



REVIEW ARTICLE

Production of higher toxic intermediates of organic pollutants during chemical oxidation processes: A review



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Abstract Incomplete degradation of organic pollutants might lead to the increased environmental risk because of the potentially toxic intermediates, especially during chemical treatment processes. However, toxicity changes of common pollutants during chemical oxidation are still unclear because the toxicity results were easily influenced by oxidation means, reaction condition, toxicity assessment method, etc. This review summarized and evaluated the toxicity test and prediction methods commonly used in oxidation process, and then the potential toxic intermediates and their possible producing pathways was proposed as for polycyclic aromatic hydrocarbon, phenols, azo dyes, organophosphorus, organonitrogens, organochlorine pesticides, pharmaceuticals of different classes. Various intermediates, especially the oxygen-containing ones, such as hydroquinone-, benzoquinone-, catechol-like products and halogenated ones are prone to have higher toxicity while some of the dimers and polymers are highly toxic and refractory. In addition, environmental elements such as DOM and halogen ion have the potential to enhance the toxicity. The strategies to reduce the residual toxicity were usually to strengthen the reaction, for example, to increase the oxidant concentration or prolong reaction time. Coupling of multiple technologies is also an effective strategy.

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1. Introduction

Chemical oxidation is a popular technology applied in the water treatment and soil remediation processes due to the benefits of its low energy consumption, low cost, and applicability for a variety of organic pollutants. The widely used chemical oxidation methods include Fenton and Fenton-like, permanganate, persulfate, peroxy-monosulfate, chlorination, sonolysis, photolytic and photocatalytic degradation, ozonation, ferrate oxidation, etc. The oxidants either

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utilize their own oxidizing properties or produce highly reactive species, such as hydroxyl radicals ($\bullet\text{OH}$), sulfate radicals, superoxide radicals ($\bullet\text{O}_2^-$), singlet oxygen, to degrade organic pollutants (Kanakaraju et al., 2018; Wang and Wang, 2020). When chemical oxidation technology is used to treat water or soil, a continuously decreased toxicity is a desirable benefit. However, in some cases the intermediates are more toxic or even less biodegradable than the parent compound, and if they were discharged to the environment, they might pose threats to the ecosystem or human health and have the potential to cause secondary environmental problems (Usman et al., 2016; Wang and Wang, 2021). For example, 2-anilino-5-[(4-methylpentan-2-yl)amino]cyclohexa-2,5-diene-1,4-dione (6PPD-quinone), an ozonation product of the globally ubiquitous tire rubber antioxidant N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), has the potential to kill adult salmon (Seiwert et al., 2022; Tian et al., 2021). Therefore, when assessing the overall performance of a chemical oxidation treatment technique, the toxicity and persistency of reaction intermediates should also be taken into account, but there is still no general agreement or standard on the assessment method. Although that some studies have measured or calculated the toxicity of oxidative intermediates (Cao et al., 2013; Li et al., 2022a; Magdeburg et al., 2012; Trovó et al., 2013), they were fragmented and most of the intermediates are less harmful than the parent compound. Seldom studies have systematically examined the potential highly toxic intermediates and their formation pathway. Therefore, it is still difficult to identify which pollutants should be given special consideration when considering chemical oxidation treatment.

In this work, the toxicity test methods suitable for evaluating toxicity change during chemical oxidation process were summarized. Then almost a thousand of articles were screened and five categories of pollutants, namely polycyclic aromatic hydrocarbons (PAHs), phenol, azo dyes, pesticide, and pharmaceuticals, obtained relatively focused attention as having the potential to increase toxicity. An inventory of potential highly toxic intermediates of these pollutants was thus established, and their generation mechanisms were summarized. Furthermore, the environmental elements that might make chemical oxidation treatments more harmful are summarized, and potential solutions to lessen residual toxicity are proposed. This review will provide insights to establish a more comprehensive approach to assess the overall effectiveness and environmental benefits of chemical oxidation treatment techniques, help identify which pollutants should be given special consideration when considering chemical oxidation treatment, and provide some reference on how to control this potential secondary risk.

2. Toxicity assessment methods

The common toxicity assessment methods reflecting oxidation effectiveness are summarized in this section. A total of 189 papers reporting changes in toxicity caused by oxidation were collected, and the application ratio of different toxicity assessment methods is summarized in Fig. 1. As some studies used more than one method, a total of 241 tests were recorded. Results indicated that the most widely used method was luminescence inhibition test, which was adopted in 34.4% of the reviewed tests, and *Alivibrio fischeri* (including *Vibrio fischeri* (*V. fischeri*)) were the most commonly used test species. The frequency of other test techniques' use is as follows: aquatic toxicity test (using indicator species like brine shrimp, fish, protozoa, and fleas) > bacteriostatic impact test > growth inhibition observation of plants. Other test methods such as genotoxicity, estrogenic activity, endocrine disrupting effects were also applied, but in only a few studies. It is noteworthy that remaining oxidants and radicals must be completely eliminated before conducting any toxicity assessments due to their

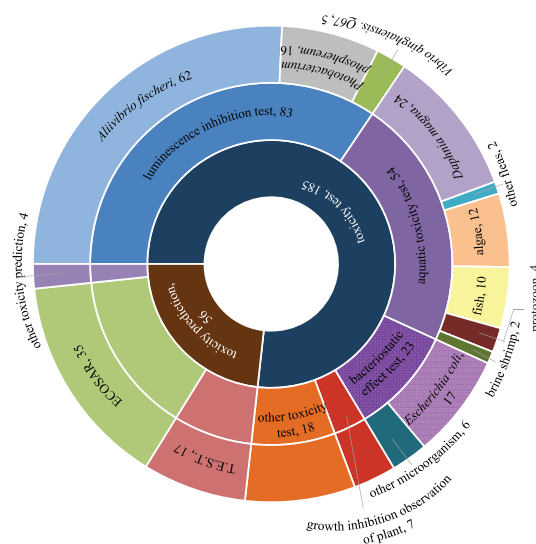


Fig. 1 Application ratio of different toxicity assessment methods in oxidation process.

obvious impact on the toxicity (Gernjak et al., 2006; Mantzavinos and Kalogerakis, 2005; Ribeiro et al., 2015).

2.1. Luminescence inhibition test

The luminescent bacteria assay is the most frequently employed acute toxicity test method due to its convenient operation, high sensitivity, and low cost (Parvez et al., 2006; Zhang et al., 2017). This method was used with various pollutants in either water or soil medium (Lu et al., 2010; Usman et al., 2016). Studies have revealed a strong association between the toxicity of organic pollutants and the luminance within a certain concentration range of pollutants (Ma et al., 2014). The marine luminescent bacterium *V. fischeri*, *Photobacterium phosphoreum* (*P. phosphoreum*) and freshwater bacterium *Vibrio qinghaiensis* Q67 are the three most commonly used luminescent bacteria (Wang and Wang, 2019; Xiong et al., 2020), in which *V. fischeri* is used in the international standard method (International Organization for Standardization, 2007), and *P. phosphoreum* is used in the national standard method of China (Ministry of Ecology and Environment of The People's Republic of China, 1995). Marine luminescent bacteria need to add a certain amount of NaCl (2%~5%) under the determination conditions, which is different from the freshwater test system. Therefore, in 1985, Chinese scholars introduced *Vibrio qinghaiensis* Q67 as the test object of chemical toxicity test and it was gradually widely used (Zhu et al., 1994). In the supporting information, Table S1 provides an overview of the most widely used international published toxicity standard test methods.

