# Oxidation of Aniline using Different Reaction Pathways

KADIR TURHAN* and SÜHEYLA UZMAN
*Department of Chemistry, Yildiz Technical University, 34220 Esenler, Istanbul, Turkey*
*E-mail: turhankadir@yahoo.com*

The goal of this study is to cleavage of aromatic ring of aniline to minimize its hazardous environmental effects. Therefore a method has been developed to remove aniline using potassium dichromate as an oxidizing agent. In the beginning of the study, chemical oxygen demand (COD) experiment was chosen as a test method to oxidize aniline. Titration part of COD experiment was replaced by UV measurement. Cerium(IV) sulfate was also used as an alternative oxidizing agent in COD experiment. As a follow-up work, experimental conditions as reported in the literature for aniline oxidation to *p*-benzoquinone were modified. Oxidation agents mentioned above lack the strength to oxidize aniline until ring opening. Therefore, ozone was used as an oxidizing agent to break down the aromatic ring of aniline in the second part of the study. In the reaction with ozone, performed at pH 9, it was observed that $CO_2$ and $H_2O$ formed through nitrobenzene, azobenzene, azoxybenzene and 2-pyridine carboxylic acid depending on ozone concentration, reaction time and bubble size of ozone. As a conclusion, ozone was excellent oxidant among the investigated three oxidant ($K_2Cr_2O_7$, $Ce(SO_4)_2$ and ozone) to cleavage of aniline ring to non-hazardous compounds.

**Key Words: Aniline, Oxidation, Environmental pollutant, Ozonization, Advanced oxidation processes.**

## INTRODUCTION

Aniline is mainly used as an intermediate chemical for the synthetic dye, agricultural, polymer, varnish, and rubber industries[1]. It is also used as a solvent and an anti-knocking compound for gasoline engines[2]. Aniline can be formed by breaking down certain pollutants found in air and smokes of burning plastics or tobacco. Exposure to airborne aniline may occur *via* respiration of contaminated air, smoking tobacco or living near by industrial sources that use large quantities of aniline. Occupational exposure to aniline may occur in industries using aniline to make intermediate chemicals. Small amounts of aniline may be found in foods, such as corn, grains, rhubarb, apples, beans and rapeseed cake. Aniline has also been found in drinking water and surface water[3].

Ingestion, inhalation or skin contact with aniline exhibits toxic effect. Significant amounts of aniline can be absorbed through the skin[4,5]. Aniline damages hemoglobin, a protein that normally transports oxygen in the blood. Acute inhalation exposure to high levels of aniline in humans has resulted in adverse effects on the lung, such as upper respiratory tract irritation and congestion.

The major effects from chronic (long-term) inhalation exposure to aniline in humans are the formation of methemoglobin, which can cause cyanosis, interference with the oxygen carrying capacity of the blood. This condition is known as methemoglobinemia and its severity depends on exposure level and time. Cyanosis, a purplish blue skin colour, following acute high exposure to aniline can cause dizziness, headaches, irregular heartbeat, convulsions, coma and possible death. Aniline severely irritates to mucous membranes and affects the eyes, skin and upper respiratory tract[1,5-8].

Other researchers investigated adsorption and oxidation of aniline by chromium ferrocyanide, Fenton's reagent and quadrivalent cerium in aqueous sulfuric acid medium[7-9]. Additionally, Ayad and Shenashin[10] studied the polyaniline film deposition from the oxidative polymerization of aniline using $K_2Cr_2O_7$. Chan and Larson[11] and Sarasa *et al.*[12] also studied on the ozonization of aniline by using advanced oxidation techniques.

Aniline in water may evaporate into air or passes through the soil to groundwater. Therefore it is required to remove aniline which is found in industrial wastewater and drinking waters to improve public health. The aim of this study is to break down the aromaticity of aniline to mitigate its hazardous environmental effects. Therefore a method has been developed to remove aniline by using potassium dichromate as an oxidizing agent and cerium(IV) sulfate as an alternative oxidizing agent. After that, ozone was also used as an oxidizing agent to break down the aromatic ring of aniline.

