Bulgarian Chemical Communications, Volume 45, Number 2 (131 – 143) 2013

Some endocrine disrupting compounds in the environment and possibilities for their removal / degradation

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Received October 18, 2011; accepted March 10, 2012

The paper presents a review of literature data on the occurrence of endocrine disruption compounds in the effluents from wastewaters treatment plants, surface, underground and drinking waters and sediments. General data concerning their action on the living organisms (mainly fish) are given. The peculiarities of the methods for removal/degradation of the pollutants *via* adsorption, ozonation, biodegradation, photolysis and photocatalysis are considered.

Keywords: environmental pollution, estrogens, photolysis, photocatalysis, TiO_2

1. INTRODUCTION

The steroids of concern for the aquatic environment due to their endocrine disruption potential are mainly estrogens and contraceptives, which include 17β-estradiol (E2, a), 17α-ethinylestradiol (EE2, b), bisphenol A (BPA, c), estrone (E1, d) and estriol (E3, e) (Fig. 1). A major source of hormone steroids is livestock (sheep, cattle, pigs, poultry, etc.) waste [1]. Steroid drugs are also frequently used in cattle as well as in other livestock to control the oestrous cycle, treat reproductive disorders and induce abortion [2]. This could greatly increase the generation of hormone steroids in urine of livestock [3]. Both natural and synthetic estrogens enter the aquatic environment via effluents of wastewater treatment plants or untreated discharges and reach concentrations (normally in the ng/l range) sufficient to exert estrogenic responses. Human-used contraceptives pills are the other source of such compounds entering the environment.

The order of aqueous solubility observed was consistent with the increasing polarities of the estrogens, firstly E2 (two hydroxy groups) and then EE2 (added ethinyl group at 17R position on the D ring). At pH=7, temperature 25.0 ± 0.5 °C the solubility in Milli-Q reagent grade water (Millipore) reported for E2 is 1.51 ± 0.04 mg/l and for EE2 – 9.20 ± 0.09 mg/l [4].

Among endocrine disrupting compounds, EE2 and BPA are the two compounds most frequently studied in environmental research [5]. EE2 is widely used as an oral contraceptive, its low removal was observed [6] and its toxicity is higher by a factor of 10-50 than that of estrone (El) and E2 [7]. Thus, reduction/elimination of EE2 could have the strongest single impact on the estrogenicity of the effluents [8].

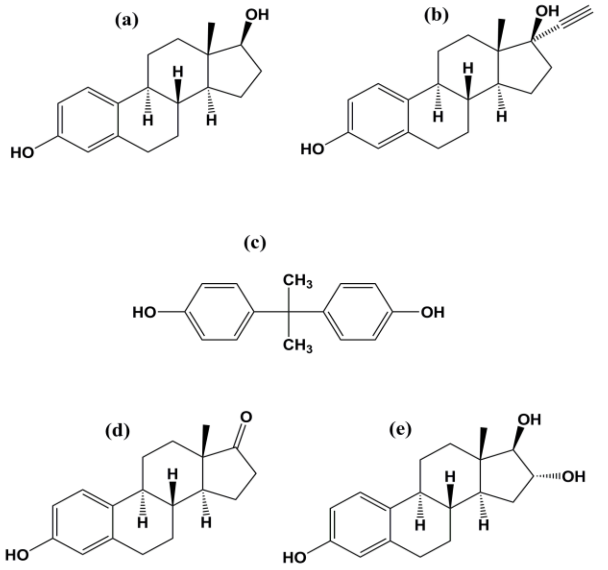

Fig. 1. Molecular structures of 17β-estradiol (E2, a), 17α-ethynylestradiol (EE2, b), bisphenol A (BPA, c), estrone (E1, d) and estriol (E3, e).

2. ESTROGEN DISRUPTING COMPOUNDS (EDCS) IN THE ENVIRONMENT

2.1. EDCs in sewage-treatment works effluents (STWE)

In 1970 Tabak *et al*. [9] reported concentrations of 2000 ng EE2/l, 25 ng E1/l, 60 ng E3/l, and 10 ng E2/l (parent compounds plus conjugates) in STWE

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from the USA [10]**.** Effluents from UK wastewater treatment works (WwTWs) were first reported to be estrogenic to fish in 1994 [11] and since then estrogenic contaminants have shown to be widespread in effluents discharging into rivers in England and Wales as well as in Europe and the USA [12–15]. The major estrogenic components in WwTWs effluents have been identified as the natural estrogens E2 and E1 and the synthetic EE2 [16]. Using an immunoassay procedure, EE2 was tentatively detected in STWE, river water, and potable water in Britain at concentrations in the low ng/l range and below [10, 17].

