Electrochemical Remediation of 17α-Ethinylestradiol

Fernando Miguel de Amorim Lino[1], Diogo Cordeiro Dias[1], Renata Crispim Batista[2], Eric de Souza Gil[1, 2*] Iranaldo Santos da Silva[3] and Lucio Angnes[3]

1. Faculty of Pharmacy, Federal University of Goias, Goiania 74605-220, Brazil

2. Postgraduate Program in Environmental Engineering, Federal University of Goias, Goiania 74603-150, Brazil

3. Institute of Chemistry, University of Sao Paulo, Sao Paulo 5509, Brazil

Abstract: Technological development has led to the emergence of new substances with many different purposes generating a new profile of pollutants in waterways. Among these, endocrine disruptors, such as 17EE (17α-ethinylestradiol), are of great importance due to their wide application and harmful consequences to the environment, human health and animals. The inefficiency of most water treatment processes in withdrawing such substances poses a global concern for the development of effective and environmentally clean methods. The electrochemical remediation processes appear as a powerful and "green" alternative for waste removal of organic or inorganic pollutants from complex environments, such as geosphere and hydrosphere. The research focus in this field is mostly related to the optimization of electronic devices with higher (photo) catalytic efficiency, whereas the starting material remains based on metal and carbon conventional electrodes. In the present study, the anodic removal process of 17α-ethinylestradiol at carbon cardboards was investigated in stationary and hydrodynamic conditions. The influence of pH and applied potential were evaluated, always taking into account the transposition of scale and environmental aspects. Thus, the principle of hormone removal showed to be strictly related to such parameters. It was observed that mild alkaline medium favors the anodic oxidation, whereas neutral and mild acid ones lead to higher adsorption at carbon surface. Also, when the applied potential was higher than 1.25 V, the electrochemical oxidation rate increased, and the adsorption was decreased. Furthermore, the removal efficiency of 17EE showed to be lower, the flow rate was higher.

Key words: Endocrine disruptors, ethinylestradiol, electrochemical remediation, carbon electrodes.

1. Introduction

For long decades, the agricultural, pharmaceutical, petrochemical and other industrial areas have originated a wide pool of new substances for many purposes. Among these, insecticides, pesticides, fertilizers, antibiotics and hormones represent, despite their benefits to humanity, have often been associated to terrible environmental impacts [1-3].

This dangerous side of technological development is the consequence of improper disposal, not only regarding the formerly mentioned products, but also their byproducts, starting materials, side-products, degradation products and also metabolites, which reach the environment and affect the biosphere [2-4].

Owing to its remarkable pharmacodynamic properties, EDs (endocrine disruptors) are one of the pollutants of greater relevance. Indeed, at very low concentrations, EDs are capable of interfering with the normal functions of human and animal bodies [1]. In humans, for example, there are common reports of impaired fertility in women, and decreased production of gametes in men. In animals, there are similar reports of decreased fertility in fish and their feminization [2].

According to the U.S. EPA (Environmental Protection Agency), "endocrine disruptor is an exogenous agent that interferes with biosynthesis, secretion, transport, binding, action and/or elimination

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*Corresponding author: Eric de Souza Gil, Professor, research fields: biossensors, bioremediation, electrochemical remediation, electroanalysis, pharmaceutical analysis and environmental analysis. E-mail: ericsgil@gmail.com.

of natural hormones in the body being responsible for the maintenance, reproduction, development and/or behavior of organisms" [3].

The EDs can affect the homeostasis of thyroid functions [4]; trigger the development of cancer [5]; increase the incidence of polycystic ovaries and disorders related to its dysfunctions (follicular growth and ovulation) [6]. Moreover, they are related to the development of obesity [7] and inducing mechanisms of insulin resistance in type 2 diabetes mellitus [8].

The EDs include a wide variety of substances, including 17EE (17α-ethynylestradiol) and all the synthetic estrogenic drugs, alkylphenols, pesticides, phthalates, polychlorinated biphenyls, bisphenol A, as well as natural estrogens (e.g., 17β-estradiol, estriol, estrone) and phytoestrogens [1-4].

The great half-life, 4 to 6 days, of 17EE, allows its long permanency in soil surface, raw sewage, treated effluent and other hydric resources [9-12]. Moreover, its intrinsic estrogenic activity is 10 times higher than estradiol, its natural counterpart, remaining viable to act in other organisms [13, 14].

