

*Full Length Research Paper*

# Photocatalytic oxidation of 17 $\alpha$ -Ethinylestradiol by UV-activated TiO<sub>2</sub> in batch and continuous-flow reactor

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In this study, the photocatalytic oxidation by UV-activated TiO<sub>2</sub> was investigated for the degradation of a 15 mgL<sup>-1</sup> solution of 17  $\alpha$ -ethinylestradiol (EE2) in an ultra-pure water matrix. The TiO<sub>2</sub> adsorption, solution pH and catalyst TiO<sub>2</sub> concentration were evaluated. Operating as a batch reactor, the system showed a 90% removal, with a 40-min retention time, a pH value of 8 a TiO<sub>2</sub> concentration of 0.1 gL<sup>-1</sup>, and a rate constant of 0.13 min<sup>-1</sup> for this experiment. The adsorption was negligible in 2 h at pH 7. As a continuous-flow reactor, the operation achieved an 87% removal with a TiO<sub>2</sub> concentration of 0.025 gL<sup>-1</sup> at pH 7. Ultraviolet-C (UVC) photolysis presented a removal of 40% in 2 h at pH 7 with the system operating in batch mode. Operating as a sequencing batch, the reactor showed remarkable efficiency in the removal of EE2 in a short period.

**Key words:** Photocatalysis, 17  $\alpha$ -ethinylestradiol, UV-activated TiO<sub>2</sub>, sequencing batch reactor, continuous flow reactor.

## INTRODUCTION

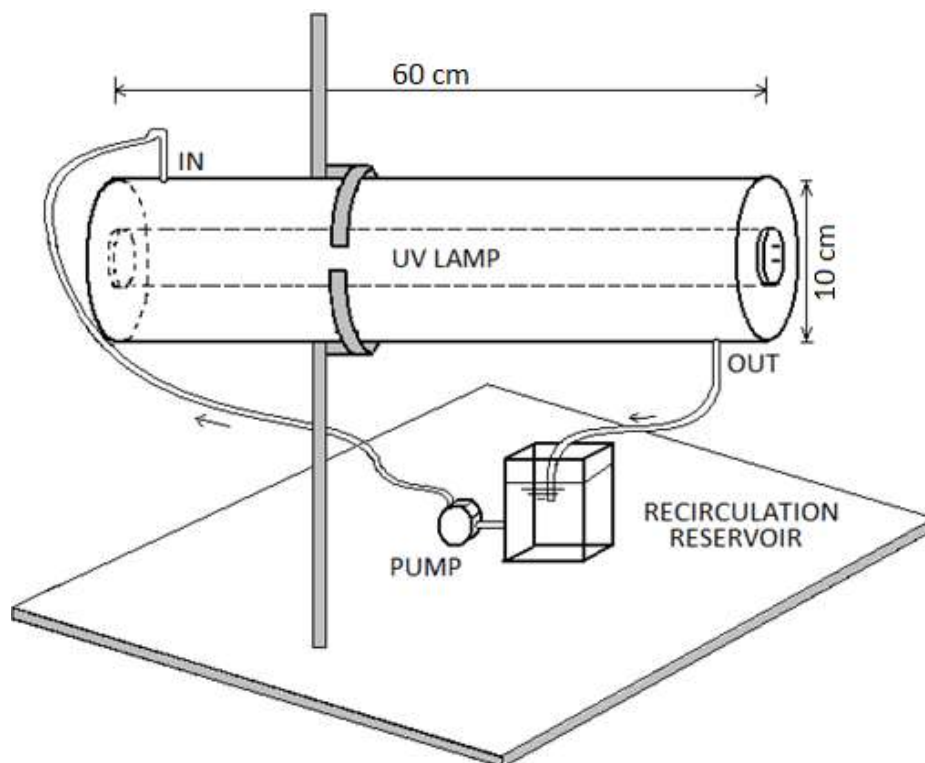
Surface waters have historically been used as wastewater receptors; however, recently, important efforts have focused on protecting water quality from recalcitrant organic compounds. Among these organic compounds, endocrine disruptor compounds (EDCs) have been reported in several water bodies worldwide (Atkinson et al., 2012; Huerta-Fontela et al., 2011;) and several researchers have reported on health and environmental injuries caused by these EDCs (Armstrong et al., 2015; Tyler et al., 2005; Zenker et al., 2014).

