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EFFECT OF CHEMICAL AND PHYSICAL VARIABLES IN THE PHOTO-ELECTROCHEMICAL REMOVAL OF ESTRIOL (E3) AND 17 α-ETHINYLESTRADIOL (EE2) IN AQUEOUS SOLUTION

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ABSTRACT

The effect of different variables in the electrochemical removal of estriol (E3) in aqueous solution was studied and it was compared with the removal of 17 α- Ethinylestradiol. The photoelectroxidations were carried out with DSA electrode (Ti/RuO_2), varying the pH, substrate concentration and supporting electrolyte, potential configuration of saline bridge, reactor volume, and light source. Results for both Estriol and 17 α- Ethinylestradiol are similar, showing to be the best removals at concentrations of 500 ug/L of substrate, volumes to be treated of 90 ml of solution, saline bridge of 30 cm in length, voltages between 0.8 and 3, concentration of Na_2SO_4 of 0.1 M, pH between 6 and10, and UV lamp of 125 W.

Keywords: Photoelectroxidationn, Estriol, Ethynilestradiol, endocrine disruptor, DSA (Ti/RUO_2)

1. INTRODUCTION

In recent decades, the interest in studying the so-called emerging pollutants has increased, as they are compounds that are used in large quantities by the population. Moreover, many of them have not been regulated in their maximum or minimum amount allowed in the environment and it is known that they return to the natural water systems, often without being treated by wastewater treatments, causing adverse effects in organisms [1]. This occurs even at very low concentrations, including ng L^{-1} [2]. The effect mostly reported in different works is the known “endocrine disruptor effect”. The environment association defines an endocrine disruptor as an exogenous agent the interferes with synthesis, secretion, transport, union, action or elimination of natural hormones, which are responsible of maintaining homeostasis, reproduction, development and or behavior [3].

Because of the aforementioned problems is that the exhaustive study of data of environmental monitoring, transport, transformation and incidence on health has allowed focusing the study on the improvement and creation of new water treatments. Among these treatments, the “treatments of Advanced Oxidation” can be found. These are based on physicochemical processes capable to produce deep changes in the chemical structure of pollutants, which involve the generation and use of transitory powerful species such as the hydroxyl radical [4]. This radical can be generated by photochemical processes or by other forms of energy [5] and it has high effectiveness for oxidizing organic matter [6].

In the present study, photoelectroxidation techniques are used to remove Estriol and α-Etthynilestradiol, 2 steroidal hormones. The first of them is a hormone of natural origin present mainly during pregnancy and the second one is a synthetic hormone used in oral contraceptives [7]. Both have been reported in natural and wastewaters [8] and there is evidence of their potential effect [9].

In the environment, these two hormones can be partially degraded by direct photolysis (absorption of the photoactive phenolic group) or indirectly (absorption of light by photosensitizing species such as nitrates or dissolved organic matter, which generate reactive oxygenated radicals). Sometimes, this depends on many factors, including climatic, which are often unpredictable.

Therefore, at the laboratory scale, various studies focused on removing hormones with physical, biological and chemical techniques have been developed, many times with promising results.

This work is aimed to know different variables both physical and chemical that could iaffect the photoelectrochemical removal of these hormones in aqueous solution, taking into account that this is a viable and efficient alternative that will allow decreasing removal times compared to the traditional electroxidation. In this photoelectrochemical removal by using an external light source, an additional flow of electrons is generated, decreasing the activation energy for transfer of charge through a semiconductor/electrolyte interface, obtaining a lower energy dissipation and the recovery of the maximum electrical or chemical energy [10].

In addition to the intrinsic advantage of using light, we will study different variables both physical and chemical that could influence in the removal of pollutants in aqueous solution, in order to apply the technique optimally.

2. MATERIALS AND METHODS

The molecular structure of the hormones under study is shown in Figure 1: Estriol (E3) and 17 α-Ethynilestradiol (EE2). Both differ from each other in the amount of OH present in each of them; in addition to the ethynil group present EE2.

Both EE2 and EE3 were obtained from Sigma Aldrich, with a purity > than 97%. The working solutions were obtained from patterns of 5.6 mg L^{-1} of Estriol and 1 mg L^{-1} of 17 α Ethynilestradiol, dissolved in ultrapure water, and filtered with PVDF filters (0.45 µm, Whatman).

