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Short Communication

Electrochemical Removal of Algestone Acetophenide and Estradiol Enanthate in Real Industrial Wastewater

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Contaminants removal from industrial effluent is a major environmental concern. In this context, Algestone Acetophenide and Estradiol Enanthate are synthetic sex hormones widely used in the manufacture of contraceptives, whose presence in waterbodies may lead to environmental hazard. Given that so far, the methods employed in the removal of these drugs have presented limited efficiency or high implementation costs, the present work presented an electrochemical reactor composed by 32 carbon steel electrodes (1728 cm^2), which was employed in a real scale model to remove these synthetic hormones in an industrial pharmaceutical effluent. After 60 minutes the removal efficiency of the hormones Algestone Acetophenide and Estradiol Enanthate was of 88.9% and of 91.8% respectively, with low energy consumption (< 0.742 $kWh.m^{-3}$). Physicochemical parameters such as color, turbidity, Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) also showed good removal efficiency too (> 50%), which implicates that the method herein depicted may be a valuable alternative to promote the removal of these contaminants in industrial wastewater.

Keywords: Synthetic Hormones, Environmental Contamination, Electrocoagulation Remediation, Mass spectrometry, Q-TOF

1. INTRODUCTION

Water contamination is a significant issue concerning anthropogenic environmental impacts [1]. In this context, drugs are noteworthy contaminants since their development aims both potency maximization and chemical stability. These features allow these compounds to remain in the environment for prolonged periods [2-4], being detected in water bodies worldwide at concentrations ranging from ng.L^{-1} to µg.L^{-1}. These characteristic raises concerns about possible environmental hazards, due to their potential to disrupt animal metabolism [2-3-5-6-7].

Urban and industrial wastewater is known to contain significant amounts of drugs. Conventional treatment systems are moreover not designed to remediate the resilient and persistent nature of many of these compounds [8-10]. Concerning most commonly used technologies of activated sludge, biotransformation is shown as an essential but insufficient step in the removal of hormones and antibiotics [11]. There have been many attempts to regulate both treatment and emission of these substances, however, they have received little attention in most countries around the world [12]. The US Environmental Protection Agency (USEPA) and the European Union has included some medicines in its list of contaminant and monitored substances [13-14]. These efforts indicate that medicines are considered an environmental threat for the future, and there is a clear need for the development of advanced treatment technologies to efficiently remove these compounds [15-16].

Electrocoagulation (EC) is a simple treatment method that uses an electric current to produce various metallic ions in solution. This event triggers the formation of hydroxo-metallic coagulants, while simultaneously producing hydrogen at the cathode, which facilitates pollutants removal by electroflotation [17-18]. The mechanism for organic pollutants removal is fairly complex, involving events such as complexation, load neutralization, entrapment, and adsorption. However, these events may coexist, henceforth increasing removal efficiency. The predominance of each mechanism depends on the nature of the organic pollutant (load, size, functional groups, hydrophobicity, etc.) as well as the type of coagulant and its dosage [19-21].

EC offers many advantages over conventional treatment methods, such as *in situ* coagulant generation, which neutralize excess of chemicals and prevents secondary pollution. This method allows moreover small equipment and easy operation, low energy consumption, high efficiency, shorter hydraulic detection time and smaller production of sludge [16-18-22]. EC has been moreover successfully employed in the treatment of wastewater from textile factories, surfactants, food, semiconductors, chemical and mechanical polishing, restaurants, heavy metals, tannery, cellulose, and paper, etc.[23-25]. However, most assays cited in the literature were performed in laboratory scale reactors and few have analyzed kinetics, modeling, cell design, cost analysis, integration with existing technologies, scale up and industrial applications, demonstrating a systematic lack of reactor design approach and scale-up [26-27].

With a EC pilot reactor and under optimal conditions, Bassala et al. [28] achieved an efficiency of <80% removal for Chemical Oxygen Demand (COD), phosphate, Total Suspended Solids (TSS) and turbidity (TBD). With an industrial reactor of 1m^3.h^{-1} capacity, Valero et al. [29] reached an efficiency of removal <74% for Total Organic Carbon (TOC), COD, Biochemical Oxygen Demand (BOD), SST and TBD. The method has been successfully applied in the remediation or pretreatment of some synthetic and industrial pharmaceutical effluents also [30], however, no industrial scale study for sex hormone removal has been found in the literature.

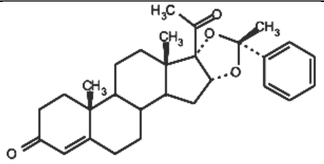
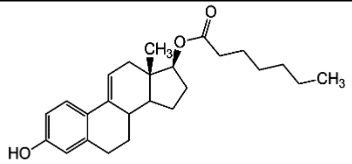
Therefore, the objective of this work was to investigate EC removal of synthetic hormones Algestone Acetophenide and Estradiol Enanthate from industrial wastewater on a real scale.

2. MATERIALS AND METHODS

2.1. Wastewater description

Wastewater samples were collected from a local pharmaceutical industry located in Goiânia-Brazil immediately after the productive steps dedicated to hormonal medicines production. The visual aspect of the wastewater had a whitish hue (Figure 1). The physicochemical characteristics of effluent samples are summarized in Table 1.