Furthermore, 17EE is broadly consumed, being one the main drugs of choice for contraception, and also on the therapy and treatment of prostatic cancer [2-4]. Therefore, considering its wide consumption, high persistency in environment and strong estrogenic activity, 17EE may have great ecological impact. Thus, the concerns regarding its disposal are of vital importance in order to avoid the harmful effects on living organisms [15].

His persistent character and continuous introduction into the environment, as well as the lack of adequate treatment plants upsurges from ecological to a public health issue [13, 16-18].

The survey of the main proposed methods to treat persistent pollutants can be based in two principles, the physical removal or the chemical transformation [10-25]. Oxidation processes such as photocatalysis [19, 20], ozonation [21-24] are good examples of chemical treatment. In turn, the use of activated charcoal [26], nanofiltration membranes [27], reverse osmosis [28, 29], represent some physical attempts of removal, though such approaches are not suitable or efficient enough, especially in macro scale. Thus, it is essential to develop and improve processes of wastewater treatment in order to decrease the contamination of aquatic systems, providing security to the population health and overall ecosystem [1].

In this sense, the electrochemical remediation processes are gaining prominence and attention in the treatment of domestic and industrial effluents. In anodic oxidation, the oxidizing agent (electron) is environmentally friendly and cleaner than the usual chemicals of strong oxidant character, which in fact might be potential pollutants [28-31].

Other advantages of electrochemical remediation include its versatility, the great energetic efficiency, the operational simplicity and the possibility of automation. Moreover, the improvement of the electrode material, in which the formation of reactive species occurs, is easily reached by using catalysts coated at the electrode surface, thus allowing higher selectivity and reaction rates [30, 31]. Commonly, glassy carbon or platinum are employed as starting material for the development of anodes of higher catalytic efficiency for remediation purposes [23-31]. Nevertheless, taking into account the possibility to apply a lab system to the large scale of treatment plants, the search for alternative materials presenting lower cost is valuable.

Thus, in this study the authors evaluated the efficiency of electrochemical oxidation of 17EE by using carbon cardboards as electrode material under different electrolyte, hydrodynamic and applied potential conditions for remediation purposes.

2. Material and Methods

2.1 Material

2.1.1 Electrode Material

CC (carbon cardboards) used to fabricate the electrode material for remediation purposes were

purchased from Shandong Longteng-Sealing Co., Ltd. articles.

2.1.2 Reagents and Solutions

The 17EE, pharmaceutical grade, was donated by Cifarma S/A (Goiania, Brazil). The sodium phosphate, potassium chloride and potassium hydroxide, used in the preparation of electrolytic solutions were all of analytical purity and obtained from Vetec S/A (Sao Paulo, Brazil).

A standard solution of 17EE was prepared in ethanol-water (1:1) at a concentration 0.25 mm. The electrolytic solutions were 0.1 m phosphate buffer, pH 7.0 or 0.1 m KCl. The influence of pH was evaluated in suitable buffers by adjusting the pH from 3.0 to 9.0.

2.2 Apparatus

2.2.1 Electroanalytical Assays

The electroanalysis was performed in order to evaluate the redox behavior of 17EE and also as a alternative tool to check its decay after continuous electrolysis. All measurements were performed using a potentiostat/galvanostat μ Autolab type III® coupled to GPES 4.9 software. A three-electrode cell system, was a GC (glassy carbon), area of 1 mm^2, the working electrode; saturated calomel (Hg/Hg_2Cl_2, KCl_{sat}), the reference electrode and platinum wire, the counter electrode. The cyclic voltammetry was performed from 0 V to 1.4 V at scan rate of 100 mV·s^{-1}, whereas the DP (differential pulse) voltammograms were performed with pulse amplitude of 50 mV, pulse width of 4 s and scan rate of 10 mV·s^{-1}.

2.2.2 ER (Electrochemical Remediation) in Different Hydrodynamic Conditions

(1) ER in stationary and stirring conditions: the evaluation of carbon cardboard as electrode material for remediation purposed was carried out in the same system as the one used for electroanalytical assays, but using carbon sheet, which was cut in order to have an area of 4 cm^2 (1 cm × 4 cm) instead carbon glassy as working electrode.

Since the CC has two equal faces, the immersion of 2 cm corresponds to the same area (Fig. 1a). The stirring was controlled by using a magnetic stirrer, Fisaton 761.

(2) ER in flow conditions: for this assay two carbon paper sheets of 1 mm thickness and area of 10 cm^2 (10 cm × 1 cm) were used as anode and cathode electrodes (Fig. 1b).

