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Selective decolorization of cationic dyes by peroxymonosulfate: non-radical mechanism and effect of chloride

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Abstract

How to effectively activate oxidants like hydrogen peroxide (H_2O_2), peroxydisulfate (PDS) and peroxymonosulfate (PMS) is the focus of advanced oxidation processes (AOPs). In this study, we have found that PMS can directly decolorize cationic dyes without activation in a wide pH range (2.0~12.0). In addition, the presence of Cl^- results in the formation of free available chlorine species and thus improves the degradation efficiency as well as broadening the scope of target pollutants. The first-order rate constant increased by 4.3 times when 2.5 mM Cl^- was added as observed by an increase from 0.021 to 0.089 min^{-1}, which further rose to 1.371 min^{-1} when Cl^- was present at a level of 50 mM. Furthermore, it was found that only PMS has such an amazing effect while H_2O_2 and PDS do not. Radical quenching experiments and electron paramagnetic resonance (EPR) studies show that the decolorization of cationic dyes by PMS does not rely on the formation of sulfate radical. A plausible mechanism is that cationic dyes (i.e., RhB^+) first formed a complex with the active component of PMS (HSO_5^-) owing to their electrical interaction. Subsequently, direct electron transfer from cationic dyes to HSO_5^- may occur and probably this is responsible for the bleaching of cationic dyes.

Key Words: peroxymonosulfate; AOPs; non-radical process; electron transfer; Rhodamine B

1. Introduction

Aqueous effluents containing dyes have increased greatly with their wide applications in many industries[1, 2]. How to best dispose of these dye effluents has been discussed for decades[1, 3]. Normally, the treatment methods used for dye effluents can be divided into three categories: biological, physical and chemical methods[3]. As physical methods only transfer wastes from one place to another and do not involve any degradation they have received the least attention. Although biological processes that rely on the activity of bacteria are economical and relatively effective, they are usually time consuming and are not applicable for toxic and low biodegradable dyes, and unfortunately, most dyes lie in both of these categories[4]. On the other hand, chemical oxidation is the most effective technique and has received the most attention[5, 6].

Over the past two decades, advanced oxidation processes (AOPs) that depend on the generation of reactive oxygen species (ROS) have been intensively developed for the remediation of wastewater[2, 7, 8]. Generally, ROS are produced from the reaction between transition metals and oxidants. The three widely applied oxidants are hydrogen peroxide (H_2O_2), peroxydisulfate (PDS) and peroxymonosulfate (PMS). AOPs can be classed as either homogeneous or heterogeneous and, in contrast with the homogenous process which is only effective at acid pH (2.5~4.0), heterogeneous AOPs can be operated in a wide pH range[9, 10]. In addition, the use of catalysts can avoid the formation of sludge and have much less problems relating to the toxicity of free metal ions. Furthermore, some light sensitive catalysts can be combined with UV, visible, and even, solar light so as to improve the efficiency of pollutant degradation[11]. Specifically, Wu et al.[12] reported that the decolorization of dyes by phase-pure layered perovskite did not need any extra oxidant or the input of external energy. Similarly, Yu et al.[13] reported that bismuth silver oxide alone is also effective for the decolorization of Rhodamine B. Indeed, heterogeneous AOPs show many advantages over homogenous AOPs but the fact that the preparation of catalyst is neither easy nor economic should not be ignored. It would be a great advance in AOPs technology if dye effluents could be degraded by oxidants without the use of any transition metal catalysts and we now report our intriguing results in this regard.

Our current research, involves evaluating the oxidation ability of the $ZnFe_2O_4$/PMS coupled system. Unfortunately, it was found that $ZnFe_2O_4$ cannot activate PMS as there was no obvious change observed when the dosage of $ZnFe_2O_4$ was altered (Figure S1). Fortunately and interestingly, it was found that PMS can directly lead to the degradation of RhB, without the aid of catalyst or other external energy. Therefore, several important factors that affect the process and the mechanism of this phenomenon were investigated. To the best of our knowledge, this is the first report of the destruction of organic pollutants by PMS alone.

2. Materials and Methods

2.1 Chemicals and Materials.

Methylene Blue (MB) was purchased from Koch-Light Laboratories Ltd., England. Orange II was bought from Panreac Quimica SA, Barcelona, Spain. Sodium chloride

(NaCl) was obtained from Merck, Taiwan. The 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) was purchased from Aladdin, China. The other main reagents, including Reactive Black 5 (RB5), Rhodamine B (RhB), phenol, methanol, and potassium peroxymonosulfate were bought from Sigma-Aldrich, Taiwan. All reagents used were at least analytical reagent and prepared in distilled water.

2.2 Procedure.

The batch trials were performed in a brown glass bottle and mechanical stirred with the desired concentration of PMS and target pollutants. The volume is 400 mL. When appropriate, the solution pH was adjusted with H_2SO_4 (0.1 M) or NaOH (0.1 M). Samples were removed at predetermined time intervals and analyzed immediately. In some cases, high purity argon was purged during the duration of the reaction in order to create an anaerobic environment. For that, the brown glass bottle was replaced with a novel reactor that has already been reported in our previous work[14].

