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Heterogeneous catalytic ozonation process for removal of 4-chloro-2-nitrophenol from aqueous solutions



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Abstract This research investigated the efficiency of nanosized ZnO in the catalytic ozonation of 4-chloro-2-nitrophenol and determined the effect of pH on heterogeneous catalytic ozonation. Use of ozone with ZnO catalyst leads to conversion of 98.7% of 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 high pH (pH 7–9). This result was not in accordance with ozonation alone, following which higher pH had positive effect on the degradation of 4-chloro-2-nitrophenol. During the catalytic ozonation of 4-chloro-2-nitrophenol, an increase of nitrate ions in water sample solution was observed. At pH = 3, the concentration of nitrate formed during nano-ZnO catalytic ozonation was 7.08 mg L⁻¹ and the amount of total organic carbon was 54.9% after 30 min.

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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 toward

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 (Saritha et al., 2007). Ozone 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. 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 (Huang et al., 2005). In this way, the combination of solid catalysts with ozone has recently demonstrated interesting capacities for the oxidation of industrial wastewater and surface waters (Allemane et al., 1993; Volk et al., 1997; Gracia et al., 2000), and for the

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removal of numerous model compounds from dilute aqueous solutions (Andreozi et al., 1996; Karpel et al., 1998). 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 (Huang et al., 2005). 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 (Jung and Choi, 2006). Additionally, nanoscale ZnO exhibits lower ionization potentials, as the particle diameter is decreased (Bahnmann et al., 1987). Jung and Choi (2006) 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 *para*-chlorobenzoic acid significantly. Huang et al. (2005) concluded that the combined use of O₃ and ZnO catalyst leads to 99.8% of trichlorophenol conversion in 30 min and 75% in the absence of the catalyst. The high reactivity of hydroxyl radicals that were generated by O₃-ZnO during the oxidation process degraded trichlorophenol effectively (Huang et al., 2005). 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) [C₆H₄ClNO₂, 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 mg L⁻¹). Nano and micro ZnO were supplied from Aldrich and Sigma-Aldrich (USA), respectively. Nanosized ZnO were < 100 nm and their surface area (15–25 m² g⁻¹) was 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 etc., were of reagent grades and were supplied from Merck, Germany.

2.2. Catalytic ozonation experiments

Catalytic activity measurements in the degradation 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 1 L of aqueous solution containing 12 mg L⁻¹ of 4C2NP and 0.3 g 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 1 L min⁻¹, having an ozone concentration of 5.64 mg L⁻¹. 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).

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 min) 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% acetic acid isocratically at a flow rate of 1.0 mL min⁻¹. 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). Total Organic Carbon (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⁻¹. The samples were acidified to pH < 4 before being sent to TOC analyzer to ensure that inorganic carbon would be released from the solution as CO₂. 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 μm micro filters to collect the filtrate.

3. Results and discussion

In a heterogeneous catalytic ozonation system, pH has two direct effects on the oxidation, i.e., ozone decomposition and the surface property of solid catalyst (Ma et al., 2005). On the other hand, in a heterogeneous catalytic system, pH could affect the surface property of metal oxides (Stumm and Morgan, 1981).

3.1. Effect of pH on ozonation

The effect of pH on ozonation was studied in a semi-batch mode. As shown in Fig. 1, in acidic conditions, the ozone was one of the main reactive species, so the degradation of 4C2NP showed low efficiency. After the pH was increased over 7, the degradation efficiency of 4C2NP began to rise obviously (Gharbani et al., 2010). At initial 5 min. of ozonation, the degradation efficiency raised from 77.3% to 99.6% as the pH increased from 3 to 9. This was due to the OH⁻ ions that functioned as the initiator of radical chain reaction to form hydroxyl radicals. From Fig. 1, it was also found that in this research, the optimum pH for ozone oxidation of 4C2NP is 9.

