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Degradation kinetics and mechanism of aniline by heat-assisted persulfate oxidation

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Abstract

Oxidation of aniline by persulfate in aqueous solutions was investigated and the reaction kinetic rates under different temperature, persulfate concentration and pH conditions were examined in batch experiments. The results showed that, the aniline degradation followed pseudo first-order reaction model. Aniline degradation rate increased with increasing temperature or persulfate concentration. In the pH range of 3 to 11, a low aniline degradation rate was obtained at strong acid system (pH 3), while a high degradation rate was achieved at strong alkalinity (pH 11). Maximum aniline degradation occurred at pH 7 when the solution was in a weak level of acid and alkalinity (pH 5, 7 and 9). Produced intermediates during the oxidation process were identified using liquid chromatography-mass spectrometry technology. And nitrobenzene, 4,4′-diaminodiphenyl and 1-hydroxy-1,2-diphenylhydrazine have been identified as the major intermediates of aniline oxidation by persulfate and the degradation mechanism of aniline was also tentatively proposed.

Key words: persulfate; oxidation; kinetic; mechanism; aniline

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Introduction

Aniline is an important industrial chemical used primarily during the synthesis of pesticides, dyes, plastics, rubber, and drugs. When released to the environment, aniline is hazardous to aquatic lives as it may damage central nervous system, cardiovascular system, liver and kidney of animals (Ye et al., 2009). It has been included in the “blacklist of environmental priority pollutants” (Zhang et al., 2007).

Several technologies such as in situ chemical oxidation (Zhang et al., 2010), photocatalysis (Gu et al., 2003; Kumar and Mathur, 2006; Wang et al., 2007), composite adsorbent (An et al., 2010), electro-catalytic oxidation (Fu et al., 2008; Li et al., 2003), reverse osmosis (Gómez et al., 2009), catalytic wet air oxidation (Gomesa et al., 2008), ferrate (Huang et al., 2001), Fenton and electro-Fenton processes (Anotai et al., 2006), aerobic co-metabolism (Li and Xie, 2007) and ultrasonic degradation (Song et al., 2007) were used to treat aniline-containing wastewaters. Among of chemical oxidation methods, potassium permanganate (KMnO₄) (Waldemer and Tratnyek, 2006), hydrogen peroxide (H₂O₂) (Watts and Teel, 2005) and ozone (O₃) (Rivas, 2006) are typical oxidants, each having its own advantages and limitations. H₂O₂ and O₃ have the limitations of being short life spans (Watts and Teel, 2006; Huling and Pivetz, 2006) and low water solubility in the case of O₃ (Watts and Teel, 2006). Sodium persulfate (Na₂S₂O₈) is recently used as an alternative oxidant for in situ chemical oxidation (ISCO) of recalcitrant organic contaminants in soil and groundwater (Anipsitakis and Dionysiou, 2004; Liang et al., 2004, 2007). As shown below, the standard oxidation-reduction potential (E⁰) for the half-reaction is higher than other oxidants (Huang et al., 2002).

\[
\begin{align*}
\text{S}_2\text{O}_8^{2-} + 2e^- & \rightarrow \text{SO}_4^{2-} & E^0 = 2.01 \text{ V} & (1) \\
\text{O}_3 + 2\text{H}^+ + 2e^- & = \text{O}_2(g) + \text{H}_2\text{O} & E^0 = 2.07 \text{ V} & (2) \\
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- & = 2\text{H}_2\text{O} & E^0 = 1.78 \text{ V} & (3) \\
\text{MnO}_4^- + 4\text{H}^+ + 2e^- & = \text{MnO}_2(s) + 2\text{H}_2\text{O} & E^0 = 7.70 \text{ V} & (4)
\end{align*}
\]

Another important feature is that persulfate is more stable in the presence of impurities such as carbonates in the aqueous phase, compared to the widely used H₂O₂ (Liang and Su, 2009). It can maintain reactive over longer time period when it is used to oxidize target contaminants in groundwater systems.

