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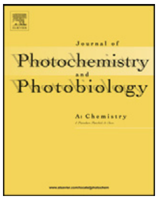

Photodegradation of 17β-estradiol in aquatic solution under solar irradiation: Kinetics and influencing water parameters

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ABSTRACT

Photodegradation of the natural steroid 17β-estradiol (E2), an endocrine disrupting hormone which is commonly released into aquatic environments, was investigated under simulated sunlight (290–700 nm) using a solar simulator in the presence of several natural water constituents including NO_3^-, Fe^{3+}, HCO_3^-, humic acid and turbidity. The E2 degradation followed pseudo-first-order kinetics, with the rate constant decreasing slightly with increasing initial constituent concentration while increasing with the square root of solar intensity in the region of 25–100 mW cm^{-2}. The rate of mineralization based on the total organic carbon (TOC) reduction was always lower than E2 degradation, although the TOC of the solution decreased steadily with irradiation time. In the presence of NO_3^-, Fe^{3+}, and humic acid, the photodegradation rate increased significantly, attributed to photosensitization by the reactive species, while HCO_3^- slowed down the degradation rate because of $OH^\bullet$ scavenging. Turbidity also reduced the photodegradation of E2 by decreasing light transmittance due to attenuation. The solution pH also had a considerable effect on the rate with maximum degradation occurring around a neutral pH of 7.

1. Introduction

The ubiquitous presence of emerging contaminants (ECs) in aquatic environments is becoming a major worldwide concern. Among the ECs, special importance is given to endocrine disrupting compounds (EDCs), as they can interfere with the normal function of hormones by interacting with the endocrine system presenting a potential threat to both aquatic life and human health [1,2]. In addition to industrial chemicals such as bisphenol-A, DDT, atrazine, methoxychlor, chlordecone, alkylphenols, PCBs and phthalic esters, several natural steroid estrogens including estrone (E1), 17β-estradiol (E2), estriol (E3) and mestranol (MeEE2) and synthetic pharmaceuticals such as diethylstilbestrol (DES), ibuprofen, norfloxacin and 17α-ethynylestradiol (EE2) were found to be the most potent of the EDCs [1–4].

Among the EDCs, natural estrogens are thought to be the most likely to cause estrogenic effects on aquatic life due to their very potent estrogenic activities, even at very low concentrations. Of the natural estrogens, 17β-estradiol is the most potent natural estrogen among those including estrone and estriol [4]. Estrogenic steroids are detected in both the influent and effluent of sewage treatment plants in different countries at various concentrations [2]. These steroid hormones make their way into the aquatic environment through sewage discharge and animal waste disposal due to both human and animal excretions. These steroids have also been detected at elevated levels in soil, ground water as well as surface water adjacent to agricultural fields fertilized with animal manure [5].

Although the concentrations of the steroid hormones in natural aquatic environments are in the low ng/L range (10–1830 ng/L), it is very important to understand the fate of these EDCs in aquatic environments. Understanding their degradation rates helps to determine their environmental impact and potential threat to aquatic life due to their extremely high biological potency and procreation toxicity [6,7]. The degradation time of these organic pollutants in the environment may vary from a few hours to months depending on various environmental parameters [8]. Among the various environmental degradation processes (abiotic/biotic), photodegradation from solar irradiation is one of the most important factors for determining the ultimate fate of the persistent pollutants in aquatic environments [9].

Solar phototransformation or degradation of organics in aquatic environments may occur by either direct or indirect photolysis. Direct photolysis is the result of light absorbance by the pollutants causing their molecular degradation. As all steroid estrogens have considerable sunlight absorbance in the ultraviolet and blue spectral region (290–360 nm) [10], it is believed that direct photolysis plays a crucial role for the photodegradation of steroid estrogens in aquatic environments [11]. For indirect photolysis, NO_3^-, Fe^{3+} and humic substances play crucial roles, which are ubiquitous in

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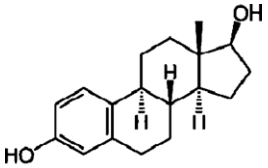


Fig. 1. Structure of 17β-estradiol (E2).

surface water and absorb solar radiation to reach an excited state, subsequently generating free radicals comprised of reactive oxygen species (ROS) (e.g., hydroxyl radicals ($OH^\bullet$), peroxyl radicals ($ROO^\bullet$), and singlet oxygen ($^1O_2$)) and other non-ROS transients [12]. Among these reactive photochemically generated species in surface waters, $OH^\bullet$ plays a very important role in the phototransformation of organic pollutants because of its very high oxidizing potential. In addition, reaction between most organics and $OH^\bullet$ occurs with rate constants that are essentially diffusion controlled [13]. The major sources of $OH^\bullet$ in natural water have been identified as NO_3^-, Fe^{3+}, and humic substance, while HCO_3^- plays a negative role due to its scavenging effect on $OH^\bullet$ in surface water [14]. Another important water parameter is turbidity, as it controls light attenuation in the water.

Steroid hormones are known to degrade rapidly in the presence of high intensity UV-C (254 nm), and many degradation studies of these hormones are available in the literature using advanced oxidation processes (AOP) such as semiconductor photocatalysis, UV/H_2O_2, UV/O_3, and O_3/H_2O_2 [15–17]. Although photodegradation of steroid hormones has been studied in engineered systems, comprehensive studies documenting their fate in the presence of sunlight are still limited. Earlier, we reported the solar degradation of estrone (E1) in water [11], however, environmental photodegradation of 17β-estradiol (E2), the most potent of natural estrogens has not yet been fully investigated. A recent study conducted by Leech et al. showed the effect of natural organic matter on the solar degradation of E2 [18]. The objective of this comprehensive study is to determine the kinetics of the photodegradation of steroid E2 (see Fig. 1) in simulated aquatic environments due to direct solar irradiation (i.e. UV-B, UV-A, and visible radiation, 290–700 nm) using a solar simulator with controlled doses of sunlight under various environmental conditions including solar intensity, initial concentration of E2, pH, natural photosensitizers (dissolved uncharacterized organic matter or the humic substances, Fe^{3+} and NO_3^-), and other water constituents such as HCO_3^- and turbidity. The extent of mineralization of E2 under various conditions was also evaluated. In addition, wherever possible, a comparative analysis of the photodegradation of E1 and E2 is provided.

