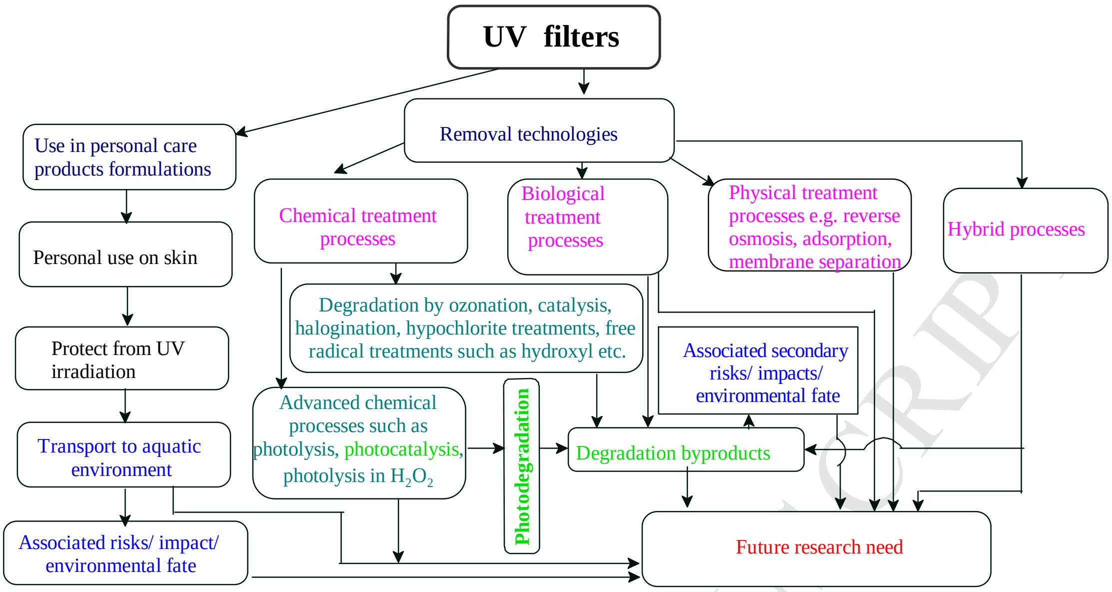
UV filters
Removal technologies
Use in personal care products formulations
Personal use on skin
Protect from UV irradiation
Transport to aquatic environment
Associated risks/ impact/ environmental fate
Chemical treatment processes
Biological treatment processes
Physical treatment processes e.g. reverse osmosis, adsorption, membrane separation
Hybrid processes
Degradation by ozonation, catalysis, halogination, hypochlorite treatments, free radical treatments such as hydroxyl etc.
Advanced chemical processes such as photolysis, photocatalysis, photolysis in H_2O_2
Photodegradation
Associated secondary risks/ impacts/ environmental fate
Degradation byproducts
Future research need

Photolytic and Photocatalytic Degradation of Organic UV Filters in Contaminated Water

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Abstract

UV filters as emerging contaminants are of great concern and their wide detection in aquatic environments indicates their chemical stability and persistence. This review summarized the photolytic and photocatalytic degradation of UV filters in contaminated water. The findings indicated that limited research has been conducted on the photolysis and photocatalysis of UV filters. Photolysis of UV filters through UV irradiation in natural water was a slow process, which was accelerated by the presence of photosensitisers e.g. triplet state of chromaphoric dissolved organic matter (^{3}CDOM*) and nutrients but reduced by salinity, dissolved organic matter (DOM) and divalent cations. UV Photocatalysis of 4-methylbenzylidene camphor and 2-phenylbenzimidazole-5-sulfonic acid was very effective with 100% removal within 30 min and 90 min using medicated TiO_2/H_2O_2 and TiO_2, respectively. The radiation source, type of catalyst and oxygen content were key factors. Future research should focus on improved understanding of photodegradation pathways and by-products of UV filters.

***Keywords**:* Photodegradation products; Photocatalysis; BP-3; BP-4; 4-MBC

1. Introduction

Different classes of UV filters (Table A1), extensively and increasingly used in recent years, are vital formulations of sunscreens products [1-3]. UV filters have unique properties as they can absorb, reflect and/or scatter UV radiation and thereby protecting our health. They are also used as sun-blocking agents for the protection of materials such as plastics, adhesives and rubber [2, 3]. UV filters are gaining growing interest due to their increased production and consumption [4], and are considered emerging contaminants due to their increasing concentrations in the aquatic environment and also for unknown risks associated with their presence [5-7]. The main concern about these compounds is their potential toxicity and adverse effects, namely as xenohormone affecting reproductive activity [8-11]. For example, camphor derivative 4-MBC, as well as benzophenone derivative 2-hydroxy-4-methoxybenzophenone (BZ-3) and 3,3,5-trimethylciclohexyl salicylate (Homosalate) have shown multiple hormonal activities including estrogenic and antiestrogenic effects [12]. Although recreational activities are direct input pathways of UV-filters into the environment, they can also come from washing, showering, rub-off to cloths, and subsequent laundering. The occurrence of UV filters has been detected in river water, lake and sea water, groundwater, sediments and even biota [13-26]. The concentrations of different organic UV filters such as benzophenone-3 (BP-3), octocrylene, octyl-dimethyl-p-aminobenzoic acid (ODPABA), 4-methylbenzylidene camphor (4-MBC), octyl methoxycinnamate, and butyl methoxydibenzoyl methane are presented in Table 1 [27].

Different methods have already been applied for the removal of UV filters. For example, adsorptive removal of 4-*tert*-butil-4’-methoxydibenzoylmethane (avobenzone), homosalate, 4-MBC, ODPABA, octocrylene and 2-ethylhexyl 4-methoxycinnamate (EMC) ($\log K_{ow} > 4.0$) onto primary sludge showed 30-70% removal efficiencies [16,28,29]. Coagulation and flocculation were not found to be effective methods for the removal of 2,4-dihydroxybenzophenone (BP-1) and 2-hydroxy-4-methoxy benzophenone-5-sulfonic acid

(BP-4) [16, 17]. Balmer et al. [30] showed moderate to lower concentrations of 4-MBC, octocrylene and EMC in the effluent after mechanical, biological, chemical and sand filtration. Liu et al. [28] investigated 6 UV filters (BP-3, 4-MBC, EMC, UV-326, UV-329, octocrylene) in a full-scale municipal wastewater treatment plant (WWTP) which consisted of primary sedimentation and secondary activated sludge treatment in South Australia; after extended period of application they observed the removal efficiencies of 5-82% [29]. Disinfection process also showed poor removal efficiencies (17-25%) of BP-3, 4-MBC, EMC and octocrylene [31]. Ozonation of BP-3 generated seven intermediate products (Figure A1) [32]. Further, chlorination process was not efficient in removing most compounds from wastewater [16, 17]. Moreover, halogenation of BP-3 and BP-4 generated halogenated by-products which may be of additional concern (Figure A2) [33, 34]. In comparison, reverse osmosis showed the highest efficiencies (> 99%) in removing some UV filters [16,17]. Membrane bioreactor showed excellent removal of BP-3 (> 96%) and octocrylene (67-96%) with a hydraulic retention time of 26 h and sludge retention time of 88 days [35].