2.2. Aquatic toxicity test

Common aquatic toxicity test methods have been summarized in Whole Effluent Toxicity methods by U.S. Environmental Protection Agency (U.S. EPA) (EPA, 2016). The test species used to assess the oxidation-induced toxicity include water flea, algae, fish, brine shrimp, protozoa, and so on.

Water fleas are widely distributed in freshwater, among which *Daphnia magna* (*D. magna*) is the most commonly used test organism to evaluate the toxicity, and its median lethal concentration (LC_{50}) and median effect concentration (EC_{50}) by activity inhibitory are usually used as acute toxicity evaluation indexes. For example, Garcia-Muñoz et al. (2020) used the 48 h LC_{50} and EC_{50} values of *D. magna* to determine the toxicity changes of glyphosate and myclobutanil pesticides in photocatalytic degradation. Dehghan et al. (2019) measured the LC_{50} of *D. magna* at 24, 48, 72 and 96 h, respectively, so as to assess the toxicity change of metalaxyl pesticides under the graphene/ Fe_3O_4 / ZnO ternary nanomaterials catalyzed photodegradation.

Algae, which are crucial to the balance and stability of aquatic ecosystems, is another widely used organism because of their small size, rapid reproduction, ease of isolation and culture. The toxicity symptoms could be observed directly at the cellular level as well. Common evaluation indexes include the inhibition effect on algae growth and the effect on photosynthesis. Zhang et al. and Rao et al. (Rao et al., 2019; Zhang et al., 2020) observed the growth inhibition to *Chlorella vulgaris* (*C. vulgaris*) to track the toxicity change during sulfamethoxazole (SMX) and diclofenac oxidation in UV-persulfate and $LaFeO_3$ -catalyzed peroxymonosulfate systems, respectively. Other algae such as *Selenastrum capricornutum*, *Chlorella pyrenoides*, and *Desmodesmus subspicatus* were also used as the test organisms in such studies (Fang et al., 2013; Kim et al., 2012; Zhang et al., 2016; Zhu et al., 2016).

Fish bioassay could be used to predict the possible effects on vertebrates, and even humans (Kime, 1999; Wester et al., 2004). Zebrafish is the most widely used fish species as the standard test organism for acute toxicity test. In addition to acute mortality, the main toxicity indicators also include embryo hatching rate, teratogenic effect, endocrine disrupting effect, etc. Willis and Oris (Willis and Oris, 2014) comprehensively evaluated the photocatalytic degradation toxicity of 4-nitrophenol with zebrafish mortality, hatching rate and phenotypic abnormalities. de Sousa Filho et al. (2019) evaluated the toxicity of etoposide solution (an antineoplastic agent) after photodegradation by using zebrafish embryo acute lethal effect, comet assay and micronucleus test.

Immobilization effects of other protozoa such as *Tetrahymena pyriformis*, *Caenorhabditis elegans*, *Chironomus riparius* and brine shrimp (*Artemia salina*) were also used at a low frequency according to our statistics.

2.3. Other toxicity tests

Microorganism test were mainly used to assess the bacteriostatic effect of antibiotics or phenol toxicity of in oxidation process, and *Escherichia coli* (*E. coli*) was the most commonly used (Carneiro et al., 2020; Huang et al., 2020; Liu et al., 2020; Olak-Kucharczyk and Ledakowicz, 2017; Zhang et al., 2018).

Seed germination rate, root elongation inhibitory effect, and growth effect (biomass, height, length, etc.) of plants such as *Lemna minor*, broad beans, onion, lettuce are also important indicators to measure the toxicity during oxidation process, which could be used in both wastewater and soil (Castro et al., 2014; Hou et al., 2014; Magdeburg et al., 2012; Zhang et al., 2004).

In addition to the above biological experiments, a few studies have looked into how other biological cells' genotoxicity, estro-

gen activity, and endocrine disrupting effects change as a result of chemical oxidation. Silva et al. (2021) tested the genetic toxicity of onion bulb root cells using granular activated carbon combined with chemical oxidant to treat wastewater. Cédât et al. (2016) tested the change of estrogenic activity in wastewater in UV photocatalysis and UV/ H_2O_2 system. Because these test methods are more complex and time-consuming than acute toxicity, their application rate is relatively low.

Since the analysis on intermediates in soil is much more difficult than that in aqueous media, studies on the toxicity changes of organic contaminants following oxidation in soil are far less common, and such studies are mainly focused on PAH and pesticides. It is noteworthy that the results of soil toxicity tests may be related to the impact on soil properties, in addition to the transformation of the contaminants themselves (O Mahony et al., 2006; Olmez-Hanci et al., 2014; Sirguey et al., 2008; Tsitonaki et al., 2008).

2.4. Toxicity prediction method

In addition to conducting overall toxicity tests on the reaction system, toxicity prediction based on intermediate identification is extensively adopted. The intermediates could be analyzed with liquid chromatography/mass spectrometry (LC/MS), gas chromatograph/mass spectrometer (GC/MS), ion chromatography, etc. Then, the toxicity of the intermediates could be predicted with quantitative structure-activity relationship (QSAR) method (Mansouri et al., 2018), or by consulting literatures. The QSAR method is used more commonly because it can eliminate the problem resulted from inconsistent toxicity data sources and is easier to operate. The free software Ecological Structure-Activity Relationship Model (ECOSAR) and Toxicity Estimation Software Tool (T.E.S.T.) developed by the U.S. EPA are the most commonly used toxicity prediction software.

2.4.1. Ecosar

ECOSAR has a QSAR database of aquatic toxicity overlaid with an expert decision tree for choosing the proper chemical categories based on chemical structures. It classifies chemicals into 111 categories of neutral organic compounds, highly toxic organic compounds, surfactants, polymers, etc., and has 704 QSAR models. It can assess the toxicity of chemicals by entering the chemical name, CAS number and other information, or drawing the compound structure diagram. ECOSAR can be used to predict chemicals' acute and chronic toxicity to aquatic organisms such as fish, aquatic invertebrates and plants. It also compares the toxicity prediction endpoint to the compound's water solubility. ECOSAR is only applicable to the prediction of acute toxicity for compounds with $\log K_{ow} \leq 5.0$ and chronic toxicity for compounds with $\log K_{ow} \leq 8.0$.

2.4.2. T.E.S.T.

Similar to ECOSAR, the user can predict the toxicity of a compound by entering its information in T.E.S.T. software. T.E.S.T. had seven toxicity endpoints, including 96-hour fathead minnow LC_{50} , 48-hour *D. magna* LC_{50} , tetrahymena pyriformis 50 percent growth inhibition concentration (IGC_{50}), oral rat 50 percent lethal dose (LD_{50}), bioconcentration factors and developmental toxicity of fish, and Ames mutagenicity. In contrast to ECOSAR, T.E.S.T. is not only suitable for aquatic toxicity prediction (Ji et al., 2020; Li et al., 2022a; Liu et al.,

2020). As a result, the toxicity of intermediate oxidation products in soil was usually predicted with T.E.S.T. (Shi et al., 2017; Wu et al., 2022; Yuan et al., 2020).

