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Review

Efficiency increased advanced oxidation processes by persalts for the elimination of pharmaceuticals in waterbodies: a short review

Melanie Voigt[1] · **Martin Jaeger**[1]

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Abstract
To achieve complete elimination of anthropogenic micropollutants in aquatic environments, advanced oxidation processes are intensively researched as remedies and potential advanced purification stages in wastewater treatment facilities. Persalts, like persulfates, percarbonates and periodates, have been investigated as potential accelerators or enhancers of these processes. This short review provides an overview of the efficiency of the persalts demonstrated for the degradation of the seven most frequently occurring pharmaceuticals in the aquatic environment: carbamazepine, ciprofloxacin, diclofenac, ibuprofen, metoprolol, paracetamol and sulfamethoxazole. While persulfates were the most commonly used, all persalts increase the effectiveness of the degradation of the pharmaceutical contaminants by increasing the formation of hydroxyl radicals, especially in the case of sodium percarbonate. Persalts are efficiently activated through UVC irradiation. The generated hydroxyl radicals are the main factor for product formation and hence dominate the chemical structures of the transformation products. From the ecotoxicological perspective, the use of persalts causes little or no hazard, if the conditions are such that acidification can be neglected. While they are transformed to stable anions on reaction, the resulting transformation products of the anthropogenic micropollutants were predicted by quantitative structure activity relation analysis to possess lower ecotoxicity than the initial drugs.

Keywords Persulfate · Percarbonate · Periodate · Micropollutants · Ecotoxicity

1 Introduction

Anthropogenic micropollutants, such as pharmaceuticals and pesticides, are regularly detected in various water bodies around the world, posing a threat to the aquatic environment [1, 2]. Due to incomplete metabolization in the body and improper disposal into the public sewage system, these pharmaceuticals reach the local sewage treatment plants. The wastewater treatment plants are very often no longer able to completely eliminate the micropollutants from the water through their conventional three purification stages consisting of mechanical, biological and chemical treatment. They eventually enter surface waters and may even penetrate into drinking water [3, 4]. In addition, medicines administered to farm animals can be discharged into the agricultural environment through excretion or manure, where they happen to be washed into nearby surface waters by rain [5, 6].

Many pharmaceuticals are a particular focus of research, as they are very frequently detected in various types of water. These include carbamazepine, ciprofloxacin, diclofenac, ibuprofen, metoprolol, paracetamol and sulfamethoxazole [7–10]. The federal environmental agencies e.g., in Germany have compiled databases in which the investigations

✉ Martin Jaeger, martin.jaeger@hs-niederrhein.de | [1]Department of Chemistry and ILOC, Niederrhein University of Applied Sciences, Frankenring 20, 47798 Krefeld, Germany.

of pharmaceuticals in water are collected from public water monitoring reports worldwide. Over 42,000 entries for the seven selected substances can be found with observed concentrations of up to several 100 mg/L [10]. More details of the focus substances are listed in Table 1.

In the last decade, it has become obvious that complete elimination of the micropollutants passing the wastewater treatment plant requires a so-called extended or advanced purification stage. Various processes have been tested, such as the use of ultrafiltration by biomembranes, constructed wetlands as an additional biological treatment stage, and the use of powdered or granulated activated carbon as an additional physical treatment stage [11–13]. The use of so-called advanced oxidation processes (AOPs) as a chemical purification stage has been investigated evenly and proved particularly promising, albeit not on real wastewater treatment plant scale [13–15].

Common AOPs include photolysis, ozonation, ultrasonic, Fenton reactions, electrochemical oxidation and hybrid methods as well as ionizing radiation like gamma and electron beam radiation [16, 17]. All of these processes generate hydroxyl radicals which, as strong oxidizing agents with an oxidation potential of 2.8 V, are found capable of completely eliminating anthropogenic micropollutants [18–20]. The degradation occurs via an indirect degradation mechanism, as the hydroxyl radicals are formed from hydrolysis [21, 22]. In contrast, direct degradation, i.e. oxidation of the compound is induced by radiation or the process' reagent itself, may also take place. Photo-irradiation may serve as an example: When the substance absorbs radiation, is hence excited and reacts or degrades from the excited state, decomposition occurs without interaction of hydroxyl radicals. An overview of extended purification processes can be found in a previous review containing more details, their application and large-scale technical implementation [13].

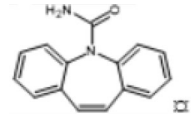
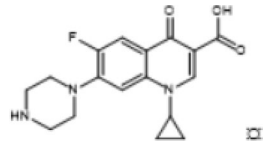
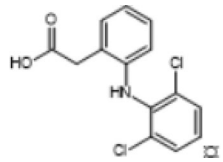
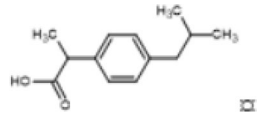
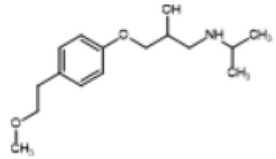
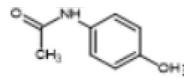
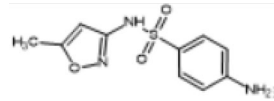
Further to the formation of hydroxyl radicals, the addition of persulfates, percarbonates and periodates can form radicals, which also have a high oxidation potential to deconstruct micropollutants [16]. Their oxidation potential, the mechanism and the efficiency will be discussed below. As a result, persalts have shifted into focus to ameliorate the removal of anthropogenic micropollutants. As a consequence, the number of publications dealing with persalts has risen in recent years, see Fig. 1.

From 2010 until 2023, more than 824 studies on AOPs using persulfate, percarbonate and periodate have been published and listed by Web of Science. Most studies report on the use of persulfate (784). In contrast, relatively few studies deal with the use of percarbonate (23) and periodate (21). The application of other persalts such as perbromate, perphosphate and pernitrate has been described very little or not at all, so that the focus of this review is set on persulfate, percarbonate and periodate.

The inorganic sulfate, iodate and carbonate products of the persalts are stable, non-reactive, and non-toxic. They may alter the pH if used in sufficient quantities and in non-buffering conditions. The generation of hydroxyl radicals was reported to lead to the formation of products that were more toxic than the initial substances, which would be detrimental to ecotoxicity [23, 24]. It is therefore essential to consider not only the efficiency of degradation using the persalts, but also the determination of the ecotoxicity of the transformation products. Such ecotoxicological testing may include luminescent bacteria or *Daphnia magna*. The transformation products are very often characterized and identified using analytical hyphenated methods such as gaschromatography or high performance-liquid chromatography coupled to mass spectrometry (GC–MS, HPLC–MS). As it is usually difficult or impossible to isolate the transformation products from the mixture in sufficient quantities and the acquisition and synthesis of the analytes are very often too expensive, time-consuming or even not possible, a theoretical predictive method needs to be used further to the in vivo and in vitro assays to assess ecotoxicity [25, 26]. The in silico quantitative structure activity relation (QSAR) analysis has established itself as an inexpensive and fast alternative to in vitro and in vivo testing [27–32]. A sum parameter may be obtained when transformation products are assayed as mixtures in order to assess their ecotoxicity [33].

For in silico methods, no organisms and chemicals are needed, since ecotoxicity is predicted from available ecotoxicity data using multivariate data analysis or statistical mathematical models, which based on molecular structure, descriptors and similarity principles [28, 34]. Yet, models rely on the availability of data from compounds of similar molecular structure. Typically, data from ecotoxicity databases are used for modeling, the best known of which is the ECOTOX database (https://cfpub.epa.gov/ecotox/) [35]. A well-known model is the Ecological Structure–Activity Relationship (ECOSAR), where the chemical structures are employed in the simplified molecular-input line-entry system (SMILES) representation. Using ECOSAR the ecotoxicity can be predicted against a variety of organisms, such as *Daphnia* (branchiopoda), fish (actinopterygii) and green algae [28, 36, 37]. The QSAR toolbox software is often used to calculate the sought ecotoxicity values. The software includes structure-based chemical classes of ECOSAR, while the physico-chemical property-based model of Veith et al. and Pavan et al. is also implemented [38, 39].

