Combined oxidative degradation of ammonia and phenol by homogeneous UV/S$_2$O$_8^{2-}$ process

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Abstract. Utilization of UV in peroxydisulfate (S$_2$O$_8^{2-}$) activation exhibits a potential for removing contaminants in wastewater. In this study, the oxidative degradation of aqueous ammonia (NH$_3$/NH$_4^+$) or/and phenol by UV/S$_2$O$_8^{2-}$ process was investigated, including the kinetic model of ammonia removal, the effect of pH on degradation efficiency and TOC removal, and influence of S$_2$O$_8^{2-}$ concentrations on contaminants removal. The results revealed that the kinetic model of ammonia removal conforms to pseudo-first-order. Strong alkaline conditions and high dosage of S$_2$O$_8^{2-}$ were profited to ammonia degradation, and the removal percent was up to 95.98% (e.g. 50 mM S$_2$O$_8^{2-}$ at pH 12). The near-neutral environment was conducive to phenol removal, and its maximal removal percent was 96.28% in 30 min at pH 8. In the combined oxidation system of ammonia and phenol, the ammonia removal quickly reached 40.90% in 30 min and got its maximum of 55.20% after 8 h, while the phenol degradation had almost no obvious decline. This study enriches our understanding of the oxidation kinetic of ammonia under UV, and provides new insights for combined oxidation of ammonia and phenol.

1. Introduction

Phenolic wastewater is either toxic or lethal to human body, water body, fish and crops, and it has been listed on the water priority control pollutants blacklist by many countries including China and the USA [1]. Alternatively, eutrophication of water body as well as some diseases was promoted by ammonia (NH$_3$/NH$_4^+$) and its metabolites, particularly nitrite (NO$_2^-$) produced from the oxidation of ammonia.

Taking into account their hazards to human beings, oxidation technologies carried out to removing the two contaminants, such as biodegradation process [2], chemical precipitation, ion exchange [3], and active carbon adsorption [4]. However, these methods are either inefficient, uneconomical, or requiring further treatment.

Peroxydisulfate ion (S$_2$O$_8^{2-}$) has drawn increasing attention as an alternative oxidant in the chemical oxidation of contaminants at mild conditions [5]. Peroxydisulfate (S$_2$O$_8^{2-}$; $E^0$ = 2.01 V) can be facilely activated by means of thermal [6], photolytic [7], radiolytic activation [8], chelated or unchelated transition metals [9], hydrogen peroxide [10] etc. to generate sulfate radicals (SO$_4^{•-}$, $E^0$=2.6 V), which emerges more aggressive oxidation. Peroxydisulfate salts are frequently used for the transformation of environmental contaminants such as bisphenol [11], phenol [12], norfloxacin [13],...
benzotriazole [14], indomethacin [15], aniline [12] to innocuous products. Principal reactions [16] in investigated system was displayed as follows:

UV irradiation: \( \text{S}_2\text{O}_8^{2-} + h\nu \rightarrow 2\text{SO}_4^{\bullet} \) (1)

Aqueous solution: \( \text{SO}_4^{\bullet} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{HO}^{\bullet} + \text{H}^+ \) (2)

Acidic conditions: \( \text{S}_2\text{O}_8^{2-} + \text{H}^+ \rightarrow \text{HS}_2\text{O}_8 \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{\bullet} + \text{H}^+ \) (3)

Alkaline conditions: \( \text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} + \text{OH}^{\bullet} \rightarrow 2\text{SO}_4^{2-} + \text{H}^+ + 2\text{HO}^{\bullet} \) (4)

Organic oxidation: \( \text{SO}_4^{\bullet} + \text{O}_j \rightarrow \text{O}_j^{\text{OX}} \) (Oj=Organic Pollutant j) (5)

In this study, UV/S\(_2\text{O}_8^{2-}\) process was conducted for removing phenol and ammonia, and the objectives of this work are to investigate: (i) the oxidative removal capacity of phenol and ammonia under different pHs and initial reactant concentrations, and (ii) the kinetics of phenol and ammonia removal.

2. Parte experimental

2.1. Reagents

In this study, deionized water was used for preparing aqueous solutions and other chemicals of analytical grade were used without further purification.

2.2. Removal testing

The UV for photocatalytic experiments was provided with 300W high pressure mercury lamps, supplied by Xujiang Electromechanical Plant, Nanjing, China. The lamps emitted predominantly UV was at a wavelength of 365 nm and the light intensity was 2.50 mW cm\(^{-2}\) at the quartz tube spot. The temperature inside the reactor was maintained at 20\(\pm\)1 \(^\circ\)C by continuous circulation of cool water. During irradiation, the supernatant of target solutions was withdrawn regularly and used to detect the residual concentrations of nitrate, nitrite, and ammonium with colorimetric methods [17] by an UV–vis spectrophotometer (Mapada, UV-6300). In the presence of phenol, 0.5 mL suspension was withdrawn regularly and centrifuged during irradiation, and the supernatant was analyzed to determine the residual concentration of phenol with the colorimetric method at 510 nm [18]. Control experiments was conducted for each group.