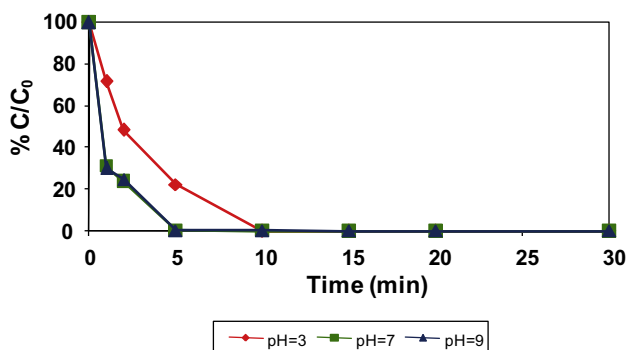


Figure 1 Effect of pH on ozonation of 4C2NP. $[O_3]_0 = 5.64 \text{ mg L}^{-1}$; $[4C2NP]_0 = 12 \text{ mg L}^{-1}$.

3.2. Effect of pH on ZnO catalyzed ozonation

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

As shown in Fig. 2, during the catalytic ozonation, the degradation of 4C2NP at pH 3 was higher than that of pH 7 and 9. After 2 min., under acidic condition (pH = 3) the degradation efficiency of 4C2NP was as high as 85.2%, 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 (Hoigne and Bader, 1985), 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 (Jung and Choi, 2006). This was due to the increased size of the ZnO particles and the subsequently decreased surface area. In the heterogeneous catalytic ozonation, the effect of pH on the catalytic

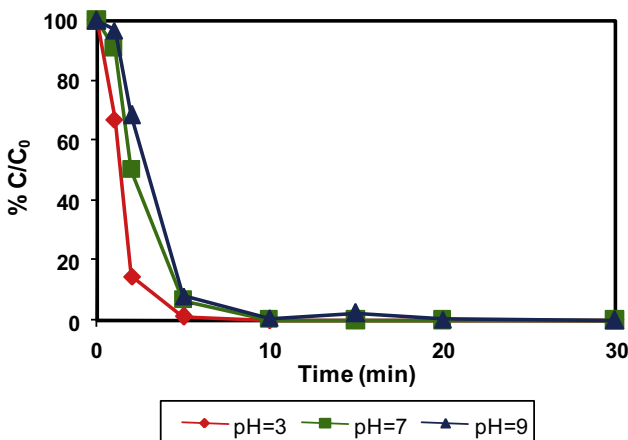


Figure 2 Effect of pH on ZnO catalyzed ozonation. $[ZnO] = 300 \text{ mg L}^{-1}$; $[O_3]_0 = 5.64 \text{ mg L}^{-1}$; $[4C2NP]_0 = 12 \text{ mg L}^{-1}$.

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_3

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_3 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, $[4C2NP]$, $[O_3]$, $[OH^0]$ and $[ZnO]$ are the concentrations 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 the direct reaction of molecular ozone with phenols was predominant during the ozonation at pH values lower than 12 (Goi et al., 2004) the equation rate can be written in the form:

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

If a reactor system is desired where compound A is to be removed by reaction with B and C and the concentration of B and C can be regarded constant, only the concentration of compound A changes and the reaction can be regarded as pseudo first order (Gottschalk et al., 2000). So, the equation rate can be expressed in the form of

$$\frac{d[4C2NP]}{dt} = -k'_{O_3} [4C2NP] \quad (3)$$

k'_{O_3} is a pseudo first-order constant rate reaction of 4C2NP with nano-ZnO/ O_3 .

The integration of Eq. (3) leads to

$$\ln \frac{[4C2NP]_0}{[4C2NP]} = k'_{O_3} \cdot t \quad (4)$$

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

Fig. 3 shows the pseudo first-order plot for removal of 4C2NP versus time at different pHs. The decomposition rate

