



ISSN 1001-0742

CN 11-2629/X

2012

Volume **24**
Number **5**

JOURNAL OF
**ENVIRONMENTAL
SCIENCES**



Sponsored by

Research Center for Eco-Environmental Sciences

Chinese Academy of Sciences

CONTENTS

Aquatic environment

Immunotoxic potential of aeration lagoon effluents for the treatment of domestic and Hospital wastewaters in the freshwater mussel <i>Elliptio complanata</i>	
Franc�is Gagn�, Chantale Andr�, Marl�ne Fortier, Michel Fournier	781
Spatial distribution of archaeal and bacterial ammonia oxidizers in the littoral buffer zone of a nitrogen-rich lake	
Yu Wang, Guibing Zhu, Lei Ye, Xiaojuan Feng, Huub J. M. Op den Camp, Chengqing Yin	790
Accelerated biodegradation of nitrophenols in the rhizosphere of <i>Spirodela polyrrhiza</i>	
Risky Ayu Kristanti, Masahiro Kanbe, Tadashi Toyama, Yasuhiro Tanaka, Yueqin Tang, Xiaolei Wu, Kazuhiro Mori	800
Sorption of 2,4-dinitroanisole (DNAN) on lignin	
Rabih Saad, Zorana Radovic-Hrapovic, Behzad Ahvazi, Sonia Thiboutot, Guy Ampleman, Jalal Hawari	808
Sewage sludge disintegration by high-pressure homogenization: A sludge disintegration model	
Yuxuan Zhang, Panyue Zhang, Boqiang Ma, Hao Wu, Sheng Zhang, Xin Xu	814
Degradation kinetics and mechanism of aniline by heat-assisted persulfate oxidation	
Xiaofang Xie, Yongqing Zhang, Weilin Huang, Shaobing Huang	821
Degradation of some typical pharmaceuticals and personal care products with copper-plating iron doped Cu ₂ O under visible light irradiation	
Jing An, Qixing Zhou	827
Preparation of high concentration polyaluminum chloride by chemical synthesis-membrane distillation method with self-made hollow fiber membrane	
Changwei Zhao, Yong Yan, Deyin Hou, Zhaokun Luan, Zhiping Jia	834
Characteristics of gas-liquid pulsed discharge plasma reactor and dye decoloration efficiency	
Bing Sun, Nyein Nyein Aye, Zhiying Gao, Dan Lv, Xiaomei Zhu, Masayuki Sato	840
Photolysis kinetics and influencing factors of bisphenol S in aqueous solutions	
Guiping Cao, Jilai Lu, Gongying Wang	846
Comparative study of leaching of silver nanoparticles from fabric and effective effluent treatment	
Aneesh Pasricha, Sant Lal Jangra, Nahar Singh, Neeraj Dilbaghi, K. N. Sood, Kanupriya Arora, Renu Pasricha	852

Atmospheric environment

Size distribution and chemical composition of secondary organic aerosol formed from Cl-initiated oxidation of toluene	
Mingqiang Huang, Weijun Zhang, Xuejun Gu, Changjin Hu, Weixiong Zhao, Zhenya Wang, Li Fang	860
Real-world fuel efficiency and exhaust emissions of light-duty diesel vehicles and their correlation with road conditions	
Jingnan Hu, Ye Wu, Zhishi Wang, Zhenhua Li, Yu Zhou, Haitao Wang, Xiaofeng Bao, Jiming Hao	865
Operating condition influences on PCDD/Fs emissions from sinter pot tests with hot flue gas recycling	
Yongmei Yu, Minghui Zheng, Xianwei Li, Xiaolei He	875
Size distribution of chemical elements and their source apportionment in ambient coarse, fine, and ultrafine particles in Shanghai urban summer atmosphere	
Senlin L�, Rui Zhang, Zhenkun Yao, Fei Yi, Jingjing Ren, Minghong Wu, Man Feng, Qingyue Wang	882
Synergistic effects of non-thermal plasma-discharge catalyst and ultrasound on toluene removal	
Yongli Sun, Libo Zhou, Luhong Zhang, Hong Sui	891
Absorption characteristics of new solvent based on a blend of AMP and 1,8-diamino- <i>p</i> -menthane for CO ₂ absorption	
Sang-Sup Lee, Seong-Man Mun, Won-Joon Choi, Byoung-Moo Min, Sang-Won Cho, Kwang-Joong Oh	897

