



Nano-Catalytic Ozonation of 4-Nitrochlorobenzene in Aqueous Solutions

S. M. TABATABAEI¹, A. MEHRIZAD², AND P. GHARBANI^{1*}

¹Department of Chemistry, Ahar Branch
Islamic Azad University, Ahar, Iran

²Department of Chemistry, Science and Research Branch
Islamic Azad University, Tabriz, Iran

p-gharbani@iau-ahar.ac.ir

Received 15 August 2011; Accepted 26 October 2011

Abstract: In this paper, efficiency of nano-ZnO particles on catalytic ozonation of 4-nitrochlorobenzene (4NCB) using semi-batch reactor has been studied at various pHs. During the catalytic ozonation, TOC and concentration of nitrate ions was monitored. Results indicate that degradation of 4NCB was improved by combination of nano-ZnO with ozone. The effect of ZnO particle size and pH are also examined. According to the results, concentration of 4NCB decreased with increasing of particle size from nanosized to microsized and pH from 3.0 to 9.0. Based on the results, it suggests radical hydroxyl does not affect on the degradation of 4NCB in catalytic ozonation, but the surface of catalyst plays main role. Kinetic studies showed degradation of 4NCB followed pseudo-first-order kinetic and maximum degradation rate was observed at pH=3.

Keywords: ZnO, Catalyst, Kinetic, Catalytic ozonation, Nano particles.

Introduction

4NCB is an important chemical intermediate that used as basic building blocks for the manufacture of numerous industrial chemicals. For example, it is utilized via chemical reaction to make industrial chemicals that are ultimately used in the preparation of dyes, pigments, pesticides and animal feed ingredients¹. PCNB is known to produce methemoglobinemia in human and animals²⁻³ and is considered hazardous⁴⁻⁵. Advanced oxidation of organic pollutants present in water is a strong method to degradation of aromatics. On the other hand, advanced oxidation processes exhibit the most effective way of oxidizing organic compounds⁶⁻⁸. Shen *et al.*, studied the kinetics and mechanism of degradation pCNB in water by ozonation. It has been deduced pCNB completely removed after 20 min of ozonation, while the degree of mineralization was slow¹. Heterogeneous catalytic oxidation of 4NCB with H₂O₂ showed that the type of catalyst and oxidation agents affected on the degradation rate⁹. A comparative study of degradation of pCNB by H₂O₂/UV and O₃/UV oxidation processes was carried out¹⁰. Reduction of concentrations of

chloronitrobenzene from 1900 $\mu\text{g/L}$ to less than 20 $\mu\text{g/L}$ could be reached by the application of 8 mg O_3/L and 3 mg $\text{H}_2\text{O}_2/\text{L}$ with a 20 minute contact time¹¹. Guittonneau *et al.*, studied the degradation of pCNB by H_2O_2 photolysis and gave a kinetic model¹². Yang *et al.* studied the ozonation of nitrobenzene catalyzed by nano- TiO_2 particles and deduced that degradation efficiency of catalytic ozonation is much higher than ozonation alone¹³.

Objective of this work is to compare the performance of ozonation and catalytic ozonation on degradation of 4-nitrochlorobenzene and determine the kinetic of reaction at various pHs. The ZnO was applied as catalyst in two different sizes, *i.e.*, nano and microsized.

Experimental

1-Chloro-4-nitrobenzen (4NCB) [$\text{C}_6\text{H}_4\text{ClNO}_2$, $M=157.6$] (Fluka Co.) was selected as a model compound. A stock solution of 4NCB was prepared at a concentration of approximately 95 μM (15 mg/L). Nano TiO_2 was purchased from Degussa (Germany). Its size was <21 nm and had a surface area in the range of 15-50 m^2/g . Nano and microsized ZnO were supplied from Aldrich and Sigma-Aldrich (USA), respectively. Nanosized ZnO was <100 nm and its surface area (15-25 m^2/g) was determined by a BET surface area analyzer. All solutions were prepared by using deionized water. All other chemicals such as acetonitrile, sodium thiosulphate, potassium iodide and *etc.*, were reagent grades and were supplied from Merck, Germany.

