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Photochemical Degradation of Organic Xenobiotics in Natural Waters

Sarka Klementova

Additional information is available at the end of the chapter

Abstract

Xenobiotics in the environment include a wide variety of compounds, e.g. pesticides, drugs, textile dyes, personal care products, stabilisers, and many others. These compounds enter natural waters by rain washing of treated areas, via leaching through soil from places of application and via waste waters of manufacturing facilities or municipal waste waters (excretion of unmetabolised drugs, disposal of unused drugs). In natural waters, physical, chemical, and biological processes contribute to the decrease of xenobiotics concentrations. For substances resistant to biological degradation processes and the chemical reactions such as hydrolysis, photoinitiated processes may represent important degradation pathways. Photochemical processes can be categorised in connection with the environmental fate of xenobiotics into two fundamental groups: those that may occur in natural waters and those that have been tested for decontamination of waste waters. The first group is focused mainly on photosensitization and homogeneous photocatalysis. The second class comprises advanced oxidation processes (AOPs) of which especially heterogeneous photocatalysis on semiconductors is the most investigated technique. The chapter covers all these processes and brings examples of their applications.

Keywords: natural waters, xenobiotics, emerging pollutants, photochemical degradation, advanced oxidation processes

1. Introduction

While most water assessments emphasise water quantity, water quality is also critical to satisfying basic human and environmental needs. The quality of the world's water is under increasing threat as a result of population growth, expanding industrial and agricultural activities, and climate change. Poor water quality threatens human and ecosystem health,

increases water treatment costs, and reduces the availability of safe water for drinking and other uses [1]. It also limits economic productivity and development opportunities. Indeed, the United Nations find that "water quality is a global concern as risks of degradation translate directly into social and economic impacts" [2].

Human society relies on rivers for many functions and services including drinking water, irrigation, navigation, transport, recreation, and waste disposal. It has been estimated that despite accounting for just 0.4% of the Earth's surface area and 0.006% of the Earth's freshwater, rivers contain 6% of all described species and provide 5.1% of global ecosystem services [3, 4].

Water quality concerns are widespread, though the true extent of the problem remains undisclosed. In developing countries, an estimated 90% of sewage and 70% of industrial waste are discharged into waterways entirely untreated [5].

In recent times, anthropogenic activities, namely the production and consumption of chemically manufactured products, have been linked to growing environmental pollution and resulting health challenges. Currently, the pollution of the global water cycle with persistent organic contaminants appears to be one of the most important challenges of the twenty-first century. The majority of these organic substances are only partially removed by conventional wastewater treatment plants; hence they enter the environment and spread across different ecological compartments.

Most of the persistent contaminants are unregulated or in the process of regulation, yet they possess possible toxic effects in long-term exposure or potent endocrine disrupting properties, which lie in their interference with the hormonal function of living organisms including humans [6, 7].

Therefore, the studies of many scientists are focused on getting information on the environmental occurrence of the compounds belonging to this vast family of species. Other studies investigate the environmental fate of these compounds as well as the feasibility of their degradation in wastewaters. Among these studies, those concentrating on the photochemical processes and techniques have recently acquired a particular attention.

2. Organic micropollutants in the environment

Chemicals of emerging concern have no clearly stated definition; therefore, no comprehensive list of them exists. Kümmerer [8] defined emerging micropollutants as unregulated compounds or those with limited regulation which are present in the environment at low range (µg/l and below), irrespective of their chemical structure, and which thus require monitoring. Marcoux et al. [9] summarised emerging micropollutants as newly detected substances in the environment or those already identified as risky and the use of which in manufactured items is prohibited, or substances already known but the recent use of which in products may cause problems during their future treatment as waste. According to the US Geological Society [10], emerging contaminants are any synthetic or naturally occurring chemical or any microorganism or metabolite that is not commonly monitored in the environment but has the potential to