As shown in Fig. 1, ECOSAR was used in 35 studies and T. E.S.T. was used 17 times. The use ratio of toxicity prediction method was about 23.2% in the collected studies.

2.5. Comparison of different toxicity assessment methods

Acute toxicity test is the most often utilized test index in the toxicity assessment of the chemical oxidation process of pollutants. Other toxicity assessment methods are relatively rarely used due to complicated procedures, long time, and lack of standard methods. However, existing studies have shown that different toxicity test methods may lead to differences in conclusions. For example, for phenol, although the oxidation intermediate is more toxic according to the toxicity database, the direct toxicity test of the reaction solution has reached the opposite conclusion (Zazo et al., 2007); for SMX, when *C. vulgaris* is used as the test substance, the solution toxicity will slightly increase after photocatalytic treatment (Zhang et al., 2020). This is consistent with the results from the *V. fischeri* assay (Zhang et al., 2016), but not the results from *D. magna* assay (Yazdanbakhsh et al., 2020). In addition, some pollutants have specific toxicity. For example, organochlorine pesticides often act by poisoning the nervous system of the target organism (Costa, 2015). For another, chemicals such as nalidixic acid, chloramphenicol and streptomycinsulfate have delayed toxicity. The standard rapid toxicity determination method will make the measured value smaller, resulting in the easily overlooked harm to the environment (Froehner et al., 2000). Therefore, diversified toxicity endpoints should be covered when selecting toxicity test indicators according to the risk assessment needs and the toxicity mechanisms of the parent compound. Toxicity test methods could reflect the real toxicity of the oxidation system objectively, but toxicity experiments are costly and the results are more sensitive to reaction conditions.

Using the prediction method to assess product toxicity can effectively reduce the number of toxicity experiments, but it has the following shortcomings: (1) Not all toxicity endpoints can be obtained in a predictive manner, especially the ecotoxicity and mammalian chronic toxicity that can be used for soil ecological and human health risk assessment; (2) Degradation products need to be identified before prediction, and inaccurate identification of degradation products may lead to misjudgment of toxicity; (3) The prediction method is only applicable to a single organic compound, while the toxicity of the pollutant oxidation process is often formed by the combination of pollutant itself and a variety of intermediate products. Using the prediction method may cause a big difference compared with the actual toxicity. The combined use of toxicity test and prediction method would deepen the understanding on mechanisms of increased toxicity.

3. Highly toxic products of typical pollutants

3.1. PAHs

PAHs are widely distributed in soil and sediment, with carcinogenic, teratogenic and mutagenic effects. Some PAHs are

difficult to biodegrade (Musa Bandowe et al., 2010; Wilson and Jones, 1993; Zhao et al., 2021). Sixteen kinds of PAHs have been listed as priority pollutants by U.S. EPA based on their wide distribution and strong toxicity.

The oxidation intermediates of PAH mainly consist of oxygen-containing polycyclic aromatic hydrocarbons (oxy-PAHs) such as quinone, ketone, aldehyde, carboxylic acid, etc. (Forsey et al., 2010; Lundstedt et al., 2006). Some oxy-PAHs have high toxicity and mutagenicity (Chesis et al., 1984; Reisen and Arey, 2002; Xue and Warshawsky, 2005), such as benzo[a]pyrene quinone and phenanthrenequinone, which show mutagenic activity and can directly react with DNA (Chesis et al., 1984). The epoxy products generated by oxidation of acenaphthene and acenaphthylene can also act as electrophilic reagents to cause DNA damage (Reisen and Arey, 2002). The main photooxidation product of phenanthrene, i.e., 9,10-phenanthraquinone, has been proved to have a stronger potency to inhibit duckweed growth and luminous intensity of luminescent bacteria than the parent compound (McConkey et al., 1997). According to the test of *Lemna gibba* L. G3 growth inhibition effects conducted to 11 main photooxidation products (anthraquinones and hydroxyanthraquinones) of anthracene, about half of the further photo-degradation products of anthraquinones were more hazardous than their parent compounds. Among them, 2-hydroxyanthraquinone is the most toxic compound in anthracene oxidation products, and is not subject to further photooxidation, showing the risk of persistent environmental damage (Mallakin et al., 1999). Liao et al. (2014) studied the formation and transformation of PAH reaction by-products in the persulfate oxidation process of PAHs from the soil of a coking plant. The results showed that there were oxy-PAH in the soil, such as 9H-fluoren-9-one, 1H-phenalen-1-one, 1(2H)-acenaphthylene and 1,8-naphthalic anhydride, and more oxy-PAHs were generated after oxidation, including naphthalene 1-(2-hydroxypropyl), 1H-phenalen-1-one, dibenzofuran, 9H-fluoren-9-one, 1,8-naphthalic anhydride. Among them, the naphthalene 1-(2-hydroxypropyl) and 1,8-naphthalic anhydride of the highest content were presumed to be the oxidation intermediates of 1-methyl anthraquinone and acenaphthylene, respectively, and the rate of further oxidative removal was slow. But fortunately, PAHs and most of its oxidation products were removed after sufficient oxidation, reducing the integrated environmental risk. Shemer and Linden (2007) used photocatalytic oxidation to degrade the mixed pollution solutions of fluorene (FLU), dibenzofuran (DBF), dibenzothiophene (DBT) in water, and found that the toxicity of the mixed solution was enhanced during the oxidation process, which may be related to the oxidation intermediate product oxy-PAHs. In addition to oxy-PAHs, the ozonation of phenanthrene will also result to the formation of biphenyl compounds, which are difficult to biodegrade (O Mahony et al., 2006; Stehr et al., 2001). Toxicity tests by Stehr et al. (2001) using *Bacillus subtilis* and garden cress *Lepidium sativum* showed that compared with phenanthrene itself, the soil after ozonation showed higher dehydrogenase inhibition toxicity or cress growth inhibition, which may be attributed to intermediate products. The main intermediate products were identified as biphenyl compounds including 2,2'-biphenyldialdehyde, 2'-formyl-2-biphenylic acid and diphenic acid. What's more, the oxidizable and biodegradable properties of pollutants were not significantly improved after

ozonation. A list of potentially produced highly hazardous intermediates from the oxidation of various pollutants is presented in Table 1.

3.2. Phenols

Phenolic compounds have gained extensive attention because of their high toxicity and the frequent presence in industrial wastewaters and natural environment (Ding et al., 1995; Ekpe et al., 2022). There have been several literatures focusing on the ecotoxicity of phenols after oxidation treatment, and most of them reported an enhanced toxicity in the early stage of phenol oxidation (Santos et al., 2004; Santos et al., 2006; Xia et al., 2017; Zazo et al., 2007). The reason was the production of intermediates such as hydroquinone, 1,4-benzoquinone and catechol, but the intermediates could further transform into low-toxicity organic acids, such as acetic, oxalic, and maleic acids. The typical evolution process of phenol was shown in Fig. 2. However, several studies found that the ecotoxicity was reduced in neutral or basic medium (Santos et al., 2006; Zazo et al., 2007).

