Review

Advanced Oxidation/Reduction Processes treatment for aqueous perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) – A review of recent advances
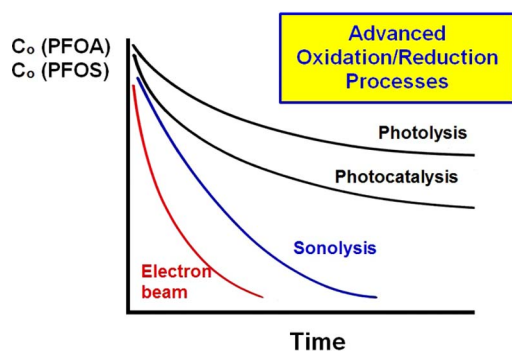
Marek Trojanowicz[a,b,*], Anna Bojanowska-Czajka[a], Iwona Bartosiewicz[a], Krzysztof Kulisa[a]

[a] Laboratory of Nuclear Analytical Methods, Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland
[b] Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Nowadays, an increasing emission of chemically resistant perfluorinated compounds (PFCs) to the natural environment, together with a global presence of those anthropogenic pollutants in both natural and treated waters and in both human and animal organisms, poses a great environmental challenge. A limited efficiency of their removal by commonly employed technologies prompts a search for more efficient and more cost-effective methods. Recent decades brought in water management an intense progress in Advance Oxidation Processes, based on decomposition of pollutants by free radicals, which can be produced in different ways. This review presents the recent advances in those methods for decomposition of the most commonly occurring PFCs in the natural environment – perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). For this purpose, there have been developed particular methods based on an oxidation and reduction of target pollutants, generally abbreviated as AO/RPs. The review, which was based on 180 cited references, includes photolytic and photocatalytic methods, electrochemical processes as well as sonolytic and radiolytic methods with the use of ionizing radiation, wet chemical oxidation methods, ozonation and Fenton processes. Attempts on comparison of the developed methods, their applications to real samples and molecular mechanisms of occurring transformations are provided.
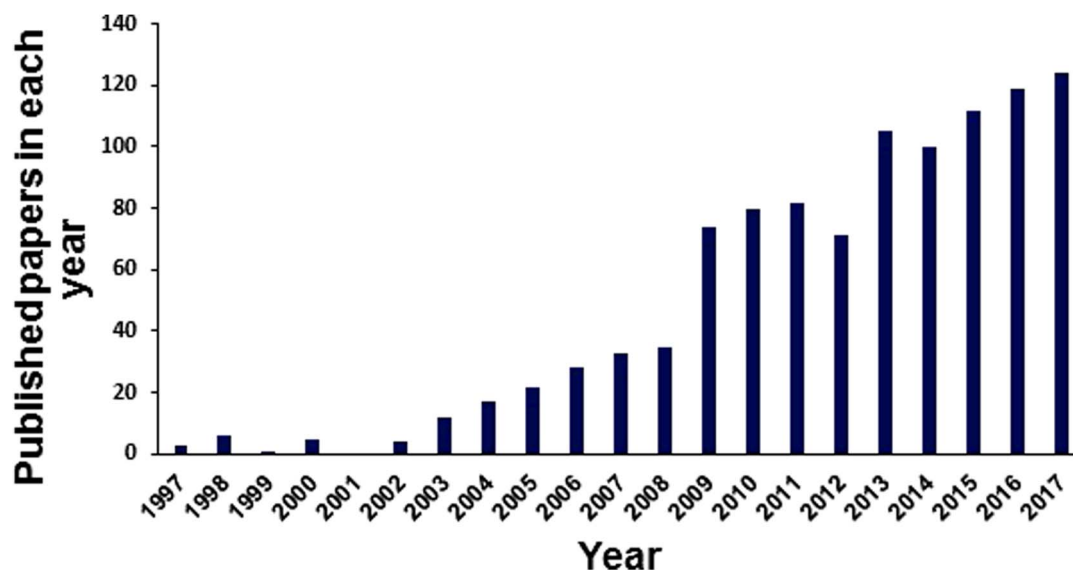
Fig. 1. Number of papers abstracted by data-base ISI Web of Science for topic keywords "perfluorinated" and "environmental" (23.10.2017).
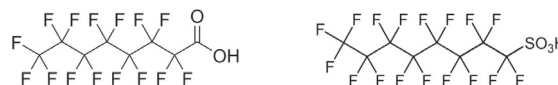
1. Introduction

The presence of fluorinated organic compounds in human serum was discovered in the late 1960s [1]. They have been produced for numerous industrial applications since 1940s as refrigerants, polymers, pharmaceuticals, adhesives, insecticides and fire retardants [2]. A particular interest in poly- and perfluorinated compounds (PFCs) erupted at the end of 1990s when a common global presence of those anthropogenic compounds was found in human serum [3], in groundwater [4] and in the tissues of wildlife including fish, birds and marine mammals [5]. This initiated, beginning in the early 2000s, a very intense development of analytical methodologies for their determination (see example reviews [6–8]), toxicological studies [9–11] and broad investigations of their sources, transport in environment and chemical transformations [12–14]. The essential increase of interest in the role of perfluorinated compounds in the natural environment can be illustrated by the number of papers published in the last two decades provided by ISI Web of Science data-base (Fig. 1).

Basic structural elements of anthropogenic PFCs are: a partially or fully fluorinated alkyl chain (a hydrophobic part) and a terminated functional group (carboxylates, sulfonates, sulfonamides, phosphonates), which constitutes a hydrophilic part of a molecule. Due to the presence of both hydrophobic and hydrophilic parts, PFCs exhibit surfactant properties, reducing surface tension stronger than other major classes of surfactants. Because of a high electronegativity and a small size of the fluorine atom, the carbon-fluorine bonds are the strongest bonds in organic chemistry [14a]. PFCs are nonflammable and resistant towards acids, bases, the majority of oxidants and reductants [15]. Those physicochemical properties are utilized for numerous applications of PFCs, including fire-fighting foams, coating of clothing fabrics, leather and paper products used for food packing. Such a broad scope of applications results in their global distribution to the natural environment, wildlife and human organisms. The consequence of this is their presence in food, which significantly contributes to human exposure to those compounds [16,17].

The most commonly encountered and investigated PFCs in the environment, food and biological samples are perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonates and sulfonamides, fluorotelomer alcohols, acids, olefins and sulfonates. Over the past few years more than 100 papers devoted to different environmental aspects of those compounds have been published every year. Due to the most frequent occurrence in both natural environment and living organisms,

the closest research attention was given to perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) – see their structures below.

Perfluorooctanoic acid (PFOA)   Perfluorooctanesulfonic acid (PFOS)

Numerous different processes are indicated as the sources of PFOA in the natural environment [13]. They include a direct production process (mostly in fabrication of ammonium perfluorooctanoate, APFO) by electrochemical fluorination, which has been used since 1950s to produce fluoropolymers. As shown in the diagram in Fig. 2A the other main sources of estimated total global historical PFCAs emissions, besides fluoropolymer manufacture from APFO, are also the use of fire-fighting foams as well as consumer and industrial products. The indirect sources of PFCAs contribute much less to total emission to the environment (about 5% according to [13]). The main indirect source is degradation of semi-volatile fluorotelomer alcohols (FTOHs) in atmosphere to yield a homologous series of PFCAs, which is an especially important source of PFCA pollution in the remote areas [12]. FTOHs are linear PFCs manufactured by telomerization process containing even-numbered alkyl carbon chains with a different number of fluorinated and two hydrogenated carbons. They are raw materials used in the manufacture of surfactants and polymeric products. They are present in these materials at low levels of unreacted residues [18], being precursors to the formation of PFCAs, and they can be also found in surface water, *e.g.* at 0.1–0.25 µg/L level even far from the location of manufacturing plants [19]. Modeling global-scale fate and transportation of PFOA emitted solely from direct sources compares favorably to observed concentration in the world's oceans [20]. The occurrence in aquatic environment and health effects of PFOA have been reviewed in recent years by several authors [21–23].

As far as the occurrence of PFOS in the environment is concerned, it also comes from manufacture releases when employed in specialized industrial processes (semiconductor, medical devices, aviation, metal plating). It is also a component of aqueous film forming foams and an impregnation agent. In an indirect way, it comes from the manufacture of perfluorooctane sulfonyl fluoride (POSF) and the breakdown of POSF-derivatives in the environment [24]. An estimated release of POSF from various sources is shown in Fig. 2B. As can be seen in the
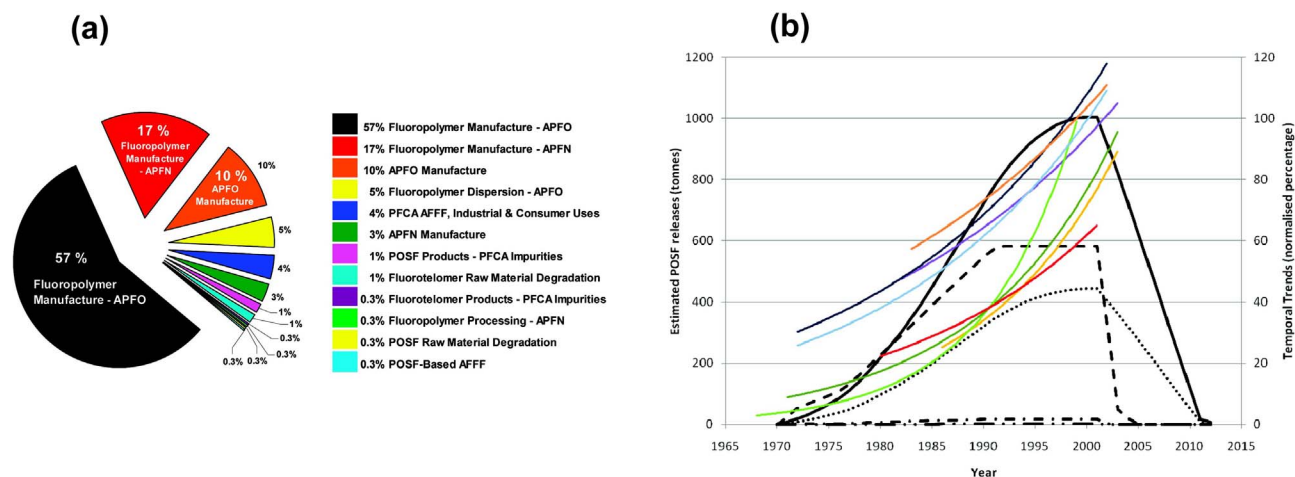
Fig. 2. The estimated sources of most commonly occurring and investigated PFCs. A. The contribution of different direct sources to total historical global PFCA emissions [13]. APFO – ammonium perfluorooctanoate, APFN – ammonium perfluorononanoate, AFFF – aqueous fire-fighting foam, POSF – perfluorooctylsulfonyl fluoride. B. Estimated perfluorooctane sulfonyl fluoride (POSF) releases from 1970 to 2012 and exponential temporal trends in biota [24]. Temporal trends in biota have been normalized to 100% for each species/data set. Usage depicted as follows: carpets (—), paper and packaging (- -), apparel (- - -), performance chemicals (–··), AFFFs (…), and biota trend lines; Ringed seals from Arctic locations; Qeqertarsuaq (purple) and Ittoqqortoormiit (yellow), Baltic guillemot eggs (pooled; light green and mean; dark green), polar bears from western (light blue) and eastern Canadian Arctic (dark blue), herring gull from Norway (orange) and laketrout from lake Ontario (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

figure, the rapid drop in the beginning of 2000s is related to the withdrawal of POSF from the market in 2002 by its main producer, the 3 M Company, in the USA. It also illustrates some trends in the content in selected biota. The world-wide distribution of PFOS into the environment is not attributed to its transport in atmosphere, as it is essentially nonvolatile, but rather its volatile precursors undergo a long range atmospheric transport prior to degrading to PFOS. In spite of some differences in the properties compared to already accepted Persistent Organic Pollutants (POP), the Stockholm Convention named POPs Review Committee (POPRC) recommended PFOS, its salts and the main production intermediate POSF to be added to the list of POPs [25,26].

Reported by many research groups data on PFOS and PFOA concentrations found in surface waters, surface water sediments, wastewater treatment plant (WWTP) effluents and sewage sludges were

compiled in the review by Zareitalabad et al. [27]. Their graphical presentation is provided in Fig. 3. As this review deals with waters and wastewaters, those two media are important to highlight. The average values for surface waters are similar for PFOA and PFOS, and they are between 1 to 10 ng/L, and can be considered as very low. In some critical cases, however, the concentration of PFOA in surface water may reach even between 10 and 50 µg/L, and in case of PFOS from 1 to 7 µg/L, which can be considered as high values. In case of effluents from WWTPs the average concentration values are from 10 to 100 ng/L for PFOA, and from 7 to 50 ng/L for PFOS. In some extreme cases the content of PFOA and PFOS may reach 1 µg/L, which is already quite substantial level taking into account the human health risk. In the abovementioned review on PFCs concentrations and their interphase distribution coefficients [27] it was concluded that the sorption of perfluorinated compounds to soils and sediments significantly
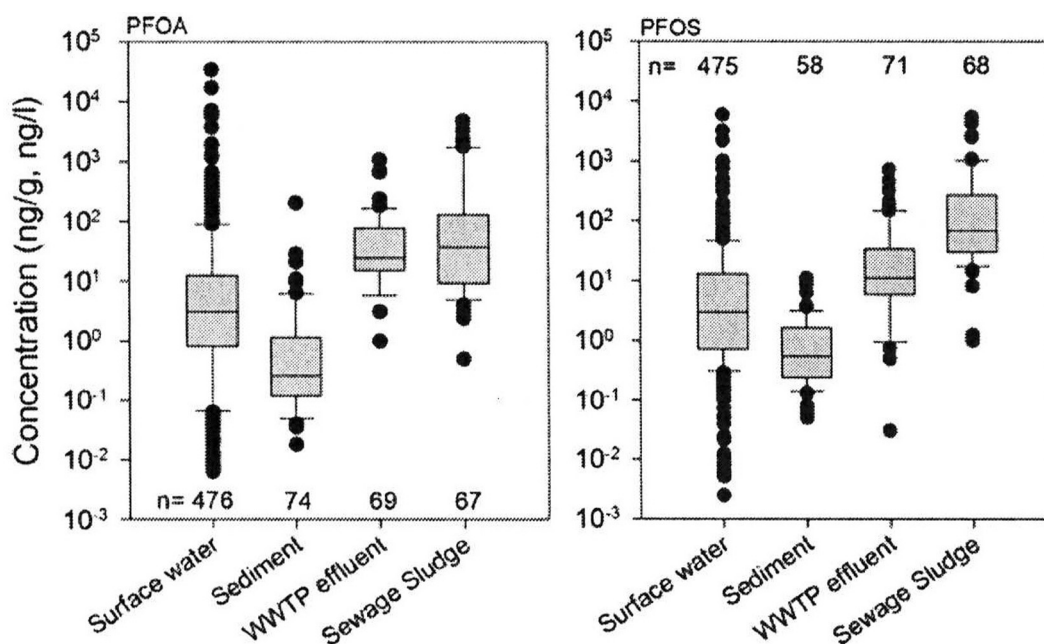

Fig. 3. Concentrations of PFOA and PFOS in surface water, surface water sediments, waste-water treatment plant effluent, and sewage sludge [27]. WWTP – wastewater treatment plant.

contributes to their fate and distribution in the environment. A various computational approaches for estimating $\log_{10}K_{oa}$ (octanol-air partitioning) values give them for PFOA in the range 5.73–7.62, and for linear PFOS in the range from 6.02 to 7.80 [26a].

In the technologies of production of PFOS precursors (*i.e.* POSF) linear isomers make up for about 70% of products, and the remaining percentage (30%) is a mixture of various branched chain isomers. This brings an essential contribution to understanding of human exposure to PFOS, based on the relative abundance and chiral signature of branched chain isomers [28], and isomer profiling can be utilized as a tool for source tracking [29]. Certain contribution to the presence of PFOA and PFOS in environment can be also assigned to the biodegradation of perfluorinated compounds with molar masses of about 2000, which are used as waterproofing and stain repellants [29a].

The common presence of those anthropogenic pollutants cause the need to establish a specific drinking water guidelines. Data from different countries on drinking water guideline values can be found *e.g.* in review by Zushi et al. [29b]. They vary from 0.04 to 0.5 µg/L in different countries. The EPA established the health advisory levels at 0.07 µg/L for combined presence of PFOA and PFOS [29c].

The common occurrence of perfluorinated surfactants in the natural environment is also a reason for an increasing interest in the development of methods of their removal from waters and wastes [30,36], including methods developed for the field applications [31], and it is rather a rare situation that they are not mentioned nowadays among surfactants posing some environmental danger [32]. The classical methods of removal of perfluorinated surfactants from waters include reverse osmosis, sorption on activated carbon, sonochemical pyrolysis and incineration. The decomposition of perfluorinated compounds with the release of total fluorine can be carried out with various combustion methods [33,34] or with the use of very strong reducing agents such as *e.g.* metallic magnesium in supercritical carbon dioxide, sodium in dry ammonia, sodium biphenyl or zero valent iron. These methods, due to the high cost of instrumentation and reagents, are employed mostly in micro-scale, for instance for analytical or synthetic purposes. For technological purposes (including environmental protection) the studies on biodegradation, especially the one with the use of advanced oxidation/reduction processes with application of radical reactions, have been carried out.

The need for development of new, effective methods of decomposition of PFCs for environmental protection can be justified by the fact that numerous studies have demonstrated an insufficient efficiency of commonly used technologies by indication of PFCs presence e.g. in drinking waters, see *e.g.* the reviews [22,35]. In a very thorough recent review Rahman et al. [35] have summarized data from many countries all over the world, showing a large number of cases where the average level of PFOA and PFOA detected in drinking water ranged from 1 to 100 ng/L, but in some cases exceeded even 1 µg/L. This essential finding takes into account the observation that ongoing human exposure to drinking water concentrations levels of 10, 40, 100 and 400 ng/L is expected to increase mean serum levels of PFOA by about 25, 100, 250 and 1000%, respectively, from background average level in human serum of about 4 ng/L [22].

One of the most common tertiary water treatment technologies is adsorption on powder or granular activated carbon, which is then followed by incineration of spent sorbent. In the examination of granular activated carbon (GAC) in treatment plants in Spain for removal of PFOS and PFOA an average elimination efficiency of 64 ± 11 and 45 ± 19% was found for PFOS and PFOA, respectively [37]. What turned out to be more effective was the reverse osmosis with ≥ 99% removal efficiency for both compounds. It was also reported, however, that activated carbon that had been used for a longer period of time (> year) was not effective in removing PFOS and PFOA [38]. The efficiency of powder activated carbon was also examined for simulated solution of aqueous film forming foam containing PFCs, where 10-time reduction of OPFCs content was observed [39]. In the study of removal

PFCAs in the drinking water production chain, that consisted of coagulation, rapid sand filtration, dune passage, aeration, ozonation, pellet softening and granular GAC filtration, it was found that none of the treatment steps are effective for PFCAs removal, except the GAC filtration [40]. In the examination of sorption of the selected four PFCs to GAC in the presence of ultrasound it was found that with the use of 20 kHz irradiation, the sorption kinetics increased from 250 to 900%, which was attributed to increase the PFCs diffusion rate into GAC nanopores [41]. The sorption kinetics enhancement increased with the lengthening of an alkyl chain. In the comparison of the removal of PFOA, PFOS and perfluorobutane from dilute solutions on GAC, zeolites with different silica content and wastewater sludges, the best results were reported for GAC, showing the highest affinity to PFCs [42]. The adsorption of PFOS on GAC was also compared with 3 non-ion-exchange polymers and 2 ion-exchange polymers. Considering both adsorption isotherms and adsorption kinetics, one of the examined hydrophobic polymers and one ion-exchange resin were found superior over the GAC employed [43]. For a relatively selective PFOS adsorption a chitosan-based molecularly imprinted polymer was prepared by crosslinking with epichlorhydrin in the presence of PFOS as a template [44]. The obtained sorbent (with its capacity of 560 µmol/g) can be used at least five times without any loss in sorption capacity when regenerated using the NaOH/acetone mixture. The obtained sorption capacity was larger than the one reported for PFOS for commercial GAC preparation 360 µmol/g reported by some other authors [42].

Among the commonly used conventional methods of decomposition of organic pollutants in waters and wastewaters there is also biodegradation. It has also been extensively examined for the removal of fluorochemicals [45], including poly- and per-fluorinated compounds [46]. Due to the presence of the strongest existing covalent bond carbon-fluorine, perfluorinated surfactants are much more stable than their hydrocarbon analogues. In the studies of defluorination of selected organofluorine sulfur compounds by *Pseudomonas* Sp. strain D2 it was found that observed for compounds containing hydrogen was not only defluorination, but also *e.g.* potassium salt of PFOS [47]. In an acidic form, protonated PFOS partly degraded with the formation of six volatile fluorinated products not containing sulfur. The biodegradation under aerobic and anaerobic conditions was investigated in wastewater samples spiked with 10 mg/L of PFOS and PFOA [48]. No degradation or mineralization was observed under aerobic conditions, while in anaerobic treatment (reductive conditions) PFOS disappeared relatively quickly within 2 days with much slower removal of PFOA, which took 25 days. Biodegradability of PFOA was also examined in both anaerobic and aerobic, 110-day incubation, employing five different microbial communities, and it was concluded that PFOA is microbiologically inert, hence its environmental persistence [49]. This gives an additional argument about the needs for search of more effective decomposition methods for perfluorinated surfactants.

2. Introduction to advanced oxidation processes employing free radicals

With rapidly widening spectrum of anthropogenic pollutants emitted to the natural environment, including pharmaceuticals, pesticide residues or pollutants of industrial origin, especially the ones recognized as persistent organic pollutants (POPs), a limited efficiency of physical purification methods and biodegradation imposed significant interest in typical chemical methods of decomposition of pollutants. Apart from the typical wet chemical oxidation methods, the recent decades have brought an increasing interest in methods based on the use of free radicals reactions as unusually reactive reagents, with particular attention paid to investigation and application of hydroxyl radicals (˙OH). In 1987 Glaze et al. [50] introduced a term *Advanced Oxidation Processes* (AOP) for water treatment processes performed at room temperature, and based on the *in-situ* generation of a powerful oxidizing agent, such as hydroxyl radicals, at a sufficient concentration
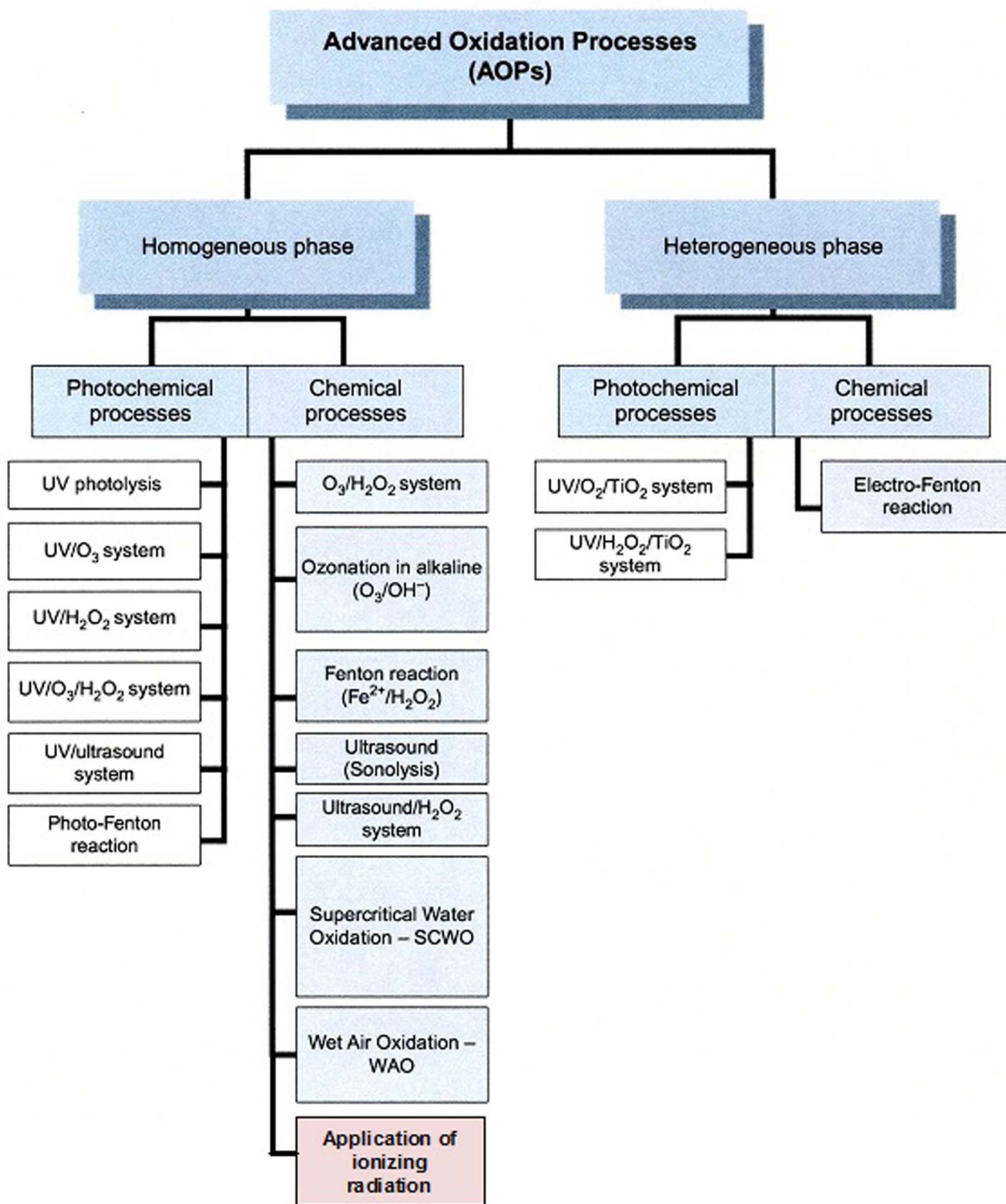
Fig. 4. Major types of Advanced Oxidation Processes in scheme adapted from [55a] with added application of ionizing radiation.

to effectively decontaminate waters. A hydroxyl radical is one of the most reactive free radicals and one of the strongest oxidants (E° = 2.33 V), reacting with various groups of organic molecules with reaction rate-constants from 10^6 to 10^{10} M^{-1} s^{-1}. The most often occurring reactions of ·OH with organic pollutants involve an addition to unsaturated carbon–carbon bonds, a substitution to aromatic rings, abstraction of hydrogen atom from target molecule or mono-electronic oxidation. ·OH radicals have also numerous environmental implications

[51] and can be generated for laboratory or industrial purposes in processes that use the combination of oxidation agents (O_3, H_2O_2), irradiation (UV, ultrasound, microwave, gamma-rays, and beam of accelerated electrons), catalysts or electrochemical reactions. The oldest method of ·OH generation is the Fenton method, based on the use of Fe (II) and H_2O_2 [52]. Later on, precisely in France in 1906, ozone was first used as a disinfectant [53]. First photocatalytic methods for environmental application were reported in 1970s, see *e.g.* [54], while the
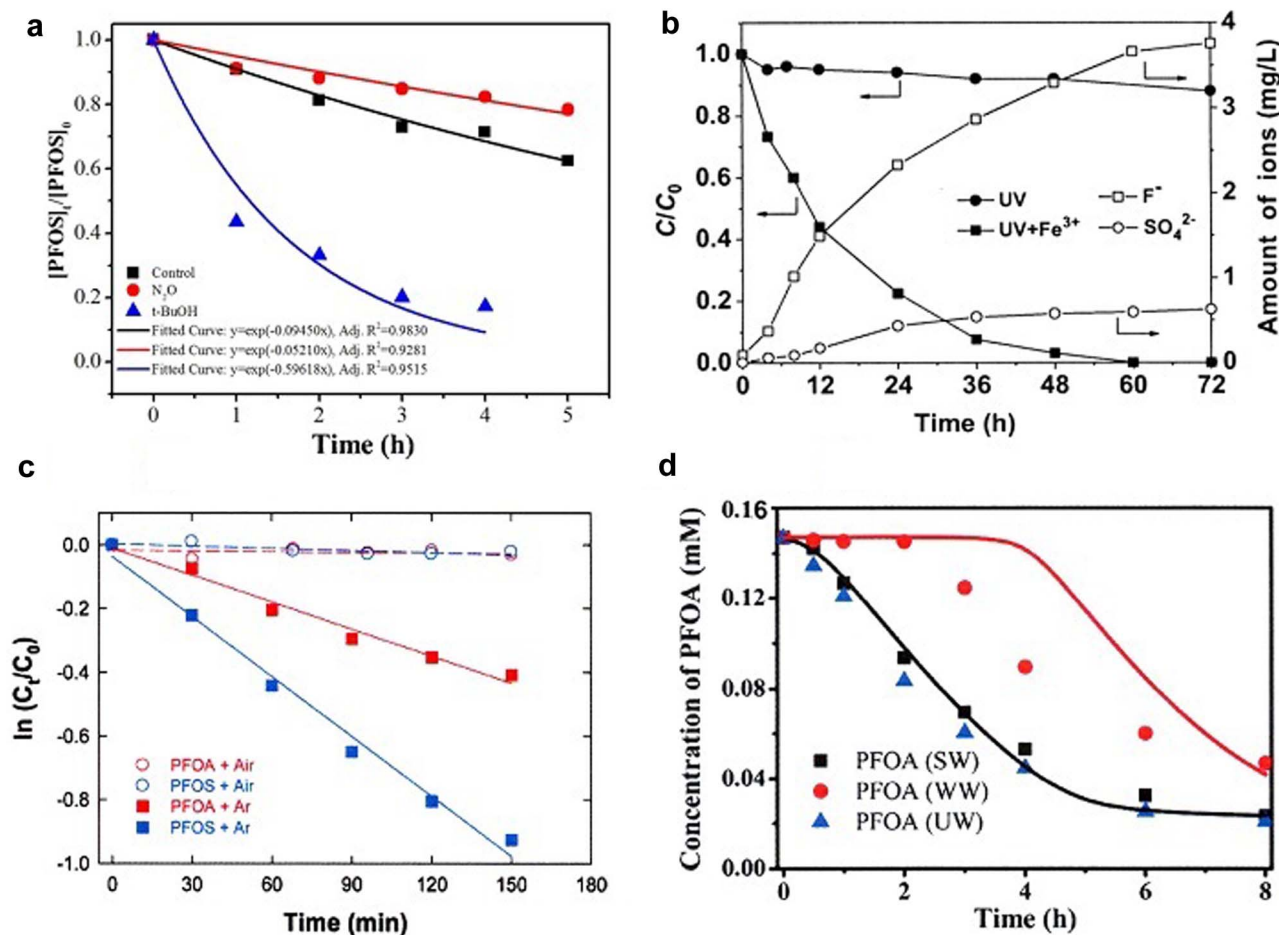
Fig. 5. The time profiles for photochemical decomposition of PFOS and PFOA in different conditions: A – decomposition of PFOS (37.2 μM) irradiated with UV at 254 nm and the fitted curves in 6.0 mM PBS (pH 7.0) with addition of either N_2O or *t*-butanol [70]. Experimental conditions: [N_2O] – 8.4 mM, [*t*-butanol] – 1.0 mM, temperature 100 °C. The control experiment was conducted under the same condition but without extra chemical additions. B – decomposition of PFOS (20 M) in the presence and absence of 100 M Fe(III), and formation of fluoride and sulfate, under UV irradiation (254 nm) at pH 3.6 [77]. C – decomposition of PFOA (0.24 M) and PFOS (0.20 M) under UV irradiation at 254 nm in 10 mM potassium iodide solution, in the presence and absence of oxygen (air vs. Ar) [78]. D – decomposition of PFOA (150 M) in different matrices under UV irradiation at 254 nm in the presence of 15 mM persulfate: UW – ultrapure water, SW – surface water, WW – wastewater [81]. The solid lines represent the modeling predictions.

first application of ionizing radiation for treatment of waters and sewage was published already in 1953 [55]. A schematic presentation of investigated and applied AOPs for various pollutants with generation of ˙OH radicals has been presented in Fig. 4.