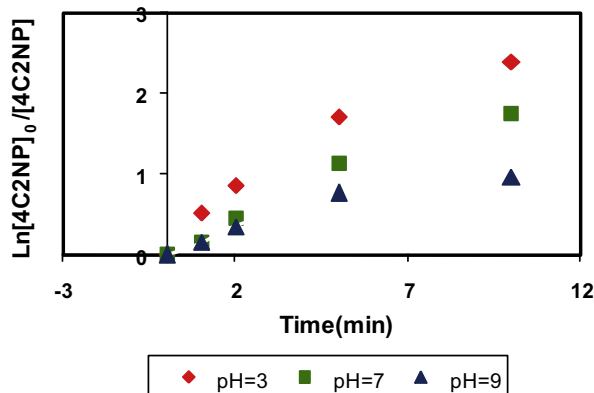


Figure 3 Kinetic degradation of 4C2NP with O_3/ZnO at various initial pH levels. $[ZnO] = 300 \text{ mg L}^{-1}$; $[O_3]_0 = 5.64 \text{ mg L}^{-1}$; $[4C2NP]_0 = 12 \text{ mg L}^{-1}$.

Table 1 The rate constant reaction of 4C2NP with O₃/ZnO at various pHs. [ZnO] = 300 mg L⁻¹; [O₃]_o = 5.64 mg L⁻¹; [4C2NP]_o = 12 mg L⁻¹.

pH	3	7	9
k (s ⁻¹)	4.47×10^{-3}	3.10×10^{-3}	1.885×10^{-3}

k = Pseudo first-order constant rate.

of 4C2NP was found to decrease with increasing pH values. This result shows the adsorption trend of 4C2NP on the nano ZnO surface, which was pH-dependent and occurred at pH < 4. Pseudo first order rate constants of 4C2NP with O₃/nano-ZnO at different pHs are shown in Table 1.

3.4. Decomposition of 4C2NP with ZnO/O₃ 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 enhanced the degradation of 4C2NP in the presence of the ZnO catalyst (Fig. 4). The corresponding results indicated that the presence of ZnO can accelerate the degradation of 4C2NP rather than the ozone oxidation alone. In addition, the ZnO has the ability to enhance the decomposition of ozone and promotes the formation of OH⁰ radicals. It can be seen that the presence of 300 mg L⁻¹ of ZnO can accelerate the degradation of 4C2NP.

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

In this part, the nano-ZnO particles ranged from < 100 nm (surface area = 15–25 m² g⁻¹) and were compared with those of micrometer size (< 5 μm). Fig. 5 shows the plot of the 4C2NP degradation by catalytic and catalytic ozonation processes. The degradation of 4C2NP by nano-ZnO (34.9%) was greater than those of the micrometer size (5.8%) at the end of the process due to increase of surface area, while in catalytic ozonation, the degraded 4C2NP by nano and micro ZnO was about 99.4% and 91.7%, respectively (at the first 5 min). So, the degradation rate of 4C2NP was shown to be ZnO size dependent.

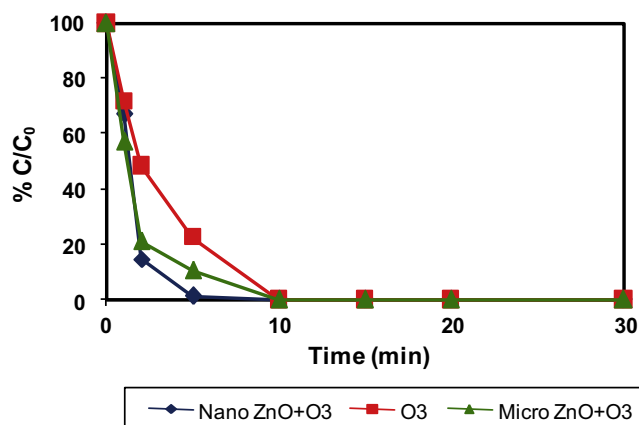


Figure 4 Degradation of 4C2NP during ozonation and catalytic ozonation. pH = 3.0; [ZnO] = 300 mg L⁻¹; [O₃]_o = 5.64 mg L⁻¹; [4C2NP]_o = 12 mg L⁻¹.

