The Open Biotechnology Journal

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Removal of Endocrine Disruptors from Urban Wastewater by Advanced Oxidation Processes (AOPs): A Review

Alessandra Cesaro and Vincenzo Belgiorno

REMOVAL OF ENDOCRINE DISRUPTORS FROM URBAN WASTEWATER BY ADVANCED OXIDATION PROCESSES (AOPs): A REVIEW

Alessandra Cesaro, Vincenzo Belgiorno

SEED - Sanitary Environmental Engineering Division, Department of Civil Engineering, University of Salerno, via Giovanni Paolo II, 84084 Fisciano (SA), Italy.

Corresponding author:

Alessandra Cesaro

SEED - Sanitary Environmental Engineering Division, Department of Civil Engineering, University of Salerno, via Giovanni Paolo II, 84084 Fisciano (SA), Italy.

Phone: +39 089 96 4181; Fax: +39 089 96 9620; E-mail: acesaro@unisa.it.

Abstract

Over the last years the growing presence of endocrine disrupting compounds in the environment has been regarded as a serious sanitary issue. The more and more frequent detection of these compounds in the effluents of wastewater treatment plants poses the risk associated to their persistence into the aquatic systems as well as to their adverse effects on both public health and environment.

As conventional systems do not allow their efficient removal, great attention has been raised towards their possible treatment by Advanced Oxidation Processes (AOPs). They rely on the action of hydroxyl radicals, which are highly reactive species, able to oxidize recalcitrant and non-biodegradable pollutants.

AOPs can either provide contaminant partial degradation or their complete removal. As their effectiveness has been proved for a wide spectrum of both organic and inorganic pollutants, they are considered a suitable option for the treatment of contaminated aqueous media, especially when combined with conventional biological processes.

This paper aims at reviewing main AOPs for the removal of endocrine disruptors, in order to highlight the most important features of different technologies, thus providing their comparative assessment. To this end, a brief overview of the most frequently detected endocrine disruptor compounds was also discussed, in order to clarify their fate into the environment as well as the contamination pathways of greatest concern for human health.

1. Introduction

In the last years the detection of increasing amounts of non-conventional pollutants in wastewater, surface water as well as drinking water has raised great concern. These contaminants, which are mainly associated to the use of substances such as pharmaceuticals, personal care products, hormones, are usually found in very low concentrations but their adverse effects on both human health and environment have been largely documented [1, 2]. For most of these contaminants there is still a regulatory lack, so that they are generally addressed as *emerging contaminants* [3].

The reduction of their presence into the environment could be pursued by either reducing the use of these substances or removing the amount which enters the water cycle. However, as emerging contaminants are related to products commonly used in everyday life, contamination control could be achieved by adequate wastewater treatments.

Conventional wastewater treatment plants are not designed to remove substances as complex as emerging contaminants, so that many of those are released along with wastewater effluents, posing a risk to both public health and environment. In municipal wastewater effluents concentrations of emerging contaminants have been found to range between 0.1 and 20 mg/L [4].

The identification of proper systems to promote their removal from urban wastewater is therefore necessary. To this end, either the upgrading of existing plants or the implementation of new technologies can be used [5].

Among the solutions that have been studied for the removal of these pollutants [6], Advanced Oxidation Processes (AOPs) are a suitable option. Their application has been studied for the degradation of several kinds of emerging contaminants, including pharmaceuticals [7, 8], personal care products [9, 10] pesticides [11, 12], organotin compounds [13], perfluorooctanoic acid [14], hormones [15, 16], surfactants [17, 18], dyes [19, 20].

Most of these contaminants are addressed as endocrine disrupting compounds (EDCs), defined by the Organization of Economic and Cooperative Development (OECD) as "an exogenous substance or mixture that alters the function(s) of the endocrine systems and consequently causes adverse health effects in an intact organism, or its progeny or (sub) populations" [21].

This work aims at reviewing main AOPs used to provide the degradation of EDCs, in order to highlight the state of the art of their application as well as to assess the comparative evaluation of the most studied processes. To this end, a brief overview of the most frequently detected endocrine disruptor compounds was also discussed, in order to clarify their sources and environmental impacts.

2. Endocrine disruptors in urban wastewater: source and impact

An endocrine-disrupting substance is a compound that alters the hormonal and homeostatic systems, acting via numerous mechanisms that converge upon endocrine and reproductive systems. The most important aspects of endocrine disruption are related to xenoestrogens, antiestrogens, antiandrogens, disruption of thyroid function, and disruption of corticoid function, and other metabolic effects [22].

Several compounds have been identified as endocrine disruptors, including [23]:

- phtalates, found in detergents as well as monomers used in plastic production;
- pesticides, which are commonly used for agricultural purposes;
- organotin compounds, used in antifouling paints in ships;

- surfactants, used in both agricultural and industrial applications;
- dioxin/furans and polycyclic aromatic hydrocarbon (PAH), which originate from the combustion of different materials;
- bisphenols, used during production processes of polymers, flame retardants and rubber chemicals;
- polychlorinated biphenyls (PCB), formerly used in several electric and electronic equipments;
- pharmaceuticals and personal care products, especially when containing parabens;
- hormones and phytoestrogens;
- Heavy metals, originating from both industrial mining and metallurgical processes.

Most EDCs are ubiquitous so that they may be found in all environmental compartments. The contamination of surface water is mainly attributed to sewage effluents from both domestic and industrial facilities. Domestic sewage is, indeed, affected by the daily produced hormones and/or ingested synthetic steroids, which are then excreted with urine and discharged into municipal systems, where they may be only partially removed before being released to surface waters (Figure 1). On the other hand, percolation from agricultural areas poses a risk for direct EDC contamination of groundwater [24, 25].
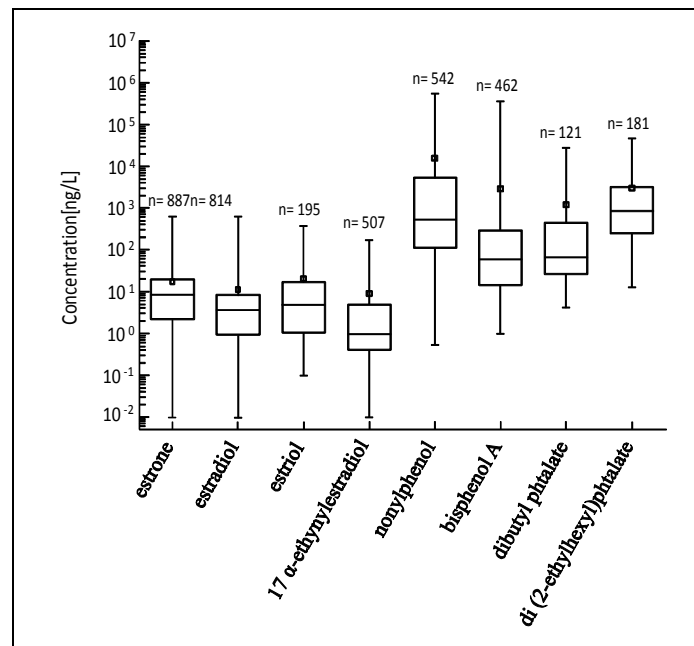
Figure 1. Concentration of selected EDCs in wasteater effluents, adapted from [26].

The presence of EDCs in the environment has been associated to different effects, including: the reduction in the breakage of eggs of birds, fishes and turtles; feminization of male fish; some problems in the reproductive system in fishes, reptiles, birds and mammals; changes in the immunologic system of marine mammals. In some cases, these effects can lead to declines in populations [23].

In human beings, endocrine disruptors contribute to the risk of cancer [27], developmental problems [28], diabetes and possibly also obesity [29] and other metabolic syndrome [30]. Moreover, these pollutants are being regarded as a highly possible promoter of infertility and subfertility [31].

As conventional treatments do not allow the complete removal of these contaminants from wastewater, more effective processes are required in order to reduce their release into the environment. To this end, Advanced Oxidation Processes have been extensively investigated. Their proper application allows the degradation of refractory compounds from the effluents of wastewater treatment plants, revealing the efficiency potential of several innovative techniques.

