



## Short Communication

# Peroxymonosulfate/base process in saline wastewater treatment: The fight between alkalinity and chloride ions

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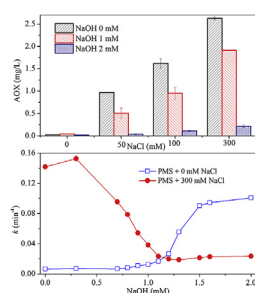
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## HIGHLIGHTS

- Negligible effects of chloride on PMS/base system at a low alkalinity are observed.
- Dye degradation is inhibited in PMS/base/Cl<sup>-</sup> system as Cl<sup>-</sup>/OH<sup>-</sup> are at high levels.
- Less AOX are formed in PMS/base/Cl<sup>-</sup> system at a high level of alkalinity.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Both Cl<sup>-</sup> and base can affect PMS activation to produce reactive chlorine or oxygen species, but the overall effects of chloride on this emerging PMS/base technology in saline wastewater treatment are unknown. Here effectiveness of PMS/base, PMS/Cl<sup>-</sup> and PMS/base/Cl<sup>-</sup> is compared with a gradient concentration of chloride and alkalinity, by probing the degradation of methylene blue (MB). Both PMS/base and PMS/Cl<sup>-</sup> systems can rapidly degrade MB due to the generation of singlet oxygen and reactive chlorine, respectively. Interestingly, dye degradation and adsorbable organic halides (AOX) formation are inhibited in the PMS/base/Cl<sup>-</sup> system as high concentrations of Cl<sup>-</sup> and base co-exist. Reaction of PMS with chloride diminishes the effective concentration of PMS by base activation, whereas in return high alkalinity decreases the oxidation capacity of reactive species. Therefore, this finding may have significant technical implications for evaluating the applicability of the emerging PMS/base technology and optimizing the conditions for AOX abatement in PMS-based processes.

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## 1. Introduction

Peroxymonosulfate (PMS) is a common oxidant used for the remediation of contaminated water or soil by generation of highly reactive radicals, such as sulfate radicals (SO<sub>4</sub><sup>•-</sup>, 2.5–3.1 V vs. NHE) and hydroxyl radicals (HO<sup>•</sup>, 1.9–2.7 V vs. NHE), through activation processes (Anipsitakis and Dionysiou, 2003, 2004; Guan et al.,

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2011). Transition metals (e.g. Co(II) (Xu et al., 2013) and Fe(II) (Zou et al., 2014; Huang et al., 2016)), radiation excitation (i.e. UV (Guan et al., 2011) and heat (Yang et al., 2010)), ultrasound (Su et al., 2012; Songlin et al., 2015), microwave (Qi et al., 2016) and electrochemistry (Govindan et al., 2014) are commonly used to activate PMS to generate  $\text{SO}_4^{\cdot-}$  and  $\text{HO}^{\cdot}$ , and the associated catalytic mechanisms have been well elucidated.

In addition to these radical-based advanced oxidation processes (AOPs), PMS can also be efficiently activated via a non-radical mechanism. The recent investigations suggest that PMS is able to be activated by benzoquinone (Zhou et al., 2015b), phosphate anions (PBS) (Lou et al., 2014), polyphosphates (Lou et al., 2017) and  $\text{Cl}^-$  (Yuan et al., 2011; Lei et al., 2016) through a non-radical pathway. Recently, activation of PMS by base has been recognized as an economical, high-efficiency method for the organic pollutant degradation. For instance, Qi et al. (2016) reported that PMS can be efficiently activated by base for degradation of a variety of organic pollutants, in which superoxide anion radical and singlet oxygen are proposed to be the primary reactive oxygen species. Chloride ion is one of the major inorganic components in wastewater from the dyeing industry (Lei et al., 2016). Impacts of  $\text{Cl}^-$  on AOPs performance vary, depending on the reactivity of peroxygens and their derived radicals, and chloride contents in wastewater to be treated. The presence of  $\text{Cl}^-$  leads to enhance degradation efficiency in the UV/PMS system (Wang et al., 2011a) and  $\text{Mn}_3\text{O}_4\text{-MnO}_2/\text{PMS}$  system (Zhao et al., 2017), while imposes inhibitory effects on performance of UV/PMS system (Khan et al., 2017; Xu et al., 2017a, 2017b) and Co/PMS system (Wang et al., 2011a). In addition, a dual effect (inhibitory and then accelerating) of chloride was observed in organics degradation with Co/PMS process (Yuan et al., 2011; Zhou et al., 2015a; Wang et al., 2017) and  $\text{Fe}^{2+}/\text{PMS}$  process (Ahmadi et al., 2017). Even such effects of chloride on radical-based systems have been investigated in the UV/PMS, Co/PMS,  $\text{Fe}^{2+}/\text{PMS}$ , and  $\text{Mn}_3\text{O}_4\text{-MnO}_2/\text{PMS}$ , there are few scattered reports available on effectiveness of non-radical systems in saline wastewater treatment. To the best of our knowledge, as yet, there is no systematic report on the effects of  $\text{Cl}^-$  on degradation of organic pollutants in the PMS/base system. It is hypothesized that both  $\text{Cl}^-$  and base would react with PMS to generate reactive chlorine or oxygen species, but overall influences of chloride on this emerging PMS/base system are completely unknown.

