



# An inescapable fact: Toxicity increase during photo-driven degradation of emerging contaminants in water environments

Yanpeng Gao<sup>1,2</sup>, Xiaolin Niu<sup>1,2</sup>, Mei Wang<sup>1,2</sup>, Guiying Li<sup>1,2</sup> and Taicheng An<sup>1,2</sup>

The occurrence of an enormous group of emerging contaminants (ECs) is of continuous concern for the safety and health of human beings, as well as the ecosystem. Photo-driven technologies especially photochemical and photocatalysis are considered to be promising for effective removal of various ECs from water. Although great advances in photo-driven performance have been achieved recently, the toxicity problem remains an important challenge yet. In this short review, we provided a general overview of the latest researches on the toxicity evolution during photo-driven degradation (including direct and indirect photochemistry, as well as photocatalysis) of ECs. Particularly, the increased toxicity was emphasized, and possible reasons were also analyzed in various photo-driven degradation of organic ECs from the viewpoint of essential characteristics and mechanisms. In light of these mechanisms, we discussed perspectives being performed by toxicologists and environmental chemists to completely eliminate toxicity in the application of photo-driven treatment technologies for ECs and their products in future research.

## Addresses

<sup>1</sup> Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, Guangdong Hong Kong-Macao Joint Laboratory for Contaminants Exposure and Health, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou, 510006, China

<sup>2</sup> Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control, Key Laboratory of City Cluster Environmental Safety and Green Development, School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou, 510006, China

Corresponding author: An, Taicheng ([antc99@gdut.edu.cn](mailto:antc99@gdut.edu.cn))

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## Introduction

During the past few decades, an increasing interest is observable in emerging contaminants (ECs) due to their adverse effect on aquatic and terrestrial organisms, as well as human health, even resulting in illness [1]. These contaminants [2] such as pharmaceuticals and personal care products (PPCPs), and endocrine-disrupting compounds (EDCs), are mostly from anthropogenic activities, and most of them can evade the conventional technologies for wastewater treatment. Accordingly, ECs are frequently detected in multiple environmental matrixes [1,3]. So far, many available approaches are being explored to address the environmental issues of ECs in a water environment. Photo-driven degradation, including photochemical and photocatalytic degradation, is an attractive option for purifying various recalcitrant ECs from water and wastewater, largely due to its environmental sustainability and economical potential.

Generally, photo-driven degradation could have the potential to overcome the energy barrier of spontaneous degradation of ECs under light irradiation [4], resulting in the transformation of ECs into transformation products (TPs) and finally products, such as CO<sub>2</sub> and H<sub>2</sub>O. Photo-driven treatment technologies could be accelerated by various photosensitizers and photocatalysts (i.e. TiO<sub>2</sub>) [5]. The energy provided by photo-irradiation can result in the excitation of ECs themselves, dissolved ions (i.e. NO<sub>3</sub><sup>-</sup>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>), oxidants (i.e. chloramine, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>), and catalysts, leading to the generation of various reactive species (RSs) such as triple excited state, hydroxyl radicals (•OH). Subsequently, these RSs can mediate the degradation of ECs in water environments. Numerous outstanding reviews have summarized the photo-driven degradation of ECs [2,3,5], which present great progress in the removal of ECs, including new approaches, process intensification, as well as removal mechanisms. However, the review about the toxicity evolution during the photo-driven degradation of ECs was relatively rare. The increased toxicity in some cases can counteract the contribution of the photo-driven degradation to the removal of ECs from water. Therefore, this opinion work mainly focused on the toxicity evolution during the photo-driven

degradation of ECs. The aim is to provide insight into a comprehensive understanding of toxicity issues on the photo-driven degradation of ECs in a water environment and analyze the potential reasons of toxicity evolution in different photo-driven scenarios. It helps to improve sustainable photo-driven treatment approaches for completely addressing the toxicity issue of ECs and their products in a water environments.

