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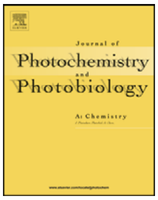

The photocatalysis of *N*,*N*-diethyl-*m*-toluamide (DEET) using dispersions of Degussa P-25 TiO_2 particles

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ABSTRACT

The photocatalysis of *N*,*N*-diethyl-*meta*-toluamide (DEET) was examined using aqueous Degussa P-25 TiO_2 dispersions and a 350 nm Hg lamp UV reactor. Various concentrations of humic acid (HA) were added to the photocatalytic sample matrix in order to simulate the influence of natural organic matter (NOM) present during water treatment. A municipal secondary treatment effluent was also used as a sample matrix to provide a field sample comparison with laboratory matrixes. Pseudo-first-order kinetic rate constants were calculated for each set of samples. Gas chromatography/mass spectrometry (GC/MS) results showed a marked decrease in the photocatalytic degradation of DEET after the addition of HA, which continued to decrease with increasing HA concentration. The rate of degradation was further reduced after the addition of the municipal secondary treatment effluent, likely due to competition from dissolved organic matter and surface interference from soluble salts.

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1. Introduction

Pharmaceuticals, personal care products, and other organic chemicals (e.g. pesticides) have received increased attention recently as many of these chemicals have been detected in drinking water sources and wastewater (WW) effluents [1,2]. A few of these organic compounds have also been detected in finished drinking water [3,4]. In order to prioritize treatment research, a literature review was conducted to establish whether or not a particular organic contaminant was detected after passing through WW treatment or water treatment processes [1–7]. The compounds chosen for further work were selected based on their ability to be detected after passing through both types of treatment. One chemical that meets these criteria is *N*,*N*-diethyl-*meta*-toluamide (DEET). DEET is used as an insect repellent by interfering with insect odor receptors thereby masking attracting odors [8].

Occurrence studies show that DEET is present in surface waters across the United States [1,9]. Studies focusing on chemical occurrence in or around WW treatment plants have reported frequent occurrence of DEET in WW effluents and receiving waters [6,10,11]. DEET has also been detected in groundwater [12] and drinking water [13]. The presence of DEET in drinking water suggests that there is some degree of recalcitrance of the compound to conventional drinking water treatment techniques, as shown by Stackelberg et al. [13].

The risk to human health from exposure to DEET in drinking water is low [14]. Toxic effects from DEET to aquatic organisms, including fish [15–17], *Daphnia magna* [18] and *Gambusia affinis* (a benthic organism) [17] typically range from LC_{50} values (lethal concentration to 50% of the test population) between 75–230 mg/L. Overall, it is thought that the risks to the environment from DEET are low, though more thorough research may be necessary to examine fate, transport and ecotoxicity of DEET [19].

There is evidence that some advanced oxidation processes can effectively (or, at least, partially) remove DEET from water. These processes include Fenton oxidation [20] and ozonation [21]. Ultraviolet (UV) light (germicidal wavelength) has less of an effect on the degradation of DEET; less than 30% removal at a fluence of 40 mJ/cm^2 [22]. However, the combination of UV light and TiO_2 semiconductors initiates photocatalytic reactions, and the application of semiconductor photocatalysis for organic waste remediation is well known [23–26]. TiO_2 photocatalysis, as with many other advanced oxidation processes, produces hydroxyl radicals; which, through charge transfer and secondary radical formation processes, lead to the oxidation/reduction of organic molecules in an aqueous system. An often used, highly photoactive form of TiO_2 is Degussa P-25. This mixture of TiO_2 is composed of 20–30% rutile and 70–80% anatase crystallites of TiO_2 with an average particle size of 21 nm. P-25 TiO_2 has a wide bandgap of 3.0–3.2 eV, which is the difference in energy between the valence and conduction bands of a semiconductor. This TiO_2 bandgap corresponds to a wavelength range of 380–400 nm. When exposed to wavelengths shorter than 380 nm, which begins in the UVA range, electron excitation from the valence band to the conduction band occurs. This is a charge sep-

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aration process, which produces electron–hole pairs that allow for oxidation/reduction chemistry. These reactions ultimately lead to the complete mineralization of the target organic molecule [25,27]. However, it is possible that the presence of dissolved organic carbon in surface waters could have a negative effect on the photocatalytic efficiency of TiO_2 with organic pollutants. This interference in photodegradation has been shown with TiO_2, humic acid (HA), and other organic molecules [28–30]. Doll and Frimmel suggested a competition and adsorption mechanism (at and below the point of zero charge for TiO_2) involving organic analytes, NOM, and TiO_2 which explains the reduction in photoactivity seen with the combination of the three components.