Terrestrial environment

Toxicity and subcellular distribution of cadmium in wheat as affected by dissolved organic acids	
Dandan Li, Dongmei Zhou	903
Changes in the sorption, desorption, distribution, and availability of copper, induced by application of sewage sludge on Chilean soils contaminated by mine tailings	
Tatiana Garrido, Jorge Mendoza, Francisco Arriagada	912
Mechanism of lead immobilization by oxalic acid-activated phosphate rocks	
Guanjie Jiang, Yonghong Liu, Li Huang, Qingling Fu, Youjun Deng, Hongqing Hu	919
Methyl-�-cyclodextrin enhanced biodegradation of polycyclic aromatic hydrocarbons and associated microbial activity in contaminated soil	
Mingming Sun, Yongming Luo, Peter Christie, Zhongjun Jia, Zhengao Li, Ying Teng	926
Inhibitory effect of nitrobenzene on oxygen demand in lake sediments	
Xiaohong Zhou, Xuying Wang, Hanchang Shi	934

Environmental health and toxicology

Endogenous nitric oxide mediates alleviation of cadmium toxicity induced by calcium in rice seedlings	
Long Zhang, Zhen Chen, Cheng Zhu	940
Species-dependent effects of the phenolic herbicide ioxynil with potential thyroid hormone disrupting activity: modulation of its cellular uptake and activity by interaction with serum thyroid hormone-binding proteins	
Sakura Akiyoshi, Gobun Sai, Kiyoshi Yamauchi	949

Environmental catalysis and materials

A screen-printed, amperometric biosensor for the determination of organophosphorus pesticides in water samples	
Junfeng Dou, Fuqiang Fan, Aizhong Ding, Lirong Cheng, Raju Sekar, Hongting Wang, Shuairan Li	956
A GFP-based bacterial biosensor with chromosomally integrated sensing cassette for quantitative detection of Hg(II) in environment	
Himanshu Priyadarshi, Absar Alam, Gireesh-Babu P, Rekha Das, Pankaj Kishore, Shivendra Kumar, Aparna Chaudhari	963



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

Xiaofang Xie¹, Yongqing Zhang^{1,2,*}, Weilin Huang³, Shaobing Huang^{1,2}

1. College of Environmental Science and Engineering and the Key Laboratory of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, South China University of Technology, Guangzhou 510006, China. E-mail: xiaofanghaha1314@126.com

2. Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Guangzhou 510275, China

3. Department of Environmental Sciences, Rutgers, The State University of New Jersey, New Brunswick, NJ 08901, USA

Received 16 June 2011; revised 16 December 2011; accepted 20 December 2011

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

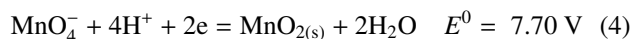
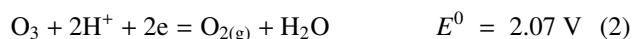
DOI: 10.1016/S1001-0742(11)60844-9

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 listed as one of the 129 priority pollutants by U.S. Environmental Protection Agency (Li and Xie, 2007). In China, 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 (*E*⁰) for the half-reaction is higher than other oxidants (Huang et al., 2002).

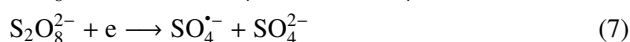
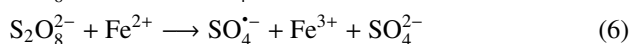


Another important feature is that persulfate is more stable in the presence of impurities such as carbonates in the aqueous phase, compared to the widely used H₂O₂ (Liang and Su, 2009). It can maintain reactive over longer time period when it is used to oxidize target contaminants in groundwater systems.

