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Degradation of p-nitrophenol by heat and metal ions co-activated persulfate

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HIGHLIGHTS

- Temperature has significant impact on the degradation of PNP.
- Co-activated persulfate exhibited chaotic and complicated effect on PNP degradation.
- The formation of precipitate restrained the diffusion of persulfate and $SO_4^{\cdot-}$.
- Degradation pathway of PNP proposed according to the intermediates formed.

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ABSTRACT

The degradation of p-nitrophenol (PNP) by thermal and metal ions (Fe^{2+} or Cu^{2+}) co-activated persulfate was studied in this work. The activation of persulfate toward PNP degradation was investigated at four temperatures *viz.* 25, 50, 60, 70 and 90 °C, and three molecular ratios between Metal ions:PS of 1:100, 1:10, 1:1 (PS was 30 mM). The results showed that the degraded rate of PNP could be enhanced either by increasing the temperature or the molecular ratio between Metal ions:PS. However, the co-activated persulfate exhibited a complicated effect on PNP degradation rather than a solely synergistic enhancement. At higher temperatures of 70 and 90 °C, the additive metal ions could act as scavenger toward $SO_4^{\cdot-}$ at such higher temperatures, then would slow down the increasing trend. In the case of co-activation system at 70 °C, a decline in PNP degradation was observed beyond 90 min comparing to the sole thermal activation. It was caused by the precipitate formed during the process, which controlled and restricted the diffusion of persulfate and $SO_4^{\cdot-}$. The concentration of persulfate remaining in the solution was measured by an iodometric method. The TOC value during the process was detected and the TOC removal efficiency reached to 85.81% at 70 °C. Furthermore, the intermediates formed during the degradation process were detected and identified by high performance liquid chromatography and mass spectrometry, and an interpretation of the degradation pathway was made based on the findings.

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1. Introduction

P-nitrophenol (PNP) is a common and prominent pollutant that exhibits acute toxicity and recalcitrant behavior and normally let out in the aquatic system from the industries such as pesticide, pharmaceutical and petrochemical [1,2]. It causes adverse health effect not only to the aquatic organisms but also to humankind through surface, ground and drinking water contamination [3]. Hence the contamination of PNP in aquatic environment has become of great concern in recent years, and the conventional wastewater treatment techniques are incapable and the strategies adopted are inadequate to treat pollutants like PNP.

The so-called advanced oxidation processes (AOPs) are proved to be effective and attractive for the treatment of PNP by in situ generation of highly powerful oxidants such as hydroxyl radicals ($^{\cdot}OH$) and sulfate radicals ($SO_4^{\cdot-}$) [1,4,5]. Among the various AOPs, the chemical oxidation involving persulfate ($S_2O_8^{2-}$) as an oxidant has been drawing an increasing attention and was found as an alternative technology for water decontamination application [6–10]. The distinctive features of the techniques are as follows: (1) persulfate is relatively stable at room temperature and can thus be diffused into considerably longer distance; (2) it has strong oxidizing power (E^0 = +2.01 V) and non-selective behavior toward

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pollutant degradation; (3) It yields $SO_4^{\cdot-}$ upon activation, which is an even stronger oxidant (E^0 = +2.60 V) than the former, having a longer half-life period than the ·OH, and can eventually enhance the oxidation efficiency in the water decontamination [6,11]. Generally, the ion of $S_2O_8^{2-}$ can be effectively activated by heat, UV light, transition metal ions (Me^{n+}), zero valent metals (e.g., iron) [12], bimetallic and trimetallic systems [13] to generate $SO_4^{\cdot-}$. Among, the heat and transition metal ions induced activation of $S_2O_8^{2-}$ have been intensively studied for the oxidation of recalcitrant toxic contaminants. The effective oxidation behavior of persulfate, activated by thermal treatment, toward 59 volatile organic compounds including benzene, toluene, ethylbenzene, xylene and chlorinated solvents has been reported by Huang et al. [8]. The degradation process of bisoprolol by thermally activated persulfate was followed pseudo-first-order kinetics and an increase in the temperature from 40 to 70 °C increased the rate constants proportionally [14]. The transition metal ions presence has also been proved to activate persulfate and enhance the oxidation efficiency of recalcitrant compounds. Romero et al. [11] reported that persulfate could be effectively activated by Fe^{2+} to improve the degradation rate of diuron compound, and an increase in the Fe^{2+} concentration accelerated the degradation of diuron at initial stages. Similarly, the effective catalytic behavior of Cu^{2+} ions on p-chloroaniline degradation using activated persulfate has been observed by Liang et al. [15]. Either as metal pollutant or a co-existing component via the application of herbicides and fertilizers, copper ions can enter into environment even to a high level of several hundreds ppm. However, to our knowledge, limited work has been carried out to investigate persulfate activated by copper ions to degrade PNP.