Catalytic Ozonation Experiments

Catalytic activity measurements in degradation of 4NCB were carried out in a semi-batch stirred reactor. A pyrex glass reactor of 150 mm diameter and 250 mm length was equipped with a ceramic diffuser. O_2/O_3 gas mixture (5.64 mg/L) was bubbled continuously through a fine-bubble ceramic diffuser into a reactor (2000 mL) containing 1 L of aqueous solution of 4NCB (15 mg/L) and 300 mg of catalyst that was completely mixed with a magnetic stirring bar. A schematic diagram of the ozonation system is shown in Figure 1.

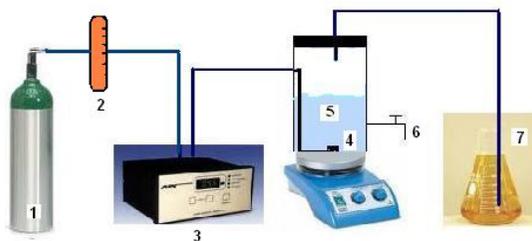


Figure 1. Schematic diagram of catalytic oxidation system. (1) Pure oxygen, (2) Flow meter, (3) Ozone generator, (4) Magnetic stirrer, (5) Ozonation reactor, (6) Water sample point, (7) KI trap.

The ozone, generated by an X200 Laboratory Ozone Generator (Baku), was produced from pure oxygen and was fed into the reactor through a porous diffuser located at the bottom of the reactor to produce fine bubbles. Gas flow was kept constant at 1 L/min, having an ozone concentration of 5.64 mg/L. The gaseous ozone concentration was measured by the iodometric method using 2% potassium iodide for ozone trapping and sodium thiosulfate as a titrant¹⁴. As soon as the ozone gas contacted the 4NCB solution, ZnO particles were dispersed in the solution. The contact time was 60 min and samples were withdrawn at different intervals (2, 5, 15, 30, 45, and 60 minutes) to determine the residual concentration of 4NCB. The change of concentration was measured by both the photometric and the HPLC methods during the reaction. The two methods gave similar results and the differences

ranged from 3.8% to 5.9%. The oxidation reaction was quenched by the addition of a small amount of sodium thiosulphate¹⁵. During the reaction, the reactor was sealed to avoid the evaporation of aqueous ozone. Triplicate experiments were conducted at 25±2 °C for verification of all results. HCl or NaOH solution was used to control the pH level during the reaction.

Analysis

The concentration of 4NCB was monitored by using high performance liquid chromatography (HPLC, Shimadzu, SCL-6A, Japan) with a UV absorbance detector (Shimadzu, SPD-6AV, Japan) and using a Spherisorb ODS-3 (5 µm, 150×4.6 mm i.d.) column. Elution was carried out by pumping acetonitrile and water (70:30 %v/v) and 0.2 cc acetic acid isocratically at a flow rate of 1.0 ml/min. Absorbance was measured at a wavelength of 279 nm using a Shimadzu UV-2501 recording spectrophotometer. The concentration of nitrate ions formed as a result of organically bounded nitrogen mineralization was measured with a spectrophotometer (HACH, DR/4000 U) at 275 nm. The pH of solution was measured with a 744 pH- meter (Ω Metrohm). TOC was measured with Shimadzu TOC-VCSH equipped with an autosampler (ASI-V) and platinum based catalyst. The carrier gas was synthetic air at the rate of 100 mL/min. Before measurement in all of the experiments, suspensions were centrifuged to collect the filtrate.

Results and Discussion

The experiments were carried out at room temperature during ozonation and catalytic ozonation.

Ozonation of 4NCB

Ozonation of 4NCB was carried out in a semi-batch reactor at a concentration of 15 mg/L using 5.64 mg/L of O₃. Calculation of consumed ozone per each mole of 4NCB was obtained by the Eq. 1¹⁶⁻¹⁷.

$$z = \frac{[O_3]_0}{[M]_0 - [M]} \quad \text{Eq. 1}$$

Where, [O₃]₀ and [M]₀ are initial concentration of ozone and 4NCB, respectively and [M] is a final concentration of 4NCB. From Table 1, maximum of ozone per mole of 4NCB is consumed at basic condition.

Table 1 Consumed mole of ozone per mole of each 4NCB.

pH	z
3	2.90
7	1.35
9	3.35

Figure 2 shows the effect of pH on the ozonation of 4NCB at different pHs. Concentration of 4NCB is plotted as a function of ozonation time.