Family/use	Emerging contaminant	Prescription 2012 (kg)	Surface waters (ng/l)
Antibacterial	Amoxicillin	158,231	2.5–245
	Erythromycin	41,057	0.5–159
	Metronidazole	12,300	1.5–12
	Ofloxacin	219	—
	Oxytetracycline	17,143	—
	Trimethoprim	10,998	1.5–108
Non-steroid anti-inflammatory drug	Paracetamol (acetaminophen)	>2,000,000	1.5–1388
	Ibuprofen	108,435	1–2370
	Naproxen	126,258	1–59
	Ketoprofen	243	1–4
Lipid regulator	Simvastatin	49,198	<0.6
	Bezafibrate	7966	10–60
Beta blocker	Propranolol	9076	0.5–107
	Atenolol	20,725	1–487
	Metoprolol	2311	0.5–10
Calcium channel blocker	Diltiazem	21,922	1–17
Hypertension	Valsartan	6484	1–55
Antidepressant	Venlafaxine	16,211	1.1–35
	Amitriptyline	10,171	<0.6–30
	Fluoxetine	5319	5.8–14
	Dosulepin	3270	0.5–25
	Nortriptyline	439	0.8–6.8
Antiepileptic	Gabapentin	104,110	0.6–1879
Hypnotic	Temazepam	883	3.2–34
	Diazepam	335	0.6–0.9
	Oxazepam	85	2.4–11
Sunscreen agent	1-benzophenone		0.3–9
	2-benzophenone		0.5–18
	3-benzophenone		15–36
	4-benzophenone		3–227
Preservative	Methylparaben		0.3–68
	Ethylparaben		1–13
	Propylparaben		0.2–7
	Butylparaben		0.3–6

Table 1. Examples of emerging contaminant occurrence for wastewaters and surface waters in the United Kingdom—based on the review by Petrie et al. [12].

enter the environment and cause known or suspected adverse ecological and/or human health effects.

An overview of micropollutants, their sources and effects, and their occurrence in different types of water including analytical detection techniques and concentration ranges is provided by an outstanding review by Tijany et al. [11]. Another comprehensive review by Petrie et al. [12] presents information about contaminants occurrence in wastewaters and surface waters in the United Kingdom, spatial distribution and seasonality, possibilities of microbial transformation, and possible ecotoxicological effects, together with some recommendations for the environmental monitoring of these substances. As can be seen from the lists of the substances covered in the above-mentioned studies as emerging xenobiotic compounds, categories such as pharmaceuticals (antibiotics, antidiabetics, antiepileptics, anti-inflammatories, analgetics, antidepressants) and personal care products (disinfectants, preservatives) are the most abundant representatives. Selected substances from the study of Petrie et al. [12] which represent the highest load on the environment are presented in **Table 1**. According to recent studies, more the 200 different pharmaceuticals alone have been reported in river waters globally to date, with concentrations mainly in the ng/l to µg/l range in surface waters [13–17], but in some cases, concentrations of even several orders of magnitude higher have been reported. Effluent concentrations from pharmaceutical formulation facilities in the USA (New York) reached 1.7 mg/l for the analgesic oxacodone and 3.8 mg/l for the muscle relaxant metaxalone [18]. Li et al. [19] found very high concentrations of tetracycline derivatives up to 800 and 2 mg/l in the effluent and receiving waters, respectively, from a sewage treatment plant serving an antibiotic manufacturing facility in China.

Besides these emerging contaminants, there are other organic pollutants, e.g. pesticides, chiefly herbicides, the presence of which in the aquatic environment has been known for a long time [20–23].

Most of the xenobiotics detected in natural waters are persistent compounds that are recalcitrant to microbial decay and resist chemical degradation through hydrolysis or other chemical reactions. Many of them contain aromatic rings, heteroatoms, and functional groups that can either absorb solar radiation or react with photogenerated transient species in natural waters (e.g. reactive oxygen species and/or photoexcited natural organic matter). Some of these compounds carry functional groups and structures such as phenol, carboxyl, nitro, and naphthyloxy that have been found to undergo photodegradation [24]; many of the pesticide compounds are chlorine derivatives, which predispose them to dechlorination and hydroxyderivative formation [25].

3. Photoinitiated reactions related to the organic xenobiotics degradation

Each reaction started by absorption of radiation may be classified as a photochemical or photoinitiated reaction. According to the mechanism of the photoinitiated reaction related to the degradation of xenobiotics, photolytic, photosensitized, and photocatalytic reactions can be distinguished.

3.1. Photolytic reactions

A photolytic reaction is usually understood as a reaction in which the absorbed quantum of radiation has enough energy to cause the breaking of a covalent bond in the substrate compound. Usually, highly energetic UV radiation (254 nm) is necessary for this purpose. The reaction includes only one reactant, the molecule that undergoes photolysis; therefore, the reaction follows first-order kinetics.

