



# Models to predict sunlight-induced photodegradation rates of contaminants in wastewater stabilisation ponds and clarifiers

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## Abstract

Two kinetic models were established for conservative estimates of photodegradation rates of contaminants under sunlight irradiation, in particular for wastewater stabilisation ponds and clarifiers in conventional wastewater treatment plants. These two models were designated for (1) contaminants with high photolytic rates or high photolytic quantum yields, whose photodegradation is unlikely to be enhanced by aquatic photosensitisers; and (2) contaminants withstanding direct photolysis in sunlit waters but subjected to indirect photolysis. The effortlessly intelligible prediction procedure involves sampling and analysis of real water samples, simulated solar experiments in the laboratory, and transfer of the laboratory results to realise water treatment using the prediction models. Although similar models have been widely used for laboratory studies, this paper provides a preliminary example of translating laboratory results to the photochemical fate of contaminants in real waters. © 2019 Hohai University. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

**Keywords:** Sunlight irradiation; Photodegradation; Contaminants; Stabilisation ponds; Solar water treatment

## 1. Introduction

Sunlight-induced photolysis is a primary transformation pathway for contaminants in surface waters (Gschwend, 2016). In past decades, numerous laboratory experiments have progressively advanced our understanding of the photochemical behaviour of a huge variety of contaminants (Afsharnia et al., 2018). The mechanism of contaminant photolysis under sunlight irradiation depends on both the properties of the compound and the chemical nature of the aquatic matrix. Contaminants with high direct photolytic rates, i.e., high quantum yields, are usually photodegraded rapidly and the impact of natural photosensitisers, such as nitrate and dissolved organic matter (DOM), is negligible (Niu et al., 2017). This is because the concentrations of reactive species (e.g.,  $^1\text{O}_2$ , triplet excited states, and  $\cdot\text{OH}$ ) photochemically generated by these photosensitisers are extremely low (Niu

et al., 2014; Romero-Maraccini et al., 2013; Niu and Croué, 2019), and their contribution to the photodegradation of these contaminants is dwarfed by the high direct photolytic rates. Comparatively, contaminants with lower direct photolytic rates, which show more intensive reactivity with photosensitized reactive species, are also subjected to impact by sunlight. Some exemplary compounds are ibuprofen (Jacobs et al., 2011), cimetidine (Niu et al., 2014; Latch et al., 2003), and amoxicillin (Xu et al., 2011).

There have been increasing amounts of publications on the photochemical fate of contaminants. These publications have documented the photodegradation rates and elucidated respective phototransformation pathways for contaminants under simulated sunlight, mostly utilising a solar simulator. A commercial sunlight simulator supplies irradiation mimicking the spectrum of natural sunlight (Niu et al., 2014; Kohn and Nelson, 2007). It is advantageous in maintaining stable and adjustable energy levels, and facilitating the control of important experimental parameters, e.g., temperature, irradiation time, wavelength range, and incident angle. However, it

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is well-known that environmentally relevant conditions are noticeably divergent; uncertainties could emanate from spatiotemporal variations and the differential physiochemical properties of the water. As a result, most laboratory-derived photochemical results are considered theoretical rather than applicable to practice. In addition to the mechanistic significance, laboratory studies will further materialize their realistic contributions if appropriate approaches are formulated to translate them into a water treatment-related scenario.

In Niu et al. (2017), sulphonamide sulfathiazole was reported to undergo direct photolysis, exhibiting a high first-order degradation rate. The authors then proposed a simplified model to predict the photodegradation rate of sulfathiazole in a real water sample. The model was demonstrated to be successful in predicting the photodegradation rate of sulfathiazole spiked in a wastewater effluent sample taken from Denmark, Western Australia (Niu et al., 2017). In other studies where the effect of indirect photolysis was significant or outperformed the effect of direct photolysis, light screening correction models were developed (Niu et al., 2016). Although transferring the sunlight simulator-based results to realistic water treatment is and will remain a challenge, the author believes in their applicability to engineered aquatic systems such as wastewater stabilisation ponds (WSP) and wastewater clarifiers, because the water quality characteristics in these engineered systems can be regularly monitored, the depth and temperature of the water can be measured, and the local solar radiation profiles might be accessible from official webpages of solar and energy research institutes.

This paper presents two models for the prediction of sunlight-induced photodegradation rates ( $k_{EST}$ ) of contaminants in WSP and clarifiers. The experimental steps pertinent to application of the models are described. The estimated  $k_{EST}$  in the present study is viewed as conservative and conceivably minimal, whereas the on-site real values are expected to be higher.