3. Degradation of endocrine disruptors by Advanced Oxidation Processes (AOPs)

AOPs refer to an oxidation process relying on free radicals, mainly hydroxyl radicals, which have been recognized as the most powerful oxidizing agent after fluorine [32].

The process involves two main steps:

- the formation of hydroxyl radicals in water;
- the reaction between free radicals and organic pollutants.

Hydroxyl radicals tend to be highly unstable and therefore highly reactive and short lived, because one of their electrons is unpaired. As they are relatively non selective species, these radicals readily attack a wide group of organic chemicals, simplifying their chemical structures. One of the main advantages of AOPs is that they neither transfer pollutants from one phase to another, as in chemical precipitation or adsorption processes, nor produce large amounts of hazardous sludge [33].

Under specific operating conditions, AOPs can even produce the complete mineralization of organic compounds to carbon dioxide and other inorganic compounds. However, as the application of AOPs for complete mineralization is generally not cost-effective [34], it is worth considering their proper combination with conventional biological systems [35].

AOPs have been largely studied as pre-treatment of biological systems, in order to enhance wastewater biological treatability [36, 37]. Similarly, AOPs can be used as post-treatment to complete the degradation partially provided by biological processes [38, 39].

The former set up is useful if oxidative reactions result in the formation of intermediates readily biodegradable; the latter may be favourable for effluents containing biodegradable fractions, which can be degraded in the biological steps, so that they will not compete for the chemical oxidant.

Hydroxyl radicals can be generated by both photochemical and non photochemical processes, as pointed out in Table 1. Different combinations of the processes listed in Table 1 have also been investigated.

Table 1. Classification of AOPs for wastewater treatment, adapted from [24]

Non photochemical processes	Photochemical processes
Sonolysis	UV irradiation/hydrogen peroxide
Ozonation	UV irradiation/ozone
Fenton reactions	UV irradiation/hydrogen peroxide/ozone
Electrochemical oxidation	UV irradiation/Ultrasound
Supercritical water oxidation	Vacuum UV photolysis
Wet air oxidation	Photo-Fenton
Ionizing radiation	Photocatalysis
Electro-beam irradiation	Photocatalysis/Ultrasound
Pulsed plasma	Microwave

The following paragraphs summarize main experimental works dealing with the application of the most studied AOPs for the degradation of EDCs, in order to define the state of the art as well as the comparative evaluation of different technical solutions.

3.1. Sonolysis

Sonolysis is a technique relying on the propagation of acoustic waves in liquids, at frequencies ranging between 20 and 1000 kHz. Under these conditions, the occurrence of cavitation phenomena, which consist in the cyclic formation, growth and collapse of micro-bubbles in the liquid, determines an intense increase in both temperature and pressure, resulting in the formation of free radicals [40]. Cavitation promotes both physical and chemical effects, although it has been extensively proved that physical phenomena are predominant at low frequency, while high frequency ultrasound mainly supports chemical effects (Figure 2).
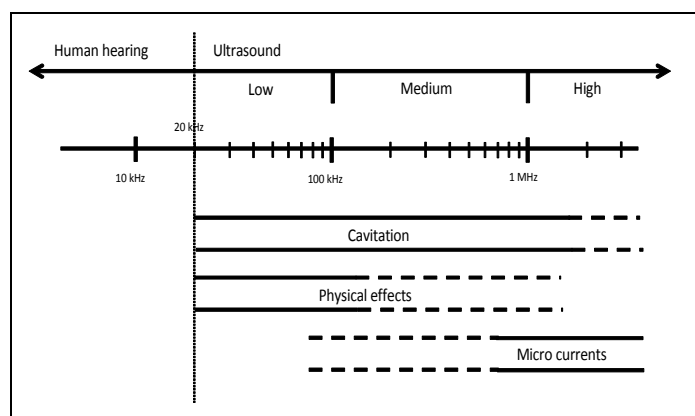
Figure 2. Ultrasound frequency fields and predominant effects.

In the study of Abu-Hassan [41], the decomposition of sodium dodecylbenzene sulfonate (SDBS), a representative Linear Alkylbenzene Sulfonates (LAS) molecule, in water by means of ultrasound irradiation at 20 kHz was investigated. Experiments were conducted at surfactant concentrations of 175, 260 and 350 mg/L. Ultrasonic power varied in the range 40-125 W and temperature values of 20, 30 and 45°C were considered. Degradation increased with increasing power and decreasing temperature. It was also found that 20 kHz ultrasound is capable of degrading SDBS in relatively concentrated model solutions, although complete mineralization may not be feasible since SDBS and its degradation by-products are resistant to total oxidation by ultrasound. This item would suggest the application of ultrasound as post-treatment of conventional biological processes to degrade SDBS.

A direct relation between degradation rate and both ultrasonic power and temperature was also reported by Chiha *et al.* [42]. They investigated the sonolytic degradation of endocrine disrupting compound 4-cumylphenol (4-CyP) in aqueous solution, founding that the degradation rate increased for increasing temperature. Such result was different from the one obtained on LAS [41], suggesting that temperature influence depends on the specific compound under investigation. The same authors also observed that the extent of degradation was inversely proportional to the initial substrate concentration and that the most favourable degradation pH was acidic media.

Similarly, the study of Suri *et al.* [15] demonstrated that the initial ultrasonic destruction of a mixture of estrogen compounds in aqueous solutions was faster at pH 3.0 than pH and 7.0 and 9.0, while the final efficiencies were comparable after about 20 min. Experimental results highlighted that sonolysis produced 80‑90% destruction of individual estrogens at initial concentration of 10 μg/L within 40-60 min of contact time.

Media characteristics in terms of pH were found to be as important as ultrasonic operating parameters for the degradation of EDCs. Torres *et al.* [43] compared the efficiency of both sonolysis and Fenton in the degradation of BPA, one of the most common EDCs, in the cases of deionised acidic water (pH 3) and natural water (pH 7.6). Ultrasound was performed at 300 kHz and 80 W. Fenton's process was operated using ferrous sulphate (100mol/L) and continuous H_2O_2 addition at the rate as it was produced when sonication was applied in water in absence of substrate. Although in deionised water both processes exhibited identical BPA elimination rate and identical primary intermediates, Fenton's process was found to be slightly more efficient than ultrasonic treatment for the removal of BPA by-products. Conversely, experiments performed in natural water highlighted Fenton process inhibition, while ultrasound action was not hampered. Further studies from the same authors [44] proved that BPA ultrasonic degradation mainly occurs via free radicals oxidation and it is highly influenced by ultrasonic power: as power increases, the number of collapsing cavities also increases, leading to enhanced BPA degradation, as also found for other kinds of compounds [45].

The improvement of sonolysis efficiency in EDC removal is thus influenced on operating conditions as well as on environmental parameters, like pH and temperature: however, their optimal combination can vary according to the target compound to be removed.

More recent studies have been directed towards the combination of sonolysis with other processes, such as ultraviolet irradiation [46, 47], photocatalysis [48], electrochemical processes [49]. The coupling of ultrasound with other processes was found to result in synergistic effects, leading to improved removal rates as well as to partial mineralization for a wide range of contaminants. Moreover, when properly coupled with other AOPs, the sonolytic input can be reduced, thus obtaining the reduction of operating costs associated with ultrasound generation.
Main findings of the experimental works discussed are summarized in Table 2.

Table 2. Application of sonolysis for the degradation of EDCs in aqueous media.

