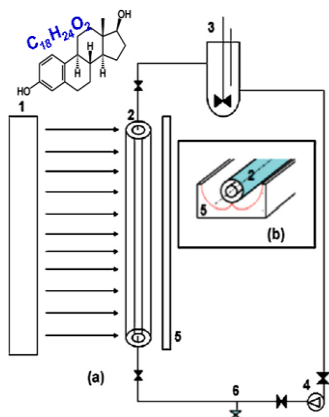


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Photodegradation of the natural steroid 17 β -estradiol (E2), an endocrine disrupting hormone, which is commonly found into aquatic environments, was investigated by Advanced Oxidation Processes. Heterogeneous photocatalysis using titanium dioxide (TiO₂) and photo-Fenton using peroxymonopersulfate (Oxone or PMS) are considered as forceful and environmental friendly processes that can be used as tertiary treatment stage to remove recalcitrant contaminants present in treated wastewater effluent. Our work focuses on the evaluation of E2 degradation using this processes. For an initial E2 concentration of 1.3 \pm 0.4 mg/L, either a 2:1 ratio of peroxymonosulfate:metal (Fe²⁺) or 0.7g/L of TiO₂ were used. Independently of the oxidation method assessed, the decomposition of E2 always followed a pseudo-first order kinetic. By-products identified during the oxidation of E2 correspond to those described in the literature. The estrogenic activity test proved that molecules inducing the estrogenic activity were destroyed.

The domestic and industrial use of water, of large amount in the developed countries, generate high quantity of residual wastewater, which direct disposal into natural channels is of considerable impact to the environment. This fact, together with the need to recuperate this water for new uses, makes practically essential the purification of wastewater to achieve the desired degree of quality.

The list of pollutants is long as well as the warning signs of water pollution surrounding us.

Reflecting a new environmental conscience, the European Directive 2000/60/CE [1] stresses the need to adopt measures against water pollution in order to achieve a progressive reduction of pollutants, especially endocrine disrupting compounds (EDCs).

Furthermore, recent update of the priority substances list in European Water Framework renders the situation even more pressing. Fifteen new molecules were proposed, which include two EDCs (17 β -estradiol and 17 α -ethinylestradiol). For this reason waste water treatment plants (WWTPs) should be designed for achieving the removal of micropollutant in order to minimize their sanitary and environmental impacts. To improve the efficiency of existing WWTPs, it is necessary to develop new eco friendly methods for the removal of emerging and recalcitrant pollutants.

A promising way to perform the mineralization of these types of substances is the application of Advanced Oxidation Processes (AOPs).

AOPs have become attractive technologies because they use cheap reactants and renewable

solar energy. Among solar-driven processes, heterogeneous photocatalysis using TiO₂ and photo-Fenton possess the highest efficiency.

AOPs are characterized by *in situ* production of hydroxyl radicals under mild experimental conditions [2]. This species exhibits a high oxidizing potential (E°=2.8 V), which permits to degrade or mineralize organic contaminants. However, due to their unselective reactivity, hydroxyl radicals are scavenged in organic matter rich environmental water.

Several improvements have been recently achieved by our research groups to increase the efficiency of titanium dioxide photocatalysis and photo-Fenton.

Concerning heterogeneous photocatalysis, the main drawbacks of the TiO₂ catalyst is its troublesome separation from purified medium after treatment. Hence, various attempts to immobilize TiO₂ on various supports have been undertaken. Macroporous reticulated materials such as aluminum foams have been proposed as supports for TiO₂ on account of their uniform cellular structure. Due to their macroscopic arrangement, they provide a large interface for exchange between the targeted molecules and the solar radiation [3, 4]. Concerning photo-Fenton, the use of sulphate radical (SO₄^{•-}, E° = 2.6V) has appeared a good alternative to HO[•] to partly overcome the inhibition induced by the environmental matrices. This is mainly due to the higher selectivity of sulphate radicals over HO[•] operating through selective oxidation and leading to higher abatement rates of pharmaceutically active compounds (PhACs) [5, 6].