2.3 Analysis.

The residual concentration of dyes was monitored at the appropriate λ_{max} using a Hewlett–Packard 8453 diode array spectrophotometer (Agilent). The concentration of phenol was determined by HPLC (Shimadzu 6A) using conditions reported previously[15]. The mineralization of pollutants was measured using a TOC analyzer (Sievers 900 Portable).

3. Results and Discussion

3.1 Effects of major factors.

3.1.1 Effect of PMS dosage.

As a preliminary step the effect of the dosage of PMS was explored. Figure 1(A) shows the degradation of RhB is apparently PMS dependent. Similar to traditional AOPs, the bleaching of RhB increased with the rise of PMS concentration. Accordingly, the rate constant that was obtained from pseudo first-order kinetic fitting (R^2 >0.9) also increased by 10 times when the PMS concentration increased from 1 to 10 mM as shown in Table 1. Nevertheless, there is a difference between our system and that of the usual AOPs. As is well known, there exists an optimum dosage of oxidants in AOPs as they will also react with the generated radicals [16, 17] but our results suggested at the given PMS dosage from 1.0 mM to 100 mM, the higher the PMS dosage, the better the removal rate.

3.1.2 Effect of RhB concentration.

Figure 1(B) shows that the initial concentration of RhB has insignificant effect on its color removal, and the first-order rate constants are all around 0.022±0.002 min^{-1}. In this case, the amount of RhB removed would increase almost proportionally with initial dye concentration. Specifically, 9.5, 18.3, 37.8 and 72.5 mg/L of RhB were removed after two hours reaction when initial dye concentrations were 10, 20, 40 and 80 mg/L, respectively. This may due to the increased collision chances between PMS and RhB, which leads to the removal of more RhB. Based on the result, it can be concluded that 2.5 mM of PMS is a sufficiently high dosage for 10 - 80 mg/L RhB and therefore over 90% of RhB were bleached in all conditions.

3.1.3 Effect of pH.

It is well known that the solution pH has a great influence on the performance of most

AOPs. Generally, while homogeneous AOPs activated by transition metal ions require an acidic pH solution[18], heterogeneous AOPs can operate in a relatively wide pH range but always perform better in slightly acidic or neutral solution[19]. To investigate the role of pH in this new kind of decolorization process, the effect of pH at 2.0, 4.5, 7.0, 10.0 and 12.0 was explored. Because PMS solution itself is a strong acid solution, the introduction of PMS will immediately lead to the fall of solution pH to around 2.5 as indicated in Table S1, when the initial solution pH was 4.5, 7.0 and 10.0. Correspondingly, similar RhB removal efficiencies (96.1% ~ 97.5%) were observed for pH_0 4.5, 7.0 and 10.0, as shown in Figure 1(C). However, if the solution pH_0 is increased from 10.0 to 12.0, the decolorization percentage declined by 31.4% in 120 min reaction and the rate constant dropped from 0.047 to 0.008 min^{-1}. This is probably because that PMS exists mostly in the form of SO_5^{2-} at pH_0 12.0 and as reported, it is less reactive than HSO_5^- [20]. Nevertheless, 66.1% of RhB was decolorized in this case. These results indicate that unlike homogeneous Fenton based AOPs, the bleaching of dyes by PMS can work in a wide pH range.

3.2 Effect of chloride ions.

Much work on the effect of Cl^- on the degradation of pollutants in AOPs has been reported as it is observed that both sulfate and hydroxyl radicals can react with Cl^- to form chlorine radicals[21, 22]. On the other hand, Cl^- is also one of the main components in wastewater so the exploration of the potential effect of Cl^- needs investigation. As can be seen from Figure 2, Cl^- plays a positive role in our system where the time for total decoloration of 10 mg/L RhB (>96.1%) decreased from more than 120 min to less than 90 min when only 1 mM Cl^{-} was added. The time can be further shortened by increasing the dose of Cl^{-}. For example, only 3 min is needed for 100% bleaching of 10 mg/L RhB in the presence of 50 mM Cl^{-}. Accordingly, with 50 mM Cl^{-}, the reaction rate constant increased 66-fold to 1.371 min^{-1}, over the rate constant at the absence of Cl^{-}. It could be surmised that the addition of Cl^{-} results in the formation of free available chlorine species as shown in Eqs. (1) and (2)[21, 23]:

$$HSO_5^{-} + Cl^{-} \rightarrow SO_4^{2-} + HOCl \quad (1)$$

$$HSO_5^{-} + 2Cl^{-} + H^{+} \rightarrow SO_4^{2-} + Cl_2 + H_2O \quad (2)$$

The observation of the production of small gas bubbles in the reactor supports the formation of gaseous chlorine as suggested by Eq. (2). HOCl and Cl_2 are both widely used as disinfectants and bleaching agents and thus the greatly improved removal of RhB is observed in the presence of Cl^{-}. Yuan et al.[22] reported that in the Co^{2+}/PMS system, the presence of Cl^{-} leads to more refractory intermediate products as they noticed a new peak in the UV/Vis spectra, but no new peak in the absence of Cl^{-}. However, in our system, whether Cl^{-} was present or not, the characteristic peaks of RhB at 260, 355 and 552 nm gradually disappear (see Figure 3) and no new peaks appeared in our system. The continuous decrease of these peaks indicated that the chromophores of RhB as well as the benzene rings are destroyed. The difference in the UV/Vis spectra between the current work and that reported by others may due to the fact that our system does not rely on the generation of radicals.