AOP	Operating conditions	Target EDCs	Work highlights	Reference
US	20 kHz; 40-125 W; 20, 30, 45°C	SDBS (175, 260 and 350 mg/L)	Degradation increase with increasing US power; Formation of by-products resistant to US oxidation.	[41]
	300, 600 kHz; 80 W; 20-50°C; pH: 2, 6.5, 10	4-CyP (0.05 - 30 mg/L)	Degradation enhanced with decreasing initial concentration of the pollutant; Most favourable pH conditions were the acidic ones.	[42]
	0.6, 2, 4 kW pH:3, 7, 9	Mixture of estrogen compounds (10 µg/L)	80-90% degradation within 40-60 min contact time.	[15]
	300 kHz 80 W pH: 3, 7.6	bisphenol A (118 µmol/L)	BPA degradation increased for increasing US power	[43, 44]
US/UV	US: 283 kHz; 40, 65 and 85 W/L UVC: 254 nm, 10 W, UVC:185 nm, 10 W + VUV: 254 nm, 10 W	Diethyl phthalate (45 µM)	US/UVC/VUV determined 99% removal as TOC and significant mineralization. Enhanced biodegradability was also observed.	[46]
	US: 518 kHz, 10 and 50 W; UV: 254 nm, 6.9 W/cm^2	Butil-paraben (up to100 mg/L)	The US/UV process applied under optimal conditions is able to oxidize 99.2 ± 1.4% of BPB and to record a partial mineralization (43.3%).	[47]
US/UV/ TiO$_2$	US: 35, 283, 450, 935 kHz; 65-70 W UV: 2.5 W/cm^2; TiO$_2$surf. area: 50 m^2/g	Diethyl phthalate (45 µM)	The sonophotocatalytic process was found to be more effective for the complete degradation and mineralization of DEP and proved to be a useful tool for enhancing the biodegradability of DEP.	[48]
US/EC	US: 20 kHz, 523 W/cm^2; BDD electrode; Current density: 10, 25, 35 and 50 mA/cm^2	Amaranth dye sol. (100 mg/L in 0.05 M K$_2$SO$_4$)	Mineralization up to 95% after 90 min of sono-electrochemical degradation.	[49]

3.2. Ozonation

Ozone is a strong oxidative agent, which decomposes in water to form hydroxyl radicals. As a consequence, ozonation relies on two main mechanisms:

- the direct action of ozone itself, which is selective;
- the indirect action of the radicals formed by ozone decomposition in water.

Direct mechanism, occurring at acidic pH, involves degradation reaction by ozone molecules acting as dipoles, as electrophilic agents and as nucleophilic agents. Under this condition, the molecular ozone reactions are limited to unsaturated aromatic and aliphatic compounds as well as to specific functional groups [50].

Degradation reactions by indirect ozone mechanism occur at basic conditions and are influenced by the presence of chemical species that can initiate (i.g., hydroxyl ion, perhydroxyl ion) promote (e.g., ozone, methanol) and/or inhibit (e.g., carbonate ion) ozone decomposition [51].

In practice, both direct and indirect reactions take place simultaneously, but when an oxidation process is specifically designed to enhance the concentration of hydroxyl radicals in a solution, it is referred to as an advanced oxidation process [52].

Ozonation efficiency depends on the compound to be removed as well as on operating conditions: basic environments enhance degradation yields by promoting the production of hydroxyl radicals, as found in studies dealing with the ozonation of pharmaceuticals [53-55].

Conversely, Zhang *et al*. [56] reported that lower pH was beneficial for EDCs removal by ozone when treating synthetic secondary effluent. This evidence was related to the lower reactivity of ozone to the inorganic and organic matters in synthetic secondary effluents as compared to the one of hydroxyl radicals, generated at high pH. As both inorganic and organic substances were not target compounds, a greater amount of ozone could be therefore preserved for the reactions with EDCs. Low pH values were found to be more effective for the degradation of some EDCs also in deionized water. The study of Wu *et al*. [57] reported that triclosan, estrone, estrion, estradiol and ethynylestradiol showed higher oxidation percentages at a pH of 6.6 than 8.6 and attributed this evidence to the relatively high ozone decomposition rate constants at a higher pH.

This trend was not confirmed by the study of Lee *et al*. [58], dealing with bisphenol A (BPA) ozonation at pH ranging between 2 and 12. Authors found that degradation rate was sensitive and proportional to the ozone feed rate, but insensitive to pH and BPA concentration. They also observed that even at extreme alkaline conditions, where hydroxyl radicals were expected to dominate over ozone, the rate of degradation remained unchanged, as a consequence of the mass transfer resistances, the deprotanation of BPA and the competition of hydroxyl radicals with ozone. Moreover, the addition of hydrogen peroxide was found to suppress the reaction by the competition between BPA and hydrogen peroxide itself for ozone and hydroxyl radicals.

More recently the oxidation potential of ozone was also studied for the degradation of caffeine, progesterone and synthetic progestogen steroids, in both ultrapure and natural water [59]. As already observed for BPA, authors found that variation in pH did not largely influence the rate constant for caffeine and progesterone. The impact of the water matrix was also minimal but varied according to the contaminant of interest. The overall removal for investigated EDCs under optimal operating conditions was found to be approximately 80%.

Environmental conditions are as important as the mass transfer of ozone in the matrix to be treated. Chan *et al*. [60] investigated an ozone membrane reactor that synergistically combined ozone oxidation, adsorption and membrane separation to treat recalcitrant EDC pollutants in water. The compact treatment unit used membranes as ozone distributor, reaction contactor and water separator: in particular, the membrane distributor was designed to generate minute ozone bubbles in water, thus enhancing the mass transfer rate. This condition led to faster reaction and higher oxidation of organic pollutants.

One of the major drawbacks of ozone application is related to the formation of by-products.

Alum *et al*. [61] monitored both concentration and estrogenic activity of BPA during 120 min ozonation, carried out under operating conditions resembling the ones applied in full-scale drinking water treatment facilities. They observed that the level of estrogenic activity first increased and then slightly reduced before reaching stability after 60 minutes. Authors attributed this trend to the formation of oxidation by-products with a higher activity than BPA as well as to a residual estrogenic response.

Similarly Larcher *et al*. [62] analysed the by-products of 17α-ethinylestradiol ozonation in terms of chemical structure, estrogenic activity as well as toxicity. Although by-products were characterized by lower estrogenic activity than parent compounds, their toxicity was found to be higher, thus indicating that the removal of EDCs is not the sole issue to consider when ozonation is applied.

Among the factors affecting by-products formation, the availability of ozone plays a key role. Several studies were, thus, based on the hypothesis that lower ozone doses could lead to a reduced generation of toxic intermediates. However this condition could also result in decreased ozonation efficiency. To overcome this obstacle, coupling ozonation with other AOPs appears as a promising strategy.

Colombo *et al.* [63] investigated the complete degradation of bisphenol A (BPA) by combined ozonation and TiO_2 photocatalysis, which allowed the complete mineralization of this compound after only 90 minutes.

The coupling of ozonation and photocatalysis led to pronounced synergistic effects, related to the interactions between ozone and nanosized titania surface. Ozone decomposition at the TiO_2 surface should lead to the formation of reactive species providing BPA degradation. Furthermore ozone may act as an electron scavenger for photo-generated electrons from TiO_2. This effect may slow down the recombination between photo-generated electrons and holes at the TiO_2 surface, thus promoting the oxidation of both BPA and its intermediates.

Ozonation has also been studied in combination with H_2O_2 addition for the removal of EDCs.
In the study of Gerrity *et al.* [64] 5 mg/L of applied ozone and 3.5 mg/L of H_2O_2 were used to degrade trace pollutants including pharmaceuticals, personal care products and steroid hormones. Results showed considerable removal efficiency, even higher than 90%, for almost all selected compounds.
The studies considered in this paragraph are summarized in Table 3.

Table 3. Application of ozonation for the degradation of EDCs in aqueous media.