Noticeable toxicity increases have been also reported during the oxidation process of cresol, nitrophenol and chlorophenol, and it could be attributed to the production of substituted hydroquinone, 1,4-benzoquinone and catechol (Santos et al., 2006; Svenson and Hynning, 1997). It is noteworthy that toxic polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) formation was observed in the oxidation of chlorophenols, which might cause further toxicity increase in oxidation process, and changing the operating conditions is conducive to mitigate toxic byproducts (Altarawneh et al., 2007; Fukushima and Tatsumi, 2001; Vallejo et al., 2013; Vallejo et al., 2015; Weber, 2007).

There was also an increase in ecotoxicity during the initial stages of bisphenol A (BPA) oxidation. A significant correlation existed between the toxicity patterns and its major transformation products, such as benzoquinone, hydroquinone, styrene, *p*-isopropyl phenol, etc. (Han et al., 2015; Olmez-Hanci et al., 2013; Zhou et al., 2020) Richard et al. (2014) found that the UV/H₂O₂ treatment of BPA revealed cytotoxic by-products but did not identify the specific compounds. In addition, the acute toxicity assay suggested that the degradation products of bisphenol S (BPS) and bisphenol F (BPF) were more toxic than their parent compounds, and the highly toxic products were identified as self-coupling dimers or polymers, such as 4,4'-dihydroxybibenzyl and 4,4'-dihydroxybiphenyl. They could undergo further oxidation into hydroxylation products during the reaction (Lu et al., 2019; Yang et al., 2020). Conversely, dimers generated during BPA oxidation seems not to increase the acute toxicity during photo-Fenton-like treatment, which might be due to the limited amount of products (Molkenthin et al., 2013).

3.3. Azo dyes

Some studies have reported the highly toxic oxidation intermediates of azo dyes (de Luna et al., 2014; Glaze, 1986; Neamtu et al., 2003; Wang et al., 2003). For example, Wang et al. (2003) confirmed the formation of high toxic by-products of *C.I. Remazol Black 5* by the luminescence test (*V. fischeri*) and the neutral red cytotoxicity assay (rat hepatoma cells).

Neamtu et al. (2003) observed the temporary increase in luminescent bacteria inhibition during the UV/H₂O₂ treatment of *C.I. Reactive Yellow 84*, *Vat Green 3*, *Reactive Black 5*, *Acid Orange 7* (AO7), and *Food Red 17* also produced more hazardous degradation products than the parent dyes, according to acute test with *Daphnia similis* and chronic tests with *Ceriodaphnia dubia* and *Pseudokirchneriella subcapitata* (de Luna et al., 2014). It has been pointed out that the reagent dosages and treatment period played a crucial role in the detoxification of dyes, meaning that the toxic intermediates could be degraded readily (Castro et al., 2014; de Luna et al., 2014; Khadhraoui et al., 2009; Zhao et al., 2010). However, seldom studies determined the structures of the highly toxic intermediate (Glaze, 1986). The toxicity of AO7 during electro-Fenton treatment increased rapidly at the early stage, in line with the emergence of intermediate hazardous aromatic compounds including 1,2-naphthaquinone (NAPQ) and 1,4-benzoquinone (BZQ), which were formed through the breakage of the azo linkage (Alderete et al., 2021; Le et al., 2016; Velegraki et al., 2006; Zhao et al., 2010). Fig. 3 is the schematic diagram on the toxicity transformation mechanism of AO7.

In addition, as the commercial azo dyes usually contain some impurities such as synthetic precursors, dispersing agents, and by-products, the toxicity of the impurities during oxidation should be paid attention (Zhang et al., 2004). As the important raw material of dyestuff, nitrobenzene and diphenylamine experienced a trend of toxicity that was initially increasing and then reducing during photocatalytic treatment. The toxic may be related with the oxygenated intermediates (Bolduc and Anderson, 1997; Li et al., 2009). Wet air oxidation of nitrotoluenesulfonic acid (NTSA) also produced some more toxic intermediates than NTSA itself such as cresol, nitrobenzene, phenol, quinolinol, 2-chlorophenol, etc (Hao and Phull, 1993).

3.4. Pesticide

3.4.1. Organophosphorus

Pesticides are produced in vast quantities and employed in a variety of agricultural processes. They were distributed in wastewaters, soil and groundwater from pesticide manufacturing plants, and chemical oxidation have been proven useful for their removal (Bhandari et al., 2020; Paul et al., 2006). The most widely utilized pesticides is organophosphorus (OP), which accounts for 40% of global use and roughly 70% of consumption in the United States (Vasseghian et al., 2022). OPs have an irreversible inhibition of acetylcholinesterase (AChE) enzyme, which would cause acetylcholine to accumulate and cholinergic receptors to become overactive in various regions of the body (Chowdhary et al., 2014; Pope, 1999). Toxicity increase of OPs during chemical oxidation have been noticed in some studies. For example, as for malathion (S-1, 2-bis(ethoxycarbonyl)ethyl-O,O-dimethyl phosphorodithioate), which has the highest rate of the total OP pesticide consumption (Vasseghian et al., 2020; Vasseghian et al., 2022), the treated effluent's luminescence and AChE toxicity all dramatically increased during the Fenton, photo-Fenton, and sono-photo Fenton processes. Malaoxon, diethyl maleate, diethyl malate, ethyl 2-hydroxysuccinate, and d-malate were recognized as the intermediates by oxidative desulfuration, the replacement of oxygen for sulfur on the P = S bond

Table 1 Potential highly toxic oxidative intermediates of various pollutants.

