



## Degradation of diphenylamine by persulfate: Performance optimization, kinetics and mechanism

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### ABSTRACT

The degradation of diphenylamine (DPA) in aqueous solution by persulfate is investigated. Effects of pH, persulfate concentration, ionic strength, temperature and catalytic ions Fe<sup>3+</sup> and Ag<sup>+</sup> on the degradation efficiency of DPA by persulfate are examined in batch experiments. The degradation of DPA by persulfate is found to follow the pseudo-first-order kinetic model. Increasing the reaction temperature or persulfate concentration may significantly accelerate the DPA degradation. Fe<sup>3+</sup> and Ag<sup>+</sup> ions can enhance the degradation of DPA, and Ag<sup>+</sup> ion is more efficient than Fe<sup>3+</sup> ion. However, the increase of either the pH value or ionic strength will decrease the rate of DPA degradation. *N*-Phenyl-4-quinoneimine, *N*-carboxyl-4-quinoneimine, 4-quinoneimine and oxalic acid are identified as the major intermediates of DPA degradation, and a primary pathway for the degradation of DPA is proposed. The degradation of DPA in surface water, groundwater and seawater is also tested by persulfate, and more than 90% of DPA can be degraded at room temperature in 45 min at an initial concentration of 20 mg L<sup>-1</sup>.

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### 1. Introduction

Diphenylamine (DPA) is widely used as the stabilizer for nitrocellulose-containing explosives and propellants, the antioxidant for various polymers and elastomers and as condensates for the insulation of rubber [1,2]. DPA is also used to prevent post-harvest deterioration of apple and pear [3,4]. In addition, DPA is a parent compound of many derivatives, which are used for the production of dyes, pharmaceuticals and photography chemicals [2]. However, DPA might lead to dermatitis (formation of vesicular and exudative eczemas) in workers exposed to DPA-containing products. Eczema formation, hypertension, tachycardia and bladder diseases were observed in humans after administration with alcoholic solution of DPA [2,5,6]. Moreover, DPA also showed damaging effects on liver, spleen and kidney in experimental animals such as dogs, rats and mice [7–9], and was hazardous to some organisms in aquatic environment [10]. In the European Union, DPA has been listed as a prior pollutant [2]. Therefore, an efficient method for the degradation of DPA is of importance.

It was reported that DPA can be biologically degraded in the laboratory under defined culture conditions [11,12]. However, the bactericidal substances (such as heavy metals) that may be found in many wastes would limit the actual effectiveness of the biodegradation process [13]. Thus, there is a strong need to look for physical and chemical methods as alternative and faster treatment processes for the degradation of DPA.

Although Fenton's reagent (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>) has been widely used for the degradation of organic pollutants [14,15], it was ineffective to DPA [16]. Potassium permanganate was also used for the degradation of organic pollutants, and was effective to DPA [16]. However, the reductive product Mn<sup>2+</sup> of permanganate might bring out the second pollution, if it was not removed by MnO<sub>2</sub> precipitate [17]. In addition, the application of potassium permanganate to treat contaminated groundwater has been limited by the concerns that residual permanganate and MnO<sub>2</sub> precipitates might alter the permeability of the aquifer and increase the dissolution of potentially toxic metals [18]. On the other hand, persulfate, as an alternative for the degradation of organic pollutants, has received considerable attention in recent years [19–23].

In this study, degradability of DPA by persulfate was studied. Effects of pH, oxidant concentration, ionic strength, temperature and catalytic ions Fe<sup>3+</sup> and Ag<sup>+</sup> on the degradation efficiency of DPA by persulfate were examined in batch experiments. The major

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intermediates of DPA degradation were identified, and a primary reaction mechanism was proposed. The degradation of DPA in surface water, groundwater and seawater was also tested by persulfate. The findings of this study could be helpful for the treatment of water, and for in situ remediation of soil and groundwater contaminated with DPA.