In order to study the effect of concentration of the analyte on the degradation rate, there were three concentration levels: 500, 700 and 1,000 µg L^{-1} of hormones, keeping three concentration of Na_2SO_4 (0.1 M) constant, whereas when performing the Na_2SO_4 concentration variation experiments (0.1 – 0.3 – 0.5 M), the concentration of hormone was kept constant (500 µg L^{-1}). Experiments of different light sources (260 W mixed lamp, 125 W mercury lamp, 20W UV lamp, and 125 W UV-C Philips lamp), saline bridge length (20-30 cm), solution volume to be treated (90-250 ml), pH (3-6-10) and Potential (0.8-6-10 V) were performed at 500 µg L^{-1} of hormone and 0.1 M de Na_2SO_4.

The dimensionally stable electrode (DSA) (Ti/RuO_2) was obtained from the cooperation of an academic of the Department of Chemical Engineering. In the experimental studies an electrode measured 16 cm^2 total surface with a thickness of 0.1 mm was used. The saline bridge was built with a U-shaped glass tube (0.5 mm Ø), filled with a 4M KNO_3 solution (Merck), gelled in 1% agarose

2.1 Electrochemical measurements and photoxidations

Pulse voltammetry and cyclical voltammetry (scanning rate = 0.1 V/s) was performed in order to observe the electrochemical performance of the hormones in the scanning range of 0 to 1 V, whereas for photoelectroxidations of the solutions, the bulk electrolysis modality with coulometry was used. The equipment used was an Electrochemical Analyzer (HCH Instruments), using the CHI 821C software, connected to a computer. The working electrodes were dimensionally stable electrode (16 cm^2 area, 0.1 mm thickness) against stainless steel electrode and Ag/AgCl electrode as counter and reference electrode, respectively, because potentiostatic oxidation was used.

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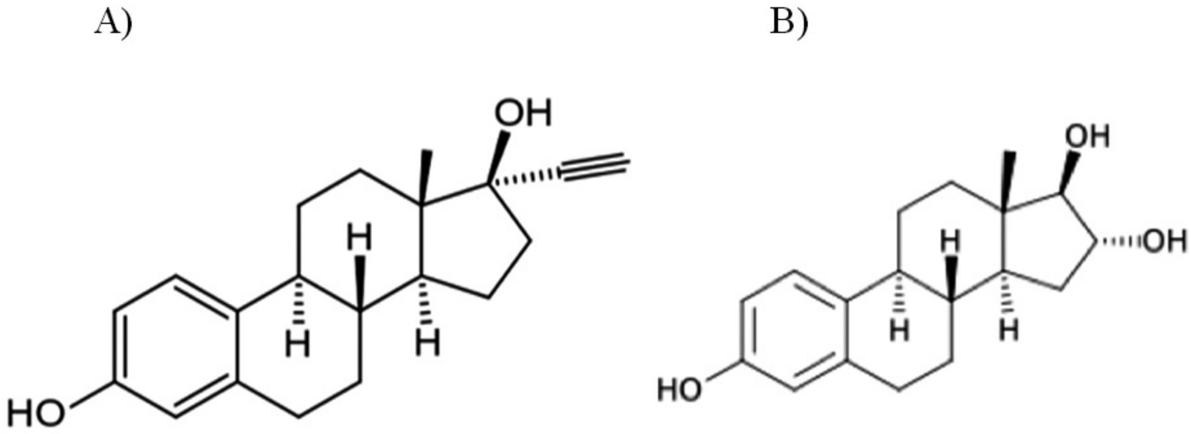

Figure 1: Chemical structure of 17 α-Ethynilestradiol (A) and Estriol (B).

All phoelectroxidations were performed in divided cells, whose content was continuously stirred with magnetic stirrer. The anode was illuminated with different light sources (mixed lamp. 20 W UV, 125 W UV) at a distance of 8 cm from the anode. This is different from the classic oxidation cells in which a single two-electrode cell is used (anode and cathode without reference electrode). This configuration was preferred to avoid the appearance of parasitic reactions in the cathode.

Anode and cathode were separated by a saline bridge (glass tube 4M gelled KNO_3). After each experiment, electrodes were washed with acetone/water (50 – 50 %v/v) and electrolyzed with diluted H_2S0_4 (0.5 M) for 5 minutes and then rinsed with abundant Milli Q water. Samples were taken every 5 minutes, which were filtered and injected in high resolution liquid chromatographer (HPLC).

2.2 Analysis of Estriol and 17 α Ethynilestradiol by high resolution chromatography (HPLC)

Concentrations of E3 and EE2 were measured by HPLC (YL Clarity 9100). Separations were performed in an RP-C8 column (125 mm X 4.6 mm, particle size, 5 μm). On the other hand, the mobile phase was acetonitrile / water (50:50 v/v) at a flow of 1 mL min^{-1}. The injection volume was 20 μL and the working wavelength for the quantitative analysis was 200 nm. Retention time of E3 was 2.05 min and for EE2 was 5.71 min. The relative standard deviations (RSD) ranged from 0.92 and 3.93% for E3 and 0.46 to 7.8 for EE2, in the range of concentrations between 20 and 1,000 μg L^{-1}. The linear adjustment of the calibration curve was $R^2 > 0.99$.