Table 1 Focus substances with their therapeutic field, target species, CAS-number, maximum observed concentration together with the observations location, and structure [10]

Substance	Therapeutic group	Target group	CAS-number	Maximum observed concentration/µg L^{-1}	Location	Structure
Carbamazepine	Antiepileptic drugs	Human	298-46-4	34	WWTP effluent, Germany	
Ciprofloxacin	Antibiotics	Human and veterinary	85721-33-1	31000	WWTP effluent, India	
Diclofenac	Analgesics	Human	15307-86-5	8000000	WWTP sludge, Canada	
Ibuprofen	Analgesics	Human	15687-27-1	22000	Sewage industrial, Kenya	
Metoprolol	Beta-blockers	Human	37350-58-6	950	WWTP effluent, India	
Paracetamol	Analgesics	Human	103-90-2	3275	WWTP influent, USA	
Sulfamethox-azole	Antibiotics	Human and veterinary	723-46-6	200000	Sewage industrial, Kenya	

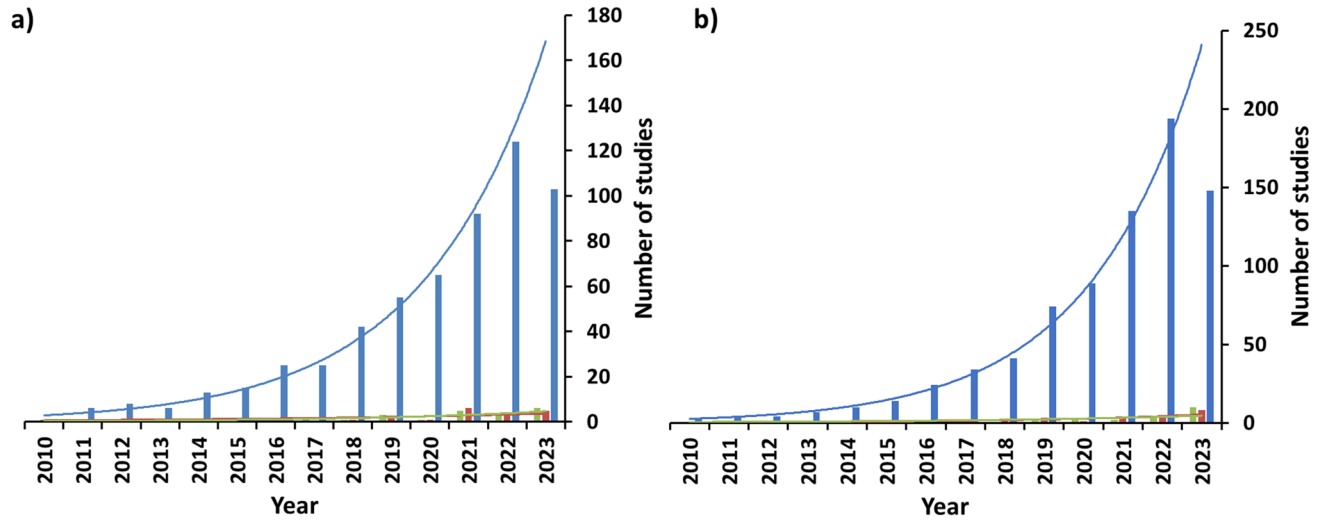


Fig. 1 Number of studies from 2010 to 2023 resulting from **a** Scifinder search and **b** web of science search "advanced oxidation process" specified by persulfate, percarbonate and periodate. Specific results for persulfate (blue), percarbonate (red) and periodate (green) are shown

In this review, the individual mechanisms resulting from the addition of the persalts persulfate, percarbonate and periodate are described and compared with each other. The efficiency of the persalts is compared on the basis of the substances carbamazepine, ciprofloxacin, diclofenac, ibuprofen, metoprolol, paracetamol, and sulfamethoxazole. Homogeneous reaction systems are considered, i.e. in the absence of catalysts, since countless catalysts are currently being tested and the consideration of heterogeneous reaction systems would exceed the scope of this short review. Finally, the ecotoxicity is assessed. To this purpose, all products reported in studies are first structurally recorded and converted into the SMILES notation such that a QSAR analysis can be performed for all seven pharmaceuticals and its reported transformation products. If possible, the analysis is compared with in vivo or in vitro studies, so that the quality of the ecotoxicity prediction can be evaluated. Furthermore, the ecotoxicity of the three persalts in the aquatic environment is also investigated. Whether the addition of persalts is beneficial for the elimination of anthropogenic micropollutants and non-hazardous for the aquatic environment will be answered.

2 Mechanism and efficiencies of persalts

The persalt-induced reactions and the mechanism of anthropogenic micropollutant degradation follow a general process, which is shown in Fig. 2.

Firstly, the persalt is activated. The activation can be achieved thermally, electrochemically, by UV irradiation, by ozonation, by sonolysis or using the Fenton reagent. After activation, the persalt generates radicals, which are hydroxyl, sulfate, iodate, superoxide, peroxomonosulfate ($SO_5^{\bullet-}$) and carbonate radicals [40–46]. In some cases, non-radical reactive species, such as singlet oxygen may be formed [47]. The species are highly reactive due to their oxidation potentials, see Table 2. They are hence able to attack the contaminating pharmaceuticals, induce break-down and eventually eliminate them from water. The radical reactions proceed via the indirect mechanisms, since the substance does not start reacting following direct activation. Degradation reactions occur hence due to the radicals generated from the persalts. The direct degradation of the substance through UV or electrochemical activation, for example, can also proceed in parallel [22, 48, 49]. The dominant mechanism and the influence of the different radicals on the degradation efficiency as well as the transformation products will be discussed below.

Fig. 2 General process of persalt-induced anthropogenic micropollutant removal

Table 2 Oxidation potential

Oxidizing species	Oxidation potential E^0/V	References
Fluorine F_2	3.0	[40–42]
Hydroxyl radical·OH	2.8	[43, 44]
Sulfate radical $SO_4^{\cdot-}$	2.4	[43, 44]
Persulfate $S_2O_8^{2-}$	2.1	[40, 41, 44]
Ozone O_3	2.1	[42–44]
Peroxymonosulfate HSO_5^-	1.8	[40, 41]
Hydrogen peroxide H_2O_2	1.8	[40–42, 44]
Permanganate MnO_4^-	1.7	[40–42, 44]
Carbonate radical $CO_3^{\cdot-}$	1.6	[45, 46]
Chlorine dioxide ClO_2	1.5	[40, 41]
Chlorine Cl_2	1.4	[40–42]
Superoxide radical $O_2^{\cdot-}$	−2.4	[44]

Sulfate and hydroxyl radicals have the highest oxidation potentials. The carbonate radical is generated from sodium percarbonate. Oxidation potentials for iodate and periodate radicals could not be found. The effectiveness of these radicals will be evaluated by the effect on degradation. Depending on the pH value and the medium investigated, different oxidation potential values are reported for hydroxyl radicals, sulfate radicals and ozone [16, 50].

Ideally the anthropogenic micropollutant is completely mineralized using persalts, so that only water, carbon dioxide and inorganic salts remain, which no longer pose a risk to the aquatic environment.

2.1 Persulfate

Most studies on the degradation of pharmaceuticals with persalts were conducted with persulfate. In dissolved, non-heterogeneous catalytic systems, two different persulfates were used as AOP promoters: peroxymonosulfate (PMS) and peroxydisulfate (PDS). They form sulfate radicals, which are essential for the successful degradation of the pharmaceuticals. Figure 3 shows the main reaction mechanism of PMS and PDS.

From PMS, two types of radicals, sulfate and hydroxyl radicals are formed. The use of PDS leads to sulfate radicals. The generation of sulfate radicals is influenced by pH. By UV irradiation or heat activation, both PDS and PMS yielded sulfate radicals, their formation being strongest at pH 5–7. Sulfate radicals were also predominantly observed in the acidic milieu. Between pH 7 and 9, both sulfate and hydroxyl radicals were reported. In the strongly alkaline regime at pH 12, sulfate radicals were observed reacting with hydroxyl anions to form hydroxyl radicals [41, 42, 51, 52]. However, both radicals could recombine in alkaline milieu in a radical termination reaction, reducing the efficiency of the degradation [41, 53].