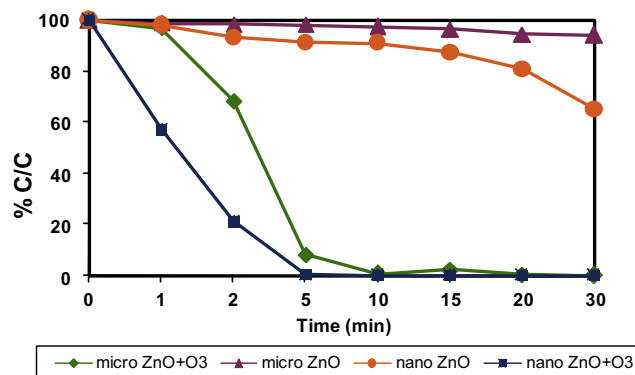


Figure 5 Effect of the particle size on the degradation of 4C2NP during catalytic ozonation. pH = 3.0; [ZnO] = 300 mg L⁻¹; [O₃]_o = 5.64 mg L⁻¹; [4C2NP]_o = 12 mg L⁻¹.

3.6. 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. Fig. 6 shows the TOC decay with time through the degradation of 1000 mL of a 12 mg L⁻¹ 4C2NP solution at pH 3.0 up to 30 min.

For the treatments, 300 mg L⁻¹ of each catalyst was added to the solution. For the nano ZnO/O₃ system, TOC concentration in water sample solution decreased rapidly during the first 2 min and then decreased much more slowly. After 30 min, change of TOC for O₃/nano ZnO, O₃/micro ZnO and O₃ systems was 54.9%, 15.8% and 7.4%, respectively.

This result indicates aqueous 4C2NP was rapidly mineralized by the heterogeneous catalytic ozonation using the nano-sized ZnO than ozonation alone. This is exactly the same as the previous reports in the heterogeneous ozonation of organic pollutants (Lin and Gurol, 1998). Fig. 6 shows that ozonation alone is the slow process and the TOC finally reduced by 7.4%, but in the O₃/nano ZnO system, TOC of solution decreased more than 54.9%. So, it can be concluded that 4C2NP cannot be totally mineralized by catalyzed ozonation, even by the O₃/nano ZnO methods. It is clear that only part of 4C2NP was

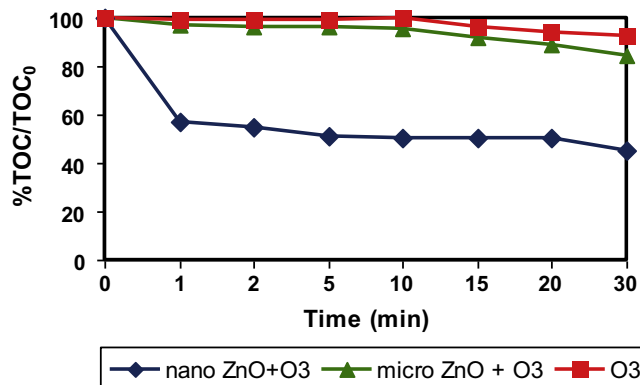


Figure 6 TOC removal with time during the ozonation and catalytic ozonation of 4C2NP. pH = 3.0; [ZnO] = 300 mg L⁻¹; [O₃]_o = 5.64 mg L⁻¹; [4C2NP]_o = 12 mg L⁻¹.

mineralized and some degradation intermediates were formed during the ozonation of 4C2NP.

During the reaction process, nitrate ions appeared from the beginning of the reaction. Conversion of nitro-group from the aromatic ring to nitrate (Goi et al., 2004) took place during the degradation of 4C2NP. The variation of nitrate ion during the ozonation and catalytic ozonation of 4C2NP was obtained (not shown here). In the initial stage of catalytic ozonation up to 1 min, nitrate formation was fast and then it became slow. The high degree of nitrogen mineralization was obtained in O₃/nano-ZnO systems (7.08 mg L⁻¹).

4. Conclusions

This study was carried out in order to evaluate the efficiency of catalytic ozonation of 4-chloro-2-nitrophenol by nanosized ZnO as a catalyst. The decomposition characteristics of 4C2NP were also studied. The following conclusions are drawn based on the experimental results and discussion:

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

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