The flow system comprising two acrylic plates, being composed of one orifice for entry and exit of electrolyte medium, separated by a spacer containing rubber slit of 0.5 cm × 10 cm × 1 cm and the two sheets of carbonaceous electrode material. The system can be seen in Fig. 1b.

The flow rate was controlled by peristaltic pump and the applied potential on the carbonaceous plates (Fig. 1) was controlled by Potentiostat PAR® Model 263A.

The evaluation of 17EE removal efficiency was performed by monitoring the absorbance decay in comparison with initial concentration. The spectrophotometric measurements were carried out at
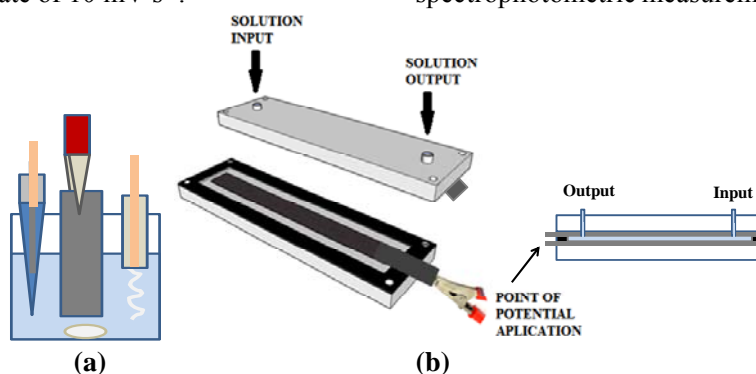

Fig. 1   (a) System for evaluation of electrochemical remediation in stationary and stirring conditions; (b) system for evaluation of electrochemical remediation in flow conditions.

HP 8452 UV-Visible A® (Diode Array Spectrophotometer).

2.3 Experimental Procedures

2.3.1 ER Parameters

The efficiency of CC for ER of 17EE was evaluated in different experimental conditions according to the applied potential, flow rate and pH of the electrolyte. All experiments were carried out at room temperature (25 °C) and the initial concentration of 17EE was of 0.25 mm 17EE.

Applied potential: The applied potential varied from 0.8 V, 1.5 V, 2.0 V and 2.5 V for all hydrodynamic and stationary conditions.

(1) ER in stationary and stirring conditions: The efficiency of CC for ER purposes was initially evaluated in not-flowing systems (Fig. 1a) in conventional electrolytic cell with 10 mL capacity provided by AutoLab® in both of static and stirring conditions.

Applied potential and time: The influence of applied potential was evaluated by fixing the time at 20 min. In turn, the ER in stationary state was evaluated as a function of time, when the 17EE was submitted to 0.8 V for 5 min, 10 min and 20 min.

Monitoring: In these studies the decay of the concentration of 17EE was determined in terms of peak currents recorded before and after electrolysis, using a working electrode of glassy carbon polished before each measurement. These measurements were obtained by cyclic voltammetry at scan range between -0.20 V to +1.00 V at 100 mV·s⁻¹.

(2) ER in flow conditions:

Flow rate: The effect of flow rate on ER of 17EE was evaluated at 0.5, 0.75, 1.0, 1.5, 2.0, 2.5 and 3.0 mL·min⁻¹.

pH: The effect of pH was evaluated in the range from 3.0 to 9.0 in order to check its influence on the electrolysis rate of 17EE. In this study the applied potential was kept at 0.9 V and the flow rate in 0.5 mL·min⁻¹.

Monitoring: The efficiency of ER assays was monitored by evaluating the decay of initial absorbance of the 0.25 mm solution of 17EE at 280 nm.

2.3.2 Stability and Reuse

The stability of the electrode material after use was evaluated, by cleaning it in 0.1 M NaOH, submitted to 1.5 V for 10 min.

