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

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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.

Keywords: by-products, combined process, cost, endocrine disruptors, risk, technology
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]:

- phthalates, 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].](image)

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).

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, finding 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 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 (100 mol/L) and continuous H₂O₂ 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]      |
| US          | 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]      |
| US          | 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]      |
| US          | 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/UV/TiO₂  | US: 518 kHz, 10 and 50 W, U: 254 nm, 6.9 W/cm²                                       | Butil-paraben (up to 100 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/EC       | US: 20 kHz, 523 W/cm²; BDD electrode; Current density: 10, 25, 35 and 50 mA/cm²    | Amaranth dye sol. (100 mg/L in 0.05 M K₂SO₄)     | 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.e., 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 deprotonation 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 TiO₂ 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 TiO₂ 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 TiO₂. This effect may slow down the recombination between photo-generated electrons and holes at the TiO₂ surface, thus promoting the oxidation of both BPA and its intermediates.

Ozonation has also been studied in combination with H₂O₂ 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 H₂O₂ 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                                                                 |
|---------------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Ozone                                      | 0-9 mgO₃/L pH: 6-9              | EE2 (50, 100, 200 µg/L)         | Removal efficiency improved at low pH values. [52]                               |
|                                             | 2 mgO₃/L pH: 6.6, 8.6           | EDCs (1-20 µg/L)                | Removal efficiency improved at low pH values. [57]                               |
|                                             | 0-3 mgO₃/L 0-15 min             | Caffeine, progesterone and its  | Variation in both pH and water matrix did not largely                        |
|                                             |                                  | steroids (2-10 mg/L)            | affect the rate constant for caffeine and progesterone; Overall removal approximately 80 %. [59] |
|                                             | 100 g/m² O₂/O₂ gas              | Potassium hydrogen phthalate    | Complete conversion of EDCs in water at less than three minutes residence time. [60] |
|                                             |                                  | (100 ppm C solution)            |                                                |
|                                             | 30 µM O₃                        | Bisphenol A                    | Reduced estrogenic activity in 60 min ozonation [61]                            |
| Ozone/TiO₂ photocatalysis                   | 3 mgO₃/L 500 W lamps           | Bisphenol A                    | Combined system showed synergistic effects. BPA mineralization occurred after only 90 min. [63] |
|                                             | 0.1-1.5 mM                       |                                |                                                |
| Ozone/H₂O₂                                  | 5 mgO₃/L 3.5 mg H₂O₂/L          | PPCPs and steroids (trace      | Approximately 90% removal was observed for each compound. [64]                 |
|                                             |                                  | concentration)                  |                                                |

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].

| 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 kW/m²)                               | 17β-estradiol, 17α-ethinylestradiol and estril | Degradation rate varied between 75% and 100%, after 126 days.                  | [70]      |
|                      | UVB: 0-500 µW/cm²                                          | Estrone and 17α-ethinylestradiol (500 ng/L) | Estrone degradation directly proportional to UVB intensity and inversely proportional to DOC concentration. | [71]      |
|                      | 1500 W xenon lamp UV filtered, 250 W/m² light power       | Estrone                              | DOC (7.7-8.9 mg/L) was found to enhance UV degradation of the target compound.   | [72]      |
| **UV/H₂O₂**          | UV: 1000mJ/cm²; low (LP)/medium pressure (MP). H₂O₂: 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/H₂O₂ was more effective than UV photolysis | [67]      |
| **UV/H₂O₂**          | 15 W, LP Hg lamps H₂O₂: 10, 50 ppm                       | Bisphenol A (13.7 mg/L)              | UV/H₂O₂ 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/H₂O₂**          | LP/MP lamps H₂O₂: various concentrations                 | Nbutylparaben, 4-t-octylphenol, trembolone, boldenone. | Highest elimination rate attained at H₂O₂ 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; H₂O₂: 0.018 mol/L | Estrone, 17β-estradiol, 17α-ethinylestradiol, estril, bisphenol A, and 4-nonylphenols (0.15 mg/gorg) | 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**        | LP Hg lamps; Fe³⁺: 5 mg/L H₂O₂: 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 micropolllutants. | [76]      |
| **UV/H₂O₂ + S₂O⁸⁻** | 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/H₂O₂ + Chlorine** | LP lamps (40-200 W); H₂O₂: ≈ 5 mg/L; Chlorine: 1-6.2 mg/L | Mix of EDCs (DOC: 46 mg/L)           | UV/Chlorine competitive from both a technical and economic point of view.       | [77]      |

