

Ozonation of alachlor catalyzed by Cu/Al₂O₃ in water

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Abstract

The Cu/Al₂O₃ catalyzed ozonation for degrading an endocrine disruptor—alachlor in water was investigated. The Cu/Al₂O₃ powders were coated on a cordierite honeycomb column, which was taken as the reactor of catalytic ozonation of alachlor. Additional uncatalyzed experiments were carried out and the results were compared to those of the catalytic runs.

The experimental results demonstrated that Cu/Al₂O₃ was a very effective catalyst for ozonation of alachlor. The removal rate of alachlor in total organic carbon (TOC) with ozonation in the absence of Cu/Al₂O₃ was only above 20% in 180 min, while the reduction of total organic carbon (TOC) in the presence of Cu/Al₂O₃ was more than 60%. Correspondingly, more inorganic ions created and less by-products produced in the Cu/Al₂O₃ catalyzed ozonation than in the uncatalyzed process. These results indicated that the use of Cu/Al₂O₃ substantially enhanced the mineralization of alachlor in ozonation. The EPR experiments verified that more •OH radicals generated in the Cu/Al₂O₃ catalyzed ozonation could bring on a higher alachlor removal rate.

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1. Introduction

Herbicides are extremely persistent in water and wastewater. They are taken as the important pollutants and hardly removed by traditional water treatment technology. It has been found that many herbicides can result in some serious illness for human body. Alachlor (2-chloro-2'-6'-diethyl-*N*-methoxymethylacetanilide), one of herbicides, is commonly used for feed control in agricultural crops. Its structure is shown in Fig. 1. It has been found in ground water and surface water in many parts of North America [1,2], and the residual levels ranging from 0.1 to 10 µg/l have been detected in surface water [3–5]. Alachlor has been classified as a carcinogen of B2 group by the EPA and has been known as a highly toxic endocrine disruptor, where the allowed maximum concentration for drinking water has been set at 2 µg/l.

Until now, there is no much study done for alachlor removal in water. Penuela and Barcelo [6] reported the experimental results of degradation in water by the pho-

tocatalysis at the presence of both FeCl₃ and TiO₂. They confirmed that the degradation kinetics of alachlor dissolved in water followed the first-order kinetics with a short half life in the range of 10–17 min. Eykholt and Davenport [7] investigated the alachlor degradation in a reactor with iron powders of 40 mesh at the room temperature and found the dechlorinated products derived from alachlor in water. Ryu et al. [8] reported the photodegradation of alachlor with the TiO₂ film immobilized on the glass tube in aqueous solution. They found that the removal rate of alachlor with Fe³⁺/UV in the presence of TiO₂ was much higher than in the absence of TiO₂. In addition, the authors detected some low molecular weight compounds in the photodegradation.

Ozone is a powerful oxidant of various organic and inorganic compounds dissolved in water. Sometimes, it can completely decompose the organic pollutants and remove them from water. However, in most cases, the ozonation can only degrade the organic compounds in water to low molecular weights substances to present a very low removal rate of total organic carbon (TOC) and chemical oxygen demand (COD). Unfortunately, some by-products in ozonation process are toxicants and harmful to human health. For those chemicals in water, advanced oxidation processes (AOPs), which involve the generation of the hydroxyl radical (•OH),

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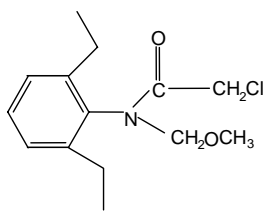


Fig. 1. Chemical structure of alachlor.

may provide more effective elimination. The O_3/H_2O_2 process has been promoted as the most practical of the AOPs because of its simplicity and ease of operation. Glaze et al. [9] concluded that at intermediate to high pH, hydrogen peroxide more effectively catalyzes the decomposition of ozone than does UV radiation or hydroxide ion. In order to improve the ozonation efficiency of organic compounds in water, several catalysts have been studied in different experimental conditions. Hewes and Davinson [10] confirmed that the ozonation removal of phenolic compounds in water could be enhanced remarkably by using the catalysts such Fe(II), Mn(II), Ni(II) or Co(II). Utrilla and Polo [11] found that the ozonation of 1,3,6-naphthalenetrisulphonic acid could be catalyzed by activated carbon in aqueous phase and basic activated carbons had greatest catalytic activity in the ozonation process. However, there are few published experimental studies on heterogeneous catalyzed ozonation of aromatic contaminants such as alachlor. Moreover, because the heterogeneous catalytic ozonation is known as the most promising process for its low cost and easy operation [12], the development of active, stable and low-cost heterogeneous catalysts and their applications in water purification has drawn a great attention [13].