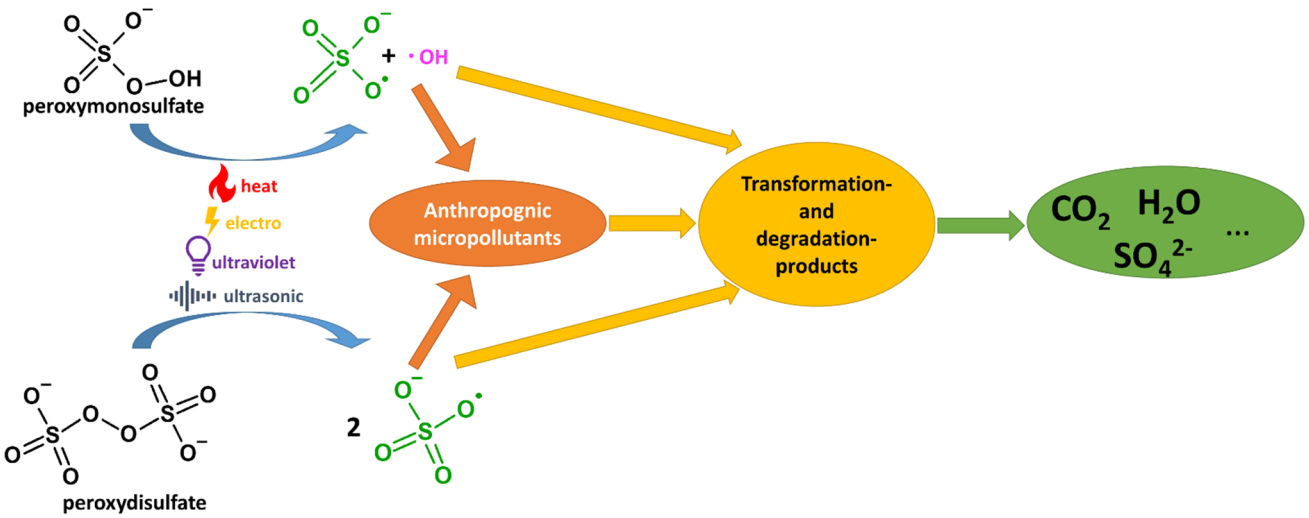


Fig. 3 Pathways of persulfate-activated degradation mechanism of anthropogenic micropollutants

The concentration of PDS or PMS influenced the degradation. Higher concentrations led to faster degradation. Yet, too high a concentration decelerated the degradation reaction due to an excess of sulfate radicals that recombine or act as scavengers. Similar observations were reported for high peroxide concentrations referred to as supersaturation [41, 42, 54–56].

An overview of the use of persulfates with carbamazepine, ciprofloxacin, diclofenac, ibuprofen, metoprolol, paracetamol and sulfamethoxazole under different conditions is given in Table 3.

From the degradation studies of carbamazepine and ciprofloxacin, it can be concluded that PMS is more effective than PDS when activated by UVC irradiation. For sulfamethoxazole, similar efficiencies were observed with both persulfates. Nevertheless, a general conclusion can be drawn from the overview: As PMS leads to sulfate and hydroxyl radical formation, PDS to sulfate radicals only, cf. Figure 3, unless high-energy irradiation methods were used, PMS is the more efficient agent as hydroxyl radicals are the more reactive and oxidizing species.

The concentration of persulfate has an impact on the degradation. For carbamazepine and metoprolol as examples, a tenfold increase in the concentration of PMS increased the degradation rate from 15 to 80% for a reaction duration of 60 min and UVA activation for carbamazepine and from 10 to 100% for metoprolol. This observation was made for ibuprofen as well, where a fivefold increase in concentration of PMS together with solar-simulating light was found to deconstruct ibuprofen from 90% after 120 min reaction time to 100% after 30 min.

As activation method, heat was reported superior to ultrasound. Increasing temperature rendered the degradation more efficient. This was demonstrated for ibuprofen, where complete degradation was observed after 20 min at 70°C as compared to 90% degradation after 60 min with ultrasound. Even more efficient than heat activation, UV radiation proved the better activator, with UVC radiation superior to UVA. This was observed for ciprofloxacin and paracetamol. In the case of sulfamethoxazole, UVC irradiation was the more effective method compared to the addition of non-activated PMS. The use of high-energy radiation, i.e. gamma radiation, yielded high elimination rates between 80 and 100% for carbamazepine and diclofenac. A wider application as advanced purification stage seems unlikely at present.

Summarizing for the seven compounds under consideration, PMS was the preferred additive among the persulfates and its activation by UVC radiation achieved the most efficient degradation rates. A higher concentration of PMS fostered the desired degradation. Scavenging and supersaturation effects were not reported.

2.2 Percarbonate and periodate

Periodate and percarbonate are also used for anthropogenic micropollutant degradation albeit less frequent. The main pathway of periodate degradation is shown in Fig. 4.

Periodate can form iodate radicals and periodate radicals. Parallel to the formation of the iodate radical, a superoxide anion radical is also formed, which further reacts with water to form hydroxyl radicals. The iodate radical can also form a periodate radical, cf. Figure 4. All occurring radicals can induce the degradation of the micropollutant via the formation of intermediate transformation products, which in turn are further degraded by the radicals. Periodate may be quickly degraded by UVC radiation. Bendjama et al. investigated the photodecomposition of 0.25 mM periodate at pH 5.6 and room temperature [87, 88]. A degradation of periodate was observed within 7 min of irradiation. As already observed for persulfates, two radicals may recombine and thus discontinue the degradation process [87, 89]. The termination reaction occurred in the presence of high periodate concentrations [90].

The mechanism of percarbonate radical generation is different from that of persulfates and periodates. Two different percarbonates come into consideration: sodium percarbonate (SPC) and peroxymonocarbonate (PMC), cf. Figure 5.

In general, PMC is unstable and the storage is difficult, hence it is not suitable for the degradation of anthropogenic micropollutants.

The most frequently used percarbonate is SPC. On dissolution in water, it immediately decomposes into sodium carbonate and hydrogen peroxide, see Eq. 1.

$$2\,Na_2CO_3 \cdot 3\,H_2O_2 \rightarrow 2\,Na_2CO_3 + 3\,H_2O_2 \quad (1)$$

Due to the formation of hydrogen peroxide, sodium percarbonate is often used as a substitute for mere hydrogen peroxide as it is easier to handle. The cost of sodium percarbonate is also three times lower than that of hydrogen peroxide [91, 92]. Hydrogen peroxide is homolyzed to hydroxyl radicals through activation via UV irradiation, see Eq. (2).

Table 3 Degradation efficiencies of carbamazepine, ciprofloxacin, diclofenac, ibuprofen, metoprolol, paracetamol and sulfamethoxazole using activated persulfates together with starting concentrations, pH and temperature

Substance	Activation	Starting concentration of the substance c_0/µM	Starting concentration of persalt c_0/mM	pH	T/°C	Efficiency	References
Carbamazepine	UVC @ 254 nm	121.16	1 (PDS)	3.5–5.5	25	76.2% in 90 min	[40, 57]
	UVC @ 254 nm	121.16	1 (PMS)	4.5	25	98.9% in 90 min	[40, 57]
	UVC @ 254 nm	0.004	1 (PDS)	8.2		50%	[58]
	UVA @ 385 nm	0.423	0.05 (PMS)	7.6		15% in 60 min	[59]
	UVA @ 385 nm	0.423	0.5 (PMS)	7.6		80% in 60 min	[59]
	Gamma radiation @ 200 Gy	42	2 (PDS)	6.5		80.9%	[41, 60]
	Gamma radiation @ 300 Gy	40	0.8 (PMS)	3.0		100%	[41, 61]
	Ultrasonic @ 40 kHz/200W	25	1 (PDS)	5.0		89.4%	[62, 63]
Ciprofloxacin	Heat @ 70 °C	30	2 (PDS)	7.0	70	92% in 180 min	[40, 64]
	Heat @ 50 °C	13	1.04 (PDS)	4.0	50	69.2% in 120 min	[41, 65]
	UVC @ 254 nm	125	2.5 (PMS)	7.0	60	100% in 60 min	[41, 66]
	UVC @ 254 nm	60.42	1.1 (PDS)	6.0		100% in 7 min	[67]
	UVC @ 254 nm	60.42	1.1 (PMS)	3.3		95% in 30 min	[67]
	UVC @ 254 nm	50	1 (PMS)	7.0	25	97% in 60 min	[40, 66]
	UVA @ 385 nm	0.30	0.05 (PMS)	7.6		70% in 60 min	[59]
	UVA @ 385 nm	0.30	0.5 (PMS)	7.6		100% in 60 min	[59]
Diclofenac	Ultrasonic @ 700 W	16.88	0.44 (PDS)	6.0	30	97% in 240 min	[40, 62, 68]
	Heat @ 60 °C	47	0.47 (PDS)	5.0	60	> 90% in 120 min	[69]
	Heat @ 70 °C	47	0.47 (PDS	7.0	70	Ca. 85% in 120 min	[69]
	Gamma radiation @ 1000 Gy		1 (PDS)	6.1		84%	[70]
Ibuprofen	Ultrasonic @ 35 kHz	24.00	0.80 (PDS)	4.9		90.4% in 60 min	[62, 71]
	Heat @ 70 °C	20.36	1 (PDS)	7.0	70	100% in 20 min	[72, 73]
	Heat @ 65 °C	20.36	1 (PDS)	7.0	65	100% in 40 min	[72]
	Solar simulated @ 290–800 nm	4.85	5 (PMS)		20	100% in 30 min	[74]
	Solar simulated @ 290–800 nm	4.85	1 (PMS)		20	90% in 120 min	[74]
	UVC @ 254 nm	0.005	1 (PDS)	8.2		40%	[58]
Metoprolol	UVC @ 254 nm	0.004	1 (PDS)	8.2		80%	[58]
	UVA @ 385 nm	0.374	0.05 (PMS)	7.6		10% in 60 min	[59]
	UVA @ 385 nm	0.374	0.5 (PMS)	7.6		100% in 60 min	[59]
Paracetamol	UVA @ 365 nm	10	2 (PDS)	7	25	95% in 30 min	[75]
	UVA @300–500 nm	50	1 (PDS)	10	20 ± 2	55% in 120 min	[76]
	UVA @300–500 nm	50	1 (PDS)	3	20 ± 2	30% in 120 min	[76]
	UVC @ 278 nm	2	0.1 (PDS)	7		95% in 30 min	[77]
	Heat @ 68 °C	330	5 (PDS)	6	68	94.2% in 120 min	[78, 79]