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

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/m² [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 H₂O₂ 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/H₂O₂, 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 H₂O₂ 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/H₂O₂ 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/H₂O₂ system proved to be the most beneficial method to degrade the selected EDCs. Although the cost of H₂O₂ addition should be taken into account, the presence of H₂O₂ (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/H₂O₂ 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/H₂O₂ system efficiency was compared to the one of UV/S₂O₅²⁻ 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/H₂O₂ 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 m³ 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/H₂O₂ 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 H₂O₂ catalyzed by ferrous (Fe (II)) or ferric ions (Fe (III)). Fenton system efficiency depends on both H₂O₂ 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 | H₂O₂: 50 mg/L; Fe⁺³ 3 mg/L and absence of light; H₂O₂: 10-50 mg/L; Fe²⁺ 0-5 mg/L UV-C/solar light | Mix of 23 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 H₂O₂ at appropriate concentrations                     | Perfluoroctanoic acid (20 µmol/L)                                             | Rapid degradation within 1 h (87.9% removal); Afterwards, H₂O₂ was consumed and reactions mainly occurred due to Fe²⁺ ions. | [80]      |
| Fenton         | H₂O₂/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         | H₂O₂/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   | H₂O₂: 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 H₂O₂/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 H₂O₂ 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⁺³/H₂O₂ 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   | H₂O₂: 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   | H₂O₂: 5 mg/L; Fe(II): 30 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/m²; UV: 254 nm; Fe²⁺: 0.1 mM                                     | Di-n-butyl phthalate (0.01 mM)                                                | Complete degradation of the target compound in 75 min. More efficient use of Fe²⁺ 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 H₂O₂/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$_2$O$_2$/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$_2$O$_2$. 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$_2$O$_2$, 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$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$) 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, the 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 H₂O₂ in the presence of Fe^{2+}; the photo-decomposition of H₂O₂; 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 (TiO₂), zinc oxide (ZnO), zinc sulfide (ZnS), ferric oxide (Fe₂O₃), silicon (Si), tin oxide (SnO₂), and cadmium sulfide (CdS) should be reported. However, TiO₂ 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 TiO₂ 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].](image-url)
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, acetaminophen (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-ethynylestradiol, 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-SnO₂, Ti/RuO₂ 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/cm²) were carried out for each anode. The best degradation results were obtained with the Ti/Sb-SnO₂ and Ti/BDD anodes, which allowed complete BPA destruction at a current density of 10 mA/cm².

The degradation of this EDC by electrochemical oxidation was also investigated by Pereira et al. [109] using a borondoped diamond (Nb/BDD) anode at a current density of 30 mA/cm². Under constant operating conditions, experiments were also performed using Ti-Pt/b-PbO₂ and TiO₂-RuO₂ 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 K₂SO₄ aqueous solution was achieved after 300 minute electrolysis at 10.8 mA/cm².

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 cm²)                                   | 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, Diphenol 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 cm²                                               | Bisphenol A, nonylphenol                                                                                | Oxidation of the alkylphenols in two-steps: oxidation generating a phenoxy radical, further oxidation to a phenoxy ion. | [106]     |
| EcO               | Anode: Co-PbO₂; Cathode: stainless steel; Density: 0-50 mA/cm²                         | 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/cm²                                               | Bisphenol A (100 mg/L)                                                                                  | Complete BPA removal was achieved at 10 mA/cm² using Ti/Sb-SrO₂ and Ti/BDD anodes.               | [108]     |
| EcO               | 3 types of anodes Density: up to 30 mA/cm²                                           | Bisphenol A (150 mg/L)                                                                                  | Nb/BDD anode presented 94% removal of BPA.                                                            | [109]     |
| EcO               | BDD anode; Density: 1.35 - 21.6 mA/cm²                                                | Metyl-paraben (100 mg/L in 0.05 mol/L K₂SO₄)                                                           | Total mineralization after 300 minute electrolysis at 10.8 mA/cm².                                    | [110]     |
| EcO/US            | DBB anode; Density: 10, 23, 35 and 50 mA/cm²; US: 20 kHz, 523 W/cm²                    | Amaranth dye solution (100 mg/L)                                                                       | The combined process allowed almost complete degradation, in the range 90-95%, even at lower current density. | [111]     |
| EcO/US/UV         | Anode: p-Si-boron-doped diamond; Cathode: stainless steel; Density: 30 mA/cm²; 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 TiO2    | TiO₂ as anode Density: 0.02-0.32 mA/cm²                                               | 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 TiO₂ 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.
References