No.	Category	pollutants	oxidizing agent	reaction medium	toxicity test method	proposed highly toxic intermediates	refractory or not	references
1	PAH	phenanthrene	simulated solar radiation (SSR)	water	luminescence of <i>Photobacterium phosphoreum</i> , growth inhibition of <i>Lemna gibba</i> (duckweed)	9,10-phenanthrenequinone (oxy-PAHs)	Y	(McConkey et al., 1997)
2	PAH	phenanthrene	ozone	soil	contact assay with <i>Bacillus subtilis</i> and Root elongation test with <i>Lepidium sativum</i>	2,2'-biphenyldialdehyde, 2'-formyl-2-biphenylic acid, diphenic acid (biphenyls)	Y	(Stehr et al., 2001)
3	PAH	anthracene	photosynthetically active radiation (PAR) and SSR	water	growth inhibition of the duckweed <i>Lemna gibba</i> L. G-3	2-hydroxyanthraquinone (oxy-PAHs)	Y	(Mallakin et al., 1999)
4	phenol	phenols	Fenton, wet catalytic oxidation, catalytic oxidation	water	Microtox toxicity test	catechol, hydroquinone, p-benzoquinone and their derivative compounds	N	(Santos et al., 2004; Santos et al., 2006; Svenson and Hynning, 1997; Zazo et al., 2007)
5	phenol	2-chlorophenol	Fenton	water	retrieve toxic equivalency factor data	PCDD/PCDF	Y	(Altarawneh et al., 2007; Vallejo et al., 2015)
6	phenol	bisphenol A	thermally activated persulfate	water	luminescence inhibition with <i>V. fischeri</i>	2,3-dimethyl benzoic acid (DMBA)	N	(Olmez-Hanci et al., 2013)
7	phenol	bisphenol A	ferrate(VI)	water	luminescence inhibition with <i>V. fischeri</i>	benzoquinone, hydroquinone, styrene	N	(Han et al., 2015)
8	phenol	bisphenol A	cyclodextrin enhanced photocatalytic system	water	T.E.S.T.	catechol derivatives formed by bond breaking such as 4-prop-1-en-2-ylbenzene-1,2-diol; hydroxylated products such as 5-hydroxybisphenol A, 4,5-bisphenol-o-quinone; isopropyl removal product such as 4,4'-dihydroxybiphenyl; coupling products	The biphenyl and coupling products are refractory	(Zhou et al., 2020)
9	phenol	bisphenol S (BPS)	peroxydisulfate (PDS) ordissolved oxygen (DO) in ultrasound (US) system	water	luminescence inhibition with <i>V. fischeri</i>	bond breaking product (p-hydroxybenzenesulfonic acid), oxygen-connected coupling product and hydroxylated product (BPS catechol)	The coupling product is refractory	(Lu et al., 2019)
10	phenol	bisphenol F	ferrate [Fe(VI)]	water	luminescence inhibition with <i>Photobacterium phosphoreum</i> and ECOSAR	coupling products and demethylation product	Y	(Yang et al., 2020)
11	azo dye	AO7	Electro-Fenton process using carbon felt cathode	water	luminescence inhibition with <i>Vibrio fischeri</i>	1,2-naphthaquinone, 1,4-benzoquinone	N	(Le et al., 2016)
12	azo dye	nitrotoluenesulfonic acid	wet air oxidation	water	toxicity test on the enriched nitrosomonas culture	cresol, nitrobenzene, phenol, quinolinol, 2-chlorophenol (oxy-products)	N	(Hao and Phull, 1993)

Table 1 (continued)

No.	Category	pollutants	oxidizing agent	reaction medium	toxicity test method	proposed highly toxic intermediates	refractory or not	references
13	pesticide	chlorpyrifos	ultrasonic irradiation	water	luminescence inhibition with <i>Vibrio qinghaiensis</i> Q67	chlorpyrifos oxon	Y	(Zhang et al., 2011)
14	pesticide	alachlor	Fenton	water	luminescence inhibition with <i>Vibrio fischeri</i>	2,6-diethylaniline	Y	(Sanchis et al., 2014)
15	pesticide	diuron	Fenton	water	luminescence inhibition with <i>Vibrio fischeri</i>	3,4-dichloroaniline	Y	(Sanchis et al., 2014)
16	pesticide	atrazine	Fenton	water	luminescence inhibition with <i>Vibrio fischeri</i>	desethyldeiso-propyl-2-hydroxyatrazine	Y	(Sanchis et al., 2014)
17	pesticide	fluopyram	UV light ($\lambda \geq 200$ nm) and SSR ($\lambda \geq 290$ nm).	water	luminescence inhibition with <i>Vibrio fischeri</i>	hydroxylated products	Y	(Dong and Hu, 2016)
18	pesticide	DDT	Fenton-like system with zero-valent iron, EDTA and air (ZVI/EDTA/Air), photodegradation, peroxymonosulfate activation by MnO ₂	soil and water	influence on algae growth	2,2-bis(4-chlorophenyl)-1-chloroethylene (4,4'-DDMU), DDE, dichlorobenzophenone	Y	(Cao et al., 2013; Hong et al., 1997; Liu et al., 2021; Megharaj et al., 1999)
19	pharmaceuticals	florfenicol	electrochemical advanced oxidation	water	luminescence inhibition with <i>Vibrio fischeri</i>	chlorine-containing hydroxylated products and inorganic chlorines	N	(Periyasamy et al., 2022)
20	pharmaceuticals	lomefloxacin	direct, indirect, and self-sensitized photolysis	water	luminescence inhibition with <i>Vibrio fischeri</i>	product derived by defluorination and piperazing ring oxidation	N	(Zhang et al., 2019)
21	pharmaceuticals	diclofenac	•OH oxidation by pulse radiolysis experiment	water	luminescence inhibition with <i>Vibrio fischeri</i>	chloroderivatives	N	(Yu et al., 2013)
21	pharmaceuticals	carbamazepine	UV-radiation, chlorine dioxide	water	luminescence inhibition with <i>Vibrio fischeri</i> , biomass growth of <i>Pseudokirchneriella subcapitata</i> , <i>daphnia</i> immobilization	Acridine, 9(10H)-acridone	UV irradiation could enhance the biodegradability of carbamazepine residues	(Donner et al., 2013; Kosjek et al., 2009)

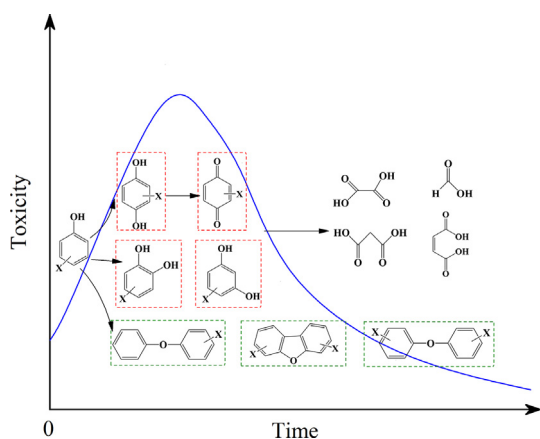


Fig. 2 The representative degradation pathway and toxicity evolution of phenol. The chemicals in red box are more toxic than the parent, and those in green are refractory in addition to highly toxic.

through oxidation, and hydrolysis processes mechanisms (Vasseghian et al., 2022). We calculated the acute toxicities of the intermediates with T.E.S.T. (version 5.1), and the results showed the malathion oxon had the higher acute oral toxicity to rat than the parent compound (see Table S2 in Supporting Information), which was consistent with the results from previous study with the LC_{50} to larval *Rana boylii* as the indicator (Sparling and Fellers, 2007). Ohashi et al. (1994) proposed the ozonation products of 17 kinds of organophosphorous pesticides, but the toxicity change was not clear. So the toxicities of the intermediates were also calculated with T.E.S.T. soft-

ware in this work and shown in Table S2. The results showed that the oxon products usually had lower acute toxicity to *D. magna* but higher oral acute toxicity to rat. It may be because that the oxon products have lower solubilities, but higher lipophilicity. Regarding chlorpyrifos, Zhang et al. (2011) found that it became more harmful as evidenced by the luminous bacterium's increasing light emission after ultrasonic irradiation for 30 min and 60 min, and this may contribute to the formation of chlorpyrifos oxon, which has been proven to be 100 times more toxic than its parent compound (Sparling and Fellers, 2007). Sheikhi et al. (2021) revealed that the main products of chlorpyrifos had lower acute and chronic toxicity than their parent, but some of the products were classified as very toxic according to the Globally Harmonized System of Classification and Labeling of Chemicals (GHS). Generally, despite the toxicity results differ with the oxidation technology, toxicity assessment method, reaction condition, and so on, much attention should be paid to the degradation byproducts' toxicity of chlorpyrifos (Liu et al., 2019; Sheikhi et al., 2021; Zhang et al., 2011).

