efficient cathodic material should possess high electrical conductivity, large surface area with good adsorption ability, and excellent chemical stability to generate a large amount of H2O2.13 Various electrocatalysts, such as carbon nanotubes,14,15 graphene,16,17 transition-metal oxides,7,18 have been investigated to promote the ORR activity and current efficiency for H2O2 generation.19

To date, numerous efforts have been devoted to improving the traditional Fenton process. However, the addition of H2O2 is an inevitable part for homogeneous and heterogeneous Fenton systems, which complicates the process. Although E-Fenton can generate H2O2 in situ, the supply of current or voltage is indispensable for all E-Fenton processes. Therefore, a more convenient and efficient Fenton system is worth investigating.

In this study, a novel Fenton-like system is developed by taking advantage of O2 and metal foam under acidic condition with Fe2+ as the catalyst. This process is performed under the condition of aeration, during which metal foams could activate dissolved O2 to produce *OH, which could then react with H+ to produce H2O2. Subsequently, a Fenton process involving Fe2+ and H2O2 can take place to produce highly reactive *OH. With the assistance of metal foams, such as Ni, Al, and Cu foams, which also offers a good alternative for rational design and application of traditional Fenton process.

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foam had the best efficiency, Al and Cu foams came next, and Ti foam had little contribution to MB degradation due to its inertness to H₂O₂ production and Fe³⁺ reduction. The effects of various parameters, such as pH value and the concentration of Fe²⁺, were also studied and discussed. The whole process was supplied with neither current nor voltage, and the addition of H₂O₂ was also unnecessary in this effective system.

2. RESULTS AND DISCUSSION

2.1. Ni-Foam-Based Fenton-Like System. Figure 1 shows the degradation of MB under various reaction scenarios. The relationship among Ni, air, and Fe²⁺ on the degradation of MB was systematically studied. The presence of single component, such as Ni, air, or Fe²⁺, had little effects on MB degradation. In the presence of Ni foam, the addition of Fe²⁺
into the solution resulted in the efficient degradation of MB. However, the combination of Ni/air or Fe²⁺/air had little effect on MB degradation. Furthermore, in the presence of both Ni foam and Fe³⁺, the removal efficiency of MB increased dramatically as a consequence of air bubbling.

According to the phenomenon mentioned above, we can conclude that both Ni foam and Fe²⁺ were essential factors for MB degradation, and bubbling air would promote the removal efficiency of MB. To elucidate the role of air on MB degradation process, experiments were conducted by supplying different gases (air, oxygen, or nitrogen) to saturate MB solution. As shown in Figure 1b, faster removal of MB was observed with higher oxygen concentration (bubbling oxygen), whereas in the absence of oxygen (bubbling nitrogen), the removal of MB was strongly inhibited. Therefore, dissolved O₂ was also essential for the degradation process.

It is likely that the above phenomenon could be attributed to the following Fenton-like reaction pathway. First, nickel foam played an important role to react with dissolved O₂ to produce O₂⁻ through eq 1 and then O₂⁻ can react with H⁺ to produce H₂O₂ through eq 2. Then, Fe²⁺ acted as the catalyst and initiated the decomposition of H₂O₂ to generate the highly reactive •OH to degrade MB, which can be described as follows:

\[
\begin{align*}
\text{Ni} + 2\text{O}_2 & \rightarrow \text{Ni}^{2+} + 2\text{O}_2^- \\
2\text{O}_2^- + 2\text{H}^+ & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \\
\end{align*}
\]

In the meantime, on the basis of the standard electrode potentials of Ni²⁺/Ni and Fe³⁺/Fe²⁺ pairs (eqs 4 and 5), Ni foam could promote the cycling of Fe³⁺/Fe²⁺ through eq 6. As a result, Fe³⁺ in this system can react with H₂O₂ continuously to generate •OH for MB degradation.

\[
\begin{align*}
\text{Ni}^{2+} + 2\text{e}^- & \rightarrow \text{Ni}, \ E_0 = -0.25 \text{ V} \\
\text{Fe}^{3+} + \text{e}^- & \rightarrow \text{Fe}^{2+}, \ E_0 = +0.77 \text{ V} \\
2\text{Fe}^{3+} + \text{Ni} & \rightarrow 2\text{Fe}^{2+} + \text{Ni}^{2+} \\
\end{align*}
\]

On the basis of the above reaction pathway and the phenomenon observed in Figure 1b, it is clear that pure oxygen can accelerate the generation of •OH to attack MB. Nevertheless, employing air was effective and more economical than employing pure O₂. Therefore, air bubbling was employed throughout the rest of the study.

