

## ENHANCEMENT OF 4-NITROPHENOL OZONATION IN WATER BY NANO ZnO CATALYST

<sup>1</sup>S. M. Tabatabaei, <sup>2</sup>S. Dastmalchi, <sup>3</sup>A. Mehrizad, \*<sup>1</sup>P. Gharbani

<sup>1</sup>Department of Chemistry, Ahar Branch, Islamic Azad University, Ahar, Iran

<sup>2</sup>Biotechnology Research Center and School of Pharmacy, Tabriz University of Medical Science, Tabriz, Iran

<sup>3</sup>Department of Chemistry, Science and Research Branch, Islamic Azad University, Tabriz, Iran

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### ABSTRACT

The removal of 4-nitrophenol (4NP) from aqueous solution by ozone combined with nano-ZnO was investigated in a laboratory-scale reactor in which pH of solution, ZnO dosage and initial 4-nitrophenol concentration were considered as variables. The degradation of 4-nitrophenol was determined using UV-Vis and HPLC methods. Interestingly, the degradation of 4-nitrophenol was high under acidic condition where the degradation was about 93% at initial phenol solution pH=3. It was due to aggregation of nano-ZnO particles above pH=6.5. This result was different from the case of ozonation alone, in which higher pH had positive effect on the degradation of 4-nitrophenol due to the formation of hydroxyl radical. As expected, degradation efficiency increased by increasing the nano ZnO dosage and initial 4-nitrophenol concentration. It was found that the nanosized ZnO enhanced the degradation of ozone and the catalytic ozonation enhanced the degradation of 4-nitrophenol on the surface of the nanosized ZnO. In addition, the degree of degradation was also determined indirectly through Total Organic Carbon (TOC) of the samples. Carbon mineralization of 4-nitrophenol was obtained as 13.68% and 60.34% during ozonation and nano-ZnO catalytic ozonation, respectively, after 30 min reaction, proving that combined ozonation and nano-ZnO for reduction of TOC is more efficient. Also a high degree of nitrogen mineralization during catalytic ozonation was achieved at pH= 3 (7.61mg/L).

**Key words:** 4-Nitrophenol; Ozonation; Nano ZnO; Total organic carbon; Nitrogen conversion

### INTRODUCTION

Nitroaromatic compounds are used in many industrial processes, including the preparation of pesticides, explosives, textiles and paper. Therefore, these compounds are often detected as water pollutants as a result of their release in industrial effluents (Sarasa *et al.*, 1998). Remediation of wastewaters containing these pollutants is very difficult, since they are usually resistant to biological degradation (O'Connor and Young, 1989). Among these nitroaromatic compounds, nitrophenols are common pollutants.

Nitrophenols (NPs) are the most common organic pollutants in industrial and agricultural effluents. Many processes have been developed for phenolic compounds removal such as adsorption (Marais and Nyokong, 2008), microbial degradation (O'Connor and Young, 1989; Movahedyan *et al.*, 2008), photocatalytic degradation (Soltanian and Havaee Behbahani, 2011), electrocoagulation (Modirshahla *et al.*, 2008) and electrochemical treatment (Cañizares *et al.*, 2004), and so on. *P*-Nitrophenol has been widely used in the production of pesticides, herbicides, dyes, and other industrial chemicals. On the other hand, 4-nitrophenol is an important intermediate for the

\*Corresponding author: E-mail: p-gharbani@iau-ahar.ac.ir  
Tel: +98 426 222 82 11, Fax: +98 426 222 78 72

manufacture of analgesic and antipyretic drugs (Chang and Chen, 2009). As a result of these widespread applications, wastewaters and water resources, including groundwater and surface waters, have become contaminated with this compound.

*P*-Nitrophenol, which is listed by the USEPA as a priority pollutant, is toxic and thereby harmful to public health and aquatic life (Shi *et al.*, 2005). In many cases, chemical industries use a large quantity of water and thus generating considerable amount of toxic and harmful industrial effluent. Sometimes conventional wastewater treatment method failed to treat persistent organic pollutant effectively. Chemical oxidation with ozone can be used to treat organic pollutants (Yogeswary and Mohd, 2007). Ozone is an allotrope of oxygen and is more powerful than chlorine and other oxidants and reacts with many compounds via direct or indirect reactions (Nabi Bidhendi *et al.*, 2006; Rajeswari and Kanmani, 2009). Although ozone has been known as a strong oxidant, it has the limitation with regards to the selectivity of organic compounds and the generation of oxidation byproducts (Langlais *et al.*, 1991).

