



RESEARCH ARTICLE

The oxidation study of N,N-diethyl-meta-toluamide in dual frequency ultrasonic reactor

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ABSTRACT

With the increasing concern of emerging contaminants (ECs), advanced oxidation processes (AOPs) have been widely investigated to fulfill the drinking water quality because of the potential adverse health effects of ECs. Accordingly, N,N-diethyl-meta-toluamide (DEET) is selected as a model compound belonging ECs to monitor its ultrasonic oxidation which is one of the most popular AOPs in a dual frequency ultrasonic reactor (DFUR) using low-frequency probe (20 KHz) and high-frequency transducer (640 KHz) type sources. DFUR was calorimetrically optimized in terms of power densities of both ultrasonic sources in order to provide the highest sonochemical yield with efficient energy output. Pseudo-first order kinetic equation was applied to results by measuring the concentration decreasing during the oxidation reactions. The pseudo-first-order rate constants, k , increased from $7.8 \times 10^{-3} \text{ min}^{-1}$ (640 kHz, $R^2=0.930$) to $13.5 \times 10^{-3} \text{ min}^{-1}$ (DFUR, $R^2=0.990$), by contrast, the rate constant was only $0.7 \times 10^{-3} \text{ min}^{-1}$ ($R^2=0.281$) for 20 kHz low-frequency ultrasonic source. DEET oxidation was evaluated with the presence of different gas saturation (Ar, Air, O₂, and N₂); addition of hydrogen peroxide (PO), persulfate (PS) and monoperoxysulfate (MPS) and PO concentration effect (molar ratio of DEET:PO; 1:1, 1:2, 1:5, 1:10 and 1:20). The DEET oxidation rate was calculated as $35.8 \times 10^{-3} \text{ min}^{-1}$ ($R^2=0.994$) in the presence of Argon gas saturation, while it was $13.5 \times 10^{-3} \text{ min}^{-1}$ ($R^2=0.990$) when no gas bubbling. Therefore, the main degradation pathway was predicted as pyrolysis taking place inside the cavitation bubble where DEET molecules can reach. On the other side, a lower degradation rate in the presence of PO, PS, and MPS than that of no additives has indicated that the bulk phase degradation pathway for some part of DEET molecules are still occurred.

Keywords: DEET, dual frequency ultrasound, emerging contaminants (ECs)

1. INTRODUCTION

N,N-diethyl-meta-toluamide, commercially called DEET, is widely used as an active ingredient in many repellent products used for insects such as mosquitoes and ticks. It is estimated that thirty percent of US population use DEET to be protected from some illness like West Nile and Zika viruses, malaria caused by mosquitoes and Lyme disease caused by ticks. Even it is not designed to directly kill the organism, it should be taken into consideration in terms of environmental risk assessment as it is registered a pesticide in EPA. Furthermore, its extensive use for common personal care products in the US (9.2 million lb in 2011) has been turning the attention on its environmental transportation mechanism especially when drinking water is taken into consideration as Emerging Contaminants (ECs) [1, 2]. DEET has been detected in

surface waters, the effluent of WW treatment plants, and even in groundwater and drinking water in the last few years. This occurrence indicates that potential recalcitrance of DEET to conventional water treatment techniques [3, 4]. Costanzo et al. [5], have reported that DEET concentrations have been detected in the range of 40-3000 ng L⁻¹ all around the world and 8-1500 ng L⁻¹ in coastal Australia in contrast to earlier assumptions that it is not a persisting compound in the aquatic environment. In a very recent study, Lesser et al. [6], analyzed a wide range of organic micropollutants including DEET in the Mezquital Valley which uses untreated wastewater for agricultural irrigation. They indicated that even though DEET was found in relatively low concentrations in wastewater, it was detected in the highest frequencies in groundwater due to its complex matrix with other micropollutants such as sulfamethoxazole. They also

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analyzed the DEET concentration in the range of 37 – 2500 ng L⁻¹ for raw wastewater consistent with all around, while DEET concentration was found in the groundwater with a concentration range of between <0.4 and 99.9 ng L⁻¹ in the same study. DEET had low removal efficiencies and quite recalcitrant to biodegradation with its concentration range of 1.4-6232 ng L⁻¹ in the urban surface water and its degradation half-life of 29 days [7]. Also, the National groundwater monitoring program in England and Wales detected DEET more than 10 times in the level of 6500 ng L⁻¹ in 2011 in groundwaters [8]. Some other publications have reported that DEET can also accumulate in sediments with discharged wastewater into surface water [9].

Despite DEET is generally depicted as safe for external use if followed its labeling recommendation, some researchers reported potential health risks even a few deaths when exposed in high concentration through extensive skin absorption or inhalation [10-12]. Furthermore, the long-term exposure of DEET and some other pesticides produced mood and cognitive changes in animal experiments that had consistency with neuro-inflammatory changes in hippocampal brain areas experienced by GW veterans [13, 14]. Even, some neurotoxicity signs and genotoxic effects were reported to be received by DEET in a few pieces of research [15]. Although, the environmental risk assessment results of DEET indicate that is unlikely to produce an adverse biological effect in aquatic systems [16]. Campos et al. [17], studied the chronic effect of DEET on some test organisms that DEET inhibited development rates leading to population-level effects at the higher concentration of DEET than the observed in water sources. In other studies, they have reported that DEET is slightly toxic to freshwater insects in the higher concentrations than observed in water sources, but they advised the further studies to be conducted on the seasonal monitoring of DEET concentration in the aquatic environment due to its widespread occurrence in a great frequency and recalcitrant persistency in the water sources.