3.2. Photosensitised reactions

A photosensitised reaction needs a sensitizer molecule. This is a molecule that can absorb radiation and transfer the absorbed excitation energy onto another molecule. The energy can be transferred either onto an organic molecule, substrate (xenobiotic compound), or onto an oxygen molecule, which results in the formation of singlet oxygen. The possible reactions are illustrated in Eqs. (1)–(5).

$$^1Sens + hv \rightarrow {}^1Sens^* \tag{1}$$

$$^1Sens^* + {}^1Substrate \rightarrow {}^1Substrate^* + {}^1Sens \rightarrow Product + {}^1Sens \tag{2}$$

$$^1Sens^* \rightarrow through\ ISC \rightarrow {}^3Sens^* \tag{3}$$

$$^3Sens^* + {}^3O_2 \rightarrow {}^1O_2 \tag{4}$$

$$^1O_2 + {}^1Substrate \rightarrow Oxidised\ product \tag{5}$$

Eq. (1) represents excitation of the sensitizer from the ground state (which is always a singlet state, i.e. all electrons in the molecule are paired) to the first excited singlet state. Eq. (2) represents energy transfer onto the substrate and its subsequent reaction into a product. Eq. (3) shows the possible conversion of the sensitizer from the first excited singlet state into the first triplet state (where two electrons are unpaired) through so-called intersystem crossing (ISC). The sensitizer in the triplet state is able to react with molecular oxygen dissolved in the reaction mixture (Eq. (4)) because the ground state of molecular oxygen with its two unpaired electrons is a triplet state. The reaction provides an excited form of oxygen, singlet oxygen, which is a powerful oxidative species; singlet oxygen then can react with organic substrate molecules and oxidise them (Eq. (5)).

Humic substances are considered to be the most common naturally occurring sensitisers.

Humic substances, comprising two major classes, humic acids and fulvic acids, are organic constituents of not only soil humus and peat but also streams, dystrophic lakes, and ocean water. They are produced by the biodegradation of dead organic matter as products of microbial metabolism although they are not synthesised as a life-sustaining carbon structures or compounds serving as energy storage. A typical humic substance is not a single, well-defined molecule, but a mixture of many molecules which typically include aromatic nuclei with carboxylic and phenolic groups as demonstrated in the structure proposed by Stevenson [26],
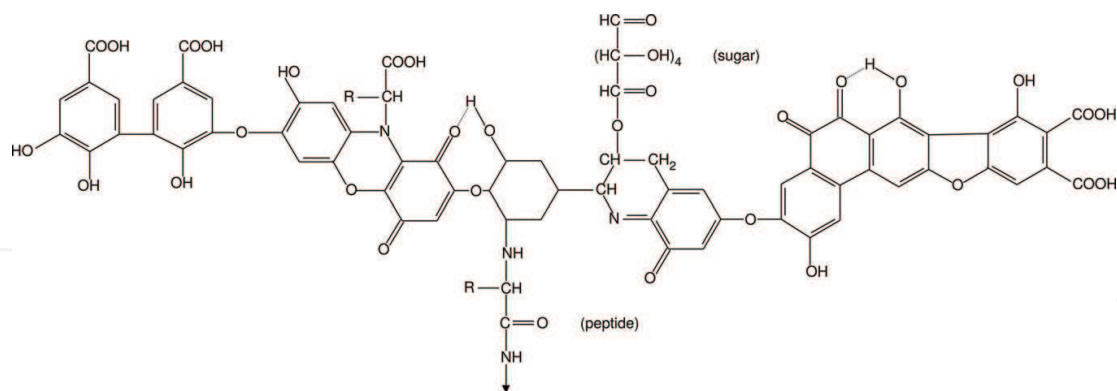
Figure 1. Proposed structure of humic acids [26].

which is illustrated in **Figure 1**. Their molecular weight ranges from a few hundred to several million of daltons [27].

The distinction between humic and fulvic acid is based on their solubility: humic acids are soluble in water at neutral and alkaline pH values and insoluble at acid pH, while fulvic acid is soluble in water across the full range of pH. Fulvic acids have usually smaller molecules and less extent of aromaticity, which results in less content of phenolic groups and more hydroxylic groups in side chains.

These functional groups contribute most to the surface charge and reactivity of humic substances. Humic and fulvic acids behave as mixtures of dibasic acids with a pK_1 value of around 4 for protonation of carboxyl groups and around 8 for protonation of phenolate groups [28].

