Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2016, 8(4):958-964

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Low Cost Commercial Anodes on the Electrochemical Remediation of the Estrogen 17α –ethinylestradiol

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ABSTRACT

Endocrine disruptors (ED) are chemicals constantly detected in water and wastewater. Ethinylestradiol (EE2) is the principal synthetic hormone used in oral contraceptive formulations and other hormonal drugs, making part of the EDs list. Electrochemical processes such as electro-oxidation and electrocoagulation are an alternative for EE2 removal from water. In this context, this study aimed to evaluate the efficiency of different anodes on the electrochemical removal of EE2 from water samples. The anodes herein used, were aluminum, for electrocoagulation, and graphite, copper and titanium, for electro-oxidation. The best result was obtained for the titanium anode, which removed 86.21% in 40 minutes of treatment. It is concluded that the electro-oxidation is an alternative method, low cost and effective for remediation of estrogen ethinylestradiol.

Key words: endocrine disruptors; estrogen; electrocoagulation; electro-oxidation.

INTRODUCTION

Some chemicals present in the environment because of rivers and soil pollution, are able to interfere with the normal function of the endocrine system of humans and animals [1]. These compounds are called endocrine disruptors (EDs) or micro-contaminants, and are constantly detected in the concentration of ng/L to µg/L in water and effluents [2].

The main contributors EDs for estrogenic activity are sex hormones such as estrone (E1), estradiol (E2) and ethinylestradiol (EE2). The EE2 is the principal synthetic hormone used in oral contraceptive formulations, hormone replacement therapy, treatment of osteoporosis, menstrual disorders and cancer prostate [3].

In trials with fish exposed to concentrations of the order of ng/L of EE2 was observed hermaphroditism, reduced amount of eggs and sperm production, decreased quality of gametes, feminization of male fish, reduced fertility and fecundity, besides behavioral changes [1,4,5].

The sewage treatment plants do not have effective methods of removal of EDs, including EE2, therefore, many end up reaching surface water without suffering changes [2,6,7].

The advanced chemical oxidation processes for the removal of micropollutants are characterized by high efficiency, but have the disadvantage consumption of chemical oxidants. In this context, the electrochemical remediation methods have gained prominence. Electrochemical remediation methods are an alternative to remove the EE2 from water. Among them, the electro-oxidation and electrocoagulation, which have advantages such as environmental compatibility, versatility, automation, low cost, high efficiency removal, security and energy efficiency [8,9].

However, the removal rates depend mainly on the efficiency of the electrode material used as anode for electrocoagulation / electro-oxidation of a specific pollutant on certain electrolytic condition.

The electrocoagulation involves the electrogeneration of coagulants from sacrificial electrodes, *i.e.* aluminum or iron anodes, whose electrodissolution leaches metallic ions that in an appropriate pH, create metal hydroxides that undergoes physico-chemical interactions with pollutants, leading to their flocculation, coagulation or precipitation [8,10].

The generation of metal ions occurs on the anode (1) forming metal complexes in acid (2) or alkaline (3) medium. At the cathode occurs the release of hydrogen gas in acidic (4) or alkaline (5) medium.

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \quad (1)$$
$$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (2)$$
$$Al^{3+}_{(aq)} + 3OH^- \rightarrow Al(OH)_3 \quad (3)$$
$$3H^+ + 3e^- \rightarrow 3/2H_{2(g)} \quad (4)$$
$$3H_2O + 3e^- \rightarrow 3/2H_{2(g)} + 3OH^- \quad (5)$$

In the electro-oxidation process the organic compounds can be removed by direct electrolysis, when electrons are transferred directly to the surface of the anode, or indirect electrolysis, when reactive oxygen species under proton and electron transfer mechanisms promote the pollutant degradation. In the indirect electrolysis, the role of electro generated hydroxyl radical, $OH^\bullet$, promoting electrochemical mineralization of pollutants is the main target. Meanwhile, the formation of other "reactive oxygen species" leading to the conversion of pollutants into biodegradable compounds has relevant secondary function (Figure 1).

