

## Short Communication

# The Effect of pH on Nanosized ZnO Catalyzed Degradation of 4-Chloro-2-Nitrophenol via Ozonation

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(Received: 18 Mar. 2012 and Accepted: 23 June. 2012)

### Abstract:

*This research evaluates the efficiency of nanosized ZnO in the catalytic ozonation of 4-chloro-2-nitrophenol and determines the effect of pH on heterogeneous catalytic ozonation. The combined use of ozone and ZnO catalyst leads to conversion of 98% 4-chloro-2-nitrophenol during 5 min. In addition, it was found that in ZnO catalytic ozonation, the degradation efficiency of 4-chloro-2-nitrophenol was higher at low pH conditions (pH 3.0) than higher pH (pH 7–9). This result was not agreed in the case of ozonation alone, following which higher pH had positive effect on the degradation of 4-chloro-2-nitrophenol. At pH=3, the amount of total organic carbon was 54%. In the degradation of 4-chloro-2-nitrophenol by catalytic ozonation, the high reaction rate constant was obtained in acidic solution.*

**Keywords:** Heterogeneous catalytic, Total organic carbon, Nano catalyst, Ozonation, Nano ZnO.

## 1. INTRODUCTION

4-Chloro-2-nitrophenol (4C2NP), selected as a model compound in the present study, is widely available in bulk drugs and pesticide wastes. It is recalcitrant and persistent towards biodegradation and is constituent intermediate of many industrial effluents. The generation of 4C2NP containing aqueous wastes during formulation, distribution and field application of pesticides is often unavoidable [1]. Ozonation is an attractive and increasingly important method for the degradation of organic pollutants in aqueous solution. However, the refractory organic compounds are not usually oxidized totally and only a small mineralization is achieved during ozonation. Moreover, the practical use of ozonation for wastewater treatment is limited by its high-energy demand. Several approaches have been taken to improve the oxidizing power of

this technique leading to reduction of the required reaction time and hence, decreasing its energy cost [2]. In this way, the combination of solid catalysts with ozone have recently demonstrated interesting capacities for the oxidation of industrial wastewater and surface waters [3-5], and for the removal of numerous model compounds from dilute aqueous solutions [6-7]. 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 mineralization of organic pollutants at room temperature [2]. Zinc oxide (ZnO) nanoparticles have been investigated in the areas of photocatalytic reactions and the catalytic ozonation due to their advantages of high catalytic capacity, low cost and low toxicity [8]. Additionally, nanoscale ZnO exhibits lower ionization potentials, as the particle diameter is decreased [9]. ZnO and

its mixed-metals (i.e. zinc ferrite) have been used as photocatalyst that decompose halogen compounds, and the photocatalytic activity is increased as the size of ZnO particles reached nanometer levels [10-11]. Jung and Choi [8] reported that the nanosized ZnO enhanced the degradation of ozone and the catalytic ozonation on the surface of the nanosized ZnO enhanced the degradation of pCBA significantly. Huang et al. [2] concluded that the combined use of O<sub>3</sub> and ZnO catalyst leads to 99.8% of 2,4,6-trichlorophenol conversion in 30 min which favorably compares to the hardly 75% reached in the absence of the catalyst. The high reactivity of hydroxyl radicals that were generated by O<sub>3</sub>-ZnO during the oxidation process degraded TCP effectively [2]. Therefore, the objectives of this study were, (1) to investigate the effect of pH on ZnO catalytic ozonation and (2) to evaluate the efficiency of the nanosized and microsized ZnO in the catalytic ozonation.

## 2. MATERIALS AND METHODS

### 2.1. Materials

4-Chloro-2-nitrophenol (4C2NP) [C<sub>6</sub>H<sub>4</sub>ClNO<sub>2</sub>, M=173.56] (Fluka Co.) was used as the probe to investigate the catalytic ozonation process. A stock solution of 4C2NP was prepared in deionized water (Millipore Milli-Q water) at a concentration of approximately 69 μM (12 mgL<sup>-1</sup>). Nano and micro ZnO were supplied from Aldrich and Sigma-Aldrich (USA), respectively. Nanosized ZnO were <100 nm and their surface area (15-25 m<sup>2</sup>g<sup>-1</sup>) were determined by a BET surface area analyzer. All solutions were prepared by using deionized water (Ultrapure system, Barnsted). All other chemicals such as sodium thiosulphate, potassium iodide and etc., were reagent grades and were supplied from Merck, Germany.