In natural waters, myriads of other sensitisers can be found—natural pigments such as heme/porphyrine-based molecules (chlorophylls, bilirubin, hemocyanin, haemoglobin), carotenoids, or flavonoids (anthocyanins), but all of these are present in extremely low concentrations in the water environment and are therefore not considered to be of real significance for photochemical transformation of organic xenobiotic compounds.

3.3. Photocatalytic reactions

Photocatalysis may occur as a homogeneous process or as a heterogeneous process.
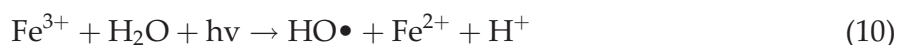
In homogeneous photocatalytic reactions, light contributes to the production of a catalytically active form of a catalyst. One example of such a reaction is the photochemically induced reduction of ferric ions in the presence of an electron donor to ferrous ions that exhibit much higher catalytic activity in comparison with the oxidised form [29, 30]. The subsequent catalytic reaction of a substrate is a 'dark' reaction, i.e. not photochemical, since the reaction does not need light. The active form of the catalyst enables the otherwise spin-forbidden reaction between a singlet substrate and triplet dissolved molecular oxygen.

Homogeneous photocatalytic reactions also include the so-called photo-Fenton reactions. Fenton's reagent is a solution of hydrogen peroxide with ferrous ions as a catalyst of an oxidative reaction with organic substrates. The reagent was described by H. J. H. Fenton in

1894. The sequence of reactions leading to the formation of reactive oxygen species (hydroxyl radicals and superoxide radicals) is represented in Eqs. (6)–(9).

$$Fe^{2+} + H_2O_2 \rightarrow HO\bullet + Fe^{3+} + HO^- \tag{6}$$

$$Fe^{3+} + H_2O_2 \rightarrow HOO\bullet + Fe^{2+} + H^+ \tag{7}$$

$$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + HO^- \tag{8}$$

Since ferrous ions are quickly reoxidised in a Fenton reaction mixture, the photochemical variant is used; in the photo-Fenton reaction, the ferric ions are photochemically reduced in situ. Additional sources of OH radicals through photolysis of H_2O_2 and through the reduction of Fe^{3+} ions under UV light (Eqs. (9) and (10)) are thus obtained.

$$H_2O_2 + h\nu \rightarrow 2\ HO\bullet \tag{9}$$

$$Fe^{3+} + H_2O + h\nu \rightarrow HO\bullet + Fe^{2+} + H^+ \tag{10}$$

Heterogeneous photocatalysis is usually understood as any photochemical reaction on a semi-conductor.

Semiconductor photocatalysis uses solid catalytic systems while the substrate to be degraded is dissolved or dissipated in the solution (or in the gaseous phase) around the catalyst. Five distinct steps in the process of the reaction on a semiconductor are involved:

- The transfer of liquid or gaseous phase reactant to the catalytic surface by diffusion.

- The adsorption of the reactant on the catalyst surface.

- The reaction of the adsorbed molecules.

- The desorption of products.

- The removal of products from the interface region by diffusion.

The initiation of the photocatalytic process involves the photochemical formation of an electron-hole pair after the absorption of a photon of sufficient energy for the excitation of an electron from the valence band of the semiconductor to its conduction band. The holes and electrons react with the solvent (water) and dissolved oxygen to produce oxidative species, mainly OH and superoxide radicals by the sequence of reactions presented in Eqs. (11)–(16).

$$h^+ + H_2O \rightarrow HO^\bullet + H^+ \tag{11}$$

$$h^+ + OH^- \rightarrow HO^\bullet \tag{12}$$

$$O_2 + e^- \rightarrow O_2^{\bullet-} \tag{13}$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \tag{14}$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \tag{15}$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow HO^\bullet + O_2 + OH^- \tag{16}$$

Various metal oxides were tested in semiconductor photocatalytic reactions. The most frequently used is not only TiO_2 [31–33] but also other materials such as ZnO [34, 35], ZnS [36], Fe_2O_3 [37], and many others including semiconductor composites as well as semiconductors doped with precious metals or modified semiconductors [31, 38–41].

Heterogeneous photocatalytic reactions are usually described by first-order kinetics though actually pseudo-first order kinetics (with OH radicals in excess to the reactant) is the relevant kinetic model.

4. Photochemistry of organic xenobiotics

4.1. Environmental relevance of the study approaches

Generally, three types of photochemical studies of xenobiotic compounds can be recognised:

- Environmental photochemical studies, i.e. field or laboratory studies under natural conditions (sun irradiation or irradiation with the source simulating as much as possible the solar spectrum, concentrations of substances the same as in natural aquatic systems).

