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RESEARCH ARTICLE
ARAŞTIRMA MAKALESİ

Assessment of environmental applicability of TiO_2 coated self-cleaning glass for photocatalytic degradation of estrone, 17β-estradiol and their byproducts

Golnar Matin[1*] ● Ali Reza Amani-Ghadim[2] ● Amir Abbas Matin[3] ● Navid Kargar[4]
Hasan Baha Buyukisik[5]

[1] Department of Marine-Inland Water Sciences and Technology, Faculty of Fisheries, Ege University, 35100 Bornova, Izmir, Turkey https://orcid.org/0000-0002-1286-8611
[2] Department of Chemistry, Faculty of Sciences, Azarbaijan Shahid Madani University, 53714-161 Tabriz, Iran https://orcid.org/0000-0003-3279-5170
[3] Department of Chemistry, Faculty of Sciences, Azarbaijan Shahid Madani University, 53714-161 Tabriz, Iran https://orcid.org/0000-0001-8264-8414
[4] Department of Marine-Inland Water Sciences and Technology, Faculty of Fisheries, Ege University, 35100 Bornova, Izmir, Turkey https://orcid.org/0000-0002-6939-0284
[5] Department of Marine-Inland Water Sciences and Technology, Faculty of Fisheries, Ege University, 35100 Bornova, Izmir, Turkey https://orcid.org/0000-0002-5855-4300

Corresponding author: golnarmatin@gmail.com

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Abstract: Optimization of photocatalytic degradation of two natural estrogenic compounds, estrone (E1) and 17β-estradiol (17β-E2) in aqueous medium was performed on TiO_2 coated Pilkington Activ™ self-cleaning glass as a novel approach to eliminate free nano-TiO_2 releasing to the intended environment after treatment. The active glass was characterized by Atomic Force Microscopy (AFM), X-ray diffraction (XRD), and Raman spectroscopy to characterize the TiO_2 nanoparticles. The main purposes were mineralization of target compounds in the treated water during the photocatalytic reaction and also to investigate the oxidation by products. Response Surface Methodology (RSM) has been applied to optimize the photocatalytic degradation by changing time, pH, and light intensity as effective factors. According to the results, time was the more effective parameter. The maximum efficiency degradation was achieved in alkaline media. Due to interactive effects between variable factors, 1 mg/L aqueous solution of E1 and 17β-E2 in water was totally decomposed by TiO_2 photocatalyzed reactions under UV-C irradiation of 10.08 W/m^2 for 52.49 min at pH 9.42. Results of GC-MS analysis were introduced 17-deoxy Estrone and 2-Hydroxyestradiol as intermediate products for E1 and 17β-E2, respectively. All of the peaks finally disappeared after 170 min. Optimized conditions were applied for real sample of wastewater, presenting 30.40% and 56.84% in the efficiency degradation of E1 and 17β-E2, respectively.

Keywords: Photocatalytic degradation, TiO_2, Endocrine Disrupting Chemicals (EDCs), Estrone, 17β-estradiol, Response surface methodology

INTRODUCTION

Endocrine Disrupting Chemicals (EDCs) comprise a group of active organic compounds which interfere with regular function of the hormonal system in the organisms (Deguchi et al., 2008; Noppe et al., 2008). EDCs are exogenous biologically active compounds by both natural and anthropogenic origins. Human's body, animals, also plants and fungi synthesize biologically derived estrogens. Synthetic EDCs can be found as a constituent component of various daily used products like plasticizers, pesticides, herbicides, detergents, pharmaceuticals, personal care products, and others (Iwanowicz & Blazer, 2011; Song et al., 2018; X. Zhang et al., 2009). Estrogenic Endocrine Disrupting Chemicals (EEDCs) have emerged as concern chemicals over the last two decades (Hamid & Eskicioglu, 2013; Mockler et al., 2017; Wert et al., 2009). Lipophilic character and long biological half-life of these group of chemicals make them more stable and easily accumulated in organisms body (Adeel et al., 2017; Cai et al., 2015). Exposure of aquatic organisms to EEDCs leads to inappropriate genetic induction for estrogen sensitive genes, abnormal development of reproductive organs and gametes, fertility reduction especially in males, reduction in the quality and quantity of male sperm, the vitellogenin elevation in male fishes, existence of intersex forms, disturbance in sex change of protandrous hermaphrodites and high female-to-male (F/M) ratios, also EEDCs modulate immune responses of fishes (Adeel et al., 2017; Blanchfield et al., 2015; Iwanowicz & Blazer, 2011; Long et al., 2014).

Factors such as distributed chemical substance type, duration and frequency of exposure, season, sex, and developmental stage could change the severity of EEDCs effects on organism (Iwanowicz & Blazer, 2011; D.-G. Wang et al., 2011). The introduction of EEDCs into the natural environment is a consequence of both natural estrogenic compounds such as estrone (E1), 17α-estradiol (α-E2),17β-estradiol (17β-E2) and estriol (E3) and synthetic ones such as ethinyl estradiol (EE2) which are the main components in oral contraceptive pills and hormone therapy, that was originated from exorcise the human urinary and fecal. Meanwhile, liquid and solid waste effluences from livestock, poultry, and fish crop farming system that contains great amounts of estrogenic compounds (Adeel et al., 2017; Song et al., 2018; Vulliet & Cren-Olivé, 2011). Degradation of E1 and 17β-E2 has concerned in this study due to their abundant excreting and toxic effects on natural environment.

Numerous studies have indicated aquatic environment sufferance from EEDCs pollution due to adverse wastewater treatment systems. Notable residual concentrations of the estrogens in treated wastewater effluents and conventional wastewater treatment plants (WWTPs), are considered as the major source for continuous entry of estrogens into the environment (Marfil-Vega et al., 2010; Wert et al., 2009; A. Zhang & Li, 2014). There is no official limitation for EEDCs in treated wastewaters, nonetheless, there has been increased concern regarding accumulation characteristic and adverse ecological and health effects of EEDCs, thereby advanced technologies and innovation needs to reinforce conventional wastewater treatment systems to decrease EEDCs effluent flowing into the aquatic environment.