The degradation pathway of DEET in conventional wastewater treatment plants (WWTP) has been studied by many researchers. For example, in a WWTP characterized by nitrification and denitrification processes, activated sludge and rotating biological contactors, DEET showed an irregular removal percentage with a 47% average ranging between 1-98% [18]. This is most probably due to the high octanol-water partitioning coefficient, K_{ow} , of DEET ($\log K_{ow}=2.02$) indicating that its tendency towards moderate hydrophobicity and low affinity for sorption according to soil column experiments [6]. In another adsorption study, DEET and some other micropollutants were subjected to treat in pilot-scale drinking water biofilters containing an Anthracite adsorption column. Even this study has shown that DEET removal was more dependent on sorption than biotransformation but its adsorption efficiency was still below 50% operated for 245 days [19]. This result has a consistency with recent adsorption studies that activated carbon (AC) adsorption of DEET was around 40% [20] and granulated activated carbon (GAC) filters

adsorption of DEET was less than 30% indicating adsorption fairly suitable method for ECs like DEET [21]. There is also one study on the biotransformation of DEET in microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) pointing out the low-level degradation (below 40%) of DEET by microorganism in their processes [22]. Even they supported their results that DEET removal from wastewater was not higher than 30% after anaerobic treatment [23]. Recently, the elimination of ECs including DEET with the membrane treatment methods have become an increasing interest. However, Huang et al. [24], achieved 82.3% removal percentage of DEET with reverse osmosis (RO) method representing the lowest removal efficiency among other organic micropollutants in the natural water.

Therefore, AOPs has recently drawn increasing attention as an emerging technology for the degradation of micropollutants and DEET since AOPs are the main sources for the production of highly reactive OH radicals ($\bullet\text{OH}$). The high oxidation capacity of $\bullet\text{OH}$ ($10^8\text{-}10^{10} \text{ M}^{-1}\text{s}^{-1}$) produced by AOPs in situ applications leads to treating a wide range of ECs with their low selectivity providing complete mineralization to CO_2 , H_2O , and inorganic ions or acids [25]. Therefore, DEET degradation has been investigated by using several AOPs including mostly ozonation [26]; ozone and biologically activated carbon system [27, 28]; photo-ozonation [29, 30]; photocatalysis [31]; photocatalysis with TiO_2 [3]; Fenton-like reaction [32] and finally electrochemical oxidation [33]. But there have not been enough studies on the ultrasonic oxidation of DEET in the literature so far. Ultrasonic oxidation processes are very effective techniques for the degradation of a wide range of problematic pollutants based on mainly hydroxyl radical ($\bullet\text{OH}$) production. Additionally, the simultaneous US at low and high frequencies can lead to improved degradation yields [34]. The principle of ultrasonic irradiation mechanism for water treatment was explained in our previous studies [25, 35].

The degradation of N,N-diethyl-m-toluamide (DEET) in dual frequency ultrasonic reactor (DFUR) including a 20 kHz low and a 640 kHz high-frequency sources was investigated in this comprehensive study as a pioneer for the literature in terms of ultrasonic DEET degradation. The enhancement effect of using dual or multiple frequencies ultrasonic sources in one reactor is probably due to obtaining a more active volume of cavitation than a single one, enhanced bubble collapse ratios resulting in higher temperature, therefore, increased sonochemical activity [36, 37]. The calorimetric experiments were firstly conducted to optimize the dual-frequency operation conditions for the enhancement of sonochemical yields. Then, DEET degradation was evaluated in terms of several operation modes of DFUR, under different gas saturation (Ar, O_2 , N_2), presence of some oxidants (PO, PS and MPS). Finally, DFUR was conducted in the addition of several PO doses which had the highest degradation efficiency for DEET degradation.

2. MATERIALS AND METHODS

2.1. Synthesis of hydrotalcite-like compounds

All chemicals were of analytical grade (99%) except for hydrogen peroxide (30%). DEET (wet basis, 99%) was purchased from Sigma-Aldrich, USA. Millipore filtered water (18 M Ω .cm) was used to dissolve DEET in all cases instead of methanol. Its highest absorbance was shifted in 192 nm instead of 230 nm [38] dissolved in methanol. Fig. 1 depicts the chemical structure of DEET.