Concentrations of up to 20 ng of E2/l and up to 62 ng of EE2/l in effluents were reported in a German study (1998, employing sophisticated modern techniques) [10, 18]**.** Steroidal estrogens have been surveyed extensively in influents and effluents from WwTWs of different countries and their concentrations generally ranged from 10 to 200 ng /l [19–25]. The median concentration of EE2 in sewage effluents in Germany, England, The Netherlands and the USA reported by several authors [10, 19, 26–33] are rather low - between 1 and 3 ng/l. Analysis of a water sample from the Tiber river (Italy) downstream of small towns whose sewages are treated by percolating filter or directly discharged into the river revealed the presence of EE2 at 0.04 ng/l [34]. Concentrations of E2 up to 20 ng/l were reported in STWE [10, 18]**.**

A suite of 30 primarily estrogenic organic wastewater contaminants was measured in several influent/effluent wastewater samples from four municipal WwTWs and effluents from one bleached kraft pulp mill. 17α-Ethinylestradiol was the more frequently detected synthetic estrogen/progesterone in the effluents occurring at or below 5 ng/l with sporadic occurrences up to 178 ng/l. The highest levels of steroidal estrogens in municipal effluents were for E1>E2>E3, all <20 ng/l [35].

In [36] data are summarized on the attempts to evaluate the estrogens emission in the environment resulting from the use of contraceptives by humans. Johnson and Williams [37] assume that 17 % of women are taking 26 μg EE2/day (the main estrogenic component of a combined oral contraceptive pill); if excreting 40 % of it are accepted, this would suggest a per capita normalized discharge of 890 ng/day. Of course this percentage does vary a little between countries, but there is a continuing trend to lower the EE2 dose in many contraceptive products. A typical wastewater discharge per capita value is 200 l/day (although often more, particularly where industrial waste streams also enter the sewage), which would suggest that 4 ng/l EE2 would be found in a raw sewage influent stream, and 0.8 ng/l EE2 in the effluent if 80 % removal takes place through sewage treatment. So if the receiving stream was composed entirely of effluent this would give only 0.8 ng/l EE2 in the receiving water, or 4 ng/l EE2 if sewage treatment had failed to remove any EE2 from the waste stream. Therefore, it is surprising to find reports of EE2 being detected at concentrations up to 178 ng/l in sewage effluent [35], up to 273 ng/l in some USA streams [38], 5 ng/l in a river estuary [39], and even 2 ng/l in drinking water [40], by researchers using GC/MS equipment [36]**.**

Generalized data on the estrogens content in STWE effluents in a number of countries are reported in [41]. Detected concentrations vary within the limits (ng/l) 1 – 5400 (E1), 0.2 – 1500 (E2), 0.1 – 3000 (E3) and 0.9 – 210 (EE2).

Despite the mentioned rather high concentrations of EE2, its common concentrations in effluents are rather close to the present detection limits of most analytical techniques causing serious difficulties in its analysis [8]. That is why one can suppose that although EE2 was not always detected, it may still be present in some effluent samples [10]**.**

2.2. EDCs in surface and underground waters

Although natural and synthetic estrogenic compounds can be biologically degraded, they cannot be completely removed in WwWTPs, thus, they are often discharged into surface waters [23, 42–44]. These estrogenic compounds are usually detected in WwWTP effluents and receiving surface waters at concentrations at the ng/l levels [35, 41, 45–51] According to Williams [52], estradiol was frequently detected (<0.4–4.3 ng/l), but ethinylestradiol was infrequently detected (<0.4–3.4 ng/l) in the River Nene and the River Lea (U.K.), upstream and downstream of sewage treatment works.

In 1998 EE2 was occasionally detected at levels below 5 ng/l in river water in Germany [10, 18]**.** Adler *et al.* [31] reported several positive detections of EE2 in ground- and drinking water in Germany. They determined EE2 in groundwater and in raw and purified drinking water at concentrations up to 2.4 ng/l [53]. Ethinylestradiol and 17β-estradiol were reported at concentrations ranging from 0.2 to 2.6 ng/l [54]. Lopez de Alda *et al.* [55] reported a maximum concentration of 22.8 ng/g for EE2 and 11.9 ng/g for E1 from two rivers in the North-East of Spain. It was shown that the higher levels of estrogens from the two drainage rivers in China could be due to untreated wastewater discharge [25]. Kolpin *et al*. [38] reported E2, EE2 and testosterone to be present in surface water at an average of 9, 73 and 116 ng/l, respectively [54].

The concentrations of E2 and EE2 in Taihu Lake (2334 km^2, in a rapid economic development and urbanization area of China) were determined using a high-pressure liquid chromatography method [56].

Data from drinking, waste, and surface water in South Korea offer the possibility to evaluate the ratio of concentrations for some types of pollutants emitted by STWE, as well as in surface and drinking waters (Table 1) [54].

Table 1. Mean values (ng/l) of some pollutants in waters

Pollutant type	Water type		
	From STWE	Surface	Drinking
Farmaceuticals	2800	390	100
Hormones	17	2	
Miscelaneius	430	88	20

The generalized data show that when EE2 is detectable, the ratio of E2 to EE2 in rivers is 9:1. This means that the concentration of EE2 was probably 0.6 ng/l, with a median concentration around half this value. These values agree well with measurements taken in The Netherlands, which reported concentrations in river water of 0.3 ng of EE2/l (5-fold lower than in drinking water) [10].

