



Synergetic effect of the mineralization of organic contaminants by a combined use of permanganate and peroxymonosulfate



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ABSTRACT

A novel bi-component oxidizing system of KMnO₄ and peroxymonosulfate (PMS, in the form of Oxone[®]) is proposed for mineralization of organic contaminants. Our results demonstrated that the combined use of KMnO₄ and PMS (CUPP) caused a synergetic effect on the mineralization of organics in solution. The reduction products of KMnO₄, suspended particulate MnO₂, activated the subsequently added PMS, promoting the sulfate radicals-involved oxidation of acid orange 7 (AO7) and degradation intermediates. The suspended amorphous MnO₂, as the PMS activator, featured a so-called sea urchin nanostructure with many flakes radiating from its center. The addition of Oxone acidified the solution and, in turn, improved the reactivity of KMnO₄. The results indicated that the time interval between KMnO₄ and Oxone additions did not impact the efficiency of the bi-component oxidizing system. The ratio of KMnO₄/PMS can be optimized to achieve the highest mineralization rate of AO7 or the best utilization of oxidants. We concluded that the combined use of KMnO₄ and PMS facilitated the utilization of both oxidants and exhibited powerful oxidizing capability without the need of an additional catalyst for PMS activation. This bi-component system can be developed as an innovative chemical oxidation technology for the transformation of a variety of organic pollutants.

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1. Introduction

Due to the increasing presence of refractory organic molecules in wastewater streams and natural media, technologies are needed to mineralize or convert them into less harmful compounds [1]. Chemical oxidation, which uses oxidants such as H₂O₂, O₃, ClO₂, KMnO₄, Na₂S₂O₈ and K₂FeO₄, is proven to be a rapid and efficient technology to treat a wide range of organic contaminants [2–4]. The oxidation potential of hydroxyl radicals (HO[•]), which can be generated, for example, by H₂O₂ involved Fenton process [5], has been estimated to be 2.8 V vs. NHE [6,7]. The high reactivity of hydroxyl radicals ensures that a broad range of organic compounds is completely oxidized. Persulfate ion (S₂O₈²⁻) is a strong oxidant that can generate free sulfate radicals under certain reaction conditions (SO₄^{-•}, E⁰ = 2.6 V) [8]. Sodium persulfate, activated by various agents (e.g. transition metals and heat) [9], has been used for *in situ* chemical oxidation (ISCO) in the remediation of soil and groundwater. In comparison with the processes involving hydroxyl radicals or sulfate radicals, permanganate is a relatively mild

oxidizing agent (E⁰ = 1.7 V) with selective oxidizing capacity to organic pollutants [10]. Permanganate has strong reactivity with electron-rich moieties, such as a wide range of chlorinated alkenes (R–C=C–R) [11]. Permanganate can be reduced to manganese species having different oxidation states such as Mn(VI), Mn(V), Mn(IV), Mn(III) and Mn(II), depending on the various reaction conditions, types of substrate and their stability [12]. In spite of its relatively low reactivity to specific organic pollutants, permanganate is still used for ISCO to remediate contaminated soil and groundwater due to its comparative stability, ease of handling, relatively low cost and effectiveness under alkaline condition [13,14].

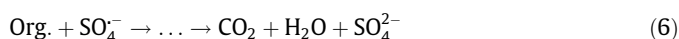
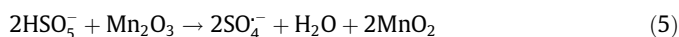
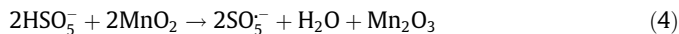
More recently, peroxymonosulfate (PMS) is also studied as a chemical oxidant for its powerful oxidizing capability [15,16]. Rastogi et al. found that PMS, in the form of Oxone triple salt, showed stronger oxidizing capability than persulfate when chelated ferrous irons were used as the activator [17]. The conjunction of PMS/Co(II) also showed a better performance than Fenton reagent in mineralization of 4-chlorophenol [18]. The catalyst-mediated decomposition of PMS can proceed according to the following radical formation reactions, where PMS ions can be reduced or oxidized [19–22].

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Owing to its unique redox properties, PMS can be effectively activated by transition metal ions, transition metal oxides and reduced graphene oxide via the reactions (1) and (2). Meanwhile, the activator can be regenerated via the reaction (3). For example, using crystallized manganese dioxide as an activator, the activation of PMS and the oxidation of organics involve the following reactions [15,23,24]:



The aim of this study is to develop a novel chemical oxidizing system, combined use of permanganate and peroxymonosulfate (CUPP), for the destruction and mineralization of organic pollutants. KMnO_4 is a cost effective and readily available chemical, but its oxidizing capability is usually not enough to mineralize organic pollutants, particularly the compounds without electron-rich moieties. PMS has a much stronger oxidizing capability; however, it needs to be activated by an additional chemical agent, which can be tedious and costly. Our hypothesis is that the combined use of the KMnO_4 and PMS facilitates the utilization of both oxidants, resulting in an efficient oxidation of organics. Their combined use will lead to several attractive advantages, including eliminating the need for an additional activator for PMS, improved cost-effectiveness when compared to the individual use of PMS, and a more efficient and thorough oxidation when compared to the individual use of KMnO_4 . An organic dye, acid orange 7 (AO7), is selected in this study as the model compound to explore the feasibility of combined use of KMnO_4 and PMS for the mineralization of organics. The efficiency of oxidation is evaluated by the extent of mineralization achieved, instead of the extent of destruction of AO7 molecules.

