Contents lists available at ScienceDirect

Science of the Total Environment

Photodegradation of free estrogens driven by UV light: Effects of operation mode and water matrix

Fan Huang, Fan Gao, Chaoran Li, Luiza C. Campos *

Department of Civil, Environmental and Geomatic Engineering, University College London, London WC1E 6BT, United Kingdom

HIGHLIGHTS

- Photolytic behaviour of estrogens under the radiation of 253.7 nm was investigated.
- Estrone (E1) was the most sensitive to the UVC radiance among the studied estrogens.
- The continuous flow mode favoured photolysis of estrogens compared to stationary mode.
- The surface water matrix taken from a local lake promoted photolysis of estrogens.

GRAPHICAL ABSTRACT
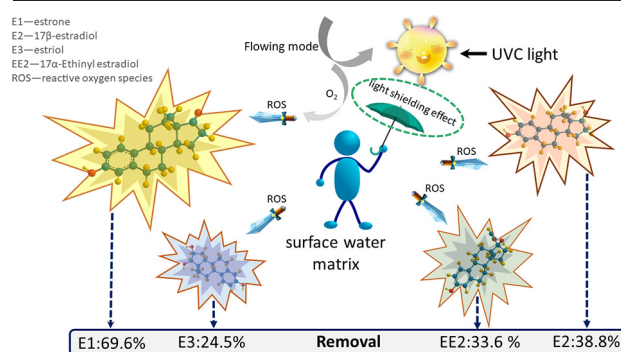
ARTICLE INFO

ABSTRACT

Estrogens are endocrine disrupting chemicals that have been frequently detected in diverse water matrices (e.g. surface water, wastewater and drinking water) and caused a series of health risks. This study was aimed at investigating the photochemical degradation of free estrogens estrone (E1), 17β-estradiol (E2), estriol (E3), and 17α-ethyl estradiol (EE2) upon the monochromatic irradiation (253.7 nm). Concerning the practical installation of photolysis treatment, exposing the impacts of photoreactor operation mode (stationary or up-flow) and the water matrix (ultrapure water or natural surface water) on the photolytic behaviour of estrogens was of high importance. The pseudo-first-order rate constants showed that E1 was the most susceptible to UV radiation among chosen estrogens due to its high molar absorption coefficient of $402.4 \, M^{-1} \, cm^{-1}$ and quantum yield of $0.065 \, mol \, E^{-1}$ at $\lambda = 253.7$ nm. Moreover, the up-flow mode and the surface water matrix collected from a lake in Regent's Park (London) were found to favour the photodegradation of estrogens due to the introduction of more dissolved oxygens and promotion of reactive oxygen species (ROS) formation. These findings may shed light on the photochemical behaviour of estrogens in some specific scenarios.

1. Introduction

Over the past decades, steroid estrogens have aroused considerable attention due to their detrimental impacts on the natural or human-based ecosystem at trace concentrations of ng L^{-1} (Dong et al., 2018; Mao et al., 2010). According to published studies, estrogens potentially induce disorders of the developmental or reproductive system in wild species and carcinogenicity in human beings (Capriotti et al., 2015; Gadd et al., 2010; Xu et al., 2007). Compared to other endocrine-disrupting chemicals (EDCs) such as nonylphenol and bisphenol A, natural estrogens estrone (E1), 17β-estradiol (E2), and estriol (E3) exhibited 1000–10,000 times greater biological efficacy (Tanaka et al., 2001). Additionally, it was also documented that synthetic estrogen 17α-Ethyl estradiol (EE2), the primary component for birth-control application, showed higher estrogenic potency than the mentioned natural estrogens due to its stronger binding affinity to the estrogen receptors (ERs) of animals and human beings (Shyu et al., 2011). Except for the health hazard presented by E1, E2, E3,

* Corresponding author.
  E-mail address: l.campos@ucl.ac.uk (L.C. Campos).

and EE2, their prevalent occurrence in multiple sources such as influents, effluents of domestic sewage treatment plants (STPs), sludge, rivers, aquatic sediments, and drinking water has been monitored all over the world (Baronti et al., 2000; Belfroid et al., 1999; Desbrow et al., 1998; Dudziak and Luks-Betlej, 2004; Fan et al., 2013; Kuch and Ballschmiter, 2001a; Kuch and Ballschmiter, 2001b; Kuster et al., 2004; Nie et al., 2009; Nieto et al., 2008; Ternes et al., 1999; Vega-Morales et al., 2011). As confirmed by previous studies, estrogens were found difficult to be eliminated through the treatment processes which were designed specifically for conventional contaminants (Fukuhara et al., 2006). For example, as one of the most common treatment techniques, the activated sludge method was widely used for the purification of wastewater. However, it was reported that estrogens were recalcitrant to the biological degradation in (Dytczak et al., 2008)'s study, especially for EE2, being removed only 5% in some cases. Removal of estrogens using membrane filtration (e.g. ultra-filtration and nanofiltration) was also investigated in a previous study (Yoon et al., 2007), and it was observed that the percentage retention varied with the characteristics of the targeted molecules and membranes, but generally limited removal (less than 60%) was observed for selected estrogens. Also, the removal of E3 was even negligible. However, the indispensable post-treatment of pollutant-concentrated sludge and the unavoidable occurrence of irreversible membrane fouling are also concerns for the practical utilization of membranes. This further indicates the requirement for a more effective and practically feasible method for alleviating the contamination of estrogens.

Therefore, advanced oxidation processes (AOPs) which include photolysis, photocatalysis, chlorination, ozonation, and Fenton reaction have been proposed for producing water with high quality (Silva et al., 2012). However, the advantages of these techniques are also accompanied by the potential formation of toxic byproducts. The concerns over chlorinated products of micropollutants transformed from their precursors were reported previously, not only due to their maintained estrogen active properties but also the far stronger binding affinity to estrogen receptors than what their parent compounds behaved (Hu et al., 2002; Xu et al., 2017). Similarly, the degradation products derived from the reaction between ozone and micropollutants (e.g. clofibric acid) were also reported to display toxicity to the *V. fischeri and D. magna* in published work (Rosal et al., 2009).

Except for acting as an experienced application for being against waterborne pathogens (S. J. Kim et al., 2016), the photolysis reaction under the ultraviolet (UV) region was previously studied for achieving the mineralisation of organic compounds (Chen et al., 2013; M. Li et al., 2017; Xu et al., 2017). Herein, the photodegradation of hormones has been also carried out in previous studies, and the destruction of surrogate estrogens was observed (Cedat et al., 2016; Frontistis et al., 2015; Li Puma et al., 2010; Bin Liu et al., 2003; Pereira et al., 2012). Additionally, in comparison with other advanced oxidation processes (e.g. UV based photocatalysis and Fenton reaction), the exemption of post-treatment such as the requirement to remove catalyst or iron slurry from treated water renders the photolysis process more suitable for practical application (Moon et al., 2011; Sanches et al., 2013).

Photolytic removal of organic compounds in an aqueous solution was mainly achieved via direct and indirect photolysis processes (Oliveira et al., 2016). For direct photolysis, the cleavage of chemical bonds occurred after the compound molecules absorbed the photon emitted by the light source (B. Liu and Liu, 2004). Specifically, the absorption of photons provides targeted molecules energy and induces the formation of excited states (e.g. singlet or triplet), then the precursor molecules undergo photochemical transformation to produce different intermediate products (Kalyanasundaram, 2012; Rosenfeldt and Linden, 2004). The occurrence of this process is mainly associated with the abilities of molecular moieties to absorb photons upon exposure to the given light source, and correspondingly these moieties are collectively termed chromophores. Therefore, functional groups such as alkenes, carbonyls, aromatic rings, heterocyclic rings, and nitro groups are particularly reactive sites for photochemical reactions (Zepp and Cline, 1977). Nevertheless, the indirect photolysis was initiated

via producing photo reactants in the presence of photosensitisers and light irradiation, and then the obtained reactive oxygen species (ROS) could further oxidize the examined pollutants (Chen et al., 2013).

The solution chemistry was one of the most important factors affecting the photodegradation performance. In order to scale up relevant techniques for practical use, the impacts of solution properties should be taken into account. Especially for the natural water matrix, the most common constituents such as natural organic matter (NOM), nitrate, and nitrite were considered the most important photosensitisers (Lin and Reinhard, 2005).

However, there have not been investigations carried out for studying the photolysis mechanisms of E1, E2, E3, and EE2 simultaneously. Furthermore, most of the current studies evaluated the photolysis behaviour of pollutants in stationary installation but did not consider the influence of flow-through conditions (Carlson et al., 2015; Frontistis et al., 2015; Rosenfeldt and Linden, 2004), while the latter was more prevalent in practical treatment facilities for the huge demand of treated water.

In this study, the photolysis of estrogens under irradiation of UV light was investigated. The photodegradation rate constants and related parameters such as molar absorption coefficients and corresponding quantum yields were examined for depicting the photochemical degradation in detail. As a novelty, the installed system in terms of the operation mode was evaluated in this study for the first time. Besides, the photolytic degradation of the chosen estrogens was also assessed in natural surface water to elucidate the relationship between water matrix and photolysis performance.

2. Methodology

2.1. Chemicals and installations

The studied estrogens (Fig. 1), i.e. estrone (E1), 17 β-estradiol (E2), estriol (E3), and 17α-ethyl estradiol (EE2), with purities greater than 98%, were purchased from Sigma-Aldrich (Dorset, UK). Their physicochemical properties are listed in Table S1 (Supplementary data). The stock solutions of estrogens were prepared by dissolving 1 mg of each of investigated estrogens in 10 mL methanol in a volumetric flask, getting stock solutions at concentrations of 100 mg L^{-1}. The stability of stock solutions was maintained for at least 3 months under −20 °C storage conditions. The working standard solution at a concentration of 1 mg L^{-1} was obtained through the dilution of stock solution with ultrapure water prior to the experiments.

The photoreactor employed for investigating the photolysis of estrogens under direct ultraviolet (UV) light was designed by J. K. Kim et al. (2013). The schematic diagram of the photolysis reactor is presented in Fig. 2. The main part of the photoreactor (diameter: 58 mm, height: 230 mm) was made of stainless steel. In the reaction chamber, a UVC lamp (11 W, 240 V) with dimensions (diameter: 19 mm, length: 251.8 mm) from Philips (Holland) was installed as the light source of irradiation. The UVC lamp emits monochromatic radiation at the wavelength of 253.7 nm according to the manufacturer.