2.3 EDCs in sediments

Given the relatively low polarity of these compounds, which are characterized by octanol–water partition coefficients mostly between 3 and 6, sorption to bed sediments appears a quite likely cumulative process. Laboratory experiments carried out to study the behavior of estrogens in the aquatic environment, predict that bed sediments act as environmental reservoirs from where both estrogens and progestogens (compounds also used in birth-control pills) can eventually become bioavailable [57]. These compounds could affect wildlife and human health by disrupting their normal endocrine systems.

Concentrations above 30 ng/g for both E2 and EE2 have been found in China river sediments due to the untreated wastewater discharge, but the common concentrations are much below such values. Average concentrations of E2 equal to 8.69, 10.3 and 7.26 ng/l in water and 5.28, 4.40 and 3.34 ng/l in the respective sediments have been found for three rivers in Tianjin area. Concerning the EE2 average concentrations, the following values are reported for the same rivers: 10.0, 9.45 and 3.54 ng/l in water and 5.09, 4.02 and 2.75 ng/l in the sediments [25]. The partitioning of estrogens between water and sediment was found to be influenced by the organic content of the sediment [25].

Data for estrogens content in rivers, estuaries and ocean sediments in a number of countries are reported in [25]. Table 2 presents data from the literature available for estrogens content in waters and sediments. 3. Action of EDCs on living organisms

The action of EDCs on living organisms is of general concern and is a significant research subject. Their presence in the environment is likely to disturb the ecosystems and to affect human health. The epidemiological data give evidence of a possible relationship between chemical exposure and observed harmful effects of endocrine disruption in the living beings [58]. Thus, the need for developing reliable detection methods, analysis tools, and adapted wastewater treatment processes is now the subject of significant interest.

Both natural and synthetic estrogens that end up in the environment have been shown to produce deleterious effects in aquatic organisms, such as feminization and hermaphroditism. The synthetic estrogenic compounds, EE2 and diethylstilbestrol (DES) have the ability to interfere with the functions of hormone systems [41].The presence of ethinylestradiol, the most potent synthetic estrogen known, in a river sediment has been associated with a striking incidence of carp species with macroscopically developed both male and female reproductive organs, and distinct high levels of plasma vitellogenin (egg yolk protein usually associated with adult females) in male fish [59]. These compounds can be extremely potent even at low concentrations; for instance, less than 1 ng/l EE2 can induce vitellogenin production in male rainbow trout [11, 60] and 4 ng/l caused male fathead minnows to fail to develop normal secondary sexual characteristics [52, 61]. Significant effect of concentrations below 1 ng/l is confirmed in [62], and sex reversal is possible in male fish at 3 ng/l [63]. “*In vitro*’ studies [11] have shown that exposure of fishes to only 0.1 ng/l of EE2 may provoke feminization in some species of male wild fishes.

Table 2. Estrogens concentration (ng/l) in waters and sediments.

Sample type	Estrogen	Values reported, sample origin, reference	
		Minimal	Maximal
STWE	E2	0.477, USA [118]	3.66, USA [118]
		3.2, Japan [117]	55, Japan [117]
		2.7, UK [10]	48, UK [10]
	EE2	0.10, Germany [119]	8.9, Germany [119]
		0.2, Netherlands [26]	7.5, Netherlands [26]
	E1	2.5 Italy[20]	82.1, Italy[20]
		1.4, UK [10]	76, UK [10]
	E3	0.43, Italy[20]	18, Italy[20]
Rivers	E2	0.11, Italy [20]	33.9, Taiwan[113]
	EE2	0.04, Italy [20]	27.4, Taiwan [113]
	E1	0.1, The Netherlands [26]	66.2, Taiwan [113]
	E3	0.33, Italy [20]	73.6, Taiwan [113]
Sediments from rivers	E2	0.71, China [25]	9.7,China [25]
	EE2	0.93, China [25]	22.8, Spain [55]
	E1	0.2, Germany [114]	21.6, China [25]
	E3		7.29, China [25]
Sediments from sea/ocean	E2	0.22, Australia [116]	2.48, Australia [116]
	EE2		0.5, Australia [116]
	E1	0.05, Japan [115]	3.6, Japan [115]
	E3	Not determined	
Drinking waters	E2	0.20, Southern Germany [119]	2.1, Southern Germany [119]
	EE2	>LOD [31]	2.4 [36,53,120]
		0.15, Southern Germany [119]	0.50, Southern Germany [119]
	E1	0.20, Southern Germany [119]	0.60, Southern Germany [119]
	E3	Data not found	Data not found

A 7-year whole lake experiment conducted at the Experimental Lakes Area in northwestern Ontario, Canada showed that chronic exposure of fathead minnow (*Pimephales promelas*) to low concentrations (5–6 ng/l) of the potent 17α-ethinylestradiol led to feminization of males through the production of vitellogenin in RNA and protein, impacts on gonadal development as evidenced by intersex in males and altered oogenesis in females, and, ultimately, a near extinction of this species from the lake. These observations demonstrate that the concentrations of estrogens and their mimics observed in freshwaters can impact on the sustainability of wild fish populations [64].

