

Review

# Critical Perspective on Advanced Treatment Processes for Water and Wastewater: AOPs, ARPs, and AORPs

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**Featured Application:** The application and limits of advanced oxidation, reduction, and oxidation/reduction processes to water and wastewater treatment are discussed.

**Abstract:** Emerging contaminants' presence in water, wastewater, and aquatic environments has been widely reported. Their environmental and health-related effects, and the increasing tendency towards wastewater reuse require technology that could remove to a greater degree, or even mineralize, all these contaminants. Currently, the most commonly used process technologies for their removal are advanced oxidation processes (AOPs); however, recent advances have highlighted other advanced treatment processes (ATPs) as possible alternatives, such as advanced reduction processes (ARPs) and advanced oxidation-reduction processes (AORPs). Although they are not yet widely diffused, they may remove contaminants that are not readily treatable by AOPs, or offer better performance than the former. This paper presents an overview of some of the most common or promising ATPs for the removal of contaminants from water and wastewater, and their application, with discussion of their limitations and merits. Issues about technologies' costs and future perspectives in the water sector are discussed.

**Keywords:** water treatment; wastewater treatment; advanced oxidation processes; advanced reduction processes; advanced oxidation-reduction processes; emerging contaminants

## 1. Introduction

The detection of emerging contaminants in the environment and in waste and supply water is increasing due to the ever-growing role of chemistry in industrial production and to advancements in analytical technology [1–3]. These, commonly addressed as a group under the term of 'contaminants of emerging concern' (CECs), are diverse and ubiquitous, frequently lumped into categories that describe their purpose, use, or other characteristic (Table 1) [4]. These contaminants could negatively affect water uses, human health, and ecosystem integrity, and cause the spread of antibiotic-resistant bacteria due to low persistent doses of residual pharmacological principles in human and animal excreta [5]. It was estimated that, just in Germany, about 16,000 tons/year of discarded pharmaceutical and personal care products (PPCPs) are flushed down toilets, or disposed of in household waste, eventually finding their way into natural waters [6]. Online measurement of these pollutants in the environment, and especially in water supply systems, is a very sensitive issue, which has not yet been satisfactorily addressed [7]. The increasing tendency towards wastewater reuse, both for non-potable and drinking uses [8], is prompting the development of more robust water and wastewater treatment through increasingly sophisticated multiple barrier treatment (MBT) schemes [9]. However, even in current state-of-the-art wastewater treatment plants (WWTPs), these contaminants may be removed but not degraded to satisfactory levels: Many current advanced processes, for example, adsorption, ion exchange, reverse osmosis, and membrane nano/ultra-filtration, only concentrate contaminants, without degrading or ultimately eliminating them, leaving this step to a subsequent

phase. Even with the use of advanced degradation technologies, these compounds may only be partly transformed, possibly into hazardous byproducts or intermediates. Furthermore, their transformation pathways may often still be undetermined [10]. Several studies have shown that many compounds subject to biological, chemical, or surface processes are not completely degraded (mineralized) but may end up as transformation byproducts in the effluent, or accumulated within the residual solid phase (i.e., excess sludge) [11–13]. These residuals, then, require additional processing to avoid byproducts' environmental dispersion. Incomplete removal (even in  $\mu\text{g/L}$ - $\text{ng/L}$  concentration ranges) of these contaminants has been related to potential long-term adverse impacts on the environment and human health.

**Table 1.** Common CEC classes (elaborated from [4]).

CEC Class	Example Compound	Definition/Use
Antibiotics	Tetracycline, Erytromycin	Medication. Inhibits or stops bacterial growth
Antimicrobials	Triclosan	Biochemical. Kill/inhibit microorganisms, incl. bacteria and fungi
Detergent metabolites	Nonylphenol	Chemical, formed by break-down of detergents by WW treatment of environmental processes
Disinfectants	Alcohols, Aldehydes, oxidizing agents	Chemicals used on non-living surfaces to destroy/neutralize/ inhibit growth of disease-causing microorganisms.
Disinfection By-Products (DBPs)	Chloroform, Nistosodimethylamine (NDMA)	Chemicals resulting from interaction of organic matter with disinfection agents (e.g., chloride) in water
Estrogenic Compounds	Estrone, Estradiol, Nonylphenol, Bisphenol A	Natural/synthetic chemicals that can elicit an estrogenic response
Explosives	TNT, RDX	TNT (2,4,6-trinitrotoluene), best known as an explosive material, is sometimes used also as reagent in chemical synthesis. RDX (cyclo trimethylenetrinitramine) is also a powerful explosive often used in mixtures with plasticizers
Fire and Flame retardants	Polybrominated Diphenyl Ethers (PBDEs)	Coatings that inhibit/resist the spread of fire
Fragrances	Galaxolide	Chemicals imparting sweet or pleasant odor
Insect repellents	DEET (N,N-diethyl-meta-toluamide)	Chemicals applied to skin or other surfaces to repel insects from that surface
PAHs (Poly-aromatic hydrocarbons)	Benzo(a)pyrene, Fluoranthene, Naphthalene	Chemical substances found in environment as result of incomplete burning of carbon-containing materials (fossil fuels, wood, garbage, etc.)
Personal Care Products (PCPs)	Para-hydroxybenzoate	Chemicals used in many personal items including toiletries and cosmetics
Per-and poly-fluoroalkyl substances	PFASs, PFOSs and PFOAs	Used in emulsion polymerization to produce fluoropolymers, characterized by high resistance to solvents, acids, and bases (e.g., polytetrafluoroethylene, commercially known as Teflon).
Pesticides and insecticides	Permethrin, Fenitrothion, Bacillus thuringiensis israelensis (B.t.i.)	Chemical substances/microbiological agents that kill/incapacitate/prevent pests from causing damage
Pharmaceuticals	Fluoxetine (Prozac), Carbamazepine, Diphenhydramine	Chemicals used in the prevention/treatment of physiological conditions
Plasticizers	Diocetyl Phthalate	Additives that increase plasticity or fluidity of materials

Table 1. Cont.

CEC Class	Example Compound	Definition/Use
Reproductive hormones	Dihydrotestosterone (DHT), Progesterone, Estrone, Estradiol	Chemicals, usually steroids, that stimulate reproductive functions
Solvents	Ethanol, kerosene	Chemical solutions (other than water) capable of dissolving other substances
Steroids	Cholesterol, Coprostanol, Estrone, Progesterone	Fat-soluble organic compounds with characteristic molecular structure, including natural and synthetic hormones
Surfactants	Sodium Lauryl Sulfate	Substances affecting the surface of a liquid

Most currently used water and wastewater process technologies, including state-of-the-art advanced oxidation processes (AOPs), have some, and occasionally significant, technological drawbacks: Almost all require extended process time (up to several hours) to achieve destruction of contaminants and often they require costly addition of chemicals or catalyzers to enhance treatment performance. This paper presents a review of some of the most common AOP process technologies used for the removal of emerging contaminants from water and wastewater, and introduces discussion about two lesser-known classes of processes, advanced reduction processes (ARPs) and advanced oxidation-reduction processes (AORPs), that may offer a similar or better performance than the former.

## 2. Advanced Treatment Processes for Emerging Contaminants

The classes of processes examined below are termed advanced treatment processes (ATPs), since they are capable of achieving degradation of specific constituents in solution, not normally achieved by other treatment options. This class covers all those unit operations that do not act on mechanical or biological principles: Coagulation-flocculation-precipitation, stripping, filtration (all types), ion exchange, absorption, electroflotation, biological and bioelectrochemical methods, etc. They may, however, be combined with these and other treatment units to improve overall pollutants' removal efficiency, i.e., in MBT schemes [9]. ATP in combination with common or modified biotreatment technologies can be the key for successful emission control for many CECs, as in many cases, they significantly increase the biodegradability of recalcitrant or inhibitory pollutants, as discussed later.

One crucial factor for assessing the feasibility of a particular treatment process is represented by the kinetic rates of the reactions involved in the degradation of target compounds. Advance treatment technologies make use of highly reactive minimally selective reagents that will achieve transformation of contaminants in solution into simpler (e.g., partial decomposition of non-biodegradable organic pollutants into biodegradable intermediates) or innocuous (e.g., mineralization to CO<sub>2</sub>, water, and residual elements) products, even though the formation of hazardous byproducts cannot be excluded a priori.

Advanced oxidation processes are aqueous phase oxidation methods, investigated and developed since the 1970s, and well established in the water sector, as they are currently considered the state-of-the-art in commercially available advanced treatment processes for many contaminants [14]. AOPs are based on the generation of highly reactive radicals (predominantly OH, hydroxyl radical) for the oxidation of organic pollutants within a solution treated by means of different activation processes (ultraviolet photolysis, Fenton processes, electrochemical oxidation, sonochemical processes, microwave, supercritical water and wet air oxidation, and others), often combined with chemicals (e.g., O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>) and/or catalysts (e.g., TiO<sub>2</sub>) [15,16]. OH is among the strongest oxidants applicable in water processes, and can unselectively oxidize virtually any susceptible compound present through the following basic pathways: Radical addition, hydrogen abstraction, electron transfer, and radical combination. The chain of reaction that is generated leads to further generation of reactive species, such as H<sub>2</sub>O<sub>2</sub> and super oxide ( $\cdot\text{O}_2^-$ ). The mechanisms of radical generation in the most common

AOPs for wastewater treatment were summarized in other works [14,17]. Figure 1 summarizes the various technologies available in the AOP and in other ATP classes. AOPs have been and are still widely researched: A non-comprehensive bibliography search counted over 20,000 published works on their application for the removal of pharmaceutical residues, endocrine disruptors, natural organic matter, bio-recalcitrant organics, generic and specific pollutants, and pathogens from water and wastewater [11–32].