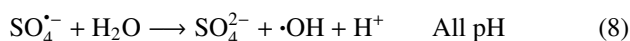
When persulfate activated by heat or a transition metal (e.g., ferrous ion), it can be converted into an even stronger oxidant, i.e., a sulfate free radical with a redox potential

* Corresponding author. E-mail: zhangyq@scut.edu.cn

of 2.4 V (Huie et al., 1991). Previous studies showed that formation of $\text{SO}_4^{\bullet-}$ can be induced via thermal (House, 1962), metal (Kolthoff and Miller, 1951), and photochemical activation (Netal et al., 1977) as shown below:



Prior experimental studies showed that persulfate oxidation reactions are usually less aggressive due to slow rates of $\text{SO}_4^{\bullet-}$ generation at relatively low temperatures in groundwater systems. Meanwhile, $\text{SO}_4^{\bullet-}$ can produce hydroxyl radical $\cdot\text{OH}$ ($E^0 = 2.7$ V) (Huang et al., 2002) in aqueous solution following the reactions below (Hayon et al., 1972; Norman et al., 1970; Pennington and Haim, 1968).



The distribution of the two free radicals is solution pH dependent. At solution pH < 7, $\text{SO}_4^{\bullet-}$ is the dominant free radical whereas $\cdot\text{OH}$ 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_2HPO_4 and 10 mmol/L NaH_2PO_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 r/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 $\text{Na}_2\text{S}_2\text{O}_3$ 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 $\text{Na}_2\text{S}_2\text{O}_8$ 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., $\ln C_t$ 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 $\ln C_t$ 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 a large temperature dependence provides that changing the system temperature is one of the ways to control the generation of sulfate free radicals.

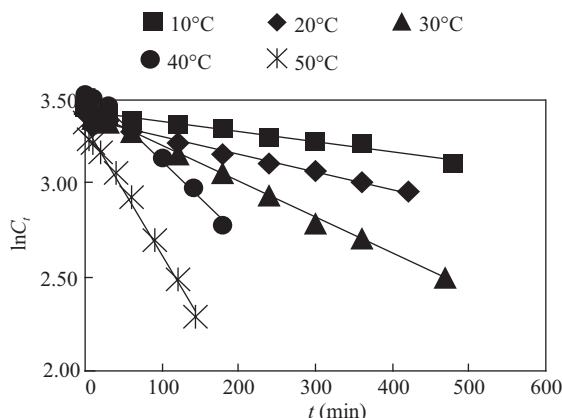


Fig. 1 Influence of temperature on the rate of aniline oxidation by persulfate.

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

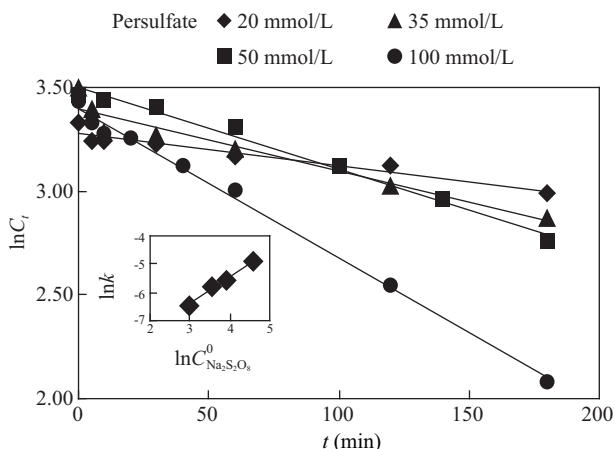


Fig. 2 Effect of initial persulfate concentration on the rate of aniline oxidation.