## EXPERIMENTAL

**Chemical oxygen demand experiments using $K_2Cr_2O_7$ and $Ce(SO_4)_2$:** Reaction mixture was prepared by mixing 20 mL of sample from stock solution of 1000 mg/L aniline, 15 mL concentrated sulfuric acid and 10 mL of 0.25 N potassium dichromate in round bottom two-neck flask for reflux at varying temperatures for different time intervals given in Table-1.

The samples were extracted with ether. Following evaporation of ether, the residue was dissolved in distilled water[13]. The absorbance spectrums of the samples were taken (Fig. 1). A similar experiment was also performed using cerium(IV) sulfate as an alternative oxidizing agent instead of potassium dichromate[10] (Fig. 2).

TABLE-1
REACTIONS CONDITIONS

| Sample | Mixture | Temp. (ºC) | Time (min) | k Constant for $K_2Cr_2O_7$ | k Constant for $Ce(SO_4)_2$ |
|--------|---------|-----------|-----------|------------------------------|------------------------------|
| 1 | Stock* | 20 | – | | |
| 2 | A** | 20 | 0 | $8.71 \times 10^{-3}$ | $9.78 \times 10^{-3}$ |
| 3 | A | 100 | 150 | $1.04 \times 10^{-1}$ | $1.07 \times 10^{-1}$ |
| 4 | A | 150 | 300 | $3.58 \times 10^{-2}$ | $5.67 \times 10^{-2}$ |
| 5 | A | 175 | 450 | $9.02 \times 10^{-2}$ | $1.03 \times 10^{-1}$ |
| 6 | A | 200 | 600 | $2.49 \times 10^{-1}$ | $3.55 \times 10^{-1}$ |
| 7 | A | 250 | 750 | $1.21 \times 10^{-1}$ | $1.57 \times 10^{-1}$ |
| 8 | A | 300 | 900 | $2.89 \times 10^{-2}$ | $1.96 \times 10^{-2}$ |

*1000 mg/L Aniline stock solution
**20 mL from aniline stock solution + 10 mL 0.25 N $K_2Cr_2O_7$ + 15 mL $H_2SO_4$



(a)                                                         (b)

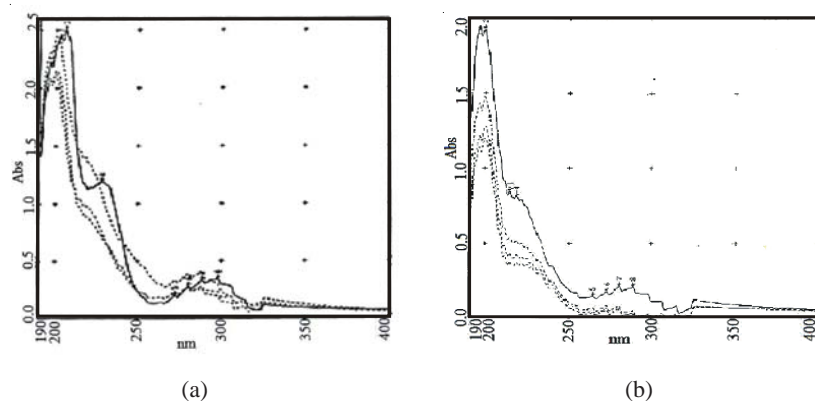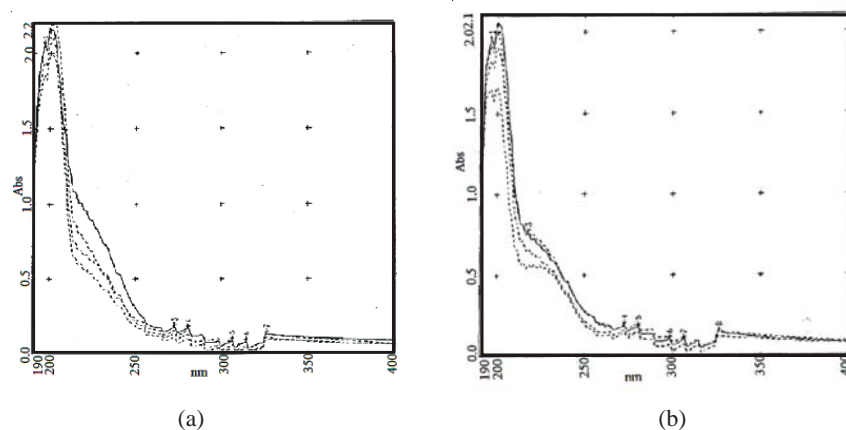Fig. 1. UV spectra of aniline reaction with $K_2Cr_2O_7$ (a) Samples 1-4 (b) Samples 5-8