3. Results and Discussion

3.1 Electrochemical Behavior of 17EE at GC Electrode

The DPV voltammogram obtained for 0.25 mm 17EE in pH 8.0 and 0.1 M phosphate buffer solution showed a anodic peak at 0.5 V (Fig. 2a), which may be related to the irreversible oxidation of phenolic moiety (Fig. 2b) [32]. Thus on successive scans it was
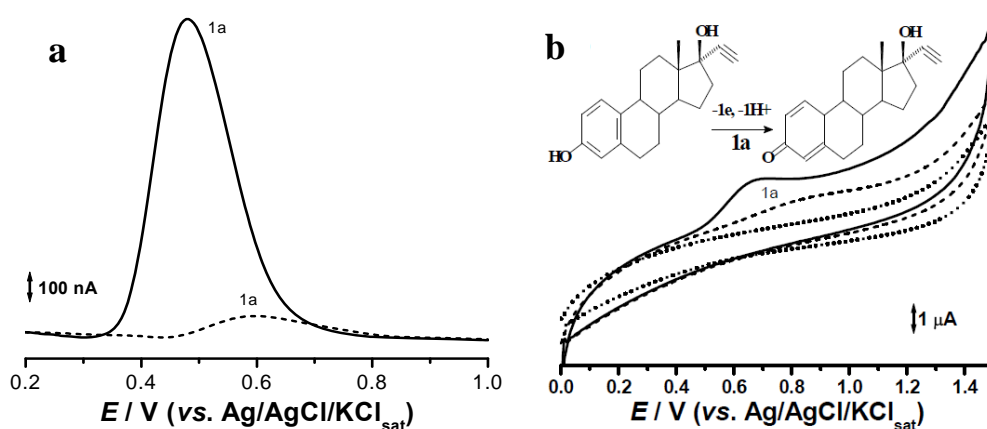

Fig. 2 (a) DP and (b) CV voltammograms, obtained at GC for 0.25 mm 17EE in pH 8.0 and 0.1 M phosphate buffer solution, 1st (——), 2nd (- - -) scans and CV blank (…).

observed higher adsorption behavior followed by blockade of electrode surface and intense fall of peak currents in both DPV and CV experiments (Fig. 2).

3.2 Influence of pH on ER

When the applied potential and hydrodynamic conditions were kept constant, it was observed that the higher the pH, higher is the ER efficiency of CC electrodes.

This behavior is in agreement with the redox behavior of 17EE at GC, in which was observed that the peak potentials decrease proportionally with the increasing of pH. Besides the higher overpotential required to the electrochemical oxidation, it was also observed stronger adsorption in acid medium, thus leading to electrode fouling and reducing the electroactive area.

3.3 Influence of Hydrodynamic Parameters

As expected, the increasing of flow rate leads to the impairment of the ER efficiency in continuous flowing systems represented in Figs. 1b and 3.

Therefore, it can be inferred that for ER in continuous flowing system, a condition that simulates effluent into water courses, is necessary to slow the flow rate to allow longer contact time between the polarized electrode and pollutant.
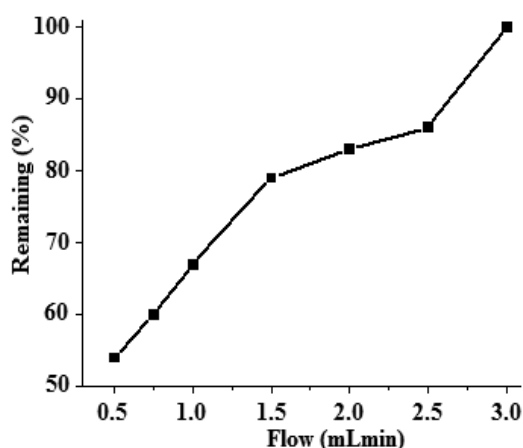
On the other hand, the 17EE decay in experiments where the solution was kept the same, thus simulating a possible ER in treatment tanks (Fig. 1a), was higher when stirred. Such fact is consistent to increase the mass transport to the electrode by the convection promoted by stirring. Indeed, in ER performed in stationary condition the mass transport is governed exclusively by diffusion. Nevertheless, the rate of stirring showed minor effect than the one observed for flow rate.

In turn, these studies in steady static condition, as well as under stirring conditions presented higher efficiency for longer times of application of pulse (Fig. 4).

3.4 Influence of Applied Potential on ER

The influence of applied potential on the efficiency of 17EE removal showed different behavior for steady and hydrodynamic conditions.

Hence, under steady state conditions, it was observed greater decay of 17EE monitored by means of peak currents decreasing.