Advanced Oxidation Processes (AOPs) are widely utilized as treatment techniques for persistent organic pollutants by high chemical stability and low biodegradability property. Photocatalytic processes are a successful way to mineralize the contaminants into carbon dioxide, water, and inorganics during AOPs (Blanco-Galvez et al., 2007). Photocatalytic treatment has proven as a convenient method for organic pollutants degradation, whereas the biological treatment processes are insufficient for treating trace levels of this group of chemicals (Mayer et al., 2019; Paredes et al., 2019). Photocatalysis are chemical processes that are considered as environmentally friendly approach in purification system (FUJISHIMA et al., 2008; Han et al., 2012a). Electronic structure, light absorption properties, charge transport features, and excited life time attribute metal oxides to their usage as photocatalyst. Among these metal oxides, TiO_2, ZnO, SnO_2, and CeO_2 due to their biocompatibility and exceptional stability in various conditions, have been extensively used as photocatalyst (Belver et al., 2019; Oturan & Aaron, 2014). Two oxidation and reduction at least occur in photocatalytic system which equilibrium between two steps is of system efficiency determination (Daghrir et al., 2013). Oxidation process in photocatalytic reactions focused on the toxic chemicals mineralization into CO_2 and H_2O. TiO_2 which has selected as catalyst in this study, is useful for the water and air purification, cleaning up and sterilization of surfaces, photolytically split water to hydrogen and oxygen, and also to perform selective reactions in organic chemistry (Kurtoglu, Longenbach, & Gogotsi, 2011). Rutile, anatase and brookite are three main types of TiO_2 structures with different stability depending on particle size by similar photocatalytic effect which has been proved by previous studies, hence it is essential to choose the more suitable structure and apply method regarding the research's purpose (FUJISHIMA et al., 2008). TiO_2 Degussa P25-slurry treatment has been attracting great interest in estrogenic pollutants elimination (Gmurek et al., 2017; Han et al., 2012a; Ohko et al., 2002; Sornalingam et al., 2016; Y. Zhang et al., 2007) although it has disadvantages such as: adversely effects of particles on UV transmission and inhibiting the photocatalysis reaction, release of free ions to the intended environment and cause to secondary pollution (Huy et al., 2019), negative effects of nano-TiO_2 as a variety of inorganic pollutant on aquatic natural life (Battin et al., 2009; Christian et al., 2008; Lee et al., 2011; Marfil-Vega et al., 2010; Mueller & Nowack, 2008; Tong et al., 2013). Also, it has been demonstrated that phosphate ions which abundantly found in waste water, adsorb on TiO_2 and inhibits the reaction rate (Blanco-Galvez et al., 2007).

To the best of our knowledge, there is no study about the photocatalytic E1 and 17β-E2 degradation with the anatase TiO_2 nanocrystals in the immobilized form on glass. To maximize the efficiency degradation, Response Surface Methodology (RSM) was applied as it has been utilized successfully to evaluate the significance of several factors affecting on the prcesses response even in the presence of complicated interactions in the processes (H.Myers et al., 2016; Khayet et al., 2011; Zodi et al., 2010). Also, some recent publications have reported the RSM prosperity for optimize the EDCs photodegradation (Chong et al., 2010; Daghrir et al., 2013).

MATERIAL AND METHOD

Experimental

Chemicals and reagents

E1 and 17β-E2 analytical standards were obtained from Sigma–Aldrich (USA). HPLC gradient grade acetonitrile and water were purchased from Chem-Lab NV (Belgium).LC-MS grade water, methanol, acetone, 1-Octanol, hydrochloric acid and sodium hydroxide were purchased from Merck (Germany). Ultrapure 18.2 MΩ.cm water was collected from a sartorius arium® 611DI purification system (Sartorius AG, Gottingen, Germany). Pilkington Activ™ TiO_2 coated glass (self-cleaning glass) was purchased from Pilkington (Pilkington UK Ltd, U.K.). Accurel® PP Q3/2 polypropylene hollow fiber (inner diameter: 600 μm, wall thickness: 200 μm, pore size: 0.2 μm) was purchased from Membrana GmbH (Wuppertal, Germany).

Apparatus and instruments

Photocatalysis reactor equipped with UV-C TUV 15W lamps (100-280 nm), model SLV/25 (Phillips, Netherlands) was made in our laboratory. Magnetic mini-stirrer from IKA (Germany) was used for solutions agitation. TiO_2 coated on self- cleaning glass was characterized by X-ray diffraction patterns (XRD) that recorded by Bruker AXS model D8 advanced diffractometer (Cu Kα radiation (λ=1.54187 Å) at 40 kV and 35 mA with Bragg angle ranging from 3 to 70). Surface morphology of the self-cleaning glass was studied by atomic force microscopy (FlexAFM, Nanosurf, Switzerland). Raman spectra were recorded by Renishaw InVia spectrometer (Renishaw RM1000, Gloucestershire, UK). A high-performance liquid chromatograph model SY-8100 from BRFL Co. (China) equipped with an isocratic pump, a reversed phase C_{18}column (250×4.6 mm I.D, 3 μm particle size) from Macherey Nagel (Germany) and a UV detector was used for following the estrogens degradation via photocatalytic reaction. A 7890 A model gas chromatograph hyphenated with a 5970-model mass spectrometer (Quadrupole mass analyzer and EI source) equipped with DB-5MS capillary column (30m×0.25 mm I.D., 0.25 μm film thicknesses) from Agilent (USA) was used for separation and identification of photocatalytic reaction byproducts. A WTW pH meter, model 3110 (Germany) was used for pH adjustments.

Photocatalytic procedure

The reactor box (50 cm × 50 cm × 120 cm) was made of medium-density fiber board and equipped by ventilation fan. Two 15W UV-C lamps were installed in the center of ceiling of the reactor to irradiate the solutions from the top with a total power of 30W. The photocatalytic glass was placed in the crystallization dishes with nickel-chrome stands in direction of the UV source.

Different radiation intensity of the experimental setup was attained by adjusting distance of active surface of glass and UV lamps. The 1 $mg.L^{-1}$ mix solution of E1 and 17β-E2 was prepared by dissolving appropriate amounts of them in methanol and diluted to the mark with ultra-pure water, stored in refrigerator at the temperature of 4 ºC, and protected from light.

Aqueous solutions of estrogenic compounds were filed in the dishes in the way that rose about 1 cm from the active level of glass. All of the solutions were stirred during tests. The experimental setup used in the photocatalytic tests consisted of irradiating solutions in selected values of independent variables proposed by RSM. The concentrations of target compounds at different conditions followed by high performance liquid chromatography that were obtained through sampling 1 mL of treated solutions. Separation of the analyses were performed on C_{18} column (250×4.6 mm I.D, 3 μm particle size), eluted by acetonitrile: water (80:20) at 1 mL min^{-1} flow rate. The E1 and 17-β E2 concentrations were measured by UV detector at 220 nm. In order to identification byproducts degradation, treated samples at optimized conditions that were obtained from RSM were analyzed by GC/MS. Separations were performed on DB-5MS capillary column (30m×0.25 mm I.D., 0.25 μm film thickness) under temperature programming. Initial temperature was set at 50 ºC for 2 min, raised to 300 ºC at 10 ºC min^{-1} rate and hold for 15 min. Ionization source (EI: 70 eV) and transfer line temperatures were set at 250 ºC and 260 ºC, respectively. Scan range was 25-500 (m/z). The efficiency degradation was calculated from the following formula:

$$X = \frac{C-C_0}{C_0} \qquad (1)$$

Where C_0 and C are the initial concentration and concentration of E1 and 17β-E2 at sampling times ($mg.L^{-1}$).

