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Enhancement of oxidation capacity of ZVI/Cu^{2+}/PMS systems by weak magnetic fields

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ABSTRACT

In this study, the effect of weak magnetic fields (WMF) on the degradation of Acid Orange 7 (AO7) solution in zero-valent iron (ZVI)/Cu^{2+}/peroxymonosulfate (PMS) systems was investigated. In the absence of a weak magnetic field, 60% of AO7 degrades in 10 min, while in the presence of a weak magnetic field the degradation rate increases to 95%. Inhibition of free radicals with *t*-butanol and methanol, and inhibition of Cu^+ with neocuproine (NPC) show that Cu^+ is the main ion that activates PMS to produce $^{\bullet}OH$ and $SO_4^{\bullet-}$ free radicals. XRD and SEM analysis showed that WMF accelerated the corrosion of ZVI to produce Fe^{2+} which can reduce Cu^{2+} to generation Cu^+, and effectively improve the catalytic efficiency of the system. This study provides a reference for studying the effect of magnetic fields on the catalytic oxidation ability of magnetic materials.

Keywords: Advanced oxidation process; Weak magnetic field; Zero-valent iron; Copper; Water treatment; Catalytic; Peroxymonosulfate

1. Introduction

Zero-valent iron (ZVI) has been widely used in the treatment of groundwater and various pollutants [1,2]. Preview research showed that ZVI can effectively reduce heavy metal ions in water [3,4], and the Fe^{2+} generated by ZVI plays an important role in reduction reaction. Other studies have also shown that the formation of Fe^{2+} by ZVI is an effective way to reduce a large number of high-valence metal ions at a low price [5,6].

Moreover, in a catalytic reaction, the low-valent metal catalyst plays an important role in generating radicals having strong oxidizing properties, as indicated in the following formula [7]:

$$M^{n+} + \text{Oxidizer} \rightarrow M^{n+1} + \text{free radical} \tag{1}$$

During this process, the low-valent metal is oxidized to a high valence state which generally is not catalytic. Among these catalytically-active metal ions, previous studies have shown that Cu^+ can effectively activate oxidants to generate various free radicals [8–11]. For example, activation of PMS generates $SO_4^{\bullet-}$, activation of H_2O_2 generates $^{\bullet}OH$ [12,13] as in the following equations:

$$Cu^+ + HSO^{5-} \rightarrow Cu^{2+} + SO_4^{\bullet-} + OH^- \tag{2}$$

$$Cu^+ + HSO^{5-} \rightarrow Cu^{2+} + {}^{\bullet}OH + SO_4^{2-} \tag{3}$$

However, the potential of Cu^{2+} to activate oxidants is low, and the conversion from Cu^{2+} to Cu^+ is often the rate-limiting step in the entire catalytic reaction. Hence, increasing the rate of conversion of Cu^{2+} to Cu^+ by increasing the rate of Fe^{2+} generated by ZVI is an effective way to enhance the catalytic effect [14,15], and is shown in the following equations [16–18]:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \tag{4}$$

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$$Fe^{2+} + Cu^{2+} \rightarrow Cu^{+} + Fe^{3+} \quad (5)$$

Theoretically, promoting the formation of Fe^{2+} in ZVI systems can accelerate the reduction of Cu^{2+} to Cu^{+}. Therefore, the formation of Fe^{2+} in this system may be the key.

Several studies have revealed that the generation of Fe^{2+} can be promoted by weak magnetic fields [19–21]. It has been confirmed that in the presence of weak magnetic fields (WMF), the Lorentz force induces convection in the solution, which narrows the diffusion layer, and the field gradient forces tend to move paramagnetic ions (especially Fe^{2+}) along the ZVI particles. Higher field gradients can lead to inhomogeneous depassivation and result in localized corrosion of the ZVI surface, eventually resulting in an increase of Fe^{2+} ions. In addition, ZVI is ferromagnetic and it can be magnetized in an external WMF. The WMF around ZVI particles is even stronger than the superimposed WMF, so the ZVI in the magnetic field is more magnetic. Further, the Cu^{2+} is also paramagnetic which may also be affected by magnetic field gradient forces. The magnetic field gradient force (FGMF) is expected to promote the transfer of Cu^{2+} to the surface of magnetized ZVI particles and promote the reaction to ZVI with Cu^{2+}. In this way, the weak magnetic field can accelerate the formation of Cu^{+} [22,23].

In summary, it is speculated that the weak magnetic field may cause the ZVI to release more Fe^{2+} ions, so that more Cu^{2+} could be reduced to Cu^{+} to enhance its catalytic ability. It is also possible to enhance its catalytic ability by accelerating the Cu^{2+} movement. Therefore, this study focused on the following aspects: (1) the effect of WMF on ZVI/Cu^{2+}/PMS systems; (2) the mechanism of WMF promoting the catalytic oxidation capability of ZVI/Cu^{2+}/PMS; and (3) influencing factors on ZVI/Cu^{2+}/PMS systems.

2. Experimental section

2.1. Chemicals

Acid Orange 7, zero-valent iron and peroxymonosulfate (PMS) were purchased from ALADIN American (Los Angeles, Southern California). The remaining analytical-grade chemicals used in this study were purchased from KELONG (Sichuan, China). All aqueous solutions were prepared with ultra-pure water. $CuSO_4$ solution was prepared using $CuSO_4·5H_2O$. The initial pH was adjusted using H_2SO_4 and NaOH.