Those numerous decades of development of AOPs brought a vast scientific and patent literature together with numerous laboratory and industrial applications. As the selected literature examples one can mention the books presenting those methods [56–58] or many review papers concerning applications in water/wastewater treatment, *e.g.* [59–61], applications of high gravity technologies successfully assisting AOPs by providing a high mass transfer [61b], figures-of-merit of AOPs for both electric- and solar-driven systems [62], applications for decomposition of particular groups of pollutants, such as endocrine disrupting chemicals [63], pharmaceuticals [63,64] or natural organic matter from drinking water [65].

A thorough review of treatment technologies for decomposition of PFOA and PFOS in aqueous solutions was published by Vecitis et al. in 2009 [30]. It included the presentation of some AOPs for PFOX oxidation, as well the as methods employed for PFOX reduction and thermolysis by incineration and sonolysis. This was based on the original papers published up to 2007, hence the subject of this review will be mostly papers published over the last decade in international journals on AOPs for decomposition of PFOA and PFOS.

3. Photochemical and photocatalytic treatment

The photochemistry is nowadays a widely used physico-chemical processing method in organic synthesis, material science and in water treatment for its purification, and has been recognized as a highly efficient and cost-effective process [65a]. The possibilities of direct and indirect photochemical degradation of PFOA and PFOS have been intensively investigated in UV range, both in the absence and presence of different supporting reagents, and especially in photocatalytic systems. There are two different aspects to these studies. The first one concerns the investigation of PFCs degradation under sunlight radiation in different chemical and environmental conditions, which brings some contribution to the evaluation of environmental degradation. The second one concerns the optimization of the irradiation processes on laboratory or technological scale dedicated to removal of PFCs from waters and wastewaters. Due to the chemical structure of compounds of interest (PFOA, PFOS) they exhibit only weak electronic absorbance bands in the 205–225 nm region, where *e.g.* perfluorooctanoate has molar absorptivity $344 \, M^{-1} \, cm^{-1}$ only at 205 nm [66]. Stronger light absorption by PFCs is observed in vacuum UV region below 200 nm, which was illustrated *e.g.* by UV spectrum for PFOA in the range from 190 to 280 nm [67]. In the same cited work the efficiency of direct photolysis of PFOA and defluorination was compared at the initial level

of 25 mg/L PFOA for irradiation at 185 and 254 nm, where much faster degradation was observed at 185 nm. After 2-h irradiation about 62% PFOA decomposition was observed with the formation of perfluorinated acids with a shorter perfluorinated alkyl chain and only about 17% yield of defluorination. A similar result of comparison of the yield of PFOA decomposition at those wavelengths, with the use as source of radiation a low-pressure UV 20 W lamp, was attributed to the fact that photo energy at 185 nm is sufficient to cleave the C−C and C−F bonds in PFOA, but at 254 nm is not sufficient to cleave the C−F bond [68]. As for the degradation mechanism, a direct photolysis into $\cdot C_7H_{15}$ and $\cdot COOH$ radicals was postulated and further reaction of $\cdot C_7H_{15}$ radical with water led to the formation of $C_6H_{15}COOH$ and fluoride. In the measurements of PFOA at the level of 0.1–2.4 µM at 185 nm it was observed that for 3-h irradiation the initial level of PFOA had no effect on the yield and the efficiency of the decomposition is close to 90%. A significant effect on lowering the yield of decomposition had matrices of tap and river waters.

In another work for the photolytic system employing a 23 W ozone-producing low-pressure mercury lamp, the yield of decomposition in the presence of nitrogen and oxygen was compared together with the effect of pH [68a]. In alkaline medium of pH 12 a much faster reaction was observed in nitrogen atmosphere than in oxygen one, which was attributed to inducing the decomposition mainly by hydrated electrons. In the most suitable conditions the 100% PFOA decomposition in 24 µM (10 mg/L) solution was observed after 60 min, with yield of fluoride release about 55%, while 80% defluorination required 3-h irradiation.

In the investigation of photochemical degradation of PFOS at 254 nm, employing a medium pressure 500 W mercury lamp, and concentration level of 37.2 µM it was found more efficient in phosphate buffer, lake water, and wastewater treatment plant (WWTP) effluent than in a pure aqueous solution, which was attributed to the presence of some dissolved organic matters [69]. In further studies the same authors investigated the role of water photolysis-derived oxidative or reductive species indicating that PFOS decomposition in a catalyst-free aqueous solution indirectly, *via* a reduction route with participation of hydrogen atom and hydrated electrons from water photolysis [70]. The PFOS photodegradation was substantially suppressed under oxygenated conditions. Those observations have been illustrated in Fig. 5A, showing the most efficient degradation (k = 0.91 h^{-1}) in the presence of *t*-butanol scavenging both $\cdot OH$ radicals and hydrogen atoms.

The investigation of photolytic processes is essential from the point of view of determination of photodecomposition rate and mechanism of degradation of those compounds in aquatic environment under the influence of sunlight. The solar radiation contains about 7% of UV radiation [71], although the Earth's atmosphere filters nearly all the light of wavelengths less than 290 nm. In spite of that fact, the interaction of sunlight with chromophoric dissolved organic matter by UV–Vis photolysis, apart from the reactions with NO_3^- and NO_2^-, are considered the main sources of $\cdot OH$ radicals in aquatic environment [51]. In one of the published approaches, the PFOA spiked solutions, including sea water, were irradiated with an artificial sunlight (290–800 nm) [72]. In employed solar sun simulator a xenon arc lamp emitting 765 W m^{-2} was employed, with blocking wavelengths below 290 nm. In the samples irradiated with a solar simulator, which corresponded to 75.6 days of natural solar irradiation, no decrease of PFOA concentration was observed at the spike level of 0.1 µg/L PFOA. The photochemical half-life of PFOA at the surface of the ocean was estimated to be at least 256 years, while in the mixing layer of the open ocean > 5000 years.

A real environmental photodegradation of selected PFCs with solar radiation was examined at an elevation of 4.200 m above sea level in Hawaii, where solar radiation intensity was approximately 40% stronger than at the sea level [73]. For the initial concentrations of 2.1 and 2.5 µM PFOS and PFOA, respectively, the reduction of concentration after 106-day irradiation was found only 29% and 5%. It was observed that long-chain perfluorinated carboxylic acids are successively dealkylated to more resistant short-chain compounds. The efficiency of

solar photodegradation of PFOA can be substantially enhanced in the presence of Fe(III) [74]. The 28 days of solar irradiation performed at 32 m above sea level on 20 mg/L PFOA solution containing 26.8 mg/L Fe(III) resulted in 97.8% of PFOA decomposition with 12.7% defluorination. It was demonstrated spectroscopically that the decomposition reaction is initiated by electron-transfer from PFOA to Fe(III), forming Fe(II) and an unstable carboxyl radical, however alternative process may involve hydroxyl radicals, which was supported by EPR measurements. Almost 100% defluorination was observed when additional 4 mM persulfate was present in irradiated solutions.

Supporting photochemical processes by an addition of different compounds to enhance the yield of formation of reactive free radicals is often employed in the degradation processes for PFOA and PFOS. In the examination of PFOA degradation at the level of 20 µM with 254 nm UV light from 9 W UV lamp it was found that the yield of the Fenton process is only slightly larger than in the presence of Fe(III) only, although it is twice as large as in the presence of added Fe(II) [75]. The effect was similar to PFOA being degraded by sunlight irradiation [74]. In the recently published paper on PFOA photodecomposition with use of a low pressure 5 W vacuum UV lamp, in the presence of Fe(III) a profound effect of $\cdot OH$ radicals was demonstrated [76]. The yield of decomposition was not affected neither by the nitrogen or oxygen content in solution and it was suppressed by the presence of persulfate, chloride and dissolved organic matter. While chloride and dissolved organic matter acted as $\cdot OH$ scavengers, persulfate consumed photoenergy by adsorption. The role of Fe(III), however, was not deeply discussed.

The role of the presence of Fe(III) and persulfate in the photolytic degradation of PFOA and PFOS was discussed in a few more papers published over the recent years. In the system with a low-pressure 23 W mercury lamp, for the initial level of 20 µM of PFOS it was shown that the presence of 0.1 mM Fe(III) accelerates 50-times the photolysis rate at 254 nm, where, besides fluoride and sulfate, also C2 to C8 PFCA were identified as the products of the decomposition [77]. It was also demonstrated, that yield of the photolysis is similar in the atmosphere of oxygen and nitrogen, while it is less effective in the presence of H_2O_2 due to the formation of additional amount of $\cdot OH$. Complete decomposition of 20 µM PFOS was obtained within 60 h and the mechanism of decomposition was based on the photolysis of PFOS complex with Fe(III), leading to unstable PFOS radical, which was desulfonated to form a perfluoroalkyl radical. Its further reaction with oxygen of hydroxyl radicals led to defluorination. As shown in Fig. 5B, this process is much slower than the one carried out under reductive conditions (Fig. 5A).

Reductive photochemical decomposition of perfluoroalkyl compounds can be carried out by hydrated electrons $e_{aq}-$ which can be generated, *e.g.* by photolysis of iodide via charge-transfer-to-solvent (CTTS) states [78–80]:

$$I^- + h\nu \rightarrow I^-_{CTTS} \rightarrow I^\cdot + e_{aq}- \tag{1}$$
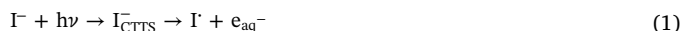
The degradation of PFCs by hydrated electrons does not occur in the presence of oxygen, because of their fast scavenging by oxygen (k = $1.9 \times 10^{10} M^{-1} s^{-1}$). The electrons react faster with PFOS than with PFOA (Fig. 5C), which is expressed by the values of apparent first-order rate-constants 6.5×10^{-3} and $2.9 \times 10^{-3} min^{-1}$ for PFOS and PFOA, respectively (data from the system with 8 W 254 nm UV lamp) [78]. From the studies of different PFCs it was found that perfluoroalkylsulfonate kinetics increased with increasing chain length, whereas in PFCAs chain length it had negligible effect. In both cases, PFOA and PFOS, the reactions with $e_{aq}-$ led to the corresponding radical ions $PFOA^{\cdot 2-}$ and $PFOA^{\cdot 2-}$, which decompose via fluoride elimination to form perfluoroalkyl radicals $C_nF_{2n}X^{\cdot-}$ (X = SO$_3$ or CO$_2$). Their further reactions with $e_{aq}-$ are as follows:

$$C_nF_{2n}X^{\cdot-} + e_{aq}- \rightarrow C_n F_{2n} X^{2-} \tag{2}$$

and they lead to the formation of sulfonate or carboxylate $C_nF_{2n-1}X^-$. The yield of defluorination was much larger for PFOS than PFOA, and

both processes were associated with the formation of numerous gaseous intermediates identified by GC/MS as shorted-chain fluorochemicals, mostly iodinated fluorocarbons [78]. No formation of shorter alkyl-chain sulfonates or carboxylates as the products of decomposition was discussed. In the later work of the same research group it was reported that the initial pH value had minimal effects on PFC photoreduction kinetics, whereas the initial substrate concentration influenced the observed degradation kinetics, especially below 1 μM of the initial concentration [79]. In the discussion about the role of PFCs degradation of hydrogen atoms formed in a slow reaction of hydrated electrons with water, it was concluded that the rate of ·H production is too slow or it cannot degrade PFCs due to a lower reaction potential (-2.1 V) than electron (-2.9 V). Compared to UV/persulfate photolysis of PFCs, the lower activity of the UV/iodide system was interpreted by triiodine scavenging of hydrated electrons. In another work on UV irradiation of PFOA in the presence of iodide, where a low-pressure 15 W mercury lamp emitting 254 nm UV was used, in deaerated solutions 93.9% of the decomposition of 25 μM PFOA was obtained with 76.8% of release of fluoride in 6 h [80]. Contrary to other works mentioned above, the yield of PFOA decomposition was much larger, compared to the potassium persulfate-containing system under oxidative conditions. Apart from fluoride, formic and acetic acids as the intermediated products in reductive degradation, six short-chains C1 to C6 PFCAs were also identified and detected during the first four hours of conducting the process. The mechanistic analysis was concluded with the indication of two major PFOA decomposition pathways – direct cleavage of C–F bonds by $e_{aq}-$ leading to elimination of fluoride and further photolytic process producing shorter PFCAs:
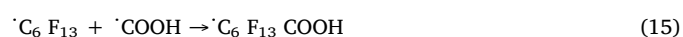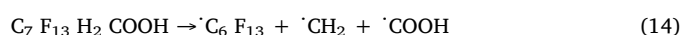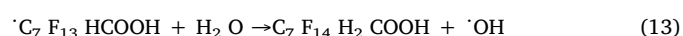
$$C_n F_{2n-1} H_2 COOH + h\nu \rightarrow \cdot C_{n-1} F_{2n-1} + \cdot \cdot CH_2 + \cdot COOH \quad (3)$$

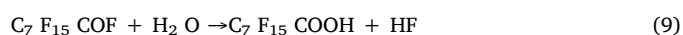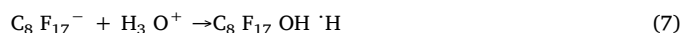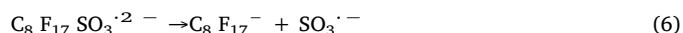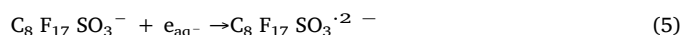$$\cdot C_{n-1} F_{2n-1} + \cdot COOH \rightarrow C_{n-1} F_{2n-1} COOH \quad (4)$$
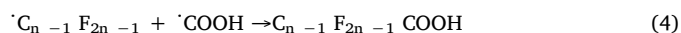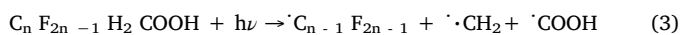
In parallel (although slower) processes, the cleavage of C–C bond occurred on the side of a carboxylic group, leading to the formation of unstable C6F13COF in direct photolysis process, which underwent further hydrolysis reaction to form C6H13COOH. The later studies of the same research group on reductive photolysis of PFOA in the presence of iodide have demonstrated a strong effect of pH of irradiated solution on the yield of PFOA degradation [80a]. From the examined pH range between 5.0 and 10.0, the best efficiency was reported for pH ≥ 8.0 and it was concluded that high pH also inhibits the generation of toxic intermediates (fluorinated and iodinated hydrocarbons). The concentration of hydrated electrons increased with the increase of pH of irradiated solution, and keeping the pH value constant during the process allowed maintaining the high degradation rate.

A much faster UV oxidative decomposition of PFOA in the presence of persulfate, compared to the above-mentioned work [80], was also reported, even for a larger initial concentration (0.15 mM) in the presence of 15 mM persulfate, employing 254 nm irradiation with the average light intensity 2.88×10^{-7} einstein $L^{-1}s^{-1}$ [81]. However, the formation of active sulfate radicals (with the oxidation potential of 2.3 V), which can be more effective oxidant in degrading organic compounds than ·OH, was substantially reduced in the presence of chloride. Through the kinetic modeling it was shown that PFOA degradation was suppressed in the presence of chloride and carbonate species and it did not occur until all the chloride was converted to chlorate. As intermediate products of PFOA oxidation by UV/persulfate process the five PFCAs with the loss of CF_2 group from PFOA were identified (C3–C7). Authors also admit that PFOA cannot be degraded by hydroxyl radicals in the presence of chloride until all the chloride in a treated sample was converted to chlorate. In order to compare the role of ·OH and $SO_4^{-}\cdot$ in the PFOA degradation, a comparison of UV/H₂O₂ and UV/persulfate was carried out, where no removal of PFOA was observed with 15 mM and even higher H₂O₂ concentrations. No mechanism of PFOA reaction with $SO_4^{-}\cdot$ was suggested, in spite of the calculation of rate-constants for PFOA and five other PFCAs. The PFOA

decomposition in pure aqueous solutions was compared to the processes conducted in matrices of surface water and wastewater (Fig. 5D). The 50% decomposition in pure water was observed after about 2.4 h, while in surface water about a 20% increase of that time need was found, and this was in satisfactorily good agreement with the kinetic modeling. However, the same degree of PFOA decomposition in wastewater matrix required about 5.5 h. In the earlier study [81a], similar conditions were employed for the decomposition of PFOA at even much higher initial concentration (1.35 mM), but with larger concentration of persulfate (50 mM). Using a UV–visible light from a xenon-mercury 200 W lamp, a 90% decomposition was achieved within about a 4-h process, which should be considered fairly effective.

The hydrated electrons for decomposition of PFOA and PFOS can also be generated in other chemical systems. The reactivity of $e_{aq}-$ produced by laser flash photolysis (266 nm) employing a Nd:YAG laser, in the 40 μM $K_4Fe(CN)_6$, nitrogen saturated solution was examined toward PFCAs, and the second-order rate-constant for PFOA was estimated to be $(1.7 \pm 0.5) \times 10^7 M^{-1} s^{-1}$ [82]. The values of the rate-constant appeared to increase with the length of perfluorinated alkyl chain. As the reaction center in PFCA is fluorine atom, the longer perfluorinated chain brought more attacking sites, which resulted in a corresponding increase in the reaction rate. In the same work, also the reactivity of PFOA with strong oxidative radicals $SO_4^{-}\cdot$ and $NO_3^{-}\cdot$ was examined, where rate-constants to be not greater than $5 \times 10^4 M^{-1}s^{-1}$ were evaluated. The photolysis carried out at 185 nm in 0.3 M chloride also generated the hydrated electrons, which allowed decomposing 30 μM PFOA with 99.6% yield after 23 h and 65% defluorination and formation PFCAs with shorter alkyl chains [83]. For PFOS decomposition, hydrated electrons can be also generated by a high photon flux UV/sulfite system with a high-pressure mercury lamp (200–400 nm) [84]. UV photon flux entering the reactor was in the range 1.98×10^{-7} to 6.6×10^{-7} einstein $cm^{-2} s^{-1}$. For the initial PFOS level of 32 μM and 10 mM Na₂SO₃, 98% PFOS was decomposed within 30 min, which was faster than those reported in other reductive methods ($k_{PFOS} = 0.118$ min^{-1}), albeit had strong dependence on the initial solution pH. The developed system demonstrated high tolerance to the presence of nitrate, which was quickly degraded (i.e. in the first 6 min). Due to a great promotion on $e_{aq}-$ production in employed system, many other potential scavengers of electrons did not affect the PFOS decomposition. In the initial stages of the decomposition process, the formation and degradation of C4–C8 PFCAs were observed as a consequence of defluorination, desulfonation, and centermost C–C fragments. The following set of equations presents the mechanism of the PFOS decomposition:

$$C_8 F_{17} SO_3^- + e_{aq-} \rightarrow C_8 F_{17} SO_3^{\cdot 2-} \quad (5)$$

$$C_8 F_{17} SO_3^{\cdot 2-} \rightarrow C_8 F_{17}^- + SO_3^{\cdot -} \quad (6)$$

$$C_8 F_{17}^- + H_3 O^+ \rightarrow C_8 F_{17} OH \cdot H \quad (7)$$

$$C_8 F_{17} OH \rightarrow C_7 F_{15} COF + HF \quad (8)$$

$$C_7 F_{15} COF + H_2 O \rightarrow C_7 F_{15} COOH + HF \quad (9)$$

$$C_7 F_{15} COOH + e_{aq-} \rightarrow \cdot C_7 F_{14} COOH + F^- \quad (10)$$

$$\cdot C_7 F_{14} COOH + H_2 O \rightarrow C_7 F_{14} HCOOH + \cdot OH \quad (11)$$

$$C_7 F_{14} HCOOH + e_{aq-} \rightarrow \cdot C_7 F_{13} HCOOH + F^- \quad (12)$$

$$\cdot C_7 F_{13} HCOOH + H_2 O \rightarrow C_7 F_{14} H_2 COOH + \cdot OH \quad (13)$$

$$C_7 F_{13} H_2 COOH \rightarrow \cdot C_6 F_{13} + \cdot CH_2 + \cdot COOH \quad (14)$$

$$\cdot C_6 F_{13} + \cdot COOH \rightarrow \cdot C_6 F_{13} COOH \quad (15)$$

As for the comparison of the obtained yield of photochemical PFOS degradation, one can find the example of degradation in aqueous solution (40 μM of the initial concentration), where irradiation with a low-pressure 32 W mercury lamp (254 nm) provided the yield
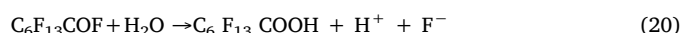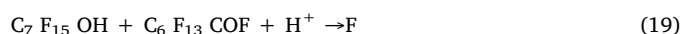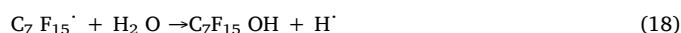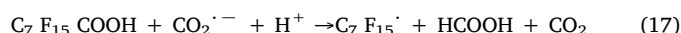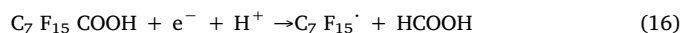
expressed by the photo-degradation rate constant $0.13 \, \text{day}^{-1}$ [85]. About 7-fold enhancement was observed for carrying out the degradation process in alkaline 2-propanol. It was also demonstrated that the degradation rate was different for different PFOS isomers, with a faster rate for linear isomer. The photochemical UV/sulfite system was also examined for reductive defluorination of PFOA employing a 10 W low-pressure mercury lamp with emission at 254 nm. [85a]. By carrying out the process under the nitrogen atmosphere and at the initial PFOA concentration level of 20 μM, a 100% decomposition was observed after an hour, while 88.5% defluorination – after 24 h. The generation of hydrated electrons was favored by increasing sulfite concentration and/or the pH. It was concluded that the photolysis of sulfite produced (apart from $e_{aq}-$) also $SO_3^{\cdot-}$ radicals, and while electrons were responsible for the PFOA defluorination, the sulfite radicals were responsible for the formation of some perfluorinated alkyl sulfonates and intermediates.

A reasonably effective photochemical oxidative decomposition of PFOA, irradiated at 254 nm, was observed in the presence of sodium bicarbonate (40 mM) and 0.075% H_2O_2 [85b]. In this case a low-pressure 400 W mercury lamp was employed with the light intensity 120,000 lux at the outer surface of the quartz reactor tube. Under such conditions, a strongly oxidizing carbonate radical anion $CO_3^{\cdot-}$ was formed and under slightly alkaline conditions (pH 8.8), for the initial PFOA concentration level 50 mg/L, the decomposition occurred with the pseudo-first-order rate-constant $0.4 \, \text{h}^{-1}$. The yield of decomposition depended significantly on the carbonate concentrate in the reacting mixture.

The use of semiconductor photocatalysts is a widely employed improvement of photolytic methods [86], which are effectively employed for treatment of various organic contaminated waters, including halogenated organics. The action was based on the promotion of electrons from valence to conductivity band and the generation of positively charged holes by the absorption of the photon flux. The electron-hole pairs can be trapped in surface states where they react with the species absorbed on the photocatalyst surface, competing with the recombination processes of the electron-hole pairs. Among the first photocatalysts employed for the photodegradation of PFOA was a heteropolyacid phosphotungstic acid $H_3PW_{12}O_{40}$, which in photocatalytic degradation at rather high initial PFOA concentration 1.35 mM, provided 50% degradation after 24 h with 20% defluorination [87]. The irradiation was carried out with UV–visible light from a 200 W xenon-mercury lamp. The decomposition was initiated by complexation of PFOA by a photo catalyst, and as a result of a photon adsorption an electron was transferred to $PW_{12}O_{40}^{3-}$, which was followed by decarboxylation and formation of the perfluoroheptyl radical. TiO_2 is widely used for environmental purposes in photocatalytic treatment due to its availability, chemical stability and low cost [88,88a]. The standard potential of a positively charged hole on TiO_2 is 3.2 V. Already in the first application to the photocatalytic degradation of PFCs it proved to be effective for the degradation of carboxylates and inactive to the sulfonates [89]. This early work has also indicated that the TiO_2 photocatalytic degradation is slow, but, in general, TiO_2 photocatalysis is affected by TiO_2 loading, pH and surface chemistry, and particularly – surface charge. The positive holes are considered to be predominating oxidative species at low pH values, whereas hydroxyl radicals play an important role at higher pH values [90]. The decomposition of 60 μM PFOA carried out in 0.l5 M $HClO_4$ took place with a pseudo-first-order rate-constant $0.71 \, \text{h}^{-1}$ with the formation of micromolar concentrations of C3–C7 PFCAs. The irradiation was conducted with a 16 W low-pressure mercury UV-lamp, and the light intensity $0.45 \, \text{mW cm}^{-2}$. It was concluded that the presence of an acid both helps to sustain the life of photoholes and improves the ionization of PFOA by increasing electron transfer from perfluorocarboxylic anions to the holes of excited TiO_2. In a similar conditions ($HClO_4$ at pH 4) PFOA was irradiated with three 6 W low-pressure lamps, emitting mainly 254 nm light with intensity $43 \, \text{mW cm}^{-2}$ [90a]. A complete degradation of PFOA in 120 μM

solution was achieved after 6 h process, but with 52% defluorination, only. The acute toxicity determined by Microtox test with *Vibrio fisheri* in such conditions was reduced by 82% after 60 min of reaction.