The removal of TOC at different amounts of added Cl^{-} was also determined as TOC is an important indication of the extent of mineralization of pollutants. It was found that the TOC removal also increased at higher Cl^- concentration. As shown in Figure 4, the TOC removal of 10 mg/L RhB after 120 min is 8.1%, 9.2%, 19.6%, 39.0%, and 50.0% at 0, 1, 2.5, 10, and 50 mM Cl^-, respectively. Although PMS alone just leads to the decolorization of RhB, PMS coupled with Cl^- is effective for the mineralization of RhB. As most dye effluents contain Cl^-, our system may provide a simple and effective technology for the treatment of dye effluents.

3.3 Possibility of employing PDS or H_2O_2.

As discussed above, the results show that PMS alone can effectively degrade dyes. Since PDS and H_2O_2 are also two widely used oxidants, there is a necessity to explore their potential possibility in the non-radical process. Figure 5 illustrates that H_2O_2 alone, or in conjunction with NaCl could not degrade dyes. Although PDS did have some effect but was far less effective than PMS and the addition of 5 mM Cl^- did not result in any improvement or inhibition in the removal of RhB. It is concluded that PMS is much more active than the other two oxidants and the structure of the three oxidants can account for the different performances in similar reaction conditions. PDS and H_2O_2 with symmetric structures are more stable than PMS and this is consistent with some reports relating to AOPs. For instance, Guan et al.[20] reported that only PMS can be easily activated by $CuFe_2O_4$ while PDS and H_2O_2 cannot and consequently, RhB was rapidly decolorized in the case of PMS.

3.4 Possibility of removing other pollutants.

In order to investigate the potential application of PMS in the decontamination of other pollutants, phenol and another three dyes: Orange II, MB and RB5 were also treated by PMS based process. Figure 6(A) shows that only MB could be effectively oxidized by PMS alone, while the other pollutants were not removed at all. However, as shown in Figure 6(B), all of these pollutants were readily degraded when 2.5 mM Cl^- were added. These results indicate that PMS alone can selectively oxidize dyes, while its combination with Cl^- can remove different kind of pollutants by the *in-situ* formation of free available chlorine species.

3.5 Mechanism study.

Methanol is a popular radical quencher for hydroxyl and sulfate radicals[24], so it was added to explore the reactive species in our system. Figure 7 (A) shows the addition of 2.5 M methanol slightly inhibits the degradation of RhB in PMS/Cl^- system but has no impact on PMS alone. It was proposed that the decolorization of RhB was not relying on the formation of radicals. To further testify this assumption, electron paramagnetic resonance (EPR) studies using DMPO as a spin-trapping agent were investigated. As can be noticed from Figure 7(B), neither DMPO-OH nor DMPO-SO_4 signals were observed in both PMS/RhB and PMS/Cl^-/RhB systems, indicating that the decolorization of RhB in the two systems is not attributed to radical attack. It should be noted that the weak signals of DMPO adducts are attributed to the background noise.

In addition, as identified above, only MB and RhB can be directly decolorized by PMS. It can thus be deduced that non-radical process is only effective for cationic dyes. The active component of PMS is HSO_5^-, and RhB actually exists in the form of cationic (RhB^+) in aqueous solution. When PMS is added to RhB, a strong electrical interaction occurs between the two ions as shown in Eqs. (3) and (4):

$$\mathrm{RhB^+ + HSO_5^- \rightarrow RhB\text{-}HSO_5} \tag{3}$$

$$\overset{2e^-\ \curvearrowright}{\mathrm{RhB\text{-}HSO_5}} + \mathrm{H^+} \rightarrow \text{oxidized RhB} + \mathrm{SO_4^{2-}} + \mathrm{H_2O} \tag{4}$$

The two-electron transfer from RhB to PMS occurs, leading to the oxidation of RhB, and a similar process should occur in the degradation of MB. However, as anionic dyes will repel HSO_5^- due to their mutually exclusive electrical interaction, the subsequent electron transfer cannot occur. The proposed mechanism is inconsistent with the recent discovery of Wang et al.[25], who reported that PMS could directly oxidize As(III) to As(V). Additionally, as mentioned above, H_2O_2 without activation cannot degrade dyes because H_2O_2 mostly exists in the molecular form in solution. The behavior of H_2O_2 is also a good support for the suggested mechanism. As a result, there is no degradation of phenol (a neutral organic molecule) and anionic dyes. The decreased removal rate at pH 12.0 (Figure 3) also supports the above discussed speculation. At pH 12.0, the attraction of HO^- to RhB^+ is dominant so the reaction as expressed by Eq. (3) will be inhibited and the extent of decolorization of RhB will be decreased. It may be postulated that oxygen is involved in the decolorization of dyes as it was reported that singlet oxygen ($^1O_2$) will be produced in a similar heterogeneous reaction[13]. However, the decolorization efficiency of RhB did not decrease in the absence of O_2 (Figure S2) when the solution was purged with high purity argon. It was concluded that O_2 did not take part in the bleaching of dyes.