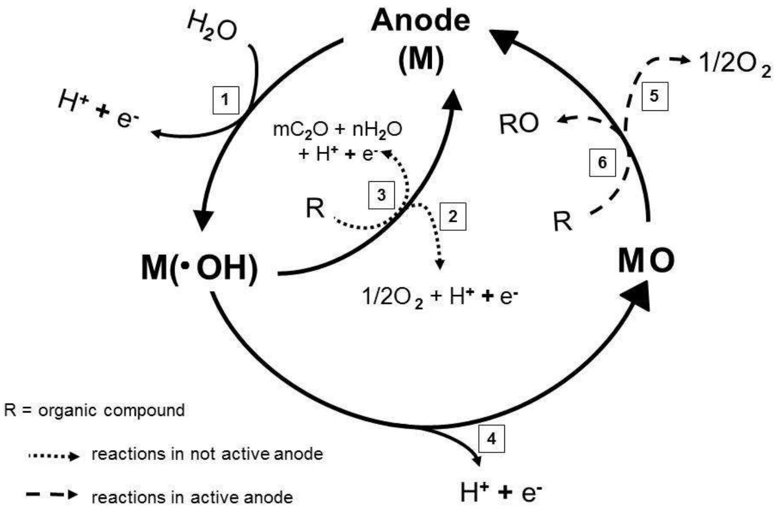

Figure 1. Electrochemical remediation mechanisms: 1) electrolysis of water and generation of radicals $OH^\bullet$; 2) evolution of oxygen by electrochemical oxidation radicals $OH^\bullet$; 3) organic compound oxidation (R) by $OH^\bullet$ radicals till mineralization; 4) superoxide formation in the electrode (MO); 5) oxygen evolution by the chemical decomposition of superoxide MO; 6) Electrochemical conversion of R, means MO

When, the $OH^\bullet$ is physically adsorbed on the anode surface, it is the so-called "non-active" electrode. Such weakly bound $OH^\bullet$, a highly oxidizing agent, can then react with organic (R) at bulk medium, hence generating organic radical ($R^\bullet$), which in presence of oxygen undergoes oxidation reactions. In the case of "active" anodes the interaction of $OH^\bullet$ onto electrode surface is stronger, producing superoxide MO. This resulting MO anode promotes the direct oxidation of pollutants [7,9,11]. The main anodic materials that have been used in electrochemical oxidation processes of water treatment are Pt, IrO_2, RuO_2 PbO_2, Ti/SnO_2 and Boron Doped Diamond (BDD) [11]. For instance, BDD and titanium coated with SnO_2 were already used on the electrochemical remediation of estrogens [6,9,12,13]. Yet, the cost of high efficiency anodes drives the search for cheaper alternatives to widen the study of electrochemical remediation application on different micropollutant targets. An alternative source for anodes is carbon graphite rods removed from ordinary batteries. Besides providing a low-cost material, the graphite salvaged from such used batteries has high purity [14]. Aluminum and copper are the main constituents of wires used in construction, being commercially accessible and having good conductivity. On the other hand, though Titanium has no low cost "appeal", it has broad applicability on the development of more expensive high efficiency electrodes [15,16].

Therefore, this study aimed to carry out electrochemical remediation EE2 with alternative and affordable anodic materials, namely graphite rod, aluminum, copper and titanium wires, in batch aqueous systems.

EXPERIMENTAL SECTION

Reagents

The pattern of 17α-ethinylestradiol hormone with a purity of 98.90% was purchased from Zhejiang Xianju Pharmaceutical Co., Ltd. All other reagents used were analytical grade and solutions were prepared with distilled water.

Electrodes

To perform the electrocoagulation aluminum (Al) electrodes were used for both the cathode and to the anode. For the electro-oxidation was used steel electrode as cathode and graphite (C) electrodes, copper (Cu) and titanium (Ti) as anodes.