In humans and animals, estrogens undergo various transformations mainly in the liver. EE2 is mainly eliminated as conjugates. Therefore, estrogens are excreted mainly as inactive conjugates of sulphuric and glucuronic acids [1]. Prolonged exposure of target tissues or cells to excessive mitogenic stimulation by natural or synthetic estrogens has long been considered an important etiological factor for the induction of estrogen-associated diseases of the endometrium, such as endometrial cancer and endometriosis [65, 66]. Although steroid conjugates do not possess direct biological activity, they can act as precursors of hormone reservoirs able to be reconverted to free steroids by bacteria in the environment. Due to the presence of microorganisms in raw sewage and sewage treatment plants, these inactive conjugates of estrogenic steroids are cleaved, and active estrogenic steroids are released to the environment [1, 19, 20].

4. EDCS REMOVAL/DEGRADATION

Most important processes that play a role in the removal of estrogens are: adsorption, aerobic or anaerobic degradation, anoxic biodegradation and photolytic degradation. In general, anaerobic conditions result in longer half-lives than aerobic conditions. EE2 shows far more persistence; therefore its estrogenic effect *in vitro* is about 2-3-fold higher compared to E2 [67]. Conventional treatment techniques, including coagulation, precipitation and activated sludge processes, may not be highly effective in removing EDCs, while advanced treatment options, such as granular activated carbon, membranes and advanced oxidation processes have shown satisfactory results. Such processes allow a high removal of recalcitrant compounds, however many by-products are released and could have an estrogenic activity higher than their precursors [58].

4.1 Sorption on activated sludge biomass

The process is an important mechanism for removal of EE2 in biological wastewater treatment [68]. Current wastewater treatment plants were normally designed for carbon, nitrogen, and phosphorus removal but partial EDCs removal is often simultaneously achieved [58]. Very few data on EDCs, and in particular on estrogens fate in STWPs processes are available in the literature [19, 58, 69, 70]. Literature data concerning this possibility are more or less contradictory probably due to variation in the ability of the bacterial populations in biosolids to degrade estrogens. Recent studies on the effectiveness of conventional wastewater treatment processes show that the STWPs are a significant EDCs point source, particularly for surface water and underground water. Therefore, future research priorities should include optimization of wastewater treatment plants to increase EDCs removal [58].

Ternes *et al*. [19] reported that 99.9 % of the E2, 83 % of the estrone and 78 % of the EE2 were removed from raw sewage in an aerator tank at a WTP in Brazil. However, in another study [71], 70–80 % of the added E2 was mineralized to CO_2 within 24 h by biosolids from wastewater treatment plants, whereas the mineralization of EE2 was lower by a factor of 25–75.

In batch experiments with activated sludge, the contraceptive EE2 was principally persistent under selected aerobic conditions, where mestranol was rapidly eliminated and small portions of EE2 were formed by demethylation. EE2 was also reported to be degraded completely within 6 days by nitrifying activated sludge and resulted in the formation of hydrophilic compounds [72]. E2 could also be degraded when incubated with aerobic and anaerobic riverbed sediments. Compared to E2, EE2 was much more resistant to biodegradation in water from English rivers [73]. Reports from laboratory biodegradation studies indicated that EE2 was highly stable and persistent in activated sludge, with no detectable degradation occurring after 120 h of treatment as compared with gestagens, which were completely metabolized within 48 h of treatment [74]. The solubility of EE2 in pure water and sewage-treatment water was reported to be 4.2 and 4.7 mg/l, respectively, which was 3 times less than the solubility of natural steroidal estrogens [9, 74]. This fact is believed to contribute to the increased resistance of EE2 to biodegradation, as compared with natural steroidal estrogens [10].

Mastrup *et al.* [75] estimated that less than 10 % of natural and synthetic estrogens are removed *via* biodegradation process, and although a considerable amount is adsorbed to the sludge, the majority of the compounds remain soluble in the effluent. Johnson *et al.* [29] could not determine whether biodegradation or sorption is the most important removal mechanism of these compounds [58].

4.2 Aquifer storage and recovery (ASR)

This is an emerging and effective management technique in reclaiming and reusing waste water. During ASR, attenuation processes such as sorption and degradation may play an important role in removing trace organic contaminants from injected waste water. E2 showed a rapid biodegradation with a DT_{50} value (time for 50 % loss) of ~2 days under aerobic conditions [76].

4.3 Adsorption on activated carbon, fullerenes and carbon nanotubes

Satisfactory results using granular activated carbon, membranes and advanced oxidation processes are shown in [77]. Adsorption of BPA, E2 and EE2 on powdered activated carbons (PAC) is feasible for their >99 % removal from raw drinking waters at initial concentrations of 500 ng/l and higher. The rank order from highest to lowest compound removal by PAC (measured by lg K_{ow}, where K_{ow} - octanol/water partition coefficients of estrogens, values given in parentheses) is: E2 (3.1–4.0) > EE2 (3.7–3.9) > BPA (3.3) [78].

Carbon nanomaterials have also shown high adsorption capacity for polyaromatic hydrocarbons [79], pesticides [80 natural organic matter [81], heavy metals [82], and fluorides [83].