Advanced oxidation processes (AOPs) have been considered to overcome these limitations in ozonation processes, because AOPs are designed to enhance the production of OH° radicals, which are known to be nonselective oxidants. Another alternative is to use a metal catalyst for the ozonation, as it can initiate the decomposition of aqueous ozone (Jung and Choi, 2006). Also, it has been clearly demonstrated that solid metal catalysts can effectively be utilized to improve the ozonation efficiency for the removal of organic compounds (Andreozzi *et al.*, 1996; Legube and Leitner, 1999). Beltran *et al.* (2003) reported that decomposition efficiency of ozone in the heterogeneous catalytic ozonation was higher than that found in the homogeneous catalytic ozonation.

Heterogeneous catalytic ozonation is a novel type of advanced oxidation which combines ozone with the adsorptive and oxidative properties of solid-phase metal oxide catalysts to achieve the

mineralization of organic pollutants at room temperature (Huang *et al.*, 2005). The most common catalysts proposed for the process of heterogeneous catalytic ozonation are metal oxides such as MnO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ZnO (Zhao *et al.*, 2002). Among them, zinc oxide appears as a very promising photocatalyst for degradation of organic solutes in aqueous systems (Daneshvar *et al.*, 2004). In some cases, ZnO has been reported to be more efficient than TiO<sub>2</sub>. Its efficiency has been reported to be particularly noticeable in the advanced oxidation of pulp mill bleaching wastewater (Yeber *et al.*, 2000).

In recent years, nanophase materials have gained more attention because of special physical and chemical features. The nanosized ZnO with the features of large volume to area ratio is a well-known catalytic material which, is used as a heterogeneous catalyst, with high catalytic activity, non-toxicity, insolubility and low cost (Huang *et al.*, 2005; Hong *et al.*, 2009). More recently, nanosized ZnO materials were tested in the catalytic ozonation of *para*-chlorobenzoic acid (Jung and Choi, 2006) and 2,4,6-trichlorophenol (Huang *et al.*, 2005). In both works, ZnO was found to promote the formation of OH° from the decomposition of ozone, leading to the enhanced degradation of the selected organic molecules. Only a few studies have assessed the effect of ozonation on the biodegradability and toxicity of NPs ozonised solutions (Adams *et al.*, 1997). They found out that ozonation of 4-nitrophenol (4NP) and 2,4-dinitrophenol (2,4-DNP) at pH=7.0 substantially enhanced their biodegradability. Stover *et al.*, (1982) found out that ozonation slightly increased the biodegradability of 2,4-DNP. These sparse data have demonstrated that further studies on the application of ozonation for the degradation of NPs, as a group of quite bio-resistant toxic compounds, are required (Ahmadimoghaddam *et al.*, 2010). A comparative assessment of O<sub>3</sub>, O<sub>3</sub>/UV, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub> (Trapido *et al.*, 2001) UV/H<sub>2</sub>O<sub>2</sub>, Fenton and photo-Fenton oxidation processes (Goi and Trapido, 2002) performance in terms of kinetic parameters of NPs removal in water was carried out. Synergistic

effects for *p*-nitrophenol degradation were observed in the ozonation with ultrasonic enhancement. The enhancements of removal rate for *p*-nitrophenol and TOC were around 11.6% and 294%, respectively in comparison with the individual ultrasound and ozonation systems (Xu *et al.*, 2005).

The present study was focused on the influence of nano-ZnO catalytic ozonation on the degradation of 4NP.

## **MATERIALS AND METHODS**

4-nitrophenol [ $C_6H_5NO_3$ ,  $M=139.11$ ] (Merck Co.) was used as the probe compound. A stock solution of 4NP was prepared in deionized water (Millipore Milli-Q water) at a concentration of approximately 16 mg/L. Nano and micro ZnO were supplied from Aldrich and Sigma-Aldrich (USA), respectively. Nanosized and microsized ZnO was <100 nm (Surface area=15-25  $m^2/g$ ) and <5 $\mu m$ , respectively. All solutions were prepared by using deionized water. All other chemicals such as sodium thiosulphate, potassium iodide etc., were reagent grades and were supplied from Merck, Germany.

Catalytic activity measurements were carried out in a semi-batch stirred reactor, where ozone gas was continuously poured through a fine-bubble ceramic diffuser into a glass reactor (2000 mL) with 1L of aqueous solution containing 16 mg/L of 4NP and 300 mg of ZnO that was completely mixed with a magnetic stirring bar. A glass reactor of 150 mm diameter and 250 mm length was equipped with a ceramic diffuser. 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 1L/min, having an ozone concentration of 5.64 mg/L. The gaseous ozone concentration was measured by the iodometric method using 2% neutral buffered potassium iodide for ozone trapping and sodium thiosulfate as a titrant (Langlais *et al.*, 1991). ZnO particles were dispersed in the solution as soon as the ozone gas contacted the 4NP solution. The contact time was 30 min and samples were withdrawn at different intervals (2, 5, 10, 15, 20, 30 minutes)

to determine the residual concentration of 4NP by both photometric and HPLC methods. Triplicate experiments were conducted at  $25\pm 2^\circ C$ .

