

Hydroxylamine Accelerates the Cycle of Fe(III)/Fe(II)-Cu(II)/Cu(I) to Enhance the Ability of Fe-Cu Bimetallic System to Activate Peroxymonosulfate to Degrade A07

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Research Article

Keywords: Bimetallic, Hydroxylamine, Peroxymonosulfate, Organic pollutants

Posted Date: December 6th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-794274/v1>

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Abstract

In this study, a new type of iron/copper bimetallic combined with hydroxylamine (HA) activated peroxymonosulfate (PMS) was constructed to treat organic pollutants. Selecting the azo dye A07 as the representative of organic pollutants, the new system can achieve nearly 100% degradation of A07 within 5 minutes. The Fe(II)/Cu(II)/HA/PMS system mainly generates $\text{SO}_4^{\cdot-}$ to achieve the degradation of A07 in acidic environment, while neutral and alkaline environments rely on $\cdot\text{OH}$. The presence of hydroxylamine accelerates the cycle of Fe(II)/Fe(III) and Cu(II)/Cu(I) in the system, and enhances the degradation ability of the system for organic pollutants. The addition of trace Cu(II) (1 μM) enhances the ability of a single Fe(II)/HA/PMS system to degrade A07 in neutral and alkaline environments without causing secondary copper pollution. The common inorganic anions Cl^- and NO_3^- in water have almost no effect on the degradation of A07 in the system. The constructed Fe(II)/Cu(II)/HA/PMS system is an efficient and clean organic pollutant wastewater treatment process, which has very promising application prospects.

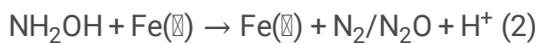
1 Introduction

Advanced oxidation processes (AOPs) based on the generation of reactive oxygen species (hydroxyl radicals, sulfate radicals, superoxide anion radicals, singlet oxygen, etc.) have shown great potential and practical value in the removal of pollutants in water in recent years (Duan et al. 2015a; Duan et al. 2015b; Indrawirawan et al. 2015; Liu et al. 2016; Yan et al. 2015). Hydrogen peroxide and persulfate are oxidants that can generate reactive oxygen species that have been widely studied in recent years (Xie et al. 2017; Wei et al. 2020). Compared with hydrogen peroxide, persulfate is more stable and easy to store and transport. In addition, compared with the $\cdot\text{OH}$ ($E_0 = 1.8\text{--}2.7$ eV) produced in the hydrogen peroxide process, the $\text{SO}_4^{\cdot-}$ ($E_0 = 2.5\text{--}3.1$ eV) produced in the persulfate process has a higher redox potential. Therefore, it can more selectively degrade organic pollutants containing carbon-carbon double bonds and benzene rings (Anipsitakis et al. 2003; Huang et al. 2005). Peroxymonosulfate (PMS, HSO_5^-) and peroxodisulfate (PDS, $\text{S}_2\text{O}_8^{2-}$) are the most concerned persulfate oxidants, because their decomposition products (SO_4^{2-}) are the least harmful to organisms (Tsitonaki et al. 2008). The main ways to activate persulfate are thermal radiation (Ghauch et al. 2015; Qi et al. 2015), alkali (Qi et al. 2016; Zhang et al. 2016a), ultraviolet radiation (Antonioni et al. 2010), transition metal ions (Ayoub and Ghauch 2014), solid catalyst, etc (Ghauch et al. 2013; Naim and Ghauch 2016).

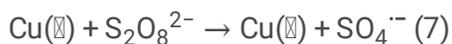
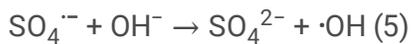
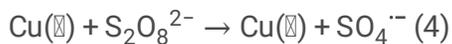
Among the above activation methods, transition metal ions have received increasing attention due to their high efficiency, low cost and environmental friendliness (Ji et al. 2014). Fe(II), as a catalytic substance in the traditional Fenton reaction, has been extensively studied in the Fenton-like advanced oxidation process. However, the Fe(II) activated persulfate process has inherent defects in wastewater treatment. For example, Wu et al. investigated the performance of Fe(II) activated PS to degrade trichloroethylene (TCE), and the results showed that the degradation efficiency of Fe(II)/PS process on TCE was only 30% within 30 minutes (Wu et al. 2015). The lower degradation efficiency is attributed to the accumulation of Fe(II) and the slow conversion of Fe(II) to Fe(III) (Chen et al. 2015; Wu et al. 2016). In addition, excessive Fe(II) will quench the reactive oxygen species such as $\text{SO}_4^{\cdot-}$ in the process (Eq. 1), leading to a decrease in the degradation efficiency of the process to pollutants (Wang et al. 2020).



In order to solve the above-mentioned defects of Fe(III) activated persulfate process for wastewater treatment, some scholars proposed to use hydroxylamine (HA, NH₂OH) as a reducing agent to improve the Fe(III) activated persulfate process (Li et al. 2020). This is because the reduction ability of hydroxylamine can greatly accelerate the cycle of Fe(III)/Fe(II) and Cu(II)/Cu(I) (Lei et al. 2015; Velosa and Nascimento 2017) (Eqs. 2 and 3). However, past studies have shown that in a neutral or alkaline environment, Fe(III) is difficult to cooperate with hydroxylamine to activate persulfate to achieve effective degradation of organic pollutants (Han et al. 2014; Jin et al. 2018). In order to broaden the pH range of the Fe(III)/hydroxylamine/persulfate system for degradation of organic pollutants, some scholars added chelating agents such as nitrilotriacetic acid, citric acid, EDDS to the system (Han et al. 2014; Jin et al. 2018; Fu et al. 2017). It is worth noting that the carbon and nitrogen commonly contained in these chelating agents may decompose into some harmful intermediate products and cause secondary pollution. Therefore, it is necessary to develop a new and clean way to broaden the pH range of the Fe(III)/hydroxylamine/persulfate system to degrade organic pollutants.



Past studies have shown that Cu(II) can activate persulfate in the presence of hydroxylamine to remove methyl orange at a pH close to neutral (Zhou et al. 2016) (Eq. 3–7). In addition, the study by Sun et al. also showed that the presence of Cu(II) can also promote the conversion of Fe(III) to Fe(II) (Sun et al. 2019) (Eq. 8). Inspired by this, some scholars have explored the performance of hydroxylamine synergistically with Fe(III)-Cu(II) bimetallic system to activate PDS to degrade organic pollutants. The results show that the presence of trace amounts of Cu(II) can increase the degradation efficiency of Fe(III)/HA/PDS process on AO7 and broaden the pH range of the process to deal with organic pollutants to alkaline (pH = 10) (Liu et al. 2020; Wang et al. 2021). Based on the above research background, it is reasonable to speculate that in the presence of hydroxylamine, trace amounts of Cu(II) can also promote the ability of Fe(III) to activate PMS to generate reactive oxygen species (ROS). However, as far as the author knows, there is no research report on Fe(III)-Cu(II) bimetallic system activating persulfate system to degrade organic pollutants. Therefore, this study explored the performance and mechanism of Fe(III)-Cu(II) bimetallic system activating PMS to degrade AO7 in the presence of hydroxylamine. We hope that this research will enrich the research on the advanced oxidation process of persulfate.