Table 3 (continued)

Substance	Activation	Starting concentration of the substance c_0/µM	Starting concentration of persalt c_0/mM	pH	T/°C	Efficiency	References
Sulfamethoxazole	Stirring @ 500 rpm	39.48	1 (PMS)	3.1	25	95% in 180 min	[80]
	UVC @ 254 nm	23.69	1 (PMS)	8		97% in 120 min	[41, 81]
	UVC @ 254 nm	20	1 (PDS)	8		100% in 120 min	[62, 82]
	UVC @ 254 nm	0.0008	0.01 (PMS)	7.5		90% in 30 min	[83]
	Heat @ 60 °C	40	2.4 (PDS)	7	60	> 80% in 120 min	[62, 84]
	Heat @ 60 °C	30	2 (PDS)		60	98% in 180 min	[85, 86]

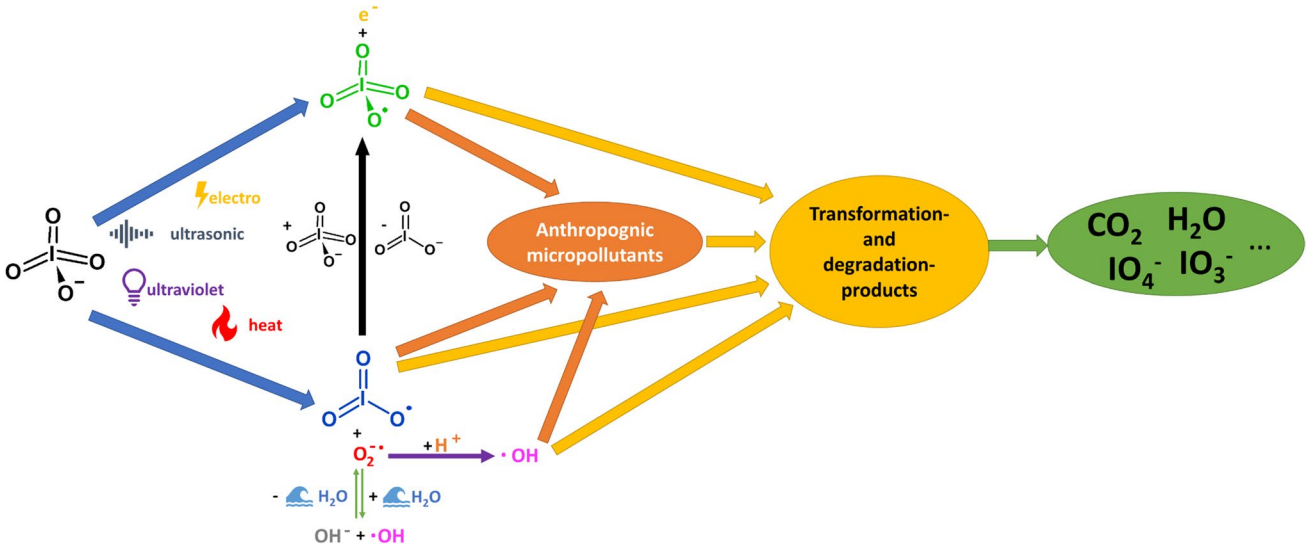


Fig. 4 Pathways of periodate-activated degradation of anthropogenic micropollutants

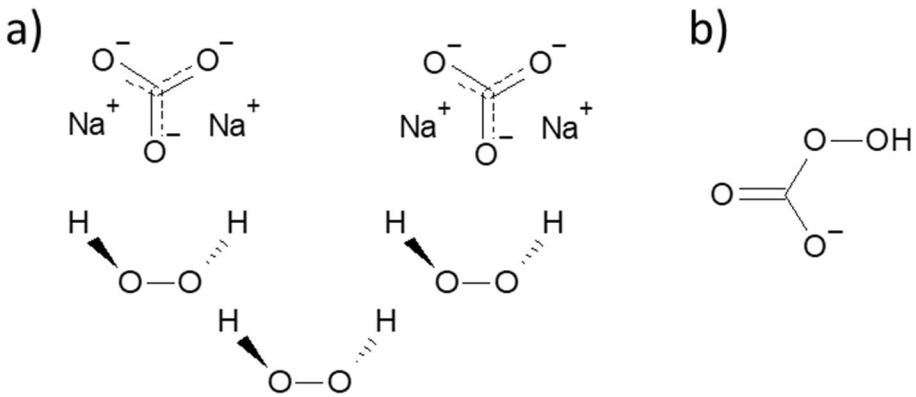


Fig. 5 Chemical structure representation of **a** SPC and **b** PMC

$$H_2O_2 \rightarrow 2\,OH^{\cdot} \tag{2}$$

The resulting hydroxyl radicals may react via electron transfer with carbonate ions, previously formed according to Eq. 1, see Eq. 3.

$$CO_3^{2-} + OH \rightarrow CO_3^{-} + OH^{-} \tag{3}$$

The degradation of the seven selected pharmaceuticals with the aid of percarbonates and periodates has been studied very little to date. It is also striking that only studies were reported where UV light was used to activate the periodate. Only the study by Chen et al. used hydrogen peroxide for its activation according to Eq. (4) [93]. In addition to the iodate radical, a superoxide anion is formed, which belongs to the reactive oxygen radical species.

$$IO_4^{-} + H_2O_2 \rightarrow IO_3 + O_2^{-} + H_2O \tag{4}$$

No study on the degradation of the seven selected pharmaceuticals using PMC could be found. That may be indeed traced back to the instability and storage difficulties of PMC. Table 4 lists the studies found that used percarbonate or periodate for the degradation of the seven selected pharmaceuticals.

Most studies reported almost complete elimination of the substance within 30 min. Due to the very low number of investigations using percarbonate and periodate salts, it is somewhat difficult to compare the efficiency. However, the use of percarbonate and UVC irradiation as activation seems to be the most effective. Carbamazepine and paracetamol could be eliminated from water by more than 90% within 2 min. Since only hydroxyl radicals are formed on percarbonate use, this radical appears to be the protagonist. All degradation experiments with percarbonate were conducted at

Table 4 Degradation efficiencies of carbamazepine, ciprofloxacin, diclofenac, ibuprofen, metoprolol, paracetamol and sulfamethoxazole using activated percarbonate or periodate together with starting concentrations, pH and temperature

Substance	Persalt	Activation	Starting-concentration of the substance c_0/µM	Starting-concentration of persalts c_0 / mM	pH	T/°C	Efficiency	References
Carbamazepine	Percarbonate	UVC @ 254 nm	5	1	7.0	25 ± 1	> 90% in 2 min	[94]
	Periodate	H_2O_2 (c_0 = 0.5 mM)	5	0.5	3.0		90% in 20 min	[93]
		UVA @ 365 nm	5	0.1	7.0		95% in 20 min	[95]
Ciprofloxacin	Percarbonate	UVC@ 254 nm and 185 nm	151	0.12	7.0		100% in 60 min	[96]
	Periodate	H_2O_2 (c_0 = 0.5 mM)	5	0.5	3.0		97% in 20 min	[93]
Diclofenac	Periodate	UVA @ 365 nm	5	0.1	7.0		100% in 10 min	[95]
Ibuprofen	Percarbonate	UVC@ 254 nm	5	1	7.0	25 ± 1	> 90% in 2 min	[94]
	Periodate	UVA @ 365 nm	5	0.1	7.0		80% in 20 min	[95]
Paracetamol	Percarbonate	UVC@ 254 nm	5	1	7.0	25 ± 1	> 90% in 2 min	[94]
Sulfamethoxazole	Percarbonate	ozone	98.7	1.19			67% in 30 min	[97]

pH 7, preventing the evaluation of pH influences. The degradation experiments using hydrogen peroxide were carried out at pH 3, the other tests at pH 7, again rendering it hard to compare.

In comparison to the persulfates, percarbonate was recognized to be the best persalt for elimination of the seven pharmaceuticals of interest. Carbamazepine, for example, was degraded to over 90% within 2 min. Among the activation methods, UVC irradiation proved to be most effective. Yet, the different quantum efficiencies would need to be taken into account, which is often not the case, as different UV sources were applied. Another reason why UVC irradiation is superior to UVA is the absorption of UV rays by the compound, see Fig. 6, leading to compound activation and further reaction i.e., according to the direct mechanism.