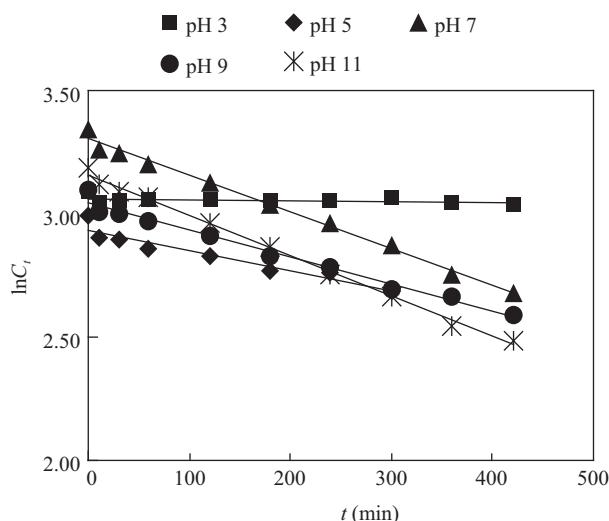


Fig. 3 Influence of pH on persulfate oxidation of aniline.

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 $\text{SO}_4^{\cdot-}$ 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 $\text{SO}_4^{\cdot-}$ is the predominant radical at pH < 7 whereas both $\text{SO}_4^{\cdot-}$ 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 $\text{SO}_4^{\cdot-}$ 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 $\text{SO}_4^{\cdot-}$ in basic solutions. Thus, it appears that the presence of various free radical scavengers in solution results in reduction in reactivity of both $\text{SO}_4^{\cdot-}$ 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; Saulea 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; Saulea 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 the byproducts.

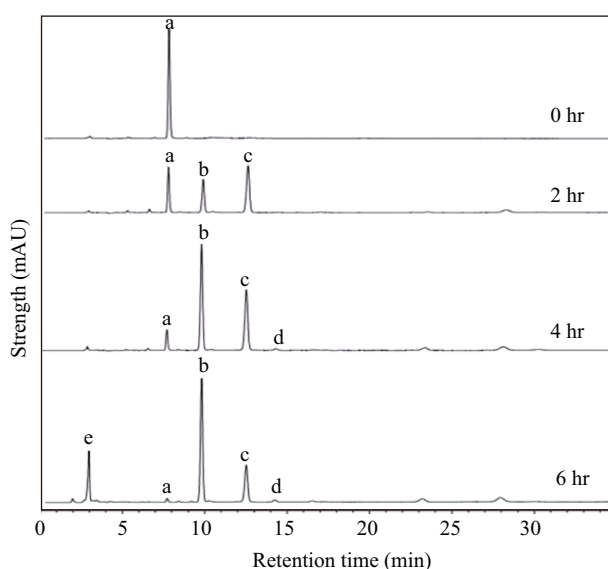


Fig. 4 HPLC typical chromatograms of intermediates (a–e) for the aniline solutions collected after 0, 2, 4 and 6 hours of persulfate oxidation in reactor.