The metal electrodes had 10 cm in length and 0.3 cm diameter when linearized approximately 4.5 cm in spiral shape and total area around 9.56 cm^2. Already the graphite electrode had 4.5 cm in length and 0.7 cm in diameter in cylindrical format and total external area around 10.66 cm^2.

Electrochemical treatment system

The experiments were performed in a beaker containing a total volume of 20mL solution, sodium acetate buffer 0.05 M pH 5 or phosphate buffer 0.05 M pH 7 and a EE2 solution at different concentrations (2-4 mg/L), prepared in 5% ethanol.

The electrodes were 4 cm away and applied voltages of 2.5, 5 or 7.5 V through an adjustable DC power supply (HF-30035, Hikari). Treatments were performed in triplicate in time of 10, 20 and 40 minutes with magnetic stirring. Figure 2 shows the scheme of the electrochemical treatment.

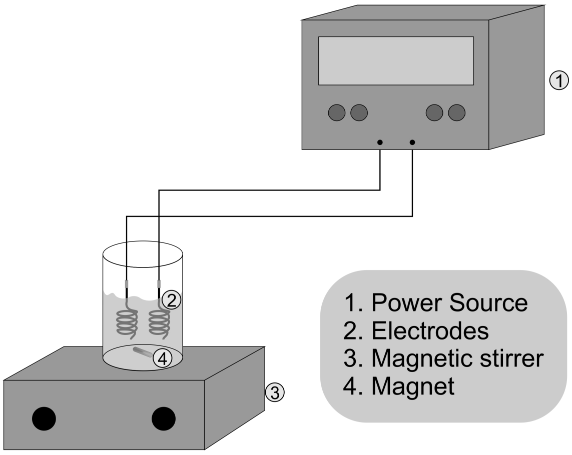

Figure 2. Diagram used for electrochemical treatment

Chromatographic analysis

The EE2 solutions before and after the electrochemical treatment were analyzed by high-performance liquid chromatography (HPLC) to determine the concentration of the hormone. a chromatographic LC-DAD Waters Alliance system comprising pump Waters 2695 detector and Waters in 2996, operated by Empower software was used. The samples were filtered through Millex filter microporus of 0.45 μM (Millex) before being analyzed

Regarding the chromatographic conditions were used: Prodigy ODS (3) (150 x 4.6 mm) column, wavelength 280 nm, HPLC grade acetonitrile mobile phase and purified Milli-Q water at 1:1 ratio with flow 0.6 mL/min, temperature of 30°C and injection volume of 10 μL sample. A calibration curve was obtained to determine the actual concentration of each solution before the treatment, besides the detection and quantification limit.

Analysis of the metals are released during the treatment

The metal analysis released by the electrodes during electrochemical remediation were carried out by optical emission spectrometry with inductively coupled plasma or Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) in a spectrometer PerkinElmer - model 7300DV whit hydride vapor generator.

Statistical analysis

The statistical data analyzes were performed using the BioEstat® program, version 5.3. The statistical differences between groups were determined by ANOVA and Tukey's test was considered statistically significant $p < 0.05$

RESULTS AND DISCUSSION

The electrochemical reactions are heterogeneous processes driven mostly by complex combination between electrode material and electrolyte composition factors. Therefore, among the myriad of experimental parameters that may be involved on the efficiency of electrochemical remediation, the electrode material deserve special attention.

In turn, the neutral pH and low ionic strength were chosen in order to mimic real situations [8]. Thus, all studies were conducted in batch conditions with magnetic stirring, by using 20 mL of electrolyte medium, which consisted in 0.05 M sodium phosphate buffer, pH 7 solution. The initial burden for EE2 was of 2.94 mg/L, whereas the applied potential was fixed in 5 V.

The results concerning the efficiency of electrochemical removal of EE2 at the different affordable electrodes, herein investigated, are presented in Figure 3.