17 $\alpha$ -Ethinylestradiol (EE2), a synthetic estrogen that is commonly used as a contraceptive and hormone replacement (Zhou et al., 2012), and other medicinal compounds reach water bodies via urine, feces or

manure (Halling-Sorensen et al., 1998). King et al. (2016) reported that the concentration of EE2 in Australian wastewater was 0.1 to 0.5 ngL<sup>-1</sup>. The removal of EE2 in both sewage treatment plants (STPs) and water treatment plants is inefficient (Nasuhoglu et al., 2012); thus, to avoid the presence of EE2 in receiving waters, it must be removed prior to entering the sewers.

In pharmaceutical industries that produce EE2, one method to address this problem is to treat hormone-carrying effluents as soon as they are produced in the oral contraceptive facilities, before their mixture with other effluents produced in the same industry. In this liquid waste, EE2 can be found at a concentration of 5 mgL<sup>-1</sup> (Nasuhoglu et al., 2012).

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**Figure 1.** Experimental setup.

The degradation of this compound has garnered attention, and several studies have utilized adsorption (Gokçe et al., 2016; Ma et al. 2016), biological (Larcher et al., 2013; Yi et al., 2011) and advanced oxidation processes for this purpose (Solcova et al., 2016; Pešoutová et al., 2014; Pessoa et al., 2014). Among these processes, advanced heterogeneous oxidation processes have been successfully used to remove water pollutants (Padovan and Azevedo, 2015; Gotostos et al., 2014; Miranda et al., 2013).

Although the removal of EE2 using photocatalytic degradation has been widely studied (Solcova et al., 2016; Pan et al., 2014; Ma et al., 2015; Wang et al., 2015), there are still gaps in the knowledge concerning the intermediates of the EE2 removal process.

These experiments represent a fast and reliable method for removing EE2 from industrial wastewater to prevent it from entering the environment in concentrations that can pose problems for animal life and human health. The purpose of this study was to evaluate EE2 removal performance in a cost-effective UV reactor using a suspension of powdered TiO<sub>2</sub> and to statistically analyze the factors related to the EE2 oxidation process.

## MATERIALS AND METHODS

### Reagents

TiO<sub>2</sub> (99.3% anatase-rutile ratio) was donated by Millennium, ultra-

pure water and acetonitrile (Sigma-Aldrich, HPLC grade) were used for chromatography, and analytical grade ethanol was used to prepare the feed solution. The EE2 standard was purchased from Zheijiang Xinaju Pharmaceutical Co. Ltd.

### EE2 feed solution preparation

The EE2 stock solution was prepared in acetonitrile at a concentration of 50 mgL<sup>-1</sup> and was subsequently diluted to 5 mgL<sup>-1</sup> in ultra-pure water to produce the feed solution. Once the reactor was filled, the catalyst was added to the recirculation basin at concentrations of 0.05 and 0.1 gL<sup>-1</sup>.

### Photocatalytic reactor

The experiments were conducted in an annular-sectioned 3.6-L reactor (600-mm height, 100-mm diameter) equipped with a recirculation reservoir, a recirculation pump and a UV lamp (15 W, 254 nm, mercury) (Figure 1).

### Operating procedure

#### Stage 1 - Batch mode operation

In stage 1, experiments were conducted using 3.6 L of the feed solution in the reactor, along with the catalyst (concentrations showed in Table 1). No oxygen was introduced during the experiments. Aliquots were obtained at 20-min time intervals during the 120-min irradiation and were filtered using a 0.45- $\mu$ m cellulose acetate membrane (Whatman 1.2- $\mu$ m pore size microfiber filter). A system temperature of 25°C was maintained.