[1]. Pomati F, Castiglioni S, Zuccato E, Fanelli R, Rossetti C, Calamari D. Effects of environmental contamination by therapeutic drugs on human embryonic cells. Environ Sci Technol 2006; 40: 2442-7.

[2]. Kümmnerer. Antibiotics in the aquatic environment - A review - Part I. Chemosphere 2009; 75: 417-34.

[3]. Bolong N, Ismail AF, Salim MR, Matsuura T. A review of the effects of emerging contaminants in wastewater and options for their removal. Desalination 2009; 239: 229-46.

[4]. Klamerth N, Rizzo L, Malato S, Maldonado MI, Agüera A, Fernández-Alba AR. Degradation of fifteen emerging contaminants at µg/L initial concentrations by mild solar photo-Fenton in MWTP effluents. Water Res 2010; 44(2): 545-54.

[5]. Larsen TA, Lienert J, Joss A, Siegrist H. How to avoid pharmaceuticals in the aquatic environment. J Biotechnol 2004; 113: 295-304.

[6]. Gogate PR., Pandit AB. A review of imperative technologies for wastewater treatment. I: oxidation technologies at ambient conditions. Adv Environ Res 2004; 8: 501-51.

[7]. Köhler C, Venditti S, Igos E, Klepiszewski K, Benetto E, Cornelissen A. Elimination of pharmaceutical residues in biologically pre-treated hospital wastewater using advanced UV irradiation technology: A comparative assessment. J Haz Mat 2012; 239-40: 70-7.

[8]. Miralles-Cuevas S, Audino F, Oller I, Sánchez- Moreno R, Sánchez-Pérez JA, Malato S. Pharmaceuticals removal from natural water by nanofiltration combined with advanced tertiary treatments (solar photo-Fenton, photo-Fenton-like Fe(III)–EDDS complex and ozonation). Sep Purif Technol 2014; 122: 515-22.

[9]. Kim I, Yamashita N, Tanaka H. Photodegradation of pharmaceuticals and personal care products during UV and UV/H2O2 treatments. Chemosphere 2009; 77: 518-25.

[10]. Li W, Nanaboinab V, Zhoua Q, Korshin GV. Effects of Fenton treatment on the properties of effluent organic matter and their relationships with the degradation of pharmaceuticals and personal care products. Water Res 2012; 46:403-12.

[11]. Zhang V, Pagilla K. Treatment of malathion pesticide wastewater with nanofiltration and photo-Fenton oxidation. Desalination 2010; 263: 36-44.

[12]. Jović M, Manojlović D, Stanković D, et al. Degradation of triketone herbicides, mesotrione and sulcotrione, using advanced oxidation processes. J Haz Mat 2013; 260: 1092-9.

[13]. Arevalo E, Calmano W. Studies on electrochemical treatment of wastewater contaminated with organotin compounds. J Haz Mat 2007; 146 (3): 540-5.

[14]. Horikoshi S, Sato S, Abe M, Serpone N. A novel liquid plasma AOP device integrating microwaves and ultrasounds and its evaluation in defluorinating perfluorooctanoic acid in aqueous media. Ultrason Sonochem 2011; 18(5): 938-42.

[15]. Suri RPS, Nayak M, Devaiah U, Helmig E. Ultrasound assisted destruction of estrogen hormones in aqueous solution: effect of power density, power intensity and reactor configuration. J Haz Mat 2007; 146: 472-8.

[16]. Chowdhury RR, Charpentier PA, Ray MB. Photodegradation of 17β-estradiol in aquatic solution under solar irradiation: kinetics and influencing water parameters. J Photochem Photobiol 2011; 219: 67-75.