3.4.2. Organonitrogens

Sanchis et al. (2014) investigated the Fenton oxidation intermediates, ecotoxicity and biodegradability of three organonitrogenous herbicides, i.e. alachlor, diuron and atrazine. The ecotoxicity was somewhat negatively impacted by the oxidation process, but fortunately, significant improvement of biodegradability was observed. The 2,6-diethylaniline, 3,4-dichloroaniline and desethyldeiso-propyl-2-hydroxyatrazine (DEIHA) partly contribute to the increase of ecotoxicity of alachlor, diuron and atrazine, respectively. Similar results were also revealed in other oxidation processes (Farré et al., 2005;

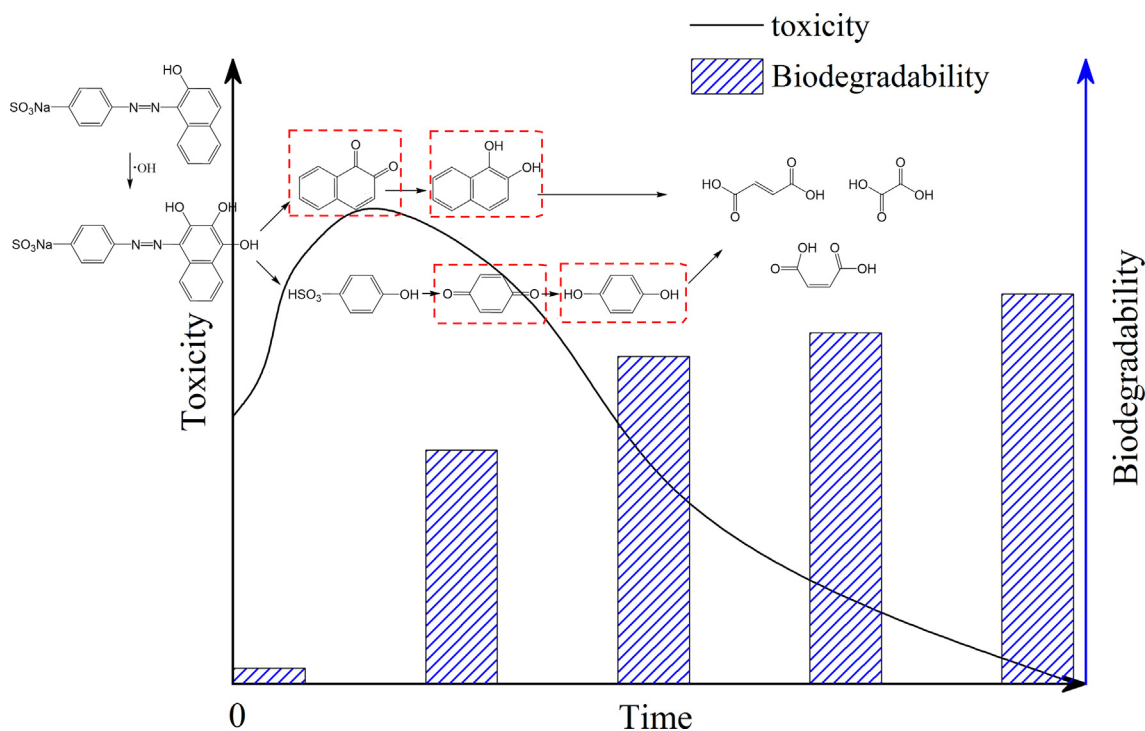


Fig. 3 The toxicity and biodegradability evolution related to the degradation intermediates of AO7. The chemicals in red box are more toxic than the parent.

Malato et al., 2003a; Osano et al., 2002). In addition to the above herbicides, the increase of ecotoxicity during oxidation processes were also observed as for isoproturon, chlorfenvin-fos, methomyl, metoxuron, fluopyram, etc. (Dong and Hu, 2016; Farré et al., 2005; Lapertot et al., 2006; Malato et al., 2003b; Parra et al., 2002). The toxic formylated and demethylated compounds forming by the $-N(R)CHO$ functions (where R might be H or CH_3) addition or $-N(CH_3)_2$ removal could account for the enhanced toxicity. The N-formylated compounds were usually formed from phenylurea herbicides in the presence of $\bullet OH$, but they seemed not to be generated when reacting with 3CDOM* (the excited triplet states of chromophoric dissolved organic matter which could be produced during direct photolysis) (Fabbri et al., 2015; Tixier et al., 2001). The hydroxylated products might also contribute to the toxicity increase (Dong and Hu, 2016; Hu et al., 2019; Li et al., 2020).

3.4.3. Organochlorine

Organochlorine pesticides (OCPs) are a major concern due to their high toxicity, stability, and resistance to degradation in the environment. Most organochlorine pesticides have been forbidden in most nations during the past 40 years, with the exception of lindane and dichlorodiphenyltrichloroethane (DDT), which still have some applications (Costa, 2015). But OCPs such as DDT, endosulfans, pentachlorophenol (PCP), toxaphenes, lindane still have widespread environmental residue (Li et al., 2016; Olisah et al., 2020; Wong et al., 2010; Yadav et al., 2016).

A trace quantity of the more hazardous 4,4'-DDMU could be produced when DDT was subjected to the Fenton or activated persulfate treatment (Cao et al., 2013; Hong et al., 1997; Liu et al., 2021). During oxidation processes of PCP, high toxicity products such as octachlorodibenzo-*p*-dioxin/furan (OCDD/OCDF), tetrachloro-1,4-benzoquinone (TCBQ) and trichlorohydroxy-1,4-benzoquinone (OH-TrCBQ) were observed and it is noteworthy that a continuous flow chemiluminescence method to monitor TCBQ and OH-TrCBQ generation during photocatalytic oxidation process of PCP was developed by Ma et al, which provide some inspiration for dynamic monitoring of highly toxic intermediate oxidation products (Ma et al., 2018; Chen et al. 2020). Other organochlorines usually experienced a toxicity decrease process (Begum et al., 2017; Ikehata and El-Din, 2006; Ribeiro et al., 2015).