**Table 1.** pH and catalyst concentration values adopted for experimental design 2<sup>2</sup>.

Factors	Lower level	Upper level
pH	7.0	8.0
TiO <sub>2</sub> concentration (g.L <sup>-1</sup> )	0.05	0.1

The concentration of TiO<sub>2</sub> and pH varied according to a 2<sup>2</sup> experimental design (Table 1). The upper and lower levels of these parameters were based on the results (Frontistis et al., 2012; Yargeau et al., 2012). The combination that presented the best results in terms of EE2 removal was applied to stage 2 in which the reactor was operated in continuous-flow mode. The concentrations of EE2 were measured using high performance liquid chromatography (HPLC). The kinetic parameters of degradation were determined according to the differential kinetics method under four separate removal conditions. The rate constants were determined using Equation 1.

$$\ln\left(\frac{-dCA}{dt}\right) = \ln k + n \ln CA \quad (1)$$

### Stage 2 - Continuous flow operation

In Stage 2, the recirculation basin did not receive the reactor effluent; instead, the effluent was directed to a treated wastewater reservoir. Initially, the influent flow rate was adjusted to have a hydraulic retention time of 120 min, with the optimal combination of pH and TiO<sub>2</sub> obtained in stage 1. In the second step, the catalyst concentration and the hydraulic detention time were varied to obtain the highest EE2 removal. Samples were obtained after 40 min and were filtered (Whatman 1.2- $\mu$ m pore size microfiber filter) to remove TiO<sub>2</sub> prior to determining the EE2 concentration.

### Photolysis and absorption

Photolysis experiments were conducted in this stage to compare the results to those of photocatalysis. The feed solution was added to the system, which was operated for 120 min using UV light without any catalyst. The sampling and analysis followed the procedure used in Stage 1.

The adsorption of EE2 on TiO<sub>2</sub> particles was also studied to evaluate its effect on the overall removal efficiency of the process. This experiment was conducted in the dark, with 0.1 gL<sup>-1</sup> of TiO<sub>2</sub> at pH 7. Santiago et al. (2013) reported EE2 adsorption at this pH value. After the system operated for 2 h, the concentration of EE2 remaining in the sample was determined using HPLC.

### Analytical procedures

To validate the chromatography method for linearity, EE2 stock solutions were prepared in ultrapure water at concentrations of 0.10, 0.25, 0.50, 0.75, 1.0, 2.5, 5.0, 7.5 and 10.0 mgL<sup>-1</sup>. Samples were obtained for HPLC analysis to construct the calibration curve (intensity versus concentration) and to determine its equation. Selectivity was also evaluated by comparing an EE2 sample (0.10 mgL<sup>-1</sup>) to ultra-pure water (Gehaka<sup>®</sup> Master P & D-TOC). The precision and accuracy of the chromatographic method were also determined by analyzing EE2 solutions with concentrations of 0.25, 2.5 and 7.5 mgL<sup>-1</sup>.

All samples were analyzed for EE2 using an HPLC instrument (Shimadzu) equipped with a C18 (ACE 5  $\mu$ m, 250 x 4.6 mm)

column, a fluorescence detector (RF 10 AXL Shimadzu) and an automatic injector (SIL-20). The mobile phase consisted of 80:20 acetonitrile:water at a flow rate of 1 mLmin<sup>-1</sup> (pump LC-20 AT Prominence) at ambient temperature. The excitation and emission wavelengths of the fluorescence detector were 280 nm and 310 nm, respectively. Data analysis was performed using the LC solution software (Shimadzu, Kyoto, Japan).

## RESULTS AND DISCUSSION

### Photolysis

Photolysis experiments were conducted in batch mode during Stage 1 to compare the results to those obtained from photocatalysis. The system operation followed the same routine as that used in Stage 1 - Batch mode operation, photocatalytic tests but without TiO<sub>2</sub>. Figure 2 shows the EE2 removal results in an ultra-pure water matrix using 254-nm UV light. These results show lower EE2 removal rates (70% in 100 min) than those of photocatalysis (90% in 20 min) (Figure 3). Removal rates greater than 75% were absent during the photolysis experiment due to the lower removal capacity of UV light without a catalyst.

