OZONATION AND PHOTOCATALYSIS OF WASTE WATER CONTAMINATED WITH 17α-ETHINYLESTRADIOL (EE2) IN CHAMBERY - FRANCE

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Abstract: Wastewater treatment plants (WWTPs) receive a large spectrum of endocrine disrupting compounds (EDCs). The classic treatment of water does not remove these molecules. They are discharged into rivers. We chose to verify the efficiency of ozonation and photocatalysis for a waste water contaminated with three concentrations of EE2 and extracted from a WWTP situated in Chambery-France. Water samples were filtered on nitrocellulose filters (porosity = 0.45µm) and conserved at 4°C. Water samples doped with EE2 were analyzed using high-performance liquid chromatography (HPLC, Hewlett-Packard, 1050 series) with a fluorescence detector (HP 1064A) (λ exc = 210 nm, λ issue = 309 nm). The consumption of ozone required to degrade small quantities of ethinylestradiol is extremely high. In fact, to eliminate 1.55×10^{-2} nmol.L^{-1} or 4.6 ng.L^{-1} of EE2, a molar quantity of ozone of 800,000 times bigger should be added to the water. This result is caused by the presence of organic substances reactive in waste water which enter in competition with the reaction between EE2 and O_3. For the photocatalysis, in only 4 hours, 23% of EE2 is degraded. The slow degradation of EE2 is caused by, the presence of the organic compounds, the low luminous flux and the small concentration of TiO2 P25 (mg.L^{-1}).

Keywords: Ozonation, Photocatalysis, EE2, Sewage water, Endocrine Disrupting Compounds (EDC).

1.   Introduction

Endocrine disrupting compounds (EDCs) are a newly defined category of environmental contaminants that interfere with the function of the endocrine system [1]. EDCs have received much more attention from the regulatory agencies since a possible relationship between EDC exposure and human/wildlife reproduction disorders was suggested [2]. These chemicals include a wide range of molecules such as estrogens, pesticides, phthalates, alkylphenols, natural hormones and pharmaceuticals [3]. Among these compounds, the synthetic estrogen ethinylestradiol (EE2), 17b-estradiol (E2), estrone (E1) and estriol (E3), are excreted by women and consequently found in wastewater [4]. Wastewater treatment
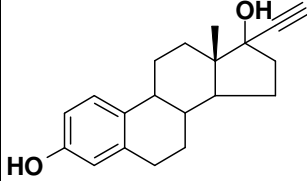
plants (WWTPs) receive these molecules from domestic and/or industrial waste, and they are not totally eliminated during the treatment processes [5-6]. At the outlets of the WWTPs, a complex mixture of molecules including the partially eliminated wastewater molecules but also their metabolites formed during treatment processes, are finally discharged into the rivers. In this context, WWTP discharges play a significant role in environmental contamination and induce a modification of the estrogenic activity of fish [7-8-9]. EE2 might be the most important endocrine disruptor in WWTP effluents together with the octyl and nonylphenols [10-11-12-13]. In our research and in order to verify the efficiency of ozonation, and photocatalysis we artificially contaminated waste water by three conccentrations of EE2: 4.6, 45, and 568 ng.L^{-1}. Water was extracted from a waste water treatment plant (WWTP) situated in Chambery-France. This WWTP of 10,000 inhabitants receives essentially domestic and industrial waste.

2.   Experimental

2.1 Materials

The 17 α-ethinylestradiol (EE2) is purchased from Sigma Aldrich and used as received without purification. The 17 α-ethinylestradiol (EE2) is in the form of a white crystalline solid, soluble in most organic solvents. The physico-chemical properties of EE2 are given in Table 1.

Table 1: Characteristics of 17 α-ethinylestradiol.

Structure	
Empirical formula	$C_{20}H_{24}O_2$
Molecular weight (g.mol^{-1})	296.4
Melting temperature (°C)	182-183°C
pKa (25°C)	10.4
Log P	3.67
DL$_{50}$ rats ingesting (mg.kg^{-1})	2.9

The photocatalyst used is Titanium dioxide Degussa P-25. Its physicochemical characteristics are shown in **Table 2**.

Table 2: Physico-chemical characteristics of the Titanium dioxide.

