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Photocatalytic (UV-A/TiO_2) and photolytic (UV-A) degradation of steroid hormones: Ethinyl Estradiol, Levonorgestrel, and Progesterone

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Abstract: In the present study, photocatalytic degradation of the steroid hormones: Ethinyl Estradiol, Levonorgestrel, and Progesterone, using immobilized TiO_2 films as a photocatalyst under UV-A light, has been investigated. The photolytic degradation (i.e. photodegradation without catalyst) of the steroid hormones also has been studied. Changes in the steroid hormones concentrations were followed by High Performance Liquid Chromatography (HPLC). The degradation of these steroid hormones followed first-order kinetics. Experiments were investigated to evaluate the effect of the addition of H_2O_2 as well as the initial concentrations of the steroid hormones. Results clearly demonstrate the efficiency of the photocatalytic and photolytic degradation of these steroid hormones in aqueous medium.

Keywords: Ethinyl Estradiol; Levonorgestrel; Progesterone; Photocatalytic degradation; Photolytic degradation; TiO_2.

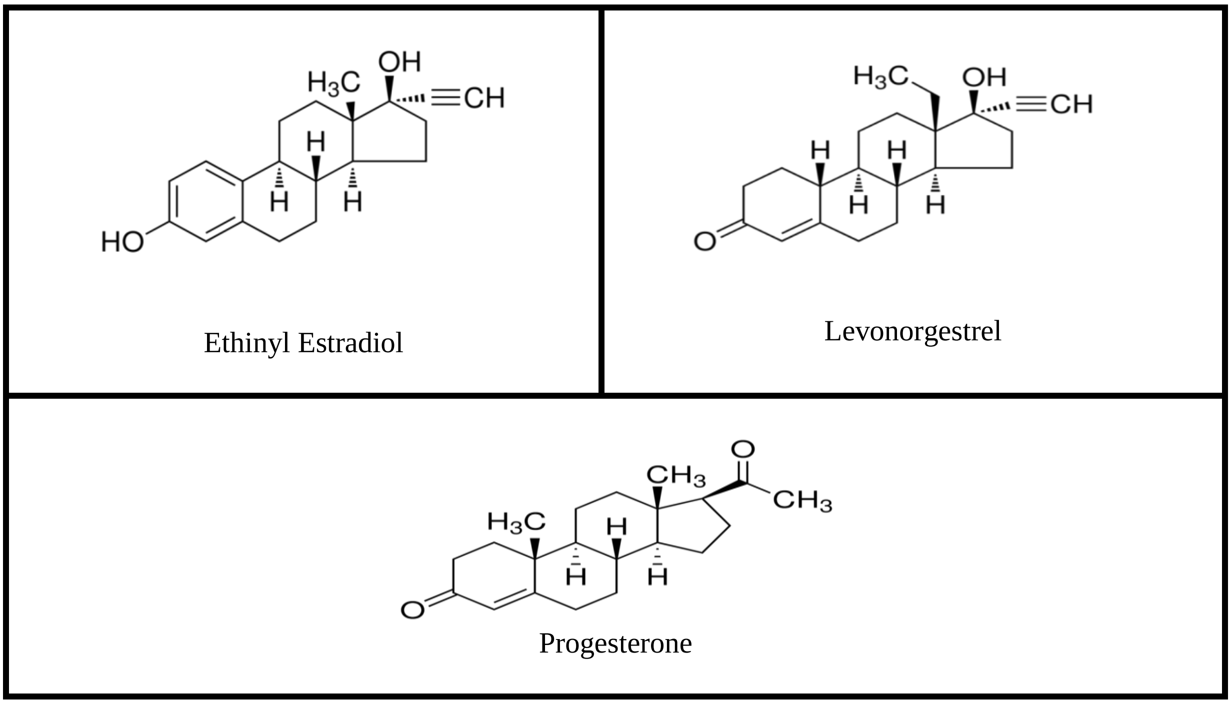
Introduction

Endocrine disrupting compounds (EDCs) are substances can cause adverse health effects in the organism[1]. EDCs, which include steroid hormones and various industrial chemicals, are classified as emerging environmental contaminants. They have the ability to interfere the normal function of hormones and the way hormones control growth, metabolism, and body functions[1-3]. The environmental exposure of EDCs may cause serious effects on human health including decreases in male sperm count and increases in testicular, prostate, ovarian, and breast cancer[4,5]. Steroid hormones have the greatest endocrine disrupting potency among all EDCs[4].