Experimental design

The photocatalytic wastewater treatment methods are influenced by various factors. Controllable variables can optimize to maximize the response (dependent variable).So in this study, solution pH, irradiation time (min) and light intensity ($W.m^{-2}$) were investigated as independent variables. Coded and actual values of RSM input variables are given in Table 1. The coded values of variables were applied for RSM optimization procedure, according to the following equation:

$$X_i = \frac{Z_i-Z_0}{\Delta Z} \qquad (2)$$

Where X_i is the dimensionless coded level, Z_i, Z_0 and ΔZare the actual value, center point of the variable and interval variation, respectively.

Table 1. Coded and actual values of operational parameters (independent variables) utilized in experimental design

Input variables	Symbol	actual values of coded levels				
		-α^a	-1	0	+1	**+α**
Light Intensity, (W/m^2)	X_1	8.29	10	12.5	15	16.70
pH	X_2	4.47	5.5	7	8.5	9.52
Time (min)	X_3	4.47	15	30	45	55.22

α=1.682

To assay the individual and interactive effects of three independent variables on the response (photocatalytic efficiency degradation), Central Composite Design (CCD) was utilized as the most popular design of RSM. 20 experiments with 8 orthogonal two levels full factorial design points (coded as ±1), six axial points (coded as ±α= 1.682) and six replications of the central points were performed based on CCD procedure. The design of experiments and analysis of experimental data were performed by Design Expert 10. The matrix of experiments is given in Table 2.

RESULTS AND DISCUSSIONS

Characterization of TiO_2 coated self- cleaning glass as photocatalyst

Surface of the proposed photocatalytic Pilkington Activ™ self-cleaning glass was studied by Atomic Force Microscopy (AFM). From the top-down view (TiO_2-coated surface of glass), the average TiO_2 nanoparticle diameter is about 90±30 nm (Figure. 1a). The hemispherical peaks are observable in the topographical view (Figure 1b). From the sectional AFM view (Figure 1c) the thickness of TiO_2 layer on the glass is about 8±3 nm. The results indicate the appropriate roughness with high surface for the photocatalyticaly active surface of glass. The top-down view (bare surface of glass) AFM images exhibit very smooth surface in comparison with active surface (Figure 1d-f).

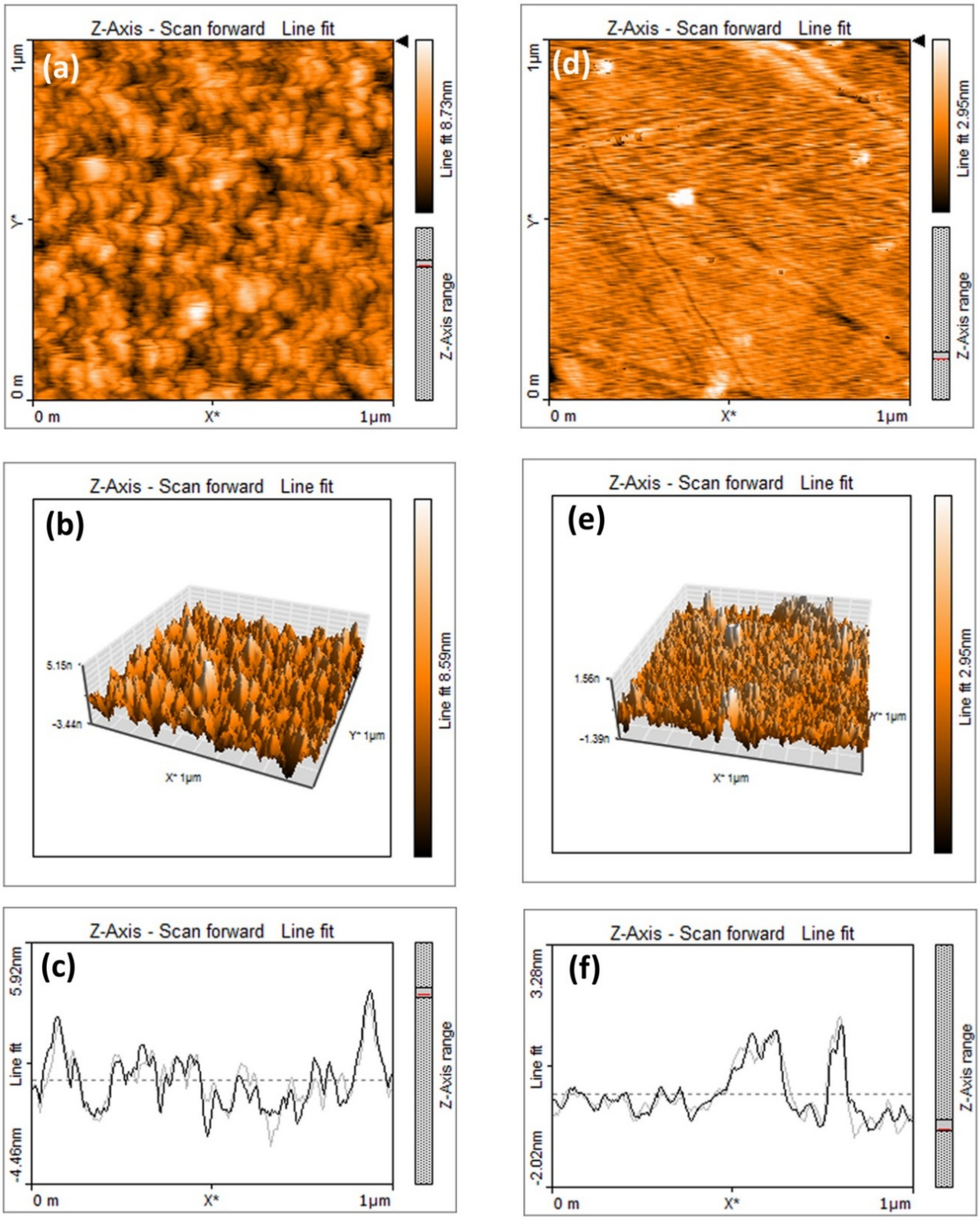


Figure 1. Demonstrates AFM images of Pilkington Activ^{TM} glass in (a, b) a top-down view and (c, d) a topographical view, (e, f) sectional view for active and bar surfaces, respectively

The existence of TiO_2 on the active surface of glass was investigated by XRD and Raman spectra. Figure 2a demonstrated Recorded XRD pattern. A sharp peak at 2θ = 25.28º confirms the existence of TiO_2 as anatase phase. No peaks related to the rutile phase of TiO_2 are observed. The characterization of TiO_2 phase coated on the active surface of glass was more investigated by Raman spectroscopy which would be considered as an accurate way for the analysis of surface morphology of thin TiO_2 films (Kurtoglu, Longenbach, & Gogotsi, 2011; Kurtoglu, Longenbach, Reddington, et al., 2011). The Raman spectra of surface film showed an obvious characteristic peak of TiO_2 anatase phase at 144, 396, 514 and 636 cm^{-1} frequencies (Figure 2b).

