

Activation of persulfate/copper by hydroxylamine via accelerating the cupric/cuprous redox couple

Peng Zhou, Jing Zhang, Juan Liang, Yongli Zhang, Ya Liu and Bei Liu

ABSTRACT

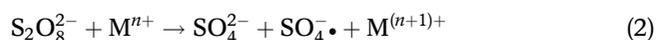
Cuprous copper [Cu(I)] reacts with sodium persulfate (PDS) to generate sulfate radical $\text{SO}_4^{\bullet-}$, but it has been seldom investigated owing to its instability and difficulty in dissolving it. This study proposes a new method to regenerate Cu(I) from cupric copper [Cu(II)] by addition of hydroxylamine (HA) to induce the continuous production of radicals through active PDS, and investigates the resulting enhanced methyl orange (MO) degradation efficiency and mechanism in the new system. HA accelerated the degradation of MO markedly in the pH range from 6.0 to 8.0 in the HA/Cu(II)/PDS process. Both $\text{SO}_4^{\bullet-}$ and hydroxyl radicals ($\bullet\text{OH}$) were considered as the primary reactive radicals in the process. The MO degradation in the HA/Cu(II)/PDS process can be divided into three stages: the fast stage, the transitory stage, and the low stage. MO degradation was enhanced with increased dosage of PDS. Although high dosage of HA could accelerate the transformation of the Cu(II)/Cu(I) cycle to produce more reactive radicals, excess HA can quench the reactive radicals. This study indicates that through a copper-redox cycling mechanism by HA, the production of $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ can be strongly enhanced, and the effective pH range can be expanded to neutral conditions.

Key words | copper, hydroxylamine, methyl orange, persulfate, sulfate radical

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INTRODUCTION

In situ chemical oxidation (ISCO) is a class of processes that have been developed over the past 20 years to treat soil and groundwater contaminated with organic pollutants (Al-Shamsi & Thomson 2013; Yan & Lo 2013). Of these ISCO processes, activated persulfate (PDS) is attractive due to its ability to generate powerful oxidizing sulfate radicals ($\text{SO}_4^{\bullet-}$), which can induce the production of another powerful and nonselective oxidizing species, hydroxyl radicals ($\bullet\text{OH}$) (Liang & Su 2009). PDS anion ($\text{S}_2\text{O}_8^{2-}$, $E^0 = 2.01 \text{ V}$) is a strongly oxidizing agent, which is usually stable, and can be activated by heat, UV light, ultrasound, and transition ions (M^{n+}) to generate sulfate radicals ($\text{SO}_4^{\bullet-}$), as respectively described by Equations (1) and (2) (Anipsitakis & Dionysiou 2004; Adewuyi 2005; Waldemer *et al.* 2007). However, the process is not yet mature and its PDS activation properties deserve detailed study.



Currently, many transition ions have been investigated for their PDS activation properties to produce $\text{SO}_4^{\bullet-}$, but not all the transition ions are efficient (Anipsitakis & Dionysiou 2004). Copper, one of the major redox-active transition metals (Balaz *et al.* 2002), is also considered to be one of the most efficient ions (Woods & Kolthoff 1965; Kolthoff & Woods 1966), but copper-catalyzed production of $\text{SO}_4^{\bullet-}$ is seldom reported.

Copper typically occurs in either the cuprous (Cu(I)) or the cupric (Cu(II)) oxidation state in natural waters. However, naturally occurring copper is mostly in the Cu(II) oxidation state, because Cu(I) is unstable and easily oxidized to Cu(II) by oxygen or other oxidants, in aqueous solutions (Gonzalez-Davila *et al.* 2009). Nevertheless, Cu(II) has a low potential to activate PDS, while Cu(I) is capable of activating PDS to produce $\text{SO}_4^{\bullet-}$ and Cu(II) following Equation (2) (Woods & Kolthoff 1965; Kolthoff & Woods 1966). Although Cu(I) could activate PDS markedly, the system has some intrinsic drawbacks, such as the instability of Cu(I), and the accumulation of Cu(II), which would cause the decline of oxidation rates (Yuan *et al.* 2012). In previous

works, the redox cycling of copper could be strongly accelerated by hydroquinone and 2,3-dihydroxybenzoic acid (Liu *et al.* 2005; Yuan *et al.* 2013), which proved that it is a possible method to enhance copper activated PDS through accelerating the redox cycling of copper.