### 2.2. Catalytic ozonation experiments

Catalytic activity measurements in removal of 4C2NP 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 12 mgL<sup>-1</sup> of 4C2NP and 300 mg of catalyst 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<sup>-1</sup>, having an ozone concentration of 5.64 mgL<sup>-1</sup>. 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 [12]. Nano-ZnO particles were dispersed in the solution as soon as the ozone gas contacted the 4C2NP solution. The contact time was 30 min and samples were withdrawn at different intervals (1, 2, 5, 10, 15, 20 and 30 minutes) to determine the residual concentration of 4C2NP by both the photometric and the HPLC methods. The two methods gave similar results and the differences ranged from 2.6% to 4.7%. 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. Triplicate experiments were conducted at 25±2°C for verification of all results. HCl or NaOH solution was used to control the pH during the reaction.

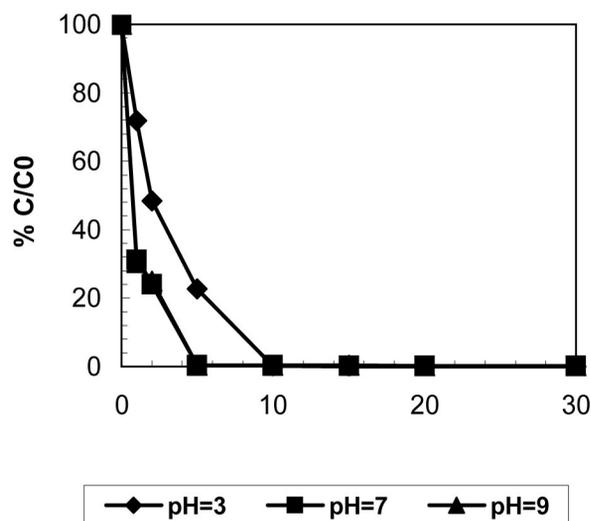
### 2.3. Analysis

4-Chloro-2-nitrophenol 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 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 1.0ml min<sup>-1</sup>. Absorbance was measured at a wavelength of 234 nm (basic & neutral solution) and 219 nm (acidic solution) using a Shimadzu UV-2501 recording spectrophotometer. 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<sup>-1</sup>.

The samples were acidified to  $\text{pH} < 4$  before being sent to TOC analyzer to ensure that inorganic carbon would be released from the solution as  $\text{CO}_2$ . 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 filtered with  $0.2 \mu\text{m}$  micro filters to collect the filtrate.

### 3. RESULTS AND DISCUSSION

In a heterogeneous catalytic ozonation system, pH has two main direct effects on the oxidation, i.e., ozone decomposition and the surface property of solid catalyst [13]. On the other hand, in heterogeneous catalytic system, pH could influence the surface property of metal oxides [14].



**Figure 1:** Effect of pH on ozonation of 4C2NP  
 $[\text{O}_3]_0 = 5.64 \text{ mgL}^{-1}$ ;  $[\text{4C2NP}]_0 = 12 \text{ mgL}^{-1}$

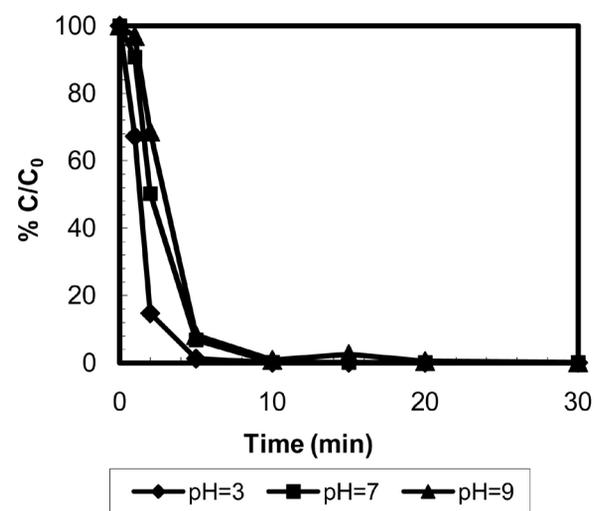
#### 3.1. Effect of pH on ozonation

The effect of pH on ozonation was studied in a semi-batch mode. As demonstrated in Figure 1, in acidic conditions, the ozone was one of the main reactive species, so the degradation of 4C2NP demonstrated low efficiency. After the pH was increased over 7, the degradation efficiency of 4C2NP began to rise obviously [15]. At initial 5 min. of ozonation, the degradation efficiency raised from 77% to 99% as

the pH increased from 3 to 9. This was due to the  $\text{OH}^-$  ions that functioned as the initiator of radical chain reaction to form hydroxyl radicals. From Figure 1, it was also noted that in this test, the optimum pH for ozone oxidation of 4C2NP is 9.