Natural steroid hormones are continuously introduced into the environment by humans and animals[4]. In addition, concentrations of steroid hormones are frequently detected in the fresh water bodies receiving effluent in North America, Europe, Japan, Brazil and China[5]. This is due to the reason that the conventional sewage treatment plants are not able to degrade residues of these chemicals, and as a result, they are released to the aquatic environment[3].

Recently, new methods have been developed for water purification. Photocatalytic degradation, using TiO_2 as photocatalyst, has been reported to be effective for the degradation of persistent pollutants[6]. That is due to the in situ generation of the strongly oxidizing hydroxyl radicals ($OH^\bullet$) which oxidize a wide range of organic pollutants[7]. TiO_2 is cheap, non-toxic, and photochemically stable[8-11]. It works at ambient conditions and may be induced by solar irradiation[12]. TiO_2 photocatalyst may be used either as an aqueous slurry or it may immobilized onto a supporting substrate[13]. The immobilization of the catalyst on a supporting substrate may be more efficient[14].

In this study, immobilized TiO_2 photocatalytic films were utilized for the degradation of the steroid hormones: Ethinyl Estradiol, Levonorgestrel, and Progesterone (Figure 1) in aqueous medium. In addition, the photolytic degradation (i.e. photodegradation without catalyst) was also used for removal of these hormones. Both methods (photocatalytic and photolytic degradation) were able to remove these contaminants from water successfully.



Ethinyl Estradiol

Levonorgestrel

Progesterone

Figure 1: Chemical structures of Ethinyl Estradiol, Levonorgestrel, and Progesterone

1. Materials and Methods

1.1. Chemicals

Ethinyl Estradiol, Levonorgestrel, and Progesterone were purchased from Chem Swiss, Switzerland, and used as received. Hydrogen peroxide (35% w/w solution) was purchased from Merck, Germany. Purified water was used for the preparation of solutions.

Titanium dioxide (Degussa P25) was mainly anatase according to the manufacturer's specifications[3]. The elementary particle in dry powder form was approximately spherical in shape and the particle size was approximately 20 nm. The specific surface area[3], as measured from N_2 adsorption at 77 K, was 48.3 m^2 g^{-1}.

1.2. Photocatalytic and Photolytic Experiments

Photocatalytic experiments with artificial irradiation were carried out in a lab-scale photochemical reactor (Figure 2). The aqueous solution was recycled over a glass slide (48 cm × 3.8 cm) on which TiO_2 particles had been deposited and fixed. The photocatalyst activation was provided by a UV lamp emitting at 365 nm (UV-A irradiation) (Nissan black light 18 W, UV ray 1.5 W). Photocatalytic experiments were carried out as follows: 1.8 L of an aqueous solution containing (1 mg/L) of the steroid hormone were recycled in the photochemical reactor with a flow rate of 300 mL/minute. The recycling was performed first in the dark (until the adsorption-desorption equilibrium was reached) and then the lamp was turned on for 5 hours. The pH of the aqueous solution was adjusted at 4.1. After each run, the photocatalyst was washed and irradiated for about hour in the presence of H_2O_2 so that it was regenerated.