The oxidation reaction was quenched by the addition of a small amount of sodium thiosulphate. During the reaction, the reactor was sealed to avoid the evaporation of aqueous ozone. HCl or NaOH solution was used to control the pH level during the reaction. 4NP was measured by using high performance liquid chromatography (HPLC, Shimadzu, SCL-6A, Japan) with a UV absorbance detector (Shimadzu, SPD-6AV, Japan) and a using a Spherisorb ODS-3 (5  $\mu m$ , 150 $\times$ 4.6 mm i.d.) column. Elution was carried out by pumping acetonitrile and water (70:30 %v/v) and 0.2 mL acetic acid isocratically at a flow rate of 1.0 mL/min. Absorbance was measured at a wavelength of 402 nm (basic and neutral solution) and 317nm (acidic solution) using a Shimadzu UV-2501 recording spectrophotometer. TOC was measured with Shimadzu TOC-VCSH equipped with an autosampler (ASI-V) and platinum-based catalyst. The concentration of nitrate ions formed because of organically bounded nitrogen mineralization was measured with a spectrophotometer (HACH, DR/4000 U) at 275 nm. Before measurement in all of the experiments, suspensions were centrifuged and then filtered with 0.2 $\mu m$  micro filters to collect the filtrate.

## **RESULTS**

### *Assay*

The validated HPLC and the UV-Visible spectrophotometer methods were used in the analysis of the 4NP. The statistical parameters and results are reported in Table 1. The differences between the concentrations obtained by UV-Vis spectrophotometer and HPLC were not significant and the results were in close agreement with each other. The standard deviation observed for HPLC and UV-Vis spectrophotometric methods were 0.85 and 0.63, respectively. From the presented results it can be concluded that both methods (UV-Vis and HPLC) can be used for the determination of 4NP. One way

Solution No.	UV-Vis Spectrophotometer	HPLC
1	5.701	5.01
2	7.4	6.6
3	6.9	5.9
4	5.1	6.2
5	5.4	6.4
6	6.9	5.9
7	6.5	5.7
8	6.1	7.1
9	7.3	7
10	7.4	5.9
Mean	6.4701	6.171
SD	0.85	0.63
CV	13.13%	10.20%

t-Test calculation was done to compare the concentrations analyzed by the two methods. t value was obtained about  $0.4 < 1.73$  ( $P=0.05$ ), confirming that the mean differences between results obtained by both methods are not significant.

*Ozonation of 4NP*

The effect of pH on ozonation of 4NP was studied in a semi-batch mode. As shown in Fig. 1, at pH=3

the degradation efficiency was low. After pH was increased over 7, the degradation efficiency of 4NP began to rise obviously. When pH increased from 3 to 9, the degradation efficiency increased from 57% to 76% (initial 5 min).

*Effect of size of ZnO particles*

Fig. 2 shows the time course of the 4NP degradation by catalytic ozonation of nano and microsized ZnO. The initial rate of 4NP degradation by nanoZnO was greater than those of microZnO. About 93% of the 4NP was degraded with nanoZnO at the first 5 minutes. while, in the presence of micro ZnO only 70% of 4NP was degraded.

*Effect of initial nano ZnO concentration*

The solution was ozonated at 5.64 mg/L dosage and using three different weight concentrations of nanoZnO particles as catalyst. The ozone contact time was controlled from 0 to 30 min. Fig. 3 presents the effect of nano ZnO concentration on degradation of 4NP during catalytic ozonation. It was found that 4NP decomposition behavior varied as a function of nanoZnO concentration and the increase of ZnO concentration from 100 to 300 mg/L led to the increase of 4NP decomposition from 69% to 93%, respectively (at initial 5 min).