The present paper is aimed to study the degradation of alachlor in the heterogeneous catalyzed ozonation using Cu/Al_2O_3 . The relative by-products produced in the ozonation of alachlor, such as inorganic ions and organic acids, were analyzed and compared in the catalyzed and uncatalyzed processes. The reaction mechanism of the Cu/Al_2O_3 catalyzed ozonation was also verified by electron paramagnetic resonance (EPR) experiment.

2. Experimental

2.1. Materials

Alachlor (99% purity) was obtained from AccuStandard Inc. (USA) and the potassium indigotrisulfonate was got from ACROS ORGANICS (New Jersey, USA). Acetonitrile of HPLC grade was purchased from Tedia Company, Inc. (USA). 5,5-Dimethyl-pyrroline-*N*-oxide (DMPO) used to detect radicals in EPR experiment was from Aldrich. Other chemicals (KI, H_2SO_4 , H_3PO_4) were of GR.

Synthetic raw stock alachlor solution was prepared by dissolving 200 mg alachlor into 1000 ml ultra-pure water

(18 M Ω) to afford a solution of 200 mg/l with pH of 6.39. The stock solution was diluted to the aqueous solutions containing 100 mg/l of alachlor for tests. Although 100 mg/l of alachlor is out of the range for source water, it is convenient for study and the same catalytic oxidation process should take place when the concentration of alachlor was μ g/l level. All the glassware equipments used in the experiments were soaked in chromic acid and then in 1% HNO_3 overnight and muffled at 400 °C for several hours after being rinsed by tap water and ultra-pure water.

The Cu/Al_2O_3 catalysts with different Cu loading were compared each other, and the catalyst coated with 10% Cu showed the best catalytic efficiency. The catalyst, Cu/Al_2O_3 (Cu loading 10 wt.%), were prepared by an impregnation method with an aqueous solution of copper nitrate, followed by evaporating for drying in a rotary evaporator under the pressure reduction at 333 K. The wet sample was dried at 393 K for 12 h and then calcined at 873 K for 3 h in air. Utilized Al_2O_3 (gamma type) had a total BET surface area of 250 m² g⁻¹. Cu/Al_2O_3 powder prepared was mounted on the square-celled extruded cordierite in a honeycomb shape (400 cell/inch², 100 mm high, 28 mm i.d.) for using as the catalyzed ozonation reactor in the experiments.

2.2. Experimental procedures

Ozone was generated by a laboratory ozonizer (Mitsubishi, ozonizer series OS-1N, Japan) rated at 0.488 mg O_3 /min. The experiments were conducted in a stainless reactor (200 mm high, 30 mm i.d.). The reactor was equipped with a Ti porous plate (10 μ m porous size) at its bottom to obtain smaller gas bubbles. The honeycomb cordierite column coated by Cu/Al_2O_3 catalyst was properly placed on the porous plate to take as the reactor of catalyzed ozonation. In the case of uncatalyzed process, a honeycomb cordierite column without Cu/Al_2O_3 but of the same size and bulk as that used in the catalyzed one was installed in the ozonation reactor. In addition, a water jacket around the reactor maintained the desired and constant temperature (20 °C) with water circulated from a water bath. Seventy five milliliters of experimental alachlor solutions was pumped by a peristaltic pump from a holding beaker. Ozone gas flowed upward through the holes of honeycomb to contact sufficiently with the coated catalyst and the treating water. To absorb the excess ozone, effluent gas was introduced into a glass bottle containing 300 ml of 2% KI solution. Alachlor concentration, total organic carbon and dissolved inorganic ions in water were determined after different time periods. The test installation is shown in Fig. 2.