2. Experimental

2.1. Chemicals

E2 (MW: $C_{18}H_{24}O_2$, CAS registry number: 50-28-2) was obtained from Sigma–Aldrich (Oakville, Ontario, Canada) and used without further purification. Acetonitrile (AcN) for HPLC analysis was of HPLC grade and purchased from Fisher Scientific (Ottawa, Ontario, Canada). Humic acid (Technical grade, CAS registry number: 1415-93-6) was also obtained from Sigma–Aldrich (Oakville, Ontario, Canada). AMCO clear turbidity standard, 1000 NTU was purchased from Fisher Scientific (Ottawa, Ontario, Canada). All other reagents used for solutions were reagent grade and used without further purification. Laboratory grade water (LGW, 18 MΩ) was prepared from an in-house Millipore purification system (Billerica, MA).

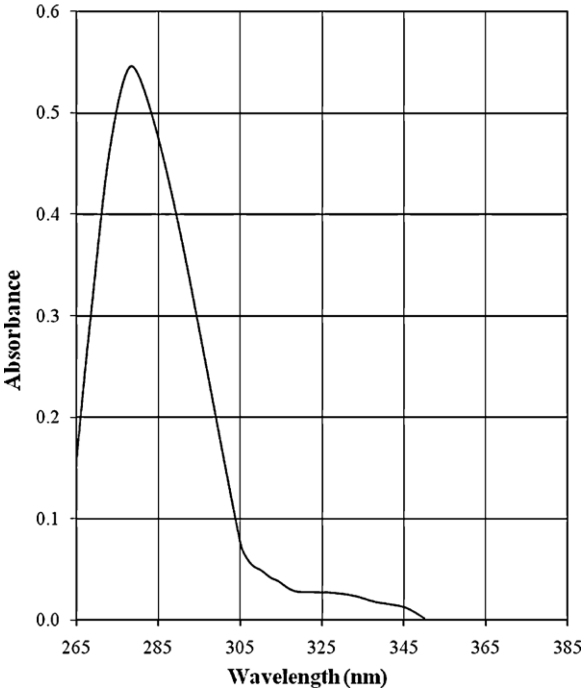


Fig. 2. Absorption spectrum of E2 over 265–385 nm at pH 6.5.

2.2. Standard and sample preparation

Stock solutions (5 ± 0.05 mg/L) of E2 (solubility: 13 mg/L at 20 °C) were prepared by dissolving an appropriate amount of E2 in purified water in a volumetric flask by stirring for 2 h to ensure complete dissolution. The working water samples were prepared by adding the stock solution to purified water to obtain the desired initial concentration. The stock and working solutions were wrapped with aluminum foil and stored at 4 °C to prevent any degradation. The natural pH of Milli-Q water is 6.5, which is also the pH of the E2 solution. All experiments were conducted at pH 6.5 except for evaluating the effect of pH and HCO_3^- on the degradation of E2, where NaOH or HCl were used to adjust the pH.

2.3. Photodegradation experiments

Photodegradation experiments were carried out using a solar simulator (Model: SS1KW, Sciencetech, ON, Canada) with a 1000 W xenon arc lamp. An air mass filter (AM filter) AM1.5G was installed in the radiation beam to produce simulated 1 SUN irradiance of 100 mW cm^{-2} at full power that matches the global solar spectrum (Class A standards as per JIS-C-8912 and ASTM 927-05) at sea level and zenith angle 37° (Fig. S1 in Supporting information). The light absorption spectra of E2 were measured and shown in Fig. 2. In spite of λ_{max} = 278 nm, E2 exhibits a slight absorption in the 300–350 nm wavelength region, which can induce photolysis of E2. Hence, photon flux from the solar simulator was calculated in the 300–400 nm range, being 5.3×10^{-5} Einstein m^{-2} s^{-1} at 1 SUN irradiation.

An open water-jacketed vertical glass vessel (length: 11 cm × diameter: 9 cm) was used as the solar photo-reactor, which was placed on a magnetic stirrer during all experiments, under aerated conditions at 350 rpm and a temperature of 22 ± 2 °C. The aqueous solution was irradiated directly from the top using a vertical solar beam of 8 in. (20.3 cm) diameter from the solar simulator. In all experiments, the total irradiated solution volume was 300 mL. The irradiation intensity was measured at the top surface of the experimental solution by a Broadband Thermopile Detector (Model: UP19K-15W, Sciencetech, ON, Canada), which allows measurement of the radiation emitted by a light source between 190 nm and 11 μm (UV–VIS–IR) and the power density on a surface (in mW cm^{-2}). The schematic of the experimental setup is shown in Fig. S2 in Supporting information. The experiments were performed using different solar intensities, initial concentrations of E2, dissolved oxygen and in the presence of different water constituents, such as pH, NO_3^-, Fe^{3+}, HCO_3^-, humic acid and turbidity.

In each experiment, a maximum of 5 irradiated samples (2 mL each) were withdrawn from the photo-reactor at different irradiation times for the kinetic study. Hence, the volume variation due to sampling was negligible. All experiments were conducted in triplicate with average error around 5% and the results presented in the following figures and tables which are the average of three experiments with reported standard deviations or error bars.

2.4. Analytical methods

2.4.1. HPLC analysis

The E2 concentration was measured by HPLC (ICS 300, Dionex), which included a DP pump, an AS auto sampler, a DC column oven and PDA UV detector, connected to Chromeleon software. Separations were carried out with an Acclaim 120 C_{18} reversed-phase column (150 mm × 4.6 mm i.d., 5 μm particle size, Dionex, USA). The injection volume was 40 μL from 2 mL HPLC vials, capped and sealed with PTFE lids. The mobile phase was a mixture of AcN and Milli-Q water (50:50, v/v) at a flow rate of 1 mL/min by the HPLC pump. The column temperature was maintained at 30 °C and detection wavelength was set at 280 nm, the maximum absorbance of E2. The retention time of E2 was 5.04 min.

2.4.2. Other analyses

The UV–Vis spectra and absorbance at wavelength 290 nm of the experimental samples were recorded using a UV–Vis spectrophotometer (UV-3600, Shimadzu) in a 1 cm path length quartz cuvette. Total organic carbon (TOC) was measured on selected samples by means of a Shimadzu TOC-V_{CPN} analyzer with an ANSI-V auto sampler, and the pH and turbidity were measured using a Beckman Coulter pH meter (model number: pHi 460) and a Micro 100 Laboratory Turbidimeter, respectively.