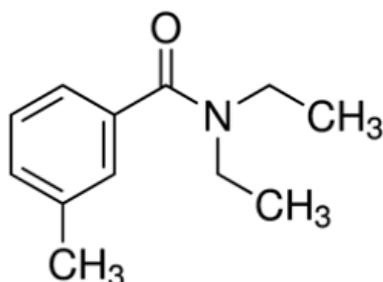


Fig 1. The chemical structure of DEET (MW=191.27 g mol⁻¹)

UES Model 15-660 ultrasound generator (640 kHz) with the power range of 100-1000 W, obtained from Ultrasonic energy system company (Panama City, Florida) was used for all experimental procedures as a high-frequency source [39]. The sound wave is transmitted via a transducer which is placed into the wall of a 580 mL glass reaction container immersed into 40-liter water cooling bath and kept at room temperature as 20 \pm 2 $^{\circ}$ C. The reaction volume in the reaction container was 500 mL containing aqueous DEET or only distilled water for the case of calorimetric experiments. Low-frequency ultrasonic horn was purchased by Sonic materials, Inc. (Danbury, Connecticut) (20 kHz) with the power range of 10-100 W. The horn was dipped into reaction solution to conduct dual-frequency as a dual-frequency ultrasonic reactor, DFUR. The illustration of the DFUR was depicted in our previous study [40].

3. RESULTS AND DISCUSSION

3.1. Analysis of DEET

The stock DEET solution was prepared in 2.614 mM concentration and, it was diluted in the desired concentration to develop a calibration curve. Calibration standards of DEET were prepared from 0 to 20 μ M concentrations for its UV-Vis absorption. The DEET degradations were observed by UV-Vis absorption at time intervals of 0, 1, 3, 5, 7, 9, 12 and 15 mins on a Cary Eclipse Spectrophotometer from Agilent Techn. with the maximum absorbance wavelength of 192 nm. All DEET solutions were fixed to 20 μ M concentration during the experimental procedure. The calibration curve of DEET to accurately monitor the final concentrations is shown in Fig 2.

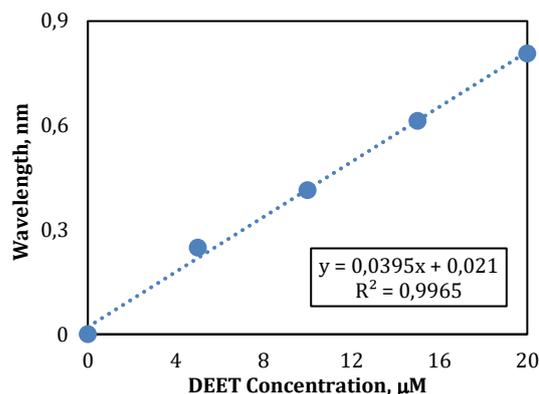


Fig 2. The calibration curve of DEET on its maximum absorbance at 192 nm dissolved in millipore filtered water.

3.2. DEET degradation in DFUR

20 kHz and 640 kHz ultrasonic sources were operated individually to calculate their power densities in each operated power (i.e. 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 W for 640 kHz and 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 W for 20 kHz) according to our previous calorimetric studies [35]. By changing the power output of 20 kHz against the fixed power of 640 kHz at 600 W, the power density of DFUR was measured. The optimum power density dissipated by solution was calculated as 10.1 \times 10⁻² WmL⁻¹ for DFUR with the highest synergistic index (0.991) combined frequency of 20 kHz of which power density was 4.1 \times 10⁻² WmL⁻¹ and 640 kHz of which power density was 8.1 \times 10⁻² WmL⁻¹ at their operating power of 60 W and 600 W, respectively. This method has provided energy savings most of which disappear in the reactor solution as heat energy. The following experiments were performed at these power settings called DFUR.

The DEET degradation and kinetic constants under three operation modes of DFUR were discussed in this section and experimental results were shown in Fig. 3. The ultrasonic degradation of DEET in DFUR was assessed by absorption abatement at 192 nm which is responsible for the aromatic compound of DEET. For this reason, 20 μ M DEET solution was sonicated by 20 kHz low frequency, 640 kHz high-frequency ultrasonic sources alone and finally irradiated with dual frequencies simultaneously for 15 mins (Fig 3). It was concluded that the contribution of 20 kHz ultrasonic source to 640 kHz high frequency for the degradation of DEET was increased, but the effect of only 20 kHz low-frequency irradiation was negligible, it could reach 2% after 15 min reaction time. The ultrasonic DEET degradation can be evaluated as low but the combination of both frequencies increased DEET degradation up to 19% while it was only 11% by high-frequency source, 640 kHz. Additionally, the pseudo-first-order degradation of DEET was used to explain the removal rates by Eq. (1):

$$\ln \frac{DEET_t}{DEET_0} = -kt \quad (1)$$

where DEET concentrations at the time of 0 and t, μ M, and k is the pseudo-first-order rate constant, min⁻¹ and t is the reaction time, min. The pseudo-first-order rate

constants, k , increased from $7.8 \times 10^{-3} \text{ min}^{-1}$ (640 kHz, $R^2=0.930$) to $13.5 \times 10^{-3} \text{ min}^{-1}$ (DFUR, $R^2=0.990$), by contrast, the rate constant was only $0.7 \times 10^{-3} \text{ min}^{-1}$ ($R^2=0.281$) for 20 kHz low-frequency ultrasonic source.