Almost all seven substances show absorption bands in the UVC range, while no absorption is visible in the UVA range. Although the direct degradation mechanism might be active, it has often been shown that the indirect radical-induced mechanism predominates [22, 98, 99].

3 Degradation and transformation products and ecotoxicological assessment

The assessment of ecological hazard or ecotoxicity is commonly achieved by in vivo assays using ecological representative species such as bacteria, algae, and fish. The tests yield values for chronic or acute toxicity, which are often made available in public domain databases. In many cases, data relevant to the aquatic environment are not available for micropollutants. In particular, toxicity data of transformation products or metabolites resulting from AOPs and sewage treatment plants stem from scientific research and remain singletons. Successful experimental toxicity determination of TPs depends on critical factors, such as the knowledge of the chemical structure and sufficient quantities for testing form isolation or chemical synthesis. In silico methods for the prediction of ecotoxicity have evolved as an alternative, faster and much less expensive approach. Yet, known weaknesses of such computational assessments are the identification of structural similarity leading to compound classification, the amount of available data for a given compound class, the type and relevance of the originally tested species, and the quality of the model and the descriptors. Among the computational approaches, quantitative structure activity relationship (QSAR) analysis has become a prominent representative [27, 29, 31, 32, 100]

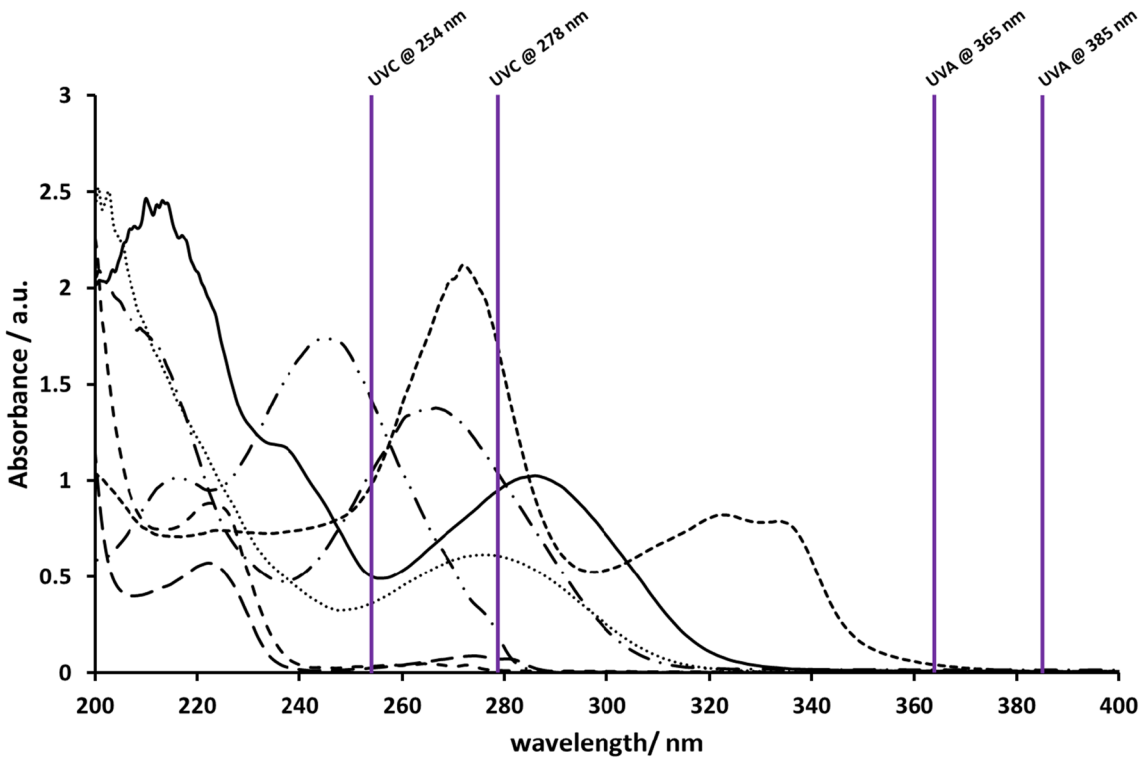


Fig. 6 Absorption spectra of carbamazepine (——), ciprofloxacin (- - -), diclofenac (···), ibuprofen (— —), metoprolol (— — —), paracetamol (– –) and sulfamethoxazole (– –); substances were dissolved in ultrapure water and with final concentrations of 20 ± 1 mg/L

For carbamazepine, ciprofloxacin, diclofenac, paracetamol and sulfamethoxazole, structures were proposed for transformation products that were formed in the presence of persalts. Before their ecotoxicity can be assessed by means of QSAR analysis, the products need to be elucidated and represented by their chemical structure so that the structures can be converted into SMILES notations, which are fed into the QSAR tools and prediction can be carried out. As examples, the structures of the reported transformation products were drawn with ACD/ChemSketch 2016.1.1 (ACDLabs, Toronto, ON, Canada) and their SMILES notations were entered into the QSAR toolbox software (LMC Oasis, Bourgas, Bulgaria). In the software, a variety of ECOSAR models are implemented. Due to the strong structural differences of the five substances, they were assigned to different ECOSAR models. As descriptor, the logarithm of the octanol–water partition coefficient, log *K*ow, was selected for prediction via a series of linear regression models [101]. The ecotoxicity of the substances was thus predicted against green algae, fish and daphnid as relevant examples for the aquatic environment. A second QSAR model, which is also implemented in the QSAR toolbox, is the model by Veith et al., which was refined by Pavan et al. [38, 102]. The lethal concentration 50% (LC_{50}) was predicted against *Pimephales promelas* based on log K_{OW} and the lowest unoccupied molecular orbital (LUMO) energy as descriptors.

The SMILES notation of the proposed structures, the conditions under which they were formed and the ECOSAR prediction models are shown in Table 5. The molecular structures are displayed in Fig. 7 in the descending order of their predicted ecotoxicological hazard.

A striking feature of the product formation is that no transformation products containing any adducts of the anionic radicals have been reported. Apparently, neither sulfate radicals nor iodate radicals nor carbonate radicals yielded stable adducts with the pharmaceutical substances. In contrast, hydroxyl radicals formed sufficiently stable transformation products, such as Cip286, where the fluorine atom was substituted by a hydroxyl group. Other products were identified having accumulated several hydroxyl groups in an aromatic moiety. Examples are Car288, Car287, Car253-2, Cip362-2, Cip334-2, Sul519, Sul286, Sul284-2, Sul270-1 and Sul190. Unfortunately, the exact position of the hydroxyl group in the ring could not be unequivocally assigned. Yet, it is important for the SMILES notation to indicate the exact position in order to recognize similarities. For the ecotoxicity prediction, it is therefore necessary to assume all possible regioisomers and assess the corresponding ecotoxicity through QSAR analysis.

As described above, ECOSAR might not yield adequate classification in some cases, so the model of Veith and Pavan et al. was also used to estimate ecotoxicity. A compilation of the structures in descending order of their predicted ecotoxicities is given in Fig. 7. The influence of the hydroxyl groups on ecotoxicity can also be recognized therefrom.

Many of the resulting products are less ecotoxic than their original substance. It is noticeable that an increasing number of hydroxyl groups in the molecule lead to decreased ecotoxicity. This is particularly evident with carbamazepine and ciprofloxacin. It is also interesting that numerous products with a smaller molecular mass, i.e. after decomposition, are often predicted to be more ecotoxic than the initial substance.

The fact that ecotoxicity decreases when persalts initiate an AOP has also been observed in vitro with other substances. Lalas et al. investigated the thermally activated persulfate oxidation of ampicillin and discovered that the transformation products did no longer exercise any hazardous effects against the microalgae *Chlorella sorokiniana* [103]. The ecotoxicity of anthraquinone dye could was also reduced by UV activated persulfates. Ramakrishnan et al. used the aquatic plant *Lemna minor* and the crustacean *Daphnia magna* for their ecotoxicological investigation [104].

For carbamazepine, in silico and in vitro ecotoxicity can be compared. Zhang et al. investigated the ecotoxicity during the degradation of carbamazepine using persulfate and UV irradiation as activation [105]. As organism, *Vibrio qinghaiensis* was studied. The acute toxicity of the AOP treated mixture showed a significant decrease of ecotoxicity, which is in good agreement with the in silico QSAR prediction above. Similar results were observed for sulfamethoxazole. Its oxidation by thermo-activated persulfate led to products which had a lower antimicrobial potency than sulfamethoxazole, and the ecotoxicity to *Vibrio fischeri* and *Daphnia magna* was reduced [106–108]. This is in line with the findings of the QSAR analysis shown in Fig. 7.