## Toxicity evolution during photo-driven degradation of organic ECs

### Direct photolysis of ECs

Photo-driven degradation of several ECs often occurs in natural environments and water treatment systems. Generally, two different mechanisms, including direct and indirect photolysis are proposed for photo-driven degradation of ECs. For direct photolysis, ECs could first absorb photon energy by themselves and then undergo heterolysis, pyrolysis, and photo-ionization of compounds, thereby forming various TPs. Accordingly, the decomposition capacity of ECs and the formed TPs in water are largely dependent on their chemical structures and photons with sufficient energy provided by light sources (e.g. solar, UV, and visible light (VL)). For instance, direct photolysis is possible in surface water when ECs can absorb radiation at wavelength ( $\lambda > 290$  nm) in sunlight. The wavelength of light is an important parameter for the decomposition of ECs and the toxicity evolution [6], e.g. shorter UV wavelength can provide higher energy in order of VUV > UVC > UVB > UVA, leading to more effective degradation of ECs in a water environment. Due to the low or no mineralization efficiencies (11–23% in 34 h) [7], direct photolysis may result in several undesired toxic TPs. These products could retain the toxicity or even be more toxic than the original ECs.

Accordingly, the generation and toxicities of TPs vary with the changes in the practical parameters such as the UV flux. Due to the insufficient capability of light absorption, the accumulation of TPs was often reported during the direct photolysis of ECs, such as solar photolysis of a mixture of pharmaceuticals [7] and UV photolysis of parabens [8]. Furthermore, due to the increase of UV flux, some toxic TPs could reduce [9]. The carcinogenic dioxins (e.g. dibenzo-*p*-dioxin) were formed in the photolysis of triclosan under UVA irradiation [10], but not detected under UVC irradiation [11]. It can be explained that UVC irradiation (250–285 nm) can provide more sufficient and higher energy to produce its excited electronic state, and then degrade into TPs via the nonreversible bond cleavage or rearrangement. By contrast, the UVA (325–380 nm) has 300 times lower intensity, thereby leading to the formation of more toxic TPs [12].

Additionally, the multiple dissociable bonds could enhance the direct photolysis of ECs. For instance, due

to the presence of different electron-withdrawing substituents, the aquatic toxicity increased after direct photolysis of lomefloxacin, while decreased for norfloxacin, and ofloxacin [13]. Moreover, the chemical speciation of ECs could significantly affect the toxicity evolution of their direct photolysis, due to the different reaction pathways under different pH values. For instance, direct ring cleavage TPs for cationic fluoroquinolones were obtained, while ring oxidation TPs were obtained for zwitterionic ones [13]. The increased estrogenic activity was also observed in photochemical degradation of ethylparaben, due to the accumulation of degradation intermediate products, photochemically generated oligomers under a water environment [8]. In short, the toxicity evolution during the direct photolysis of ECs could be mainly affected by the wavelength of light, the chemical structure of toxic ECs, and the speciation of ECs, as well as their degradation mechanisms.

### Indirect photolysis of ECs

Compared to direct photolysis, indirect photolysis of ECs is less wavelength-dependent, and especially significant, because they can degrade ECs that resist direct photolysis. In indirect photolysis of ECs, light can act on the substances presented originally in a water environment such as humic acid or inorganic substances. And then various highly reactive species (RSs) (e.g.,  $\bullet\text{OH}$ ,  $^1\text{O}_2$ ,  $\text{O}_2^{\bullet-}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HOO}\bullet$ ,  $\text{Cl}\bullet$ ,  $\text{CO}_3^{\bullet-}$ ) can be generated to degrade ECs in water environment [14]. Among them, several ROSs can rapidly degrade the ECs with large bimolecular rate constants (around  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). Unfortunately, the concentration of these ROSs is often rarely high in the natural environment [15]. Thus incomplete mineralization of ECs usually gives rise to TPs, thereby potentially imposing adverse effects on aquatic organisms and human health. Many previous researches revealed that TPs of several ECs were becoming more toxic than the parent compounds, for instance, parabens [16], triclosan [17], synthetic musks [18,19], and phthalates [20]. The toxicity evolution largely depends on the transformation mechanisms of TPs. For example, the toxicity on luminescence inhibition was observed to be up to three times higher under aerobic than under anaerobic conditions, because of the formation of toxic product 3-hydroxy-propylparaben originating from  $\text{O}_2$  [21]. While the opposite conclusion was obtained in the UV photolysis of doxazosin [22]. Therefore, researches on formation mechanisms of TPs should be paid much attention to in future research.