3. Results and discussion

3.1. Kinetics of solar photolysis of E2 in aqueous solution

Prior to undertaking the various solar degradation studies on E2, a 10 h control experiment was carried out in the dark by covering the reactor with aluminum foil at an E2 concentration of 5 μg/L at pH 6.5 to determine the extent of dark reaction. There was no evidence of E2 degradation at ambient conditions in the absence of solar light. Thereafter, the kinetic experiments were carried out with an initial E2 concentration of 5 μg/L at 1 SUN solar irradiation, pH 6.5, and with normal dissolved air, nitrogen purged and aerated conditions. The results show that the E2 concentration decayed exponentially with time. All experiments produced linear plots of $\ln(C_{E2}/C_{0_{E2}})$ versus time as shown in Fig. 3, indicating the photodegradation of E2 in aqueous solution under solar irradiation followed pseudo-first-order kinetics. The pseudo-first-order degradation rate constant and half-life of E2 can be calculated as per Eqs. (1) and (2):

$$\ln\left(\frac{C_{E2}}{C_{0_{E2}}}\right) = -kt \quad (1)$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (2)$$

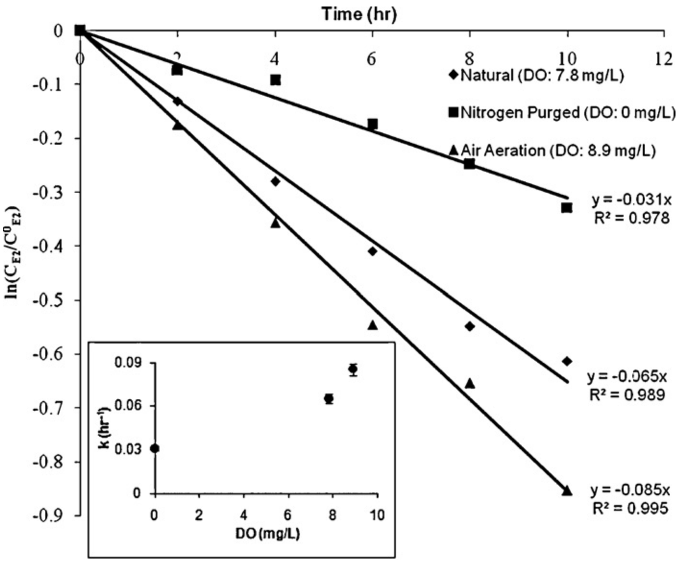


Fig. 3. Solar photodegradation of E2 and pseudo-first order rate constant k at normal, nitrogen purged and aerated conditions. $C_{0_{E2}} = 5$ μg/L, pH = 6.5, solar intensity = 1 SUN and irradiation time = 10 h.

where $C_{0_{E2}}$ and C_{E2} are the concentrations of E2 at time zero and reaction time k in h, k is the pseudo-first-order degradation rate constant (h^{-1}) and $t_{1/2}$ is the half-life.

E2 degraded due to direct photolysis under solar irradiation in the range of 290–700 nm in the absence of free radicals, which are generally produced in the presence of photosensitizers in natural water. The value of the pseudo-first-order rate constant k of E2 under 1 SUN irradiation in natural conditions was measured as $0.0652 \pm 0.0033\ h^{-1}$. Although the absorption maxima of E2 is at 278 nm, E2 has an extended light absorption band from 290 to 340 nm (see Fig. 2); i.e. UV-B and UV-A region, which is present in natural solar irradiation (UV-A: 6.3% and UV-B: 1.5%) [19].

The direct photolysis of E2 occurs in the region where the solar spectrum overlaps with the E2 light absorption band. In order to determine the extent of direct photolysis of E2, control experiments were conducted by purging air from the reactor using nitrogen. As seen in Fig. 3, the degradation of E2 was substantially decreased in the absence of air (DO: 0 mg/L for nitrogen purged condition). Comparing the degradation rates in the presence of nitrogen ($k = 0.0311 \pm 0.0016\ h^{-1}$ at DO: 0 mg/L) with that of in the presence of naturally dissolved oxygen ($k = 0.0652 \pm 0.0033\ min^{-1}$ at DO: 7.8 mg/L) as shown in Fig. 3, inset, it can be inferred that about 48% degradation of E2 occurred due to direct photolysis.

The degradation rate constant increased by ≈32% in the presence of additional air ($k = 0.0855 \pm 0.0040\ h^{-1}$ at DO: 8.9 mg/L) than that found in naturally dissolved air due to photooxidation as shown below:

$$E2 + h\upsilon \xrightarrow{O_2} \text{Photoproducts} \quad (3)$$

The extent of mineralization was determined by measuring the total organic carbon (TOC) at various experimental conditions, which indicate that only about 8 ± 0.3% TOC degraded in 10 h in the presence of nitrogen (DO: 0 mg/L) as compared to 13 ± 0.6% and 15 ± 0.7% TOC removal in the presence of naturally dissolved oxygen (DO: 7.8 mg/L) and additional aeration (DO: 8.9 mg/L), respectively. TOC degradation in the presence of nitrogen indicates that the intermediates formed during solar irradiation also undergo photolysis. As anticipated, the presence of oxygen helps the degradation of both E2 and its intermediates. Previously, mineralization of estrone (E1) under similar operating conditions was found to be much higher than E2 indicating that the primary photochemical process of photon absorption is important for total degradation of estrogenic compounds [11]. This is also reflected by the much higher photolysis rate of E1 ($0.534 \pm 0.012\,\mathrm{h}^{-1}$), which is about 17.5 times higher than E2. The half-life of E2 at 1 SUN intensity is ≈10 h, whereas it is only about 50 min for E1; accordingly about 67% degradation of E1 occurred due to photolysis as opposed to 48% degradation by photolysis of E2 [11].