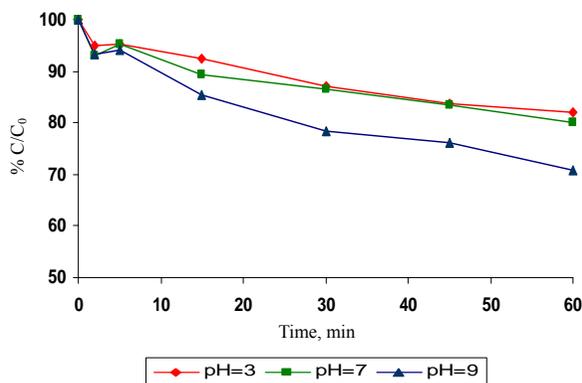


Figure 2. Effect of pH on ozonation of 4NCB $[O_3]_0 = 5.64$ mg/L; $[4NCB]_0 = 15$ mg/L.

As shown, after 60 min, 4NCB degradation was 17.91, 19.94, and 29.1% at pH 3, 7 and 9, respectively. Ozone is a dipolar molecule, *i.e.*, it had both electrophilic and nucleophilic property. On the base of results, it can be deduced the initial attack of ozone was occurred via nucleophilic nature of ozone, as the nitro and chloro electron withdrawing groups decrease the electron density of the ring and deactivate it against the electrophilic attack of O_3 ¹⁸.

Results show that ozonation alone is not significantly affect on degradation of 4NCB, so combination of catalyst with ozone was tested. For this, two different kind of catalysts was used, *i.e.*, TiO_2 and ZnO. The performance of both is examined and results showed nano-ZnO has the most effect on the removal of 4NCB compare to TiO_2 (Figure 3).

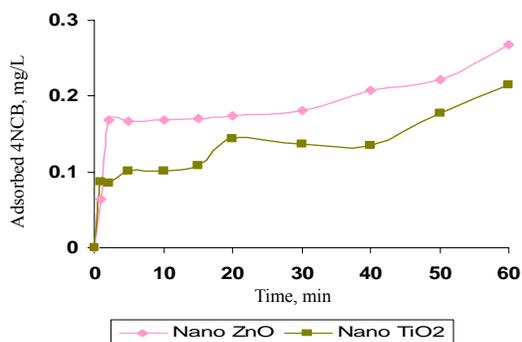


Figure 3. Evolution of the remaining concentration of 4NCB with time during catalytic ozonation by nano TiO_2 and ZnO $[4NCB]_0=15$ mg/L; $[ZnO]_0=300$ mg/L; $[TiO_2]_0=300$ mg/L; pH= 7.11.

To investigate the effects of particle size of catalyst, two different size of ZnO were applied, *i.e.*, micro and nano sized. As shown in Figure 4, nano ZnO has the higher performance, due to its high surface area.

Finally, nano sized ZnO selected as an appropriate catalyst during catalytic ozonation of 4NCB.

Catalytic ozonation of 4NCB

Degradation of 4NCB by nano-ZnO catalytic ozonation at different pHs showed the maximum decomposition took place at acidic medium (Figure 5).

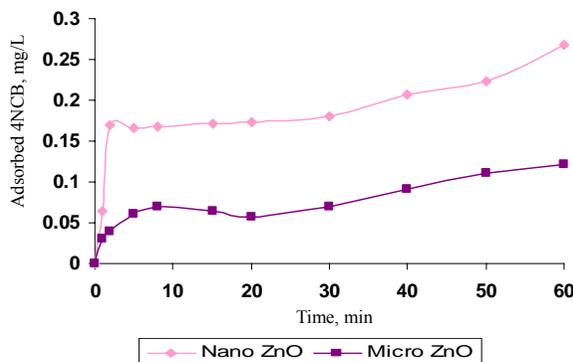


Figure 4. Evolution of the remaining concentration of 4NCB during catalytic ozonation at different ZnO particle size, $[4\text{NCB}]_0 = 15 \text{ mg/L}$; $[\text{ZnO}]_{\text{Micro}} = 300 \text{ mg/L}$; $[\text{ZnO}]_{\text{Nano}} = 300 \text{ mg/L}$; $\text{pH} = 7.11$.

