Degradation of N,N-diethyl-m-toluamide (DEET) by sono-Fenton process: Complex by-products from synergistic effect

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C. T. Aravindakumar[1,2]*. (1) School of Environmental Sciences (2) Inter University Instrumentation Centre, Mahatma Gandhi University, Kottayam 686560, Kerala, India, cta@mgu.ac.in*

DEET (N,N-diethyl-m-toluamide) is a widely used insect repellent world over and is listed under the category of pharmaceuticals and personal care products (PPCPs) within contaminants of emerging concern (CECs). A detailed investigation on the sonochemical degradation of DEET was carried out in aqueous medium. Presence of inorganic ions (except NO_3^-), organic matter and surfactants showed a positive effect on the degradation. Significant TOC reduction (≈96%) was achieved at 90 min of sonolysis which is the highest figure compared to all other reported AOP based degradation of DEET. The addition of Fe^{2+} (5×10^{-5} M) exhibited a positive synergy and leads to remarkable enhancement in the degradation efficiency up to 99%. The degradation products of both the sonolysis and sono-Fenton were analyzed by using LC-Q-ToF-MS. Fourteen sonochemical and six sono-Fenton degradation products were identified. Based on the identified intermediates, possible degradation pathways are proposed. Sonolysis mainly proceeds through hydroxylation (mono and poly) along with oxidation, demethylation, aromatic ring cleavage and hydrolysis. Whereas, majority of the sono-Fenton products are observed to be the breakdown products after dimerization followed by radical reactions. This study provides new insights on complex breakdown products of DEET dimers formed during sono-Fenton, which has high relevance in its degradation protocol in natural environment as well as waste water treatment.

Introduction

Degradation studies of DEET have gained scientific attention worldwide for more than two decades because of its continuous release into water bodies as a contaminant of emerging concern (CEC). DEET is a widely used insect repellent world over. Studies reporting the occurrence of DEET in water are increasing exponentially at global level. The ubiquitous occurrence of DEET in the aqueous environment mostly results from the incomplete removal of the compound by conventional wastewater treatment plants [1]. So, upgradation of the existing treatment methods with advanced treatment processes is essential for the better attenuation of this micro pollutant. Since aquatic systems appear to be the main environmental sink for DEET, studies on degradation of this compound in aqueous medium using a suitable treatment technique is a very relevant topic of investigation [2,3]. To date, sonochemical degradation of DEET in aqueous medium has not been investigated in detail and thus is the focus of this study. The specific objectives are (i) to evaluate the influence of pH, inorganic anions, organic matter (humic acid) and additives like Fe^{2+} and surfactants on the efficiency of degradation, (ii) to analyze the extent of mineralization, and (iii) to identify the degradation products using high resolution mass spectrometric (HRMS) technique (LC–Q-ToF–MS) followed by the elucidation of a possible mechanism of the degradation process. In order to see the workability of this technique in the context of water treatment, the efficiency of degradation and mineralization were also monitored in river water.

Experimental

The experiments were carried out in a sonoreactor with a frequency of 620 kHz and at a power of 30 W (L3 ELAC Nautik). The degradation of DEET was monitored by using high performance liquid chromatography (Shimadzu prominence UFLC, LC 20 AD) connected with a diode array detector (SPD-M20 A). TOC was analyzed by using a TOC analyzer (Skalar, Formacs^{HT} TOC/TN analyzer, HTAccess^{TM} V3) with a non-dispersive IR (NDIR) detector. The degradation products obtained during sonolysis were analyzed by using Waters Xevo G2 Q TOF with electrospray ionization (ESI) source coupled to Acquity H class UPLC system with BEH C18 column, 50×2.1 mm, 1.7 µm. The anions and cations released during the sonolysis were analysed by Dionex ICS-1100 ion chromatography with conductivity detector.

Results and Discussion

The degradation of DEET initiated by ultrasound (at frequency 620 kHz, power 30 W and pH 6) followed a pseudo-first-order kinetics under sonochemical degradation. 74% of degradation was observed in 90 min of sonolysis and the corresponding rate constant is 0.01553 min^{-1}. Reaction with $HO^{\bullet}$ was reported as the predominant oxidation pathway of DEET in previous studies with other AOPs. The sonochemical degradation at acidic and alkaline pH is presented in Figure 1 together with near natural pH (6) of the solution.