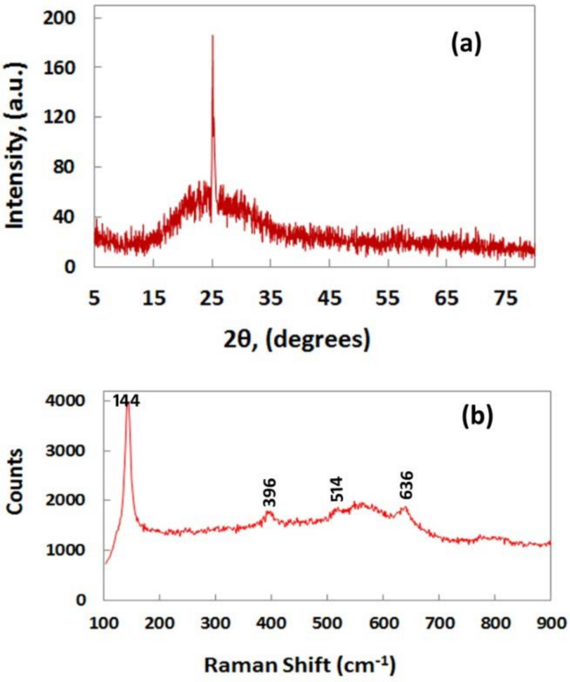


Figure 2. (a) XRD pattern and (b) Raman spectra of Pilkington Activ™ glass active surface

Photocatalytic performance of Pilkington ActivTM **glass in degradation of E1 and 17β**-E2

Figure 3 demonstrated the efficiencies degradation of E1 and 17β-E2 vs. time in adsorption (in dark), direct photolysis (without active glass), and photocatalytic (with active glass under UV irradiation) processes. Under UV light irradiation, the efficiency degradation of E1 and 17β-E2after 120 min was 61.26 and 41.52%, respectively. The removal efficiency of estrogenic compounds in dark (adsorption process) was negligible. As shown in Figure 3 significantly greater degradation of each estrogenic compound is obtained from the coated TiO_2 on the active surface of Pilkington Activ™ glass in compared to direct photolysis. At the same UV irradiation (10.08 W/m^2) and time (120 min) more than 90% of degradation occurs in the existence of coated TiO_2 on the active surface of Pilkington Activ™ glass for both E1 and 17β-E2. The observed difference in efficiencies degradation is due to the fact that the dominant mechanism of degradation becomes hydroxyl or superoxide anion radical mediated advanced oxidation when active glass is placed in the exposing of UV light.

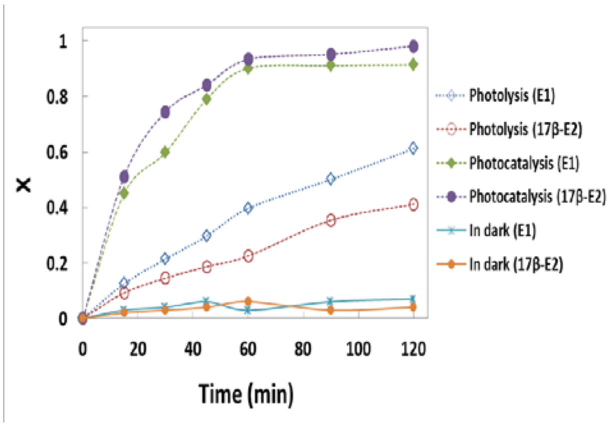


Figure 3. Efficiency Degradation E1 and 17β-E2 indirect photolysis (in absence of active glass and UV irradiation) and photocatalysis (by existence of active glass and UV light intensity of 10.08W/m^2)

Modeling, effect of operational parameters and optimization of the photocatalytic degradation process by RSM

Model development and analysis

A second-order polynomial or quadratic regression equation (Eq. (3)) was utilized to fit the experimental results that were achieved from CCD. This response surface modelprovides polynomial experimental results estimation.

$$y = b_0 + \sum_{i=1}^{n} (b_i X_i) + \sum_{i=1}^{n} (b_{ii} X_{ii}^2) + \sum_{i,j=1}^{n} (b_{ij} X_i X_j) \qquad (3)$$

Wherey and bare the predicted responses (efficiency degradation, %) and regression of coefficients. For each experiment, the efficiency degradation was experimentally obtained from the experimental design results (Table 2), the quadratic equations for specifying the photocatalytic degradation of E1 and 17β-E2 by TiO_2 coated self-cleaning glass were obtained from the least square approximation.

The equations are presented as equations 4 and 5 for E1 and 17β-E2, respectively:

$$y_{E1} = 0.66 - 0.021X_1 - 0.015X_2 + 0.19X_3 + 0.022X_1^2 + 0.022X_2^2 - 0.047X_3^2 \\ -1.125\times10^{-3}X_1X_2 + 1.125\times10^{-3}X_1X_3 + 1.125\times10^{-3}X_2X_3 \tag{4}$$

$$y_{17\beta-E2} = 0.73 - 0.035X_1 - 0.019X_2 + 0.18X_3 + 0.046X_1^2 + 0.067X_2^2 - 0.053X_3^2 \\ -8.625\times10^{-3}X_1X_2 - 3.875\times10^{-3}X_1X_3 - 2.625\times10^{-3}X_2X_3 \tag{5}$$

Table 2. Applied central composite design matrix and efficiency degradation values for photocatalytic degradation of the estrogens

Run order	L.I (W/m^2)	pH	Time (min)	Degradation efficiency E1		Degradation efficiency **17β**-E2	
				Experimental	Predicted	Experimental	Predicted
1	15	8.5	15	0.45	0.431	0.578	0.583
2	15	8.5	45	0.791	0.811	0.902	0.907
3	12.5	9.52	30	0.708	0.699	0.894	0.886
4	15	5.5	15	0.471	0.466	0.621	0.626
5	12.5	7	30	0.62	0.6611	0.752	0.731
6	12.5	7	30	0.675	0.661	0.711	0.731
7	12.5	4.47	30	0.784	0.749	0.964	0.956
8	10	8.5	15	0.477	0.478	0.622	0.627
9	12.5	7	30	0.671	0.661	0.721	0.731
10	8.29	7	30	0.802	0.759	0.964	0.956
11	12.5	7	30	0.658	0.661	0.749	0.731
12	12.5	7	30	0.64	0.661	0.751	0.731
13	10	8.5	45	0.818	0.853	0.971	0.976
14	12.5	7	55.22	0.909	0.844	0.931	0.923
15	10	5.5	15	0.498	0.508	0.64	0.645
16	12.5	7	30	0.697	0.661	0.701	0.731
17	12.5	7	4.77	0.193	0.214	0.247	0.239
18	16.70	7	30	0.688	0.687	0.772	0.764
19	10	5.5	45	0.83	0.878	0.99	0.995
20	15	5.5	45	0.812	0.840	0.965	0.970

Table 3. Analysis of variance (ANOVA) for the developed models

Source	DF*	ANOVA for E1 degradation				**ANOVA for 17β**-E2 degradation			
		SS**	Adj-MS***	F-Value	P-Value	SS	Adj-MS	F-Value	P-Value
Regression	9	0.54	0.06	35.55 (Critical F-value=3.02)	0.0001<	0.63	0.07	62.02 (Critical F-value =3.02)	0.0001<
Residual error	10	0.017	1.685×10^{-3}	-	-	0.011	1.133×10^{-3}	-	-
Lack-of-fit	5	13×10^{-3}	2.627×10^{-3}	3.53 (Critical F-value =5.05)	0.0962	8.77×10^{-3}	1.754×10^{-3}	3.42 Critical F-value =5.05)	0.1017
Pure error	5	3.72×10^{-3}	7.438×10^{-3}	-	-	2.56×10^{-3}	5.13×10^{-4}	-	-
Total	19	0.56	-	-	-	0.64	-	-	-

* DF = Degrees of freedom. ** SS = Sum-of-squares. ***Adj-MS = Adjusted mean squares.