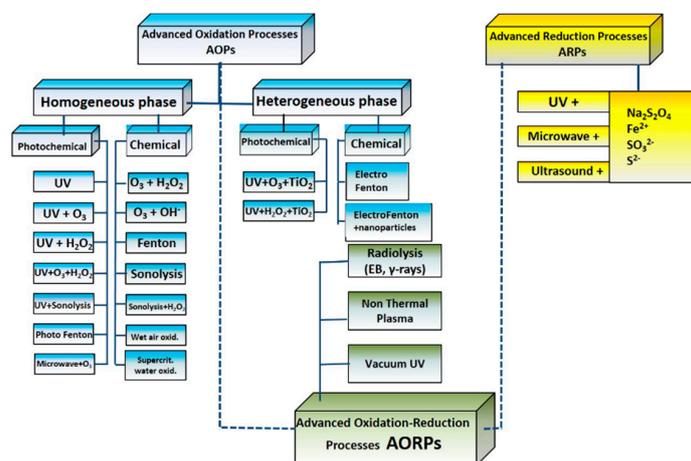


Figure 1. Various process technologies in the ATP realm.

AOPs promote the degradation of organic compounds into simpler molecules: Partial decomposition of non-biodegradable organics may lead to more biodegradable intermediates or, more rarely, to their mineralization and to the destruction of pathogenic organisms, by the effect of strong oxidants. The oxidation potential is hence the strength and, at the same time, the limit of AOPs: Some contaminants, such as, for example, chlorinated and brominated compounds, are poorly or not degraded at all by oxidation.

While AOPs and their applications in the water sector are well known, advanced reduction processes (ARPs) are a recently emerged class of processes combining activation methods similar to those used by AOPs (UV, ultrasound, microwave) and reductive agents (sulfite, ferrous iron, sulfide, dithionite) to generate reactive radicals capable of strong reducing reactions (hydrated electrons,  $e^-_{aq}$ , hydrogen  $\cdot H$ , and sulfite radicals  $\cdot SO_3^-$ ). These, unlike those generated by AOPs, can easily degrade oxidized contaminants in solution [33,34]. Reductants are selected for ARPs based on the applied activation method's capacity to produce reducing radicals, or other effective reducing agents.

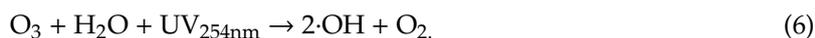
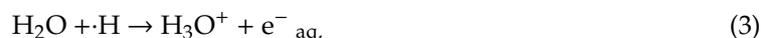
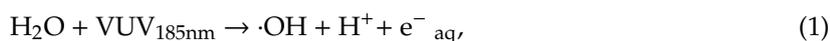
Dithionite (i.e., sodium hydrosulfite,  $Na_2S_2O_4$ ), for example, is a water-soluble salt used as reducing agent in aqueous solutions. By cleaving the S-S bond upon absorption of 315-nm UV radiation, dithionite can be broken into two sulfur dioxide radical anions ( $\cdot SO_2^-$ ), a strong reductant. Additionally, sulfite ( $SO_3^{2-}$ ), upon irradiation, will react to create a sulfite radical anion ( $\cdot SO_3^-$ ) and  $e^-_{aq}$ , also a strong reductant, while the sulfite radical could act indifferently as an oxidant or reductant, accepting an electron to form sulfite or donating one to form sulfate. Sulfide,  $S^{2-}$ , adsorbs UV light at 230 nm, promoting the formation of hydrogen in solution, similarly to ferrous iron.

While the chemical mechanisms of reducing radical formation are fairly well known, little research has been conducted so far on the application of these processes to water treatment and contaminant degradation. Preliminary results [33] have demonstrated that ARPs can degrade a wide variety of contaminants, including: Perchlorate (a highly oxidized chlorine form normally difficult to reduce) [35], 1,2 dichloroethane [36], perfluorooctanoic acid (PFOA, a synthetic, difficult to treat, fluorinated organic acid) [37], 2,4-dichlorophenol (2,4-DCP), a chlorinated highly toxic phenol derivative used as herbicide preparation intermediate [38], several halogenated compounds [39], nitrate (a ubiquitous groundwater contaminant that can be removed by chemical or electrochemical methods) [40,41], and metals (e.g., arsenic, selenium) [42]. Despite these encouraging results, however, this technology has not

reported real-scale applications so far. Considering the fact that some CECs can only be removed by strong reduction reactions, these processes will likely gain greater consideration in the near future.

Advanced oxidation-reduction processes (AORPs), a third class of ATPs, combine both types of radical reactions to directly degrade contaminants. They are perhaps the most interesting development in advanced treatment technology. Concurrently generated radicals carry out simultaneous oxidation and reduction reactions, achieving accelerated destruction of a wide range of contaminants [43]. AORPs are chemical-less high-rate energy-efficient processes, with a wide applicability range. AORPs may be activated by high-energy inputs, such as photoionization (Vacuum UV -VUV- with irradiation at 185 nm and 254 nm) [44], non-thermal plasma electric discharges [45], or ionizing radiations [46].

In the VUV process, photoionization and homolysis of water molecules occur with the absorption of high-energy photons in water, according to the following reactions:



In non-thermal plasma processes (NTPs), high-voltage electrical pulses generate a corona discharge, which in turn excites electrons in the air above a liquid solution with an ionization effect, producing singlet oxygen atoms, which generate ozone and hydroxyl radicals in the underlying water layer [47]. In other alternative NTP configurations, dielectric barrier discharges, corona discharges in aerosols or in the water matrix itself, are applied without substantial differences in the products of the reactions sequence previously indicated (Equations (1)–(6)). NTP technology is confined to thin-layer low-flow applications, due to the limited water penetration of excited electrons. An example of a pilot-scale NTP unit is schematized in Figure 2. This “electrode-to-plate” scheme consists of two units: In the first, water flowing in a thin film (~5 mm) over a ground electrode (anode) is exposed to high-voltage pulses from a carbon fiber electrode (cathode). Electric pulses with a frequency in the range 500–1000 Hz, at maximum voltage of 8.0 kV, 100 A current, are released by a generator. Upon leaving this reactor, water enters an ozone contactor, where it is mixed with ozone-rich air (generated in the previous reactor’s headspace). Other configurations, such as wetted-wall or falling film reactors, have been used experimentally [48,49].

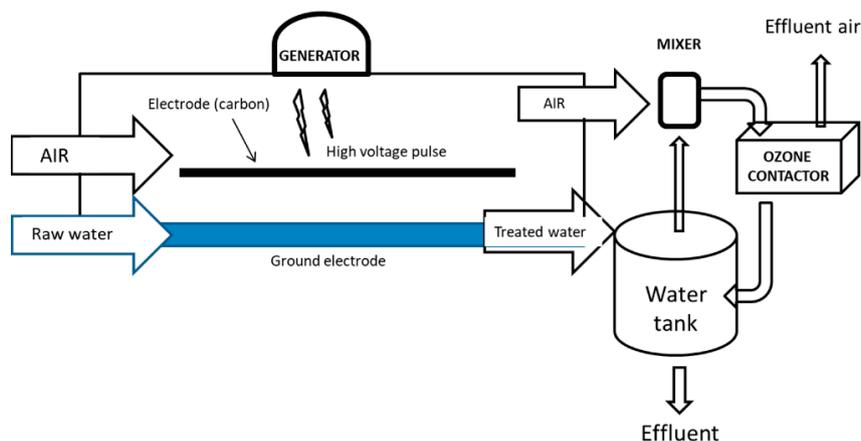


Figure 2. NTP “electrode-to-plate” reactor scheme described in [45].

The most common AORP technology, however, operates through the use of ionizing radiations (Figure 3). Ionizing radiation is defined as any electromagnetic wave (at a frequency higher than  $10^{17}$  Hz) carrying sufficient energy to ionize or remove electrons from an atom. Unlike non-ionizing radiation (e.g., radiofrequency, infrared, and UV), with the kinetic energy of particles (photons, electrons, etc.) too small to generate charged ions when passing through matter, the energy of ionizing radiation particles can form ions by losing electrons (i.e., ionize) from target atoms. Two types of electromagnetic waves can do that: X-rays, and  $\gamma$ -rays, emitted by radionuclides, such as  $^{60}\text{Co}$  and  $^{137}\text{Cs}$ . The same effect may be achieved by particulate radiation, consisting of subatomic particles (electrons, protons, etc.) carrying energy in kinetic form, such as those emitted by electron accelerators (electron beam, EB). These types of ionizing sources do not have the capability of making their targets radioactive, although they can break chemical bonds and damage DNA. Neutron radiation, such as that emitted from nuclear fission, on the other hand, is not able to directly ionize atoms (due to its lack of charge) but can make them unstable, turning materials radioactive, and must not be confused with the former.