Knowledge of the ecotoxicological potential of persalts themselves is also important when considering their use in advanced purification stages. Do they have adverse effects on the aquatic environment since persalts cannot simply be removed from water? Liang et al. investigated the acute toxicity potential of PDS [109]. They found that peroxodisulfate $S_2O_8^{2-}$ is more ecotoxic than its decomposition product sulfate. The LC_{50} value at 96 h for peroxodisulfate was above 500 mg/L against the common carp *Cyprinus carpio* [109]. In the ECOTOX database, values between 22 mg/L and 1667 mg/L are listed for LC_{50} after 2 days against several aquatic organisms. The LC_{50} values of PMS after 4 days are reported between 0.5 and 53 mg/L, such that PMS can be assumed to have a higher ecotoxicity than PDS. For sodium carbonate, LC_{50} values between 5 mg/L and 780.5 mg/L within 1 day were observed against different aquatic microorganism, meaning that it might be a little more ecotoxic than PDS but not as much as PMS. For periodate,

Table 5 Degradation and transformation products, persalts and activators, SMILES notation and assigned ECOSAR models of carbamazepine, ciprofloxacin, diclofenac, paracetamol and sulfamethoxazole

Substance	Condition	SMILES	ECOSAR-models	References
Carbamazepine		NC(=O)N1c2ccccc2C=Cc2ccccc21	Substituted Urea (1.0);	
Car288	Gamma-induced, PDS			[60]
Car288a		O=C(O)N1c2c(cccc2O)C(O)C(O)c2ccccc21	Benzyl Alcohols (1.0); Phenols (1.0);	
Car288b		O=C(O)N1c2ccccc2C(O)C(O)c2ccc(O)cc21	Benzyl Alcohols (1.0); Phenols (1.0);	
Car288c		O=C(O)N1c2ccccc2C(O)C(O)c2cc(O)ccc21	Benzyl Alcohols (1.0); Phenols (1.0);	
Car288d		O=C(O)N1c2ccccc2C(O)C(O)c2c1cccc2O	Benzyl Alcohols (1.0); Phenols (1.0);	
Car287	Gamma-induced, PDS; Gamma-induced, PMS			[60, 61]
Car287a		NC(=O)N1c2c(cccc2O)C(O)C(O)c2ccccc21	Benzyl Alcohols (1.0); Phenols (1.0); Substituted Urea (1.0);	
Car287b		NC(=O)N1c2ccccc2C(O)C(O)c2ccc(O)cc21	Benzyl Alcohols (1.0); Phenols (1.0); Substituted Urea (1.0);	
Car287c		NC(=O)N1c2ccccc2C(O)C(O)c2cc(O)ccc21	Benzyl Alcohols (1.0); Phenols (1.0); Substituted Urea (1.0);	
Car287d		NC(=O)N1c2ccccc2C(O)C(O)c2c1cccc2O	Benzyl Alcohols (1.0); Phenols (1.0); Substituted Urea (1.0);	
Car269	Gamma-induced, PMS	OC1c2ccccc2N2c3c(cccc3NC2=O)C1O	Benzyl Alcohols (1.0); Substituted Urea (1.0);	[61]
Car267	Gamma-induced, PDS	NC(=O)N1C2=C(C=Cc3ccccc31)C(=O)C=CC2=O	Substituted Urea (1.0); Quinones (1.0)	[60]
Car253-1	Gamma-induced, PDS; Gamma-induced, PMS	NC(=O)N1c2ccccc2C=C(O)c2ccccc21	Substituted Urea (1.0); Vinyl/ Allyl Alcohols (1.0)	[60, 61]
Car253-2	Gamma-induced, PDS; Gamma-induced, PMS			[60, 61]
Car253-2a		NC(=O)N1c2c(C=Cc3ccccc31)cccc2O	Phenols (1.0); Substituted Urea (1.0);	
Car253-2b		NC(=O)N1c2ccccc2C=Cc2ccc(O)cc21	Phenols (1.0); Substituted Urea (1.0);	
Car253-2c		NC(=O)N1c2ccccc2C=Cc2cc(O)ccc21	Phenols (1.0); Substituted Urea (1.0);	
Car253-2d		NC(=O)N1c2ccccc2C=Cc2c1cccc2O	Phenols (1.0); Substituted Urea (1.0);	
Car249	Gamma-induced, PDS	O=C1C=CC2=NC(=O)N3C2=C1C=Cc1ccccc13	Vinyl/Allyl Ketones (1.0)	[60]
Car239	Gamma-induced, PMS	NC(=O)N1c2ccccc2CCc2ccccc21	Substituted Urea (1.0);	[61]
Car224	Gamma-induced, PMS	O=Cc1cccc2Nc3ccccc3C(=O)c21	Aldehydes (Mono) (1.0)	[61]
Car208	Gamma-induced, PMS	c1cccc2Nc3ccccc3C=3OC=3c12		[61]
Car180	Gamma-induced, PMS	c1c2ccccc2nc2ccccc12	NEUTRAL ORGANICS (1.0)	[61]
Car152	Gamma-induced, PMS	Nc1ccccc1CC(=O)O	Anilines (Hindered) (1.0);	[61]
Ciprofloxacin		O=C(O)C1=CN(c2cc(c(F)cc2C1=O)N1CCNCC1)C1CC1	Aliphatic Amines (1.0); Vinyl/Allyl Ketones (1.0);	
Cip366	UVC, PMS	O=C(O)N(C1CC1)c1cc(c(F)cc1C(=O)CC(=O)O)N1CCNCC1	Aliphatic Amines (1.0)	[66]
Cip362-1	Heat-activated, PDS	O=CN(CCNC=O)c1cc2c(cc1F)C(=O)C(=CN2C1CC1)C(=O)O	Amides (1.0); Vinyl/Allyl Ketones (1.0)	[64]
Cip362-2	Heat-activated, PDS			[64]
Cip362-2a		O=C(O)C=1C(=O)c2c(O)c(O)c(cc2N(C=1O)C1CC1)N1CCNCC1	Aliphatic Amines (1.0); Phenol Amines (1.0); Phenols, Poly (1.0); Vinyl/Allyl Ketones (1.0)	

Table 5 (continued)