## 2. Materials and methods

### 2.1. Materials

Analytical-reagent grade or better chemicals as well as Milli-Q water were used in the experiments. DPA and potassium persulfate were purchased from Sigma (St. Louis, MO, USA). Acetonitrile and methanol were obtained from BDH (Poole, UK). All other reagents were purchased from Aldrich (Milwaukee, WI, USA). The buffer solution used to control pH value was prepared by mixing  $1.85 \text{ g L}^{-1}$  of  $\text{Na}_2\text{HPO}_4$  and  $1.52 \text{ g L}^{-1}$  of  $\text{NaH}_2\text{PO}_4$  in deionized water. The pH values of all solutions were adjusted with 1 M of NaOH or  $\text{H}_2\text{SO}_4$  whenever required. Potassium chloride was used as ionic strength adjuster in the phosphate-buffered solutions. The DPA stock solution was prepared by dissolving 40.0 mg of DPA in 1 L of water and then stored in a refrigerator.

### 2.2. Degradation experiments

The reaction was carried out in graduated and plugged test tubes (internal volume 50 mL). Reaction mixtures were obtained by taking an appropriate amount of DPA stock solution, and the buffer solution. The reaction was initiated by adding persulfate solution. The final volume of the reaction mixture was 50 mL. The reaction was terminated immediately by adding 1 M of  $\text{Na}_2\text{SO}_3$  solution to the reaction mixtures. The reactions were performed at room temperature ( $23 \pm 1^\circ\text{C}$ ).

At regular time intervals, the sample aliquots were taken from the tubes and then filtered through  $0.2\text{-}\mu\text{m}$  membrane. To measure the residual DPA concentration after a certain reaction period,  $20\ \mu\text{L}$  of filtrate was injected into the column of high-performance liquid chromatography.

Each experiment was conducted in triplicate. The data presented in the text and figures were the mean values of the results from the experiments.

### 2.3. Analytical methods

The HPLC system used throughout this study consisted of two Waters 510 pumps (Waters, Milford, MA, USA), a sample injector (Rheodyne, Cotati, CA, USA) with a  $20\text{-}\mu\text{L}$  loop and a Waters 996 photodiode array detector. Evaluation and quantification were made on a Millennium chromatography data system (Waters). The column used was a reversed-phase Spherisorb  $\text{C}_{18}$  column ( $250 \text{ mm} \times 4.6 \text{ mm i.d.}$ ,  $5\ \mu\text{m}$ , Waters). The mobile phase was acetonitrile–water (70:30, v/v) with a flow-rate at  $1.00 \text{ mL min}^{-1}$ , and the effluent was monitored at 280 nm. The peak identification was based on the retention time and the UV spectrum (obtained from photodiode array detector) against the standard. Routine sample calculation was made by comparison of the peak area with that of the standard.

## 3. Results and discussion

### 3.1. Kinetics of DPA degradation

Reaction kinetics could be simplified in many cases by using one-reactant concentration in large excess (20–500-fold) and by

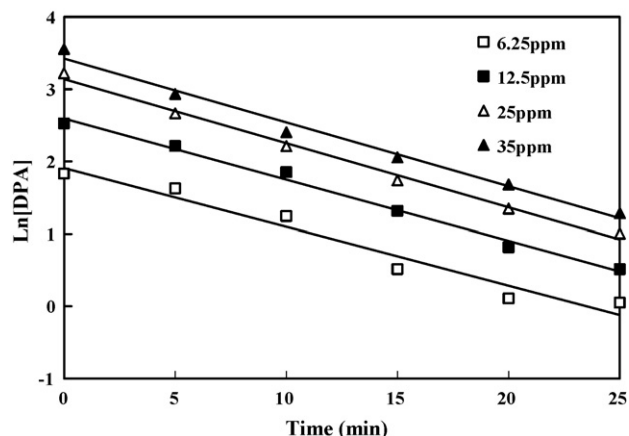


Fig. 1. Kinetics of DPA degradation.  $[\text{Persulfate}]_0 = 3 \text{ mg mL}^{-1}$ , pH 7.

