Separation and Purification Technology 140 (2015) 6–12

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Degradation and detoxification of diazinon by sono-Fenton and sono-Fenton-like processes

Chikang Wang *, Yiheng Shih

Department of Environmental Engineering and Health, Yuanpei University of Medical Technology, 306 Yuanpei St., Hsinchu, Taiwan

ARTICLE INFO

Article history:
Received 9 September 2014
Received in revised form 7 November 2014
Accepted 13 November 2014
Available online 21 November 2014

Keywords:
Diazinon
Mineralization
Sono-Fenton
Sono-Fenton-like
Toxicity

ABSTRACT

The degradation of the organophosphorus pesticide diazinon by means of sono-Fenton and sono-Fenton-like systems was investigated in this study. The effects of a combination of transition metals, the concentration of Fenton's reagent and temperature on diazinon degradation were examined. An initial concentration of 50 mg L^{-1} diazinon was used in this study as a model solution. For the sono-Fenton and sono-Fenton-like experiments, an ultrasonic probe at a frequency of 20 kHz was employed. The optimal experimental conditions were determined to be as follows: 20 mg L^{-1} Fe^{2+}, 150 mg L^{-1} H_2O_2, 25 °C and pH 3. According to the results, the diazinon removal efficiency after 60 min was 98.3%, and the mineralization efficiency was 29.9%. It was also found that the toxicity of the diazinon solution was efficiently reduced by a sono-Fenton process. The most important mechanism of degradation was the substitution of sulfur by oxygen on the P=S bond in diazinon through oxidation.

1. Introduction

Pesticides are well known to be carcinogenic, mutagenic, teratogenic and simultaneously resistant to destruction in environment [1]. Fourteen types of organophosphorus pesticides, such as azinphos-methyl, diazinon, dichlorvos, malathion, and parathion, are extensively used in Taiwan for agricultural activities. However, organophosphorus pesticides are extremely toxic, acting as an inhibitor of acetylcholinesterase in insects, which disrupts the nervous system of simpler organisms, and are responsible for toxicity in humans [2]. The application of organophosphorus pesticides leads to the common occurrence of organophosphorus pesticides residues in food crops, natural water systems and soil [3].

Diazinon (O,O-diethyl O-(2-isopropyl-6-methylpyrimidin-4-yl)thiophosphate) is a commonly used insecticide in the organophosphate chemical family and was commercially introduced in 1952 [5]. Diazinon has been classified by the WHO as moderately hazardous Class II, and the oral LD_{50} for rats is 18 mg/kg (MSDS). Additionally, high diazinon residues were found in urbane waterways and effluents from sewage treatment plants [4] where the residual concentrations of diazinon were among 0.41–1 μg L^{-1}. It appears to be persistent enough to significantly affect water resources in the environment. Hence, understanding how to effectively degrade the diazinon residues in aqueous phase requires consideration.

Biological remediation processes have been proven that they are not suitable for rapid removal of the diazinon from contaminated water [5,6], and therefore, alternative treatment methods are required. Among several available treatment methods, the advanced oxidation processes (AOPs) are the most promising alternative to treat the diazinon because they involve the generation of hydroxyl radicals ($^{\cdot}OH$), which are nonselective of species and highly reactive oxidants [7–13]. Matouq et al. [8] used an ultrasound (frequency of 1.7 MHz and 125 W) equipped with a 40–60 mL reactor to treat 800–1800 mg L^{-1} diazinon and found that degradation increased with the concentration of diazinon, and when the solution volume increased, the ability to degraded pesticides decreased. The experimental results showed that the optimal conditions for the degradation of diazinon were an initial concentration of 1200 mg L^{-1} and a 50 mL solution volume. Zhang et al. [14] used a ultrasound (frequency of 25 kHz and 100–500 W) equipped with a 150 mL reactor to treat 2.38–80 mg L^{-1} diazinon and found that both ultrasonic power and the initial concentration of diazinon significantly influenced the percent of degradation of diazinon. Although the above studies showed that the diazinon could be readily degraded by ultrasound, they were both conducted with small reactors (0.04–0.15 L) and half of the diazinon still remained in the water sample after 120 min of treatment. Hence, ways to enhance the degradation of diazinon and shorten the treatment duration based on an ultrasonic system require

---

* Corresponding author.
E-mail addresses: ckwang@mail.ypu.edu.tw, ckwang168@yahoo.com.tw (C. Wang).

http://dx.doi.org/10.1016/j.seppur.2014.11.005
1383-5866/

further investigation. Wang et al. [15] used the sono-Fenton process (namely, a combination of ultrasound and Fenton's reagents) to degrade ethylenediamine and found that more than 71% of ethylenediamine was degraded within a very short time. Additionally, the toxicity of ethylenediamine wastewater was reduced by the sono-Fenton process. However, additional amounts of Fe^{2+} will increase the toxicity of the treated wastewater and the formation of ferric hydroxide sludge, so many researchers have tried to replace the Fe^{2+} by transition metals such as Ag^+ and Co^{2+} [16–19].

Hence, a sono-Fenton-like process, namely, a combination of ultrasound and H_2O_2 with alternative transition metals (Fe^{2+}, Ag^+ and Co^{2+}), was designed in this study to degrade the diazinon. The objectives were to investigate the feasibility of sono-Fenton and sono-Fenton-like processes on the degradation of diazinon and to understand the effects of different combinations of transition metals and the dosage of Fenton's reagents and temperatures. Additionally, the toxicity measured by the cell viability before and after treatments and the possible degradation by-products and mechanisms were proposed.