The objective of this study was to assess the effectiveness of TiO_2 photocatalysis on the degradation of DEET, calculate kinetic rate constants, and examine the macroscopic effects of dissolved organic carbon (in the form of HA) on the photocatalytic degradation of DEET. UV/TiO_2 degradation of DEET was also assessed in an actual secondary effluent from a WW treatment plant in a suburban/agricultural setting. The study was performed on a bench scale with increasingly complex matrixes containing DEET. The focus was to best gain an understanding of the overall impact of the photocatalysis of DEET in an interfering matrix. All experiments were performed at a natural, unadjusted pH in order to best represent treatment conditions.

2. Experimental

2.1. Chemicals

DEET (97%, Aldrich, St. Louis, MO) and P-25 titanium dioxide (Degussa, Frankfurt, Germany) were used as-received. A 250 mg/L stock DEET solution was prepared in methanol and diluted to 0.100 mg/L standards for analysis. HA (soil humic acid standard (IS102H), International Humic Substances Society, St. Paul, MN) was available in powder form and used in stock solutions. A stock HA solution was prepared by adding 20 mL 0.01N sodium hydroxide (from 1N NaOH stock, Fisher, Fair Lawn, NJ) to dissolve the HA followed by neutralization (pH 7.10) with 0.1 M hydrochloric acid (Fisher, Fair Lawn, NJ) and diluting to 100 mL with 18.2 MΩ water. A secondary water treatment effluent was obtained from a local municipal wastewater treatment plant. Samples were obtained in 1 L aliquots in a high-density polyethylene bottle and stored at 4 °C. The water treatment plant utilized activated sludge as the treatment mechanism followed by sand filtration. The sample was collected by removing water from the post-sand filtration tank and placing it into the container.

For GC/MS analysis, aqueous samples were extracted and concentrated (4:1) with methyl *tert*-butyl ether (HPLC grade, Fisher, Fair Lawn, NJ) and sodium chloride (Fisher, Fair Lawn, NJ). Phenol-d_6 (99 at% D, Isotec, Miamisburg, OH) was used as an internal standard during GC/MS analysis. Ion chromatography (IC), inductively coupled plasma (ICP) spectroscopy, total organic carbon (TOC) analyses, and pH analyses were performed on neat aqueous samples. Dissolved organic carbon (DOC) analysis samples were filtered using 25 mm Whatman glass microfiber filters (GF/F, Maidstone, England) prior to analysis.

2.2. Sample preparation and instrumental methods

Prior to GC/MS analysis, all samples were prepared in triplicate using a liquid–liquid extraction/concentration method. The extraction used 8 mL aliquots of the aqueous sample, 2 mL MTBE/phenol-d_6, and 6.0 g of NaCl. The MTBE was spiked with phenol-d_6 as an internal standard. The mixtures were placed in 60 mL vials and tumbled at 85 rpm for 15 min using an end-over-end shaker. The MTBE top layer was extracted and used for GC/MS analysis. Filtration of the TiO_2 particles was not necessary due to the hydrophilic nature of the photocatalyst. Blank samples of MTBE were analyzed every three to four samples in order to detect and prevent any sample carryover.

Liquid samples were analyzed using a Varian CP-3800 gas chromatograph with detection by a Varian Saturn 2200 mass spectrometer (Walnut Creek, CA). Samples were quantified by peak area integration using the Varian software provided, based on a selected ion range (118:120 + 188:190 for DEET and 70:72 + 98:100 for phenol-d_6) of the target analytes. All accepted samples showed a %R.S.D. <20%. The determination of the sample concentrations was based on a linear regression analysis with a calibration curve ranging from 0.005 to 0.120 mg/L and a method detection limit (MDL) of 0.0005 mg/L. This concentration range was chosen as the optimal range based on the instrumental method used. The gas chromatograph column conditions were 40 °C held for 3.00 min followed by a temperature increase to 300 °C at a rate of 9.0 °C/min and held for 2.00 min. The helium carrier gas flow rate was set at 9.0 mL/min. The column used was a Varian VF-5ms 30 m × 0.25 mm i.d. capillary GC column (Lake Forest, CA).