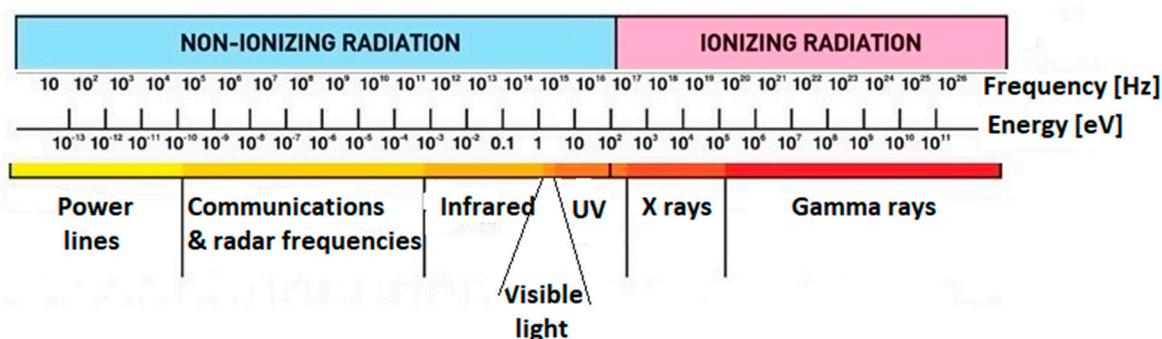
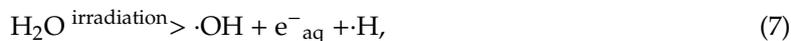


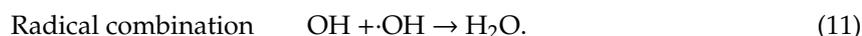
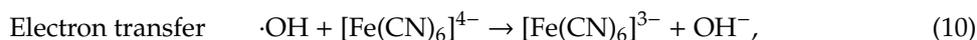
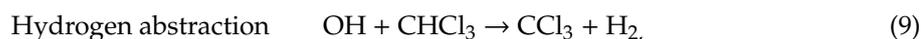
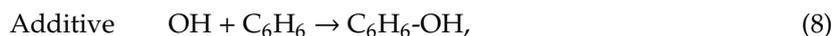
Figure 3. Non-ionizing and ionizing radiation ranges: frequency and energy.

Ionizing irradiation therefore results in the cleavage of one or more molecular bonds, dissociating the exposed molecules (radiolysis) without radioactivity induction. The process differs from “conventional” AOPs, for instance, photolysis, where lower energy UV sources are used in conjunction with chemicals or catalyzers. Irradiation of a dilute (total solute concentration lower than 10%) solution with ionizing radiation instantaneously ( $t \leq 10^{-12}$  s) splits water molecules into strongly oxidative hydroxyl radicals ( $\cdot\text{OH}$ ), and strongly reductive species ( $e^-_{\text{aq}}$ ,  $\cdot\text{H}$ ), in addition to other species, such as  $\text{H}^+$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_3\text{O}^+$ , and  $\cdot\text{O}$ , without chemical or catalyst addition [50].

The yields of reactive species formed in this process are expressed by the G-value, a measure of the number of molecules formed/consumed per unit of absorbed energy. For example, in the simplest water radiolysis reaction:



the *G-Values* of the generated species are 0.28, 0.28, and 0.06, respectively, much higher than in other conventional AOPs [51]. However, the possible reaction mechanisms of hydroxyl radicals are the same as those in AOPs, i.e.,:



Gamma rays are still used in many experimental radiolysis studies, but, due to their high organic matter penetration, they require strong precautions and shielding protection to avoid harm to living cells. Furthermore,  $\gamma$ -ray sources are highly radioactive isotopes requiring periodical replacement and special (and costly) high-risk handling procedures. The efficiency of a  $\gamma$ -irradiation process depends on the

“age” of the radiation sources, which determines the deliverable dose. EB technology, instead, does not rely on constantly decaying isotopes but on electromagnetic particle generation, and can therefore be turned off when the process is not needed, much like a television set. Old cathodic tube television sets were actually quite similar, in principle, but at lower energy, to modern electron accelerators (Figure 4). Safety and practical considerations have therefore contributed to widespread industrial adoption of EB, commercially used in many manufacturing processes requiring an improvement of the material properties by molecular modification (e.g., submarine data cables, membranes grafting, medical hydrogels), sterilization or disinfection (including food processing), and environmental areas (industrial flue gas treatment, sludge processing, textile effluents processing) [52]. However, despite the advantages of this practical process, few full-scale water and wastewater treatment applications have been reported to date [53].

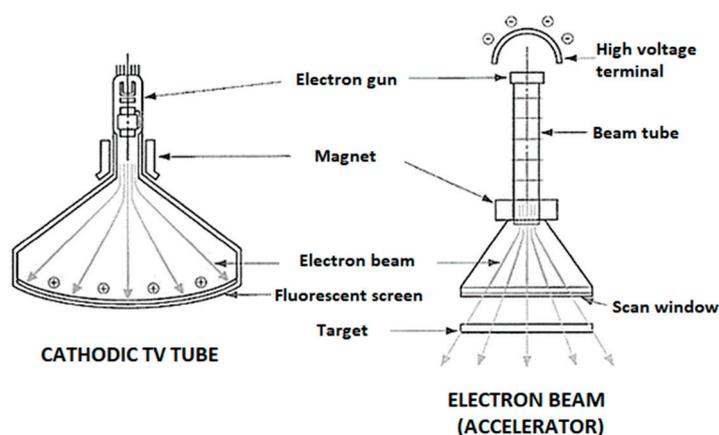


Figure 4. Cathodic tube television set (left) vs. EB (right).

Studies on radiolytic processes for water treatment date back to the 1950s, when this technology was initially tested on domestic and industrial wastewater [51]. Since at that time CECs had not yet been addressed nor identified, treatment of organic matter solely in terms of COD, though successful, immediately appeared anti-economical, given the availability of cheaper established biological processes, and the high cost of irradiation equipment at the time. Some applications were also attempted with the use of X-rays [54], which have not been followed up further, due to the low specific efficiency of this source. While  $\gamma$ -rays are still often used in laboratory studies, optimal irradiation dose-rates can be achieved more easily, in practice, with EB systems. The dose-rate parameter, one of the main indicators for process applicability, and the process time are in fact much more favorable for EB irradiation than for  $\gamma$  or X-rays, as reported in Table 2. Dose-rate determines the process contact time for an established irradiation dose, as indicated in the table: A dose of 1 kGy represents a relatively low value used, for example, to achieve wastewater disinfection, and is in the low range of those commonly used in the pretreatment of foods in industrial distribution applications. It should also be noted that although 1 Curie (37 GBq in SI units) corresponds to a very high value of radioactivity, it still generates a low dose-rate even compared to small EB units.

**Table 2.** Achievable dose-rates and process contact times of different radiation sources.

Radiation Source Rated Strength	Energy [kW]	Calculated Dose-Rate [MGy h <sup>-1</sup> ]	Process Contact Time for 1 kGy Dose [s]
<i>X-ray</i>			
250 kV	$0.5 \times 10^{-8}$	$1.8 \times 10^{-5}$	$2.0 \times 10^5$ (=55.6 h)
<i><sup>60</sup>Co <math>\gamma</math>-source (Ci = Curie)</i>			
$0.5 \times 10^6$ Ci*	0.18	0.65	5.5
$1.0 \times 10^6$ Ci*	0.36	1.30	2.8
<i>Electron Beam (MeV = <math>10^6</math> electron-Volt)</i>			
1 mA, 1 MeV	2	$7.2 \times 10^3$	0.2
10 mA, 10 MeV	100	$3.6 \times 10^5$	$10^{-5}$
50 mA, 10 MeV	500	$1.8 \times 10^6$	$2 \times 10^{-6}$

### 3. Applications and Limits of ATPs in Water and Wastewater Treatment

While oxidation is considered a key removal mechanism for many compounds, especially when achieved by strong oxidants, such as chlorine, ozone, or AOPs, as discussed in the previous section, not all CECs are susceptible to destruction by it. Table 3 summarizes selected organic compounds' removal rates in solution by different radicals, and the relative importance of each reactive species in the process. It can be seen that several compounds (e.g., halogenated substances) respond poorly to oxidation but are well degraded by reduction. Others, such as, for example, trihalomethanes, are not degraded at all by oxidation, and seem to be poorly degraded also by reduction, although recent reports claimed an 82% total THMs removal by means of an AORP VUV/UV-C process [55] and complete degradation by a UV-C/free chlorine process [56].

**Table 3.** Organic compounds' removal rates by different radicals, and the relative importance of each species in the process (modified from [50]).

Compound	Bimolecular Reaction Rate Constants [10 <sup>9</sup> M <sup>-1</sup> s <sup>-1</sup> ]			Relative Importance of Radical Species in Compound Removal (%)		
	·OH	e <sup>-</sup> <sub>aq</sub>	·H	·OH	e <sup>-</sup> <sub>aq</sub>	·H
<i>Compounds highly susceptible to oxidation</i>						
Ethylbenzene	7.5	-	-	100	0	0
DBCP	0.73	-	-	100	0	0
NDMA	0.33	-	-	100	0	0
Atrazine	2.6	-	-	100	0	0
Simazine	208	-	-	100	0	0
$\alpha$ -Xylene	6.7	-	2	94	0	6
Toluene	5.1	0.011	2.6	90	~0.1	~10
<i>Compounds highly susceptible to reduction</i>						
Chloroform	0.054	11	0.073	0.4	99	0.1
Ethylenedibromide	0.26	14	NF	2	98	0
Bromoform	0.11	26	1.9	0.5	97.5	2
<i>Other compounds</i>						
CHBrCl <sub>2</sub>	-	21	-	0	10	0
CHBr <sub>2</sub> Cl	-	20	-	0	10	0

The effectiveness of an ATP depends on the reactivity of the radical species generated. This is indicated by the redox potential, a measure of a species' tendency to reduce or oxidize, measured in volts (V). The standard oxidation-reduction potential,  $E_0$ , is defined relative to a standard reference hydrogen electrode (SHE), which is arbitrarily given a potential of 0 V. A high positive value of  $E_0$ ,

therefore, indicates a high capacity to oxidate; a high negative value, on the contrary, a high capacity to reduce. Table 4 compares the  $E_0$  values of different radical and commonly used chemical reagents.