To prove the reaction pathway proposed above, it is instrumental to measure the concentrations of H₂O₂ and Ni²⁺ in the process. Figure 2a shows the accumulation of H₂O₂ in the presence of Ni foam with continuous air bubbling. It is clear that H₂O₂ was generated likely through eqs 1 and 2. In the absence of MB, the concentration of H₂O₂ increased dramatically to about 7.5 mg L⁻¹ in 30 min and then reached a plateau. Ni²⁺ and Fe²⁺ were also measured during the MB degradation process. With the increase of reaction time, the concentration of Ni²⁺ had a similar tendency to H₂O₂, which was in accordance with eqs 1 and 2. The Fe²⁺ concentration remained unchanged during MB degradation (Figure 2c), which suggests the efficient Fe³⁺/Fe²⁺ cycling promoted by Ni foam. This is a robust evidence to support the presence of eq 6 in this system. According to eq 6, Ni foam could reduce Fe³⁺ to Fe²⁺. Therefore, it is expected that the introduction of Fe³⁺ is also beneficial for MB degradation. To investigate the effect of Fe³⁺, 0.25 mM Fe³⁺ was added into the system to degrade MB at pH 3. Under the same conditions, although Fe³⁺ could contribute to MB degradation, its efficiency was much lower than that of Fe²⁺. Figure 2d reveals that 56% of MB was degraded in 5 min with the addition of Fe³⁺, whereas Fe²⁺ could facilitate 94% degradation of MB. The difference between Fe²⁺ and Fe³⁺ was due to the fact that Fe²⁺ could be oxidized by H₂O₂ immediately to produce •OH for MB degradation. However, Fe³⁺ had to be reduced by Ni foam to generate Fe²⁺ first and then •OH can be produced via a Fenton reaction. Therefore, Fe²⁺ was a superior catalyst to Fe³⁺ in the metal foam-based Fenton-like system.

Scanning electron microscopy (SEM) images show that Ni foam (Figure 3a) maintained its three-dimensional porous structure after the reaction (Figure S1), which is beneficial for the mass transfer of air. However, its surface morphology changed dramatically as a result of chemical reaction. As
demonstrated in Figure 3b,c, the original Ni foam featured smooth surface in both microscale and nanoscale. On the contrary, there was distinct corrosion on the surface of the used Ni foam (Figure 3d). The size of the defects on the surface of the Ni foam ranges from nanometers to micrometers as a result of the chemical reaction depicted in eqs 1−6. The defects on the surface of the Ni foam also indicate that nickel was leached during the reaction, which was in agreement with the increasing Ni²⁺ concentration during the reaction (Figure 2b).

2.2. Quenching of *OH and *O₂⁻ in the Fenton-Like Process. To have a better understanding of the reaction pathway during the Fenton-like process, 2-propanol was used as an efficient *OH scavenger,²⁸,³⁰ and p-benzoquinone as an *O₂⁻ scavenger. As demonstrated in Figure 4, the addition of both p-benzoquinone and 2-propanol could inhibit the degradation of MB dramatically. When 1 mM p-benzoquinone or 2-propanol was introduced, there was no obvious change of MB concentration in the Ni foam/air/Fe²⁺ system for 60 min, indicating the complete inhibition of the degradation process. This phenomenon suggests that the degradation of MB in this system was based on both *OH and *O₂⁻ radicals. Here, *O₂⁻ radical likely served as the precursor to generate *OH for MB degradation rather than as a direct oxidant, as shown in eqs 2 and 3. This is demonstrated by Figure 1a that the combination of Ni and air had little effect on MB removal. In such case, *O₂⁻ and H₂O₂ were produced; however, they did not have the capability to degrade MB. The introduction of Fe²⁺ to initiate Fenton reaction was crucial for the fast MB degradation. It is also evident that the quenching of *OH completely inhibited the degradation of MB (Figure 4b). We therefore conclude that *OH was the main radical that degraded MB in this system.