Rather high adsorption capacity for EE2 was observed for fullerenes and single-wall carbon nanotubes (SWCNTs), which have the smallest diameters. Multi-wall carbon nanotubes (MWCNTs) with outer diameters of 8-15, 20-30 and 30-50 nm exhibit similar adsorption capacity towards both EE2 and BPA, but their activity decreased with diameter enhancement. Apparently, in case of SWCNTs the adsorption capacity depends on the nature of the pollutant. In the presence of EE2, SWCNTs adsorption ability is two times lower than in presence of BPA [42].

4.4 Ozonation

Conventional ozonation of Lake Zurich water was shown to degrade ethinylestradiol by > 99 % [84, 85]. Doses of ozone typically applied for the disinfection of drinking waters were sufficient to reduce estrogenicity by a factor of more than 200. However, it proved impossible to completely remove estrogenic activity due to the slow reappearance of 0.1-0.2 % of the initial EE2 concentration after ozonation. The oxidation products formed during ozonation of EE2 were identified by LC-MS/MS and GC/MS using model compounds. Oxidation products of the natural steroid hormones E2 had significantly altered chemical structures as compared to the parent compounds, explaining the diminished estrogenic activity after ozonation [86].

4.5 Molecularly imprinted polymers (MIP).

The feasibility of removing estrogenic compounds from environmental water by the MIP was demonstrated using lake water spiked with α-estradiol. In addition, the MIP reusability without any deterioration in performance was demonstrated for at least five repeated cycles [87].

4.6 Enzymatic waste treatment and biodegradation.

Several oxidoreductase enzymes (*e.g.* peroxidases, polyphenol oxidases) have been shown to be effective for the removal of aromatic compounds, such as phenols, nonylphenol, and bisphenol A (BPA). Technical feasibility of laccase-catalyzed treatment of municipal wastewater contaminated by steroid estrogens (E1, E2, E3, and EE2) is reported in [88]. The municipal waste water used in the study, contained 25.3 ng/l of E2 and 6.25 ng/l of EE2. The results showed that pH has a significant influence on laccase-catalyzed treatment efficiency. The experimental results showed that 20 U/ml (1 U = 1 μmol/min) of initial laccase activity was required to completely remove each estrogen from synthetic water within a 1 h treatment period and 15 U/ml was required to achieve 100 % removal of EE2 [88].

The possibilities for biodegradation of estrogens and some of their conjugates are also tested. The study of Blánquez demonstrates the feasibility of estrogenic compounds biodegradation by suspended fungal biomass (white-rot fungi) using a continuous bioreactor. The feasibility of E2 and EE2 removal by *Trametes versicolor* was demonstrated in batch and continuous cultures. In batch, E2 and EE2 initially supplied at 10 mg/l were removed by more than 97 % in 24 h, which corresponds to volumetric removal rates of 0.43 and 0.44 mg/(l.h), respectively [89].

4.7 Mn(III) as an oxidizing agent.

The authors [90] structurally identify the oxidation products of EE2. From HPLC analysis of the reaction products, a single compound with a molecular mass of 294 was found to be predominant. As the molecular mass of EE2 is 296, it is believed that this compound has been formed by the removal of two hydrogen atoms from EE2. Due to the formed double bond the resulting compound is believed to be more easily oxidized or hydrolyzed in the further treatment (e.g. activated sludge) than the parent one.

4.8 Photolysis

Photolysis reactions have been extensively studied for estrogens removal from aqueous environment [91-94]. It is shown that the photolysis (under high-pressure mercury lamp, $\lambda \geq 365$ nm, 125 W [94]) of both estrogens causes breakage and oxidation of benzene rings to produce compounds containing carbonyl groups [58]. However, according to [95], while EE2 underwent photodegradation in aqueous solutions under irradiation with UV disinfection lamp ($\lambda = 254$ nm, 30 W), no photodegradation was observed under high pressure mercury lamp ($\lambda \geq 365$ nm, 250 W). The photodegradation of EE2 induced by high-pressure mercury lamp ($\lambda \geq 313$ nm, 250 W) in aqueous solution was investigated in [96] and it was shown that the process could be accelerated by Fe^{3+}. Ferric ions can promote the photodegradation of EE2 in aqueous solutions at a pH value of 2.0–5.0 [97].

The phototransformation of E2 and EE2 in dilute non buffered aqueous solution (pH 5.5–6.0) occurs with a quite low quantum yield of about 0.06 upon polychromatic ($\lambda > 290$ nm) or at 254 nm irradiation [95]**.** Increasing the initial concentration of EE2 lowers the photodegradation rate. The latter reached its lowest value at a pH about 5.0; higher pH values of 6.0 – 8.0 benefited the process [97].

The photodegradation of 1.6–20.0 mg/l EE2 in aqueous solutions at a given initial pH value of 6.8 is a pseudo-first order reaction. The pseudo-first order law is also found for the photolysis reaction of E2 in aqueous solutions (3.0–20 mg/l) [94]**.**

According to Rosenfeldt [98], EDCs are more effectively degraded utilizing UV/H_2O_2 advanced oxidation as compared to direct UV photolysis treatment. However, mineralization of the pollutant would require extended UV treatment times. The breakdown products, as compared to their parent compounds, must be assessed through toxicological testing.