**Table 4.** Oxidation and reduction potential of different radical and commonly used reagents.

Reactive Species	Generated by			Standard Redox Potential, $E_0$ (V)		
	AOP	ARP	AORP			
Hydroxy radical ( $\cdot\text{OH}$ )	X		X	2.86	↑	↑
Oxygen atom ( $\cdot\text{O}$ )	(X)		(X)	2.42		
Ozone molecule ( $\text{O}_3$ )	(X)		(X)	2.07	A	
Peracetic Acid	=	=	=	1.81	O	
Hydrogen peroxide ( $\text{H}_2\text{O}_2$ )	X		X	1.78	P	
Hypochlorite ( $\text{HClO}$ )	=	=	=	1.63	↓	A
Chlorine ( $\text{Cl}_2$ )	=	=	=	1.36		O
Oxygen molecule ( $\text{O}_2$ )	=	=	=	1.23		R
Ferric Iron ( $\text{Fe}^{3+}$ )	=	=	=	0.77	↓	P
<b>Hydrogen (H)</b>	=	=	=	<b>0</b>	↑	
Ferrous Iron ( $\text{Fe}^{2+}$ )	=	=	=	-0.44	A	
Sulfur dioxide radical ( $\cdot\text{SO}_2^-$ )		X	X	-0.66	R	
Hydrogen radical ( $\cdot\text{H}$ )	=	X	X	-2.3	P	
Hydrated electron ( $e^-_{\text{aq}}$ )		X	X	-2.87	↓	↓

In addition to the  $E_0$  potential, reaction rates are paramount for the efficiency of process development: Literature-reported reaction rate constants determined for different organic compounds reacting with ozone and hydroxyl radicals show that the latter originates rates eight to nine orders of magnitude ( $10^8$ – $10^9$ ) faster than the former. Hence, a process generating large amounts of OH radicals will be much faster than one based on ozone, or on lower concentrations of hydroxyl radicals, although the mere oxidative potential of the two basic species is not that different, as seen in Table 4.

In radiolytic processes, the kinetics is determined by the reaction order and the values of rate constants for specific reactions. The irradiation process yield is commonly expressed by G values, i.e., the number of molecules of reactant consumed per 100 eV of energy absorbed, the value of the dose constant,  $d$ , and the dose magnitude required for 50% ( $D_{0.5}$ ) or 90% ( $D_{0.9}$ ) decomposition of chemical solutes [57]. *G-values*, commonly reported in the applied radiolysis literature, however, are not useful in practice to predict the required decomposition dose for a compound, since this depends on its actual concentration in solution, while G values are often calculated according to a linear kinetics approximation, not fully representative of the actual reaction. The dose constant,  $d$ , represents decomposition rates as a function of the absorbed radiation dose, calculated as the slope of the line obtained from plotting  $\ln(C_D/C_0)$  against the absorbed dose. This is considered a more reliable parameter than the former, because it represents the entire irradiation process. Large values of  $G_0$  and  $d$  indicate high pollutant decomposition yields; their increase corresponds to a lower required dose for pollutant decomposition. Experimental dose-constants serve as a first approximation of the irradiation required to remove a major component compound from a multi-component solution; however, for these and other considerations exposed below, the actual required dose depends on the overall matrix composition, and on compounds' decomposition pathway(s). Dose estimates can also be used for a preliminary evaluation of treatment costs (equipment size and energy requirements).

An important factor affecting the efficiency of all ATPs is the composition of the original water matrix, which may contain natural compounds acting as radical scavengers. Reaction rates involving scavengers may be of the same magnitude as those involving target pollutants; as a result, the pollutant decomposition yield in real conditions may significantly differ from that assessed in a pure solution. Some examples of scavenger species, typically occurring in natural waters and wastewater, are summarized in Table 5, together with the rate constants of their reaction with the main radical species. In addition to those reported in the table, the presence of other scavengers in wastewater

may include both organic (e.g., humic and fulvic acids, natural organic matter—NOM, aminoacids, proteins, carbohydrates) and inorganic species (e.g., sulfide, bromide).

**Table 5.** Scavenger molecules' removal rates by different radicals (data from [50]).

Scavenger	Bimolecular Reaction	Bimolecular Reaction	Bimolecular Reaction
	Rate Constants [10 <sup>9</sup> M <sup>-1</sup> s <sup>-1</sup> ]	Rate Constants [10 <sup>9</sup> M <sup>-1</sup> s <sup>-1</sup> ]	Rate Constants [10 <sup>9</sup> M <sup>-1</sup> s <sup>-1</sup> ]
	OH	e <sup>-</sup> <sub>aq</sub>	H
O <sub>2</sub>	-	19	<0.001
HCO <sub>3</sub> <sup>-</sup>	0.0085	<0.001	<0.001
CO <sub>3</sub> <sup>2-</sup>	0.39	0.00004	-
Cl <sup>-</sup>	3	<0.001	<0.00001
NO <sub>2</sub> <sup>-</sup>	11	0.0035	0.71
NO <sub>3</sub> <sup>-</sup>	-	9.7	0.0014
Dissolved Organic Carbon (DOC)	0.2	-	-

As a consequence of the introduction of ATPs in water and wastewater treatment, the generation of by-products from CECs transformation, water or wastewater original matrix oxidation, or reactions with disinfecting chemicals may be observed. Some of these by-products may be proven or potential carcinogenic, or carcinogenic precursor compounds, or induce otherwise undesired contamination if released into the environment. This may occur when insufficient applied oxidation or reductants doses do not result in complete mineralization of the target pollutants. For example, UV irradiation alone is considered the least effective AOP for organic contaminants' removal. An indication that this process cannot be considered as a feasible standalone process was shown in a study proving that, while it could remove 50–80% of targeted antibiotics, it required doses 100 times greater than those required for disinfection alone to achieve this target. This would be highly expensive, and such high doses unpractical to deliver [58]. Preference should therefore be given to processes with a high radical yield and reaction rates, with reduced process contact time, and in which doses could be rapidly adjusted, when needed. In addition to the greater radical generation capacity, the achievable EB dose-rates are about 100 times higher than a gamma's source, requiring very short irradiation exposure.

The literature on radical reactions in water solutions is established [34], with works on the kinetics of decomposition of various types of environmental pollutants. However, studies have mostly been carried out on single-component synthetic solutions. Prediction (modeling) of specific pollutant's degradation in pure monocomponent solutions can be achieved in most cases by using reaction rate constants as a function of the solute concentration, pH, and operational conditions, but the influence of the actual solution matrix on the process can be determined, to date, only experimentally. Hence, ATP application cannot be based solely on reaction yield calculations but must be empirically tested in real conditions. While most AOPs and ARPs require the addition of chemical substances and/or catalyzers in order to increase the intensity of the reactions, in radiolytic processes (especially with EB technology), this is not strictly necessary. However, in the presence of external additives, which interact with radiolytic reaction products, increased radical generation may occur. For example, N<sub>2</sub>O added to an irradiated solution exhibits fast reactivity with both e<sup>-</sup><sub>aq</sub> and ·H, converting the former to ·OH.

Studies showed that oxidants, such as hypochlorite (NaOCl) [59] or ozone [60], added to irradiated solutions could significantly enhance process yields. When irradiation is carried out in air-saturated solutions, ·O<sub>2</sub><sup>-</sup> and ·HO<sub>2</sub> radicals are present, as a result of the oxygen reaction with e<sup>-</sup><sub>aq</sub> and ·H. H<sub>2</sub>O<sub>2</sub>'s presence, which reacts with those radicals, could be an additional source of hydroxyl radicals, although excessive peroxide concentrations may act as scavengers. Hydrated electrons predominate when irradiated neutral solutions are saturated with N<sub>2</sub> or Ar gas, while at pH < 2, ·H radicals predominate. Due to technological reasons, the most practical process modification to increase the concentration of hydroxyl radicals in irradiated solutions is the moderate addition of O<sub>3</sub> or H<sub>2</sub>O<sub>2</sub>.

### 3.1. Applications of ATPs in Water and Wastewater Treatment

During the last decade, a dramatic rise in ATPs research, development, and applications was observed, due to increasing concerns about CECs' presence in water and wastewater, and to the increasing diffusion of water reuse projects for high-quality use [8]. While ozonation, activated carbon adsorption, and membrane filtration processes are, at the moment, the most common consolidated processes for advanced wastewater treatment [61], none of them are technically defined as a proper ATP. In fact, ozone alone in pure water does not generate radicals, unless combined with UV or peroxide, although studies on the side reactions of ozone with phenols or amine groups show its  $\cdot\text{OH}$  generation potential in the presence of dissolved organic matter (DOC). Ozone doses  $\geq 0.25$  g  $\text{O}_3$ /g DOC were shown to be sufficient to remove at least 80% of some CECs with high ozone reactivity in different wastewater treatment plant effluents [62]. For this reason, wastewater effluent ozonation could be classified as an AOP under specific circumstances [63]. Ozone-resistant compounds include pesticides (e.g., prometon, aldicarb), aromatic compounds, and chlorinated solvents [64].