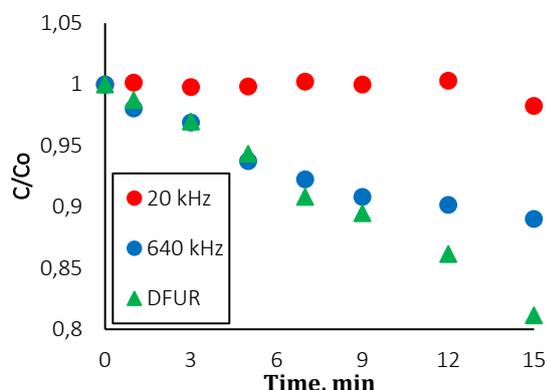


Fig 3. Time-dependent ultrasonic DEET degradation by 20 kHz, 640 kHz and DFUR ($[DEET]_0 = 20 \mu\text{M}$)

3.3. DEET degradation in DFUR under different gas saturation

In this experimental setup, the initial DEET solution was individually saturated with Ar, air, O_2 , and N_2 before the experiment for 15 min and during ultrasonic irradiation in DFUR for 15 min. The time-dependent DEET concentration under different gas saturation in DFUR was plotted in Fig 4. The presence of dissolved gases in the ultrasonically induced solutions is a crucial parameter since they become a nucleation site for cavitation bubbles and also enhance the final temperature of the collapsing bubble due to their specific heat capacities [41]. Therefore, additional pyrolysis reactions take place inside of a cavitation bubble which is the main degradation reaction for hydrophobic compounds like DEET. As its hydrophobic tendency, DEET is supposed to reach the interior of a

cavitation bubble formed during ultrasonic irradiation. Our results were consistent with the idea that pyrolysis played a significant role during DEET degradation due to faster degradation (nearly two-fold) than that of no gas bubbling and the highest rate constant ($35.8 \times 10^{-3} \text{ min}^{-1}$) under Ar saturation. After then, the pseudo-first-order degradation constants followed the order of $25.1 \times 10^{-3} \text{ min}^{-1}$, $15.0 \times 10^{-3} \text{ min}^{-1}$, $13.5 \times 10^{-3} \text{ min}^{-1}$, and $5.5 \times 10^{-3} \text{ min}^{-1}$ for the O_2 , N_2 , NA (Not applicated any gas) and air, respectively. Since oxygen provides additional pathways to form $\bullet\text{OH}$, DEET degradation was higher compared to N_2 saturated solution and N_2 could be responsible for the consumption of $\bullet\text{OH}$ [42, 43]. However, DEET degradation slowed down during the air bubbling to DFUR probably due to the interference of the propagation of ultrasonic waves through the solution [44]. The Pseudo first-order kinetic constants of DEET degradation in the presence of various gas saturation are shown in Table 1 as well.

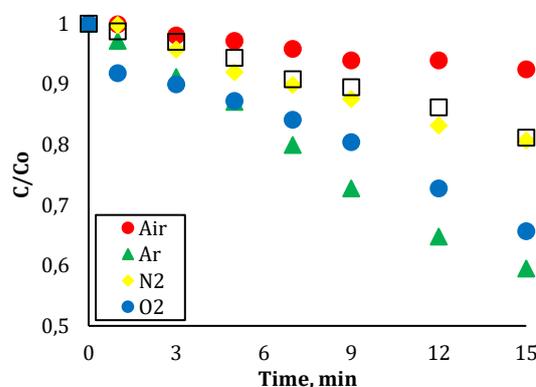


Fig 4. The effect of different gas saturation on the degradation of DEET ($[DEET]_0 = 20 \mu\text{M}$, gas flow rate = 1 ml min^{-1})

Table 1. Pseudo-first-order kinetic constants of DEET degradation in the presence of various gas saturation

Gas saturation	Ar	O_2	N_2	NA	Air
$k, \text{ min}^{-1}$	35.8×10^{-3} $R^2=0.994$	25.1×10^{-3} $R^2=0.968$	15.0×10^{-3} $R^2=0.992$	13.5×10^{-3} $R^2=0.990$	5.5×10^{-3} $R^2=0.960$
Additives	PO	MPS	PS	NA	
$k, \text{ min}^{-1}$	10.1×10^{-3} $R^2=0.971$	7.5×10^{-3} $R^2=0.921$	6.4×10^{-3} $R^2=0.921$	13.5×10^{-3} $R^2=0.990$	

3.4. Effect of PO, PS and MPS on DEET degradation

AOPs in the presence of some oxidants such as PO, PS and MPS which can be activated by ultrasonic, light or heat sources cause to form different radicals such as $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ and $\text{S}_2\text{O}_8^{\bullet-}$ [45, 46]. Therefore, DEET degradation was studied by the addition of these three radical sources with the same molar ratio of DEET to enhance the efficiency of DFUR and the results are depicted in Fig. 5. The pseudo-first-order rate constants were kinetically evaluated from Fig. 5 as

$10.1 \times 10^{-3} \text{ min}^{-1}$ ($R^2=0.971$), $7.5 \times 10^{-3} \text{ min}^{-1}$ ($R^2=0.921$) and $6.4 \times 10^{-3} \text{ min}^{-1}$ ($R^2=0.921$) for the presence of PO, MPS and PS which was slower (already depicted in Fig 3 as $13.5 \times 10^{-3} \text{ min}^{-1}$) than that of no catalyst addition. The slower degradation rate of DEET under these oxidants can mostly be attributed to hydroxyl radical scavenging effect of PO beyond a critical dose [47] which is continuously produced by recombining of hydroxyl radicals in a cavitation collapse according to following equations (Eq. 2-3) [25]:



Additionally, some other researchers indicated that the interaction between hydroxyl ions and sulfate radicals can produce $\bullet\text{OH}$ [48] which is associated with DEET degradation in bulk solution. However, it was discussed that DEET degradation mostly took place interior gas phase of a cavitation bubble in the previous section. Although DEET degradation increased in the presence of Ar gas supporting the degradation via pyrolysis, we can draw a conclusion that another degradation pathway is either the bulk solution phase where additional $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$ and $\text{S}_2\text{O}_8^{\bullet-}$ mostly reside and act as a scavenger. Therefore, a slower degradation rate in the presence of PO, PS, and MPS due to partition of these ions in bulk phase can be supported with the idea of DEET degradation occurring in the bulk phase following pyrolysis.

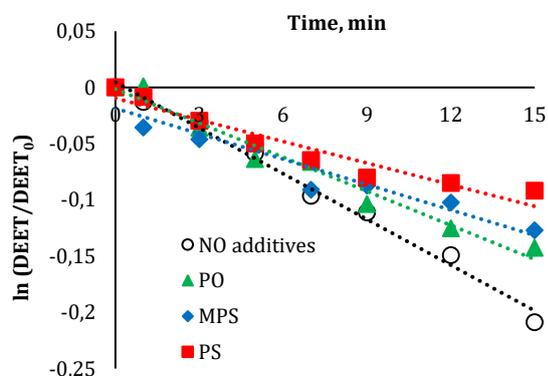


Fig 5. Determinations of pseudo-first-order kinetic plots of DEET degradation with the addition of PO, PS, MPS additives in DFUR ($[\text{DEET}]_0 = [\text{PO}] = [\text{PS}] = [\text{MPS}] = 20 \mu\text{M}$, 1:1 molar ratio of DEET and additives)

3.5. Effect of PO dose on DEET degradation

In order to efficiency assessment of PO for the degradation of DEET, different DEET:PO molar ratio in the range between 1:1, 1:2, 1:5, 1:10 and 1:20 was subjected to sonicate in DFUR. Although the

4. CONCLUSIONS

DEET considered an emerging water contaminant, quite recalcitrant to biodegradation, was selected as a model compound for the study of a DFUR applying simultaneously 20 kHz as the low-frequency and 640 kHz as the high-frequency ultrasonic source. Considering calorimetric measurements, the optimum power density dissipated to the solution was calculated as $10.1 \times 10^{-2} \text{ W mL}^{-1}$ for DFUR, while the power densities were $4.1 \times 10^{-2} \text{ W mL}^{-1}$ for 20 kHz and $8.1 \times 10^{-2} \text{ W mL}^{-1}$ for 640 kHz US source, individually. The DEET degradation was monitored as a function of treatment time and nicely fit to pseudo-first-order kinetic model. Treatment of DEET was negligible by separate 20 kHz low-frequency US in 15 min reaction period, but the simultaneous operation of 20 kHz low-frequency US and 640 kHz high-frequency US i.e. DFUR provided nearly two times higher degradation

degradation rate of DEET slowed down in the presence of low dose PO (20 μM), the higher dose of PO was widely examined so as to define the DEET degradation pathway through the bulk phase in ultrasonically induced solution. The application of pseudo-first-order kinetic equation (Eq. 1) is plotted in Fig. 6 by evaluating their rate constant for the degradation of DEET in DFUR. The DEET degradation rate was almost zero in the presence of a higher ratio 1:10 and 1:20, but it slowed down even in a lower ratio of DEET:PO (1:1, 1:2, 1:5, 1:10 were only shown in the Fig 6). The degradation rate constants decreased from $10.1 \times 10^{-3} \text{ min}^{-1}$ ($R^2=0.971$) of which DEET:PO molar ratio 1:1 to $5.7 \times 10^{-3} \text{ min}^{-1}$ ($R^2=0.896$) and $5.7 \times 10^{-3} \text{ min}^{-1}$ ($R^2=0.956$) which were associated with the molar ratio of 1:2 and 1:5. However, DEET had its highest degradation rate in the absence of PO that provides information about its degradation pathway both through the interior gas phase and gas-liquid interface of a cavitation bubble in DFUR used in this study. Because, 20 kHz and 640 kHz ultrasonic sources form $\bullet\text{OH}$ in the reactor that is, over those of $\bullet\text{OH}$ act as a scavenger according to Eq. (3). Therefore, there is still DEET degradation occurring via pyrolysis inside of the gas phase of a cavitation bubble but degradation via $\bullet\text{OH}$ occurring in the bulk solution phase is inhibited.