### Adsorption experiments

EE2 adsorption on the catalyst may interfere with the ability to compare the results obtained from the photocatalysis experiment. The results of the adsorption test confirmed that the loss of EE2 was lower than 5%, thus demonstrating that adsorption onto TiO<sub>2</sub> particles may be considered negligible.

### Removal of EE2 in the ultra-pure water matrix: Stage 1

The focus of this research is to study the effect of the photoactivation of the catalyst by UV light under the conditions explained above. The paired electron-hole creates hydroxyl radicals that have high oxidative power. The degradation of EE2 under 254-nm UV light for the studied pH and TiO<sub>2</sub> conditions is presented in Table 1 (Figure 3). The reactor was most effective in reducing the EE2 concentration at pH 7 and at a catalyst concentration of 0.1 gL<sup>-1</sup>. Low concentrations of TiO<sub>2</sub> particles permit the passage of light, thereby enhancing the catalyst

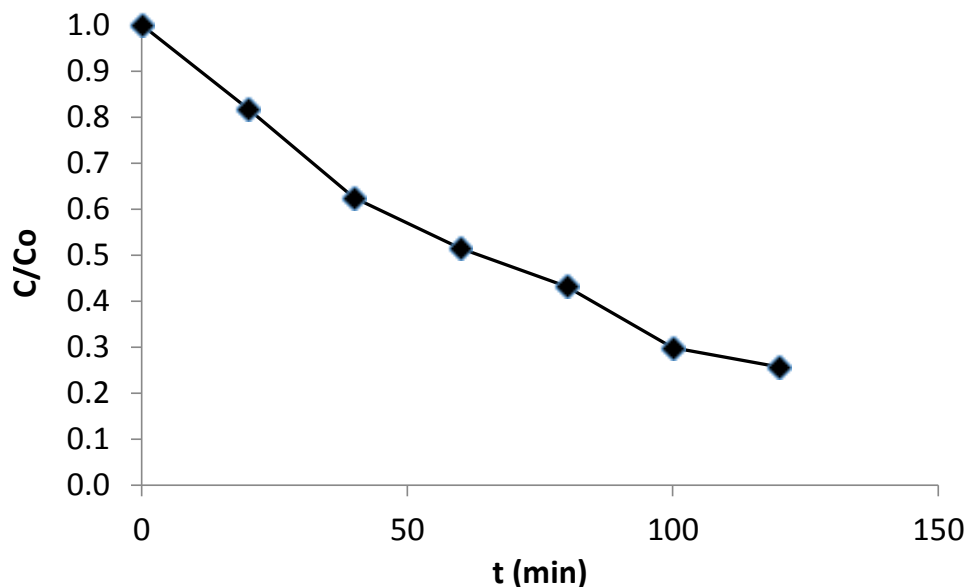


Figure 2. Variation of EE2 concentration during photolysis.

