

# Review on endocrine disrupting-emerging compounds in urban wastewater: occurrence and removal by photocatalysis and ultrasonic irradiation for wastewater reuse

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## Abstract

Because of the vast use of organic chemicals in modern society, almost any wastewater stream from industrial processes or households contains such compounds and disposal without proper treatment will therefore result in exposure to humans and the environment. Some of them may exhibit endocrine disrupting effects (EDCs) and they widely exist in wastewater. The current effluent standards for Urban Wastewater Treatment Plants (UWWTPs) still include the conventional parameters of BOD, COD, pH, suspended solids, nitrogen, phosphorus, total number of *E. coli* etc. No limits for dangerous substances such as heavy metals or xenobiotic organic compounds exist in many countries. In the framework of the Water Frame Directive (WFD), environmental quality standards including 33 priority pollutants and some other xenobiotics have been proposed by the EU. As a consequence, member states have to establish monitoring programs for a number of priority and emerging pollutants. The integrated use of conventional biological treatment with advanced oxidation processes (AOPs) such as ozone oxidation, photocatalysis, Fenton and Photo-Fenton oxidation have been applied in order to increase the biodegradability and also the detoxification of the effluent streams. The use of AOPs seems to be favorable for reuse applications that require high quality of treated water, like for example groundwater recharge and indirect potable reuse. However, total dissolved solids (TDS) which can be increased if AOPs are applied have to be removed before reuse. This paper aims at providing an updated review on EDCs and their removal by photocatalysis (PC)

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and ultrasound oxidation (US) from aqueous spiked solutions and wastewater. The recently established reuse limits in Italy are evaluated according to AOPs requirements discussed in this paper.

*Keywords:* Endocrine disrupting compounds; Photocatalysis; Reuse; Ultrasound; Urban wastewater

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## 1. Introduction

One of the principal environmental objectives of the EC Water Framework Directive (WFD), Article 4, is to ensure achievement and maintenance of “good status” for all community waters including inland surface and ground waters, transitional and coastal waters by 2015 [1]. In this framework, a number of xenobiotics (a class of chemical compounds foreign to the body of the living organisms and resistant to environmental degradation) which are continuously released into the environment, such as polycyclic aromatic hydrocarbons (PAHs), alkylphenols (APs), organotins (OTs), volatile organic compounds (VOCs), pesticides and heavy metals have been listed as priority substances. A recent proposal issued by the EU Parliament and Council regulates their concentrations in surface waters [2]. The priority list of WFD includes 33 substances characterized by high toxicity, high environmental persistence and high lipophilicity leading to bioaccumulation in food webs and by increased risk for the environment and human health. Several of them (e.g. PAHs, APs, OTs, brominated flame retardants) have been already proven to be or are potential endocrine disruptors (EDCs) [3,4]. These compounds, a wide class of natural and synthetic chemicals, are referred to as EDCs because they interfere with the normal functioning of the endocrine system. The U.S. Environmental Protection Agency (EPA) defines environmental EDCs as xenobiotics (agents foreign to an organism) that interfere with the “synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior.

The effects suggested as being related to endocrine disruption have been reported in mollusks, crustacean, fish, reptiles, birds and mammals in various parts of the world as early as the 1930s [5].

Substances like phthalates, pesticides, polychlorinated biphenyls (PCBs), dioxins, polycyclic aromatic hydrocarbons (PAHs), alkylphenols (APs) and bisphenols are present more frequently in wastewater treatment plant effluents than other environmental matrices. Most EDCs are synthetic organic chemicals (xenobiotics) introduced to the environment by anthropogenic inputs but they can also be naturally generated estrogenic hormones (e.g. estrone, 17 $\beta$ -estradiol), and therefore are ubiquitous in aquatic environments receiving sewage effluents [6]. Recent studies show that sewage treatment plants (STPs) are a significant point source, particularly for surface water and groundwater of EDCs including Nonylphenol monoethoxylate (NPE1); Nonylphenol diethoxylate (NPE2), Nonylphenol triethoxylate (NPE3) and: Octylphenol (OP) at  $\mu\text{g/L}$  levels [3]. Another group of compounds of particular interest and unknown fate and impact originating from STPs is pharmaceutical residues. For instance, in a monitoring campaign in Italy, France, Greece and Sweden, carbamazepine, clofibrate, phenazone and aminopyrine, clofibric acid, diclofenac, fenofibrate, fenoprofen, flurbiprofen, gemfibrozil, ibuprofen, ketoprofen and naproxen belonging to different therapeutic pharmaceuticals classes were found in the effluent of the STPs [7]. A predictive model proposed to assess the presence of the pharmaceutical residues showed a high risk ratio of the occurrence of the most consumed pharmaceuticals in Italy [8].