(a)                                                         (b)

Fig. 2. UV spectra of aniline reaction with $Ce(SO_4)_2$ (a) Samples 1-4 (b) Samples 5-8

### *p*-Benzoquinone experiments

*p*-**Benzoquinone experiment (I):** The mixture of aniline (4.4 mL) with water (100 mL) and concentrated sulfuric acid (20 mL) was stirred at 0-5 ºC. After 1 h, potassium dichromate solution (6.73 g/85 mL of water) added in portions of about 1 g at a time, care was taken so that the temperature does not rise above 5°C. The mixture was left on a cool place overnight and then an additional quantity of potassium dichromate solution (9.42 g/145 mL of water) was added under conditions similar to the above. Dark coloured solution was allowed at room temperature for 18 h. Then it was extracted three times with ether. The ethereal solution dried with calcium chloride and ether removed by evaporation. Raw product was purified by steam distillation. Product forms gold yellow colour needle crystals with a characteristic pungent odour with 70 % yield (m.p. 112.8 ºC, Lit: 112.7 ºC)[10]. After interpretation of spectroscopic data, it was inferred that the product was *p*-benzoquinone. IR (KBr, cm$^{-1}$): $\nu$ 3050 C-H stressed bond, 1648 C=O, C=C stretch bending, 1291 C-O stretch bending, 1124 C-C stretch bending, 963 and 894 C-H out-of-plane bending; MS: m/z (rel. abund): 108 [M$^+$] (100), 82 (70), 80 (60), 58 (100).

*p*-**Benzoquinone experiment (II):** Aniline (4.4 mL) and water (100 mL) were mixed together slowly by a magnetic stirrer in a 1000 mL two-neck flask in an ice-salt bath. Thermometer and dropping funnel were mounted to the necks of flask. In a separate 1000 mL flask, 400 mL concentrated sulfuric acid and 16.0 g potassium dichromate mixed. This mixture added to the stirred solution above *via* dropping funnel during 13 h period. Temperature was kept[14] in between 0-2 ºC. A dark blue solution was formed. A precipitation occurred in dropping funnel during treatment of the solution with ether for extraction. A 1.5 L of distilled water was used to dilute the mixture to dissolve the precipitant. This solution was extracted three times with ether, the ethereal solution dried with sodium sulfate and ether removed by evaporation. Identification techniques used in previous experiment were also applied to this raw product. Yield in this experiment was found as 79 % (m.p. 112.7 ºC, Lit: 112.7 ºC)[10]. This product has also been identified as *p*-benzoquinone after interpretation of IR, GC (MS data). IR (KBr, cm$^{-1}$): $\nu$ 3050 C-H stretch bending, 1645 C=O, C=C stretch bending, 1296 C-O stretch bending, 1130 C-C stretch bending, 965 and 901 C-H out-of-plane bending; MS: m/z (rel.abund): 108 [M$^+$] (100), 82 (70), 80 (60), 58 (100).

### Ozonization of aniline

Aniline solution was prepared from pure standard (Merck, 99.9 % of purity) with distilled water. The concentrations of aniline solutions were 25, 50, 75 and 100 mg/L, respectively.

