



Pretreatment of heterocyclic pesticide wastewater using ultrasonic/ozone combined process

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Abstract

Ultrasonic/O₃ combined process was employed to pretreat heterocyclic pesticide wastewater for increasing biodegradability and reducing biological toxicity. Influences of ultrasonic frequency, ultrasonic power, probe diameter, initial pH and O₃ dosage on the COD removal were studied. The results showed that the ultrasonic/O₃ process significantly improved the biodegradability and reduced the biological toxicity of the wastewater. The ratio of BOD₅/COD was increased from 0.03 to 0.55 and the EC₅₀ increased from 11% to 52% under ultrasonic/O₃ treatment. Low ultrasonic frequency brought better COD removal. Initial pH was found to have a high influence on the COD removal and alkaline conditions were more favorable. The influences of ultrasonic power and probe diameter were small. With an increase in O₃ dosage, COD removal was effectively improved. The optimal operational parameters for the combined process on COD removal were ultrasonic frequency 20 kHz, initial pH 9.00, ultrasonic power 300 W and dosage of O₃ 454.8 mg/(L·min), under which the efficiency of COD removal reached 67.2%.

Key words: heterocyclic pesticide wastewater; ultrasonic; O₃; BOD₅/COD; biological toxicity

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Introduction

Large amounts of pesticide is produced and used in China. Pesticide industry generates approximately 150 million tons of wastewater annually (Wang and Li, 2008). Pesticide wastewater contains high concentrations of pollutants, which are in general toxic and refractory, therefore biological treatment processes were shown inefficient for this wastewater without a proper pretreatment.

Advanced oxidation processes (AOPs) have attracted much attention for the high efficiencies in the pretreatment of pesticide wastewaters and less secondary pollution. Ozonation is one of the AOPs widely used for wastewater pretreatment, in which ozone, as a strong oxidant, breaks down organic compounds into smaller molecules. The pollutants are therefore transformed to be more biodegradable (Esplugas et al., 2002; Contreras et al., 2003), although some authors indicated that the oxidized intermediates could have new toxicity to pure bacteria/mixed microorganisms at early stage of ozonation (Shang et al., 2006; Dantas et al., 2008). However, ozonation has its limitations: (1) ozone generation results in high energy consumption and could cause a cost increase; (2) ozonation is selective in some cases, and complete mineralization of

organics is difficult. Ozonation was thus generally used to treat wastewaters with low concentrations; its application in high strength wastewater, e.g., heterocyclic pesticide wastewater, is rare.

More recently, ultrasonic/O₃ combined process was studied to improve the efficiencies of wastewater treatment (He et al., 2005). Ultrasonic has been used as a wastewater treatment technology (Qi et al., 1996; Shen et al., 2005; Wu et al., 2004; Jing et al., 2004); the principle is that ultrasonic waves break down complicated organic pollutants through ultrasonic cavitation, which leads to an extreme surrounding with high temperatures up to 5000°C and pressures 100 MPa (Legube et al., 1999; Peyton and Glaze, 1988). Significant improvements in the efficiency of COD removal by ultrasonic/O₃ combined process have also been reported (Hu et al., 1999; Terese and Philippe, 1994). In the combined system, ultrasonication and ozonation were believed to enhance each other in the oxidation of organic pollutants.

This article presents the effectiveness of the pretreatment of heterocyclic pesticide wastewater by ultrasonic/O₃ combined process. The biodegradability and biological toxicity were then analyzed to explore the mechanisms of ultrasonic/O₃ in the wastewater pretreatment.

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1 Materials and methods

1.1 Pesticide wastewater

The heterocyclic pesticide wastewater was collected from a pesticide company in Anhui Province (China). The wastewater contained various heterocyclic compounds with structures close to pyridine and pyrimidine. The characteristics of the pesticide wastewater are followed as: pH 13–14, COD ($22,000 \pm 1000$) mg/L, BOD₅ 650.1 mg/L, BOD₅/COD 0.03 and EC₅₀ 11%.