The removal of EDCs in wastewater treatment processes depends on the inherent physicochemical properties of the pollutants and on the nature of the treatment process involved. It is generally recognized that there are four main removal pathways for organic compounds during the conventional wastewater treatment: (i) adsorption onto suspended solids or association with fats and oils, (ii) aerobic and anaerobic degradation, (iii) chemical (abiotic) degradation by processes such as hydrolysis and (iv) volatilization. A compound's physicochemical data can be used to predict physical processes, such as sorption, volatilization and dissolution. The important properties to be considered are octanol-water partition coefficient ( $K_{ow}$ ), aqueous solubility, acid dissociation constant and Henry's Law constant ( $H_c$ ). Knowledge of chemical partitioning between the aqueous and solid phase is needed to assess pathways of EDCs transport and transformation [9]. However, many of those EDCs, and other emerging pollutants are partially or at a low grade removed from wastewater in conventional treatment systems. Several studies confirmed that in activated sludge treatment plants the EDCs are relatively removed. Sorption and biodegradation are considered as the principal mechanisms for steroid estrogens removal, influenced by hydraulic retention time (HRT) and high sludge retention time used in STPs [10,11]. Due to the possibility of maintaining high retention time, membrane bioreactors are able to host diverse microbial culture which can induce degradation. Thus compared to other biological treatment methods membrane bioreactors show better removal effectiveness [12]. Regarding the physical treatment methods, the non polar and hydrophobic nature of many EDCs chemicals causes them to sorb onto particulates. This suggests that the general effect of wastewater treatment processes would be to concentrate organic pollutants, including EDCs, in the sewage sludge while mechanical separation techniques, such as sedimentation, would result in significant removal

from the aqueous phase to primary and secondary sludges. The result of this is that the treated wastewater is discharged relatively free of EDCs but absorbed on sewage sludge which could constitute a new source of pollution if applied as fertilizer on agricultural fields [13]. Thus there is an even increasing interest towards the direction of developing reliable detection methods [14] and also treatment processes able to reach final concentrations in the effluents below estrogenic limits of these emerging pollutants [13]. The use of advanced oxidation processes (AOPs) such as photocatalysis (PC) [15–19], ozone based technologies [20–21] and ultrasound oxidation [22–24] have been investigated in respect to their ability to increase the biodegradability as well as the detoxification of effluent streams containing polar and hydrophilic chemicals.

This paper provides a discussion on wastewater management and reuse with special reference to health and regulatory aspects in respect to EDCs and their removal by photocatalytic oxidation and ultrasound irradiation considering the Water Framework Directive [1–2], the present reuse limits for urban wastewaters that are applied by WHO [25] and those that are applied in Italy [26].

## **2. Removal of endocrine disrupting compounds from urban wastewater using photocatalysis and ultrasonic irradiation (US) processes**

Photocatalysis is a chemical oxidation process in which a metal oxide semiconductor immersed in water and irradiated by near UV light ( $\lambda < 385$  nm) results in the formation of free hydroxyl (OH) radicals. Although several semiconductors exist,  $TiO_2$  is the most widely used catalyst, mainly because of its photo-stability, non-toxicity, low cost and water insolubility under most environmental conditions. Photocatalysis process has been found to be effective for the degradation of EDCs in wastewater (Table 1). As seen in Table 1,

Table 1  
Removal of some EDCs during TiO<sub>2</sub> based photocatalytic suspended systems

Compound	Concentration (mg/L)	Removal (%)	pH	Reaction time	Catalyst and oxidant concentrations	References
17β-Estradiol	0.82	98 <sup>a</sup>	5.5	3.5 h	1.0 g/L of TiO <sub>2</sub>	[18]
Atrazine	25	99 <sup>a</sup>	6.94	60 min	1.0 g/L of TiO <sub>2</sub>	[27]
Atrazine	25	86.1 <sup>a</sup>	2.03	60 min	1.0 g/L of TiO <sub>2</sub>	[27]
Atrazine	25	67.6 <sup>a</sup>	9.99	60 min	1.0 g/L of TiO <sub>2</sub>	[27]
2,4-Dichlorophenol	22.5	96 <sup>a</sup>	6.6	2 h	0.2 g/L of TiO <sub>2</sub>	[28]
Methomyl	18	67 <sup>b</sup>	7	400 min	0.2 g/L of TiO <sub>2</sub>	[29]
Bisphenol A	100	63 <sup>a</sup>	6	1 h	10 g/L of TiO <sub>2</sub>	[30]
Bisphenol A	20	95 <sup>a</sup>	3	1 h	2 g/L of TiO <sub>2</sub> (pH = 3)	[17]
Bisphenol A	20	99 <sup>a</sup>	10	1 h	2 g/L of TiO <sub>2</sub> (pH = 3)	[17]
Bisphenol A	20	62.5 <sup>b</sup>	3	1 h	2 g/L of TiO <sub>2</sub> (pH = 3)	[17]
Bisphenol A	20	12.5 <sup>b</sup>	10	1 h	2 g/L of TiO <sub>2</sub> (pH = 3)	[17]
Aldrin	5	71 <sup>a</sup>	–	8 h	0.2 g/L of TiO <sub>2</sub>	[31]
Aldrin	5	68 <sup>a</sup>	–	8 h	0.2 g/L of TiO <sub>2</sub> + 3 g/L H <sub>2</sub> O <sub>2</sub>	[31]
Aldrin	5	90 <sup>a</sup>	–	8 h	0.2 g/L of TiO <sub>2</sub> + 6 g/L H <sub>2</sub> O <sub>2</sub>	[31]
Malathion	70	50 <sup>a</sup>	–	1 h	0.1 g/L of TiO <sub>2</sub>	[32]
Atrazine	90	81 <sup>a</sup>	–	4 h	0.1 g/L of TiO <sub>2</sub>	[32]
Lindane	0.1	99 <sup>a</sup>	7.3	30 min	0.5 g/L of TiO <sub>2</sub>	[33]
3-Amino-2-chloropyridine	64.2	98 <sup>a</sup>	4.6	1.5 h	2 g/L of TiO <sub>2</sub>	[34]
3-Amino-2-chloropyridine	321.2	98 <sup>a</sup>	4.6	7 h	2 g/L of TiO <sub>2</sub>	[34]
Malathion	10	94 <sup>a</sup>	7	250 min	1 g/L of TiO <sub>2</sub>	[35]
Diazinon	10	99 <sup>a</sup>	7	220 min	1 g/L of TiO <sub>2</sub>	[35]
Malathion	10	99 <sup>a</sup>	7	3 h	1 g/L of TiO <sub>2</sub> + 20 mg/L H <sub>2</sub> O <sub>2</sub>	[35]
Diazinon	10	99 <sup>a</sup>	7	160 min	1 g/L of TiO <sub>2</sub> + 20 mg/L H <sub>2</sub> O <sub>2</sub>	[35]