2 Materials And Methods

2.1 Materials

AO7 ($C_{16}H_{11}N_2NaO_4S$, > 85%), $FeCl_3 \cdot 6H_2O$ (99%), $CuSO_4 \cdot 5H_2O$ (99%), hydroxylamine sulfate ($H_6N_2O_2 \cdot H_2SO_4$, HA, 99%), $KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$ (PMS, $\geq 47\%$ $KHSO_5$ basis), *tert*-butyl alcohol (TBA, $\geq 99\%$) and ethanol (EtOH, > 95%) were purchased from Aladdin Pharmaceutical Company (Shanghai, China). Sodium hydroxide (NaOH) was purchased from Sinopac Chemical Reagent Corporation. The reagents used in the experiment are all analytically pure, and ultrapure water is used to prepare the required solution before each experiment.

2.2 Experimental procedure

The degradation experiment of AO7 was conducted in a 250 mL beaker. A certain concentration of AO7, $Fe(III)$, $Cu(II)$, HA solution is uniformly mixed and then magnetically stirred. Add a certain amount of PMS to start the reaction (keep the initial total volume of the mixed solution at 50 mL). At a specified time interval (10, 30, 60, 90, 180 and 300 s) after the reaction started, 1 mL of the reaction liquid was taken out, and 1 mL of ethanol was added to quench the reaction. The absorbance was measured with an ultraviolet-visible spectrophotometer (UV-1810, Youke). Except for exploring the effect of pH of the solution on the degradation of AO7, all other experiments were conducted under the background pH of the mixed solution. Solution pH was adjusted by 0.1 mol/L H_2SO_4 and 0.1 mol/L NaOH. In addition, the degradation experiments of AO7 were repeated three times at room temperature (20 ± 1 °C), and the experimental results were averaged.

3 Results And Discussion

3.1 Role of HA in the $Fe(III)/Cu(II)/HA/PMS$ system

The reduction ability of HA is the key to the degradation of AO7 by the $Fe(III)/Cu(II)/HA/PMS$ system (Eqs. 2 and 3), so it is necessary to consider the effect of HA on the degradation of AO7 by the system. The effect of HA dosage on the degradation of AO7 in the $Fe(III)/Cu(II)/HA/PMS$ system is shown in Fig. 1a. No degradation of AO7 was observed in the $Fe(III)/Cu(II)/PMS$ system without HA. This indicates that it is difficult for $Fe(III)-Cu(II)$ bimetallics to activate PMS to generate reactive oxygen species to achieve effective degradation of AO7. After adding 0.05 mM HA, 29.59% of AO7 was degraded within 5 min with $k = 0.059 \text{ min}^{-1}$ (Fig. 1b). As the dosage of HA increased to 0.5 mM, the degradation efficiency of $Fe(III)/Cu(II)/HA/PMS$ system on AO7 was significantly improved, reaching 95.52% with $k = 0.569 \text{ min}^{-1}$ within 5 min. Further increasing the dosage of HA (1 mM) cannot improve the degradation efficiency of $Fe(III)/Cu(II)/HA/PMS$ system on AO7, but it can accelerate the degradation process of AO7 by the system (k increased from 0.569 min^{-1} to 0.868 min^{-1}). Therefore, the presence of HA is the key to the $Fe(III)-Cu(II)$ bimetallic system to activate PMS, and its optimal dosage is 0.5 mM.

3.2 Role of $Fe(III)$, $Cu(II)$, PMS in the $Fe(III)/Cu(II)/HA/PMS$ system

The effect of $Fe(III)$ dosage on the degradation of AO7 in $Fe(III)/Cu(II)/HA/PMS$ system is shown in Fig. 2a. The $Cu(II)/HA/PMS$ system without $Fe(III)$ added almost no degradation of AO7, which indicates that $Cu(II)$ alone or $Cu(II)$ reduced by HA is difficult to activate PMS to degrade AO7. When $Fe(III)$ dosage was 5 μM , only 38.46% of AO7 was degraded within 5 min with $k = 0.099 \text{ min}^{-1}$ (Fig. 2b). Adding 50 μM $Fe(III)$ into the system, the degradation efficiency of $Fe(III)/Cu(II)/HA/PMS$ system on AO7 reached 95.37% with $k = 0.569 \text{ min}^{-1}$. Further increasing the dosage of $Fe(III)$ cannot improve the degradation efficiency of the system for AO7. In the past reports on $Fe(III)$ activation of PMS or PS degradation of organic pollutants, excessive $Fe(III)$ may remove $SO_4^{\cdot -}$, leading to a decrease in degradation efficiency (Eq. 1) (Zhang et al. 2016b). However, this study did not observe a

decrease in degradation efficiency, which indicates that the Fe(II)-Cu(II) bimetallic system can overcome the defects of Fe(II) system activating PMS to degrade pollutants.

The effect of Cu(II) dosage on the degradation of A07 in Fe(II)/Cu(II)/HA/PMS system is shown in Fig. 3a. Compared with the control group, the system with 0.5 μM Cu(II) added significantly improved the degradation efficiency of A07, from 83.84–95.37% (k increased from 0.345 min^{-1} to 0.574 min^{-1} , show in Fig. 3b). Further increasing the dosage of Cu(II) has almost no effect on the degradation of A07 in the Fe(II)/Cu(II)/HA/PMS system. However, when the dosage of Cu(II) was increased to 50 μM , the degradation efficiency of Fe(II)/Cu(II)/HA/PMS system on A07 decreased slightly to 93.08% with $k = 0.482 \text{ min}^{-1}$. Excessive Cu(II) will cause a large amount of Cu(II) reduced by HA in the system to compete with pollutants for $\text{SO}_4^{\cdot-}$ and/or $\cdot\text{OH}$, resulting in a decrease in the degradation efficiency of the system for A07 (Eqs. 9 and 10) (Buxton et al. 1988; Liang and Su 2009). The above studies show that in the process of Fe(II)-Cu(II) bimetallic system coupled with hydroxylamine to activate PMS, trace amounts of Cu(II) (1 μM) can greatly promote the degradation efficiency of A07. Surprisingly, the concentration of 1 μM Cu(II) is lower than the Cu(II) concentration (15.6 μM) stipulated by China's Surface Water Level II Standard. In addition, the concentration of Cu(II) added in Fe(II)-Cu(II) bimetallic system is much lower than other advanced oxidation processes based on Cu(II) (Zhou et al. 2016; Lee et al. 2016). This means that the Fe(II)/Cu(II)/HA/PMS system can not only achieve high-efficiency degradation of organic pollutants, but also will not cause the secondary pollution of Cu(II).