Metal concentrations (As, Al, Cd, Cr, Cu, Fe, Pb, Mg, Mn, K, P, Ni, Na, Si, Zn, Ca, Ag, Ba) of aqueous samples were measured using a PerkinElmer Optima 2100 DV optical emission spectrometer (Shelton, CT). Anion analysis of municipal secondary effluent samples was performed using a Dionex ICS 3000 (Sunnyvale, CA) ion chromatograph with an RFIC IonPac AG18 2 mm × 50 mm guard column and an AS18 2 mm × 250 mm IC column. UV–vis spectra were determined using a Hach DR/4000U spectrophotometer (Loveland, CO). Water (18.2 MΩ) was used as the blank/background for all UV–vis scans. TOC and DOC analyses were performed using a Phoenix 8000 UV/Persulfate TOC analyzer (Tekmar-Dohrmann, Cincinnati, OH).

2.3. Experimental methods

Various experiments were performed in order to better understand the photolytic relationship between DEET, HA, and municipal effluents, which may affect overall removal. First, the photocatalysis of DEET in the presence of aqueous P-25 TiO_2 dispersions was explored. This provided a baseline rate of degradation which facilitated the addition of other components (i.e. HA, secondary effluent) into the DEET/TiO_2 system. DEET was also irradiated with no TiO_2 present in order to determine if photocatalysis was the dominant mechanism in the loss of DEET concentration. Different HA concentrations were added (10.0, 1.00, and 0.100 mg/L) to the DEET/TiO_2 system, and the effect on DEET concentration was observed. Since HA is likely susceptible to oxidation and could effect DEET degradation, it was also necessary to observe the effective photocatalytic degradation of HA alone in the presence of TiO_2. The HA organic carbon concentration was determined using TOC analysis after samples were irradiated. If a change was observed, then a decrease in HA concentration after increasing irradiation time would most likely signify photocatalytic degradation. The loss of carbon would be due to the release of CO_2 during the mineralization of the HA. In order to better simulate an actual treatment model, a municipal secondary effluent was used as the matrix for the DEET/TiO_2 system. The effects of organic carbon and soluble salts present in the effluent on DEET degradation rates were observed. Soluble salts (NaCl, $MgSO_4$, KCl, and $CaCl_2$), which can be present during water treatment, were also added to a DEET/TiO_2 system in 18.2 MΩ water and irradiated 30 min in order to examine the effects of the salts on TiO_2 photocatalysis. The concentration of salts added were based on ICP analysis and contained 40.0 mg/L NaCl, 13.0 mg/L $MgSO_4$, 5.0 mg/L KCl, and 72.0 mg/L $CaCl_2$.

2.4. Irradiated samples

Samples were irradiated using a Rayonet photochemical reactor (RPR-100) containing 350 nm Hg lamps. The lamps provide approximately 24 W of UV light and 1.5 to 5 × 10^{16} photons/(s cm^3). Approximately 90% of the light provided is in the 350 nm range, and the intensity of light was 9200 μW/cm^3. The samples were stirred during irradiations using a magnetic stirrer. Aliquots of 10.0 mL containing 0.100 mg/L DEET were placed in 16 mL glass vials containing a small stir bar. Samples were stirred in order to irradiate the maximum surface area of TiO_2 particles and help aerate the sample. The air present in the headspace of the vial provided the oxygen necessary for the photocatalytic process. This concentration of DEET was chosen because it is large enough to observe a noticeable trend in photocatalytic degradation kinetic rates but small enough to remain within an environmentally relevant regime. Irradiated dispersions of aqueous samples containing 2.5 mg P-25 TiO_2 and 10.0, 1.00, and 0.100 mg/L HA were examined. Samples containing no HA were also analyzed. The concentration of DEET was measured by GC/MS after varying the irradiation time (0, 5, 10, 15, 20, 25, and 30 min) of the samples and changing the concentration of HA. A municipal secondary effluent sample was used as the matrix for one set of irradiation experiments where a 0.100 mg/L DEET concentration was used and no other components were added. The experimental procedure for the secondary effluent samples was the same as the procedure for the samples containing HA. For samples containing no DEET, TOC measurements were used to determine organic carbon concentrations in 10.0 mg/L HA samples after irradiation. Samples containing 40 mL 10.0 mg/L HA and 2.5 mg P-25 TiO_2 were irradiated for 15 and 30 min using 350 nm lamps. Samples were filtered using glass microfiber filters to remove TiO_2 particle aggregates.