　　　The ozonization reaction was carried out in the system, which was shown in Fig. 3. The reactor capacity was 3,000 mL. Ozonization experiments were performed in a 2,000 mL volume ozone bubble column between 0 and 2 h at semi-batch supplied with counter current recirculation of the liquid to the gas flow. Fischer 502 model ozone generator was used for the production of ozone from pure oxygen (99.9 %). The oxygen flow rate to the generator was adjusted at 120 L/h and monitored with a rotameter integrated into the ozone generator. The ozone stream was continuously introduced in the sample through a porous sparger as microbubbles from the bottom of the ozone contactor. The diffusion rates of the ozone-oxygen mixture, introduced from the bottom of the reactor through a sintered glass diffusing plate, were 2, 4 and 6 L/h. Excess ozone was passed into gas absorption bottle containing KI solution (2 % wt). The excess amount of ozone was determined by the titration of the solutions in the bubblers using sodium thiosulfate and starch as indicator and calibration curve was established[15,16]. All tubing from the ozone generator to the reactor and the gas absorption bottles were made of glass. The fittings in the system are made of teflon. The medium dosages of ozone consumed were calculated for all the experiments, which were performed at room temperature at 20 ± 1 ℃.
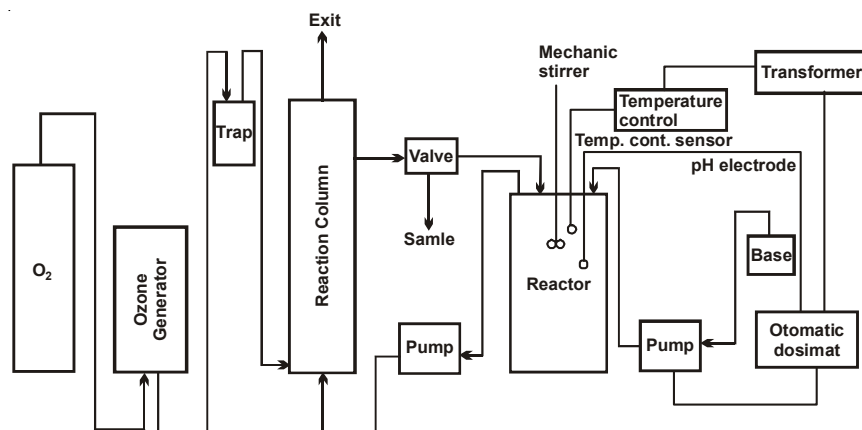


Fig. 3. Scheme of ozonization

　　　75 mL of samples were collected from upper reaction column end at different time intervals during the ozonization reaction for the determination of the reaction by products. Ozonization of aniline was carried out at four different initial aniline concentrations of 25, 50, 75 and 100 mg/L, with three different ozone concentrations of 2, 4 and 6 L/h for each initial aniline concentration.

The aromatic compounds were determined by means of a liquid-liquid extraction of the aqueous samples with methylene chloride[16]. The GC/MS apparatus used for quantification of aniline was A HP5890 Plus II Gas Chromatograph equipped with a flame ionization detector (FID). The chromatographic conditions were as follows: Column DB-WAX; injection volume: 2 μL in splitless (0.8 min); injection temperature: 300 ºC; carrier gas: helium (30 cm/s); auxiliary gas: nitrogen and temperature programme: 60(1)-25-120(3)-4-250. IR spectrum was taken with Perkin Elmer spectrum 10 Model apparatus.

## RESULTS AND DISCUSSION

It has been found that aniline as starting material maintained its structural integrity and concentration after examination of UV spectra of samples from COD experiments. It was observed that ring opening of aniline did not occur in modified *p*-benzoquinone experiment. The results from *p*-benzoquinone(I) are not conclusive. However, the modified method for the oxidation of aniline with $K_2Cr_2O_7$ gives higher yield *p*-benzoquinone compare with the literature value[17].