When persulfate activated by heat or a transition metal (e.g., ferrous ion), it can be converted into an even stronger oxidant, i.e., a sulfate free radical with a redox potential.
of 2.4 V (Huie et al., 1991). Previous studies showed that formation of SO$_4^{2-}$ can be induced via thermal (House, 1962), metal (Kolthoff and Miller, 1951), and photochemical activation (Netal et al., 1977) as shown below:

$$\text{S}_2\text{O}_8^{2-} + \text{heat} \rightarrow \text{SO}_4^{2-} \quad (5)$$

$$\text{S}_2\text{O}_8^{2-} + \text{Fe}^{2+} \rightarrow \text{SO}_4^{2-} + \text{Fe}^{3+} + \text{SO}_4^{2-} \quad (6)$$

$$\text{S}_2\text{O}_8^{2-} + e \rightarrow \text{SO}_4^{2-} + \text{SO}_2 \quad (7)$$

Prior experimental studies showed that persulfate oxidation reactions are usually less aggressive due to slow rates of SO$_4^{2-}$ generation at relatively low temperatures in groundwater systems. Meanwhile, SO$_4^{2-}$ can produce hydroxyl radical (-OH (E$_0$ = 2.7 V) (Huang et al., 2002) in aqueous solution following the reactions below (Hayon et al., 1972; Norman et al., 1970; Pennington and Haim, 1968).

$$\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{-OH} + \text{H}^+ \quad \text{All pH} \quad (8)$$

$$\text{SO}_4^{2-} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{-OH} \quad \text{Alkaline pH} \quad (9)$$

The distribution of the two free radicals is solution pH dependent. At solution pH < 7, SO$_4^{2-}$ is the dominant free radical whereas -OH dominates at solution pH > 9 and both free radicals are important at pH 7–9 (Liang and Su, 2009).

Thus, the purpose of this work was to develop a persulfate-based in situ oxidation technology for treating aniline polluted water by measuring both the kinetics and mechanism of the chemical oxidation of aniline by persulfate under different aqueous pH, temperature and oxidant concentration conditions. Intermediates of the oxidation process were also identified based on liquid chromatography-mass spectrometry (LC-MS) techniques.

1 Materials and methods

1.1 Chemicals

All chemicals used in the experiment were of analytical or reagent grades. Disodium hydrogen phosphate dodecahydrate, sodium phosphate monobasic dehydrate, concentrated sulfuric acid, sodium hydroxide, sodium persulfate, sodium thiosulfate pentahydrate, hexane and aniline were purchased from Tianjin Kermel Chemical Reagent Co. Ltd. (China). Acetonitrile was obtained from Sigma-Aldrich Chemical Company (USA).

1.2 Analysis

Concentrations of aniline in all aqueous solutions were analyzed with a Shimadzu LC-20A high performance liquid chromatography (Japan) equipped with Ultraviolet (UV) detector (SPD-M20A, Shimadzu, Japan) set at 236 nm. The column used was a reversed-phase C18 column (5 mm × 250 mm). Mobile phase was a mixture of acetonitrile-water (55:45, V:V) and the flowrate was set at 0.50 mL/min. The peak identification was based on the retention time and the UV spectrum of external standards.

The intermediates were identified on an Agilent 1200 series LC (USA) equipped with Agilent 6460 triple quad mass spectrometer with a reversed-phase C18 column (5 mm × 250 mm). The mobile phase was also the mixture of acetonitrile-water (55:45, V:V) and the flow rate was set at 0.50 mL/min. The mass spectrometer was operated under electrospray positive ionization at a fragmentor voltage of 100 V with mass scan range of 50–3000 amu. The ionization source conditions were set at the drying gas flow of 3 mL/min at 325°C, sheath gas flow of 12 mL/min at 350°C and the nebulizer pressure at 40 psig.

1.3 Experiment

The reaction of persulfate oxidation of aniline was carried out in a series of 250 mL Erlenmeyer flasks operated as completely-mixed batch reactor systems. The standard stock solution of aniline was prepared by dissolving 0.09 g pure aniline with ultrapure water in a 100 mL volumetric flask. Buffer solution was prepared by mixing 15 mmol/L Na$_2$HPO$_4$ and 10 mmol/L NaH$_2$PO$_4$ in Milli-Q water and was purged with N$_2$ for 20 min to eliminate oxygen. The aniline stock solution (0.50 mL) was then added into the Erlenmeyer flasks and mixed with the phosphate-buffer. The reactor was placed in a lab shaker at 125 t/min and the temperature of the shaker was set at a desired temperature. After 10 min, an aliquot (0.5 mL) of the solution was collected from the reactor to determine the initial concentration of aniline. After sampling, sodium persulfate solution (5 mL and 50 mmol/L) in excess was added to the reactor. At the predesigned time intervals, an aliquot (0.5 mL) of the solution was sampled and mixed with 0.5 mL of Na$_2$S$_2$O$_3$ solution (2 mol/L) in a 2 mL vial to quench the reaction. The solution pH was measured at both the beginning and end of the experiment. To examine the effects of solution pH, temperature and the Na$_2$S$_2$O$_3$ concentration on the reaction rates, similar experimental procedure was followed for operating the batch reactor systems at different initial conditions. In all experiments, duplicate reactor systems were run simultaneously.