2.3. Kinetic model expression

The kinetic model of ammonia oxidation conformed to the pseudo-first-order, due to concentrations of peroxydisulfate were elevated well above that of contaminants in the oxidation of pure ammonia in UV/S\(_2\text{O}_8^{2-}\) processes.

**Figure** 1. The natural logarithm of the ratio between initial and detected concentration of NH\(_3\)-N plotted as a function of UV irradiation time at different initial concentrations of S\(_2\text{O}_8^{2-}\) (a) 15 mM S\(_2\text{O}_8^{2-}\), (b) 50 mM S\(_2\text{O}_8^{2-}\).
3. Results and discussion

3.1. Kinetic model of NH₃-N oxidation

The ratio of initial and periodically detected concentrations of ammonia was plotted versus UV irradiation time as shown in Fig. 1. The plots of C₀/Cᵢ versus time were linear (0.9421< R²<0.9888) at various initial peroxydisulfate concentrations, suggesting a pseudo-first-order achieved. The reaction rate constants (k) were evaluated and shown in Table 1.

As it can be seen from Figure 1, the reaction rate constant (k) increased as the pH rise from 2 to 12 with 15 mM S₂O₈²⁻, while under 50 mM S₂O₈²⁻ condition, it went down and then went up. Under acidic environment (e.g. pH 2 to 7), the active species in the solution mainly existed in the form of SO₄⁻•, while in alkaline conditions, especially pH>10, the active species was HO• that mainly contributed to the degradation of contaminations in solution [19].

At low dosage of peroxydisulfate (15 mM), SO₄• was predominant due to sufficient UV irradiation (Eq. (1)), corresponding to the sulfate concentration in Figure 6(a) (e.g. a, c and e). Nevertheless, the subordinate reaction (Eq. (3)) decreasing oxidation efficiency of peroxydisulfate compared to Eq. (1) was continuously secondary as the pH value increased (e.g. below pH 7). Subsequently, the subordinate reaction (Eq. (4)) was gradually more critical as the pH value increased (e.g. above pH 7), from which hydroxide free radical was generated as supplementary and maintained the optimum and equivalent oxidation efficiency of peroxydisulfate. Accordingly, the rate constants order was arranged as $k₁<k₂<k₃<k₄$ in Table 1.

### Table 1. Reaction rate constants under different conditions

| Initial concentration of S₂O₈²⁻ (mM) | pH  | first-order rate constant, k (s⁻¹) | correlation coefficients, R² |
|-------------------------------------|-----|-----------------------------------|------------------------------|
| 15                                  | 2   | $k₁=3.23×10^{-3}$                 | 0.9882                       |
| 15                                  | 8   | $k₂=3.52×10^{-5}$                 | 0.9747                       |
| 15                                  | 10  | $k₃=3.70×10^{-5}$                 | 0.9932                       |
| 15                                  | 12  | $k₄=4.62×10^{-5}$                 | 0.9662                       |
| 50                                  | 2   | $k₅=8.23×10^{-5}$                 | 0.9421                       |
| 50                                  | 8   | $k₆=7.28×10^{-5}$                 | 0.9799                       |
| 50                                  | 10  | $k₇=6.49×10^{-5}$                 | 0.9577                       |
| 50                                  | 12  | $k₈=10.84×10^{-5}$                | 0.9888                       |

When pouring superabundant S₂O₈²⁻ (50 mM) into solutions resulted in insufficient UV irradiation, the reaction (Eq. (3)) dominated decreasingly as the pH increased (e.g. below pH 7). Furthermore, a significant role was played for Eq. (2) during the pH at a range of 7 to 10, and the decrease of rate constant k was observed with increasing ionic strength of the medium due to negative ion effect 40. Simultaneously, Eq. (4) had strongly dependence on hydroxyl ion concentration, with unremarkable effect at low ion concentration (e.g. pH 8 and 10) but significance at higher, (e.g. pH 12). Consequently, the rate constants order was arranged as $k₅<k₇<k₈<k₉<k₁$.