maintaining constant pH value with the buffer solution. Under these conditions, the reaction kinetics was fixed with respect to the concentrations of  $\text{H}^+$  and the excess reactant, thus isolating the rate dependence of the limiting reactant. Pseudo-first-order rate constants for the variable reactant ( $k_{\text{obs}}$ ) could be obtained from the slope of linear regression of  $\ln[\text{concentration}]$  as a function of time. In this study, the concentration of persulfate would remain nearly constant during the initial stage of the reaction because DPA concentrations used ( $6.25\text{--}50 \mu\text{g mL}^{-1}$ ) were much lower than that of persulfate ( $3 \text{ mg mL}^{-1}$ ). As shown in Fig. 1, the plots of  $\ln[\text{DPA}]$  versus time were linear ( $0.987 < R^2 < 0.994$ ) at various initial DPA concentrations, suggesting a first-order reaction with respect to DPA. The observed rate constant ( $k_{\text{obs}}$ ) obtained in this experiment was  $1.428(\pm 0.061) \times 10^{-3} \text{ s}^{-1}$ , which was approximately 228 times of that ( $6.25 \times 10^{-6} \text{ s}^{-1}$ ) obtained from the microbial degradation of DPA [11]. Therefore, the chemical degradation of DPA by persulfate was much faster than the microbial degradation.

### 3.2. Effect of pH on the degradation of DPA

The pH value of the solution was usually an important parameter affecting oxidative degradation of organic pollutants. Therefore, the role of initial pH on the degradation of DPA by persulfate was investigated. As shown in Fig. 2, increasing the pH value would result in more DPA remaining in aqueous solutions. That is, the degradation rate of DPA decreased with the increase of pH value. The linear plots of  $\ln[\text{DPA}]$  versus time indicated that

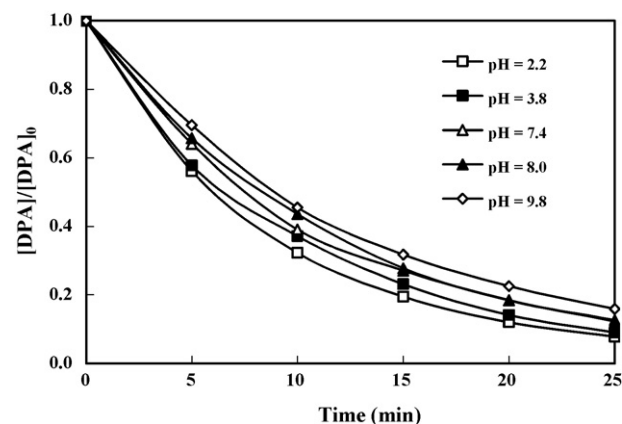


Fig. 2. Effect of pH on the degradation of DPA.  $[\text{DPA}]_0 = 20 \mu\text{g mL}^{-1}$  and  $[\text{persulfate}]_0 = 3 \text{ mg mL}^{-1}$ .

the reaction was pseudo-first-order with respect to DPA in all pH solutions with the correlation coefficients ( $R^2$ ) of 0.999, 0.995, 0.999, 0.998 and 0.997 at pH 2.2, 3.8, 7.4, 8.0 and 9.8, respectively. The slopes of these linear plots, i.e., the observed rate constants ( $k_{\text{obs}}$ ) were  $1.70 \times 10^{-3}$ ,  $1.63 \times 10^{-3}$ ,  $1.42 \times 10^{-3}$ ,  $1.35 \times 10^{-3}$  and  $1.21 \times 10^{-3} \text{ s}^{-1}$ , which revealed that  $k_{\text{obs}}$  decreased as pH increased. The results obtained in this study were also in agreement with the previous finding that the rate of methyl *tert*-butyl ether (MTBE) degradation by persulfate decreased with the increase in the pH value [19]. This might be due to the rapid decay of sulfate radicals resulting from the reactions with hydroxyl ions [24]. In addition, carbon dioxide formed from DPA degradation could lead to the formation of bicarbonate and carbonate ions under alkaline solutions, which might inhibit DPA oxidation [25].