1.2 Experimental setup

The ultrasonic/O₃ combined process is illustrated in Fig. 1. A ultrasonic generator (JY92-IIN, Ningbo Xinzhi, China) and an air-fed ozonator (3S-A5, Beijing Tonglin, China) were used to provide ultrasonic and O₃, respectively. A cooling water system was employed to keep the reactor at $(25 \pm 1)^\circ\text{C}$. The gas mixture of air and ozone was introduced into the reactor via a porous diffuser. A rotameter was adopted to adjust the gas flow. The ozone residue was adsorbed by KI solutions.

1.3 Treatment of pesticide wastewater

The assays were started by simultaneously introducing ultrasonic and O₃ into a 100 mL of pesticide wastewater. The effects of ultrasonic frequency, power and probe diameter, initial pH of the solution, and dosage of O₃ on COD removal were investigated. Samples were taken every 20 min for COD tests during a period of 2 hr. Under the optimized condition, BOD₅ and biological toxicity of the wastewater were measured to estimate the biodegradability improvements. The products from ultrasonic/O₃ treatment were analyzed by gas chromatography-mass spectrometer (GC-MS). Water samples were pre-concentrated through liquid phase extraction (LPE) using dichloromethane. Treatment of the pesticide wastewater by sole ultrasonic and sole O₃ were also investigated.

1.4 Analytical methods

Ozone concentration was determined by indigo disulphonate spectrophotometry (CJ/T 3028.2-94). O₃ dosage is defined as the average amount of O₃ put into one

liter wastewater per minute. COD was measured by using a COD analyzer (CTL-12, Chengde Huatong, China) according to fast digestion-spectrophotometric method (HJ/T 399-2007). BOD₅ measurement was conducted in an Oxitop system (WTW, Germany) according to standard methods (GB 7488-87). Biological toxicity was determined by using a toxicity analyzer (DXY-3, Nanjing Kuake, China). *T*₃ luminescent bacteria were obtained from Institute of Soil Science, Chinese Academy of Sciences, China. The toxicity is described as EC_{50,15 min} (% V/V), the percentage of initial solution that causes 50% of inactivation in 15 min of contact.

Pesticide wastewater (300 mL) and dichloromethane (100 mL) were mixed thoroughly for at least 30 min in a funnel. The obtained organic phase was concentrated to 5–6 mL by a rotary evaporator (RE-52AA, Shanghai Yarong, China) at 40°C and further enriched to 1 mL by a pressure blowing concentrator (KL-521, Chengdu Yayuan, China). The solution was dehydrated using anhydrous sodium sulfate. The enriched samples were then analyzed using a GC-MS system (Trace DSQ, Thermo Finnigan, USA). The splitless injection volume was 2 μL. Separation was achieved by a DB-17 column (30 m × 0.25 mm × 0.25 μm, Agilent, USA). The oven temperature program was 1.0 min at 50°C, 6°C/min to 250°C (10 min). Helium was the carrier gas with a flow rate of 0.8 mL/min. Electron impact (EI) mass spectra were monitored from 29 to 540 *m/z*. The ion source and interface temperatures were set at 190 and 250°C, respectively.

2 Results and discussion

2.1 COD removal by ultrasonic/O₃ process

2.1.1 Comparison of ultrasonic, O₃ and ultrasonic/O₃ processes

In the assays with sole ultrasonic, COD removal from the pesticide wastewater was improved at a low ultrasonic frequency: 33.7% at 20 kHz vs. 5.8% at 60 kHz (Fig. 2). The efficiency of COD removal in the presence of O₃ was obviously higher than that by sole ultrasonic. A highest COD removal of 67% was observed when the wastewater was pretreated by the ultrasonic (20 kHz)/O₃ combined