2.3. Analytical methods

The concentrations of dissolved ozone were measured colorimetrically by the indigo method [14]. The adsorption measurements were performed at 600 nm with a Model DR/2010 portable datalogging spectrophotometer (Hach, USA) and

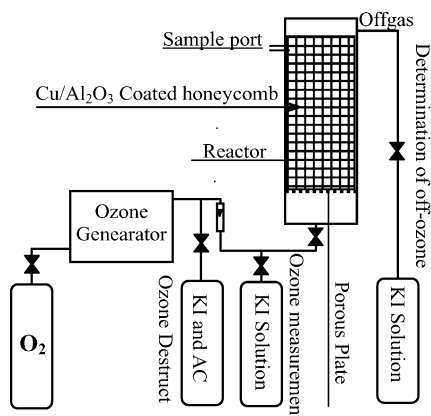


Fig. 2. Schematic of the Cu/Al₂O₃ catalytic ozonation of alachlor in water.

the gaseous ozone concentration was iodometrically determined before the ozone was introduced into the reactor. The applied quantity of ozone ($Q_{\text{applied ozone}}$) was calculated by a simple formula

$$Q_{\text{applied ozone}} = Q_{\text{introduced ozone}} - (Q_{\text{ozone in off-gas}} + Q_{\text{residual ozone}})$$

The concentration of residual alachlor in water was measured by HPLC (Shimadzu, 10A) using a Merck-Hitachi with UV-Vis detector. Liquid chromatography was carried out with a flow rate of 1.0 ml/min of acetonitrile/water mixture (80:20 v/v) on a ZORBAX Extend-C18 column (250 mm long, 4.6 mm i.d. Agilent, USA) with a column temperature of 40 °C. The injection volume of sample for analysis was 20 μ l. Detection was performed at 215 nm, and quantification was done using a five-point calibration curve.

The variations of inorganic ions (Cl^- , NO_2^- , NO_3^-) in water were measured using an ion chromatograph (Dix-4000, Dionex Co.) equipped with a conductivity detector and an AS4A-SC column (4 mm, Dionex Co.). The eluent was 1.8 mM Na₂CO₃ and 1.7 mM NaHCO₃ solution. TOC was determined using a Phoenix 8000 TOC analyzer (USA, Tekmar-Dohrmann Co.).

Aliphatic carboxylic acids produced during the ozonation period were analyzed using an ion chromatograph (Dix-500, Dionex Co.) equipped with a conductivity detector and an AG9-HC guard column (Dionex Co.). The eluent was 1.8 mM Na₂CO₃ and 1.7 mM NaHCO₃ solution.

For the determination of hydroxyl radicals generated in the ozonation process, EPR experiment was applied. A nitron spin-trapping reagent DMPO was used in the process. Because the powdered catalyst was easy to be tested, and the fixed and powdered catalyst should follow the same mechanism in the catalyzed ozonation, the powdered Cu/Al₂O₃ was selected for EPR experiments. Alachlor stock solution, O₃ and the catalyst powder were mixed with DMPO in ultra-pure water (18 M Ω). Immediately after the mixing, 25 μ l of the sample solution was transferred into a capillary tube, and EPR spectra were recorded in the X-band on

a Bruker ESP spectrometer at room temperature. EPR measurements were conducted under the following conditions: modulation amplitude 2.0 G; microwave power 10.00 mW; modulation frequency 100 kHz, sweep width 100.0 G, receiver gain 1.00e + 005.