The reaction products of aniline with the oxidizing agents used above maintain ring structure in this study. This point out, that the used oxidizing agents are not suitable to open the aromatic ring system. Therefore oxidation of aniline with ozone was studied in the second part of this work.

Total organic carbon (TOC) analysis was performed to check concentration change in samples from aniline with ozone reaction mixture. Results are shown in Fig. 4a-d.

In the reaction of ozone with aniline at pH 9, in addition to nitrobenzene, azobenzene, azoxybenzene and 2-pyridine carboxylic acid were found. At pH 9, $OH^\bullet$ radicals are nonselective in their action on organic matter and can degrade the azobenzene formed. However, final concentration of azobenzene after 25 min of treatment is much higher when the experiment is carried out at pH 9. The evolution of the formation of azoxybenzene is similar to azobenzene, although it is only detected when the ozonization is carried out at pH 9. The compounds identified as by-products of aniline ozonization are in accordance with those reported by Chan and Larson[11] who describes the formation mechanisms of azobenzene and azoxybenzene from the reaction of ozone with aniline[18]. Besides those compounds, 2-pyridine carboxylic acid was also found in our experimental results[19] as reported by Sarasa *et al.*[12].

Other research groups have reported the acute toxicity of nitrobenzene, however, fewer data have been published[11,20] on toxicity of azobenzene, azoxybenzene and 2-pyridine carboxylic acid. When comparing toxicity data, it can be concluded that ozonization by products of aniline are less toxic than raw material.
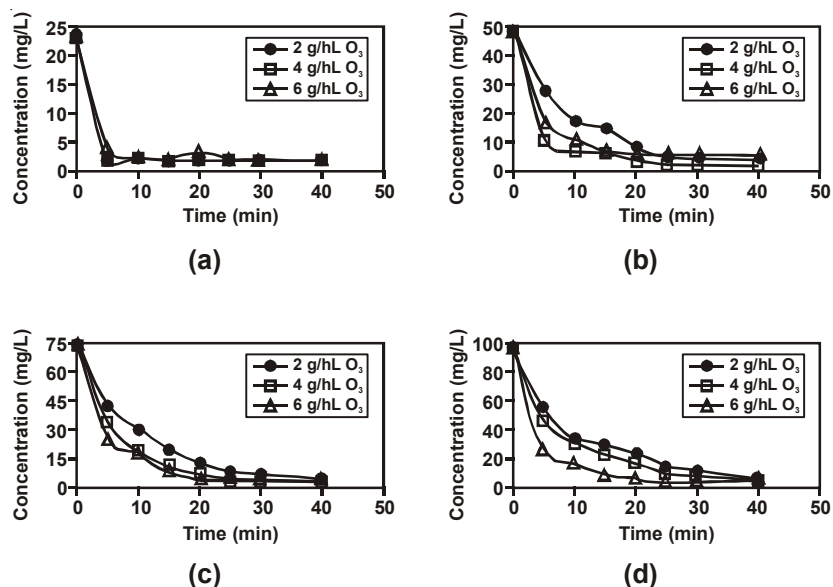
Fig. 4.    Change in aniline concentration after reaction with ozone at different
          initial aniline [(a) 25 mg/L, (b) 50 mg/L, (c) 75 mg/L and (d) 100 mg/L]
          and ozone concentrations.

Among the by products formed, the most interesting compound is nitrobenzene: it is included in the Priority pollutant list[21] and there is an effluent limitation of US EPA applicable to the process wastewater discharges containing nitrobenzene resulting from the manufacture of organic chemicals, plastics and synthetic fibers[22].

In this study, the degradability of aniline in aqueous solutions using three different oxidant ($K_2Cr_2O_7$, $Ce(SO_4)_2$ and ozone) was investigated. It was found that $K_2Cr_2O_7$ and $Ce(SO_4)_2$ are not efficient oxidant to cleavage of aniline ring whereas, indirect reaction of ozone with aniline yields azoxybenzene and 2-pyridine carboxylic acid besides nitrobenzene and azobenzene at pH 9. Further oxidation of these intermediate products forms $CO_2$, $NH_3$ and $H_2O$ depending upon concentration and bubble size of ozone and reaction time. Ozone as an effective oxidizer is perfect agent for oxidation of aniline-like organic pollutants to less hazardous chemicals in water treatment plants. The kinetics of reaction is under investigation for further research.

