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Technical Note

Degradation of DEET by ozonation in aqueous solution

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ABSTRACT

This study was undertaken in order to understand the factors affecting the degradation of an insect repellent, *N,N*-diethyl-*m*-toluamide (DEET) by ozonation. Kinetic studies on DEET degradation were carried out under different operating conditions, such as varied ozone doses, pH values of solution, initial concentrations of DEET, and solution temperatures. The degradation of DEET by ozonation follows the pseudo-first-order kinetic model. The rate of DEET degradation increased exponentially with temperature in the range studied (20–50 °C) and in proportion with the dosage of ozone applied. The ozonation of DEET under different pH conditions in the presence of phosphate buffer occurred in two stages. During the first stage, the rate constant, k_{obs}, increased with increasing pH, whereas in the second stage, the rate constant, k_{obs2}, increased from pH 2.3 up to 9.9, however, it decreased when the pH value exceeded 9.9. In the case where buffers were not employed, the k_{obs} were found to increase exponentially with pH from 2.5 to 9.2 and the ozonation was observed to occur in one stage. The rate of degradation decreased exponentially with the initial concentration of DEET.

GC/MS analysis of the by-products from DEET degradation were identified to be *N,N*-diethyl-formamide, *N,N*-diethyl-4-methylpent-2-enamide, 4-methylhex-2-enedioic acid, *N*-ethyl-*m*-toluamide, *N,N*-diethyl-*o*-toluamide, *N*-acetyl-*N*-ethyl-*m*-toluamide, *N*-acetyl-*N*-ethyl-*m*-toluamide 2-(diethylamino)-1-*m*-tolylethanone and 2-(diethylcarbamoyl)-4-methylhex-2-enedioic acid. These by-products resulted from ozonation of the aliphatic chain as well as the aromatic ring of DEET during the degradation process.

1. Introduction

DEET (*N,N*-diethyl-*m*-toluamide), an active compound in insect repellents was first introduced by the US Army in 1946 for protection against insect bites has been in the market for more than 50 years (USEPA, 1998). Contaminations of DEET have been studied and reported in various aquatic environments, such as groundwater (Barnes et al., 2004; Costanzo et al., 2007), streams (Kolpin et al., 2004), seawater, effluents from sewage plant (Weigel et al., 2004), and even drinking water treated by conventional water-treatment systems (Stackelberg et al., 2004).

DEET has been reported to have potential carcinogenic properties in human nasal mucosal cells (Tisch et al., 2002). Ingestion of low doses of DEET in children has been reported to result in coma and seizures (Petrucci and Sardini, 2000). Currently, there is no legislation controlling the amounts of both usage and discharge of DEET into the environment. Thus, greater attention should be paid to removing this chemical, especially in the production of drinking water.

Ozonation is a water-treatment technology which has been projected to be the fastest growing water-disinfection method in the market (Sowmya, 2008). During ozonation, organic pollutants undergo a series of oxidation processes, and in some cases, highly toxic by-products can be produced (Ikehata et al., 2006). These undesired degradation by-products may become new chemical entities in the environment following the discharge of incompletely treated effluents into the environment. Thus, evaluation and determination of by-products from ozonation are important considerations for environmental protection purposes.

The objectives of this work are (i) to study the influences of several operating parameters on the ozone degradation of DEET, such as temperature, pH, initial concentration, and ozone dose (ii) to identify major by-products of DEET degradation, and (iii) to propose the reaction mechanism for DEET degradation by ozonation.

Earlier studies have confirmed the presence of DEET at trace levels in the environment. The concentrations of DEET used in this experiment are higher than those found in aquatic environments and may not be directly relevant to the environment. This method will enable observation of DEET reduction over at least an order of magnitude without extensive sample preparation procedures.

2. Materials and methods

2.1. Chemicals

DEET was obtained from Aldrich, USA, and used without further purification. All the stock solutions were prepared by dissolving DEET in ultrapure deionized water (Elga, USA). All solvents were

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of high-performance liquid chromatography (HPLC) grade and were used without purification. HPLC grade solvents, sulfuric acid and hydrochloric acid were purchased from Merck (Germany). Phosphate buffer (0.5 M) was prepared using sodium dihydrogen-phosphate (Aldrich, USA) and/or disodium hydrogen-phosphate (Riedel-de Haën, Germany) and the pH was adjusted using either phosphoric acid (Merck, Germany) or sodium hydroxide (Fluka, Germany) solutions. Tert-butanol was purchased from Riedel-de Haën (Germany).

2.2. Degradation of DEET by ozonation

Ozonation experiments were performed in a 1000 mL cylindrical jacketed beaker. Ozone was continuously bubbled into stirred DEET solution through a gas-dispersion tube placed at the bottom of the reactor. Ozone was produced from purified oxygen (99.8%) by an OZX03 K-model ozone generator (Enaly Trade Co. Ltd., Canada). Ozone doses were determined by the iodometric method. Reaction temperatures were maintained at the desired value ±0.1 °C using a circulating water bath. Samples were withdrawn at defined time intervals and nitrogen gas was used to remove the residual ozone. The degradation of DEET was studied under various initial concentrations of DEET ranging from 5 to 25 mg L^{-1}, pH values ranging from 2.3 to 11.7 (pH was adjusted using 50 mM phosphate buffer), reaction temperatures ranging from 20 to 50 °C, and ozone dosages ranging from 0.51 to 0.76 g h^{-1} (Supplementary Material (SM), Table SM-1). The pH value of the DEET solutions without pH adjustment was 6.5. Values for the unbuffered solutions were adjusted with sulfuric acid to pH $\leqslant$ 6.5 and with sodium hydroxide to pH > 6.5. Some runs were carried out in the presence of t-butanol (50 mM) as the hydroxyl radical scavenger.