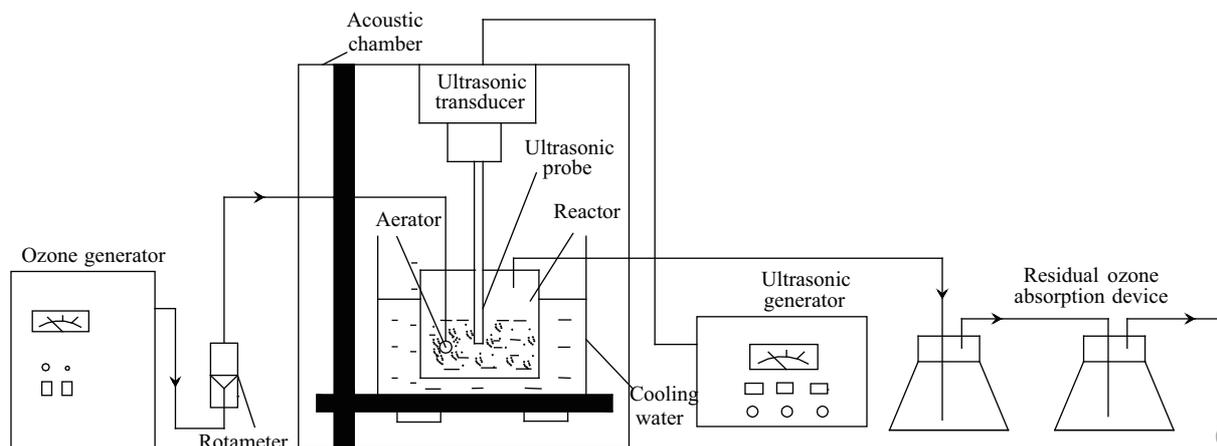


Fig. 1 Schematic diagram of the ultrasonic/O₃ combine process.

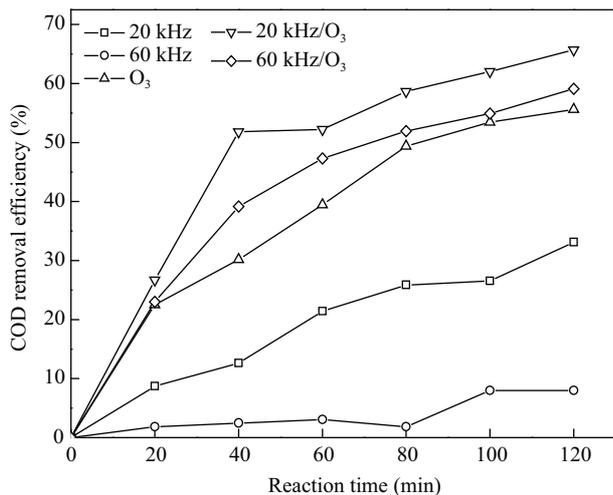


Fig. 2 Comparison of COD removal by different processes. Conditions using only ultrasonic: pH 9.00, ultrasonic frequency 20 or 60 kHz, probe diameter 10 mm, power 300 W; conditions using only O₃: pH 13.34, O₃ dosage 454.8 mg/(L·min); Conditions using ultrasonic/O₃: pH 9.00, ultrasonic frequency 20 or 60 kHz, probe diameter 10 mm, power 300 W, O₃ dosage 454.8 mg/(L·min).

process. Ultrasonic and O₃ could enhance each other in the COD degradation as expected: (1) ultrasonic broke O₃ into micro-bubbles and improved the mass transfer O₃ to the solution; (2) the produced micro-bubbles intensified the cavitation effect of ultrasonic.

The relationship plots of the logarithm to COD concentrations and reaction time were drawn and kinetic study in Table 1 indicated that COD removal by the three processes had a good agreement with a first-order equation. The kinetic rate constants of the reactions with O₃ were more than twice higher than that with sole ultrasonic. Among the O₃ involved processes, the k_1 was in the order of ultrasonic (20 kHz)/O₃ > ultrasonic (60 kHz)/O₃ > O₃.