## REFERENCES

1. S. Budavari, The Merck Index, An Encyclopedia of Chemicals, Drugs and Biologicals, Merck and Co. Inc., Rahway, NJ, USA, edn. 11, p.104 (1989).
2. U.S. Environmental Protection Agency, Pollution Prevention and Toxics, OPPT Chemical Fact Sheets, Office of Research and Development (1994).
3. U.S. Environmental Protection Agency, Health and Environmental Effects Profile for Aniline, Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Cincinnati, OH (1985).
4. P.H. Howard, Handbook of Environmental Fate and Exposure Data, Lewis Publishers, Chelsea, MI (1989).
5. U.S. Department of Health and Human Services, Hazardous Substances Data Bank (HSDB, online database), National Toxicology Information Program, National Library of Medicine, Bethesda, MD (1993).
6. R. Schrebler, H. Gomez, R. Cordova, L.M. Gossa and J.R. Vilche, *Synth. Metals*, **93**, 187 (1998).
7. A. Tanveer, H. Tarannum and R.A. Shah, *J. Coll. Interface Sci.*, **245**, 251 (2002).
8. M.C. Lu, Y.F. Chang, I.M. Chen and Y.Y. Huang, *J. Environ. Menage.*, **75**, 177 (2005).
9. M. Verma, *J. Sci. Rev.*, **7**, 5 (1985).
10. M.M. Ayad and M.A. Shenashin, *European Polym. J.*, **40**, 197 (2004).
11. W.F. Chan and R.A. Larson, *Ozone Sci. Eng.*, **17**, 619 (1995).
12. J. Sarasa, S. Cortes, M.P. Ormad, R. Gracia and J.L. Ovelleiro, *Water Res.*, **36**, 3035 (2002).
13. L.S. Clesceri, A.E. Greenberg and A.D. Eaton, Standard Methods, for the Examination of Water and Wastewater, Ed. American Public Health Association, American Water Works Association, Water Environment Federation, edn. 20, p. 312 (1998).
14. K. Turhan, Chemical Oxidation of Aniline, M.Sc. Thesis, Yildiz Technical University, Institute of Science and Technology, Istanbul (1993).
15. H. Bader and J. Hoigné, *Water Res.*, **15**, 449 (1981).
16. L.S. Clesceri, A.E. Greenberg and R.R. Trussell, Standard Methods for the Examination of Water and Wastewater, Washington DC: APHA-AWWA-WPCF, edn. 17 (1989).
17. A.I. Vogel, A.R. Tatchell, B.S. Furniss, A.J. Hannaford and P.W.G. Smith, Vogel's Textbook of Practical Organic Chemistry, Longman Group Ltd., London, edn. 5, p. 1025 (1996).
18. J. March, Advanced Organic Chemistry, Reactions, Mechanisms and Structure, New York, USA, Wiley, edn. 3 (1985).
19. K. Turhan, Investigation of Decomposition Kinetics of Aromatic Compounds with Ozone in Aqueous Solutions, Ph.D. Dissertation, Yildiz Technical University, Istanbul (2001).
20. R. Atkinson, E.C. Tuazon, T.J. Wallington, S.M. Aschmann, J. Arey, A.M. Winer and J.N. Pitts, *Environ. Sci. Tech.*, **21**, 64 (1987).
21. US EPA, Priority Pollutant List promulgated by the US EPA under authority of the Clean Water Act of 1977, Fed. Regist., Vol. 44, p. 233 (1979).
22. US EPA. EPA CFR40 Subchapter N. Effluent Quidelines and Standards, Part 414. Organic Chemicals, Plastics and Synthetic Fibers (1995).