2.2. Batch experiments and catalyst characterization

Experiments were designed to study the effects of ZVI/Cu^{2+}/PMS on the degradation of AO7 in the presence of magnetic fields. A ring magnet with an outer diameter of approximately 12 cm, an inner diameter of 6 cm and a magnetic force of approximately 1,000 mt was used as a source of WMF. The weak magnetic field was provided by placing the magnet on the bottom of the beaker. The 25 mg L^{-1} AO7 solution was stirred at 320 rpm by a mechanical stirrer (D2004W, Shanghai Sile Instrument Co. Ltd.) at room temperature (25°C ± 2°C). The initial pH of the simulated wastewater containing AO7 was adjusted with 0.1 M sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4). The experiments were started by the addition of 0.05 g ZVI powder, 0.2 mL PMS (0.5 mol L^{-1}), and 0.5 mL Cu^{2+} (25 mg L^{-1}). In order to study the influence of the magnetic field on the reaction, the reactor was placed about 7 cm above an 1T magnet. At a given reaction time interval, samples were removed using a 10 mL syringe and solids removed by filtration through a 0.22 μm superfine membrane. The absorbance of the remaining liquid was measured on a Cary 50 UV–Vis spectrophotometer (Varian, USA) at a wavelength of 484 nm.

After the experiment, the ZVI powder was recovered after separation in a magnetic field, washed with deionized water, and dried in a low-temperature freeze-drying oven for 40 min. Powder X-ray diffraction (XRD, UItima IV, Rigaku, Japan) was used to analyze the structure of various samples. The specific structure of the ZVI powder was characterized by scanning electron microscopy (SEM, Quanta 250, FEI United States), performed on an FEI Inspect F50.

A 0.1 mmol L^{-1} inhibitor was used in the free radical inhibition experiment. Radical inhibitors were tert-butanol (TBA), ethanol (EtOH), benzoquinone (BQ) and furfuryl alcohol (FFA). The concentration of TFe leached was measured by UV–vis spectrophotometer, with o-phenanthroline spectrophotometry. The spectrophotometric method was used to determine the concentration of Cu^{+} (TCu^{+}) after the Cu^{+} was chelated with neocuproine (NPC).

3. Results and discussion

3.1. Effect of WMF on ZVI/Cu^{2+}/PMS

Fig. 1 shows the ability of different systems to degrade dyes and the effect of weak magnetic fields on them. As can be seen from Fig. 1a, Cu^{2+}/PMS did not have the ability to degrade the dye regardless of the presence or absence of a weak magnetic field, indicating that Cu^{2+} is not an efficient activator for PMS. Fig. 1b shows that ZVI alone had no significant effect on the degradation of the dye, and the effect did not change when the weak magnetic field was present. However, ZVI/PMS could remove nearly 30% of AO7, and the removal rate increased to 70% with the existence of a weak magnetic field. A possible explanation for this might be that the PMS can be activated by ZVI to produce oxidative factors, and presumably WMF may affect the catalytic ability of the system through acting on the ZVI.

As shown in Fig. 1c, about 70% of the dye in ZVI/Cu^{2+}/PMS was degraded in 10 min, implying that ZVI and Cu^{2+} have synergistic effects on the degradation of AO7. However, in a weak magnetic field environment, the AO7 was completely degraded in the ZVI/Cu^{2+}/PMS system after 10 min. The above results clearly demonstrated that the weak magnetic field can effectively improve the catalytic effect of the ZVI/Cu^{2+}/PMS system.

3.2. Mechanism discussion

3.2.1. Identification of free radicals

Previous research showed that there are three main types of reactive radicals generally formed from the activation of PMS by metal irons, sulfate, peroxysulfate, and hydroxyl radicals [23]. Therefore, radical quenching tests were performed to identify the main radical species.

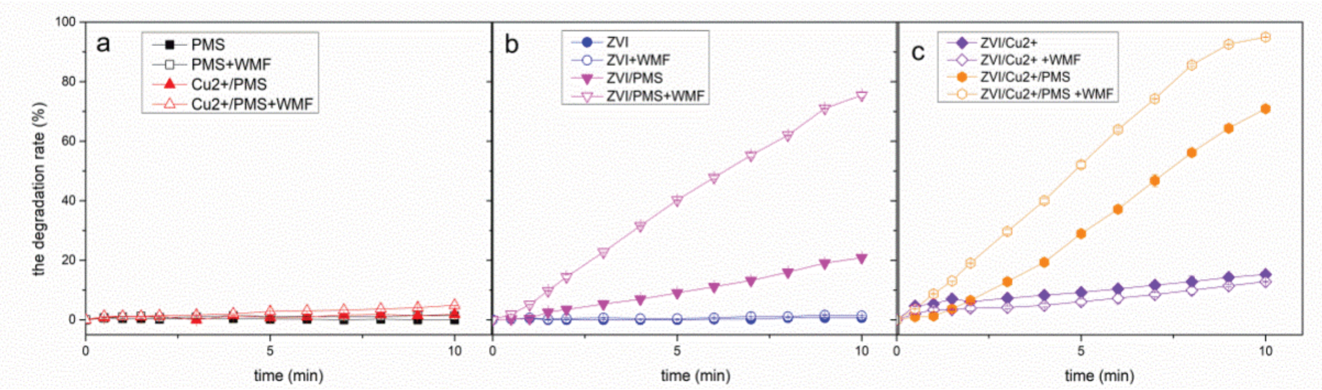

Fig. 1. Effect of weak magnetic field on catalytic ability of ZVI/Cu^{2+}/PMS system. Reaction conditions: AO7 = 25 mg L^{-1} 300 mL, [ZVI] = 0.2 g L^{-1}, [Cu^{2+}] = 0.05 mg L^{-1}, [PMS] = 4×10^{-4} mol L^{-1}, pH = 4.0.