3.2. Effect of pH on NH₃-N removal

The effect of different pHs on NH₃-N removal in the UV/S₂O₈²⁻ process was investigated as shown in Figure 2 and Figure 3. It was revealed that NH₃-N removal percent was 69.71% at low S₂O₈²⁻ dosage (e.g. S₂O₈²⁻ 15mM, pH12), compared to 95.98% that of high dosage (e.g. S₂O₈²⁻ 50mM, pH12). This demonstrated that high concentration of S₂O₈²⁻ was profitable to NH₃-N removal and NH₃-N was almost completely oxidized to NO₃-N due to more reactive species (e.g. SO₄⁻•, HO•) generated in concentrated solution. Alternatively, total-N remained in concentrated solution while decreased in dilute solution. It can be speculated that a certain nitrogenous material (N₂ approximately) was divorced from solution abounding with activated species under abundant UV irradiation and relatively deficient S₂O₈²⁻ conditions.
3.3. Phenol removal in blend solutions

Photocatalytic degradation of phenol was surveyed in the absence and presence of ammonia as shown in Figure 4. Concentrations of phenol in solutions were both decreased to below 20 mg L\(^{-1}\),
regardless of the absence and presence of ammonia, and its removal rate was up to 96.28% in 30 mins. Moreover, as can be seen that the pH close to neutral was profitable for the removal of phenol (Figure 4 b) compared to that of acidic (Figure 4) and alkaline (Figure 4 c) conditions, which conformed to the maximal concentration of sulfate ions in Figure 6 b. The presence of ammonia showed a promoting tendency to the removal of phenol under strong acidic (e.g. pH 2) and alkaline (e.g. pH 12) environment in UV/S₂O₈²⁻ processes, especially the latter, but exhibited a retarding effect under the pH close to neutral (e.g. pH 8).

Figure 4. Photocatalytic degradation of phenol with 50 mM K₂S₂O₈ in the absence and presence of NH₃-N under UV irradiation at different pHs. (a) pH 2, (b) pH 8 and (c) pH 12.

3.4. NH₃-N removal in blend solutions
Ammonia removal efficiency were also investigated in blend solutions of phenol and ammonia (Figure 5). In the present of phenol, the removal percent quickly reached 40.90% in 30 minutes and got its maximum 55.20% after 8 hours. It was indicated that ammonia removal was accelerated in the first 30 minutes with the assistance of phenol, compared with the results shown in Figure 3. It probably attributed to phenol or undetermined intermediates which promoted the activation of peroxydisulfate in the initial phase. The concentrations of nitrate and ammonia were almost at the same level after 8 hours, while the total nitrogen content decreased slightly compared to the beginning and it was presumably nitrogen escaping from the solution.

Figure 5. Concentrations of NO₃⁻, NO₂⁻ and NH₄⁺ plotted as a function of UV irradiation time at different pHs in the presence of 50 mM K₂S₂O₈ and 100 ppm phenol. (a) pH 2, (b) pH 8 and (c) pH 12.

3.5. Production of sulfate ions and TOC analysis
Concentrations of sulfate ions and TOC were investigated after the photocatalytic reaction in the UV/S₂O₈²⁻ systems. Results showed that the generated sulfate ions in the presence of 50 mM S₂O₈²⁻ first decreased (e.g. pH from 2 to 8) and then increased (e.g. pH from 8 to 12) with the increase of pH in the pure ammonia system (Figure 6 A). However, it exhibited a reversed trend in the pure phenol system (Figure 6 b). As for blend system of two contaminants, the generated sulfate ions declined with
the increase of pH from 2 to 12 (Figure 6 c). It was relied on that in most cases SO₄• prevails in acidic media and HO• generated from the reactions of SO₄• with HO predominates in alkaline media [20]. SO₄• with highly selectivity than HO• are prone to react by electron transfer reactions, especially compounds with aromatic rings. Removal percentage of TOC (Figure 7) revealed that it was that probably residual intermediate possessed the ability of forming complexes with perdisulfate and the formation was controlled by pH values. The mechanism and pathway of the reactions need to be further investigated in subsequent experiments.

Figure 6. Concentration of SO₄²⁻ after the photocatalytic reaction in the presence of K₂S₂O₈ in the system of (a) pure NH₃-N, (b) pure phenol and (c) NH₃-N and phenol.

Figure 7. Removal percent of TOC in the system of (a) pure phenol at pH 2, (b) NH₃-N and phenol at pH 2, (c) pure phenol at pH 8, (d) NH₃-N and phenol at pH 8, (e) pure phenol at pH 12 and (f) NH₃-N and phenol at pH 12.

4. Conclusion
UV/S₂O₈²⁻, one of significant Advanced Oxidation Process (AOPs), was applied into removal of ammonia and phenol within coking wastewater. The oxidation of ammonia in this UV/S₂O₈²⁻ process formulated a pseudo-first-order kinetic model well, but that of phenol needed to further investigate. The optimum pH of ammonia oxidation was 12 in the presence of 50 mM S₂O₈²⁻ and UV. In the combined oxidation system of ammonia and phenol, the ammonia removal was accelerated initially but retarded after 30 min (with maximum efficiency of 55.20%), while the phenol degradation had almost no obvious decline. This study enriches our understanding of the oxidation kinetic of ammonia under UV, and provides new insights for combined oxidation of ammonia and phenol.

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