## 2. Materials and methods

### 2.1. Chemicals and wastewater samples

Target contaminants with high purity standards are purchased. Water samples are collected and filtered through a 0.45- $\mu\text{m}$  membrane before use. Important model parameters include pH, ultraviolet-visible (UV-Vis) absorption spectrum (280–600 nm), nitrate concentration, temperature, and depth of the ponds/tanks.

### 2.2. Analytical instruments

Analytical instruments include a pH meter, an ion chromatograph (IC), a thermometer, a high-pressure liquid chromatography (HPLC) system coupled with a UV detector or a diode-array detector (DAD), and an HPLC column that enables the separation of target compounds.

### 2.3. Photo-experiments

Photo-experiments are performed in a sunlight simulator (e.g., SUNTEST), which usually generates irradiance in the wavelength range of 280–600 nm (Niu et al., 2014, 2017). The experimental setup varies, but some well-developed examples are available (Romero-Maraccini et al., 2013; Niu et al., 2014; Lee et al., 2013; Boreen et al., 2003; Remucal and McNeill, 2011; Kohn and Nelson, 2007; Sharpless et al., 2014). Briefly, reactors (e.g., Pyrex beakers) containing solutions of the target contaminants (initial concentrations 5–10  $\mu\text{mol/L}$ ) are seated in a water bath under the xenon lamp. The reaction solutions are mixed using a multi-point magnetic stirring plate. Samples are aliquoted at certain time intervals and analysed by HPLC.

## 3. Prediction models

### 3.1. Prediction models for contaminants with high photolytic rates

Sunlight is a key indigenous force governing the fate and transport of contaminants, bacteria, and DOM in surface waters, WSP, and clarifiers (Gruchlik et al., 2018; Niu et al., 2019; Gladly-Croue et al., 2018). A fundamental obstacle hindering direct translation of laboratory photodegradation results to engineered waters is the heterogeneity of irradiance in experimental solutions and real waters, mainly owing to light attenuation. The light attenuation factor ( $S_\lambda$ ) has been used to compensate for this effect in experiments conducted in the laboratory (Canonica et al., 2008; Niu et al., 2014; Kohn and Nelson, 2007) and is determined using Eq. (1):

$$S_\lambda = \frac{1 - 10^{-\alpha_\lambda z}}{2.303\alpha_\lambda z} \quad (1)$$

where  $\alpha_\lambda$  is the UV-Vis absorption ( $\text{cm}^{-1}$ ), and  $z$  is the optical length of the water (cm) (Leifer, 1988). In waterways such as rivers and lakes, the depth is unlikely to be identical at different locations. Nonetheless, engineered aquatic systems such as WSP and clarifiers have measurable, uniform dimensions. Hence, light attenuation models were used in this study to convert photodegradation results observed in synthetic water to those in real waters.

The light attenuation correction factor  $CF_w$  of engineered waters has been previously applied in simulated photochemical and photobiological studies (Niu et al., 2016; Kohn and Nelson, 2007; Romero-Maraccini et al., 2013) and is described in Eq. (2):

$$CF_w = \frac{\sum_\lambda (I_{0,\lambda} \varepsilon_\lambda)}{\sum_\lambda \left( I_{0,\lambda} \varepsilon_\lambda \frac{1 - 10^{-\varepsilon_\lambda z}}{2.303 \varepsilon_\lambda z} \right)} \quad 280 \text{ nm} \leq \lambda \leq m \quad (2)$$

where  $\lambda$  is the wavelength,  $m$  is the longest wavelength at which the compound displays considerable absorption on the

UV-Vis absorption spectrum,  $I_{0,\lambda}$  is the initial irradiance at the surface of an irradiated solution, and  $\varepsilon_\lambda$  is the molar absorptivity of the target compound. Contaminants with high photolytic rates are characterised by very short photochemical lifetimes. Eq. (3) is used to predict the photodegradation rate, regardless of the complexity of the water:

$$k_{\text{EST}} = \frac{k_{\text{d,obs}}}{CF_{\text{w}}} \quad (3)$$

where  $k_{\text{d,obs}}$  is the direct photolytic rate of the compound observed in buffered water, the pH value of which is adjusted to the same level as the natural water.

A previous paper examining the photochemical fate of sulfathiazole showcased the validation of this model (Niu et al., 2017). Fitted using Eq. (3), the photodegradation rate was directly proportional to the inverse of  $CF_{\text{w}}$  (300–350 nm) (Fig. 1 in Niu et al. (2017)). Alternatively, one could spike the target contaminants into real waters and obtain the photodegradation rate in the sunlight simulator ( $k_{\text{s,obs}}$ ). The predicted photodegradation rate  $k_{\text{EST}}$  could be calculated using Eq. (4).

$$k_{\text{EST}} = \frac{CF_{\text{s,w}}k_{\text{s,obs}}}{CF_{\text{w}}} \quad (4)$$

where  $CF_{\text{s,w}}$  is the correction factor calculated for the experiments performed in the sunlight simulator (e.g., in painted glass beakers (Niu et al., 2014; Romero-Maraccini et al., 2013)).