<sup>a</sup>Direct analysis of EDC.

<sup>b</sup>TOC measurement.

Bisphenol A (BPA) was degraded by different TiO<sub>2</sub> photocatalysts at pH values of 3.0 and 10 [17]. The mineralization of BPA was found to be strongly dependent on the pH. BPA was completely mineralized at pH 3.0 after 120 min of UV irradiation. Microtox® toxicity analyses showed that oxidation intermediates formed at pH 10 were less toxic compared to the BPA molecule. Coleman et al. [18] investigated the effects of silver and platinum metals on the photocatalytic degradation of several EDCs (natural estrogens such as 17β-estradiol and estriol, synthetic estrogens such as 17α-ethynylestradiol, xenoestrogens such as bisphenol A, resorcinol and

2,4-dichlorophenol) in water using immobilised TiO<sub>2</sub> and a TiO<sub>2</sub> slurry system. The authors found no effect of the addition of silver or platinum on the photocatalytic degradation or mineralisation of the EDCs examined. Therefore they concluded that it is not required to add expensive metals to photocatalytic systems for the removal of low EDCs concentrations. 0.82 mg/L of 7α-ethynylestradiol was degraded at 98% during 3.5 h of oxidation using 1 g/L of TiO<sub>2</sub>.

As shown by Malygina et al. [36], steroid estrogens, natural β-estradiol (E2) and synthetic 17α-ethynylestradiol (EE2) are easily photocatalytically degraded on UV-irradiated TiO<sub>2</sub> surface

at very low (10 mg/L) concentrations of the photocatalyst. No degradation of urea was observed during their study on the  $\text{TiO}_2$  surface under the experimental conditions. The alkaline media exhibited the highest efficiency in both photocatalytic oxidation and adsorption of steroid estrogens.

The photodegradation of the two natural female hormones, estrone (E1) and  $17\beta$ -estradiol (E2) was studied in two UV-photo-reactors in the presence of  $\text{TiO}_2$  by Zhang and Zhou [37]. The degradation of E1 and E2 followed the pseudo-first-order kinetics. More rapid degradation was observed in reactor 2 (15 W) where 98% of both compounds disappeared within 1 h, due to the shorter wavelength of UV-light in reactor 2 (fixed at 253 nm) than in reactor 1 (238–579 nm). The effects of different initial chemical concentrations, pH value, the presence of dissolved organic matter and hydrogen dioxide, and the catalyst concentration on the degradation rate of E1 and E2 in aqueous solutions were assessed in detail. The findings showed that the extent of photodegradation of E1 and E2 was increased when pH value increased from 2 to 7.6. The presence of humic acid enhanced the degradation of E1 and E2 in both reactors as a result of the photosensitisation effect of humic acid chromophore. The degradation rate also increased with an increase in  $\text{H}_2\text{O}_2$  concentration or increasing catalyst concentration. The results therefore suggest that photocatalysis can be a very effective method for rapidly removing certain EDCs from water.