The experimental and predicted efficiencies degradation of E1 and 17β-E2 (from Eqs. (4) and (5)) has shown in Table 2.

Table 3 demonstrates the analysis of variance (ANOVA) results. The ANOVA is carried out to evaluate the significance and adequacy of the obtained response surface models. Based on the ANOVA results, the Fisher F-values of both regressions were remarkably higher than the tabulated F-value (35.55 and 62.02 for E1 and 17β-E2, respectively at 95% significance) implying that the obtained models predict the experimental results, suitably. Furthermore, P-values that are related to the Fisher test are lower than 0.05 signifying that the response surface models are significant by a statistical point of view. The next criterion for evaluating the achieved models was Lack of Fit (LOF) test. Indeed, it compares the residual with pure error. The pure error calculated by the replicated experiments at the central level of variables from the ANOVA results, the F-values that are related to the LOF of response surface models were less than tabulated ones. Also, the P-values of LOF test were equal to0.0962 and 0.1017, respectively. The results of LOF have shown the insignificant lack of fit for the developed models for predicting the degradation efficiency of E1 and 17β-E2.

The coefficient of determination (R^2) and Adj-R^2 values, which compared experimental and predicted degradation efficiencies, were equal to 96.97% and 94.24% for developed model of E1 degradation and they were equal to 98.24% and 96.60%, for 17β-E2, respectively (Figure 4).

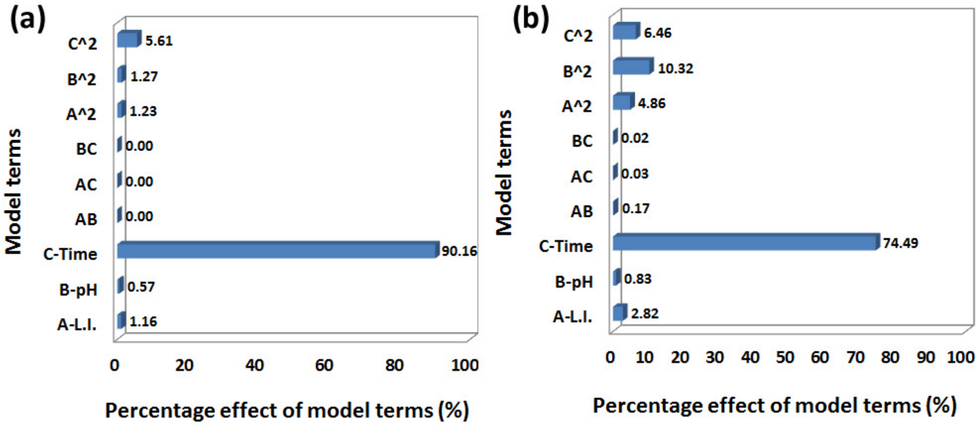


Figure 4. Experimental degradation efficiency vs. calculated ones by developed models for a) E1 and b) 17β-E2

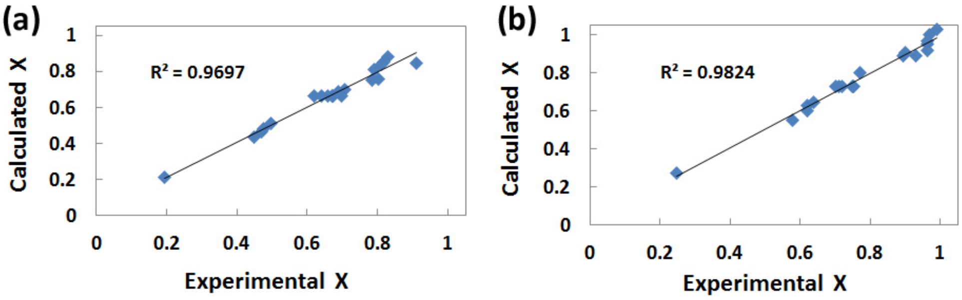


Figure 5. Experimental efficiency degradation vs. calculated ones by developed models for a)E1 and b) 17β-E2

Determination of importance of model terms

The well-known Pareto analysis was used in order to determine the effective terms in the response surface models. In Pareto analysis the percentage of independent variables (P_i) was calculated to evaluate the effectiveness of model parameters using the following formula:

$$P_i = \left(\frac{b_i^2}{\sum_{i=1}^{n} b_i^2} \right) \times 100 \qquad i \neq 0 \qquad (6)$$

According to the Pareto results (Figure 5), during the photocatalytic degradation process the irradiation time showed the most effect (90.16% and 74.49% for E1 and 17β-E2, respectively) on the efficiency degradation of the studied hormones. The coefficient of the quadratic effects of time, pH and light intensity were also significant. In this mechanism, the maximum efficiency degradation is achieved by alkaline media. Therefore, pH effect as 10.32% quadratic terms predicted by Pareto is expectable.

Optimized conditions for photocatalytic degradation of E1 and 17β-E2

The main purpose in designing experiments by RSM is achieving the optimized conditions of operational factors to attain the desired response. The optimized values of the variables for obtaining the maximum efficiency degradation of E1 and 17β-E2 are given in Table 4. Other experiments were performed to optimized conditions proposed by RSM and experimental efficiency degradations for both estrogenic compounds that were obtained to verify the optimized values of the factors. The experimental results demonstrated that the maximum degradation efficiency was equal to 0.921 and 0.986 for E1 and 17β-E2 which were in a good agreement with the predicted ones.

