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Degradation of antipyrine by heat activated persulfate

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ABSTRACT

Heat activated persulfate is an emerging water treatment technology utilizing highly active sulfate radicals ($SO_4^{\cdot-}$) as the principal oxidizing agent. The objective of this study was to evaluate the degradation of antipyrine, a representative pharmaceutically active compound, in a heat-activated persulfate system. Bench-scale kinetics tests were conducted to evaluate the impacts of key factors controlling the treatment performance, including pH, chloride, alkalinity, dissolved oxygen, dissolved organic matters, chemical addition mode, and water matrices. Under different experimental conditions, the antipyrine degradation exhibited a pseudo-first-order kinetics pattern ($R^2 > 0.95$). Solution pH influenced the treatment efficiency because the fractions of different oxidizing agents were pH-dependent. $SO_4^{\cdot-}$ predominated under an acidic condition, while hydroxyl radicals ($OH^{\cdot}$) gradually prevailed at a basic condition. Chloride could enhance the degradation at an appropriate concentration ($[Cl^{-1}]$:[persulfate] = 10:1 in this study achieved a 80% removal of antipyrine within 2 h), but inhibited the treatment at other levels. The alkalinity species apparently reduced the reaction rate (k_{obs} decreased from $7.5 \times 10^{-3}\ s^{-1}$ to $3.4 \times 10^{-3}\ s^{-1}$ when $[HCO_3]_0$:$[Persulfate]_0$ was increased from 0:1 to 200:1). Dissolved organic matter decreased the antipyrine degradation rate by 76% when initial DOC increased from 0 to 10 mg/L due to their competition for sulfate radicals. Anaerobic condition (dissolved oxygen = 0.01 mg/L) improved the k_{obs} by 20% compared with an aerobic condition (dissolved oxygen = 8.20 mg/L). A single step of persulfate addition favored the antipyrine degradation rate. The findings demonstrate that the heat-activated persulfate oxidation is a promising technology for water pollution caused by emerging contaminants such as pharmaceuticals, and the treatment is optimized only after the impacts of water characteristics and operation methods are carefully considered.

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1. Introduction

Inappropriate usage or disposal of pharmaceuticals and personal care products (PPCPs) poses a great threat to water resources [1–4]. Many PPCPs are chemically and/or biologically persistent, and have been frequently detected as emerging contaminants in raw water, drinking water, and treated wastewater [5,6]. Antipyrine is a persistent analgesic and antipyretic drug. In Germany, antipyrine is consumed approximately at a rate of 0.35 g/year person [7]. Although removal of numerous PPCPs from water has been intensively investigated over the past decade, the publications regarding fate of antipyrine are scarce. Results of the few available studies demonstrate that traditional water treatment is very ineffective for antipyrine in water. For example, conventional aerobic biological treatment in wastewater treatment plants only achieved up to 30% removal of antipyrine [8]. Chlorination with 0.4 mg/L chlorine could merely degrade 48% of 50 μg/L antipyrine in tap water [9]. Consequently, there is an urgent demand in development of technically effective advanced treatment technologies for controlling the antipyrine-induced water pollution [10].

Among advanced water treatments, advanced oxidation technologies have attracted great attention because the principal oxidizing agents (hydroxyl or sulfate radicals) are able to chemically destruct molecular structures of target pollutants, and transform them into less toxic pollutants and even non-toxic water and carbon dioxide. Particularly, persulfate ($S_2O_8^{2-}$, PS)-based AOTs have recently emerged as an alternative for decomposition of organic pollutants in contaminated soil and water [11]. Persulfate is a strong oxidizing agent itself, with a redox potential of 2.2 V [12]. Once activated by appropriate methods (UV, heat, or metals), persulfate can transform to much more active sulfate radicals ($SO_4^{\cdot-}$) as follows [13,14].

Abbreviations: AP, antipyrine; AOT, advanced oxidation technology; DO, dissolved oxygen; DOC, dissolved organic carbon; E_0, redox potential; ISCO, *in situ* chemical oxidation; k_{obs}, pseudo-first-order degradation rate; $k_{obs\text{-}original}$, pseudo-first-order degradation rate in blank test; $OH^{\cdot}$, hydroxyl radicals; PPCPs, pharmaceuticals and personal care products; PS, persulfate; $SO_4^{\cdot-}$, sulfate radicals.

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$$S_2O_8^{2-} + \text{heat/UV} \rightarrow 2SO_4^{\cdot -} \quad (1)$$

$$S_2O_8^{2-} + Me^{n+} \rightarrow SO_4^{\cdot -} + Me^{(n+1)+} + SO_4^{2-} \quad (2)$$

Sulfate radicals ($SO_4^{\cdot -}$), similar to hydroxyl radicals ($OH^{\cdot}$), have an extremely high redox potential ($E_0 = 2.6$ V). Generally, $OH^{\cdot}$ preferably adds to C=C bonds or cleaves hydrogen from C—H bonds, whereas $SO_4^{\cdot -}$ directly gains electrons from organic compounds to produce organic radical cations [15]. Among the three activation methods, heat activation has been increasingly applied in in situ chemical oxidation (ISCO) for environmental remediation [16,17]. Compared with the other two activation methods, heat activation can effectively generate $SO_4^{\cdot -}$, locally increase temperature in solution, shorten reaction time, and minimize the amount of persulfate wasted [14,18]. However, most of the previous studies regarding utilization of sulfate radicals were primarily focused on remediation of industrial hazardous waste-contaminated soil or groundwater [19–21], and few publications reported sulfate radicals-induced oxidation for removal of emerging contaminants [22–24]. To the best of our knowledge, there has not been any study on sulfate radical oxidation of antipyrine in water.