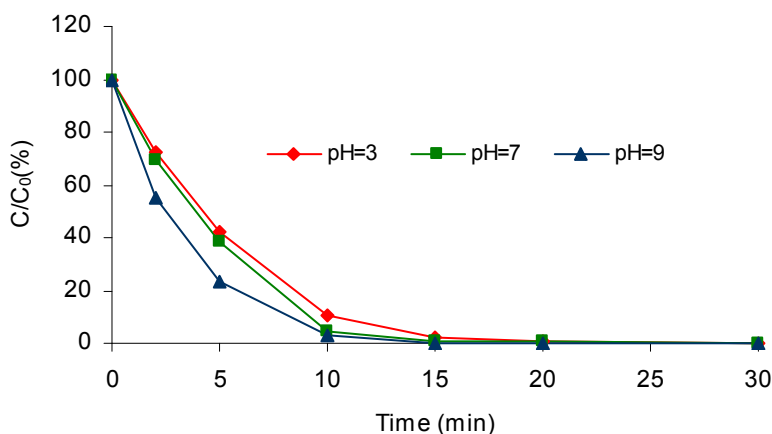


Fig. 1: Effect of pH on degradation of 4NP by ozone:  $[O_3]_0 = 5.64$  mg/L;  $[4NP]_0 = 16$  mg/L

*Effect of initial 4NP concentration*

The influence of the initial 4NP concentration on the decomposition of 4NP was carried out and the results are presented in Fig. 4. The decomposition of 4NP increased as the initial 4NP concentration was increased. It was about 63%, 68%, 75% and 93% for 10, 12, 14 and 16 mg/L of 4NP, respectively.

*Effect of initial pH*

Since pH is a main factor for both ozone stability and catalyst surface properties in aqueous solution, it is important to examine the influence of pH on catalytic ozonation. As shown in Fig. 5, adsorption of 4NP on nano ZnO surface varied slightly with pH of the solution and reached

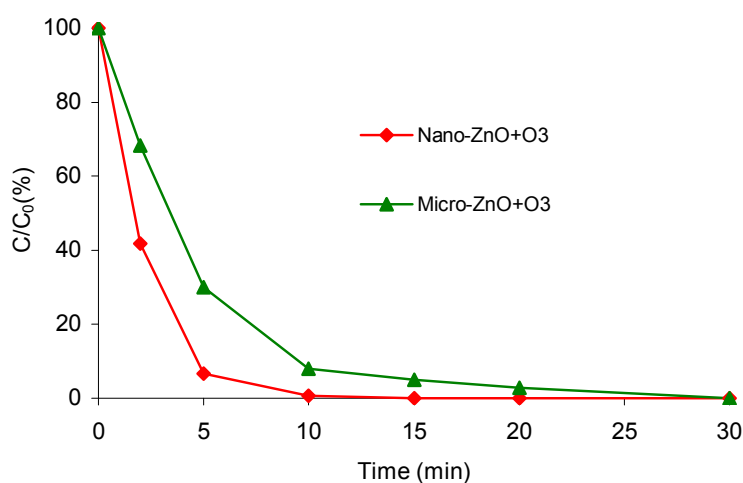


Fig. 2: Effect of size of ZnO particles on 4NP degradation: [4NP]<sub>0</sub>=16 mg/L; [O<sub>3</sub>]<sub>0</sub> = 5.64 mg/L; [ZnO]<sub>Micro</sub>=300 mg/L; [ZnO]<sub>Nano</sub>=300 mg/L; pH= 6.5

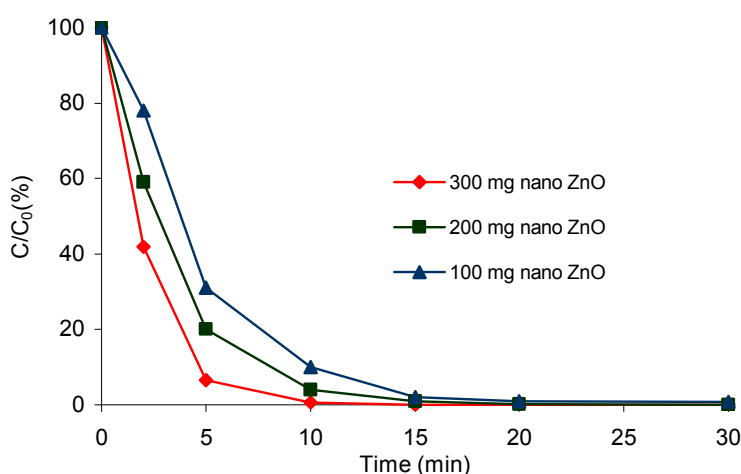


Fig. 3: Effect of initial nano ZnO concentration on catalytic ozonation of 4NP: [O<sub>3</sub>]<sub>0</sub> = 5.64 mg/L; [4NP]<sub>0</sub>=16 mg/L; pH=6.5