For the purpose of improving reaction rates, we could reasonably take into account that some reducing agents with low reaction rates to reactive species which accelerate the redox cycles of Cu(II) to Cu(I). NH_2OH (HA) have been introduced into the Fenton process and the Fe(II)/PMS process to enhance the generation of reactive radicals and extend the pH range by accelerating the redox cycle of Fe(III)/Fe(II) (Chen *et al.* 2011; Zou *et al.* 2013). HA is also capable of reducing Cu(II) into Cu(I), so it was assumed that HA would also enhance the PDS/copper process (Adams & Overman 1909).

To our knowledge, there has been no literature to investigate the reduction of Cu(II) to Cu(I) in a PDS/copper system. Therefore, the aim of this study is to investigate the activation of PDS/copper by HA, focusing on the extension of the applied pH range, the role of HA, the identification of primary reactive oxidants, and proper dosage of main reagents in the process. Methyl orange was selected as the simple target compound in the Cu(II)/PDS process with the addition of HA.

MATERIALS AND METHODS

Materials

Hydroxylamine hydrochloride (HA, $\geq 99\%$), Sodium persulfate (PDS, $\geq 98.0\%$), methyl orange (MO), copper sulfate, absolute ethyl alcohol (ETOH), *tert*-butyl alcohol (TBA), phosphoric acid, monosodium phosphate, and sodium dihydrogen phosphate were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd.

Procedures

All experiments were performed in a 500 mL round-bottomed flask at $20 \pm 1^\circ\text{C}$. The reactor was operated in batch mode with rapid mixing provided at the bottom of the reactor. MO and Cu(II) with desired concentrations were spiked into the solution of the reactor buffered with 15 mmol/L phosphate buffer. Each run was initiated by adding the desired dosage of sodium persulfate and hydroxylamine. pH changed by less than 0.2 units during the process. Samples were withdrawn at predetermined

intervals and then subjected to analysis with MO using a UV-vis spectrometer. Every experiment was carried out at least two times and the standard deviation obtained was less than 2.0%.

Analysis

Methyl orange was measured by a UV-vis spectrometer (MAPADA, UV-1800) at 463 nm using a 1 cm quartz cuvette. The pH changed less than 0.2 units during the process, and we produced the standard concentration-absorbency curve at different pH values for each experiment to work out the accurate MO degradation. The products of MO degradation were examined with the gas chromatography/mass spectroscopy (GC/MS) technique, operating on a QP2010Plus GC/MS analyzer. pH was measured by a pH meter (PHB-4).

RESULTS AND DISCUSSION

Effect of HA addition on MO degradation in the HA/Cu(II)/PDS process

Figure 1(a) shows the degradation of MO in PDS, Cu(II)/PDS, HA/PDS, and HA/Cu(II)/PDS processes. As shown, 29.6% and 30.5% of the MO was degraded in 60 min in the PDS process and the Cu(II)/PDS process, respectively, suggesting that Cu(II) can hardly activate PDS. Surprisingly, more than 60% of MO was degraded in 60 min in the Cu(II)/PDS process with the addition of HA. Note that only 24% of MO was degraded by the HA/PDS process. It was obvious that the addition of HA strongly enhanced oxidation in the Cu(II)/PDS process. As a typical reducing agent, HA could accelerate the transformation from Cu(II) to Cu(I). This allows Cu(I) to function as an activator of PDS to generate $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ following Equations (3)–(6) (Kolthoff & Woods 1966; Pennington & Haim 1968; Hayon *et al.* 1972). The mechanism of the HA/Cu(II)/PDS process is shown in Figure 1(b).