Thus, it can be stated that different physical and biological processes may not be effective to remove UV filters from contaminated water. A few review articles on UV filters have been published which mainly focused on the occurrence and fate of the UV filters in different water [6, 29, 36-39]. However, no comprehensive review on the photolytic and photocatalytic degradation of UV filters has been conducted. It is therefore necessary to understand the photolytic and photocatalytic degradation mechanism of UV filters in contaminated water. In this review we assess recent findings on the removal of UV filters through photolytic and photocatalytic degradation, focusing on the degradation pathways and effectiveness in removing UV filters from contaminated water together with future perspectives.

2. Photolytic and photocatalytic degradation of UV filters

Photodecomposition is one of the most important abiotic processes affecting the fate of UV absorbing compounds in the aquatic environment and photocatalysis has been suggested as an effective method to degrade UV filters [40]. However, UV filters transformation appears to be a complex process, barely addressed to date as they designed not to be degraded in UV light. The photodegradation of UV filters may produce transformation products which pose additional environmental stress. The mechanisms of photodegradation of UV filters include (i) direct or indirect photolysis by the dissociation of adsorbing molecule and produced free radicals or reactive fragments, and (ii) photo-isomerization which yields species that probably absorb less UV light than the parent species [27].

Among different classes of UV filters, photodegradation and photo-stability of benzophenone derivatives UV filters has been studied extensively using $OH^{\bullet}$ [40, 41]. Typical surface-water conditions, direct photolysis and reactions with $OH^{\bullet}$ and ^{3}CDOM* would be the main processes of BP-3 photo-transformation. The reaction with $OH^{\bullet}$ would prevail at low dissolved organic carbon (DOC) concentration, direct photolysis at intermediate DOC concentration (5 mg L^{-1}), and reaction with excited ^{3}CDOM* at high DOC concentration. Furthermore, two methylated derivatives were tentatively identified which were probably produced by reactions between BP-3 and fragments arising from photodegradation [42]. In another study, other intermediates such as benzoic acid (maximum concentration ~10% of initial BP-3) and benzaldehyde (1%) were identified [34]. Gago-Ferrero et al. [40] reported that after 24 h of UV irradiation, BP-3 was not photodegraded but BP-1 was readily photodegraded. Similarly, Rodil et al. [41] observed high stability of BP-3, which was further confirmed under UV and artificial solar light [43]. Liu et al. [43] also observed solar radiation exposure of 50 days resulted in 8% loss of BP-3 in pure water; however, the loss was almost 31% in solution containing 50 mg L^{-1} of humic acid. They identified one major photoproduct as 2,4-dimethylanisole, formed by the loss of hydroxyl and benzoyl groups (Figure A3).

Laboratory-scale irradiation experiments revealed that photodegradation of benzophenones [benzophenone (BP), 4-hydroxybenzophenone (4H-BP), BP-3, BP-1 and 2,2'-dihydroxy-4-methoxybenzophenone (BP-8)] followed pseudo-first-order kinetic models with $t_{1/2}$ of 17-99 h [44]. They also found that the photolytic behaviour of benzophenone UV filters differed significantly between natural water. The photostability of benzophenone UV filters after 24 h exposure in distilled water (C_t/C_o in percentage) followed the order: BP-8 > BP-3 > 4H-BP > BP > BP-1 (Figure 1a). UV filters can undergo photodegradation reactions under the influence of sunlight due to direct or indirect photolysis [44]. Direct photolysis of benzophenones from natural water with DOM, bicarbonate, nitrate, nitrite and chloride can react with target pollutants in surface waters and affects their photolysis rate and environmental half-life. Lake and surface water matrices containing DOM, nutrients, salinity and pH also affect the direct photolysis (Table A2). Salinity and high DOM concentration were found to reduce the direct photolysis of those benzophenones while nutrients (e.g. nitrates) in lake water increased the photolysis during solar irradiation (Table A2) [44]. The kinetic rate constant and $t_{1/2}$ of benzophenones under solar photolysis in lake water followed the order: BP-8 ($0.207\ d^{-1}$, 3.35 d) > BP-1 ($0.153\ d^{-1}$, 4.53 d)> BP-3 ($0.074\ d^{-1}$, 9.38 d) > 4H-BP ($0.073\ d^{-1}$, 9.52 d) > BP ($0.057\ d^{-1}$, 12.2 d). Photosensitisers (e.g. DOM) in natural waters may compete with the target UV filters acting as a filter hindering light transmission and reduced photolysis in seawater. Lake water was found to be positive effect on the solar photolysis followed by deionized water and seawater [44]. Finally, the catalysis of BP-3 was studied [45] using a hybrid Cu-Mn-O catalyst with a chemical composition of $Cu_{1.4}Mn_{1.6}O_4$ along with other two catalysts Mn_3O_4 and Mn_2O_3, with the highest degradation (81.5%) being observed for BP-3 after 240 min of experiments. They mentioned that degradation was mainly related to presence of hydroxyl radicals but they did not perform the experiments under UV light. So photocatalytic degradation can be a potential alternative and fast removal process for benzophenone UV filters.

Photochemical behaviour of *p*-aminobenzoic acids derivatives such as ODPABA was studied by Sakkas et al. [46] using xenon light source and under natural sunlight conditions in sea water, swimming pool water and distilled water. They observed several derivative products due to the loss of methyl groups, through addition of two chlorine atoms and addition of OH group in the aromatic ring (Figure 2a). It is notable from Figure 2a that methyl functional *P*-amino functional group in benzyl ring had been replaced with hydrogen ion (no carbon bond cleavage) and different derivative products were produced along with halogenated derivatives. The stability of ODPABA was also studied by Gackowska et al. [47] using a medium-pressure mercury lamp (TQ 150 W) under UV radiation (for 3 h) and using sodium hypochlorite. They identified three degraded products namely (i) ethylhexyl alcohol (*m/z* 130, 112, 98, 57); (ii) octyl para-aminobenzoic acid (*m/z* 249, 137, 120); (iii) octylmethyl-para-aminobenzoic acid (*m/z* 263, 151, 134). Hence the demethylation reactions of amino group occurred in the presence of UV radiation (Figure 2b). Sodium hypochlorite application produced nine degraded products including chlorinated products after 3 h application [47]. On the removal of UV filter *p*-amino benzoic acid, it was found that DOM (such as fulvic and humic acids) inhibits the photolysis due to light screening effect, energy transfer, electron transfer and proton abstraction mechanism [48].