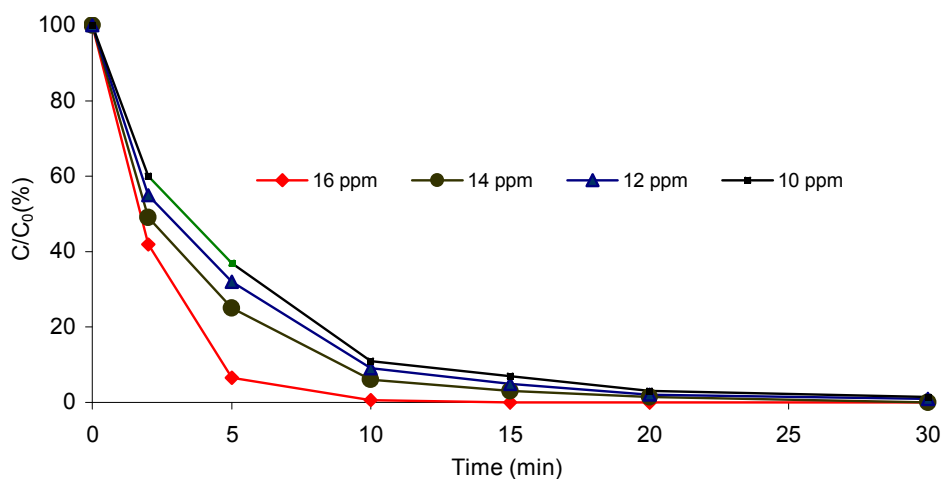


Fig. 4: Effect of initial 4NP concentration on catalytic ozonation of 4NP:  $[O_3]_0 = 5.64$  mg/L; nano ZnO=300 mg/L; pH=6.5

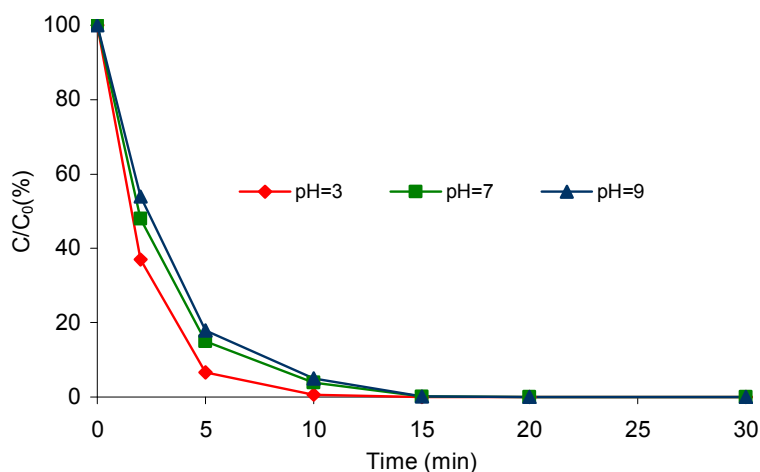


Fig. 5: Effect of pH on catalytic ozonation of 4NP:  $[O_3]_0 = 5.64$  mg/L;  $[4NP]_0 = 16$  mg/L; nano ZnO =300 mg/L

maximum at pH=3.

Among the factors that contribute to the degradability improvement is the nitrogen mineralization, transformation of aromatics to aliphatic by ring opening reactions and ring hydroxylation (Dieckmann and Gray, 1996; Adams *et al.*, 1997). The formation of nitrate as a result of mineralization of organically bounded

nitrogen during 4NP catalytic ozonation is shown in Fig. 6. Nitrate formation was fast at the initial stage of ozonation until 86%–93 % (initial 5 min.) of 4NP was degraded and then the degradation slowed down. Further formation of nitrate during the catalytic ozonation was observed even when 100% of NP was degraded (Fig. 6 ).

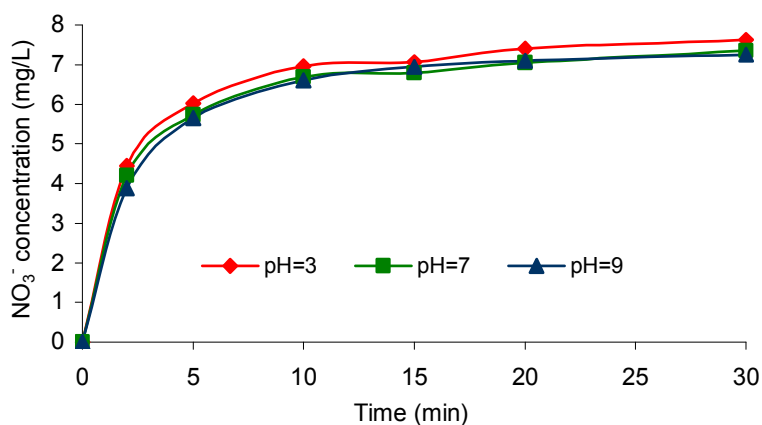


Fig. 6: Formation of nitrate ion during the catalytic ozonation of 4NP at different pHs  
[O<sub>3</sub>]<sub>0</sub> = 5.64 mg/L; [4NP]<sub>0</sub> = 16 mg/L; nano ZnO = 300 mg/L