#### 3.2. Effect of pH on ZnO catalyzed ozonation

The effect of pH on ZnO catalyzed ozonation is shown in Figure 2. It was found from Figure 2, the degradation efficiency of 4C2NP changed with the variation of pH in the solution. From the experimental results, it can be found that in ZnO heterogeneous catalytic ozonation, the surface property of metal oxides rather than  $\text{OH}^-$  ions in the solution was the main factor determining the catalytic activity.



**Figure 2:** Effect of pH on ZnO catalyzed ozonation.  
 $[\text{ZnO}] = 300 \text{ mgL}^{-1}$ ;  $[\text{O}_3]_0 = 5.64 \text{ mgL}^{-1}$ ;  $[\text{4C2NP}]_0 = 12 \text{ mgL}^{-1}$

As shown in Figure 2, during the catalytic ozonation, the degradation of 4C2NP at pH of 3 was higher than pH of 7 and 9. After 2 min., under acidic condition (pH=3) the degradation efficiency of 4C2NP was as high as 85%, while in the solutions with pH 7–9, the degradation efficiency of 4C2NP was about 31–49%. It is clear that pH affects the aggregation of ZnO particles. It is already well known that nanosized particles tend to form aggregates when they are suspended in water [16], and it depends on the concentration of particles

and the pH of solution. The size of ZnO reaches to 350 nm at pH = 7.5 and the decomposition rate was decreased with an increase in the pH [8]. This was due to increase size of the ZnO particles and the subsequently decreased surface area. In the heterogeneous catalytic ozonation, the effect of pH on the catalytic reaction between the catalyst and ozone can be largely explained by the electrostatic interactions.

### 3.3. Reaction rate constant of 4C2NP with nano-ZnO/O<sub>3</sub>

A kinetic study of 4C2NP removal in the presence of nano ZnO was carried out at different pHs (3, 7 and 9). The equation rate of 4C2NP decomposition with nano-ZnO/O<sub>3</sub> can be written as:

$$\frac{d[4C2NP]}{dt} = -k_{O_3} \cdot [4C2NP][O_3][ZnO] + k_{OH^0} [4C2NP][OH^0][ZnO] \quad (1)$$

Here, [4C2NP], [O<sub>3</sub>], [OH<sup>0</sup>] and [ZnO] are the concentration of 4C2NP, ozone, hydroxyl radicals and zinc oxide, respectively.

$k_{O_3}$  and  $k_{OH^0}$  are the rate constants of 4C2NP with ozone and hydroxyl radicals, respectively.

As direct reaction of molecular ozone with phenols was predominant during the ozonation at pH values lower than 12 [17], therefore, the equation rate can be written in the form:

$$\frac{d[4C2NP]}{dt} = -k_{O_3} \cdot [4C2NP][O_3][ZnO] \quad (2)$$

In addition, ozone and zinc oxide concentration in the solution can be assumed to be constant[18]. So, the term of  $k_{O_3} \cdot [O_3][ZnO]$  is constant and the can be simplified to,

$$\frac{d[4C2NP]}{dt} = -k' [4C2NP] \quad (3)$$

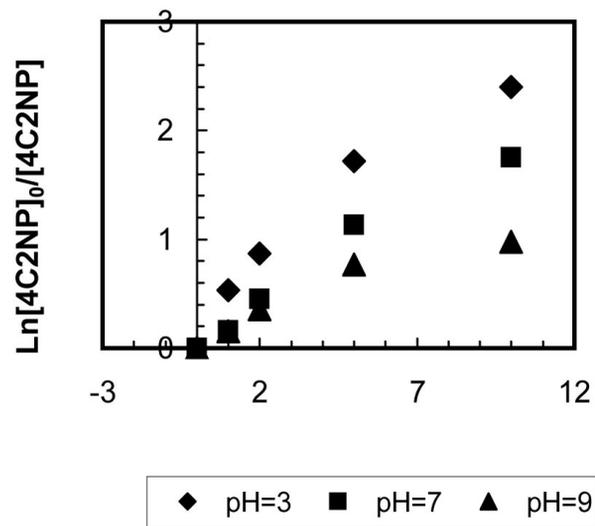
$k'$  is a pseudo first-order constant rate reaction of 4C2NP with Nano-ZnO/O<sub>3</sub>.