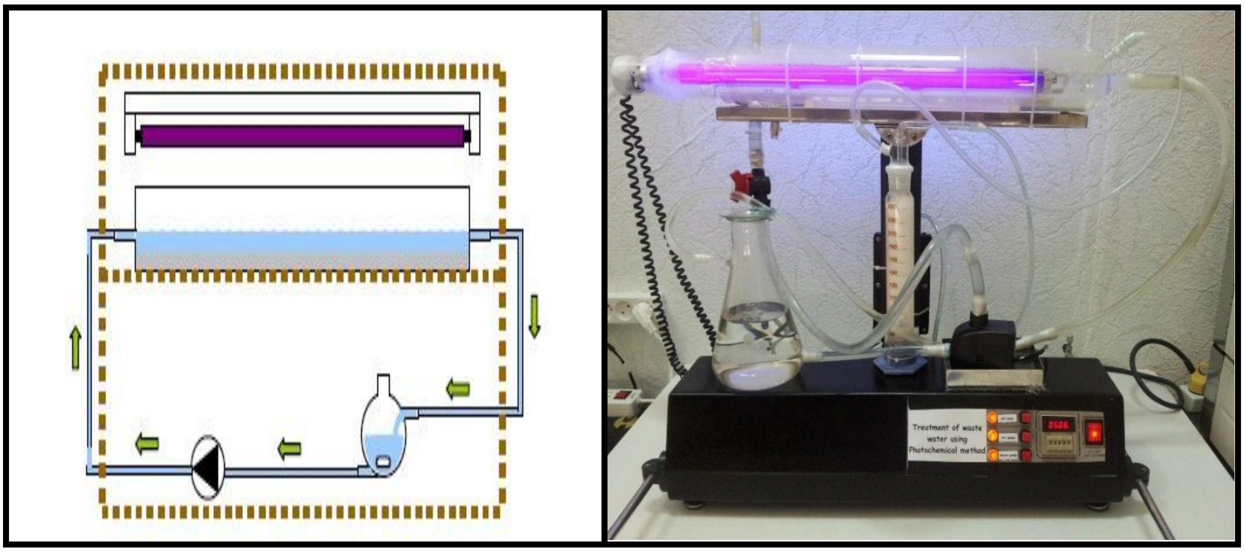


Figure 2: The lab-scale photochemical reactor

Photolytic experiments were carried out as follows: 1.8 L of an aqueous solution containing (1 mg/L) of the steroid hormone were recycled in the photochemical reactor with a flow rate of 300 mL/minute without catalyst. The recycling was performed for 5 hours in the presence of UV-A irradiation and H_2O_2 if needed. The pH of the aqueous solution was adjusted at 4.1.

1.3. Catalyst

The surface of the glass slide was washed in a solution of NaOH before deposition of TiO_2 on the glass supporting substrate. This treatment may increase the number of OH groups[15]. TiO_2 (Degussa P25) suspension having a concentration of 8 g/L was prepared in purified water with the aid of sonication. The pH of the suspension was adjusted at 3.0. An amount of the suspension was poured on the glass slide. Then, the glass slide was dried out for a few hours at 100°C. After that, the glass slide was heated at 475°C for 4 hours. According to (Zahraa et al., 2006)[15], reaction between OH groups from the surface of the catalyst and the glass support could happen during the heating, resulting loss of a water molecule. This reaction creates an oxygen bridge and thus increases the adhesion of the catalyst to the glass supporting substrate.

In order to increase the total thickness of the TiO_2 layer, the deposition process could be carried out several times in a row[15].

1.4. Analytical Procedures

High performance liquid chromatography (HPLC/UV-DAD, LA Chrom ELITE, VWR Hitachi, Germany) was employed to monitor the concentrations of the steroid hormones during the photocatalytic and photolytic reactions at specific time intervals. Separation was achieved on Thermo Hypersil C18 column (150 mm, 4.6 mm i.d., 5 μm). The chromatographic conditions of the analytical procedures are shown in Table I.

Table I: The chromatographic conditions of the analytical procedures

Analyte	Ethinyl Estradiol	Levonorgestrel	Progesterone
Mobile phase	Water : Acetonitrile (50:50, v/v)	Water : Acetonitrile (45:55, v/v)	Water : Acetonitrile (40:60, v/v)
Flow rate	1 mL/minute	1 mL/minute	1 mL/minute
Column temperature	40°C	40°C	40°C
Detection wavelength	205 nm	245 nm	245 nm
Injection volume	50 μL	50 μL	50 μL

2. Results and Discussion

2.1. Results of The Photocatalytic Degradation

The results of the photocatalytic degradation of the steroid hormones are summarized in Table II. Where **A%** is the adsorption of the steroid hormone on the surface of the photocatalyst, as percentage, and **X_{300}%** is the degradation of the steroid hormone after 5 hours (300 minutes) of the photocatalytic reaction, as percentage. These factors were calculated by the following formulas:

Table II: The results of the photocatalytic degradation of the steroid hormones (without any addition of H_2O_2)

Parameter		**Steroid Hormone**	
	Ethinyl Estradiol	**Levonorgestrel**	**Progesterone**
Adsorption-desorption equilibrium time	1 hour	1 hour	2 hours
A%	14.99	11.61	73.58
X_{300}%	54.21	47.62	80.78
Total removal%	61.07	53.70	94.92
K_{deg} (minute^{-1})	0.00250	0.00212	0.00500
Kinetics	first-order kinetics	first-order kinetics	first-order kinetics

$$\mathbf{A\% = [(C_i - C_0)/C_i] \times 100}$$

$$\mathbf{X_{300}\% = [(C_0 - C_{300})/C_0] \times 100}$$

In which: **C_i** is the initial concentration of the steroid hormone, **C_0** is the equilibrium concentration of the steroid hormone when the adsorption-desorption equilibrium is reached, and **C_{300}** is the concentration of the steroid hormone after 5 hours (300 minutes) of the photocatalytic reaction.

In general, the photodegradation of organic compounds follows first-order kinetics[16] according to the following equation:

$$\mathbf{\ln (C_0/C) = K_{deg}.t}$$

According to our results, plotting **$\ln (C_0/C)$** versus time **(t)** corresponds to a straight line, and the slope equals the apparent first-order constant **(K_{deg})**, thus implying that the photocatalytic degradation kinetics of these steroid hormones perfectly fit first-order kinetics (Figure 3).

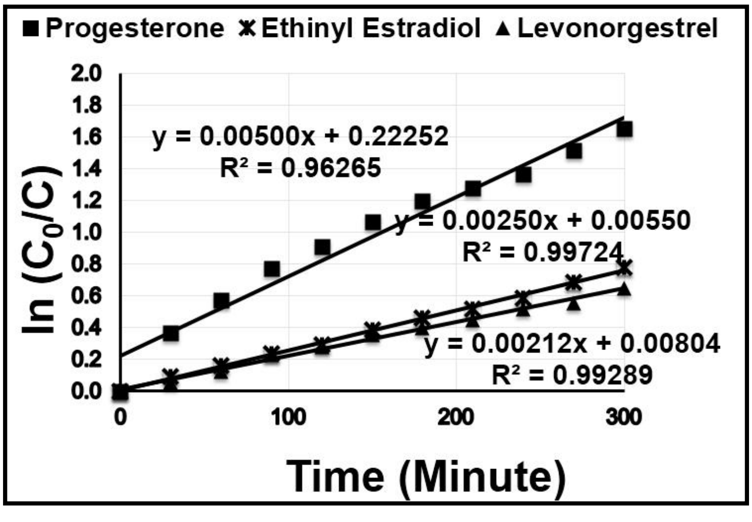


Figure 3: The kinetics of the photocatalytic degradation of the steroid hormones (without any addition of H_2O_2)

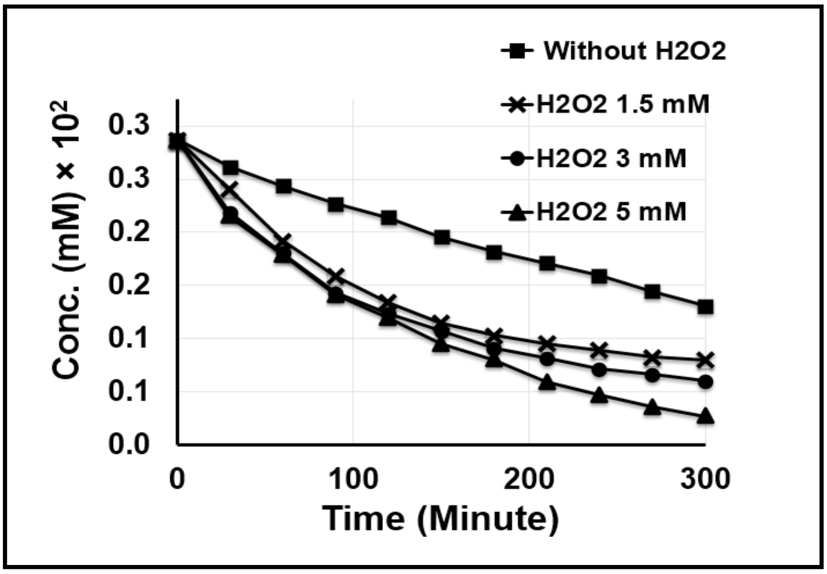


Figure 4: The effect of H_2O_2 addition on Ethinyl Estradiol photocatalytic degradation