Fig. 2a shows the inhibitory effect of inhibitors on the degradation of AO7 during the ZVI/Cu^{2+}/PMS/WMF process. Furfuryl alcohol inhibited almost all free radicals [26]. When 0.2 mL of furfuryl alcohol was added to the solution, the system could hardly degrade AO7. Therefore, the catalysis of the system is mainly related to free radicals. In order to further verify the conjecture, TBA and EtOH were used as quenching agents to determine $^{\bullet}OH$ and $SO_4^{\bullet-}$. As illustrated in Fig. 1c, the degradation rate of AO7 reached 95% within 10 min when no quencher was added, while the degradation rate dropped to 75% within 10 min when 7 mL TBA was added to the solution. Moreover, the addition of 10 mL ethanol decreased the AO7 degradation removal from 95% to 25%, inhibiting nearly 70% of degradation. Nevertheless, the inhibitory effect of furfuryl alcohol was still around 20% more than that of ethanol. In this situation, benzoquinone can inhibit nearly 25% of the degradation of AO7, similar to the uninhibited result of the addition of methanol. These results indicate that $^{\bullet}O^{2-}$, $^{\bullet}OH$ and $SO_4^{\bullet-}$ were present in the system, but the amount of $SO_4^{\bullet-}$ was much more than $^{\bullet}OH$ and $^{\bullet}O^{2-}$. As discussed above and in previous studies, various free radicals in the system may be generated by the following equation [10,15,23]; as indicated in the following equations:

$$Cu^{+} + HSO^{5-} \rightarrow Cu^{2+} + SO_4^{\bullet-} + OH^{-} \tag{6}$$

$$Cu^{+} + HSO^{5-} \rightarrow Cu^{2+} + {}^{\bullet}OH + SO_4^{2-} \tag{7}$$

$$Fe^{2+} + HSO^{5-} \rightarrow Fe^{3+} + SO_4^{\bullet-} + OH^{-} \tag{8}$$

$$Fe^{0} + O_2 + 2H^{+} \rightarrow Fe^{2+} + H_2O_2 \tag{9}$$

$$Cu^{2+} + H_2O_2 \rightarrow Cu^{+} + {}^{\bullet}O^{2-} + 2H^{+} \tag{10}$$

As shown in Fig. 2b, after the addition of free radical inhibitors, the inhibited degradation rate was higher in the presence of a magnetic field than in the absence of a magnetic field. Thereby, WMF may have contributed to the

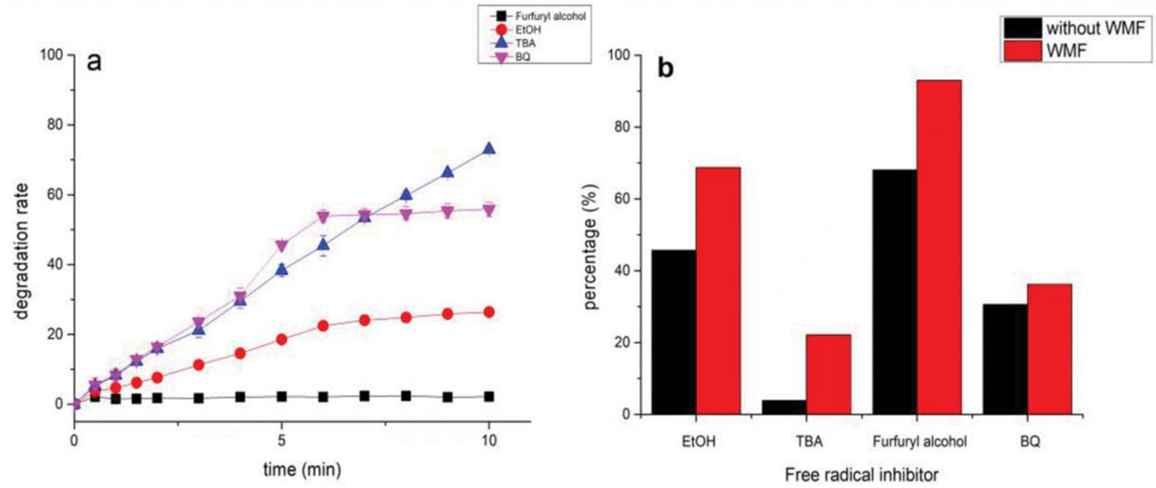

Fig. 2. Free radical exploration experiment: (a) degradation rate after addition of free radical inhibitors and (b) percentage inhibition of WMF and without WMF inhibition. Reaction conditions: AO7 = 25 mg L^{-1} 300 mL, [ZVI] = 0.2 g L^{-1}, [Cu^{2+}] = 0.05 mg L^{-1}, [PMS] = 4×10^{-4} mol L^{-1}, pH = 4.0.

increase in the amount of the free radicals. It was also shown that the content of the various free radicals increased by varying degrees when a weak magnetic field was present. In the weak magnetic field conditions, the percentage of inhibition of TBA and EtOH increased significantly, but there was only a slight increase in the percentage of BQ inhibition. According to Eqs. (6)–(8), the generation of ${}^{\bullet}OH$ and $SO_4^{\bullet-}$ may be related to Fe^{2+} and Cu^{+}. It is speculated that a weak magnetic field may enhance the catalytic ability of the system by increasing the content of Fe^{2+} and Cu^{+}. However, the increase in the number of superoxide radicals by the weak magnetic field was not significant. According to Eq. (9), it indicates that WMF may contribute to the increase in free radical content in the system by accelerating the generation of Fe^{2+} and Cu^{+}.

3.2.2. Effective species to activate PMS

As shown in Figs. 3a and b, the content of Fe^{2+} and Cu^{+} in water was determined. In the presence of a weak magnetic field, the TFe content in the solution is slightly less than that without a weak magnetic field, but the Cu^{+} content in the solution increased significantly when a weak magnetic field was present. Therefore, it is inferred that Cu^{+} was the main influencing factor for increasing the amount of free radicals in the system. To verify this conjecture, NPC was added as an inhibitor of Cu^{+}. As shown in Fig. 3c, after Cu^{+} was inhibited, the degradation effect of the system was only 30%, which is consistent with the degradation effect of the system after adding EtOH. In this case, the generation of ${}^{\bullet}OH$ and $SO_4^{\bullet-}$ in the system was mainly brought around by the Cu^{+}.