Cinnamates derivatives UV filter such as EMC photolysis was carried out with and without UV radiation exposure equipped with medium pressure mercury lamp and sample was irradiated for 180 min. It was observed that only ~6% degradation occurred after 180 min, although a maximum of ~24% occurred within the first 30 min exposure to UV irradiation. The change in the percentage of degradation was due to isomerisation of EMC [49].

The application of hybrid system such as chlorination and photolysis with sodium hypochlorite was studied for the degradation of dibenzoyl methane derivative such as avobenzone (4-*tert*-butil-4’-methoxydibenzoylmethane), with 25 transformed compounds being identified although their toxicities remaining largely unknown [50] (Figure A4). Although avobenzone was stable in organic solvents under UV irradiation, photochemical degradation in water was occurred with the formation of two pairs of corresponding substituted benzoic aldehydes and acids. The longer was the irradiation, the higher were the levels of these products. UV-C was found to be very effective.

The recent studies of photocatalysis have shown it to be very effective in the removal of UV filters [51-53]. The photocatalysis and identification of intermediate compounds of 4-MBC in the presence of medicated TiO_2/H_2O_2 was studied by Sakkas et al. [52]. They pointed out that the transformation of 4-MBC (*m/z* 254) occurred in three different steps as demethylation of the bridged structure, hydroxylation of the methylbenzylidene moiety, and bihydroxylation/demethylation reaction. The complete disappearance of the initial compound occurred within 30 min of irradiation [52]. The species formed during the reformations were identified (Figure 2b). Similarly, Soto-Vázquez et al. [53] studied the photocatalaytic degradation of 2-phenylbenzimidazole-5-sulfonic acid using zinc-oxide-nanoparticles and detected very effective degradation. The photocatalytic activity of the calcined zinc oxide nanoparticles proved to be very high since more than 90% of degradation of 2-phenylbenzimidazole-5-sulfonic acid reached after 180 min of reaction time (Figure 1b). The effects of different factors (i.e. radiation source, oxygen source, and catalyst) on the catalytic reaction were evaluated, which were all required to act synergistically in the photodegradation process [53]. They observed the degradation of 2-phenylbenzimidazole-5-sulfonic acid was ~1%, ~1%, ~18% under white light in the absence of oxygen, catalysis by nZnO in the absence of light, and photolysis under white light with no catalyst, respectively after 180 min of application. On the other hand, Pang et al. [54] found 100% catalytic degradation of 2-phenylbenzimidazole-5-sulfonic acid within 3-30 min using modified $LaCoO_3$ catalysts (Figure 1b). They observed eight intermediate products of this UV filter and proposed a catalytic degradation pathway (Figure A5). Ji et al. (2013) observed very effective photocatalytic degradation of 2-phenylbenzimidazole-5-sulfonic acid using TiO_2 photocatalyst under high pressure UV irradiation (HPK 125W, Heraeus) [55], with the complete disappearance of the compound and its intermediates being observed within 90 min irradiation, in addition to significant reduction of total organic carbon content. The possible degradation pathway is shown in Figure 3, with the hydroxyl radical as the predominant reactive species. The photodegradation reactions of 2-phenylbenzimidazole-5-sulfonic acid followed the pseudo-first-order kinetics [55]. Hence, the photocatalytic degradation of UV filters is very effective with potential for wide applications.

3. Future research priorities

So far eleven different groups of UV filters were detected in different water, among them only a few (BP-1, BP-3, BP-4, ODPABA, 4-MBC) were investigated for photodegradation. Further research is needed to:

- Compare photocatalysis of different classes of UV filters using different catalysts.
- Develop new photocatalyst to increase their performance, selectivity and longevity.
- Focus more on utilizing solar irradiation facilitated visible light photodegradation.
- Study the fate of UV filters as a mixture in the environment.
- Evaluate different treatment technologies such as adsorption, biodegradation, membrane filtration, along with photocatalysis for UV filters removal from contaminated water.
- Identify photodegradation pathways and products.
- Improve understanding of mechanistic role of free radicals in the photodegradation of UV filters.

4. Conclusions

This review summarized the current literature on the photolytic and photocatalytic removal of UV filters in contaminated water, which has not been widely researched up to now. Photolytic degradation was found to be a very slow process while photocatalysis far more efficient. UV filter compounds should be further researched to identify their environmental fate, key transformation processes and by-products, and potential risks from the parent and degradation products, in contaminated water. To minimize their environmental impact, better control and removal technologies are needed with improved efficiency, selectivity, energy demand, and environmental quantum yield. The mechanisms involved in photolysis and photocatalysis processes, in particular radicals, should be fully evaluated.

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(Photocatalysis of 2-phenyl-5-sulfobenzimidazole occurred within 90 min using TiO_2 photocatalysts)

Photolytic and Photocatalytic Degradation of Organic UV Filters in Contaminated Water

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Appendix Containing:

2 Tables

5 Figures

Table A1. Physicochemical properties of major organic UV filters (data taken and modified from ref. [1]).

Family	**Compound (Abbreviation) and CAS number**	**Boiling Point (^{o}C)**	**log K_{ow}**	**Solubility in water at 25 ^{o}C (mg/L)**
Benzophenone derivatives	2,4-Dihydroxybenzophenone (BP1), CAS: 131-56-6	374.6	2.19	4.13x10^{3}
	2,2',4,4'-Tetrahydroxybenzophenone (BP2) CAS: 131-55-5	444.6	2.78	3.99x10^{2}
	2-Hydroxy-4-methoxybenzophenone (BP3) CAS: 131-57-7	363.4	3.79	6.90x10^{1}
	2-Hydroxy-4-methoxy benzophenone-5-sulfonic acid (BP4), CAS: 4065-45-6	497.6	0.37	2.50x10^{5}
	2-Hydroxy-4-methoxy benzophenone-5-sodium sulfonate (BP5), CAS: 6628-37-1	698.3	-1.42	5.05x10^{5}
	2,2′-Dihydroxy-4,4′-dimethoxybenzophenone (BP6), CAS: 131-54-4	421.9	3.90	3.10x10^{1}
	2,2'-Dihydroxy-4-methoxybenzophenone (BP8), CAS: 131-53-3	398.2	3.82	5.30x10^{1}
	2,2′-Dihydroxy-4,4′-dimethoxybenzophenone-5,5′-disulfonic acid disodium salt (BP9), CAS: 76656-36-5	852.1	-2.78	8.89x10^{5}
	4-Hydroxybenzophenone (4H-BP), CAS: 1137-42-4	339.6	3.07	4.06x10^{2}
	4,4'-Dihydroxybenzophenone (4DHB), CAS: 611-99-4	374.6	2.19	1.91x10^{3}
	Diethylamino hydroxybenzoyl hexyl benzoate (DHHB), CAS: 302776-68-7	504.8	6.54	8.19x10^{-3}
	2,3,4-Trihydroxybenzophenone (234THB), CAS: 1143-72-2	409.4	2.91	3.811x10^{2}
p-Aminobenzoic acids derivatives	2-Ethylhexyl 4-(dimethylamino)benzoate (EDP), CAS: 21245-02-3	344.5	5.77	2.00x10^{-1}
	Ethyl *p*-aminobenzoate (Et-PABA), CAS: 94-09-7	278.9	1.86	1.31x10^{3}
	Octyl-dimethyl-*p*-aminobenzoic acid (ODP) CAS: 58817-05-3	351.6	5.84	1.70x10^{-1}
	p-Aminobenzoic acid (PABA), CAS: 150-13-0	307.7	0.83	6.11x10^{3}
	Amyl *p*-dimethylaminobenzoate (APABA) CAS: 14779-78-3	314.1	4.37	5.33x10^{0}