The integration of equation (3) leads to:

$$\ln \frac{[4C2NP]}{[4C2NP]_0} = -k' t \quad (4)$$

$[4C2NP]_0$  is initial concentration of 4C2NP.

Figure 3 shows the pseudo first-order plot for removal of 4C2NP versus time at different pHs. The decomposition rate of 4C2NP was found to decrease with increasing pH values. This result indicates adsorption trend of 4C2NP on the nano ZnO surface, which was pH-dependent and occurred at pH<4 (Table 1).



**Figure 3:** Kinetic degradation of 4C2NP with O<sub>3</sub>/ZnO at various initial pH.

$[ZnO] = 300 \text{ mgL}^{-1}$ ;  $[O_3]_0 = 5.64 \text{ mgL}^{-1}$ ;  $[4C2NP]_0 = 12 \text{ mgL}^{-1}$

**Table 1:** The rate constant reaction of 4C2NP with O<sub>3</sub>/ZnO at various pHs

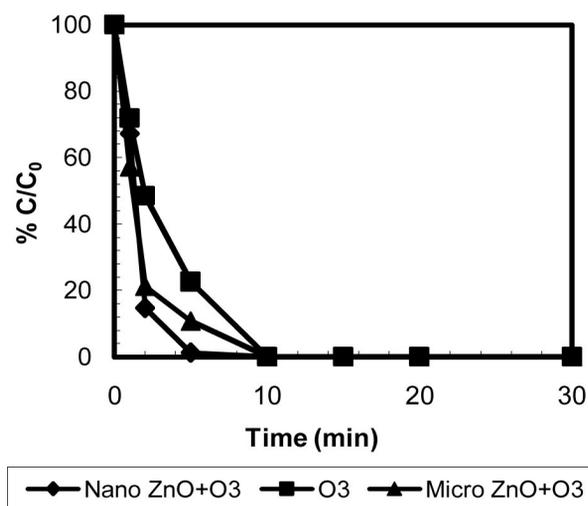
$[ZnO] = 300 \text{ mgL}^{-1}$ ;  $[O_3]_0 = 5.64 \text{ mgL}^{-1}$ ;  $[4C2NP]_0 = 12 \text{ mgL}^{-1}$

$k'$  = pseudo first-order constant rate

pH	3	7	9
$k' \text{ (s}^{-1}\text{)}$	$4.47 \times 10^{-3}$	$3.10 \times 10^{-3}$	$1.885 \times 10^{-3}$

### 3.4. Decomposition of 4C2NP with nano ZnO/O<sub>3</sub> at pH=3

During the ozonation and the catalytic ozonation, the concentration of 4C2NP was measured. The results obtained show that the presence of the catalyst also enhances the degradation of 4C2NP in the presence of the nano-ZnO catalyst (Figure 4). The corresponding results indicate that the presence of nano-ZnO can accelerate the degradation of 4C2NP rather than the ozone oxidation alone. Furthermore, the nano-ZnO has the ability to enhance the decomposition of ozone and promotes the formation of OH<sup>°</sup> radicals.



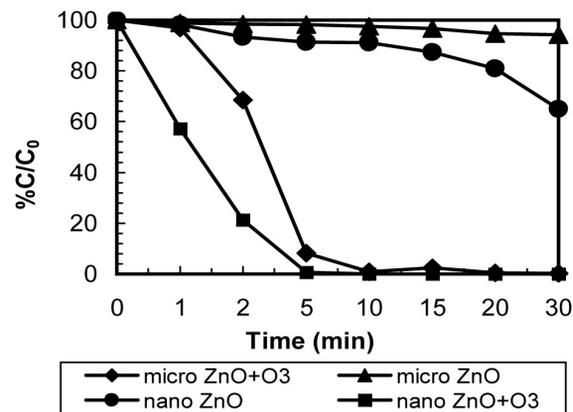
**Figure 4:** Degradation of 4C2NP during ozonation and catalytic ozonation  
 $pH = 3.0$ ;  $[ZnO] = 300 \text{ mgL}^{-1}$ ;  $[O_3]_o = 5.64 \text{ mgL}^{-1}$ ;  
 $[4C2NP]_o = 12 \text{ mgL}^{-1}$

It can be seen that the presence of  $300 \text{ mgL}^{-1}$  of nano-ZnO can accelerate the degradation of 4C2NP. The maximum degradation is approximately 99% in the presence of nano ZnO (at first 5 min.).