Since UV irradiation alone is, as mentioned, the least effective AOP process in CECs removal, its combination with photocatalysis was tested, using  $\text{TiO}_2$  as the catalyst at a concentration between 0.2 and 2 g  $\text{TiO}_2$ /L, to enhance free hydroxyl radical formation. This approach removed endocrine-disrupting compounds between 12 and 99%, requiring contact times between 0.5 and 8 h [65]. Photocatalysis also showed bisphenol A (BPA) removal up to 99% with a process time up to 140 min, with a mineralization ratio of just 40% (the other 60% consisting of intermediate by-products of an undetermined nature). Reducing the contact time to 20 min, conversion was reduced to 35%, with a 10% mineralization fraction only [66]. UV can also be combined with other oxidants, such as  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ , to increase the process effectiveness. Wang and Xu carried out a wide review of AOP applications in the treatment of water from various sources, as summarized in Table 6 [18]. An updated review was recently published by Cuerda-Correa et al. [67].

**Table 6.** Application of AOPs for the removal of different types of compounds (data from [18]).

Contaminant	Type of Process	Remarks/Results
<i>Aromatic compounds</i>		
Phenol	Ultrasound + $\text{O}_3$ UltraSound + $\text{Fe}_2\text{O}_3/\text{SBA}-15$ + $\text{H}_2\text{O}_2$	Complete elimination of TOC 30% TOC degradation @584 kHz, with 0.6 g/L SBA-15 catalyst
<i>p</i> -Chlorophenol	$\text{O}_3$	95% <i>p</i> -chlorophenol, 26% DOC removed after 9 min
4-Chloro-3-methyl phenol	Anodic oxidation (Ti/SnO <sub>2</sub> -Sb/PbO <sub>2</sub> anode)	Complete 4-chloro-3-methyl phenol removal after 90 min, 49% TOC removal after 8 h
Nitrobenzene	Heterogeneous Catalytic ozonation (Cu-cordierite + $\text{O}_3$ )	77.9% nitrobenzene, 62.3% TOC removed in 20 min
<i>p</i> -Nitrophenol	Anodic oxidation (Ti/B-doped diamond BDD, Ti/SnO <sub>2</sub> -Sb/PbO <sub>2</sub> , Ti/SnO <sub>2</sub> -Sb anodes) Sono-Fenton	TOC removal 98% in Ti/BDD anode cell with applied charge of 3.2 Ah/L 66.4% degradation observed for 0.5% <i>p</i> -nitrophenol concentration ( <i>w/v</i> )
Nitrophenols	Anodic oxidation (Ti/Bi-PbO <sub>2</sub> anode)	Degradation efficiency in the order: 2,6-dinitrophenol > 2,5-dinitrophenol > 2,4-dinitrophenol > 2,4,6-trinitrophenol
2,6-dimethylaniline	Homogeneous Fenton	Nearly complete degradation was after 10 min
2,4-Dinitrotoluene	Homogeneous catalytic ozonation (Mn <sup>2+</sup> + $\text{O}_3$ + oxalic acid)	65% degradation in 15 min

Table 6. Cont.

Contaminant	Type of Process	Remarks/Results
2,4,6-trinitrotoluene	Electro-Fenton	Nearly complete TOC mineralization
4-Chlorobenzoic acid	Electrolysis-ozonation	Complete degradation after 30 min
Aniline, nitrobenzene, 4-chlorophenol	Photoelectro-Fenton (electrolysis and UVA)	Nearly complete mineralization after 50 min
<i>Dyes</i>		
Diacryl Red X-GRL	Photolysis	70% degradation in 5 h
CI Reactive Yellow 145	UV/O <sub>3</sub>	80% TOC removal in 2.5 h with 175 W UV irradiation
Rhodamine B	UV/H <sub>2</sub> O <sub>2</sub>	73% decoloration achieved
CI Reactive Black 5	Photocatalysis (UV + SrTiO <sub>3</sub> /CeO <sub>2</sub> )	Complete decolorization after 120 min, 57% TOC removal in 5 h at pH = 12.0
Acid Orange 7	Photocatalysis (UV/TiO <sub>2</sub> )	90% reduction after 4-h
CI Direct Red 23	Ultrasound/O <sub>3</sub>	98% removal after 1 min
CI Reactive Blue 19	Ultrasound/O <sub>3</sub>	65% TOC removed in 2 h
Crystal violet	Homogeneous Fenton (Fe <sup>2+</sup> /Fe <sup>3+</sup> + H <sub>2</sub> O <sub>2</sub> )	Complete degradation after 10 min at pH = 3
Orange II	Heterogeneous Fenton (FeVO <sub>4</sub> + H <sub>2</sub> O <sub>2</sub> )	94.2% degradation in 60 min
Levafix Blue CA, Levafix Red CA	Electro-Fenton	Complete decolorization and 90–95% mineralization achieved
<i>Pharmaceutical compounds</i>		
Amoxicillin, ampicillin, cloxacillin	Photo-Fenton	Complete degradation of antibiotics in 2 min
Paracetamol Triclosan	Photocatalysis (UV/TiO <sub>2</sub> ) Sonolysis	>80% degradation in 5 h Complete degradation
Levodopa, paracetamol	Sonolysis	At initial concentration of 25 mg/L, 91% levodopa, 95% paracetamol removed in 4 h
Ibuprofen	Electron-Fenton, UVA and solar photoelectro-Fenton	Solar photoelectron-Fenton achieved highest mineralization (92%)
Propranolol	Ozonation	Nearly all antibacterial compounds quantitatively deactivated
Antibacterial compounds	Ozonation	
<i>Pesticides</i>		
Linuron	Photocatalysis (TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub> /visible light) Photolysis	>70% decomposition 91% degradation after 16-h irradiation
2,4-dichlorophenoxyacetic Acid	Sonolysis Ozonation (30 mg/L) with MnO <sub>x</sub> /MZIW catalyst (1.5 g/L)	90% degradation in 100 min 82% TOC removal at pH = 3.7
Methamidophos	Anoxic oxidation with Si/BDD electrodes	Complete mineralization
Atrazine	Photoelectrocatalysis	Complete removal
Diuron	Photolysis	88% degradation after 16-h irradiation
Chlorotoluron	Photolysis	71% degradation after 16 h
Pesticide mix (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon)	Solar photo-Fenton	All pesticides mineralized after 12–25 min

Table 6. Cont.

Contaminant	Type of Process	Remarks/Results
<i>Other pollutants</i>		
Oxalic acid	Photocatalysis (visible+TiO <sub>2</sub> -based catalysist)	92% removed (89% TOC removal)
PFOS+PFAS	Sonolysis	28% PFOS and 63% PFAS removed after 60 min
Polypropylene	Sonolysis with p-xylene as solvent	>60% degraded
Arsenite (As(III))	Photocatalysis (UV + TiO <sub>2</sub> )	Complete removal by oxidation to As(V) followed by adsorption
	Sonolysis	Complete oxidation after 30 min sonication
Coliphages	Photocatalysis	99.75–99.94% removal rate
Olive mill wastewater	Fenton process (Fe <sup>0</sup> +H <sub>2</sub> O <sub>2</sub> )	Complete color removal and 50% decrease of phenolic compounds after 3 h
Industrial Wastewater	Sono-Fenton	70% TOC removal after 150 min

As it can be seen from Table 6, most conventional AOPs may require extended process times for contaminants' degradation, ranging from a fraction to several hours to achieve at least a 1-log reduction of the original contaminants' mass. It may also be noticed that, when reporting the results of their studies, researchers refer to the fate of the primary target contaminant with the words "removed", "degraded", or "decomposed" without specifying (save for rare occasions) if the actual contaminant's "end-of-life" (i.e., mineralization) was reached, or the nature of the degradation products. It is conventionally agreed that CEC compounds' complete destruction (i.e., mineralization) should be required to eliminate any possible residual risk; however, this could require treatment processes more advanced than those currently available, even in facilities of last-generation design.

The application of ARPs was initially tested for the removal of bromate (a DBP considered a possible human carcinogen [68,69]), and in recent laboratory studies, it showed its potential towards the degradation of chlorinated organic compounds like vinyl chloride, mono-chloroacetic acid, and 1,2-DCA [39]. Due to the fact that ARPs have received attention as a water treatment process only recently, little is known about the effect of the matrix composition on the specific degradation processes taking place. Table 7 summarizes the reported experimental ARPs applications in water treatment.

Table 7. Application of ARPs for removal of different types of compounds. Adapted from [33,35,38,69–73].

Contaminant	Type of Process	Remarks/Results
<i>Chlorinated compounds</i>		
2,4-Dichlorophenol	UV + sulfite	> 70% removal
1,2-Dichloroethane	UV + sulfite	90% removal in 20 min at pH = 8.2–11, in 130 min at pH = 7.0
Vinyl chloride	UV + sulfite	100% degradation with 120 mg/L sulfite in 15 min
Monochloroacetic acid	UV + sulfite	100% degradation in 3 min
Trichloroethylene	Sulfite-mediated UV irradiation	97.6% removal in 3 h
<i>Perfluorinated Compounds</i>		
PFOA	UV + potassium iodide (KI)	93.6% removal in 6 h
	UV + sulfite	<10% removal in 20 h
<i>Pharmaceutical compounds</i>		
Atenolol	UV/SO <sub>3</sub> <sup>2-</sup>	approx. 70% reduction in 15 min. Little toxicity reduction

Table 7. Cont.