Continue

Family	Compound (Abbreviation) and CAS number	Boiling Point (^{o}C)	log K_{ow}	Solubility in water at 25 ^{o}C (mg/L)
o-Aminobenzoic acids derivatives	Menthyl *o*-aminobenzoate (MOABA) CAS: 134-09-8	374.3	6.28	7.40x10^{-2}
Camphor derivatives	3-(4’-Methylbenzylidene) camphor (4-MBC), CAS: 36861-47-9	349.4	5.92	2.00 x10^{-1}
	Terephthalylidene dicamphor sulfonic acid (Ecamsule) (TDSA), CAS: 92761-26-7	757.5	3.83	1.50 x10^{-1}
	Camphor benzalkonium methosulfate (CBM), CAS: 52793-97-2	638.2	3.11	7.34 x10^{0}
	Benzylidene camphor sulfonic acid (BCSA) CAS: 56039-58-8	472.0	2.22	1.20 x10^{2}
	Polyacrylamidomethyl benzylidene camphor (PBC), CAS: 113783-61-2			
	3-Benzylidene-camphor (3BC), CAS: 15087-24-8	337.6	5.37	6.90 x10^{-1}
Benzotriazole derivatives	2-(2H-Benzotriazol-2-yl)-4,6-bis(2-phenyl-2-propanyl)phenol (UV-234), CAS: 70321-86-7	599.7	7.67	1.65x10^{-3}
	2-(3-*tert*-butyl-2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole (UV 326), CAS: 3896-11-5	450.1	5.55	6.80 x10^{-1}
	2-(5-Chloro-2H-benzotriazol-2-yl)-4,6-bis(2-methyl-2-propanyl)phenol (UV-327), CAS: 3864-99-1	473.3	6.91	2.63x10^{-2}
	2-(2H-Benzotriazol-2-yl)-4,6-bis(2-methyl-2-butanyl)phenol (UV-328), CAS: 25973-55-1	477.8	7.25	1.48x10^{-2}
	2-(2’-hydroxy-5’-octylphenyl)-benzotriazole (UV 329), CAS: 3147-75-9	454.6	6.21	1.70 x10^{-1}
	Methylene bis-benzotriazolyltetramethyl butylphenol (MBBT), CAS: 103597-45-1	818.5	12.46	4.47x10^{-10}
	Drometrizole Trisiloxane (DTS), CAS: 155633-54-8	528.6	10.82	6.40x10^{-7}
Salicylate derivatives	2-Ethylhexyl salicylate (ES), CAS: 118-60-5	344.9	5.97	7.20 x10^{-1}
	3,3,5-trimethylciclohexyl salicylate (Homosalate) (HMS), CAS: 118-56-9	355.9	6.16	4.20 x10^{-1}
	Benzylsalicylate (BZS), CAS: 118-58-1	354.9	4.31	2.46 x10^{1}
	Triethanolaminium salicylate (TAS), CAS: 2174-16-5	460.9	-0.53	4.24x10^{4}

Continue

Family	Compound (Abbreviation) and CAS number	Boiling Point (^{o}C)	log K_{ow}	Solubility in water at 25 ^{o}C (mg/L)
Triazine derivatives	Diethylhexyl butamido triazone (DBT) CAS: 154702-15-5	893.5	14.03	$1.33x10^{-11}$
	Ethylhexyl triazone (EHT), CAS: 88122-99-0	874.4	17.05	$1.45x10^{-14}$
	Bis-ethylhexyloxyphenol Methoxyphenyl triazine (BEMT) CAS: 187393-00-6	786.6	9.29	$1.45x10^{-16}$
	Tris-biphenyl triazine (TBPT) CAS: 31274-51-8	792.2	10.38	$5.56x10^{-7}$
Cinnamates derivatives	2-Ethylhexyl 4-methoxycinnamate (EMC) CAS: 5466-77-3	360.5	5.80	$1.50\ x10^{-1}$
	Isoamyl 4-methoxycinnamate (IMC) CAS: 71617-10-2	324.4	4.33	$4.86\ x10^{0}$
	2-Ethoxyethyl 4-methoxycinnamate (Cinoxate) (EOMC) CAS: 104-28-9	185.5	2.65	$5.00\ x10^{2}$
	Isopropyl 4-methoxycinnamate (IPMC) CAS: 5466-76-2	296.4	3.35	$4.80\ x10^{1}$
	4-Hydroxy-3-methoxycinnamic acid (ferulic acid) (FA), CAS: 1135-24-6	354.2	1.51	$5.97\ x10^{3}$
zoyl methane deriva	4-*tert*-butil-4'-methoxydibenzoylmethane (Avobenzone) (BMDM), CAS: 70356-09-1	409.3	4.51	$1.52\ x10^{0}$
Benzimidazole derivative	2-Phenyl-5-benzimidazole sulfonic acid (PBSA), CAS: 27503-81-7	566.1	-0.16	$2.36x10^{4}$
	Disodium phenyl dibenzimidazole tetrasulfonate (DPDT), CAS: 180898-3-7		-2.00	$2.00\ x10^{1}$
Crylene derivative	2-Ethylhexyl 2-cyano-3,3-diphenylacrylate (OC), CAS: 6197-30-4	472.9	6.88	$3.81x10^{-3}$
Other	1-(3,4-dimethoxyphenyl)-4,4-dimethyl-1,3-pentanedione (PD), CAS: 135099-97-7	348.8	1.61	$8.24\ x10^{2}$

Table A2. Effects of different water and chemical species on the photolysis and solar photolysis of benzophenone derivative UV filters.

