Advanced Removal of 17 α-Ethynilestradiol Using Photocatalytic Ozonation Techniques

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ABSTRACT

Synthetic estrogens such as 17α-ethinylestradiol are among the most commonly found chemicals in surface and treated waters. Because it is a hormone, this compound has a high potential to act as an endocrine disruptor. The advanced oxidative processes (AOPs) are one of the techniques that have a good efficiency in the removal of these compounds, being the ones used in this work the photolysis, photocatalysis with titanium dioxide and the photocatalytic ozonation. To perform the experiment, a PVC tube reactor with a working volume of 4 L was prepared. Inside it, 2 ultraviolet lamps (UVC) of 15 w each were inserted. In a 2 L recirculation reservoir, connected to the tube, was installed a pump with a flow of 180 $L.h^{-1}$ and ozone. The equipment was batch operated for 2 hours, the samples were collected every 10 min and analyzed in HPLC. In addition, a study was made of the influence of the variation of the catalyst concentration, on the removal efficiency. Photolysis presented efficiency of 87.6%, photocatalysis with TiO_2 0.2 $g.L^{-1}$ 91.28% and photocatalytic ozonation 99.2%. The process did not show interference by adsorption of the hormone on the catalyst or the filter.

KEYWORDS: 17α-ethinylestradiol, photocatalysis, titanium dioxide, photocatalytic ozonation.

INTRODUCTION

Pharmaceutical industry has invested in developing of products that go along the modern life style and attend to the needs of their customers. However, as a consequence of the production of complex chemical compounds, a significant number of environmental-offensive byproducts is generated (SILVA; COLLINS, 2011). Some of these substances are called emerging pollutants that are potentially toxic compound in concentrations of µgL or ngL (MOREIRA; GONÇALVES, 2011).

Among them are endocrine disruptors (ED), according with USEPA, external agent that interferes in synthesis, transport, bonding, action or elimination of natural hormones responsible for maintenance, reproduction, development or behavior of organisms. ED include substances with different structures including natural or synthetic estrogens (BILA; DEZOTTI, 2007).

Estrogens can be natural as 17 β-estradiol (E2), estryol (E3), estrona (E1) that produced by human body or synthetic as 17α-ethynilestradiol (EE2) that is developed in pharmaceutical industries for hormonal reposition and as a contraceptive method (REIS FILHO; ARAUJO;VIEIRA, 2006) in the form of 30 or 50 µg per pill (BEAUSSE, 2004). EE2 is considered one of the most powerful of estrogenic compounds, since it is biodegradation-resistant because of the ethylene group in its structure (CARGOUET et al 2004).

This substance reaches the environment by the pharmaceutical industry wastewater or by human urine and feces released with incomplete treatment (REIS FILHO; ARAUJO;VIEIRA, 2006).

Authors report that the exposition to estrogenic compounds is related with sperm reduction, ovulation inhibition, alteration of menstrual cycle and testicles and breast cancer. In fish, BERGAMASCO in 2010 reported high rates of hermaphroditism that are related with the presence of EE2 in the environment.

Since EE2 is not removed completely in conventional domestic or industrial wastewater treatment plants, the assessment of advanced processes application is needed to avoid the impact on water bodies. Researchers that work with advanced oxidation processes have reported important advances in the removal this pollutant from the water. Huber et al., (2004), Zhang et al., (2006) Larcher et al. (2012); Frontisis et al., (2012), Zhang et al., (2012), Pan et al., (2014).

AOPs are degradation reactions capable of transform organic pollutants in CO_2 and H_2O and inorganic anions. So that these reactions can occur, it is required the presence of hydroxyl radicals that can be generated by O_3, H_2O_2, TiO_2, ZnO and UV radiation.

Ozonation allied to catalysis with a UV-irraditaed TiO_2 suspension has been tested in order to reduce reaction times, which lowers the volumes needed for reaction to take place. The presence of dissolved O3 is fundamental for these reactions to take place, been the suspension of TiO2 a condition that makes the contact with pollutant more intensive.

MATERIALS AND METHODS

Experimental

Catalytic reaction

The removal of EE2 was performed in a 3.6L, 100mm-diameter sequencing batch annular reactor (SBR) with two UVC-15W lamps (Osram) and a recirculation reservoir with a recycling pump (180 L.h^{-1} SarloBetter). Ozone was provided by means of a diffuser connected to a ozone generator (4 mg.h^{-1} Ozoneline). Fig. 1 shows the configuration of the reactor system.