According to the literature (James & Rod 1987; Yuan *et al.* 2012), different Cu(I) species may exist in the HA/Cu(II)/PDS process, such as Cu^+ , Cu_3PO_4 , CuClOH^- , CuCO_3^- , CuHCO_3 , CuCl , CuCl_2^- , and CuCl_3^{2-} . Thus, the Cu(I) mainly exist in the form of compounds, so Cu(I) can activate PDS in nearly neutral conditions. Nevertheless, it is possible that only part of the Cu(I) species can effectively activate PDS. This is most possibly due to the high activity of Cu^+ , CuCl , and CuClOH^- in inducing the generation of

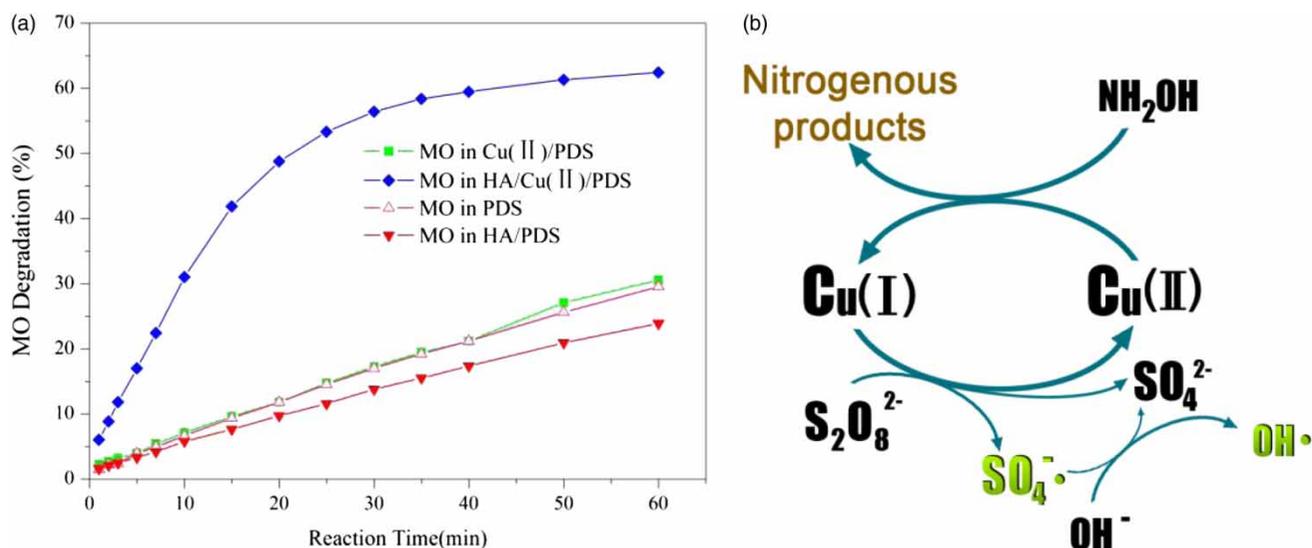
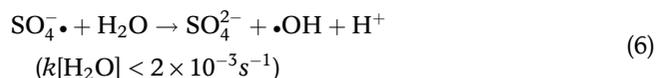
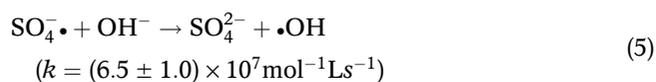
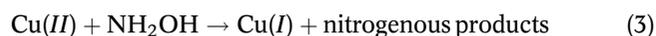


Figure 1 | (a) Time-dependent degradation of MO by PDS, Cu(II)/PDS, HA/PDS, and HA/Cu(II)/PDS processes. [Cu(II)]₀ = 10 μM mol L⁻¹, [PDS]₀ = 1 m mol L⁻¹, [HA]₀ = 0.5 m mol L⁻¹, [MO]₀ = 18.3 μ mol L⁻¹, pH = 7 ± 0.1. (b) The mechanism of HA/Cu(II)/PDS process.

active radicals (James & Rod 1987; Yuan *et al.* 2012) and with varying pH value, the proportion of different Cu(I) species would be changed.