PMS is the source of the reactive oxygen species in the Fe(II)/Cu(II)/HA/PMS system, so the dosage of PMS has a crucial influence on the efficiency of the system to degrade A07. Figure 4a shows the effect of PMS dosage on the degradation of A07 in the Fe(II)/Cu(II)/HA/PMS system. The degradation efficiency of A07 increases with the increase of PMS dosage, from 17.62% at 0.1 mM to 95.52% at 1 mM, and the reaction rate constant k is increased by nearly 285 times (k increased from 0.002 min^{-1} to 0.569 min^{-1} , show in Fig. 4b). Less PMS dosage ($\leq 0.5 \text{ mM}$) will result in a significant shortage of reactive oxygen species that can be produced in the system (Qi et al. 2014), and the reaction in the system will be terminated within 3 minutes, resulting in a lower degradation efficiency of A07 ($\leq 76.68\%$). However, excessive PMS will also inhibit the degradation efficiency of A07 by the system (Qi et al. 2016). When the dosage of PMS was increased to 3 mM, the degradation efficiency of the system for A07 was only 66.03% with $k = 0.206 \text{ min}^{-1}$. Excessive PMS will remove $\text{SO}_4^{\cdot-}$, resulting in a decrease in the degradation efficiency of A07 by the system (Eq. 11). Therefore, 1 mM PMS is the most suitable dosage for Fe(II)/Cu(II)/HA/PMS system to degrade A07.



3.3 Trace Cu(II) enhances the degradation of A07 by Fe(II)/HA/PMS system in a wide pH range

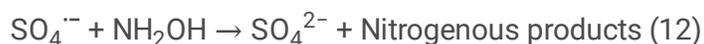
The pH of wastewater has a vital influence on the degradation of organic pollutants by persulfate advanced oxidation system. Figure 5 compares the effect of initial pH (2–10) on the degradation of A07 in different systems. When the initial pH is 4–6, Fe(II)/Cu(II)/HA/PMS or a single Fe(II)/HA/PMS system can achieve high-

efficiency degradation of AO7 within 5 minutes (> 94%). However, when the pH further increased to neutral or alkaline, the degradation efficiency of AO7 for both systems significantly decreased. The degradation efficiency of Fe(III)/HA/PMS system for AO7 decreased sharply from 94.12% at pH = 6 to 56.20% at pH = 7 (k decreased from 0.438 min^{-1} to 0.099 min^{-1} , show in Table 1). The decrease in AO7 degradation efficiency can be attributed to three explanations. First, the increase of pH will cause the precipitation of Fe(III) hydroxide to reduce the Fe(III) that can be used to activate PMS in the system; Secondly, in a neutral or alkaline environment, $\text{SO}_4^{\cdot-}$ will be partially or completely converted into $\cdot\text{OH}$ with lower selectivity and shorter half-life, resulting in a decrease in the degradation efficiency of AO7 (Eqs. 5 and 6); Finally, HA ($\text{pK}_a = 5.96$) will exist in the form of NH_2OH in a neutral or alkaline environment. Past studies have shown that NH_2OH will react with $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, resulting in the reduction of reactive oxygen species that can be used to degrade AO7 in the system (Liu et al. 2017) (Eqs. 12 and 13). However, the degradation efficiency of Fe(III)-Cu(II) bimetallic system to AO7 at pH = 7 is higher than that of single Fe(III) activated PMS system (68.69% with $k = 0.149 \text{ min}^{-1}$). This advantage remains as the initial pH rises to alkaline except for pH = 10. This suggests that a trace amount of Cu(II) ($1 \mu\text{M}$) enhances the ability of a single Fe(III)-activated PMS system to degrade organic pollutants in neutral and alkaline environments. This is in agreement with the findings of Liu et al. (2020) and Wang et al. (2021) using Cu(II)/Fe(II)-coupled hydroxylamine activated PDS systems for the degradation of AO7. Notably, when the initial pH was in an extremely acidic environment (pH = 2), no significant degradation of AO7 was found for the above two systems. And when the initial pH increased to 3, the degradation efficiency of both systems for AO7 was about 80%. This can be attributed to the fact that at $\text{pH} < 3$, the reduced Fe(II) forms the non-reactive iron species $(\text{Fe}^{2+}(\text{H}_2\text{O}))^{2+}$, which is common in Fenton-like reactions, making the above two systems unable to degrade AO7 (Masomboon et al. 2009). In contrast to the two systems mentioned above, the single Cu(II)/HA/PMS system was unable to degrade AO7 at an initial $\text{pH} < 5$. The degradation efficiency of the Cu(II)/HA/PMS system for AO7 increased slightly with increasing pH, from 5.94% at pH = 5 to 13.26% at pH = 10 (k increased from 0.009 min^{-1} to 0.016 min^{-1}). The Cu(II) in the system is reduced to Cu(I) under the reduction of HA (Eq. 3). Subsequently, as the pH increases, Cu(I) will be converted into Cu(OH) and $\text{Cu}(\text{OH})_2^-$ which have a stronger ability to activate PMS, leading to an increase in the degradation efficiency of AO7 by the system (Brandt and Eldik 1995). However, under alkaline environment ($\text{pH} > 7$), the improvement of the efficiency of trace amount of Cu(II) ($1 \mu\text{M}$) for the degradation of AO7 by Fe(III)/HA/PMS system (< 10%) was lower than that of the degradation of AO7 by Cu(II)/HA/PMS system (about 13%). This may be due to the fact that Cu(I), Cu(OH) and $\text{Cu}(\text{OH})_2^-$ partially reduced by HA participated in the process of reducing Fe(III) to Fe(II) (Eq. 8), while Fe(III) is difficult to activate PMS in an alkaline environment (Chen et al. 2015).

Table 1

Pseudo-first-order kinetic fitting parameters of the degradation of A07 by different system at different pH.

System		pH = 2	pH = 3	pH = 4	pH = 5	pH = 6	pH = 7	pH = 8	pH = 9	pH = 10
Cu(II)/HA/PMS	k (min^{-1})				0.009	0.014	0.013	0.018	0.016	0.016
	R^2				0.806	0.945	0.857	0.823	0.861	0.860
Fe(II)/HA/PMS	k (min^{-1})		0.296	0.545	0.559	0.438	0.099	0.080	0.043	0.035
	R^2		0.999	0.951	0.936	0.886	0.997	0.994	0.959	0.960
Fe(II)/Cu(II)/HA/PMS	k (min^{-1})		0.314	0.609	0.621	0.478	0.149	0.116	0.043	0.030
	R^2		0.999	0.930	0.926	0.875	0.979	0.994	0.963	0.962