The relationship between degradation of E2 and EE2 and the removal of their estrogenic activity as measured by an *in vitro* estrogen activity assay, using UV photolysis and UV/H_2O_2 advanced oxidation processes, is examined [99].

Survey of the treatability of endocrine disruptors in water by advanced oxidation processes is made by Gültekin *et al.* [100].

4.9 Photocatalytic degradation

Photocatalysis vs. *photolysis*

Photocatalytic degradation of 17β-estradiol on immobilised TiO_2 was first reported by Coleman *et al.* [91]. The wavelength of light emitted from the lamp used includes the UVB (medium wave-range 280-315 nm; λ_{max} = 290 nm) and UVC (short wave or germicidal-range between 200 nm and 280 nm; λ_{max}=254 nm) regions of the spectrum. So, experiments with TiO_2 are therefore photolysis and photocatalysis. The same group reported [101, 102] that photocatalysis coupled with photolysis is much more effective in degrading estrogens than photolysis alone caused by a 125 W medium pressure mercury lamp emitting radiation in the UVA (longwave or blackwave range between 315-400 nm; λ_{max} = 365 nm), UVB and UVC regions of the spectrum. The photocatalytic treatment of E2 and EE2 completely removes the estrogenic activity in less than 60 min, compared to the photolytic process which requires 2-3 times longer treatment for EE2 and 8-9 times for E2 [101]. Other groups also reported that photocatalytic oxidation is much more efficient than direct photolysis in the degradation of E2, EE2 and E1 [101, 102, 103].

Photocatalytic reaction order

The authors [91] modeled the degradation kinetics using an apparent first order Langmuir-Hinshelwood kinetic rate equation. With the increase of E2 initial concentration, the rate of the reaction increases proportionally for both photocatalysis and photolysis, confirming that the reactions are first order [104]. First order kinetics is proven or accepted in practically all of the studies on this subject.

Photocatalytic reactors and irradiation sources

A quartz coil reactor and Hanovia 125 W medium pressure mercury lamp (emitting in UVB and UVC spectral regions) is used by Coleman *et al.* [104]; the TiO_2 is immobilized onto a quartz coil. Degussa P25 TiO_2, immobilized on a Ti-6Al-4V alloy film illuminated by 150 W xenon lamp is applied in [91]. Photocatalytic decomposition of 17-β-estradiol (E2) on TiO_2 immobilized on polytetrafluoroethylene mesh sheets is presented in [105]. The latter group reported results obtained in two kinds of reactors with different efficiency.

A quartz water-jacketed reactor with titanium dioxide immobilized on titanium alloy with a 125 W Philips high-pressure mercury lamp placed 3 cm from the reactor was used by Coleman *et al.* [101] for removal of estrogenic activity of several estrogens. Rate constants of UVA photolysis of the steroid substrates were 0.011 min^{-1} for E2 and 0.035min^{-1} for EE2 and the photocatalytic values - 0.106 min^{-1} for E2 and 0.086 min^{-1} for EE2.

A borosilicate glass spiral reactor (volume 85 ml) with TiO_2 immobilized onto the inside wall of the reactor was used in [106]. A black light blue fluorescent lamp (NEC, 15 W, emission range 300–400 nm with maximum at ~350 nm,) was fitted through the centre of the coil.

Zhang [107] also suggests that photocatalysis using P25-TiO_2 can be a very effective method of rapid removal of certain EDCs including E2 from water in two UV-photo-reactors. The water solutions were stirred with a magnetic stirrer for 30 min before TiO_2 was added at a concentration of 1 g/l. In reactor 1 (150 W UV-lamp), 97 % of the compounds were degraded within 4 h of irradiation. Even more rapid degradation was observed in reactor 2 (15 W-lamp), where 98 % of both compounds disappeared within 1 h due to the shorter wavelength of UV-light in this reactor (fixed at 253 nm) than in reactor 1 (238–579 nm) [107].

Influence of TiO_2 and pollutant concentrations on the estrogen removal efficiency

It was found that the efficiency of photocatalytic degradation of E2 in aqueous medium mediated with Degussa P25-TiO_2 increases with increasing concentration of TiO_2 but decreases for TiO_2 concentrations higher than 0.5 g/l due to light scattering [108]. The influence of the pollutant concentration on the photocatalytic process rate is seen from the data in Table 3 [104].

Table 3. Influence of the pollutant concentration on the rate constant and degradation rate of E2 by photolysis and photocatalytic process

E2, μmol/l	Rate constant, $k.10^{-3}$ min^{-1} [104]		Degradation rate, $r.10^{-3}$ μmol/l.min [104]	
	Photo-lysis	Photo-catalysis	Photo-lysis	Photo-catalysis
0,1	125	86	12	9
3	134	174	402	522

Estrogenic activity removal

Degradation of E2 in water by Degussa P25-TiO_2 photocatalysis has been investigated by Ohko *et al.* They showed experimentally and theoretically that the estrogenic activity of E2 is lost in the first step of the photocatalytic reactions. Thus, the authors conclude that TiO_2 photocatalysis could be applied to water treatment as a method for efficient removal of natural and synthetic estrogens without generating biologically active intermediates [92].