2.1.1. Effect of addition of H_2O_2

Literature shows that the addition of H_2O_2 improves the photocatalytic degradation process[17]. The effect of the addition of various concentrations of H_2O_2 (1.5-5 mM) on Ethinyl Estradiol photocatalytic degradation was studied. The results shown in (Table III and Figure 4) demonstrate that the addition of H_2O_2 had enhanced the photocatalytic degradation of Ethinyl Estradiol. Generally, the addition of H_2O_2 is expected to improve the photocatalytic degradation due to the generation of the strongly oxidizing hydroxyl radicals ($OH^\bullet$) which oxidize the organic pollutant as follows[17,18]:

Table III: The effect of H_2O_2 addition on Ethinyl Estradiol photocatalytic degradation

Parameter	**Without H_2O_2**	**H_2O_2 1.5 mM**	**H_2O_2 3 mM**	**H_2O_2 5 mM**
X_{300}%	54.21	72.09	78.99	90.45
K_{deg} (minute^{-1})	0.00250	0.00431	0.00507	0.00758
Kinetics	first-order kinetics			

$$\mathbf{H_2O_2 + e^- \rightarrow OH^- + OH^\bullet}$$
$$\mathbf{H_2O_2 + O_2^{\bullet -} \rightarrow OH^- + OH^\bullet + O_2}$$
$$\mathbf{OH^\bullet + \text{steroid hormone} \rightarrow \text{hormone intermediate}}$$
$$\mathbf{OH^\bullet + \text{hormone intermediate} \rightarrow \text{mineralization product}}$$

Figure 5 shows that there is no effect of the addition of H_2O_2 on the kinetics of Ethinyl Estradiol photocatalytic degradation, where the Ethinyl Estradiol photocatalytic degradation demonstrated first-order kinetics in the various concentrations of H_2O_2.

To exclude the possibility that increased degradation in the presence of H_2O_2 is due to the bleaching and/or photobleaching rather than the photocatalytic degradation[18], Ethinyl Estradiol at a concentration of 1 mg/L was subject to photolytic degradation (i.e. photodegradation without catalyst) with 5 mM H_2O_2 yielding only 32.44% degradation.

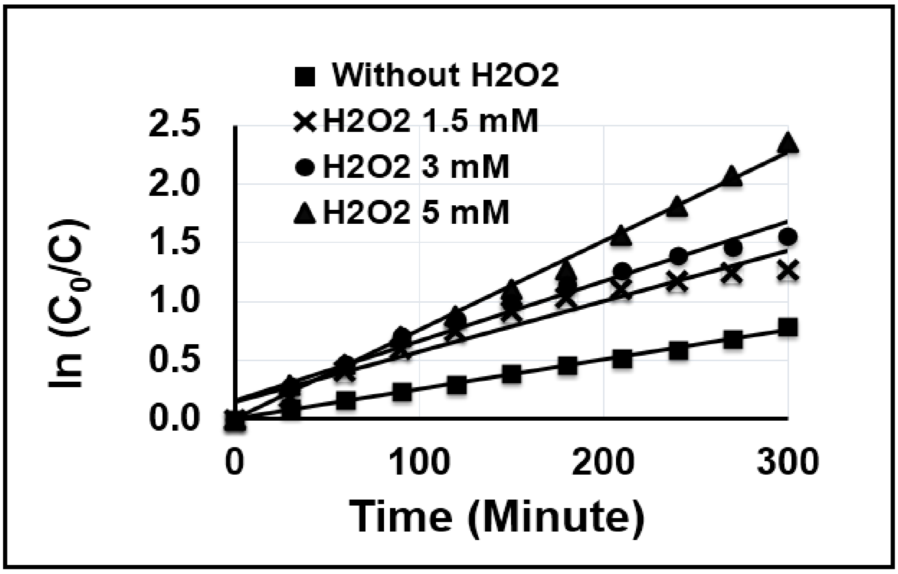


Figure 5: The Kinetics of the photocatalytic degradation of Ethinyl Estradiol in the presence of H_2O_2