AOP	Operating conditions	Target EDCs	Work highlights	Reference
Ozone	0-9 mgO$_3$/L pH: 6-9	EE2 (50, 100, 200 µg/L)	Removal efficiency improved at low pH values.	[52]
	2 mgO$_3$/L pH: 6.6, 8.6	EDCs (1-20 µg/L)	Removal efficiency improved at low pH values.	[57]
	0-3 mgO$_3$/L 0-15 min	Caffeine, progesterone and its steroids (2-10 mg/L)	Variation in both pH and water matrix did not largely affect the rate constant for caffeine and progesterone; Overall removal approximately 80 %.	[59]
	100 g/m^3 O$_3$/O$_2$ gas	Potassium hydrogen phthalate (100 ppm C solution)	Complete conversion of EDCs in water at less than three minutes residence time.	[60]
	30 µM O$_3$	Bisphenol A	Reduced estrogenic activity in 60 min ozonation	[61]
Ozone/TiO$_2$ photocatalysis	3 mgO$_3$/L 500 W lamps	Bisphenol A (0.1-1.5 mM)	Combined system showed synergistic effects. BPA mineralization occurred after only 90 min.	[63]
Ozone/H$_2$O$_2$	5 mgO$_3$/L 3.5 mg H$_2$O$_2$/L	PPCPs and steroids (trace concentration)	Approximately 90% removal was observed for each compound.	[64]

If intended to mineralize EDCs, ozonation is not a suitable process as ozone doses required can easily determine the formation of by-products more toxic than the former. This drawback can be overcome by reducing ozone doses. This, in turn, could be obtained by combining ozonation with either different AOPs for complete pollutant removal or conventional biological treatments when ozone is intended to improve pollutant biodegradability.

Alternatively, ozonation can be used as post-treatment: the tertiary treatment of secondary effluent by an ozone-biofiltration system was found to effectively remove EDCs [65].

3.3. UV based processes

Ultraviolet (UV) light is a radiation in the range 200-280 nm in the UV spectrum. The extensive studies carried out for disinfection purposes [66] addresses the evaluation of UV based oxidation processes for EDC removal [67], as summarized in Table 4.

The related degradation pathways are direct photolysis and hydroxyl radical reactions, which can be generally captured in the following parameters: quantum yield, molar absorption and hydroxyl radical reaction rate constant. These parameters can be considered to predict removal rates of different UV-based AOPs, which only differ on how the hydroxyl radicals are generated [68].

Table 4. Application of UV-based processes for the degradation of EDCs in aqueous media.

AOP	Operating conditions	Target EDCs	Work highlights	Reference
UV	Hg/Xe arc lamps Sunlight	ED phthalate esters (250 µM)	Target compound acquired estrogenic activity by light exposure.	[69]
	Direct sunlight (5.2 kWh/m^2)	17β-estradiol, 17α-ethinylestradiol and estriol	Degradation rate varied between 75% and 100%, after 126 days.	[70]
	UVB: 0-500 µW/cm^2.	Estrone and 17a-ethinylestradiol (500 ng/L)	Estrone degradation directly proportional to UVB intensity and invesrely proportional to DOC concentration.	[71]
	1500 W xenon lamp UV filtered, 250 W/m^2 light power	Estrone	DOC (7.7-8.9 mg/L) was found to enhance UV degradation of the target compound.	[72]
UV/H$_2$O$_2$	UV: 1000mJ/cm^2; low (LP)/medium pressure (MP). H$_2$O$_2$: 0-15 mg/L	Mixture of bisphenol A, ethinyl estradiol, and estradiol	MP UV radiation source was more effective than LP one for direct photolysis degradation; UV/H$_2$O$_2$ was more effective than UV photolysis	[67]
UV/H$_2$O$_2$	15 W, LP Hg lamps H$_2$O$_2$: 10, 50 ppm	Bisphenol A (13.7 mg/L)	UV/H$_2$O$_2$ was highly effective in estrogenic activity reduction below detectable levels, although the UV fluence levels utilized were 50-100 times higher than the ones typically applied	[73]
UV/H$_2$O$_2$	LP/MP lamps H$_2$O$_2$: various concentrations	Nbutylparaben, 4-t-octylphenol, trenbolone, boldenone.	Highest elimination rate attained at H$_2$O$_2$ of 0.01 M; The degradation time for 50% reduction of initial concentrations ranged from few minutes to few seconds, depending on target compound and its initial concentration.	[74]
	LP Hg lamps (75 W), 40 min irradiation time; H$_2$O$_2$: 0.018 mol/L	Estrone, 17β-estradiol, 17α-ethinylestradiol, estriol, bisphenol A, and 4-nonylphenols (0.15 mg/g$_{DW}$)	Removal efficiency between 67 and 97%, after 2 min, depending on the compound. Improved performances due to metal ion presence in the sludge.	[75]
UV Fenton Photo-Fenton	LP Hg lamps; Fe^{2+}: 5 mg/L H$_2$O$_2$: 10 - 50 mg/L	Mix of 25 pharmaceuticals, 2 corrosion inhibitors and 5 pesticides at real concentration in wastewaters (COD: 0-150 mg/L)	Photo-Fenton (UV254) was the most efficient at natural pH; Dissolved organic matter played a key role in improving indirect degradation of micropollutants.	[76]
UV/H$_2$O$_2$ UV/S$_2$O$_8^{2-}$	UV-C 0.125-5.0 mM reagents	nonionic surfactant TX-45 (20 mg/L)	TOC removals were higher than 80%; Similar degradation products were identified.	[18]
UV/H$_2$O$_2$ UV/Chlorine	LP lamps (40-200 W); H$_2$O$_2$: ≈ 5 mg/L; Chlorine: 1-6.2 mg/L	Mix of EDCs (DOC: 46 mg/L)	UV/Chlorine competitive from both a technical and and economic point of view.	[77]

Okamoto *et al.* [62] studied the degradation of endocrine disrupting phthalate esters under both UV light and sunlight irradiation. They also assessed photodegradation products and their estrogenic activity, finding that these EDCs acquire unequivocal estrogenic activity by light exposure.

Direct solar irradiation was also studied for the degradation of 17β-estradiol, 17α-ethinylestradiol and estriol, with an average irradiance value of 5.2 kWh/m^2 [70]. Authors observed that after 126 days, the degradation rate varied between 75% and 100% and significant changes in the shape of UV-Vis spectra were also observed.

Further studies on the degradation kinetics of 17α-ethinylestradiol allowed to verify its persistence to simulated sunlight, especially in presence of dissolved organic carbon (DOC), acting as a competitive inhibitor to direct photolysis. Differently, estrone, another steroidal estrogen, was observed to degrade with a pseudo-first-order rate law constant that was directly proportional to UVB radiation intensity and inversely proportional to DOC concentration [71]. Similar results were obtained by Caupos *et al.* [72]

While the effectiveness of direct UV photolysis is governed by the absorption spectra of the contaminant and the quantum yield, the addition of H_2O_2 often significantly lowers the UV dose required for oxidation compared to direct photolysis, enhancing process yields, as found by Rosenfeldt and Linden [67]. They studied the degradability of bisphenol A (BPA) by low and medium pressure mercury UV lamps, reporting 5% and 10-25% reduction by direct photolysis and UV lamps, respectively. When the same samples were exposed to UV/ H_2O_2, under operating conditions usually applied in full-scale drinking water treatment facilities, BPA degradation enhanced up to 90% and its estrogenic activity was reduced by nearly 100%, despite UV source.

The positive effect of H_2O_2 addition during the UV irradiation was also reported by Chen *et al.* [73] for BPA as well as by Błędzka et al. [74], studying the degradation of nbutylparaben (BP), 4-t-octylphenol (OP), trenbolone (TB) and boldenone (BD) in aqueous solution.

The latter authors investigated the application of direct photolysis (254 nm irradiation), UV/H_2O_2 process as well as photosensitized oxidation using mainly singlet molecular oxygen. Results showed that 254 nm radiation provided an efficient degradation of chosen EDCs but process rate was low. Relatively high values of rate constants were obtained in photosensitized oxidation, indicating that in surface waters some EDCs can undergo spontaneous degradation quite efficiently in the presence of natural sensitizers. Although the possibility of using cheap solar energy and air as a source of oxygen seemed attractive, authors pointed out the need to overcome the drawbacks related to sensitizer photostability and their separation from treated water. UV/H_2O_2 system proved to be the most beneficial method to degrade the selected EDCs. Although the cost of H_2O_2 addition should be taken into account, the presence of H_2O_2 (0.01 M) in the reaction mixture during photolysis led to a strong reaction rate increase. The degradation time for 50% reduction of starting concentration of BP, OP and TB ranged from few minutes to few seconds, depending on target compound and its initial concentration.