2 Results and discussion

2.1 Effect of temperature on the degradation of aniline

Figure 1 presents the degradation of aniline under different temperatures at pH 7. It indicates that the reaction rate data fits well to the pseudo first-order reaction model (i.e., lnC$_i$ versus t), represented by relatively high values of the goodness of fit ($R^2 > 0.96$). The higher is the temperature, the faster is the aniline degradation. As shown in the Fig. 1, the best fit lines of lnC$_i$ versus t have slopes increasing as a function of temperature indicating that the rate constant ($k$) of aniline degradation increased as a function of temperature. The activation energy ($E_a$) obtained by fitting the temperature dependent rate constants into an Arrhenius equation is 49.97 kJ/mol during the range of 10–50°C. Such as a large temperature dependence provides that changing the system temperature is one of the ways to control the generation of sulfate free radicals.
2.2 Effect of persulfate concentration on the degradation of aniline

Figure 2 presents the time dependent aniline concentration profiles for the reaction systems initiated at four different starting concentrations \( C_0 \) of persulfate and solution pH 7. The rates of aniline degradation were faster at higher concentrations of initial \( \text{Na}_2\text{S}_2\text{O}_8 \). A plot of \( \ln k \) against \( \ln C_0 \) of persulfate yielded a straight line with a slope of 0.98, indicating that the rate of aniline degradation was directly proportional to initial \( \text{Na}_2\text{S}_2\text{O}_8 \) concentration. Our results were in agreement with a previous finding (Huang et al., 2002) rather than another early study (Li et al., 2009) that the degradation rate did not increase further when the initial persulfate concentration was higher 46.88 mmol/L.

2.3 Effect of pH on the degradation of aniline

Figure 3 shows time-dependent aniline concentration profiles measured at room temperature under different solution pH conditions. The aniline degradation was also fit to the pseudo first-order reaction model. It clearly shows that acidic conditions slowed the rate of aniline degradation. The rate constants of aniline degradation in different pH solutions in the following sequence: pH 11 > pH 7 > pH 9 > pH 5 > pH 3. Within the observed pH range of 3–11, strong acid system (pH 3) resulted in a low aniline degradation rate and strong alkalinity (pH 11) lead a high degradation rate. However maximum aniline degradation occurred at pH 7 when the solution was in a weak level of acid and alkalinity (pH 5, 7 and 9).

A possible explanation is that the predominant radical formed in acidic solution was \( \text{SO}_4^{2-} \) rather than \( \cdot \text{OH} \), however the latter has a higher redox potential. Liang and Su (2009) used nitrobenzene (NB) as a chemical probe to identify the active radical species. They found that \( \text{SO}_4^{2-} \) is the predominant radical at pH < 7 whereas both \( \text{SO}_4^{2-} \) and \( \cdot \text{OH} \) are presented at pH 9 and \( \cdot \text{OH} \) is the predominant radical at higher solution pH. It should be noted that both \( \text{SO}_4^{2-} \) and \( \cdot \text{OH} \) can react rapidly with other chemicals in the background solution. As reported by Huang et al. (2002) and Li et al. (2009), the oxidation rates of methyl tert-butyl ether systems (Huang et al., 2002) and persulfate-diphenylamine (Li et al., 2009) decreased as a function of solution pH. They explained that the results were due to the rapid decay of sulfate radicals and hydroxyl radicals as they react with hydroxyl ions. Meanwhile, carbon dioxide formed from organic pollutants degradation could speed up the formation of bicarbonate and carbonate in alkaline solutions, resulting inhibition of the oxidation reaction. Liang et al. (2009) showed that the maximum rate of trichloroethylene (TCE) degradation by persulfate occurred at pH 7, and they believed that more \( \cdot \text{OH} \) free radicals were generated at neutral pH condition and that the \( \cdot \text{OH} \) free radicals were scavenged at faster rate by \( \text{SO}_4^{2-} \) in basic solutions. Thus, it appears that the presence of various free radical scavengers in solution results in reduction in reactivity of both \( \text{SO}_4^{2-} \) and \( \cdot \text{OH} \).