The toxicity evolution is also largely dependent on the number of RSs produced by different forms of indirect photolysis. For instance, dioxins are favorably formed in the photochemical transformation of triclosan via the cyclization of intermediates at a low concentration of  $\bullet\text{OH}$  [17]. However, at sufficient  $\bullet\text{OH}$ , the

intermediates can preferentially react with  $\bullet\text{OH}$  continuously, instead of dioxins formation. Furthermore, the formation and toxicities of TPs generated by indirect photolysis varies with the changes in the practical parameters, such as the UV flux and oxidant dose (e.g.  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ). The toxic TPs were only observed in UV/ $\text{H}_2\text{O}_2$  when the UV flux was low, while ECs were completely destroyed with the increased UV flux [9]. Based on the enough RSs, indirect photolysis is applied in water treatment processes. Various methods such as UV/ozonation, UV/ $\text{H}_2\text{O}_2$ , Fenton and photo-Fenton processes, were all used to enhance the generation of RSs, further effectively reducing the accumulation of toxic TPs [23]. Nevertheless, the toxicity still increased in the initial step of indirect photolysis of several ECs, due to the rapid formation of toxic TPs [24]. For instance, the acute toxicity increased by almost five times for the UV photodegradation of imipramine in 5 min [24]. Additionally, the estrogenic activity increased by 30% in UV irradiation of ethylparaben for 40 min [8]. Furthermore, on prolonging the reaction time, enough RSs are provided continuously, and further the toxicity could decrease with the TPs oxidation into low toxic products. In summary, raising the formation rate and concentration of RSs could be helpful to reduce ECs quickly and decrease the accumulation of their toxic TPs in a water environment. Additionally, understanding the formation mechanisms of toxic TPs also deserved much attention.

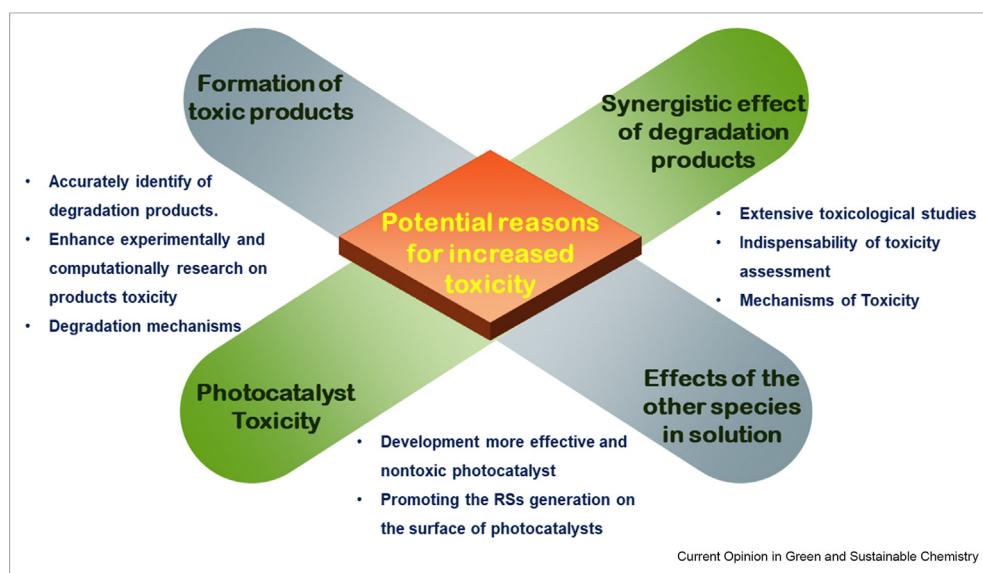
### Photocatalytic degradation of ECs

Compared with the indirect photolysis of ECs in natural water, photocatalytic degradation often exhibits higher