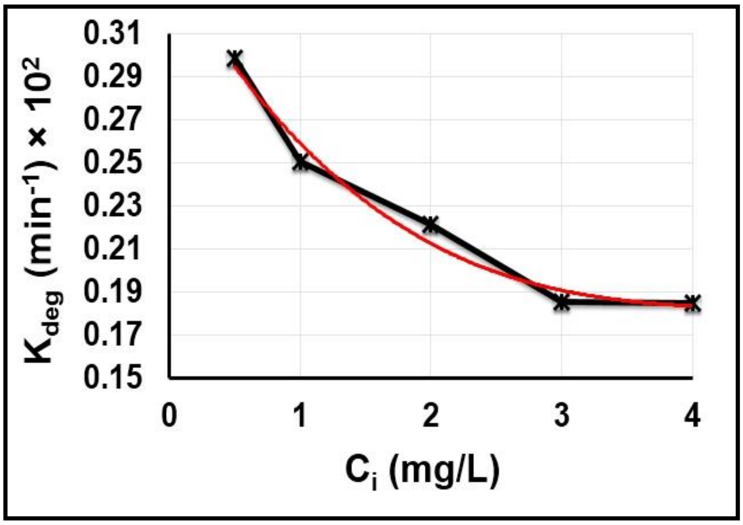


Figure 6: The effect of the initial concentration of Ethinyl Estradiol on the photocatalytic efficiency

2.1.2. Effect of initial concentration

The effect of the initial concentration of Ethinyl Estradiol on the photocatalytic efficiency was studied with concentrations from 0.5 to 4 mg/L (Table IV and Figure 6). It was found that the degradation decreases at an increased initial concentration of Ethinyl Estradiol. Therefore, the photocatalytic degradation will work faster at a low concentration of pollutants[17]. According to (Hapeshi et al., 2010)[12], increased concentration of the pollutant could occupy more active sites of photocatalyst, which inhibits generation of the oxidizing species and decreases the photocatalytic degradation.

Table IV: The effect of the initial concentration of Ethinyl Estradiol on the photocatalytic efficiency

C_i (mg/L)	0.5	1	2	3	4
K_{deg} (minute^{-1})	0.002987	0.002503	0.002212	0.001854	0.001846
X_{300}%	59.53	54.21	47.69	42.87	41.18

2.2. Results of the Photolytic Degradation

The results of the photolytic degradation of the steroid hormones are summarized in Table V. Where **X_{300}%** is the degradation of the steroid hormone after 5 hours (300 minutes) of the photolytic reaction, as percentage. It was calculated by the following formula:

Table V: The results of the photolytic degradation of the steroid hormones

Steroid Hormone	C_{H2O2} (M)	K_{deg} (minute^{-1})	X_{300}%	Kinetics
Ethinyl Estradiol	0	0.00091	23.97	first-order kinetics
	0.06	0.00536	79.38	first-order kinetics
	0.1	0.00688	86.87	first-order kinetics
	0.2	0.00915	93.46	first-order kinetics
Levonorgestrel	0	0.00196	45.46	first-order kinetics
	0.06	0.00216	51.75	first-order kinetics
	0.3	0.00638	85.73	first-order kinetics
	0.4	0.00731	90.07	first-order kinetics
Progesterone	0	0.00684	88.93	first-order kinetics

$$X_{300}\% = [(C_i - C_{300})/C_i] \times 100$$

In which: **C_i** is the initial concentration of the steroid hormone, and **C_{300}** is the concentration of the steroid hormone after 5 hours (300 minutes) of the photolytic reaction.