Ohko *et al.* [92] concluded in their study on E2 degradation by TiO_2 photocatalysis that the phenol moiety of the E2 molecule should be the starting point of the photocatalytic oxidation. In addition, since the intermediate products do not have a phenol ring, the authors presumed that their estrogenic activities are negligible [58, 92]. The association of the oxidative degradation of some EDCs with the aromatic moieties in their structure is accepted in [77], as well.

Nevertheless, the degradation of estrogen conjugates is also a rather important problem and their photocatalytic destruction had been an object of investigations. Estradiol and its conjugates estradiol-3-glucuronide and estradiol-17-glucuronide were subjected to photodegradation using TiO_2 immobilized on glass beads as a catalyst. Estradiol and its 17-glucuronide were almost completely degraded in presence of UV irradiation (4 W, λ_{max}=365 nm) in 4 h [109].

Estrogen susceptibility to degradation

The quantum yield of estrogen solutions degradation under UVA radiation in the absence of catalyst follows the sequence E1 > E3 > E2 > EE2, reflecting the much higher rate of decomposition of E1 compared to other estrogens. In the presence of TiO_2, the quantum yield follows the sequence E3 > EE2 > E1 > E2, although the difference among the estrogens is not significant [102].

In the presence of the illuminated (150 W xenon lamp) Degussa P25 TiO_2, E2 (0.05–3 μmol/dm^3) was 50 % degraded in 40 min and 98 % degraded in 3.5 h [91]. Photocatalytic decomposition of E2 over TiO_2 immobilized on polytetrafluoroethylene mesh sheets is performed in two types of reactors [103]. In the first one E2 concentration was decreased by 85 % in the dark (no UV illumination) after reaching absorption equilibrium for 1 h. UV illumination applied for 1 h after the dark period lead to decomposition of 98 % of the initial E2, with first-order rate constant of the photocatalytic decomposition of 0.033 min^{-1}. In the second reactor, 90 % of E2 disappeared after 20 min (first-order rate decomposition constant of 0.050 min^{-1}) [103]. More recently, the same group reported a first-order rate constant of 0.15 min^{-1} obtained for E2 under relatively weak UV illumination (1.2 mW/cm^2) [105].

A recombinant yeast assay to measure estrogenic activity, which provided detection limits within the reactor of 53 ng/l for E2 and EE2, and 100 ng/l for estrone is used for the study of the efficiency of the photocatalytic degradation of hormones. Pseudo-first-order kinetic data showed that photocatalysis over immobilized TiO_2 was equally effective at removing the estrogenic activity of all three steroid substrates in aqueous solutions (initial concentrations of 10 mg/l) with a 50 % reduction in estrogenicity within 10 min and 100 % within 1 h. In control experiments without TiO_2 catalyst, the rate of UVA photolysis of the steroid substrates varied, but was most effective with EE2 followed by estrone, and was least effective with E2 (0.42, 0.2 and <0.1 times the rate achieved with photocatalysis, respectively). The application of photocatalysis for the removal of steroid compounds within STW effluent released into the aquatic environment is discussed [101].

An interesting cross-relation between the irradiation light wavelength and the chemical nature of the estrogen is reported by Li Puma *et al.* [102] studying the degradation of multicomponent mixtures of E1, E2, EE2 and E3 in a slurry with P25-TiO_2 The E3 was low sensitive to a process under UVA irradiation, however, E1, E2 and EE2 were removed reaching 49, 20 and 25 % conversion, respectively, after 180 min of irradiation. Under UVC irradiation the conversions of E2, EE2 and E3 after 180 min were 60 %, but the reaction was much faster for E1, which was almost completely (98 %) degraded.

The research of Karpova *et al.* concerns the competitive photocatalytic oxidation and adsorption of steroid estrogens on TiO_2 in the presence of ethanol and urea. Degussa P25 TiO_2 under near-UV irradiation (1.1 mW/cm^2, 365 nm) was used as a photocatalyst. The presence of urea had a negligible effect on the oxidation of EE2 and a moderate one on E2 destruction. The process with E2 in the presence of urea proceeded a little faster than in its absence at pH 7–10, but the effect was moderate as well [110].

The comparison of some main parameters (rate constant, degradation rate and time for degradation of a part of the pollutant) for the photolysis and photocatalytic process is seen from the data in Table 4 [101, 104].

Table 4. Rate constants, degradation rates and time for pollutant removal resulted in photolysis and photocatalysis

Estrogen	Rate constant, $k.10^{-3}$ min^{-1}		Degradation rate, r. 10^{-3} μmol/l.min [104]		Time (min) for removal (%) of the pollutant [101]					
					50		90		100	
	Photo-lysis	Photo-catalysis	Photo-lysis	Photo-catalysis	Photo-lysis*	Photo-catalysis	Photo-lysis*	Photo-catalysis	Photo-lysis*	Photo-catalysis
E2	134[104]; 11[101]	174[104]; 106[101]; 33 [103]; 50 [103]	402	522	195	10	248	24	485	55
EE2	195[104]; 35[101]	231[104]; 86[101]	585	694	23	8	72	28	120	50
Estriol	93[104]	156[104]	280	468						
Estrone	12[101]	86[101]			68	7	195	18	360	60

* Under UVA irradiation.