4. Conclusions

Two systems, namely PMS and PMS/Cl^- were investigated for degradation of RhB.

The results demonstrated that PMS can selectively degrade cationic dyes through a two electron transfer process that does not rely on the generation of radicals. In addition, Cl^- that widely exists in wastewater can accelerate the degradation of dyes by in situ generation of free available chlorine species. Unlike PMS alone, the PMS/Cl^- system is very effective for all the pollutants studied. It is suggested that either PMS or its combination with Cl^- can serve as an effective and simple technology for the decolorization/degradation of organic contaminants. Additionally, this study suggests that the role of PMS and Cl^- in PMS based AOPs should be reinvestigated and this will be our focus in future work.

Supplementary Material

Supplementary Material associated with this article is available free of charge via the Internet at http://www.sciencedirect.com.

Acknowledgments

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Figure captions

Figure 1. Effects of (A)PMS dosage, (B)RhB concentration and (C) initial pH on the degradation of RhB. Conditions: (A) [RhB] = 10 mg/L, $pH_0 = 4.5 \pm 0.1$; (B) [PMS] = 2.5 mM, $pH_0 = 4.5 \pm 0.1$; (C) [RhB] = 10 mg/L, [PMS] = 2.5 mM, Time = 120 min.

Figure 2. Effect of chloride ion on the degradation of RhB by PMS. Conditions: [RhB] = 10 mg/L, [PMS] = 2.5 mM, $pH_0 = 4.5 \pm 0.1$.

Figure 3. Changes in the UV-vis spectra of RhB on reaction with PMS in the absence (A) and presence (B) of chloride ion Conditions: [RhB] = 10 mg/L, [PMS] = 2.5 mM, $[Cl^-]$ = 2.5 mM, $pH_0 = 4.5 \pm 0.1$.

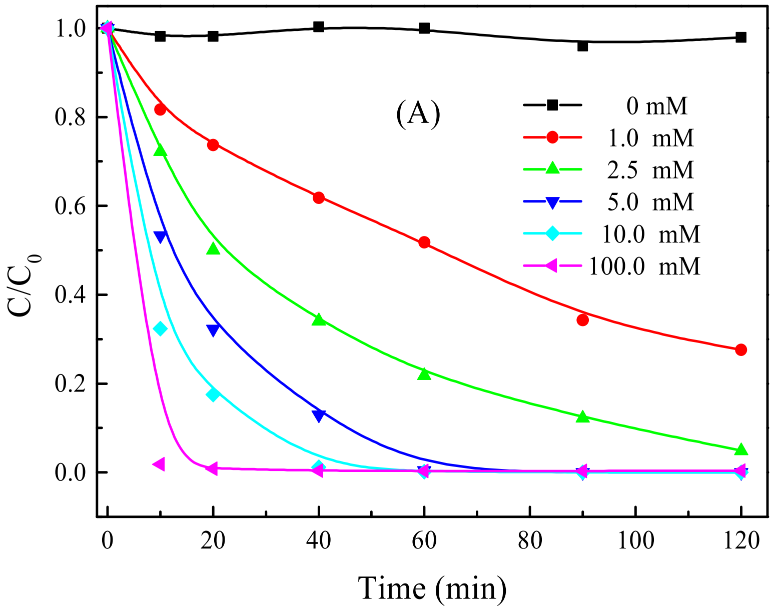
Figure 4. TOC removal of RhB using different concentrations of chloride ion. Conditions: [RhB] = 10 mg/L, [PMS] = 2.5 mM, $pH_0 = 4.5 \pm 0.1$. Time = 120 min.

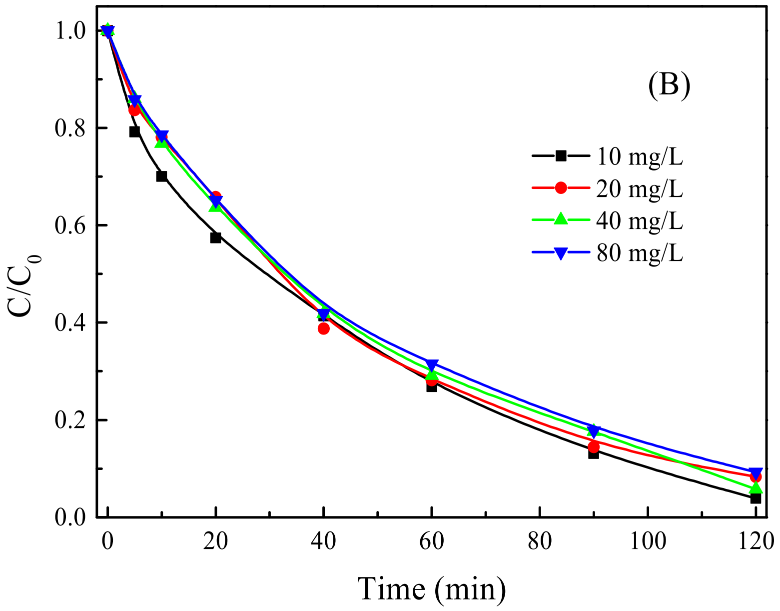
Figure 5. Degradation of RhB with PDS and H_2O_2 in the presence or absence of chloride ion. Conditions: [RhB] = 10 mg/L, [PMS] = 2.5 mM, $[Cl^-]$ = 2.5 mM, $pH_0 = 4.5 \pm 0.1$.