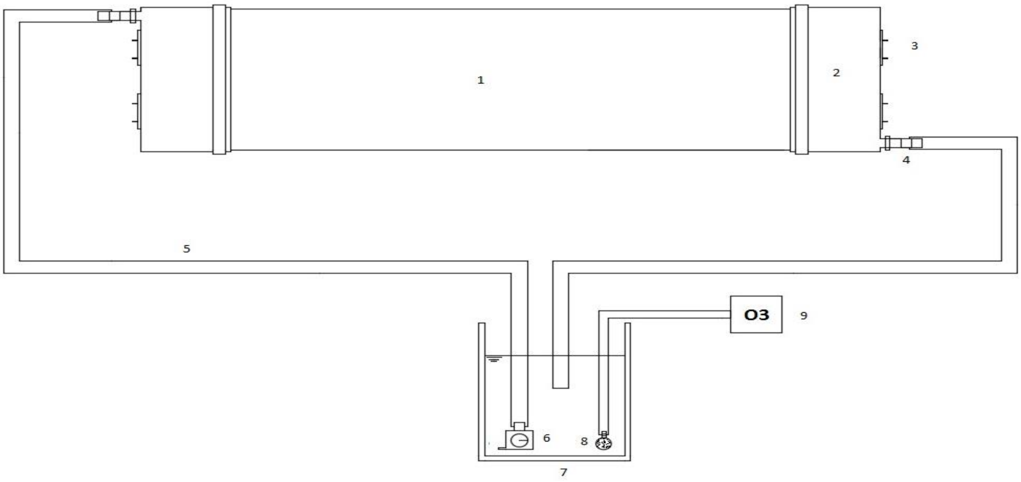

Fig. 1. Experimental setup of the bench scale system including SBR. 1) Reactor body; 2) closing caps; 3) UVC lamps; outlet; 5) inlet; 6) pump; 7) Recirculation reservoir; 8) Ozone diffuser 9) ozone generator

Influent was prepared in order to simulate the presence of EE2 in an industrial effluent. In this way, EE2 (98.9 % pure from Zhejiang Xinaju Pharmaceutical Co. Ltd) was previously diluted in methanol to a concentration of 40 mg.L^{-1}. This solution was subsequently diluted to 5 mg.L^{-1} in ultra-pure water (MS2000 Gehaka), this concentration is similar to that from pharmaceutical wastewater (NASUHOGLU et al 2012).

The TiO_2 (Millennium) was used in suspension in order to reach better contact with the liquid.
Experimental procedure was performed in three stages, being stage 1 with application of UVC radiation (photolysis), stage 2 with application of UVC/TiO_2 (photocatalysis) and stage 3 with application of UVC/TiO_2/O_3 (catalytic ozonation).

In Stage 2 TiO_2 concentration varied from 0.05, 0.2 and 0.5 g.L^{-1} in order to verify variation effect on EE2 removal (PAN et al, 2014).

Each SBR run had a duration of 120 min, taking 10mL samples every 10 min. Before the first sampling, SBR was let to function during 3 min to promote complete mixing of reactants.

Samples were initially filtered in filter paper (Whatman 40) and taken to chromatographical analysis according the following technique using a UHPLC (Flexar, Perkin Elmer) equipped with a C-18 100 x 4.6 mm column (Perkin Elmer) and a PDA detector. The mobile phase was a mixture of acetonitrile and water in the proportion of 80:20 with flow rate of 0.8 mL.nim^{-1}. Wave length for EE2 detection was 280 nm in excitation and 310nm in emission. Injection volume was 20 µL and analyte was retained for 1.4 min.

EE2 adsorption on TiO_2

In order to verify the adsorption of EE2 on TiO_2 particles, an experiment was performed using a solution containing EE2 and TiO_2 in the concentrations of 5 and 0.2 g.L^{-1} respectively. That suspension was kept under agitation for 2 h, samples were taken every 30 min and submitted to the analytical procedure described before.

RESULTS AND DISCUSSION

Photolysis

This stage was intended to verify the efficiency of the removal of EE2 using UVC light emission. EE2 decay with time is showed in Fig. 2.