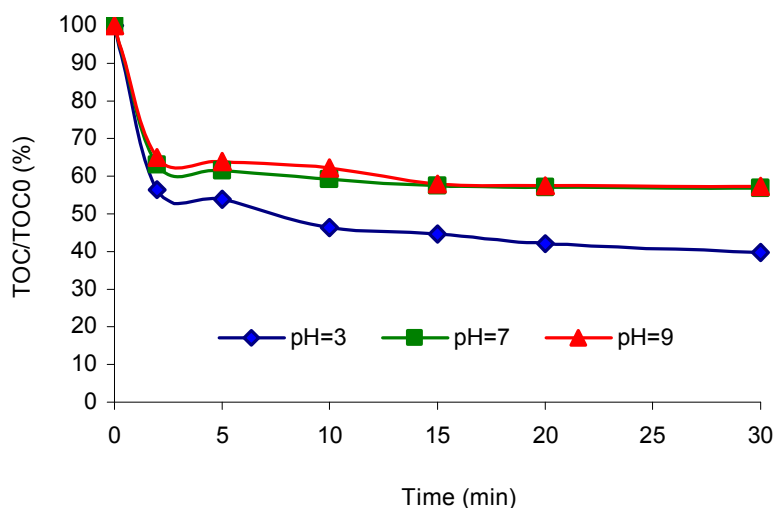


Fig. 7: TOC removal during the degradation of 4NP by catalytic ozonation at different pH:  
[O<sub>3</sub>]<sub>0</sub> = 5.64 mg/L; [4NP]<sub>0</sub> = 16 mg/L; nano ZnO = 300 mg/L

TOC yields the quantity of organic matter transformed in CO<sub>2</sub>. During ozonation it does not give a quantitative value for the oxidation evolution (Beltran, 2004). The degree of carbon mineralization during catalytic ozonation of 4NP is shown in Fig. 7.

## DISCUSSION

From Fig. 1, it was noted that the optimum pH for degradation of 4NP by ozone is 9 in this test. This was due to the OH<sup>-</sup> ions generated at pH=9, that functioned as the initiator of radical chain reaction. While in acidic condition, the ozone molecule was one of the main reactive species, so



the degradation of 4NP exhibited low efficiency (Gharbani *et al.*, 2010).

The degradation rate of 4NP was shown to be ZnO size dependent. The decay rate increased with decrement of particle size of ZnO due to high surface area of nanoparticles. So, the degradation was followed by nano ZnO (Huang *et al.*, 2005).

It is evident that removal of 4NP was due to the action of some ozone absorbed species or free radicals generated probably on the catalyst surface or in the aqueous bulk solution. Catalyst dose exerted a positive influence on 4NP conversion in catalytic ozonation process (Yang, 2007). It is believed that the production of hydroxyl radicals and ozone loss was accelerated on the surface of ZnO during catalytic ozonation (Jung and Choi, 2006). So, it can be concluded that the 4NP concentration drop is duo to the enhanced ozone decomposition by nano ZnO (Huang *et al.*, 2005; Jung and Choi, 2006).

The degradation increased by increasing of initial concentration of 4NP. The results may be explained by the fact that, the initial concentration provides the necessary driving force to overcome the resistances to the mass transfer of 4NP between the aqueous and the solid phase. (Yang *et al.*, 2007).

During catalytic ozonation, the maximum degradation of 4NP was occurred at pH=3. It is already well known that nanosized particles including metal oxides form aggregates when suspended in water (Huang *et al.*, 2005), and this property of them depends on the concentration of particles and the pH of solution. It is well known that pH affects on the aggregation of nano ZnO particles. For pH>6.5, nano ZnO particles aggregates and forms large clusters. The size of ZnO reaches to 350 nm at pH=7.5 (Jung and Choi, 2006) and due to decrease in surface area, its efficiency is decreased. Therefore, this factor was under consideration in the present study. Cleavage of nitro-group from the aromatic ring and its conversion to nitrate occur during the degradation of 4NP. Nitrite ion that was followed in the reaction was subsequently oxidized in nitrate

ion. Among the inorganic nitrogen species, nitrate was the predominant one. This can be explained by the cleavage of nitro-group from nitrated aliphatic intermediates (Goi *et al.*, 2004), which are formed during catalytic reaction. Fig. 6 shows that the degree of nitrogen mineralization during 4NP catalytic ozonation at pH= 3 was a little higher than at initial pH= 9.