The aims of the present study are (1) to test the effect of different concentration of chloride ions on the extent of pollutant degradation in PMS/base systems and (2) to examine the conversion of adsorbable organic halides (AOX). Methylene blue is selected as a typical model cationic dye, as it represents a class of non-biodegradable dye and is widely used in the textile industry. Also, the primary reactive oxygen species are identified with chemical quenching experiments. Reaction mechanism in PMS/base/ $\text{Cl}^-$  systems is discussed.

## 2. Materials and methods

### 2.1. Materials

Methylene blue (MB,  $\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}\cdot\text{XH}_2\text{O}$ , 95%), Oxone<sup>®</sup> ( $[\text{2KHSO}_5\cdot\text{KHSO}_4\cdot\text{K}_2\text{SO}_4]$  salt, 95%) were obtained from Sigma-Aldrich. Sodium chloride (NaCl, 99.5%), sodium hydroxide (NaOH) were purchased from Sinopharm Chemical and used without further purification. Methanol (MeOH) and tert-butyl alcohol (TBA), as a radical scavenger for  $\text{SO}_4^{\cdot-}$  and  $\text{HO}^{\cdot}$ , respectively, were purchased from Sinopharm Chemical. Superoxide dismutase from bovine erythrocytes (SOD, Sigma) was used to quench superoxide. L-histidine (Sigma) was used as a singlet oxygen scavenger. All

chemical reagents and organic solvents were of high purity reagent grade and were used without further purification.

### 2.2. Experimental methods

Stock solution of MB was pre-prepared with Milli-Q water, and the initial concentration ( $C_0$ ) was fixed at 0.1 mM except for experiments concerning the effect of initial MB concentration. Stock solutions of sodium hydroxide and PMS (typically 60 mM) were also freshly prepared by dissolving weighed amounts of sodium hydroxide and PMS in Milli-Q water. Stock solution of sodium chloride was pre-prepared with Milli-Q water. All the experiments were conducted in 50 mL beakers without the pH being controlled. Changes in pH during the reaction are recorded in Table S1. Appropriate concentrations of MB, NaOH, NaCl, PMS were orderly added into the beakers in this order immediately at ambient temperature.

### 2.3. Analytical methods

The concentration of MB was quantified on a Hitachi U-2910 spectrophotometer by monitoring the absorbance at 663 nm. AOX determination was carried out by instrumental analysis (AOX, multi X 2500, Jena, Germany) after enrichment on activated carbon. The measurement range of AOX analysis was from 1 to 100  $\mu\text{g}$  (calculated as the absolute content of chloride). Samples were pre-treated with the Automatic Preparation Unit2 (Jena, Germany), an automatic adsorption system for sample preparation (Fang et al., 2016).

## 3. Results and discussion

### 3.1. Degradation kinetics

Fig. 1 shows the different effects of chloride and NaOH on the PMS-based oxidation of MB. PMS itself can partly oxidize MB, while dye degradation is greatly accelerated upon the addition of either 2 mM NaOH or 300 mM  $\text{Cl}^-$ , demonstrating both alkalinity and chloride are capable of activating PMS to effectively oxidize organic pollutants. However, while 2 mM NaOH and 300 mM  $\text{Cl}^-$  are simultaneously added, MB decomposition is inhibited as compared to those in the PMS/base and PMS/ $\text{Cl}^-$  systems. This indicates that

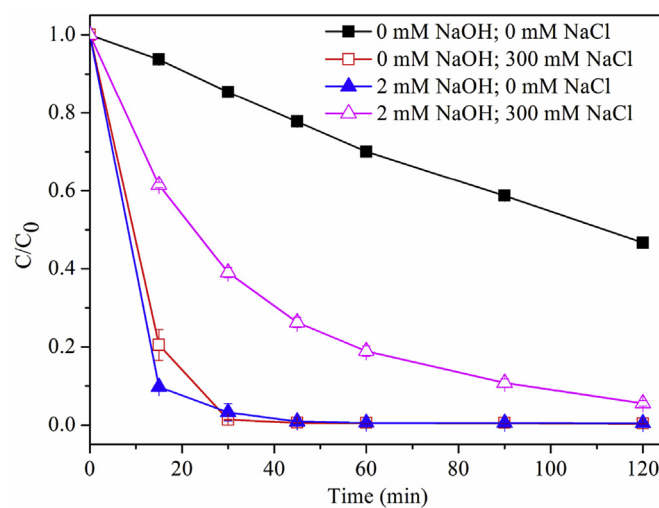


Fig. 1. Effect of NaCl on MB degradation in the base/PMS system without pH adjustment. Conditions: [PMS] = 1 mM, [MB] = 0.03 mM, [NaOH] = 0 or 2 mM, [NaCl] = 0 or 300 mM.

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