As shown in Fig. 2, the degradation of DPA by persulfate could even be performed in alkaline solutions at pH of 9.8 although the reaction rate was lower than that in acidic condition. This result was much more practical in field application. Generally speaking, the pH values of soil and groundwater are between 5 and 9. Furthermore, most oxidants reported in the literature for the degradation of organic pollutants were either less effective or not effective under alkaline conditions [15,17]. Therefore, persulfate could be used in remediation of soil and groundwater contaminated with DPA in a wider range of pH values.

### 3.3. Effect of persulfate concentration on the degradation of DPA

Effect of persulfate concentrations ( $1.2\text{--}9.0 \text{ mg mL}^{-1}$ ) on the degradation of DPA ( $20 \mu\text{g mL}^{-1}$ ) was studied at pH 2.2. Linear plots of  $\ln([\text{DPA}]/[\text{DPA}]_0)$  versus time were obtained at the initial persulfate concentrations of 1.2, 2.4, 3.6, 4.8 and  $9.0 \text{ mg mL}^{-1}$ , with the correlation coefficients ( $R^2$ ) of 0.995, 0.997, 0.998, 0.999 and 0.999, respectively (Fig. 3). The  $k_{\text{obs}}$  values were obtained from the slopes of the lines, and were  $6.35 \times 10^{-4}$ ,  $1.25 \times 10^{-3}$ ,  $1.72 \times 10^{-3}$ ,  $2.36 \times 10^{-3}$  and  $4.20 \times 10^{-3} \text{ s}^{-1}$  at the initial persulfate concentrations of 1.2, 2.4, 3.6, 4.8 and  $9.0 \text{ mg mL}^{-1}$ , respectively. The results showed that the rate of DPA degradation increased as the initial persulfate concentration increased. It should be pointed out that the degradation rate did not increase further when the initial persulfate concentration was higher than  $9.0 \text{ mg mL}^{-1}$ . For example, the  $k_{\text{obs}}$  value was  $4.22 \times 10^{-3} \text{ s}^{-1}$  at an initial persulfate concentration of  $12.0 \text{ mg mL}^{-1}$ , which was almost the same as that at  $9.0 \text{ mg mL}^{-1}$  of persulfate. When the natural logarithm of the pseudo-first-order rate constant ( $\ln k_{\text{obs}}$ ) was plotted versus the natural logarithm of the initial persulfate concentration, the slope of the linear regression was 0.934 ( $R^2 = 0.999$ ). Thus, the reaction

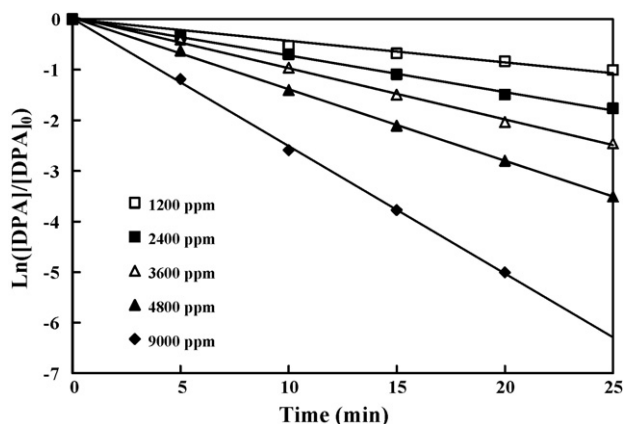


Fig. 3. Effect of concentration of persulfate on the degradation of DPA.  $[\text{DPA}]_0 = 20 \mu\text{g mL}^{-1}$ , pH 2.2.

was approximately first order to persulfate. This indicated that an oxidizing species (mostly likely  $\text{SO}_4^{\bullet-}$  under the experimental conditions) might dominate the reaction with DPA although numerous oxidizing species (e.g.,  $\text{SO}_4^{\bullet-}$ ,  $\text{HO}^{\bullet}$  and  $\text{S}_2\text{O}_8^{2-}$ ) could exist in the system and react with DPA [19].