3. Results and discussion

3.1. The removal efficiency of alachlor in catalyzed and uncatalyzed ozonation

Fig. 3 shows the removal rate of alachlor as a function of ozonation time. Alachlor could be effectively degraded with a percentage of above 95% within 30 min ozonation both in the uncatalyzed and catalyzed ozonations. However, TOC removal rate presented an obvious difference in two cases. In addition, there was only about 1% alachlor adsorbed onto Cu/Al₂O₃ catalyst with ozone absent. While the catalyzed ozonation led to over 60% TOC removal after reacting for 180 min, the uncatalyzed process gave only a modest decrease in TOC and an equivalent reduction of alachlor was only about 20%. The TOC present in solution is an important parameter to evaluate degraded degree of organic matters and their removal efficacy for a given water treatment process. Therefore, above results demonstrated that in the experimental condition of our study, alachlor could not be degraded to CO₂ and H₂O completely by ozone alone, and Cu/Al₂O₃ showed a great catalytic effect on the mineralization of alachlor in the ozonation process.

3.2. The main products of alachlor in catalyzed and uncatalyzed ozonation

The difference of TOC removal in the catalyzed and uncatalyzed ozonation processes indicated that the degraded products would present some differences in the two cases. In order to determine these differences to overall process of alachlor degradation, the relative products of alachlor in the catalyzed and uncatalyzed ozonation processes were detected and analyzed.

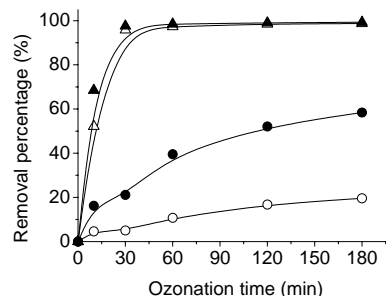


Fig. 3. Removal efficiency of alachlor and its corresponding TOC in the catalyzed and uncatalyzed ozonation processes: (○) TOC uncatalyzed; (●) TOC catalyzed; (Δ) alachlor uncatalyzed; (▲) alachlor catalyzed; experimental temperature: 20 °C, alachlor concentration: 100 mg/l.

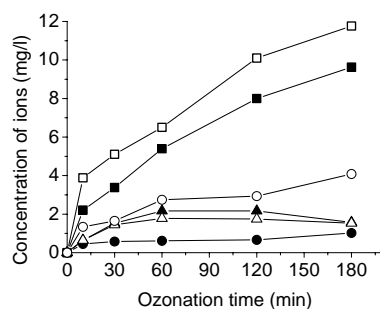


Fig. 4. Inorganic ions produced in the two ozonation processes: (■) Cl⁻ uncatalyzed; (□) Cl⁻ catalyzed; (▲) NO₂⁻ uncatalyzed; (△) NO₂⁻ catalyzed; (●) NO₃⁻ uncatalyzed; (○) NO₃⁻ catalyzed; experimental temperature: 20 °C; alachlor concentration: 100 mg/l.

Based on the high catalytic efficiency of Cu/Al₂O₃ on the ozonation of alachlor, the ultimate products such as inorganic ions arising from the alachlor degradation were followed with ozonation time. Fig. 4 depicts the formation of Cl⁻, NO₂⁻ and NO₃⁻ produced from the mineralization of organic chlorine linked to the side chain of alachlor and nitrogen linked to the aromatic ring during two ozonation processes. Nitrogen was principally mineralized into nitrate. Nitrite ions were initially formed, but they were quickly oxidized to nitrate, and the formation rate of NO₂⁻ was very slow in the whole reaction process. By comparing the formation rate of Cl⁻ and NO₃⁻, it was found that the oxidation of side chain of the alachlor molecular happened more easily than the cleavage of the ring. The results revealed that the first step of alachlor ozonation was mainly the dechlorination. Moreover, after being oxidized for 180 min by ozone alone, alachlor nearly disappeared completely and 90.1% of chlorine was converted into Cl⁻, but there was only 13.7% of nitrogen converted into nitrite and nitrate ions. This implied that other (in-)organic chlorine-containing and nitrogen-containing compounds were still present in the solution. However, the conversion percentage of chlorine and nitrogen of alachlor increased to 90.5 and 26.7%, respectively, in the catalyzed ozonation. It also can be found that there were more Cl⁻, NO₃⁻ and less NO₂⁻ created in catalyzed process than those produced in the uncatalyzed one. This could be due to the stronger oxidation ability of the catalyzed ozonation than that of the uncatalyzed one. Therefore, more complete dechlorination, denitration and cleavage of the aromatic ring happened in the catalyzed ozonation process.