3.4 The effect of anions and humic acid on the degradation of A07 in Fe(II)/Cu(II)/HA/PMS system

There are many inorganic anions and natural organic matter (NOM) in natural water, and the presence of these substances has a non-negligible effect on the degradation of organic pollutants by advanced oxidation processes. In order to explore the ability of the Fe(II)/Cu(II)/HA/PMS system to degrade organic pollutants in a complex water environment, we selected Cl^- , NO_3^- , CO_3^{2-} which are common in water as the representative anions, and selected humic acid as a representative of natural organic matter. The effect of the addition of the above substances on the degradation of A07 in the Fe(II)/Cu(II)/HA/PMS system is shown in Fig. 6a. Compared with the control group, the addition of 2 mM Cl^- or NO_3^- had almost no effect on the degradation of A07 by the system, and the degradation efficiency of A07 only decreased by 1.48% and 1.63%, respectively. However, in the report that Li et al. (2019) and Bu et al. (2017) used Fe(II) and Fe(III) to activate PDS to degrade organic pollutants, it was found that the presence of Cl^- and NO_3^- would consume $\text{SO}_4^{\cdot-}$ in the system, thus inhibit the degradation of organic pollutants by the system (Eqs. 14 and 15). The above comparison shows that the Fe(II)/Cu(II)/HA/PMS system can enhance the impact resistance of the advanced oxidation process based on iron in the degradation of organic pollutants in water. Compared with the control group, the presence of CO_3^{2-} greatly reduced the degradation efficiency of A07 from 95.52–9.71% (k decreased from 0.569 min^{-1} to 0.016 min^{-1} , show in Fig. 6b). CO_3^{2-} will be hydrolyzed to HCO_3^- in the water and make the water present an alkaline environment (Eq. 16). As mentioned earlier, higher pH will inhibit the degradation of A07 by the system. In addition, HCO_3^- will react with $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ to form less oxidizing $\text{CO}_3^{\cdot-}$ (Eqs. 17 and 18), which greatly

weakens the system's ability to oxidize A07 (Luo et al. 2016; Zhou et al. 2013). The addition of 40 mg/L humic acid reduced the degradation efficiency of A07 by 41.46% (k decreased from 0.569 min^{-1} to 0.146 min^{-1}). The abundant electron sites on the surface of humic acid will attract electrophilic $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ (Eq. 19), thereby competing with pollutants for reactive oxygen species in the system, leading to a decrease in the degradation efficiency of A07 (Gara et al. 2009).

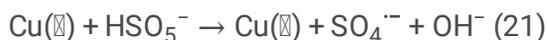


3.5 Possible mechanism of HA enhancing the degradation ability of the system

Investigating the reactive oxygen species involved in the degradation of A07 in the system is necessary to further explore the mechanism of degradation of A07 in the $\text{Fe}(\text{III})/\text{Cu}(\text{II})/\text{HA}/\text{PMS}$ system. $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ are considered to be common reactive oxygen species in the advanced oxidation process of homogeneous persulfate (Wang et al. 2019). The reaction rate of *tert*-butanol (TBA) with $\cdot\text{OH}$ ($6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) is much higher than $\text{SO}_4^{\cdot-}$ ($8.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$), so we choose TBA as the scavenger of $\cdot\text{OH}$ in the system; Similarly, ethanol (EtOH) has a high rate constant between $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, so we choose it as a scavenger of $\text{SO}_4^{\cdot-}$ ($1.6 \times 10^7 - 7.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) and $\cdot\text{OH}$ ($1.2 \times 10^9 - 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Zhou et al. 2016; Wang et al. 2021). The effect of adding 0.1 M (100 times the amount of PMS) scavenger on the degradation of A07 in the $\text{Fe}(\text{III})/\text{Cu}(\text{II})/\text{HA}/\text{PMS}$ system is shown in Fig. 7. In an acidic environment (pH = 3), the addition of 0.1 M TBA has almost no inhibitory effect on the degradation of A07 in the $\text{Fe}(\text{III})/\text{Cu}(\text{II})/\text{HA}/\text{PMS}$ system. Compared with the control group, the addition of 0.1 M EtOH reduced the degradation efficiency of A07 from 80.74–29.60%. This indicates that the reactive oxygen species involved in the degradation of A07 in the system is mainly $\text{SO}_4^{\cdot-}$ in an acidic environment. On the contrary, in a neutral (pH = 7) or alkaline (pH = 10) environment, the inhibitory effects of TBA and EtOH on the degradation of A07 in the system are almost the same. This indicates that in the neutral and alkaline environment, the main oxygen species for degradation of A07 in the $\text{Fe}(\text{III})/\text{Cu}(\text{II})/\text{HA}/\text{PMS}$ system is $\cdot\text{OH}$.

Based on the above analysis, the mechanism by which HA enhances the degradation of A07 in $\text{Fe}(\text{III})/\text{Cu}(\text{II})/\text{PMS}$ system can be summarized in Fig. 8. In an acidic environment, HA can reduce $\text{Fe}(\text{III})-\text{Cu}(\text{II})$ in the system to $\text{Fe}(\text{II})-\text{Cu}(\text{I})$ (Eqs. 2 and 3) respectively. In addition, $\text{Cu}(\text{II})$ can also participate in the process of reducing $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ (Eq. 8). The reduced $\text{Fe}(\text{II})$ in the system can activate PMS to produce $\text{SO}_4^{\cdot-}$ to degrade A07 (Eq. 20), while the reduced $\text{Cu}(\text{I})$ does not participate in the process of activating PMS (Fig. 5). Similarly, in a neutral or alkaline environment, HA and $\text{Cu}(\text{I})$ reduced by HA are involved in the process of reducing $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ (Eqs. 2 and 3). However, unlike the acidic environment, $\text{Fe}(\text{III})$ and $\text{Cu}(\text{II})$ in the system are both involved in the process of

activating PMS to produce reactive oxygen species (Eqs. 20 and 21) (Fig. 5). Then the $\text{SO}_4^{\cdot-}$ in the system is converted to $\cdot\text{OH}$ through the reaction of Eqs. 5 and 6 to achieve the degradation of A07.



4 Conclusion

Based on the iron/peroxymonosulfate advanced oxidation process to treat organic pollutants, this study constructed a new type of bimetallic Fe(II)-Cu(II) coupling hydroxylamine activated peroxymonosulfate by adding hydroxylamine and Cu(II). The presence of hydroxylamine and Cu(II) accelerates the Fe(II)/Fe(II)-Cu(II)/Cu(II) cycle in the system. When the initial dosages of Fe(II), Cu(II), HA, and PMS were 50 μM , 1 μM , 0.5 mM, and 1 mM, respectively, Fe(II)/Cu(II)/HA/PMS system could degrade 95.52% of A07 within 5 minutes. Adding a trace amount of Cu(II) (1 μM) can not only enhance the system's ability to degrade pollutants, but also will not cause secondary pollution. Therefore, the new bimetal Fe(II)-Cu(II) coupled with hydroxylamine activated peroxymonosulfate advanced oxidation system constructed in this research is very promising.

Declarations

Author contribution

Ming Zhang: investigation, data curation, writing—original draf; Kuo Zhang: investigation, data curation, writing—original draf; Runjuan Zhou: methodology, writing—reviewing and editing; Jinpeng Wang: conceptualization, methodology, supervision, writing—reviewing and editing.

Funding

This work was supported by the National Natural Science Foundation of China (Grant No. 51409001) and Natural Science Foundation of Anhui Province (2008085ME159).

Data availability

The dataset analyzed during the current study is not publicly available due to ethical concerns but are available from the corresponding author on reasonable request.

Ethics approval

All authors declare that they have not violated academic ethics and ethics.

Consent to participate

All authors declare to participate in the creation of the article.

Consent for publication

All authors agree to the publication of the article.

Competing interests

The authors declare no competing interests.