The light intensity in the reactor was determined using a radiometer (Apogee MQ-100, USA), getting a mean photon flux value of 65.87 μmol m^{-2} s^{-1} (21.5 W m^{-2}) via averaging the photon flux measured at the surface of the quartz sleeve. The rubber stopper, which tightly matches the top opening of the reaction chamber, allows to hold the UV lamp vertically and seal the reaction chamber in the meantime. In addition, the UV lamp is wrapped by a quartz sleeve for protecting the lamp from contacting the solution directly. The reaction chamber is embedded in a cooling-water jacket, and the ongoing cooling water inside is aimed at preventing heat impact induced by the UV lamp and keeping solutions around ambient temperature during the photolysis reaction. For achieving equilibrium of light intensity, the UV lamp was pre-operated for at least 15 min before experiments (Kim et al., 2013).

In order to evaluate the impact of the flow mode of the fluid on the photolysis performance, the photoreactor was selectively connected or disconnected with the feeding tank coupled with a peristaltic pump (Watson Marlow 501 U), the valves on the inlet and outlet of the reaction chamber were correspondingly controlled and then made available to feed
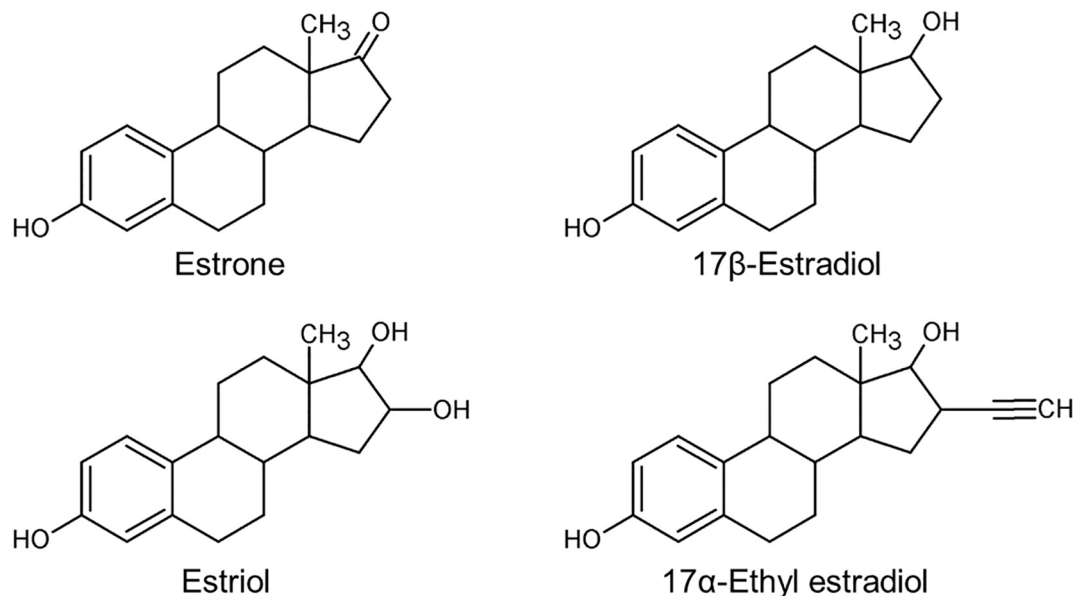
Fig. 1. The chemical structures of the target estrogens in this study.

contaminant-containing solutions with continuous up-flow mode (15, 30, 45, 60, and 75 mL min^{-1} were tested) from the inlet to the outlet of the chamber or to add the fixed amount of solution from the top opening of the reaction chamber directly for investigating the photolysis performance under stationary mode.

2.2. Irradiation experiments

The irradiation experiments were conducted at the Environmental Engineering Laboratory of the Civil, Environmental, and Geomatic Engineering Department (CEGE) at University College London.

Then aliquots (10 mL) of a mixed working standard solution of E1, E2, E3, and EE2 (1 mg L^{-1}) was added to an empty 1 L volumetric flask. To be free of solvent effect, the methanol was evaporated before adding ultrapure water (18 MΩ resistance) to the etched graduation marking. Then the free estrogen solution with a nominal concentration of 10 μg L^{-1} with a

dissolved organic carbon (DOC) concentration of 0.024 ± 0.033 mg L^{-1} was finally obtained. The spiked concentration of the targeted compounds was slightly higher than their naturally occurring level (ng L^{-1} ~ μg L^{-1}) (Souissi et al., 2012) due to the limitation of the analytical instrument. The pH of the mixed estrogen solution prepared using ultrapure water was determined as 6.58.

The stationary and continuous modes of the estrogen solution were applied for investigating the percentage removal of estrogens under the irradiation of a UVC lamp. For the stationary mode, prior to the experiment the inlet and outlet of the photolysis chamber were closed, and then 600 mL of prepared estrogen solution with a concentration of 10 μg L^{-1} was taken and transferred into the pre-cleaned photoreactor directly, setting the irradiation time as 15, 30, 40, 60, 120, 180 and 240 min; for the up-flow mode, the pre-calibrated peristaltic pump was employed to connect the feeding tank containing the prepared estrogen solution (10 μg L^{-1}) to the inlet of the photolysis chamber. Then the estrogen solution was treated
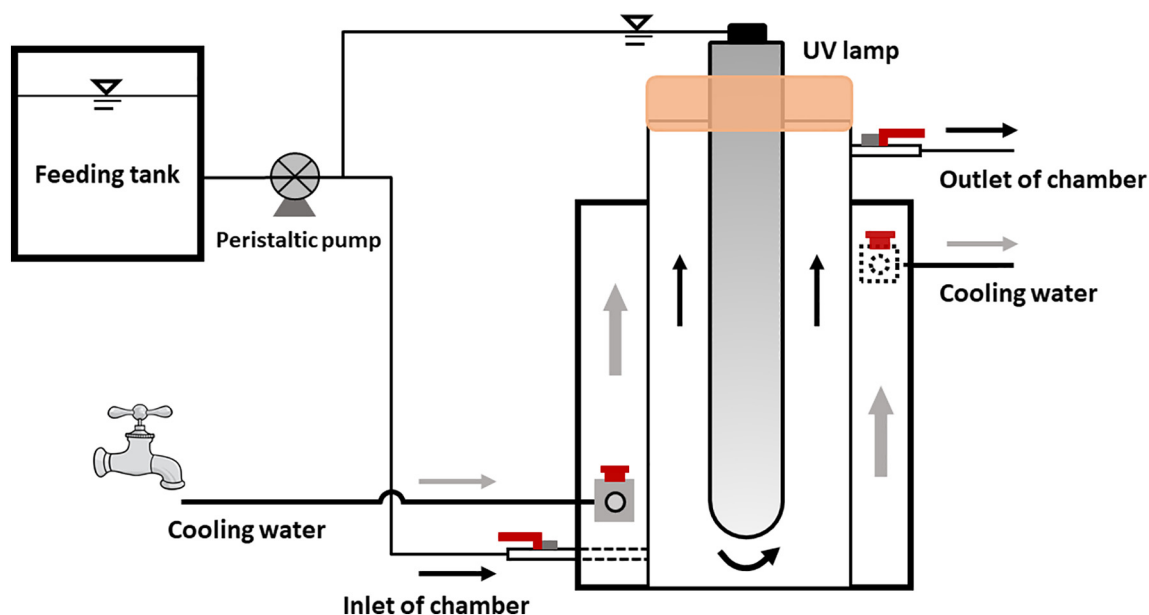

Fig. 2. Schematic diagram of the photoreactor.

using flow rates of 15, 30, 45, 60, and 75 mL min^{-1} for evaluating their effect on photodegradation of the targeted estrogens, and consequently, the theoretical hydraulic time of 40, 20, 13.3, 10, and 8 min in the photolysis chamber were also verified based on the corresponding flow rate and volume information of the chamber (600 mL), respectively.

The impacts of naturally occurring NOM on photochemical degradation of estrogens were studied using the same experimental design described above but with natural surface water collected from a lake of Regent's Park, London (51°31′27.9″N 0°09′13.7″W) with the same spiked concentration (10 μg L^{-1}). To avoid the impact of different pH values, the pH of spiked surface water was adjusted to 6.58 using NaOH and HCl. Additionally, based on the method developed by Shi et al. (2010), the surface water sample was sterilized by combining filtration through a 0.45 μm membrane filter and radiation under ultraviolet light for 30 min prior to the photolysis experiment for exempting overestimation of the removals due to the presence of the enzymatic and microbial activity.

The spiked ultrapure water and natural surface water with the same concentration of estrogens were put under dark conditions (via being wrapped with aluminum foil) as a control group for verifying if there was a loss of compounds due to the ambient background.

Cooling water (16.3 ± 0.7 °C) was introduced into the outer jacket for preventing thermolysis as a result of overheating over the irradiation time, thus keeping the temperature of the liquid in the reaction chamber ranging from 34.5 °C to 38.6 °C.

2.3. Analysis of the samples

A sample with 500 mL volume was collected after the photolysis experiment and then filtered through a 0.45 μm membrane filter using the vacuum filtration apparatus. The filtered sample was concentrated and analysed according to the SPE protocol, developed derivatization, and the LC-MS method described in our previous study (Huang et al., 2021).

In addition, the water samples used for investigating the matrix influences were characterised concerning water quality parameters (e.g. DOC, UV$_{254}$, and IC) following the method reported in the Supplementary data (Text S1). The transmittance of UV light (UVT) at 254 nm to the solution was calculated by (M. Zhang et al., 2021):

$$\%UVT = 10^{-A} \tag{1}$$

where A (cm^{-1}) is the UV$_{254}$ absorbance of solutions.

2.4. Rate constants, molar absorption coefficient, and quantum yields

Rate constants for the photolysis of estrogens under the irradiance at a wavelength of 254 nm were determined using the pseudo-first-order reaction kinetics which is commonly applied to describe the rate of photolytic removal of estrogen (Nasuhoglu et al., 2012; Whidbey et al., 2012).

The pseudo-first-order rate constants were calculated by the linear regression of natural logarithmic concentration of compounds against irradiation time as follows:

$$\ln \frac{C}{C_0} = -k_1 t \tag{2}$$

where C_0 (μg L^{-1}) and C (μg L^{-1}) are the concentration of estrogen at the beginning and concentration after exposure to irradiance for time t (min), respectively; k_1 is the pseudo-first-order rate constant (min^{-1}). The half-life ($t_{1/2}$) of the compound in the photolysis process could be obtained via the equation:

$$t_{1/2} = \frac{\ln 2}{k_1} \tag{3}$$

The absorption spectra of chosen estrogen were profiled over the range of 200–400 nm wavelength using the Agilent Cary 60 UV–Vis (Cheshire, UK) coupled with Cary WinUV software. The estrogen single solution

with a concentration of 100, 50, 10, 5, and 1 mg L^{-1} was obtained via diluting each of their stock solutions, and 5% methanol was contained in the final solutions. Each sample was loaded into a 1 cm path length quartz cuvette and its absorbance was measured against the corresponding background solvent which contained methanol at the same concentration for correcting their respective baselines. The equation for calculating the molar absorption coefficient ε(λ) (M^{-1} cm^{-1}) of individual estrogen was as follows (Bonneau et al., 1991):

$$a(\lambda) = \varepsilon(\lambda) \times M_{estrogen} \times l \tag{4}$$

where a(λ) (cm^{-1}) is the absorbance of solutions containing nominated molar concentrations (M$_{estrogen}$, mol L^{-1}) of individual estrogen with a cell path length (l), being 1 cm in this study.