### 3.5. Effect of the particle size of ZnO on 4C2NP degradation

In this part, the nano-ZnO particles were ranged from  $<100 \text{ nm}$  (surface area=  $15\text{-}25 \text{ m}^2\text{g}^{-1}$ ) and was compared with those of micrometer size ( $<5 \mu\text{m}$ ). Figure 5 shows the profile of the 4C2NP degradation by catalytic and catalytic ozonation processes. The degradation of 4C2NP by nano-ZnO (34%) was

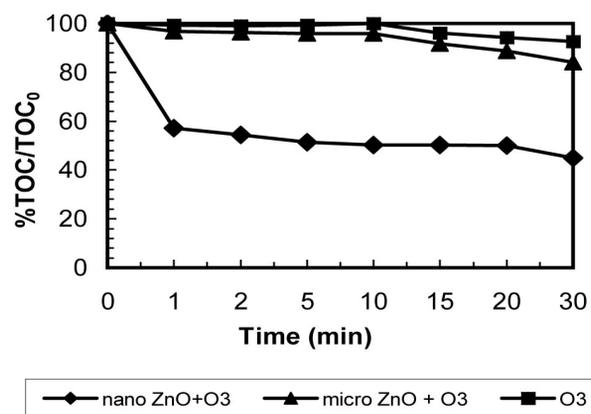
greater than those of the micrometer size (5 %) at the end of process due to increase of surface area. But in catalytic ozonation, the degraded 4C2NP by nano and micro ZnO was about 99 % and 91 %, respectively (at 5 min). So, the degradation rate of 4C2NP was shown to be ZnO size dependent.



**Figure 5:** Effect of the particle size on the degradation of 4C2NP during catalytic ozonation  
 $pH = 3.0$ ;  $[ZnO] = 300 \text{ mgL}^{-1}$ ;  $[O_3]_o = 5.64 \text{ mgL}^{-1}$ ;  
 $[4C2NP]_o = 12 \text{ mgL}^{-1}$

#### 3.5.1. TOC analysis

The degradation of 4C2NP was studied by ozonation and ozonation catalyzed with nano and micro ZnO in acidic solution to compare the oxidizing power of the different systems. Figure 6 shows the TOC decay with time through the degradation of 1000 ml of a  $12 \text{ mg L}^{-1}$  4C2NP solution at pH 3.0 up to 30 min.



**Figure 6:** TOC removal with time during the ozonation and catalytic ozonation of 4C2NP.  
 $pH = 3.0$ ;  $[ZnO] = 300 \text{ mgL}^{-1}$ ;  $[O_3]_o = 5.64 \text{ mgL}^{-1}$ ;  
 $[4C2NP]_o = 12 \text{ mgL}^{-1}$

This result indicates that 4C2NP was rapidly mineralized in water by the heterogeneous catalytic ozonation using the nanosized ZnO/ozonation in comparison to ozonation alone. This is exactly the same as the previous reports in the heterogeneous ozonation of organic pollutants[19]. The mineralization percentage of the above-mentioned methods changes with increasing degradation time. Figure 6 shows that in ozonation alone, TOC finally reduced by 7%, but in the O<sub>3</sub>/nano ZnO and O<sub>3</sub>/micro ZnO processes, TOC of solution decreased more than 54% and 15%, respectively. However, it can be concluded that 4C2NP cannot be totally mineralized from catalyzed ozonation, even by the O<sub>3</sub>/nano ZnO methods. It is clear that only part of 4C2NP was mineralized and some degradation intermediates were formed during the ozonation of 4C2NP.

#### 4. CONCLUSIONS

This study was carried out in order to evaluate the efficiency of nanosized ZnO as a catalyst for the heterogeneous catalytic ozonation. The decomposition characteristics of 4C2NP were also studied. The following conclusions are drawn based on the experimental results and discussion:

ZnO catalyst in water enhanced the decomposition rate of 4C2NP by the catalytic reaction on the ZnO surface. The enhancement of reaction rates in the presence of this catalyst was even more prominent in a nanometer ZnO particle size. The rate of 4C2NP decomposition on the surface of ZnO was strongly pH dependent and in the ZnO catalyzed ozonation, the oxidation efficiency of 4C2NP was higher at low pH (pH =3) than higher pH (pH =9).

#### ACKNOWLEDGEMENTS

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

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