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Figures

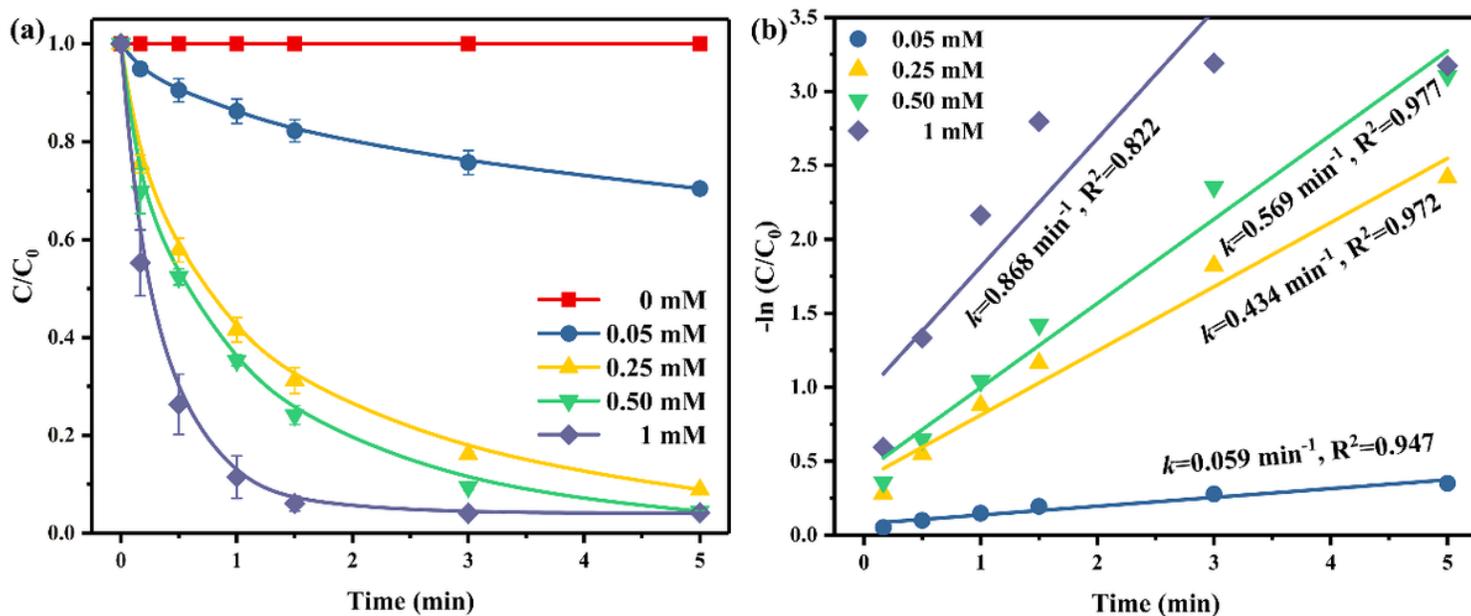


Figure 1

(a) The effect of HA dosage on the degradation of A07 in $\text{Fe(II)}/\text{Cu(II)}/\text{HA}/\text{PMS}$ system and (b) its kinetics fitting. ($[\text{A07}]_0=100 \text{ mg/L}$, $[\text{Fe(II)}]_0=50 \text{ }\mu\text{M}$, $[\text{Cu(II)}]_0=1 \text{ }\mu\text{M}$, $[\text{PS}]_0=1 \text{ mM}$)

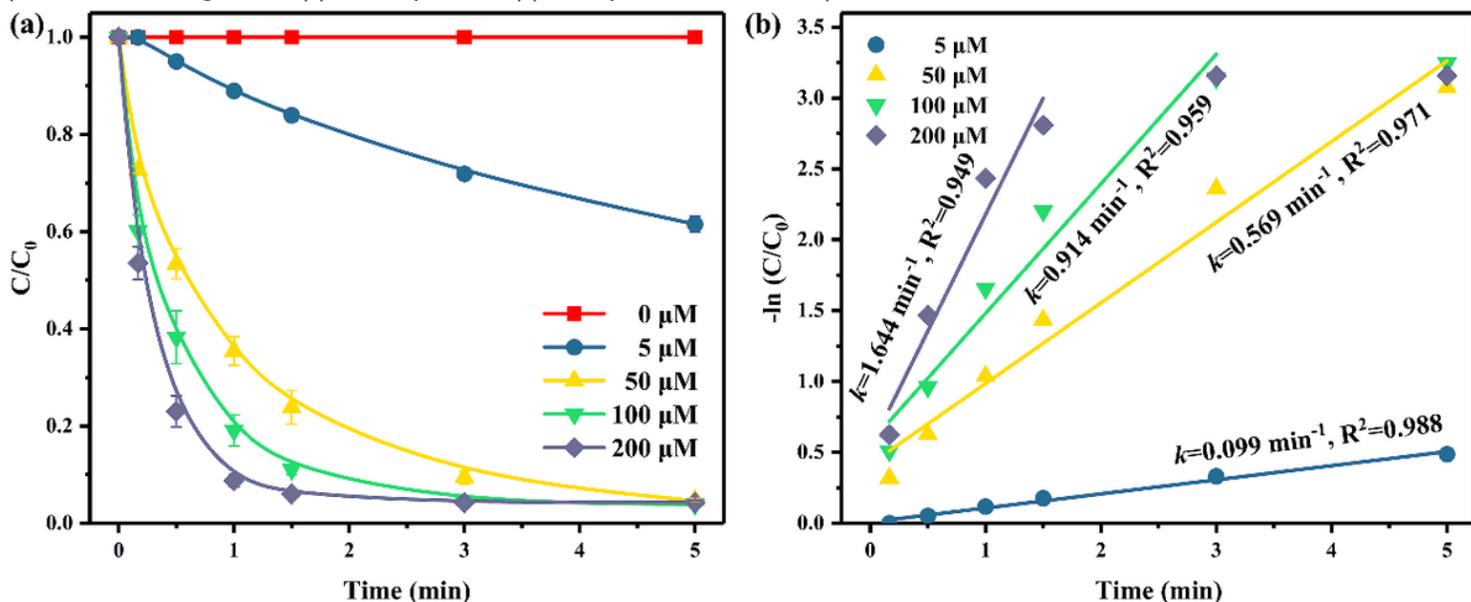


Figure 2

(a) The effect of Fe(II) dosage on the degradation of A07 in Fe(II)/Cu(II)/HA/PMS system and (b) its kinetics fitting. ([A07]₀=100 mg/L, [Cu(II)]₀=5 μM, [HA]₀=0.5 mM, [PMS]₀=1 mM)