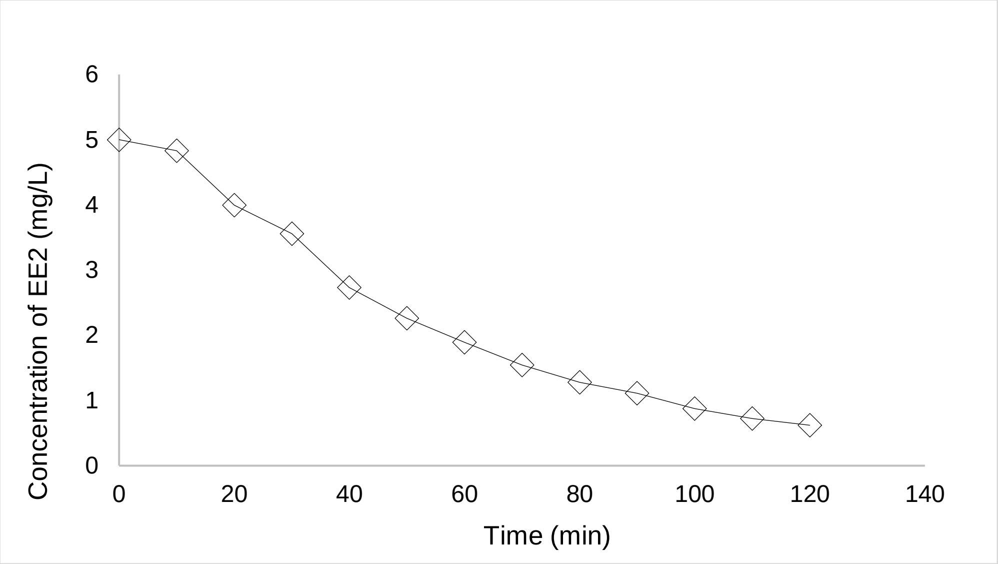

Fig. 2. Variation of EE2 concentration with time after UVC light application

As can be seen, after 120 min the concentration of hormone had a decay of 88% dropping the concentration of EE2 from 5 to 0.59 mg.L^{-1}. This efficiency was better than expected considering the 75% EE2 removal efficiency presented by TERAN et al in 2017, using a reactor similar to the one used in this research. The fact that two 15W UVC lamps were used in this work instead of one used by the authors, can justify this observation.

Photocatalysis with 0.2 g.L^{-1} TiO$_2$

This stage consisted in the determination of efficiency in the hormone removal by means of photocatalysis using TiO_2 in the concentration of 0.2, 0.5 and 0.05 g.L-1. The results of this stage are shown in Fig. 3.

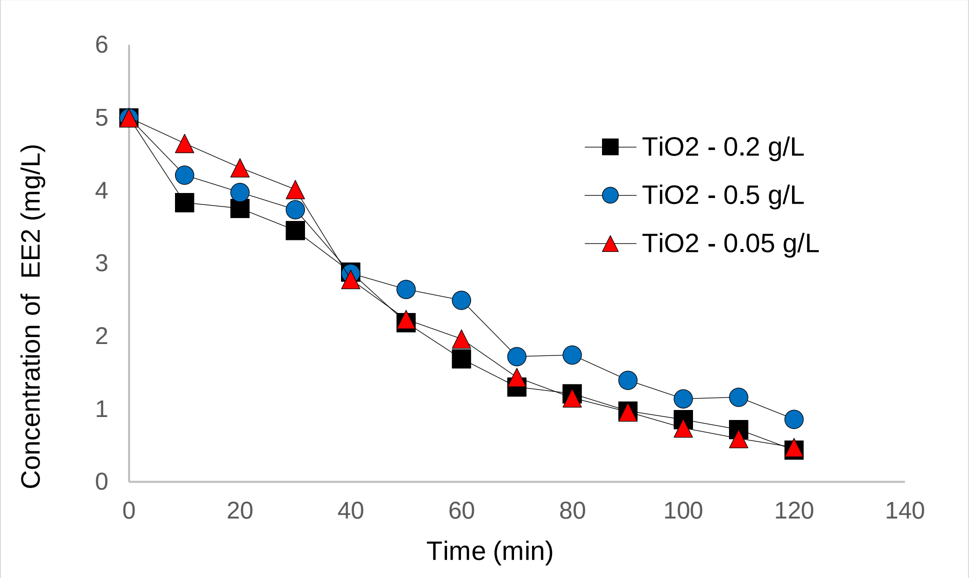

Fig. 3. Variation of EE2 concentration with time after UVC/light application with different concentrations of TiO$_2$

Fig. 3 shows that, for TiO_2 concentration of 0.2 g.L^{-1}, after 120 min hormone concentration dropped from 5 to 0.44 mg.L-1 presenting a removal of 91.3%That is similar to that removal reached by Nasuhoglu (2012) in 30 min. The reason of that may be that the authors used 1.6 L of raw influent and greater volumes like the one used in this work, can cause variations of light distribution into the reactor, turning the activation of the catalyst more difficult which results in low removal of pollutant in a short period of time. So, in order to increase photocatalysis efficiency, considering equal volume of liquid, we must increase contact time to promote a more uniform light distribution and activate more particles of the catalyst.