3.5. Pharmaceuticals

3.5.1. Fluoroquinolones (FQs)

FQs, the powerful and broad-spectrum antimicrobial agents, have been employed more often in both human and veterinary medicine since the late 1980 s (Feng et al., 2018; Redgrave et al., 2014). Although in most cases the oxidation was a detoxification process as for FQs, some studies have revealed its toxicity increase during oxidation processes (Bobu et al., 2013; Carneiro et al., 2020; Feng et al., 2018; Yang et al., 2016). For example, Qiu et al. (2019) found that the acute toxicity indicated by death and incubation number of zebrafish embryos of pefloxacin reaction solutions was firstly shown to increase and then be followed by a drop with increasing irradiation time of photolysis, but they did not identify the effective intermediates. The basic structure of FQ is shown in Fig. 4,

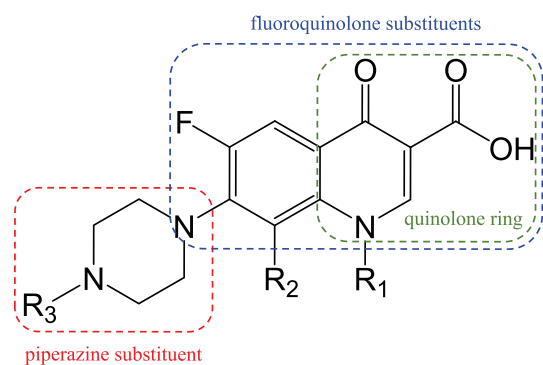


Fig. 4 The characteristic structure of fluoroquinolone.

and according to previous studies, FQs were often oxidized by cleavage or oxidation of piperazine ring, and decarboxylation of quinolone substituents. When FQs contain more than one fluorine, defluorination was also a degradation route (Li et al., 2022a; Zhang et al., 2019; Zhu et al., 2016). The toxicity of ofloxacin during the electrochemical oxidation on a BDD electrode process was evaluated with the EC_{50} values by the algal (*desmodesmus subspicatus*) growth inhibition tests. The toxicity significantly increased, and it is revealed that the oxidation of the piperiziny ring is not sufficient to eliminate the toxicological effects of FQs and would even increase it (Zhu et al., 2016). Similar conclusion has also been driven by Zhang et al. and Ge et al. (Ge et al., 2018; Zhang et al., 2019). Zhang et al. (2019) found that the degradation products of lomefloxacin exhibited greater toxicity, and the possible intermediate was formed by defluorination and breakage of piperiziny ring. Ge et al. (2018) examined the photomodified toxicity of gatifloxacin using an *E. coli* activity assay. The light-irradiated solutions' antibacterial activity did not considerably decline during the first photodegradation phase ($0 - t_{1/2}$) as the photoreactions had not alter the core aromatic backbone of quinolone substituents. Li et al. (2022a) investigated the intermediates of ofloxacin treated with heat-activated persulfate and calculated their oral rat LD_{50} values, mutagenicity and developmental toxicity with T.E.S.T. and ECOSAR respectively. The products formed by β -elimination on the piperazine substituent appeared to have a higher mutagenicity and developmental toxicity, while products formed by the cleavage of quinolone seemed to be more mutagenic. A greater acute toxicity to rats was seen when the quinolone and piperazine rings were both removed. In conclusion, the destruction of fluorinated aromatic ring might be the key of detoxification, which required further investigation.

3.5.2. Sulfonamides (SAs)

The toxicity increase of SAs during oxidation or photolysis was also found in many previous studies (Qiu et al., 2019; Trovó et al., 2009; Xu et al., 2014; Zhang et al., 2016). Li et al. (2021) reviewed the abiotic transformation and ecotoxicity alteration of SAs during water treatment and environmental processes. The typical structural transformation of SAs include oxidation of aniline moiety, SO_2 extrusion, cleavage of sulfonamide group, transformation on the heterocyclic ring, and so on (Zhang et al., 2020). The typical transformation processes are summarized in Fig. 5, and the highly toxic intermediates are identified according to the previous studies. The

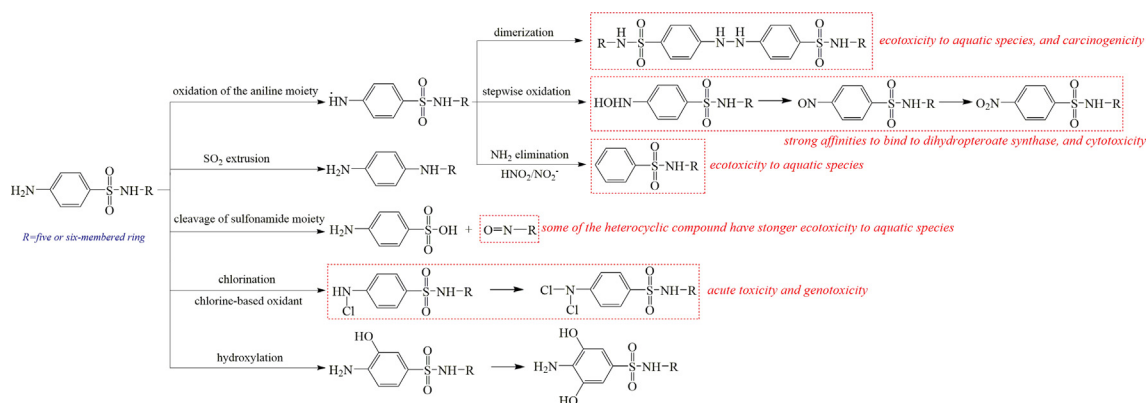


Fig. 5 Typical transformation pathways and product toxicity of SAs. The chemicals in red box are more toxic than the parent.

formed dimers connecting through --NH--NH-- have been previously demonstrated to be more detrimental to aquatic species, and exhibit carcinogenicity (Zhuang et al., 2019). Additionally, it has been established that the nitroso-, nitro-, and hydroxylamine-SAs were more hazardous than the parent SAs due to their stronger propensities to bind to dihydropteroate synthase (Majewsky et al., 2014; Shad et al., 2018), and the hydroxylamine-SAs usually have a higher cytotoxicity. Both acute and chronic toxicity of SO_2 extrusion products to typical aquatic species were also revealed to be much higher than the parent compound (Kråkström et al., 2020; Yang et al., 2018). One important product, 2-aminopyrimidine, which is formed through the cleavage of sulfonamide bond (S-N) during several advanced oxidation processes (AOPs) (Fabińska et al., 2014; Neafsey et al., 2010; Wang et al., 2010; Zou et al., 2014), showed substantially higher acute and chronic toxicity for aquatic species than sulfadiazine based on ECOSAR computation [143]. In addition, acute toxicity and genotoxic potentials were increased during chlorination processes with the emergency of DBPs of SAs (Fu et al., 2018; Zhang et al., 2020).

3.5.3. Others

Apart from fluoroquinolones and sulfonamides, high toxic intermediates have also been found in other pharmaceuticals. Typically, the halogen-containing chemicals have potential high toxicity via transformation. For example, propranolol (PRO), one of the most commonly used beta blockers, enhanced the luminescence inhibition during UV-LED/chlorine treatment, which might be correlated with the chlorine-containing by-products (Xiong et al., 2020). Diclofenac (DCF), a synthetic non-steroidal anti-inflammatory medication, is one of the most widely prescribed painkillers. Hydroxylation, ring-opening, decarboxylation and cyclation reaction might occur during the processes, and the toxicity of DCF solution experienced an increase stage during some processes (Calza et al., 2006; Lu et al., 2017; Wang et al., 2015; Yu et al., 2013; Zhao et al., 2009). The toxicity might be related with the production of the chloroderivatives (Lu et al., 2017). Most of the chlorine-containing products, such as hydroxylated DCF, chlorinated DCF, 2,6-dichloro-N-(2-methylphenyl)aniline, might be responsible for the toxicity (Gao et al., 2022; Li et al., 2017; Qiu et al., 2020). Similarly, the increase of toxicity occurred during the florfenicol (FLO)

degradation due to chlorinated byproducts and inorganic ones (ClO_2 , ClO_3 and ClO_4) formed, which are more toxic than the parent FLO (Periyasamy et al., 2022). Similar phenomenon was also observed on nitrogenous heterocyclic compounds. Carbamazepine produced acridine and acridone during UV-radiation and chlorine dioxide oxidation, which have been found to have higher ecotoxicity (Donner et al., 2013; Kosjek et al., 2009).