Further, after the addition of Cu^{+} inhibitors, there was no significant difference in the catalytic ability of the system with or without WMF. Referring to Fig. 3b, it is inferred that the reason for the WMF's enhanced catalytic ability was to increase the production of Cu^{+}.

3.3. SEM and XRD characterization

In order to further study the influence of WMF on the coupling of zero-valent iron and Cu^{2+}, the SEM images were examined. As seen in Fig. 4, the SEM image shows that the ZVI particles are irregular spheres with a rough surface. When there was no weak magnetic field, the surface of the iron powder was still rough, similar to the iron powder before reaction. However, after the addition of WMF, the surface became smooth, and this phenomenon was not observed in the absence of WMF. Previous studies have shown that in the presence of WMF, the Lorentz force caused convection in the solution, which narrowed the diffusion layer. The weak magnetic field gradient forces made the paramagnetic ions (especially Fe^{2+}) tend to move toward the ZVI, resulting in certain areas having higher electric field gradient is higher. These may lead to higher electric field gradient ZVI surface passivation; eventually causing the local corrosion [24,25]. Moreover, the local corrosion caused by the weak magnetic field can result in more Fe^{2+} dissolution. Under the action of an external magnetic field and an induced magnetic field, the Lorentz force FL caused convection in the electrolyte, and the dissolved Fe^{2+} was adsorbed on the surface of ZVI without being released into the solution. As a result of this, the ZVI surface was relatively smooth in the presence of a magnetic field, and also explains why the amount of Fe^{2+} in solution slightly decreased with the addition of a magnetic field.

XRD analysis was performed to study the specific substances adsorbed on the surface of ZVI. As shown in Fig. 5, there were no other substances on the iron powder before the reaction. After the reaction, the surface of the iron powder not only contained Fe^{0} but also contained a small amount of Cu^{0}. According to the above analysis, it is inferred that the following reactions occur on the surface of ZVI [26].

$$Fe^{0} \rightarrow Fe^{2+} + 2e^{-} \tag{11}$$

$$Cu^{2+} + 2e^{-} \rightarrow Cu^{0} \tag{12}$$

$$Fe^{2+} + Cu^{2+} \rightarrow Cu^{+} + Fe^{3+} \tag{13}$$

Besides, whether or not there was a weak magnetic field, the ferromagnetism of ZVI itself provides the ability to attract the paramagnetic ion Cu^{2+} to its surface for reaction. This provides an explanation as to why there was little difference between the XRD images of ZVI reacting

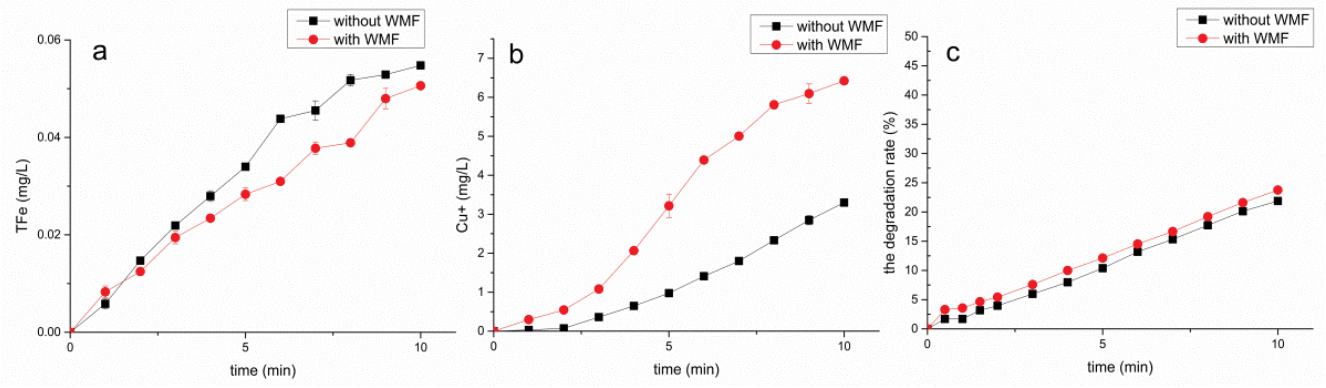

Fig. 3. (a) Iron ion concentration, (b) Cu^{+} concentration, and (c) degradation effect after adding Cu^{+} inhibitor. Reaction conditions: AO7 = 25 mg L^{-1} 300 mL, [ZVI] = 0.2 g L^{-1}, [Cu^{2+}] = 0.05 mg L^{-1}, [PMS] = 4×10^{-4} mol L^{-1}, pH = 4.0, [NPC] = 0.1 mmol L^{-1}.

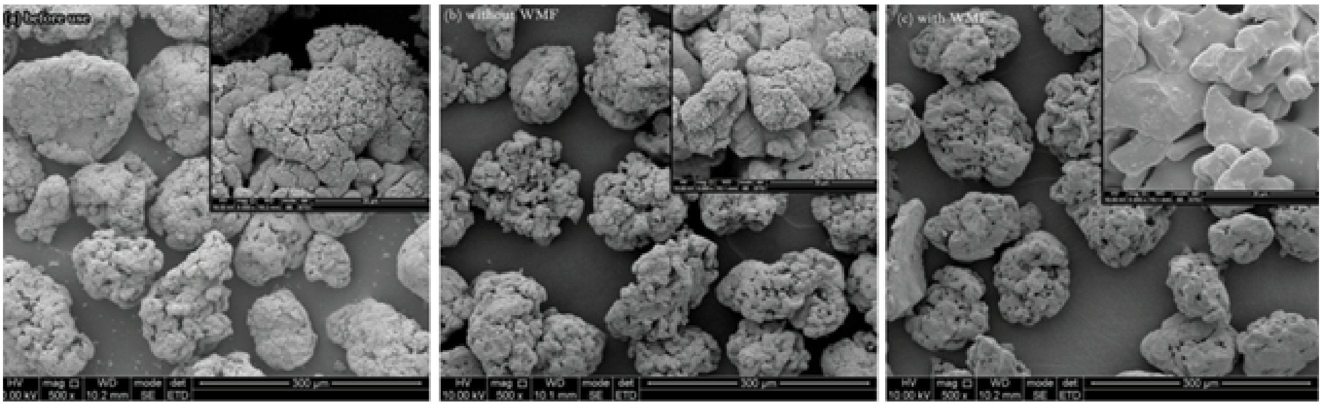

Fig. 4. SEM image of (a) iron before use, (b) iron after reaction without WMF and (c) iron after reaction with WMF.