Crystal structure	Specific surface $(m^2.g^{-1})$	Particle size (nm)	PZC
80% anatase 20% rutile	50-55	30	6

Water samples were taken from the waste water treatment plant (WWTP) situated in Chambery-France. The extracted water was filtered on nitrocellulose filter (porosity = 0.45µm) and conserved at 4°C. The principal physico-chemical characteristics of waste water are presented in **Table 3**.

Table 3: Physico-Chemical characteristics of waste water extracted from WWTP of Chambery-France

pH	Alkanility (A) (°f)	Total Organic Carbon (TOC) (mg C L^{-1})	Chemical Oxygen Demand (COD) (mg O_2 L^{-1})	Biological Oxygen Demand (BOD) (mg O_2 L^{-1})
7.03	22.5	4.95	30	3

2.2 Ozonation procedure

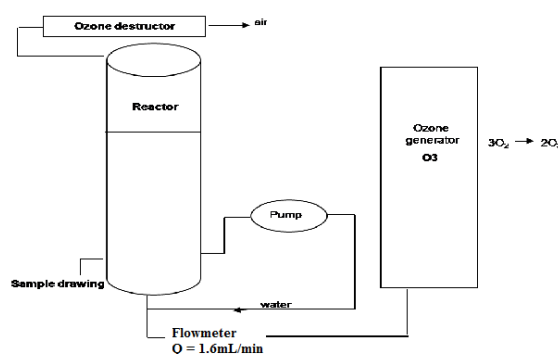Experimental set up for ozonation is shown in **Figure 1.**

Figure 1: Schematic of the ozonation pilot plant

The pilot plant consists of a cylindrical glass reactor (450 mm high water column, 5000 mL maximum capacity), an ozone generator 5LO Trailigaz model, the flow of liquid is made with a magnetic driven pump, a valve adjustment to adjust the speed from 0 to 60 L.h^{-1} , and an ozone destructor. Ozone is produced from pure oxygen and fed into the reactor through a porous glass diffuser located at the bottom of the reactor to produce bubbles. Production of

ozone is controlled by changing the power input of ozone generator. The gas flow rate is adjustable by a valve. In all ozonation experiments, the power of the ozone generator is set to 50 W with gas flow rate of 1.6 $L.h^{-1}$.

2.3 Sample preparation

The ozonation of waste water was done after being doped by three concentrations of EE2: 4.6, 45 and 568 $ng.L^{-1}$ that are respectively equal to 0.0155; 0.132 and 1.92 $nmol.L^{-1}$. For every studied concentration, the ozone dose to degrade the EE2 molecule was determined. An ozonated water solution is prepared by bubbling ozonized air in a phosphate buffer solution (ionic strength $I = 10^{-2}$ $mol.L^{-1}$, pH = 2 to 12). This solution was used to adjust a variety of vials containing a constant volume of doped ethinylestradiol diluted with a variable volume of phosphate buffer as a function of O_3 during 2 hours of oxidation.

2.4 Adsorption experiments

750 mL of doped EE2 are placed in the reactor at neutral pH. It is then placed for 24 hours under magnetic stirring in the dark and in the presence of 66 $mg.L^{-1}$ of TiO_2. This time is necessary to reach the equilibrium between adsorption and desorption.

2.5 Photocatalytic experiments

The photoreaction is carried out in a Pyrex cylindrical reactor of a volume of 1 liter. The radiant flux is provided by a high-pressure mercury lamp Philips HPK 125 W which provides maximum energy at 365 nm. An optical filter is installed to cut-off any radiation of wavelength below 300 nm. A circulating water system is installed to avoid heating of the solution subjected to UV irradiation. The radiant flux is measured with a VLX-3W radiometer with a CX-365 detector (UV-A). A value of 2.2 $mW.cm^{-2}$ is found corresponding to about $5.71x10^{16}$ $photons.s^{-1}$. The photodegradation of waste water was realized after being doped by 0.0034 $\mu mol.L^{-1}$ (= $1\mu g.L^{-1}$) of EE2 in the presence of 66 $mg.L^{-1}$ of TiO_2 P25.