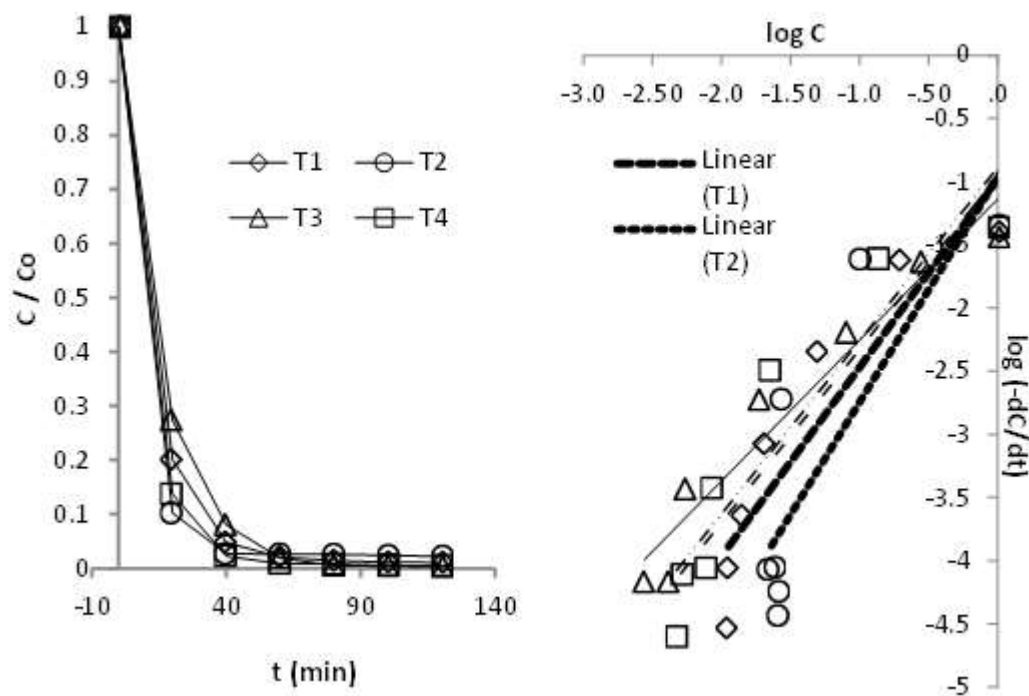


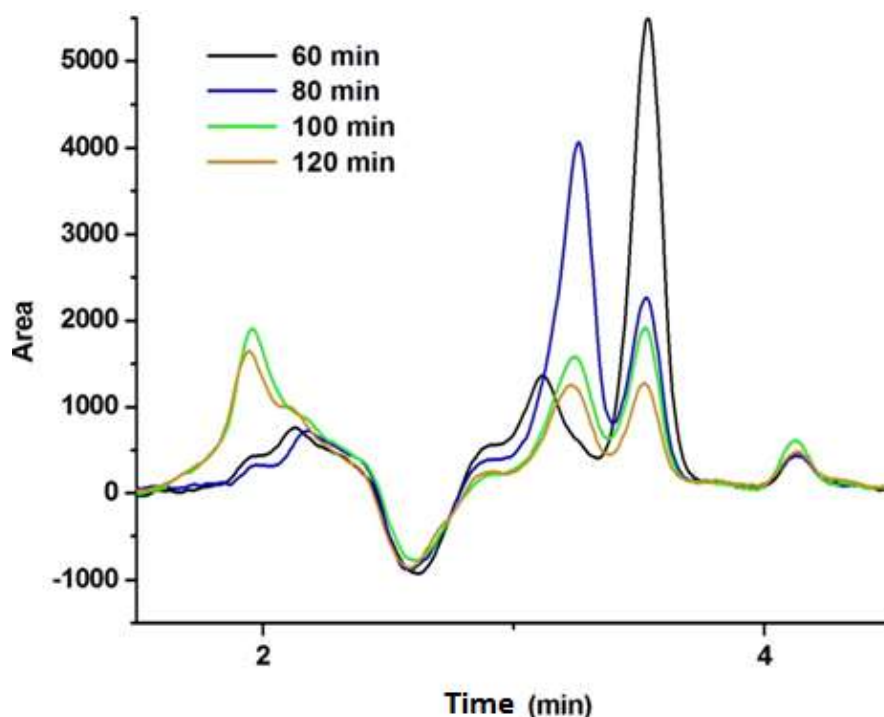
Figure 3. Degradation profiles of EE2 concentration during photocatalysis in Stage 1. a) conditions for T1: pH = 7,  $TiO_2$  concentration =  $0.05 \text{ g.L}^{-1}$ ; conditions for T2: pH = 7,  $TiO_2$  concentration = 0.1; conditions for T3: pH = 8,  $TiO_2$  concentration =  $0.05 \text{ g.L}^{-1}$ ; conditions for T4: pH = 8,  $TiO_2$  concentration =  $0.1 \text{ g.L}^{-1}$ . b) Linear regression for curves showed in (a).  $C/Co$  represents the removal rate of EE2 in time.

photoactivation. The photocatalytic removal of EE2 is considerably higher than the photolytic removal of EE2, as shown by the difference observed at 40 min, when nearly 90% of the hormone was removed.