The experimental results proved that the decomposition of alachlor in ozonation produced mainly three kinds of organic by-products: acetic acid, oxalic acid and propionic acid. The concentrations of these organic acids produced in the catalyzed and uncatalyzed ozonation were very different. Table 1 is the comparison of three by-products, concentration of alachlor in the two ozonation processes. In the ozonation without Cu/Al₂O₃ catalyzing, the concentration of three organic acids was all much higher than in the presence of catalyst. After 180 min catalyzed ozonation, the concentra-

Table 1
Comparison of concentration of three by-products between catalyzed and uncatalyzed ozonation

By-products	Acetic acid (mg/l)	Oxalic acid (mg/l)	Propionic acid (mg/l)
Without Cu/Al ₂ O ₃	53.4	36.3	6.5
Catalyzed by Cu/Al ₂ O ₃	11.7	1.0	0.7

Initial concentration of alachlor: 100 mg/l; experimental temperature: 20 °C.

tion of acetic acid, oxalic acid and propionic acid in water decreased 78.1, 97.3 and 89.2%, respectively, comparing to the uncatalyzed ozonation reaction. This result agrees with the TOC removal efficiency of two ozonation processes, and shows further the high catalytic capacity of Cu/Al₂O₃ on ozonation mineralization of alachlor.

3.3. Effect of •OH in catalyzed ozonation of alachlor

Ozone may either react directly with organic compounds, or decompose to generate some more reactive species, such as the hydroxyl radical (•OH), which control subsequent oxidation reactions. •OH is one of the most important oxidants due to its high reactivity and unselecting towards organic compounds [15]. The proposed heterogeneous catalytic ozonation mechanism were expressed as: (i) simultaneous adsorption of ozone and organic molecules on the catalyst surface, (ii) decomposition of ozone on the metallic sites and production of surface bound hydroxyl radicals that is more reactive than ozone, (iii) oxidation of adsorbed organic molecules by adjacent hydroxyl radicals. Oxidation proceeds through several oxidized intermediates whilst hydroxyl radicals are continuously generated by dissolved ozone that is transferred to the catalyst surface. The affinity of the oxidation products to the catalyst decreases and final oxidation products desorb from the catalyst surface [16]. Only about 2 μg l⁻¹ Cu²⁺ releasing from the Cu/Al₂O₃ catalyst was detected in solution after the catalyst being used for several times, which could verify that homogeneous reaction could be neglected and the heterogeneous catalytic ozonation was a dominated mechanism in this study. To investigate the effect of •OH on the Cu/Al₂O₃ catalyzed ozonation of alachlor in the aqueous solution, EPR experiment was carried out. As shown in Fig. 5, a much stronger signal of •OH which had the typical spectrum of 1:2:2:1 was presented in the catalyzed ozonation than that in the uncatalyzed process. This indicated that more •OH was produced when Cu/Al₂O₃ was used as a kind of catalysts in ozonation process. •OH has the oxidation potential as high as 2.80, and it can oxidize organic substances easily. The greater rate of decomposition of alachlor and higher ozonation efficiency in the presence of Cu/Al₂O₃ could, therefore, be explained by an increase in free radical hydroxyl concentration. Consequently, •OH formation and effect by the applying of catalyst becomes more important for TOC removal in ozonation process.

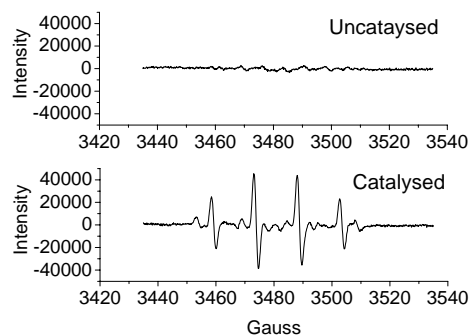
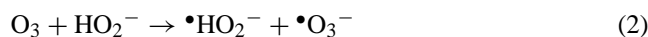


Fig. 5. Comparison of the intensity of DMPO-OH adduct signals with catalyzer existed or not. DMPO and O₃ concentrations are 25 and 0.568 mM, respectively.