3. RESULTS AND DISCUSSION

3.1 Pulse and cyclic voltammetry

Pulse and cyclic voltammetry (0 – 1 V), of 200 mg L^{-1} for E3 and EE2 in 0.1 M Na_2SO_4, shows a defined oxidation peak around 0.62 and 0.68 V against Ag/AgCl (Fig. 2). In inverse exploration 1 – 0 V no peak corresponding to the reduction is observed. This suggests that the electrochemical oxidation of E3 and EE2 in Ti/RuO_2 is totally irreversible.

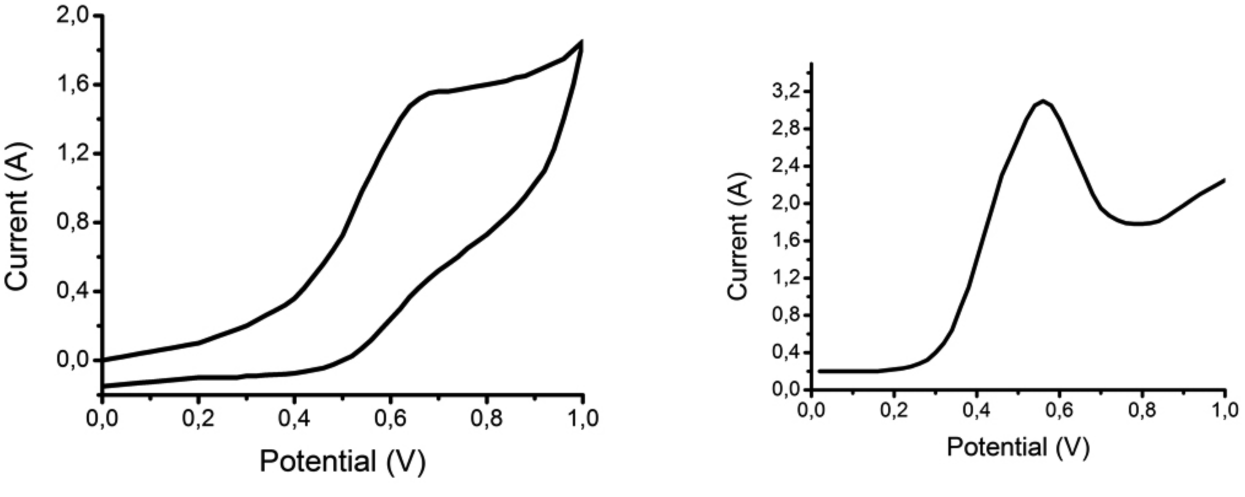

Figure 2: Cyclic (A) and pulse (B) voltamperogram of 200 mg L^{-1} E3, 0.1 M Na_2SO_4.

3.2. Effect of Light source

In this experience, the removal efficiency of 500 μg L^{-1} of hormones, with and without exposition to different sources of artificial lights was compared. As can be observed in Figure 3, in the experiments performed in absence of light (electrolysis), removals of 40% for E3 and 25% for EE2 were obtained at 120 min of reaction (0.8 V, 0.1M Na_2S0_4, pH 6), with degradation rates 6-7 times lower for E3 and EE2 at 90 min reaction, respect to experiments performed with 125 W ultraviolet radiation. In the latter conditions, higher removals up to 100% for E3 and 92% for EE2 can be obtained after 120 min of reaction (125 W UV-lamp) (Figure 3). When comparing artificial light sources, differences are also evidenced. By using lamps the emit in the visible light spectrum (mixed lamps), radiations 3-4 times higher for E3 and EE2 are obtained after 60 min of reaction, respect to the 125 W UV light source. Finally, if UV Light sources with different power are compared, it will be evidence that the speed of the reactions will be favored at higher powers, this due to the higher number of target photons/molecules.

The degradation of hormones in water under different experimental conditions have been studied in several works and in general, the photolysis achieves degradations in the range of 1-35% for EE2. Results will depend on the type of matrix, power of the light source, and the concentration of the compound, as well as the intrinsic properties such as its molar extinction coefficient and its quantum performance [11], though in general the removals are insignificant.