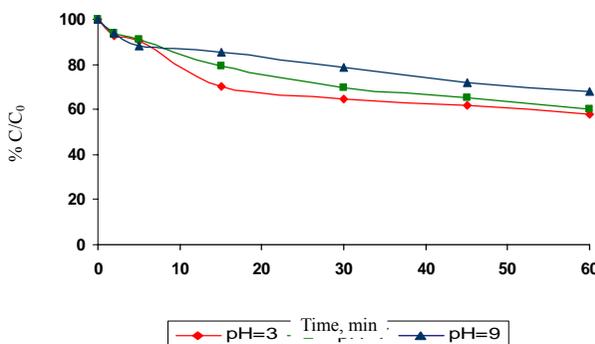


Figure 5. Effect of pH on nano-ZnO catalyzed ozonation of 4NCB $[\text{ZnO}] = 300 \text{ mg/L}$; $[\text{O}_3]_0 = 5.64 \text{ mg/L}$; $[4\text{NCB}]_0 = 15 \text{ mg/L}$.

It is clear pH affects the aggregation of nano-ZnO particles. Nano-ZnO particles significantly enlarged above $\text{pH} > 6.5$. At $\text{pH} 7.5$, the size of the ZnO reaches up to 350 nm^{19} . It is well known nano particles of metal oxides when suspended in water, formed aggregate²⁰. Result proved that though formation of free radicals at high pH, OH° dose not affect on catalytic ozonation process and the main factor is the surface of catalyst. So, due to increase of particle surface area at $\text{pH} = 3$, degradation of 4NCB is reached to 42.3%, while at $\text{pH} 7$ and 9 was 40.10 and 32.13%, respectively.

During catalytic ozonation of 4NCB, nitrogen was principally mineralized into nitrate. Concentration of nitrate formed during reaction was monitored (Figure 6) and results showed much formation of nitrate ions is obtained at $\text{pH} 3$ (4.15 mg/L). The remaining nitrogen atoms could be in nitro form or may be converted to nitro-intermediates that more resistant to ozone attack²¹.

TOC is total organic carbon that represents the total amount of organically bound carbon present in dissolved and particulate matter in water¹⁶. In ozonation processes, TOC slowly decrease with time in many cases¹⁵⁻¹⁶, but ozonation processes catalyzed by transition

metals have found to improve the TOC removal as compared to ozonation alone²². The effect of pH on mineralization of 4NCB in aqueous solution was shown during catalytic ozonation (Figure 7).

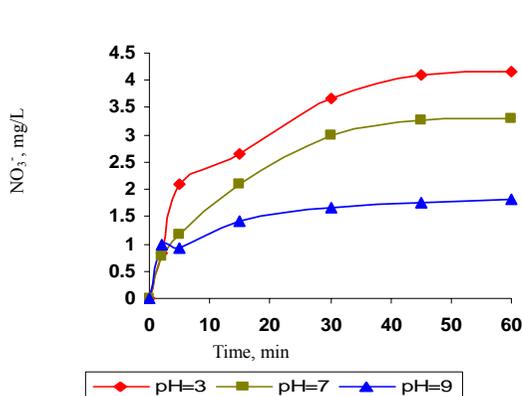


Figure 6. Released nitrate ion during the catalytic ozonation of 4NCB at different pHs. [ZnO] = 300 mg/L; [O₃]₀ = 5.64 mg/L; [4NCB]₀ = 15 mg/L.

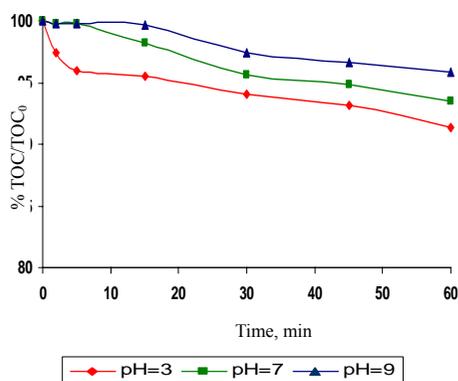


Figure 7. Changes of TOC during catalytic ozonation of 4NCB at different pHs. [ZnO] = 300 mg/L; [O₃]₀ = 5.64 mg/L; [4NCB]₀ = 15 mg/L.