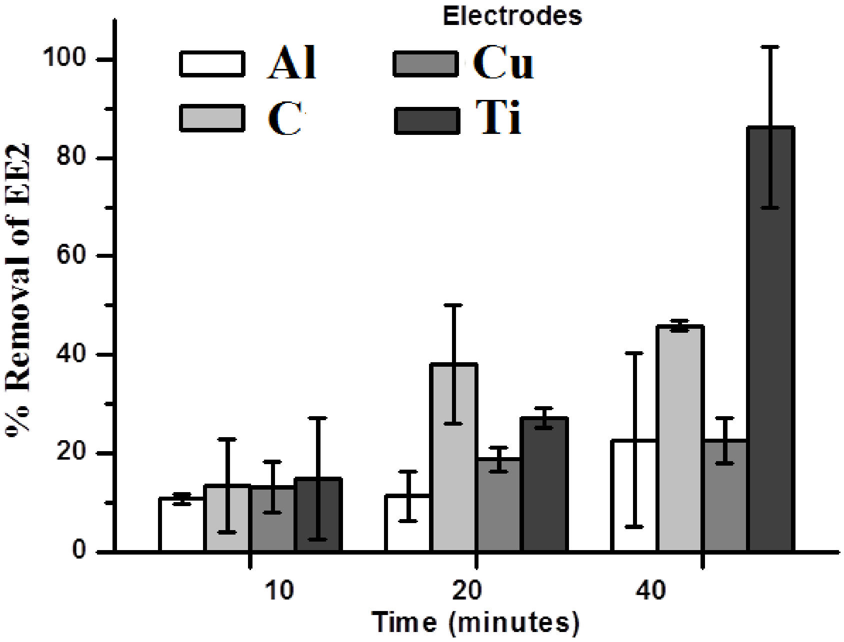

Figure 3. Electrochemical removal of EE2 with different anodic materials as a function of time (10, 20 and 40 min)

The efficiency of Al electrodes for EE2 removal, which occur by electrocoagulation mechanism, was the lowest, ranging from 10.77% to 22.74% (Figure 3).

At similar experimental conditions, the antibiotic tetracycline was almost completely removed by using aluminum electrodes, in only 20 minutes [10]. Also, the Al anode was applied on the electrochemical remediation of pharmaceutical effluents, presenting higher efficiency, 24% reduction of Chemical Oxygen Demand (COD), 35% of Biochemical Oxygen Demand (BOD) and 70.25% of color removal in 25 minutes. Therefore, the efficiency of anodes for electrocoagulation relies upon the type of chemical compound under treatment.

In turn, graphite, one the most widely used electrode material, though it is prominently used in electroanalysis, has been also applied on the electrokinetic soil remediation [19-21], as well as, at electrochemical removal of pesticides in contaminated aquatic systems [22,23]. The main advantage of C electrodes is its relative low cost [24].

Moreover, the electrochemical EE2 removal, using graphite anode reached 45.94% in 40 minutes (Figure 3). Such results are even better than the one observed for other treatment systems based on C electrodes [25, 26]. Moreover, it must be highlighted the null cost of our salvageable device.

Regarding the Ti anode efficiency, when applying 5 V for 40 minutes it was possible to remove 86.21% of EE2.

A Ti/PbO_2 anode reached the total organic removal of 51.4% in 30 minutes of electrolysis, also at 5 V [27], whereas a Ti/RuO_2 anode, allowed the complete removal of phenol in 50 minutes under applied potential of 16.7 V [28]. Thus, the feasibility of our commercially available system is reinforced by its lower effective area, less than 8 cm^2, in comparison to the 30 cm^2 of Ti/PbO_2 [27] and 12 cm^2 of Ti/RuO_2 [28].

The Table 1 presents other good results obtained for electrochemical remediation of estrogens at different electrode materials.