In river water, the average lifetime of EE2 is at least 10 days, with daily exposures of 12 hours at sunlight. However, this type of natural system where no control of all variables can not be maintained, degradation is limited for instance, by the turbidity of the water and attenuation of light in the depths, among other variables [12]. Better results have been reported in other works in the degradation of endocrine disrupting compounds, but when combined with Iron, H_2O_2, TiO_2, O_3, among others. Thus, the removal % of BPA can be increased from 60% through photolysis until 100% at 60 min with self-organized matrix nanotubular TIO_2 electrodes, using a 125 W mercury lamp, 1.5 V at pH 6 [13].

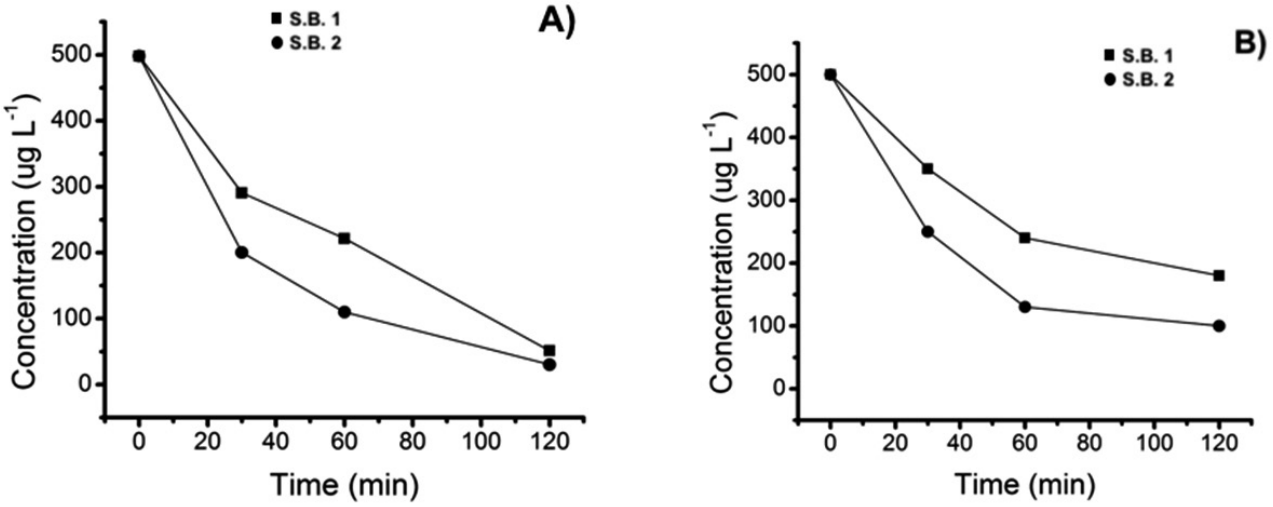

Figure 3: Effect of Light on the degradation of 500 µg L^{-1} de E3 (A) and EE2 (B), 0.1 M Na_2SO_4, pH 6, 0.8 V,

3.3. Saline bridge configuration effect and solution volume

When performing experiments varying the solution volume and keeping constant the concentration of hormone (500 µg L^{-1}), supporting electrolyte (0,1M) at a voltage of 0.8 V, an increase in the removal at a volume of 90 mL can be observed (Fig. 3). This can be due to the shorter path of the analyte to the electrode, in comparison to the distance between what the analyte must travel in a larger size reactor.

When the reactor is 90 mL, high removals of the species under study are obtained especially in the first minutes of reaction, which would indicate that the removal is a first-order reaction. Another factor to be considered is that the electrode is the same for both cases, having the same contact surface but for a larger volume. These results (250 mL) could be improved by increasing the size of the electrode, proportionally to the increase in volume.

Regarding the configuration of the saline bridge, a greater longitude favors removals, since there is more KNO_3 being driven through it [12, 14, 15].

