Heterogeneous photocatalysis and photo-Fenton of estradiol in wastewater

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CONTEXT

•The European Directive 2000/60/CE stresses the need of adopting measures against water pollution in order to achieve a progressive reduction of pollutants and recuperate water for new uses.

Fig 1 : Crossed benefits of wastewater reuse.

PRINCIPLE

•Advanced Oxidation Processess (AOPs) are promising ways to perform the mineralization of pollutants. AOPs are characterized by the in situ production of hydroxyl radicals, which are highly reactive species capable of oxidizing organic materials in a non-selective way.

Fig 2 : Mechanism of AOP

OBJECTIVE - APPROACH

- The main objective of this to study was to compare the 17-β Estradiol (E2) degradation in wastewater by different AOPs including UV, UV+oxidant, UV-TiO_2, photo-Fenton, UV-photosphere, UV-graphenesphere, UV-oxone (a photo-Fenton like process based on peroxymonopersulfate as oxidant).

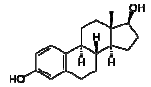


Fig 3 : Molecule of estradiol

Approach :

1. The disappearance of target contaminant
2. The elucidation of estrogenic
3. Validate the model by solar experiments.

EXPERIMENTS – ANALYSIS

1 - UV Lamp λ = 365nm
2 – Tubular reactor
3 – Storage tank
4 - Peristaltic pump
5 - Reflector CPC
6 – withdrawing valve

Fig 4 : Artificial UV disinfection pilot

The total volume of the reactor was 1L and it was equipped with an irradiation source centred to 365 nm and 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 backside.

Fig 5 : HPLC

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 280 nm and the emission wavelength was 305 nm

Assay n	Oxidation process	n	$t_{1/2}$ (min)	k (h-1)	r^2	k ratios kn/k_1	k ratios kn/k2
1	UV	0	161.81	0.0036	0.9970	1(reference)	0.0046
2	OX+Uv						2
3	Fe/Uv						8
4	TiO2/Uv						nce)
5	Photosphe						5
6	Graphenespl						1
8	Photo fenton						23

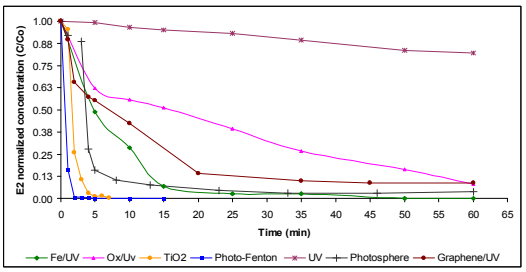
n= reaction order
$t_{1/2}$ = half-life (min)
k=kinetic constant
r^2=determinatin coefficient

Fig 6 : cell line Heln Er for evaluation of estrogenic activity

Estrogens control transcriptional responses through binding to two different nuclear receptors, estrogen receptor α (ERα) and β (ERβ). The HELN-ERα and HELN-ERβ cells stably express full-length ERα and ERβ, respectively, and are derived from HELN cells (HeLa cells stably transfected with an ERE-driven luciferase plasmid). This method was used to evaluate estrogenic activity

RESULTS

• Study of E2 degradation in presence of different oxidation systems



$$Ln\left(\frac{C_{E2}}{Co_{E2}}\right) = -kt$$

$$t_{1/2} = \frac{Ln2}{k}$$

• Kinetics

Assay	Oxidation process	n	$t_{1/2}$ min	k	R^2	k_n/k_1	k_n/k_4
1	UV	0	161	0.0036	0.9970	*1(reference)*	0.005
2	UV+Ox	1	17.4	0.0398	0.9615	11	0.05
3	UV-Fe	1	4.46	0.1553	0.9095	43	0.2
4	UV-TiO_2	1	0.89	0.7774	0.9596	216	*1(reference)*
5	UV-photosphere	2	2.64	0.3790	0.9756	105	0.5
6	UV-graphenesphere	2	4.76	0.2100	0.9347	58	0.3
7	UV-oxone	2	0.015	68.10	0.9816	18917	87

n=reaction order
T ½= hlaf-life (min)
K= kinetic constant
R2= determination

➢For an initial E2 concentration of 1.3 ± 0.4 mg/L, either a 2:1 ratio of peroxymonosulfate: metal (Fe^{2+}) or 0.7 g/L of TiO_2 were used. The same amount was used for all tests and to ensure good replication of the experimental procedures, kinetics experiments were carried out in triplicate.

➢E2 concentration decayed exponentially with time

➢Half-lives of E2 degradation were consistently decreased from 161.81 min (UV-irradiation) to 0.015 min when the oxidation power of UV light was enhanced by means of photo Fenton using peroxymonopersulfate.

➢Byproducts 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.

➢Estrogenic activity was evaluated using cell line Heln Er, during photo Fenton using peroxymonopersulfate and photocatalysis with TiO_2, a loss of activity was observed within 5 minutes (data not show)

CONCLUSION

- Homogeneous photo – Fenton using peroxymonopersulfate as oxidant and heterogeneous photocatalysis using TiO_2 were the most effective technologies for the fast removal of estrogenic hormone.
- Both processes were very fast considering that 95% of E2 was removed in few minutes. Moreover, UV-oxone was more efficient than UV-TiO2 since with the first technology the complete mineralization of E2 was achieved within 2 minutes without the production of dangerous by-products.

PERSPECTIVES

- Treatment of larger volumes
- Application of AOP outdoor in wastewater treatment plants
- Identification of intermediates and residual toxicity.
- Definition of molecules mainly responsible of eventual toxicity

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