A more recent study investigated the removal of six phenolic EDCs (estrone, 17β-estradiol, 17α-ethinylestradiol, estriol, bisphenol A, and 4-nonylphenols) from waste activated sludge using the combined UV/H_2O_2 process. Under the optimal reaction conditions, the removal efficiencies of target compounds at the reaction time of 2 min were found to range between 67 and 97% [75]. Authors also pointed out the key role of the sludge matrix in the degradation of EDCs, highlighting that metal ions in the sludge enhanced the removal of the selected compounds, promoting Fenton-type reactions which produced additional hydroxyl radicals.

Another parameter influencing the efficiency of UV based AOPs is the presence of dissolved organic matter (DOM). It can be oxidized competing with the EDC degradation present at much lower concentrations and/or attenuating the UV process. Conversely, it can be involved in other positive mechanisms which can improve the indirect degradation of micropollutants, as found by De la Cruz et al. [76].

In the study of Olmez-Hanci et al. [18], UV/H_2O_2 system efficiency was compared to the one of UV/$S_2O_8^{-2}$ to degrade a nonionic surfactant. Both combined processes exhibited remarkable removals in terms of TOC, higher than 80%. The identification and structural characterization of degradation products showed that they were similar, despite the reagent used during UV irradiation, suggesting comparable degradation pathways for both investigated processes.

Process costs of the UV/H_2O_2 state of the art process are mainly due to the electrical energy consumption: it was estimated that 70-90% of the consumable operating costs for 1 m^3 of treated water can be attributed to electrical energy consumption [77]. Even taking into account the variety of energy and chemical pricing at different places, the main saving for AOPs is the reduction of energy. To this end UV/HOCl process compared to the UV/H_2O_2 process could provide relevant yield improvement of over 30-70% for different EDCs as well as 30-50% reduction for operational process costs. Moreover important reduction in capital costs due to smaller numbers of AOP reactor chambers can be expected for full scale applications [77].

3.4. Fenton-like reaction

In Fenton processes, oxidation occurs via hydroxyl radicals that are rapidly generated through the decomposition of H_2O_2 catalyzed by ferrous (Fe (II)) or ferric ions (Fe (III)). Fenton system efficiency depends on both H_2O_2 and Fe (II) dosages, concentration and properties of effluent organic matter as well as on the solution pH [78], which should be kept in the acid range. In combination with UV-vis light, oxidation rates are strongly increased, likely due to the photolysis of iron aqua complex (Fe(OH)$^{2+}$) providing a new importance source of hydroxyl radicals [79].

Several studies have been carried out on the Fenton-like processes for the degradation of EDCs (Table 5), including perfluorooctanoic acid [80], steroid estrogens [81], phthalic acid esters and bisphenol A [82], pesticides [83].

Table 5. Application of Fenton-like processes for the degradation of EDCs in aqueous media.

AOP	Operating conditions	Target EDCs	Work highlights	Reference
Dark/Photo-Fenton	H_2O_2: 50 mg/L, Fe^{2+} 5 mg/L and absence of light; H_2O_2: 10-50 mg/L, Fe^{2+} 0-5 mg/L UV-C/solar light.	Mix of 25 pharmaceuticals, 2 corrosion inhibitors and 5 pesticides at real concentration in wastewaters (COD: 0-150 mg/L)	DOM presence enhanced Fe(III) photo-Fenton yields; UV-C degradation efficiency higher than sunlight one.	[76]
Photo-Fenton	9 W UV lamp Ferrous sulfate and H_2O_2 at appropriate concentrations	Perfluorooctanoic acid (20 µmol/L)	Rapid degradation within 1 h (87.9% removal); Afterwards, H_2O_2 was consumed and reactions mainly occurred due to Fe^{3+} ions.	[80]
Fenton	H_2O_2/ Fe (III): 10; pH. 3; Various Fe concentrations	17β-estradiol, 17α-ethinylestradiol	Removal efficiencies of 95% and 98% at ferric concentration of 58.6 mg/L were obtained.	[81]
Fenton	H_2O_2/Fe(II) molar ratio:7; Fe(II):0.05 (ph=2) - 0.06 (pH=3.0) mol/L	Phthalic acid esters and bisphenol A (0.08-1.5 mg/L)	Removal efficiencies up to 88%-increased performances for higher EDC concentrations.	[82]
Photo-Fenton	H_2O_2: 20-50 mg/L; Fe^{3+}: 0-4 mg/L UV-C (70 W/m²)	Mix of 22 EDCs, including pharmaceuticals, corrosion inhibitors and pesticides	When Fe (III) was added, almost no dissolved fraction could be measured, so homogeneous photo-Fenton was probably not occurring.	[83]
Fenton	Different molar ratio H_2O_2/Fe(II) pH: 3	PPCPs (each present as 1 µg/L)	20 mg/L Fe(II) allowed complete removal of all PCPPs, except atrazine and iopromide.	[84]
Photo-Fenton	Different Fe and H_2O_2 concentrations; UV-C: 254 nm, UV-A: 350 nm, vis: 420 nm.	BPA (50 mg/L)	Complete degradation after 2-3 min treatment, despite irradiation source. Toxicity disappearance along with BPA removal.	[85]
Fenton	Fe^{2+}/H_2O_2 molar ratio: 0.012 to 0.100; pH: 3	BPA (13- 300 mg/L)	Complete BPA degradation and significant DOC and TOC conversion.	[86]
Photo-Fenton	H_2O_2: 5 mg/L; Fe(II): 50 mg/L; Solar light	Mix of 15 EDCs, including pharmaceuticals, corrosion inhibitors and pesticides (100 µg/L)	Significant degradation within 4-5 hours.	[4]
Photo-Fenton	H_2O_2: 5 mg/L; Fe(II): 50 mg/L; pH: 3, 7.6-8.3	Mix of 62 EDC present in real wastewater (3 ng/L to 66.379 ng/L)	Complexing agents have to be used to keep the iron in solution. EDDS is a suitable agent.	[87]
US/Photo-Fenton	US: 400 kHz, 0.3 W/mL; UV: 254 nm; Fe^{2+}: 0.1 mM	Di-n-butyl phthalate (0.01 mM)	Complete degradation of the target compound in 75 min. More efficient use of Fe^{2+} in comparison to conventional Fenton	[88]

Li et al. [84] studied the effects of Fenton treatment on the degradation of trace level pharmaceuticals and personal care products (PPCPs) commonly occurring in wastewaters. They found that Fenton oxidation at 20 mg/L Fe(II) dose and 2.5 H_2O_2/Fe (II) molar ratio completely removed all selected compounds with the exception of atrazine and iopromide. DOC removal up to 30% was also achieved, while breakdown of high molecular weight molecules into smaller fragments took place. Similarly, Molkenthin *et al*. [85] observed the complete degradation of BPA, along with significant DOC removal by UV-A (near-UV), UV-C (short-UV) and visible-light assisted Fenton-like treatment. BPA removal was always rapid and complete after 2 or 3 min treatment, with a degradation rate slightly variable depending on the irradiation source, according to the following order: UV-C > UV-A > visible light. However, in the presence of UV-A light, DOC abatement was appreciably faster than Photo-Fenton-like treatment with UV-C light irradiation. Despite the irradiation source, the inhibitory effect of 50 mg/L BPA on V. Fischeri was originally around 90-91% : it slowed down to 15-16% when BPA was completely degraded and, after 5 min treatment, toxicity decreased to "stimulative" values, suggesting its tight relation with BPA presence.

The removal of BPA was also investigated by a combined Fenton/nanofiltration process. Escalona *et al*. [86] showed that BPA could be almost completely degraded by Fenton process, along with 78.2 and 59.1% conversions for COD and TOC, respectively. The subsequent nanofiltration of the Fenton treated effluent allowed a rejection of COD, TOC, colour and Fe^{2+} always higher than 81%.