Compound name	Positive effect (species)	Negative effect (species)	Reference
BP-3	$OH^{\bullet}$, O_2, ^{3}CDOM*, humic acid, solar light	Cu^{2+}, Fe^{3+}, DOM	[2, 3]
BP	Lake water, nutrients, $OH^{\bullet}$	Salinity, DOM	[4]
BP-1	Lake water, nutrients, $OH^{\bullet}$	Salinity, DOM	[4]
BP-3	Lake water, nutrients, $OH^{\bullet}$	Salinity, DOM	[4]
BP-8	Lake water, nutrients, $OH^{\bullet}$	Salinity, DOM	[4]
4-H BP	Lake water, nutrients, $OH^{\bullet}$	Salinity, DOM	[4]

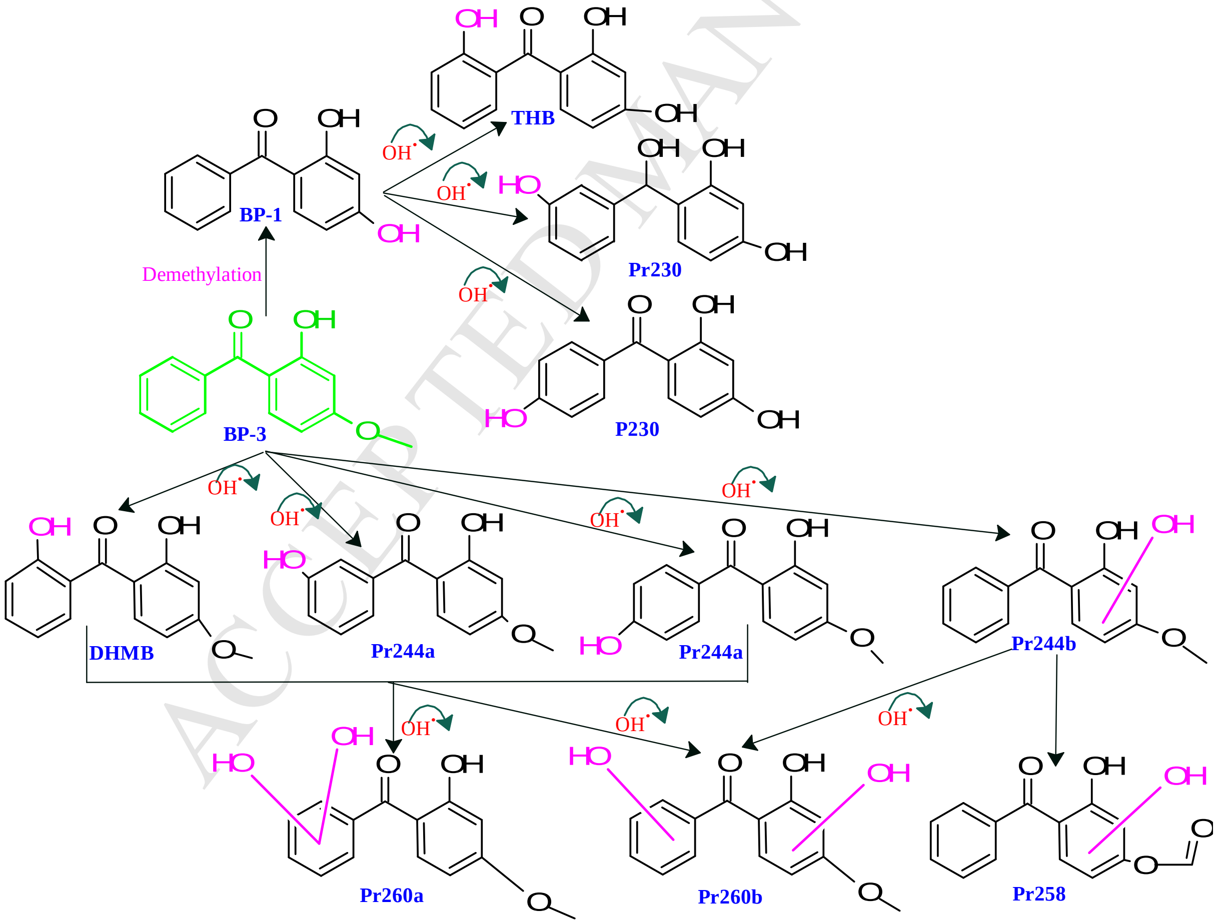

Figure A1. Proposed BP-3 degradation pathways during ozonation, adopted from ref. [5].

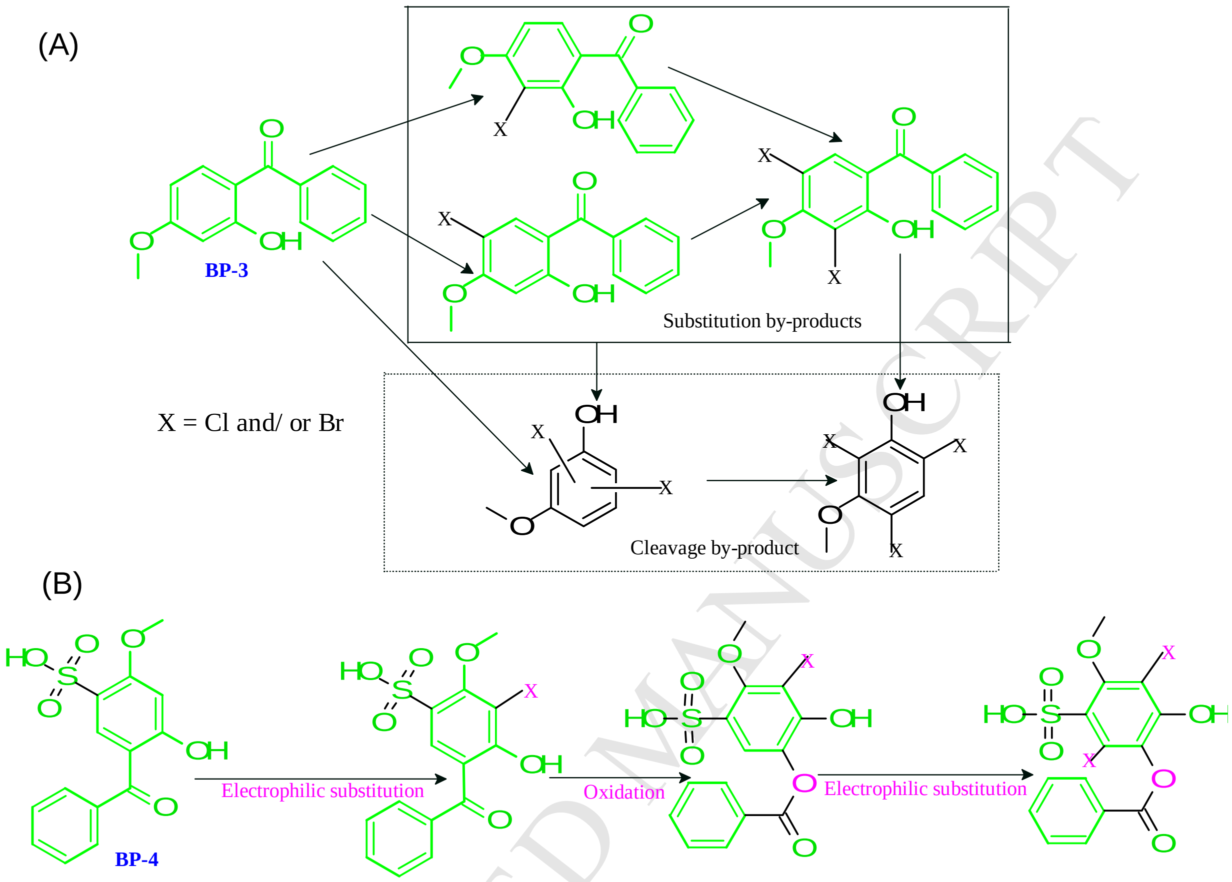

Figure A2. Proposed degradation pathway for BP-3, adopted from ref. [6] (Figure A), and for BP-4 in chlorine-containing water samples, adopted from ref. [7] (Figure B).