3. Results and discussion

3.1. Photocatalysis of DEET with TiO_2

The photocatalytic degradation of DEET over time in the presence of 0.25 g/L P-25 TiO_2 was examined. The TiO_2 concentration was based on TiO_2 concentrations found in the literature [31–33]. This concentration would limit the scattering effects caused by large amounts of photocatalyst, but still allow reasonably fast kinetics. The initial concentration of DEET was 0.100 mg/L, and the system pH was approximately 8.00. The pH was not adjusted, as to best simulate natural water conditions prior to and during treatment. Results of irradiated samples showed that there was a decrease in concentration of DEET over time. In order to ensure that the degradation of DEET by TiO_2 was the dominant mechanism, 0.100 mg/L DEET was irradiated without TiO_2 for 30 min in 5 min increments. It was shown that there was no statistical change in concentration due to the direct photolysis of DEET with 350 nm lamps based on a 95% confidence interval. Also, no adsorption at the surface of the TiO_2 particles was observed between unirradiated samples containing only DEET and samples containing DEET/TiO_2. Based on this information, it was determined that the photocatalytic degradation of DEET on the TiO_2 particles was the dominant mechanism of degradation.

Irradiated samples showed that after 5 min of irradiation, there was already a marked change in the concentration of DEET. The percent change between the initial DEET concentration and the concentration after 5 min irradiation with TiO_2 was 31.5%. The degradation of DEET continued with increased irradiation time. After 30 min of irradiation, the percent drop in concentration was 78.2%.

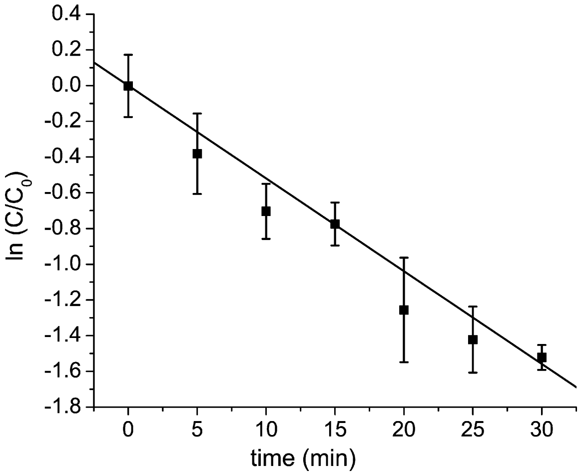

Fig. 1. Pseudo-first-order photocatalytic degradation plot of DEET in the presence of an aqueous P-25 TiO_2 dispersion.

The rate constant of the DEET photocatalytic degradation was calculated using a pseudo-first-order kinetics model, which is generally expected from a TiO_2 photocatalytic system [34–37]. The pseudo-first-order rate constant, k, was determined from the slope of $\ln(C/C_0)$ versus irradiation time, which follows:

$$\ln\left(\frac{C}{C_0}\right) = -kt \qquad (1)$$

where C is the concentration at time t and C_0 is the initial concentration. The rate constant was calculated to be 0.0519 ± 0.0021 min^{-1}. The plot used to determine the rate constant for the photocatalytic degradation of DEET in the presence of TiO_2 can be seen in Fig. 1.

3.2. Photocatalysis of DEET with TiO_2 in the presence of HA

Three concentrations of HA were examined in 0.100 mg/L DEET solutions containing 0.25 g/L TiO_2 particles. Samples were irradiated for 30 min in 5 min increments. The purpose of the addition of HA into the system was to examine the effects of dissolved and/or suspended organic matter on the photocatalytic degradation of DEET. The DEET concentration was measured before and after irradiation for each set of HA concentrations. The three HA concentrations used were 0.100, 1.00, and 10.0 mg/L, with the pH measured to be 7.87, 8.29, and 7.84, respectively. The rate constant was calculated for each system based on the change in DEET concentration for each sample.

A decrease in the concentration of DEET for each of the systems over time was observed. A plot using a pseudo-first-order kinetic equation for the HA samples can be seen in Fig. 2. Using Eq. (1), the pseudo-first-order rate constants for 0.100, 1.00, and 10.0 mg/L were calculated and can be seen in Table 1. The rate of degradation decreases with increasing HA concentration. Overall, there is a decrease in the photocatalytic degradation rate between samples with no HA and samples which contained various amounts of HA.

There are two contributing factors which may inhibit the photocatalytic degradation rate of DEET in samples containing HA. HA contains many aliphatic and aromatic organic molecules. These

Table 1
Pseudo-first-order rates for samples containing DEET in the presence of an aqueous P-25 TiO_2 dispersion and different concentrations of HA.