A significant improvement of photocatalytic decomposition of PFOA by TiO_2 under 254 nm UV irradiation was observed by replacing $HClO_4$ under N_2 atmosphere with oxalic acid as a hole-scavenger [91]. The irradiation was carried out with a low-pressure 23 W mercury lamp emitting 254 nm light with the light intensity $5.9–6.1 \, \text{mW cm}^{-2}$. Under such conditions the formation of carboxyl anion radicals ($CO_2^{\cdot-}$) was confirmed by EPR, which primarily induced the PFOA decomposition, while the addition of potassium persulfate as an electron-scavenger inhibited the PFOA decomposition. Based also on some earlier works, it was generally assumed that decarboxylation of carboxylic acids by TiO_2 is initiated by photo-generated holes, however the authors [91] suggest that in the presence of oxalate acting as a hole scavengers, the photo-generated electrons of TiO_2 with carboxyl anion radicals may initiate the decarboxylation of PFOA with a series of the following reactions:

$$C_7F_{15}COOH + e^- + H^+ \rightarrow C_7F_{15}^{\cdot} + HCOOH \quad (16)$$

$$C_7F_{15}COOH + CO_2^{\cdot-} + H^+ \rightarrow C_7F_{15}^{\cdot} + HCOOH + CO_2 \quad (17)$$

$$C_7F_{15}^{\cdot} + H_2O \rightarrow C_7F_{15}OH + H^{\cdot} \quad (18)$$

$$C_7F_{15}OH + C_6F_{13}COF + H^+ \rightarrow F \quad (19)$$

$$C_6F_{13}COF + H_2O \rightarrow C_6F_{13}COOH + H^+ + F^- \quad (20)$$

The formation of PFCAs with a shorter alkyl chain was confirmed by LC/MS. Fig. 6 shows the efficiency of PFOA decomposition under different conditions as well as the formation of decomposition products. A significant improvement of the yield of photocatalytic degradation of PFOA with the use of TiO_2 can be obtained by using Cu/Fe-modified [92] or Pb-modified [93] photocatalyst. In both works published by the same research group, where the same irradiation source was used as mentioned above [85b] modifications of photocatalyst were made by a photodeposition from a given metal salts in oxalic acid solution. Although for decomposition of PFOA at the initial concentration of 50 mg/L and at the same dose of photocatalyst (0.5 g/L), different values of pseudo-zero-order rate-constants were reported for non-modified TiO_2 ($0.0001 \, \text{min}^{-1}$, and $0.0158 \, \text{h}^{-1}$ [93]), in both cases a significant enhancement of degradation was reported for the metal-modified TiO_2. As presented in the recent paper, the 90% decomposition of 50 mg/L PFOA was observed in about 12 h with the use of Cu-modified TiO_2 [92] and in 4.5 h with the use of Pb-modified TiO_2 [93]. This was interpreted by producing traps to capture photo-induced electrons, which resulted in reducing electron-hole recombination during photocatalytic reactions, and, in consequence, leading to enhancement of PFOA decomposition. The enhancement of the catalytic capability in the case of metal-modified catalyst was attributed to the formation of PFOA-metal-TiO_2 complexes, which added a certain pre-concentrating step to the whole process.

In recent years, in numerous works on photocatalytic decomposition of PFOA in the presence of TiO_2, the application of various nanostructured preparations of the photocatalyst, which may potentially enhance the photocatalytic activity by a high specific surface area or additional ion-exchangeable or sorptive capabilities, has been reported. In the study of the role of oxygen in photocatalytic pathways of PFOA, a commercial nano-sized TiO_2 was employed containing two crystalline forms: 75% anatase and 25% rutile [94]. The irradiation was carried out with an iron halogenide 500 W UV lamp, emitting light at wavelength of 315–400 nm, and irradiation the reactor with a specific power of $75 \, \text{W/m}^2$. The evaluated rate-constants for PFOA decomposition for oxygen saturated solution $0.3346 \, \text{h}^{-1}$ was twice larger than in air-saturated solution and more than 40-times larger than in nitrogen saturated solution. The oxygenated conditions favored the formation of oxygen-centered perfluorinated radicals as major intermediates and the isolation in pure form COF_2 allowed to identify a new chemical route in
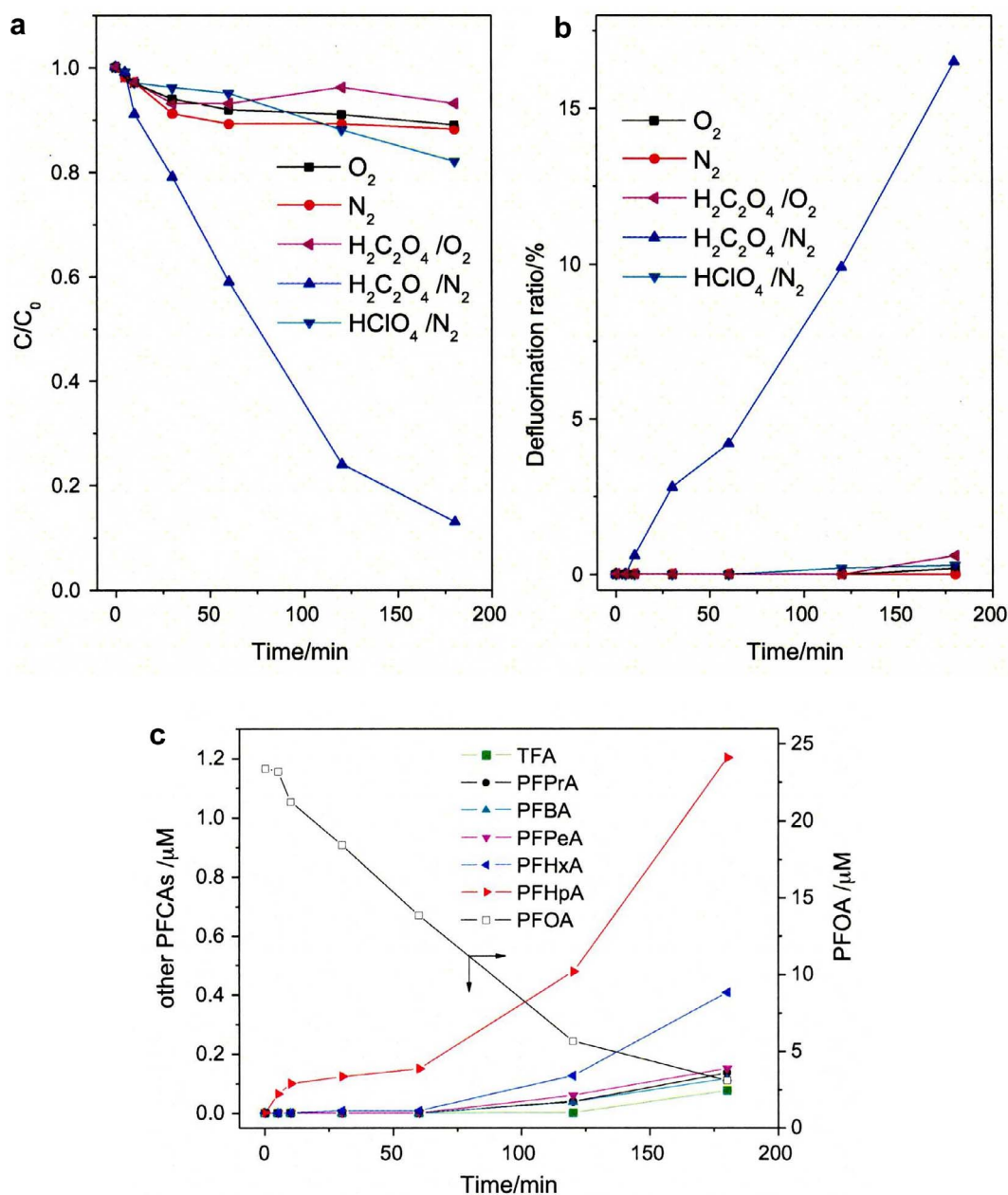
Fig. 6. Photocatalytic decomposition of PFOA (24 M) by TiO$_2$ under UV irradiation at 254 nm in the presence of oxalic acid [91]. a – time profile of PFOA decomposition under different conditions and in the presence of 0.5 g/L TiO$_2$ and 3 mM oxalic acid; b – time profile of defluorination in the same conditions as in a; c – time profile of PFOA decomposition, and formation of its shorter-chain PFCAs intermediates in the presence of 0.5 g/L TiO$_2$ and 3 mM oxalic acid. TFA-trifluoroacetic acid, PFPrA-pentafluoropropionic acid, PFBA-heptafluorobutyric acid, PFPeA-nonafluoropentanoic acid, PFHxA-undecafluorohexa-noic acid, PFHpA-perfluoroheptanoic acid.

the photocatalytic oxidation of PFOA. Then the titanate nanotubes, synthesized by microwave hydrothermal method, were employed for the photocatalytic PFOA decomposition carried out with 400 W UV lamp (254 nm), and it was found that all of the ion-exchange, electrostatic interactions, and hydrophobic interactions participated in the photocatalytic process [95]. At pH 4, 85% PFOA was decomposed after 24 h for the initial concentration 50 mg/L. For photocatalytic applications, the commercial TiO$_2$ was also modified by noble metallic nanoparticles (Pt, Pd, Au) using a chemical reduction method with KBH$_4$ [96]. In the used set up a high-pressure mercury lamp (125 W, central wavelength 365 nm) with light intensity 5.3 mW/cm^2 was used. For the initial PFOA concentration 60 mg/L the largest value of the rate-constant of pseudo-first-order kinetics 0.7267 h^{-1} was obtained for Pt modifications and it was 12.5 times larger than the one for unmodified TiO$_2$. This improvement of the yield of photocatalytic activity was

attributed to nanoparticles acting as electron sinks to store the excess electrons in a conduction band.

Two other nanotechnological approaches in using TiO$_2$ for photocatalytic PFOA decomposition are worth mentioning here. The preparation of TiO$_2$-multiwall carbon nanotubes (MWCNT) composite can be an appropriate way to reduce recombination of electron-hole pair in order to obtain higher photocatalytic activity. This was reported for the composites synthesized using sol-gel method [97]. The photocatalytic reactions were carried with a 300 W medium pressure mercury lamp (mainly emitting 365 nm light) with a cylindrical quartz cold trap placed in the center of a 250 mL reactor. With the optimized tetra-butyl titanate/MWCNT ratio and its dosage, almost 100% PFOA degradation was obtained after 8-h irradiation (at 365 nm) for the initial concentration 30 mg/L. It was concluded that incorporation of TiO$_2$ on MWCNT increased the adsorption of PFOA and its contact with the

Table 1
Available second order rate-constants for reactions of PFOA and PFOS with selected radicals and hydrated electron.

Substrate	Radical	Chemical form of substrate	Rate-constant (M^{-1} s^{-1})	Reference
PFOA	$\cdot$OH	NH_4 salt	$\leq 3 \times 10^7$	Szajdzińska-Piętek, Gębicki [141]
		–	$\leq 10^5$	Vecitis et al. [30]
		–	$< 10^6$	Vecitis et al. [122]
	$e_{aq}-$	NH_4 salt	$1.3–5.1 \times 10^7$	Szajdzińska-Piętek, Gębicki [141]
		Na salt	$1.7 (\pm 0.5) \times 10^7$	Huang et al. [82]
	$\cdot$H	Acid	9.0×10^7	Kciuk et al. [142]
	$SO_4\cdot$	–	$2.59 (\pm 0.16) \times 10^5$	Qian et al. [81]
		–	$\leq 5.0 \times 10^4$	Huang et al. [82]
	$NO_3\cdot$	–	$\leq 5.0 \times 10^4$	Huang et al. [82]
PFOS	$\cdot$OH	NH_4 salt	$\leq 3 \times 10^7$	Szajdzińska-Piętek, Gębicki [141]
		$N(C_2H_5)_4$ salt	No reaction	Szajdzińska-Piętek, Gębicki [141]
		–	$< 1 \times 10^6$	Vecitis et al. [122]
	$e_{aq}-$	$N(C_2H_5)_4$ salt	7.3×10^7	Szajdzińska-Piętek, Gębicki [141]

catalyst, and, similarly to other TiO_2 applications, PFOA was degraded by stepwise losing a moiety of CF_2. Recently, for the same purpose the molecularly imprinted polymer (MIP)-modified TiO_2 nanotubes have been reported [98]. In developed experimental setup, a quartz tube containing a low-pressure UV lamp (23 W, UV-C light at 254 nm) was placed at the reactor center. Not only did this approach allow to obtain the effective PFOA decomposition (84% after 8 h) and defluorination, but it also enhanced the selectivity for target species in the treatment of effluents. The mechanism of decomposition involved the photo-generated holes, which are main oxidants for PFOA decomposition.

In spite of the different, afore-presented attempts to increase the photocatalytic activity of TiO_2 toward PFOA, generally this photocatalyst exhibits relatively low activity. This can be attributed to the inertness of PFOA to hydroxyl radicals (see the list of reported data on reaction rate-constants in Table 1), which are also generated in the TiO_2 photocatalytic process. Apart from the different modifications of TiO_2 and careful optimization of photocatalytic treatment condition, an alternative way is to search for some other semiconductor materials showing better activity than TiO_2. The materials examined for this purpose include indium oxide [99,100], gallium oxide [101], and SiC/graphene composites [102]. In the first application of In_2O_3 for PFOA decomposition it was demonstrated that it shows about 8.4 times higher activity than TiO_2 [99]. The experiments were carried out in a tubular quartz reactor equipped with a low-pressure 23 W mercury lamp. It was found that strong bidentate biding of carboxylic group of PFOA to the In_2O_3 surface was beneficial for PFOA to be decomposed by photo-generated holes. The binding for TiO_2 is monodentate and it was evaluated as weaker. Hence, the holes of TiO_2 are transformed rather to hydroxyl radicals, which are less reactive with PFOA. Similarly to TiO_2, however, the main decomposition products are also C2–C7 PFCAs and inorganic fluoride. A further significant enhancement of photocatalytic activity toward PFOA was obtained by the preparation of In_2O_3 porous nanoplates by an ethylenediamine-assisted hydrothermal process [100]. For the initial level of PFOA $\sim$30 mg/L, and irradiation with a low-pressure 15 W mercury lamp emitting 254 nm UV light, the decomposition half-life of PFOA took only 4.4. min and the pseudo-first-order reaction rate-constant was evaluated as 9.5 h^{-1}. Strong binding of PFOA to Ga_2O_3 was also attributed to high photocatalytic activity toward PFOA [101]. This was examined for the nanostructured sheaf-like Ga_2O_3, which was prepared by a PVA-assisted hydrothermal method. In the degradation of PFOA at the initial level of 500 μg/L the rate constant was estimated to be 4.85 h^{-1}.

Very recently, a completely different nanostructured material have also been examined for photocatalytic decomposition of PFOA. Although the obtained decomposition rate 0.096 h^{-1} for the initial PFOA concentration 120 μM was clearly lower than the ones for In_2O_3 and Ga_2O_3, with the SiC/graphene nanocomposite employed, the mechanism of processes occurring at the catalyst surface differed a lot [102]. During the UV irradiation in a cylindrical 80 mL reactor with a

5 W UV lamp (254 nm), the reactive Si-H bonds in reaction with the C−F bonds in PFOA formed the bond between Si and F on the surface of the catalyst. The photoinduced hydrodefluorination included the replacement of F atoms by hydrogen via Si−H/C−F redistribution, generation of CH_2 carbene from hydrogen-containing perfluoro-alkyl chains, and the C−C bonds scission.

Concluding the presentation of photocatalytic methods of PFOA decomposition reported so far, the developed In_2O_3 porous nanoplates provide a superior activity, however it should be also mentioned that several other PFCAs formed during PFOA decomposition have increased with reaction time within 120 min, which makes the total picture of PFCAs removal more complicated [100]. The same observation was reported in several works on photocatalytic PFOA decomposition employing TiO_2, see *e.g.* [91,93].

4. Ozonation

Ozonation as an efficient method of water treatment has been employed for decades and has been reported in numerous books [103] and review articles [104,105]. Ozonation reactions with organic pollutants of waters take place directly with O_3 molecule or indirectly with the ozone decomposition leading to the generation of hydroxyl radicals. They involve the following main reaction:

$$O_3 + H_2O \rightarrow 2 \cdot OH + O_2 \quad (k = 1.1 \times 10^4 \ M^{-1} \ s^{-1}) \quad (21)$$
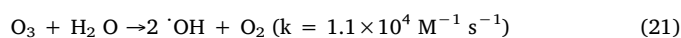
The second-order rate constants for oxidation with ozone vary between $< 0.1 \ M^{-1} \ s^{-1}$ and about $7 \times 10^9 \ M^{-1} \ s^{-1}$ [104]. Due to its electronic configuration and structure, ozone can react as electrophilic or nucleophilic reagent, and, because of its high reactivity, ozone is very unstable in water and this instability strongly depends on pH. Ozone is also one of the strongest oxidants, reacting according to the following equation:

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \quad (E_o = 2.07V) \quad (22)$$
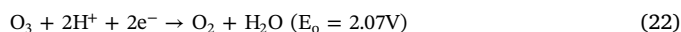
Hence, it finds wide application in water disinfection, oxidation of some inorganic pollutants, and, most importantly, oxidation of organic micropollutants, and therefore ozonation belongs to most commonly employed AOPs. Its efficiency can be additionally enhanced in the presence of appropriate catalysts [105], and ozonation belongs to AOPs only in alkaline media or when it is combined with the use of catalysts or UV light irradiation. In homogeneous catalytic ozonation, transition metal ions are involved (Co(II), Mn(II), Ni(II), Fe(II), Mn(IV)), while in heterogeneous catalytic ozonation – metal oxides (MnO_2, TiO_2) or metals on metal oxide supports. The main catalytic mechanism is based on either the enhancement of ozone decomposition with the formation of hydroxyl radicals, or the formation of complexes by target molecule with catalyst, and their oxidation. In the comparison of the efficiency of $\cdot$OH radical formation during ozonation and AOPs, it was found that ozone-based AOPs are more energy-efficient than the UV/H_2O_2

processes [106].

In one of the first attempts to use several different AOPs for decomposition of different fluorinated surfactants, the decomposition of PFOS using ozonation, O_3/UV, O_3/H_2O_2 and the Fenton process was examined [107]. The monitoring of decomposition was carried out by mass spectrometry during the treatment period of 120 min using the solid-phase preconcentration, and in the case of PFOS no decomposition was detected. Different results were reported, however, on PFCs stability from the monitoring of drinking water treatment processes [37,38] or water reclamation plants [108] in different countries. Water samples, including raw river waters and samples collected at various stages of drinking water production in several countries, contained PFOA and PFOS at ng/L level with maximum contents for PFOS 7.6 and PFOA 72 ng/L. In the reported cases, the ozonation didn't affect the removal of those two PFCs according to this evaluation. Although the use of activated carbon was more efficient, the presence of those PFCs in treated waters led to the conclusion about the need for their regular monitoring in finished waters. However, there is data indicating some efficiency of the ozonation step in the removal of perfluorinated surfactants in water treatment processes. This was studied *e.g.* for several PFCs at water reclamation plants in Australia [108]. It was demonstrated that the concentrations of PFOA and PFOA in influent (WWTP effluent) ranged up to 3.7 and 16 ng/L, respectively, and they were reduced to 0.7 and 12 ng/L in the finished water of the ozonation plant. Importantly, it was pointed out that all those levels are well below provisional health-based drinking water guideline suggested for PFOA and PFOA. In the removal of PFOS and PFOA from surface waters in a drinking water treatment plant, in the ozonation step only 9% removal of PFOA and 2% for PFOS was reported [37]. In fact, this data is not surprising in the context of the above-mentioned discussion on photolytic and photocatalytic decomposition of those compounds, where only reductive processes proved to be effective.

Very recently, an interesting comparison of the ozonation of PFOA with both UV photolysis and photocatalytic ozonation has been reported [109]. The comparison of the PFOA decomposition and defluorination with investigated methods for the initial PFOAS concentration 10 mg/L is shown in Fig. 7. With the ozone dosage of 25 mg/h only about 0.5% PFOA was decomposed in a 4-h reaction time, but when the ozonation was carried out simultaneously with TiO_2-based photocatalytic decomposition, the yield of PFOA decomposition increased up to 99.1% with 44.3% defluorination. One should mention that the efficiency of both ozonation and photocatalytic ozonation, essentially depended on the ozone dosage. Earlier on, it was reported by some other authors [110] that at extremely high ozone dosage 8.7 g/h at pH 11, 99% of PFOA can be decomposed in 4 h. In the photocatalytic ozonation, the ozone dosage and pH of treated solution also affected the efficiency of defluorination, however in this case, a lowering pH enhances the defluorination. In the discussion on the decomposition mechanism it was also pointed out that in the photocatalytic ozonation the photo-generated holes play a dominant role consuming an electron from the absorbed PFOA anion, while hydroxyl radicals accelerate the decomposition by oxidizing perfluoroalkyl radical. So, after the set of the following reactions:

$$C_7F_{15}COO^- + H^+ \rightarrow C_7F_{15}COO^\cdot \tag{23}$$

$$C_7F_{15}COO^\cdot \rightarrow C_7F_{15}^\cdot + CO_2 \tag{24}$$

$$C_7F_{15}^\cdot + {}^\cdot OH \rightarrow C_7F_{15}OH \tag{25}$$

$$C_7F_{15}OH \rightarrow C_6F_{13}COF + H^+ + F^- \tag{26}$$

$$C_6F_{13}COF + H_2O \rightarrow C_6F_{13}COO^- + H^+ F^- \tag{27}$$
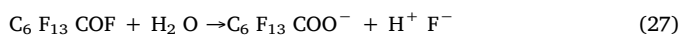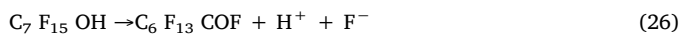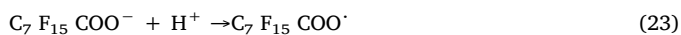
PFOA anion was converted to $C_6H_{13}COO^-$, and, following the same mechanism, PFCAs with shorted alkyl chains can be produced, which was confirmed experimentally.
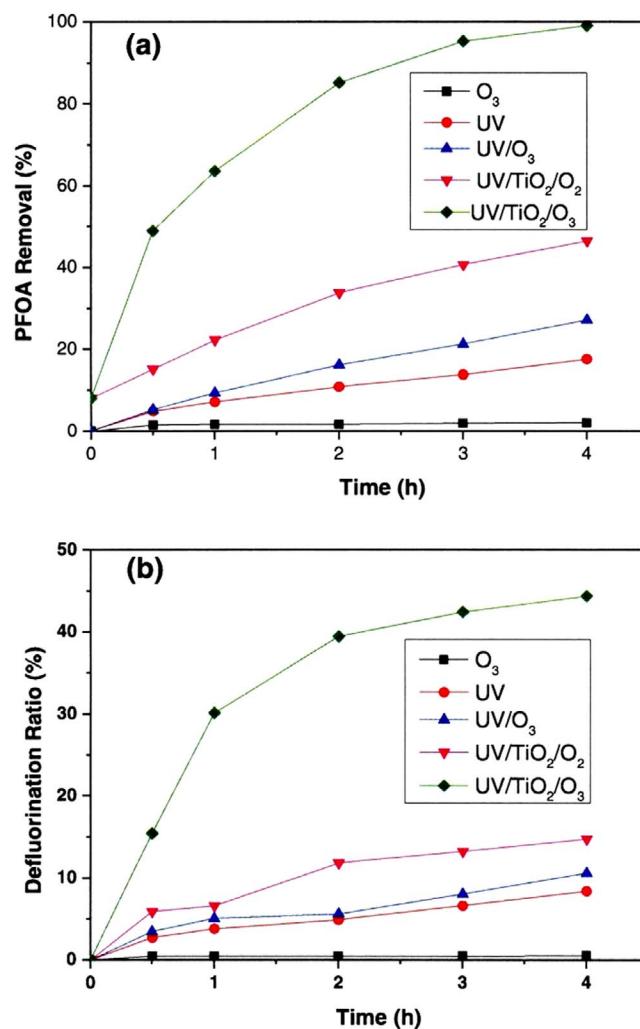
Fig. 7. Comparison of photocatalytic processes of PFOA (10 mg/L) degradation (a) and defluorination ratio (b) under UV irradiation at 254 nm, and under different chemical conditions [109]. Reaction condition: flow-rate of oxygen 1.0 L/min, ozone dosage 25 mg/h, catalyst dosage 0.2 g/L, volume of PFOA solution 1.0 L, temperature 25 °C.