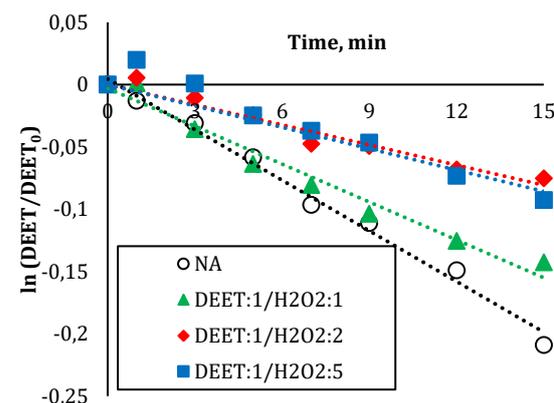


Fig. 6. Determinations of pseudo-first-order kinetic plots of DEET degradation in the presence of different DEET:PO molar ratio of 1:2, 1:5, 1:10 and 1:20 ($[\text{DEET}]_0 = 20 \mu\text{M}$)

efficiency than that of 640 kHz high-frequency US alone. Among other gas saturation (O_2 , N_2 , and air), Argon enhanced the final temperature of collapsing bubble due to its highest specific heat capacity and pyrolysis played a significant role for DEET degradation by increasing the degradation rate constant nearly three-fold than that of no additional gas bubbling to reaction solution in DFUR.

Slower degradation rate in the presence of PO, PS and MPS additives can be probably attributed to the partition of these ions in bulk phase supporting the idea of some part of DEET degradation occurring in the bulk phase where additional $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$ and $\text{S}_2\text{O}_8^{\bullet-}$ mostly reside and act as scavenger following pyrolysis. To assess the degradation part of DEET which takes place in the bulk phase, effect of PO concentration on the degradation of DEET was examined and the higher dose of PO even stopped the degradation of DEET in bulk phase indicating the hydroxyl radical scavenging effect of PO beyond a critical dose and small part of

DEET degradation in bulk phase. Finally, this study has proven that combined low and high frequency US, DFUR, provides better cavitation yields for DEET as a hydrophobic compound of which degradation pathway mostly takes place in a cavitation bubble inside and gas-liquid interface.

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REFERENCES

- [1]. USEPA, Registration eligibility decision (Red) DEET (EPA738-R-98-010). Office of pesticides and Toxic substances, US EPA, Washington DC, 1998.
- [2]. USEPA, DEET (N,N-Diethyl-meta-toluamide) Interim Registration Review Decision Case Number 0002. <https://www.regulations.gov/document?D=EPA-HQ-OPP-2012-0162-0012> (2014) Access Date: 2.10.2018.
- [3] W.A. Adams and C.A. Impellitteri, "The photocatalysis of N,N-diethyl-m-toluamide (DEET) using dispersions of Degussa P-25 TiO₂ particles," *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 202, pp. 28–32, 2009.
- [4] E. Mena, A. Rey, E.M. Rodríguez and F.J. Beltrán, "Reaction mechanism and kinetics of DEET visible light assisted photocatalytic ozonation with WO₃ catalyst," *Applied Catalysis B: Environmental*, Vol. 202, pp. 460–472, 2017.
- [5] S.D. Costanzo, A.J. Watkinson, E.J. Murby, D.W. Kolpin and M.W. Sandstrom, "Is there a risk associated with the insect repellent DEET (N,N-diethyl-m-toluamide) commonly found in aquatic environments?," *Science of the Total Environment*, Vol. 384, pp. 214–220, 2007.
- [6] L.E. Lesser, A. Mora, C. Moreau, J. Mahlknecht, A. Hernandez-Antonio, A.I. Ramírez and H. Barrios-Pina, "Survey of 218 organic contaminants in groundwater derived from the world's largest untreated wastewater irrigation system: Mezquital Valley, Mexico," *Chemosphere*, Vol. 198, pp. 510-521, 2018.
- [7] N.H. Tran, K.Y.H. Gin and H.H. Ngo, "Fecal pollution source tracking toolbox for identification, evaluation and characterization of fecal contamination in receiving urban surface waters and groundwater," *Science of the Total Environment*, Vol. 538, pp. 38–57, 2015.