HA sample concentration (mg/L)	k (min^{-1})	95% Confidence level
10.0	0.0306	0.0032
1.00	0.0318	0.0038
0.100	0.0373	0.0022

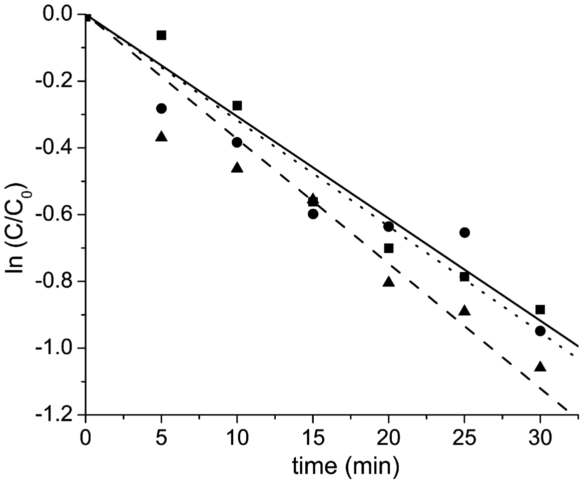

Fig. 2. Pseudo-first-order photocatalytic degradation plot of DEET in the presence of an aqueous P-25 TiO_2 dispersion and different concentrations of HA: (■) 10.0 mg/L (—); (●) 1.00 mg/L (- - -); (▲) 0.100 mg/L (– – –).

molecules are subject to the same chemistry as the target analyte. As photoactive sites at the surface of the TiO_2 particle become occupied by HA, fewer sites are available for the oxidation/reduction of DEET. This competition between molecules would lead to a slower degradation of the target analyte, DEET. As the concentration of HA molecules increases, the degradation rate of DEET would also decrease. A change in HA concentration in the presence of TiO_2 particles was observed as a color change between solutions containing no DEET. As irradiation time increased, the solutions appeared less dark, which would indicate a lower HA concentration. A series of samples containing TiO_2 and HA in water was irradiated for 15 and 30 min, and the decrease in HA concentration with increasing irradiation time was measured using TOC. Results showed the initial C concentration to be 3.37 mg/L for samples containing 10.0 mg/L HA and TiO_2. The C concentration fell to 1.44 mg/L after 15 min and 0.59 mg/L after 30 min. Lower HA concentration samples, 1.00 and 0.100 mg/L, displayed similar trends. The loss of HA was expected, as the photocatalytic degradation of humic acid in the presence of TiO_2 is well known [38–40]. The second contributing factor which would slow the DEET degradation rate involves UV light attenuation and its ability to reach the surface of the TiO_2 particles. UV–vis spectrophotometer results show that there is a measurable amount of light absorbed by the HA samples at 350 nm. This wavelength represents the maximum of the spectral range of the irradiator lamps used in this study and is adequate for the electron excitation at the surface of P-25 TiO_2. At 350 nm, the amount of light absorbed is 33.2% for samples containing 10.0 mg/L HA, 4.1% for samples containing 1.00 mg/L HA, and 0% for samples containing 0.100 mg/L HA. Since a measurable portion of UV light is absorbed by the HA at 350 nm, photons may not be able to reach a portion of the photoactive sites at the surface of the TiO_2 particles. This would lead to lower photoactivity and reduce the degradation rate of DEET. However, initial experiments showed no quantifiable correlation between the amount of light absorbed by HA and the percent change in degradation rates between all samples. The change in DEET degradation rates between samples containing 10.0, 1.00, and 0.100 mg/L HA was calculated to be 41.0%, 38.7%, and 28.1%, respectively. While the absorption of light at higher HA concentrations may reduce photoactivity, the change in degradation rate for the lower HA concentration samples does not correlate to the amount of light absorbed. Further study of the correlation between absorbed light and HA concentration is needed in order to confirm that the competition between analyte and HA at the TiO_2 surface is the dominant mechanism that leads to a reduced degradation rate.

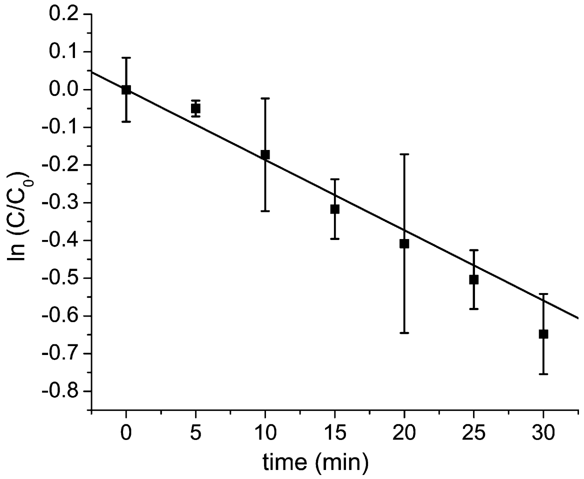

Fig. 3. Pseudo-first-order photocatalytic degradation plot of DEET in the presence of a P-25 TiO_2 dispersion in a municipal secondary treatment effluent matrix.