5. Electrochemical oxidation

The generation of strongly oxidizing hydroxyl in aqueous solutions at near ambient temperature and pressure, which is a basic attribute of AOPs, can also be carried out electrochemically on the anode surface under the application of high current density:

$$H_2O \rightarrow {}^\cdot OH + H^+ + e^- \tag{28}$$

This process has been applied in the decomposition of numerous anthropogenic pollutants in water and wastewater treatment as well as in the remediation of environmental pollution in general [111,112]. They are carried out with the use of electrodes whose material ensures sufficiently high overpotential of oxygen evolution, providing the possibility of $^\cdot OH$ generation at lower potential values. Such materials include *e.g.* boron-doped diamond (BDD) and certain undopped or doped oxides (PbO_2, SnO_2, RuO_2, TiO_2). The doping with additive metal ions may introduce some catalytic activity. These materials should be chemically inactive to prevent passivation and they should exhibit a long life span. From the practical point of view, they should also be inexpensive to fabricate and robust during operation. Below the potential of oxygen evolution, there exists a large electrode potential window for the direct electron transfer reactions, which can be potentially utilized for the direct oxidation of pollutants unreactive towards $^\cdot OH$. This may concern *e.g.* perfluorinated compounds [113]. There are

Fig. 8. Proposed pathways for the electrochemical oxidation of PFCs based on activation energy calculations [111]. Cycle 1 shows the most energetically favorable reaction pathway.
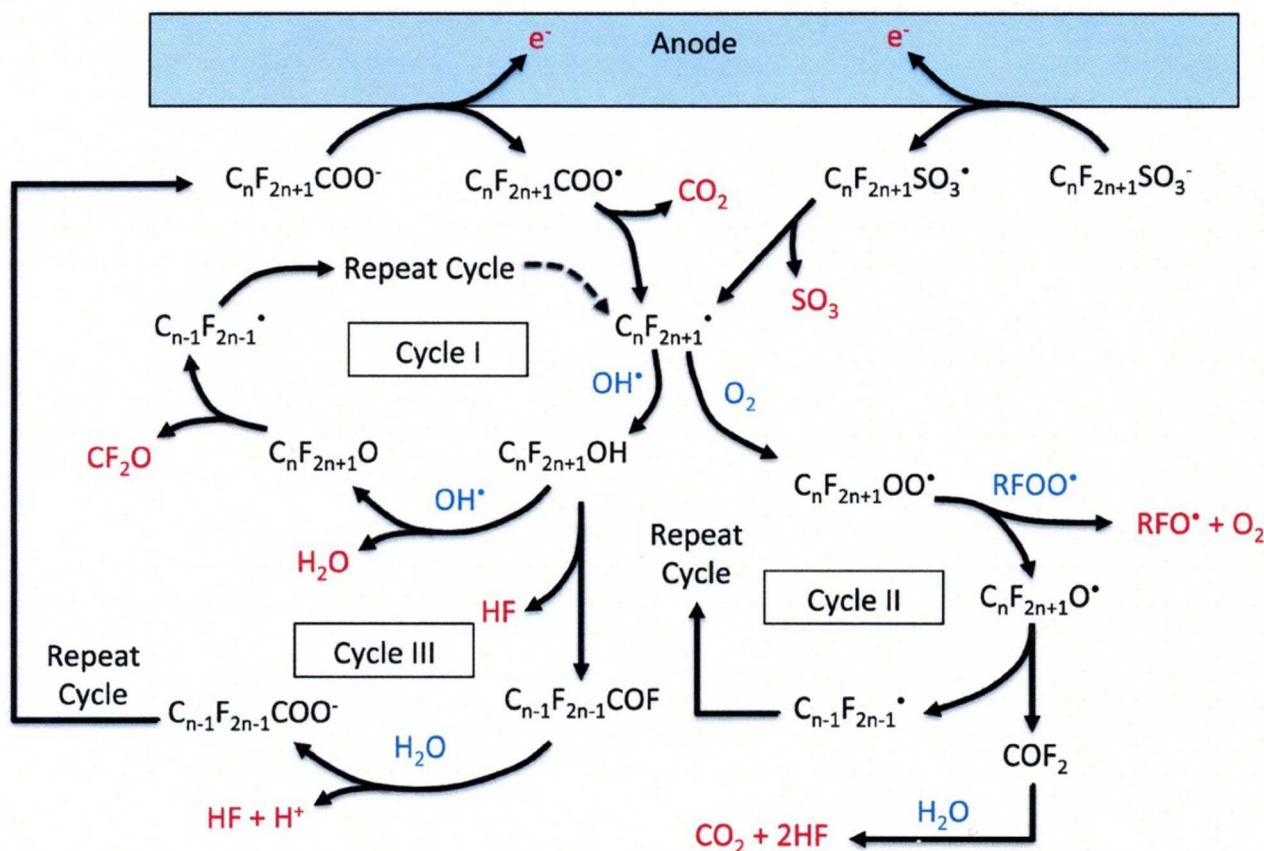
often utilized processes combining reactions with hydroxyl radicals and direct electron transfer reaction of organic pollutant [111].

Another application of electrochemical processes in AOPs is combining them with the Fenton method, which is considered to be the most popular chemical AOP [112a]. This mostly concerns the generation of the Fenton's reagent, partially or completely by the electrode reactions, i.e. cathodic H_2O_2 generation and/or cathodic Fe(II) generation.

In the first attempt to report electrochemical AOP to decompose PFCs, the oxidation of PFOS was examined with BDD electrode [114]. Similarly to PFOA oxidation investigated at SnO_2-Sb-Bi/Ti anodes [111], the oxidation of both discussed perfluorinated compounds was initiated by a direct electron transfer reaction, with PFC radicals releasing functional groups to form a perfluoro radical. Three different sequences of further possible transformations have been shown in the scheme in Fig. 8, reproduced from [111], which was based on original research. The cycle I leading to shorter chained PFC and based on the reaction with anodically formed ˙OH, was evaluated as the most energetically favorable reaction pathway.

The same electrode material was employed for hydrothermal enhanced electro-chemical oxidation of PFOA [115]. The elevation of anodic oxidation process in the autoclave up to 100 °C decreased the apparent rate constant by 4 times compared to the value at 20 °C for the initial PFOA concentration 200 mg/L. It was concluded that not only did the elevation of temperature enhance the mass transport to the electrode surface, but it also improved the physical and electrochemical properties of the anode. Also, the hydrothermal condition promoted a high formation of hydroxyl radical. As it was earlier demonstrated that at higher current then $0.6 \, mA/cm^2$ the direct electron oxidation at the electrode surface is not the main mechanism [116], at employed density $20 \, mA/cm^2$ the main mechanism of PFOA degradation is the hydroxyl radical-mediated oxidation. Apart from inorganic fluoride and

short-chain PFCAs, also dicarboxylic perfluorinated acids were postulated as the products of the oxidation. In the treatment of 200 mg/L PFOA solution the 93.6% decomposition was observed after the 6-h degradation. The electrochemical mineralization of PFOA was also investigated using a Cs-doped modified porous nanocrystalline PbO_2 film anode, where ˙OH, oxygen and water played different roles [117]. Theoretic quantum calculations and experimental data indicated that the degradation was initiated by the electron transfer process of PFOA on anode, which after decarboxylation was followed by the reaction of C_7H_{15}˙ radical with ˙OH, and ended in mineralization to CO_2 and HF, as the electrolysis system can supply enough ˙OH radicals. During this process, no short-chain PFCAs were generated and the apparent rate-constant for PFOA decomposition was evaluated as $0.013 \, min^{-1}$ for the initial PFOA concentration 250 µM.

The electrochemical decomposition of both PFOA and PFOS was examined in a natural sample of groundwater impacted by aqueous film foams at the level of 13 and 15 µg/L of PFOA and PFOS, respectively [118]. The study was carried out with the use of a commercially-produced Ti/RuO_2 at current densities from 1 to $20 \, mA/cm^2$. The obtained results compare favorably with those obtained in other metal oxide anodes. The PFOS electrochemical decomposition has been very recently examined with the use of nanostructured anode materials based on TiO_2 nanotube arrays [119]. Composite electrode material Ti/TiO_2-NTs/Ag_2O/PbO_2, prepared in a multistep procedure, had a long life span of 47 h and high oxygen evolution potential of 2.12 V, while the pseudo first-order rate-constant for PFOS degradation was evaluated to be $0.0165 \, min^{-1}$ for 93 µM of the initial PFOS concentration. It was also mentioned that although BDD electrodes have a higher oxygen evolution potential and stronger oxidation capacity [114], the fabrication of reported electrode material is less expensive than BDD. The degradation mechanism of PFOS was initiated by desulfation at the anode to form C_7H_{15}˙ and after several further steps including

combining with $^{\cdot}OH$, $C_7H_{15}COO^-$ was obtained and then gradually degraded into short-chain PFCAs.

In further technological applications of this methodology in treatment of natural waters or wastewaters, several challenges remain, *e.g.* formation of ClO_4^- from chloride oxidation or relatively limited electroactive surface area of electrodes [111].

6. Sonolysis

The main mechanism, on which the sonochemical degradation of organic pollutants is based, is water pyrolysis leading to the formation of hydroxyl radicals, oxygen atoms (O) and hydrogen atoms (H). Ultrasonic pressure waves, induced by ultrasonic irradiation of aqueous solutions, cause the formation of vapor bubbles. They undergo a quasi-adiabatic compression raising internal vapor temperatures near 4000 K, whereas the bubble-water interface temperature is estimated to be 600–1000 K [120]. The products of water pyrolysis may react with components in the gas phase of bubbles or compounds of that partition at the bubble interface such as perfluorinated surfactants. Those surface-active properties might even give some additional selectivity factor to the sonolytic decomposition compared to other components in the treated samples.

In the early work on sonolytic decomposition of PFOsA and PFOS, for the initial concentrations 20 μM of both PFCs in argon atmosphere, the pseudo-first-order rate-constants were 0.032 and 0.016 min^{-1} for PFOA and PFOS respectively [121]. They were about two times larger than in oxygenated solutions and it was concluded that the main reaction mechanism is pyrolysis of PFCs at the interfacial region between the cavitation bubbles and the bulk solution. During both PFOA and PFOS decomposition, the formation and decomposition of PFCAs with shorter perfluoroalkyl chain was observed with different kinetics.

In the later, detailed work on the mechanism of sonolysis applied to PFOA and PFOS decomposition the nearly immediate production of mineralized fluoride, sulfate, CO and CO_2 was observed [122]. The initial degradation step occurring at the bubble interface involved the loss of ionic functional group while the series of pyrolytic reactions led to complete mineralization. The suggested pathway of sonochemical degradation of PFOS has been shown in Fig. 9A. A degradation half-life for both PFOA and PFOS is 30 min or less and this method can be successfully used in a wide range of concentrations from ppb to ppm. The plots of degradation for PFOS and PFOA can be seen in Fig. 9B. The main experimental factors optimized for carrying sonolytic degradation are frequency of ultrasonic radiation and power density expressed in watts for volume of irradiated solutions. For the initial concentrations 0.20 μM PFOS and 0.24 μM PFOA, the values of a quasi-first-order reaction rate-constants were 0.027 and 0.041 min^{-1} for PFOS and PFOA, respectively. This gives half-lives of decomposed species 25.7 and 16.9 min, respectively. Those rate constants decreased slightly at higher initial concentrations. A large number of fluorinated volatile species were detected after the sonolysis. The transformation mechanism of fluoro-radicals into CO and CO_2 was widely discussed in the cited paper [122] and it was concluded from both experimental data and kinetic estimations that those sono-intermediates are quickly transmitted into inorganic products as a result of reactions with $^{\cdot}OH$, H and O atoms and water.

Several later works of the same research group reported different aspects of the application of this treatment method in the decomposition of PFCs in natural environmental samples. In its application to treatment of groundwater containing PFCs, it was shown that much higher content of other organic components did not affect the PFCs' decomposition rate due to preferential adsorption of perfluorinated surfactants at the bubble-water interface [123]. The studies on kinetic effects of matrix inorganics on sonochemical degradation of PFOA and PFOS in groundwater demonstrated that the effect of inorganic anions over the range between 1 and 10 mM follows the Hofmeister series, which was originally based on salting-out abilities of proteins. The

extent of hydration of anions and the ability to enhance hydrophobic interactions were also indicated [124]. The presence of perchlorate or nitrate enhanced the rate-constants of the sonolytic decomposition, while the presence pf sulfate or bicarbonate decreased the degradation rate. This effect was interpreted as resulting from both ionic partition and interaction with the bubble-water interface. For inorganic cations, the negligible effect was observed on the kinetics of PFCs decomposition, while enhanced kinetics at pH below 4 was attributed to the proton interaction with the bubble-water interface.

At least two papers reported the studies on effect of the presence of other surfactants in a sonochemically treated solution of perfluorinated compounds. The sonolytic degradation of PFOA was examined in the presence of known amounts of a cationic surfactant CTAB (hexadecyltrimethylammonium bromide), anionic surfactant SDS (sodium dodecyl sulfate) and a non-ionic Triton X-110 (octylphenol ethoxylate) [125]. It was found that the addition of CTAB enhanced the yield of the sonolytic decomposition and the extension of this enhancement increased with CTAB concentration and was pH-dependent. The best degradation efficiency (79%) for the initial PFOA concentration 120 μM with 120 min irradiation was obtained at 0.12 mM CTAB and pH 4.0. The SDS and Triton X-100 inhibited the degradation process. The sonolytic decomposition efficiency was also investigated for real aqueous forming foam preparation FC-600 (3M, USA), which contains 1–5% fluorinated surfactants (including PFOA and PFOA) and many other constituents [126]. It was found that FC-600 matrix had a minor effect on the kinetics of PFOS decomposition and that also other FC-600 components were sonolytically decomposed.

The ultrasonic irradiation may successfully enhance the yield of other methods of removal of perfluorinated surfactants. For instance, it was shown for several perfluorochemicals (including PFOA and PFOS), pure aqueous solutions and landfill groundwater matrix that their sorption kinetics on granular activated carbon can be enhanced from 2.5 to 9 times at the initial level of 50 mg/L PFC with 20 kHz ultrasound irradiation [127]. The equilibrium sorption was enhanced by ultrasound only by 5–50% and pronounced kinetic effect was interpreted as a result of the increasing PFC diffusion rate into the activated carbon nanopores. The ultrasonic irradiation for PFOS decomposition was also hyphenated with vacuum UV irradiation at 185 nm [128]. In this case, however, an increase of yield of PFOS decomposition at the initial concentration 10 mg/L in vacuum UV-ultrasonic system, compared to only sonolytic treatment, was only 12% after 4 h treatment.

The sonication-assisted oxidative photocatalytic decomposition was reported for PFOA in alkaline medium with sol-gel TiO_2, but, since at the initial level of 50 mg/L about 70% decomposition required even 8 h irradiation, it proved not very effective too [128a].

7. Application of ionizing radiation

Often ignored, even in competent and thorough reviews on Advanced Oxidation Processes (see *e.g.* [129–132]), radiolysis with the use of ionizing radiation proves to be a very efficient AOP for the decomposition of organic pollutants in waters and wastewaters of different origin [133]. Irradiation of treated solutions for environmental purposes in carried out by γ-rays from radioisotope sources (^{60}Co or ^{137}Cs) or with the use of beams of electrons (EB) accelerated in different type of accelerators, which are commonly employed in various fields of processing of materials, sterilization disposable medical products, and pasteurizing and preserving foods [133a]. Basic differences between these two kinds of irradiations are their energy, depth of penetration of irradiated materials and so called dose-rate, which is a measure of amount of energy provided in a given time period. Generally, γ-rays are mostly employed for environmental purposes in research studies, while in technological applications for water and wastewater treatment the EB applications predominate.

In the case of diluted aqueous solutions irradiated either by γ-rays or EB, the fastest predominating reaction is the radiolysis of water. When
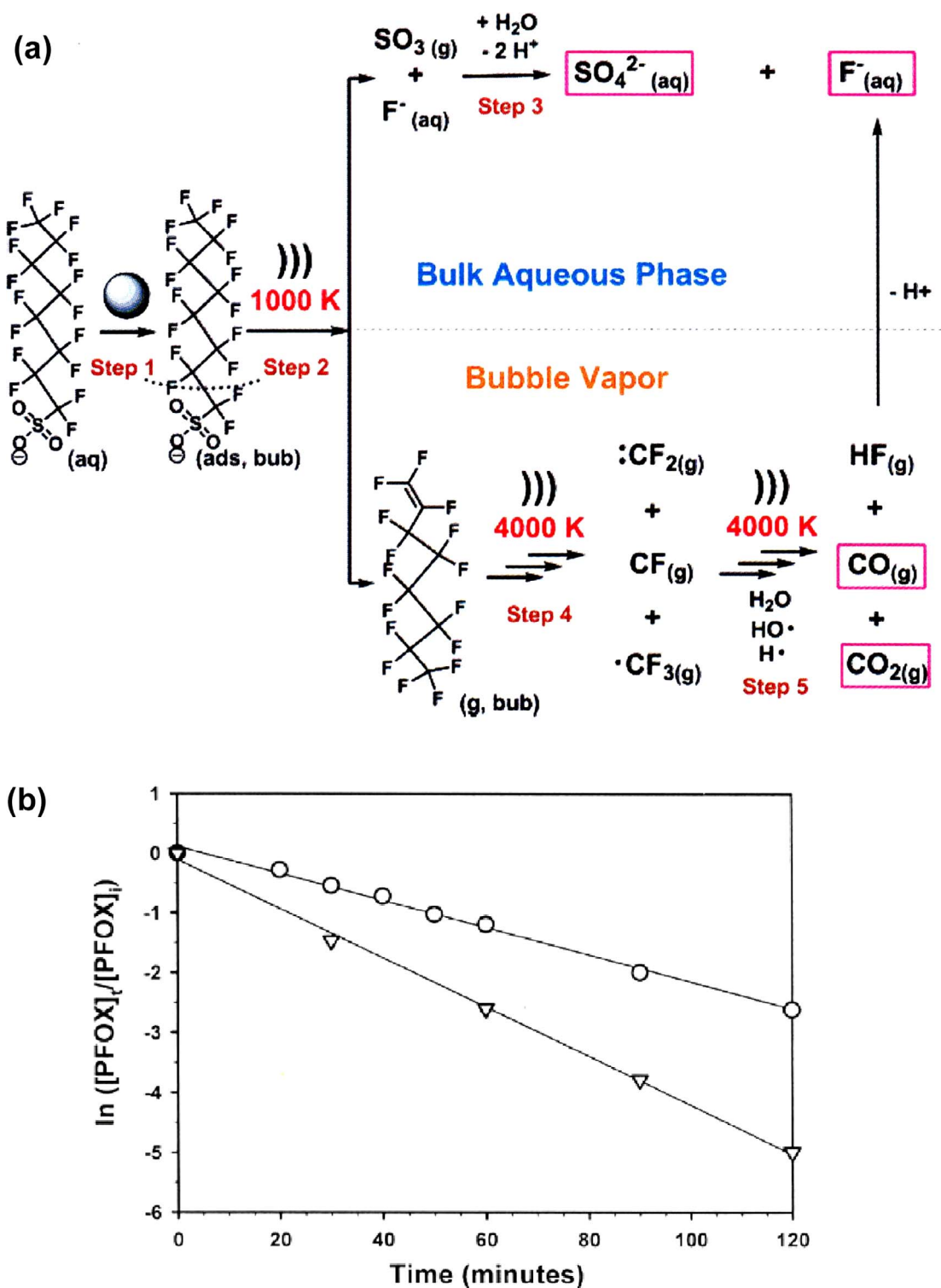
Fig. 9. Sonolytic decomposition of PFCs induced by high-frequency ultrasound [122]. A – scheme of PFOS degradation and transformation into inorganic compounds; B – pseudo-first-order plots of the degradation of PFOS (0.20 M) and PFOA (0.24 M) under ultrasonic irradiation at 354 kHz in the presence of Ar at 10 °C.

irradiation was carried out in non-aerated solutions, the main products of radiolysis were ·OH radicals and hydrated electrons $e_{aq}-$ formed almost in the same amounts, and at lower concentrations of ·H, H_2O_2, H_2 and H^+ ions. The reactive products of water radiolysis may react with compounds present in irradiated solutions. There are at least two basic advantages of this method compared to other AOPs employed for environmental purposes. The first one is the formation of a strongly oxidizing hydroxyl radical as well as a strongly reducing species such as

hydrated electrons and hydrogen atoms. It means that in the presence of different types of pollutants in the treated solutions, such processes can occur simultaneously. Obviously, in aerated solutions, the reduction process will occur simultaneously with the reduction of dissolved oxygen. The second essential advantage is the fast rate of the radiolytic formation of those reactive radicals, and also usually fast rate of their reactions with decomposed pollutants. This is reflected by much shorter time of the radiolytic decomposition process compared to other AOPs.

By the appropriate adjustment of pH of irradiated solutions, and/or addition of scavengers of radicals or reagents enhancing the yield of formation of particular radicals, one can adjust the conditions of irradiation to obtain a predomination of particular active species, as well as the acceleration of their formation. Due to essentially different dose-rates from different sources, the radiolytic processes carried out with γ-rays may take hours, while with EB irradiation, they can be shortened to seconds.

The first applications of the ionizing radiation in water and waste-water treatment, in their disinfection and removal of both organic pollutants and trace metals, were already reported in 1950s. Since then, these processes were the subject of hundreds of research papers and numerous pilot installations were constructed in different countries, see book edited by Cooper et al. [133] and several review articles [134–136]. The EB irradiation was successfully employed *e.g.* for removal of hydrocarbon surfactants from industrial and domestic effluents [137], decomposition of multi-class hydrocarbon surfactants and their biotransformation products in sewage treatment plant effluents [138], while as illustration of one recent applications of gamma-irradiation can be showed a degradation of pharmaceutical sulfamethoxazole [138a,166].

The applications of ionizing radiation in the degradation of fluorinated organic compounds reported so far concerned the studies on degradation of fluoroorganic polymers such as poly(perfluoro ethers) [139] or γ-irradiation-induced decomposition of polymer type perfluorosulfonic acid [140]. Published in 2000, the first work on the application of ionizing radiation involving perfluorinated surfactants reported the use of electron beam from a 6 MeV accelerator for the determination of rate constants of PFOA and PFOS with $\cdot$OH radicals and hydrated electron [141]. The studies were carried out in nanosecond pulse radiolysis system with spectrophotometric detection with the use of aqueous solutions of ammonium perfluorooctanoate and tetraethylammonium perfluorooctano sulfonate. The values obtained have been listed in Table 1 and until now this work constitutes the main source of those constants. Two values of rate-constant for ammonium perfluorooctanoate 5.1×10^7 and $1.3 \times 10^7 \, M^{-1} \, s^{-1}$ were determined for the free surfactant below the critical micelle concentration (CMC) and for the micellized surfactant, respectively. Recently, the second order rate constant for the reaction of PFOA anion with $\cdot$H radical has been evaluated as $9.0 \times 10^7 \, M^{-1} \, s^{-1}$ [142]. The data listed in Table 1 demonstrates that the reactions of PFOA and PFOS with $\cdot$OH radicals or hydrated electrons are 2–3 orders of magnitude lower than those of many other organic molecules that can be encountered as environmental pollutants, see *e.g.* [143]. On the other hand, the evaluated rate-constants showed that both surfactants PFOS and PFOA may potentially react with all the main products of water radiolysis, hence the application of such method requires a careful optimization of experimental conditions.

So far, only two papers have been published on this subject in recent years, reporting the use of γ-rays [144], and electron beam [145] for the decomposition of PFOA. The γ-irradiation was carried out at the initial PFOA concentration 20 mg/L in deaerated solutions, at pH range from 3 to 13, which gave a large span of pseudo-first-order reaction rate-constants for PFOA decomposition from $0.034 \, h^{-1}$ at pH 7.0 up to $0.654 \, h^{-1}$ for pH 13. Experiments carried out under different conditions demonstrated that both reductive species, hydrogen atom and hydrated electrons, which can be eliminated by H_2O_2 or O_2, are essential for the PFOA degradation. Since the increasing *t*-butanol (scavenger of $\cdot$OH radicals) concentration brought smaller release of fluoride, it means that the C−F bond could not be broken effectively in the absence of $\cdot$OH radicals. The authors concluded that both $\cdot$OH and $e_{aq}-$ contribute to PFOA degradation by γ-irradiation. The suggested pathways of radiolytic PFOA degradation (Fig. 10) implies the synergistic effects of both radicals involved in the cleavage of C−C and C−F bonds, leading to complete mineralization. As transient products in early stages of the degradation process, shorter alkyl chain C4–C7
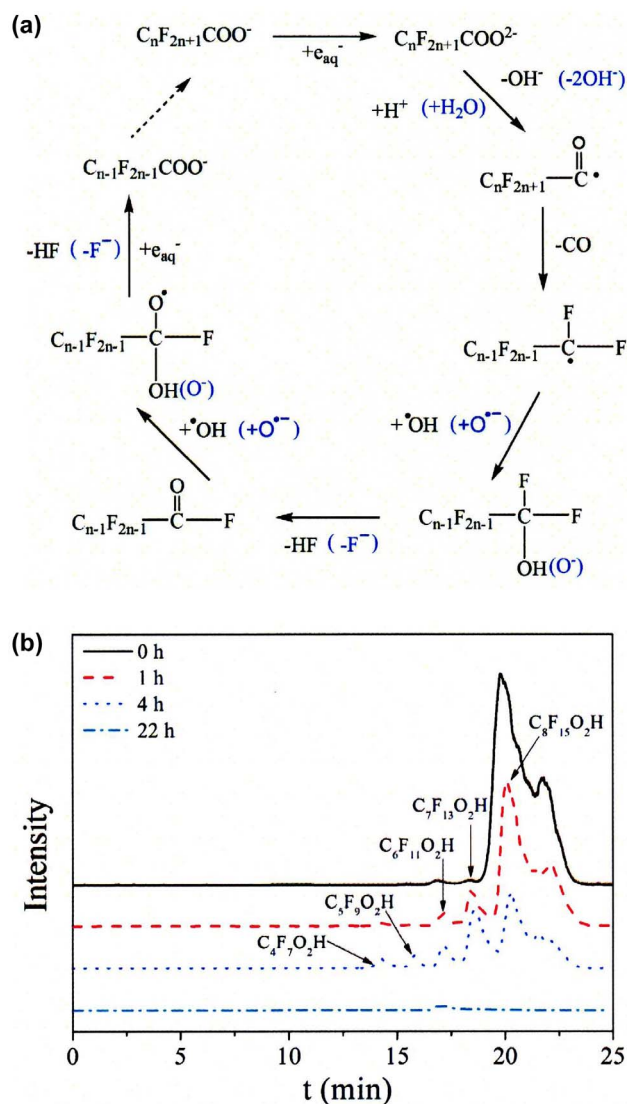
Fig. 10. Proposed PFOA degradation pathway (A) and LC/MS trace of the intermediate products of shorter-chain PFCA anions at various irradiation times (B) for γ-irradiation of 20 mg/L deaerated PFOA solution with dose-rate 96 Gy/min [144].

PFCAs were detected at the absorbed dose range from 5.8 to 23 kGy, decomposed at 128 kGy absorbed dose.

Very recently, the first attempt on the use of irradiation with the beam of accelerated electrons (EB) has been reported for the PFOA decomposition of PFOA, with EB generated by a 10 MeV accelerator with beam power 18 kW [145]. The decomposition experiments were carried out for solutions with the initial PFOA concentration 0.5 mg/L, prepared in phosphate buffer of 0.1 mM total phosphate concentration in the anaerobic chamber. It was observed that at the absorbed dose 10 kGy, which corresponds to absorbed energy 10 kJ/kg, the defluorination efficiency 34.6% can be elevated up to 93.3% after the addition of 20 mg/L nitrate. This was interpreted by an additional formation of radicals, as nitrates are strong scavengers of hydrated electrons forming nitrate radical $NO_3^{\cdot 2-}$, which can reduce organic compounds. However, this radical reacts with water forming nitrogen dioxide radical $NO_2\cdot$, which can oxidize organic compounds [145a], therefore the evaluation of the mechanism of occurring processes requires further investigation. The improvement of the PFOA degradation with increasing alkalinity was interpreted by the formation of carbonate radical $CO_3\cdot^{-}$ as a result of scavenging $\cdot$OH radicals, and this radical can additionally oxidize PFOA anion to PFOA$\cdot$ radical. The increasing amount of fulvic acid in irradiated PFOA solutions resulted in a

decrease of the yield of the PFOA decomposition, but it was also noticed that fulvic acid accelerates the degradation of shorter-chain PFCAs. Based on the technical data of the employed electron accelerator provided in the paper, the dose-rate can be estimated to be about 8 kGy/s, which means that 90% defluorination for irradiation in the presence of 20 mg/L nitrate took only about 1 s, which is a few orders of magnitude faster than in all other methods presented and discussed in this review. Under nearly the same conditions, except that no nitrate was added, the yield of defluorination dropped down to about 35%. The presence of dissolved oxygen significantly decreased the efficiency of defluorination (to 1/3 of that observed for anaerobic conditions) due to scavenging of reductive radicals formed in water radiolysis. The pseudo-first-order reaction rate-constants were not given for examined systems with EB irradiation.

8. Wet chemical oxidation and reduction methods

Frequently indicated advantages of the above discussed photolytic, electrochemical, sonolytic and radiolytic methods, is the possibility of carrying out processes of treatment of waters and wastewaters without the necessity to add other chemicals to treated solutions. As it was also demonstrated in many examples, some chemical additives are used in some cases to improve the yield of decomposition processes, of which the best examples are numerous photocatalytic methods. However, generating particularly active reagents for decomposition of organic pollutants, free radicals in particular, can be carried out chemically in the specially selected reaction systems and this has been developed since decades for treatment of waters and wastewaters. One of such systems – ozonation – was already discussed above. The evolution of several other chemical systems for the decomposition of perfluorinated surfactants will be discussed below, based on the original research papers published in recent years.