Apart from the molar absorption coefficient, quantum yield, Φ (λ) (E mol^{-1}) was also determined to describe the mechanism of photodegradation using the equation proposed by (Schwarzenbach et al., 2016):

$$\Phi(\lambda) = \frac{k_1(\lambda)}{k_s(\lambda)} \tag{5}$$

$$k_s(\lambda) = \frac{E_p^0 \varepsilon_\lambda \left[1 - 10^{-a(\lambda)z}\right]}{a(\lambda)z} \tag{6}$$

where, k_1 (s^{-1}) is the pseudo-first-order rate coefficient obtained from the irradiance exposure at a wavelength of 254 nm; k_s value with a unit (E mol^{-1} s^{-1}) refers to the specific photon absorption rate of the studied compounds under the radiation region of λ. In Eq. (6), E_p^0 (λ) in a unit of mE cm^{-2} s^{-1} is the photon fluence rate determined on the surface of the solution; z is the path length (cm) solution penetrated by the irradiance, according to the aforementioned dimension information of photolysis reactor and diameter of the lamp, it was assumed that the emission from the UVC lamp was perpendicular to the surface of the solution in the photolysis chamber without deviation (Carlson et al., 2015). As presented in Fig. 3, in the cylindrical chamber, the optical path length of the solution traveled by the light ray was z, which was also confirmed via the top and side views of the system, being verified as 1.95 cm in this study.

2.5. Statistical analysis

All experiments in this study were conducted in triplicate for checking the repeatability. The statistical analysis was carried out using OriginPro 2019 software. The availability of pseudo-first-order kinetic in each irradiation experiment was evaluated via the linear fit option of the analysis method. The statistically significant differences in the operation mode (stationary and continuous mode) and water matrix (ultrapure water and surface water) accounting for the photolysis performance of examined estrogens were estimated using the one-way ANOVA method ($p = 0.05$).

3. Results and discussion

3.1. Photolysis of estrogens in ultrapure water

For dark controls of both stationary and continuous operation mode for up to 4 h, no significant loss of estrogens was illustrated via the minor difference (−2.90% to 1.45%) between the concentrations before and after reaction under the dark condition, which specifically indicated that the participation of hydrolytic and thermolytic destruction, biodegradation, and adhesion of estrogen to the inner wall of the photolysis chamber could be ignored.

The photolytic removal of E1, E2, E3, and EE2 in ultrapure water matrix by the irradiance of UVC lamp was indicated via the pseudo-first-order kinetics derived via plotting ln(C/C$_0$) against irradiation time (Fig. 4), the corresponding rate constants (k$_1$), photodegradation half-life (t$_{1/2}$) and correlation coefficients (R^2) are reported in Table 1. The significant linear
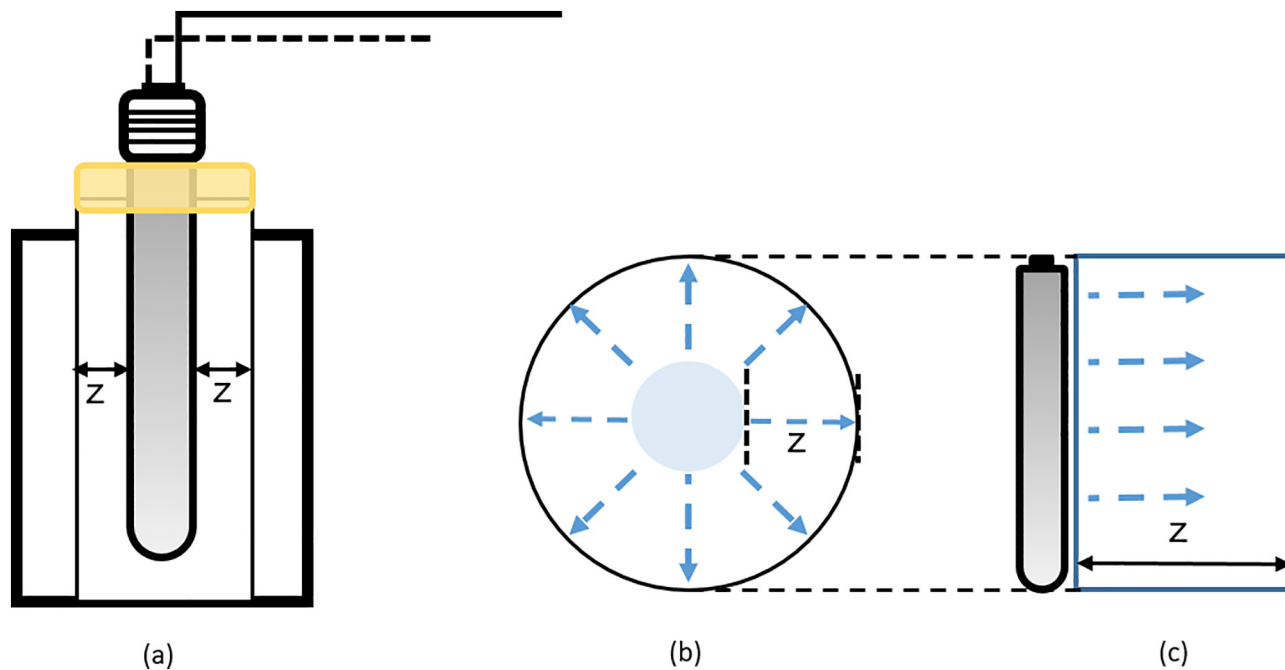
Fig. 3. The simplified schematic for calculating z - the length of path solution penetrated by the irradiance. (a) the simplified structure of the photolysis chamber; (b) top view of the photolysis chamber; (c) side view of the photolysis chamber.

correlation coefficients (R^2: 0.980–0.994, $p < 0.05$) demonstrated that the obtained data fit well with the pseudo-first-order kinetics.

For the photolysis of four representative estrogens, their removal performances were found to follow the order E1 > E2 > EE2 > E3 in terms of the steepness of linear models, which were further evidenced by their pseudo-first-order rate constant and degradation half-life. E1 was degraded under irradiation at λ = 254 nm with a rate constant of 0.0177 min^{-1} for stationary mode, which corresponded to the degradation half-life of 39.8 min. In contrast to E1, E3 was found to be far more resistant to direct photolysis with the rate constant of 0.0023 min^{-1} under the identical exposure condition and approximately 7.6 times longer photodegradation half-life than that of E1. The acquired degradation rate constants of E2 and EE2 were similar and slightly higher than E3.

It was confirmed from previous studies that the photolytic removal of compounds was mainly associated with their decadic molar absorption coefficients and quantum yields at a given range of λ (Pereira et al., 2012).

Therefore, these two parameters were investigated for explaining the differences in the photochemical destruction of selected estrogens in our study.

The spectra of studied estrogens within a range of 200–400 nm wavelength were detected, then the obtained molar absorption coefficient data implied the capacity of surrogate compounds to absorb the photon delivered by the light from the installed UVC lamp and played an important role in the photolysis reaction (Yuan et al., 2009). According to published work, the photon absorbed by targeted molecules could be capable of driving their photochemical reaction (Wells, 1972). As indicated in Fig. 5, the absorbance of radiation for estrogen molecules was more abundant in the UVC range (100–290 nm) than in regions UVA (320–400 nm) and UVB (290–320 nm) (Dale Wilson et al., 2012; Lindblad et al., 2020). Moreover, the negligible absorption probability in the visible light region was also noticed. Therefore, the irradiation used for investigating the photolysis of estrogens was selected as UVC. As the most common commercially accessible UVC lamp emitting UV light with specific wavelengths of 253.7 nm was
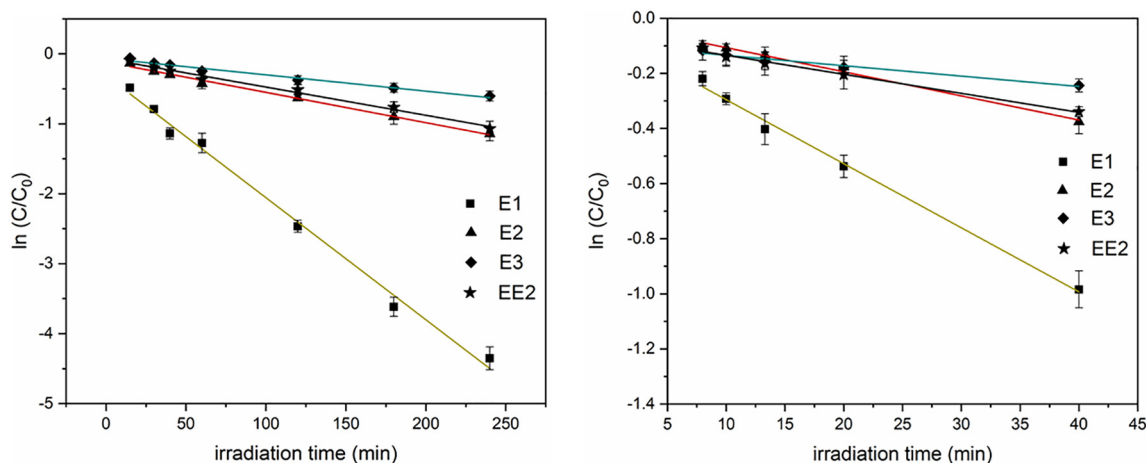

Fig. 4. The photolytic removal of chosen estrogens in ultrapure water matrix under different operational modes of the photolysis reactor. A) running in stationary mode; B) running in up-flow mode.

Table 1
Time-based pseudo-first-order rate constant (k₁), correlation factor (R²), photodegradation half-life (t₁/₂), quantum yields (Φ) for the photolysis experiment of estrogens in ultrapure water with stationary and continuous mode under the irradiation of UVC lamp.