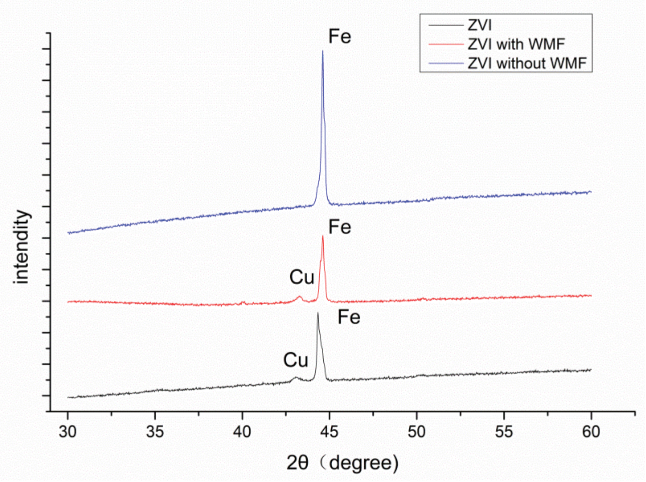

Fig. 5. XRD image of iron powder surface.

with a weak magnetic field and ZVI reacting in the absence of a weak magnetic field. Previous studies have shown that after weak magnetic field superposition, the ZVI's own ferromagnetism enables it to be magnetized. Thus, a strong non-uniform stray field was generated on the surface of ZVI particles, and the magnetic flux density exceeded the external stray field. Afterwards, the magnetic field gradient force (FGMF) can attract Cu^{2+} ions in the direction of the increasing magnetic field intensity, enhancing the movement of Cu^{2+} to ZVI. In other words, a weak magnetic field can increase the production of Cu^{+} ions by speeding up the medium drive between Cu^{2+} and ZVI. Nevertheless, Cu^{+} is non-paramagnetic and could not be attracted by magnetic ZVI. This is a possible explanation as to why that the Cu^{+} content in the solution increased when the weak magnetic field was present [12,22,27–29].

As discussed above, Cu^{+}, as the main function of the system, can effectively activate PMS to produce sulfate radicals and hydroxyl free radicals, and the Cu^{+} content can be increased by WMF. On one hand, the weak magnetic field accelerates the local corrosion on the ZVI surface through the influence of the Lorentz force, and causes ZVI to release more Fe^{2+}, which promotes the reaction of Eq. (2) and enhances the production of Cu^{+} ion. Furthermore, the magnetic field can also magnetize ZVI to accelerate the paramagnetic ion Cu^{2+} movement to its surface by the Lorentz force and magnetic field gradient force. In this case, the magnetic field enhances the reaction rate of Fe^{2+} and Cu^{2+} and promotes the formation of Cu^{+} by accelerating the movement of the materials. The specific mechanism diagram is as follows (Fig. 6).

3.4. Impact factor

3.4.1. Effect of WMF on AO7 removal by ZVI at different pHs

Fig. 7 illustrates the effect of pH on AO7 removal by ZVI. The pH of the solution was maintained at pH 2, 3, 4, 5 and 6 and the rest of the conditions were consistent. At pH 2, the removal rate of AO7 was very fast, and more than 95% of AO7 was removed after 5 min of reaction. However, when the solution was maintained at pH 6, only 60% of AO7 was removed from the solution during the 5 min of mixing. These results showed that, as pH decreased, the reaction rate increased significantly. Low pH favored the total reaction

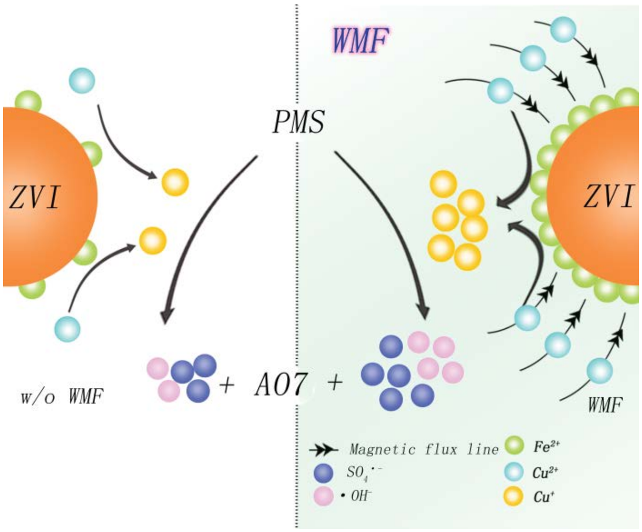

Fig. 6. Schematic illustration of the role of WMF in enhancing the reaction.