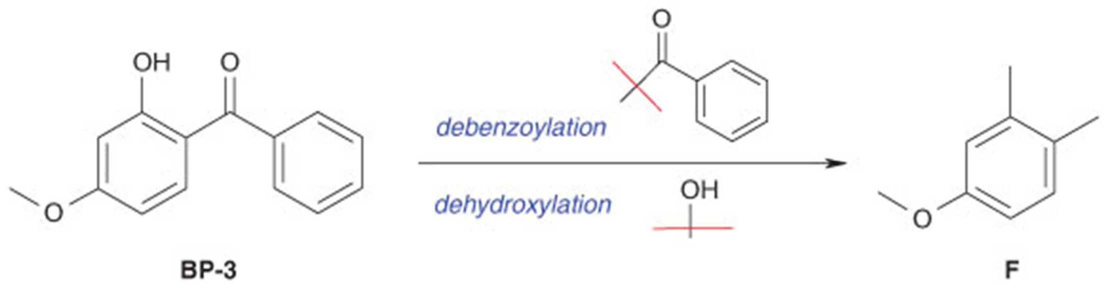

Figure A3. Photolysis of BP-3 under UV radiation in the presence of humic acid (from ref. [8]).

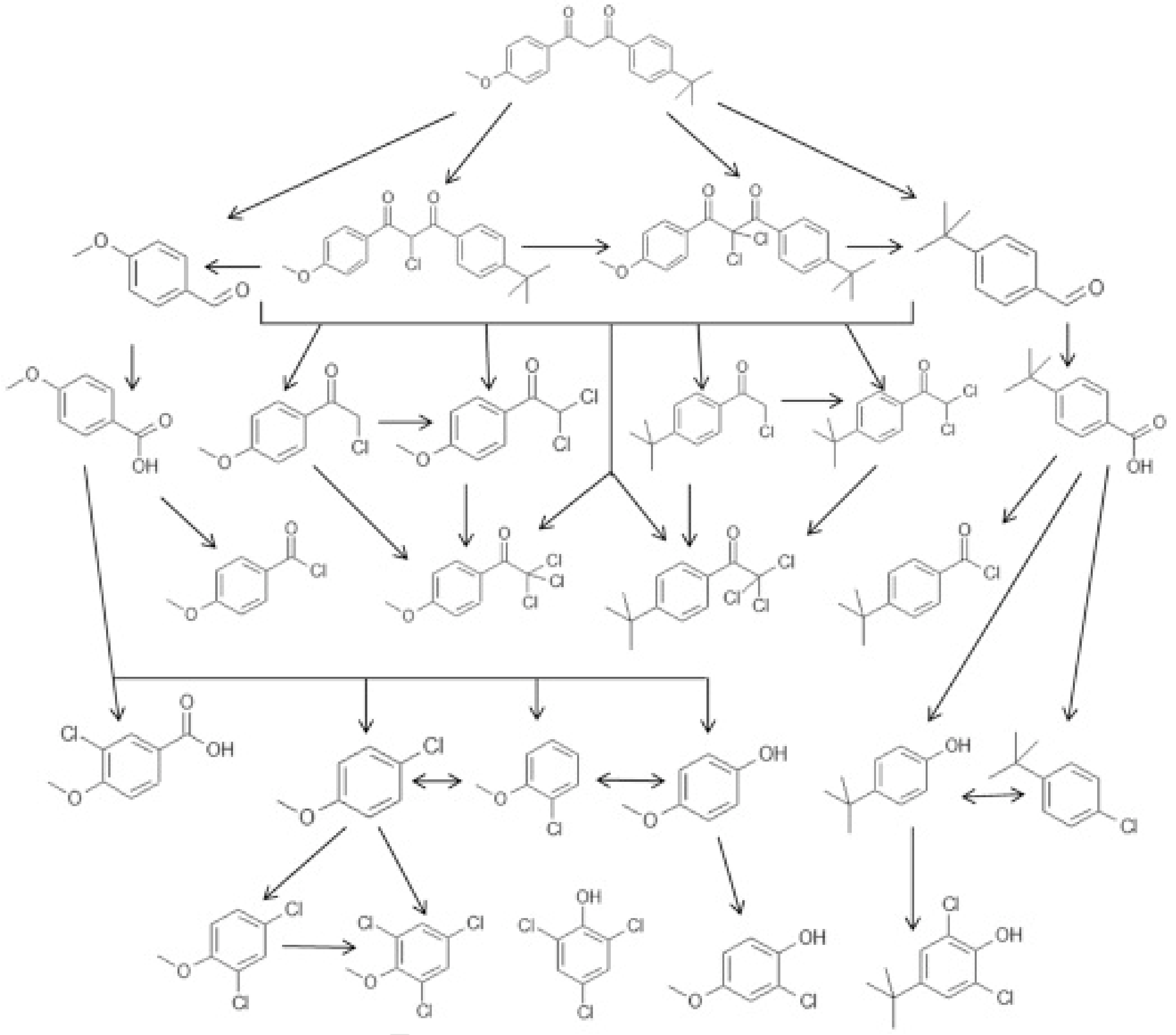

Figure A4. Transformation pathways of avobenzone under aquatic chlorination and UVC irradiation (from ref. [9]).