The great differences in the photocatalytic process conditions explain the differences in the mentioned parameters, so the cited values can be used for general evaluation of the process. Data summarized in [111] show variation in the rate constant (n.10^{-3} min^{-1}) from 14 to 174 for E2 and from 86 to 231 reaching (in the cited paper) 399 for E2 at 365 nm-irradiation and 315 and full destruction for 15 min at UVC irradiation.

Doping as a tool for increasing TiO_2 efficiency

It was found that the addition of silver or platinum to TiO_2 (doping by photodeposition) has no effect on the photocatalytic degradation or mineralization of all EDCs at the concentrations found in water. This was attributed to the high concentration of holes and hydroxyl radicals in the system compared to the low amount of organic matters to be degraded [106]**.**

For the first time data on the effect of TiO_2 modification by N-doping or MWCNT, are obtained in [111]. The sorption ability and photocatalytic activity (measured by degradation rate constant and percentage of the pollutant conversion) of the catalysts under UV (150 W, emission maximum at 365 nm) illumination are determined. The commercial product TiO_2 P25 showed significant degradation efficiency for both estrogens under UV irradiation. However, in some cases the activity of the commercial product declines after the first 15-30 min of illumination and plateau trends are registered at longer irradiation times. That is why, as a final result, the catalysts TiO_2-MWCNTs and TiO_2-N show similar or better efficiency despite the fact that their main component - pure sol-gel synthesized TiO_2 - is much less effective than the Degussa TiO_2 P25.

The sorption and photocatalytic performance of the commercial product Degussa P25, the sol-gel prepared TiO_2 calcined at different temperatures and the same doped with carbon nanotubes against the estrogen EE2 under UVC irradiation is studied in [112]. It is found that the commercial product TiO_2 P25 shows significant degradation efficiency for EE2 providing its full destruction for 30 min. The pure TiO_2 sol-gel synthesized at 700 ^oC is ~6-fold less effective than the Degussa P25. Higher rutile content, larger morphological grains and other surface properties (acidity, hydrophobicity, etc.) seem to be among the factors responsible for this effect. The addition of carbon nanotubes to a similar (produced at lower temperature) TiO_2 has no significant positive influence at the applied photocatalytic test conditions.

Estrogens degradation under visible light illumination

For the first time the photocatalytic destruction of E2 and EE2 under visible light irradiation (150 W halogen lamp) is tested in [111]. The observed rather high efficiency of Degussa TiO_2 P25 under these conditions suggests that the measured band-gap energy value can not be regarded as a direct response to the level of photocatalytic activity. Full destruction of E2 and >99.7 % of EE2 is reached after 2 h irradiation with visible light.

5 CONCLUSION

The literature review shows that both natural and synthetic estrogens are a common pollutant of surface waters, sediments and even drinking waters. Extremely important sources of estrogens found in the environment are the not treated wastewaters, such as effluents from livestock farms. Despite the occasionally reported rather high concentrations, the normal presence of endocrine disrupting compounds ranges from 0.1 to dozen of nanograms per liter. The laboratory tests, as well as the environmental monitoring unambiguously show that their presence in the environment even at such low concentrations is likely to disturb the ecosystems and to affect human health. Thus, the need for developing reliable detection methods, analysis tools, and adapted wastewater treatment processes is now a subject of significant interest. The advanced oxidation processes and especially photocatalysis gained approval as a prospective method for degradation of these emerging environmental contaminants.

The data for the photocatalytic degradation rate constants and the time for degradation of different estrogens vary within rather wide limits, depending on the type of catalyst, irradiation conditions and chemical nature of the estrogen. Full destruction of EE2 can be ensured for 15 min at UVC irradiation and for 1 h in presence of E2 or EE2 under UVA treatment. The recent investigations show that full destruction of E2 and >99.7 % of EE2 can be reached after 2 h irradiation with visible light.

***Acknowledgement**: The study is performed with the financial support of the Bulgarian Fund for Scientific Investigations (contract DO 02-93/08).*

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НЯКОИ СЪЕДИНЕНИЯ С ЕНДОКРИННО ВЪЗДЕЙСТВИЕ В ОКОЛНАТА СРЕДА И ВЪЗМОЖНОСТИТЕ ЗА ТЯХНОТО ОТСТРАНЯВАНЕ/РАЗГРАЖДАНЕ

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Постъпила на 18 октомври, 2011 г.; приета на 10 март, 2012 г.

(Резюме)

Работата представя преглед на литературните данни за присъствието на съединения с ендокринно въздействие в изходните води от пречиствателните станции за отпадни води, повърхностни, подземни и питеййни води и седименти. Дадени са общи данни за тяхното въздействие върху живите организми (главно риба). Разгледана е спецификата на методите за отстраняването/разграждането на замърсителите чрез адсорбция, озониране, биоразграждане, фотолиза и фотокатализ.