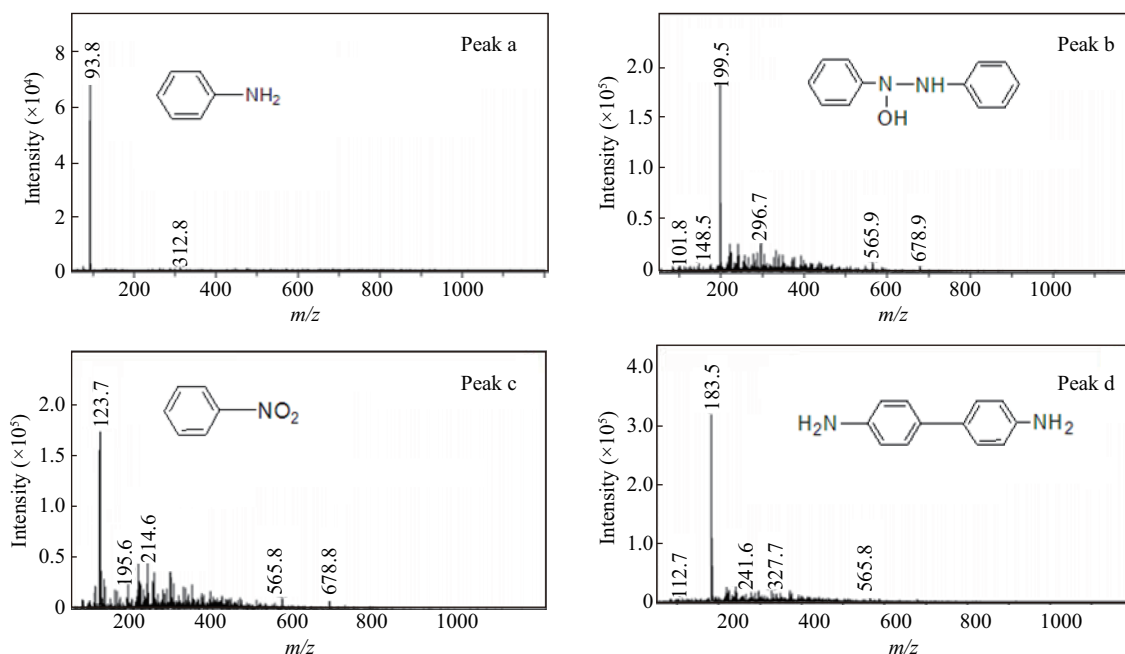


Fig. 5 Proposed intermediates and mass spectra of the degradation products.

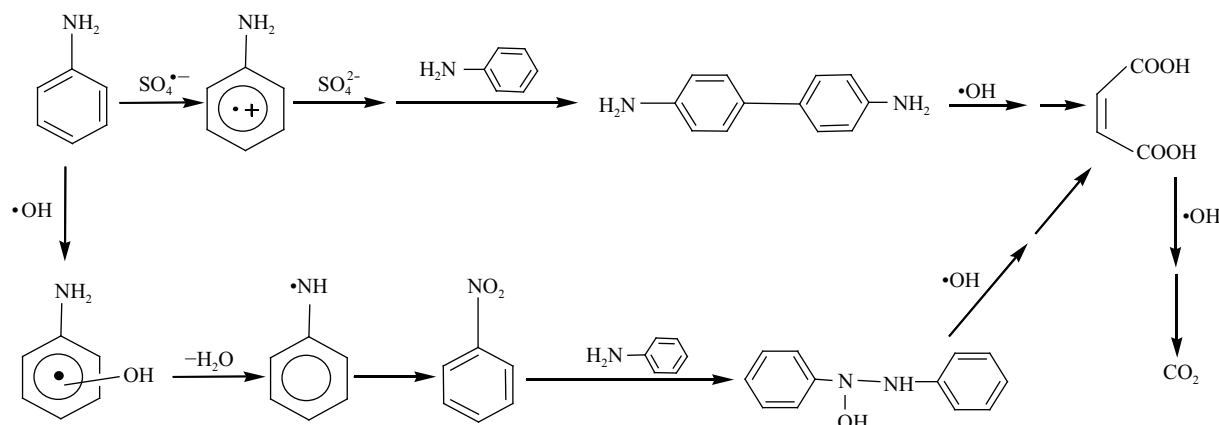


Fig. 6 Proposed reaction pathways for mineralization of aniline.

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.

Acknowledgments

This work was supported by the Foundation of Science and Technology Planning Project of Guangdong Province (No. 2010B050200007), the Fundamental Research Funds for the Central Universities (No. 2011ZM0054), and the Research Fund Program of Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology (China) (No. 2011K0013).