The highest mineralization extents was achieved at pH=3(8.26%), while during ozonation it drops maximum to 2.1% (not shown here). It means that only part of 4NCB was mineralized and some by product formed during reaction that can not mineralized¹. So, this system dose not follow a free radical pathway²³.

Catalytic Ozonation Kinetic

The rate constant of reaction was obtained following 4NCB degradation at its maximum wavelength (279 nm) at pHs 3, 7, and 9.

The reaction form of 4NCB with nano-ZnO/O₃ can be written as:

$$\frac{d[4NCB]}{dt} = -k_{O_3} \cdot [4NCB][O_3][ZnO] + K_{OH^\ominus} \cdot [4NCB][OH^\ominus][ZnO] \quad \text{Eq. 2}$$

Where [4CNB], [ZnO] and [O₃] are the concentrations of 4CNB, zinc oxide, ozone and k_{o₃} and k_{OH^o} are the corresponding kinetic rate constant of 4NCB with O₃ and OH^o, respectively.

According to Goi *et al.*, direct reaction of molecular ozone with aromatic was predominant during the ozonation at pH values lower than 12²⁴. Therefore, the rate equation can be written in the form

$$\frac{d[4NCB]}{dt} = -K_{O_3} \cdot [4NCB][O_3][ZnO] \quad \text{Eq. 3}$$

In addition, ozone and zinc oxide concentration in the solution can be assumed to be

constant thus the term $k_{O_3} \cdot [O_3][ZnO]$ is constant and the Eq. 3 can be simplified to,

$$\frac{d[4NCB]}{dt} = -K'[4NCB] \quad \text{Eq. 4}$$

So, the reaction can be regarded as pseudo first order²⁵. The integration Eq. 4 Leads to

$$\ln \frac{[4NCB]}{[4NCB]_0} = -k' \cdot t \quad \text{Eq. 5}$$

Here, k' is the overall pseudo-first-order rate constant.

Figure 8 shows the pseudo first-order plot of 4NCB removal versus time at different pHs. The decomposition rate of 4NCB was found to decrease with increasing pH values. This result shows adsorption trend of 4NCB on the nano ZnO surface, which was pH-dependent and was occurred at $pH < 6$. Also, the decay rate of 4NCB improved by increase of process time.

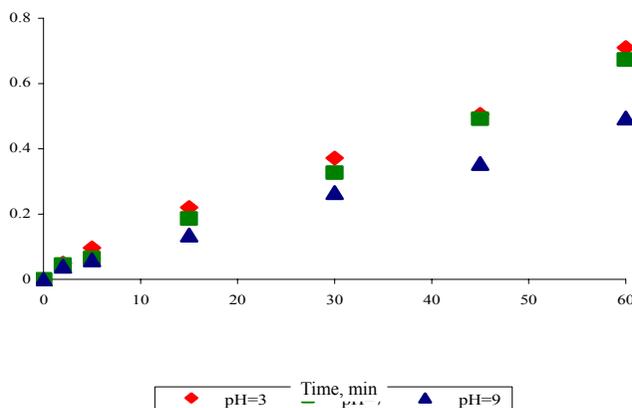


Figure 8. Determination of the rate constant for the reaction of 4NCB and O_3/ZnO at various pHs $[ZnO] = 0.3 \text{ mg/L}$; $[O_3]_0 = 5.64 \text{ mg/L}$ and $[4NCB]_0 = 15 \text{ mg/L}$.

Rate constant reaction (k') of 4NCB and O_3/ZnO at different pHs are summarized in Table 2. As shown in Table 2, k' is higher at acidic condition.