2.3. Effects of Fe²⁺ Concentration and Initial pH on MB Degradation. Solution pH and concentration of Fe²⁺ are known factors affecting the efficiency of Fenton process.³³ Figure 5a reveals that initial pH value had a great impact on the degradation of MB. The system reached the maximal MB removal efficiency at pH 3. With the increase of pH, the MB removal decreased, which was likely caused by the formation of Fe²⁺-based hydroxyl complexes under high pH value. Figure 5a also reveals that when the pH value lowered to less than 3 the MB degradation efficiency decreased. This can be attributed to the scavenging effect of *OH by H⁺.³⁴ The MB removal underwent a gradual acceleration when Fe²⁺ concentration increased from 0.025 to 0.25 mM (Figure 5b). The increased degradation of MB was ascribed to the enhanced H₂O₂ decomposition associated with the increase of Fe²⁺. However, when Fe²⁺ concentration continued to rise, the MB removal...
decreased. This is because excessive amount of Fe^{2+} would consume OH\textsuperscript{-}, \textsuperscript{33,35,36} which resulted in the formation of Fe^{3+} and OH\textsuperscript{-} and consequently iron hydroxides, thus terminating the Fenton reaction (eq 7). Therefore, the optimal conditions for this Fenton-like process are initial pH = 3 and Fe^{2+} concentration = 0.25 mM.

\[
\text{Fe}^{2+} + \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^{-} \quad (7)
\]

2.4. Comparison of Ni Foam and Ni Plate. To illustrate the role of Ni foam on MB degradation, Ni plate was also employed as another Ni source for comparison. Ni foam resulted in much faster MB degradation than Ni plate (Figure 6a). In Ni foam system, the MB removal reached 94% in 5 min; however, only less than 50% MB removal was achieved in the Ni plate system. The superior efficiency of Ni foam likely originated from its macroporous structure possessing more specific surface area, which can provide more reactive sites for H_{2}O_{2} production. Therefore, the employment of Ni foam is another key factor to obtain high reaction efficiency. Figure 6b shows the degradation of three other pollutants based on our proposed Fenton-like process. It is obvious that the proposed Fenton-like process is suitable for other pollutants (such as orange II, methyl orange, and phenol). The results indicate that this process may be a general approach for wastewater treatment.

2.5. Degradation of MB Based on Other Metal Foams. In the Fenton-like system discussed above, Ni foam played an important role in degrading MB by facilitating effective O_{2}\textsuperscript{-} production as well as Fe^{3+}/Fe^{2+} cycling. Some other metals, such as Al and Cu, which have similar properties as Ni, may also have the ability to activate O_{2} and circulate Fe^{3+}/Fe^{2+}. We propose that the Ni-foam-based Fenton-like process is a general approach to produce OH for pollutant degradation, which could be applied to other metal foams. Figure 7a shows the removal of MB in Fenton-like systems based on different metal foams. Three typical metals (Ni, Al, and Cu) that could reduce Fe^{3+} were chosen; another metal (Ti) that does not have the ability to reduce Fe^{3+} was also selected for comparison. It is obvious that Ni foam had the best efficiency to degrade MB. The MB removal reached 94% in 30 min. MB removal by Al foam reached 88% in 60 min, whereas Cu foam could remove 50% of MB. However, almost no MB removal was observed for Ti foam. This phenomenon confirms that metals that have the ability to reduce Fe^{3+} to Fe^{2+} can be employed in this Fenton-like system, whereas other inactive metals (such as Ti) are inefficient in this system.
Furthermore, the differences in MB removal for the above metals were in good accordance with their H₂O₂ production capability. As demonstrated in Figure 7b, Ni foam exhibited the best H₂O₂ accumulation. For Al foam and Cu foam, H₂O₂ concentration could achieve 3.8 and 1.8 mg L⁻¹, respectively. As a result, their corresponding MB degradation efficiency fell far behind Ni foam. As a comparison, no H₂O₂ was detected in Ti foam system due to its inertness to oxygen.

The performance of different metal foams with same surface area of 0.5 m² is demonstrated in Figure S2. It is revealed that Ni foam still demonstrates the best MB removal efficiency, Cu and Al foams come next, and Ti foam has little efficiency. Furthermore, the differences in MB removal for the above metals (based on surface areas) were also in good accordance with their H₂O₂ production capability. It is found that Ni foam has the best H₂O₂ production efficiency (18.5 mg L⁻¹ in 1 h). For Cu foam and Al foam, H₂O₂ concentration could achieve 3.8 and 0.93 mg L⁻¹ in 1 h, respectively. As a result, their corresponding MB degradation efficiency fell far behind Ni foam. On the contrary, no H₂O₂ was detected in the Ti foam system due to its inertness to oxygen. This phenomenon is in agreement with previous comparison based on the mass.