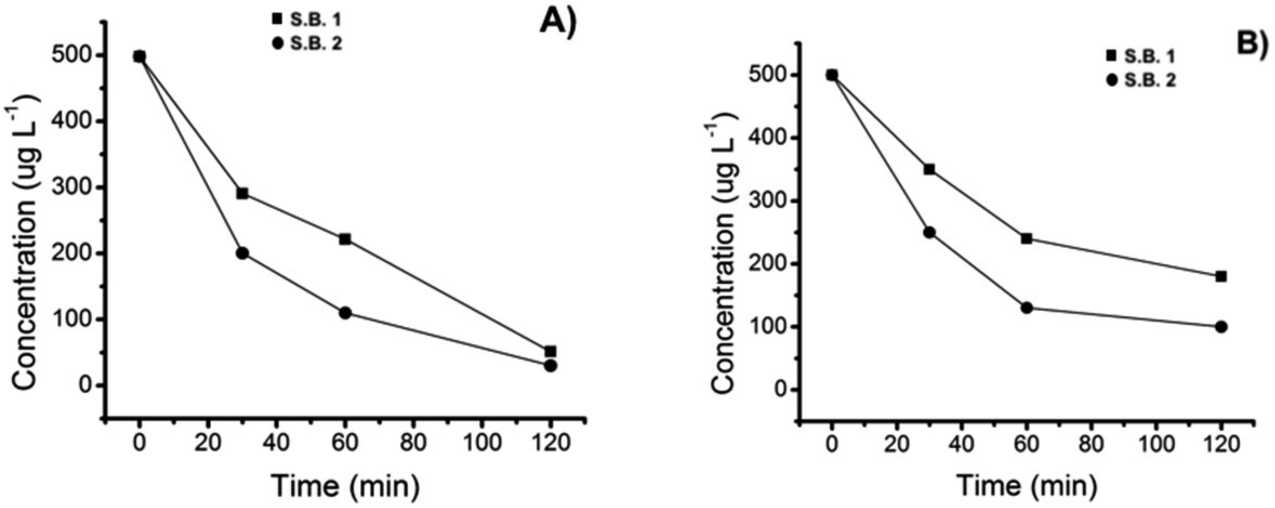

Figure 4: Effect of saline bridge length (A) on the removal of 500 µg L^{-1} of E3 (A) and EE2 (B) at 0.8 V, 0.1 M of Na_2SO_4, pH 6.

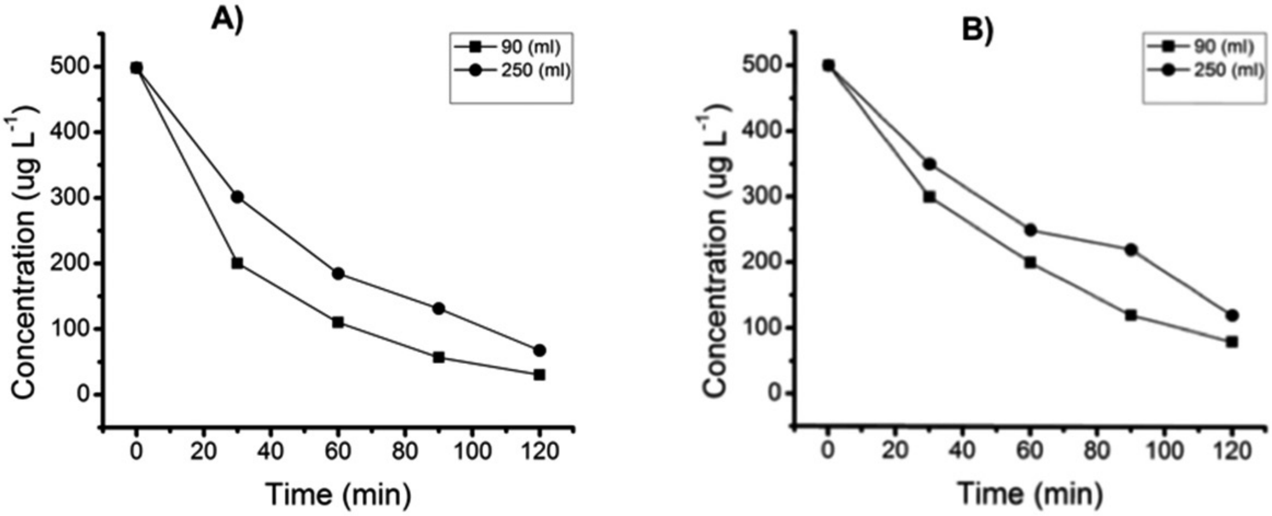

Figure 5: Effect of the volume of the solution to be treated in the removal of 500 µg L^{-1} de E3 (A) and EE2 (B) a 0,8 V, 0,1 M of Na_2SO_4, pH 6.

3.4. Effect of the supporting electrolyte concentration

When carrying out the experiences of hormone removal (500 µg L^{-1}), 0.8 V, at different concentrations of Na_2SO_4, removals higher than concentrations of 0.1 M are obtained, as well as a significant decrease, for instance at 0.5 M de Na_2SO_4. This suggests that at these concentrations the work is being performed with an excess of electrolyte, which causes an increase in the viscosity of the medium and hence, a lower transport of analyte to the electrode and a lower removal. In the work by Brugnera [13], the effect of the supporting electrolyte is also studied, but at lower concentrations. Thus, a maximum of mineralization at concentrations of 0.1 M are obtained.