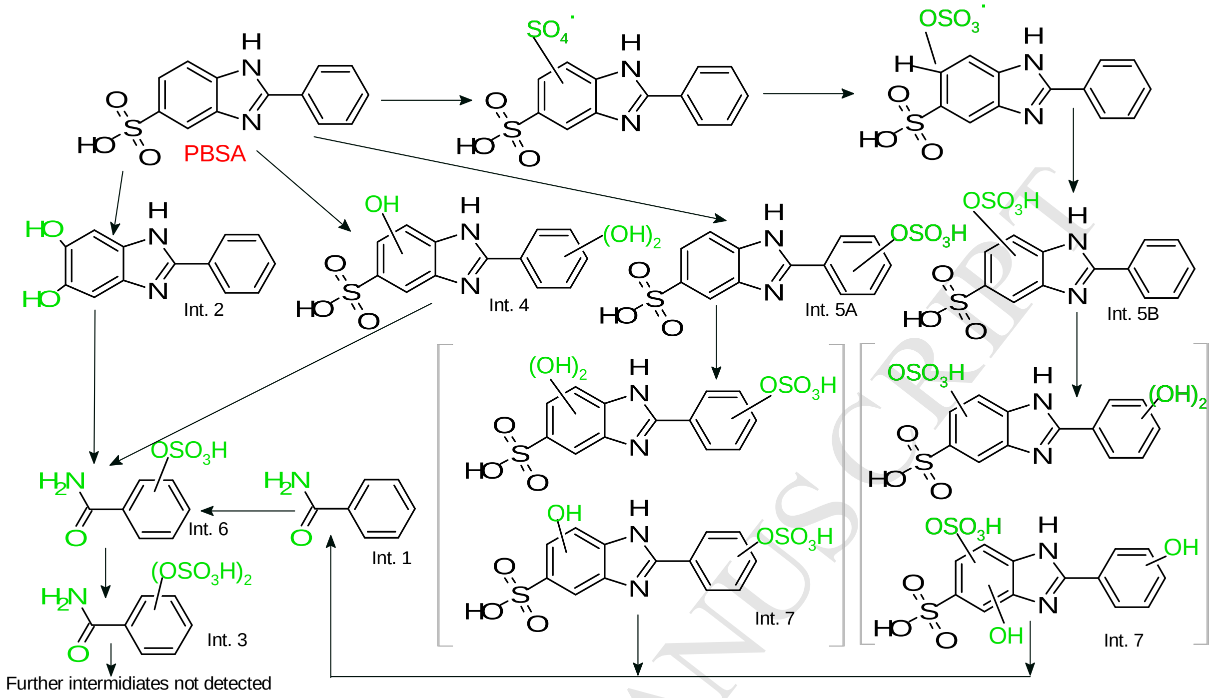

Figure A5. Catalytic degradation pathway of 2-phenylbenzimidazole-5-sulfonic acid by $LaCoO_3$ based catalyst activation of peroxymonosulfate (from ref. [10]).

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Table 1. The concentration of different organic UV filters present in various types of water. Data taken from ref. [27].

Water source	BP-3	OD-PABA	4-MBC	Octyl methoxycinnamate	Octocrylene	Butyl methoxydibenzoyl methane
Swimming pool (ng L^{-1})	3.3-3300	2100	5.9-7.9	3.6-5.4		n.d.
Shower wastes (ng L^{-1})	8.3-9900	5300-6200	3.3-4.3	3.8-4.4		n.d.
Ionian sea (ng L^{-1})	1.4-2.2		trace			n.d.
Game pool (ng L^{-1})	4.8-6.6		4.3-6.5	2.6-3.4		n.d.
Bathing waters (12pm) (ng L^{-1})	5.1-7.9		11.9-14.3	6.5-8.3		
Zurich lake (ng L^{-1})	<2-4		<2-22	<2-25	<2	<20
Huttnersee lake (ng L^{-1})	5-125		<2-82	<2-19	<2-27	
Swiss lakes (ng L^{-1})	<2-35		<2-28	<2-7	<2-5	
WWTP Influent (mg L^{-1})	0.7-7.8		0.6-6.5	0.5-19	0.1-6.1	
WWTP effluent (mg L^{-1})	<0.01-0.3		0.06-2.7	<0.01-0.1	<0.01-0.3	

n.d.: not detected

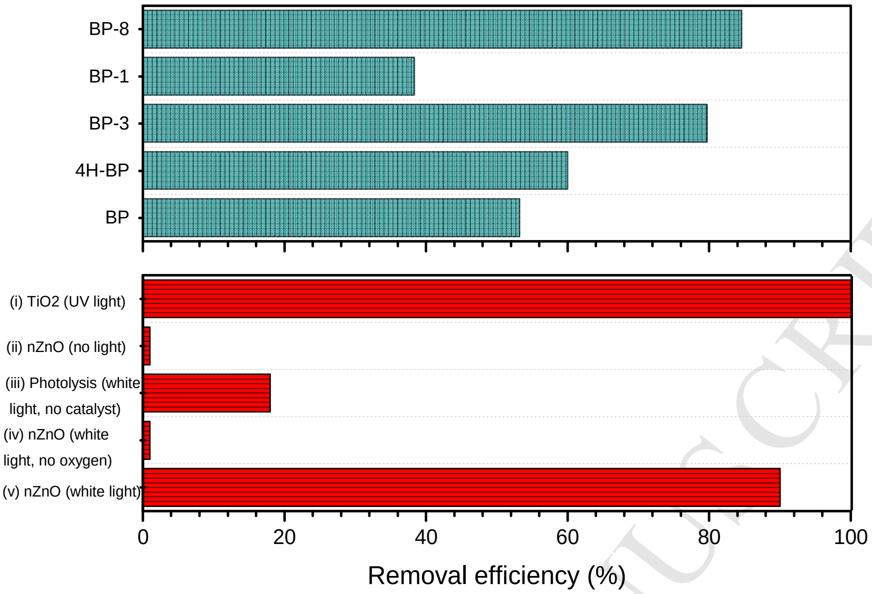

Figure 1. The photostability of benzophenone UV filters after 24 h exposure under a medium pressure mercury UV lamp (125 W) in distilled water [44] (a). Comparative degradation of 2-phenylbenzimidazole-5-sulfonic acid UV filter using (i) TiO_2 photocatalyst under UV (high pressure mercury lamp, 125 W) [55], (ii) nZnO catalyst in the absence of light, (iii) Photolysis in the absence of the catalyst under white light irradiation (53,000 lux), (iv) nZnO catalyst in the absence of oxygen, (v) nZnO under white light irradiation (53,000 lux) [53], (b).