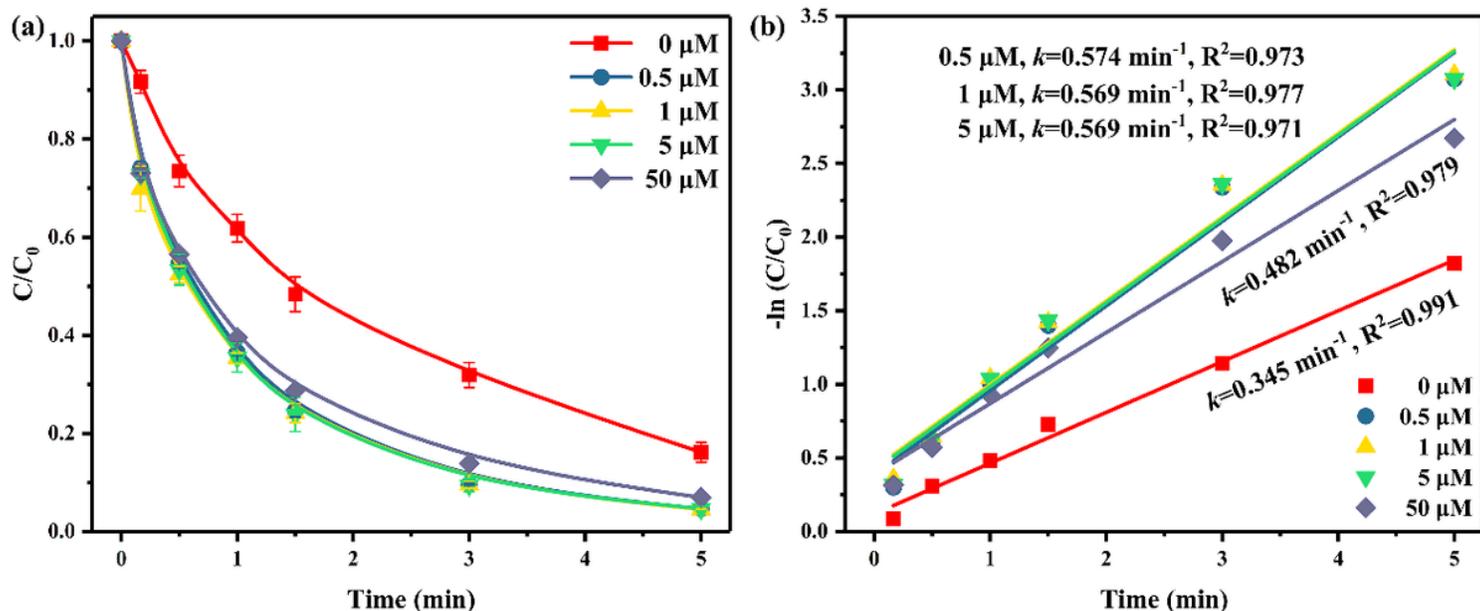


Figure 3

(a) The effect of Cu(II) dosage on the degradation of A07 in Fe(II)/Cu(II)/HA/PMS system and (b) its kinetics fitting. ([A07]₀=100 mg/L, [Fe(II)]₀=50 μM, [HA]₀=0.5 mM, [PMS]₀=1 mM)

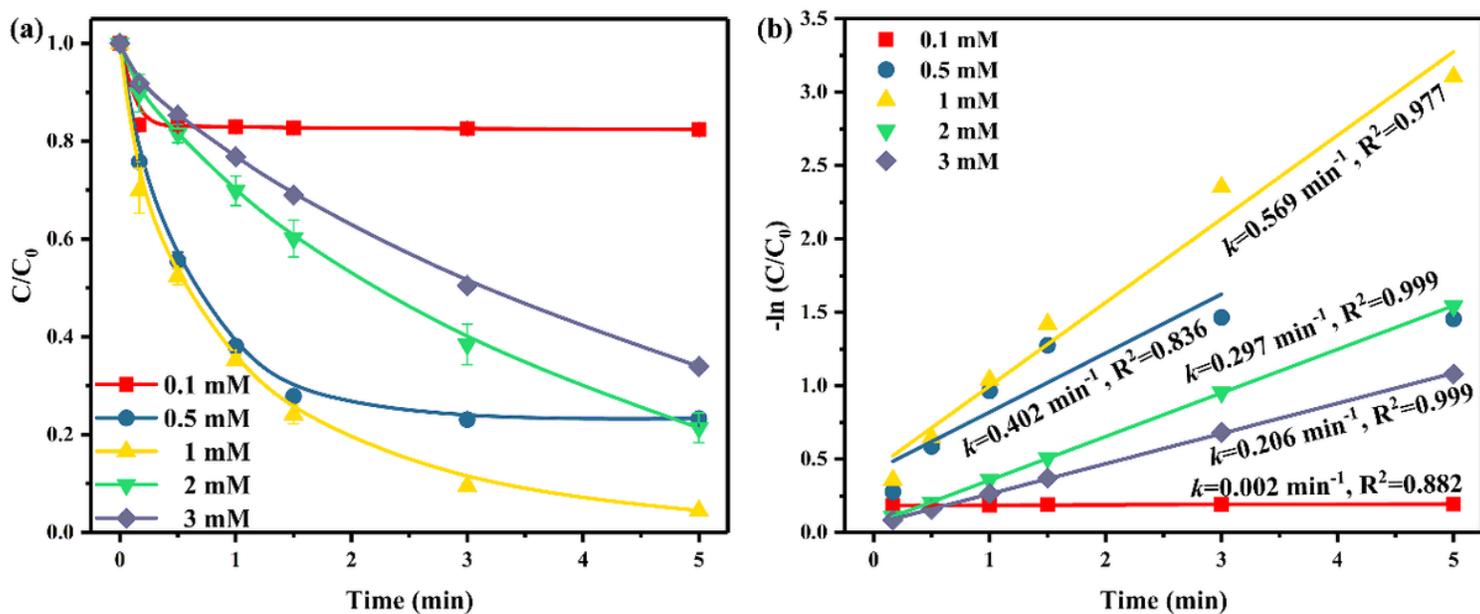


Figure 4

(a) The effect of PMS dosage on the degradation of A07 in Fe(II)/Cu(II)/HA/PMS system and (b) its kinetics fitting. ([A07]₀=100 mg/L, [Fe(II)]₀=50 μM, [Cu(II)]₀=1 μM, [HA]₀=0.5 mM)