mineralization efficiency for refractory ECs. Fewer kinds but higher concentration of RSs are continuously generated from the wide band-gap photocatalysts such as semiconductors  $\text{TiO}_2$ ; that is, once the provided photons energy is equal to or greater than the band gap of photocatalyst, semiconductor photocatalysts can absorb the energy, and then form a pair of conduction band electron ( $e_{\text{cb}}^-$ ) and valence band hole ( $h_{\text{vb}}^+$ ). Furthermore, the  $e_{\text{cb}}^-$  and  $h_{\text{vb}}^+$  could individually react with molecular oxygen and water, generating various RSs, including  $\bullet\text{OH}$ ,  $\bullet\text{O}_2^-$ , and  $^1\text{O}_2$ . Especially  $\bullet\text{OH}$  as the dominant RSs, can non-selectively degrade ECs via three mechanisms [25], including  $\bullet\text{OH}$ -addition, dehydrogenation, and single-electron transfer reactions. Thus, most ECs can be effectively photo-catalytically degraded with various photocatalysts such as  $\text{TiO}_2$  [26,27] and its composites [28].

So far, approximately 44% of researches on photocatalysis evaluated the toxicity of TPs nowadays, by using bioassays with bacteria, invertebrates, microalgae, plants (phytotoxicity), mammalian cells (genotoxicity) [29]. Most indicated the decrease of the toxicity during the photocatalytic degradation of ECs. However, few researches reported the drastic increase in toxicity, especially the initial step of the photocatalytic degradation of ECs. For example, the toxicity of acyclovir to *P. phosphoreum* increased gradually from 12.3% to 41.2% inhibition when acyclovir was degraded under UV irradiation for 60 min [30]. Additionally, *Vibrio fischeri* tests showed that the toxicity value  $\text{EC}_{50}$  decreased from 27% to 6% under photocatalytic degradation of sulfamethoxazole using Au- $\text{TiO}_2$  [31]. In general, the increased

Figure 1



The potential reasons for the increased toxicity during photo-driven degradation of ECs, and the corresponding strategy for research.

toxicity is mainly attributed to the possible formation of toxic TPs (Figure 1). It may be conjectured that the concentration of the generated RSs cannot meet the conditions for the rapid formation of TPs, thereby either leading to the accumulation of TPs in a water environment. This conclusion was confirmed in the previous study using photocatalysts P25/polydopamine (PDA) [32]. Additionally, both experimental and theoretical approaches are applied to reveal the toxicity evolution in the photocatalytic degradation of ECs and the formation of toxic TPs. For example, as for the preservative parabens [16,27,33], the increase of aquatic toxicity is mainly attributed to the initial formation of mono-hydroxylated paraben. And then the decreases of toxicity are also observed soon with the subsequent formation of di-hydroxylated paraben, TPs with ring cleavage, and ultimately to produce CO<sub>2</sub> and H<sub>2</sub>O. A similar evolution of toxicity is also observed in the •OH mediated transformation of ECs, including bezafibrate, ibuprofen, diclofenac, and carbamazepine [9].

Several results from the experimental evaluation of toxicity could clearly imply that more toxic TPs are generated and decomposed. However, identification of the toxic TPs is still a great challenge, due to the lack of the standard sample of TPs, often low concentrations, and the complexity of the matrices [34]. Several computational approaches (Figure 2) are performed to screen the toxic TPs using EOCSAR, VEGA platform, Toxtree, EPIWEB, TEST, COMPTOX, CAESAR, VEGA, and ACD/Percepta [35]. Several toxic TPs were found to be formed during photocatalytic degradation of parabens [16], pemetrexed [36], synthetic musk [19], and imatinib [37], although some parent compounds with negligible toxicity. Although longer time could achieve for the complete photocatalytic degradation