2.3. Degradation by-products study

Initial DEET concentration of 10 mg L^{-1} was selected for identification of the by-products of DEET degradation. Ozonation was carried out at 25 °C at an ozone dosage of 0.51 g h^{-1} and without pH adjustment. A small sample (20 mL) was withdrawn every 2 min throughout a 1 h period and nitrogen gas was used to remove the residual ozone. Sample extraction was carried out on a Lichrolut vacuum manifold (Merck, Germany) using 200 mg Lichrolut EN SPE (solid-phase extraction) cartridges (Merck, Germany). SPE cartridges were serially conditioned with 3 mL of ethyl acetate and 3 mL of dichloromethane, followed by 9 mL of acidified deionized water (pH 2). Samples were adjusted to pH 2 and then loaded onto the SPE cartridges. The flow rate was adjusted to 1 mL min^{-1}. The cartridges were dried under a stream of purified nitrogen (99.999%), and the retained organic components were eluted with three 0.3 mL aliquots of ethyl acetate. The extract was dried by evaporation and then dissolved in 20 μL of ethyl acetate; a 1.2 μL aliquot of the solution was injected into GC/MS.

2.4. Analytical methods

The concentration of DEET was monitored using a HPLC (Thermo Finnigan, Spectra System P2000) equipped with a UV detector (UV 2000), degasser (SCM1000) and a chromolith RP-18 (100 × 4.6 mm) monolithic column (Merck, Germany). The mobile phase used was a mixture of acetonitrile (Solvent A) and deionized water (Solvent B). The flow rate was maintained at 1.0 mL min^{-1} for all runs. Gradient elution was carried out as follows: the initial mobile phase was a mixture of 20A:80B (v/v); subsequently, it was increased to 40A:60B (v/v) over a period of 10 min. A 5 min reequilibration using 20A:80B (v/v) was carried out between sample injections. The detection wavelength was 210 nm.

The analysis of degradation by-products was carried out using a Hewlett-Packard Model 6890 GC, with a HP-5 (5% phenylmethylpolysiloxane) column of dimensions 30 m × 0.25 mm × 0.25 μm. Helium (purity 99.999%) was used as the carrier gas, with an average velocity of 40 cm s^{-1}, and the temperature for the GC oven was programmed for an initial temperature of 60 °C maintained for 2 min, which was further increased to 280 °C at the rate of 6 °C min^{-1} and was maintained at this temperature for 2 min. The temperatures of the injection port and the transfer line were maintained at 290 and 300 °C, respectively. The data for quantitative analysis was acquired in the electron impact mode (70 eV), scanning in the range of 50–550 amu at 1.5 s $scan^{-1}$.

3. Results and discussion

3.1. Rate of degradation and kinetic study

In this study, degradation of DEET by ozonation involving a gas–liquid heterogeneous system followed the pseudo-first-order kinetic model. The pseudo-first-order kinetic plots are shown in Fig. 1 and the rate constants obtained are presented in Table SM-1.

3.1.1. Influence of temperature

This study shows that the rate of DEET degradation increases exponentially with temperature (Fig. SM-1a). Temperature is an important factor that influences the solubility of ozone. According to Song et al. (2007), the solubility of ozone in aqueous solution decreases with increase in the temperature of the solution; however, from our observation, the rate of degradation of DEET increases with temperature. This may indicate that the solubility of ozone is not a major factor that influences the decomposition of DEET and that the removal of DEET from water can be accelerated by increasing the reaction temperature.

3.1.2. Influence of initial DEET concentration

The rate of DEET degradation is found to decrease exponentially (Fig. SM-1b) with an increase in the initial concentration of DEET. Because ozone inlet concentration and flow rate are maintained constant throughout the experiment, the amount of ozone introduced into the aqueous phase and the amount of hydroxyl radical produced are presumed to be constant. Higher concentration of degradation by-products were produced initially, when the concentration of DEET was high. However, due to the nonselective behavior of hydroxyl radicals, there is competition between the degradation by-products and DEET for the reaction with hydroxyl radicals, thereby reducing the rate of DEET degradation later on. Thus, as reported by Wu et al. (1998) in the treatment of reactive-dye wastewater, the concentration of degradation products produced during ozonation is a major factor in reducing the rate of DEET degradation.

3.1.3. Influence of pH

Experiments were carried out in both buffered and unbuffered conditions. For buffered condition, the pH did not change (decrease) more than ±0.1 pH units throughout the experiments. However, for those without buffer, the pH was found to decrease during the ozonation process except for the initial pH of 2.5 and 11.4 (Fig. SM-2).

Under buffered conditions, the amount of hydroxyl radical remained constant during the ozonation process and the ozonation was observed to occur in two stages (Fig. 1ci). As suggested by Chen et al. (2003), the change in k_{obs} is possibly due to the decrease of the concentration of selected organic compounds in the