[17]. Singla R, Grieser F, Ashokkumar M. The mechanism of sonochemical degradation of a cationic surfactant in aqueous solution. Ultrason Sonochem 2011; 18(2): 484-8.

[18]. Olmez-Hanci T, Arslan-Alaton I, Genc B. Degradation of the nonionic surfactant Triton™ X-45 with HO and SO4 - Based advanced oxidation processes. Chem Eng J 2014; 239: 332-40.
[19]. Banerjee P, DasGupta S, De S. Removal of dye from aqueous solution using a combination of advanced oxidation process and nanofiltration. J Haz Mat 2007; 140: 95-103.
[20]. Grčić I, Papić S, Mesec D, Koprivanac N, Vujević D. The kinetics and efficiency of UV assisted advanced oxidation of various types of commercial organic dyes in water. J Photochem Photobiol A: Chem 2014; 273: 49-58.
[21]. Lister AL, van der Kraak GJ. Endocrine disruption: why is it so complicated? Water Qual Res J Canada 2001; 36: 175-90.
[22]. De Coster S, van Larebeke N. Endocrine-Disrupting Chemicals: Associated Disorders and Mechanisms of Action. J Environ Public Health 2012; 2012: 1-52.
[23]. Esplugas S, Bila DM, Krause LGT, Dezotti M. Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. J Haz Mat 2007; 149: 631-42.
[24]. Gültekin I, Ince NH. Synthetic endocrine disruptors in the environment and water remediation by advanced oxidation processes. J Environ Manage 2007; 85: 816-32.
[25]. Lapworth DJ, Baran N, Stuart ME, Ward RS. Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. Environ Pollut 2012; 163: 287-303.
[26]. Sun Y, Huang H, Sun Y et al. Occurrence of estrogenic endocrine disrupting chemicals concern in sewage plant effluent. Front Environ Sci Eng 2014; 8(1): 18-26.
[27]. Pisapia L, Del Pozzo G, Barba P, et al. Effects of some endocrine disruptors on cell cycle progression and murine dendritic cell differentiation. Gen Comp Endocrinol 2012; 178: 54-63.
[28]. Birnbaum LS, Fenton SE. Cancer and developmental exposure to endocrine disruptors. Environ Health Persp 2003; 111: 389-94.
[29]. García-Mayor RV, Larrañaga Vidal A, Docet Caamaño MF, Lafuente Giménez A. Endocrine disruptors and obesity: obesogens. Endocrinologia Nutrición (English Edition), 2012; 59: 261-7.
[30]. Lee DH, Lee IK, Porta M, Steffès M, Jacobs Jr DR. Relationship between serum concentrations of persistent organic pollutants and the prevalence of metabolic syndrome among non-diabetic adults: results from the National Health and Nutrition Examination Survey 1999-2002. Diabetologia, 2007; 50: 1841-51.
[31]. Fei C, McLaughlin JK, Lipworth L, Olsen J. Maternal levels of perfluorinated chemicals and subfecundity. Hum Reprod 2009; 24: 1200-5.
[32]. Metcalf & Eddy. Ingegneria delle acque reflue. Trattamento e riuso. 4th ed. McGraw Hill: Milano 2006.
[33]. Ince NH, Apikyan IG. Combination of activated carbon adsorption with light-enhanced chemical oxidation via hydrogen peroxide. Water Res 2000; 34: 4169-76.
[34]. Oller I, Malato S, Sánchez-Pérez JA. Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination-A review. Sci Total Environ 2011; 409: 4141-66.
[35]. Cesaro A, Naddeo V, Belgiorno V. Wastewater Treatment by Combination of Advanced Oxidation Processes and Conventional Biological Systems. J Bioremed Biodeg 2013; 4(8): 1-8.
[36]. Jamil TS, Ghaly MY, El-Seesy IE, SouayaER, Nasr RA. A comparative study among different photochemical oxidation processes to enhance the biodegradability of paper mill wastewater. J Haz Mat 2011; 185: 353-8.
[37]. Estrada AL, Li YY, Wang A. Biodegradability enhancement of wastewater containing cefalexin by means of the electro-Fenton oxidation process. J Haz Mat 2012; 227-228: 41-8.
[38]. Moreira FC, Vilar VJP, Ferreira ACC et al. Treatment of a pesticide-containing wastewater using combined biological and solar-driven AOPs at pilot scale. Chem Eng J 2012; 209: 429-41.