Table 1. Hormone electrochemical removal

Electrode (Area)	Burden (mg/L)	Remediation Conditions	Removal rate	Reference
Ti (7.61 cm^2)	2.94	40 min/5 V	86.21% of EE2	This study
GCGR (2000 cm^2)	0.001	180 min*/0.5 and 1 $mA.cm^{-2}$	98% of E1, E2 and EE2	[6]
BDD (4 cm^2)	0.5	40 min/25$mA.cm^{-2}$	100% of E2	[9]
BDD (19 cm^2)	0.1	7 min /2.1$mA.cm^{-2}$	100% of EE2	[12]
Ti/SnO_2 (6 cm^2)	2	60 min/10$mA.cm^{-2}$	~100% of EE2	[13]

*Note: GCGR = Glassy carbon granules in reactor; BDD = Boron Doped Diamond; E1 = Estrone; E2 = Estradiol; EE2 = Ethinylestradiol, *Flow condition*

On the other hand, as expected the worst performance was obtained by using Cu anode. The EE2 removal with this anode ranged between 13.14% and 22.55% for the time of treatment herein investigated (Figure 3).

Moreover, it was noticed great vulnerability to corrosion process. Indeed, the treated solution get blue color, this indicated the presence Cu^{2+} ions. Indeed, it was possible to detect 148.25 mg/L of this metal after 40 minutes of treatment (Table 2).

In order to check the stability of the electrode materials, the leaching of metallic ions were investigated by ion chain plasma spectrometry, ICP-OES after each treatment (Table 2).

Table 2. Metal quantified by ICP-OES analysis after electrochemical treatment of an aqueous solution containing EE2 hormone (2.94 mg/L)

Electrodes	Al^0/Steel Al (mg/L)	Cu^0/Steel Cu (mg/L)	Ti^0/Steel Ti (mg/L)
10 min	0.030 (± 0.010)	64.417 (± 6.869)	<0.08
20 min	0.040 (± 0.014)	127.375 (± 9.878)	<0.08
40 min	0.029 (± 0.003)	148.250 (± 10.136)	<0.08
Control	0.0270 (± 0.008)	0.0233 (± 0.009)	<0.08

Besides the best response of Ti anode, it was not possible to determine such metal ion in solution even after 40 minutes of treatment (Table 1).

In order to evaluate other parameters that may influence the efficiency of electrochemical remediation, namely the pH, applied potential and initial burden of pollutant, the further assays were carried out only with Ti anode and steel cathode.

Since, electrochemical reactions can leads to the production of insulating films over the electrode surface, thus requiring greater over potentials, the effect of initial burden, on the removal efficiency must be evaluated. In this study, the hormone concentrations ranged from 2.62 to 3.21 mg/L, being observed that at higher initial burden the effective removal decreases for a fixed applied potential (Figure 4A). This result is consistent with insulating reactions over the electrode surface that are higher at higher concentrations. Such, polymeric reactions are higher at acidic than neutral or alkaline pH [29]. Moreover, at neutral pH, the water electrolysis to generate hydroxyl radicals is favored, since they have equivalent amounts of H^+ and OH^- ions in the reaction medium, as shown in equation:

$$\text{Anode} + H_2O \rightarrow \text{Anode}(OH^\bullet) + H^+ + e^-.$$

In turn, at acid pH the reaction is hampered, since at larger amount of H^+, the equilibrium is shifted, decreasing the production of hydroxyl radical.

Regarding the applied potential, the higher the overpotential, the higher the electrochemical oxidation (Figure 4C).