The intermediates of MO degradation in the HA/Cu(II)/PDS process were examined by the GC/MS technique. The GC retention time (t_R), molecular weight (M_W), and main fragments are summarized in Table 1. The identified intermediate 5 indicates dissociation of the C–N bond close to the side of benzenesulfonic group, due to the attack of reactive radicals. The intermediates 1 and 4 are due to recombination of the radical fragments derived from opening the benzene ring by oxidation, which proved the strong oxidizability of the HA/Cu(II)/PDS process. Thus, the degradation of MO is not only because of the oxidation of the chromophoric group. Moreover, the GC chromatogram of the intermediates of MO degradation in the HA/Cu(II)/PDS process is shown in Figure S1 (see Supplementary Information, available in the

Table 1 | GC/MS results

Intermediate	t_R (min)	M_W	Main fragment ions (m/z)
Methyl methacrylate (1)	3.61	100	100, 82, 69, 55, 41/40
aniline (2)	5.11	93	92/91, 77, 65, 51, 31
<i>N,N</i> -Dimethylbenzene-1,4-diamine (3)	8.25	136	121, 106/105, 91, 77, 65, 51, 33
Oct-1-en-3-ol (4)	18.26	128	127, 113, 99, 85, 71, 57, 43/42
4-Diazenyl- <i>N,N</i> -dimethylbenzenamine (5)	20.83	149	149, 121, 105, 93, 76, 66/65, 50

online version of this paper). The absolute intensity of intermediates increased first and then decreased, which proved that the HA/Cu(II)/PDS process can further degrade the intermediates of MO degradation.

Effect of pH

Figure 2 shows the effect of pH on MO degradation in the HA/Cu(II)/PDS process. The effective pH value of degradation of MO ranges from 4 to 8. The MO degradation increased with the increase of pH from pH 3 to 7; a further increase of pH resulted in a decrease of MO degradation. These results show that the HA/Cu(II)/PDS process is efficient near neutral pH, which overcomes the drawbacks of Fenton or Fenton-like processes with an effective pH range under acidic conditions (Chen *et al.* 2011; Zou *et al.*

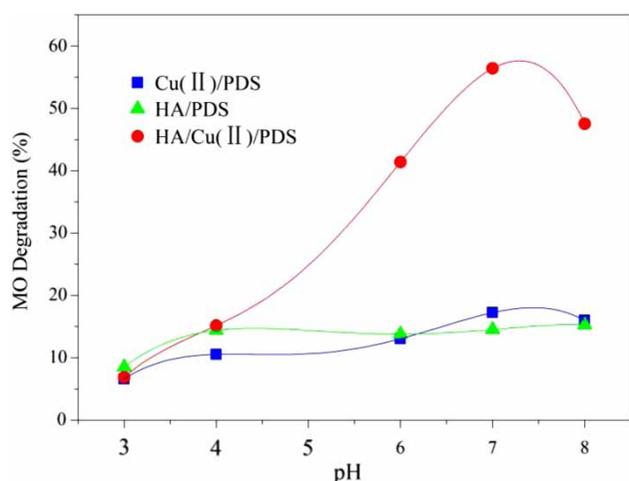
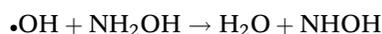


Figure 2 | Effect of pH on MO degradation in the HA/Cu(II)/PDS process. $[Cu(II)]_0 = 10 \mu\text{mol L}^{-1}$, $[PDS]_0 = 1 \text{ mmol L}^{-1}$, $[HA]_0 = 0.5 \text{ mmol L}^{-1}$, $[MO]_0 = 18.3 \mu\text{mol L}^{-1}$, reaction time = 30 min, $\text{pH} = 7 \pm 0.1$.

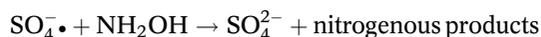
2013). When both pK_{a1} of HA and pH are equal to 5.96 (Robinson & Bower 1961), HA is in a neutral condition.

Beyond this point, the protonation ratios of HA decrease with the increase of pH. The fact that the degradation of MO increased with the decrease of the ratio of $\text{NH}_3\text{OH}^+/\text{HA}$ as pH increased from 3 to 7 may prove that the unprotonated HA is more effective at reducing Cu(II) into Cu(I) to induce the generation of reactive radicals. However, the degradation of MO decreased with the increase of pH range from 7 to 8, which is different from the increase in degradation of MO observed at pH 3 to 7. Although low ratios of $\text{NH}_3\text{OH}^+/\text{HA}$ can accelerate the transformation from Cu(II) to Cu(I) to produce more reactive radicals, high pH can increase the rate constant between HA with both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ via Equations (7) and (8) (Buxton *et al.* 1988; Neta *et al.* 1988). Moreover, the solubility product (K_{sp}) of $\text{Cu}(\text{OH})_2$ is 1.6×10^{-19} , so a large percentage of Cu(II) translates to $\text{Cu}(\text{OH})_2$ which may not be effective in the HA/Cu(II)/PDS process at pH greater than 7.0 (Kang *et al.* 2014). In addition, the higher proportion of reactive oxidant $\cdot\text{OH}$ may decrease the degradation of MO due to the higher reaction rate between $\cdot\text{OH}$ and HA with pH increase.