Quantum yield (Φ) is an important parameter to measure the efficiency of photodegradation and is defined as the number of moles of reactant transformed divided by the number of moles of photons absorbed by the reactant, in this case by E2:

$$\Phi = \frac{\text{Number of molecules reacted (or produced)}}{\text{Number of photons of light absorbed}} \tag{4}$$

Under polychromatic irradiation in dilute aqueous solution, the rate of disappearance of an absorbing compound (E2) is given by [10]:

$$-\frac{dC_{\mathrm{E2}}}{dt} = \sum \Phi_\lambda I_{0,\lambda}(1 - 10^{\varepsilon_\lambda C_{\mathrm{E2}} z_0}) \tag{5}$$

where Φ_λ is the quantum yield (in mol Einstein^{-1}), ε_λ (M^{-1} cm^{-1}) the molar absorption coefficient, $I_{0,\lambda}$ (Einstein L^{-1} s^{-1}) the photon rate at the wavelength λ, z_0 (cm) and C_{E2} (M) are the reactor optical path length and the concentration of the compound E2, respectively. When the concentration of the absorbing compound is low enough (this is usually the case in natural water), Eq. (5) can be simplified by integrating to Eq. (6):

$$\sum \Phi_\lambda = \frac{k}{2.303 \times I_{0,\lambda} \times \varepsilon_\lambda \times z_0} \tag{6}$$

where k (s^{-1}) is the pseudo-first-order rate constant. The average quantum yield can be calculated by integrating the 1 SUN solar intensity over the wavelength range of 300–400 nm, which gave the value of 0.0033 mol Einstein^{-1} for E2 in Milli-Q water, which is comparable to the quantum yield of E2 (Φ = 0.0048 mol Einstein^{-1}) determined previously by Lin and Reinhard [20]. The difference in quantum yield can be attributed to the wavelength of light used and other experimental conditions used in the work of Lin and Reinhard [20]. The calculated quantum yield of E2 under natural solar irradiation is much lower than the quantum yield (Φ = 0.067 mol Einstein^{-1}) under monochromatic (λ = 254 nm) irradiation determined by Mazellier et al., because E2 has a very small absorbance in the wavelength range of 300–400 nm [21]. The quantum yield of E1 is 0.0246 mol Einstein^{-1}, which is 7.45 times higher than E2, attributed to its higher absorbance in the UV-A and UV-B regions of solar light (ε_{290}(E2) = 1010 M^{-1} cm^{-1} and ε_{290}(E1) = 2186 M^{-1} cm^{-1}) [11].

3.2. *Effect of initial concentration on photodegradation of E2*

As E2 has been detected at various concentrations in natural surface water in recent years, it is important to investigate the effect of E2 concentration on its photolysis by solar irradiation. Experiments were carried out at different initial E2 concentrations of 5, 10, 20, 30, 40 and 50 μg/L to investigate the effect of concentration on the degradation rate. As shown in Table 1, solar photodegradation of E2 in aqueous solution decreased only slightly (about 10% reduction in rate-constant for tenfold increase in concentration) with increasing E2 initial concentration. This is a common trend for photochemical degradation of organic compounds, where the photolysis rate can be decreased due to photon limitations occurring at higher initial concentrations of the organics [22]. However, due to the small absorbance of E2, the small range of concentration tested, and the presence of sufficient solar photon flux, the effect of concentration of E2 is minimal.

Table 1
Pseudo-first-order rate constant, *k* and half-life for solar photodegradation at different E2 initial concentrations (intensity 1 SUN, 100 mW cm^{-2}).

E2 concentration (μg/L)	k (h^{-1})	$t_{1/2}$ (h)	R^2
5	0.0652 ± 0.0033	10.63	0.9896
10	0.0633 ± 0.0024	10.94	0.9787
20	0.0616 ± 0.0025	11.24	0.9864
30	0.0603 ± 0.0017	11.49	0.9693
40	0.0598 ± 0.0026	11.59	0.9723
50	0.0589 ± 0.0022	11.76	0.9815

Table 2
Pseudo-first-order rate constant, *k* and half-life for solar photodegradation at different solar intensities of E2.

Solar intensity	k (h^{-1})	$t_{1/2}$ (h)	R^2
1/4 SUN (25 mW cm^{-2})	0.0329 ± 0.0016	21.07	0.9829
1/2 SUN (50 mW cm^{-2})	0.0433 ± 0.0022	16.01	0.9746
3/4 SUN (75 mW cm^{-2})	0.0575 ± 0.0026	12.05	0.9909
1 SUN (100 mW cm^{-2})	0.0652 ± 0.0033	10.63	0.9896

3.3. *Effect of solar intensity on photodegradation of E2*

The variation of solar light intensity during the day and over the year is an important parameter to consider when evaluating solar driven processes, because the photon generation rate changes with different solar intensities. Therefore, experiments were carried out at four different solar intensities of 1/4 SUN (25 mW cm^{-2}), 1/2 SUN (50 mW cm^{-2}), 3/4 SUN (75 mW cm^{-2}) and 1 SUN (100 mW cm^{-2}) simulated by adjusting the power output from the xenon arc lamp, and using the same experimental conditions discussed earlier to determine the effect of solar intensity on the photodegradation of E2. As shown in Table 2, the solar photodegradation of E2 follows pseudo-first-order kinetics for all solar intensities, and the rate constant increases with increasing light intensity. Fig. 4 shows that k (h^{-1}) is directly proportional to the square root of solar intensity over the range tested as per the following equation:

$$k = 0.006 \times I^{0.5} \tag{7}$$

where I is the solar intensity in mW cm^{-2}. The enhanced solar photodegradation rate at higher intensity is obviously due to higher photon flux. The relatively lower dependence of photodegradation on intensity is due to photooxidation in the presence of the oxygen as was seen earlier. The photolysis corresponds to only 48% of the

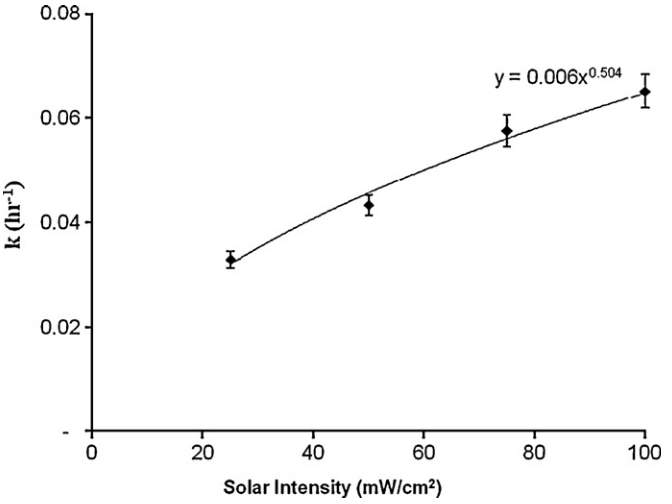


Fig. 4. Effect of solar intensity on solar photodegradation rate constant of E2. $C_{0_{\mathrm{E2}}}$ = 5 μg/L, pH = 6.5 and irradiation time = 10 h.