In contrast, similar studies performed in hydrodynamic conditions, at flow rate of 0.5 mL·min^{-1} showed that the decay increases with peak potential until 1.0 V, and then decreases (Fig. 5). This may be associated with formation of bubbles at higher peak. Besides the ohmic drop, the bubbles may avert the 17EE molecules from the electrode interface region,
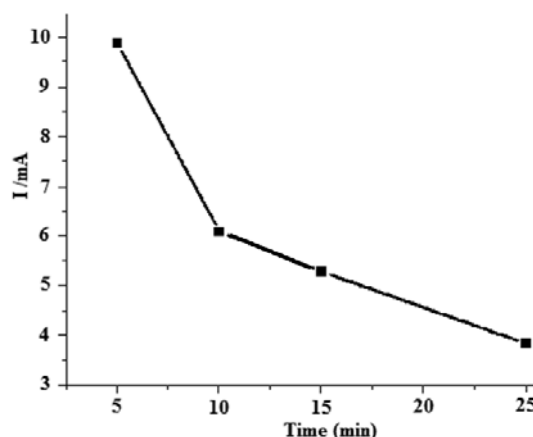

Fig. 3 Decay of 17 EE absorbance as function of flow rates. Applied potential of 0.9 V, CC anode of 10 cm^2 in continuous flowing of 0.1 M pH 9.0 KCl solution is contained 0.25 mm 17 EE.

Fig. 4 Decay of 17 EE currents as function of time. ER at CC anode of 4 cm^2, applied potential of 0.9 V in 10 mL pH 7.0 KCl static solution containing 0.25 mm 17EE.
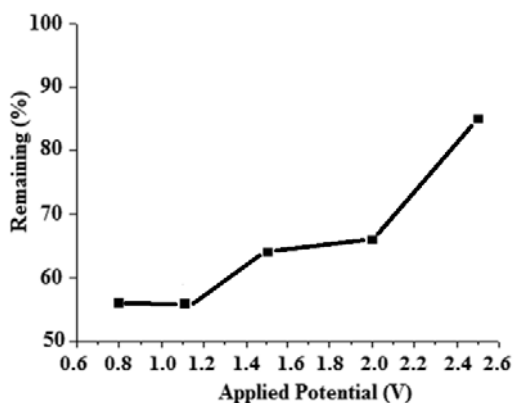
Fig. 5 Decay of the concentration of 17EE as a function of applied potential under continuous flow rate of 0.5 mL·min^{-1}, in pH 9.0 0.1M KCl.
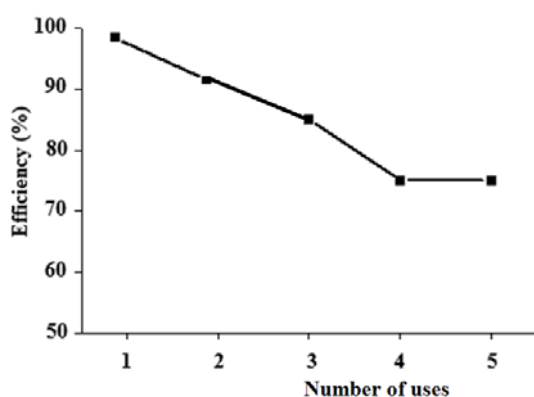

Fig. 6 Efficiency (%) of ER according to the number of uses after surface renewal.

thus hampering electron transfer and oxidative process and also avoiding the physical removal by adsorption.

3.5 Recovery of CC Anodes

Considering the adsorptive character of most of all organic pollutants, also observed for 17EE at CC anodes during the ER. Some attempts on the renewal of CC were investigated in order to make its reuse possible. Indeed, it was achieved by flowing a 0.1 M NaOH solution in the flowing system apparatus (Fig. 1b) at flow rate of 0.5 mL·min^{-1} and by applying 1.5 V.

Nevertheless, a small decay on efficiency was observed in further assays (Fig. 6).

4. Conclusions

The efficiency of ER of 17EE when using CC as anode was showed to occur by physical and chemical

mechanisms, the first carried out by electrochemical adsorption of 17EE at CC and the second by chemical oxidation by radical electrogenerated at potentials higher than 1.2 V.

Therefore, both the hydrodynamics and applied potential may have great influence in the ER process.

Thus, when simulating the flowing course of sewage plants, the slow rate must be reduced in order to allow a longer contact time. Meanwhile, owing to the larger contact area of the proposed ER system in Fig. 1b, too high potential may generate bubbles, that may interfere on the heterogeneous anodic reaction.

Yet in the ER system simulating waste treatment tanks, the chemical process showed to have larger influence. In this case, the direct anodic oxidation and also the chemical attack of reactive species such as hydroxyl radical's electrogenerated at the electrode surface may be involved on the 17EE decay. Therefore, higher potentials and stirring may favor the ER model showed in Fig. 1a.

Finally, taking into account the larger possibilities to increase the catalytic efficiency of CC, such materials showed to be promising materials for ER purposes.

Acknowledgments

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