- Studies relevant to environmental conditions (irradiation sources simulating part of the solar spectrum, concentrations of organic substrates usually higher than those found in natural waters).

- Other photochemical studies, using short wavelengths not relevant to environmental conditions, addition of chemicals such as O_3, H_2O_2, additional components such as semiconductors acting as photocatalysts.

The first two approaches enable us to quantify transformation rates, identify photoproducts, and estimate the importance of the photochemical reactions to the mass balance of pollutants in the natural environment or at least (in the second case) make an extrapolation to the environmental conditions relatively straightforward.

The third approach is not aimed at the elucidation of environmental processes; its goal lies in the removal of polluting substances remaining in wastewaters after the application of the classical procedure consisting of microfiltration, ultrafiltration, reverse osmosis, activated carbon absorption, and sand filtration [42]. To achieve this goal, techniques involving advanced oxidation processes (AOPs) are usually applied [43, 44].

For environmental photochemical studies or for those relevant to the environmental condition, solar spectrum radiation must be considered. UV region represents only a small part of the solar spectrum; it is estimated that the region from 290 to 380 nm forms ca 5% of the overall ultraviolet plus visible range [45]. Although UV solar radiation reaching the Earth's surface represents a small part of the solar spectrum, it plays an important role in its photochemical effects since it contains the radiation of highest energies. Nevertheless, considering photochemical reactions of xenobiotics, it is necessary to keep in mind that these compounds often exhibit negligible or none absorption in the region of wavelengths longer than 290 nm, since

their absorption lies in the shorter UV wavelength range; therefore, many of the compounds cannot react directly under sun irradiation. Homogeneous photocatalytic degradation in the presence of dissolved metal ions, photosensitized reactions, or heterogeneous photocatalytic degradation on particulate metal compounds may contribute to the photochemical degradation of xenobiotics.

4.2. Examples of xenobiotic photodegradation studies

Pharmaceuticals and personal care products have been increasingly detected in aquatic field samples not only in Europe—e.g. in Italy [46, 47], Spain [48], United Kingdom [12, 49], Poland [50], and a EU-wide monitoring survey [16], but also in the USA [51, 52], China [53], and Japan [54].

The ecological impact of xenobiotics of the families of pharmaceuticals and personal care products is presently not sufficiently understood, partially because the environmental persistence of nearly all of these compounds has not yet been investigated. There are several indications that photochemical degradation may be a central factor in determining the environmental fate of these compounds. One of the supporting evidence lies in the structure of these substances—they often contain structural features that have been found photodegradable in other categories of compounds such as pesticides [30, 55].

As pointed out by Boreen et al. [24], the pesticides, carbaryl and napropamide, which photodegrade readily [55], contain the naphthoxy chromophore group that is found in pharmaceuticals, such as the non-steroid anti-inflammatory drugs, naproxen and nabumetone, and the beta-blocker, propranolol. The structure of carbaryl and naproxen is shown in **Figure 2**.

Because many of the pharmaceutical pollutants in surface waters have already eluded the biodegradation procedures of wastewater treatment, photochemistry in sunlit surface waters may be expected to play a much larger role than any naturally occurring biodegradation processes. Nevertheless, some compounds may evade photochemical degradation through sorption to suspended particles, which may be the case for substances such as the tetracyclines that have a high affinity for soil particles [56].

Many studies concerning emerging contaminants are focused on antibacterials, especially those used in both human and veterinary medicine, such as fluoroquinolones. Several representatives of fluoroquinolones are illustrated in **Figure 3**. Photochemical degradation of three representants of this group, norfloxacin, enrofloxacin, and ciprofloxacin, was studied, e.g., by
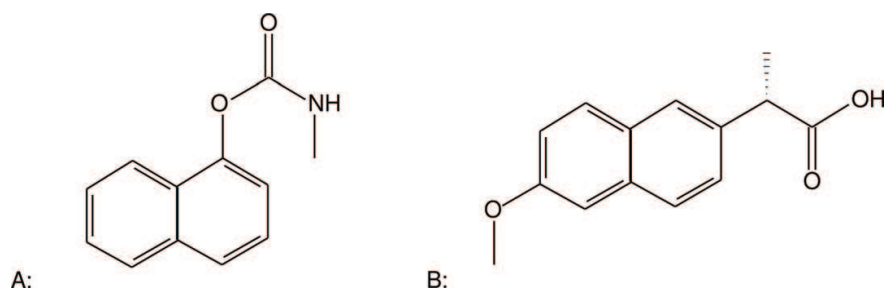