Contaminant	Type of Process	Remarks/Results
Lincomycin	Photolysis	approx. 80% reduction at pH = 8 w/ 0.1 mM $\text{SO}_3^{2-}$ , 90% reduction at pH = 10 w/ 5 mM $\text{SO}_3^{2-}$ , 120 min
Ibuprofen	Photolysis w/ $\text{SO}_3^{2-}$	approx. 50% reduction at pH = 8 (not dependent on sulfite conc.), 80% reduction at pH = 6, w/ 5 mM $\text{SO}_3^{2-}$ , 120 min
Carbamazepine	UV/sulfite	100% removal after 30 min
Diatrizoic acid (diatrizoate)	UV/sulfite	100% removal of parent compound in 8 h, complete removal of halogenated by-products in 24 h
<i>Pesticides</i>		
Atrazine	UV/sulfite	Completely transformed after 4 h
Bromoxynil	UV/sulfite	100% removal after 30 min
Dinoseb (6-sec-butyl-2,4-dinitrophenol)	UV/sulfite	100% removal in 30 min
<i>Other pollutants</i>		
Perchlorate	UV/Sulfite	$\text{ClO}_4^-$ half-life in process 7–15 h >75% removal at pH = 11 in 22 h
Nitrate	UV/Sulfite	>98% removal at pH = 7 in 30 min
Bromate	Photocatalysis, various light sources and catalysts	up to 90% removal at process times between 15 and 60 min
DBPs	Photoreduction (Visible light + Ag@BiVO <sub>4</sub> @RGO catalyst)	99.1% removal at 90 min
Oxyanion compounds	UV + TiO <sub>2</sub> + BrO <sub>3</sub> <sup>-</sup>	100% removal in 10 min at acidic pH

Although, as mentioned, few full-scale applications of AORPs were reported to date, many lab-scale or pilot studies on the application of this class of processes are found in the literature, as summarized in Table 8.

Table 8. Application of AORPs for the removal of different types of compounds. Data from [6,74–77].

Contaminant	Type of Process	Remarks/Results
<i>Chlorinated compounds</i>		
2,4-Dichlorophenol	$\gamma$ -irradiation	complete degradation at 10 kGy
Monochloroacetic acid		
Tetrachloroethylene.	EB	80% removal at 2 kGy
Trichloroethylene	EB	80% removal at 2 kGy
Carbon tetrachloride	EB	80% removal at 2 kGy
<i>Perfluorinated Compounds</i>		
PFOA + BrO <sub>3</sub> <sup>-</sup>	EB 10 MeV, 18 kW	100% removal at pH = 7.3
<i>Aromatic hydrocarbons</i>		
BTX	EB	80% removal at 2 kGy
Toluene, ethylbenzene, o-, m-, p-xylenes, chlorobenzene	EB	55–85% removal at 10 kGy Up to 99.5% removal at < 5 kGy
<i>Pharmaceutical compounds</i>		
Carbamazepine	EB EB with 10 mM H <sub>2</sub> O <sub>2</sub>	90% removal at 1 kGy 90% removal at 0.88 kGy, in 20 s 95% removal at 2 kGy in 45 s
Diclofenac	$\gamma$ irradiation	90–100% removal at 1–6 kGy in 1–20 min
MCPA	$\gamma$ irradiation	97% removal at 4 kGy
Iopromide	EB	90% removal at 19.7 kGy

Table 8. Cont.

Contaminant	Type of Process	Remarks/Results
<i>Pesticides</i>		
Diazinon	$\gamma$ -irradiation	Complete degradation at irradiation of 6 kGy, reduction at drinking water MRL at 1.5 kGy
PCB	$\gamma$ -irradiation	96% degradation at < 0.1 kGy
Prochloraz, Imidacloprid, Carbofuran, Dimetoato	EB	99% removal at 5 kGy
<i>Other pollutants</i>		
Perchlorate	EB	30–40% removal at <5 kGy
Trihalomethanes	$\gamma$ -irradiation/EB	87–95% removal at 2–6 kGy Up to 99.9% removal at < 5 kGy
DBPs		
MTBE	EB	Up to 68% removal at < 5 kGy
NDMA	EB	Up to 88% removal at < 5 kGy

In addition to the performance reported in the removal of emerging contaminants, irradiation-based AORPs have proven highly effective in the removal of natural dyes from food industry wastewater. Observed efficiencies were up to 48% for pure tincture and up to 100% for dilute solutions at a 32 kGy irradiation dose [78]. In municipal wastewater effluent disinfection, 95% removal of coliforms at a 0.2 kGy dose and 99% removal at a 0.5 kGy dose were measured [79].

As previously mentioned, the efficiency of a treatment should not only be evaluated on its degradation efficiency of specific compounds but also on the generation of intermediates of a lesser or non-toxic nature. A study on E-beam irradiation on real pharmaceutical industrial wastewater showed that when EB was applied as pre-treatment technology before biological treatment, almost complete detoxification of wastewater was achieved, compared to non-irradiated wastewater. The cytotoxicity of un-irradiated and irradiated wastewater was tested against *E. coli*, *P. aeruginosa*, and *B. subtilis*, indicating the high potential of irradiation processes to eliminate cytotoxicity [80].

Among AORPs, radiation processes have been recognized as a more environmentally friendly technology compared to chemical processes, with the greatest progress in the latter years in the EB accelerator technology sector in terms of a larger capacity, wider range of applications, reliability, and cost reduction, substantially gaining researchers' appreciation in the mitigation of many pollution problems. Furthermore, among the studied AORPs, EB irradiation may be the most suitable in industrial-scale operations due to the ease of implementation and achievable reaction yield.

### 3.2. ATP Efficiency Enhancement and Process Combination

While conventional AOPs and ARPs rely heavily on chemicals or catalysts for the generation of reaction-driving radicals, radiolysis-based AORPs do not necessarily require such additions, due to the high intensity of the energy transfer occurring in these processes. However, even their efficiency may be further increased by appropriate process management, with possible synergetic effects of irradiation and the addition of nanoparticles (NPs) of various nature on solutes' decomposition, enhancing radical production and the reaction yield [81].

Most ATPs' performance may be enhanced by the application of advanced materials of different nature and/or NPs, including semiconductors, nanoclays, nanocatalysts, nanoclusters, nanorods, and nanocomposites. Nanotechnology consists of the manipulation of materials, including TiO<sub>2</sub>, palladium, Fe<sub>3</sub>O<sub>4</sub>, cerium oxide, graphene oxides, magnetic chitosan, and others, at a scale of <100 nm, taking advantage of unique phenomena that may occur realized at that size scale due to their high surface area to volume ratios, greatly improving adsorption properties. Research recently addressed wastewater treatment also with the use of complex nanocomposites, such as

$\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$  magnetic nanoparticles, and bismuth silver oxide [82]. Polymeric dendrimers are randomly hyper-branched polymers consisting of spherical macromolecules with a dense shell morphology between 2 and 20 nm size. They are very efficient adsorbents for the removal of toxic metal ions, radionuclide, and organic solutes from water [83]. Metal/metal oxide nanoparticles, including silver, gold, and palladium, have also been widely investigated for wastewater treatment: Noble metal-structured photocatalysts can significantly improve the photoactivity of the semiconductor NPs, depending on the substrate to be degraded [84]. Nanosized silver showed strong antimicrobial properties; gold-impregnated palladium NPs have been used to destroy TCE from groundwater, with a 2200 times better performance than palladium catalyst alone; other metal oxide nanoparticles, such as  $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{CeO}_2$ , have demonstrated a capacity for the degradation of organic pollutants in solutions [82]. Carbon-based nanomaterials, such as fullerenes, carbon nanotubes (CNTs), nanosize diamonds and nanosize wires, graphene oxide [85], and chitosan [86], have been used as sorbents for organic compounds in aqueous solutions. In particular, graphene, a two-dimensional recently identified form of carbon, is the thinnest and the strongest material ever measured, and has received much attention in various scientific applications due to its chemical stability, higher mobility as a charge carrier, and large surface area. One major drawback of pure graphene in water treatment applications is its hydrophobic nature; however, its oxide and reduced oxide (also known as functionalized graphene) are derived hydrophilic materials, suitable for such applications that were tested extensively in combination with AOPs. Studies have shown that graphene-based materials can improve the generation of hydroxyl and sulfate radicals in solutions treated with Fenton processes (enhancing the ferrous ion regeneration rate in conventional Fenton, hydrogen peroxide generation capacity in electro-Fenton processes, and hydroxyl radical generation in photo-Fenton processes), significantly improve the performance of catalytic ozonation, and enhance the activation of sulfate radicals from persulfate and peroxymonosulfate in ARPs [85].

Gamma radiation was observed to induce catalytic degradation of p-nitrophenol (PNP) in the presence of titanium dioxide ( $\text{TiO}_2$ ) nanoparticles in aqueous solution. In the presence of low  $\text{TiO}_2$  doses (0–2.0 g/L), the catalytic effect of NPs on PNP decomposition was not obvious, since this compound could be removed well by irradiation alone; however, the removal of total organic carbon (TOC) and total nitrogen (TN) was significantly accelerated in the presence of  $\text{TiO}_2$ . TOC removal increased from 16% to 42%, and PNP mineralization was dramatically enhanced [87]. An innovative Fe/C nanomaterial fabricated with Fe-based metal organic frameworks (MOFs) was shown to catalyze  $\gamma$ -induced degradation of the antibiotics, cephalosporin C (CEP-C) and sulfamethazine (SMT), in aqueous solutions [88]. An increase of the  $\text{H}_2\text{O}_2$  yield (at  $\text{pH} < 4$  or  $>$  than 11) was observed in radiolysis of aerated solutions with added  $\text{Al}_2\text{O}_3$  NPs. It was also observed that the addition of  $\text{Al}_2\text{O}_3$  could inhibit scavenging of  $\cdot\text{OH}$  radical precursors by solute  $\text{NO}_3^-$  [89]. Growing research interest in the field of radiation-induced heterogeneous chemical transformations in solutions with nanocatalyst addition could provide significant progress to irradiation-based processes in the future.