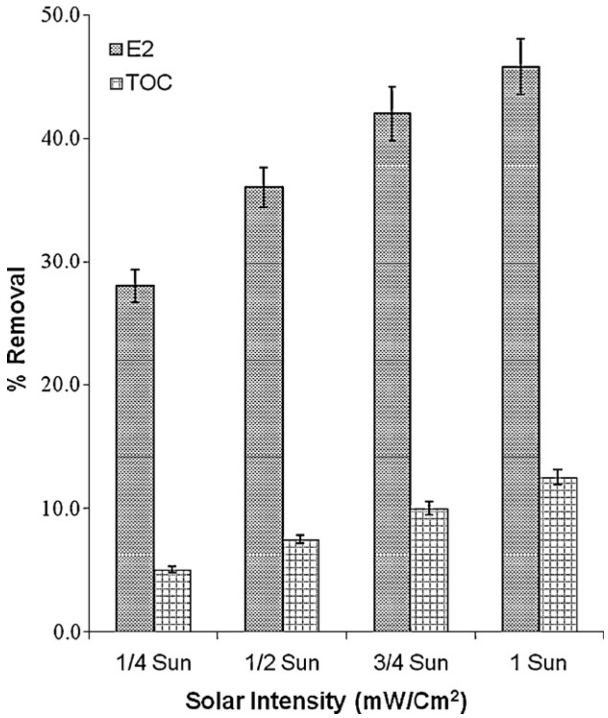


Fig. 5. Comparison between mineralization and degradation efficiencies of E2 at different solar intensities. $C_{0_{E2}} = 5\,\mu g/L$, pH = 6.5, initial TOC = 0.004 mg/L and irradiation time = 10 h.

total degradation in the presence of naturally dissolved air/oxygen. E1 with higher light absorption than E2 and a higher degree of photolysis (67% as compared to 48% of E2) shows a stronger dependence of the degradation rate on solar intensity [11].

3.4. Mineralization

Complete mineralization is an important parameter in the fate of environmental pollutants, as the degradation photoproducts or intermediates may exhibit more toxicity than the parent organic pollutants. In order to determine the extent of mineralization of E2, TOC values of the solution were monitored during solar photodegradation. Due to the variation of solar light intensity during the day and over the year, the TOC removal of E2 solution was evaluated as a function of four different solar intensities (1/4 SUN, 1/2 SUN, 3/4 SUN and 1 SUN) with initial concentration of E2 = 5 μg/L (initial TOC = 0.004 mg/L) and solution pH 6.5 for 10 h of irradiation. The results indicate that TOC removal increases with solar intensity as shown in Fig. 5. It was found that mineralization of E2 increased with solar intensity as well as the irradiation time, although the mineralization of E2 was always significantly lower than the degradation of E2 itself. Even at the maximum solar intensity of 1 SUN, the extent of mineralization was only 13 ± 0.6%, whereas E2 degradation was 46 ± 0.23% after 10 h of irradiation. The significant difference between the rates of degradation and mineralization implies that the photoproducts of E2 oxidation are much slower than E2 photodegradation under the present experimental conditions [11]. It is possible that the aromatic ring of E2 was easily broken due to photolysis, while the aliphatic rings were not destroyed due to their higher stability [16].

3.5. Effect of water parameters on solar photodegradation of E2

3.5.1. Influence of pH

Water pH is one of the most important parameters influencing the solar photodegradation of organic compounds in natural aquatic environments. To evaluate the effect of pH on photodegradation, experiments were carried out at a pH range of 3.0–9.0 using a solar intensity of 1 SUN and E2 initial concentration of 5 μg/L. The results are presented in Fig. 6. In this work, any extreme pH changes were avoided to maintain environmentally relevant conditions. The results show that the photodegradation rate of E2 was significantly dependent on the solution pH, i.e. the photodegradation rate constant in the alkaline regime was higher than that in the acidic regime, with maximum degradation occurring around pH 7. Since these experiments were conducted in the absence of anions such as NO_3^-, Fe^{3+} or humic acid, which are known to produce $OH^\bullet$ in surface water in the presence of sunlight, the effect of pH on E2 degradation cannot be related to $OH^\bullet$. The acid dissociation constant for E2 is ≈10.4 [23], therefore E2 remains protonated in the test pH range, although some dissociation would occur at higher pH values. At pH values above the pK_a, the phenol group on E2 structure would form phenoxide ions, facilitating faster degradation than the un-dissociated E2. Similar trends were reported for the degradation of estrone and 17α-ethynylestradiol in engineered systems [11,24] as well as for the solar degradation of phenol and chlorophenol. Here, the photolysis rate of phenols was much lower at a pH below the pK_a due to a lower rate of photolysis of the nonionized form relative to the phenoxide ion [25]. The drop in photolysis rate is due to a lower molar absorbance of light (≥290 nm) with the nonionized E2 than that of ionized E2. The molar absorbance of E2 decreased from $9.07 \times 10^3\ cm^{-1}\ M^{-1}$ at pH 12.3 to $1.81 \times 10^3\ cm^{-1}\ M^{-1}$ at pH 3.6, therefore ionized E2 is easier to be excited and degraded than nonionized E2 [23].

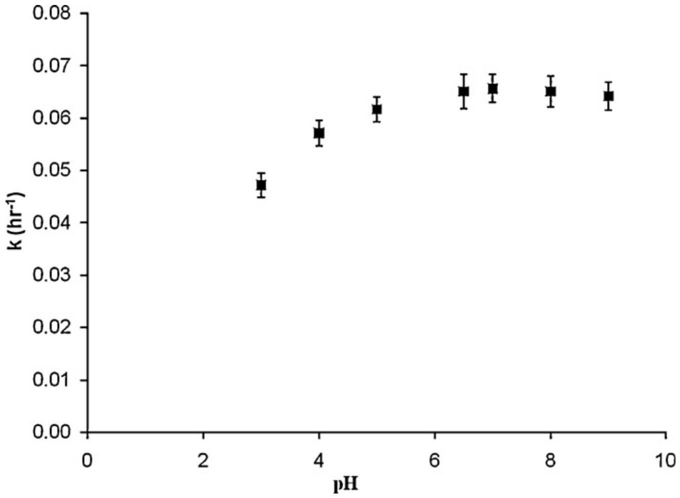


Fig. 6. Influence of pH on solar photodegradation of E2. $C_{0_{E2}} = 5\,\mu g/L$, solar intensity = 1 SUN and irradiation time = 2 h.