2.1.2 Influencing factors on COD removal

The influence of initial pH on COD removal of the pesticide wastewater is illustrated in Fig. 3a. Higher COD removal efficiencies were observed under alkaline conditions. Under pH < 8.90, COD removal was improved with an increase in the initial pH of the solution. The highest efficiency of 60.12% was achieved at pH 8.90. The influence of solution pH on COD degradation could be attributed to the resulted variation in the amount of free radicals

Table 1 Kinetic rate constants (k_1) for the COD removal by different processes

Process	k_1 (min ⁻¹)	R^2
Ultrasonic (20 kHz)	3.2×10^{-3}	0.9750
O ₃	6.7×10^{-3}	0.9655
Ultrasonic (60 kHz)/O ₃	7.1×10^{-3}	0.9326
Ultrasonic (20 kHz)/O ₃	8.4×10^{-3}	0.8872

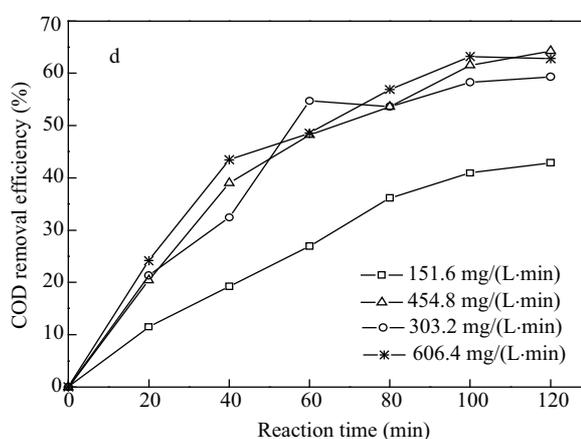
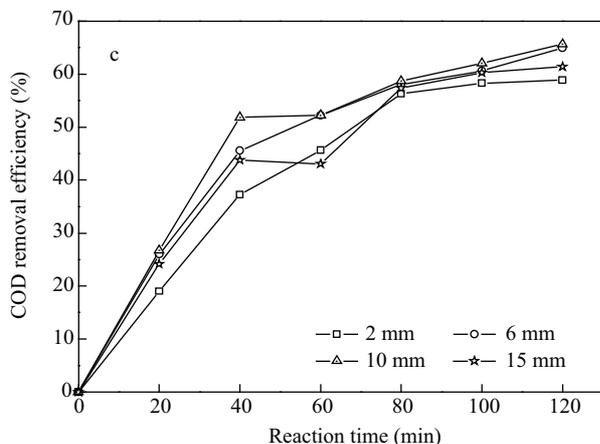
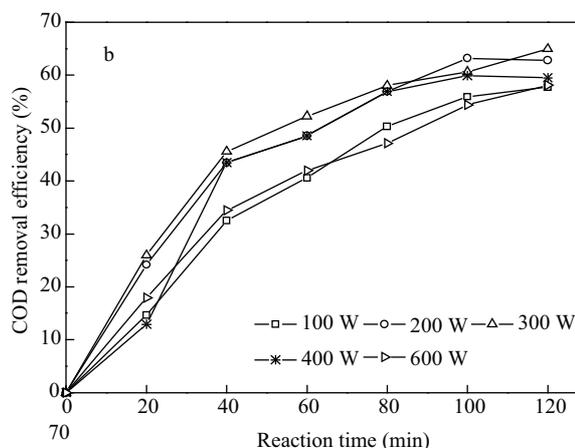
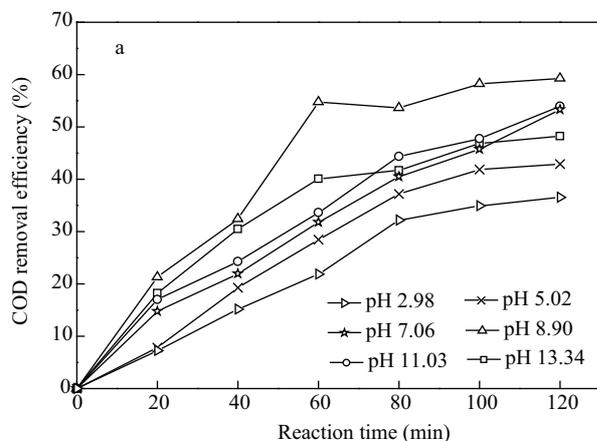


