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Degradation of acephate using combined ultrasonic and ozonation method

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Abstract

The degradation of acephate in aqueous solutions was investigated with the ultrasonic and ozonation methods, as well as a combination of both. An experimental facility was designed and operation parameters such as the ultrasonic power, temperature, and gas flow rate were strictly controlled at constant levels. The frequency of the ultrasonic wave was 160 kHz. The ultraviolet-visible (UV-Vis) spectroscopic and Raman spectroscopic techniques were used in the experiment. The UV-Vis spectroscopic results show that ultrasonication and ozonation have a synergistic effect in the combined system. The degradation efficiency of acephate increases from 60.6% to 87.6% after the solution is irradiated by a 160 kHz ultrasonic wave for 60 min in the ozonation process, and it is higher with the combined method than the sum of the separated ultrasonic and ozonation methods. Raman spectra studies show that degradation via the combined ultrasonic/ozonation method is more thorough than photocatalysis. The oxidability of nitrogen atoms is promoted under ultrasonic waves. Changes of the inorganic ions and degradation pathway during the degradation process were investigated in this study. Most final products are innocuous to the environment.

Keywords: Acephate; Ultrasonic wave; Ozonation; Degradation pathway

1. Introduction

Acephate is a low-toxicity pesticide. Due to its wide applicability, pesticide wastewater discharge may cause poisoning in humans. Many studies have investigated effective methods for degrading acephate, most of which involve the biodegradation method, photocatalytic decomposition, and electrolyzed water treatment (Phugare et al., 2012; Hao et al., 2011; Han et al., 2009). In addition, there are other mainstream pesticide wastewater degradation methods called advanced oxidation processes (AOPs). In these methods, the oxidant breaks down organic compounds by dissolving them in water (Chen et al., 2013). These processes have attracted great interest in the pesticide wastewater treatment field.

Ozonation is an AOP, and ozone (O_3) is widely used in wastewater pretreatment as a strong oxidant. It generates a single atom of oxygen (O) and a hydroxyl radical (•OH) with a strong oxidation capacity, which can decompose the organic compounds in water instantly (Esplugas et al., 2002; Yang et al., 2012). Because the oxidability of hydroxyl radicals is as strong as fluorine, O_3 water can not only break the acephate's carbon chain in the molecular structure, but also oxidize the nitro or amino group and completely change the

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molecular structure of organics. Thus, the toxicity of pesticides can be degraded (Li et al., 2012; Xu et al., 2002). Moreover, excess O_3 can be safely decomposed into oxygen, and most products can be discharged into the environment directly, because they are water-soluble. The degradation efficiency of pesticides during ozonation increases when the ultrasonic wave is involved (Naddeo et al., 2009). First, the degradation process is feasible when the ultrasonic wave is used alone. Instantaneous negative pressure is generated in liquid when there is sufficient ultrasonic power. When the medium molecular spacing exceeds the critical molecular spacing, cavitation bubbles are formed. At the moment that bubbles explode, local high-temperature and high-pressure environments are produced. The water molecules crack and become strong oxidants such as •OH, HO_2, and •O (Shriwas and Gogate, 2011; Matouq et al., 2008; Xiong et al., 2012; Golash and Gogate, 2012). Zhang et al. (2010) investigated degradation behavior of ultrasonic waves, and found that products of malathion and chlorpyrifos in apple juice increased significantly with ultrasonic treatment. The maximum degradation efficiencies were achieved for malathion (41.7%) and chlorpyrifos (82.0%) after ultrasonic treatment at 500 W for 120 min. Second, when the ultrasonic and ozonation methods are combined, the ultrasonic wave breaks O_3 into micro-bubbles and improves the solubility of O_3 in solution. Meanwhile, micro-bubbles enhance the intensity of ultrasonic cavitation (Sivakumar and Pandit, 2001; Wang et al., 2006). An appropriate frequency value of ultrasonic wave can be chosen to create a sonochemical reaction, which provides its maximum yield according to the distribution of bubbles in liquid (Zhu et al., 2011). A Gaussian-shape distribution of gas bubble radii is to be expected in water:

$$N(R) = A \exp\left[-\frac{(R-R_0)^2}{2\delta^2}\right] \tag{1}$$

where $N(R)$ is the number of bubbles with a radius of R in a unit volume of liquid; R_0 is the bubbles' most probable value of radii in a certain volume of liquid, and also the center value of the distribution curve; δ is the scale factor of this Gaussian function; and A is a coefficient. $N(R)$ is at its highest value when $R = R_0$. The frequency effect of the low-frequency ultrasound using the electrical detection method was investigated by Huang et al. (1995). The experimental data showed that the optimum frequency should be about 159.54 kHz and the bubbles' most probable value of radii was 17.88 μm.

It is difficult to use the traditional treatment methods to effectively solve the secondary pollution problem, especially in chemical water treatment. Sonochemical degradation is a purely physical wastewater treatment method, and O_3 is much safer compared to other chemical reagents. The ultrasonic method combined with ozonation (the combined ultrasonic/ozonation method) is still a recommended method in the wastewater treatment field. In the past few years, many studies (Liu et al., 2008; Naddeo et al., 2009; Krishnamoorthya et al., 2013) have been performed using the ultrasonic method to degrade different organic compounds, but investigation of acephate degradation using the sonochemical method has rarely been carried out. This study examined the performance of the combined ultrasonic/ozonation method in degrading the acephate solution. We observed the variation of degradation efficiency with time using only the ultrasonic method, only the ozonation method, and the combined ultrasonic/ozonation method under a 160 kHz ultrasonic wave, in order to find the relationship between the promotion effect and the degradation efficiency throughout the processes. The products of inorganic ions were measured separately for comparison with the results presented in Han et al. (2009) using photocatalytic decomposition.

2. Materials and methods

2.1. Pesticide solution

The raw material of the pesticide solution was the water-dispersible granules of acephate, with a purity of 97%, which is produced by India United Phosphide Co., Ltd. The granules were dissolved in water, with a concentration of 100 mg/L. The solution was stored in a brown glass bottle and the pH value was stable at 7.9 after the solution became motionless.

2.2. Experimental setup

The experimental facility of the combined ultrasonic/ozonation process is illustrated in Fig. 1. The reactor was a cylindrical steel structure with a diameter of 90 mm, a height of 120 mm, and a maximum capacity of 500 mL. An ultrasonic transducer with a frequency of 160 kHz was glued to the bottom of the reactor, with a maximum power of 50 W. The lateral wall of the reactor was filled with cooling water in order to keep the solution temperature at (25±1)°C. An ultrasonic wave generator (developed by the authors) was used to drive the 160 kHz ultrasonic transducer. An air-fed ozonator (YL-G3500, from Beijing Yilang Technology Co., Ltd., in China) was used, with an O_3 amount of 3 500 mg/h. The gas was transmitted into the reactor via a porous diffuser and the gas flow rate was maintained by a rotameter (LZB-3WB, from Changzhou Ruiming Instrument Co., Ltd., in China) at 2 L/min. An ultraviolet-visible (UV-Vis) spectrophotometer (T6S, from Beijing Persee Instrument Co., Ltd., in China) was used to detect the

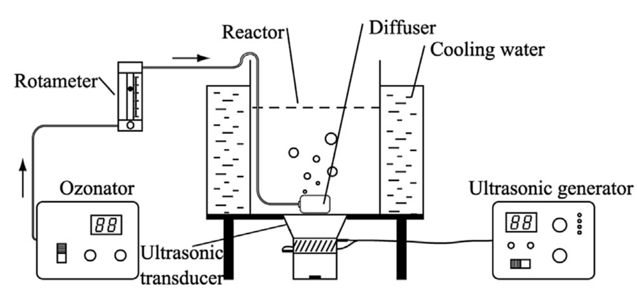

Fig. 1. Schematic diagram of combined ultrasonic/ozonation process.