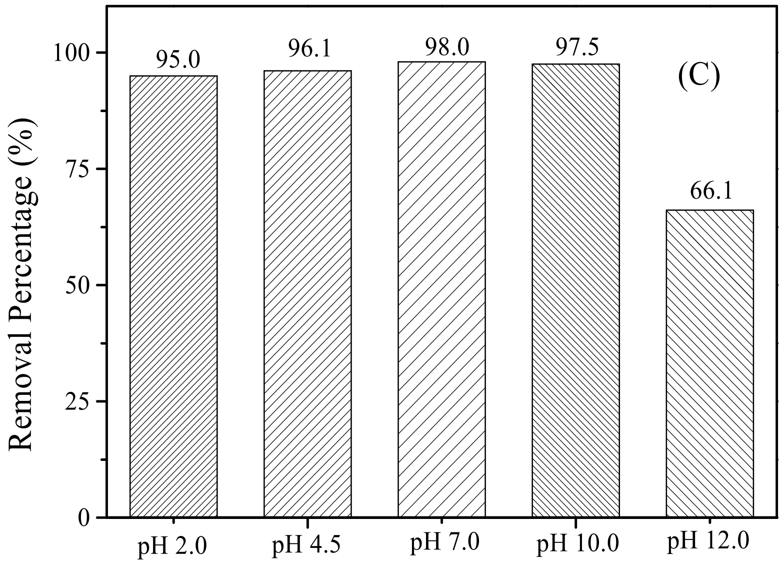
Figure 6. Degradation of other organic pollutants with PMS (A) or PMS/Cl^- (B) and UV-vis spectra changes of MB in PMS system (insert figure). Conditions: [MB] = [RB5] = [Orange II] = 10 mg/L, [phenol] = 0.1 mM, [PMS] = 2.5 mM, $[Cl^-]$ = 2.5 mM, $pH_0 = 4.5 \pm 0.1$.

Figure 7. Effect of methanol on the degradation of RhB (A) and EPR spectra in. PMS/RhB and PMS/RhB/Cl^- systems (B). Conditions: [RhB] = 10 mg/L, [PMS] = 2.5 mM, $[Cl^-]$ = 2.5 mM, $pH_0 = 4.5 \pm 0.1$, [methanol] = 2.5 M, [DMPO] = 10 mM.

Table 1. Kinetic coefficients under various operating conditions (RhB = 10 mg/L).


(A)
C/C$_0$
Time (min)
0 mM
1.0 mM
2.5 mM
5.0 mM
10.0 mM
100.0 mM
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100
120


(B)
C/C$_0$
Time (min)
10 mg/L
20 mg/L
40 mg/L
80 mg/L
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100
120