Compounds	Stationary mode				Continuous mode			
	k_1 (min⁻¹) (R²)	$t_{1/2}$ (min)	k_s (λ = 254 nm) (E mol⁻¹ s⁻¹)	Φ (mol E⁻¹)	k_1(min⁻¹) (R²)	$t_{1/2}$ (min)	k_s (λ = 254 nm) (E mol⁻¹ s⁻¹)	Φ (mol E⁻¹)
E1	0.0177 (0.994)	39.8	0.00473	0.065	0.0233 (0.995)	29.7	0.00522	0.107
E2	0.0043 (0.993)	161.2	0.00445	0.016	0.0088 (0.991)	78.8	0.00490	0.035
E3	0.0023 (0.980)	301.4	0.00250	0.015	0.0039 (0.981)	177.7	0.00276	0.029
EE2	0.004 (0.988)	173.3	0.00371	0.018	0.0069 (0.993)	100.5	0.00409	0.034

applied correspondingly. Similarly, the photolysis of estrogens under the irradiation of UVC light at 253.7 nm was also conducted in previous studies (Li Puma et al., 2010; B. Liu and Liu, 2004; Nasuhoglu et al., 2012; Trudeau et al., 2011; Z. Zhang et al., 2010), and some of the results indicated the better photolysis performance achieved by UVC compared to UVB or UVA irradiation.

The molar absorption coefficients of the target estrogens at a given wavelength (λ) of 253.7 nm are presented in Table 2. The values of 402.4 M cm⁻¹ for E1, 378.0 M⁻¹ cm⁻¹ for E2, 212.7 M⁻¹ cm⁻¹ for E3 and 315.6 M⁻¹ cm⁻¹ for EE2 were found, collectively being within the similar range (less than 400 M⁻¹ cm⁻¹) determined for E1, E2, and EE2 in published work (Carlson et al., 2015; Rosenfeldt and Linden, 2004).

As another important parameter governing photolytic degradation rate, the quantum yield of chosen estrogens under UVC lamp with λ = 253.7 nm ranged from 0.013 to 0.056 mol E⁻¹ under the stationary mode, where E1 exhibited the highest quantum yield while the values of the remaining three compounds were nearly the same, ranging from 0.013 to 0.016 mol E⁻¹. Overall, the quantum yield values determined in this study are within the range obtained in other studies. For example, as reported by Lin and Reinhard (2005), the quantum yields of E1, E2, E3, and EE2 under irradiation by the monochromatic light source with a wavelength of 254 nm were 0.0296, 0.0048, 0.0048, and 0.0048, respectively. Rosenfeldt and Linden (2004) and Mazellier et al. (2008) found 0.043–0.067 mol E⁻¹ for E2 and 0.026–0.062 mol E⁻¹ for EE2 under exposure to the same wavelength. Although similar values were expected for the four chosen estrogens owing to their similar chemical structures, the differences observed in previous work and this study was surprising. The structures of E1, E2, E3, and EE2 (Fig. 1), all have a typical steroid structure with a phenolic A ring, and the apparent discrepancies between them are different functional groups on the D ring.

According to a previous study carried out by Chan et al. (2013), it was emphasized that the phenolic A ring was the most sensitive chromophore and responsible for the lowest energy $\pi \rightarrow \pi^*$ absorption band in the estrogen molecules, in another word, phenolic A ring was the primary contributor upon the excitation state under the UV region irradiation. Thus, the different photodegradation tendencies among the assayed estrogens in this study were decided by the functional group constitutions on D ring. Differing from E2, E3, and EE2, aside from the phenolic ring, the carbonyl group on the C17 position of E1 also contributes to the excitation dynamics due to the existence of a weak $^1n\pi^*$ absorption band (Chan et al., 2012). Similarly, Ahmad et al. (2016) and Lin and Reinhard (2005) also reported that the carbonyl group, which is linked to the C-17 position of E1, was considered as one of the most important chemical groups for initiating the photochemical reactions.

In summary, the relatively greater molar absorption coefficient and quantum yield achieved for E1 may explain its higher photodegradation than E2, E3, and EE2 which have different molecular structures.

3.2. Influence of operation mode

The variation of the tracer concentration at the outlet of the photoreactor at flow rates of 15, 30, 45, 60, and 75 mL min⁻¹ is shown in Fig. S1 (Supplementary data). According to the Eq. ES.1 (Supplementary data), the mean hydraulic time of 40, 20, 13.3, 10, and 8 min respectively corresponding to flow rates of 15, 30, 45, 60, and 75 mL min⁻¹ matched with the experimental residence time (Table S2) (e.g. 41.41 min for 15 mL min⁻¹, 21.39 min for 30 mL min⁻¹, 13.88 min for 45 mL min⁻¹, 10.72 min for 60 mL min⁻¹ and 8.49 for 75 mL min⁻¹) calculated based on the data derived from the residence time distribution curve. This
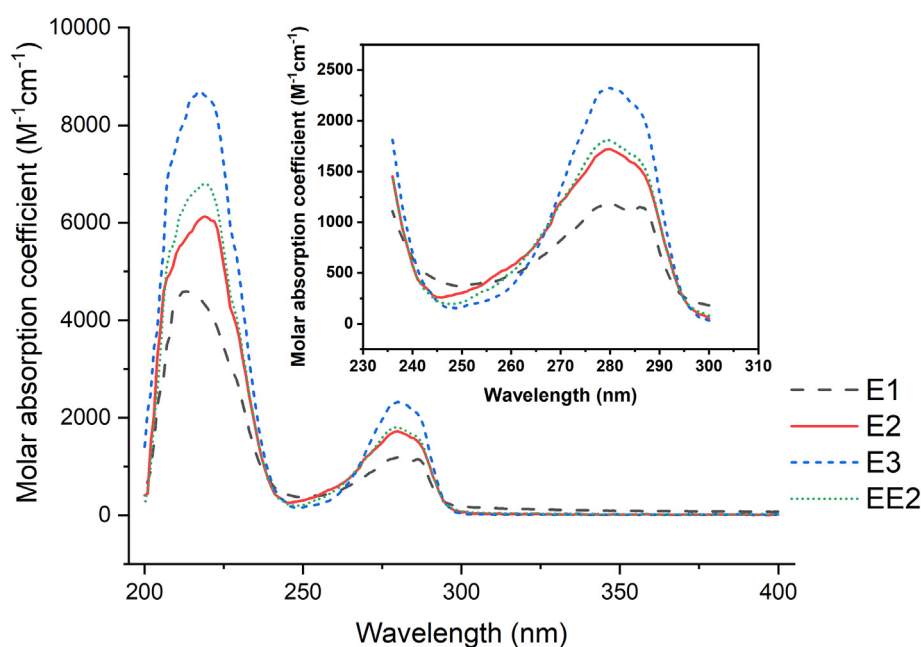

Fig. 5. Molar absorption coefficients of estrogens over a wavelength range of 200–400 nm.

Table 2
Molar absorption coefficients of the targeted estrogens at λ = 253.7 nm.

Compound	$\varepsilon_{253.7\ nm}$ ($M^{-1}\ cm^{-1}$)
E1	402.4
E2	378.0
E3	212.7
EE2	315.6

phenomenon indicated that the dead flow and sorption to the apparatus of the photoreactor did not occur (Levenspiel, 1998).

The dispersion values D estimated based on the data in obtained residence time distribution and Eq. E. S3 for the tested flow rates are presented in Table S2, ranging from 0.021 to 0.037. It has been reported previously that the assayed reactor with a D value less than 0.05 could be regarded as plug flow status. Therefore, the mean hydraulic time of 40, 20, 13.3, 10, and 8 min are valid for the calculation of pseudo-first-order kinetics of estrogen photolysis in the continuous flowing mode.

The influence of the photolysis reactor operation mode on the degradation of estrogens was estimated by irradiating the same spiked ultrapure water solution under the same condition besides changing a stationary mode to a continuous flow mode. The degradation of the chosen estrogen in the continuous mode was closely analogous to that observed in the stationary mode, following the same order E1 > E2 > EE2 > E3. Regarding the residence time as the time-span of irradiation, the photolysis rate constants obtained from the pseudo-first-order kinetics with significant correlation coefficients (R^2:0.981–0.995, $p < 0.05$) for E1, E2, E3, and EE2 were 0.0233, 0.0088, 0.0039 and 0.0069 min^{-1}, respectively. Accordingly, their $t_{1/2}$ values were in the range of 29.7–177.7 min. In addition, the quantum yields increased to 0.107 mol E^{-1} for E1, 0.035 mol E^{-1} for E2, 0.029 mol E^{-1} for E3, and 0.034 mol E^{-1} for EE2.

It was noteworthy that both larger photolysis rate constant and higher quantum yields for all four estrogens were determined in the continuous flow mode in comparison with that derived from the stationary mode, according to the data presented in Table 1. Therefore, this indicated that a shorter irradiation time was required for reaching the same photochemical removal of targeted compounds in continuous flow mode. Particularly, after the analysis using the one-way ANOVA method, the difference of k_1 between the stationary and continuous mode for each estrogen was significant ($p < 0.05$).

Concerning the impact of stationary and continuous flow modes, there has not been a relevant discussion reported before. During the operation of the stationary mode, all outlets and the top opening of the photoreactor were closed via turning off the valves and covered with a tightly fitted rubber stopper, respectively. In contrast, the valves of outlets remained open for delivering the solution from the feeding tank to the reactor outlet when the photolysis process ran in the continuous mode. Therefore, the continuous operation mode was assumed to increase the dissolved oxygen concentration of the solution in the photolysis reactor compared with the stationary mode. Subsequently, the presence of oxygen probably promoted the oxidation of organic compounds with UV exposure.

This assumption was also mentioned by Pailthorpe et al. (1973). Since in the presence of dissolved oxygen, hydroxyl radicals ·OH could be produced by water molecules upon absorption of photons emitted by the UV lamp (A. Zhang and Li, 2014). The detailed reaction occurred as follows:

$$H_2O + h\nu \rightarrow e_{aqu}^- + H\cdot + \cdot OH + H^+ \qquad (7)$$

The oxidation potential of 2.80 V owned by ·OH was capable of increasing the decomposition percentage of estrogens via oxidation reaction via ·OH (Buxton et al., 1988). A similar acceleration of photolytic removal was also observed in studies of mineralising diafenthiuron, CGA-140408, CGA-177960, naproxen under aerated conditions (Keum et al., 2002; Marotta et al., 2013). Additionally, the photolytic removal of organic compounds (e.g. 4-chlorophenol, EE2, and aniline) was also found to be

elevated in the presence of dissolved oxygen (Du et al., 2011; Ren et al., 2019; Zhao et al., 2013).