The photocatalysed degradation of various selected pesticide derivatives, namely N,N-Dimethyl- $\alpha$ -phenyl benzene acetamide (Diphenamid), 1,2-diethyl phthalate (DEP), 5-bromo-3-sec-butyl-6-methyl uracil (Bromacil), 3-tert-butyl-5-chloro-6-methyluracil (Terbacil), and 2,4,5-tribromoimidazole (TBI), as well as that of two selected priority organic pollutants, namely benzidine and 1,2-diphenylhydrazine (DPH) has been investigated in aqueous suspensions of titanium dioxide ( $\text{TiO}_2$ ) under a variety of conditions

employing a pH-stat technique by Muneer and Bahnemann [38]. The degradation was studied by monitoring the change in substrate concentration of each model compound employing HPLC analysis and the decrease in total organic carbon (TOC) content, respectively, as a function of irradiation time. The degradation kinetics were studied under different conditions such as reaction pH, substrate and photocatalyst concentration, type of  $\text{TiO}_2$  photocatalyst and the presence of alternative additives such as  $\text{H}_2\text{O}_2$ ,  $\text{KBrO}_3$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  besides molecular oxygen. The degradation rates and the photonic efficiencies were found to be strongly influenced by the above parameters.

It is true to say that only very recently has considerable interest been shown in the application of an innovative treatment for hazardous chemical destruction based on the use of ultrasound. The chemical effects of ultrasound derive from acoustic cavitation, i.e., the formation growth and implosive collapse of cavitation bubbles in a liquid. Extreme temperatures of several thousand degrees and pressures of several hundred atmospheres are developed locally within the bubbles during their collapse with these bubbles serving as hot spot microreactors in an otherwise cold liquid. Destruction of chemicals is usually achieved through a combination of pyrolytic reactions occurring inside or near the bubble and hydroxyl radical-mediated reactions occurring in the liquid bulk [39].

Linear alkylbenzene sulfonates (LAS) are the worlds most widely used synthetic detergents in both household and industrial cleaning products. Thus these compounds are frequently found in urban wastewaters. Although they are not characterised as EDCs, might break down to EDCs and therefore there is a need to be removed from the wastewaters. The decomposition of sodium dodecylbenzene sulfonate (SDBS) in water by means of ultrasound irradiation at 20 kHz has been investigated by Abu-Hassan et al. [23]. Experiments were conducted at surfactant concentrations of 175, 260 and 350 mg/L, liquid

volumes of 120, 170 and 220 mL, temperatures of 20, 30 and 45°C and applied power of 40, 80 and 125 W. The extent of degradation was followed by monitoring the substrate and organic carbon concentrations, while hydrogen peroxide concentration was also measured. Eighty percent SDBS conversion was achieved after 120 min of sonication at 125 W and 30°C; nonetheless, SDBS and its degradation intermediates proved difficult to oxidise as only about 20–25% of the initial carbon content was transformed to carbon dioxide. Degradation appears to occur at the bubble-liquid interface through hydroxyl radical-mediated reactions whose role was established by performing experiments in the presence of radical scavengers, namely potassium bromide and sodium benzoate. Degradation was increased with increasing power and decreasing temperature and volume.

The ultrasound induced destruction of a mixture of estrogen compounds in aqueous solutions was studied in a batch reactor using a 0.6 kW sonication unit and in a continuous flow reactor using a 1.0 kW sonication unit by Suri et al. [40]. Increasing the temperature and fluid pressure was detrimental to the reaction efficiency. The initial destruction was faster at pH 3.0 than pH and 7.0 and 9.0, while the final efficiencies were similar after about 20 min. Under high initial concentration of 290 µg/L, the initial degradation was fast, while the following reaction proceeded slowly. The pseudo first-order rate constants in 2.0 kW systems, under pH 3.0, 7.0 and 9.0 with individual initial concentration of 1 µg/L, and 10 µg/L were reported. The tendency of estrogens to be degraded by sonolysis in pH 7.0 mixture solution under the studied conditions was 17α-dihydroequilin > 17α-estradiol > equilin > estrone > 17β-estradiol > ethinyl estradiol > gestodene > levonorgestrel/norgestrel. Under initial concentration of about 0.5 mg/L of each estrogen compound spiked in pharmaceutical wastewater, the estrogens removal ranged from 40 to 80%.

Two advanced oxidation processes (AOPs), Fenton's reagent and ultrasonic cavitation, were tested for the degradation of bisphenol A (BPA) by Torres et al. [41]. Ultrasound was performed at 300 kHz and 80 W, while Fenton process was operated using ferrous sulphate 100 µmol/L and continuous H<sub>2</sub>O<sub>2</sub> addition at the same rate as it is produced in the sonochemical method. Experiments carried out in deionised water show that both processes exhibit identical BPA elimination and primary intermediates, indicating the predominance of the same reaction way: •OH radical attack. Chemical oxygen demand (COD) and total organic carbon (TOC) analyses show that the Fenton process is slightly more efficient for removal of BPA by-products in deionised water. However, in experiments conducted in real natural water containing neutral pH and high ion concentrations the Fenton process was completely inhibited while the ultrasonic one was not hampered. Conversely, at relative low BPA concentrations the ultrasonic treatment was more efficient in the natural water than in the deionised one. This unexpected result was attributable to bicarbonate species present in the natural water.

Concluding, it can be said that the use of AOPs seems to be efficient in degrading and removing EDCs and therefore could be applied in treatment and reuse schemes where the final effluent to be reused must be of high purity (Table 1). In any case though, the total dissolved solids (TDS) which can potentially be increased if AOPs are applied have to be removed before any reuse application.