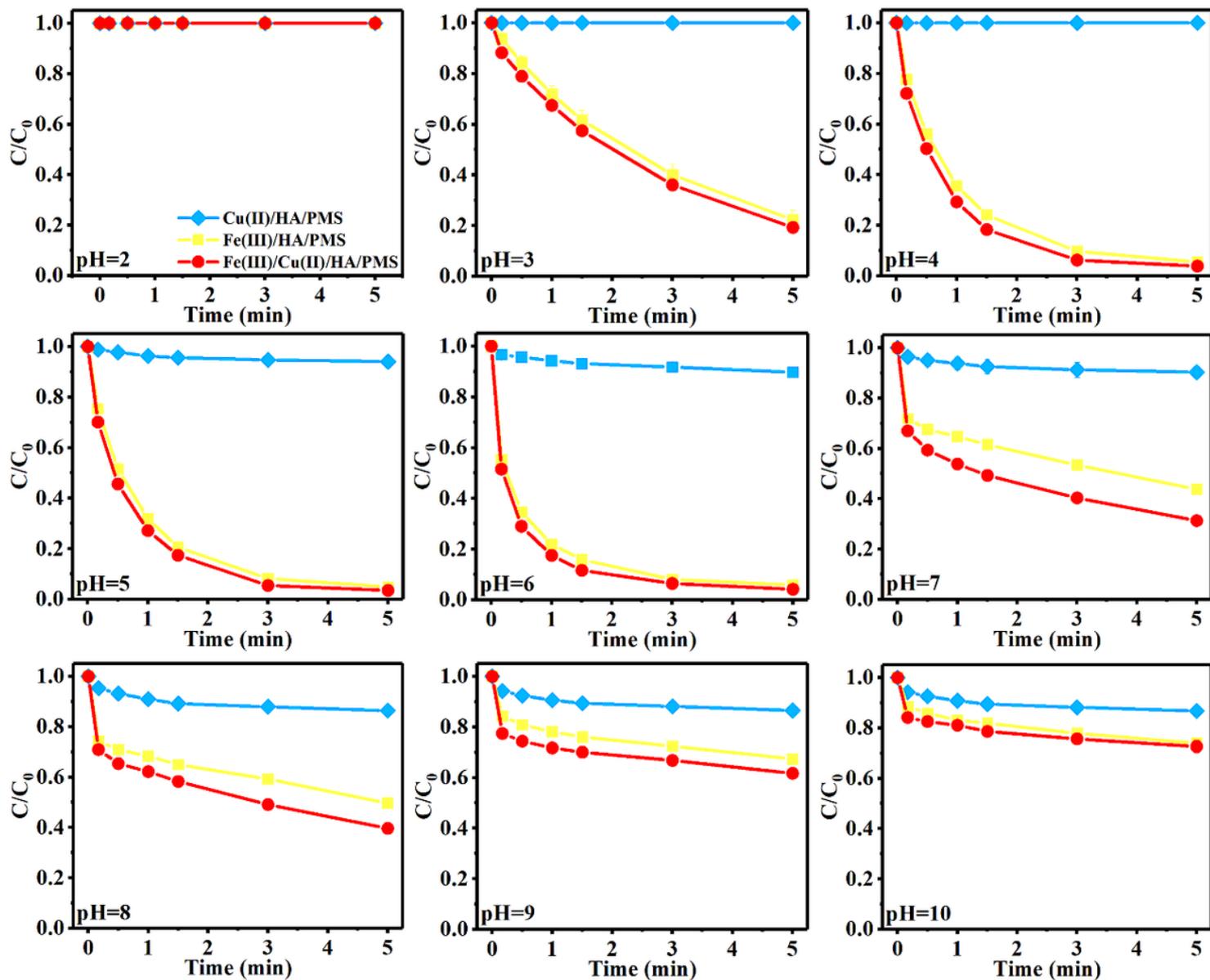


Figure 5

The effect of pH on the degradation of AO7 in different systems. ($[AO7]_0=100$ mg/L, $[Fe(\text{II})]_0=50$ μ M, $[Cu(\text{II})]_0=1$ μ M, $[HA]_0=0.5$ mM, $[PMS]_0=1$ mM)

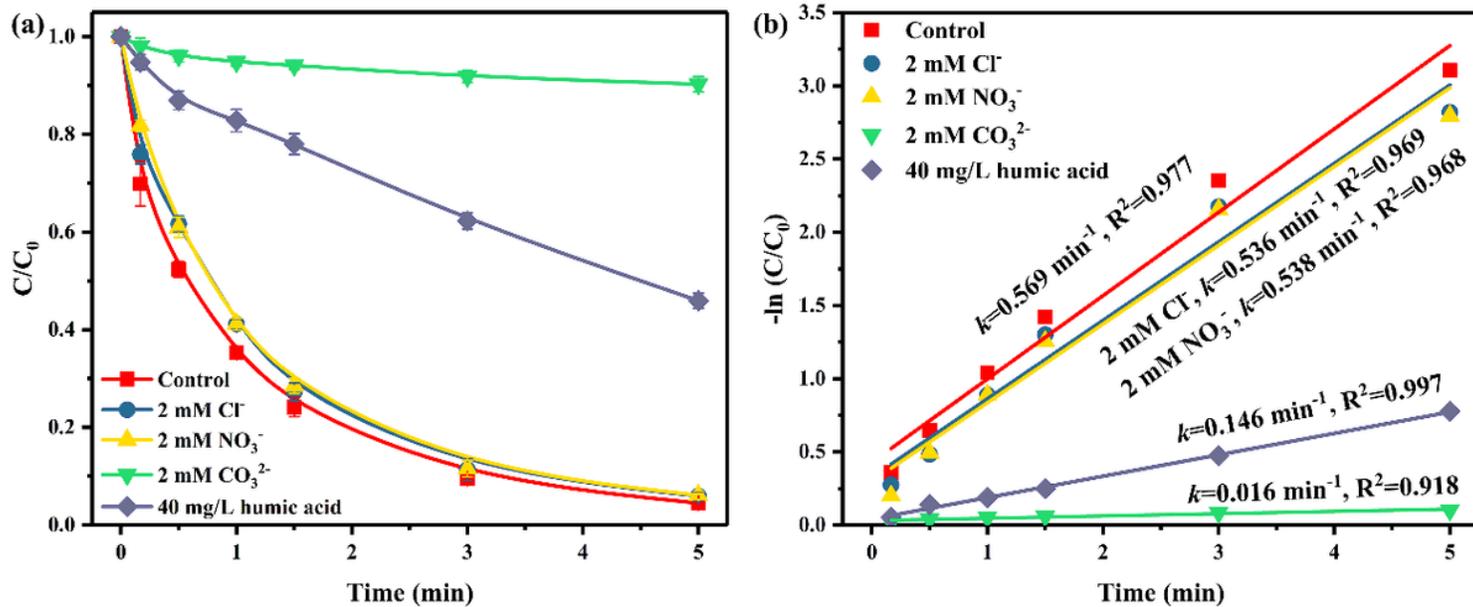


Figure 6

(a) The effect of anions and humic acid on the degradation of AO7 in Fe(III)/Cu(II)/HA/PMS system and (b) its kinetics fitting. ($[AO7]_0=100 \text{ mg/L}$, $[Fe(III)]_0=50 \text{ } \mu\text{M}$, $[Cu(II)]_0=1 \text{ } \mu\text{M}$, $[HA]_0=0.5 \text{ mM}$, $[PMS]_0=1 \text{ mM}$)