3.3. The impact of the solution matrix

To understand the impacts of the solution matrix on the photolytic decomposition of estrogens, the irradiation experiment with continuous flow mode was conducted using the surface water spiked with the same 10 µg L^{-1} of mixed estrogens. Based on the characterisation of the water samples (Table 3) in terms of the DOC, UV$_{254}$, SUV$_{254,}$ and IC, the results indicated that the spiked natural water matrix had a DOC content of 3.75 ± 0.25 mg L^{-1}, UV$_{254}$ of 0.067 ± 0.002 cm^{-1} and SUVA$_{254}$ of 1.79 ± 0.14 L mg^{-1} m^{-1}. The higher absorbance illustrated that the greater content of chromophore was contained in the natural surface water, which further indicated that the natural surface water was more sensitive to photons at λ = 253.7 nm (Silva et al., 2016a; Silva et al., 2016b). From another perspective, the higher absorbance was likely indicative of the existence of the inner filter effect of the surface water matrix (Oliveira et al., 2016). Additionally, the relatively rich ion composition in the surface water matrix was also profiled. SUVA$_{254}$ was employed here to indicate the concentration of organic compounds, the value obtained via dividing UV$_{254}$ absorbance by the DOC concentration could illustrate the dissolved aromatic carbon content in water samples (Weishaar et al., 2003). The higher SUVA$_{254}$ values refer to the greater molecular complexity such as higher aromaticity, on the other hand, they also demonstrated decreased biodegradability (Hozalski et al., 1995).

Fig. 6 described the time-based pseudo-first-order rate constants of the four surrogate estrogens in ultrapure water and natural surface water matrix when the flow rate was fixed as 15 mL min^{-1}. Contrary to the decline of photolysis removal for methyl triclosan presented by W. Liu et al. (2018), as a result of the drastically decreased transmittance of UV light (namely light-shielding effects) with the presence of NOM, the higher content of DOC and dissolved solids in natural water matrix did not impede the decomposition of estrogens in this study, instead, a higher removal rate for all chosen estrogens was noticed. However, there were no statistically significant differences between ultrapure water and surface water for E2 and E3 ($p > 0.05$), while a significant enhancement was found for E1 ($p < 0.05$) only at a 95% confidence interval. The degradation rate constants, correlation coefficients, and $t_{1/2}$ were calculated using pseudo-first-order kinetics (Table 4). The contribution of the solution matrix to the acceleration of photodegradation rate could be calculated in accordance with:

$$Contribution\ of\ solution\ matrix\ (\%) = \frac{(k_{1,matrix} - k_{1,ultrapurewater})}{k_{1,matrix}} \times 100 \qquad (8)$$

Compared to the photolytic degradation in ultrapure water, the degradation rate constants for E1, E2, E3, and EE2 were 0.03, 0.0098, 0.0055, and 0.0085 min^{-1}, respectively. As a result, their $t_{1/2}$ values were accordingly shortened to 23.1, 70.3, 126.8, and 81.2 min, respectively. The shortened time of the photolysis process was attributed to the replacement of the water matrix, and its contribution to the change of rate constants for targeted estrogens ranged from 12.8% to 40.8%. Similarly, the enhancement of photodegradation for E1, E2, and E3 in the presence of humic acids or fulvic acids, which are the most common constituents of NOM in water, has also been reported by Y. Zhang et al. (2007), Chen et al.

Table 3
The water quality parameters of spiked surface water in terms of DOC, UV$_{254}$, and representative ions are characterised by IC with the standard deviation (SD).

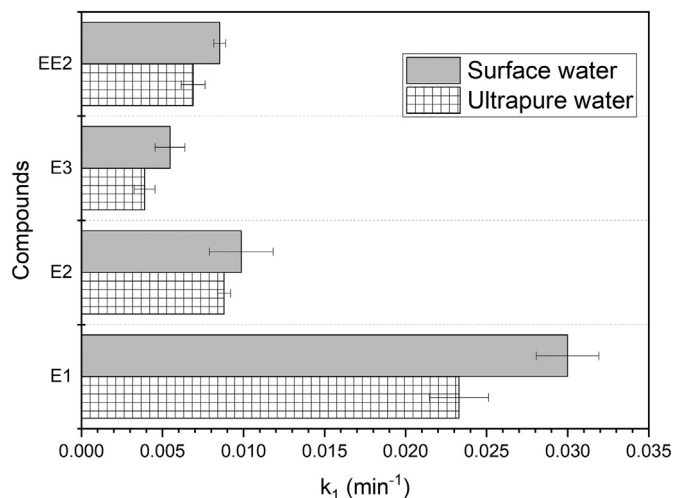| Water quality parameters	Spiked surface water sample
DOC (mg L^{-1})	3.75 ± 0.23
UV$_{254}$ (cm^{-1})	0.0671 ± 0.002
SUVA$_{254}$ (L mg^{-1} m^{-1})	1.79 ± 0.14
Nitrite, NO_2^- (mg L^{-1})	N.A
Nitrate, NO_3^- (mg L^{-1})	6.63 ± 0.61
Chloride, Cl^- (mg L^{-1})	74.23 ± 5.68

Fig. 6. The time-based photolytic degradation rate constants of estrogens in ultrapure water and natural surface water.

(2013), Oliveira et al. (2016) and Caupos et al. (2011). Furthermore, the great increase in phototransformation of EE2 in natural water under UV light irradiation was also described by Canonica et al. (2008).

NOM in water samples has dual effects on the behaviour of photochemical destruction: 1) the inhibitory effect: NOM is well-known as an absorber of UV light so that the available light for phototransformation of estrogens was diminished due to the photon competition of NOM or scattering of radiation; 2) the promotion effect: the transformation of NOM took place once they absorbed light and the property of acting as a photosensitiser allowed the further occurrence of indirect photolysis (Atkinson et al., 2011; Canonica et al., 2008; Nasuhoglu et al., 2012).

In our study, even though the occurrence of light-screening was proven based on the UV_{254} value, the calculated UVT of 85.7% for spiked surface water and 94.5% for spiked ultrapure water showed that the loss of available light was not great because the difference between their transmittance values was less than 10%. Consequently, it was inferred that the inhibitory impact was limited to some extent.

As for the promotion effect, upon the absorption of photons, NOM worked as a photosensitiser due to the involvement of aromatic, carboxyl groups, and carbonyl-type chromophores in its complex structure, and then the photo-induced transformation occurred with the production of ROS, which specifically contained singlet oxygen($^1O_2$), superoxide radical ($O_2^{\bullet-}$), hydroperoxyl radicals ($HO_2\bullet$) and hydroxyl radicals ($\bullet OH$) (Alegría et al., 1999; Atkinson et al., 2011; Caupos et al., 2011; W. Liu et al., 2018). The emerging ROS subsequently participated in the oxidation reaction with targeted compounds (Leech et al., 2009):

$$DOC + O_2 + h\upsilon \rightarrow ROS_{DOC} \tag{9}$$
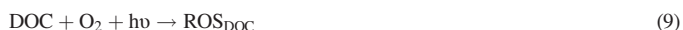
$$ROS_{ss} = ROS_{DOC} + ROS_{estrogen} \tag{10}$$

Table 4
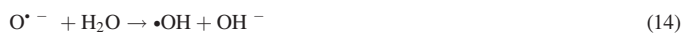The pseudo-first-order parameters for photochemical removal of estrogens in the surface water matrix.

Compounds	Natural water			Contribution of solution matrix (%)	p-value$_{,k1}$
	k_1 (min^{-1})	R^2	$t_{1/2}$ (min)		
E1	0.030	0.996	23.1	28.6	0.024
E2	0.0098	0.989	70.3	12.8	0.474
E3	0.0055	0.995	126.8	40.8	0.118
EE2	0.0085	0.990	81.2	23.2	0.0497

$$ROS_{ss} + estrogen \rightarrow products. \tag{11}$$

In Y. Li et al. (2021)'s work, the impacts of NOM derived from Suwannee River on the photolysis of 2,4-dichloro-6-nitrophenol was studied and the result showed that NOM at low concentration (< 5 mg L^{-1}) favoured the photodegradation of the targeted compound, being consistent with what was observed in our study.

The opposite impacts in terms of the presence of NOM, enhancement, or hindrance observed in different studies might be ascribed to the types and content of the NOM used in studies (Atkinson et al., 2011; Ge et al., 2009; A. Zhang and Li, 2014). For example, the inverse correlation between aromaticity of humic substances and the impact on the photolysis removal rate constant was observed by Silva, Lima, Otero, et al. (2016), who suggested that the humic substances with more aromatic or chromophoric groups might induce more suppression on the rate of photodegradation.

Apart from NOM, nitrate and nitrite were also regarded as important photosensitisers due to their capacity to produce the photoreactions after exposure to light and then affect the photolysis of organic compounds (Chowdhury et al., 2011; Hao et al., 2019; Oliveira et al., 2016). In assayed surface water sample, the concentration of nitrite was negligible while the average concentration of nitrate was characterised as 6.63 mg L^{-1}. As discussed by Chen et al. (2013), once nitrate absorbed the light within the UV range ($\lambda < 350$ nm), its photolysis reaction took place and further $\bullet OH$ was formed according to the following reactions (Machado and Boule, 1995):

$$NO_3^- + h\upsilon \rightarrow NO_2^- + O \tag{12}$$

$$NO_3^- + h\upsilon \rightarrow NO_2\bullet + O^{\bullet-} \tag{13}$$

$$O^{\bullet-} + H_2O \rightarrow \bullet OH + OH^- \tag{14}$$

The low molar extinction coefficient of nitrate within the UV visible wavelength range (the maximum value was determined as 7.2 M^{-1} cm^{-1} at $\lambda = 302$ nm) indicated that the light-shielding impact could be neglected (Machado and Boule, 1995). Therefore, the influence of nitrate on photodegradation was simpler compared with the dual effect of NOM.

Additionally, being one of the most prevalent constituents in studied water, the chloride ion (Cl$^-$) was also found to behave with dual effects in previous publications (Mihas et al., 2007; Oliveira et al., 2016; Zhai et al., 2008). Specifically, under irradiation of light with $\lambda > 200$ nm, the Cl$^-$ in solutions were found capable of inducing the formation of single oxygen ($^1O_2$) and then increased the photolysis rate of florfenicol and thiamphenicol (Ge et al., 2009). However, in some other research, the chloride ion could scavenge hydroxyl radicals in solutions and exhibit the suppression of the indirect photolysis process (Sornalingam et al., 2016). In light of the experiments conducted by Ge et al. (2009), the effects of Cl$^-$ on the photolysis process were light source-dependent.

Carbonate (CO_3^{2-}) and bicarbonates (HCO_3^-) ions are the most common salts in the natural environment, although their concentrations were not profiled in the surface water matrix used in this study. Within a normal pH range (6–9) of natural surface water, bicarbonate ion is the dominant form of inorganic carbon (Vione et al., 2006). According to previous work (Buxton et al., 1988; Vione et al., 2006), carbonate and its conjugated acid-bicarbonate did not show UV absorption but both were the scavengers of OH$\bullet$. This was proved by Chowdhury et al. (2011)'s study, the photolysis of E2 was inhibited along with the increasing concentration of HCO$_3^-$ by scavenging OH$\bullet$, even though the free radicals CO$_3\bullet$ was produced in the following reaction:

$$\bullet OH + HCO_3^- \rightarrow HCO_3^\bullet + H_2O$$
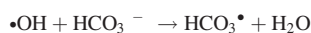
Similarly, the negative impact of carbonate/bicarbonate on the photodegradation of EE2 in pH = 8 deionised water was reported by Albalawi and Zuo (2018), who also indicated that the oxidization of estrogens with HCO$_3\bullet$ was apparently weaker than that with OH$\bullet$. The inverse result was observed by Kang et al. (2018) and Orellana-García et al. (2015) that carbonate and bicarbonate was found to favour the UV photolysis of

bisphenol A and herbicide amitrole due to the formation of $HCO_3\bullet$ and $CO3\bullet^-$. The differences may be tightly related to the properties of targeted pollutants and the pH value of solutions, which needs to be explored further.