The removal rates for the experiments are presented in Table 2. The degradation of EE2 was faster than that reported in another study (Pereira et al., 2011) in which UV and  $H_2O_2$  were used. UV showed a significant

**Table 2.** EE2 removal kinetic parameters of degradation for several pH and catalyst concentrations.

Experiment	pH	Catalyst conc. (g.L <sup>-1</sup> )	Rate constant (min <sup>-1</sup> )	Reaction order	Linear equation	R <sup>2</sup>
T1	7.0	0.05	0.1169	1.4959	$\log(-dC/dt) = 1.4959 \log C - 0.93187$	0.8533
T2	7.0	0.1	0.12320	1.78027	$\log(-dC/dt) = 1.78027 \log C - 0.90912$	0.6955
T3	8.0	0.05	0.07295	1.11616	$\log(-dC/dt) = 1.11616 \log C - 1.13696$	0.9394
T4	8.0	0.1	0.13039	1.3703	$\log(-dC/dt) = 1.3703 \log C - 0.88476$	0.8691

**Figure 4.** HPLC chromatogram of EE2 in experimental system.

improvement in the conversion of EE2.

Increasing the TiO<sub>2</sub> concentration can lead to a significant improvement in the conversion of EE2, unless high concentrations of suspended catalyst cause photon scattering, thereby reducing the activation of the TiO<sub>2</sub> powder in regions away from the UV lamp and close to the reactor walls. The results of the T2 and T4 experiments show higher values of the rate constant, indicating higher efficiency. Therefore, these experiments require lower activation energy, can occur at lower temperatures than those applied in the other experiments, and have better results than those obtained under the other conditions tested. Both T2 and T4 used 0.1 gL<sup>-1</sup> of catalyst, and in both experiments, the changes in pH did not appear to have a great effect. Additionally, this concentration did not prevent UV light from penetrating into the liquid column, as shown by the efficiency results.

Despite a better performance by T2 in the first 20 min, the T4 experiment showed the best overall results

starting at 40 min (Figure 3), including the highest value of the rate constant (Table 2). T4 also showed a better fitted curve, as indicated by the R<sup>2</sup> value.

### Residual EE2 concentration in the experimental system

In the experimental system, liquid chromatography was used to determine the residual EE2 concentrations over time (Figure 4). With the current facilities available in our laboratory, it was not possible to identify this unknown intermediate. The removal results in the chromatograms for the reaction times of 60, 80, 100 and 120 min are also shown.

### Removal of EE2 in the ultra-pure water matrix: Stage 2

To represent full-scale applications, in Stage 2, the

reactor was operated in continuous-flow mode, with a hydraulic detention time (HDT) of 40 min at pH 7. For  $\text{TiO}_2$  concentrations of 0.1, 0.05 and  $0.025 \text{ gL}^{-1}$ , the removal rates were of 37, 62 and 87%, respectively, indicating that lower catalyst concentrations favored higher EE2 removal in this operating mode. Greater UV light penetration appeared to enhance the pollutant removal in the continuous-flow reactor. The  $\text{TiO}_2$  concentration showed only a minor effect in the batch mode in which the liquid passed through the reactor several times over 40 min; in this case, a higher concentration of  $\text{TiO}_2$  ( $0.1 \text{ gL}^{-1}$ ) produced better results. In continuous-flow mode, the removal rates were 37, 62 and 87% for  $\text{TiO}_2$  concentrations of 0.1, 0.05 and  $0.025 \text{ gL}^{-1}$ , respectively.