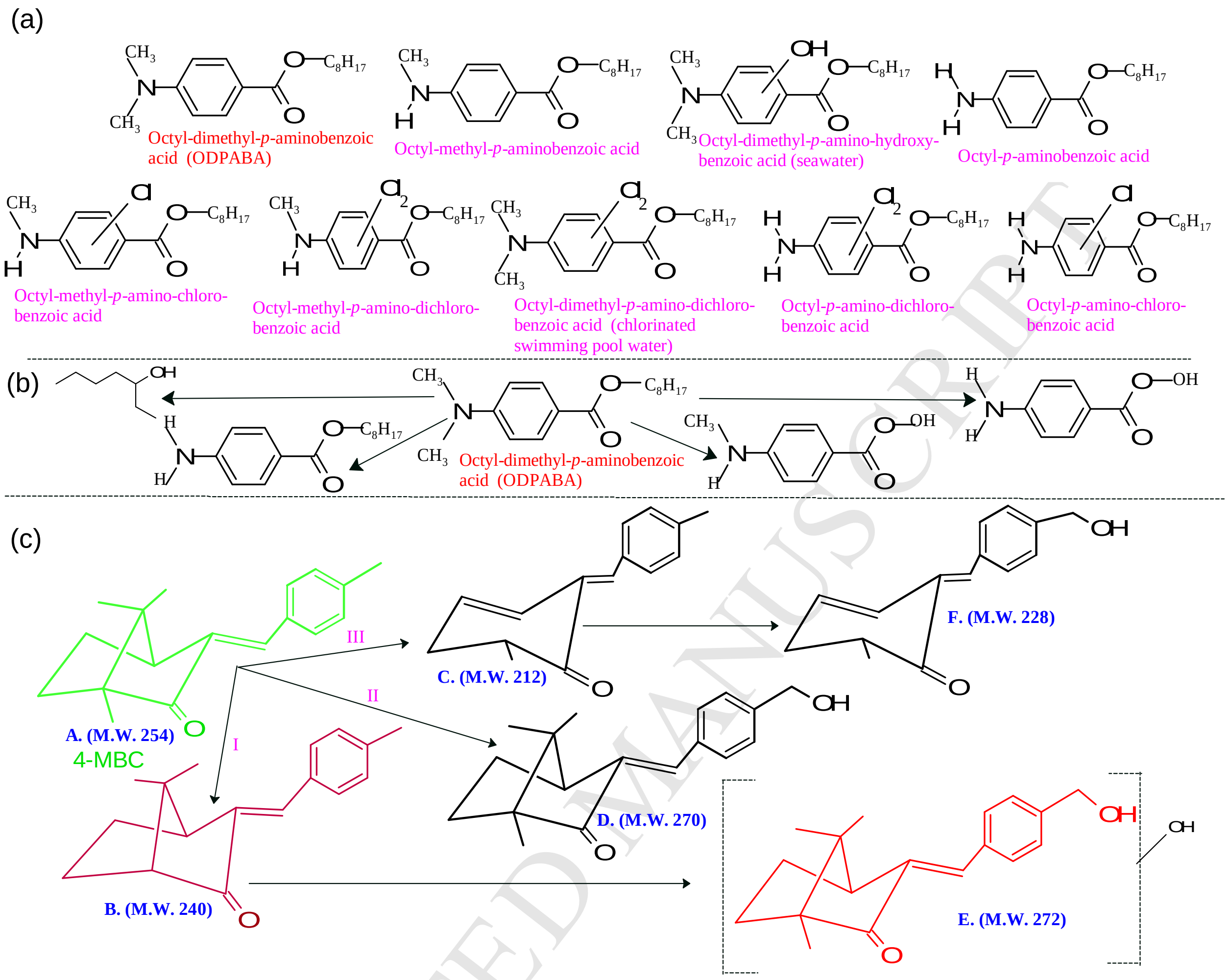

Figure 2. Major photodegradation intermediates of ODPABA in seawater and in chlorinated swimming pool water, adopted from ref. [46] (a). Products of ODPABA conversion under photolysis (b). Possible photocatalytic transformation pathways of 4-MBC UV filter using TiO_2/H_2O_2 medicated photocatalyst (Xenon arc lamp, 1500 W, Solarbox, Milan, Italy), adopted from ref. [52] (c).

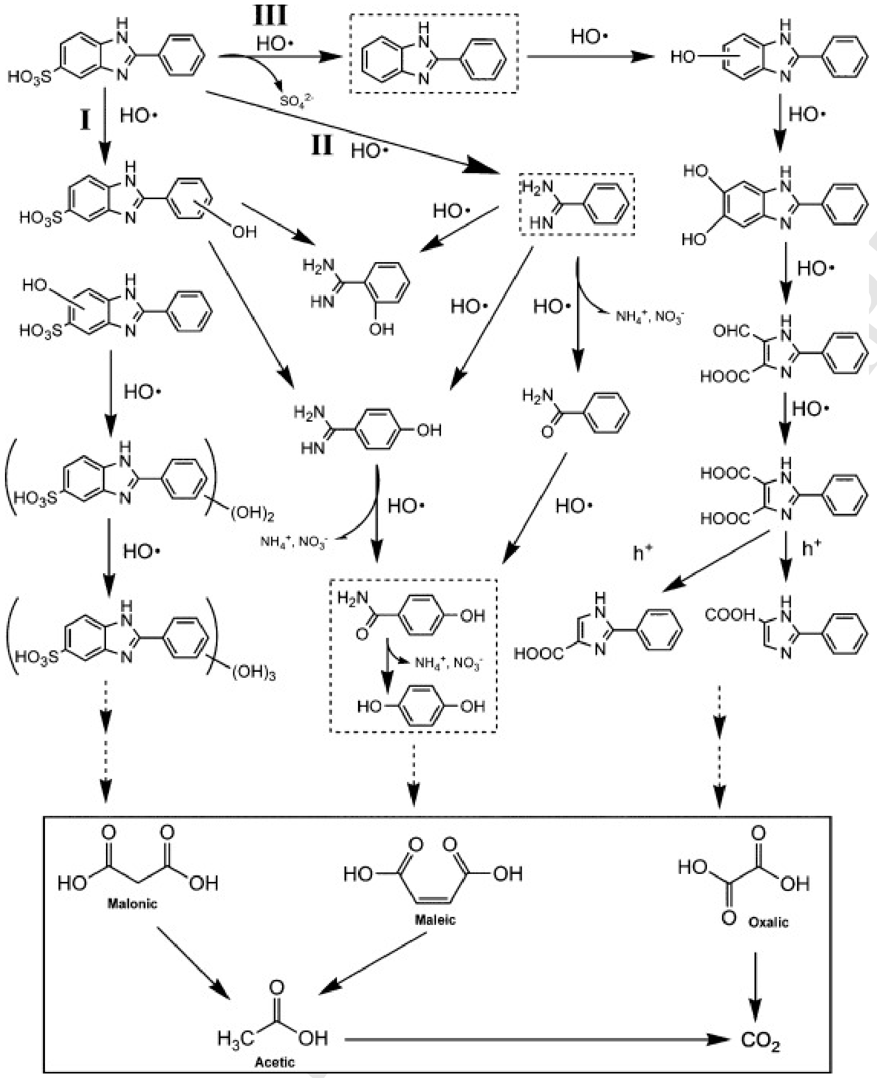

Figure 3. Possible photocatalytic degradation pathways of 2-phenylbenzimidazole-5-sulfonic acid in illuminated aqueous TiO_2 suspensions (taken from ref. [55]).

Highlights

- Photolysis of UV filters was a slow process.
- Presence of photosensitisers (e.g. ^{3}CDOM*) increased photolysis.
- Salinity and DOM decreased the photolysis of UV filters.
- Photocatalysis was very effective for UV filters removal.
- Radiation source, catalyst and O_2 content were key factors for photocatalysis.