Table 4. Optimum values of factors to obtain the maximum photocatalytic degradation of the E1 and E2

Degradation process	Predicted optimized values of factors			Predicted degradation efficiency	Experimental degradation efficiency
	Light intensity (W/m^2)	pH	Time (min)		
E1	10.084	9.421	52.498	0.915	0.921
17β-E2	10.084	9.421	52.498	1.040	0.986

Effects of variables on estrogens' efficiency degradation

Figure 6 demonstrates the three-dimensional response surface plots for investigating the effect of pH and light intensity and irradiation time on the degradation of studied hormones. It is clear that the efficiency degradation of hormones increased by irradiation time increasing. Also, the light intensity had a negligible effect on photocatalytic degradation in comparison with irradiation time. The photocatalytic degradation mechanism is summarized as follow:

$$\mathrm{TiO_2 + h\nu \rightarrow h^+ + e^-} \quad (7)$$

$$\mathrm{h^+ + e^- \rightarrow heat} \quad (8)$$

$$\mathrm{H_2O + TiO_2 \rightarrow H_2O_{ads} - TiO_2} \quad (9)$$

$$\mathrm{OH^- + H^+ + TiO_2 \rightarrow OH^-_{ads} - TiO_2 + H^+} \quad (10)$$

$$\mathrm{Estrogen + TiO_2 \rightarrow [Estrogen]_{ads} - TiO_2} \quad (11)$$

$$\mathrm{H_2O_{ads} - TiO_2 + h^+ \rightarrow {}^{\cdot}OH_{ads} - TiO_2 + H^+} \quad (12)$$

$$\mathrm{OH^-_{ads} - TiO_2 + h^+ \rightarrow {}^{\cdot}OH_{ads} - TiO_2} \quad (13)$$

$$\mathrm{{}^{\cdot}OH_{ads} + [Estrogen]_{ads} \rightarrow [Intermediate]} \quad (14)$$

$$\mathrm{OH^-_{ads} + TiO_2h^+ \rightarrow {}^{\cdot}OH_{ads}} \quad (15)$$

$$HO_2^{\cdot} + H^+ + \mathrm{e^-} \rightarrow H_2O_2 \quad (16)$$

$$H_2O_2 + \mathrm{e^-} \rightarrow \mathrm{{}^{\cdot}OH_{ads}} + OH^- \quad (17)$$

$$\mathrm{O_2^{\cdot -}} + H^+ \rightarrow HO_2^{\cdot} \quad (18)$$

$$HO_2^{\cdot} + H^+ + \mathrm{TiO_2e^-} \rightarrow H_2O_2 \quad (19)$$

$$H_2O_2 + \mathrm{TiO_2e^-} \rightarrow \mathrm{{}^{\cdot}OH_{ads}} + OH^- \quad (20)$$

$$\mathrm{{}^{\cdot}OH_{ads} + [Estrogen]_{ads} \rightarrow [intermediates]} \quad (21)$$

$$\mathrm{O^{\cdot -}_{2(ads)} + [Estrogen]_{ads} \rightarrow [intermediates]} \quad (22)$$

The reaction between hydroxide ions and positive holes on TiO_2 surface can lead to formation of hydroxyl radicals (Eq. 13). The hydroxyl radicals can be easily formed in alkaline media by oxidizing more hydroxide ions. The photocatalytic efficiency degradation of both estrogens is enhanced in alkaline solution more significantly, even though the efficiency increases for both acid and alkaline pH. From Eqs. 14 - 17, the formation of the superoxide anion radicals and their conversion of the hydroxyl radicals is favorable at low pH. Even though at the acidic solution, oxygen reduction by electrons in conduction band may play an important role in the degradation, highest efficiency degradation of target compounds were observed under alkaline conditions. For achieve better sight in photocatalytic degradation of E1 and 17β-E2, in comparison to other previous studies was reported in Table 5.

Table 5. A compilation of comparative studies on AOPs in degradation of EEDCs

Degradation Process	Target	Experimental conditions	Intermediates	Efficiency %	Ref.
Photocatalytic	E1	P25 TiO_2* suspension 50 mg L^{-1} /UVA 60 min /Irradiating Batch system	-	95	(Han et al., 2012b)
Photocatalytic	17β-E2	P25 TiO_2* suspension 100 mg L^{-1} /UV-C 60 min /Irradiating Batch system		>85	(Orozco-Hernández et al., 2019)
Photocatalytic	17β-E2 (C₀=0.003 mg/L)	P25 TiO_2 suspension 1.00 g L^{-1} /UVA 180 min / irradiation intensity: 6mW.cm^{-2} / Irradiating Batch system	10ϵ-17β-Dihydroxy-1,4-estradien-3-one and testosterone like species	100	(Ohko et al., 2002)
Photocatalytic	17β-E2	1.8 × 10^{-5} M $FeCl_3$/$NaNO_2$ under natural light irradiation / 1440 min / Irradiating Batch system	-	>86.6	(L. Wang et al., 2007)
Photocatalytic	E1 and 17β-E2	PTT*** / UV-C -LED / ~120 / irradiation intensity: 0.390 mW.cm^{-2}		100 for E1 and inefficient degradation of 17β-E2	(Arlos et al., 2016)
Photocatalytic	E1 and 17β-E2	Anatase TiO_2 as glass coated immobilized form / UV-C 52.5 min / irradiation intensity: 10.084 W.cm^{-2} / Irradiating Batch system	17-deoxy Estrone & 2-Hydroxyestradiol	>92 for E1 and >98 for 17β-E2	This study

*P25 TiO_2 : Titanium dioxide, anatase nanopowder, Particle Size ≤ 25 nm, CAS Number: 1317-70-0
**EDDS: Ethylenediamine-N,N´-disuccinic acid
***PTT: Porous Titania-TiO_2