The potential of ATPs and in particular EB technology to remove toxic organic substances was widely documented, as shown in Tables 6–8. The possibility of combining these and other conventional processes to maximize efficiency and cost-effectiveness was also demonstrated. Kim et al. showed that the EB irradiation and activated sludge process combination was a highly effective method for enhancing the biodegradability of textile wastewater [90]. The effect of ionizing radiation on the biodegradability and toxicity of individual drugs was also studied: Changes in the biodegradability and toxicity of aqueous solutions containing sulfamethoxazole (SMX) by ionizing radiation showed that SMX biodegradability was improved by applying small (0.4 Kgy) irradiation doses. At the 2.5 Kgy dose, full SMX conversion to biologically treatable substances was noted [91]. The combination of radiolytic treatment with conventional processes was studied in a significant number of applications to wastewaters of different origins. The application of  $\gamma$ -irradiation to landfill leachates showed considerable biodegradability improvement [92]; cellulosic wastewater showed accelerated enzymatic hydrolysis [93]; pulp mill effluents registered increased removal of adsorbable organic halogen (AOX)

in biological treatment (from 50% to 96%) following  $\gamma$ -irradiation [94], and significant improvement of COD removal after EB pre-treatment [95]. The combined EB irradiation and activated sludge treatment of textile dyeing effluents achieved equal treatment levels at more than halved biological process HRTs [53]. The biodegradability of textile dyeing wastewater was reported to increase from the 0.34–0.61 range, to between 0.87 and 0.96 after irradiation [96]. Studies highlighted that other intermediate processes (i.e., coagulation prior to irradiation) could be appropriate for some (e.g., textile) wastewaters [97].

The combination of EB irradiation and ozone (3 ppm) resulted in an eightfold reduction of the required dose for 95% trichloroethylene removal from contaminated groundwater, increasing the equipment irradiation capacity from 146 to 1200 m<sup>3</sup>/h while reducing treatment costs threefold from 0.25 to 0.075 US\$/m<sup>3</sup> [98].

A hybrid process combining microfiltration membrane separation with EB irradiation was tested for the production of safe water from secondary effluents. The EB's high effectiveness in modifying the effluent organic matter structure significantly reduced membrane fouling and improved permeate quality at an irradiation dose of 1 kGy, without significantly changing the overall process energetic consumption [99]. Hybrid radiolytic approaches (coagulation, biological treatment, and  $\gamma$ -irradiation) were tested for the decomposition of real pharmaceutical wastewater. The sequence of coagulation, irradiation, and biological treatment accounted for synergistic degradation and detoxification of recalcitrant pharmaceutical wastewater, with an overall improved COD removal at over 90% [100]. The study confirmed that irradiation pre-treatment is a realistic approach for the treatment of recalcitrant wastewaters. In particular, due to the very short process contact time, EB-based AORPs do not require large additional units, and can therefore be easily inserted in existing facilities' treatment trains with minimal disruption, to improve treatment efficiency.

### 3.3. Energy Demand and Cost-Effectiveness of ATPs

The sustainability of a treatment technology is determined by its competitive performance, economic feasibility, and reliable operational practice. While these factors have been deemed acceptable so far for many conventional AOPs currently in use, the high capital investment and energy demand by innovative AORPs, in particular EB, still raise doubts about their sustainability among water practitioners, although several studies have demonstrated the economic feasibility of these processes.

Direct cost comparison of different technologies is not immediate, as it may depend on local site conditions and market factors. The cost of ozone and UV technology, for example, can roughly be estimated as indicated in Table 9, based on a commercial survey of primary suppliers for the EU market today. These figures include only the generation equipment for typical disinfection uses (dedicated AOP applications will require different doses) and not the structural costs necessary for installation, such as buildings and process tanks. For UV systems, significant differences may arise depending on the specific system configuration (e.g., horizontal vs. inclined lamp installation). Process contact volumes may increase significantly the capital cost (CAPEX), depending on the required contact time, which may range from 10–15 min for O<sub>3</sub> disinfection, to several hours for AOP removal of specific compounds.

**Table 9.** Investment and operational cost of ozone and UV facilities for water treatment.

<i>Ozone generator</i>	CAPEX: approx. 50,000 Euro (~56,000 US\$) per kg O <sub>3</sub> /h (suggested dose for disinfection 10 g/m <sup>3</sup> ) OPEX: approx. 2.5–4 Euro/kg O <sub>3</sub> (inclusive of LOX gas and energy)
<i>UV system</i>	CAPEX: can be determined by the approximate formula (44.4 Q + 26,000), where Q is the treated flow in m <sup>3</sup> /h and the result is expressed in Euro (for standard disinfection dose –surface water discharge–only. Values should be doubled for irrigation reuse) OPEX: electric energy consumption (in kWh) for disinfection dose can be estimated as [0.33 × (0.02 Q + 30)]. In addition, the cost for periodical (every 14,000 h of operation) lamp substitution (in Euro/h) can be estimated as [0.037 × (0.016 Q + 17)]

Given the scarce diffusion of EB systems in water applications, it is difficult to provide an upfront reliable cost figure for this technology. The cost of an accelerator ( $C_{EB}$ ) is generally proportional to the installed electron energy ( $E$  in MeV), power ( $P$ , in kW) through a factor ( $f$ ) that depends on site-specific conditions, accelerator type, and manufacturer according to the following relationship:

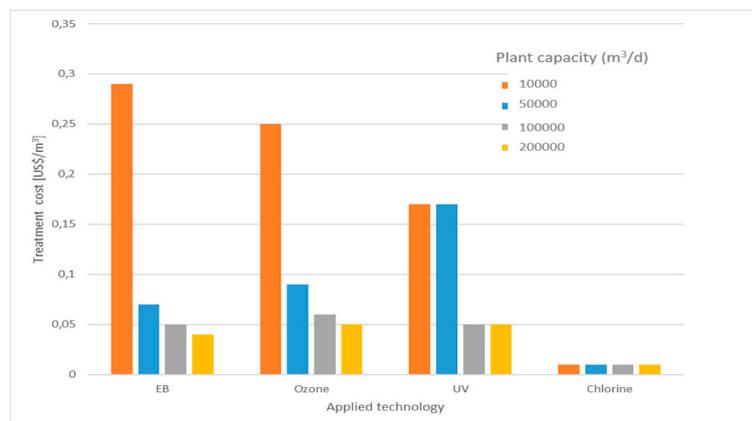
$$C_{EB} = fE \sqrt{P}, \quad (12)$$

as suggested by Zimek and Kaluska [101]. Available cost figures from 2012 [53] suggested that the specific price tag (US\$/W) of electron accelerators (at 1 MeV electron energy) decreases with the installed power according to the approximate relationship:

$$c_{EB} = 220 P^{0.665}, \quad (13)$$

that would make the cost of this technology more affordable with increasing treatment capacity (both in treated flow and irradiation dose).

This is confirmed by preliminary comparative calculations estimating the total cost of 3-log disinfection of municipal effluents for irrigation water reuse, summarized in Figure 5 [102]. It can be seen that at increasing capacity, the irradiation technology-specific cost becomes similar or lower than that of conventional AOP processes, save for chlorination. Since all these processes (except chlorination) are based on energy conversion (electric to radiation, or to oxidants), it is safe to assume that similar economies of scale would be seen also in uses different from simple disinfection. From the OPEX point of view, it was noted that, generally, EB is energetically more efficient than other AOPs, such as ozonation and UV irradiation [50].



**Figure 5.** Specific total disinfection costs (US\$/m<sup>3</sup> treated) of urban effluents for irrigation reuse according to different technologies (data from [102]).

O<sub>3</sub> production from liquid oxygen generally requires 8–9 kWh/kg (may decrease to 7 kWh/kg in large facilities with capacity > 25 kg/h). Production from ambient air requires the circulation of higher air flows (about fivefold, due to O<sub>2</sub> air content); therefore, the overall specific consumption is higher in this case. UV irradiation normally absorbs about one third of the total installed nominal power. It has been shown that process efficiency does not depend solely on the conversion from electric current to UV-C radiation but also on the system configuration: Even if last-generation horizontal lamps are individually more efficient (42% electric to UV-C conversion) than inclined ones (35% conversion), due to the more advantageous installation geometry, the latter result in a lower overall specific energy demand. In this respect, an important feature of EB equipment is the high conversion efficiency of electric power to irradiation, in excess of 95% for modern accelerators. This results in high radicals' generation efficiency of over 1.0 M<sub>OH</sub>/kW.

The energy demand and efficiency of water treatment facilities is a currently an issue of great relevance, associated with process sustainability and their environmental impact [103].

A method to estimate the energy efficiency of different ATPs was suggested as the determination of the electrical energy per order (EE/O) of a process for a specific contaminant [104]. Defined as the amount of kWhs required to reduce a pollutant concentration by an order of magnitude in 1 m<sup>3</sup> of solution, it is easily applicable to any energy-driven process, and could also include the embedded energy contained in chemical additives or catalysts (i.e., the energy required for their production and supply to the process).