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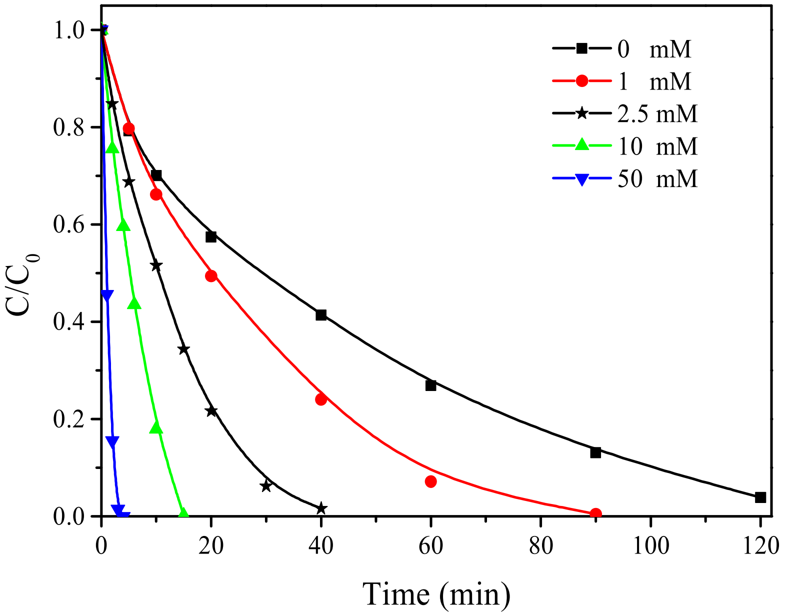
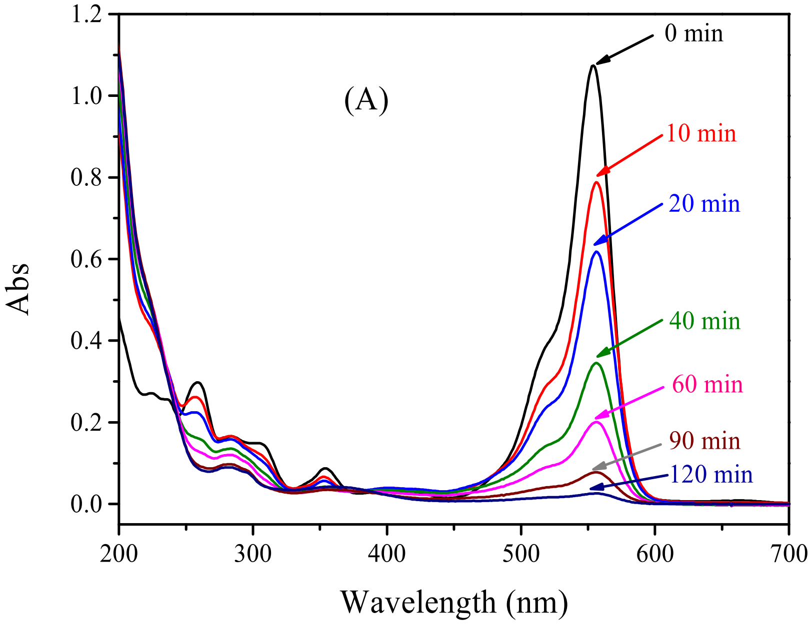
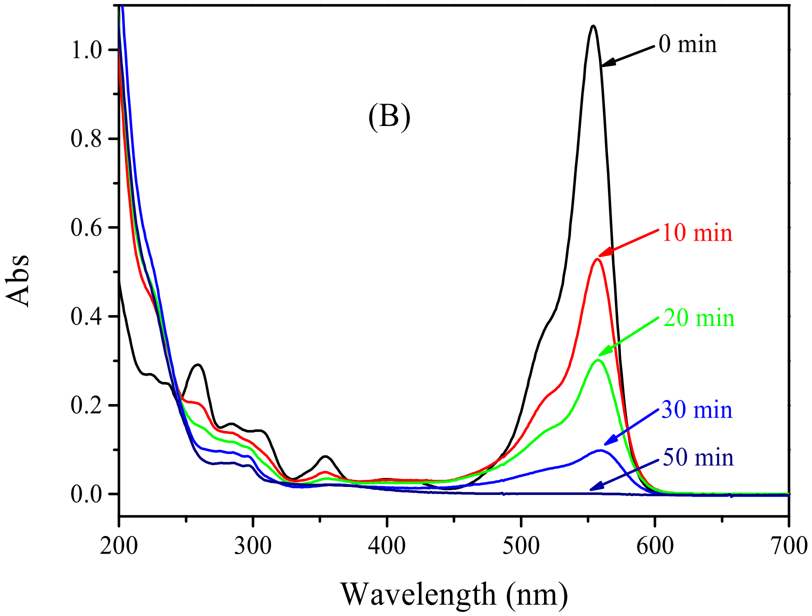


Figure 2. Effects of chloride ion on the degradation of RhB by PMS. Conditions: [RhB] = 10 mg/L, [PMS] = 2.5 mM, pH$_0$ = 4.5 ± 0.1.





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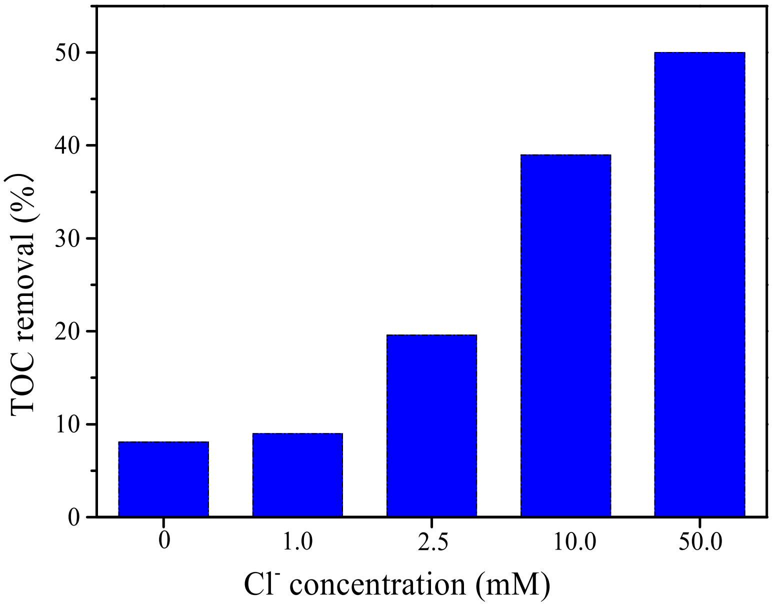