Figure 2. Chemical structure of the pesticide carbaryl (A) and anti-inflammatory drug naproxen (B).
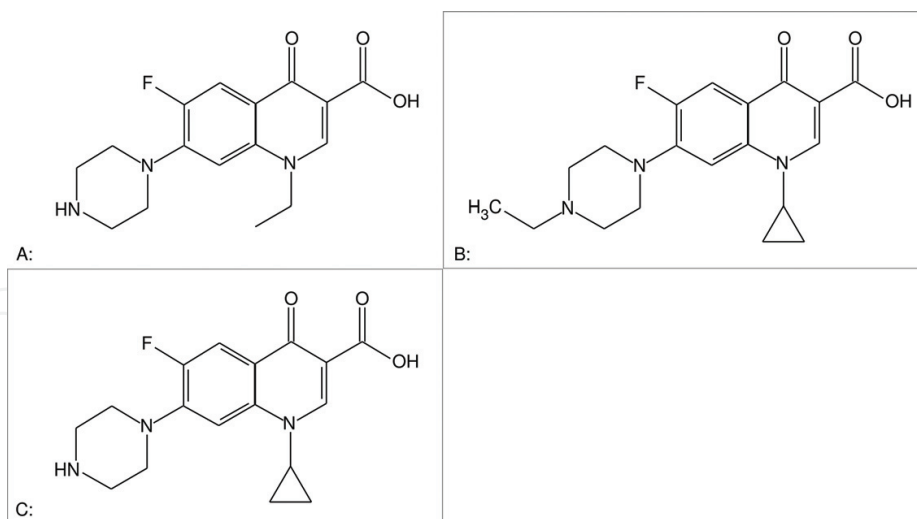
Figure 3. Examples of fluoroquinolone antibiotics: A—norfloxacin, B—enrofloxacin, and C—ciprofloxacin.

Babić et al. [57]. The source of radiation used in the study was a xenon lamp (emitting radiation in the 300–800 nm range); experiments were done in three matrices—MiliQ water, river water, and synthetic wastewater. It has been demonstrated that solar irradiation contributes significantly to the degradation of all three fluoroquinone derivatives—the mother compounds were degraded in 10 min after exposition to the radiation. Similar results were provided by the study of Sturini et al. [58] in which the reaction mixtures of two other fluoroquinolones, marbofloxacin and enrofloxacin, were investigated. The degradation was completed in about 1 h by exposure to solar light (Pavia, Italy, summer–noon time). The structure of the primary photoproducts showed that the degradation pathway proceeds via oxidative degradation of the piperazine side chain, reductive defluorination, and fluorine solvolysis.

Another important group of pharmaceutical products in connection with water pollution is antidepressants. Antidepressants are a class of pharmaceuticals used primarily to treat the symptoms of depression but can also be used to treat a wide variety of other medical conditions including sleep and eating disorders, alcohol and drug abuse, post-traumatic stress disorders, panic, and chronic pain. They are commonly prescribed for long-term use, leading to an increasing production volume compared to many other types of pharmaceuticals. According to Kessler et al. [59], almost 15 million American aged 18 and older suffer from a diagnosable major depressive disorder, thus giving rise to a market for branded antidepressants estimated to be worth US $14 billion [60].

Jeong-Wook Kwon and Armbrust [61] studied the laboratory persistence of fluoxetine (**Figure 4**), an antidepressant known under the brand names Prozac or Sarafen, which belongs to the selective serotonin reuptake inhibitor (SSRI) class of antidepressants. In the study, fluorescent lamps with a wavelength output of between 290 and 400 nm were adopted. In the experiments, fluoxetine was photochemically stable in buffered solutions as well as in two lake waters, the half-lives being greater than 100 days. This is not surprising since fluoxetine has a negligible absorption of radiation with wavelengths longer than 270 nm. The only exception was synthetic
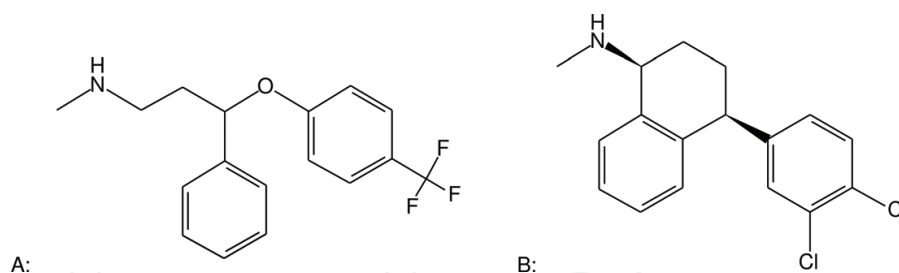
Figure 4. Structure of fluoxetine (A) and sertraline (B).