Table 2. The rate constant reaction of 4NCB with O_3/ZnO at various pHs. $[ZnO] = 300 \text{ mg/L}$; $[O_3]_0 = 5.64 \text{ mg/L}$ and $[4NCB]_0 = 15 \text{ mg/L}$.

pH	k', s^{-1}
3	1.98×10^{-4}
7	1.85×10^{-4}
9	1.38×10^{-4}

$k' = \text{Pseudo rate constant.}$

Conclusion

Semi-batch experiments were carried out to investigate the effect of pH on nano-ZnO

catalyzed ozonation of 4NCB. Unlike ozonation, the higher degradation of 4NCB was obtained at acidic condition, *i.e.*, OH^o has no main role. However the 4NCB is a recalcitrant compound and even in catalytic ozonation, its degradation reached to maximum 42.3% after 60 min. Nitrate ions detected during the reaction is confirmed conversion of nitrogen to nitrate. TOC was partly changes during process, that means only part of 4NCB was mineralized. Pseudo first rate constant of reaction was obtained at different pHs. The rate of 4NCB degradation was pH dependent and was faster at pH=3 ($1.98 \times 10^{-4} \text{ S}^{-1}$) due to high surface area of nano ZnO.

Acknowledgment

This work was supported by School of Pharmacy, Tabriz-Iran, and East Azerbaijan Water and Waste Water Company.

References

1. Shen J M, Chen Z L, Xu Z Z, Li X Y, Xu B B and Qi F, *J Hazard Mater.*, 2008, **152**, 1325.
2. Linch A L, *Am Ind Hyg Assoc J.*, 1974, **35**, 426.
3. Travlos G S, Mahler J, Ragan H A, Chou B J and Bucheret J R, *Fundam Appl Toxicol.*, 1996, **30**, 75.
4. Watanabe T, Ishihara N and Ikeda M, *Int Arch Occup Environ Health.*, 1976, **37**, 157.
5. Davydova S G, *Hyg Sanit.*, 1976, **32**, 161.
6. Glaze W H, Kang J W and Chapin D H, *Ozone Sci Eng.*, 1987, **9**, 335.
7. Carey J H, An introduction to advanced oxidation processes (AOP) for destruction of organics in wastewater. Proceedings of a Symposium on Advanced Oxidation Process for Contaminated Water and Air, 4–5 June, 1990, Toronto, Canada.
8. Ollis D, Pelizzetti E and Serpone N, *Environ Sci Technol.*, 1991, **25**, 1522.
9. Hofmann J, Freier U, Weeks M and Demund A, *Top Catal.*, 2005, **33**, 243.
10. Guittonneau S, De Laat J, Duguet J P, Bonnel C and Dore M, *Ozone Sci Eng.*, 1990, **12**, 73.
11. Duguet J P, Anselme C, Mazounie P, and Mallevalle J, *Ozone Sci Eng.*, 1990, **12**, 281.
12. Guittonneau S, De Laat J, Dore M, Duguet J P, and Suty H, *Environ Technol.*, 1990, **11**, 57.
13. Yang X Y, Ma J, Qin Q D, and Zhai X D, *J Mol Catal A: Chem.*, 2007, **267**, 41.
14. Langlais B, Reckhow D A and Brink D R, *Ozone in Water Treatment: Application and Engineering*; Lewis publishers, USA, 1991.
15. Gharbani P, Khosravi M, Tabatabaei S M, Zare K, Dastmalchi S, and Mehrizad A, *Int J Environ Sci Technol.*, 2010, **7**, 377.
16. Beltran F J, *Ozone Reaction Kinetics for Water and Wastewater Systems*, Lewis Publishers/CRC Press Company, USA, 2004.
17. Benitz F J, Acero J L, Real F J, and Garcia J, *Chemosphere*, 2003, **51**, 651.
18. Andrew Hong P K, and Zeng Y, *Water Res.*, 2002, **36**, 4243.
19. Jung H and Choi H, *Appl Catal B: Environ.*, 2006, **66**, 288.
20. Huang W J, Fang G C, and Wang C C, *Colloid Surf A*, 2005, **260**, 45.
21. Paprocki A, Santos H S, Hammerschitt M E, Pires M and Azevedo M N, *J Braz Chem Soc.*, 2010, **21**, 452.
22. Legube B, Karpel N, and Leitner V, *Catal Today*, 1999, **53**, 61.
23. Martins R C and Quinta-Ferreira R M, *Appl Catal B*, 2000, **90**, 268.
24. Goi A, Trapido, and Tuhkanen T, *Adv Environ Res.*, 2004, **8**, 303.
25. Gottschalk C, Libra J A, and Saube A, *Ozonation of Water and Wastewater*. Wiley-VCH publisher, 2000.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