$$\text{pH } 4.0 \quad k < 5.0 \times 10^8 \text{ mol}^{-1} \text{Ls}^{-1} \quad (7)$$

$$\text{pH } 8.0 \quad k = 9.5 \times 10^9 \text{ mol}^{-1} \text{Ls}^{-1}$$



$$\text{pH } 4.1 \quad k = 1.5 \times 10^7 \text{ mol}^{-1} \text{Ls}^{-1} \quad (8)$$

$$\text{pH } 8.5 \quad k = 8.5 \times 10^8 \text{ mol}^{-1} \text{Ls}^{-1}$$

Identification of primary reactive oxidants

It has been reported that two different reactive radicals, $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, can be generated for catalyst-mediated decomposition of PDS systems (Liang & Su 2009). As shown in Equations (3)–(6), both radicals could be generated in the HA/Cu(II)/PDS process. However, the HA/Cu(II)/PDS process is complex, and $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ are reactive intermediates with very short lifetimes. Thus, the existence and effect of $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ are indirectly proved at different pH values through inhibition by absolute ethyl alcohol (EtOH) and tert-butyl alcohol (TBA). Owing to high rate constants with $\text{SO}_4^{\cdot-}$ (1.6×10^7 – $7.7 \times 10^7 \text{ mol}^{-1} \text{Ls}^{-1}$) (Neta *et al.* 1988) and $\cdot\text{OH}$ (1.2×10^9 – $2.8 \times 10^9 \text{ mol}^{-1} \text{Ls}^{-1}$) (Buxton *et al.* 1988), EtOH is an effective quencher for both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$. In contrast, due to the high rate constant with $\cdot\text{OH}$ ($6.0 \times 10^8 \text{ mol}^{-1} \text{Ls}^{-1}$) (Buxton *et al.* 1988) and the much slower rate constant with $\text{SO}_4^{\cdot-}$ ($8.0 \times 10^5 \text{ mol}^{-1} \text{Ls}^{-1}$) (Neta *et al.* 1988), TBA is an effective quencher for $\cdot\text{OH}$ but not for $\text{SO}_4^{\cdot-}$. Based on these properties, the quenching experiment with EtOH and TBA could allow us to differentiate between the contributions of $\text{S}_2\text{O}_8^{2-}$, $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$.

Figure 3 shows the inhibition effect of EtOH and TBA on the degradation of MO in the HA/Cu(II)/PDS process at pH 6–8 which were highly effective pH levels, as shown in Figure 2. Due to the addition of 30 mmol L^{-1} TBA, the inhibition of MO degradation in the HA/Cu(II)/PDS process increased with pH increase ranging from 6 to 8. It can be inferred that the proportion of $\cdot\text{OH}$ increased with pH increase ranging from 6 to 8. Moreover, with the pH increase,

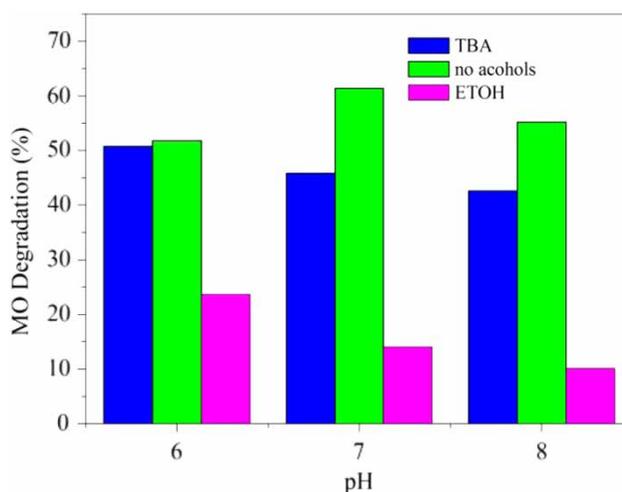


Figure 3 | Inhibition of radical scavengers on MO degradation in the HA/Cu(II)/PDS process at pH 6, 7 and 8. $[Cu(II)]_0 = 10 \mu\text{mol L}^{-1}$, $[PDS]_0 = 1 \text{ mmol L}^{-1}$, $[HA]_0 = 0.6 \text{ mmol L}^{-1}$, $[MO]_0 = 18.3 \mu\text{mol L}^{-1}$, $[TBA]_0 = 30 \text{ mmol L}^{-1}$, $[EtOH]_0 = 30 \text{ mmol L}^{-1}$, reaction time = 60 min.