The single strategy, *i.e.*, the heat [16,17] or transition metal ions [18] induced treatment, has been extensively studied to elucidate fundamental mechanisms and kinetics of persulfate activation in aqueous media. However, to our knowledge, there have only been few studies on the synchronized effect of both heat and metal ions together so far. Since the presence of transition metal ions in the water body is quite normal, their role played in the degradation of organic pollutants would be of more practical study. Among the various transition metals, Fe^{2+} and Cu^{2+} were most studied ones that could activate persulfate effectively. On the other hand, they were also common metal ions in the environment. For these reasons, Fe^{2+} and Cu^{2+} were chosen as the representative transition metal to study the co-activation effect by heat and metal ions in this study. Hence, the main objectives of this work were: (1) to study the efficiency of metal ions (Fe^{2+} or Cu^{2+}) activated persulfate on PNP degradation at ambient temperature; (2) to investigate the effect of different activation temperature of persulfate on PNP degradation; (3) to elucidate the impact of Fe^{2+} or Cu^{2+} at different molecular ratio between Metal ions:PS on PNP degradation in the process of persulfate activation by thermal treatment. These findings would definitely be useful to enhance the performance of persulfate in degrading the PNP contaminated wastewater.

2. Materials and methods

2.1. Chemicals

All agents such as sodium persulfate (PS, 99%, $Na_2S_2O_8$) and p-nitrophenol (PNP) were purchased from Sinopharm Chemical Reagent Company (Shanghai, China) and used without further purification. Solutions were prepared by dissolving the chemical agents into deionized (DI) water with a resistivity of 18.25 MΩ cm^{-1} and pH of 6.8. The initial pH of every experiment performed was adjusted with 1 mol L^{-1} H_2SO_4 and 1 mol L^{-1} NaOH solutions.

2.2. Batch oxidation experiments

Stock solutions of PNP and persulfate were freshly prepared using DI water and the dilutions were made prior to every batch experiment using DI. The degradation experiments were carried out in a 50 ml sealed vial with an initial PNP concentration of 0.72 mmol L^{-1} and $Na_2S_2O_8$ concentration of 30 mmol L^{-1}. To study the effect of activation temperature on the degradation of PNP, the experiments were carried out with a thermo regulated water bath fixing respective reaction temperature (25, 50, 60, 70 and 90 °C) constantly. To investigate the degradation behavior of PNP with Fe^{2+} or Cu^{2+} activated persulfate, three different molecular ratio between metal ions (Cu^{2+}, Fe^{2+}):PS *viz.* 1:100, 1:10, 1:1 were employed in the batch experiments at room temperature (25 °C). To determine the synchronized effect of persulfate activated by both heat and metal ions addition, the Cu^{2+} or Fe^{2+} concentration of 30 mmol L^{-1} were taken using $CuSO_4$ or $FeSO_4$ respectively, with varying required reaction temperatures. Also, the molecular ratio between Metal ions (Cu^{2+}, Fe^{2+}):PS was varied as 1:100, 1:10 and 1:1 at 70 °C to elucidate the influence of the metal ion. Control tests were conducted in parallel in the absence of persulfate for each experiment. All degradation experiments were conducted with three duplicate samples and average data were reported. The final results are given as mean (±s) where s represents the standard deviation.

2.3. Analysis

The concentration of PNP was determined with a UV–vis spectrophotometer (Cary 50, USA) at an absorbance of 400 nm [1] and the pH of the aqueous solutions was monitored using a pH meter (Sartorius PB-10 meter with Sartorius pH/ATC electrode). The concentration of persulfate existed in the solution was determined by using an iodometric method [19].

The intermediates formed in the degradation reaction were monitored by high performance liquid chromatography (HPLC, Shimadzu, Japan) equipped with an UV detector and a C_{18} reverse-phase column (4.6 mm × 250 mm, Agilent, USA) at 40 °C. The mobile phase was methanol/water/acetic acid with a ratio of 35/65/0.5 (v/v). The injection volume of the sample was 20 μl and the flow rate was 0.8 ml/min. The wavelength of the UV absorbance detector was fixed at 254 nm [2]. X-ray fluorescence spectrometry (XRF, EDAX Inc., USA) was used for elemental analysis of precipitate formed during the reaction. Total organic carbon (TOC) was measured using a TOC analyzer (multi N/C, Germany). A liquid chromatography–mass spectrometry (LC–MS, LC–MSD Trap1100 Agilent) was used to identify the reaction intermediates formed. The mass spectrometer was operated in negative electrospray ionization (–ESI) mode. The optimum conditions for MS scan were as follows: dry temperature of 325 °C, nebulizer pressure of 40 psi, nitrogen gas flow rate of 10 L min^{-1}, capillary voltage of 3.5 kV and scan range of 50–500 *m*/*z*. The conditions for LC–MS *viz.* column, oven temperature and mobile phase, were similar to those for HPLC analysis.

3. Results and discussion

3.1. Degradation of PNP by sole heat-activated persulfate

Fig. 1 shows the changes in the concentration of PNP with respect to the temperatures employed to activate the persulfate. As seen, the PNP is a highly recalcitrant molecule and will not self-decompose even at an elevated temperature of 90 °C in the absence of persulfate. With the presence of persulfate, however, the degradation of PNP was progressively increased as the

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