This study compares the effectiveness of solar TiO₂ photocatalysis and photo-Fenton, using peroxymonopersulfate (Oxone or PMS), for the removal of 17β-estradiol (E2) as model contaminant. The efficiency of these processes was evaluated through

- 1) the disappearance of target contaminant monitored by HPLC;
- 2) the elucidation of estrogenic activity using cell lines;
- 3) analytical determinations by LC coupled to high resolution mass spectrometry to identify and monitor transformation products.

Material and methods. Experiments were conducted on wastewater effluent from the municipal WWTP of Perpignan (France) spiked with Estradiol (1.3±0.4 mg/L). Degradation experiments were performed by using a photochemical reactor described elsewhere [2]. The total volume of the reactor was 1L and it was equipped with an irradiation source centered to 365 nm, having an irradiance of 35 W m⁻². All the surface of the reactor was uniformly irradiated thanks to a compound parabolic collector (CPC) positioned at the back side. E2 kinetic of degradation was followed by HPLC using Accucore C18 column (2.6μ, 100mm x 2.1mm) and was detected by fluorescence detector in which the excitation wavelength was 280nm and the emission wavelength was 305nm. Identification of intermediates was carried out by LC-HRMS using LC-QTOF instrumentation.

Results and discussion. Elimination of E2 in WWTP effluent by heterogeneous photocatalysis using titanium dioxide (TiO₂) and photo-Fenton using peroxymonopersulfate (Oxone or PMS) was studied.

Kinetic parameters of tested oxidation reactions have been listed in table 1. Results show that the E2 concentration decayed exponentially with time. All experiments produced linear plot of Ln(C_{E2}/C_{0E2}) versus time as reported in Fig.1, indicating that the photodegradation of E2 in aqueous solution under solar irradiation followed pseudo-first-order kinetics. The pseudo-first-order degradation rate constant and half time of E2 can be calculated as per Eq. (1) and (2):

$$\ln\left(\frac{C_{E2}}{C_{0E2}}\right) = -kt \quad (1)$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (2)$$

Table 1. Kinetic parameters of different processes under UV irradiation

Process	K _{app} (min ⁻¹)	Half – life (min)
UV	0.004	161
Oxone	0.04	17
Fe(II)	0.14	4.5
Oxone/Fe(II)	0.59	0.29
P25	0.78	0.9
P25/Oxone	0.85	0.81
Photosphere	0.14	5

[Oxone] = 0.2mM; [Fe²⁺] = 0.1mM; [TiO₂] = 0.7g/L

To ensure good replication of the experimental procedures, kinetics experiments were carried out in duplicate.

Homogeneous photo-Fenton using peroxy-monopersulfate as oxidant and heterogeneous photocatalysis using TiO₂ were highly effective for E2 removal.

Nonetheless, the effluent's inherent estrogenicity can be only partly removed. Decrease of estrogenic activity test implies that the estrogenic activity inducing molecules have been destroyed [7]. In fact, estrogenic activity was evaluated using cell line HELEN ER. During PMS/Fe and TiO₂, a loss of activity was observed within 5 minutes.

By-products identified during the oxidation of E2 correspond to those described in the literature. The first step is the formation of estrone followed by a polyhydroxylation and ring opening.

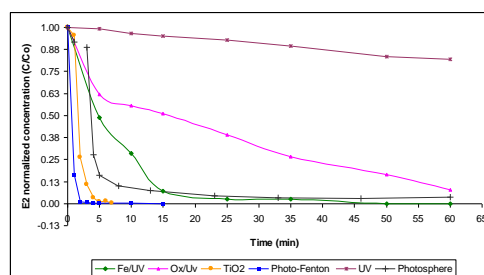


Figure 1. E2 degradation in presence of different oxidation systems.

Conclusion. Homogeneous photo-Fenton using peroxymonopersulfate as oxidant and heterogeneous photocatalysis using TiO₂ are effective technologies for the fast removal of estrogenic hormones. Both processes were very fast because after 5 min, 95% of E2 was removed, but photo - Fenton process was more efficient than

TiO₂ because the mineralization of E2 was achieved within 2 min (Fig. 1). Hence advanced oxidation processes can represent a powerful mean for the further purification of WWTP effluents.

Acknowledgements

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