The absorption spectra of Ethinyl Estradiol, Levonorgestrel, and Progesterone show no absorption in the region 320–400 nm, where the UV-A lamp emits. Therefore, the photolytic degradation cannot be caused by the direct absorption of UV-A irradiation from the pollutants[12]. It may be caused by the photo-oxidation of pollutants from the singlet oxygen generated photochemically from the oxygen dissolved in the reaction mixture[12].

To exclude the possibility that increased degradation in the presence of H_2O_2 is due to bleaching rather than photolytic degradation; Ethinyl Estradiol and Levonorgestrel at concentration of 1 mg/L were subject to bleaching experiments in the presence of high concentrations of H_2O_2 without UV-A irradiation. It was clear that the absence of UV-A irradiation led to a significant reduction of the degradation even in the presence of high concentrations of H_2O_2. Results are shown in Table VI.

Table VI: The effect of UV-A irradiation on the photolytic degradation

Steroid Hormone	Ethinyl Estradiol	Levonorgestrel
C_{H2O2} (M)	0.2	0.4
Degradation% (with UV-A irradiation)	93.46	90.07
Degradation% (without UV-A irradiation)	22.28	15.84

Figures 7, 8 and 9 show the decrease of the areas of the chromatographic peaks of Ethinyl Estradiol, Levonorgestrel, and Progesterone during the photolytic reaction.

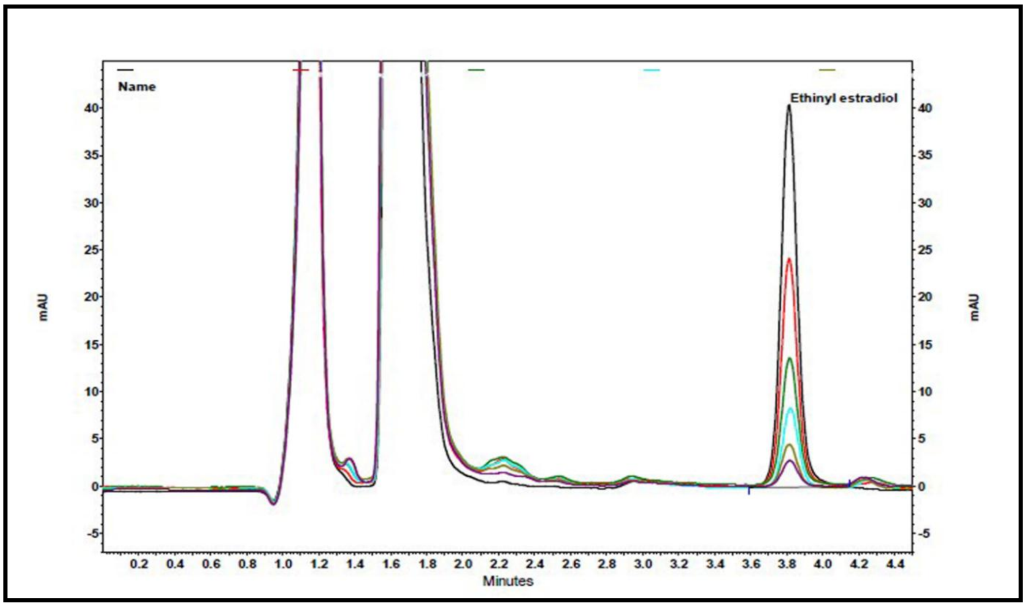


Figure 7: The decrease of the area of the chromatographic peak of Ethinyl Estradiol during the photolytic reaction