### 3. Reuse limits

Wastewater reuse is a resource of growing global importance which must be carefully managed in order to obtain substantial benefits and to minimise serious risks. In 1996 the EPA formed the Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC) to recommend a conceptual framework, priorities, screening and testing methodologies for EDCs. In 2001, the

Table 2

Limits for reuse of wastewater in Italy concerning EDCs and some other persistent compounds as well as microbiological concerns [26]

Parameter	Unit	Limit	Parameter	Unit	Limit
Total phenols	mg/L	0.1	Benzene	mg/L	0.001
Pentachlorophenol	mg/L	0.003	Benzo(a)pyrene	mg/L	0.00001
Total aldehydes	mg/L	0.5	Total organo-nitrogen-solvent	mg/L	0.01
Tetrachloroethylene + trichloroethylene	mg/L	0.01	Total surfactants	mg/L	0.5
Total chlorinated solvents	mg/L	0.04	Chlorinated pesticides (each)	mg/L	0.0001
THMs	mg/L	0.03	Phosphorated pesticides	mg/L	0.0001
Total aromatic organic solvent	mg/L	0.01	Other pesticides (total)	mg/L	0.05
Microbiological parameters	Unit		Limit		
<i>Escherichia coli</i>	UFC/100 mL		10 for the 80% of samples, 100 maximum value		
<i>Salmonella</i>	–		Absent for the 100% of samples		

EPA formed the Endocrine Disruptor Methods Validation Subcommittee (EDMVS) to evaluate the battery of test suggested by EDSTAC. California is considering establishing regulations based on the potential impacts of EDCs and Pharmaceuticals and Personal Care Products (PPCPs), where municipal wastewater effluent is recycled for indirect potable reuse. Because California's criteria often establish precedents for programs throughout the world, other regulatory agencies will likely adopt similar choices in their own water recycling programs [42].

Although several studies have shown that EDCs represent a threat for both the humans and environment, for many of EDCs no reuse standards exist in many countries yet. While the WFD [1] leads the Member States towards the promotion of (1) wastewater reuse through, i.e., reuse for irrigation, (2) lower water consumption and (3) recycling of processed wastewater in industries, and also despite the fact that many of the EDCs are included in lists referring to environmental quality standards for surface water quality [2], no European regulations on water reuse have been set yet. These legislative actions are expected however to promote the removal of EDCs before final discharge or reuse in the near future. In Italy,

very strict limits for municipal wastewater reuse are set (Table 2). However the limits are not categorised according to the reuse application.

It is obvious that in every wastewater treatment and reuse scheme, protecting public health is critical. The overall conclusion from the epidemiological data on adverse effects on human health from EDCs is that in general, low level environmental exposure to EDCs has not yet been demonstrated to cause harm. However pharmacological dosing with estrogens (particularly diethylstilbestrol), accidental and occupational exposure to agricultural chemicals, industrial chemical accidents and accidental consumption of contaminated foodstuffs have been clearly associated with harm [5]. Although the scientific community is far from establishing consensus on the adverse human health effects from EDCs, some scientists for example suggest that certain drinking water disinfection by-products (DBPs) may act as EDCs [43].

The stability and persistence of some EDCs contribute to the increased ground and surface water contamination and bioaccumulation risk in the trophic chain [13]. For this reason wastewater that could come in contact with the public should be appropriately treated to increase EDCs

Table 3

Removal of some EDCs during chlorination [13 and literature cited therein]

Compound	Concentration	Removal (%)	Reaction time	Added use
17 $\beta$ -Estradiol	50 $\mu\text{g/L}^{\text{a}}$	100	10 min	1.46 mg/L of sodium hypochlorite
17 $\beta$ -Estradiol	10 $^{-7}$ M $^{\text{b}}$	100	36 h	1.5 mg/L of chlorine
17 $\beta$ -Ethinylestradiol	0.02 mmol/L $^{\text{b}}$	0	5 min	1 mmol/L of chlorine

<sup>a</sup>Wastewater from secondary treatment.<sup>b</sup>Synthetic water.

removal and reduce potential for by-product formation (DBPs). The strict Italian wastewater reuse limits are able to monitor the disinfection by-products formation before discharging the treated effluent. Although the removal of some of EDCs is evaluated in respect to disinfection (chlorination) as seen in Table 3, there are still intensive studies currently carried out to monitor EDCs before and after the disinfection process.