The surface morphologies of the three metals before and after reaction vividly reveal the occurrence of the Fenton-like reaction. As demonstrated in Figure 8a,c, the surfaces of the original Al and Cu foam are smooth without obvious defects. However, after the Fenton-like process, their surfaces became fairly rough with numerous nanosized defects. The dramatic changes in the surface morphology were caused by the following two reasons. First and foremost, metal foams were corroded by oxygen, which produced *O₂⁻ and then H₂O₂. Second, metal foams reacted with Fe³⁺ to produce Fe²⁺, which activated H₂O₂ to produce highly oxidative *OH. On the contrary, the surface of Ti foam remained smooth and untouched after the reaction, as Ti was unreactive to either *O₂⁻ production or Fe³⁺ reduction.

In summary, the reaction pathways for the proposed Fenton-like process are depicted in Scheme 1. Initially, metal foam (denoted M in Scheme 1) can activate the dissolved O₂ in water to produce *O₂⁻, which then reacts with H⁺ in the solution to produce H₂O₂ in situ. The added Fe²⁺ reacts with H₂O₂ to generate *OH for MB degradation. In the meantime, metal foam plays another role in reducing Fe³⁺ to Fe²⁺. As a result of Fe³⁺/Fe²⁺ cycling, *OH will be continuously produced by the above Fenton-like process for pollutant degradation.

3. CONCLUSIONS

In this study, a novel Fenton-like system was developed by introducing aeration and metal foam under acidic condition. Metal (Ni, Al, and Cu) foam plays dual roles in this process that it can not only activate dissolved O₂ to produce H₂O₂ but also facilitate Fe³⁺/Fe²⁺ cycling for continuous Fenton reaction. The production of both *O₂⁻ and *OH in this process was demonstrated, whereas *O₂⁻ was the precursor for H₂O₂ production and *OH was responsible for MB removal. Nickel foam had the best activity for H₂O₂ generation and MB removal, whereas Ti had little contribution to the reaction due to its inertness to oxygen. The optimum conditions for this Fenton-like process were determined to be pH value = 3 and Fe²⁺ concentration = 0.25 mM, under which 94% of MB can be removed in 5 min by employing Ni foam. The novel Fenton-like system in this study would have good potential in wastewater treatment due to its high efficiency and low cost.

4. EXPERIMENTAL SECTION

4.1. Materials. All chemicals used in this study were of analytical grade. Hydrogen peroxide, FeSO₄·7H₂O, Fe(NO₃)₃·9H₂O, isopropanol, and p-benzoquinone were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Potassium titanyl oxalate and methyl blue were purchased from Mclean. Nickel, aluminum, copper, and titanium foams were obtained from Suzhou Jiashide Metal Foam Co., Ltd., China. All of the chemicals were used without further purification. Deionized
water was used throughout the experiments. Prior to the degradation experiment, metal foams were washed by 0.1 M HCl and deionized water to remove the oxides and grease on the surface.

4.2. MB Degradation and H2O2 Accumulation. MB solution (500 mg L−1) was kept as a stock solution. MB solution used in the degradation reaction was obtained by diluting from the stock solution. The degradation of MB was conducted in a 250 mL beaker containing metal foam (2 cm × 2 cm × 2 mm) and 200 mL of MB solution with an initial concentration of 20 mg L−1. Prior to the Fenton-like reaction, air was bubbled into the reactor for 30 min and then Fe3+ was added. H2O2 was generated in a system containing metal foam and deionized water but without MB during bubbling air. The initial pH was adjusted to the designated value using 0.1 M HCl or 0.1 M NaOH.

4.3. Characterization. The MB and H2O2 concentrations were measured by a UV−vis spectrophotometer (TU1810, Universal Analysis, Beijing, China). H2O2 was determined using the potassium titanium oxalate method at its maximum absorption wavelength of 400 nm. The MB concentration was measured at its maximum absorption wavelength of 664 nm. The standard curves of H2O2 and MB are shown in the Supporting Information (Figures S3 and S4). The Ni2+ concentration was detected by an atomic absorption spectrophotometer (TAS-990F, Universal Analysis, Beijing, China). The specific surface area (Brunauer−Emmett−Teller) was measured by nitrogen adsorption/desorption (Microertics ASAP2020 instrument). SEM measurement was performed on a Zeiss Supra 55 scanning electron microscope.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00977.

Calibration curves of H2O2 and MB, SEM image of Ni foam after the reaction (PDF)

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Notes
The authors declare no competing financial interest.

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