3.3. Photocatalytic degradation of DEET with TiO_2 in wastewater treatment plant secondary effluent

Samples containing 0.100 mg/L DEET and 0.25 g/L TiO_2 in wastewater treatment plant secondary effluent were irradiated for 30 min in 5 min increments. The concentration of DEET in each sample was measured to determine the rate of degradation. After 5 min irradiation, the concentration of DEET only showed a change of 4.9%. After 30 min irradiation, the change in concentration increased to 47.7%. The pseudo-first-order degradation rate constant, k, was calculated using Eq. (1) to be $0.0186 \pm 0.0019\ \mathrm{min}^{-1}$ based on the plot from Fig. 3.

The degradation rate for samples in the secondary effluent matrix was shown to be much slower than samples prepared in deionized water and samples containing HA. Filtered secondary effluent samples had a DOC content of 4.38 mg/L. Although the effluent samples were retrieved after sand-filtration, it is possible that dissolved organics and minerals present in the effluent compete with the photocatalytic degradation of DEET, thereby slowing the degradation rate. UV–vis spectrophotometer results showed no light scattering or absorption at 350 nm. Therefore, light would have been able to reach the TiO_2 surface to allow for electron excitation. However, ICP spectroscopy measurements of unfiltered secondary effluent samples showed significant concentrations of calcium, sodium, magnesium, potassium, and phosphorous. The concentration of the most prevalent metals in the effluent can be seen in Table 2(a). Ion chromatography results showed that the secondary effluent sample contained significant concentrations of Cl^-, SO_4^{2-}, and NO_3^{2-} (see Table 2(b)). Most likely, the elements and anions detected were present in the form of sol-

Table 2

(a) ICP metals analysis of municipal secondary treatment effluent (cations). (b) IC/MS analysis of municipal secondary treatment effluent (anions).

Name	Concentration (mg/L)
(a) ICP results	
Magnesium	15.46
Potassium	6.52
Phosphorous	0.67
Sodium	43.51
Calcium	65.01
(b) IC results	
Cl^-	112.2
SO_4^{2-}	60.5
NO_3^-	39.6

uble salts in the treated water. Experiments showed that there was a marked decrease in photocatalytic degradation efficiency in samples containing various salts, including NaCl, $MgSO_4$, KCl, and $CaCl_2$. The ratios of salts used in these experiments were based on ICP spectroscopy measurements of the municipal secondary treatment effluent. Samples with no salts present were shown to have 42.1% higher DEET removal than samples which contained salts. This difference in efficiency corresponds to the results obtained during the DEET photocatalytic degradation kinetic experiments, which compared samples containing DEET/TiO_2 in 18.2 MΩ water and in a municipal secondary effluent water matrix. Based on the decrease in photoefficiency, it appears that the presence of the salts affects the oxidation/reduction chemistry that occurs from the radical cations and anions produced during electron excitation. Based on previous studies, this decrease in efficiency has been attributed to the quenching of radicals and scavenging of valence band holes at the surface of the TiO_2 particles [41,42] and the lack of adsorption of the analyte at the surface of the photocatalysts due to the formation of an inorganic salt layer [43]. Both events would lead to the overall reduction of photoefficiency in a municipal secondary treatment effluent containing salts.

4. Conclusions

Samples containing DEET and P-25 TiO_2 dispersions were irradiated in 18.2 MΩ water, HA, and municipal secondary effluent matrixes. The rate constant for each system was calculated, and it was shown that as HA concentration increased, the photocatalytic degradation rate decreased. The decrease likely stems from both the attenuation of UV light needed for electron excitation and photoactive surface site competition between the target analyte and HA. Samples containing a municipal secondary effluent were shown to have the lowest photocatalytic degradation rate. Following analysis of the secondary effluent, it was determined that the decrease in rate was due to the presence of both dissolved organic matter and salts in the treated water, which were believed to compete with analyte oxidation/reduction, quench reactive species at the surface of the TiO_2, and prevent efficient charge transfer at the surface by forming at salt layer.

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