Fig. 3 Influences of initial pH (a), ultrasonic power (b), probe diameter (c), and dosage of O₃ (d) on COD removal. (a) ultrasonic frequency 20 kHz, ultrasonic power 300 W, probe diameter 10 mm, O₃ dosage 454.8 mg/(L·min); (b) ultrasonic frequency 20 kHz, pH 9.00, probe diameter 10 mm, O₃ dosage 454.8 mg/(L·min); (c) ultrasonic frequency 20 kHz, pH 9.00, ultrasonic power 300 W, O₃ dosage 454.8 mg/(L·min); (d) ultrasonic frequency 20 kHz, pH 9.00, ultrasonic power 300 W, probe diameter 10 mm.

(Staehelin and Holgne, 1985) and the form of compounds in the solution (Li et al., 2008). pH affects O_3 decomposition in water. With an increase in pH, the generation of hydroxyl radicals from the reaction between O_3 and OH^- was accelerated rapidly. However, under strong alkaline conditions, the increase in pH reduced the solubility of O_3 and caused a decrease in the mass transfer driving force. The CO_2 produced by the organics degradation was transformed into CO_3^{2-}/HCO_3^- at higher pH levels, which were free radical scavengers and could have trapped some hydroxyl radicals and thus slowed the COD degradation (Staehelin and Holgne, 1985). Moreover, under highly alkaline conditions, the organic pollutants existed in ionic forms after reacting with hydroxyls. They were less likely to enter the cavitation bubbles by evaporation, and could only be removed from the gas-liquid surface of cavitation bubbles. All these facts could have led to the decreased COD removal efficiencies at $pH > 8.90$.

The influences of ultrasonic power and ultrasonic probe diameter on COD removal from the pesticide wastewater were small according to Fig. 3b and c. The COD removal efficiency was improved by 7% with an increase in the ultrasonic power from 100 to 300 W, and dropped down back to the level at 100 W when the ultrasonic power was further increased to 600 W. A higher ultrasonic power provided more energy, which created more ultrasonic and then more micro-bubbles for the reactions. However, when the ultrasonic power was too high, the bubbles would grow bigger and caused a sound energy barrier, which was believed to reduce the energy for reactions (Sivakumar and Pandit, 2001). Extra energy under high ultrasonic power was also wasted as the form of heat as revealed by the drastic increase in the solution temperature. The ultrasonic probe diameter influenced the COD degradation marginally. Big ultrasonic probe gave a larger radiation area for reactions, whereas it reduced the ultrasonic intensity. A slightly higher efficiency of COD removal was observed with the ultrasonic probe of 10 mm in diameter.

As shown in Fig. 3d, the COD removal from the pesticide wastewater was markedly improved (from 40% to 60%) with an increase in the O_3 dosage from 151.6 to 303.2 mg/(L·min); further increase in the O_3 dosage could only give a small improvement of COD removal. This could be due to the solubility of O_3 in water.

2.1.3 Biodegradability and biological toxicity after ultrasonic/ O_3 treatment

Table 2 reveals the variation of COD and BOD_5 after treatments by the ultrasonic, O_3 and ultrasonic/ O_3 . COD removal and BOD_5 production were observed for all the three processes, resulting in an increase in the BOD_5/COD ratio. Low ultrasonic frequency (20 kHz) was more effective in the COD degradation and its conversion to BOD_5 than high ultrasonic frequency (60 kHz), which agreed with the results in Section 2.1.1. The COD removal and the BOD_5/COD were greatly improved by supplementing O_3 in the wastewater treatment. A BOD_5/COD ratio of 0.33 was achieved by the sole O_3 , indicating the resulted wastewater was turned to be biodegradable