### 3.4. Effect of ionic strength on the degradation of DPA

Effect of ionic strength on the degradation of DPA by persulfate was studied with the concentrations of KCl ranging from 0.016 to 0.64 M. The linear plots of  $\ln([\text{DPA}]/[\text{DPA}]_0)$  versus time indicated that the reaction was pseudo-first-order with respect to DPA in different ionic strength solutions, with the correlation coefficients ( $R^2$ ) of 0.998, 0.992, 0.995 and 0.996 at different KCl concentrations of 0.016, 0.064, 0.24 and 0.64 M, respectively. The  $k_{\text{obs}}$  values were  $1.41 \times 10^{-3}$ ,  $1.18 \times 10^{-3}$ ,  $1.03 \times 10^{-3}$  and  $7.55 \times 10^{-4} \text{ s}^{-1}$  at different KCl concentrations of 0.016, 0.064, 0.24 and 0.64 M, respectively. The results showed that  $k_{\text{obs}}$  decreased as ionic strength increased. This trend was similar to that of MTBE degradation by persulfate. The higher the ionic strength of the solutions, the slower MTBE degraded [19]. A previous study reported that the increase of ionic strength decreased the rate of persulfate decomposition in a 0.1 M of  $\text{HClO}_4$  solution [26]. In addition, the activities of persulfate and other reactive species could be decreased as a result of high-ionic strength [19]. In this study, when  $\ln k_{\text{obs}}$  was plotted versus  $\ln[\text{KCl}]$ , the slope of the linear regression was 0.160 ( $R^2 = 0.939$ ), suggesting an approximately 0.2-reaction order with respect to KCl.

### 3.5. Effect of catalytic ions $\text{Fe}^{3+}$ and $\text{Ag}^+$ on the degradation of DPA

It was discovered that if only  $\text{Ag}^+$  or  $\text{Fe}^{3+}$  was added in the solution instead of persulfate, DPA did not show any decomposition. This indicated that  $\text{Ag}^+$  or  $\text{Fe}^{3+}$  alone could not decompose DPA at all. However,  $\text{Ag}^+$  or  $\text{Fe}^{3+}$  ions could significantly accelerate degradation of DPA in the presence of persulfate, and  $\text{Ag}^+$  ion was more efficient than  $\text{Fe}^{3+}$  ion (Fig. 4). It was reported that  $\text{Ag}^+$  was the most efficient metal ion for the activation of persulfate among nine transition metals tested by Anipsitakis and Dionysiou [27]. In fact, persulfate oxidation was usually carried out under heat-, photo- or metal ion-catalyzed conditions because the reaction rate could be greatly accelerated. Highly reactive species such as sulfate radicals ( $\text{SO}_4^{\bullet-}$ ) and hydroxyl radicals ( $\text{HO}^{\bullet}$ ) could be quickly generated as a result of decomposition of persulfate ions in aqueous solutions,