Although EE/O is not directly related to the total process costs (it only reflects operational costs, it could provide an indication about the feasibility of alternative process approaches, with rapid determination of their operating costs, known as the expected reduction in contaminant concentration (in orders of magnitude) and the local cost of electricity. Of course, there are other factors (chemical needs, operation/maintenance costs, capital amortization, etc.) that go into a complete cost analysis. EE/O values may vary widely (even more than one order of magnitude) when considering common ATPs, and largely depend on a process efficiency in radicals' generation but are also affected by matrix interference (scavengers), specific process equipment (e.g., lamp efficiency for UV systems), and operating conditions. As an example, Table 10 reports the calculated EE/O values for the decomposition of antibiotics (sulfamethazole and chlortetracycline) and other contaminants by different ATPs [104,105]. Lower values indicate higher treatment efficiency.

**Table 10.** EE/O values for the decomposition of solute contaminants by different ATPs.

Contaminant	EB	Ozonation	UV (210 nm) + H <sub>2</sub> O <sub>2</sub>	UV + TiO <sub>2</sub>
Chlortetracycline	0.19	7.15	15.5	
Methylene Blue	0.6		0.63	16.4
Phenol	1.5		3.6	336
Sulfamethazole	0.46	27.53	1.5	
Other pollutants (typical values)	<3		<3	>50

A study examining different wastewaters, two textile and one municipal effluent, evaluated different treatment options (primary and activated sludge, low-dose EB, and chlorination) to establish the reliability and optimum conditions for different treatment processes. EB was used for disinfection (municipal effluent) and treatment (textile effluent). The evidence of the study indicated that as far as cost estimates, EB at doses between 1 and 3 kGy compared to conventional methods was less expensive than activated sludge for treatment (but more expensive than chlorination for disinfection, as also shown in Figure 4) [97].

As noted earlier, the appropriate combination of different conventional (e.g., biological) and advanced processes (e.g., EB and O<sub>3</sub>) may result in more efficient and economic treatment of specific pollutants. Klein et al. conducted a pilot study on the treatment of landfill leachate containing significant concentrations of recalcitrant organic substances with a scheme consisting of an activated sludge pre-treatment combined with the Fenton process and biological post-oxidation. The results indicated that the combined treatment according to the suggested scheme proved more efficient, both in efficacy and cost, than individual biological or chemical processes [106]. Pikaev et al. compared pilot plant results obtained by combined EB and ozone treatment and conventional (biological plus disinfection) treatment of municipal wastewater from the town of Raduzhnyi (Russia). The combined EB+O<sub>3</sub> treatment cost was estimated at 17–30% of the cost of conventional treatment, depending on the influent COD concentration, to achieve comparable effluent quality [107]. Other authors compared the cost of using EB and  $\gamma$  radiation under different conditions. In general, the cost of running an EB unit was estimated at approximately half of that of a  $\gamma$  unit, and up to 60% lower than that of conventional technology [108]. A comparative treatment study of low (COD = 11,940 mg/L) and high (COD = 52,856 mg/L) real pharmaceutical wastewater indicated a treatment cost of EB

radiolysis at 0.50 US\$/m<sup>3</sup>, activated sludge treatment at 2.35 US\$/m, and EB/biological combination at 2.85 US\$/m<sup>3</sup> for low-strength wastewater, whereas for the high-strength effluent, costs were 0.67, 0.7, and 1.37 US\$/m<sup>3</sup>, respectively. Activated sludge HRT was 2 days, and the EB treatment contact time was 3 and 4 min, respectively, for low- and high-strength wastewater but decreased to 2 and 1 min, respectively, with the addition of H<sub>2</sub>O<sub>2</sub> to the process. Peroxide addition, however, increased the combined treatment cost to 7.87 and 11.48 US\$/m<sup>3</sup>, respectively, in the low- and high-strength cases [80].

Waite et al. compared the cost of effluent disinfection in a 1.5 MeV EB facility to that of a UV peroxidation process. The reported total operating cost of the latter was US\$ 0.68/m<sup>3</sup>, and the calculated costs for EB treatment (including capital amortization and running costs) ranged between US\$ 0.66 and 0.066 depending on the applied treated flow (36–480 m<sup>3</sup>/h) [109]. It should be noted that the previous estimate was based on an EB installation cost of US\$ 2.35 million (in 1998). Although a direct estimate of the current cost of an equivalent facility is quite difficult, the industrial diffusion of this technology and new accelerator construction technology can now offer better economic and technical characteristics than those available in the late 1990s.

An analysis of EB irradiation of municipal sewage sludge showed that operational irradiation costs were poorly sensitive to delivered doses: At 6.7 kGy irradiation, the energy cost for treatment was estimated at 1.10 US\$/kg, increasing to 1.26 US\$/kg (+14.5%) when raising the irradiation dose to 25.7 kGy (+283.6%) [110]. This indicates that once the accelerator is in place, increasing the irradiation doses (in response to new contaminants' presence or increased removal requirements) has minimal impact on the cost of treatment, resulting in an unparalleled adaptation flexibility and operability of this specific process. Other AOPs' (e.g., ozone and UV) cost are, on the contrary, directly proportional to the oxidant or irradiation doses, as shown in Table 9.

#### 4. Discussion

Recent development of highly performant advanced treatment processes, in addition to traditional AOPs, has opened new horizons in the field of water purification and production. Although not all the proposed processes will turn out to be industrially applicable in the end, some are well beyond the stage of laboratory testing and have already seen real-world application. Table 11 summarizes the pros and cons of some of the processes examined in this paper.

**Table 11.** Pros and cons of ATP technologies.

Technology	Pros	Cons	Notes
AOPs			
UV	Established disinfection technology.	Low energy transfer yields. UV exposure is mutagenic for bacteria and is suspected of antibiotic resistance buildup. Not highly efficient in contaminants removal.	UV penetration affected by turbidity and presence of nitrates. Cost is almost linear with flow capacity.
UV + H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub>	Higher degradation rates compared to individual processes. Higher yield of hydroxyl radicals.	Cost of chemicals. May require long process contact time. Affected by scavengers' presence. Potential for bromate byproducts.	Proven technology. Specific energy efficiency (EE/O) higher than ozonation alone but lower than other AOPs. Cost is directly proportional to treatment capacity.
H <sub>2</sub> O <sub>2</sub> + O <sub>3</sub>	More effective than the individual processes.	High cost. Ozone may generate toxic byproducts.	pH and chemical ratios control required.
UV + TiO <sub>2</sub>	Catalyst is costly but can be recycled.	No full-scale applications reported.	pH sensitivity. Oxygen sparging required.
Sonication	Energy use similar to UV systems.	Need for supplemental oxidants. High cost.	Not commercially applicable.

Table 11. Cont.

Technology	Pros	Cons	Notes
ARPs			
UV/MW/US + chemicals	Capable of degrading oxidated compounds.	Need of chemical addition. High energy requirements. No full-scale applications.	Emerging technology not proven at full scale. No reliable estimates about application costs.
AORPs			
$\gamma$ -irradiation	Popular AORP technology for laboratory studies.	High process time compared to EB. Radiation sources entail high handling risks and process safety issues. No full-scale applications in the water sector.	$\gamma$ -irradiation effects are very similar to EB's, but with lower dose delivery. Similarly to EB, there is controversial public perception about radiation technologies.
EB	Extremely fast process. High reliability. Minimal byproducts formation. High flexibility of process operation and combination.	Relatively poorly known technology in the water sector, due to controversial public and technical perception. High total investment costs (but may be comparable to other AOPs).	No extensive use yet, although a few full-scale facilities exist. Preliminary cost analysis seems to indicate competitiveness with conventional technologies in some cases. This technology could easily be combined with other processes to increase overall efficiency.
Nonthermal plasma, Vacuum UV	Promising results in lab-scale applications	Technologies not mature for full scale applications.	Newly proposed technologies yet to be field validated. Uncertainty about cost and reliability.

Despite many real -scale applications of some of these processes with real wastewaters, there is a need for a deeper understanding of their reaction kinetics in complex systems, to enable better design of combination treatment schemes. For all processes examined, an understanding of chemical reaction mechanism (in the form of reliable chemical models) is needed to address issues about contaminant decomposition and byproduct formation in complex solutions. It was shown, for example, that ionizing radiation together with oxidants, such as ozone or hydrogen peroxide, may further improve an individual process removal efficiency but may also induce secondary scavenging effects in solution.

There appears to be a general lack of comparative investigations between consolidated AOP processes and innovative ARPs/AORPs, and of their combinations with other conventional processes. This prevents reaching conclusive evaluations about the most suitable and cost-effective solution for advanced treatment of water/wastewater for specific uses. It should also be considered that site-specific conditions may lead to different conclusions for different sites.

## 5. Conclusions

Despite the absence, so far, of explicit regulations concerning the elimination of CECs from water and wastewater, the recognized need for highly efficient non-selective purification processes and ongoing related research has generated increased knowledge about the degradation of numerous classes of industrial and emerging environmental pollutants.

In particular, a significant understanding and development of advanced treatment processes based on free radicals' efficient reactions was achieved recently. One of the most efficient ways for the production of such radicals consists of ionizing radiation-based processes, showing the highest free radical yield per unit energy input, and a wider range of reacting compounds to tackle a larger spectrum of contaminants. Controversial perception about radiation technology, however, has so far slowed down its application in the water sector, notwithstanding the many notable application examples in other industrial sectors, including the food and medical industry. Compared to other technologies, ionizing radiations could provide economical, reliable, and safer operations that would not be affected by seasonal variations in effluent composition, and could reduce the generation of secondary toxic intermediates.

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