In our study, it was difficult to calculate the detailed positive or negative impacts on the direct and indirect photolysis of estrogens induced by each component in the natural water matrix due to its complex constitution. But it could be concluded that the enhancement effect on the photolysis of estrogens resulting from the surface water matrix was more remarkable than its inhibitory effects in this study. Further identification of ROS in the future is required for understanding the mechanisms of photochemical destruction of estrogens comprehensively. Moreover, the yields of ROS produced in presence of the surface water matrix concerning the constitutions and the molecular size distribution of NOM should also be studied to obtain a deep insight into the photodegradation process.

In the UV photolysis process, though the removal of estrogens was observed in both ultrapure water and natural water matrix, the degradation percentage of E1, E2, E3, and EE2 was still limited (69.6%, 38.8%, 24.5%, and 33.6%, respectively), considering the relatively prolonged time of 40 min under UVC irradiation. The photolytic performance was comparable with what was reported for the removal of E1 (80%) and E2/E3/EE2 (25%) under nearly the same time of UVC irradiation in Li Puma et al. (2010)'s work.

However, longer irradiation time was deemed to increase the financial budget and energy cost drastically. So, it may be more appropriate to add an extra barrier with low-cost demand such as a biofiltration process to achieve an effective removal of estrogen. In a previous study, the integration of UV pretreatment with biofilter was found to provide 60% extra removal compared with the sum of performance behaved by the single process of UV photolysis or biofilter (Moussavi and Mohseni, 2007).

4. Conclusion

In this study, the removal of estrogens E1, E2, E3, and EE2 under irradiation of UVC lamp were well-described by the pseudo-first-order kinetics with correlation coefficients $R^2 > 0.981$. According to their photolysis rate constants and $t_{1/2}$, the order of recalcitrance to the employed UV light followed E3 > EE2 > E2 > E1. Out of all studied estrogens, E1 had the largest molar absorption coefficient of 402.4 M^{-1} cm^{-1} and quantum yield of 0.065 mol E^{-1} at λ = 253.7, which further explained that E1 was more prone to photodegradation than the other three estrogens under the identical exposure conditions.

The operation mode of the photolysis reactor (stationary and continuous flow mode) was found to produce a significant difference in the photolytic performance of all selected compounds, whose $t_{1/2}$ values were respectively shortened to 29.7 min, 78.8, 177.7, and 100.5 min for E1, E2, E3 and EE2 using the continuous flow mode. Compared with the $t_{1/2}$ calculated for the stationary mode (39.8 min for E1, 161.2 min for E2, 301.4 min for E3, and 173.3 min for EE2), the increased time-based rate constants in the flow-through system were mainly attributed to higher content of dissolved oxygen, which promoted the oxidation of estrogens.

Simultaneously, the impact of the surface water matrix on the photolysis of estrogens was also assessed by comparing the rate constants with those derived from the spiked ultrapure water treatment. The obtained short $t_{1/2}$ ranging over 23.1 to 126.8 min indicated the enhancement of estrogen photodegradation with involvement of surface water matrix, even though a statistically significant difference was only attained for E1. It was assumed that the most common constituents such as NOM, nitrate, and chloride ion worked together under the UVC irradiation to achieve an overall positive impact on the photolysis performance.

However, it was also observed that the degradation percentage of E1, E2, E3, and EE2 under UVC irradiation was still limited for the operation time of 40 min, being 69.6%, 38.8%, 24.5%, and 33.6%, respectively. Therefore, improvement of this technique via changing the irradiation source or combining it with other treatment processes (e.g. biodegradation) will be investigated in the future. Additionally, considering the practical utilization of this photodegradation method, the optimisation of operating parameters should be further conducted on a pilot scale.

CRediT authorship contribution statement

Fan Huang: Conceptualisation, methodology, validation, formal analysis, investigation, writing - original draft, visualization. **Fan Gao:** partial investigation, formal analysis. **Chaoran Li**: formal analysis, writing - review & editing. **Luiza C. Campos**: Resources, supervision, project administration, writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.155515.

References

Ahmad, I., Ahmed, S., Anwar, Z., Sheraz, M.A., Sikorski, M., 2016. Photostability and photostabilization of drugs and drug products. Int. J. Photoenergy 2016, 1–19. https://doi.org/10.1155/2016/8135608.

Albalawi, F., Zuo, Y., 2018. Photodegradation of 17α-ethynylestradiol (EE2) in the presence of humic acid and carbonate ions in water solutions. Int. J. Chem. Eng. Appl. 9 (2), 71–75. https://doi.org/10.18178/ijcea.2018.9.2.701.

Alegría, A.E., Ferrer, A., Santiago, G., Sepúlveda, E., Flores, W., 1999. Photochemistry of water-soluble quinones. Production of the hydroxyl radical, singlet oxygen and the superoxide ion. Journal of Photochemistry and Photobiology A: Chemistry 127 (1), 57–65. https://doi.org/10.1016/S1010-6030(99)00138-0.

Atkinson, S.K., Marlatt, V.L., Kimpe, L.E., Lean, D.R., Trudeau, V.L., Blais, J.M., 2011. Environmental factors affecting ultraviolet photodegradation rates and estrogenicity of estrone and ethinylestradiol in natural waters. Arch. Environ. Contam. Toxicol. 60 (1), 1–7. https://doi.org/10.1007/s00244-010-9515-4.

Baronti, C., Curini, R., D'Ascenzo, G., Di Corcia, A., Gentili, A., Samperi, R., 2000. Monitoring natural and synthetic estrogens at activated sludge sewage treatment plants and in a receiving river water. Environ. Sci. Technol. 34 (24), 5059–5066. https://doi.org/10.1021/es001359q.

Belfroid, A.C., Van der Horst, A., Vethaak, A.D., Schäfer, A.J., Rijs, G.B.J., Wegener, J., Cofino, W.P., 1999. Analysis and occurrence of estrogenic hormones and their glucuronides in surface water and waste water in the Netherlands. Sci. Total Environ. 225 (1), 101–108. https://doi.org/10.1016/S0048-9697(98)00336-2.

Bonneau, R., Carmichael, I., Hug, G., 1991. Molar absorption coefficients of transient species in solution. Pure Appl. Chem. 63 (2), 289–300.

Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O− in aqueous solution. J. Phys. Chem. Ref. Data 17 (2), 513–886. https://doi.org/10.1063/1.555805.

Canonica, S., Meunier, L., von Gunten, U., 2008. Phototransformation of selected pharmaceuticals during UV treatment of drinking water. Water Res. 42 (1–2), 121–128. https://doi.org/10.1016/j.watres.2007.07.026.

Capriotti, A.L., Cavaliere, C., Piovesana, S., Stampachiacchiere, S., Samperi, R., Ventura, S., Lagana, A., 2015. Simultaneous determination of naturally occurring estrogens and mycoestrogens in milk by ultrahigh-performance liquid chromatography-tandem mass spectrometry analysis. J. Agric. Food Chem. 63 (40), 8940–8946. https://doi.org/10.1021/acs.jafc.5b02815.

Carlson, J.C., Stefan, M.I., Parnis, J.M., Metcalfe, C.D., 2015. Direct UV photolysis of selected pharmaceuticals, personal care products and endocrine disruptors in aqueous solution. Water Res. 84, 350–361. https://doi.org/10.1016/j.watres.2015.04.013.

Caupos, E., Mazellier, P., Croue, J.P., 2011. Photodegradation of estrone enhanced by dissolved organic matter under simulated sunlight. Water Res. 45 (11), 3341–3350. https://doi.org/10.1016/j.watres.2011.03.047.

Cedat, B., de Brauer, C., Metivier, H., Dumont, N., Tutundjan, R., 2016. Are UV photolysis and UV/H2O2 process efficient to treat estrogens in waters? Chemical and biological assessment at pilot scale. Water Res. 100, 357–366. https://doi.org/10.1016/j.watres.2016.05.040.

Chan, K.Y., Gavaghan, B.M., Stoeckel, A.W., Irizarry, K., Hare, P.M., 2012. Solvent effects on the steady state photophysics of estrone and 17beta-estradiol. Photochem. Photobiol. 88 (2), 295–303. https://doi.org/10.1111/j.1751-1097.2011.01066.x.

Chan, K.Y., Courtois, B., Loose, K., Hare, P.M., 2013. Solvent-dependent fluorescence lifetimes of estrone, 17beta-estradiol and 17alpha-ethinylestradiol. Photochem. Photobiol. 89 (2), 294–299. https://doi.org/10.1111/php.12011.

Chen, Y., Zhang, K., Zuo, Y., 2013. Direct and indirect photodegradation of estriol in the presence of humic acid, nitrate and iron complexes in water solutions. Sci. Total Environ. 463–464, 802–809. https://doi.org/10.1016/j.scitotenv.2013.06.026.

Chowdhury, R.R., Charpentier, P.A., Ray, M.B., 2011. Photodegradation of 17β-estradiol in aquatic solution under solar irradiation: kinetics and influencing water parameters. J. Photochem. Photobiol. A Chem. 219 (1), 67–75. https://doi.org/10.1016/j.jphotochem.2011.01.019.

Dale Wilson, B., Moon, S., Armstrong, F., 2012. Comprehensive review of ultraviolet radiation and the current status on sunscreens. Retrieved from https://pubmed.ncbi.nlm.nih.gov/23050030The Journal of clinical and aesthetic dermatology 5 (9), 18–23. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3460660/.

Desbrow, C., Routledge, E.J., Brighty, G.C., Sumpter, J.P., Waldock, M., 1998. Identification of estrogenic chemicals in STW effluent. 1. Chemical fractionation and in vitro biological screening. Environ. Sci. Technol. 32 (11), 1549–1558. https://doi.org/10.1021/es9707973.

Dong, X., He, L., Hu, H., Liu, N., Gao, S., Piao, Y., 2018. Removal of 17β-estradiol by using highly adsorptive magnetic biochar nanoparticles from aqueous solution. Chem. Eng. J. 352, 371–379. https://doi.org/10.1016/j.cej.2018.07.025.