- [8] D.J. Lapworth, N. Baran, M.E. Stuart and R.S. Ward, "Emerging organic contaminants in groundwater: A review of sources, fate and occurrence," *Environmental Pollution*, Vol. 163, pp. 287-303, 2012.
- [9] S. Merel and S.A. Snyder, "Critical assessment of the ubiquitous occurrence and fate of the insect repellent N,N-diethyl-m-toluamide in water," *Environment International*, Vol. 96, pp. 98–117, 2016.
- [10] H. Qiu, H.W. Jun and J.W. McCall, "Pharmacokinetics, formulation, and safety of insect repellent N,N-diethyl-3-methyl benzamide (DEET): a review," *Journal of the American Mosquito Control Association*, Vol. 14, pp. 12–27, 1998.
- [11] J.C. Veltri, T.G. Osimitz, D.C. Bradford and B.C. Page, "Retrospective analysis of calls to poison control centers resulting from exposure to the insect repellent N,N-diethyl-m-toluamide (DEET) from 1985–1989," *Journal of Toxicology: Clinical Toxicology*, Vol. 32, pp. 1–16, 1994.
- [12] F.B. Antwi, L.M. Shama and R.K.D. Peterson, "Risk assessments for the insect repellents DEET and picaridin Frank B. Antwi," *Regulatory Toxicology and Pharmacology*, Vol. 51, pp. 31–36, 2008.
- [13] R.F. White, L. Steele, J.P. O'Callaghan, et al., "Recent research on Gulf War illness and other health problems in veterans of the 1991 Gulf War: Effects of toxicant exposures during deployment," *Cortex*, Vol. 74, pp. 449-475, 2016.
- [14] C.J. Carter and R.A. Blizard, "Autism genes are selectively targeted by environmental pollutants including pesticides, heavy metals, bisphenol A, phthalates and many others in food, cosmetics or household products," *Neurochemistry International*, Vol. 101, pp. 83-109, 2016.
- [15] D.N. Roy, R. Goswami and A. Pal, "The insect repellents: A silent environmental chemical toxicant to the health," *Environmental Toxicology and Pharmacology*, Vol. 50, pp. 91–102, 2017.
- [16] J.M. Brausch and G.M. Rand, "A review of personal care products in the aquatic environment: Environmental concentrations and toxicity," *Chemosphere*, Vol. 82, pp.1518–1532, 2011.
- [17] D. Campos, C. Gravato, C. Quintaneiro, O. Koba, T. Randak, A.M.V.M. Soares and J.L.T. Pestana, "Are insect repellents toxic to freshwater insects? A case study using caddisflies exposed to DEET," *Chemosphere*, Vol. 149, pp. 177-182, 2016.
- [18] M. Sgroi, P. Roccaro, G.V. Korshin, V. Greco, S. Sciuto, T. Anumol, S.A. Snyder and F.G.A. Vagliasindi, "Use of fluorescence EEM to monitor the removal of emerging contaminants in full scale wastewater treatment plants," *Journal of Hazardous Materials*, Vol. 323, pp. 367–376, 2011.
- [19] K.E. Greenstein, J. Lew, E.R.V. Dickenson and E.C. Wert, "Investigation of biotransformation, sorption, and desorption of multiple chemical contaminants in pilot-scale drinking water biofilters," *Chemosphere*, Vol. 200, pp. 248-256, 2018.
- [20] O.M. Rodriguez-Narvaez, J.M. Peralta-Hernandez, A. Goonetilleke and E.R. Bandala, "Treatment technologies for emerging contaminants in water: A review," *Chemical Engineering Journal*, Vol. 323, pp. 361–380, 2017.
- [21] S. Zhang, S.W. Gitungo, L. Axe, R.F. Raczko and J.E. Dyksen, "Biologically active filters-An advanced water treatment process for contaminants of emerging concern," *Water Research*, Vol. 114, pp. 31-41, 2017.
- [22] C.M. Werner, C. Hoppe-Jones, P.E. Saikaly, B.E. Logan and G.L. Amy, "Attenuation of trace organic compounds (TOCs) in bioelectrochemical