8.1. Fenton methods

The Fenton reaction, in which from the interaction of Fe(II) with H_2O_2, the hydroxyl radical are generated in a sequence of several consecutive reactions, has been of great interest for many decades now due to its relevance to biological systems, syntheses, natural waters' chemistry and also its potential in the treatment of organic pollutants [146]. The main occurring reaction is the following:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + {}^{\cdot}OH \qquad (29)$$

with the participation of another reaction:

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2^{\cdot} + H^+ \qquad (30)$$

which is slower than the previous one by a few orders of magnitude, the role of iron in generation ${}^{\cdot}OH$ radicals is of a catalytic character, therefore it can be used at relatively small concentration, which minimizes ferric hydroxides production during the process. Usually the molar ratio of peroxide-to-iron employed in the water treatment is almost 1:10. As it was commonly assumed that ${}^{\cdot}OH$ radicals cannot effectively decompose high-energy C−F bonding, in comparison to other AOPs, the Fenton reaction has rarely been examined for perfluorinated surfactants. Modified Fenton methods, such as photo-assisted Fenton reaction *e.g.* for PFOA decomposition [75], electro-Fenton processes, combining Fenton reactions with heterogeneous catalysis or the use of chelated iron [146] have been more often investigated.

One of such examples concerning the PFOA decomposition was already mentioned above [75]. In the reaction of 20 μM PFOA with Fe^{2+} (4 mM) and H_2O_2 (40 mM) at pH 3.0 no fluoride release was observed after 24 h. When, in the same system, the process was additionally UV irradiated at 254 nm, 46% defluorination was noticed and the suggested interpretation of the process involved two stages. In the first one (about 1 h) PFOA was quickly decomposed with 90% yield, with

hydroxyl radicals being generated fast, and this accelerated PFOA decarboxylation. This is associated with about 36% defluorination. In the second stage, when H_2O_2 was completely consumed, further defluorination was attributed to the reaction of PFOA with Fe^{3+} ions, with the electron transfer between Fe^{3+} and PFOA. No decomposition of PFOA by the Fenton reaction at the initial concentration 100 μM and temperature 25 °C was observed, as well as in the reaction with 53 mM sodium persulfate [147]. An increase of temperature for the reaction with persulfate up to 70 °C provided the complete decomposition after 18 h, however the process carried out in the presence of humic acid was found more efficient. In the case of Fenton-like reaction (with Fe^{3+}) in the presence of humic acid, the oxidation of the acid took place with simultaneous quantitative and irreversible entrapment of PFOA. In the presence of leftover Fe(III) acting as a coagulant and a neutralizer in the reaction mixture (to pH 7.0), the precipitate with entrapped PFOA is formed, which means its removal from the treated solution at 25 °C and at time shorter than 100 min.

8.2. Sulfate radical oxidation

As it was already mentioned, sulfate radical (apart from hydroxyl radical) belongs to the strongest oxidants. The evaluated rate-constants for the reaction with PFOA given by different authors ranged between 10^4 and $10^5 M^{-1} s^{-1}$ (Table 1). It was already pointed out that those radicals can be favorably produced by the photolysis of persulfate aqueous solutions both at ambient [81] and elevated temperatures [148]. At the initial PFOA concentration 374 μM, in the reaction with 50 mM persulfate at 80 °C after 6 h the concentration dropped below 1.5 μM, which was associated with the defluorination with 77.5% yield and the formation of CO_2 with 70% yield. As minor products shorter-chain PFCAs were detected (Fig. 11). The satisfactory yield of this
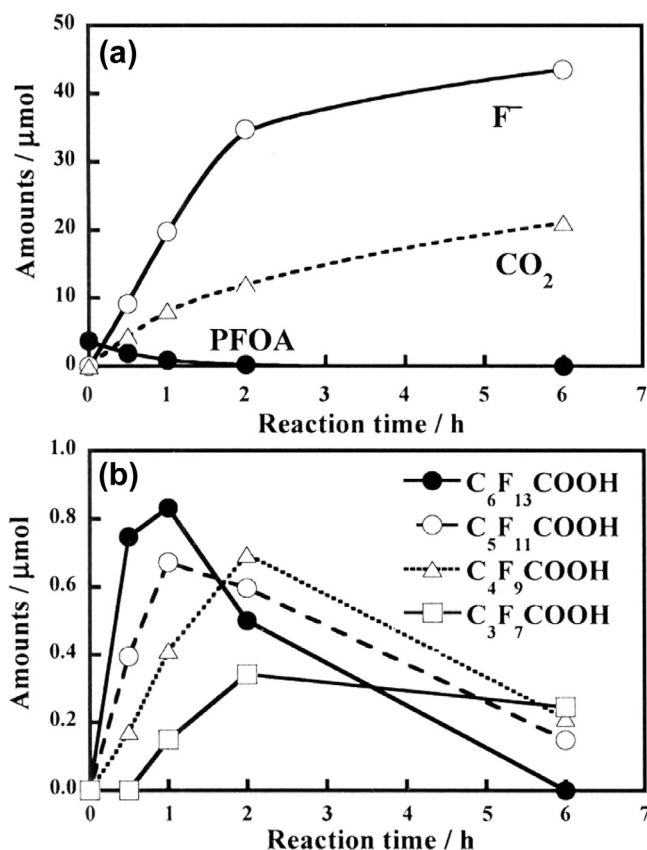

Fig. 11. Time profiles of the PFOA decomposition in hot water at 80 °C, containing 50 mM potassium persulfate and 374 μM PFOA [148]: A – decomposition of PFOA, and formation of fluoride and CO_2, B – formation and decomposition of shorter-chain PFCAs.

process was expressed by the pseudo-first-order reaction rate-constant $1.36 \, h^{-1}$. The occurring reaction:

$$SO_4^{\cdot -} + PFOA \rightarrow SO_4^{2-} + PFOA^{\cdot +} \qquad (31)$$

was not affected neither by aeration or deaeration of the reacting solution. An increase of persulfate concentration in the reaction mixture did not cause a linear increase of the yield of PFOA decomposition because of the competing reaction:

$$SO_4^{\cdot -} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\cdot -} \qquad (32)$$
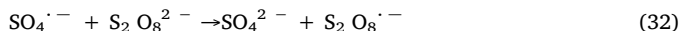
The reaction of PFOA decomposition was initiated by the cleavage of the C—C bond between C_7H_{15} radical and COOH group, and then the resulting radical reacted with water or $\cdot OH$ forming alcohol $C_7H_{15}OH$, which underwent HF elimination to form $C_6H_{13}COF$. The hydrolysis of that acid fluoride produced shorter-chain PFOA. Further elevation of temperature up to 150 °C in an autoclave reactor resulted in a dramatic decrease of the yield of decomposition. Very recently, the same approach has been employed to investigate PFOA decomposition at environmentally relevant concentrations 0.121–6.04 μM (50–2500 μg/L) at the temperature range between 20 and 60°C [149]. For the potential use for in-situ groundwater remediation, the PFOA removal was also examined in the presence of soluble fuel components (BTEX). The measured half-life of 0.242 μM PFOA decreased from 754–1746 days at 20 °C to 3.1–3.9 days at 60 °C, with pseudo-first-order reaction rate-constants for PFOA reaching $0.199 \, h^{-1}$ at 60 °C. The decomposition was preceded by sequential removal CH_2 groups to form shorter chain PFCs. The presence of the 40-times higher concentration of benzene, toluene, ethylbenzene and xylene did not affect the yield of decomposition. It was also reported, however, that the reaction with 60.5 mM sodium persulfate at the temperature range between 5 and 100 °C did not cause any decomposition of PFOS at its concentration 0.92 μM. Different results were reported earlier in time, even for much higher initial concentrations of PFOS (186 μM) [150]. This particular work reported a thorough study on PFOS decomposition by persulfate oxidation, and compared different methods of activation of that process. The employed activation methods involved UV irradiation at 254 nm, ultrasound treatment, addition of Fe(II) as a catalyst and hydrothermal conditions at elevated temperature. The obtained pseudo-first-order reaction rate-constants for all these variants at pH 3.1 were 0.018, 0.005, 0.013 and $0.025 \, h^{-1}$, showing the best yield for hydrothermal process. The essential role of the amount of persulfate and initial pH on the yield of those processes was also demonstrated, with conclusion on acidic conditions as the most suitable ones for the PFOS decomposition with sulfate radicals. In the proposed mechanism of decomposition, PFOS lost an electron to sulfate radicals and then it was desulfonated to form $\cdot C_8F_{17}$ radical. From the examination of persulfate oxidation processes for perfluorinated carboxylic acids, it was concluded that decomposition of PFCAs runs easier than the decomposition of PFOS, and the formation and decomposition of PFCAs during PFOS degradation was transient. In the process of UV/persulfate oxidation of PFOS, which occurred at almost similar rate as in the case of a hydrothermal one, it was shown that 50% decomposition of PFOS took place after 12 h about.

For the application of persulfate oxidation to PFOA removal from ground waters, milder conditions were also examined with the additional acidification to pH 2 [151]. In the degradation of 20 μM PFOA with 2 mM persulfate at 50 °C 89.9% of decomposition after 100 h was observed, however with defluorination yield only 23.9%. Based on EPR measurements it was concluded that both $SO_4^{\cdot -}$ and $\cdot OH$ radicals contributed to the PFOA decomposition. The effect of temperature in the range between 60 and 130 °C on PFOA decomposition by persulfate was also examined using microwaves to generate sulfate radicals [152,153]. As it is illustrated by plots in Fig. 12A, the most suitable temperature was 90 °C, where for 253.8 μM concentration of PFOA after 4 h 99.3% PFOA was decomposed with 74.3% defluorination ($0.67 \, h^{-1}$
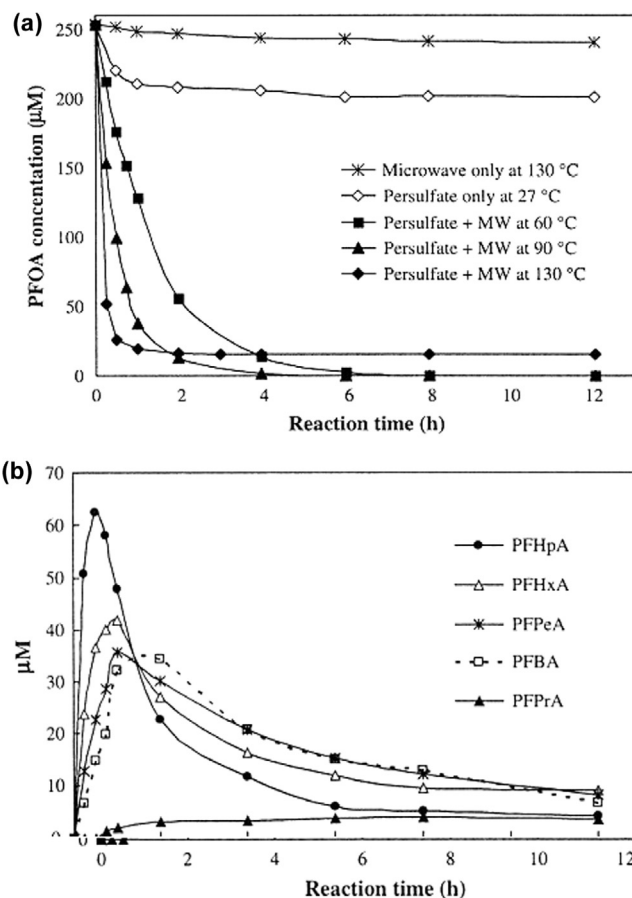
Fig. 12. Decomposition of PFOA (253.8 μM) under different experimental conditions (A), and time profile of concentrations of intermediates at 90 °C (B), using microwave-induced persulfate oxidation [152]. In B: PFHpA-perfluoroheptanoic acid, PFHxA-undecafluorohexanoic acid, PFPeA-perfluoropentanoic acid, PFBA-heptafluorobutyric acid, PFPrA-pentafluoropropionic acid.

pseudo-first-order rate-constant for PFOA decomposition) [152]. At 130 °C almost all persulfates were converted into sulfates, hence almost no PFOA was decomposed. Favorable acidic conditions for the decomposition were justified by the formation of $\cdot OH$ radicals under alkaline conditions:

$$SO_4^{\cdot -} + OH^- \rightarrow SO_4^{2-} + \cdot OH \qquad (33)$$
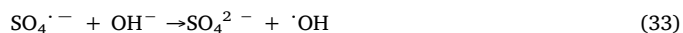
and poor activity of $\cdot OH$ towards PFOA, which is, however, not that obvious considering reported values of the second-order reaction rate-constants (see Table 1). Similarly to other works on persulfate oxidation, the transient formation of shorter-chain PFCAs during PFOA decomposition process was observed (Fig. 12B). The yield of defluorination is very close to that one of CO_2 formation, illustrating the completeness of mineralization. After 12 h of carrying out the decomposition process under optimized conditions it reached about 90%. It was also demonstrated that short-chain PFCAs are easier to decompose in the reaction with sulfate radical than PFOA (see also Fig. 12A and B). In the next work by the same research group [153], it was reported that introducing zero-valent iron (ZVI) to persulfate solution accelerated the PFOA decomposition. This was interpreted by the formations of ferrous ions, which may lower the activation energy of persulfate to produce sulfate radicals. This resulted in an almost twofold increase of the pseudo-first-order reaction rate-constant.

The process of sulfate radical oxidation of PFOA can also be successfully hyphenated with the adsorption on powdered activated carbon [154]. When thermolytic persulfate oxidation under acidic conditions is carried out, the activated carbon catalyzes the PFCA

transformation to shorter-chain-length perfluorinated compounds and reacts with the transformation products to produce covalently bound PFOA. At the initial PFOA concentration 0.5 μM, covalent bonding resulted in the removal of 10–40% PFOA, which makes chemisorption new mechanism of PFOA removal. This can be explained by the formation of the oxidized functional groups on the activated carbon surface as a result of the reaction with reactive radicals $SO_4^{\cdot-}$ and $\cdot OH$ during the persulfate treatment process. The active carbon can also enhance the persulfate decomposition by serving as an electron donor:

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\cdot-} + SO_4^{2-} \tag{34}$$
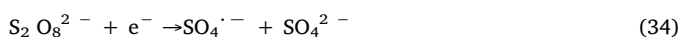
Although both high reaction temperature (80 °C) and large amounts of activated carbon needed in the reaction make this method impractical for drinking water treatment, it can be employed for effluents containing high concentration of PFOA.

Very recently, a completely different way of the application of persulfate for PFOA degradation has been proposed [155]. The developed process was based on the use of hydrogen peroxide and persulfate activated by iron-modified siliceous sedimentary rock, diatomite, which generates a strongly reductive superoxide radical anions $O_2^{\cdot-}$ ($E^0 = -0.33$ V). The formation of this radical may occur by generation of HO_2^- through the activation of H_2O_2 by Fe(III) ions:

$$H_2O_2 + Fe^{3+} \rightarrow HO_2^{\cdot} + Fe^{2+} + H^+ \tag{35}$$

$$HO_2^{\cdot} + Fe^{3+} \rightarrow Fe^{2+} + HO_2^- \tag{36}$$
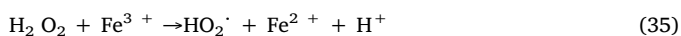
and they further react with persulfate, so the overall reaction is as follows:

$$S_2O_8^{2-} + 2H_2O_2 \rightarrow 2SO_4^{2-} + 2O_2^{\cdot-} + 4H^+ \tag{37}$$

For the initial PFOA concentration 10 mg/L (24 μM) at pH 9.0 and optimized concentrations of H_2O_2 and persulfate, 63% of PFOA was decomposed after 6 h treatment in the presence of iron-modified diatomite.

8.3. Reduction with elemental iron

Elemental (zero-valent) iron (ZVI) is even a stronger reductant ($E^0 = -0.447$ V) than the above-mentioned superoxide radical anion, hence numerous attempts on its application can be found for reductive degradation of organic pollutants, *e.g.* [156,156a] or selected metal ions [157]. It can be employed as uncoated particles of metal powders or Fe nanoparticles, coated with stabilizing agents. In recent years a particular attention was focused on the application of nano zerovalent iron (nZVI), although data about the toxicity of that form of reagent and also consequences of its application in remediation of waters and wastewaters are still not sufficiently recognized [157a]. A valuable approach to reduce the risk of their aggregation can be the application of continuous preparation of nZVI in the same reactor where degradation of pollutant(s) is conducted [157b].

The first application of ZVI for the PFOS decomposition was reported in subcritical water and it served to enhance the reaction rates [158]. The reduction process was carried out in a pressurized reactor at 350 °C with the addition of iron powder. For the initial PFOS concentration 372 μM complete decomposition was observed after 5 h (k = 0.59 h^{-1}) with ~30% yield of defluorination. The yield of decomposition depended essentially on the temperature employed.

Much milder conditions can be applied when for the same purpose nanoscale Fe(0) preparations are used [159]. This was recently shown also for PFOS and several other PFCs with the use of Mg-aminoclay coated ZVI nanoparticles, which due to the presence of free amino groups interact with the negatively charged PFCs when ionized ($-NH_3^+$). From the experiments carried out at 20 °C and 55 °C it was observed that the removal yield decreased with the increased temperature, which can be an evidence of the adsorption being prior to the reduction. The results of the removal of several examined PFCs,

including PFOA and PFOS, are shown in Fig. 13 for the initial concentration 200 μg/L. The removal of PFOS was almost completed during the first 20 min and the removal efficiency for the examined PFCs slightly decreased with the aging of coated ZVI nanoparticles (~15% after 3 days). The products of the reactions have not been investigated.

8.4. Biochemically driven transformations

A short presentation of the reported studies on biodegradation of PFOA and PFOS was already given in the Introduction, see the Refs. [43–47]. It included typical microbiological treatments are widely employed in wastewater treatment plants. As an addition to the above-discussed numerous physico-chemical and chemical methods developed for the decomposition of most commonly occurring perfluorinated pollutants, the two examples of processes employing biocatalytic transformations can also be given. Reductive dehalogenation based on the participation of cofactor vitamin B_{12} (cyanocobalmin) was examined for PFOA decomposition with Ti(III)-citrate in alkaline solution at 70 °C [160]. It was noticed that branched isomers which are usually present in technical grade PFOS can be degraded while linear isomers are resistant to this reductive procedure. It was suggested that the enhanced susceptibility of branched PFOS isomers to biocatalytic dehalogenation may be related to the stabilizing effect of branched structures on radical intermediates formed from the reduction attack. The LC/MS analysis carried out after 7 days indicated the removal of isomer 5- and 6-CH_3-PFOS by 80 ± 1%, 4-CF_3-PFOS by 48 ± 1% and 1-CH_3-PFOS by 44 ± 2%.

Another biocatalytic degradation concerns the PFOA decomposition via reaction with horseradish peroxidase (HRP), hydrogen peroxide and a phenolic co-substrate 4-methoxyphenol [161]. For the initial PFOA concentration of 850 μM the 68% removal was observed after over 6 h (k = 0.003 min^{-1}). One of the mechanism of degradation involved the generation of nonspecific methoxy radicals which attack the intermediate degradation by-products to produce a short-chain-length compound. Very little (> 1%) fluoride release and a significant reduction of Microtox toxicity (98%), suggest a stepwise decomposition pathway. Moreover, the detected products of GC/MS suggest an interpretation that the PFOA detoxification proceeds via the combination of decomposition and humification reactions. This was presented by the authors in details including for example some ring-closing steps with the formation of dodecafluorocyclohexane.

9. Discussion

Almost decades of particular interest in organic perfluorinated compounds in terms of the protection of the natural environment from these anthropogenic pollutants resulted in hundreds of research papers on their analytical determination. Furthermore, their presence and transport in the environment as well as their toxicity have been widely discussed (the keyword "perfluorinated" brings up above 8 thousand of published papers in the ISI Web of Knowledge database). A rapidly increasing interest was observed in the development of methods and technologies for their removal from the environment. Vast literature on the development of efficient Advanced Oxidation/Reduction Processes, of which recent advances are reviewed in this work, is focused on PFOA and PFOS that are most commonly occurring in the environment. A wider spectrum of PFCs in terms of their removal/decomposition was examined and reported so far only in few works including photolytic methods [73,78,79,81a,82], sonolysis [127] or wet oxidation methods [148,152,159]. That wider scope of target pollutants was also discussed in reporting the fate of PFCs in drinking water treatment [35,40,108] or their removal during wastewater treatment [36]. In the environmental photolytic degradation larger resistivity of PFCAs with shorter perfluoroalkyl chain was observed [73]. However, in the photolytic decomposition – both under oxidative conditions (with persulfate) and
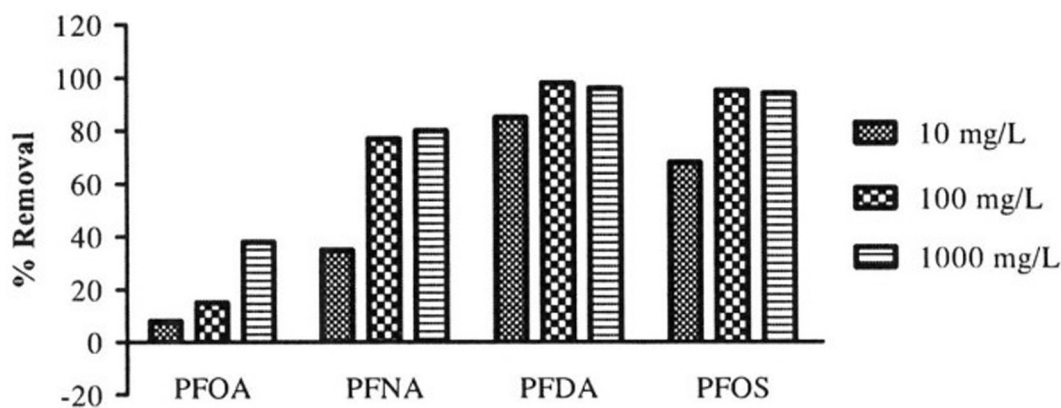
Fig. 13. The yield of the reductive decomposition of perfluorinated compounds (200 μg/L) at different dosage of Mg-aminoclay coated nanoscale zero valent iron (10–1000 mg/L) at pH 3, reaction temperature 20 °C and reaction time 1 h [159]. PFNA-perfluorononanoic acid, PFDA-perfluorodecanoic acid.

reductive ones (with iodide), it was reported that yield of those processes depended significantly on the number of carbon atoms in the alkyl chain in perfluorinated sulfonic acids, albeit less in the case of PFCAs [78,79]. In some of the earlier works, both in oxidative photolysis with persulfate [81a] and in reductive laser flash photolysis with $K_4Fe(CN)_6$ [82], it was shown that the rate constants for PFCAs decomposition increase with the lengthening of a perfluorinated chain. An increase of PFCs kinetics of sorption to granulated activated carbon in the presence of ultrasound was observed with the lengthening of perfluoroalkyl chain [127]. The increase of defluorination yield with the number of carbon atoms in the chain was observed in persulfate oxidation carried out in hot water (80 °C) [148], whereas a reversed trend was reported for C3–C7 PFCAs using the microwave-hydrothermal persulfate oxidation [152]. Then, in comparison of the yield of reductive C8-C10 PFCAs decomposition using Mg-aminoclay coated nanoscale ZVI, an increase in removal was observed with the lengthening of perfluoroalkyl chain [159]. This data suggests that the effect of this element on the PFCs' structure requires further studies and a more detailed interpretation.

9.1. Comparison of the decomposition yield for PFOA and PFOS

In the numerous papers one can find various comparisons of the efficiency of different treatment methods for decomposition of the most commonly occurring PFOA and PFOS, although, as illustrated in Tables 2 and 3, the PFOA, as a target pollutant, has been examined more often than PFOS. For these both compounds, the treatment studies are carried out with a wide range of initial concentrations reaching 3 and 4 orders of magnitude, which significantly hindered the comparisons and evaluation of methods. Comparisons of decomposition efficiency for both compounds were carried out for different methods, including both oxidative and reductive processes. Practically, only in two papers from the cited literature a very similar reactivity of both compounds at the same initial concentration was demonstrated. This included photochemical oxidation with persulfate [79] and anodic electrochemical oxidation with Ti/RuO_2 anode [118]. A more efficient reduction of PFOS than PFOA was observed mainly in reductive processes such as photolysis in the presence of iodide [78,79], or reduction by zero-valent iron [159]. Although in the reductive photolytic process under a catalyst-free conditions at pH 7.0 and 90 °C, where hydrated electrons were pointed out as key reacting species, the PFOA was decomposed at a high-rate of 2.78 h^{-1}, while the PFOS at 0.058 h^{-1} [70].

On the contrary, a more efficient decomposition of PFOA than of PFOS was observed in several oxidative processes such as *e.g.* ozonation in the presence of H_2O_2 [110], in sonolysis [121,122,124] or in hydrothermal persulfate oxidation [149]. However, an opposite observation for the sonolysis of PFOA was made since it brought larger yield

(than for PFOS) with higher efficiency in argon saturated solution than in aerated ones [121]. For most of those processes the pseudo-first-order reaction rate-constants were evaluated and they are listed in Tables 2 and 3.

9.2. Comparison of different decomposition methods

It is difficult to compare the efficiency of different decomposition methods developed for the decomposition of perfluorinated compounds. The yield of decomposition significantly depends on the structure of a target compound, its initial concentration, the matrix of the treated solutions and various physico-chemical parameters of the employed process. This efficiency is most commonly characterized by the time of decomposition/removal or by the values of pseudo-first-order reaction rate-constant. The papers which reported them have been listed in Tables 2 and 3.

Such comparisons carried out experimentally by several research groups were particularly valuable. For instance, the efficiency of photocatalytic PFOA decomposition was examined under different chemical conditions for the initial concentration 10 mg/L and it was also compared with ozonation, direct UV photolysis at 254 nm and the ozonation supported by photolysis and photocatalysis [109]. As can be seen in Fig. 7, both yield of PFOA decomposition and release of inorganic fluoride are evidently the largest in the case of photolytic process conducted with TiO_2 simultaneously with ozonation. Compared to the data reported for other photochemical and photocatalytic methods included in Table 2, one can notice that, even for a larger initial level of PFOA, 10-times shorter time $t_{0.9}$ for 90% decomposition (15 min) was reported for photocatalytic decomposition with the use of In_2O_3 as the catalyst [100]. Much shorted $t_{0.9}$ was observed in photochemical reductive PFOA decomposition carried out in the presence of sulfite [85] as well as in the ozonation in the presence of H_2O_2 in alkaline medium, where about 18 min was required for 90% decomposition of PFOA in 12 μM solution [110].

Another interesting comparison was reported for the yield of wet persulfate oxidation methods conducted both for PFOS [150] and PFOA [155] under different conditions. In the case of PFOS, for the initial concentration 186 μM the oxidation by persulfate [91] was supported by UV irradiation, sonication, and Fe(II) catalysis, and the most effective conditions were the hydrothermal ones at 80 °C [150]. In this case the reported rate-constant was only 0.00042 min^{-1}, and, as it can be seen from Table 2, photolysis in the presence of sulfite conducted at 32 μM PFOS concentration [84] or sonolysis-assisted sorption on granular activated carbon at 100 μM PFOS [127] proved to be much more efficient. In the case of PFOA, at the initial concentration 25 μM wet oxidation by persulfate was conducted with additional activation by H_2O_2 or under alkaline conditions, but the best yield was obtained in

Table 2
Characteristics of selected processes of PFOA decomposition in pure aqueous solutions.