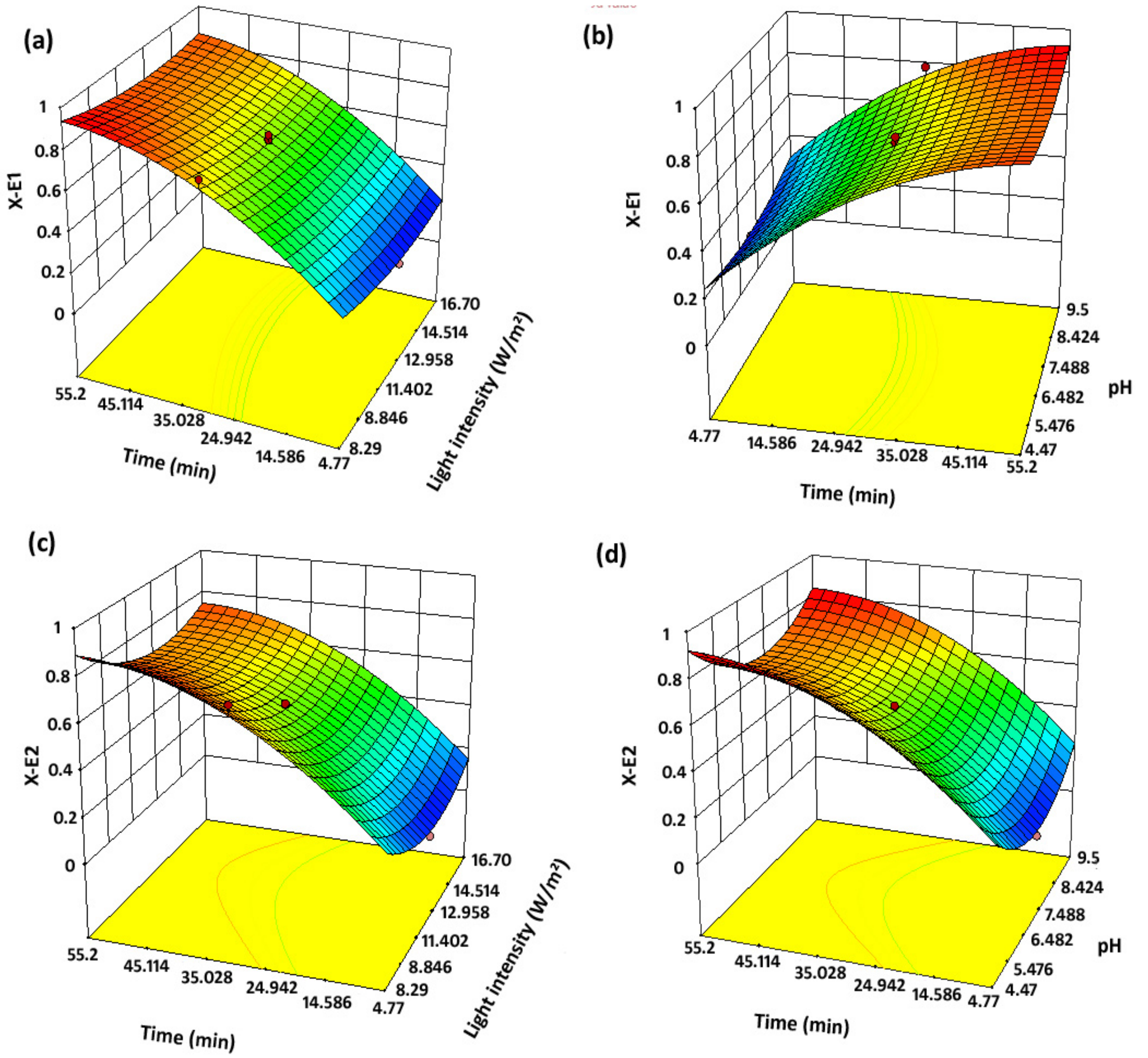


Figure 6. Response surface plots for investigating the time and light intensity effects on photocatalytic degradation of (a) E1 and (c) 17 β-E2 and effect of pH on (b) E1 and (d) 17 β-E2 efficiency degradation

For identification of the active species in the photocatalytic degradation process, a series of experiments were accomplished. Hydroxyl radicals($OH^{\cdot}$), trapped photogenerated holes on the TiO_2 and superoxide anion radicals(O_2^{-}) are the main reactive oxidative species in photocatalytic degradation of estrogenic hormones. In the new series of experiments, three test were separately conducted in the existence of tert-butyl alcohol (t-BuOH), benzoquinone (BQ), and ammonium oxalate (AO) as a hydroxyl radical, superoxide anion radicals and photogenerated holes scavengers, respectively. The photocatalytic tests were performed at the optimized conditions obtained from RSM (Table 4). Figure 7 shows the ranking of different radical scavengers effect of efficiency degradation was in order of BQ > t-BuOH >AO. Therefore, the superoxide anion radicals and hydroxyl radicals are the main oxidative specie for degradation of both estrogenic compounds.

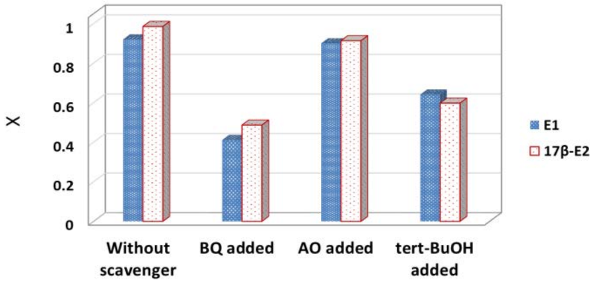
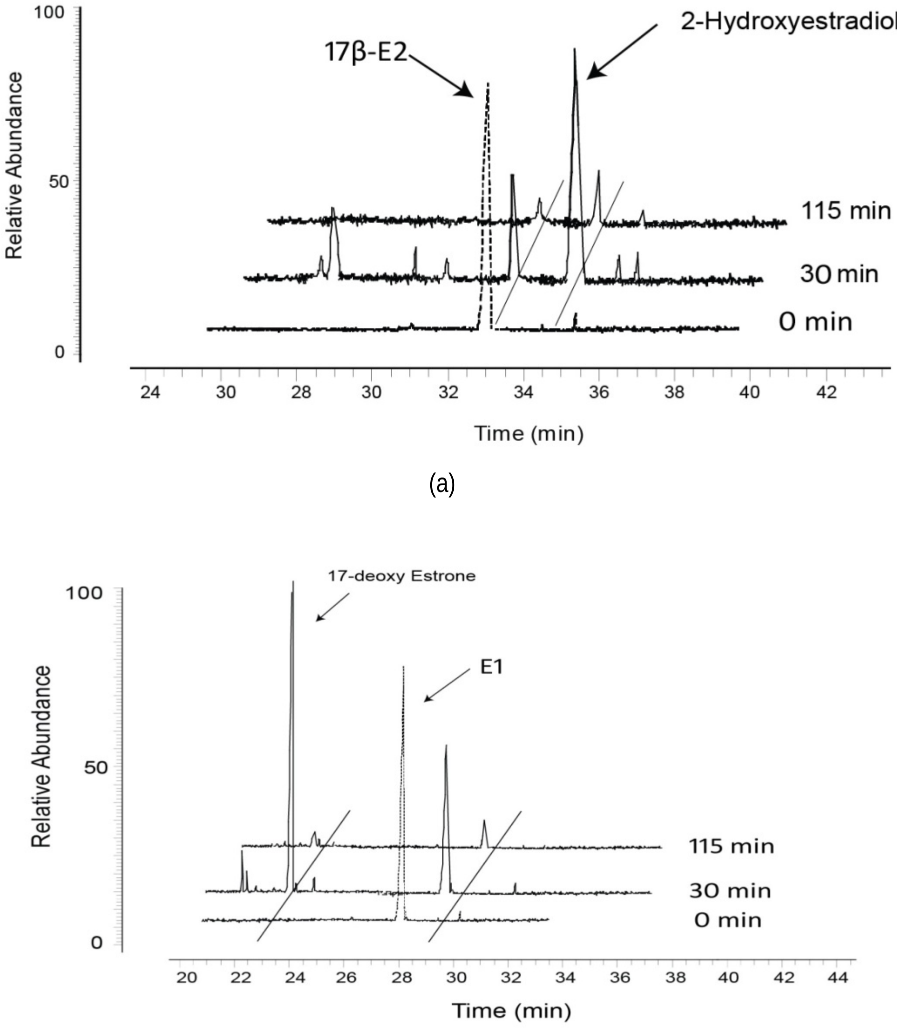


Figure 7. Effect of different radical scavengers on photocatalytic degradation of of E1 and 17β-E2 (1 mg/L of mix solution, light intensity=10.08 W/m2, pH=9.421 and irradiation time=52.5 min)

HPLC and GC/MS study of the photocatalytic degradation of E1 and **17β**-E2 in aqueous media

Photocatalytic tests were also performed at the optimized conditions that were proposed by RSM and the degradation of E1 and 17β-E2 was studied by high performance liquid chromatography with determining the changes in the hormones concentrations during tests. The chromatograms of mixed estrogen solutions under optimized pH, light intensity, and varying times were investigated. It has clearly shown that E1 and 17β-E2 peaks were disappeared during 0-115min of UV-C irradiation with 10.08W/m^2 light intensity and 9.42 solution pH in the existence of self-cleaning glass as proposed photocatalyst. From comparison of the HPLC chromatograms, it could be seen growth of the new peaks at retention times 4.45 and 5.15 min, which was related to degradation byproducts of the studied hormones. The first peak growth was continued till 115 min and then with further light irradiation that was disappeared (HPLC chromatogram for170 min). The second peak reached to maximum at 22.5 min and at longer irradiation times the peak disappears from 22.5 up to 60 minutes.