Substance	Condition	SMILES	ECOSAR-models	References
Cip362-2b		O = C(O)C = 1C(=O)c2cc(O)c(c(O)c2N(C = 1O)C1CC1)N1CCNCC1	Aliphatic Amines (1.0); Phenol Amines (1.0); Phenols, Poly (1.0); Vinyl/Allyl Ketones (1.0	
Cip362-3	Heat-activated, PDS	O = C(O)C1 = CN(C2CC2)c2cc(c(F)cc2C1 = O)N1CC(=O)NCC1O	Amides (1.0); Vinyl/Allyl Ketones (1.0)	[65]
Cip360	Heat-activated, PDS	O = C(O)C1 = CN(C2CC2)c2cc(c(F)cc2C1 = O)N1CC(=O)NCC1 = O	Amides (1.0); Vinyl/Allyl Ketones (1.0)	[65]
Cip348-1	UVC, PMS; Heat-activated, PDS	O = C(O)C = 1C(=O)c2cc(F)c(cc2N(C = 1O)C1CC1)N1CCNCC1	Aliphatic Amines (1.0); Vinyl/Allyl Ketones (1.0)	[64, 66]
Cip348-2	Heat-activated, PDS	OC1NCCN(C1)c1cc2c(cc1F)C(=O)C(=CN2C1CC1)C(=O)O	Aliphatic Amines (1.0); Vinyl/Allyl Ketones (1.0)	[65]
Cip346	UVC, PMS	O = C1CN(CCN1)c1cc2c(cc1F)C(=O)C(=CN2C1CC1)C(=O)O	Amides (1.0); Phenol Amines (1.0); Vinyl/Allyl Ketones (1.0)	[66]
Cip344	UVC, PMS	O = C1CN(CCN1)c1cc2c(cc1O)C(=O)C(=CN2C1CC1)C(=O)O	Amides (1.0); Phenols (1.0); Phenol Amines (1.0); Vinyl/Allyl Ketones (1.0)	[66]
Cip334-1	UVC, PMS; Heat-activated, PDS	O = CN(CCN)c1cc2c(cc1F)C(=O)C(=CN2C1CC1)C(=O)O	Aliphatic Amines (1.0); Amides (1.0); Vinyl/Allyl Ketones (1.0)	[64–66]
Cip334-2	Heat-activated, PDS			[64]
Cip334-2a		Oc1c(cc2c(c1O)C(=O)C(O) = C(O)N2C1CC1)N1CC-NCC1	Aliphatic Amines (1.0); Phenol Amines (1.0); Phenols, Poly (1.0); Vinyl/ Allyl Alcohols (1.0); Vinyl/Allyl Ketones (1.0)	
Cip334-2b		Oc1cc2c(c(O)c1N1CCNCC1)N(C(O) = C(O)C2 = O)C1CC1	Aliphatic Amines (1.0); Phenol Amines (1.0); Phenols, Poly (1.0); Vinyl/ Allyl Alcohols (1.0); Vinyl/Allyl Ketones (1.0)	
Cip330	UVC, PMS; Heat-activated, PDS	O = C(O)C1 = CN(c2cc(c(O)cc2C1 = O)N1CCNCC1)C1CC1	Aliphatic Amines (1.0); Phenols (1.0); Phenol Amines (1.0); Vinyl/Allyl Ketones (1.0)	[64–66]
Cip322-1	Heat-activated, PDS	O = CN(CCN)c1cc2c(cc1F)C(=O)C(=CN2CC)C(=O)O	Aliphatic Amines (1.0); Amides (1.0); Vinyl/Allyl Ketones (1.0)	[64]
Cip322-2	Heat-activated, PDS	NCC(O)Nc1cc2c(cc1F)C(=O)C(=CN2C1CC1)C(=O)O	Aliphatic Amines (1.0); Vinyl/Allyl Ketones (1.0)	[65]
Cip320	Heat-activated, PDS	O = C(O)C1 = CN(CC)c2cc(c(F)cc2C1 = O)N1CCNCC1	Aliphatic Amines (1.0); Vinyl/Allyl Ketones (1.0)	[64]
Cip306	UVC, PMS; Heat-activated, PDS	O = C(O)C1 = CN(c2cc(NCCN)c(F)cc2C1 = O)C1CC1	Aliphatic Amines (1.0); Vinyl/Allyl Ketones (1.0)	[64–66]
Cip291	Heat-activated, PDS	O = C(O)C1 = CN(c2cc(NC = O)c(F)cc2C1 = O)C1CC1	Amides (1.0); Vinyl/Allyl Ketones (1.0)	[64]
Cip286	Heat-activated, PDS	Oc1cc2c(cc1N1CCNCC1)N(C = CC2 = O)C1CC1	Aliphatic Amines (1.0); Phenols (1.0); Phenol Amines (1.0); Vinyl/Allyl Ketones (1.0)	[64, 65]
Cip264	UVC, PMS	Fc1cc2c(cc1NCCN)N(C(=O)C2 = O)C1CC1	Aliphatic Amines (1.0)	[66]
Cip263	UVC, PMS; Heat-activated, PDS	O = C(O)C1 = CN(c2cc(N)c(F)cc2C1 = O)C1CC1	Anilines (Unhindered) (1.0); Vinyl/Allyl Ketones (1.0)	[64–66]
Cip251	Heat-activated, PDS	O = C(O)C1 = CN(CC)c2cc(N)c(F)cc2C1 = O	Anilines (Unhindered) (1.0); Vinyl/Allyl Ketones (1.0)	[64]
Cip245	Heat-activated, PDS	O = C(O)C1 = CN(c2cc(N)ccc2C1 = O)C1CC1	Anilines (Unhindered) (1.0); Vinyl/Allyl Ketones (1.0)	[64]
Cip233	Heat-activated, PDS	O = C(O)C1 = CN(CC)c2cc(N)ccc2C1 = O	Anilines (Unhindered) (1.0); Vinyl/Allyl Ketones (1.0)	[64]
Diclofenac		Clc1cccc(Cl)c1Nc1ccccc1CC(=O)O		

Table 5 (continued)

Substance	Condition	SMILES	ECOSAR-models	References
Dic328	US, PDS	Clc1cc(O)cc(Cl)c1Nc1ccc(O)cc1CC(=O)O	Phenols, Poly (1.0)	[68]
Dic312-1	US, PDS	Clc1ccc(O)c(Cl)c1Nc1ccccc1CC(=O)O	Phenols (1.0)	[68]
Dic312-2	US, PDS	Clc1cc(O)cc(Cl)c1Nc1ccccc1CC(=O)O	Phenols (1.0)	[68]
Dic312-3	US, PDS	Clc1cccc(Cl)c1Nc1ccc(O)cc1CC(=O)O	Phenols (1.0)	[68]
Dic310	US, PDS	O=C1C=C\C(=N/c2c(Cl)cccc2Cl)C(CC(=O)O)=C1	Schiff Bases-Azomethine (1.0); Vinyl/Allyl Ketones (1.0)	[68]
Dic282	US, PDS	Clc1cccc(Cl)c1Nc1ccccc1C(=O)O		[68]
Dic278	US, PDS	Clc1cccc(Cl)c1N1c2ccccc2CC1=O	Amides (1.0)	[68]
Dic177	US, PDS	ONc1c(Cl)cccc1Cl		[68]
Paracetamol		Oc1ccc(NC(C)=O)cc1	Amides (1.0); Phenols (1.0); Phenol Amines (1.0)	
Par167	UVC, SPC	Oc1ccc(NC(C)=O)cc1O	Amides (1.0); Phenol Amines (1.0); Phenols, Poly (1.0)	[94]
Par150	UVC, SPC	O=C1C=C/C(=N\C(C)=O)C=C1	Amides (1.0); Vinyl/Allyl Ketones (1.0)	[94]
Par138-1	UVC, SPC	Oc1ccc(NC=O)cc1	Amides (1.0); Phenols (1.0); Phenol Amines (1.0)	[94]
Par138-2	UVC, SPC	Oc1ccc2NCOc2c1	Phenols (1.0)	[94]
Par126	UVC, SPC	Nc1cc(O)c(O)cc1	Anilines (Unhindered) (1.0); Phenol Amines (1.0); Phenols, Poly (1.0)	[94]
Par111	UVC, SPC	Oc1ccc(O)cc1	Hydroquinones (1.0); Phenols, Poly (1.0)	[94]
Par110-1	UVC, SPC	Nc1ccc(O)cc1	Anilines (Unhindered) (1.0); Phenols (1.0); Phenol Amines (1.0)	[94]
Par110-2	UVC, SPC	O=C1C=CC(O)C=C1	Vinyl/ Allyl Alcohols (1.0); Vinyl/Allyl Ketones (1.0)	[94]
Par109	UVC, SPC	O=C1C=CC(=O)C=C1	Quinones (1.0)	[94]
Sulfamethoxazol		Cc1cc(NS(=O)(=O)c2ccc(N)cc2)no1	Amides (1.0); Anilines (Unhindered) (1.0)	
Sul519	UVC, PDS			[82]
Sul519a		Cc1cc(NS(=O)(=O)c2cc(O)c(/N=N/c3ccc(cc3)S(=O)(=O)Nc3cc(C)on3)cc2)no1	Amides (1.0); Phenols (1.0); Phenol Amines (1.0)	
Sul519b		Cc1cc(NS(=O)(=O)c2ccc(/N=N/c3ccc(cc3)S(=O)(=O)Nc3cc(C)on3)cc2O)no1	Amides (1.0); Phenols (1.0); Phenol Amines (1.0)	
Sul502	UVC, PDS	Cc1cc(NS(=O)(=O)c2ccc(/N=N/c3ccc(cc3)(=O)(=O)Nc3cc(C)on3)cc2)no1	Amides (1.0)	[82]
Sul288-1	UVC, PDS	OC1N=C(NS(=O)(=O)c2ccc(N)cc2)OC1(C)O	Amides (1.0); Anilines (Unhindered) (1.0); Esters (1.0)	[82]
Sul288-2	UVC, PDS	OC1C(NS(=O)(=O)c2ccc(N)cc2)=NOC1(O)C	Aliphatic Amines (1.0); Amides (1.0); Anilines (Unhindered) (1.0)	[82]
Sul286	Heat-activated, PDS			[84]
Sul286a		Cc1cc(NS(=O)(=O)c2ccc(N)c(O)c2O)no1	Amides (1.0); Anilines (Unhindered) (1.0); Phenol Amines (1.0); Phenols, Poly (1.0)	
Sul286b		Cc1cc(NS(=O)(=O)c2cc(O)c(N)c(O)c2)no1	Amides (1.0); Anilines (Unhindered) (1.0); Phenol Amines (1.0); Phenols, Poly (1.0)	

Table 5 (continued)