3.5.2. Influence of NO_3^-

NO_3^- is generally present in natural surface water at various concentrations depending on the agricultural and geographic location [26]. Hence experiments were carried out for several NO_3^- concentrations using $NaNO_3$ stock solution in the range of 0–40 mg/L, which are similar to natural surface water conditions, using a solar intensity of 1 SUN and E2 initial concentration of 5 μg/L with the results shown in Fig. 7. Solar photodegradation of E2 in the presence of NO_3^- also follows pseudo-first-order kinetics and the degradation efficiency was enhanced markedly with increasing concentration of NO_3^- with the degradation rate increased proportionately with increasing concentrations of NO_3^-. It is well known that NO_3^- produces $OH^\bullet$ when excited by solar ultraviolet light at wavelengths between 290 and 330 nm with quantum yield (Φ) ranging from 0.009 to 0.017 [27]. The mechanism of $OH^\bullet$ generation

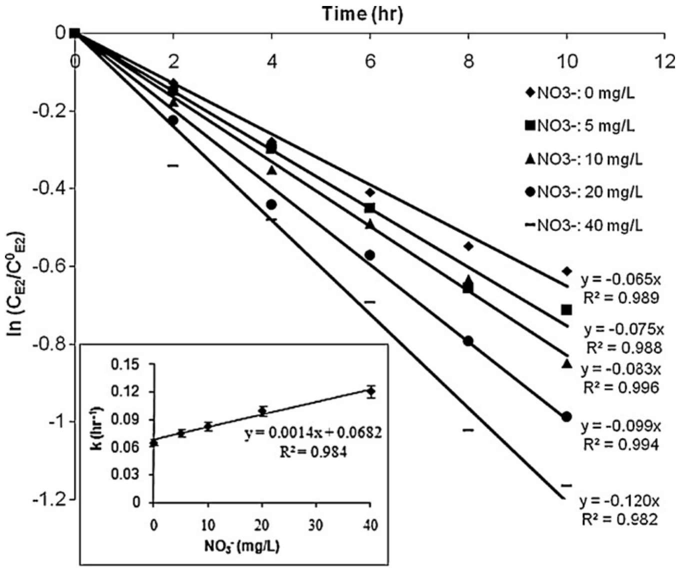


Fig. 7. Influence of NO_3^- concentration on solar photodegradation of E2. $C_{0_{E2}}$ = 5 μg/L, pH = 6.5, solar intensity = 1 SUN and irradiation time = 10 h.

from NO_3^- photolysis at λ_{max} = 302 nm (ε = 7.2 M^{-1} cm^{-1}) results in two primary photochemical processes as per reactions (8) and (9), and according to reaction (10), $OH^\bullet$ should be proportional to NO_3^- and if its reaction with E2 is equimolar, the degradation rate of E2 should also be proportional to NO_3^- [26–28]. Similar results were obtained for the photodegradation of diuron and monolinuron in the presence of NO_3^- by other researchers [26,27].

$$NO_3^- \xrightarrow{h\upsilon} NO_3{}^{\bullet -} \rightarrow NO_2^- + O(^3P) \tag{8}$$

$$NO_3^- \xrightarrow{h\upsilon} NO_3{}^{\bullet -} \rightarrow NO_2 + O^{\bullet -} \tag{9}$$

Followed by:

$$O\bullet^- + H_2O \rightarrow OH\bullet + OH^- \tag{10}$$

$$E2 + OH\bullet \rightarrow \text{Photoproducts} \tag{11}$$

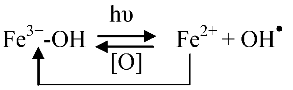
Increasing the nitrate concentration by 4 times, the photodegradation rate constant increased by 1.8 times, with the rate constant following the linear relationship with NO_3^- concentration.

$$k = 0.0014C + 0.0682 \tag{12}$$

where k is the pseudo-first order rate constant of E2 degradation in h^{-1}, and k is the nitrate concentration in mg/L.

3.5.3. Influence of Fe^{3+}

Dissolved iron is often present in natural surface water at various concentrations depending on the geographical location. It has been shown that Fe^{3+}–aquo complexes strongly absorb solar irradiation (λ > 290 nm) at acidic pH between 2.5 and 5 and yield $OH^\bullet$ and Fe^{2+} according to the following reaction [29]:



$$Fe^{3+}\text{-}OH \underset{[O]}{\overset{h\upsilon}{\rightleftharpoons}} Fe^{2+} + OH^\bullet \tag{13}$$

Among the Fe^{3+}–aquo complexes (Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$, dimer $Fe(OH)_2^{4+}$, $Fe(OH)^{2+}$) is the predominant photoreactive species in terms of $OH^\bullet$ generation with the highest quantum yield as per the following reaction [29,30]:

$$Fe(OH)^{2+} \xrightarrow{h\upsilon} Fe^{2+} + OH\bullet \tag{14}$$

Hence experiments were conducted using 30, 50 and 70 μmol/L Fe^{3+} concentrations (by spiking $FeCl_3$ stock solution) at three different pH values of 3, 4 and 5 using a solar intensity of 1 SUN and E2 initial concentration of 5 μg/L with the results shown in Table 3. The results show that the photodegradation rate of E2 was enhanced considerably in the presence of Fe^{3+} for all pH values due to the presence of $OH^\bullet$. The effect is more pronounced at pH 3 where, a 38% increase in rate occurred by increasing the Fe^{3+} concentration to 70 μmol/L. Here, the photodegradation rate increased by 8% with increasing Fe^{3+} concentration from 30 μmol/L to 50 μmol/L and about 5% by increasing Fe^{3+} concentration from 50 to 70 μmol/L for all experimental pHs (3–5) due to the increased $OH^\bullet$ production rate with higher Fe^{3+} concentration. However, the results indicate that degradation rate had reached a plateau with increasing Fe^{3+} concentration which needs to be investigated further.