humic water in which the half-life was 21 day. Therefore, a photosensitised reaction with humic substances as sensitisers either for direct energy transfer or for reactive oxygen species (singlet oxygen) production can be hypothesised to be responsible for photoinitiated degradation in synthetic humic water.

The environmental fate of another SSRI antidepressant representant, sertraline, known under the brand name Zoloft, was explored by Jakimska et al. [62]. Simulated solar radiation (xenon lamp) was used for the experiments in eight different matrices: wastewater influent and effluent, untreated and treated water, river water, ultrapure water (pH 3 and 10), and methanol. The half-lives fell in the range of several days for most of the samples (from 4.9 days for wastewater effluent to 16.8 days for treated water); the only exceptions were ultrapure water with pH adjusted to 3 (127 days) and methanol (129 days). Since the authors observed a delay time in several cases, they proposed an autocatalytic mechanism as a plausible explanation for this observation.

Advanced oxidation treatment and the photochemical fate of three selected antidepressants in a solution of river humic acid was the subject of a study by Santoke et al. [63]. They focused on two antidepressants from the class of serotonin-norepinephrine reuptake inhibitors, SNRIs, duloxetine (brand name Cymbalta) and venlafaxine (brand name Effexor), which act on the two named neurotransmitters in the brain and are therefore more widely used than the older selective serotonin reuptake inhibitors, SSRIs, which act on only one neurotransmitter. The third substance, bupropion (brand name Wellbutrin or Zyban), is a norepinephrine-dopamine reuptake inhibitor, used both as an antidepressant and as a smoking cessation aid [64]. A Rayonet RPR-100 photochemical reactor with sixteen 350 nm fluorescent lamps and a solar simulator with a xenon lamp were employed for irradiation, commercially available Suwannee River humic acid was used as a sensitiser. In this study, concentrations of individual reactive species (singlet oxygen, hydroxyl radicals, hydrated electrons, and triplet excited state dissolved organic matter) were evaluated through specific probe reactions. Of the three antidepressant studied, only duloxetine was susceptible to direct photoreaction; venlafaxine and bupropion underwent indirect photoreaction to only a limited extent. The hydroxyl radicals were proven to be more important in the degradation of all three compounds in water to which humic acid had been added, compared to singlet oxygen or the hydrated electron. Pathways for the reaction of the antidepressants with hydroxyl radicals include hydroxylation and fragmentation. In the case of duloxetine, excited triplet state dissolved organic matter accounts partially for the photodegradation.

A significant group of organic xenobiotics in aquatic systems is parabens, p-hydroxybenzoic acid esters (**Figure 5**), widely used as preservatives in food products, cosmetics, toiletries, and pharmaceuticals. Parabens were first used as antimicrobial preservatives in pharmaceutical products in the mid-1920s and remained as preservative favourites for almost a century since they met several of the criteria of an ideal preservative: they exhibit a broad spectrum of antimicrobial activity, they have been considered safe to use, and they are stable over the broad pH range and sufficiently soluble in water to produce the effective concentration in the aqueous phase. In recent years, concern has been raised about their safety since several parabens have been reported to have estrogenic activity in experimental cell systems and animal models. Several studies, e.g. studies of Gomez et al. [65], Thuy et al. [66], and Chuang and Luo [67], investigated the photocatalytic degradation of parabens, namely ethylparaben and butylparaben, on TiO_2, focusing on operational parameters such as pH values and the initial concentration of parabens. Ethylparaben and butylparaben were demonstrated to have similar properties in terms of the values of adsorption constants and intrinsic reaction rates. The pH dependence was not significantly pronounced, but the reaction rate was slightly higher at pH = 4 than at other values (6, 9, 11). A study of transformation product led to a proposed pathway including an attack of the hydroxyl radical on the alkyl chain and the opening of the aromatic ring through hydroxylation to form alkyl carboxylic acid.