#### 4. Discussion

Although AOPs were found to be effective to mineralize many organic compounds reducing the TOC of effluents, in many cases, they can cause harmful by-products formation in the effluent [44]. Therefore, the optimization of the efficiency of these processes gains importance not only for the economic viewpoint but also for safe disposal of the treated effluents. Another point to keep in mind is that, the effluent produced by various AOPs process though not toxic, might after final disinfection be transformed to a toxic one. This is an important issue since the interferences of many emerging pollutants in wastewater (i.e., EDCs formation during disinfection) have not been described well yet due to the complex mixture composition of wastewater. The presence of DBPs should be evaluated in particular when the effluent is to be reused. In fact, a recent study compared the differences in DBPs formation potentials (DBPFP) between a wastewater effluent and surface water by means

of chlorine use [45]. Surface water samples with higher anthropogenic impacts were found to have higher overall DBPFP primarily due to the higher concentration of dissolved organic carbon. On the other hand, although effluent-derived organic matter was found to be less reactive with chlorine, it had higher proportions of brominated DBP, which may be associated with greater health risks [45].

As seen in Table 1 photocatalytic process is very promising to remove many of EDCs. However these studies should be evaluated on the basis of complex and mixed matrices such as real fresh water, wastewater, and sludge. This process has been applied in full scale using solar energy to destruct EU priority pollutants [46]. Although this process was found very effective for microbial removal [47], (i.e., as the tertiary treatment at UWWTPs), the reactivation of bacteria needs to be hindered by disinfection before reuse. In this case the interaction among the by-products and the chlorine should be considered. The other promising innovative AOP is US which can result in the partial degradation or removal of EDCs. However there have been no large scale applications in respect to this process so far. Thus, the data related to this method should be refined with further and more in-depth investigations.

Recent investigations in aqueous solutions to degradate some biorecalcitrant pesticides (alachlor, atrazine, chlorfenvinfos, diuron, isoproturon and pentachlorophenol) by homogeneous and

heterogeneous photocatalytic ozonation showed that this combination was found as the most efficient technique [48]. The same pesticides were introduced to a combined process of ozone and photo-Fenton reagents to increase their biodegradability efficiently as alternative AOPs [49]. However, their possible use for the final effluent also can be investigated in further studies.

## 5. Conclusions

EDCs have been a general concern and they are currently being investigated in different aspects. The removal of them has not been achieved adequately in conventional chemical and biological processes and/or their sorption capacity on the sludge causes further concerns for sludge management. Therefore various advanced oxidation processes (AOPs) have been investigated to remove them from water and wastewater. In particular, photocatalysis and ultrasound oxidation technologies have been found to be effective in respect to the removal of these compounds in aqueous solutions and with some exception for photocatalysis at full scale plants. Therefore these methods can contribute towards the production of safer effluents for reuse. The application of these processes on actual mixed matrices needs to be further investigated and the combined application of AOPs with biological treatment merits further investigation so as to optimise the technical efficiency and the cost as well.

The wastewater reuse guidelines have to be upgraded so as to take into consideration the fate of EDCs, emerging pollutants and also that of the various disinfection by-products. Therefore the need for more detailed analytical and toxicological supporting data is crucial. Furthermore, standardised analytical methods for the determination of EDCs and other emerging pollutants should be developed in respect to all relevant environmental matrices, i.e., water, wastewaters, sludge and sediments.

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## References

- [1] EC, Directive of the European Parliament and of the Council 2000/60/EC establishing a framework for community action in the field of water policy, Official Journal, 2000, C513, 23/10/2000.
- [2] Proposal for a directive of the European Parliament and of the Council on environmental quality standards in the field of water policy and amending Directive 2000/60/EC (presented by the Commission) [COM(2006), 398 final, SEC(2006) 947], Brussels, 17.7.2006, COM(2006) 397 final.
- [3] G.G. Ying, B. Williams and R. Kookana, Environmental fate of alkylphenols and alkylphenol ethoxylates — a review, *Environ. Int.*, 28 (2002) 215–226.
- [4] A.S. Stasinakis, N.S. Thomaidis, A. Nikolaou and A. Kantifes, Aerobic biodegradation of organotin compounds in activated sludge batch reactors, *Environ. Pollut.*, 134 (2005) 431–438.
- [5] WHO (World Health Organization), Global assessment of the state-of-the-science of endocrinedisruptors, [www.who.int/ipcs/publications/new\\_issues/endocrine\\_disruptors/en/\(2002\)](http://www.who.int/ipcs/publications/new_issues/endocrine_disruptors/en/(2002)).
- [6] G.R. Boyd, H. Reemtsma, D.A. Grimm and S. Mitra, Pharmaceuticals and personal care products (PPCPs) in surface and treated waster of Louisiana, USA and Otario, Canada, *Sci. Tot. Environ.*, 311 (2003) 135–149.
- [7] R. Andreozzi, M. Raffeale and P. Nicklas, Pharmaceuticals in STP effluents and solar photodegradation in aquatic environment, *Chemosphere*, 50 (2003) 1319–1330.
- [8] E. Zuccato, S. Castiglioni and R. Fanelli, Identification of the pharmaceuticals for human use contaminating the Italian aquatic environment, *J. Hazard. Mater.*, 122 (2005) 205–209.
- [9] J.W. Birkett and J.N. Lester, *Endocrine Disrupters in Wastewater and Sludge Treatment Processes*, Lewis Publishers, 2003.