### 3.2. Prediction models for contaminants with low direct photolytic rates

Eqs. (5) through (7), derived from models utilized in several previous studies (Niu et al., 2016; Liang et al., 2015), are used providing that the compound has a relatively lower direct photolytic quantum yield and that a crucial contribution is exerted from photosensitization in the matrix.

$$CF_{\text{DOM}} = \frac{\sum_{\lambda} (I_{0,\lambda} \alpha_{\lambda} z)}{\sum_{\lambda} (I_{0,\lambda} \alpha_{\lambda} S_{\lambda} z)} \quad 280 \text{ nm} \leq \lambda \leq 600 \text{ nm} \quad (5)$$

$$k_{\text{obs}} = \frac{k_{\text{d,obs}}}{CF_{\text{w}}} + \frac{k_{\text{DOM}}}{CF_{\text{DOM}}} \quad (6)$$

$$k_{\text{EST}} = \frac{k_{\text{d,obs}}}{CF_{\text{w}}} + \frac{k_{\text{DOM}}}{CF_{\text{DOM}}} \quad (7)$$

Unlike Eq. (3), which is applicable regardless of the complexity of real waters, Eqs. (5) through (7) are only applicable to specific waters. First, the direct photolytic rate in buffered water ( $k_{\text{d,obs}}$  in Eq. (3)) is procured at the same pH as the real water. Target water samples spiked with the standard compound are irradiated in the sunlight simulator and the first-order degradation rate  $k_{\text{obs}}$  is obtained. Nitrate photochemistry and the photo-Fenton process are not modelled in this study, but they should be individually accounted for if nitrates are

abundant in the target water. The contribution of DOM photosensitization is expressed as  $k_{\text{DOM}}$ , or  $k_{\text{DOM}}/CF_{\text{DOM}}$  after considering the light screening correction.  $CF_{\text{DOM}}$ , the light screening correction factor for DOM-photosensitized reactions, is obtained differently from  $CF_{\text{w}}$ , by integrating in the wavelength range of 280–600 nm, the typical absorption range of DOM.  $CF_{\text{DOM}}$  and  $CF_{\text{w}}$  are generated from Eqs. (1), (2), and (5). This permits  $k_{\text{DOM}}$  to be obtained (Eq. (6)) and used in Eq. (7) to predict the photodegradation rate  $k_{\text{EST}}$ . Using the available values of  $k_{\text{d,obs}}$ ,  $k_{\text{DOM}}$ , and water depth  $z$ , new values of  $CF_{\text{w}}$  and  $CF_{\text{DOM}}$  are determined, with which  $k_{\text{EST}}$  (Eq. (7)) can be determined.

For compounds showing insubstantial absorption in the wavelength range of 280–600 nm (i.e., no assumed direct photolysis,  $k_{\text{d,obs}} \approx 0$ ), but showing a definite degree of degradation due to indirect photolysis, it is fair to simply neglect the impact of direct photolysis in Eq. (7) and count DOM photosensitization as the sole contributor (Eq. (8)).

$$k_{\text{EST}} = \frac{k_{\text{DOM}}}{CF_{\text{DOM}}} \quad (8)$$

### 3.3. Contaminants with other photochemical mechanisms

The aforementioned two models conform to contaminants undergoing direct photolysis and/or indirect photolysis. Implementing these two models might be hazardous for contaminants involved in a different photochemical mechanism. For instance, the fluoroquinolone antibiotics family represented by norfloxacin, ciprofloxacin, and levofloxacin have been demonstrated to be strong photosensitizers, and self-sensitized photodegradation has been proposed as the photodegradation mechanism (Niu et al., 2016; Liang et al., 2015). Knowledge of DOM's role in the photodegradation of fluoroquinolones remains incomplete. Niu et al. (2018) found that DOM quenched the triplet excited states of norfloxacin. Hence, although we could subject an appreciable amount of contaminants to these two models, uncommon cases should be treated with additional caution.

### 3.4. Sunlight irradiance and temperature

The irradiance spectrum of SUNTEST at 400 W/m<sup>2</sup> was compared to the local solar irradiation at noon, July 2013, in Thuwal (Jeddah, Saudi Arabia) (Niu et al., 2014), and the natural sunlight irradiance was found to be approximately twice that of the simulated sunlight at 400 W/m<sup>2</sup>. Similarly, another study delineated an energy level of 510 W/m<sup>2</sup> at noon, June 2005, in Berkeley (CA, USA). It is noteworthy that both measurements were conducted at noon, while fluctuation of solar irradiance throughout the day is definite. Solar incident angle also impacts sunlight input into the aquatic system. Based on the locations and irradiation intensities in the places of interest, one should either set the energy level of the sunlight simulator accordingly or take the local irradiance into account during data processing. For example, 400–500 W/m<sup>2</sup>

was used for the sunlight simulator when the experiments were performed in Saudi Arabia, although the local natural sunlight at noon was much higher (Niu et al., 2014).