[39]. Prieto-Rodríguez L, Oller I, Klamertha N, Agüera A, Rodriguez EM, Malato S. Application of solar AOPs and ozonation for elimination of micropollutants in municipal wastewater treatment plant effluents. Water Res 2013; 47: 1521-8.

[40]. Furuta M, Yamaguchi M, Tsukamoto T. et al. Inactivation of Escherichia coli by Ultrasonic irradiation. Ultrason Sonochem 2004; 11: 57-60.

[41]. Abu-Hassan MA, Kim JK, Metcalfe IS, Mantzavinos D. Kinetics of low frequency sonodegradation of linear alkylbenzene sulfonate solutions. Chemosphere 2006; 62:749-55.

[42]. Chiha M, Hamdaoui O, Baup S, Gondrexon N. Sonolytic degradation of endocrine disrupting chemical 4-cumylphenol in water. Ultrason Sonochem 2011; 18: 943-50.

[43]. Torres RA, Abdelmalek F, Combet E, Pétrier C, Pulgarin C. A comparative study of ultrasonic cavitation and Fenton’s reagent for bisphenol A degradation in deionised and natural waters. J Haz Mat 2007; 146: 546-51.

[44]. Torres RA, Pétrier C, Combet E, Carrier M, Pulgarin C. Ultrasonic cavitation applied to the treatment of bisphenol A. Effect of sonochemical parameters and analysis of BPA by-products. Ultrason Sonochem 2008; 15:605-11.

[45]. Naddeo V, Belgiorno V, Kassinos D, Mantzavinos D., Meric S. Ultrasonic degradation, mineralization and detoxification of diclofenac in water: optimization of operating parameters. Ultrason Sonochem 2010; 17: 179-85.

[46]. Na S, Jinhua C, Cui M, Khim J. Sonophotolytic diethyl phthalate (DEP) degradation with UVC or VUV irradiation. Ultrason Sonochem 2012, 19: 1094-8.

[47]. Daghrir R, Dimboukou-Mpiry A, Seyhi B, Drogui P. Photosonochemical degradation of butyl-paraben: Optimization, toxicity and kinetic studies. Sci Total En 2014; 490: 223-34.

[48]. Na S, Ahn YG, Cui M, Khim J. Significant diethyl phthalate (DEP) degradation by combined advanced oxidation process in aqueous solution. J Env Manag 2012; 101: 104-10.

[49]. Steter JR, Barros WRP, Lanza MRV, Motheo AJ. Electrochemical and sonoelectrochemical processes applied to amaranth dye degradation. Chemosphere 2014; 117: 200-7.

[50]. Beltrán FJ. Ozone reaction kinetics for water and wastewater systems. 1st ed. Lewis Publishers, CRC Press: USA 2005.

[51]. Koprivanac N, Kušić H. In: Hazardous Materials and Wastewater: Treatment, Removal and Analysis, Nova Science Publishers, Inc: uppauge, NY, SAD 2007; pp. 149-99.

[52]. Rodriguez A, Rosal R, Perdigón-Melón JA et al. Ozone-based technologies in water and wastewater treatment. Hdb Env Chem 2008; 5 (S/2): 127-75.

[53]. Arslan-Alaton I, Dogruel S. Pre-treatment of penicillin formulation effluent by advanced oxidation processes. J Haz Mat 2004; 112: 105-113.

[54]. Arslan-Alaton I, Dogruel S, Baykal E, Gerone G. Combined chemical and biological oxidation of penicillin formulation effluent. J Environ Manag 2004; 73: 155-63.

[55]. Cokgor EU, Arslan-Alaton I, Karahan O, Dogruel S, Orhon D. Biological treatability of raw and ozonated penicillin formulation effluent. J Haz Mat 2004; 116: 159-66.

[56]. Zhang Z, Zhu H, Wen X, Si X. Degradation behavior of 17α-ethinylestradiol by ozonation in the synthetic secondary effluent. J Environ Sci 2012; 24: 228-33.
[57]. Wu Q, Shi H, Adams CD, Timmons T, Ma Y. Oxidative removal of selected endocrine-disruptors and pharmaceuticals in drinking water treatment systems, and identification of degradation products of triclosan. Sci Total Environ 2013; 439: 18-25.