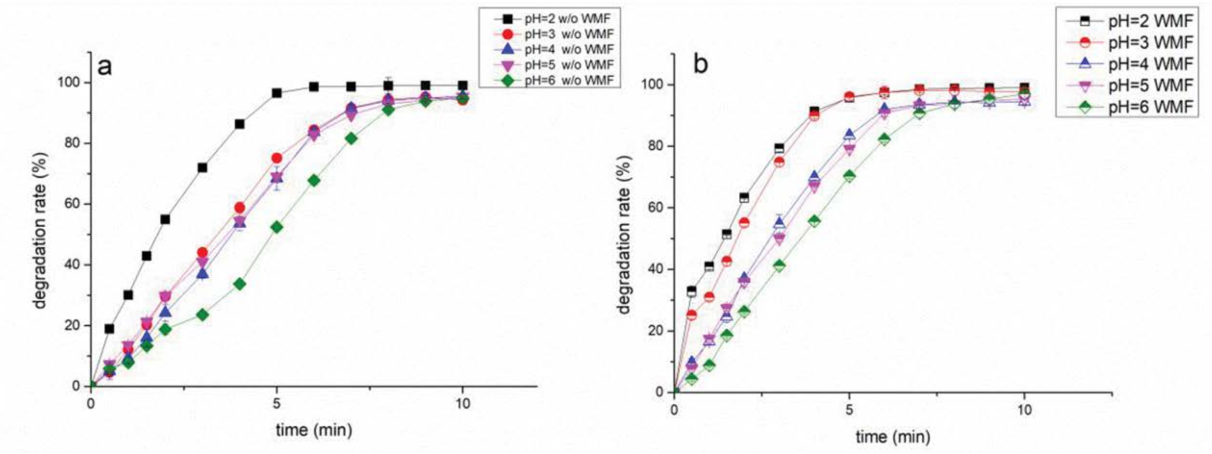

Fig. 7. Effect of WMF on AO7 removal by ZVI at different pHs. (a) W/o WMF and (b) with WMF. Reaction conditions: AO7 = 25 mg L^{-1} 300 mL, [ZVI] = 0.2 g L^{-1}, [Cu^{2+}] = 0.05 mg L^{-1}, [PMS] = 4 × 10^{-4} mol L^{-1}.

of AO7 with ZVI/Cu^{2+}/PMS, which may be due to the following reasons: (1) lower pH can accelerate ZVI corrosion, (2) H^+ can react with OH^- and promote the reaction (Eq. (6)) to proceed in the forward direction, accelerating the production of free radicals.

3.4.2. Effect of WMF on AO7 removal by ZVI/Cu^{2+}/PMS at different ZVI dosages

The influence of ZVI dosage on the AO7 removal rate is shown in Fig. 8. It was observed that 0.04 g of ZVI removed only 55.2% of AO7 in 10 min. As the ZVI dose increased to 0.6 and 0.7 g, 70.1% and 75.9% of AO7 were removed from the solution during the 5 min of mixing. Obviously, the removal rate of AO7 increased with the increase of the ZVI dosage. According to Eq. (3), increasing the amount of ZVI made the reaction proceed in the positive direction, thereby increasing the content of Fe^{2+} in the system, The Fe^{2+} can effectively reduce Cu^{2+} to generate Cu^+, and more Cu^+ is more conducive to activate PMS to generate free radicals. In this case, the oxidation effect of the system was enhanced.

3.4.3. Effect on AO7 removal by ZVI/Cu^{2+}/PMS at different Cu^{2+} dosages

As shown in Fig. 9, the degradation effect of the system was enhanced with the increase of Cu^{2+} dosage regardless of the magnetic field. Cu^{2+} can be converted to Cu^+ ions by the action of ZVI, and Cu^+ can effectively activate PMS to generate free radicals. Therefore, the content of Cu^+ increased as the content of Cu^{2+} increased, and the oxidation capacity of the system was enhanced.

3.4.4. Effect on AO7 removal by ZVI/Cu^{2+}/PMS at different PMS dosages

As shown in Fig. 10, as the amount of PMS increased, the reaction rate increased significantly. PMS was the main source of HSO^{5-} and was the cause of sulfate in the system.

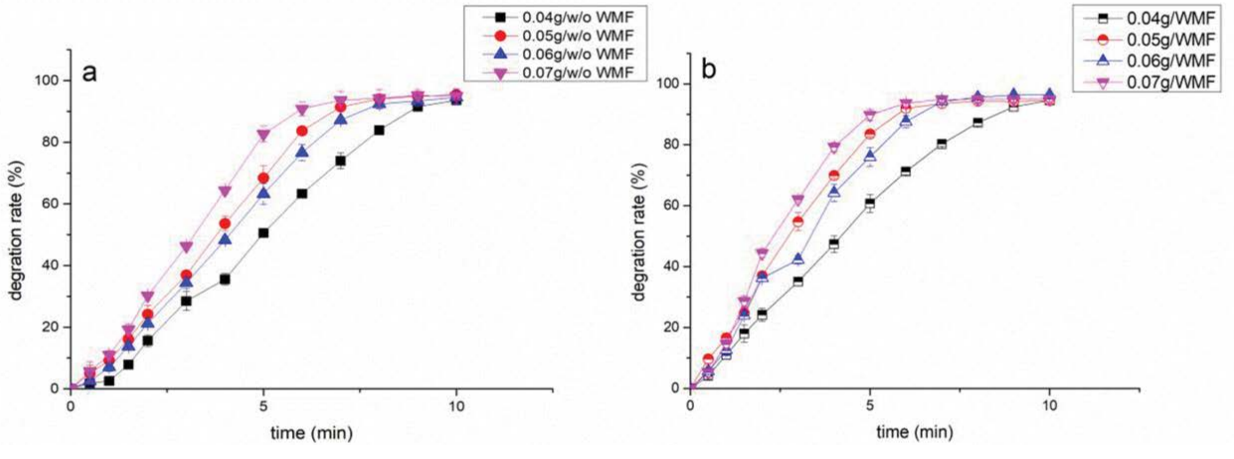

Fig. 8. Effect of ZVI dosage. (a) W/o WMF and (b) with WMF. Reaction conditions: AO7 = 25 mg L^{-1} 300 mL, [Cu^{2+}] = 0.05 mg L^{-1}, [PMS] = 4 × 10^{-4} mol L^{-1}, pH = 4.0.