2.6 Analytical methods

Residual EE2 is determined using high-performance liquid chromatography (HPLC, Hewlett-Packard, 1050 series) with a fluorescence detector (HP 1064A) (λ exc = 210 nm, λ issue = 309 nm). The eluent is acetonitrile: water (70:30, v/v). pH is measured with a Tacussel LPH330T pH-meter equipped with a Radiometer Analytical combined electrode and previously calibrated with standard buffers (pH 4 - 7). Samples are extracted using solid phase extraction (SPE) cartridges in order to monitor low concentrations of EE2 between $4\mu g.L^{-1}$ and $4ng.L^{-1}$. The aqueous sample (200 mL) from the oxidation experiments is passed through the preconditioned SPE cartridge. Conditioning is performed successively with 10

mL acetonitrile and 10 mL distilled water successively. The analytes are eluted with 5 ml acetonitrile. The solvent is evaporated by a gentle stream of nitrogen and the residue is dissolved immediately in 200 µl acetonitrile. Thus the analytes are concentrated to a factor of 1000. The analysis is done by HPLC / fluorescence (λ exc. = 210 nm λ issue. = 309 nm).

3.   Results and discussions

The ozonation of waste water was done after being doped by 3 concentrations of EE2: 4.6, 45, and 568 ng.L^{-1} that are respectively equal to 0.0155, 0.132, and 1.92 nmol.L^{-1}. An example of the degradation of EE2 at 45 ng.L^{-1} (= 0.132 nmol.L^{-1}) is represented in **Figure 2**. From this figure, proportionality between the residual of EE2 degraded and the concentration of O_3 introduced was observed. The global consumption of ozone (Number of moles of ozone consumed per mole of degraded EE2) was reported in **Table 4** for waste water and ultrapure water.
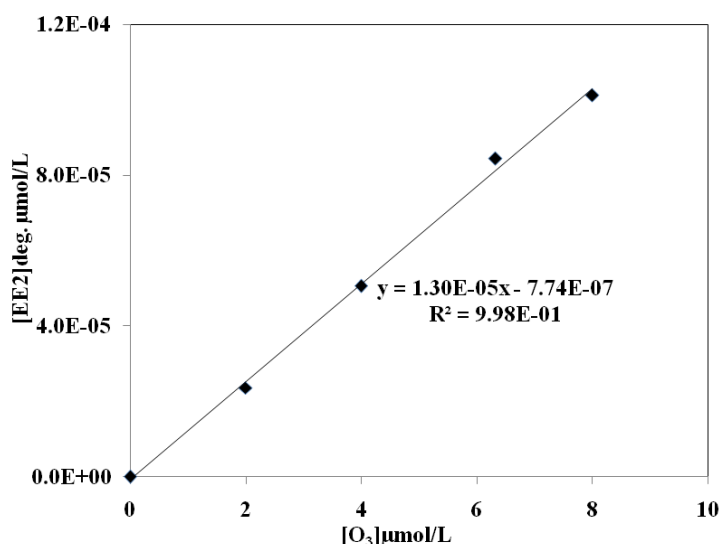

Figure 2: Degradation of EE2 doped in waste water (pH = 7.03; [EE2] = 45ng.L^{-1})

Table 4: Evolution of the global consumption of ozone in function of the initial concentration of EE2 in waste water

[EE2]$_o$ (nmol.L^{-1})	[EE2]$_o$ (ng.L^{-1})	Global consumption of ozone (Number of moles of ozone consumed per mole of degraded EE2)	
		Waste water (experimental values)	Ultrapure water (calculated values)
1.92	568	17,900	99
0.152	45	76,900	182
0.0155	4.6	800,000	787

The representation of the above results given on a logarithmic scale (**Figure 3**) shows that, for this water, the global consumption of ozone per degraded mole of EE2 evolves linearly in function of the initial concentration of EE2.
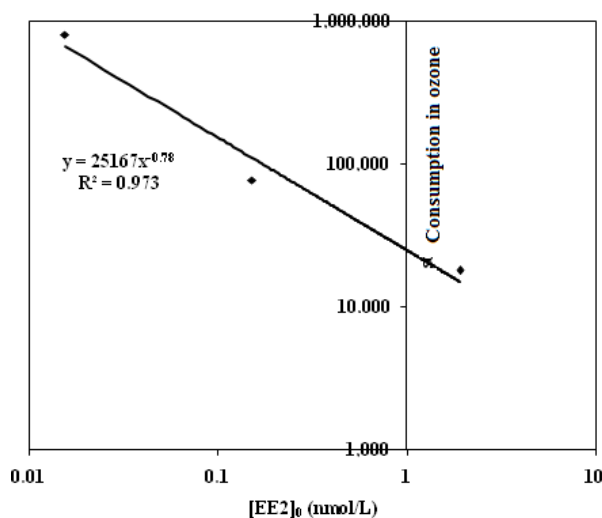