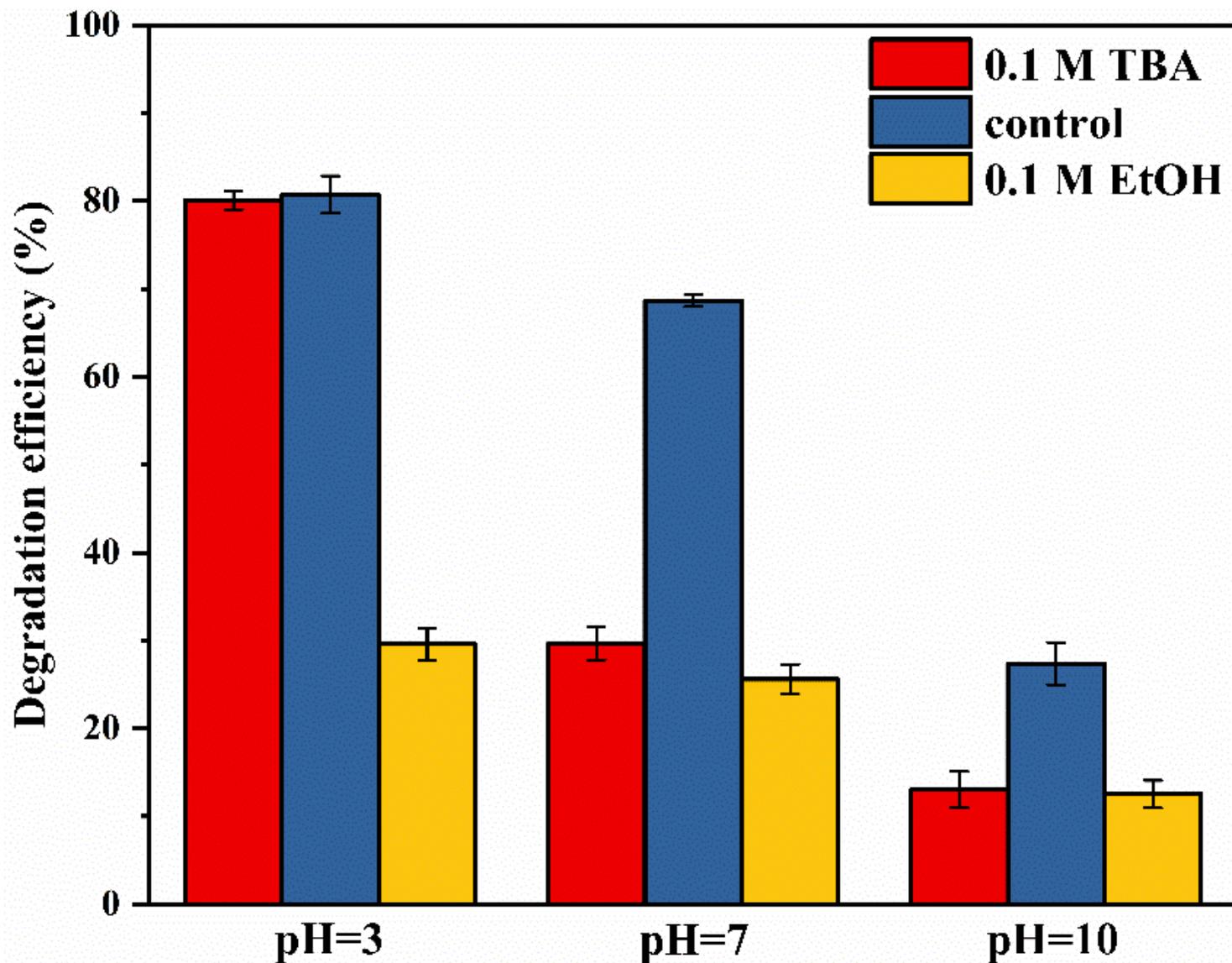


Figure 7

Identification of reactive oxygen species during the degradation of A07 in Fe(II)/Cu(II)/HA/PMS system. ([A07]₀=100 mg/L, [Fe(II)]₀=50 μM, [Cu(II)]₀=1 μM, [HA]₀=0.5 mM, [PMS]₀=1 mM)

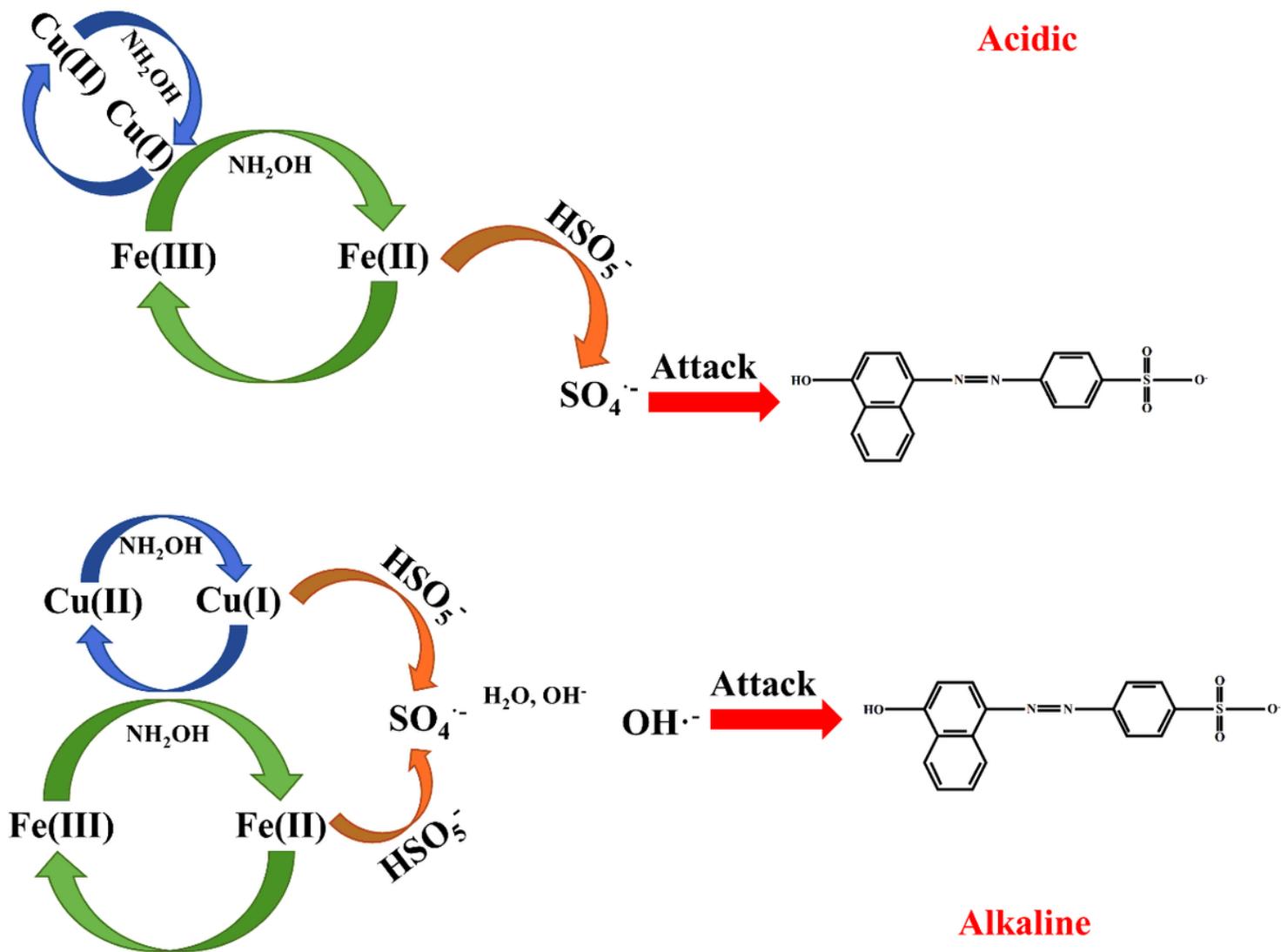


Figure 8

The mechanism of HA enhancing Fe(II)-Cu(I) bimetallic system to activate PMS to degrade A07.