On the other hand, an obvious pH shift from 6.39 to 3.98 in the uncatalyzed ozonation within 180 min was observed. However, pH of the catalyzed solution remained nearly stable at 6.15–6.45 throughout the ozonation process. The ozonation of organic substances generally occurs via one of two pathways: (i) direct reaction with the molecular ozone and (ii) indirect reaction with the radical species produced as the result of the decomposition of ozone in water. At higher pH, the main reacting route followed the radical way, but followed the selective direct reaction pathway at lower pH. Since the oxidation potential (2.80) of hydroxyl radicals is much higher than that of molecular ozone, radical oxidation is much faster than the direct oxidation too. At higher pH, HO₂⁻ ion created from the reaction between O₃ and OH⁻, and •OH would be inspired consequently as shown in Eqs. (1)–(4) [17]. Therefore, with the pH decreasing of alachlor solution in the uncatalyzed ozonation, the direct reaction between alachlor and ozone played the dominant role. Contrarily, indirect reaction between alachlor and hydroxyl radical became the main pathway in the catalyzed process, which resulted in the higher TOC removal rate and more complete decomposition of alachlor in ozonation.



3.4. The catalytic efficiency of Cu/Al₂O₃ in its repeated use

In order to investigate whether the Cu/Al₂O₃ catalyst could be used successfully in batch operations for removing organic pollutants from water, the tests were carried out using the same Cu/Al₂O₃ coated reactor and measured the catalytic efficiency indicated by TOC removal rate. The experimental results are shown in Table 2. After 10 times uses of Cu/Al₂O₃, the TOC removal efficiency kept almost at a constant rate, which suggested that the catalytic capacity of Cu/Al₂O₃ was not decreasing with its reused times in the water treatment condition. On the other hand, only about

Table 2
The catalytic efficiency of Cu/Al₂O₃ on ozonation when being used repeatedly

	TOC removal percentage (%)				
	10 min	30 min	60 min	120 min	180 min
Unanalyzed	4.59	4.99	10.7	16.7	19.6
Catalyzed (one time)	16.2	21.2	39.5	52.1	58.4
Catalyzed (two times)	16.5	20.2	42.7	53.5	57.6
Catalyzed (four times)	16.3	20.7	38.1	51.8	58.3
Catalyzed (eight times)	15.8	19.9	37.5	51.5	58.9
Catalyzed (10 times)	15.9	19.7	37.8	51.7	58.6

10, 30, 60, 120 and 180 min are the reaction conditions.

2 μg l⁻¹ Cu²⁺ releasing from the Cu/Al₂O₃ catalyst was detected in solution after being used for three times, and less metal loss was observed with the next continuous application of the catalyst. When the operations were repeated by 10 times, there was no Cu²⁺ detected in water. This demonstrated that the Cu/Al₂O₃ was a stable and effective catalyst in the ozonation of organic pollutants, and the Cu/Al₂O₃ coated cordierite honeycomb could be taken as a kind of useful reactor for carrying out the catalytic ozonation of alachlor.

4. Conclusions

Cu/Al₂O₃ has very effective catalytic activity in the ozonation process. Although the degradation rates of alachlor were almost same in the Cu/Al₂O₃ catalyzed and uncatalyzed ozonation process, the TOC removal efficiencies showed a great difference in the two cases. The use of Cu/Al₂O₃ in ozonation of alachlor could increase the TOC removal rates from 20 to 60%.

More inorganic ions, such as Cl⁻ and NO₃⁻, produced in catalyzed process than in unanalyzed one, which verified the catalytic potential of Cu/Al₂O₃ in the ozonation of alachlor. In addition, the production of by-products (three kinds of organic acids) was restrained by using Cu/Al₂O₃ as a catalyst in ozonation of alachlor. EPR experiments confirmed that larger amount of •OH radicals generated when the catalyst was applied, and the indirect reaction of •OH and alachlor should be the main pathway in Cu/Al₂O₃ catalyzed ozonation.

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