Iron dosage up to 4 mg/L was used in the study of De la Cruz et al. [83], supporting the potential use of UV-C/H_2O_2/Fe (natural pH) at pilot scale in a continuous water flow, for the degradation of EDCs in an effluent from a municipal wastewater treatment plant. Degradation greater than 80% with very low reaction times (10 s) was achieved only adding UV light and H_2O_2. Authors also observed that iron addition to the reactor did not improve the process, but degradation rates were equal to, or lower than, experiments using only iron already present in water. This result could also be related to wastewater pH, which was in the range 6-7 as any adjustment was provided. Under this condition, Fe (III) catalyst begins to precipitate in the form of hydrous oxyhydroxides, thus reducing its activity.

However, when dissolved organic matter (DOM) is present, some compounds can complex with ferric ions. These complexes can be useful to keep the iron soluble when the solution is at neutral pH, as observed in a previous study from the same authors [76]. They investigated both Fenton and photo-Fenton processes to degrade 32 selected pollutants including pharmaceuticals, corrosion inhibitors and biocides/pesticides found in the effluent of a municipal wastewater treatment plant (MWTP) based on activated sludge. In particular, Fenton technique was developed with 50 mg/L of H_2O_2, and 5 mg/L of Fe(II) in the absence of light. Photo-Fenton was studied using both UV254 and artificial sunlight irradiation as well as varying H_2O_2 concentrations between 10 and 50 mg/L; experiments were also performed without iron addition, as 1.48 mg/L of total iron was already present in wastewater. Fenton process could completely remove only the norfloxacin after 30 min, whereas degradation yields lower than 15% were found for 10 of the 30 compounds detected in wastewater. The addition of light to the Fenton improves noticeably the global degradation, which increased from 31% with the Fenton process up to a 97% adding UV254, under the same operating conditions. Enhanced removal were attributed to the photochemistry of the Fe(III) which was probably complexing with organic ligands present in the solution as well as to the action of the UV light itself and its interaction with H_2O_2 and the organic matter. In photo-Fenton processes, UV254 allowed 100% degradation after 90 min, much higher efficiency compared with sunlight (47% degradation after 90 min).

Conversely, Klamerth *et al*. [4] proved the degradation efficiency of solar photo-Fenton (5 mg/L of Fe(II), 50 mg/L of H_2O_2) for fifteen emerging contaminants (initial concentration of 100 µg/L) including pharmaceuticals, pesticides and personal care products commonly detected in wastewaters and introduced. Despite the mild operating conditions, most contaminants were reduced below the instrumental detection limit by increasing irradiation time up to 4-5 hours. Further studies pointed out that photo-Fenton at pH 3 allowed the reduction of treatment time, but the water must be previously acidified and neutralised afterwards for reuse, with consequent operating costs [87]. At neutral pH, the removal of over 95% of the contaminants can be also achieved. However, as Fe precipitates at neutral pH, the use of complexing agents which are able to form photoactive species, do not pollute the environment or increase toxicity, and reduce the biodegradability of the water, have to be used to keep the iron in solution. To this end, a promising process was recognized to be photo-Fenton modified with Ethylenediamine-N,N'-disuccinic acid (EDDS), an aminopolycarboxylic acid. It does not lower the pH, thereby not requiring water neutralization afterwards. The main drawback is the treatment cost, as EDDS was also degraded during the process [87].

More recently Fenton process has been investigated in combination with ultrasound.

Xu *et al.* [88] studied the effects of a homogeneous sono-photo- Fenton reaction on the degradation of Di-n-butyl phthalate (DBP), assumed as model compound. The process involved ultrasound at 400 kHz, with 0.3 W/mL power density as well as UV irradiation at 254 nm; Fe^{2+} initial concentration was set at 0.1 mM. The combined process allowed the complete degradation of DBP within 75 min. The relative degradation performance for the alternative processes was found to be in the order: $US/UV/Fe^{2+} > US/Fe^{2+} > US/UV > US > UV/Fe^{2+} > UV$. The synergistic effects were attributed to the enhanced generation of hydroxyl radicals via three main mechanisms: a Fenton reaction from ultrasonically generated H_2O_2 in the presence of Fe^{2+}; the photo-decomposition of H_2O_2; the photo-decomposition of $[Fe(OH)^{2+}]$ resulting from the Fe^{2+} photo-oxidation and hydrolyzation process. Moreover, the sono-Fenton process was recognized to utilize more efficiently Fe^{2+}, resulting in higher DBP removal yields.

Fenton systems are easy to handle and to operate: adjusting working conditions accordingly, Fenton reactions may conveniently be applied to degrade different emerging contaminants with endocrine disrupting properties, even at very low concentrations.

On the other hand, although the drawbacks associated to the narrow pH range of operation can be overcome as pointed out in the most recent studies, further efforts should be addressed towards the identification of suitable Fe complexes to face the issues of their recovery.

3.5. Heterogeneous photocatalysis

Photocatalysis is a photochemical reaction accelerated by the presence of a catalyst: when this catalyst occurs in a different phase than the reaction medium, the process is named heterogeneous photocatalysis.

Among the most spread photocatalysts, titanium dioxide (TiO_2), zinc oxide (ZnO), zinc sulfide (ZnS), ferric oxide (Fe_2O_3), silicon (Si), tin oxide (SnO_2), and cadmium sulfide (CdS) should be reported. However, TiO_2 has been the most widely cited photocatalyst in literature due to its considerable activity, high stability, non-environmental impact and low cost [89].

In heterogeneous photocatalytic processes, UV irradiation induces the formation of electron-hole pairs (Figure 3), whose charge carriers react with chemical species such as water molecule and molecular oxygen in the air to produce hydroxyl radicals, which contribute to the decomposition of organic molecules at the TiO_2 surface [90].

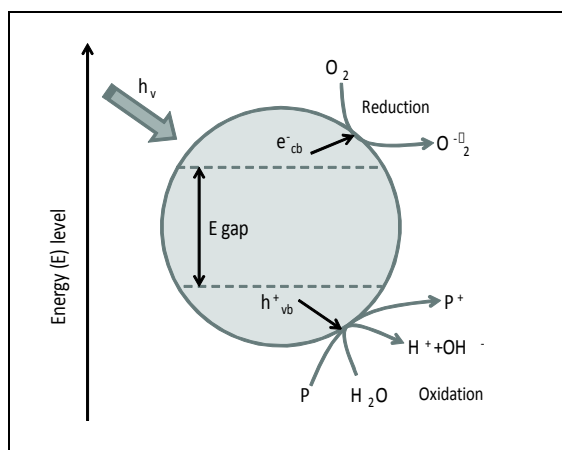Light sources play thus a key role in the definition of the process efficiency.

Figure 3. Scheme of electron-hole pair formation and related chemical reactions, adapted from [91].

Several studies report the successful application of heterogeneous photocatalysis process using TiO_2 for the removal of different kinds of EDCs (Table 6), including pesticides [92] as well as estrogens [93].

Table 6. Application of heterogeneous photocatalysis for the degradation of EDCs in aqueous media.