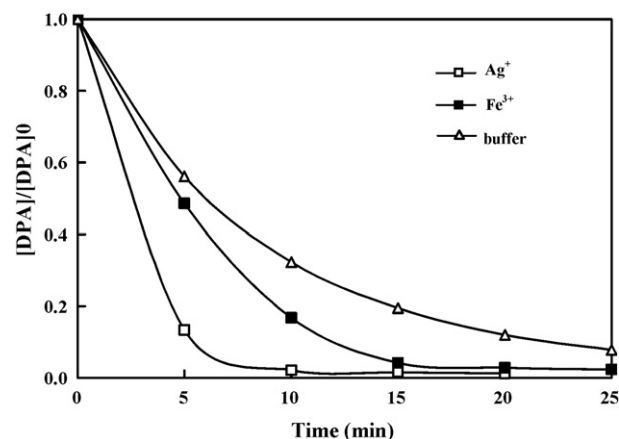


Fig. 4. Effects of catalytic ions  $\text{Fe}^{3+}$  and  $\text{Ag}^+$  on the degradation of DPA.  $[\text{DPA}]_0 = 20 \mu\text{g mL}^{-1}$ ,  $[\text{persulfate}]_0 = 3 \text{ mg mL}^{-1}$  and  $[\text{Fe}^{3+}] = [\text{Ag}^+] = 2 \times 10^{-4} \text{ M}$ , pH 2.2.

which were able to oxidize many organic substances into carbon dioxide [19].

### 3.6. Effect of temperature on the degradation of DPA

The degradation reaction of DPA was significantly influenced by temperature, as the  $k_{\text{obs}}$  values were  $1.38 \times 10^{-3}$ ,  $2.39 \times 10^{-3}$ ,  $2.84 \times 10^{-3}$  and  $3.92 \times 10^{-3} \text{ s}^{-1}$  at 23, 34, 43 and 52 °C, respectively. That is, the higher the temperature, the faster the DPA degradation. In addition, the activation energy of the degradation reaction could be obtained based on the experimental data using the Arrhenius equation,  $k = A \exp(-E_a/RT)$ , where  $A$  is the frequency factor,  $E_a$  is the activation energy,  $R$  is the universal gas constant and  $T$  is the temperature in Kelvin [19]. The plot of  $\ln k_{\text{obs}}$  versus  $1/T$  was linear ( $R^2 = 0.976$ ), and  $E_a$  was  $27.54 \text{ kJ mol}^{-1}$  (or  $6.58 \text{ kcal mol}^{-1}$ ). The  $E_a$  for the reaction of DPA with persulfate was smaller than that ( $24.5 \text{ kcal mol}^{-1}$ ) for the reaction of MTBE with persulfate [19], which indicated that DPA was easier to be degraded than MTBE using persulfate as an oxidant.

### 3.7. Mechanism of DPA degradation

To explore the mechanism of DPA degradation, the intermediates formed during the degradation of DPA by persulfate were identified by HPLC–MS and GC–MS. Instrumental library searches, comparison with available standard compounds, and mass fragmentation pattern were used to identify the suspected intermediates. The separation and identification methods of DPA and the intermediates were very similar to those reported in literature [28–30]. *N*-Phenyl-4-quinoneimine, *N*-carboxyl-4-quinoneimine, 4-quinoneimine and oxalic acid were identified as primary intermediates formed during the degradation of DPA.

Hydroxyl and sulfate radicals are thought to be the primary oxidizing species produced by decomposition of persulfate, which can oxidize many organic pollutants into carbon dioxide [19]. Comparing the above results with literature [2,28], a primary pathway might be proposed for the degradation of DPA by persulfate (Fig. 5). In this pathway, the degradation of DPA by persulfate involved oxidation and ring opening reactions, which was very different from the degradation of DPA by microorganisms, because DPA was cleaved into aniline and benzene by reduction, or cleaved into aniline and phenol by hydrolysis during the degradation of DPA with different bacteria [2]. The proposed pathway was also different from the controlled oxidation of DPA by persulfate in aqueous-organic micellar solutions where the product was a polymer that could be used as functional material [31].