Figure 3: Evolution of the consumption of ozone in function of the initial concentration of EE2 in waste water

The reported results in **Table 4** and **Figure 3** show that the consumption of ozone required to degrade small quantities of ethinylestradiol is extremely high. In fact, to eliminate 1.55×10^{-2} nmol/L or 4.6 ng/L of EE2, a molar quantity of ozone of 800,000 times bigger should be added to the water. This quantity of ozone is superior to the one that should be added to an ultrapure water at the same pH. This result is caused by the presence of organic substances reactive in waste water. These substances enter in competition with the reaction between EE2 and O_3. For waste water the global rate of ozone decomposition is the result of, the reaction rate of ozone with ethinylestradiol and its intermediate products (IP), participating reactions like autodecomposition of ozone and the reaction of ozone with the organic compounds (OC) present in the water:

$$OC_{water} + O_3 \rightarrow OC_{ox} \; k_{OC}$$
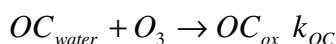
The global rate of the decomposition of ozone in waste water is the following:

$$v = -\frac{d[O_3]}{dt} = k_1[O_3][EE_2] + \sum k_{IP}[O_3][IP] + k_3[O_3] + \sum k_{OC}[O_3][OC]$$

In the case of waste water, the added ozone is consumed by the organic compounds for a water doped at approximately 4 ng.L^{-1} of EE2, the consumption of ozone is almost 1000 times superior to that of ultrapure water. A dose if 0.6 mg of ozone should be applied to treat one liter of waste water. This quantity of ozone is higher than that determined by Hubber *et*

al. [14] who obtained that 0.1 mg.L^{-1} (= 2 µmol.L^{-1}) and 0.2 mg.L^{-1} (= 4 µmol.L^{-1}) of ozone are needed to degrade 0.5 µmol.L^{-1} of EE2 (148 µg.L^{-1}) doped in extracted water from la Seine river in Paris and another river in Finland respectively. The difference of consumption is caused by the characteristics of water. The ozone dose determined in this research to treat this waste water is similar to the ozone dose published by Thomas *et al.* [15] who estimate that 5 to 10 mg.L^{-1} of ozone are necessary to degrade pharmaceutical products, estrogen, and micropolutants.

4.   Photodegradation of waste water

Waste water taken from waste water treatment plant of Chambery-France was artificially contaminated by ethinylestradiol. The photodegradation of waste water was realized after being doped by 0.0034 µmol.L^{-1} (= 1µg.L^{-1}) of EE2 in the presence of 66 mg.L^{-1} of TiO2 P25 and luminous flux of 2.2 mW.cm^{-2}. The photodegradation of the molecule was preceded by a study of the adsorption during 24 hours. The quantity of EE2 adsorbed corresponds to 2.3x10^{-3} µmol.L^{-1}. **Figure 4** shows that under a luminous flux of 2.2 mW.cm^{-2}, the degradation of EE2 is weak. The disappearance of EE2 is not observed. In only 4 hours, 23% of EE2 is degraded. The slow degradation of EE2 could be due to the presence of the organic compounds in the solution that enter in competition with the photodegradation of EE2, the weak irradiation and the small concentration of TiO2.

Conclusion

Ozone is a strong oxidant that is well adopted to eliminate EE2. The dose of ozone to be applied to waste water can be modeled in function of the initial concentration of pollutant, therefore, this dose does not take into consideration the quantity of ozone necessary to have a total degradation (mineralization) of this pollutant. The photocatalysis is an advanced oxidation process. More developed studies will be useful as the dependence of the concentration of TiO2 P25 and the luminous flux intensity.

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