AOP	Operating conditions	Target EDCs	Work highlights	Reference
TiO_2 photocatalysis	Bi^{3+}-doped TiO_2 UV-A light	Organophosphate insecticide methylparathion (20 mg/L).	Bi-TiO_2 photocatalysts provided higher yields than TiO_2. Optimal Bi^{3+} conditions ranged between 0.7 and 1.5%.	[92]
TiO_2 solar photocatalysis	TiO_2:0.2-0.5 g/L Solar light	Mix of 9 EDCs (order of magnitude ng/L)	3 hour irradiation was useful to decrease most pollutant concentrations below detection limit values.	[94]
TiO_2 photocatalysis	UV: 350-420 nm, vis: 410-550 nm, UV-vis: 350-550 nm; TiO_2: 0.5 g/L	BPA (20 mg/L)	UV and UV-vis irradiation were more effective. Visible radiation can be effectively used with carbon-doped TiO_2.	[95]
Ag/TiO_2 and Pt/TiO_2 photocatalysis	Black light blue fluorescent lamp (300-400 nm); Various catalyst use.	Estrogen (3 μM) BPA, resorcinol and 2,4-dichlorophenol (equivalent to 50-2000 μg carbon)	Enhanced removal of EDCs only at high contaminant concentration.	[96]
TiO_2 photocatalysis	TiO_2: 0-125 mg/L; UVA HP Hg lamps (150 W).	BPA (10 mg/L)	BPA removal strongly affected by catalyst characteristics, with the highest extent of mineralization observed in the presence of high specific surface area.	[97]
TiO_2 photocatalysis	TiO_2: 0.8 g/L; UVA black light lamps (365 nm).	EDCs in secondary effluents from wastewater treatment plant	Inorganic ions and DOM were found to inhibit photocatalysis, thus requiring proper wastewater pretreatment.	[98]
TiO_2/Fe(III) photocatalysis	TiO_2:0.1 g/L; Fe(III): 32.8 mg/L; Black light lamps.	Testosterone, bisphenol A, acettaminophen (1-3 mg/L).	Fe(III) addition determined a significant increase in the removal of EDCs, up to 97%.	[99]

A recent study investigated TiO_2-based solar photocatalysis as tertiary treatment to remove several emerging pollutants from wastewater treatment plant effluents [94]. Titanium dioxide was added in the range 0.2-0.5 g/L. Process efficiency was compared with that of photo-Fenton process, employing ferrous sulphate as iron source (initial concentration 5 mg/L) and hydrogen peroxide in concentrations ranging between 5 and 10 mg/L. TiO_2 photocatalysis was more effective than photo-Fenton. After 3 h of irradiation, the concentration of pollutants under investigation was mostly decreased below their limit of quantification. Moreover, after 1 h of treatment, more than 99% inactivation of faecal coliforms indicated significant disinfection of the effluent.

However, the photocatalytic efficiency of TiO_2 under sunlight has been reported to be lower than the one occurring under UV light, as UV radiation, which only accounts for 4% of the solar spectrum. In order to extend the use of TiO_2 to the visible light region, Manassero *et al*. [95] compared the degradation of BPA under UV, visible and UV–visible radiation using undoped and carbon-doped TiO_2 in a slurry reactor. They observed that considerably higher reaction rates were obtained with UV and UV–visible radiation, but when the carbon-doped TiO_2 was used, it was found to be effectively activated also by visible radiation. BPA degradation was thus significant, yielding similar reaction rates under UV and visible radiation.

Deposition of metals onto titanium dioxide has also been widely used as a technique to improve its photocatalytic activity. Coleman *et al*. [96] studied the effects of silver (Ag) and platinum (Pt) metals on the photocatalytic degradation of 17β-oestradiol, oestriol, 17α-ethynyloestradiol, bisphenol A, resorcinol and 2,4-dichlorophenol in water over TiO_2. At high concentration of EDCs, a significant increase in the reaction rate was observed for bisphenol A and resorcinol over Pt/TiO_2. However, there was a decrease in reaction rate for bisphenol A over Ag/TiO_2 and no significant effect with resorcinol, indicating that the reactions are metal specific, substrate specific and may depend on the

substrates molecular structure. The high variability of photocatalytic yields in terms of EDC removal would not justify the costs of metal addition in water, especially when considering that EDCs are trace contaminants, thus present in very low concentrations.

More recent studies are directed towards the testing of TiO_2 polymorphs (anatase, rutile, brookite) and their mixtures (anatase/rutile, anatase/TiO_2-B) in heterogeneous photocatalytic oxidation process. Kaplan et al. [97] investigated the efficiency of bare TiO_2 catalysts on the degree of bisphenol A removal, finding that it is strongly affected by catalyst morphology, crystallite size, structure and specific surface area. The highest extent of mineralization was observed in the presence of high specific surface area nanotubular anatase/TiO_2-B nanocomposite. Interestingly, when anatase and rutile particles were physically mixed, an additional beneficial effect on BPA degradation was observed, likely due to a synergistic effect between the respective phases.

Several factors have thus been recognized to influence heterogeneous photocatalysis efficiency. However, as most research has been performed by means of lab or bench scale tests, the influence of the aqueous matrix composition has been neglected. Zhang *et al*. [98] studied the influence of water composition on TiO_2 photocatalytic removal of EDCs and estrogenic activity. To this end, secondary effluent samples were collected at a municipal wastewater treatment plant. It was found that the adsorption of inorganic ions on the surface of TiO_2 could inhibit both EDC removal and estrogenic activity. Dissolved organic matter played a more significant role than inorganic ions in the inhibition of the process, leading to a temporary increase of estrogenic activity. These results highlight the need for wastewater treatment prior to heterogeneous photocatalysis, in order to improve the matrix characteristics for the proper application of the advanced process.

TiO_2 photocatalysis yields can be also enhanced by its proper combination with other AOPs.
In the work of Rodriguez *et al*. [99] TiO_2 photocatalytic system was improved by Fe(III) addition (2.8 mg/L as ferric perchlorate). A significant increase, ranging between 85 and 97%, was achieved in the degradation of a mixture of BPA, testosterone and acetaminophen. The same study proved that the combination of ozone with photocatalytic systems can further enhance process yields. The heterogeneous O_3/TiO_2/Fe(III)/UVA system at pH 3 proved to be highly reactive towards the mixture of EDCs under investigation, with 82% TOC conversion in 50 min. This result was reasonably attributed to the development of photo-Fenton processes occurring in ozonated system during the first 40-50 min, which was confirmed by the absence of Fe(II) consumption. The same photocatalytic system in absence of ozone provides approximately 10% TOC removal.

Experimental results suggest the efficiency of photocatalysis and the possibility of enhancing degradation yields by the proper combination with other AOPs. In this case, however, the assessment of the overall process efficiency is not enough to promote their successful up-scale, as the integration of different processes brings increase in both capital and operating costs. Such issue is even more stressed when energy consuming technologies, like ozonation, are intended to be used. This could be the main reason why most research has been performed at bench and pilot scale.
Further studies should thus be addressed towards the definition of economic indicators, taking into account specific energy consumption of the technologies involved in the proposed combined systems.

3.6. Electrochemical oxidation

The electrochemical method for the degradation of EDCs is a relatively new technology. Because of the large capital investment and the expensive electricity supply, electrochemical water or wastewater technologies has not found wide application worldwide. However, the need for more sophisticated processes has attracted a great deal of attention towards this kind of processes [100].

Electrochemical degradation relies on the action of free radicals, mainly hydroxyl radicals that can be generated either by direct or indirect electrochemistry. In the former case, pollutants are oxidized after adsorption on the surface of the electrode and destroyed by the anodic electron transfer reaction (anodic oxidation processes). In an indirect oxidation process, strong oxidant such as hypochlorite, Fenton's reagent [101] or oxidized metallic ion can be regenerated by the electrochemical reactions during electrolysis. The pollutants are then destroyed in the bulk solution by oxidation reaction of the regenerated oxidant [102]. Indirect oxidation has been recognized to be responsible for the highest removal rates attained using electrochemical methods, mainly due to the generation of hydroxyl radicals [103].

Jiang et al. [104] studied the potential of electrochemical oxidation to remove EDCs from wastewater samples and found that the concentrations of different contaminants were effectively reduced between 10 and 100 ng/L. Similarly, the successful application of electrochemical processes has been reported for the removal of BPA [105], steroids [106] as well as estrogens [107].

In the degradation efficiency of selected EDCs anode characteristics play a key role.

Experiments carried out on the kinetics, pathways and mechanisms of electrochemical degradation of bisphenol A (BPA), with initial concentration of 100 mg/L, on four types of anodes, Ti/borondoped diamond (BDD), Ti/Sb-SnO$_2$, Ti/RuO$_2$ and Pt showed that there were considerable differences among the anodes in their effectiveness and performance of BPA electrolysis [108]. Electrochemical experiments with two current densities (10 and 50 mA/cm^2) were carried out for each anode. The best degradation results were obtained with the Ti/Sb-SnO$_2$ and Ti/BDD anodes, which allowed complete BPA destruction at a current density of 10 mA/cm^2.