[58]. Lee J, Park H, Hoon J. Ozonation characteristics of bisphenol A in water. Environ Technol 2003; 24:241-248.

[59]. Broséus R, Vincent S, Aboulfadl K et al. Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment. Water Res 2009; 43: 4707-17.

[60]. Chan WK, Jouët J, Heng S, Yeung KL, Schrotter JC. Membrane contactor/seperator for an advanced ozone membrane reactor for treatment of recalcitrant organic pollutants in water. J Solid State Chem 2012; 189:96-100.

[61]. Alum A, Yoon Y, Westerhoff P, Abbaszadegan M. Oxidation of bisphenol A, 17β-estradiol and 17α-ethynyl estradiol and byproduct estrogenicity. Environ Toxicol 2004; 19: 257-64.

[62]. Larcher S, Delbès G, Robaire B, Yargeau V. Degradation of 17α-ethinylestradiol by ozonation - Identification of the by-products and assessment of their estrogenicity and toxicity. Environ Int 2012; 39: 66-72.

[63]. Colombo A, Cappelletti G, Ardizzone S et al. Bisphenol A endocrine disruptor complete degradation using TiO₂ photocatalysis with ozone. Environ Chem Lett 2012; 10: 55-60.

[64]. Gerrity D, Gamage S, Holady JC, et al. Pilot-scale evaluation of ozone and biological activated carbon for trace organic contaminant mitigation and disinfection. Water Research 2011; 45: 2155-65.

[65]. Jin P, Jin X, Wang XC, Shi X. An analysis of the chemical safety of secondary effluent for reuse purposes and the requirement for advanced treatment. Chemosphere 2013; 91: 558-62.

[66]. Unluturk S, Atilgan M, Handan Baysal A, Tari C. Use of UV-C radiation as a non-thermal process for liquid egg products (LEP). J Food Eng 2008; 85: 561-8.

[67]. Rosenfeldt EJ, Linden KG. Degradation of endocrine disrupting chemicals bisphenol A, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation processes. Environ Sci Technol 2004; 38: 5476-83.

[68]. Wols BA, Hofman-Caris CHM. Review of photochemical reaction constants of organic micro pollutants required for UV advanced oxidation processes in water. Water Res 2012; 46: 2815-27.

[69]. Okamoto Y, Hayashi T, Toda C et al. Formation of estrogenic products from environmental phthalate esters under light exposure. Chemosphere 2006; 64: 1785-92.

[70]. Fonseca AP, Lima DLD, Esteves VI. Degradation by solar radiation of estrogenic hormones monitored by UV-visible spectroscopy. Water Air Soil Pollut 2011; 215:441-7.

[71]. Atkinson SK, Marlatt VL, Kimpe LE, Lean DRS, Trudeau VL, Blais JM. Environmental factors affecting ultraviolet photodegradation rates and estrogenicity of estrone and ethinylestradiol in natural waters. Arch Environ Contam Toxicol 2011; 60:1-7.

[72]. Caupos E, Mazellier P, Croue JP. Photodegradation of estrone enhanced by dissolved organic matter under simulated sunlight. Water Res 2011; 45: 3341-50.

[73]. Chen PJ, Linden KG, Hinton DE, Kashyawada S, Rosenfeldt EJ, Kullman SW. Biological assessment of bisphenol A degradation in water following direct photolysis and UV advanced oxidation. Chemosphere 2006; 65: 1094-102.

[74]. Będzka D, Gmureka M, Gryglik M, Olak M, Miller JS, Ledakowicz S. Photodegradation and advanced oxidation of endocrine disruptors in aqueous solutions. Catal Today 2010; 151: 125-30.

[75]. Zhang A, Li Y. Removal of phenolic endocrine disrupting compounds from waste activated sludge using UV, H₂O₂, and UV/H₂O₂ oxidation processes: effects of reaction conditions and sludge matrix. Sci Total Environ 2014; 493: 307-323.
[76]. De la Cruz N, Giménez J, Esplugas S, Grandjean D, de Alencastro LF, Pulgarín C. Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. Water Res 2012; 46: 1947-57.