$\text{SO}_4^{\cdot-}$ can react with OH^- to induce the production of $\cdot\text{OH}$ following Equation (4) which is significantly faster than Equation (5) (Liang & Su 2009). Due to the fact that the reaction rate constant of HA with $\cdot\text{OH}$ is higher than the rate constant between HA and $\text{SO}_4^{\cdot-}$, there are more reactive radicals reacting with HA to inhibit the degradation of MO with pH increase, which conforms to Figure 2. On the other hand, with the addition of 30 mmol L^{-1} EtOH, the degradation efficiency of MO was decreased from 51.74%, 61.34%, and 55.19% to 23.65%, 14.04%, and 10.09% at pH 6, 7, 8, respectively, which can mean that $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ are two of the reactive oxidants in the HA/Cu(II)/PDS process and the addition of EtOH weakly inhibited the MO degradation which indicated the absence of radicals in the PDS process and the HA/PDS process (shown in Figure S2, see Supplementary Information, available in the online version of this paper). Hence, the primary reactive oxidants were PDS, $\text{SO}_4^{\cdot-}$ and $\text{OH}\cdot$ in the HA/Cu(II)/PDS process.

Kinetics of MO degradation

In principle, the contaminant disappearance should be describable with a pseudo-first-order rate constant that is the sum of second-order terms for each oxidant as in Equation (9) where k'' represents the second-order rate constants for the reaction of the contaminant with each reactive intermediate (Waldemer et al. 2007). Under most conditions, the dominant term in Equation (9) is presumed to be the one involving $\text{SO}_4^{\cdot-}$ (Kolthoff et al. 1951; Peyton 1993) which is in agreement with the HA/Cu(II)/PDS process in Figure 3, but it is not known how the relative significance of these terms varies with system parameters.

$$k_{\text{obs}} = k''_{\text{SO}_4^{\cdot-}}[\text{SO}_4^{\cdot-}] + k''_{\text{OH}\cdot}[\text{OH}\cdot] + k''_{\text{S}_2\text{O}_8^{2-}}[\text{S}_2\text{O}_8^{2-}] + k''_{\text{other}}[\text{other}] \quad (9)$$

To investigate the kinetics of MO degradation, different dosages of HA in the HA/Cu(II)/PDS process were studied. The degradation of MO in the HA/Cu(II)/PDS process consists of three stages, which are the fast stage (k_1), the transitory stage (k_2) and the low stage (k_3). Furthermore, the fast stage and the low stage agree with first-order kinetic models, and the transitory stage fits with second-order kinetic model. Rate constants (k , k_1 , k_2 , k_3) and R^2 ($R^2 > 0.964$) of the three stages are shown in Table S1 and Table S2 (see Supplementary Information, available in the online version of this paper). Increased k_1 and k_2 were observed with the increase of HA concentration in the range of 0.1 mmol L^{-1} to 0.75 mmol L^{-1} . The

reaction rate of the fast stage depends on the initial HA concentration. After that, the increase of HA concentration resulted in decrease of k_1 and k_2 . k_3 was significantly less than k_1 with no apparent relationship between the two values. From the comparison between Tables S1 and S2 (see Supplementary Information) the predominant increase of MO degradation in the HA/Cu(II)/PDS process occurs in the fast stage. k_1 is significantly higher than k of the PDS process, the HA/PDS process and the Cu(II)/PDS process. On the contrary, k_3 is lower than k in the same processes resulting in the activation of copper/PDS, which was facilitated in the fast stage by HA via acceleration of the Cu(II)/Cu(I) redox couple.