Substance	Condition	SMILES	ECOSAR-models	References
		Cc1cc(NS(=O)(=O)c2cc(O)c(N)cc2O)no1	Amides (1.0); Anilines (Unhindered) (1.0); Hydroquinones (1.0); Phenol Amines (1.0); Phenols, Poly (1.0)	
Sul284-1	UVC, PDS	Cc1cc(NS(=O)(=O)c2ccc(cc2)[N+]([O-])=O)no1	Amides (1.0)	[82]
Sul284-2	Heat-activated, PDS			[84]
Sul284-2a		Cc1cc(NS(=O)(=O)c2cc(O)c(N=O)cc2)no1	Amides (1.0); Phenols (1.0); Phenol Amines (1.0)	
Sul284-2b		Cc1cc(NS(=O)(=O)c2ccc(N=O)cc2O)no1	Amides (1.0); Phenols (1.0); Phenol Amines (1.0)	
Sul272	UVC, PDS	OC1N=C(NS(=O)(=O)c2ccc(N)cc2)OC1C	Amides (1.0); Anilines (Unhindered) (1.0); Esters (1.0)	[82]
Sul270-1	Heat-activated, PDS			[84]
Sul270-1a		Cc1cc(NS(=O)(=O)c2cc(O)c(N)cc2)no1	Amides (1.0); Anilines (Unhindered) (1.0); Phenols (1.0); Phenol Amines (1.0)	
Sul270-1b		Cc1cc(NS(=O)(=O)c2ccc(N)cc2O)no1	Amides (1.0); Anilines (Unhindered) (1.0); Phenols (1.0); Phenol Amines (1.0)	
Sul270-2	Heat-activated, PDS	Cc1cc(NS(=O)(=O)c2ccc(NO)cc2)no1	Amides (1.0)	[84]
Sul254	UVC, PDS	Cc1cnc(NS(=O)(=O)c2ccc(N)cc2)o1	Amides (1.0); Anilines (Unhindered) (1.0)	[82]
Sul190	Heat-activated, PDS			[84]
Sul190a		Nc1ccc(cc1O)S(O)(=O)=O	Anilines (Unhindered) (1.0); Phenols (1.0); Phenol Amines (1.0)	
Sul190b		Oc1cc(N)ccc1S(O)(=O)=O	Anilines (Unhindered) (1.0); Phenols (1.0); Phenol Amines (1.0)	
Sul133	Heat-activated, PDS	OC1(C)ON=C(N)C1O	Aliphatic Amines (1.0)	[84]
Sul99	UVC, PDS; Heat-activated, PDS	Cc1cc(N)no1	Anilines (Unhindered) (1.0)	[82, 84]
Sul94	Heat-activated, PDS	Nc1ccccc1	Anilines (Unhindered) (1.0)	[84]

Hyphenated numbers indicate regioisomers, lower case letters a to d indicate tentative regioisomers with respect to the same ring. All structures are listed in Fig. 7

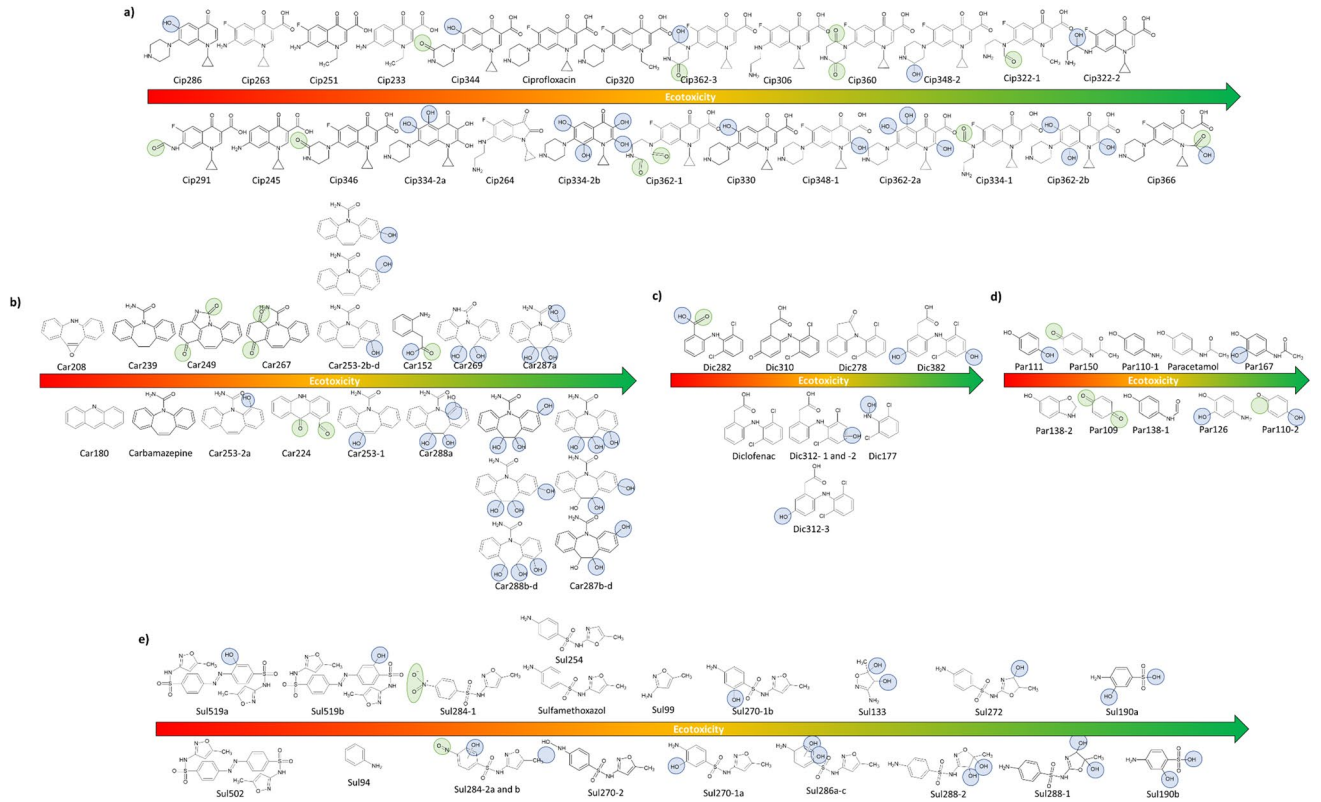


Fig. 7 Structures, including tentative regioisomers, of transformation products of **a** ciprofloxacin, **b** carbamazepine, **c** diclofenac, **d** paracetamol and **e** sulfamethoxazole, cf. Table 5, in descending order of ecotoxicity values predicted by QSAR analysis

only three LC_{50} entries are listed against different algae species. They are about 130 mg/L observed after 0.05 days. Yet, the ecotoxicity values reported for assays and the values calculated from the ECOSAR models were based on different organisms. While the difference rendered a direct comparison difficult, a general ecotoxicity trend could still be derived and evaluated.

In general, the use of persalts in confined areas such as wastewater treatment plants does not seem critical for the aquatic environment, as in most cases several 100 mg/L are required to have an ecotoxicological effect. The persalts are reactive, hence not persistent, and decompose into stable anionic salts such that it is unlikely that the reactive, ecotoxicological hazardous forms enter the aquatic environment via the effluent at relevant concentrations. Nevertheless, the persalts may induce acidification, which may be detrimental to microorganisms. Yet, the dilution of the effluent and the water's buffer capacity may mitigate these effects.

4 Conclusion

In this short review the application of the three persalts, persulfate, periodate and percarbonate for the targeted removal of the pharmaceuticals carbamazepine, ciprofloxacin, diclofenac, ibuprofen, metoprolol, paracetamol and sulfamethoxazole, which occur worldwide in the aquatic environment was summarized. The efficacy of the persalts was found different and strongly depending on activation. The use of UVC irradiation proved to be very successful, as the persalts form anionic radical salts, which induce a decomposition of the micropollutants following the indirect mechanism. At the same time, the substances are able to absorb in the UV region from which degradation according to the direct mechanism is initiated. Particularly effective are the persalts that generate hydroxyl radicals, which are the most reactive species to indirectly degrade anthropogenic micropollutants. As a consequence, the use of sodium percarbonate proves the most effective way of degrading the substances. Limiting factors for using UV irradiation are often high energy costs and the penetration depth of the radiation in waters containing e.g., natural organic matter.

The dominance of hydroxyl radicals was also evident in the chemical structures of the transformation products. In the studies reviewed, mainly products were reported from degradation processes, where hydroxyl radicals were added to the molecule and atoms such as fluorine were substituted by hydroxyl groups.

From an ecotoxicological point of view, degradation by persalts is beneficial for the environment, as the pharmaceuticals investigated were deconstructed and their ecotoxicological potentials were minimized by the use of persalts. This was found from in silico QSAR analysis but also from in vivo and in vitro assays. It must be taken into account that if persalts are to be used, they cannot be removed from the water. Upon application, the pH might be lowered and cause undesired effects to microorganisms. Due to a potential application in the confinement of sewage treatment plants, the risk needs consideration but may be minimized. The reactive persalts themselves readily transform into stable, non-toxic forms whose occurrence should be much less harmful to the aquatic environment than the presence and spread of pharmaceuticals.

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Declarations

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