[77]. Sichel C, García C, Andre K. Feasibility studies: UV/chlorine advanced oxidation treatment for the removal of emerging contaminants. Water Res 2011; 45: 6371-80.

[78]. Trapido M, Kulik N, Goi A, Veressinina Y, Munter R. Fenton treatment efficacy for the purification of different kinds of wastewater. Water Sci Technol 2009; 60(7): 1795-801.

[79]. Yaping Z, Jiangyong H, Hongbin C. Elimination of estrogen and its estrogenicity by heterogeneous phot-Fenton catalyst β-FeOOH/resin. J Photochem Photobiol 2010; 212: 94-100.

[80]. Tang H, Xiang Q, Lei M, Yan J, Zhu L, Zou J. Efficient degradation of perfluorooctanoic acid by UV-Fenton process. Chem Eng J 2012; 184: 156-62.

[81]. Ifelebuegu AO, Ezenwa CP. Removal of endocrine disrupting chemicals in wastewater treatment by Fenton-like oxidation. Water Air Soil Poll 2011; 217: 213-20.

[82]. He PJ, Zheng Z, Zhang H, Shao LM, Tang QY. PAEs and BPA removal in landfill leachate with Fenton process and its relationship with leachate DOM composition. Sci Total Environ 2009; 407: 4928-433.

[83]. De la Cruz N, Esquius L, Grandjean D, et al. Degradation of emergent contaminants by UV, UV/H2O2 and neutral photo-Fenton at pilot scale in a domestic wastewater treatment plant. Water Res 2013; 47: 5836-545.

[84]. Li W, Nanaboina V, Zhou Q, Korshin GV. Effects of Fenton treatment on the properties of effluent organic matter and their relationships with the degradation of pharmaceuticals and personal care products. Water Res 2012; 46: 403-12.

[85]. Molkenthin M, Olmez-Hanci T, Jekel MR, Arslan-Alaton I. Photo-Fenton-like treatment of BPA: effect of UV light source and water matrix on toxicity and transformation products. Water Res 2013; 47: 5052-64.

[86]. Escalona I, Fortuny A, Stüber F, Bengoa C, Fabregat A, Font J. Fenton coupled with nanofiltration for elimination of Bisphenol A. Desalination 2014; 345: 77-84.

[87]. Klamerth N, Malato S, Agüera A, Fernández-Alba AR. Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: A comparison. Water Res 2013; 47: 833-40.

[88]. Xu LJ, Chu W, Graham N. Degradation of di-n-butyl phthalate by a homogeneous sono-photo-Fenton process with in situ generated hydrogen peroxide. Chem Eng J 2014; 240: 541-7.

[89]. Augugliaro V, Litter M, Palmisano L, Soria J. The combination of heterogeneous photocatalysis with chemical and physical operations: a tool for improving the photoprocess performance. J Photochem Photobiol C: Photochem Reviews 2006; 7: 127-44.

[90]. Nakata K, Ochiai T, Murakami T, Fujishima A. Photoenergy conversion with TiO2 photocatalysis: New materials and recent applications. Electrochim Acta 2012; 84: 103-11.

[91]. Umar M, Aziz HA. In: Organic pollutants: monitoring, risk and treatment, Ed. M. Nageed Rusheb 2013; 8: 195-208. ISBN 978-953-51-0948-8.

[92]. Rengaraj S, Li XZ, Tanner PA, Pan ZF, Pang GKH. Photocatalytic degradation of methylparathion-An endocrine disruptor by Bi3+-doped TiO2. J Mol Catal A Chem 2006; 247: 36-43.

[93]. Silva CP, Otero M, Esteves V. Processes for the elimination of estrogenic steroid hormones from water: a review. Environ Pollut 2012; 165: 38-58.
[94]. Bernabeu A, Vercher RF, Santos-Juanes L, et al. Solar photocatalysis as a tertiary treatment to remove emerging pollutants from wastewater treatment plant effluents. Catal Today 2011; 161: 235-40.

[95]. Manassero A, Satuf ML, Alfano OM. Evaluation of UV and visible light activity of TiO$_2$ catalysts for water remediation. Chem Eng J 2013; 225: 378-86.

[96]. Coleman HM, Chiang K, Amal R. Effects of Ag and Pt on photocatalytic degradation of endocrine disrupting chemicals in water. Chem Eng J 2005; 113: 65-72.