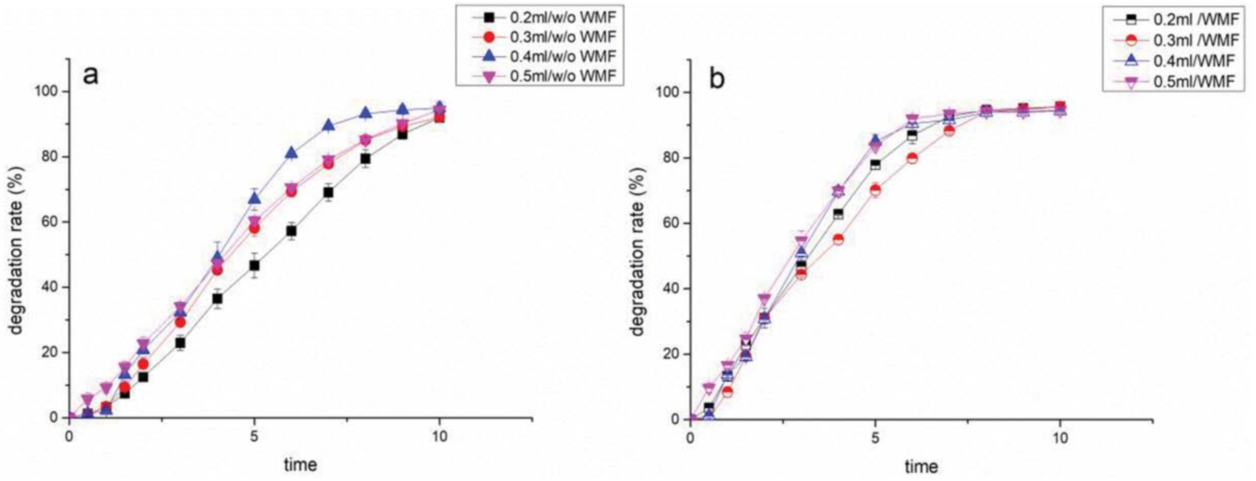

Fig. 9. Effect of Cu^{2+} dosage. (a) W/o WMF and (b) with WMF. Reaction conditions: AO7 = 25 mg L^{-1} 300 mL, [ZVI] = 0.2 g L^{-1}, [PMS] = 4×10^{-4} mol L^{-1}, pH = 4.0.

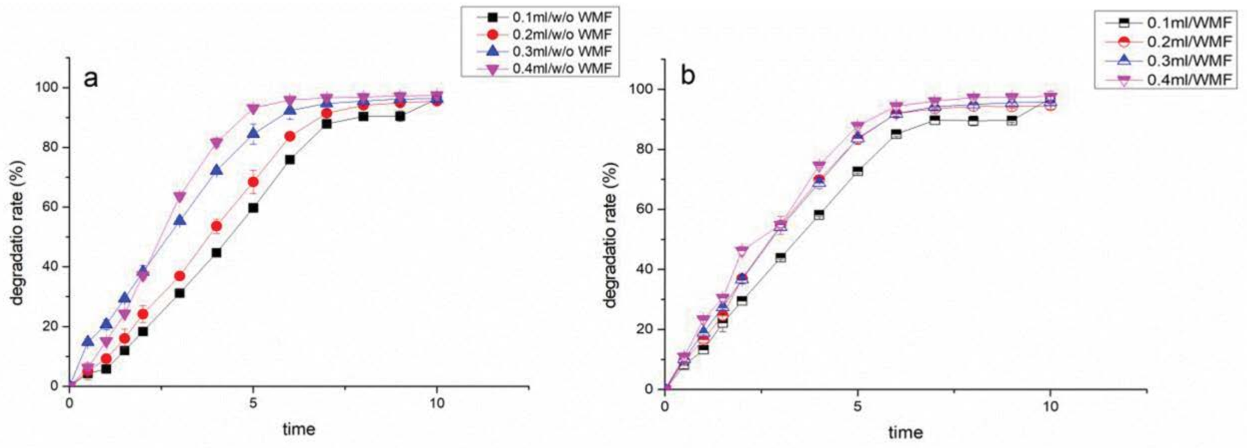

Fig. 10. Effect of PMS dosage. (a) W/o WMF and (b) with WMF. Reaction conditions: AO7 = 25 mg L^{-1} 300 mL, [ZVI] = 0.2 g L^{-1}, [Cu^{2+}] = 0.05 mg L^{-1}, pH = 4.0.

Therefore, as the PMS content in the solution increased, the amount of HSO^{5-} in the solution increased. This promoted the production of sulfate radicals, which were the major contributors to the system. In this case, increasing the amount of PMS can increase the reaction rate.

3.4.5. AO7 concentration effects on AO7 removal

As shown in Fig. 11, the system was able to almost completely degrade 10, 15 and 20 mg L^{-1} AO7 solution within 10 min. About 60% of 25 mg L^{-1} of AO7 was degraded within 10 min. After the magnetic field was added, the degradation rate was increased to 95%. This shows that the system has a good oxidation efficiency. Comparison between Figs. 11a and b shows that higher the concentration of AO7, the more obvious the effect of adding WMF. Therefore, in order to better study the role of the magnetic field, a high concentration of solution was selected for the study.

3.4.6. Effect on AO7 removal by ZVI/Cu^{2+} at different WMF strength

The magnetic field intensity was changed by the distance between the magnetic field and the beaker (Fig. 12). With the increase of WMF, the reaction rate greatly increased. The probable reason was that the stronger the magnetic field, the more ZVI would be magnetized, then the ZVI would have a stronger ability to attract Cu^{2+}, and Cu^{2+} could move to the surface of ZVI more quickly, which accelerated the reaction.