- [10] W. Korner, U. Bolz, B. Submuth, G. Hiller, W. Schuller, V. Hanf et al., Input/output balance of estrogenic active compounds in a major municipal sewage plant in Germany, *Chemosphere*, 40 (2000) 1131–1142.
- [11] A.C. Johnson and J.P. Sumpter, Removal of endocrine disrupting chemicals in activated sludge treatment works, *Environ. Sci. Technol.*, 35 (2001) 4697–4703.
- [12] N. Cicek, J.P. Franco, M.T. Suidan, V. Urbain and J. Manem, Characterization and comparison of a membrane bioreactor and a conventional activated sludge system in the treatment of wastewater containing high molecular weight compounds, *Water Environ. Res.*, 71 (1999) 64–70.
- [13] M. Auirol, Y. Filali-Meknassi, R.D. Tyagi, C.D. Adams and R.Y. Surampalli, Endocrine disrupting compounds removal from wastewater: a new challenge, *Process Biochem.*, 41 (2006) 525–539.
- [14] M.O. Buffle, J. Schumacher, E. Salhi, M. Jekel and U. von Gunten, Measurement of the initial phase of ozone decomposition in water and wastewater by means of a continuous quench-flow system: application to disinfection and pharmaceutical oxidation, *Water Res.*, 40 (2006) 1884–1894.
- [15] J. Arana, J.A. Herrera Melian, J.M. Dona Rodriguez, O. Gonzalez Diaz, A. Viera, J. Perez Pena, P.M. Marrero Sosa and V. Espino Jimenez, TiO<sub>2</sub>-photocatalysis as a tertiary treatment of naturally treated wastewater, *Catal. Today*, 76 (2002) 279–289.
- [16] N.M. Al-Bastaki, Performance of advanced methods for treatment of wastewater: UV/TiO<sub>2</sub>, RO and UF, *Chem. Eng. Process.*, 43 (2004) 935–940.
- [17] K. Chiang, T.M. Lim, L. Tsen and C.C. Lee, Photocatalytic degradation and mineralization of bisphenol A by TiO<sub>2</sub> and platinumized TiO<sub>2</sub>, *Appl. Catal. A*, 261 (2004) 225–237.
- [18] H.M. Coleman, K. Chiang and R. Amal, Effects of Ag and Pt on photocatalytic degradation of endocrine disrupting chemicals in water, *Chem. Eng. J.*, 113 (1) (2005) 65–72.
- [19] R. Andreozzi, M. Canterino, R. Lo Giudice, R. Marotta, G. Pinto and A. Pollio, Lincomycin solar photodegradation, algal toxicity and removal from wastewaters by means of ozonation, *Water Res.*, 40 (2006) 630–638.
- [20] T.A. Ternes, J. Stuber, N. Herrmann, D. McDowell, A. Ried, M. Kampmann and B. Teiser, Ozonation: a tool for removal of pharmaceuticals, Contrast media and musk fragrances from wastewater? *Water Res.*, 37 (2003) 1976–1982.
- [21] R. Andreozzi, M. Canterino, R. Marotta and P. Nicklas, Antibiotic removal from wastewaters: the ozonation of amoxicillin, *J. Hazard. Mater.*, 122 (2005) 243–250.
- [22] C. Stavarache, B. Yim, M. Vinatoru and Y. Maeda, Sonolysis of chlorobenzene in Fenton-type aqueous systems, *Ultrasonics-Sonochemistry*, 9 (2002) 291–196.
- [23] M.A. Abu-Hassan, J.K. Kim, I.S. Metcalfe and D. Matzavinos, Kinetics of low frequency sonodegradation of linear alkylbenzene sulfonate solutions, *Chemosphere*, 62 (2006) 749–755.
- [24] Y. Jiang, Ch. Petrier and T.D. Waite, Sonolysis of 4-chlorophenol in aqueous solution: effects of substrate concentration, aqueous temperature and ultrasonic frequency, *Ultrasonics-Sonochemistry*, 13 (2006) 415–422.
- [25] WHO (World Health Organization), WHO Guidelines for the safe use of wastewater excreta and greywater. Vol II: Wastewater Use in Agriculture, 2006.
- [26] Decreto Legislativo (D.Lgs) (N.152/2006), 3 April 2006, No. 152, published in *Gazzetta Ufficiale*, no. 88, 14/04/2006, Suppl Ordinario, no. 96, Italy.
- [27] S. Parra, S.E. Stanca, I. Guasaquillo and K.R. Thampi, Photocatalytic degradation of atrazine using suspended and supported TiO<sub>2</sub>. *Appl. Catal. B: Environ.*, 51 (2004) 107–116.
- [28] S. Malato, J. Blanco, A. Vidal and C. Richter, Photocatalysis with solar energy at a pilot-plant scale: an overview, *Appl. Catal. B: Environ.*, 37 (2002) 1–15.
- [29] S. Malato, J. Blanco, A. Vidal, D. Alarcon, M.I. Maldonado, J. Caceres and W. Gernjak, Applied studies in solar photocatalytic detoxification: an overview, *Solar Energy*, 75 (2003) 329–336.
- [30] S. Kaneco, M.A. Rahmana, T. Suzuki, H. Katsumata and K. Ohta, Optimization of solar photocatalytic degradation conditions of bisphenol A in water using titanium dioxide, *J. Photochem. Photobiol. A: Chem.*, 163 (2004) 419–424.
- [31] E.R. Bandala, S. Gelover, M.T. Leal, C. Arancibia-Bulnes, A. Jimenez and C.A. Estrada, Solar photocatalytic degradation of Aldrin, *Catal. Today*, 76 (2002) 189–199.