Du, Y., Fu, Q.S., Li, Y., Su, Y., 2011. Photodecomposition of 4-chlorophenol by reactive oxygen species in UV/air system. J. Hazard. Mater. 186 (1), 491–496. https://doi.org/10.1016/j.jhazmat.2010.11.023.

Dudziak, M., Luks-Betlej, K., 2004. Ocena obecności estrogenów - steroidowych hormonow plciowych - W wybranych wodach rzecznych w polsce. Ochr. Sr. 26 (1), 21–24.

Dytczak, M.A., Londry, K.L., Oleszkiewicz, J.A., 2008. Biotransformation of estrogens in nitrifying activated sludge under aerobic and alternating anoxic/aerobic conditions. Water Environ. Res. 80 (1), 47–52. https://doi.org/10.1002/j.1554-7531.2008.tb00348.x.

Fan, Z., Hu, J., An, W., Yang, M., 2013. Detection and occurrence of chlorinated byproducts of bisphenol a, nonylphenol, and estrogens in drinking water of China: comparison to the parent compounds. Environ. Sci. Technol. 47 (19), 10841–10850. https://doi.org/10.1021/es401504a.

Frontistis, Z., Kouramanos, M., Moraitis, S., Chatzisymeon, E., Hapeshi, E., Fatta-Kassinos, D., Mantzavinos, D., 2015. UV and simulated solar photodegradation of 17α-ethynylestradiol in secondary-treated wastewater by hydrogen peroxide or iron addition. Catal. Today 252, 84–92. https://doi.org/10.1016/j.cattod.2014.10.012.

Fukuhara, T., Iwasaki, S., Kawashima, M., Shinohara, O., Abe, I., 2006. Adsorbability of estrone and 17beta-estradiol in water onto activated carbon. Water Res. 40 (2), 241–248. https://doi.org/10.1016/j.watres.2005.10.042.

Gadd, J.B., Tremblay, L.A., Northcott, G.L., 2010. Steroid estrogens, conjugated estrogens and estrogenic activity in farm dairy shed effluents. Environ. Pollut. 158 (3), 730–736. https://doi.org/10.1016/j.envpol.2009.10.015.

Ge, L., Chen, J., Qiao, X., Lin, J., Cai, X., 2009. Light-source-dependent effects of Main water constituents on photodegradation of phenicol antibiotics: mechanism and kinetics. Environ. Sci. Technol. 43 (9), 3101–3107. https://doi.org/10.1021/es8031727.

Hao, Z., Guo, C., Lv, J., Zhang, Y., Zhang, Y., Xu, J., 2019. Kinetic and mechanistic study of sulfadimidine photodegradation under simulated sunlight irradiation. Environmental sciences. Europe 31 (1). https://doi.org/10.1186/s12302-019-0223-z.

Hozalski, R.M., Goel, S., Bouwer, E.J., 1995. TOC removal in biological filters. J. AWWA 87 (12), 40–54. https://doi.org/10.1002/j.1551-8833.1995.tb06464.x.

Hu, J.Y., Aizawa, T., Ookubo, S., 2002. Products of aqueous chlorination of bisphenol a and their estrogenic activity. Environ. Sci. Technol. 36 (9), 1980–1987. https://doi.org/10.1021/es011177b.

Huang, F., Karu, K., Campos, L.C., 2021. Simultaneous measurement of free and conjugated estrogens in surface water using capillary liquid chromatography tandem mass spectrometry. Analyst https://doi.org/10.1039/D0AN02335C.

Kalyanasundaram, K., 2012. Photochemistry in microheterogeneous systems. Elsevier.

Kang, Y.-M., Kim, M.-K., Zoh, K.-D., 2018. Effect of nitrate, carbonate/bicarbonate, humic acid, and H2O2 on the kinetics and degradation mechanism of bisphenol-a during UV photolysis. Chemosphere 204, 148–155. https://doi.org/10.1016/j.chemosphere.2018.04.015.

Keum, Y.S., Kim, J.H., Kim, Y.W., Kim, K., Li, Q.X., 2002. Photodegradation of diafenthiuron in water. Pest Manag. Sci. 58 (5), 496–502. https://doi.org/10.1002/ps.483.

Kim, J.K., Alajmy, J., Borges, A.C., Joo, J.C., Ahn, H., Campos, L.C., 2013. Degradation of humic acid by photocatalytic reaction using nano-sized ZnO/Laponite composite (NZLC). Water Air Soil Pollut. 224 (11). https://doi.org/10.1007/s11270-013-1749-0.

Kim, S.J., Kim, D.K., Kang, D.H., 2016. Using UVC light-emitting diodes at wavelengths of 266 to 279 nanometers to inactivate foodborne pathogens and pasteurize sliced cheese. Appl. Environ. Microbiol. 82 (1), 11–17. https://doi.org/10.1128/AEM.02092-15.

Kuch, H.M., Ballschmiter, K., 2001. Determination of endocrine-disrupting phenolic compounds and estrogens in surface and drinking water by HRGC-(NCI)-MS in the picogram per liter range. Environ. Sci. Technol. 35 (15), 3201–3206. https://doi.org/10.1021/es010034m.

Kuch, H.M., Ballschmiter, K., 2001. Determination of endocrine-disrupting phenolic compounds and estrogens in surface and drinking water by HRGC−(NCI)− MS in the picogram per liter range. Environ. Sci. Technol. 35 (15), 3201–3206.

Kuster, M., López, José, de Alda, M., Barceló, D., 2004. Analysis and distribution of estrogens and progestogens in sewage sludge, soils and sediments. TrAC Trends Anal. Chem. 23 (10–11), 790–798. https://doi.org/10.1016/j.trac.2004.08.007.

Leech, D.M., Snyder, M.T., Wetzel, R.G., 2009. Natural organic matter and sunlight accelerate the degradation of 17ss-estradiol in water. Sci. Total Environ. 407 (6), 2087–2092. https://doi.org/10.1016/j.scitotenv.2008.11.018.

Levenspiel, O., 1998. Chemical Reaction Engineering. John Wiley & Sons.

Li Puma, G., Puddu, V., Tsang, H.K., Gora, A., Toepfer, B., 2010. Photocatalytic oxidation of multicomponent mixtures of estrogens (estrone (E1), 17β-estradiol (E2), 17α-ethynylestradiol (EE2) and estriol (E3)) under UVA and UVC radiation: photon absorption, quantum yields and rate constants independent of photon absorption. Appl. Catal. B Environ. 99 (3–4), 388–397. https://doi.org/10.1016/j.apcatb.2010.05.015.

Li, M., Wen, D., Qiang, Z., Kiwi, J., 2017. VUV/UV light inducing accelerated phenol degradation with a low electric input. RSC Adv. 7 (13), 7640–7647. https://doi.org/10.1039/c6ra26043h.

Li, Y., Qin, H., Wang, L., Lu, J., Chovelon, J.M., Zhou, Q., Ji, Y., 2021. Aquatic photolysis of 2,6-dichloro-6-nitrophenol-the toxic nitrated byproduct of 2,4-dichlorophenol. Chemosphere 132986. https://doi.org/10.1016/j.chemosphere.2021.132986.

Lin, A.Y.-C., Reinhard, M., 2005. Photodegradation of common environmental pharmaceuticals and estrogens in river water. Environ. Toxicol. Chem. 24 (6), 1303–1309. https://doi.org/10.1897/04-236R.1.

Lindblad, M., Tano, E., Lindahl, C., Huss, F., 2020. Ultraviolet-C decontamination of a hospital room: amount of UV light needed. Burns 46 (4), 842–849. https://doi.org/10.1016/j.burns.2019.10.004.

Liu, B., Liu, X., 2004. Direct photolysis of estrogens in aqueous solutions. Sci. Total Environ. 320 (2–3), 269–274. https://doi.org/10.1016/j.scitotenv.2003.08.005.

Liu, B., Wu, F., Deng, N.-S., 2003. UV-light induced photodegradation of 17α-ethynylestradiol in aqueous solutions. J. Hazard. Mater. 98 (1–3), 311–316. https://doi.org/10.1016/s0304-3894(02)00321-7.

Liu, W., Jin, L., Chen, K., Li, Y., Dahlgren, R.A., Ma, M., Wang, X., 2018. Inhibitory effects of natural organic matter on methyltriclosan photolysis kinetics. RSC Adv. 8 (38), 21265–21271. https://doi.org/10.1039/c8ra03512a.

Machado, F., Boule, P., 1995. Photonitration and photonitrosation of phenolic derivatives induced in aqueous solution by excitation of nitrite and nitrate ions. J. Photochem. Photobiol. A Chem. 86 (1), 73–80. https://doi.org/10.1016/1010-6030(94)03946-R.

Mao, L., Lu, J., Habteselassie, M., Luo, Q., Gao, S., Cabrera, M., Huang, Q., 2010. Ligninase-mediated removal of natural and synthetic estrogens from water: II. Reactions of 17β-estradiol. Environmental science & technology 44 (7), 2599–2604. https://doi.org/10.1021/es903058k.

Marotta, R., Spasiano, D., Di Somma, I., Andreozzi, R., 2013. Photodegradation of naproxen and its photoproducts in aqueous solution at 254 nm: a kinetic investigation. Water Res. 47 (1), 373–383. https://doi.org/10.1016/j.watres.2012.10.016.

Mazellier, P., Meite, L., De Laat, J., 2008. Photodegradation of the steroid hormones 17beta-estradiol (E2) and 17alpha-ethynylestradiol (EE2) in dilute aqueous solution. Chemosphere 73 (8), 1216–1223. https://doi.org/10.1016/j.chemosphere.2008.07.046.

Mihas, O., Kalogerakis, N., Psillakis, E., 2007. Photolysis of 2,4-dinitrotoluene in various water solutions: effect of dissolved species. J. Hazard. Mater. 146 (3), 535–539. https://doi.org/10.1016/j.jhazmat.2007.04.054.

Moon, B.-H., Park, Y.-B., Park, K.-H., 2011. Fenton oxidation of Orange II by pre-reduction using nanoscale zero-valent iron. Desalination 268 (1), 249–252. https://doi.org/10.1016/j.desal.2010.10.036.

Moussavi, G., Mohseni, M., 2007. Using UV pretreatment to enhance biofiltration of mixtures of aromatic VOCs. J. Hazard. Mater. 144 (1–2), 59–66. https://doi.org/10.1016/j.jhazmat.2006.09.086.

Nasuhoglu, D., Berk, D., Yargeau, V., 2012. Photocatalytic removal of 17α-ethinylestradiol (EE2) and levonorgestrel (LNG) from contraceptive pill manufacturing plant wastewater under UVC radiation. Chem. Eng. J. 185–186, 52–60. https://doi.org/10.1016/j.cej.2012.01.012.