The four detected intermediates of DPA degradation could be further degraded by persulfate under the experimental conditions. A representative graph showing the fate of these four intermediates in a persulfate solution is presented in Fig. 6. *N*-Carboxyl-4-quinoneimine was a primary intermediate in the early stage of the reactions and reached the highest concentration among the intermediates, and then rapidly degraded as the reaction proceeded. The concentration of *N*-carboxyl-4-quinoneimine was higher than that of *N*-phenyl-4-quinoneimine, 4-quinoneimine or oxalic acid, hinting that it could be more persistent toward radical oxidation because of the carboxylic structure in its molecule. The four detected intermediates were also observed in a previous study where DPA was degraded with an advanced oxidation process  $\text{TiO}_2/\text{UV}$ , although none was identified [32]. The degradation patterns of the three unidentified intermediates by  $\text{TiO}_2/\text{UV}$  were similar to the results obtained by the present study. This implied that the degradation of DPA in persulfate system was most likely due to its reaction with sulfate and hydroxyl radicals.

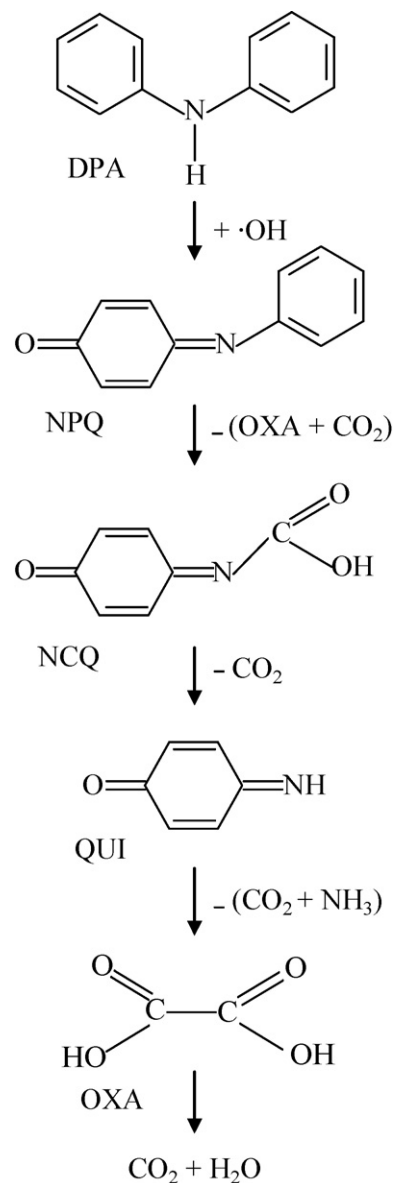


Fig. 5. Proposed primary pathway for the degradation of DPA. DPA = diphenylamine, NPQ = *N*-phenyl-4-quinoneimine, NCQ = *N*-carboxyl-4-quinoneimine, QUI = 4-quinoneimine and OXA = oxalic acid.

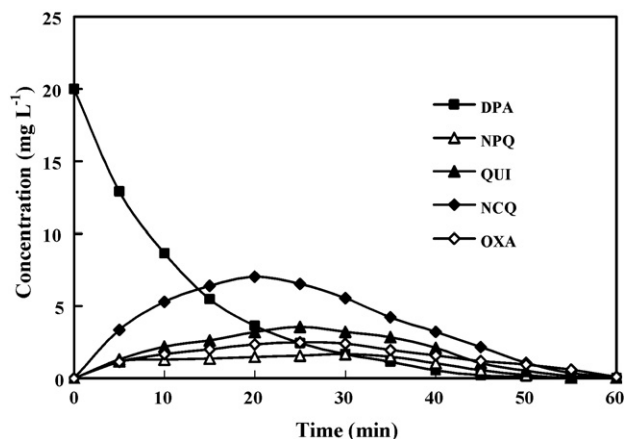


Fig. 6. DPA degradation and its by-products formation profiles over time.  $[\text{DPA}]_0 = 20 \text{ mg L}^{-1}$  and  $[\text{persulfate}]_0 = 3 \text{ mg mL}^{-1}$ , pH 2.2.