It is clear that, at least 100% degradation of 4NP (at initial 10 min.) led to the 55% removal of TOC. Carbon mineralization was very slow during the degradation of 4NP by ozonation (about 13%, not shown here), while catalytic ozonation could improve TOC removal (up to 55%). TOC barely decreases with time in many cases during ozonation processes and this is very often observed in ozonation processes. On the other hand, TOC gives a measure of the carbon mineralization achieved in the ozonation process (Beltran, 2004).

From this study it can be concluded that use of nano-ZnO powder as catalyst for the catalytic ozonation of 4NP in water significantly accelerated its removal compared with ozonation alone; The oxidation efficiency was higher at low pH (pH =3) and increased by increasing the nano ZnO dosage and 4NP concentration. Thus, in nano ZnO catalytic ozonation, the adsorption of organic micropollutants on catalyst was an important step, which would have a direct influence on the catalytic effectiveness of the heterogeneous catalytic system. Also, catalytic ozonation notably enhanced the carbon mineralization.

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## REFERENCES

- Adams, C. D., Cozzens, R. A., Kim, B. J., (1997). Effects of ozonation on the biodegradability of substituted phenols. *Water Res.*, **31**:2655–2663.
- Ahmadimoghaddam, M., Mesdaghinia, A., Naddafi, K., Nasser, S., Mahvi, A.H., Vaezi, F., Nabizadeh, R., (2010). Degradation of 2,4-Dinitrophenol by Photo Fenton Process. *Asian J.Chem.*, **22**: 1009 –