References

- An F Q, Feng X Q, Gao B J, 2010. Adsorption property and mechanism of composite adsorbent PMAA/SiO₂ for aniline. *Journal of Hazardous Materials*, 178(1-3): 499–504.
- Anipsitakis G P, Dionysiou D D, 2004. Radical generation by the interaction of transition metals with common oxidants. *Environmental Science and Technology*, 38(13): 3705–3712.
- Anotai J, Lu M C, Chwprecha P, 2006. Kinetics of aniline degradation by Fenton and Electro-Fenton processes. *Water Research*, 40(9): 1841–1847.
- Brillas E, Mur E, Sauleda R, Sánchez L, Peral J, Domènech X et al., 1998. Aniline mineralization by AOP's: anodic oxidation, photocatalysis, electro-Fenton and photoelectro-Fenton processes. *Applied Catalysis B: Environmental*, 16(1): 31–42.
- Canle L M, Santaballa J A, Vulliet E, 2005. On the mechanism of TiO₂-photocatalyzed degradation of aniline derivatives. *Journal of Photochemistry and Photobiology A: Chemistry*, 175(2-3): 192–200.
- Chen X Y, Xue Z Y, Wu D, Wang W P, Zhu F X, Wu C Z, 2009. Advanced oxidation technology based on sulfate radical and application in water treatment. *Water Treatment*, 35(5): 16–20.
- Fu N, Tu X Y, Pan Y, Liu W W, 2008. The treatment of high-concentration aniline wastewater via hydro-thermal electrolysis of catalysis oxidation. *Environmental Chemistry*, 27(5): 578–582.
- Gai K, 2003. The detection of the intermediate products of aniline in degradation process by HPLC. *Journal of Baoji College of Arts and Science (Natural Science)*, 23(4): 271–272.
- Gomesa H T, Machado B F, Ribeiro N, Moreira I, Rosário M, Silva A M T et al., 2008. Catalytic properties of carbon materials for wet oxidation of aniline. *Journal of Hazardous Materials*, 159(2-3): 420–426.
- Gómez J L, León G, Hidalgo A M, Gómez M, Murcia M D, Griñán G, 2009. Application of reverse osmosis to remove aniline from wastewater. *Desalination*, 245(1-3): 687–693.
- Gu H F, An T C, Wen S, Chen W G, Zhu X H, Fu J M et al., 2003. Sonophotocatalytic degradation of aniline and its derivatives. *Acta Scientiae Circumstantiae*, 23(5): 593–597.
- Hayon E, Treinins A, Wilf J, 1972. Electronic spectra, photochemistry, and autoxidation mechanism of the sulfite-bisulfite-pyrosulfite systems. SO₂⁻, SO₃⁻, SO₄⁻, and SO₅⁻ radicals. *Journal of the American Chemical Society*, 94(1): 47–57.
- House D A, 1962. Kinetics and mechanism of oxidations by peroxydisulfate. *Chemical Reviews*, 62(3): 185–203.
- Huang H, Sommerfeld D, Dunn B C, Lloyd C R, Eyring E M, 2001. Ferrate(VI) oxidation of aniline. *Journal of the Chemical Society, Dalton Transactions*, (8): 1301–1305.
- Huang K C, Couttenye R A, Hoag G E, 2002. Kinetics of heat-assisted persulfate oxidation of methyl *tert*-butyl ether (MTBE). *Chemosphere*, 49(4): 413–420.
- Huie R E, Clifton C L, Neta P, 1991. Electron transfer reaction rates and equilibria of the carbonate and sulfate radical anions. *International Journal of Radiation Applications and*