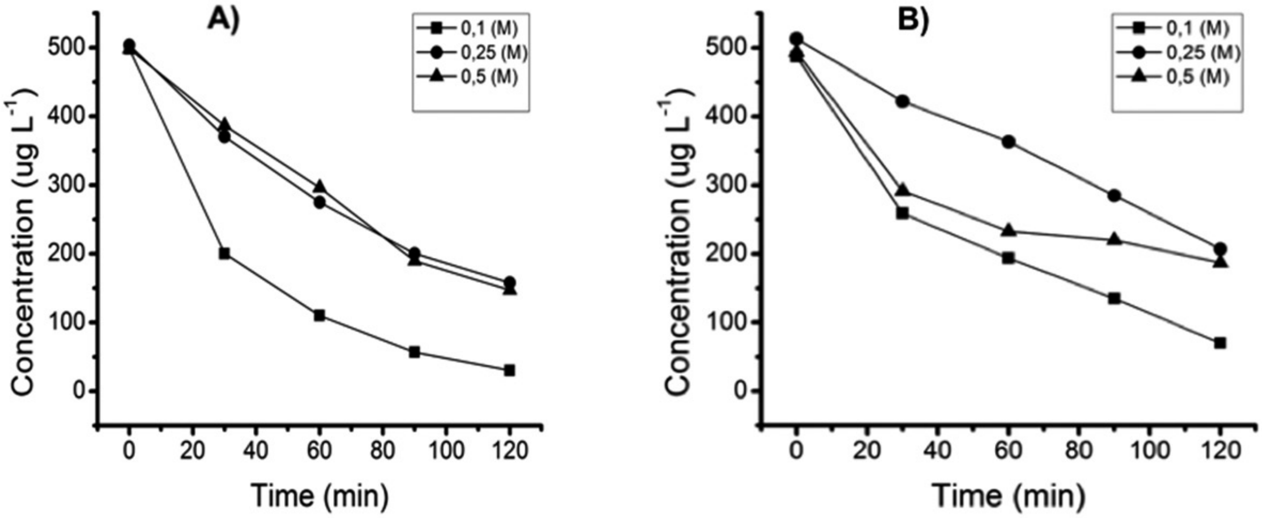

Figure 6. Effect of the variation of concentration of the supporting electrolyte (Na_2SO_4) in the removal of 500 µg L^{-1} of E3 (A) and EE2 (B) at 0.8 V, pH 6.

3.5. Effect of pH variation

Removal of hormones is directly affected by pH. Thus, it can be observed in Figure 7 that as pH increases, removals also do so. The above is explained by observing the chemical structures of hormones (Figure 1), which are weak acids, with a pKa >10. This indicates that they are fully ionized at a pH > 10, leaving the structure negatively charged and it will facilitate the displacement to the anode (positively charged) where the removal takes place.

On the other hand, the isoelectric point of RuO_2 is found at pH 6.5, which indicated that E3 and EE2 are preferentially absorbed when the surface of RuO_2 is in the charged form [16].

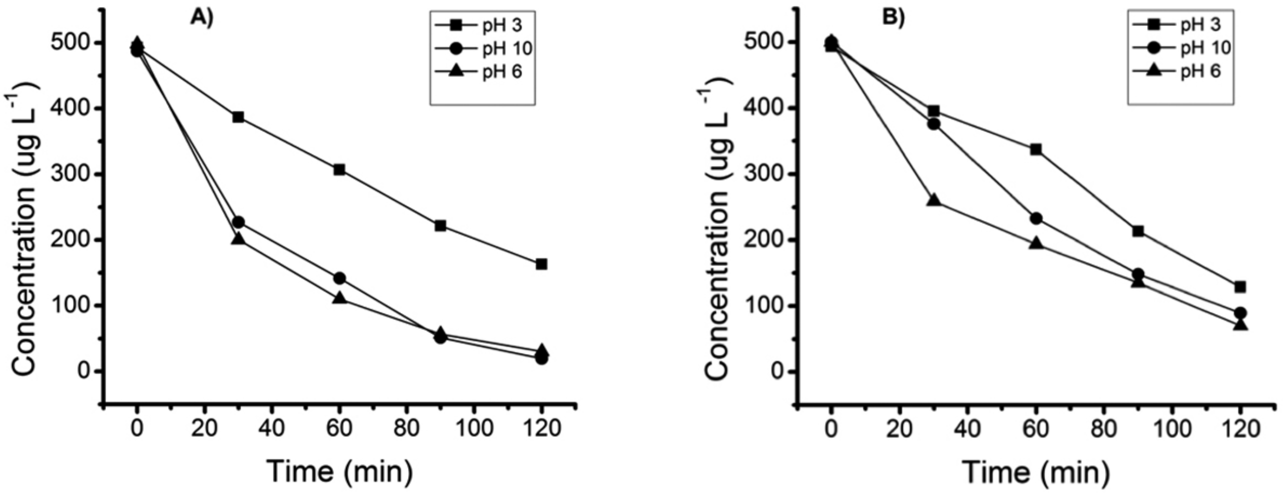

Figure 7: Effect of pH variation on the removal of 500 µg L^{-1} of E3 (A) and EE2 (B) at 0.8 V and 0.1 M Na_2SO_4.