Table 2 Comparison of biodegradability before and after treatments

Experimental mode	COD (mg/L)	COD removal efficiency (%)	BOD_5 (mg/L)	BOD_5/COD
Original wastewater	22000	0	650	0.030
Ultrasonic (60 kHz)	20734	5.8	867	0.042
Ultrasonic (20 kHz)	15236	33.7	1267	0.083
O_3	9100	58.6	2980	0.33
Ultrasonic (60 kHz)/ O_3	8562	61.1	3550	0.41
Ultrasonic (20 kHz)/ O_3	7217	67.2	4000	0.55

($BOD_5/COD > 0.3$). By ultrasonic/ O_3 combined processes, the BOD_5/COD ratio was even more increased. For example, the ratio of BOD_5/COD 0.55 was obtained in the assays with ultrasonic (20 kHz)/ O_3 . This BOD_5/COD ratio was much higher than the sum of those by sole ultrasonic and sole O_3 , suggesting a synergy effect between ultrasonic and O_3 in improving the biodegradability of the pesticide wastewater.

The influence of different processes on the biological toxicity of the pesticide wastewater is shown in Fig. 4. Higher EC_{50} values mean a lower toxicity to the T_3 luminescent bacteria. The biological toxicity was slightly lowered after the ultrasonic treatment as revealed by the EC_{50} increasing from 11% to 16%. The sole O_3 and ultrasonic/ O_3 combined processes reduced the toxicity of the wastewater greatly: the EC_{50} was increased up to 46% and 52%, respectively. The improvement of biodegradability reflects the reduction of biological toxicity, so that the results of the biological toxicity agreed with those of the biodegradability, which demonstrated the effectiveness of ultrasonic/ O_3 in the detoxication of the tested pesticide wastewater.

2.2 Product analysis

The composition of the pesticide wastewater before and after treatments is illustrated by the results of GC-MS in Fig. 5. The original pesticide wastewater

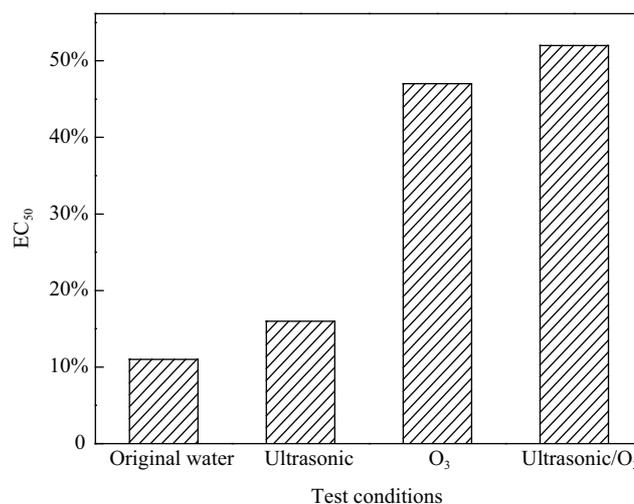


Fig. 4 Evolution of biological toxicity after treatments by different processes. Conditions using ultrasonic: pH 9.00, ultrasonic frequency 20 kHz, probe diameter 10 mm, power 300 W; conditions using O_3 : pH 13.34, O_3 dosage 454.8 mg/(L·min); conditions using ultrasonic/ O_3 : pH 9.00, ultrasonic frequency 20 kHz, probe diameter 10 mm, power 300 W, O_3 dosage 454.8 mg/(L·min).