Treatment process	Conditions of treatment	Initial concentration, μM	Decomposition reaction-rate constant, min^{-1}	Time required for 90% decomposition, h	Reference
Photochemical	185 nm	48	0.0075	~3	Chen et al. [67]
		2.4	–	3	Giri et al. [68]
		24	–	1	Wang et al. [68a]
	Solar, Fe(III)	48	–	~15 days	Liu et al. [74]
	254 nm, Fe(III)	36	0.0031	60	Liang et al. [76]
	254 nm, iodide	0.24	0.0014	–	Park et al. [78]
		25	0.0073	~4.5	Qu et al. [80]
	266 nm, iodide	25	0.0295	~1.5	Qu et al. [80]
	UV–Vis light, persulfate	1350	–	~4	Hori et al. [81]
	254 nm, persulfate	150	0.005	~8	Qian et al. [81]
	185 nm, chloride	30	0.0063	~2.3	Guo et al. [83]
	254 nm, sulfite	20	–	0.5	Song et al. [85]
	254 nm, carbonate, H_2O_2	121	0.0067	~9	Phan Thi et al. [85b]
Photocatalytic	254 nm, TiO_2	60	0.0118	–	Panchangam et al. [90]
	254 nm, TiO_2, oxalate	24	0.0116	~3.5	Wang et al. [91]
	254 nm, Cu-modified TiO_2	121	0.0031	12	Chen et al. [92]
	254 nm, Pb modified TiO_2	121	0.0086	4.5	Chen et al. [93]
	315–400 nm, nano-TiO_2, oxygen	4000	0.0056	~5	Sansotera et al. [94]
	254 nm, nano-TiO_2	121	–	36	Chen et al. [95]
	365 nm, TiO_2- PtNPs	145	0.0121	3.5	Li et al. [96]
	365 nm, TiO_2-MWCNT	72.5	–	~8	Song et al. [97]
	254 nm, TiO_2 – MIP	72.5	0.0044	~10	Wu et al. [98]
	254 nm, In_2O_3	100	0.0063	~5	Li et al. [99]
	254 nm, In_2O_3 NPs	~72.5	0.158	15 min	Li et al. [100]
	254 nm, Ga_2O_3 NPs	1.21	0.0810	~40 min	Shao et al. [101]
	254 nm, SiC/graphene	120	0.0016	~16	Huang et al. [102]
Ozonation	With UV or H_2O_2	24.1 mM	–	(No decomp. in 2 h)	Schröder et al. [107]
	With UV 254 nm, TiO_2	24.1	–	2.5	Huang et al. [109]
	With H_2O_2, pH 11	12	0.0716	~30 min	Lin et al. [110]
Electrochemical	BDD electrode, 100 °C	483	0.0074	5	Xiao et al. [115]
	Ce-PbO_2 electrode	250	0.013	1	Niu et al. [117]
	Ti/RuO_2 electrode	0.031	0.073	6	Schaefer et al. [118]
	Ti/SnO_2-Sb-Bi electrode	100	0.322	1.5	Zhuo et al. [113]
Sonolysis	200 kHz, 200 W	20	0.032	~1	Moriwaki et al. [121]
	354 kHz, 250 W/L	0.24	0.041	1	Vecitis et al. [122]
	612 kHz, 250 W/L	0.21	0.0366	1	Cheng et al. [124]
	40 kHz, 150 W, with surfactant	120	–	~3.5	Lin et al. [125]
	20 kHz, with sorption on GAC	120	–	~1	Zhao et al. [127]
	40 kHz, with TiO_2 photocatalysis	120	0.00218	> 8	Panchangam al. [128]
Ionizing radiation	Gamma, pH 13, N_2-saturated	48.3	0.011	3.5 h	Zhang et al. [144]
	Electron beam, pH 7.2, 20 mg/L nitrate	1.21	–	~1 s[*]	Wang et al. [145]
Fenton methods	With UV 254 nm, pH 3	20	–	1	Tang et al. [75]
	With persulfate, 70 °C With humic acid	100	–	~2 25 min	Santos et al. [147]
Persulfate (PS) oxidation	50 mM PS, 80 °C, pressurized air	3.74	0.023	~1.5	Hori et al. [148]
	42 mM PS, 60 °C, pH 3.1	0.241	0.0033	~5	Park et al. [149]
	2 mM PS, 50 °C, pH 2	20	0.00038	100	Yin et al. [151]
	50 mM PS, MWV assisted, 90 °C, pH 2	253.8	0.011	~1.5	Lee et al., [152]
	5 mM PS, 90 °C, ZVI	240.7	0.0147	Max. decomp. ~75%	Lee et al. [153]
	10 mM PS, activated carbon, pH 8.2	0.5	–	Max. removal ~50%	Sun et al. [154]
	0.3 M PS, H_2O_2, Fe-modified diatomite, pH 5	24	–	6 (70% decomp.)	Silva-Rackov et al. [155]
Zero valent iron	Clay coated FeNPs, pH 3	0.48	–	Max. decomp. ~40%	Arvaniti et al. [159]
Enzymatic	HRP, H_2O_2, phenolic co-substrate	850	0.003	6 (~75% decomp.)	Colosi et al. [160]

BDD – boron doped diamond, GAC-granulated activated carbon, HRP – horse radish peroxidase, MWV – microwave, NPs – nanoparticles, ZVI – zero-valent iron.

[*] Measured defluorination only, and not PFOA decomposition.

Table 3
Characteristics of selected processes of PFOS decomposition for environmental protection examined in pure aqueous solutions.

Treatment process	Conditions of treatment	Initial concentration, μM	Decomposition reaction-rate constant, min^{-1}	Time required for 90% decomposition, h	Reference
Photolytic	254 nm	37.2	0.0152	~5	Lyu et al. [70]
	254 nm, with Fe(III)	20	1.67 d^{-1}	36	Jin et al. [77]
	254 nm, with iodide	0.20	0.003	–	Park et al. [78]
	200–400 nm, with sulfite	32	0.118	20 min	Gu et al. [84]
	254 nm, with 2-propanol	40	0.93 d^{-1}	4 days	Yamamoto et al. [85]
Ozonation	H_2O_2, pH 11	10	0.0374	~0.5	Lin et al. [110]
Electrochemical	Ti/RuO$_2$ electrode	0.036	0.006	6	Schaefer et al. [118]
	Ti/TiO$_2$-NTs/Ag$_2$O/PbO$_2$ electrode	93	0.0165	> 3	Zhu et al. [119]
Sonolysis	200 kHz, 200 W	20	0.016	≥ 1 h	Moriwaki et al. [121]
	354 kHz, 250 W/L	0.20	0.027	2	Vecitis et al. [122]
	612 kHz, 250 W/L	0.20	0.0192	2	Cheng et al. [124]
	20 kHz, with sorption on GAC	100	–	~0.5	Zhao et al. [127]
	600 kHz, with UV 185 nm	20	–	4	Yang et al. [128]
Persulfate (PS) oxidation	18.5 mM PS, hydrothermal at 80 °C	186	0.00042	–	Yang et al. [150]
	15 mM PS, UV 254 nm	150	–	> 8	Qian et al. [81]
	2 mM PS, 50 °C	20	0.00047	> 30	Yin et al. [151]
Zero valent iron	Subcritical water, 350 °C	372	0.0098	~3	Hori et al. [158]
	Subcritical water, clay coated FeNPs, pH 13	0.40	–	~20 min	Arvaniti et al. [159]
Reduction with Ti(III)-citrate	70 °C, pH 9.0, vitamin B$_{12}$	60 (branched isomers)	0.00034	~7 days	Ochoa-Herrera et al. [160]

GAC – granulated activated carbon, NT – nanotube, NP – nanoparticle.

H_2O_2 catalyzed process using iron-modified diatomite [155]. The obtained yield was, however, evidently worse than the one reported in a much earlier paper with persulfate oxidation at 80 °C with pressurized air [148].

Among the attempts at objective comparison of different AOPs intensively developed for purification of wastewaters and water management, the concept of the evaluation of electric energy consumption, which was published as IUPAC Technical Report in 2001 [62], found numerous applications in the field. For high contaminant concentrations, the comparison of electric energy per mass should be considered, while for low contaminant concentrations the electric energy per order of magnitude changes the concentration of a pollutant (EE/O). That commonly cited recommendation has found numerous applications, *e.g.* in comparing different AOPs for decolorization of textile wastewater [162] in the degradation of hormone estrone [163] or in comparing the photodegradation of various pharmaceuticals by AOPs [164]. The energy consumption approach was also recently employed for the comparison of different AOPs in the PFOA degradation [125]. The calculated G_{50} value corresponded to the ratio of 50% of the initial amount of PFOA (C$_o$) to the energy input required for its decomposition:

$$G_{50} = 1.8 \times 10^6 C_o V_o M (Pt_{50})^{-1} \tag{38}$$

where V_o is the volume of treated solution (in liters), M – the molecular weight of a pollutant, P – the power of the reactor (in watts), and t_{50} – the time required for 50% decomposition (in seconds). As it is shown in Table 4A, the photocatalytic decomposition employing In$_2$O$_3$ was found the most energy efficient method [99]. This is a somewhat surprising result in terms of data listed in Table 2, as the time required for 90% decomposition was 5 h and the rate-constant value was quite low 0.0063 min^{-1} for that method. Shorter decomposition time was observed together with larger rate-constant values for electrochemical oxidation [113] and microwave-assisted persulfate oxidation [152], for which G_{50} values were much higher. This indicated real difficulties in the comparison of different AOPs. It is worth mentioning that in the photocatalytic methods with In$_2$O$_3$ catalyst reported by the same research group the exchange of conventional reagent In$_2$O$_3$ [99] by the

In$_2$O$_3$ porous nanoplates [100] for the same level of the initial level of PFOA resulted in both an essential increase of the rate-constant from 0.0063 to 0.158 min^{-1}, shortening the $t_{0.9}$ value from about 5 h to 15 min (Table 2).

The values of EE/O parameter were calculated for the comparison of energy efficiency of different photolytic processes of PFOS decomposition [70]. They were additionally compared to the one for the selected sonolytic process [121] and also to the decomposition using dc plasma generated within gas bubbles [164a]. As shown in Table 4B, this comparison was made for relatively narrow range of the PFOS initial concentrations between 20 and 100 μM. The best energy efficiency was evaluated for direct UV photolysis under strong alkaline conditions, carried out in 6 mM phosphate buffer solution [70], although it should be taken into account that in this particular case a much larger power of radiation source was used than in many other developed UV methods. Under such conditions the largest value of rate-constant, comparable to sonolysis was obtained too. Generally, the obtained rate-constants were smaller for PFOS than for PFOA (see Table 4A and B), although different sets of methods are included in those two attempts to compare various methods.

The energy efficiency for the ozonation treatment of PFOA and PFOS under alkaline conditions in both the absence and presence of H_2O_2 was calculated (in kJ/μM units) and compared to the values evaluated for selected reports on direct photolysis, photocatalysis, sonication-assisted photocatalysis and photolytic oxidation with persulfate [110]. In the alkaline ozonation method the energy required for PFOA decomposition was smaller than the one needed for PFOS. The ozonation with H_2O_2 proved more efficient than without H_2O_2. Furthermore, direct photolytic or photocatalytic methods required more energy than ozonation, while sonication and photolytic persulfate oxidation exhibited similar energy efficiency. The sonication-assisted photocatalytic process required less energy, but the degradation process was slower than ozonation (see Table 2).

As it was already mentioned and as it was shown in Table 2 too, the process of PFOA decomposition can be carried out a several orders of magnitude faster with the use of the beam of accelerated electrons (EB).

Table 4
Energy efficiency evaluated for PFOA (A) and PFOS (B) decomposition using different treatment. In A – energy consumption G_{50} calculated as amount of decomposed PFOA (50% of initial concentration) per energy input required [125], in B – energy consumed EE/O in kWh per one order of magnitude change of initial PFOA concentration per cubic meter of the treated solution [70].

A (PFOA)

Treatment method	Initial PFOA concentration, μM	Rate-constant, min^{-1}	G_{50}, g/kWh	Reference
Electrochemical/Ti/SnO$_2$-Sb anode	120.8	**0.322**	0.1471	Zhuo et al. [113]
Microwave-hydrothermal/Fe-activated	240.7	0.0147	0.0178	Lee et al. [153]
Microwave/persulfate oxidation	253.8	0.011	0.0901	Lee et al. [152]
UV/carbonate	121	0.0067	0.0303	Phan Thi et al. [85b]
Photocatalytic/TiO$_2$/oxalic acid	240	0.0116	0.0864	Wang et al. [91]
Photocatalytic/In$_2$O$_3$	100	0.0063	**0.2138**	Li et al. [99]
Photochemical/persulfate	1350	–	0.0205	Hori et al. [81]
Photocatalytic with sonication	120	0.00218	0.0295	Panchangam et al. [128]
Sonication	120	–	0.0186	Lin et al. [125]
Sonication with CTAB	120	–	0.0552	

B (PFOS)

Treatment method	Initial PFOS concentration, μM	Rate-constant, min^{-1}	EE/O, 10^3 kWh/m^3/order	Reference
Direct UV, 32 W	40	0.00009	18.19	Yamamoto et al. [85]
UV in iso-propanol, 32 W	40	0.00065	2.59	Yamamoto et al. [85]
UV with iodide, 8 W	20	0.0030	3.41	Park et al. [79]
UV with persulfate, 8 W	20	0.0040	2.56	Park et al. [79]
UV with Fe(III), 23 W	20	0.00117	1.90	Jin et al. [77]
UV at 100 °C, pH 11.8, 500 W	37.2	0.0151	**1.27**	Lyu et al. [70]
Sonolysis, Ar saturated solution	20	**0.016**	8.00	Moriwaki et al. [121]
Plasma bubble	100	0.0025	3.99	Yasuoko et al. [165]

Its duration depends mostly on the construction and operational parameters of the electron accelerator employed. There have not been reported any attempts to evaluate the energy efficiency of such processes for PFCs decomposition so far, although some data on other pollutants can be found in the literature. For instance, the EE/O values were evaluated for the decomposition of 0.5 mM phenol and 10 μM Methylene Blue using three different AOPs [165]. The most favorable results were reported for EB irradiation, while less favorable for UV/H$_2$O$_2$ homogeneous process. The poorest energy efficiency was reported for the photocatalytic process with TiO$_2$. A similar evaluation was conducted for the decomposition of two antibiotics, comparing EB process with ozonation and direct photolysis at 254 nm [166]. For the initial concentration of target pollutants 30 mg/L, the best EE/O values were reported for the radiolytic decomposition using electron beam. The calculation of EE/O values were also employed during the optimization of working parameters for the PFOA decomposition using UV-persulfate oxidation process [81].

The above-mentioned significant advantage of the use of ionizing radiation for the decomposition of organic pollutants is extremely short duration of the process (see examples for PFOA in Table 2), however this concerns only the processes carried out with the use of electron beams. For both gamma and EB irradiation, their rate significantly depends on the parameters of gamma-source and electron accelerator, as well as on the chemical conditions of the process. Fig. 14 shows the comparison of these two processes (gamma and EB) for the PFOA decomposition under experimental conditions where hydrated electrons predominated as the products of water radiolysis. In this case, the time for 90% PFOA decomposition of 1 mg/L was 0.5 h for γ-irradiation, and 4 s for 50% decomposition in EB process, whereas the required absorbed dose of radiation was 5 and 80 kGy, respectively. One must admit, however, that those values are significantly larger than the ones required for instance for the decomposition of pharmaceutical residues [167], which can be attributed to much higher chemical resistance of PFCs.

Combining various mechanisms of the decomposition of pollutants into processes, that one may refer to as hyphenated processes, is an evident trend observed in recent years in search for improving the

efficiency of various AOPs. Several such AOPs were also developed for the decomposition of PFOA and PFOS. They can be, e.g. photolytic or photocatalytic processes combined with sonolytic treatment. The photolytic support of PFOS sonolysis with vacuum UV at 185 nm, for the initial concentration range between 10 and 30 mg/L, enhanced the yield of decomposition only about 12% [128], while in the decomposition of 120 μM PFOA the sonication enhanced the photocatalytic decomposition from 22% to 45% after the 7-h process [128a]. It was already mentioned that the sonication increased the sorption of PFCs on the granular activated carbon from 2.5 to 9 times [127]. Different processes were employed for the activation of wet persulfate oxidation of PFOS, including sonolysis, photolysis at 254 nm, catalysis with Fe(II). Although the best efficiency was obtained for carrying out the oxidation process at the elevated temperature (80 °C), the reported pseudo-first-order reaction rate-constant 0.025 h^{-1} for the initial PFOS concentration 186 μM was not impressive at all [150]. Much more efficient decomposition was reported for 253.8 μM PFOA where oxidation with 50 mM persulfate at pH 2 and 90 °C was carried out in the microwave-assisted mode, with the rate-constant equal 0.67 h^{-1} [152]. Even further enhancement of such a process was also observed by additional synergetic effect of the presence of zero-valent iron in PFOA solution [153].

In spite of a wide investigations and discussion about toxicity of PFCs for humans and other living organisms, this subject is almost neglected in studies of AO/RPs for their decompositions. One of the reason of that can be their low toxicity towards bioluminescent bacteria commonly used in Microtox® tests for the monitoring of toxicity of environmental pollutants. In studies employing *Photobacterium phosphoricum* for PFOA ammonium salt a 30 min EC$_{50}$ values were determined in the range from 730 up to even 3150 mg/L, what means a very low toxicity [153a]. Using toxicity assessment based on the bioluminescence inhibition of *Vibrio fisheri*, a 30 min EC$_{50}$ values were determined as 130 mg/L for PFOS and 55.1 mg/L for PFOA [153b], while by other authors a 15 min EC$_{50}$ was reported as 22.8 mg/L [90a]. To our best knowledge, in two cases of PFOA decomposition processes, only, the changes of Microtox toxicity based on *Vibrio fisheri* were examined. This concerns the abovementioned photocatalytic
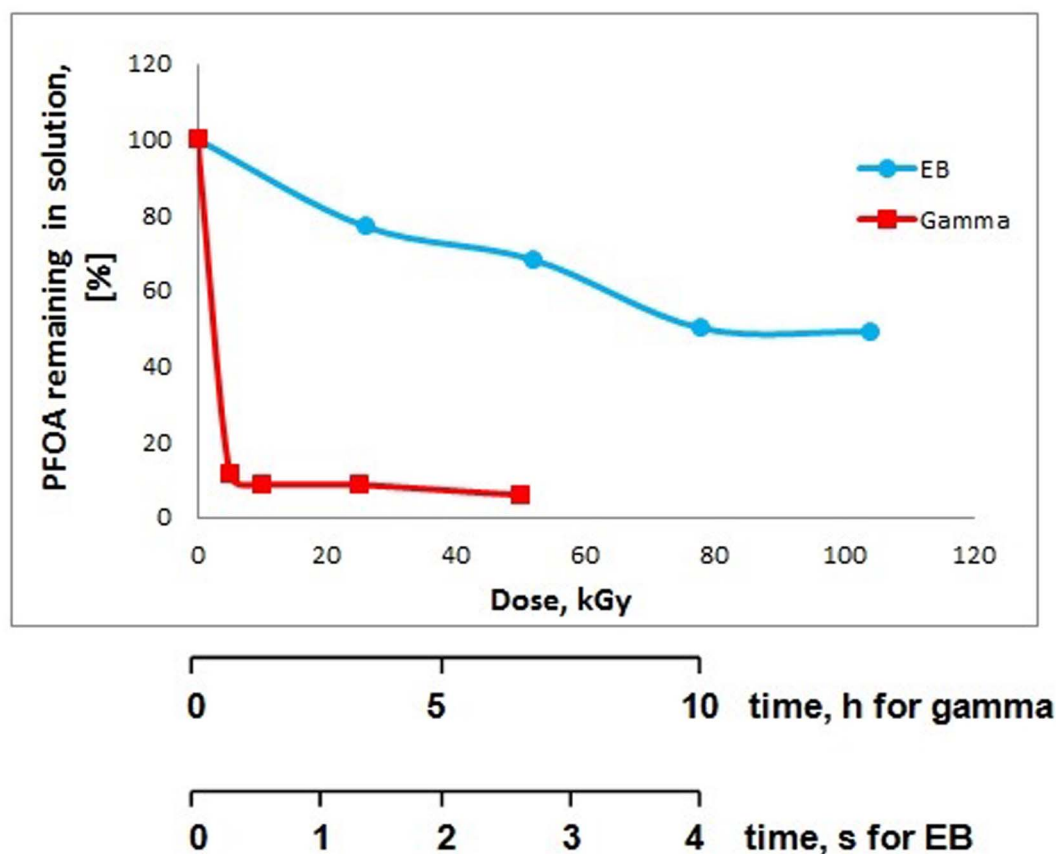
Fig. 14. Efficiency of radiolytic processes shown with appropriate time scales for PFCA decomposition at initial concentration 1 mg/L in Ar-saturated solution at pH.12.5 containing 0.2 M t-butanol using: ■ – gamma radiation from the ^{60}Co source with dose-rate 4.8 kGy/h, and ● – electron beam irradiation from accelerator with dose-rate 20 kGy/s.

decomposition with TiO_2, where for PFOA initial level 120 μM after 60 min process the acute toxicity was almost completely removed (greater than 81.9%) [90a]. In peroxidase-mediated degradation of PFOA with a phenolic substrate, for treatment of PFOA with initial concentration 850 μM, after 120 min treatment the initial value of

Microtox toxicity TU equal 137 dropped down to 24 [161], although a high initial value of Microtox toxicity is much higher than reported by other authors [153a,153b].

Table 5
Application of discussed AO/RPs in decomposition of PFOA and PFOS in natural matrices.

Matrix	Method of treatment	PFC	Examined concentrations	Time needed for 90% decomposition	Rate-constant, min^{-1}	Reference
Groundwater	Sonochemical	PFOA PFOS	100 g/L	~80 min ~3 h	0.0291 0.0135	Cheng et al. [124]
	Electrochemical with Ti/RuO$_2$ anode	PFOA PFOS	13 g/L 18 g/L	6 h 6 h	0.0073 0.0065	Schaefer et al. [118]
Landfill groundwater	Ultrasonic-assisted sorption on GAC	PFOA PFOS	50 mg/L	~60 min ~30 min	–	Zhao et al. [127]
Lake water WWTP effluent	UV, 90 °C	PFOS	37.2 M	≥6 h	0.0027 0.0017	Lyu et al. [69]
Lake water Municipal wastewater	UV (254 nm) – persulfate	PFOA	62 mg/L 62 mg/L	~8 h 6 h	–	Qian et al. [81]
Industrial wastewater	Ozonation, pH 11	PFOA PFOS	33.6 g/L 8.04 g/L	5 h 1 h	– –	Lin et al. [110]
Aqueous soil slurry	Persulfate oxidation, 60 °C	PFOA	1 mg/L	25% in 7 days, and next 30% in next 7 days	0.0033 (in water)	Park et al. [149]
Antireflective coating agent	Zero-valent Fe reduction in subcritical water, 350 °C	PFOS	55.9–118.8 mg/L	6 h	–	Hori et al. [158]
Aqueous film-forming foam agent (1/5000 diluted)	Sonochemical	PFOS	1110 ± 460 μg/L	1.5 h	–	Vecitis et al. [126]

9.3. Decomposition of PFCs in natural samples

Several research groups have already examined PFOA and PFOS decomposition using various AO/RPs in natural matrices (Table 5). The processed real samples included industrial and municipal wastewaters [110], antireflective coating agent [158] and diluted solution of aqueous film-forming foam (AFFF) agent [126], whereas the spiked natural matrices included groundwaters [118,124,127], lake waters, municipal wastewaters [69,81] and soil slurry [149].

In the two cases the matrix of the analyzed samples did not affect the yield of decomposition. This was observed for instance in ultrasonic-assisted sorption of PFOA and PFOS on granulated activated carbon employed for spiked landfill groundwater [127] as well as in the case of diluted solutions of AFFF agent treated by the sonolytic decomposition of 1110 ± 460 µg/L PFOS required about 1.5 h, while 0.2 µM in pure water – about 2 h [122,124]. However, a pronounced effect of matrices was observed in the case of spiked water in sonochemical treatment, which was attributed to the presence of bicarbonate [124], or in the photolytic oxidation of PFOA by persulfate in lake water and municipal wastewater, which was attributed to the presence of chloride [81]. Particularly large effect of matrix was reported for persulfate oxidation of PFOA, where the decomposition of 100 µg/L in water required about 50 min treatment, while for 1 mg/L in aqueous soil slurry – several days treatment [149]. A less pronounced, but also quite large matrix effect was observed in the decomposition of PFOS by ZVI in subcritical water carried out in antireflective coating agent, compared to pure aqueous solutions [158].

Concluding these considerations, there are not much data reporting the decomposition of PFOA and PFOS in real samples among original works in cited in this review, and all of them are listed in Table 5. It is not a simple question to answer if they are efficient enough to meet water quality standards. As it should be obvious from whole this work, the efficiency of particular treatment method depends first of all on initial level of PFCs, and a remaining level after treatment depends on the time of conducting the process. For instance, according to above-mentioned EU Directive, the maximum allowable concentration of PFOS in inland surface water is given as 36 µg/L, while in other surface waters 7.2 µg/L [158a]. Those levels when compared to data in Table 5, show that many of reported methods can be effectively employed even within a time span employed in carried out investigations. As the time needed to reach the permissible levels of PFCs significantly depends on their initial concentrations, a drawing a general conclusion about methods which are really applicable is impossible, as each real case is an individual situation.

The reported so far applications of AO/RPs in real treatment installations are very scarce and concern ozonation or UV irradiation without or with the presence of H_2O_2, only [35,157]. Results of those studies were extensively presented and discussed by Rahman et al. [35], and based on that review work, Table 6 was completed, providing a synthetic picture of that aspect. The negative values of recovery reported in several cases correspond to a larger values of PFCs concentrations observed in the effluent, compared to the influent. The reported applications deal mostly with treatment of river waters to produce drinking waters in installations involving different sets of purification operations. A drawing more general conclusions based on those data, seems however to be a very difficult task. There are both numerous examples of efficient removal of PFCs in different systems, which are absent or in decreased concentration in final drinking water, and inefficiency of those methods, or even increase of PFCs concentrations in effluents.

Several different treatment trains were examined, for instance, in studies of treatment of PFCs in different U.S. full-scale water treatment systems, where among other operations included in different configurations also ozonation or UV irradiation in the presence of H_2O_2 were used [157]. Although authors of that work generally concluded that all of these processes proved mostly ineffective in PFOA and PFOS removal, in two cases UV irradiation was slightly effective for both pollutants (10% removal), but in systems with ozonation, additional increase of PFOA and PFOS was observed in the effluent. The observed inefficiency was attributed to the resistance of PFCs to oxidizing processes.

In any of cases reported so far, were not employed a most efficient AO/RPs discussed above, so this evidently requires further works to be done.

9.4. Mechanisms of decomposition

In the majority of original works presented in this review, apart from the optimization of conditions for conducting the decomposition process with largest yield, particular attention was paid to the investigation of the mechanism of decomposition under different conditions of carrying out the discussed processes. There are both oxidative and reductive ways to employ radical reactions, hence commonly used AOPs abbreviation was modified to AO/RPs. Some of these mechanisms were already presented in different sections of this review.

A factor which has to be also mentioned here, is the chemical form (protonated/non-protonated) in which given PFC occurs in environmental sample. There is a controversy in the literature on pK_a values for PFOA, which are ranged from 0 [158b] to 3.8 ± 0.1 [158c]. If the latter value is correct, their initial form will be strongly affected by pH of the treated solutions, with protonated form in acidic solutions, and prevailing anion form in neutral and basic solutions. This is taken into account by numerous authors in proposing different starting species for composing the pathway of degradation, see e.g. schemes shown for PFOA in Figs. 8 and 10, and reactions (16)–(20), and also (23)–(27). The pK_a values for perfluorinated sulfonic acids, including PFOS, are in the range of −5 to −9, [26a] and for potassium salt of PFOS this value was given also as −3.5 [122]. So, under all possible environmental conditions, except strongly acidic wastewaters, e.g. industrial ones, they are effectively ionized. This is commonly taken into account in proposing the degradation pathways, see e.g. schemes shown for PFOS in Figs. 8 and 9, and reactions (5)–(15).