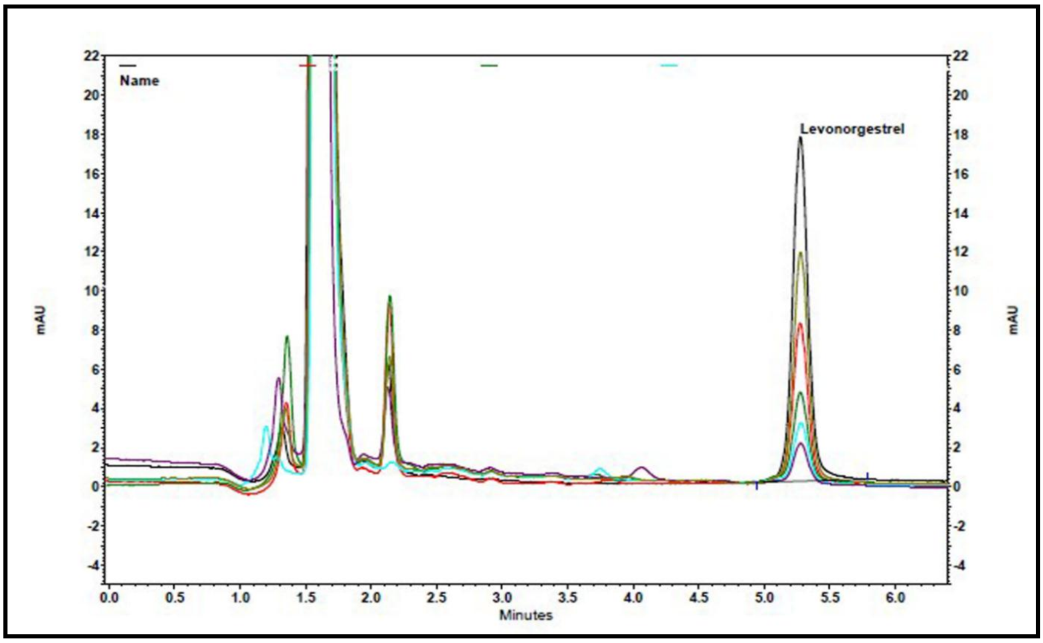


Figure 8: The decrease of the area of the chromatographic peak of Levonorgestrel during the photolytic reaction

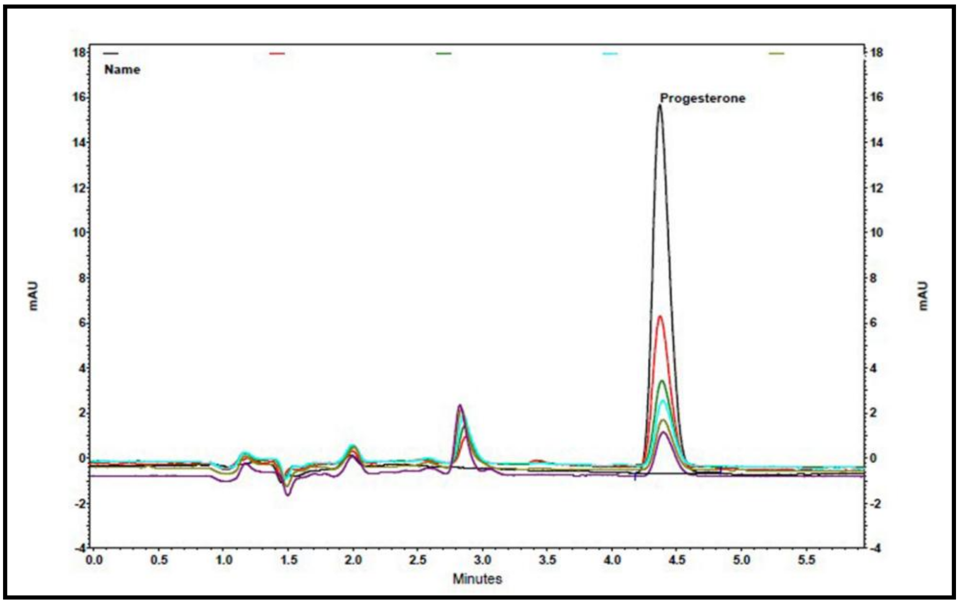


Figure 9: The decrease of the area of the chromatographic peak of Progesterone during the photolytic reaction

3. Conclusion

To summarize, thin TiO_2 photocatalytic films immobilized on glass plates were utilized for the degradation of the steroid hormones: Ethinyl Estradiol, Levonorgestrel, and Progesterone. In addition, the photolytic degradation (i.e. photodegradation without catalyst) of the steroid hormones has been studied. The results showed the possibility of dispensing with the photocatalyst using UV-A irradiation with relatively high concentrations of H_2O_2. It was found that both techniques: photolytic and photocatalytic degradation were effective for the elimination of the studied steroid hormones in aqueous medium.

4. Acknowledgement

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