- Instrumentation. Part C. Radiation Physics and Chemistry*, 38(5): 477–481.
- Huling S G, Pivetz B E, 2006. *In Situ* Chemical Oxidation, EPA/600/R-06/072. Office of Research and Development, National Risk Management Research Laboratory, U. S. EPA.
- Jin A T, Lu M C, Chewprecha P, 2006. Kinetics of aniline degradation by Fenton and electro-Fenton processes. *Water Research*, 40(9): 1841–1847.
- Kolthoff I M, Miller I K, 1951. The chemistry of persulfate. I. The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium. *Journal of the American Chemical Society*, 73(7): 3055–3059.
- Kumar A, Mathur N, 2006. Photocatalytic degradation of aniline at the interface of TiO_2 suspensions containing carbonate ions. *Journal of Colloid and Interface Science*, 300(1): 244–252.
- Li J, Xie C J, 2007. Study on aerobic co-metabolism biodegradation of aniline in wastewater. *Chinese Journal of Environmental Engineering*, 1(6): 51–55.
- Li S X, Wei D, Mak N K, Cai Z W, Xu X R, Li H B et al., 2009. Degradation of diphenylamine by persulfate: Performance optimization, kinetics and mechanism. *Journal of Hazardous Materials*, 164(1): 26–31.
- Li Y J, Wang F, Zhou G D, Ni Y M, 2003. Aniline degradation by photocatalytic oxidation. *Chemosphere*, 53(10): 1229–1234.
- Liang C J, Bruell C J, Marley M C, Sperry K L, 2004. Persulfate oxidation for in situ remediation of TCE. I. activated by ferrous ion with and without a persulfate–thiosulfate redox couple. *Chemosphere*, 55(9): 1213–1223.
- Liang C J, Liang C P, Chen C C, 2009. pH dependence of persulfate activation by EDTA/Fe(III) for degradation of trichloroethylene. *Journal of Contaminant Hydrology*, 106(3–4): 173–182.
- Liang C J, Su H W, 2009. Identification of sulfate and hydroxyl radicals in thermally activated persulfate. *Industrial and Engineering Chemistry Research*, 48(11): 5558–5562.
- Liang C J, Wang Z S, Bruell C J, 2007. Influence of pH on persulfate oxidation of TCE at ambient temperatures. *Chemosphere*, 66(1): 106–133.
- Netal P, Madhavan V, Zemel H, Fessenden R W, 1977. Rate constants and mechanism of reaction of $\text{SO}_4^{\cdot -}$ with aromatic compounds. *Journal of the American Chemical Society*, 99(1): 163–164.
- Norman R O C, Storey P M, West P R, 1970. Electron spin resonance studies. Part XXV—Reactions of the sulphate radical anion with organic compounds. *Journal of the Chemical Society, B: Physical Organic*, 1087–1095.
- Oliviero L, Barbier J Jr, Duprez D, 2003. Wet air oxidation of nitrogen-containing organic compounds and ammonia in aqueous media. *Applied Catalysis B: Environmental*, 40(3): 163–184.
- Pennington D E, Haim A, 1968. Stoichiometry and mechanism of the chromium (II) peroxydisulfate reaction. *Journal of the American Chemical Society*, 90(14): 3700–3704.
- Rivas F J, 2006. Polycyclic aromatic hydrocarbons sorbed on soils: a short review of chemical oxidation based treatments. *Journal of Hazardous Materials*, 138(2): 234–251.
- Sauleda R, Brillas E, 2001. Mineralization of aniline and 4-chlorophenol in acidic solution by ozonation catalyzed with Fe^{2+} and UVA light. *Applied Catalysis B: Environmental*, 29(2): 135–145.
- Song S, He Z Q, Chen J M, 2007. US/O_3 combination degradation of aniline in aqueous solution. *Ultrasonics Sonochemistry*, 14(1): 84–88.
- Waldemer R H, Tratnyek P G, 2006. Kinetics of contaminant degradation by permanganate. *Environmental Science and Technology*, 40(3): 1055–1061.
- Wang L, Zhang C B, Wu F, Deng N S, 2007. Photodegradation of aniline in aqueous suspensions of microalgae. *Journal of Photochemistry and Photobiology B: Biology*, 87(1): 49–57.
- Watts R J, Teel A L, 2005. Chemistry of modified Fenton's reagent (catalyzed H_2O_2 propagation-CHP) for in situ soil and groundwater remediation. *Journal of Environment Engineering*, 131(4): 612–622.
- Watts R J, Teel A L, 2006. Treatment of contaminated soils and groundwater using ISCO. *Journal of Hazardous, Toxic, and Radioactive Waste*, 10(1): 2–9.
- Ye Z L, Sun X, Zheng L, Hou H Q, 2009. Study on degradation mechanism of aniline solution by potassium ferrate. *Environmental Pollution and Control*, 31(4): 1–4.
- Zhang X, Dong X Q, Zhang M H, 2007. Catalytic supercritical water oxidation of aniline. *Chemical Industry and Engineering Progress*, 26(3): 413–416.
- Zhang Y Q, Huang W L, Fennell D E, 2010. *In situ* chemical oxidation of aniline by persulfate with iron(II) activation at ambient temperature. *Chinese Chemical Letters*, 21(8): 911–913.