The objective of this study was to evaluate the technical feasibility of heat activated persulfate oxidation of antipyrine. Our motivation of this study is to explore a new pathway to effectively control the pollution caused by micro-pollutants such as pharmaceutically active compounds, as well as provide a prototype to utilize emerging oxidizing agents to address new water pollution issues. Factors affecting the treatment, including chloride, alkalinity, pH, dissolved oxygen (DO), dissolved organic matter, and chemical addition mode were assessed. These factors were selected because they were demonstrated to significantly influence the degradation efficiency during sulfate radical-induced oxidation of organic pollutants [25–27].

2. Experimental

2.1. Chemicals

All chemicals were at least analytical grade, except as noted. All the solutions were prepared using the ultrapure water produced from a Milli-Q Academic water purification system. Antipyrine (The physical and chemical properties of antipyrine are shown in Table.1.), methanol (HPLC grade, ⩾99.9%) and humic acid were purchased from Sigma–Aldrich. Sodium persulfate ($Na_2S_2O_8$, ⩾99.5%) were purchased from Sinopharm Chemical Reagent Co., China. All the other chemicals were purchased from Sinopharm Chemical Reagent Co., China. Ethanol (EtOH, ⩾99.7%) and tert butyl alcohol (TBA ⩾ 99.5%) were used as radical scavengers. Sodium phosphate (Na_2HPO_4, ⩾99.0%) and monobasic sodium phosphate (NaH_2PO_4, ⩾99.0%) were used to prepare appropriate pH buffer solution. The solution at pH 7.0 and 9.0 was prepared with 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4. Solution at pH 4.5 was prepared with 0.2 M NaH_2PO_4 and 10 M HCl. And the solution at pH 11.0 was prepared with 0.2 M Na_2HPO_4 and 1 M NaOH. If needed, 10 M HCl and 1 M NaOH were used to adjust solution pH to a desirable level. Sodium chloride (NaCl, ⩾99.9%), sodium carbonate (Na_2CO_3, ⩾99.8%), and sodium bicarbonate ($NaHCO_3$, ⩾99.5%) were used to study the effects of chloride and alkalinity on the treatment.

2.2. Experimental procedure

All the tests were conducted in triplicate in 45-mL culture bottles containing 40 mL antipyrine solution. Prior to addition of persulfate, the reactors were pre-heated in a water bath (low-temperature stirring reaction bath, Zhengzhou Great Wall Scientific Industrial and Trade Co., China) for 2 h to allow the solutions to reach 60 °C. The oxidation was initiated once appropriate volumes of 0.1 M sodium persulfate stock solution were added. During the treatment, a rapid shaking (~100 rpm) ensured a complete solution mixing state. At each sampling time (0, 20, 40, 60, 80, 100, 120 min), 0.6 mL homogenously mixed sample was collected from each culture bottle, and added to a 1.0 mL sample bottle pre-filled with 0.2 mL ethanol that quenched the oxidation caused by any residual persulfate. The samples were prepared for further analysis. For the experiments of identification of radical species in Section 2.2, TBA or EtOH was added with 1000 fold mole ratio of TBA/PS or EtOH/PS before reaction was initiated.

2.3. Chemical analysis

Antipyrine was measured using a high-performance liquid chromatograph (HPLC) (Waters 2010, USA) equipped with a Symmetry C18 column (dimensions 250 mm × 4.6 mm, 5 μm, Waters, USA) and a UV detector (Waters 2489) at 260 nm. The mobile phase was a mixture of Milli-Q water and HPLC-grade methanol (v:v = 20:80) at a flow rate of 0.8 mL/min. Dissolved oxygen (DO) was measured by a dissolved oxygen meter (Digital Precision Meter Multi 3410 WTW, USA). Solution pH was measured with a Mettler Toledo pH meter. Symbols in figures represent the average values of data obtained from the triplicate testing. All the standard deviations are below 5%. Statistical analysis was performed using Origin 8.0.

3. Results and discussion

3.1. Effect of solution pH

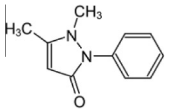
Effect of solution pH (4.5–11.0) on the antipyrine degradation ($[\text{Antipyrine}]_0 = 0.0265$ mM and $[Na_2S_2O_8]_0 = 1.85$ mM) is shown in Fig. 1. All the antipyrine decomposition well followed a pseudo-first-order kinetics pattern. The overall rate law for the antipyrine degradation can be expressed in Eq. (3).

$$-[\text{Antipyrine}]/\mathrm{dt} = k_{obs}[\text{Antipyrine}]_0 \quad (3)$$

where k_{obs} is the pseudo-first-order rate constant, and [Antipyrine] is the molar concentration of antipyrine at any specific time. In Fig. 1, the $k_{obs\text{-}origin}$ indicates the k_{obs} obtained in the tests without addition of any scavenger. Of note, the kinetics equation reflects the overall antipyrine degradation due to the mixed oxidizing agents (e.g., $SO_4^{\cdot -}$, $HO^{\cdot}$, and $S_2O_8^{2-}$) present in our reactors. Similar models were reported in previous studies using a heat-activated persulfate system [28–30].

The antipyrine degradation rate continuously decreased from pH 4.5 ($6.85 \times 10^{-3}\ s^{-1}$) through pH 7 ($3.92 \times 10^{-3}\ s^{-1}$) to pH 9 ($3.07 \times 10^{-3}\ s^{-1}$), but significantly increased to $6.33 \times 10^{-3}\ s^{-1}$

Table 1
Physical and chemical characteristics of antipyrine.

Name	Molecular structure	Formula	Molecular weight	Solution (g/L), 20 °C	log Kow	Density (g/cm^3)	Melting point (°C)	Boiling point (°C)
Antipyrine		$C_{11}H_{12}N_2O$	188.23	1000	0.38	1.07	110–113	319

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