3.5.4. Influence of HCO_3^-

Carbonate and bicarbonates, which are responsible for alkalinity, are the most common inorganic salts present in natural surface water. Studies have shown that CO_3^- and HCO_3^- do not absorb solar UV radiation, but act as $OH^\bullet$ scavengers [31]. Since inorganic carbon exists mainly in the form of HCO_3^- at natural pH, experiments were carried out for several HCO_3^- concentrations (using $NaHCO_3$ stock solution) in the range of 50–200 mg/L as $CaCO_3$ in the presence of 40 mg/L NO_3^-, which produces $OH^\bullet$ when excited by ultraviolet light at wavelength 290–330 nm [27–32]. The experiments were conducted at an intensity of 1 SUN and E2 initial concentration of 5 μg/L. The results shown in Table 4 indicate that the degradation rate decreased markedly with increasing HCO_3^- concentration. This is due to the fact that HCO_3^- acts as a $OH^\bullet$ scavenger according to reaction (15), with a second order rate constant 8.5×10^6 M^{-1} S^{-1}; the reaction produces $CO_3^\bullet$, which is a weak oxidizing agent that hardly reacts with E2 [31,33].

$$HCO_3^- + OH\bullet \rightarrow CO_3\bullet + H_2O \tag{15}$$

Although the solution pH increased from 6.5 to 8.8 due to the increase in alkalinity, the effect of increasing pH on degradation rate is minimal in this pH range as can be seen in Fig. 6.

3.5.5. Influence of humic acid

Humic substances (HS), the largest fraction of dissolved organic matter (DOM) are ubiquitous in the aquatic environment. They are formed during the abiotic and microbiological transformations of plant and animal materials, and can be categorized as humic and fulvic acids, and humin depending on their solubility [11,34]. Humic acid is the predominant constituent in HS with an average molecular weight of 2000–5000 g/mol containing a high portion of oxygen-containing functional groups (e.g., phenolic hydroxyl, carboxyl groups, and carbonyl-type chromophores). The chromophoric HS absorbs solar radiation mostly between 300 and 500 nm to reach an excited state, hence generating free radicals (e.g., hydroxyl radicals ($OH^\bullet$), peroxyl radicals ($ROO^\bullet$), and singlet oxygen ($^1O_2$)) that cause photooxidation of organic contaminants [34,35]. Since the presence of humic acid has a significant effect in natural aquatic environments, it is very important to study the influences of humic acid on the photodegradation of E2 to predict the transport and fate of organic contaminants in natural water.

Prior to photodegradation studies, the dark adsorption of E2 by humic acid was conducted in batch mode. In these experiments, 10–400 μg/L of E2 was put in 0.1 mg of humic acid in 100 mL solutions in 150 mL bottles. The temperature of all solutions was controlled at 24 °C with the tests conducted in an orbital-shaker at 100 rpm. The samples were then removed at various times for analysis by HPLC. The sorption equilibrium data of E2 on humic acid

Table 3
Influence of Fe^{3+} on solar photodegradation of E2 (intensity 1 SUN).

pH	k (h^{-1}) without Fe^{3+}	k (h^{-1}) at Fe^{3+} = 30 μM	k (h^{-1}) at Fe^{3+} = 50 μM	k (h^{-1}) at Fe^{3+} = 70 μM
3	0.0472 ± 0.0023	0.0564 ± 0.0027	0.0616 ± 0.0027	0.0651 ± 0.0039
4	0.0571 ± 0.0025	0.0629 ± 0.0033	0.0678 ± 0.0035	0.0714 ± 0.0057
5	0.0616 ± 0.0023	0.0660 ± 0.0031	0.0731 ± 0.0032	0.0782 ± 0.0054

Table 4
Influence of HCO_3^- on solar photodegradation of E2 in the presence of 40 mg/L NO_3^- (intensity 1 SUN).

	HCO_3^- (mg/L as $CaCO_3$)			
	0	50	100	200
pH	6.47	7.96	8.40	8.76
k (h^{-1})	0.1210 ± 0.0054	0.1167 ± 0.0057	0.1021 ± 0.0042	0.0834 ± 0.0043
% reduction	–	3.55	12.51	18.32

were plotted in Fig. 8 and modeled using the Freundlich Eqs. (16) and (17) as follows:

$$q_e = K_F C_e^n \tag{16}$$

$$\ln q_e = \ln K_F + n \ln C_e \tag{17}$$

where q_e is the equilibrium solid-phase solute concentration (μg/mg), C_e is the aqueous-phase solute concentration (μg/L), K_F is the Freundlich capacity parameter, and n is the isotherm nonlinearity index. The parameter K_F has units of $(\mu g/mg)/(\mu g/L)^n$ and n is unitless. Fig. 8 shows the adsorption isotherms of E2 on humic acid modeled by the Freundlich equation with K_F is 1.02 $(\mu g/mg)/(\mu g/L)^n$ and $n = 0.04$. Dark adsorption studies show that the maximum 10% E2 is adsorbed onto the humic acid (Fig. S3 in Supporting information).

Photodegradation experiments were also carried out at several humic acid concentrations in the range of 0–10 mg/L at 2 h solar irradiation and an intensity of 1 SUN, while the E2 initial concentration was maintained at 5 μg/L. The degradation rate of E2 with humic acid concentration is shown in Fig. 9. The photodegradation rate increased considerably (≈22%) by the addition of 2 mg/L humic acid compared to pure E2 solution due to photooxidation resulting from $OH^\bullet$ as per reactions (18)–(22). Further degradation was also observed with increasing humic acid concentration up to 8 mg/L, but the rate of increase was much lower at higher concentrations.

$$HS \xrightarrow{h\upsilon} HS^{\bullet -} \tag{18}$$

$$HS^{\bullet -} + O_2 \rightarrow \text{Oxidized-HS} + O_2^{\bullet -} \tag{19}$$

$$2O_2^{\bullet -} + 2H^+ \rightarrow H_2O_2 + O_2 \tag{20}$$

$$H_2O_2 \xrightarrow{h\upsilon} 2OH^\bullet \tag{21}$$

$$E2 + OH^\bullet \rightarrow \text{Photoproducts} \tag{22}$$

Beyond 8 mg/L humic acid concentration, the degradation rate reached a plateau due to the scavenging of reactive oxygen species as well as increased light attenuation with increasing humic acid concentration [36]. The transmittance of humic acid solution was decreased from 89% to 71% at 290 nm for 2 mg/L to 10 mg/L humic acid concentration, respectively, indicating absorption of light by humic acid. Although indirect photolysis probably increases with humic acid concentration, the direct photolysis rate is decreased due to the absorption of photons by humic acid. As humic acid is a very week acid, solution pH does not change significantly due to its addition; it varied from 6.5 for 2 mg/L to 6.2 for 10 mg/L of humic acid in water, whereas the natural pH of E2 in Milli-Q water is around 6.5. Hence, the effect of pH change due to different humic acid concentrations is minimal. The effect of humic acid concentration on the degradation rate was higher for E1 than