## Conclusions

The applicability of photocatalysis for the degradation of 17  $\alpha$ -ethinylestradiol using UV-activated  $\text{TiO}_2$  was demonstrated in an ultra-pure water matrix. These experiments showed a high degree of EE2 oxidation, although the process was more effective in Stage 1 (batch mode) than in stage 2 (continuous flow).

The experimental results indicated that the pH value had only a small influence on the oxidation process of EE2 and that a catalyst concentration of  $0.1 \text{ mgL}^{-1}$  of  $\text{TiO}_2$  showed higher removal rates for both of the pH values tested. However, pH 8.0 resulted in by-product formation; for 40 min of operation, Stage 1 obtained 90% degradation, and stage 2 obtained 87% degradation of 17  $\alpha$ -ethinylestradiol.

These results provide a good foundation for applying the photocatalytic oxidation of 17  $\alpha$ -ethinylestradiol using a UV-activated  $\text{TiO}_2$  process, thereby avoiding the adverse environmental effects of this compound.

## Symbols

- C:** EE2 concentration corresponding to time  $t$ ,  $\text{ML}^{-3}$   
**CA:** Concentration of constituent named A,  $\text{ML}^{-3}$   
**Co:**  $t = 0$  time EE2 concentration,  $\text{ML}^{-3}$   
**t:** Time, T  
**k:** Reaction rate constant,  $\text{T}^{-1}$   
**n:** Order of the reaction

## CONFLICT OF INTERESTS

The author has not declared any conflict of interests.

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## REFERENCES

- Armstrong BM, Lazorchak JM, Murphy CA, Haring HJ, Jensen KM, Smith ME (2015). Determining the effects of a mixture of an endocrine disrupting compound, 17  $\alpha$ -ethinylestradiol, and ammonia on fathead minnow (*Pimephales promelas*) reproduction. *Sci Total Environ.* 120:108-114.
- Atkinson SK, Marlatt VL, Kimpe LE, Lean DRS, Trudeau VL, Blais JM (2012). The occurrence of steroidal estrogens in south-eastern Ontario wastewater treatment plants. *Sci. Total Environ.* 430:119-125.
- Frontistis Z, Kassinos-Falta D, Mantzavinos D, Xekoukoulotakis NP (2012). Photocatalytic degradation of 17 $\alpha$ -ethinylestradiol in environmental samples by ZnO under simulated solar radiation. *J. Chemical Tec. Biotechnol.* 87:1051-1058.
- Gokçe CE, Arayici S (2016). Investigation of the environmental distribution of endocrine disrupting materials in sewage sludge. *Desalin. Water Treat.* 57:2564-2569.
- Gokçe CE, Arayici S (2016). Adsorption of 17 $\beta$ -estradiol and estrone by activated carbon derived from sewage sludge. *Desalin. Water Treat.* 57:2503-2514.
- Gotostos MJN, Chia-Chi, De Luna SMDG, Ming-Chun L (2014). Kinetic study of acetaminophen degradation by visible light photocatalysis. *J. Environ. Sci. Health Part. A* 49:892-899.
- Halling-Sorensen B, Nielsen SN, Lanzky PF, Ingerslev F, Lutz-heft HCH, Jorgensen SE (1998). Occurrence, fate and effects of pharmaceutical substances in the environment—a review. *Chemosphere* 36:357-393.
- Huerta-Fontela M, Galceran MT, Ventura F (2011). Occurrence and removal of pharmaceuticals and hormones through drinking water treatment. *Water Res.* 45:1432-1442.
- King O, Merwe J, McDonald JA, Leusch FDL (2016). Concentrations of levonorgestrel and ethinylestradiol in wastewater effluents: Is the progestin also cause of concern? *Environ. Toxicol. Chem.* 35:1378-1385.
- Larcher S, Yargeau V (2013). Biodegradation of 17 alpha-ethinylestradiol by heterotrophic bacteria. *Environ. Pollut.* 173:17-22.
- Ma X, Zhang C, Deng J, Song S, Li Q, Guo Y, Li C (2015). Simultaneous Degradation of Estrone, 17 $\beta$ -Estradiol and 17 $\alpha$ -Ethinyl Estradiol in an Aqueous UV/H<sub>2</sub>O<sub>2</sub> System. *Environ. Res. Public Health* 12:12016-12029.
- Ma W, Nie C, Gao X, Qu D, Lun X, Chen B (2016). Sorption characteristics and factors affecting the adsorption behavior of bisphenol A and 17 $\beta$ -estradiol/ethinyl estradiol in river- and farmland-based artificial groundwater recharge with reclaimed water. *Desalin. Water Treat.* 57:8015-8025.
- Miranda CY, Contreras J, Zaror CD, Mansilla HD (2013). Phenylmercury degradation by heterogeneous photocatalysis assisted by UV-A light. *J. Environ. Sci. Health Part A* 48:1642-1648.
- Nasuhoglu D, Berk D, Yargeau V (2012). Photocatalytic removal of 17- $\alpha$ -ethinylestradiol (EE2) e levonorgestrel (LNG) from contraceptive pill manufacturing plant wastewater under UV radiation. *Chem. Eng. J.* 185-186: 52-60.
- Padovan RN, Azevedo EB (2015). Combining a sequencing batch reactor with heterogeneous photocatalysis ( $\text{TiO}_2/\text{UV}$ ) for treating a pencil manufacturer's wastewater. *Braz. J. Chem. Eng.* 32:99-106.
- Pešoutová R, Střítešský L, Hlavínek P (2014). A pilot scale comparison of advanced oxidation processes for estrogenic hormone removal from municipal wastewater effluent. *Water Sci. Technol.* 70:70.
- Pessoa GP, Souza NC, Vidal CB, Alves, PIM, Firmino RF, Nascimento AB, Santos (2014). Occurrence and removal of estrogens in Brazilian wastewater treatment plants. *Sci. Total Environ.* 490:288-295.
- Santiago DE, Doña-Rodríguez JM, Araña J, Fernandez-Rodríguez C, Gonzalez-Diaz OJ, Perez-Peña AMT (2013). Optimization of the degradation of imazalil by photocatalysis: Comparison between commercial and lab-made photocatalysts. *Applied Catalysis B*, 138-139:391-400. <http://doi.org/10.1016/j.apcatb.2013.03.024>