3.6. Effect of variation in potential

By varying the potential applied to the photoelectrochemical removal of E3 and EE2 it can be observed that the best removal potentials are found at a potential of 0.8 V compared to higher voltages. This can be attributed to the predominance of collateral parasitic reactions, such as the reaction of evolution of oxygen. This trend can be observed in other studies such as that by Nájera [17], where they refer to the influence of of the density of the applied current on the removal efficiency of a GES-EE2 mixture. In this study, three levels of densities of current of 16, 32 and 48 mA cm^{2} were tested. As shown here, in some cases as the density of current increases (48 mA cm^{2}), a limit value will be reached, where the reaction stabilizes. In other cases, there is a decrease in the efficiency of the anodic oxidation, so the density of the current and voltage is not capable to control the efficiency of the oxidative system.

On the other hand, although the potential applied is low, it is still more positive than the flat band potential, so there is a potential gradient on the film of ruthenium oxide, which will result in an electric field that keeps the photogenerated charges. Therefore, the adsorption of E3 and EE2 and/or the generation and separation of electron-hole pairs that are accelerated under this gradient will be favored. Thus, a quick decomposition is promoted [18] (Rajeshwar and Ibanez 1997).

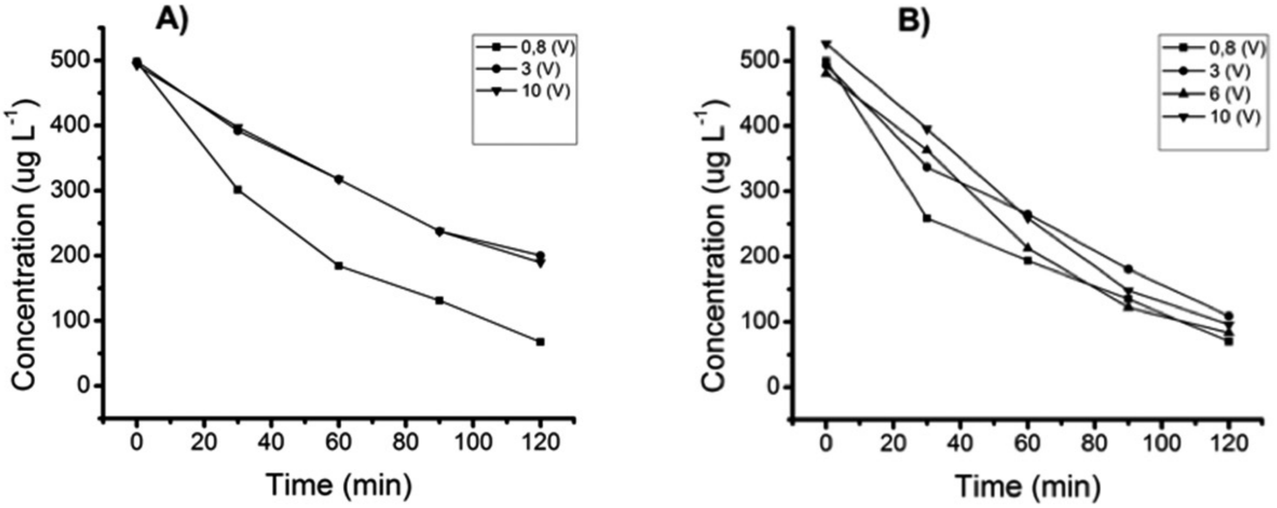

Figure 8: Effect of variation of potential on the removal of 500 µg L^{-1} of E3 (A) and EE2 (B), 0.1 M Na_2SO_4, at pH 6

3.6. Effect of substrate variation concentration

A total of three concentrations of E3 and EE2 (500, 750, 1000 µg L^{-1}) were studies to observe the effect of concentration on the removal on the surface of the Ti/RuO_2 electrode.. Figure 9 shows concentration removal with the decrease of the initial concentration. Thus, it is observed in Fig. 9 A that the removal at 30 min is five times higher when working at concentration 500 µg L^{-1} than 1000 µg L^{-1}, and double removal of concentration at 120 min of reaction.