[97]. Kapla R, Erjavec B, Pintar A. Enhanced photocatalytic activity of single-phase, nanocomposite and physically mixed TiO$_2$ polymorphs. In press on Appl Catal A Gen.

[98]. Zhang W, Li Y, Su Y, Ma K, Wang Q. Effect of water composition on TiO$_2$ photocatalytic removal of endocrine disrupting compounds (EDCs) and estrogenic activity from secondary effluent. J Haz Mat 2012; 215-216: 252-8.

[99]. Rodriguez EM, Fernández G, Alvarez PM, Beltrán FJ. TiO$_2$ and Fe(III) photocatalytic ozonation processes of a mixture of emergent contaminants of water. Water Res 2012; 46: 152-66.

[100]. Chen G. Electrochemical technologies in wastewater treatment. Sep Purif Technol 2004; 38: 11-41.

[101]. Nidheesh PV, Gandhimathi R. Trends in electro-Fenton process for water and wastewater treatment: An overview. Desalination 2012; 299: 1-15.

[102]. Chiang LC, Chang JE, Wen TC. Indirect oxidation effect in electrochemical oxidation treatment of landfill leachate. Water Res 1995; 29: 671-8.

[103]. Aquino JM, Rocha-Filho RC, Ruotolo LAM, Bocchi N, Biaggio SR. Electrochemical degradation of a real textile wastewater using β-PbO$_2$ and DSA(R) anodes. Chem Eng J 2014; 251: 138-45.

[104]. Jiang JQ, Yin Q, Zhou JL, Pearce P. Occurrence and treatment trials of endocrine disrupting chemicals (EDCs) in wastewaters. Chemosphere 2005; 61: 544-50.

[105]. Kuramitz H, Matsushita M, Tanaka S. Electrochemical removal of bisphenol A based on the anodic polymerization using a column type carbon fiber electrode. Water Res 2004; 38: 2331–8.

[106]. Ngundi MM, Sadik OA, Yamaguchi T, Suye S. First comparative reaction mechanisms of β-estradiol and selected environmental hormones in a redox environment. Electrochem Commun 2003; 5: 61-67.

[107]. Korshin GV, Kim J, Gan L. Comparative study of reactions of endocrine disruptors bisphenol A and diethylstilbestrol in electrochemical. Water Res 2006; 40: 1070-8.

[108]. Cui YH, Li XY, Chen G. Electrochemical degradation of bisphenol A on different anodes. Water Res 2009; 43: 1968-76.

[109]. Pereira GF, Rocha-Filho RC, Bocchi N, Biaggio SR. Electrochemical degradation of bisphenol A using a flow reactor with a boron-doped diamond anode. Chem Eng J 2012; 198-199: 282-8.

[110]. Steter JR, Rocha RS, Dionisio D, Lanza MRV, Motheo J. Electrochemical oxidation route of methyl paraben on a boron-doped diamond anode. Electrochim Acta 2014; 117: 127-33.

[111]. Barros RP, Steter JR, Lanza MRV, Motheo AJ. Degradation of amaranth dye in alkaline medium by ultrasonication coupled with electrochemical oxidation using a boron-doped diamond anode. Electrochim Acta 2014; 143: 180-7.

[112]. Martín de Vidales MJ, Barba S, Sáez C, Cánizares P, Rodrigo MA. Coupling ultraviolet light and ultrasound irradiation with conductive-diamond electrochemical oxidation for the removal of progesterone. Electrochim Acta 2014; 140: 20-6.
[113]. Frontistis Z, Daskalaki VM, Katsaounis A, Poulos I, Mantzavinos D. Electrochemical enhancement of solar photocatalysis: Degradation of endocrine disruptor bisphenol-A on Ti/TiO$_2$ films. Water Res 2011; 45: 2996-3004.

[114]. Alvarez-Guerra E, Dominguez-Ramos A, Irabien A. Design of the Photovoltaic Solar Electro-Oxidation (PSEO) process for wastewater treatment. Chem Eng Res Des 2011; 89: 2679-85.

[115]. Kapalka A, Főti G, Comninellis C. Kinetic modelling of the electrochemical mineralization of organic pollutants for wastewater treatment. J Appl Electrochem 2008; 38: 7-16.