Effect of PDS, HA, and Cu(II) on MO degradation

To investigate the application of the HA/Cu(II)/PDS system, different dosages of PDS, HA, and Cu(II) were tested in the HA/Cu(II)/PDS process, as shown in Figure 4. With the increase of initial PDS concentration, MO degradation was strongly enhanced and optimal Cu(II) concentration is about $10 \mu\text{mol L}^{-1}$ but the optimal HA concentration was increased with increase of PDS concentration. Thus, although proper HA concentration could increase the MO degradation in the Cu(II)/PDS process, the main contribution of MO degradation is PDS. Increased degradation of MO was observed with the increase of initial HA concentration. Exceeding the optimal concentration resulted in the decrease of MO degradation. It can be inferred that the more HA that was used to accelerate the transformation from Cu(II) to Cu(I) to activated PDS, the more reactive radicals were generated. However, a large amount of reactive radicals could be quenched by HA with high rate constants, especially when the HA concentration was high enough via Equations (7) and (8) (Buxton et al. 1988; Neta et al. 1988), resulting in decrease in MO removal. Moreover, increase of initial Cu(II) concentration could result in the increase of MO degradation but exceeding the optimal concentration resulted in the decrease of MO degradation. This is because Cu(I) may react with $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ with a high rate constant following Equations (10) (Buxton et al. 1988) and (11) (Liang & Su 2009) to inhibit MO degradation in the HA/Cu(II)/PDS process. Therefore, a proper dosage of PDS, HA, and Cu(II) should be selected in the application in order to improve the degradation of probe compounds at the highest extent and reduced cost.

Furthermore, it should be noted that HA is a kind of toxic compound and the addition of HA in Cu(II)/PDS is far from practical. Our work just introduced an interesting phenomenon and proposed a preliminary interpretation that HA could accelerate the reaction rates and expand effective pH

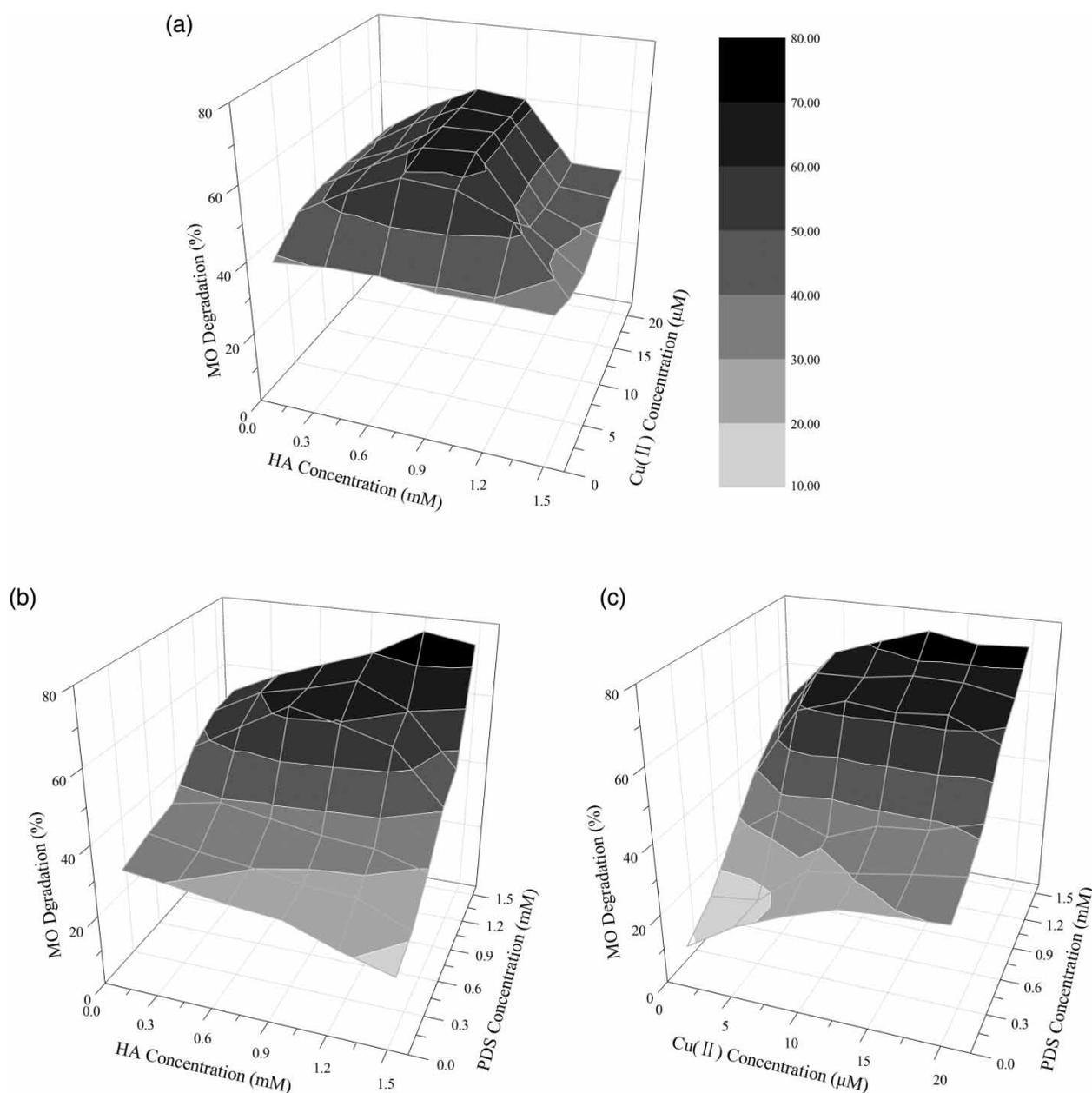
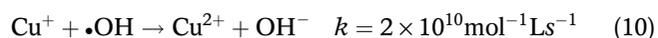