4. The enhanced toxicity induced by environmental elements

Environmental elements such as dissolved organic matter (DOM) and halides have been reported to have the potential to enhance the toxicity after oxidation. The enhanced toxicity on *V. fischeri* and *D. magna* have been reported for DOM-spiked ofloxacin solutions after photo-Fenton processes. However, the increased toxic effects might be attributed to the byproducts generated from DOM but not from the transformation intermediates of ofloxacin (Michael et al., 2010; Michael et al., 2013). Li et al. (2022b) found that a ClO_2 pre-oxidation process might be useful in reducing the genotoxicity and cytotoxicity of UV/chlorine-treated DOM-containing water. On the contrary, sometimes DOM helps reduce the toxicity. For example, the cross-coupling products combining SAs and natural organic matter (NOM) constituent via the amide nitrogen might lessen ecotoxicity due to their lower mobility (Li et al., 2020; Wang et al., 2020). Franklin pointed out that the DOM source affects DBP formation, and the organic nitrogen and protein-like content drove differences (Franklin et al., 2021), and Xie et al. discovered that organic matters with a molecular weight (MW) of between 1 k and 100 k Da are more likely to generate organic halogens than those with a MW of lower than 1 k Da and higher than 100 k Da. (Xie et al., 2020).

Halides are also noteworthy and usually have a combined effect with DOM. The growth inhibition ratios of SMX to *C. vulgaris* increased with increasing halogen ion (Cl^- , Br^-) content under the UV/PS and UV/ NaClO oxidation system (Zhang et al., 2020). Similar results were found in the Co(II)/peroxymonosulfate, ozone system, electrochemical oxidation, and so on (Fang et al., 2016; He et al., 2022; Xiang et al., 2019; Xu et al., 2022). It has been reported that the cytotoxic index value of brominated byproducts was much higher than chlorinated ones, and iodo-products which have mammalian

cell toxicity should also been addressed (Richardson et al., 2008). The halogenated organic products, which were formed from reactions of pollutants with halogen radicals or hypohalous acid, can interpret the phenomenon of toxicity enhancement. The description on increased toxicity induced by interaction between DOM and halogen elements is available in an excellent review compiled by Yang et al. and Ike et al. (Ike et al., 2019; Yang et al., 2022). An interaction between NO_2^- and DOM was also found to be have the potential to enhance the toxicity (Yang et al., 2021; Yang et al., 2022).

5. Strategies to reduce the residual toxicity

As in most cases the high toxicity resulted from the inadequate degradation of pollutants, it is necessary to take some measures to strengthen the reaction, for example, to increase the oxidant concentration or prolong reaction time. Sanchis et al. (2014) has proved that the detected toxicity products decreased significantly as the amount of oxidant increased. According to Liu et al. (2017), prolonging the photo-Fenton oxidation time could lessen the toxicity of methylene blue solution. Furthermore, coupling of multiple technologies is an effective strategy. For example, the coupling of ozone and electrochemical methods can reduce the toxicity of the phenol degradation process (Gao et al., 2022), and combining solar photo-Fenton and biological treatment can effectively remove the pharmaceuticals in wastewater and alleviate the residual toxicity (Sirtori et al., 2009). Likewise, biodegradation after Fenton-like oxidation could effectively reduce the toxicity of petroleum-contaminated soil (Lu et al., 2010), and the products of carbamazepine were also proved to be more susceptible to biological treatment than the parent (Kosjek et al., 2009). Membrane technology can be also used following AOPs to further remove toxicity. Żyła et al. (2019) found that the combined use of UV/ H_2O_2 and nanofiltration process facilitated the chemical conversion of the tested chemicals as well as the elimination of their poisonous oxidation byproducts from the solution, and Zhi et al. (2020) draw the similar conclusion.

Optimization of oxidation catalytic materials to regulate the reactive oxygen species (ROS) generation is another way to change the pollutant conversion pathways and reduce product toxicity. For example, Chen et al. (Chen et al., 2020; 2022) synthesized the polydopamine modified TiO_2 nanoparticles (P25/PDA) and TiO_2 /polydopamine/ bismuth oxybromide (P25/PDA/BiOBr) materials respectively to improve the PCP photodegradation process and depress generation of TCBQ and OH-TrCBQ through regulating the dominant ROS to be H_2O_2 , $\bullet\text{O}_2^-$, electrons, et al., but not $\bullet\text{OH}$.

In addition, controlling environmental conditions was also effective in some cases. Chen et al. and Sun et al. (Chen et al., 2021; Sun et al., 2019) proved that pH might affect the generation of nitro(so) and chlorinated products as well as toxicity alterations when phenol was treated with UV light and monochloramine. The pH was also an influencing factor on the formation of DBPs and toxicity variation during the UV/chlorine AOPs. Moreover, the contribution of various ROS and the degradation pathway during SMX oxidation varied intensively under different pH. The residual toxicity was better eliminated along with the increase of pH (pH-dependent transformation products and residual toxicity evaluation of sulfamethoxazole degradation through non-radical oxygen

species involved process). The presence of humic substances would change oxidative conversion pathways of PCP and avoid OCDD formation in some cases (Fukushima et al., 2003; Fukushima et al., 2010; Fukushima and Tatsumi, 2001).

6. Conclusion and perspectives

Incomplete degradation of organic pollutants in wastewater or soil would lead to unintended formation of potentially toxic intermediates, and sometimes the complete conversion of the parent compound or even a decrease in the amount of organic carbon in the reaction solution is insufficient to detoxify it. Therefore, only monitoring the pollutant attenuation is not enough to reflect the treatment effect, and analysis on intermediates or toxicity is necessary. Acute toxicity test is commonly used in the oxidation process to assess the negative environmental impacts of the intermediates, and the luminescence inhibition is the predominant indicator. The prediction based on QSAR following product identification is also frequently applied. As each method has pros and cons of its own, combination of both is recommended. Although test species, reaction conditions, oxidation methods, and evaluation endpoints all had an impact on toxicity, particular attention should be paid to all substances that have the potential to produce more hazardous intermediates. Higher toxic intermediates have been found as for PAH, phenols, azo dyes, organophosphorus, organonitrogens, organochlorine pesticide, pharmaceutical chemicals, and so on. The hydroquinone-, benzoquinone-, catechol-like and halogenated products usually have higher ecotoxicity while the dimers and polymers are refractory and prone to accumulate in the soil. In addition, DOM and halogen ion have the potential to enhance the oxidative toxicity. The strategies to reduce the residual toxicity were also summarized in this work. For the deeper understanding of the oxidation product toxicity of pollutants, more efforts can be made from the following aspects: (1) to investigate the occurrence and distribution of persistent oxidation products; (2) to study the toxicity effects of the products at multiple trophic levels; (3) to strengthen the residual toxicity studies in soil; (4) to consider the toxicity change as a standardized measure of remediation effectiveness; (5) to further clarify the relationship between the transformation pathway of the pollutants and key action species.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.arabjc.2023.104856>.

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