2. Materials and methods

2.1. Standards and reagents

Diazinon (analytical standard) was purchased from Sigma–Aldrich. Other chemical reagents used in this study including H_2SO_4, NaOH, $FeSO_4{\cdot}7H_2O$, $AgNO_3$, $Co(NO_3)_2{\cdot}6H_2O$ and an aqueous solution of H_2O_2 (30%, w/w in water) were of the purest grade commercially available and were used without further purification. During the analytical process, dichloromethane and n-hexane were used to isolate the diazinon and oxidation by-products from aqueous solution via a liquid–liquid extraction procedure. To investigate the mineralization of diazinon, profiles of total organic carbon (TOC) concentration were measured and potassium hydrogen phthalate ($C_8H_5KO_4$) was used as the standard chemical.

2.2. Ultrasonic device and treatment conditions

Ultrasonic treatment was carried out with a sonicator (Microson VCX 750, USA) equipped with a sealed converter (Model CV 33, 63.5 mm in diameter and 183 mm in length) and a titanium probe tip (Part. No. 630-0210, 25 mm in diameter and 122 mm in length). The ultrasonic transducer operated at 20 kHz continuously, with a maximum output power of 750 W. A diazinon sample (1000 mL) was added to a cylindrical reactor (working volume of 1 L with a cooling jacket) and treated through dipping the titanium probe tip in diazinon sample 50 mm below the surface. A circulating temperature controller was equipped to maintain the reaction temperature (15–55 °C); other reaction parameters were designed at H_2O_2 concentrations of 0–150 mg L^{-1}, Fe^{2+} concentrations of 0–20 mg L^{-1} and ultrasonic powers of 100 W. We used the calorimetric method to make sure the energy efficiency of ultrasonic horn was about 51.9% so that the actually calorimetric power in our system should be as maximum as 51.9 W. In addition to H_2O_2 and Fe^{2+}, Co^{2+} and Ag^+ (both 10 mg L^{-1}) were also evaluated to investigate the effect of transition metals on the degradation of diazinon. Fig. 1 shows the schematic diagram of the sono-Fenton and sono-Fenton-like systems. Aeration of the reactor during the reaction was maintained at 0.2 L min^{-1} to provide sufficient dissolved oxygen. The reactor was equipped with pH and ORP (oxidation–reduction potential) meters (Suntex PC-3200, Taiwan) to monitor the profiles of pH and ORP values.

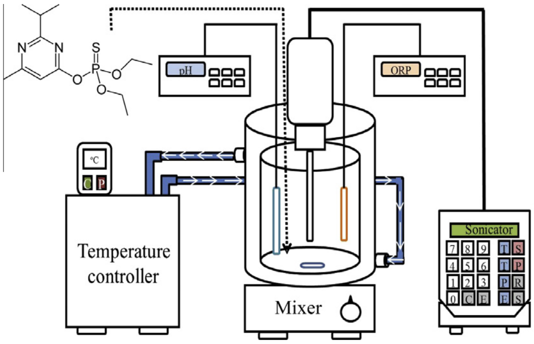

Fig. 1. Schematic diagram of the experimental apparatus designed for the degradation of diazinon.

2.3. Sample extraction

The extraction of diazinon is a modification of the standard method established by the Environmental Protection Agency of Taiwan (NIEA W662.50C). An aliquot of diazinon sample (10.0 mL) was mixed with 1.0 mL of n-hexane in a brown Pyrex glass tube (20 mL). The mixture was shaken vigorously for 30 min at a mixing speed of 150 rpm. For the qualification of diazinon and oxidation by-products by gas chromatography/mass spectrometry detector (GC/MS) during the oxidation process, 1.0 mL dichloromethane was used as the extraction solvent.

2.4. GC and TOC analysis

The concentration of diazinon was detected with a gas chromatography/flame ionization detector (GC/FID-Varian GC 3400, Mulgarve, Victoria, Australia) equipped with a DB-1 fused silica capillary column (30 m × 0.53 mm i.d., 1.50 μm). Nitrogen gas was used as a carrier gas (15 mL min^{-1}); hydrogen gas (33 mL min^{-1}) and air (400 mL min^{-1}) were used for the GC/FID. The GC oven temperature program was as follows: initial temperature of 120 °C held for 1 min, then from 120 to 240 °C at 20 °C min^{-1}, and finally, held for 7 min at 240 °C. The injector and detector temperatures were set at 250 °C and 260 °C, respectively. Sample solution (1.0 μL) was injected in splitless mode. The mineralization of diazinon was investigated by determining the TOC concentration using a total organic carbon analyzer (TOC-500, Shimadzu, Japan).

2.5. GC/MS analysis

GC/MS qualitative analysis was performed on a Shimadzu GC/MS-GC2010 Plus (Shimadzu Co., Kyoto, Japan). The sample solution was injected with an AOC-20i autosampler (Shimadzu Co., Kyoto, Japan). The GC analysis was performed with a HP-5MS column (length 30 m, thickness 0.25 μm, diameter 0.25 mm). The oven temperature program was started at 80 °C and increased to 180 °C at a rate of 20 °C min^{-1}, was held for 2 min, then further increased to 250 °C at a rate of 5 °C min^{-1}, and was held for 5 min at 240 °C. The injector and detector temperatures were 250 °C and 280 °C, respectively. High purity helium (99.99%) was used as a carrier gas (1.5 mL min^{-1}), and the sample was analyzed in splitless mode. Mass spectra were obtained by electron-impact (EI) at 70 eV using the full-scan mode. The spectrum of diazinon analysis by the GC/FID and GC/MS is shown in Fig. 2.

2.6. Toxicity analysis

The toxicity of diazinon samples (before and after treatments) was performed by assessing the cell viability, where the viability was defined by cell counting. The steps for cell counting are shown below. The water samples were first sterilized by filtration through a 0.25-μm Millipore membrane filter (Millipore, Bedford, USA). The