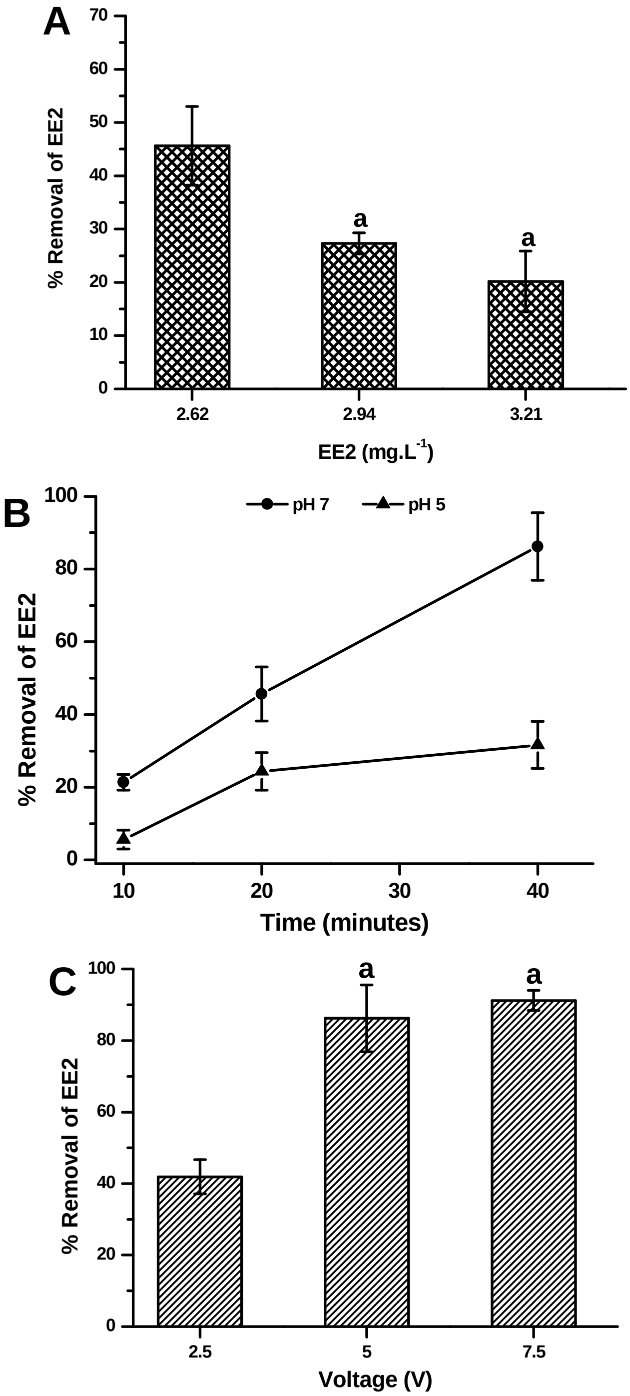

Figure 4. Effect of concentration load (A), pH (B) and applied potential (C) on the electrochemical removal efficiency of EE2 at Ti anode. Same letters are not statistically different from each other at 5% by Tukey's test

The anodic removal percentages for EE2 concentration load of 2.62, 2.94 and 3.21 mg/L were of 45.64%, 27.3% and 20.17% respectively (Figure 4A). Similar profile was observed for Ti/SnO2 [13] and BDD [9] anodes, in which at higher concentration loads of EE2 the electrochemical remediation efficiency have fallen deeply, thus being in agreement with our prior arguments [29].

The efficiency of EE2 removal was higher at neutral pH, reaching 80%, whereas in slightly acidic environment it not exceeds 22% (Figure 4B). It is easily explained by the fact that the anodic oxidation, as well as, the hydroxyl radical is hampered at higher protonated medium, whereas insulating reactions are favored at this condition [29].

The removal efficiency of Ti anode for EE2 increased twice, when the applied potential changed from 2.5 to 5 V. Nevertheless, the efficiency increment decelerates for higher applied potentials, exhibiting only a slight enhancement for 7.5 V, which was statistically insignificant (Figure 4C). Therefore, taking into the low energetic consume, the applied potential of 5V may be the best choice. Indeed, similar assumptions were obtained for similar electrodes [30].

CONCLUSION

The EE2 is an electroactive molecule and can be removed by electrochemical processes, such as electro-oxidation or electrocoagulation with Ti, C and Al anodes. Whereas, the Ti anode, at neutral pH, applied potential of 5 V and under the lowest load concentration of EE2 (2.62 mg/L) presented the higher efficiency, being almost complete after 40 minutes of electrolysis.

Thus, it is concluded that the electro-oxidation is an alternative and effective method for remediation of EE2, opening the perspective of application to other estrogens.

Acknowledgements
The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for funding and scholarships.

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