- 1016.
- Andreozzi, R., Insola, A., Caprio, V., Marotta, R., Tufano, V., (1996). The use of manganese dioxide as a heterogeneous catalyst for oxalic acid ozonation in aqueous solution. *Appl. Catal. A*, **138**: 75-81.
- Beltran, F. J., (2004). *Ozone Reaction Kinetics for Water and Wastewater Systems*. Lewis publishers.
- Beltran, F. J., Rivas, F. J., Montero-de-Espinosa, R., (2003). Ozone enhanced oxidation of oxalic acid in water with cobalt catalysts. I. Homogeneous catalytic ozonation. *Ind. Eng. Chem. Res.*, **42**: 3218-3224.
- Cañizares, P., Sáez, C., Lobato, J., Rodrigo, M. A., (2004). Electrochemical treatment of 4-nitrophenol containing aqueous wastes using boron-doped diamond anodes. *Ind. Eng. Chem. Res.*, **43**: 1944-1951.
- Chang, Y.C., and Chen, D.H., (2009). Catalytic reduction of 4-nitrophenol by magnetically recoverable Au nanocatalyst. *J. Hazard. Mater.*, **165**: 664-669.
- Daneshvar, N., Salari, D., Khataee, A.R., (2004). Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO<sub>2</sub>. *J. Photoch. Photobio A*, **162**: 317- 322.
- Dieckmann, M. S., and Gray, K. A., (1996). A comparison of the degradation of 2-nitrophenol via direct and sensitized photocatalysis TiO slurries. *Water Res.*, **30**: 1169-1183.
- Gharbani, P., Khosravi, M., Tabatabaei, S.M., Zare, K., Dastmalchi, S., Mehrizad, A., (2010). Degradation of trace aqueous 4-chloro-2-nitrophenol occurring in pharmaceutical industrial wastewater by ozone. *Inter. J. Environ. Sci. Technol*, **7**:377-384.
- Goi, A., and Trapido, M., (2002). Hydrogen peroxide photolysis, Fenton reagent and photo-Fenton for the degradation of nitrophenols: a comparative study. *Chemospher*, **46**: 913-922.
- Goi, A., Trapido, M., Tuhkanen, T., (2004). A study of toxicity, biodegradability and some by-products of ozonised nitrophenols. *Ad. Environ. Res.*, **8**: 303-311.
- Huang, W. J., Fang, G. C., Wang, C. C., (2005). A nanometer-ZnO catalyst to enhance the ozonation of 2,4,6-trichlorophenol in water. *Colloids Surf. A*, **260**: 45-51.
- Hong, R.Y., Li, J.H., Chen, L.L., Liu, D.Q., Li, H.Z., Zheng, Y., Ding, J., (2009). Synthesis, surface modification and photocatalytic property of ZnO nanoparticles. *Powder Technology*, **189**: 426-432.
- Jung, H., and Choi, H., (2006). Catalytic decomposition of ozone and para-chlorobenzoic acid(pCBA) in the presence of nanosized ZnO. *Appl. Catal. B: Environ.*, **66**: 288-294.
- Langlais, B., Reckhow, D. A., Brink, D. R., (1991). *Ozone in Water Treatment: Application & Engineering*. Lewis Publisher.
- Legube, B., and Leitner, N.K.V., (1999). Catalytic ozonation: a promising advanced oxidation technology for water treatment. *Catal. Today*, **53**: 61-72.
- Marais, E., and Nyokong T., (2008). Adsorption of 4-nitrophenol onto Amberlite® IRA-900 modified with metallophthalocyanines. *J. Hazard. Mater.*, **152**: 293-301.
- Modirshahla, N., Behnajady, M.A., Mohammadi-Aghdam, S., (2008). Investigation of the effect of different electrodes and their connections on the removal efficiency of 4-nitrophenol from aqueous solution by electrocoagulation. *J. Hazard. Mater.*, **154**: 778-786.
- Movahedian, H., Assadi, A., Amin, M.M., (2008). Effects of 4-chlorophenol loadings on acclimation of biomass with optimized fixed time sequencing batch reactor. *Iran J. Environ. Health Sci & Eng.*, **5** : 225-234
- Nabi Bidhendi, G.R., Hoveidi, H., Jafari, H.R., Karbassi, A.R., Nasrabadi, T., (2006). Application of ozonation in drinking water disinfection based on an environmental management strategy approach using swot method, *Iran. J. Environ. Health. Sci. Eng.*, **3**: 23-30.
- O'Connor, O.A., Young, L.Y., (1989). Toxicity and anaerobic biodegradability of substituted phenols under methanogenic conditions. *Environ. Toxicol. Chem.*, **8**: 853-862.
- Rajeswari, R., and Kanmani, S., (2009). TiO<sub>2</sub>-based heterogeneous photocatalytic treatment combined with ozonation for carbendazim degradation. *Iran. J. Environ. Health. Sci. & Eng.*, **6**: 61-66.
- Sarasa, J., Roche, M. P., Ormad, M. P., Gimeno, E., Puig, A., Ovelleiro, J. L., (1998). Treatment of a wastewater resulting from dyes manufacturing with ozone and chemical coagulation. *Water Res.*, **32** :2721-2727.
- Shi, H.x., Xu, X.W., Xu, X.H., Wang, D.H., Wang, Q.D., (2005). Mechanistic study of ozonation of p-nitrophenol in aqueous solution. *J. Environ.Sci.*, **17**: 926-929.
- Soltanian, G.R., Havaee Behbahani, M., (2011). The effect of metal oxides on the refinery effluent treatment. biological treatment. *Iran J. Environ. Health Sci & Eng.*, **8** : 147-156.
- Stover, E.L., Wang, L. W., Medley, D.R., (1982). Ozone assisted biological treatment of industrial wastewaters containing biorefractory compounds. *Ozone Sci. Eng.*, **4**:177-194.
- Trapido, M., Veressinina Y., Kallas, J., (2001). Degradation of aqueous nitrophenols by ozone combined with UV-radiation and hydrogen peroxide. *Ozone Sci. Eng.*, **32**: 333-342.
- Xu, X.W., Shi, H.X., Wang, D.H., (2005). Ozonation with ultrasonic enhancement of p-nitrophenol wastewater. *J. Zhejiang Univ. Sci.*, **6B**: 319-323.
- Yang, Y., Ma, J., Qin, Q., Zhai, X., (2007). Degradation of nitrobenzene by nano-TiO<sub>2</sub> catalyzed ozonation. *J. Molec. Catal. A: Chem.*, **267**: 41-48.
- Yeber, M.C., Rodriguez, J., Freer, J., Durán, N., Mansilla, H.D., (2000). Photocatalytic degradation

- of cellulose bleaching effluent by supported TiO<sub>2</sub> and ZnO. *Chemosphere*, **41**: 1193-1197 .
- Yogeswary, P., Rashid Mohd, M., (2007). Degradation of phenol by catalytic ozonation. *J. Chem.Natur. Resour. Engin.*, **2** : 34-46
- Zhao, L., Sun, Z., MA, J., (2009). Novel Relationship between Hydroxyl Radical Initiation and Surface Group of Ceramic Honeycomb Supported Metals for the Catalytic Ozonation of Nitrobenzene in Aqueous Solution. *Environ. Sci. Technol.*, **43**: 4157-4163.