JOURNAL OF ENVIRONMENTAL SCIENCES

Editors-in-chief

Hongxiao Tang

Associate Editors-in-chief

Nigel Bell Jiuhui Qu Shu Tao Po-Keung Wong Yahui Zhuang

Editorial board

R. M. Atlas University of Louisville USA	Alan Baker The University of Melbourne Australia	Nigel Bell Imperial College London United Kingdom	Tongbin Chen Chinese Academy of Sciences China
Maohong Fan University of Wyoming Wyoming, USA	Jingyun Fang Peking University China	Lam Kin-Che The Chinese University of Hong Kong, China	Pinjing He Tongji University China
Chihpin Huang "National" Chiao Tung University Taiwan, China	Jan Japenga Alterra Green World Research The Netherlands	David Jenkins University of California Berkeley USA	Guibin Jiang Chinese Academy of Sciences China
K. W. Kim Gwangju Institute of Science and Technology, Korea	Clark C. K. Liu University of Hawaii USA	Anton Moser Technical University Graz Austria	Alex L. Murray University of York Canada
Yi Qian Tsinghua University China	Jiuhui Qu Chinese Academy of Sciences China	Sheikh Raisuddin Hamdard University India	Ian Singleton University of Newcastle upon Tyne United Kingdom
Hongxiao Tang Chinese Academy of Sciences China	Shu Tao Peking University China	Yasutake Teraoka Kyushu University Japan	Chunxia Wang Chinese Academy of Sciences China
Rusong Wang Chinese Academy of Sciences China	Xuejun Wang Peking University China	Brian A. Whitton University of Durham United Kingdom	Po-Keung Wong The Chinese University of Hong Kong, China
Min Yang Chinese Academy of Sciences China	Zhifeng Yang Beijing Normal University China	Hanqing Yu University of Science and Technology of China	Zhongtang Yu Ohio State University USA
Yongping Zeng Chinese Academy of Sciences China	Qixing Zhou Chinese Academy of Sciences China	Lizhong Zhu Zhejiang University China	Yahui Zhuang Chinese Academy of Sciences China

Editorial office

Qingcai Feng (Executive Editor) Zixuan Wang (Editor) Suqin Liu (Editor) Zhengang Mao (Editor)
Christine J Watts (English Editor)

Journal of Environmental Sciences (Established in 1989)

Vol. 24 No. 5 2012

Supervised by	Chinese Academy of Sciences	Published by	Science Press, Beijing, China
Sponsored by	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences		Elsevier Limited, The Netherlands
Edited by	Editorial Office of Journal of Environmental Sciences (JES) P. O. Box 2871, Beijing 100085, China Tel: 86-10-62920553; http://www.jesc.ac.cn E-mail: jesc@263.net , jesc@rcees.ac.cn	Distributed by	Domestic Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China Local Post Offices through China Foreign Elsevier Limited http://www.elsevier.com/locate/jes
Editor-in-chief	Hongxiao Tang	Printed by	Beijing Beilin Printing House, 100083, China
CN 11-2629/X	Domestic postcode: 2-580	Domestic price per issue	RMB ¥ 110.00

ISSN 1001-0742



jesc.ac.cn