Nie, Y., Qiang, Z., Zhang, H., Adams, C., 2009. Determination of endocrine-disrupting chemicals in the liquid and solid phases of activated sludge by solid phase extraction and gas chromatography-mass spectrometry. J. Chromatogr. A 1216 (42), 7071–7080. https://doi.org/10.1016/j.chroma.2009.08.064.

Nieto, A., Borrull, F., Pocurull, E., Marce, R.M., 2008. Determination of natural and synthetic estrogens and their conjugates in sewage sludge by pressurized liquid extraction and liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 1213 (2), 224–230. https://doi.org/10.1016/j.chroma.2008.10.043.

Oliveira, C., Lima, D.L.D., Silva, C.P., Otero, M., Esteves, V.I., 2016. Photodegradation behaviour of estriol: an insight on natural aquatic organic matter influence. Chemosphere 159, 545–551. https://doi.org/10.1016/j.chemosphere.2016.06.046.

Orellana-García, F., Álvarez, M.A., López-Ramón, M.V., Rivera-Utrilla, J., Sánchez-Polo, M., 2015. Effect of HO, SO4− and CO3−/HCO3 radicals on the photodegradation of the herbicide amitrole by UV radiation in aqueous solution. Chem. Eng. J. 267, 182–190. https://doi.org/10.1016/j.cej.2015.01.019.

Pailthorpe, M.T., Bonjour, J.P., Nicholls, C.H., 1973. The photolysis of tryptophan in the presence of oxygen. Photochem. Photobiol. 17 (4), 209–223. https://doi.org/10.1111/j.1751-1097.1973.tb06350.x.

Pereira, V.J., Galinha, J., Barreto Crespo, M.T., Matos, C.T., Crespo, J.G., 2012. Integration of nanofiltration, UV photolysis, and advanced oxidation processes for the removal of hormones from surface water sources. Sep. Purif. Technol. 95, 89–96. https://doi.org/10.1016/j.seppur.2012.04.013.

Ren, D., Chen, F., Ren, Z., Wang, Y., 2019. Different response of 17α-ethinylestradiol photodegradation induced by aquatic humic and fulvic acids to typical water matrixes. Process Saf. Environ. Prot. 121, 367–373. https://doi.org/10.1016/j.psep.2018.11.018.

Rosal, R., Gonzalo, M.S., Boltes, K., Leton, P., Vaquero, J.J., Garcia-Calvo, E., 2009. Identification of intermediates and assessment of ecotoxicity in the oxidation products generated during the ozonation of clofibric acid. J. Hazard. Mater. 172 (2–3), 1061–1068. https://doi.org/10.1016/j.jhazmat.2009.07.110.

Rosenfeldt, E.J., Linden, K.G., 2004. Degradation of endocrine disrupting chemicals bisphenol a, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation processes. Environ. Sci. Technol. 38 (20), 5476–5483. https://doi.org/10.1021/es035413p.

Sanches, S., Penetra, A., Rodrigues, A., Cardoso, V.V., Ferreira, E., Benoliel, M.J., Pereira, V.J., 2013. Removal of pesticides from water combining low pressure UV photolysis with nanofiltration. Sep. Purif. Technol. 115, 73–82. https://doi.org/10.1016/j.seppur.2013.04.044.

Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2016. Environmental Organic Chemistry. John Wiley & Sons.

Shi, Y., Xu, L., Gong, D., Lu, J., 2010. Effects of sterilization treatments on the analysis of TOC in water samples. J. Environ. Sci. 22 (5), 789–795. https://doi.org/10.1016/s1001-0742(09)60178-9.

Silva, C.P., Otero, M., Esteves, V., 2012. Processes for the elimination of estrogenic steroid hormones from water: a review. Environ. Pollut. 165, 38–58. https://doi.org/10.1016/j.envpol.2012.02.002.

Shyu, C., Cavileer, T.D., Nagler, J.J., Ytreberg, F.M., 2011. Computational estimation of rainbow trout estrogen receptor binding affinities for environmental estrogens. Toxicol. Appl. Pharmacol. 250 (3), 322–326. https://doi.org/10.1016/j.taap.2010.11.005.

Silva, C.P., Lima, D.L., Groth, M.B., Otero, M., Esteves, V.I., 2016. Effect of natural aquatic humic substances on the photodegradation of estrone. Chemosphere 145, 249–255. https://doi.org/10.1016/j.chemosphere.2015.11.068.

Silva, C.P., Lima, D.L., Otero, M., Esteves, V.I., 2016. Photosensitized degradation of 17beta-estradiol and 17alpha-ethinylestradiol: role of humic substances fractions. J. Environ. Qual. 45 (2), 693–700. https://doi.org/10.2134/jeq2015.07.0396.

Sornalingam, K., McDonagh, A., Zhou, J.L., 2016. Photodegradation of estrogenic endocrine disrupting steroidal hormones in aqueous systems: Progress and future challenges. Sci. Total Environ. 550, 209–224. https://doi.org/10.1016/j.scitotenv.2016.01.086.

Souissi, Y., Bourcier, S., Bouchonnet, S., Genty, C., Sablier, M., 2012. Estrone direct photolysis: by-product identification using LC-Q-TOF. Chemosphere 87 (2), 185–193. https://doi.org/10.1016/j.chemosphere.2011.12.016.

Tanaka, H., Yakou, Y., Takahashi, A., Higashitani, T., Komori, K., 2001. Comparison between estrogenicities estimated from DNA recombinant yeast assay and from chemical analyses of endocrine disruptors during sewage treatment. Water Sci. Technol. 43 (2), 125–132. https://doi.org/10.2166/wst.2001.0081.

Ternes, T.A., Stumpf, M., Mueller, J., Haberer, K., Wilken, R.D., Servos, M., 1999. Behavior and occurrence of estrogens in municipal sewage treatment plants — I. Investigations in Germany, Canada and Brazil. Sci. Total Environ. 225 (1), 81–90. https://doi.org/10.1016/S0048-9697(98)00334-9.

Trudeau, V.L., Heyne, B., Blais, J.M., Temussi, F., Atkinson, S.K., Pakdel, F., Lean, D.R.S., 2011. Lumiestrone is photochemically derived from estrone and may be released to the environment without detection. Front. Endocrinol. 2. https://doi.org/10.3389/fendo.2011.00083.

Vega-Morales, T., Sosa-Ferrera, Z., Santana-Rodriguez, J.J., 2011. Determination of various estradiol mimicking-compounds in sewage sludge by the combination of microwave-assisted extraction and LC-MS/MS. Talanta 85 (4), 1825–1834. https://doi.org/10.1016/j.talanta.2011.07.051.

Vione, D., Falletti, G., Maurino, V., Minero, C., Pelizzetti, E., Malandrino, M., Arsene, C., 2006. Sources and sinks of hydroxyl radicals upon irradiation of natural water samples. Environ. Sci. Technol. 40 (12), 3775–3781. https://doi.org/10.1021/es052206b.

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ. Sci. Technol. 37 (20), 4702–4708. https://doi.org/10.1021/es030360x.

Wells, C.H.J., 1972. Introduction to molecular photochemistry [By]. Chapman and Hall, C.H.J. Wells.

Whidbey, C.M., Daumit, K.E., Nguyen, T.H., Ashworth, D.D., Davis, J.C., Latch, D.E., 2012. Photochemical induced changes of in vitro estrogenic activity of steroid hormones. Water Res. 46 (16), 5287–5296. https://doi.org/10.1016/j.watres.2012.07.016.

Xu, B., Li, K., Qiao, J., Liungai, Z., Chen, C., Lu, Y., 2017. UV photoconversion of environmental oestrogen diethylstilbestrol and its persistence in surface water under sunlight. Water Res. 127, 77–85. https://doi.org/10.1016/j.watres.2017.09.059.

Xu, X., Roman, J.M., Issaq, H.J., Keefer, L.K., Veenstra, T.D., Ziegler, R.G., 2007. Quantitative measurement of endogenous estrogens and estrogen metabolites in human serum by liquid chromatography-tandem mass spectrometry. Anal. Chem. 79 (20), 7813–7821.

Yoon, Y., Westerhoff, P., Snyder, S.A., Wert, E.C., Yoon, J., 2007. Removal of endocrine disrupting compounds and pharmaceuticals by nanofiltration and ultrafiltration membranes. Desalination 202 (1–3), 16–23. https://doi.org/10.1016/j.desal.2005.12.033.

Yuan, F., Hu, C., Hu, X., Qu, J., Yang, M., 2009. Degradation of selected pharmaceuticals in aqueous solution with UV and UV/H(2)O(2). Water Res. 43 (6), 1766–1774. https://doi.org/10.1016/j.watres.2009.01.008.

Zepp, R.G., Cline, D.M., 1977. Rates of direct photolysis in aquatic environment. Environ. Sci. Technol. 11 (4), 359–366.

Zhai, G., Liu, J., He, B., Zhang, J., Zhou, Q., Jiang, G., 2008. Ultraviolet degradation of methyltins: elucidating the mechanism by identification of a detected new intermediary product and investigating the kinetics at various environmental conditions. Chemosphere 72 (3), 389–399. https://doi.org/10.1016/j.chemosphere.2008.02.048.

Zhang, A., Li, Y., 2014. Removal of phenolic endocrine disrupting compounds from waste activated sludge using UV, H2O2, and UV/H2O2 oxidation processes: effects of reaction conditions and sludge matrix. Sci. Total Environ. 493, 307–323. https://doi.org/10.1016/j.scitotenv.2014.05.149.

Zhang, Y., Zhou, J.L., Ning, B., 2007. Photodegradation of estrone and 17beta-estradiol in water. Water Res. 41 (1), 19–26. https://doi.org/10.1016/j.watres.2006.09.020.

Zhang, Z., Feng, Y., Liu, Y., Sun, Q., Gao, P., Ren, N., 2010. Kinetic degradation model and estrogenicity changes of EE2 (17alpha-ethinylestradiol) in aqueous solution by UV and UV/H2O2 technology. J. Hazard. Mater. 181 (1–3), 1127–1133. https://doi.org/10.1016/j.jhazmat.2010.05.132.

Zhang, M., Ghosh, S., Kumar, M., Santiana, M., Bleck, C.K.E., Chaimongkol, N., Shuai, D., 2021. Emerging pathogenic unit of vesicle-cloaked murine norovirus clusters is resistant to environmental stresses and UV254 disinfection. Environ. Sci. Technol. 55 (9), 6197–6205. https://doi.org/10.1021/acs.est.1c01763.

Zhao, G., Lu, X., Zhou, Y., 2013. Aniline degradation in aqueous solution by UV-aeration and UV-microO3 processes: efficiency, contribution of radicals and byproducts. Chem. Eng. J. 229, 436–443. https://doi.org/10.1016/j.cej.2013.06.011.