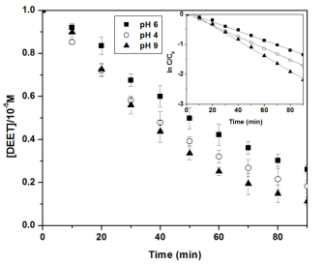

Figure 1. Degradation of DEET at varying pH, $[DEET]_0 = 10^{-5}$ M, Frequency = 620 kHz, Power = 30 W; *Inset: first order kinetic plot*.

Carbon and nitrogen mineralization was examined in terms of TOC reduction and release of NO_3^- and ammonium ions. Around 96% TOC reduction was achieved at 90 min ultrasonic irradiation of DEET with an initial concentration of 1×10^{-5} M. Continuous release of nitrogen as NO_3^- and ammonium ions was also observed during the process. The release of ammonium ions is probably due to the conversion of bound nitrogen in the compound into ammonium ions. The release of NO_3^- ion is likely to be the result of $HO^\bullet$ attack at NH_2 group of DEET. Stoichiometric amounts of nitrogen release as NO_3^- and ammonium ions had been already reported in the photocatalytic transformation study of DEET.

Effect of Fe^{2+} (Sono-Fenton reaction)

In sonolysis, the presence of Fe^{2+} can augment the degradation by initiating Fenton process and seldom it act as $HO^\bullet$ scavenger. The degradation rate was increased drastically with the addition of Fe^{2+}. The pseudo-first-order rate constant of sonolysis in the presence of Fe^{2+} (0.06795 min^{-1}) was almost four times higher than sonolysis alone (0.01553min^{-1}). Also, the degradation percentage was increased from 74% to 91%, 96% and 99% with the addition of 5×10^{-6}, 1×10^{-5} and 5×10^{-5} M of Fe^{2+}, respectively. This enhancement in the degradation rate was mainly due to the production of additional $HO^\bullet$ through Fenton chemistry. Once Fe^{2+} is added to the system, it can initiate reactions with sonochemically generated hydrogen peroxide as follows (reactions (1) - (4)).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + HO^- \quad (1)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^{2+} + H^+ \quad (2)$$
$$Fe(OOH)^{2+} \rightarrow Fe^{2+} + HOO^\bullet \quad (3)$$
$$Fe^{3+} + HOO^\bullet \rightarrow Fe^{2+} + O_2 + H^+ \quad (4)$$

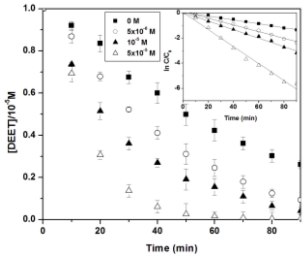

Figure 2. Degradation of DEET in the presence of Fe^{2+}, $[DEET]_0 = 10^{-5}$ M, Frequency = 620 kHz, Power = 30 W.

Analysis of sono-Fenton degradation products and possible pathways

Degradation products formed during sono-Fenton were analyzed as it showed a remarkable enhancement in the degradation rate of DEET. Based on the structural educidation of the products, the following degradation pathways is proposed (Figure 3) [4-6].

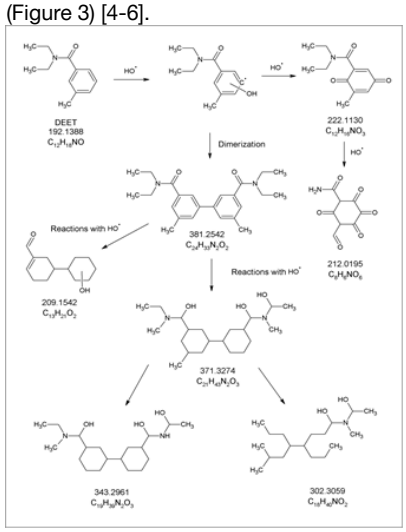

Figure 3. Transformation pathway of DEET during ferro-sonolysis.

Conclusions

This study demonstrates that sonolysis is an effective treatment method for the removal of DEET in aqueous medium with highest mineralization rate and minimal byproduct formation that are less toxic. It is very probable that the dimeric products may be formed in water bodies having the presence of DEET since the presence of Fe2+ and free radicals is very likely in aquatic matrices [7].

References

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