For EE2 (Figure 9B) as well as estriol, removals are favored at lower initial concentration, doubling at 120 min of reaction at 500 µg L^{-1} compared to 1,000 µg L^{-1}. It is known that an increase in the initial concentration of a compound increases its concentration gradient and the mass transference through the diffusion layer and therefore, its degradation in the electrode. However, many times the electrode is saturated at high concentrations of the analyte [10] or the electrogenerated hydroxyl radicals are depleted due to competitive reaction for the OH radical. This leads to a parallel consumption of it, for example the oxidation of many compounds (intermediates) with OH [19].

On the other hand, the degradation profile follows the performance first-order kinetics, where reaction rates depend on the concentration as concentration increases (500 to 1,000 µg L^{-1}) and the degradation rate decreases. This leads to a decrease in the kinetic coefficient of 0.023 to 0.006 min $^{-1}$ for E3 and 0.016 to 0.006 min $^{-1}$ for EE2.

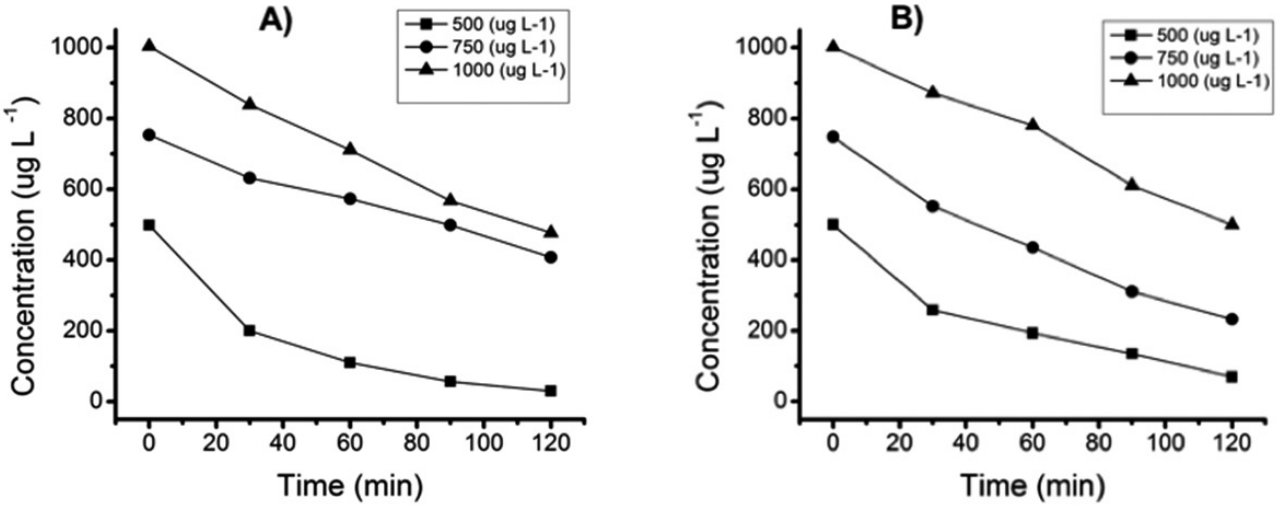

Figure 9: Effect of the concentration variation of E3 (A) and EE2 (B) at 0.8 V, 0.1 M Na_2SO_4, at pH 6.

4. CONCLUSIONS

There are different variables that affect the renoval of E3 and EE2. Thus, it can be concluded that a greater length of the saline bridge (30 cm) and smaller volume of solution (900 ml) favor the removals of hormones, especially during the first 30 min of reaction. In turn, the source light has direct implications on the efficiency of percentages of removal, as well as the light source with 125 W of power. This allows us to obtain removals greater than 90%, at a potential of 0.8 V, 500 µg L^{-1} de hormone, natural pH and 0.1 M of Na_2SO_4.

On the other hand, the effect of concentration of the supporting electrolyte allows concluding that 0.1 M concentration of Na_2SO_4 is more effective than higher salt concentrations. The pH is also a significant factor, since at higher pH; removals also increase, favoring the transport of the analyte to the anode (see discussion).

Regarding the effect of the potential, lower potentials (0.8 V) present better efficiencies in the percentages of removal (30% higher at 120 min of reaction) respect to 3 V and 10 V. However, no significant differences are observed for EE2 at 120 min when using potentials of 0.8-6-1 V. This concludes that 0.8 V is more efficient, also due to an economic factor.

Finally, concentrations of 500 µg L^{-1} allow obtaining removals of Estriol five times higher than for 1000 µg L^{-1} and double removal for EE2 at 120 min of reaction.

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