Figure 4 | Effect of PDS, HA, and Cu(II) concentration on MO degradation in the HA/Cu(II)/PDS process. $[MO]_0 = 18.3 \mu\text{mol L}^{-1}$, reaction time = 90 min, $\text{pH} = 7 \pm 0.1$. (a) $[PDS]_0 = 1 \text{ mmol L}^{-1}$, $[Cu(II)]_0 = 1\text{--}20 \mu\text{mol L}^{-1}$, $[HA]_0 = 0.1\text{--}1.5 \text{ mmol L}^{-1}$. (b) $[PDS]_0 = 0.1\text{--}1.5 \text{ mmol L}^{-1}$, $[Cu(II)]_0 = 10 \mu\text{mol L}^{-1}$, $[HA]_0 = 0.1\text{--}1.5 \text{ mmol L}^{-1}$. (c) $[PDS]_0 = 0.1\text{--}1.5 \text{ mmol L}^{-1}$, $[Cu(II)]_0 = 1\text{--}20 \mu\text{mol L}^{-1}$, $[HA]_0 = 0.75 \text{ mmol L}^{-1}$.

range. The ultimate aim is to find an environmentally friendly chemical with a feasible reaction rate with $\cdot\text{OH}$ and $\text{SO}_4\cdot^-$ to reduce the cost and accelerate the generation of active radicals.



CONCLUSION

This study sets up the HA/Cu(II)/PDS process to utilize HA to reduce Cu(II) to Cu(I) to induce the production of $\text{SO}_4\cdot^-$ and $\cdot\text{OH}$ through the activation of PDS. The MO degradation in the HA/Cu(II)/PDS process can be divided into three stages: the fast stage, the transitory stage, and the low stage. The fast and low stages fit well

with pseudo-first-order kinetic models, and the transitory stage agrees with a second-order kinetic model. HA can strongly enhance MO degradation in the HA/Cu(II)/PDS process, which countered the drawbacks of accumulation and sedimentation of Cu(II) and instability of Cu(I) and the HA/Cu(II)/PDS process excellently showed high degradation of MO in nearly neutral conditions, which enhanced the application of the HA/Cu(II)/PDS process. However, owing to the reactions between HA and reactive oxidants, the addition of HA may reduce the use of PDS in the HA/Cu(II)/PDS process. High dosage of PDS can enhance the MO degradation in the HA/Cu(II)/PDS process, and the optimal dosage of Cu(II) is about $10 \mu\text{mol L}^{-1}$. Although this study provided promising results, further research is required to better understand the problem. Future studies may not only be confined to HA; other reducing agents which can react with Cu(II) to generate Cu(I) may act similar to HA in the HA/Cu(II)/PDS process.

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