- systems," *Water research*, Vol. 73, pp. 56-67, 2015.
- [23] W. Xue, C. Wu, K. Xiao, X. Huang, H. Zhou, H. Tsuno and H. Tanaka, "Elimination and fate of selected micro-organic pollutants in a full-scale anaerobic/anoxic/aerobic process combined with membrane bioreactor for municipal wastewater reclamation," *Water Research*, Vol. 44(20), pp.5999-6010, 2010.
- [24] H. Huang, H. Cho, K. Schwab, J.G. Jacangelo, "Effects of feedwater pretreatment on the removal of organic microconstituents by a low fouling reverse osmosis membrane," *Desalination*, Vol. 281, pp. 446-454, 2011.
- [25] Z. Eren, "Ultrasound as a basic and auxiliary process for dye remediation: A review," *Journal of Environmental Management*, Vol. 104, pp. 127-141, 2012.
- [26] Q. Sui, J. Huang, S. Deng, G. Yu and Q. Fin, "Occurrence and removal of pharmaceuticals, caffeine and DEET in wastewater treatment plants of Beijing," *China Water Research*, Vol. 44, pp. 417-426, 2010.
- [27] D. Gerrity, S. Gamage, J.C. Holady, D.B. Mawhinney, O. Quinones, R.A. Trenholm and S.A. Snyder, "Pilot-scale evaluation of ozone and biological activated carbon for trace organic contaminant mitigation and disinfection," *Water Research*, Vol. 45, pp. 2155-2165, 2011.
- [28] Y. Sun, B. Angelotti, M. Brooks, B. Dowbiggin, P.J. Evans, B. Devins and Z.W. Wang, "A pilot-scale investigation of disinfection by-product precursors and trace organic removal mechanisms in ozone-biologically activated carbon treatment for potable reuse," *Chemosphere*, Vol. 21, pp. 539-549, 2018.
- [29] A.M. Chávez, A. Rey, F.J. Beltrán and P.M. Álvarez, "Solar photo-ozonation: A novel treatment method for the degradation of water pollutants," *Journal of Hazardous Materials*, Vol. 317, pp. 36-43, 2016.
- [30] E. Mena, A. Rey, E.M. Rodríguez and F.J. Beltrán, "Nanostructured CeO₂ as catalysts for different AOPs based in the application of ozone and simulated solar radiation," *Catalysis Today*, Vol. 280, pp. 74-79, 2017.
- [31] M. Antonopoulou, C.G. Skoutelis, C. Daikopoulos, Y. Deligiannakis and I.K. Konstantinou, "Probing the photolytic-photocatalytic degradation mechanism of DEET in the presence of natural or synthetic humic macromolecules using molecular-scavenging techniques and EPR spectroscopy," *Journal of Environmental Chemical Engineering*, Vol. 3, pp. 3005-3014, 2017.
- [32] Y. Li, J. Sun and S.P. Sun, "Mn²⁺-mediated homogeneous Fenton-like reaction of Fe(III)-NTA complex for efficient degradation of organic contaminants under neutral conditions," *Journal of Hazardous Materials*, Vol. 313, pp. 193-200, 2016.
- [33] J. Radjenovic, A. Bagastyo, R.A. Rozendal, Y. Mu, J. Keller and K. Rabaey, "Electrochemical oxidation of trace organic contaminants in reverse osmosis concentrate using RuO₂/IrO₂-coated titanium anodes," *Water Research*, Vol. 45, pp. 1579-1586, 2011.
- [34] P.R. Gogate, V.S. Sutkar, A.B. Pandit, "Sonochemical reactors: Important design and scale up considerations with a special emphasis on heterogeneous systems," *Chemical Engineering Journal*, Vol. 166, pp. 1066-1082, 2011.
- [35] Z. Eren and N.H. Ince, "Sonolytic and sonocatalytic degradation of azo dyes by low and high frequency ultrasound," *Journal of Hazardous Materials*, Vol. 177(1-3), pp.1019-1024, 2010.
- [36] M. Lee and J. Oh, "Synergistic effect of hydrogen peroxide production and sonochemiluminescence under dual frequency ultrasound irradiation," *Ultrasonics Sonochemistry*, Vol. 18, pp. 781-788, 2011.
- [37] A. Brotchie, M. Ashokkumar, F. Grieser, "Effect of Water-Soluble Solutes on Sonochemistry under Dual-Frequency Sonication," *J. Phys. Chem. C*, Vol. 11, pp. 3066-3070, 2007.
- [38] G. Markovic, D. Agbaba, D.Z. Stakic and S. Vladimirov, "Determination of some insect repellents in cosmetic products by high-performance thin-layer chromatography," *Journal of Chromatography A*, Vol. 847(1-2), pp. 365-368, 1999.
- [39] Z. Eren and K. O'Shea, "Hydroxyl Radical Generation and Partitioning in Degradation of Methylene Blue and DEET by Dual-Frequency Ultrasonic Irradiation," *Journal of Environmental Engineering*, Vol. 145/10, 04019070, 2019.
- [40] Z. Eren and K. O'Shea, "Definition of the optimum conditions of dual frequency (20 kHz+640 kHz) ultrasonic system by decolorization of Crystal Violet dye," *Journal of the Faculty of Engineering and Architecture of Gazi University*, Vol. 35(3), pp. 1257-1268, 2020.
- [41] M. Siddique, R. Farooq and G.J. Price, "Synergistic effects of combining ultrasound with the Fenton process in the degradation of Reactive Blue 19," *Ultrasonics Sonochemistry*, Vol. 21, pp. 1206-1212, 2014.
- [42] H. Ferkous, O. Hamdaoui and S. Merouani, "Sonochemical degradation of naphthol blue black in water: Effect of operating parameters," *Ultrasonics Sonochemistry*, Vol. 26, pp. 40-47, 2015.
- [43] A. Torres, C. Petrier, E. Combet, M. Carrier, C. Pulgarin, "Ultrasonic cavitation applied to the treatment of bisphenol A. Effect of sonochemical parameters and analysis of BPA by-products," *Ultrasonics Sonochemistry*, Vol. 15(4), pp. 605-611, 2008.
- [44] T.J. Mason and J.P. Lorimer, "The uses of power ultrasound in chemistry and processing, Applied Sonochemistry," Wiley-VCH Verlag, Weinheim, 303 pp, 2002.
- [45] K. Shang, X. Wang, J. Li, H. Wang, N. Lu, N. Jiang and Y. Wu, "Synergetic degradation of Acid Orange 7 (AO7) dye by DBD plasma and persulfate," *Chemical Engineering Journal*, Vol. 311, pp. 378-384, 2017.
- [46] K.Y.A. Lin and Y.C. Chen, "Accelerated decomposition of Oxone using graphene-like carbon nitride with visible light irradiation for enhanced decolorization in water," *Journal of the Taiwan Institute of Chemical Engineers*, Vol. 60, pp. 423-429, 2016.

- [47] N.H. Ince, "Critical effect of hydrogen peroxide in photochemical dye degradation," *Water Research*, Vol. 33(4), pp. 1080-1084, 1999.
- [48] Y. Jin, S.P. Sun, X. Yang and X.D. Chen, "Degradation of ibuprofen in water by FeII-NTA complex-activated persulfate with hydroxylamine at neutral pH," *Chemical Engineering Journal*, Vol. 337, pp. 152-160, 2018.