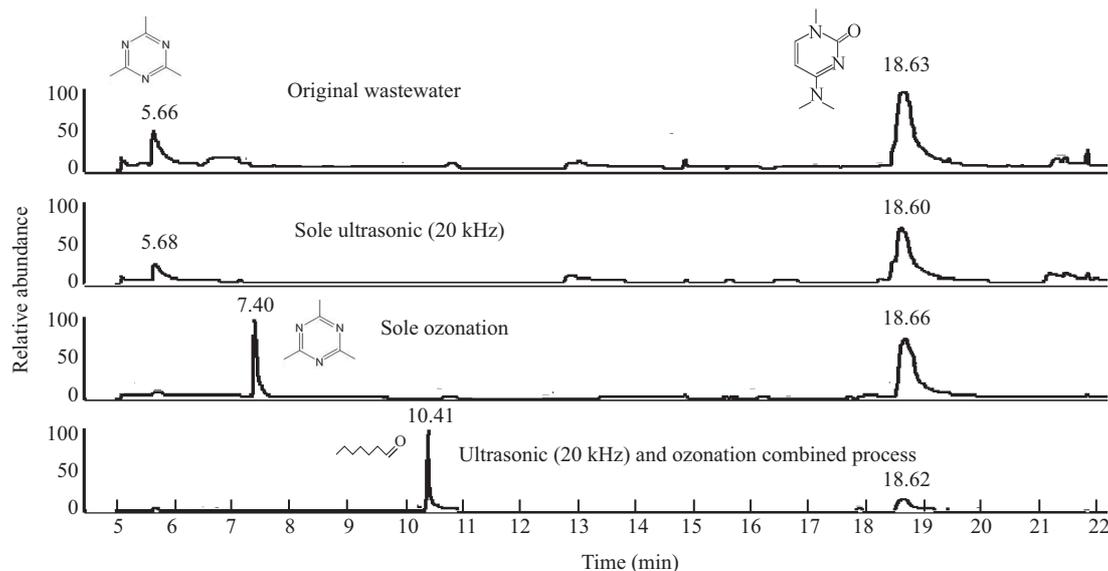


Fig. 5 GC-MS results of pesticide wastewater before and after treatments. Conditions using ultrasonic: pH 9.00, ultrasonic frequency 20 kHz, probe diameter 10 mm, power 300 W; conditions using O_3 : pH 13.34, O_3 dosage 454.8 mg/(L·min); conditions using ultrasonic/ O_3 : pH 9.00, ultrasonic frequency 20 kHz, probe diameter 10 mm, power 300 W, O_3 dosage 454.8 mg/(L·min).

ter contained complicated components with mainly two heterocyclic compounds in large quantity. The components with the retention times of 5.66 min and 18.60 min could be attributed to 1,3,5-triazine,2,4,6-trimethyl- $(C_6H_9N_3)$ and 2(1H)-pyrimidinone, 4-(dimethylamino)-1-methyl- $(C_7H_{11}N_3O)$, respectively. The concentrations of these compounds were reduced to some extent after the ultrasonic treatment. When O_3 was introduced to the wastewater, 1,3,5-triazine,2,4,6-trimethyl was nearly eliminated as well as a small reduction in 2(1H)-pyrimidinone, 4-(dimethylamino)-1-methyl. A new compound was produced with a retention time of 7.40 min, which was probably 1,3,5-triazine,hexahydro-1,3,5-trimethyl- $(C_6H_{15}N_3)$. After treatment by the ultrasonic/ O_3 combined process, the two original components were both degraded and were partially transformed into other smaller compounds. The degradation of the component with a retention time of 18.62 min could be responsible for the improvement in the biodegradability and the reduction in the biological toxicity of the pesticide wastewater.

3 Conclusions

Ultrasonic/ O_3 combined processes were shown as an effective pretreatment method for the heterocyclic pesticide wastewater. 67.2% of COD was removed from the wastewater under an optimal condition: ultrasonic frequency 20 kHz, ultrasonic power 300 W, initial pH 9.00 and O_3 dosage 454.8 mg/(L·min). Ultrasonic frequency, initial pH of the solution and O_3 dosage had great influences on the COD removal from the wastewater, whereas the influences of ultrasonic power and ultrasonic probe diameter were small. The BOD_5/COD of the pesticide wastewater was increased from 0.03 to 0.55 and the EC_{50} was increased from 11% to 52% by the ultrasonic (20 kHz)/ O_3 treatment, indicating a significant improvement in the biodegradability of the wastewater and a significant reduction in

the biological toxicity. This could be attributed to the removal of the complicated compounds and the conversion to smaller molecules.

Acknowledgments

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