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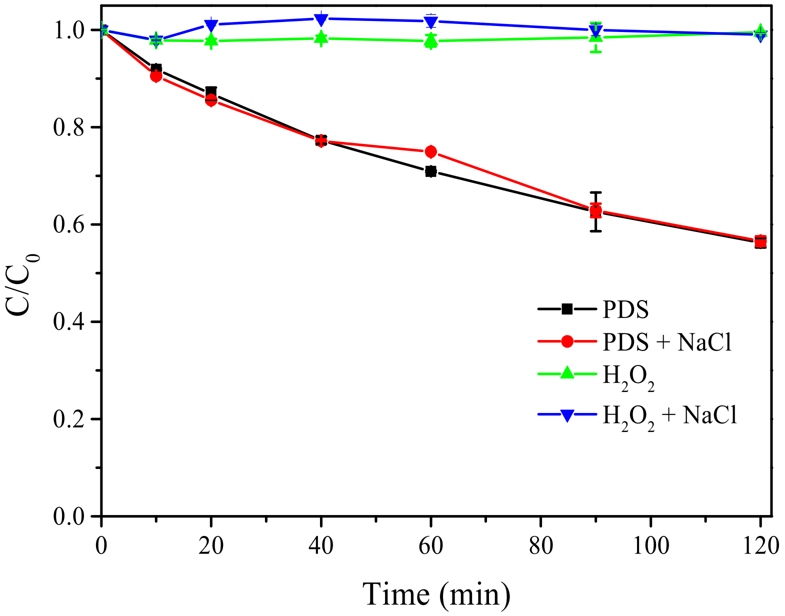

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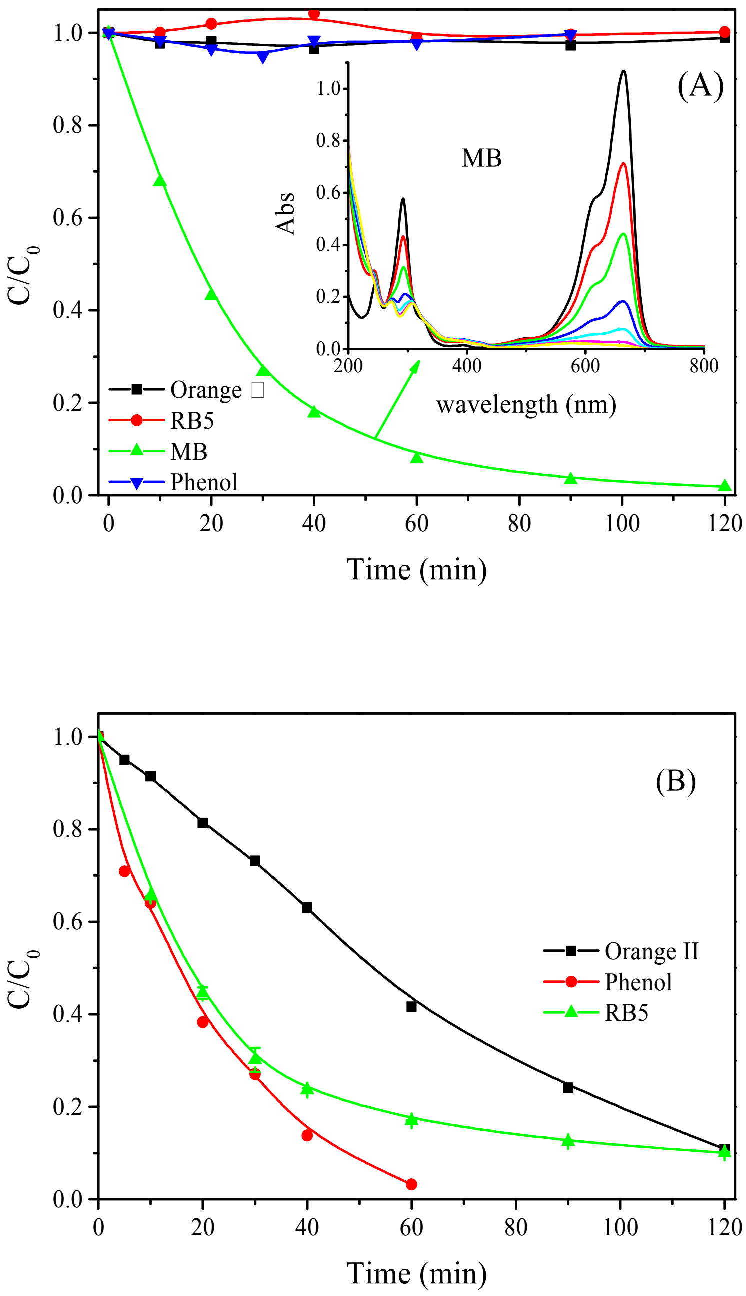


Figure 6. Degradation of other organic pollutants with PMS (A) or PMS/Cl$^-$ (B) and UV-vis spectra changes of MB in PMS system (insert figure). Conditions: [MB] = [RB5] = [Orange II] = 10 mg/L, [phenol] = 0.1 mM, [PMS] = 2.5 mM, [Cl$^-$] = 2.5 mM, pH$_0$ = 4.5 ± 0.1.