In the oxidative processes, in the first stage as a result of the oxidation of neutral or anionic form of PFCs perfluorinated radicals are formed, e.g. PFOA˙ or PFOA˙⁺. Such oxidation reactions can be carried out with $SO_4^{˙-}$ radicals with persulfate oxidations methods, e.g. [150], by photogenerated hole of a photocatalyst (˙TiO_2 or h^+) [90,94,128a], by anodic oxidation e.g. [111], by $CO_3^{˙-}$ radical in direct photolysis in the presence of H_2O_2 and bicarbonate [85b] or by hydroxyl radicals ˙OH in the UV-Fenton process [75]. Especially the role of hydroxyl radicals in those processes is ambiguous. The second-order reaction rate-constants of ˙OH radicals with PFOA and PFOS haven't been precisely evaluated yet (see Table 1), however their values are estimated to be $\leq 3 \times 10^7 M^{-1} s^{-1}$ [141] or even $\leq 10^5 M^{-1} s^{-1}$ for the PFOA [30]. Some authors express the opinion that ˙OH radicals cannot directly oxidize PFCs, see e.g. [81,107,121,144]. On the other hand, besides the above-mentioned UV-Fenton process [75], it was reported that ˙OH radicals react with non-terminal C−C bonds in electrochemical processes [115] and they are predominant reactive species in vacuum UV photolysis with Fe(III) [76]. The next step of the oxidation processes is the decarboxylation of either PFOA radicals, see e.g. [85b,109,111,128a,151] or PFOS radicals, e.g. [77,111,119,150] to form fluorocarbon radicals $C_7F_{15}˙$ and $C_8F_{17}˙$ from PFOA and PFOS, respectively. The next stage can be the hydrolysis of those radicals leading to the formation of e.g. $C_7H_{15}OH$, which was observed in photolytic processes [67,85b], photocatalytic processes [67] and microwave-induced persulfate oxidation [152]. The next most commonly postulated step, however, is the oxidation of those fluorocarbon radicals with ˙OH or oxygen, which can lead to the formation of unstable fluorocarbon alcohols or peroxyradicals, e.g. $C_8F_{17}OO˙$ [77,111,119]. The oxidation with ˙OH was postulated e.g. in electrochemical processes [111,113,117,119], in persulfate oxidation [128a], photolysis

Table 6

The efficiency of removal of PFOA and PFOS form different natural waters or wastewaters in full-scale treatment plants with multistep procedures involving ozonation or photolytic treatment by UV (adopted from review by Rahman et al. [35]

Configuration of multistep treatment	Treated medium	Initial concentration in influent, ng/L	Removal, %	Reference
PFOA				
Processes including UV irradiation				
DBF, UV, Cl_2	Groundwater	11	0	[157]
MF/RO, UV/H_2O_2, SAT	Potable water (indirect use facility)	15	100	[157]
Processes including ozonation				
COA/FLOC/SED, SF, O_3, GAC, Cl_2,	River water	15–24	0 to −220	[38]
	Lake water	42	6.5–9.2	
RSF, O_3, GAC, Cl_2	River water	25–64	−28 to −31	
		19–58	15–35	
Cl_2, COA/FLOC, RSF, O_3, GAC		13	52	[37]
Cl_2, COA/FLOC, RSF, O_3, GAC, UF, RO		6.9	89	
COA/FOC, RSF, O_3, GAC, SSF		4.4	−16	[40]
De-nitrification, pre-O_3, COA/FLOC/SED, DAFF, O_3, GAC, O_3	Treated wastewater	6.1–16	−24 to 32	[108]
PFOS				
Processes including UV irradiation				
MF/RO, UV/H_2O_2, SAT	Potable water (indirect use facility)	41	100	[157]
Clarifier/lamellar settler, UF, RO, UV/H_2O_2, stabi-lization/disifection (addition of lime, CO_2, NaOCl)	Treated wastewater	23–39	100	[108]
Processes including ozonation				
O_3, COA/FLOC, DBF, Cl_2	Surface water	1.4	0	[157]
RSF, O_3, GAC, Cl2	River water	0.87–3.2	50 to −222	[157]
COA/FLOC/SED, SF, O_3, GAC, Cl_2		0.26–3.3	60 to −185	[38]
COA/FLOC, RSF, O_3, GAC, SSF		< 0.23	< 97	[40]
Cl_2, COA/FLOC, RSF, O_3, GAC		116	69	[37]
Cl_2, COA/FLOC, RSF, O_3, GAC, UF, RO		86	86	[37]
De-nitrification, pre-O_3, COA/FLOC/SED, DAFF, O_3, GAC, O_3	Treated wastewater	0.6–3.7	81–100	[108]

Cl_2 – chlorination, COA/FLOC/SED – coagulation/flocculation/sedimentation, DAFF – dissolved air flotation and sand filtration, DBF – deep bed filtration, GAC – granular activated carbon, MF/RO – microfiltration/reverse osmosis, RSF – rapid sand filtration, SAT – solid aquifer treatment, UV – medium pressure ultraviolet.

[77], photolytic ozonation [109] or photocatalytic [94] and radiolytic [144] processes. As an alternative route, the oxidation with oxygen was indicated in electrolytic processes [111,113], photolysis [77] and photocatalytic decomposition [90]. In the ultrasound-assisted photolytic decomposition, the oxidation with $O_2^{\cdot -}$ superoxide radical was postulated [128]. A further sequence of hydrolytic and defluorination reactions of perfluorinated alcohols or peroxyradicals led to the formation of $C_6F_{13}COOH$ in the case of the degradation of PFOA, and PFOA in the case of the degradation of PFOS, as it was observed *e.g.* in photocatalytic ozonation [110] (see reactions (23)–(27)) and in electrochemical oxidations (Fig. 8).

The reductive processes employed for the decomposition of PFCs are based mostly on the use of hydrated electrons as particularly strong reducing agents, although, as it was already mentioned, weaker reductants such as superoxide radicals $O_2^{\cdot -}$ [155], carboxyl anion radicals $CO_2^{\cdot -}$ [91] or zero-valent iron (ZVI) [158,159] can be used for the same purposes. In the processes involving electrons, in the first stage the anion radicals (e.g. $C_7F_{15}COO^{\cdot 2-}$) were formed, which was described for instance in the photolytic decomposition in the presence of iodide [73] or in gamma-radiolysis [144] (Fig. 10A). From those unstable radicals fluorine atoms can be released [78], or radicals $C_7F_{15}CO^{\cdot}$ can be formed, and then by the loss of carbonyl the fluorocarbon radicals $C_7F_{15}^{\cdot}$ are formed. The direct cleavage of the C−F bond by electrons was also observed for PFOA parallel with the formation of $C_6F_{13}COF$ [80], although the process was slower.

The C−C bond is weaker than the C−F one, hence there is also postulated as the first stage of PFOA decomposition the cleavage of the C−C bond, *e.g.* in the photocatalytic process with TiO_2 and oxalate [91], according to the following reaction:

$$C_7F_{15}COOH + e^- \rightarrow C_7F_{15}^{\cdot} + HCOO^- \tag{39}$$

or in the gamma radiolytic process [144] (Fig. 10A).

In the photolytic decomposition of PFOS in the presence of sulfite

and after the formation of $PFOS^{\cdot 2-}$ radicals, two parallel processes were postulated [84], see the reactions (5)–(15). They can include defluorination from α-position of fluoroalkyl chain and desulfonation with the formation of $C_8F_{17}OH$. In the photocatalytic decomposition of PFOA in the presence of oxalate, apart from the predominating reduction with carboxyl anion radicals, direct decarboxylation with the formation of $C_7F_{15}^{\cdot}$ radicals was also postulated as showed by the reactions (16)–(20). The above-mentioned direct cleavage of the C−F bonds [78,80] led to the formation of $C_7F_{14}HCOOH$ and $C_7F_{13}H_2COOH$ acids, which underwent further reactions (12)–(15) leading to $C_6F_{13}COOH$ [85].

In the numerous works cited in this review the authors discuss a possible parallel process that may take place during the whole treatment procedure, hence an unambiguous determination of the mechanisms governing such processes is a difficult task. When the complete decomposition of target perfluorinated compounds is associated with only partial defluorination, completely different, new fluorinated organic compounds can be formed. The identification of products formed in this case is still a rarely discussed subject and it requires further investigation.

10. Conclusions

The main conclusions that one may draw from the presented review are as follows:

1. Radical reactions can be effectively carried out used in different methods both in oxidative and reductive modes for decomposition of PFOA and PFOS where different molecular mechanisms of decomposition/degradation take place.
2. Complete description of a decomposition method should include the kinetic parameters, duration of the treatment process with the particular level of concentration of a decomposed compound, energy

efficiency and the examination of matric effects.

3. In the developed methods very wide spans of the initial concentrations of PFOA and PFOS were investigated, which makes it difficult to objectively compare these methods.

4. In most of the developed treatment methods for sub-milimolar concentrations of PFCs, a period of time for complete decomposition is usually counted in hours, whereas in the selected ones only in a fraction of an hour. The extremely short time, however, is needed for the treatment with the beam of accelerated electrons.

5. The number of reported applications of the developed methods in real samples is still very limited, but the ones that have already been published indicate a great variety of possible practical applications.

6. In almost all of the reported methods, the formation of PFCs with shorter perfluorinated alkyl chain as the product of decomposition was indicated, however, in many cases their further decomposition occurred slower than the one of PFOA or PFOS. This is the reason why in many cases the extent of defluorination or total demineralization is much smaller than the decomposition of the target compound. The possibility of the formation of other fluorinated organic compounds should be taken into account when only partial defluorination is observed.

The challenges and perspectives in terms of the present status of development of those methods can be indicated as follows:

1. Numerous AO/RPs were investigated in details, with the elucidation of molecular mechanism of radical reactions, optimization of treatment conditions, and even examining of the real matrices effects, but besides few exceptions, concerning ozonation and UV irradiation, most of those methods were not examined so far in real WWTP processes for removal of PFCs where conventional methods routinely used are not sufficiently effective.

2. A practical applications of discussed methods require scaling up the laboratory instrumentation to a large-scale technological installations with yield in the range of hundreds m³/h, as in such scale only the real cost-efficiency can be evaluated.

3. For especially efficient laboratory photocatalytic methods it is necessary to develop an appropriate preparation of a large-volume immobilized photocatalyst beds, and examination of their long-term stability and functioning.

4. A larger attention should be focused on testing of different forms of toxicity changes of treated media.

5. Substantially larger research activity should be devoted to development of AO/RPs which do not require the use of additional chemicals (vacuum UV, sonolysis, electrochemical, use of ionizing radiation), and their applications in the most favorable configurations with other treatment methods to obtain the best cost-efficiency of the treatment.

When the preparation of this review was in progress, another very thorough and competent review on the decomposition of PFCs was published by Hoffmann's group [168]. It reported a wider scope of PFCs and discussed in detail AOPs, sorptive processes and also high-voltage electric discharge. The recent original paper on the transformation of perfluorinated compounds (*e.g.* fluorotelomer compounds) in natural waters by AOPs into PFCAs, which can be one of the sources of their presence in finished drinking waters, is worth mentioning here [169].

Yet another problem, although also associated with the global proliferation of PFCs and their common presence in the human blood, is the elimination of PFCs from the human body. Although already reviewed [170], it is the subject of a growing number of the original publications.

Acknowledgements

References

[1] D.R. Taves, Evidence that there are two forms of fluoride in human serum, Nature 217 (1968) 1050–1051.

[2] B.D. Key, R.D. Howell, C.S. Criddle, Fluorinated Organics in the Biosphere, Environ. Sci. Technol. 31 (1997) 2445–2454.

[3] G.W. Olsen, J.M. Burris, J.H. Mandel, L.R. Zobel, Serum perfluorooctanoate and hepatic and lipid clinical chemistry tests in fluorochemical production employees, J. Occup. Environ. Med. 41 (1999) 799–806.

[4] C.A. Moody, J.A. Field, Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams, Enviorn. Sci. Technol. 34 (2000) 3864–3870.

[5] J.P. Giesy, K. Kannan, Global; distribution of perfluorooctane sulfonate in wildlife, Environ. Sci. Technol. 35 (2001) 1339–1342.

[6] P. De Voogt, M. Saez, M, Analytical chemistry of perfluoroalkylated substances, Trends Anal. Chem. 25 (2006) 326–342.

[7] U. Berger, M.A. Kaiser, A. Kärrman, J.L. Barber, S.P.J. Van Leeuwen, Recent developments in trace analysis of poly- and perfluoroalkyl substances, Anal. Bioanal. Chem. 400 (2011) 1625–1635.

[8] M. Trojanowicz, M. Koc, Recent developments in methods for analysis of perfluorinated persistant pollutants, Microchim. Acta 180 (2013) 957–971.

[9] F.M. Hekster, R.W.P.M. Laane, P. de Voogt, P, Environmental and toxicity effects of perfluoroalkylated substances, Rev. Environ. Contam. Toxicol. 179 (2003) 99–121.

[10] C. Lau, K. Anitole, C. Hodes, D. Lai, A. Pfalhles-Hutchens, J. Seed, Perfluoroalkyl acids : a review of monitoring and toxicological findings, Toxicol. Sci. 99 (2007) 366–394.

[11] K. Sttenland, T. Fletcher, D.A. Savitz, Epidemiologic evidence on the health effects of perfluorooctanoic acid (PFOA), Environ. Health. Persp. 118 (2010) 1100–1108.

[12] D.A. Ellis, J.W. Martin, A.O. De Silva, S.A. Mabury, M.D. Hurley, M.P.S. Andersen, T.J. Wallington, Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids, Environ. Sci. Technol. 38 (2004) 3316–3321.

[13] K. Prevedouros, I.T. Cousins, R.C. Buck, S.H. Korzeniowski, Sources, fate and transport of perfluorocarboxylates, Environ. Sci. Technol. 40 (2006) 32–44.

[14] M. Houde, A.O. De Silva, D.C.G. Muir, R.L. Letcher, Monitoring of perfluorinated compounds in aquatic biota: an updated review, Environ. Sci. Technol. 45 (2011) 7962–7973;
(a) D. O'Hagan, Understanding organofluorine chemistry. An introduction to the C-F bond, Chem. Soc. Rev. 37 (2008) 308–319.

[15] G. Ding, W.J.G.M. Peijnenburg, Physicochemical properties and aquatic toxicity of poly- and perfluorinated compounds, Crit. Rev. Environ. Sci. Technol. 43 (2013) 598–678.

[16] W. D'Hollander, P. de Voogt, W. De Coen, L. Bervoets, Perfluorinated substances in human food and other sources of human exposure, Rev. Environ. Contam. Toxicol. 208 (2010) 179–215.

[17] Y. Pico, M. Farre, M. Llorca, D. Barcelo, Perfluorinated compounds in food: a global perspective, Crit. Rev. Food Sci. Nutr. 51 (2011) 605–625.

[18] B.S. Larsen, P. Sthur, B. Szostek, S.F. Bachmura, R.C. Rowand, K.B. Prickett, S.H. Korzeniowski, R.C. Buck, Method development for the determination of residual fluorotelomer raw materials and perfluorooctanoate in fluorotelomer-based products by gas chromatography and liquid chromatography mass spectrometry, J. Chromatogr. A 1110 (2006) 117–124.

[19] C. Bach, V. Boiteux, J. Hemard, A. Colin, C. Rosin, J.-F. Munoz, X. Dauchy, Simultaneous determination of perfluoroalkyl iodides, perfluoroalkane sulfonamides, fluorotelomer alcohols, fluorotelomer iodides and fluorotelomer acrylates and methacrylates in water and sediments using solid-phase microextraction-gas chromatography/mass spectrometry, J. Chromatogr. A 1448 (2016) 98–106.

[20] J. Armitage, I.T. Cousins, R.C. Buck, K. Prevedouros, M.H. Russel, M. Macleod, S.H. Korzeniowski, Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sourcers, Enviorn. Sci. Technol. 40 (2006) 6969–6975.

[21] L. Ahrens, Polyfluorooalkyl compounds in the aquatic environment: a review of their occurrence and fate, J. Environ. Monit. 13 (2011) 20–31.

[22] G.B. Post, P.D. Cohn, K.R. Cooper, Perfluorooctanoic acid (PFOA), an emerging drinking water contaminant: a critical review of recent literature, Environ. Res. 116 (2012) 93–117.

[23] E. Hampton (Ed.), Perfluorooctanoic acid (PFOA). Global occurrence, exposure and health effects, Nova Publishers, New York 2016150 pp.

[24] A.G. Paul, K.C. Jonjes, A.J. Sweetman, A first global production, emission, and environmental inventory for perfluorooctane sulfonate, Environ. Sci. Technol. 43 (2009) 386–392.

[25] T. Wang, Y. Wang, C. Liao, Y. Cai, G. Jiang, Perspectives on the inclusion of perfluorooctane sulfonate into the Stockholm convention on persistent organic pollutants, Environ. Sci. Technol. 43 (2009) 5171–5175.

[26] Listing of POPs in the Stockholm Convention, http://chm.paps.int/TheConvention/ ThePOPs/ListingsofPOPs
(a) S. Rayne, K. Forest, Perfluoroalkyl sulfonic and carboxylic acids: A critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods, J. Environ. Sci. Health Part A 44 (2009) 1145–1199

[27] P. Zareitalabad, J. Siemens, M. Hamer, W. Amelung, Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater – A review on concentrations and distribution coefficients, Chemosphere 91 (2013) 725–732.

[28] A. Miealles-Marco, S. Harrad, Perfluorooctane sulfonate: a review of human

exposure, biomonitoring and the environmental forensics utility of its chirality and isomer distribution, Enviorn. Int. 77 (2015) 148–159.

[29] J.P. Benskin, A.O. De Silva, MJ.W. Martin, Isomer profiling of perfluorinated substances as a tool for source tracking: A review of early findings and future applications, Rev. Environ. Contam. Toxicol. 208 (2010) 111–160;
(a) A. Yamamoto, H. Hisatomi, T. Ando, S. Takemine, T. Terao, T. Tojo, M. Yagi, D. Ono, H. Kawasaki, R. Arakawa, Use of high-resolution mass spectrometry to identify precur-sors and biodegradation products of perfluorinated and poly-fluorinated compounds in end-user products, Anal. Bioanal. Chem. 406 (2014) 4745–4755;
(b) Y. Zushi, J.N. Hogarth, S. Masunaga, Progress and perspective of per-fluorinated compound risk assessment and management in various countries and institutes, Clean Tech. Environ. Policy 14 (2012) 9–20;
(c) Fact Sheet: PFOA and PFOS drinking water health advisories. US Environmental Agency, EPA 800-F-16-003, November 2016.

[30] C.D. Vecitis, H. Park, J. Cheng, B.T. Mader, M.R. Hoffmann, Treatment technol-ogies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA), Front. Environ. Sci. Engin. China 3 (2009) 129–151.

[31] V.A.E. Espana, M. Mallavarapu, R. Naidu, Treatment technologies for aqueous perfluo-rooctanesufonate (PFOS) and perfluorooctanoate (PFOA): a critical review with an emphasis on field testing, Environ. Technol. Innov. 4 (2015) 168–181.

[32] Ch. Cowan-Ellsberry, S. Belanger, P. Dorn, S. Dyer, D. McAvoy, H. Sanderson, D. Versteeg, D. Ferrer, K. Stanton, Environmental safety of the use of major sur-factant classes in North America, Crit. Rev. Environ. Sci. Technol. 44 (2014) 1893–1993.

[33] P.B. Sweetster, Decomposition of organic fluorine compounds by Wickbold oxy-hydrogen flame combustion method, Anal. Chem. 28 (1956) 1766–1768.

[34] P. Ventkateswalu, Determination of fluorine in biological materials: a review, Adv. Dent. Res. 8 (1994) 80–86.

[35] M.F. Rahman, S. Peldszus, W.B. Anderson, Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substance (PFASs) in drinking water treatment: a review, Water Res. 50 (2014) 318–340.

[36] O.S. Arvaniti, A.S. Stasinakis, Review on the occurrence, fate and removal of perfluorinated compounds during wastewater treatment, Sci. Total Environ. 524–525 (2015) 81–92.

[37] C. Flores, F. Ventura, J. Martin-Alonso, J. Caixach, Occurrence of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in N.E. Spanish surface waters and their removal in a drinking water treatment plant that combines conventional and advanced treatments in parallel lines, Sci. Total Environ. (2013) 461618–462626.

[38] S. Takagi, F. Adachi, K. Miyano, Y. Koizumi, H. Tanaka, I. Watanabe, S. Tanabe, K. Kannan, Fate of perfluorooctanesulfonate and perfluorooctanoate in drinking water treatment processes, Water Res. 45 (2011) 3925–3932.

[39] M. Pabon, J.M. Corpart, Fluorinated surfactants: synthesis, properties, effluent treatment, J. Fluorine Chem. 114 (2002) 149–156.

[40] Ch. Eschauzier, E. Beerendonk, P. Scholte-Veenendaal, P. De Voogt, Impact of treatment processes on the removal of perfluorooalkyl acids from the drinking water production chain, Environ. Sci. Technol. 46 (2012) 1708–1715.

[41] D. Zho, J. Cheng, C.D. Vecitis, M.R. Hoffmann, Sorption of perfluorochemicals to granular activated carbon in the presence of ultrasound, J. Phys. Chem. A 115 (2011) 2250–2257.

[42] V. Ochoa-Herrera, R. Sierra-Alvarez, Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge, Chemosphere 72 (2008) 1588–1593.

[43] S.T.M.L.D. Senevirathana, S. Tanaka, S. Fujii, C. Kunacheva, H. Harada, B.R. Shivakoti, R. Okamoto, A comparative study of adsorption of perfluorooctane sulfonate (PFOS) onto granular activated carbon, ion-exchange polymers and non-ion-exchange polymers, Chemosphere 80 (2010) 647–651.

[44] Q. Yu, S. Deng, G. Yu, Selective removal of perfluorooctane sulfonate from aqu-eous solution using chitosan-based molecularly imprinted polymer adsorbents, Water Res. 42 (2008) 3089–3097.

[45] R. Nataraja, R. Azerad, B. Bader, E. Copin, Microbial cleavage of C-F bond, J. Fluorine Chem. 126 (2005) 425–436.

[46] J.R. Parsons, M. Saez, J. Dolfing, P. de Vogt, Biodegradation of perfluorinated compounds, Rev. Environ. Contam. Toxicol. 196 (2008) 53–71.

[47] B.D. Key, R.D. Howell, C.S. Criddle, Defluorination of organofluorine sulfur compounds by *Pseudomonas* Sp. strain D2, Environ. Sci. Technol. 32 (1998) 2283–2287.

[48] H.F. Schroder, Determination of fluorinated surfactants and their metabolites in sewage sludge samples by liquid chromatography with mass spectrometry and tandem mass spectrometry after pressurised liquid extraction and separation on fluorine-modified reversed-phase sorbents, J. Chromatogr. A 1020 (2003) 131–151.

[49] J.S.-C. Liou, B. Szostek, C.M. DeRito, E.L. Madsen, Investigating the biodegrad-ability of perfluorooctanoic acid, Chemosphere 80 (2010) 176–183.

[50] W.H. Glaze, J.W. Kang, D.H. Hapin, The chemistry of water-treatment processes involving ozone, hydrogen-peroxide and ultraviolet radiation, Ozone Sci. Eng. 9 (1987) 335–352.

[51] S. Gligorovski, R. Strekowski, S. Barbati, D. Vione, Environmental implications of hydroxyl radicals (˙OH), Chem. Rev. 115 (2015) 13051–13092.

[52] H.J.H. Fenton, Oxidation of tartaric acid in the presence of iron, J. Chem. Soc. Trans. 65 (1894) 899–910.

[53] W.H. Glaze, Drinking-water treatment with ozone, Environ. Sci. Technol. 21 (1987) 224–229.

[54] J.H. Carey, J. Lawrence, H.M. Tosine, Photodechlorination of PCBs in the presence of titanium dioxide in aqueous suspensions, Bull. Environ. Contam. Toxicol. 16

(1976) 697–701.

[55] C.G. Dunn, Treatment of water and sewage by ionizing radiations, Sewage Ind. Wast. 25 (1953) 1277–1281;
(a) A.K. Biń, S. Sobera-Madej, Comparison of the advanced oxidation processes (UV, UV/H$_2$O$_2$ and O$_3$) for the removal; of antibiotic substances during waste-water treatment, Ozone Sci. Eng. 34 (2012) 136–139.

[56] T. Oppenländer, Advanced Oxidation Processes (AOPs): Principles, Reaction Mechanis-ms, Reactor Concepts, Wiley VCH, Weinheim, 2003.

[57] S. Parsons (Ed.), Advanced Oxidation Processes for Water and Wastewater, IWA Publishing, 2004.

[58] M.I. Stefan (Ed.), Advanced Oxidation Processes for Water Treatment: Fundamentals and Applications, IWA Publishing, 2016.

[59] J.L. Wang, L.J. Xu, Advanced Oxidation Processes for wastewater treatment: Formation of hydroxyl radical and application, Crit. Rev. Environ. Sci. Technol. 42 (2012) 251–325.

[60] M.A. Oturan, J.-J. Aaron, Advanced Oxidation Processes in water/wastewater treatment: Principles and applications. A review, Crit. Rev. Environ. Sci. Technol. 44 (2014) 2577–2641.

[61] A.R. Ribeiro, O.C. Nunes, M.F.R. Pereira, A.M.T. Silva, An overview on the ad-vanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU, Environ. Int. 75 (2015) 33–51;
(a) G. Boczkaj, A. Fernandes, Wastewater treatment by means of advanced oxi-dation processes at basic pH conditions: a review, Chem. Eng. J. 320 (2017) 608–633;
(b) W. Jiao, S. Luo, Z. He, Y. Liu, Applications of high gravity technologies for wastewater treatment: a review, Chem. Eng. J. 313 (2017) 912–927.

[62] J.R. Bolton, K.G. Bircher, W. Tumas, C.A. Tolman, Figures-of-merit for the tech-nical development and application of advanced oxidation technologies for both electric- and solar-driven systems, Pure Appl. Chem. 73 (2001) 627–637.

[63] S. Esplugas, D.M. Bila, L.G.T. Krause, M. Dezotti, Ozonation and advanced oxi-dation technologies to remove endocrine disrupting chemicals (EDCs) and phar-maceuticals and personal care products (PPCPs) in water effluents, J. Hazard. Mater. 149 (2007) 631–642.

[64] M. Klavarioti, D. Mantzavinos, D. Kassinos, Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environ. Int. 35 (2009) 402–417.

[65] A. Matilainen, M. Sillanpa, Removal of natural organic matter from drinking water by advanced oxidation processes, Chemosphere 80 (2010) 351–365;
(a) D. Cambie, C. Bottechia, N.J.W. Straathof, V. Hesel, T. Noël, Applications of continuous-flow photochemistry in organic synthesis, material science, and water treatment, Chem. Rev. 116 (2016) 10276–10341.

[66] P. Mukerjee, M.J. Gumkowski, C.C. Chan, R. Sharma, Determination of critical miceli-zation concentration of perfluorocarboxylates using ultraviolet spectro-scopy: Some unusual counterion effects, J. Phys. Chem. 94 (1999) 8832–8835.

[67] J. Chen, P. Zhang, J. Liu, Photodegradation of perfluorooctanoic acid by 185 nm vacuum ultraviolet light, J. Environ. Sci. 19 (2007) 387–390.

[68] R.R. Giri, H. Ozaki, T. Okada, S. Taniguchi, T. Takanami, Factors influencing UV photodecomposition of perfluorooctanoic acid in water, Chem. Eng. J. 180 (2012) 197–203;
(a) Y. Wang, P. Zhang, Effects of pH on photochemical decomposition of per-fluorooctanoic acid in different atmospheres by 185 nm vacuum ultraviolet, J. Environ. Sci. 26 (2014) 2207–2214.

[69] X.-J. Lyu, W.-W. Li, P.K.S. Lam, H.-Q. Yu, Photodegradation of perfluorooctane sulfonate in environmental matrices, Sep. Pur. Technol. 151 (2015) 172–176.

[70] X.-J. Lyu, W.-W. Li, P.K.S. Lam, H.-Q. Yu, Insights into perfluorooctane sulfonate photodegradation in a catalyst-free aqueous solution, Sci. Rep. 5 (2015) 9353.

[71] http://www.ces.fau.edu/nasa/module-2/radiation-sun.php.

[72] S. Vaalgamma, A.V. Vähätalo, N. Perkola, S. Huhtala, Photochemical reactivity of perfluorooctanoic acid (PFOA) in conditions representing surface water, Sci. Total Environ. 409 (2011) 3043–3048.

[73] S. Taniyasu, N. Yamashita, E. Yamazaki, G. Petrick, K. Kannan, The environmental photolysis of perfluorooctanesulfonate, perfluorooctanoate, and related fluor-ochemicals, Chemosphere 90 (2013) 1686–1692.

[74] D. Liu, Z. Xiu, F. Liu, G. Wu, D. Adamson, et al., Perfluorooctanoic acid de-gradation in the presence of Fe(III) under natural sunlight, J. Hazard. Mater. 262 (2013) 456–463.