- Solcova O, Spacilova L, Maleterova Y, Morozova M, Ezechias M, Kresinova Z (2016). Photocatalytic water treatment on TiO<sub>2</sub> thin layers, *Desalin. Water Treat.* 57:11631-11638.
- Tyler CR, Spary C, Gibson R, Santos EM, Shears J, Hill EM (2005). Accounting for differences in estrogenic responses in rainbow trout (*Oncorhynchus mykiss*: Salmonidae) and roach (*Rutilus rutilus*: Cyprinidae) exposed to effluents from wastewater treatment works. *Environ. Sci. Technol.* 39:2599-2607.
- Wang Y, Li Y, Zhang W, Wang Q, Wang D (2015). Photocatalytic degradation and reactor modeling of 17 $\alpha$ -ethynylestradiol employing titanium dioxide-incorporated foam concrete. *Environ. Sci. Pollut. Res. Int.* 22:3508-3517.
- Yi T, Mackintosh S, Aga DS, Harper WF (2011). Exploring 17 alpha-ethynylestradiol removal, mineralization, and bioincorporation in engineered bioreactors. *Water Res.* 45:(3)1369-1377.
- Zenker A, Cicero MR, Prestinaci F, Bottoni P, Carere M (2014). Bioaccumulation and biomagnification potential of pharmaceuticals with a focus to the aquatic environment. *J. Environ. Manage.* 133:378-387.
- Zhou Y, Zha J, Wang Z (2012). Occurrence and fate of steroid estrogens in the largest wastewater treatment plant in Beijing, China. *Environ. Monit. Assess.* 184:6799-6813.