The degradation of this EDC by electrochemical oxidation was also investigated by Pereira et al. [109] using a boron-doped diamond (Nb/BDD) anode at a current density of 30 mA/cm^2. Under constant operating conditions, experiments were also performed using Ti-Pt/b-PbO$_2$, and TiO$_2$-RuO$_2$ anodes. The Nb/BDD anode presented the best performance, with a 94% removal of BPA. The slight difference with the results of the study of Cui et al. [108] should be attributed to the different operating conditions as well as to the BPA initial concentration value, which was higher in experiments performed by Pereira et al. [109]. The same kind of anode was used in the study of Steter et al. [110] to explore the removal of methyl-paraben. The total mineralization of 100 mg/L of the target compounds in 0.05 mol/L K$_2$SO$_4$ aqueous solution was achieved after 300 minute electrolysis at 10.8 mA/cm^2.

Main findings from the reviewed studies are reported in Table 7.

Table 7. Application of electrochemical oxidation (EcO) processes for the degradation of EDCs in aqueous media.

AOP	Operating conditions	Target EDCs	Work highlights	Reference
EcO	Graphite felt and titanium electrodes (area: 34 cm^2)	Bisphenol A, 17β-estradiol, estrone (0.1-1 mg/L)	Degradation of target EDCs in the range 10-100 ng/L.	[104]
EcO	Carbon fiber anode; Reference electrode: Ag/AgCl	Bisphenol A, Bisphenol S, Diphenoli acid (1 mM BPA, BPS and DPA in 0.1 M Sodium sulfate solution)	Complete removal in 10 min treatment.	[105]
EcO	Pt electrodes areas: 0.02 and 0.196 cm^2	Bisphenol A, nonylphenol	Oxidation of the alkylphenols in two-steps: oxidation generating a phenoxy radical, further oxidation to a phenoxonium ion.	[106]
EcO	Anode: Co-PbO$_2$; Cathode: stainless steel; Density: 0-50 mA/cm^2.	Bisphenol A (BPA) Diethylstilbestrol (DES)	The degradation of the target compounds accompanied by the generation of identified and non-identified chlorinated by-products.	[107]
EcO	4 types of anodes Density: 10-50 mA/cm^2.	Bisphenol A (100 mg/L)	Complete BPA removal was achieved at 10 mA/cm^2 using Ti/Sb-SnO$_2$ and Ti/BDD anodes.	[108]
EcO	3 types of anodes Density: up to 30 mA/cm^2	Bisphenol A (150 mg/L)	Nb/BDD anode presented 94% removal of BPA.	[109]
EcO	BDD anode; Density: 1.35 - 21.6 mA/cm^2	Metyl-paraben (100 mg/L in 0.05 mol/L K$_2$SO$_4$)	Total mineralization after 300 minute electrolysis at 10.8 mA/cm^2.	[110]
EcO/US	DBB anode; Density: 10, 23, 35 and 50 mA/cm^2; US: 20 kHz, 523 W/cm^2	Amaranth dye solution (100 mg/L)	The combined process allowed almost complete degradation, in the range 90-95%, even at lower current density. At higher current density values, TOC removal was also achieved.	[111]s
EcO/US/UV	Anode: p-Si-boron-doped diamond; Cathode: stainless steel; Density: 30 mA/cm^2. US: 24 kHz, 200 W; UV: 254 nm, 4 W.	Progesterone	CDPEO was found to be a synergistic process, not only from the improvement of rate but also from the energy point of view.	[112]
EcO/solar TiO$_2$ photocatalysis	TiO$_2$ as anode Density: 0.02-0.32 mA/cm^2.	Bisphenol A (120-820 μg/L)	Promotion of photocatalysis was associated with the efficient separation of photo-generated holes from electrons. The presence of dissolved species may partly impede the removal of BPA from secondary treated effluents.	[113]

More recent trends are directed towards the coupling of electrochemical processes with other AOPs.

The combined sonolysis/electrochemical process was tested for the degradation of amaranth dye [111] and, along with UV light, for the one of progesterone [112]. Similarly, an electrochemical process was applied to enhance the solar photocatalytic oxidation of BPA on TiO$_2$ film [113].

Electrochemical oxidation provides high pollutant removal and the technology is characterized by simple equipment, easy operation and versatility. The main drawback of electrochemical oxidation is its high investment and operational costs in comparison with conventional technologies [114]. Operational costs are mainly associated to energy consumption, which varies according to the electric potential as well as to the electrochemical oxidation index. The latter represents the average current efficiency for pollutants oxidation and is linked to treatment duration [115].

Recent research is therefore directed towards the combination of this kind of AOPs with renewable energy sources, in order to reduce both economic and environmental impact associated with the high energy demand of electrochemical oxidation.

4. Conclusive remarks

The continuous release of EDCs in wastewater effluents poses a serious issue related to the risk for both public health and environment. The need for adequate removal of these compounds has raised the interest towards AOPs. Their action mechanisms, based on free hydroxyl radicals, allow the degradation of a wide spectrum of contaminants.

AOPs can be adopted alone to treat specific industrial wastewaters. However their combination with conventional biological system has been recognized to be more sustainable to achieve either the increase of the biodegradability of contaminants or their complete removal.

Broad scientific literature has been produced on photocatalysis, but research has also been focused on sonolysis, ozonation as well as electrochemical methods.

Degradation yields for different kinds of EDCs have been reported to be high (80 - 90%) and extensive operating conditions have been found to determine even the occurrence of mineralization phenomena. However, if intended to remove all contaminants, AOPs could prove to be disadvantageous because of two main reasons:

- the possible formation of by-products and/or intermediates, which can be more toxic than parent compounds and sometimes difficult to degrade further. This item is more frequently associated with the application of chemically-based AOPs, such as ozonation, but it is also highly dependent on the compound to be degraded as well as on the characteristics of the aqueous media. Only few works have been carried out on real wastewaters, whereas most research has been performed on synthetic solutions. Although this approach promotes a clear identification of the potential of AOPs in the degradation of EDCs, it tangles the identification of mechanisms occurring in wastewaters due to the presence of different contaminants;
- the operating costs related to energy consumption, which is the main disadvantage of some technologies including ultrasound, UV as well as electrochemical systems.

In order to improve the cost-effectiveness of energy-consuming AOPs, the use of alternative systems has been studied. A step in this direction has been proved by the use of renewable energy sources to power the processes as exemplified in the case of solar photocatalysis. Similarly, the proper combination of AOPs can be a suitable strategy.

Coupling different advanced oxidation systems allows the reduction of the extent of single processes, without hampering overall degradation yields. On the contrary, different combinations of AOPs have been reported to result in synergistic effects, which enhance the removal rates and/or the degradation yields of EDCs. Moreover, when chemical processes are involved in combined systems, lower reagent dosage determines a reduction in inhibiting by-products formation.

Further studies should be directed towards the in-depth analysis of the mechanisms behind by-products formation from the application of different AOPs and their combination to EDC contaminated wastewaters, as well as to the evaluation of their toxicity. Results would realistically address the choice of the most suitable AOPs for the treatment of aqueous matrix contaminated by different kinds of EDCs. They would also suggest the most suitable application of AOPs as pre- or post-treatment when they are intended to be applied in combination with conventional biological systems for the upgrade of existing plants.

To this end, evaluation of the operating costs associated to different technological solutions is necessary.

Application of AOPs to degrade EDCs in aqueous media is likely to be an expensive venture: initial concentrations of contaminants are so low that treatment cost per unit mass can be much higher than the one associated to less effective conventional processes.

In order to reduce treatment costs, the segregation of wastewater flows originated from different sources appears interesting. The separation of wastewater streams, differently characterized in terms of EDC types and concentrations,

would allow the identification of the most efficient process for their removal, along with the reduction of the flow rates to be processed. This in turn would result in the reduction of the specific treatment costs.

Such a strategy could improve the competitiveness as well as a more sustainable application of AOPs, which could be limited to specific user bases, thus providing a solution for the expected enhanced water quality demand.

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