3.4.7. Summary of influencing factors

In summary, the ZVI/Cu^{2+}/PMS system has a better catalytic oxidation effect in the solution with a lower pH value, and the increase of the dosage of each component can effectively promote the following two reactions in the positive direction, thereby enhancing the oxidation of the system.

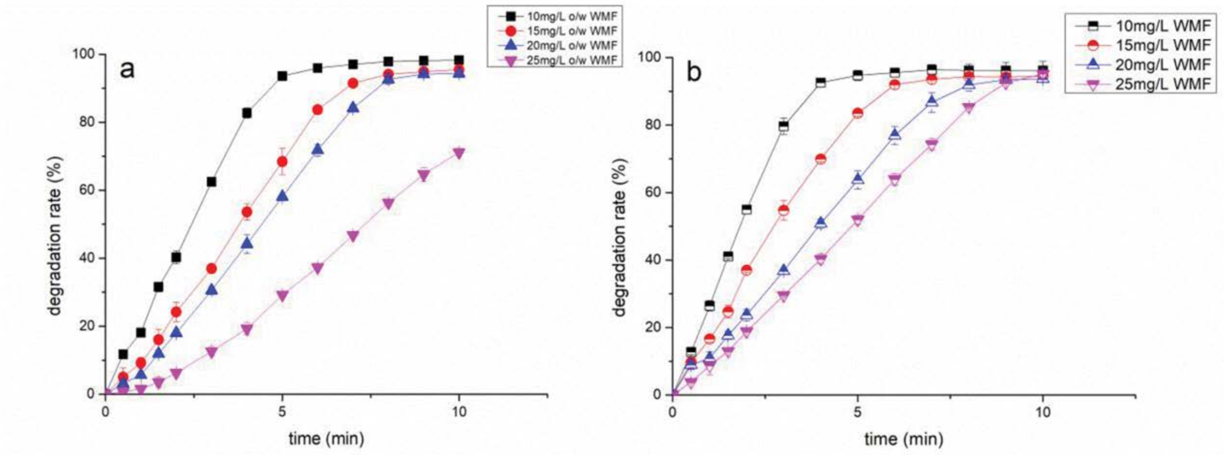

Fig. 11. Effect of AO7 concentrates on AO7 removal by ZVI. (a) W/o WMF and (b) with WMF. Reaction conditions: AO7 300 mL, [ZVI] = 0.2 g L^{-1}, [Cu^{2+}] = 0.05 mg L^{-1}, [PMS] = 4 × 10^{-4} mol L^{-1}, pH = 4.0.

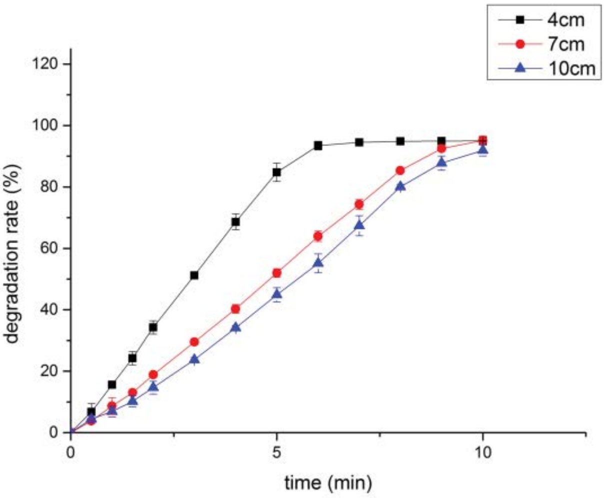

Fig. 12. Effect on AO7 removal by ZVI/Cu^{2+} at different WMF strength. Reaction conditions: AO7 = 25 mg L^{-1} 300 mL, [ZVI] = 0.2 g L^{-1}, [Cu^{2+}] = 0.05 mg L^{-1}, [PMS] = 4 × 10^{-4} mol L^{-1}, pH = 4.0.

$$Fe^{2+} + Cu^{2+} \rightarrow Cu^{+} + Fe^{3+} \tag{14}$$

$$Cu^{+} + HSO^{5-} \rightarrow Cu^{2+} + SO_4^{\bullet -} + OH^{-} \tag{15}$$

$$Cu^{+} + HSO^{5-} \rightarrow Cu^{2+} + {}^{\bullet}OH + SO_4^{2-} \tag{16}$$

When the dosage was [ZVI] = 0.2 g L^{-1}, [Cu^{2+}] = 0.05 mg L^{-1}, [PMS] = 4 × 10^{-4} mol L^{-1}, and the pH value was 4.0, the system achieved the best effect. Enhancement of the weak magnetic field can also effectively improve the catalytic oxidation effect of the system.

4. Conclusions

The present study demonstrated that WMF can effectively improve the oxidizing ability of ZVI/Cu^{2+}/PMS systems. Due to the magnetic field gradient force, a weak magnetic field can cause local corrosion of ZVI to produce more Fe^{2+} which can reduce Cu^{2+} to Cu^{+}. In addition, the weak magnetic field not only adsorbs the paramagnetic ion Fe^{2+} on the ZVI surface but also moves the paramagnetic ion Cu^{2+} along the magnetic field line to the ZVI surface. In this way, the reduction of Cu^{2+} by Fe^{2+} is accelerated to result in more Cu^{+} formation. In addition, through free radicals and Cu^{+} inhibition experiments, it is concluded that Cu^{+} is the substance that mainly activates PMS to generate $^{\bullet}OH$ and $SO_4^{\bullet -}$. Therefore, a weak magnetic field accelerates the rate of Cu^{+} formation and thus promotes the free radicals production ability which can enhance the oxidation capacity of the system. An increased magnetic field strength and decrease in the solution pH can further enhance the oxidation efficiency. The results obtained help in understanding the effect of WMF on the interaction between ZVI, Cu^{2+} and PMS. Therefore, this study is of theoretical significance in understanding the effects of WMF on metal-based catalysts.

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