2. Materials and method

2.1. Chemicals

Oxone ($\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot 0.5\text{K}_2\text{SO}_4$, >95% purity) was purchased from Sigma-Aldrich. Other chemicals with purity ranging from 97% to 99.9% were purchased from Sinopharm Chemical Reagent, China and used as received. Deionized water was used in all experiments. KMnO_4 was dissolved in deionized water to make a concentrated stock solution (~100 mM), which was boiled and stored in the dark. Prior to use, the KMnO_4 solution was determined by sodium oxalate titration.

2.2. Preparation of different types of MnO_2

Stock solutions containing suspended particulate MnO_2 were prepared following the procedure similar to the method reported by Perez-Benito et al. [25]. In brief, solutions containing suspended particulate MnO_2 were prepared by stoichiometrically mixing 0.1 M KMnO_4 with 0.1 M required $\text{Na}_2\text{S}_2\text{O}_3$ in deionized water. Prior to use, the solution was stirred violently to make a homogeneous distribution of the suspended particulate MnO_2 . Synthesis of nano-crystalline α - MnO_2 followed the hydrothermal method

based on the redox reactions of Mn^{2+} ions with persulfate. Detailed procedures are available in the literature [23].

2.3. Tests for AO7 oxidation

The AO7 oxidation experiments were conducted in a 150 mL erlenmeyer flask. A predetermined amount of AO7 was mixed with the oxidants (individual or combined use of KMnO_4 and Oxone). The initial concentration of AO7 was controlled at 50 mg/L, and the volume of the solution was kept at 50 mL. The temperature of the solution was maintained at 30 °C by a water-bathing shaker. If not otherwise specified, the pH of the AO7 solution (~45 mL) was adjusted to 5 before adding any oxidant. Diluted H_2SO_4 and NaOH were used to adjust pH. For the combined use of KMnO_4 and Oxone, the time interval between their additions was 1 h except in the investigation on the effect of time interval. At the end of oxidation experiments, the solutions were sampled and the concentrated NaNO_2 (~5 g/L) solution was added to quench the oxidation process. After that, excess HONH_3Cl was added into the sample solution to convert the MnO_2 to Mn(II) , avoiding the adsorption effect of suspended amorphous MnO_2 . Preliminary experiments showed that the treating process allowed an accurate TOC analysis on the liquid samples. Total organic carbon (TOC) content of the quenched sample solution was determined and the mineralization rate of the AO7 solution (i.e. $1 - [\text{TOC}]_t / [\text{TOC}]_0$) was calculated. Three kinds of MnO_2 were investigated to elucidate their catalytic activities on AO7 oxidation and their adsorption capabilities. In the adsorption experiments, the AO7 solution was centrifuged and the supernatant was further filtered with a 0.22 μm PVDF syringe filter before concentration measurement [23]. Experiments were carried out in duplicate, and the data referred to in this paper are the mean value.

2.4. Analytical methods

The concentration of KMnO_4 was determined using UV–vis spectrophotometry (Shanghai spectrum Ltd., China) at a maximum absorption wavelength of 525 nm [26]. The UV–vis spectrum measurement showed that the decoloration of AO7 ($\lambda_{\text{max}} = 484 \text{ nm}$) was very fast (<5 min) in the presence of KMnO_4 . The daughter compounds of AO7 does not interfere the photometric measurement of KMnO_4 . 2-naphthol was measured using a High Performance Liquid Chromatography consisting of a Shimadzu 15C HPLC pump and a UV/Visible Detector. TOC of the solution was measured by a Multi N/C 2100 TOC analyzer (Analytik Jena, Germany). The turbidity of solution during testing was measured by a turbidity meter (HACH 2100P, USA). Particle size distribution of the suspended particulate MnO_2 was measured by a Microtrac S3500 apparatus (Micro Instruments, USA). The pH value of the reaction solution was measured or monitored using a pH probe (Fondriest environmental company, USA), which was connected with a computer via a USB interface. The MnO_2 materials were characterized by a scanning electron microscopy (SEM, Zeiss Sigma FESEM) and an X-ray diffraction analyzer (Shimadzu X-ray 6000). For the SEM observation of suspended particulate MnO_2 , a piece of nickel foam was soaked in the solution for several seconds to collect the particles. In selected experiments, residual oxidants after reaction were determined by iodometric titration [27,28]. The solution was centrifuged and filtrated to separate the MnO_2 precipitates and the supernatant was collected for titration. For the combined use of oxidants, the residual PMS was calculated by subtracting the contribution of residual KMnO_4 from the total $\text{Na}_2\text{S}_2\text{O}_3$ consumption. The residual KMnO_4 was determined by the UV–vis spectrophotometry at 546 nm.

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