Increasing catalyst concentration to 0.5 g.L^{-1} caused the reduction of efficiency to 82.80 % in 120 min. Several authors (Suave et al 2012, Méndez-Arriaga et al 2008 and Gogate and Pandit 2004), showed that when catalyst concentration increases efficiency of removal tends to decrease due to shading effect caused by excess of TiO_2 that would not let UVC radiation to activate a greater part of TiO_2 particles.

The reduction of catalyst concentration to 0.05 g.L^{-1} produced an efficiency of 90.55%, very close to that from 0.2 g.L-1 indicating that this lower concentration can be used without prejudicing the systems efficiency in the removal of EE2.

as these pollutants frequently show first order decay reactions, its original concentrations affect the overall reaction.

Photocatalytic ozonation

The last stage consisted in verifying the efficiency of the reactor by means of the application of UVC/TiO_2/O_3. So, 400 mg.h-1 of O_3 were applied to the system along with UVC radiation and TiO_2 in the concentration of 0.2 g.L^{-1}, the one that reached the best result in the previous stage. The decaying curve is showed in Fig. 4.

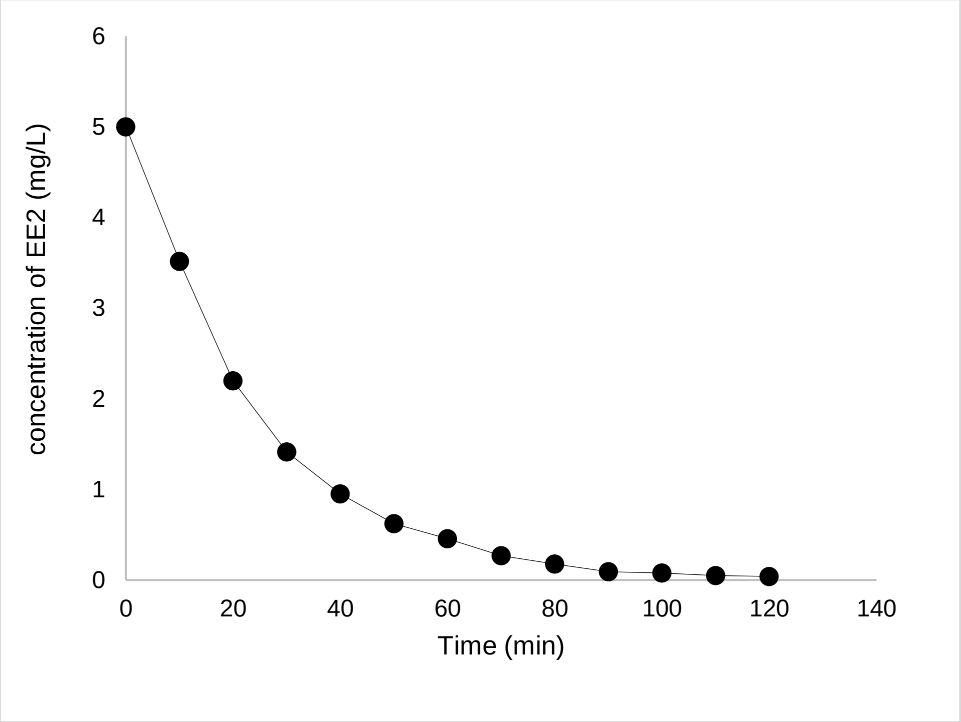

Fig. 4 Decaying curve of EE2 after the application of 0.2 g.L^{-1} TiO_2, UVC radiation and 400 mg.h^{-1} of O_3.

After 2 h of treatment was verified that efficiency attained was of 99.29 % dropping the concentration of EE2 from 5 to 0.04 mg.L^{-1}. That indicted that the combination of processes UVC/TiO_2/O_3 was very effective and fast, showing a sudden drop to 56.05 % in the first 20 min and 94.62 % in 70 min, better that all removals reached in previous stages.

The processes combination resulted in a greater production of •OH radicals being electron hole the mechanism responsible for oxidation in photocatalysis and molecule decomposition and UVC interaction the mechanisms responsible for oxidation due to O_3 presence.

A kinetic study was made in order to quantify the removal rates. Fig. 5 along with Table 1 show the linear regression results.