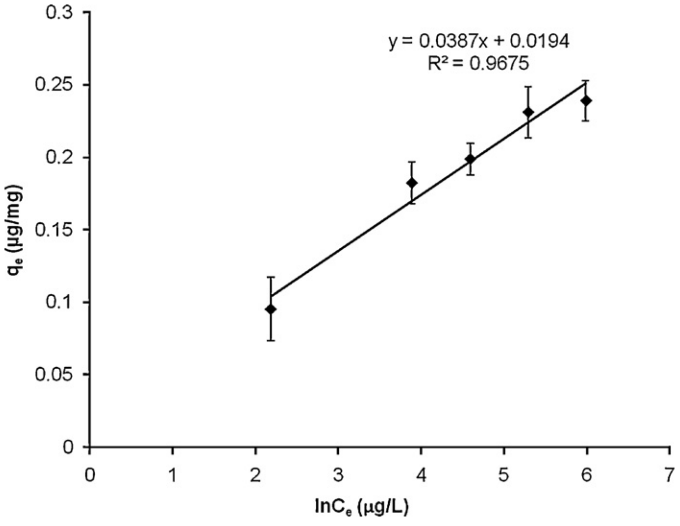


Fig. 8. Freundlich adsorption isotherm of E2 on humic acid. $C_{0_{E2}}$ = 10, 50, 100, 200 and 400 μg/L, time = 30 min. and temperature = 24 °C.

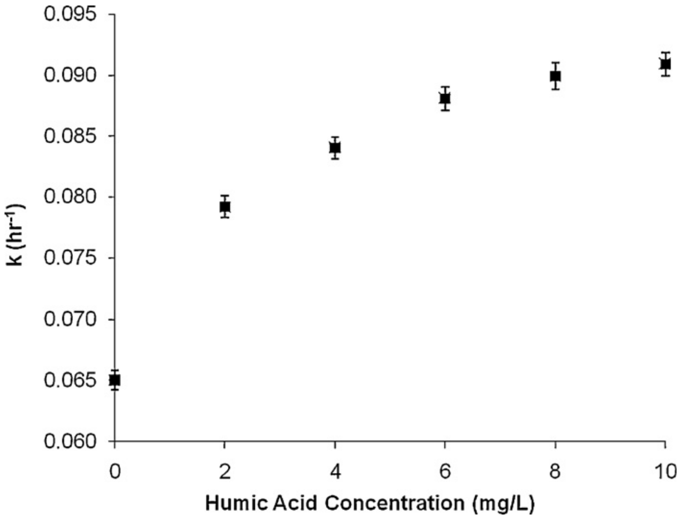


Fig. 9. Influence of humic acid concentration on solar photodegradation of E2. $C_{0_{E2}}$ = 5 μg/L, solar intensity = 1 SUN and irradiation time = 2 h.

Table 5
Influence of turbidity on solar photodegradation of E2 (intensity 1 SUN).

	Turbidity (NTU)					
	0.1	5	10	20	40	60
k (h^{-1})	0.0652 ± 0.0033	0.0616 ± 0.0027	0.0594 ± 0.0029	0.0549 ± 0.0026	0.0494 ± 0.0023	0.0472 ± 0.0024
Transmittance at 290 nm (%)	99.1	95.4	91.4	83.5	67.6	51.7

E2 (a maximum difference of 56% was observed for similar condition) [11], indicating that the sensitized photooxidation rate of E1 is also higher than E2, and the primary photochemical process of proton absorption by the parent compound enhances the overall degradation.

3.5.6. *Influence of turbidity*

Turbidity measured in Nephelometric Turbidity Units (NTU) is an optical property of a liquid that causes light to be scattered and absorbed rather than transmitted and is the ultimate measure of water clarity and cloudiness. In natural aquatic systems, sunlight penetration depends on the reflection from the water surface and attenuation in water by absorption and scattering. The movement of the water body and angle of incidence for sunlight are responsible for reflection, while attenuation is greatly influenced by the water depth and turbidity, which is caused by organic matter (OM), phytoplankton, color, mineral content and suspended sediment [37]. Here, experiments were carried out for several solution turbidity values in the range of 0–60 NTU (desired experimental turbidity was produced by adding clear turbidity standard, 1000 NTU to E2 solution) at an intensity of 1 SUN with E2 initial concentration of 5 μg/L and the results are shown in Table 5. The degradation of E2 in different turbid solutions decreased with increasing turbidity attributed to the reduction in light penetration. The transmittance of E2 solution was measured at 290 nm and it varied from 99.1% for 0.1 NTU ($k = 0.0652 \pm 0.0033\,\mathrm{h}^{-1}$) to 51.7% for 60 NTU ($k = 0.0472 \pm 0.0019\,\mathrm{h}^{-1}$); a drop of 47.8% in transmittance corresponds well with the 38% drop in reduction in the rate constant of E2, which is consistent with the intensity of 1/2 SUN ($k = 0.0433 \pm 0.0022$). Therefore the effect of turbidity is directly related to photon attenuation and subsequent decrease in photolysis. Since these experiments were not conducted in the presence of a photosensitizer, the effect of turbidity on photooxidation due to reactive radicals cannot be characterized.

4. Conclusions

Photodegradation of E2 in aqueous solution occurs under simulated solar irradiation as per pseudo-first-order reaction kinetics. The quantum yield was evaluated to be 0.0033 mol Einstein^{-1} in Milli-Q water in direct photolysis. About 48% of E2 degraded due to direct photolysis, while the rest of the degradation is due to subsequent photo-oxidation in the presence of molecular oxygen. The half-life of E2 varied from 10 to 21 h depending on the solar intensity and concentration. The effects of several water constituents such as pH, NO_3^-, Fe^{3+}, HCO_3^-, humic acid and turbidity on photodegradation of E2 were evaluated. The degradation rate increased in the presence of NO_3^-, Fe^{3+}, and humic acid due to photosensitization, whereas HCO_3^- slowed down the degradation rate because of the $OH^\bullet$ scavenging effect with the maximum degradation occurring at neutral pH. Turbidity also reduced the photodegradation of E2 due to a reduction in light penetration. Although the TOC analysis showed a steady degradation of TOC indicating a gradual mineralization of E2, TOC removal is always significantly lower than the degradation of E2, indicating stability of the photoproducts of E2. As all natural estrogens have very similar structures and properties of E2, the other steroid hormones also are expected to be removed from the natural aquatic system by direct and indirect photoreactions, and the half-life may be rather short in full sun and in clear water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.01.019.

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