The test solutions of individual hormones were examined by GC/MS in order to identify reaction byproducts. Figure 8 shows the total ion chromatograms of GC/MS analysis. As can be seen the peaks that are related to the E1 and 17β-E2 were disappeared photocatalytic degradation. However, the byproduct peaks grew at the first minutes of processes and then omitted. The proposed byproduct compounds are 2-hydroxyestradiol as intermediate compound before complete oxidation and mineralization of 17β-E2 and 17-deoxy estrone as intermediate compound in photocatalytic degradation of E1 which were identified by mass spectra of GC/MS analysis.



(a)

(b)

Figure 8. Total ion chromatogram of individual (a) 17β-E2 and (b) E1 during photocatalytic degradation process that performed at optimized conditions proposed by RSM

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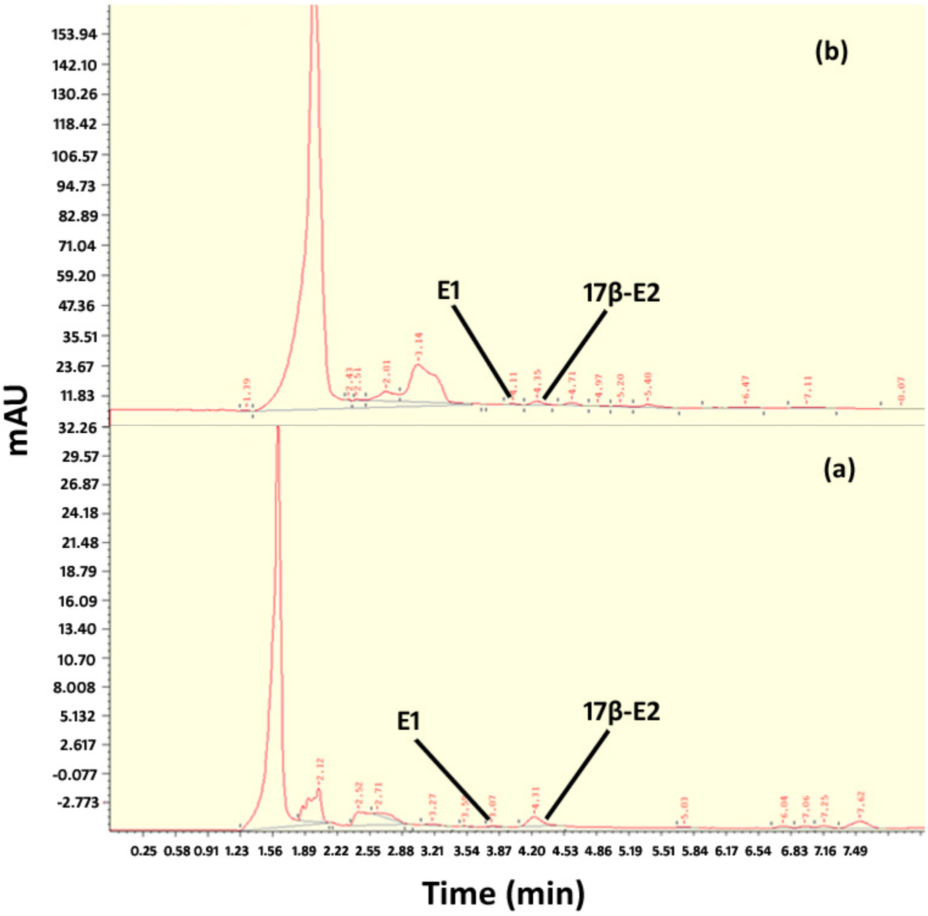

Figure 9. HPLC chromatograms of real sample of wastewater effluent of MBR system before (a) and after (b) photocatalytic degradation at RSM optimized conditions

Evaluation of applicability the method for real wastewater matrix

To evaluate the optimized method applicability, a real sample from effluent of a WWTP which membrane bioreactor (MBR) technology employed as treatment process, were collected. Profile of mentioned WWTP's influent was in the ration of 40% domestic (originated from ~ 7000 personnel) and 60% industrial approximately.120 mL of real sample was treated under optimized conditions that were established by RSM. 50 mL of treated samples were extracted following the hollow-fiber liquid-phase micro extraction procedure.

HPLC analyses were performed and Figure 9 shows the HPLC chromatograms. Efficiency degradation of E1 and 17β-E2 was equal to 30.40% and 56.84%, respectively; which is lower than performance of the system for synthetic wastewater; it can be in the result of containing complex matrices of organic matter and other competing chemicals in real samples and higher level of organic content of them naturally(Bodhipaksha et al., 2017); in addition, phosphate ions which abundantly found in wastewater, can inhibit the reaction rate by adsorption on TiO_2 crystals (Blanco-Galvez et al., 2007). This result highlights the importance of moderation of AOPs in pilot tests before real scale application. Regard to main role of superoxide and the hydroxyl radicals in the case, existence of effective electron scavenger (e.g. phosphate and nitrate anions) over illuminated TiO_2 being able to compete successfully with molecular oxygen for the photogenerated electrons (Gu et al., 2002).

CONCLUSION

Deficiency of conventional WWT systems to decrease EEDCs effluent flowing on the aquatic environment alert needs an advanced treatment systems development. E1 and 17β-E2 as a representing estrogenic compound undergo photocatalytic degradation process under UV irradiation in the existence of TiO_2coated on Pilkington Activ™ glass. UV irradiation is conducted at room temperature which is near to realistic conditions for feature real scale tests. The optimal efficiency degradation was obtained in alkaline pH under 10.08 W/m^2 UV light irradiation and after52.49min of process which were obtained from RSM. According to the Pareto analysis, the irradiation time is the most important parameter in treatment process which should be suit to remove of primary compounds. Anatase crystal phase of TiO_2 as glass coated immobilized form is used by obtaining self-cleaning commercial glass Pilkington Activ™ which is available to purchase for real scale photo reactors is advantageous due to eliminate secondary pollution of aquatic ecosystems. The results of this study provide new insight for the benefits and efficiency of using the TiO_2 coated self-cleaning glass to purify the wastewater. In comparison with other previous studies, achieved results in this study provide further justification for AOP development applications in real scale WWT systems. Presented evidences advices to ideal management practices, use this material in reinforce treatment systems after further ecotoxicological researches, approach for the degradation of organic micro pollutants especially EEDCs in WWTPs.

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