Temperature variation also affects the precision of the prediction models. A rearranged form of the Arrhenius equation is given to evaluate the effect of temperature differences between experimental solutions and real waters (Eq. (9)):

$$\ln k_{\text{EST}_2} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) + \ln k_{\text{EST}_1} \quad (9)$$

where  $k_{\text{EST}_1}$  is the predicted photodegradation rate at temperature  $T_1$  (K), the temperature set and maintained in the simulated experiments (e.g., 298 K in Niu et al. (2014));  $k_{\text{EST}_2}$  is the eventually predicted photodegradation rate at temperature  $T_2$  (K), the temperature of the water in the WSP or clarifiers;  $R$  is the universal gas constant (8.314 J/(mol·K)); and  $E_a$  is the activation energy (J/mol), with the value varying with the experimental condition of photolysis or photosensitization. For example, photocleavage of the S–N bond in five-membered sulphonamide antibiotics, i.e., direct photolysis, had an estimated  $E_a$  value of about  $1.2 \times 10^4$  J/mol (Ge et al., 2018). With sulfathiazole as an example, the photodegradation rate in buffered water (pH = 8.0,  $T = 298$  K) was  $3.76 \text{ h}^{-1}$  (Niu et al., 2017). Assuming real water temperature ranges from 5°C to 45°C (278–318 K), the calculated deviation of  $k_{\text{EST}}$  is 30%–40% for a temperature from 25°C to 45°C (or 25°C to 5°C). The impact of temperature on the indirect photolysis of five-membered sulphonamides is even more severe because  $E_a$  for the reactions between reactive species and these sulphonamides was estimated in the range of  $0.84 \times 10^5$  to  $1.5 \times 10^5$  J/mol (Ge et al., 2018). Therefore, the author suggests an experimental temperature in the lab not higher than the natural water, circumventing the additional data processing as shown in Eq. (9). Besides, even one is voluntary to proceed according to Eq. (9), in most instances, the  $E_a$  value of an emerging contaminant or an as-yet unregulated compound is unavailable from the literature.

#### 4. Conclusions

It is worth noting that the real waters described in this paper were pre-filtered (0.45 μm) to remove particulate materials. In other words, the methods and models discussed in this paper solely relate to the contribution of sunlight irradiation to the fate of contaminants. For contaminants reliant on photosensitization for photodegradation,  $k_{\text{EST}}$  in Eq. (7) could be arguably overestimated. This is because  $CF_{\text{DOM}}$  in Eq. (7) is integrated over a wide wavelength range of 280–600 nm. The quantum yield for DOM to photochemically produce reactive species is wavelength-dependent. For example, DOM-photosensitized production of hydroxyl radical had different quantum yields at different wavelengths (Vaughan and Blough, 1998). The quantum yield in a longer wavelength range, e.g., 500–600 nm, is likely much lower than that in the range of 280–400 nm. If the photodegradation results are

processed in a narrower wavelength range instead of 280–600 nm of Eq. (5),  $CF_{\text{DOM}}$  increases, and consequently a lower  $k_{\text{EST}}$  will be obtained instead.

By measuring the water depth and temperature, sampling and characterising the target water, and conducting simulated experiments with standard target compounds, these models could produce constructive results pertinent to the photochemical fate of contaminants in WSP and clarifiers. The methods and models discussed in this paper are theoretically straightforward and operationally user-friendly. Although contaminant removal through exposure to solar irradiation is nonselective, researchers could conduct experiments and construct prediction models for specific compounds of concern. The process could enlighten researchers and water utilities on whether specific contaminants are obliterated by sunlight or whether they persist in the ponds. Also, further development of the current models has the prospect of unleashing the potential to facilitate solar water treatment by supervising the design and operation of such open water treatment units. In addition, experimental results have already demonstrated the effect of solar irradiation in virus and bacteria inactivation (Wenk et al., 2019; Romero-Maraccini et al., 2013; Glady-Croue et al., 2018). In a similar fashion, prediction models could be established to translate experimental results of microbial contaminant photo-inactivation to solar water treatment. Further work should be conducted (1) to utilise the photochemical and photobiological results generated in the laboratory for realistic water treatment; and (2) to disseminate, revamp, and improve the approaches in this paper with the ultimate aim of extensively bridging laboratory-based aquatic studies and practical treatment of waterborne hazardous materials.

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