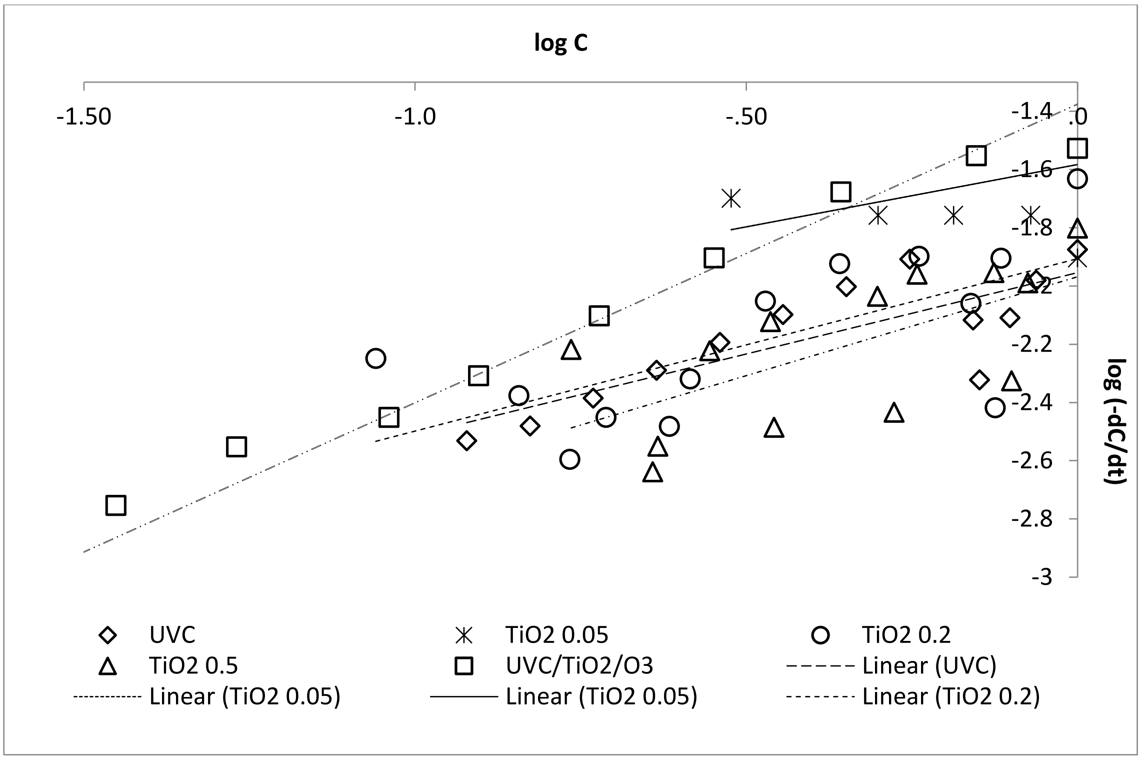

Fig. 5. Linear regression of degradation profiles of EE2 concentration during application of UVC; TiO2 concentration = 0.05 g.L-1; TiO2 concentration = 0.2 g.L-1; TiO2 concentration = 0.5 g.L-1 and UVC/TiO2/O3.

The removal rates for the experiments are presented in Table 2. As pointed before, the degradation of EE2 was faster with the combination of processes, presenting a rate constant o 0.041 min-1, which was expected due to the enhanced formation of oxidative radicals.

Despite a similar performance, experiments 1 and 2 present different rate constants, indicating that when a concentration of 0.05 g.L-1 of TiO2 is applied, reaction takes place in less time because it did not prevent UVC radiation to activate the catalyst. In the other hand, when UVC/TiO2/O3combinations is applied, the rate constant doubles the valor of that from 0.05 g.L-1 of TiO2.

Table 1. EE2 removal kinetic parameters of degradation for several experimental conditions.

Experiment	Catalyst Conc. (g.L^{-1})	Rate constant (min^{-1})	Reaction Order	R	Efficiency after 120 min %
Photolysis	0	0.011	0.559	0.787	75
1	0.05	0.026	0.428	0.642	90
2	0.2	0.0124	0.592	0.704	91
3	0.5	0.010	0.679	0.642	83
UVC/TiO2/O3	0.2	0.041	1.025	0.991	99

CONCLUSION

Photolysis and photocatalyst showed efficiency in the removal of EE2 in a typical concentration of an industrial wastewater, being the TiO_2 concentration of 0.2 g.L^{-1} the one that presented better efficiency after 120 min of treatment.

Photocatalytic ozonation was the most effective process because of the generation of •OH radicals in more than one way resulting not only in higher efficiency but in shorter residence times. Efficiencies reached 90.8 % after 60 min and 99.2 % after 120 min of treatment.

About the effect of TiO_2 concentration, it was proved that mass increment resulted in a depletion in the removal of the hormone due to the interference caused by the excess of particles that increased turbidity preventing light to activate the catalyst. A value of 0.05 g.L^{-1} seems to be an adequate value for de conditions imposed to the system.

As verified, adsorption on TiO_2 particles played a minor role in the overall process.

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