- [32] L. Muszkat, L. Bir and L. Feigelson, Solar photocatalytic mineralization of pesticides in polluted water, *J. Photochem. Photobiol. A: Chem.*, 87 (1995) 85–88.
- [33] A. Vidal, A.I. Diaz, A. El Hraiki, M. Romero, I. Muguruza, F. Senhaji and J. González, Solar photocatalysis for detoxification and disinfection of contaminated water: pilot plant studies, *Catal. Today*, 54 (1999) 283–290.
- [34] B.F. Abramovic, V.B. Anderluh, A.S. Topalov and F.F. Gaál, Titanium dioxide mediated photocatalytic degradation of 3-amino-2-chloropyridine, *Appl. Catal. B: Environ.*, 48 (2004) 213–221.
- [35] R. Doong and W. Chang, Photoassisted titanium dioxide mediated degradation of organophosphorus pesticides by hydrogen peroxide, *J. Photochem. Photobiol. A: Chem.*, 107 (1997) 239–244.
- [36] T. Malygina, S. Preis and J. Kallas, 1st European Conference on Environmental Applications of Advanced Oxidation Processes, E-proceedings, September 2006, Chania Crete, Greece.
- [37] Y. Zhang and J.L. Zhou, Photocatalytic degradation of estrogens in water, in: 1st European Conference on Environmental Applications of Advanced Oxidation Processes, E-proceedings, September 2006, Chania Crete, Greece.
- [38] M. Muneer and D. Bahnemann, Semiconductor-mediated photocatalytic degradation of various pesticides derivatives and other priority organic pollutants in aqueous suspensions, in: 1st European Conference on Environmental Applications of Advanced Oxidation Processes, E-proceedings, September 2006, Chania Crete, Greece.
- [39] M. Papadaki, R. Emery, M. Abu-Hassan, A. Diaz-Bustos, I. Metcalfe and D. Mantzavinos, Sonocatalytic oxidation processes for the removal of contaminants containing aromatic rings from aqueous effluents, *Separation, Purification Technol.*, 34 (2004) 35–42.
- [40] R.P.S. Suri, H. Fu and R. Chimchirian, Ultrasound induced destruction of estrogen hormones in aqueous systems, in: 1st European Conference on Environmental Applications of Advanced Oxidation Processes, Book of abstracts, Chania, Crete, Greece, September 2006, p. 243.
- [41] R.A. Torres, F. Abdelmalek, E. Combet, C. Petrier and C. Pulgarin, A comparative study of ultrasonic cavitation and Fenton's reagent for bisphenol A degradation in natural waters, in: 1st European Conference on Environmental Applications of Advanced Oxidation Processes, E-proceedings, September 2006, Chania Crete, Greece.
- [42] USEPA Guidelines for Water Reuse, EPA/625/R-04/108, 2004. [www.epa.gov](http://www.epa.gov).
- [43] K. Fent, A.A. Weston and D. Caminada, Ecotoxicology of human pharmaceuticals, *Aquatic Toxicol.*, 76 (2006) 122–159.
- [44] A.R. Fernandez-Alba, D. Hernando, A. Aguera, J. Caceres and S. Malato, Toxicity assays: a way for evaluating AOPs efficiency, *Water Res.*, 36 (2002) 4255–4262.
- [45] T. Sirivedhin and K.A. Gray, 2. Comparison of the disinfection by product formation potentials between a wastewater effluent and surface waters, *Water Res.*, 39 (2005) 1025–1036.
- [46] M. Hincapié, M.I. Maldonado, I. Oller, W. Gernjak, J.A. Sánchez-Pérez, M.M. Ballesteros and S. Malato, Solar photocatalytic degradation and detoxification of EU priority substances, *Catal. Today.*, 101 (2005) 203–210.
- [47] M. Bekbölet, Photocatalytic bactericidal activity of TiO<sub>2</sub> in aqueous suspensions of *E. coli*, *Water Sci. Technol.*, 35 (11–12) (1997) 95–100.
- [48] M.J. Farré, M.I. Franch, S. Malato, J.A. Ayllón, J. Peral and X. Doménech, Degradation of some biorecalcitrant pesticides by homogeneous and heterogeneous photocatalytic ozonation, *Chemosphere*, 58 (2005) 1127–1133.
- [49] M.J. Farre, M.I. Franch, J.A. Ayllon, J. Peral and X. Domenech, Biodegradability of treated aqueous solutions of biorecalcitrant pesticides by means of photocatalytic ozonation, *Desalination*, 211 (2007) 22–33.