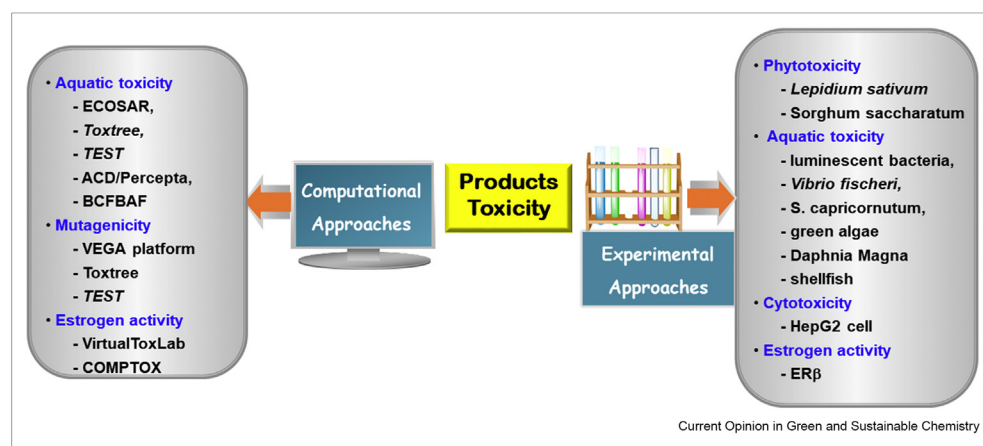
and/or mineralization of ECs, as well as their toxic TPs under certain reactive species, the increased operational cost is often considered for practical application of photocatalysis in water treatment. To balance the generation of toxic TPs and economic effectiveness, the toxicity assessment and formation mechanisms of toxic TPs are of crucial significance. Additionally, the possible toxicity had resulted from the photocatalysts, such as the metal release from the dissolution and/or photo-dissolution of the metal-containing photocatalysts [29]. We should pay much attention to improving purification conditions based on the researches on their formation mechanisms, further avoiding the generation and/or accumulation of toxic TPs during the photocatalytic degradation of ECs.

### Outlook and perspectives

In short, toxicity elimination should be a final goal for the photo-driven degradation of ECs, rather than the decrease of concentration only. So far, very limited available information was reported yet on the toxicity evolution of TPs during the photo-driven degradation of ECs. The existing researches observed that the increased toxicity in several ECs, despite the fact that the original ECs can be completely eliminated. Accordingly, further investigation on the toxicity evolution is still needed, which is crucial for evaluating the efficiency of toxicity decrease in a real water environment. Moreover, the following suggestions are still necessary for future research.

- 1) **Indispensability of toxicity assessment.** For practices, despite the fact that photo-driven degradation can rapidly eliminate target ECs, it is also important to further evaluate the treatment efficiency and toxicity evolution of TPs. Namely, the performance of a

Figure 2



The common experimental and computational approaches for toxicity assessment during the photo-driven degradation (including photolysis and photocatalysis) of ECs.



photo-driven degradation system should include the toxicity evolution together with the removal of original ECs, as well as TPs.

- 2) **Extensive toxicological studies.** The existing toxicological studies during the photo-driven degradation of ECs mainly focused on aquatic toxicity towards luminescent bacteria, green algae, and fish. But the adverse effects on human health are largely unclear yet. Thus, extensively effective studies on human health are still urgently required in future research. Moreover, the recognized assessment approach should be developed considering the integration of different species belonging to different functional levels.
- 3) **Identification of toxic degradation products.** It is very important to highlight the potential toxicity of individual TPs and further elucidate the formation mechanisms of toxic TPs, as well as the identification of TPs. In particular, several unidentified products could cause serious damage to humans, although at a low concentration.
- 4) **Toxic action of mechanisms.** The existing researches mainly focused on the toxicity evolution during the photo-driven degradation of individual ECs or one kind of ECs, but their toxic action of mechanisms and the toxicity resulted from the interaction between different ECs degraded TPs were rarely concerned, as well as the toxicity interaction between photocatalyst and degradation products.

### 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.

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