2.4 Mechanism of aniline degradation

To explore the mechanism of aniline degradation, the intermediates formed during the degradation by persulfate were identified by using high performance liquid chromatography-mass spectrometry (HPLC-MS) based on previous literature (Gai, 2003) and mass fragmentation pattern. The samples collected at the different times (0, 2, 4 and 6 hr) of reaction solutions were dissolved by ultrapure water after extracted with hexane to HPLC and HPLC-MS analysis. Figure 4 demonstrates typical chromatograms of...
the intermediates for the aniline solutions collected after 0, 2, 4 and 6 hr. All of the peaks which had a response on mass spectrometry were marked.

The predominant species b, c and d were characterized by \( m/z \) values of 200, 124, and 184 and the chromatographic response intensity is shown in Fig. 5. The chemical structures for the predominant degradation products were also proposed on the basis of the results of the HPLC-MS fragmentation analysis and the chromatographic retention time. HPLC and HPLC-MS analysis evidenced three main products. Along the degradation time, the chromatographic peak areas of species with \( m/z \) 124 characterized by nitrobenzene progressively increased to a maximum and then decreased. On the contrary, the peak areas of the species characterized by \( m/z \) 200 and 184 were increased along the degradation time. The chromatographic peak appeared at 3 min of retention time was not detected in mass spectrum. Some intermediates (such as phenol, azobenzene and benzoquinone) which were identified as major products of aniline mineralization in some previous literature (Brillas et al., 1998; Jin et al., 2006; Sauleda and Brillas, 2001; Canle et al., 2005; Oliviero et al., 2003) failed detection under the experimental conditions in this study. The specific reasons need to be further investigated.

From the above discussion, two main destruction pathways might be proposed for the degradation of aniline by persulfate at pH 7.00 (Fig. 6). First, formation of the nitrobenzene has been reported during previous study (Liang et al., 2009, Brillas et al., 1998; Sauleda and Brillas, 2001; Canle et al., 2005) under different process. Hydroxyl radicals attacked the aromatic ring, aniline followed eliminated HO- and accomplished deprotonation to form the aniliny radical, the aniliny radical is further oxidized to nitrobenzene. And nitrobenzene may be further oxidized to more stable small molecules such as oxalic acid. Another important intermediates observed in this study was 4-4’-diaminodiphenyl. The reaction between sulfate radicals and aromatic compounds was considered complete by electron transfer (Chen et al., 2009). The presence of 4-4’-diaminodiphenyl indicated the bimolecular reaction between the anilinium/aniliny radicals (Canle et al., 2005). The second pathway implied that the degradation of aniline in persulfate system was most likely due to its reaction with sulfate and hydroxyl radicals. As hydroxyl and sulfate radicals are thought to be the primary oxidizing species produced by decomposition of persulfate (Huang et al., 2002; Li et al., 2009). The byproduct characterized by \( m/z \) 200 was proposed 1-hydroxy-1,2-diphenylhydrazine. It may fit the condensation of nitrobenzene and aniline, and this result also evidenced by that the change of concentration of nitrobenzene and aniline, and this result also evidenced by the change of concentration of nitrobenzene and the byproducts.

![Fig. 4 HPLC typical chromatograms of intermediates (a–e) for the aniline solutions collected after 0, 2, 4 and 6 hours of persulfate oxidation in reactor.](image)

![Fig. 5 Proposed intermediates and mass spectra of the degradation products.](image)
3 Conclusions

This study investigated the degradation kinetics and mechanism of aniline by heat-assisted persulfate oxidation. The affecting factors including temperature, oxidant concentration, and pH were examined in designed batch experiments. The aniline degradation was found to follow a pseudo first-order reaction model. The results indicated that the reaction was significantly influenced by temperature, oxidant concentration and pH. Increasing the reaction temperature or oxidant concentration can significantly accelerate the aniline degradation in persulfate/aniline system. In the pH range of 3 to 11, a low aniline degradation rate was obtained at strong acid system (pH 3), while a high degradation rate was achieved at strong alkalinity (pH 11). Maximum aniline degradation occurred at pH 7 when the solution was in a weak level of acid and alkalinity (pH 5, 7 and 9). Through the analysis of mass spectrum and the studies of previous literature of aniline degradation, three intermediates were detected in our work, characterized by m/z 124, 200 and 184, and identified as nitrobenzene, 1-hydroxy-1,2-diphenylhydrazine and 4-4'-diaminodiphenyl, respectively.

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