[75] H. Tang, Q. Xiang, M. Lei, J. Yan, L. Zhu, J. Zou, Efficient degradation of per-fluorooctanoic acid by UV-Fenton process, Chem. Eng. J. 184 (2012) 156–162.

[76] X. Liang, J. Cheng, C. Yang, S. Yang, Factors influencing aqueous per-fluorooctanoic acid (PFOA) photodecomposition by VUV irradiation in the pre-sence of ferric ions, Chem. Eng. J. 298 (2016) 291–299.

[77] L. Jin, P. Zhang, T. Shao, S. Zhao, Ferric ion mediated photodecomposition of aqueous perfluorooctane sulfonate (PFOS) under UV irradiation and its me-chanism, J. Hazard. Mater. 271 (2014) 9–15.

[78] H. Park, C.D. Vecitis, J. Cheng, W. Choi, B.T. Mader, M.R. Hoffmann, Reductive defluorination of aqueous perfluorinated alkyl surfactants: Effects of ionic head-group and chain length, J. Phys. Chem. 113 (2009) 690–696.

[79] H. Park, C.D. Vecitis, J. Cheng, N.F. Dalleska, B.T. Mader, M.R. Hoffmann, Reductive degradation of perfluoroalkyl compounds with aquated electrons gen-erated from iodide photolysis at 254 nm, Photochem. Photobiol. Sci. 10 (2011) 1945–1953.

[80] Y. Qu, C. Zhang, F. Li, J. Chen, Q. Zhou, Photo-reductive defluorination of per-fluorooctanoic acid in water, Wat. Res. 44 (2010) 2939–2947;
(a) Y. Qu, C. Zhang, P. Chen, Q. Zhou, W. Zhang, Effect of initial solution pH on photo-induced reductive decomposition of perfluorooctanoic acid, Chemosphere 107 (2014) 218–223.

[81] Y. Qian, X. Guo, Y. Zhang, Y. Peng, P. Sun, et al., Perfluorooctanoic acid degradation using UV-persulfate process: Modeling of the degradation and chlorate formation, Environ. Sci. Technol. 50 (2016) 772–781;
(a) H. Hori, A. Yamamoto, E. Hayakawa, S. Taniyasu, N. Yamashita, S. Kutsuna, Efficient decomposition of environmentally persistent perfluorocarboxylic acids by use of persulfate as a photochemical oxidant, Environ. Sci. Technol. 39 (2005) 2383–2388.

[82] L. Huang, W. Dong, H. Hou, Investigation of the reactivity of hydrated electron toward perfluorinated carboxylates by laser flash photolysis, Chem. Phys. Lett. 536 (2007) 124–128.

[83] R. Guo, C. Zhang, G. Zhang, Q. Zhou, Degradation of perfluorooctanoic acid by UV/chloride process, Chem. J. Chin. Univ. 8 (2016) 1499–1508.

[84] Y. Gu, W. Dong, C. Luo, T. Liu, Efficient reductive decomposition of perfluorooctanesulfonate in a high photon flux UV/sulfite system, Environ. Sci. Technol. 50 (2016) 10554–10561.

[85] T. Yamamoto, Y. Noma, S. Sakai, Y. Shibata, Photodegradation of perfluorooctane sulfonate by UV irradiation in water and alkaline 2-propanol, Environ. Sci. Technol. 41 (2007) 5660–5665;
(a) Z. Song, H. Tang, N. Wang, L. Zhu, Reductive defluorination of perfluorooctanoic acid by hydrated electrons in a sulfite-mediated UV photochemical system, J. Hazard. Mater. 262 (2013) 332–338;
(b) L. Phan Thi, H. Do, Y. Lee, S. Lo, Photochemical decomposition of perfluorooctanoic acids in aqueous carbonate solution with UV irradiation, Chem. Eng. J. 221 (2013) 258–263.

[86] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysts, Chem. Rev. 95 (1995) 69–96.

[87] H. Hori, E. Hayakawa, H. Einaga, S. Katsuna, K. Koike, et al., Decomposition of environmentally persistent perfluorooctanoic acid in water by photochemical approaches, Environ. Sci. Technol. 38 (2004) 6118–6124.

[88] U.I. Gaya, A.H. Abdullah, Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamental, progress and problems, J. Photochem. Photobiol. C 9 (2008) 1–12;
(a) M. Pelaez, N.T. Nolan, S.C. Pillai, M.K. Seery, P. Falaras, A.G. Kontos, P.S.M. Dunlop, J.W.J. Hamilton, J.A. Byrne, K. O'Shea, M.H. Entezari, D.D. Dionisou, A review on the visible light active titanium dioxide photocatalysts for environmental applications, Appl. Catal. B Environ. 125 (2012) 331–349.

[89] S. Katsuna, Y. Nagaoka, K. Takeuchi, H. Hori, TiO$_2$-induced heterogenous photodegradation of a fluorotelomer alcohol in air, Environ. Sci. Technol. 40 (2006) 6824–6829.

[90] S.C. Panchangam, A.Y. Lin, K.L. Shaik, C. Lin, Decomposition of perfluorocarboxylic acids (PFCAs) by heterogeneous photocatalysis in acid aqueous medium, Chemosphere 77 (2009) 242–248;
(a) I.H. Cho, Degradation and reduction of acute toxicity of environmentally persistent perfluorooctanoic acid (PFOA) using VUV photolysis and TiO$_2$ photocatalysis in acidic and basic aqueous solutions, Toxicol. Environ. Chem. 93 (2011) 925–940.

[91] Y. Wang, P. Zhang, Photocatalytic decomposition of perfluorooctanoic acid (PFOA) by TiO$_2$ in the presence of oxalic acid, J. Hazard. Mater. 192 (2011) 1869–1875.

[92] M. Chen, S. Lo, Y. Lee, C. Huang, Photocatalytic decomposition of perfluorooctanoic acid by transition-metal modified titanium dioxide, J. Hazrad. Mater. 288 (2015) 168–175.

[93] M. Chen, S. Lo, Y. Lee, J. Kuo, C. Wu, Decomposition of perfluorooctanoic acid by ultraviolet light irradiation with Pb-modified titanium dioxide, J. Hazard. Mater. 303 (2016) 111–118.

[94] M. Sansotera, F. Persico, V. Rizzi, W. Panzeri, C. Pirola, et al., The effect of oxygen in the photocatalytic oxidation pathways of petrfluorooctanoic acid, J. Fluorine Chem. 179 (2015) 159–168.

[95] Y. Chen, S. Lo, J. Kuo, Effects of titanate nanotubes synthesized by a microwave hydrothermal method on photocatalytic decomposition of perfluorooctanoic acid, Water Res. 45 (2011) 4131–4140.

[96] M. Li, Z. Yu, Q. Liu, L. Sun, W. Huang, Photocatalytic decomposition of perfluorooctanoic acid by noble metallic nanoparticles modified TiO$_2$, Chem. Eng. J. 286 (2016) 232–238.

[97] C. Song, P. Chen, C. Wang, L. Zhu, Photodegradation of perfluorooctanoic acid synthesized TiO$_2$-MWCNT composites under 365 nm UV irradiation, Chemosphere 86 (2012) 853–859.

[98] Y. Wu, Y. Li, A. Tian, K. Mao, J. Liu, Selective removal of perfluorooctanoic acid using molecularly imprinted polymer-modified TiO$_2$ nanotube arrays, Int. J. Photoenergy (2016) 7368795.

[99] X. Li, P. Zhang, L. Jin, T. Shao, Z. Li, J. Cao, Efficient photocatalytic decomposition of perfluorooctanoic acid by indium oxide and its mechanism, Environ. Sci. Technol. 46 (2012) 5528–5534.

[100] Z. Li, P. Zhang, J. Li, T. Shao, J. Wang, L. Jin, Synthesis of In$_2$O$_3$ porous nanoplates for photocatalytic decomposition of perfluorooctanoic acid (PFOA), Cat. Commun. 43 (2014) 42–46.

[101] T. Shao, P. Zhang, L. Jin, Z. Li, Photocatalytic decomposition of perfluorooctanoic acid in pure water and sewage water by nanostructured gallium oxide, Appl. Cat. B: Environ. 142–143 (2013) 654–661.

[102] D. Huang, L. Yin, J. Niu, Photoinduced hydrodefluorination mechanisms of perfluoro-, octanoic acid by the SiC/graphene catalyst, Environ. Sci. Technol. 50 (2016) 5857–5863.

[103] B. Langlais, D.A. Reckhow, D.R. Brink (Eds.), Ozone in Water Treatment: Application and Engineering, Lewis Publishers, Chelsea, Michigan, 1991.

[104] U. von Gunten, Ozonation of drinking water: Part I. Oxidation kinetics and product formation, Water Res. 37 (2003) 1443–1467.

[105] J. Nawrocki, B. Kasprzyk-Hordern, The efficiency and mechanisms of catalytic ozonation, Appl. Catal. B: Environ. 99 (2010) 27–42.

[106] E.J. Rosenfeld, K.G. Linden, S. Canonica, U. Von Gunten, Comparison of the efficiency of ˙OH radical formation during ozonation and the advanced oxidation processes O$_3$/H$_2$O$_2$ and UV/H$_2$O$_2$, Wat. Res. 40 (2006) 3695–3704.

[107] H.F. Schröder, R.J.W. Meesters, Stability of fluorinated surfactants in advanced oxidation processes – A follow up of degradation products using flow injection-mass spectrometry, liquid chromatography-mass spectrometry and liquid chromatography-multiple stage mass spectrometry, J. Chromatogr. A 1082 (2005) 110–119.

[108] J. Thompson, G. Eagesham, J. Reungoat, Y. Poussade, M. Bartkow, et al., Removal of PFOS, PFOA and other perfluoroalkyl acids at water reclamation plants in South East Queensland Australia, Chemosphere 82 (2011) 9–17.

[109] J. Huang, X. Wang, Z. Pan, X. Li, Y. Ling, L. Li, Efficient degradation of perfluorooctanoic acid (PFOA) by photocatalytic ozonation, Chem. Eng. J. 296 (2016) 329–334.

[110] A.Y. Lin, S.C. Panchangam, C.Y. Chang, P.K. Hong, H.F. Hsueh, Removal of perfluorooctanoic acid and perfluorooctane sulfonate via ozonation under alkaline condition, J. Hazard. Mater. 243 (2012) 272–277.

[111] B.P. Chaplin, Critical review of electrochemical advanced oxidation processes for water treatment applications, Environ. Sci. Proc. Imp. 16 (2014) 1182–1203.

[112] I. Sires, E. Brillas, M.A. Oturan, M.A. Rodrigo, M. Panizza, Electrochemical advanced oxidation processes: today and tomorrow. A review, Environ. Sci. Pollut. Res. 21 (2014) 8336–8367;
(a) E. Brillas, I. Sires, M.A. Oturan, Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry, Chem. Rev. 109 (2009) 6570–6631.

[113] Q.F. Zhuo, S.B. Deng, B. Yang, J. Huang, G. Yu, Efficient electrochemical oxidation of perfluorooctanoate using a Ti/SnO$_2$-Sb-Bi anode, Environ. Sci. Technol. 45 (2011) 2973–2979.

[114] K.E. Carter, J. Farrell, Oxidative destruction of perfluorooctane sulfonate using boron-doped diamond film electrodes, Environ. Sci. Technol. 42 (2008) 6111–6115.

[115] H. Xiao, B. Lv, G. Zhao, Y. Wang, M. Li, D. Li, Hydrothermally enhanced electrochemical oxidation of high concentration refractory perfluorooctanoic acid, J. Phys. Chem. A 115 (2011) 13836–13851.

[116] T. Ochiai, Y. Izuka, K. Nakata, T. Murakami, D.A. Tryk, et al., Efficient electrochemical decomposition of perfluorocarboxylic acids by the use of a boron-doped diamond electrode, Diamond Rel. Mater. 20 (2011) 64–67.

[117] J. Niu, H. Lin, C. Gong, X. Sun, Theoretical and experimental insights into the electrochemical mineralization mechanism of perfluorooctanoic acid, Environ. Sci. Technol. 47 (2013) 14341–14349.

[118] C.E. Schaefer, C. Andaya, A. Urtiaga, E.R. McKenzie, C.P. Higgins, Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in groundwater impacted by aqueous film forming foams (AFFFs), J. Hazard. Mater. 295 (2015) 170–175.

[119] Q. Zhuo, M. Luo, Q. Guo, G. Yu, S. Deng, et al., Electrochemical oxidation of environmentally persistent perfluorooctane sulfonate by a novel lead dioxide anode, Electrochim. Acta 213 (2016) 358–367.

[120] A. Kotronaru, G. Mills, M.R. Hoffmann, Ultrasonic irradiation of para-nitrophenol in aqueous solution, J. Phys. Chem. 95 (1991) 3630–3638.

[121] M. Moriwaki, Y. Takagi, M. Tanaka, K. Tsuruho, K. Okitsu, Y. Maeda, Sonochemical decomposition of perfluorooctano sulfonate and perfluorooctanoic acid, Environ. Sci. Technol. 39 (2005) 3388–3392.

[122] C.D. Vecitis, H. Park, J. Cheng, B.T. Mader, M.R. Hoffmann, Kinetics and mechanism of the sonolytic conversion of the aqueous perfluorinated surfactants, perfluorooctanoate (PFOA), and perfluorooctane sulfonate (PFOS) into inorganic products, J. Phys. Chem. A 112 (2008) 4261–4270.

[123] J. Cheng, C.D. Vecitis, H. Park, B.T. Mader, M.R. Hoffmann, Sonochemical degradation of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in landfill groundwater: Environmental matrix effects, Environ. Sci. Technol. 42 (2008) 8057–8063.

[124] J. Cheng, C.D. Vecitis, H. Park, B.T. Mader, M.R. Hoffmann, Sonochemical degradation of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in groundwater: Kinetic effects of matrix inorganics, Environ. Sci. Technol. 44 (2010) 445–450.

[125] J. Lin, C. Hu, S. Lo, Effect of surfactants on the degradation of perfluorooctanoic acid (PFOA) by ultrasonic (US) treatment, Ultrason. Sonochem. 28 (2016) 130–135.

[126] C.D. Vecitis, Y. Wang, J. Cheng, H. Park, B.T. Mader, M.R. Hoffmann, Sonochemical degradation of perfluorooctanesulfonate in aqueous film-forming foams, Environ. Sci. Technol. 44 (2010) 432–438.

[127] D. Zhao, J. Cheng, C.D. Vecitis, M.R. Hoffmann, Sorption of perfluorochemicals to granular activated carbon in the presence of ultrasound, J. Phys. Chem. A 115 (2011) 2250–2257.

[128] S. Yang, J. Sun, Y. Hu, J. Cheng, X. Liang, Effect of vacuum ultraviolet on ultrasonic defluorination of aqueous perfluorooctanesulfonate, Chem. Eng. J. 234 (2013) 106–114;
(a) S.C. Panchangam, A.Y. Lin, J. Tsai, C. Lin, Sonication-assisted photocatalytic decomposition of perfluorooctanoic acid, Chemosphere 75 (2009) 654–660.

[129] P. Fernandez-Castro, M. Vallejo, M.F. San Roman, I. Ortiz, Insight on the fundamentals of advanced oxidation processes. Role and review of the determination methods of reactive oxygen species, J. Chem. Technol. Biotechnol. 90 (2015) 796–820.

[130] I. Oller, S. Malato, J.A. Sanchez-Perez, Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination – A review,

Sci. Total Environ. 409 (2011) 4141–4166.

[131] S.G. Babu, M. Ashokkumar, B. Neppolian, The role of ultrasound on advanced oxidation processes, Top Curr. Chem. (2016) 374–406.

[132] M. Cheng, G. Zeng, D. Huang, C. Lai, P. Xu, C. Zhang, Y. Liu, Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: a review, Chem. Eng. J. 284 (2016) 582–598.

[133] W.J. Cooper, R.D. Curry, K.E. O'Shea (Eds.), Environmental Applications of Ionizing Radiation, Wiley, New York, 1998;
(a) M.N. Martins, T.F. Siva, Electron accelerators: history, applications, and perspectives, Radiat. Phys. Chem. 95 (2014) 78–85.

[134] N. Getoff, Factors influencing the efficiency of radiation-induced degradation of water pollutants, Radiat. Phys. Chem. 65 (2002) 437–446.

[135] L. Wojnarovits, E. Takacs, Irradiation treatment of azo dye containing wastewater: an overview, Radiat. Phys. Chem. 77 (2008) 225–244.

[136] M.A. Rauf, S.S. Ashraf, Radiation induced degradation of dyes – An overview, J. Hazard. Mater., 166 (2009) 6–16. sis on anionic surfactants, Radiat. Phys. Chem., 71 (2004) 461–463.

[137] M.C.F. Moraes, M.F. Romanelli, H.C. Sena, G. Pasqualini da Silva, M.H.O. Sampa, S.I. Borrely, Whole acute toxicity removal from industrial and domestic effluents treated by electron beam radiation: emphasis on anionic surfactants, Radiat. Phys. Chem. 71 (2004) 461–463.

[138] M. Petrovic, P. Gehringer, H. Eschweiler, D. Barcelo, Radiolytic decomposition of multiclass surfactants and their biotransformation products in sewage treatment plant effluents, Chemosphere 66 (2007) 114–122;
(a) H.Y. Kim, T. Kim, S.M. Cha, S. Yu, Degradation of sulfamethoxazole by ionizing radiation: Identification and characterization of radiolytic products, Chem. Eng. J. 313 (2017) 556–566.

[139] J. Pacansky, R.J. Waltman, Electron beam irradiation of poly(perfluoro ethers): Identification of gaseous products as a result of main chain scission, J. Phys. Chem. 95 (1991) 1512–1518.

[140] Y. Akiyama, H. Sodaye, Y. Shihabara, Y. Honda, S. Tagawa, S. Nishijima, Study on gamma-ray-induced degradation of polymer electrolyte by pH titration and solution analysis, Pol. Degr. Stab. 95 (2010) 1–5.

[141] E. Szajdzińska-Piętek, J.L. Gębicki, Pulse radiolytic investigation of perfluorinated surfactants in aqueous solutions, Res. Chem. Intermed. 26 (2000) 897–912.

[142] G. Kciuk, A. Bojanowska-Czajka, K. Kulisa, M. Trojanowicz, unpublished results.

[143] T. Csay, R. Homolk, E. Illes, E. Takacs, L. Wojnarovits, The chemical background of advanced oxidation processes, Isr. J. Chem. 54 (2014) 233–241.

[144] Z. Zhang, J. Chen, X. Lyu, H. Yin, G. Sheng, Complete mineralization of perfluorooctanoic acid (PFOA) by γ-irradiation in aqueous solution, Sci. Rep. (2014), http://dx.doi.org/10.1038/srep07418.

[145] L. Wang, B. Batchelor, S.D. Pillai, V.S.V. Botlaguduru, Electron beam treatment for potable water reuse: Removal of bromate and perfluorooctanoic acid, Chem. Eng. J. 302 (2016) 58–68;
(a) L.G. Forni, V.O. Mora-Arellano, J.E. Packer, R.L. Wilson, Nitrogen dioxide and related free radicals: Electron-transfer reactions with organic compounds in solutions containing nitrite or nitrate, J. Chem. Soc. Perkin Trans. 2 (1986) 1–6.

[146] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol. 36 (2006) 1–84.

[147] A. Santos, S. Rodriguez, F. Pardo, A. Romero, Use of Fenton reagent combined with humic acids for the removal of PFOA from contaminated water, Sci. Total Environ. 563–564 (2016) 657–663.

[148] H. Hori, Y. Nagaoka, M. Murayama, S. Katsuna, Efficient decomposition of perfluorocarboxylic acids and alternative fluorochemical surfactants in hot water, Environ. Sci. Technol. 42 (2008) 7438–7443.

[149] S. Park, L.S. Lee, V.F. Medina, A. Zull, S. Waisner, Heat-activated persulfate oxidation of PFOA, 6:2 fluorotelomer sulfonate, and PFOS under conditions suitable for in-situ groundwater remediation, Chemosphere 145 (2016) 376–383.

[150] S. Yang, J. Cheng, J. Sun, Y. Hu, X. Liang, Defluorination of aqueous perfluorooctane-sulfonate by activated persulfate oxidation, PLoS One 8 (2013) e74877.

[151] P. Yin, Z. Hu, X. Song, J. Liu, N. Lin, Activated persulfate oxidation of perfluorooctanoic acid (PFOA) in groundwater under acidic conditions, Int. J. Environ. Res. Publ. Health 13 (2016) 602.

[152] Y. Lee, S. Lo, P. Chiueh, D. Chang, Efficient decomposition of perfluorocarboxylic acids in aqueous solution using microwave-induced persulfate, Wat. Res. 43 (2009) 2811–2816.

[153] Y. Lee, S. Lo, P. Chiueh, Y. Liou, M. Chen, Microwave-hydrothermal decomposition of perfluorooctanoic acid in water by iron-activated persulfate oxidation, Wat. Res. 44 (2010) 886–892;
(a) https://www.pca.state.mn.us/sites/default/files/pfos-report.pdf.
(b) www.conffidence.eu/wp.../OpenDay_WP1b_Llorca-poster4.pdf.

[154] B. Sun, J. Ma, D.L. Sedlak, Chemisorption of perfluorooctanoic acid on powdered activated carbon initiated by persulfate in aqueous solution, Environ. Sci. Technol. 50 (2016) 7618–7624.

[155] C.K.O. da Silva-Rackov, W.A. Lawal, P.A. Nfodzo, M.M.G.R. Vianna, C.A.O. do Nascimento, H. Choi, Degradation of PFOA by hydrogen peroxide and persulfate activated by iron-modified diatomite, Appl. Catal. B: Environ. 192 (2016)

[156] Y.H. Kim, E.R. Carraway, Dechlorination of pentachlorophenol by zero valent iron and modified zero valent irons, Environ. Sci. Technol. 34 (2000) 2014–2017;
(a) F. Fu, D.D. Dionysiu, H. Liu, The use of zero-valent iron for groundwater remediation and wastewater treatment: a review, J. Hazrad. Mater. 267 (2014) 194–205.

[157] K.J. Cantrell, D.I. Kaplan, T.W. Wietsma, Zero-valent iron for the in-situ remediation of selected metals in groundwater, J. Hazard. Mater. 42 (1995) 201–212;
(a) M. Stefaniuk, P. Oleszczuk, Y.S. Ok, Review on nano zerovalent iron (nZVI): From synthesis to environmental applications, Chem. Eng. J. 287 (2016) 618–632;
(b) W. Jiao, Y. Qin, S. Luo, Z. He, Z. Feng, Y. Liu, Simultaneous formation of nanoscale zero-valent iron and degradation of nitrobenzene in wastewater in an impinging stream- rotating packed bed reactor, Chem. Eng. J. 321 (2017) 564–571;
(c) O. Quinones, S.A. Snyder, Occurrence of perfluoroalkyl carboxylates and sulfonates in drinking water utilities and related waters from the United States, Environ. Sci. Technol. 43 (2009) 9089–9095;
(d) S. Takagi, F. Adachi, K. Miyano, Y. Koizumi, H. Tanaka, M. Mimura, I. Watanabe, S. Tanabe, K. Kannan, Perfluorooctanesulfonate and perfluorooctanoate in raw and treated tap water from Osaka, Japan, Chemosphere 72 (2008) 1409–1412;
(e) T.S. Appleman, C.P. Higgins, O. Quinones, B.J. Vanderford, C. Kolstad, J.C. Zeigler-Holady, E.R.V. Dickenson, Treatment of poly-and perfluoroalkyl substances in U.S. full-scale water treatment systems, Water Res. 51 (2014) 246–255.

[158] H. Hori, Y. Nagaoka, A. Yamamoto, T. Sano, N. Yamashita, S. Taniyasu, S. Kutsuna, Efficient decomposition of environmentally persistent perfluorooctanesulfonate and related fluorochemicals using zero-valent iron in subcritical water, Environ. Sci. Technol. 40 (2006) 1049–1054; (a) Directive 2013/39/EU of the European Parliament and of the Council, https://www.ecolex.org/details/legislation/directive-201339eu-of-the-european-parliament-and-of-the-council-amending-directives-200060ec-and-2008105ec-as-regards-priority-substances-in-the-field-of-water-policy-lex-faoc127344/; (b) K.-U. Goss, The pKa values of PFOA and other highly fluorinated carboxylic acids (vol 73, pg 2323, 1951), Environ. Sci. Technol. 42 (2008) 5032-5032; (c) D.C. Burns, D.A. Ellis, H. Li, C.J. McMurdo, E. Webster, Experimental pKa determination for perfluorooctanoic acid (PFOA) and the potential impact of pKa concentration dependence on laboratory-measured partitioning phenomena and environmental modeling, Environ. Sci. Technol. 42 (2008) 9283–9288.

[159] O.S. Arvaniti, Y. Hwang, H.R. Andersen, A.S. Stasinakis, N.S. Thomaidis, M. Aloupi, Reductive degradation of perfluorinated compounds in water using Mg-aminoclay coated nanoscale zero valent iron, Chem. Eng. J. 262 (2015) 133–139.

[160] V. Ochoa-Herrera, R. Sierra-Alvarez, A. Somogyi, N.E. Jacobsen, V.H. Wysocki, J.A. Field, Reductive defluorination of perfluorooctane, Environ. Sci. Technol. 42 (2008) 3260–3264.

[161] L.M. Colosi, R.A. Pinto, Q. Huang, W.J. Weber Jr., Peroxidase-mediated degradation of perfluorooctanoic acid, Environ. Toxicol. Chem. 28 (2009) 264–271.

[162] J.C. Cardoso, G.G. Bessegato, M.V.B. Zanoni, Efficiency comparison of ozonation, photolysis, photocatalysis and phtoelectrocatalysis methods in real textile wastewater decolorization, Water Res. 98 (2016) 39–46.

[163] S. Sarkar, S. Ali, G. Rehmann, M.B. Ray Nakhla, Degradation of estrone in water and wastewater by various advanced oxidation processes, J. Hazard. Mat. 278 (2014) 16–24.

[164] Z. Shu, J.R. Bolton, M. Belosevic, M.G. El Din, Photodegradation of emerging micropollutants using the medium-pressure UV/H$_2$O$_2$ advance oxidation process, Water Res. 47 (2013) 2881–2889;
(a) K. Yasuoka, K. Sasaki, R. Hayashi, An energy-efficient process for decomposing perfluorooctanoic and perfluorooctano sulfonic acids using dc plasmas generated within gas bubbles, Plasma Sour. Sci. Technol. 20 (2011) 034009.

[165] J.R. Bolton, J.E. Valladares, J.P. Zanin, W.J. Cooper, M.G. Nickelson, D.C. Kajdi, T.D. Waite, C.N. Kurucz, Figures-of-merit for advanced oxidation technologies: a comparison of homogeneous UV/H$_2$O$_2$, Heterogeneous UV/TiO$_2$ and electron beam processes, J. Adv. Oxid. Technol. 3 (1998) (1998) 174–181.

[166] T. Kim, S.D. Kim, H.Y. Kim, S.J. Kim, M. Lee, S. Yu, Degradation and toxicity assessment of sulfamethoxazole and chlortetracycline using electron beam, ozone and UV, J. Hazard. Mater. 227–228 (2012) 237–242.

[167] J. Wang, L. Chu, Irradiation treatment of pharmaceutical and personal care products (PPCPs) in water and wastewater: an overview, Radiat. Phys. Chem. 125 (2016) 56–64.

[168] N. Merino, Y. Qu, R.A. Deeb, E.L. Hawley, M.R. Hoffmann, S. Mahendra, Degradation and removal methods for perfluoroalkyl substances in water, Environ. Eng. Sci. 33 (2016) 615–649.

[169] T. Anumol, S. Dagninio, D.R. Vandervort, S.A. Snyder, Transformation of poly-fluori-nated compounds in natural waters by advance oxidation processes, Chemosphere 144 (2016) 1780–1787.

[170] S.J. Genuis, D. Birkholz, N. Ralitsch, N. Thibault, Human detoxification of per-fluoro-nated compounds, Public Health 124 (2010) 367–375.