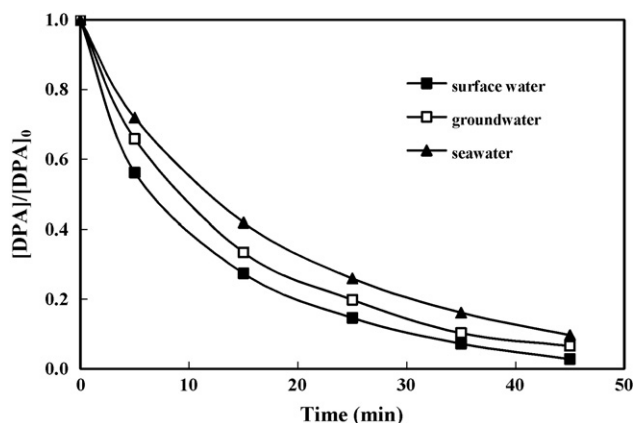


Fig. 7. Degradation of DPA in surface water, groundwater and seawater by persulfate.  $[DPA]_0 = 20 \text{ mg L}^{-1}$  and  $[\text{persulfate}]_0 = 3 \text{ mg mL}^{-1}$ .

### 3.8. Degradation of DPA in surface water, groundwater and seawater by $K_2S_2O_8$

The experiments were conducted to investigate the degradation of DPA by persulfate at room temperature in surface water, groundwater and seawater samples which were spiked with DPA. The results showed that DPA was rapidly degraded by persulfate under the experimental conditions (Fig. 7). The degradation percentages of DPA were, respectively, 97.2%, 93.5% and 90.4% in the surface water, groundwater and seawater in 45 min at an initial DPA concentration of  $20 \text{ mg L}^{-1}$ . Surface water, groundwater or seawater could contain many different compounds or ions, and some of them (such as KCl) might decrease the rate of DPA degradation, but others (such as  $\text{Fe}^{3+}$ ) might accelerate the reaction rate as above discussed in Sections 3.4 and 3.5 in this paper.

## 4. Conclusions

Degradation of diphenylamine in aqueous solution by persulfate was investigated. The results showed that the degradation efficiency of DPA by persulfate was significantly influenced by pH, persulfate concentration, ionic strength, temperature and catalytic ions  $\text{Fe}^{3+}$  and  $\text{Ag}^+$ . The degradation of DPA was found to follow a pseudo-first-order kinetic model. Increasing the reaction temperature or persulfate concentration may significantly accelerate the DPA degradation. Both  $\text{Fe}^{3+}$  and  $\text{Ag}^+$  ions could improve the degradation of DPA, and  $\text{Ag}^+$  ion was more efficient than  $\text{Fe}^{3+}$  ion. However, increasing either the pH value or ionic strength will decrease the reaction rate. *N*-Phenyl-4-quinoneimine, *N*-carboxyl-4-quinoneimine, 4-quinoneimine and oxalic acid were identified as major intermediates of DPA degradation, and a primary reaction mechanism was proposed. The results indicated that more than 90% of DPA in surface water, groundwater and seawater could be degraded by persulfate at room temperature in 45 min at an initial concentration of  $20 \text{ mg L}^{-1}$ . The results obtained in this study are helpful for the treatment of water contaminated with DPA. On the other hand, in situ chemical oxidation is a promising technology for the remediation of contaminated soil and groundwater. Hydrogen peroxide, permanganate and ozone are widely used oxidants in this process. Persulfate is much more stable in the subsurface as compared to hydrogen peroxide and ozone [19]. Persulfate could be effectively transferred to the contaminated zones and react with the contaminants because of its high solubility and stability under normal subsurface conditions. Furthermore, DPA could be degraded by persulfate at room temperature, without light, heat or catalyst. Thus, persulfate could be

used for in situ remediation of soil and groundwater contaminated with DPA.

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