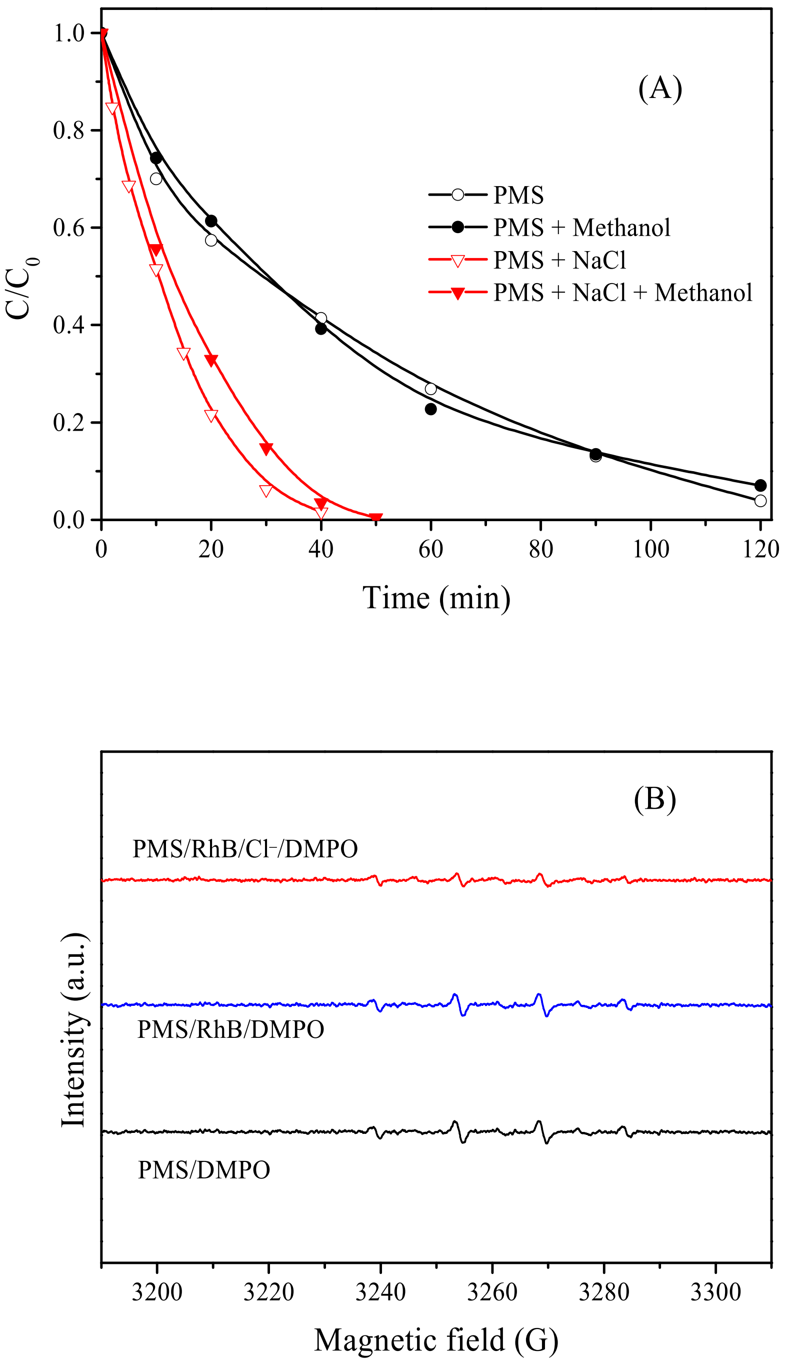
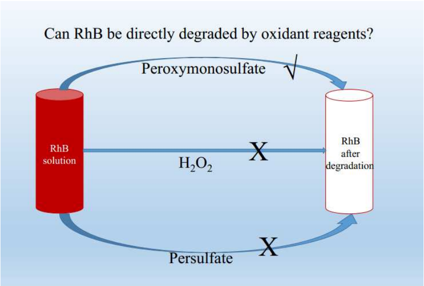


Figure 7. Effect of methanol on the degradation of RhB (A) and EPR spectra in PMS/RhB and PMS/RhB/Cl⁻ systems (B). Conditions: [RhB] = 10 mg/L, [PMS] = 2.5 mM, [Cl⁻] = 2.5 mM, pH_0 = 4.5 ± 0.1, [methanol] = 2.5 M, [DMPO] = 10 mM.

Table 1.
Kinetic coefficients under various operating conditions (RhB = 10 mg/L).

Run No.	[PMS] (mM)	pH_0	[Cl^-] (mM)	k (min^{-1})	R^2
1	1.0	4.5	0	0.010	0.963
2	2.5	4.5	0	0.021	0.979
3	5.0	4.5	0	0.050	0.991
4	10.0	4.5	0	0.110	0.975
5	2.5	2.0	0	0.021	0.992
6	2.5	10.0	0	0.047	0.905
7	2.5	12.0	0	0.008	0.982
8	2.5	4.5	1.0	0.042	0.978
9	2.5	4.5	2.5	0.089	0.973
10	2.5	4.5	10.0	0.170	0.973
11	2.5	4.5	50.0	1.371	0.902

Graphical abstract



PMS alone is able to decolorize cationc dyes withou the need for any catalysts.