Klementova et al. [68] studied a set of pharmaceuticals of different classes including three parabens: methylparaben, ethylparaben, and propylparaben—both in homogeneous photocatalytic reaction mixture irradiated in the Rayonet RPR reactor with fluorescent lamps emitting wavelengths 300–350 nm and on TiO_2 with the lamps emitting in the region of 350–410 nm. Parabens were the most resistant substrates of all studied compounds. In the homogeneous reaction mixture, methylparaben exhibited mild photodegradation (40% of the substrate degraded in 90 min of irradiation) only in an extremely high, environmentally irrelevant, concentration of added Fe(III)—25 mg/l. Ethylparaben and propylparaben were more reactive than methylparaben—40% of ethylparaben and 60% of propylparaben were degraded after 90 min of irradiation in the presence of 5 mg of Fe(III) per 1 L of the reaction mixture. The measurement of the reduced form of iron (i.e. of the active catalytic form) in the reaction mixture revealed that steady state concentration of Fe(II) was attained in less than 5 min of irradiation; the steady state concentration of Fe(II) reached values between 60 and 70% of the total added ferric ions in the reaction mixtures of all parabens.

On TiO_2, methylparaben was again the least reactive substrate of the parabens studied—its degradation does not reach more than about 20% of the original amount in 120 min of
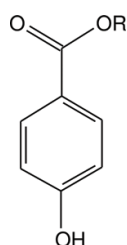

Figure 5. General chemical structure of a paraben.

irradiation. Ethylparaben and methylparaben reactivity was similar—48 and 52% of degraded ethylparaben and propylparaben, respectively.

An additional measurement of total organic carbon (TOC) in the reaction mixture [69] revealed that although the extent of the substrates degradation on TiO_2 is lower than in the homogeneous photocatalytic reaction, the decrease of organic carbon is higher in the reaction on TiO_2 compared with the homogeneous catalytic reaction. It means that mineralisation to CO_2 is more efficient with TiO_2 as the catalyst.

As accentuated earlier, organic xenobiotics reported in natural waters represent not only an extremely variegated, complex chemical system, including the above-mentioned drugs and preservatives, but also all groups of pesticides, chemicals used in the dye industry, explosives (TNT and its derivatives), solvents, and many others. For all these categories of compounds, the photochemical degradation processes, especially AOPs techniques, have been investigated. To mention just several of them, let us start with the photo-Fenton process. Yardin and Chiron [70] and Kröger and Fels [71] used it for the mineralisation of TNT and its derivatives. Haseneder et al. [72] and Santos et al. [73] employed the process for the degradation of polyethylene glycol, a substance with a wide range of application in both the industrial and pharmaceutical sectors. González et al. [74] and Dias et al. [75] achieved a significant mineralisation of the antibiotic sulfamethoxazole in wastewaters with this technique. Peternel et al. [35] and Sohrabi [76] conducted studies on the elimination of the persistent, non-biodegradable dyes, textile dye Red 45 and edible dye Carmoisine, respectively, by the photo-Fenton process.

A combination of ozone and UV radiation was shown to be effective in the degradation of dinitrotoluene and trinitrotoluene [77] as well as for some insecticides of the carbamate group such as carbofuran [78], for an industrial solvent N-methyl-2-pyrolidone [79], and for the reduction of trihalomethanes formation during drinking water treatment [80].

Heterogeneous photocatalysis with TiO_2 as the photocatalyst has been used for the degradation of sulfosalicylic acid in effluent [81]; the plant growth regulator 2,4-dichlorophenoxyacetic acid [82]; neonicotinoid insecticides [83]; the textile fibre reactive azo dye Procion Red MX-5B [84]; the extremely recalcitrant dye C.I. Reactive Red 2, RR2 [85]; and drugs such as paracetamol [86, 87]; tetracycline and beta-blockers [87], the calcium channel blocker verapamil, the corticosteroid cortisol, and the female sex hormone 17β-estradiol [68].

5. Conclusions

The photochemical reactions of pharmaceutical compounds as well as of many other contaminants are likely to play a major role in their fate in the aquatic environment. More information on their photodegradation pathways and on the degradation products and their persistence in the environment is essential for a better understanding of the impact of these contaminants on aquatic organisms and humans. The newly designed and quickly developing current advanced oxidation techniques are expected to help in the safe, efficient, and economic removal of the majority of these contaminants from wastewater effluents.

Acknowledgements

Conflict of interest

Hereby, I solemnly declare that I am the only author of the presented chapter and that no conflict of interest for a given manuscript exists that could inappropriately influence my judgement.

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