Table 1. Physicochemical properties of effluent from hormone production plant.

	Acetophenide Algestone[31]	**Estradiol Enanthate**[32]
Structure		
Solubility (mg.L^{-1}) (Estimated by Log K_{ow})	0.02864	0.006894
Log K_{ow}	5.53	7.40

For this study, no additions of chemical compounds were made for correction purposes.

2.2. Electrocoagulation at industrial scale

2.2.1. Electrochemical reactor

The electrochemical reactor (model C320-1.0, maximum flow of 1.0 m^3.h^{-1} and dimensions 3233 x 1104 x 1082 mm) was designed by AQUA ETE Tecnologia em Efluente Ltda. (Aparecida de Goiânia-GO, Brazil) presenting industrial scale system capacity of 0.25 to 5.0 m^3.h^{-1} (Figure 1).

The EC system was pre-molded and fixed on a metal support, which was installed next to the passage boxes of raw effluent outside the productive area. The effluent was pumped continuously into the lung tank (equalization tank, c.a. 200 L capacity).

A second pump installed in the lung tank launched the raw effluent into the electrolytic box.

The effluent was received in the electrolytic box through a gutter and by gravity directed to two EC chambers where 32 electrodes were arranged.

Figure 1. Industrial scale EC treatment system **(**https://www.aquaete.com.br/produtos)

The 32 electrodes of the EC system consisted of two sets of 16 parallel units (one set for each chamber of the box), which were made of 1020 carbon steel. Each electrode presented 20 x 27 x 6.35 cm and 1728 cm^2 total surface (Figure 2).

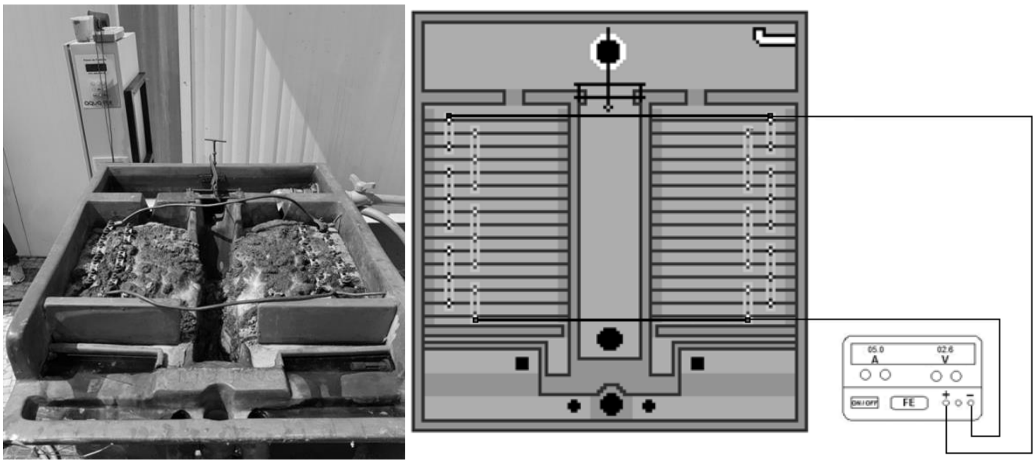


Figure 2. The industrial scale electrolytic case for flow up to 1 $m^3.h^{-1}$.

2.2.2. Operational electrocoagulation conditions

The effluent circulated in the two EC box areas with downward flow, while the electric current passed continuously through the electrodes. The flocculated material, overflowed at the top of the chambers was led to the tailing tanks, while the treated liquid part was directed for final separation by sedimentation.

The sediment flakes in the sedimentation tank and the mainstream tailings were directed to a new treatment in the electrolytic box, while the treated effluent was collected through a pipeline for analysis and evaluation of the system efficiency.

The initial treatment conditions were: electric current 15.4 A; applied potential of 26.2 V. Temperature and electric parameters were monitored during the treatment at 0 and 60 minutes. The temperature changing were monitored in an Infrared Temperature Tester Thermometer GM300 (Benetech, Shenzhen Jumaoyuan Science And Technology Co., Ltd, Shenzhen, China), whereas the current and potential with a Digital Clamp AC/DC Voltmeter F203 (Chauvin Arnoux Metrix, France).

Electrical conductivity, color, BOD, COD, pH, and turbidity were monitored in this study since they are good indicators of wastewater quality. The tests were performed according to the techniques recommended by the Standard Methods for the examination of Water and Wastewater [33].

2.2.3. Electrode efficiency

The efficiency of the EC process is based on electrogenerated iron ions and electrode durability, which was theoretically deduced by Faraday's law (Eq. 1) [34]. In this sense, Faraday's Law was used to calculate the mass (m) of iron generated electrolytically, considering the experimental conditions of I = 15.4-28 A (current intensity), t = 3600 s (time of EC process), M = iron molar mass (55.845 $g.mol^{-1}$) as well as the Faraday's Constant (F = 96486 $C.mol^{-1}$) and cation charge (z = 2^+ and 3^+).

$$m = I.t.M / z.F \qquad \text{Eq. (1)}$$

2.2.4. Electrical energy consumption

Electrical energy consumption is the major operating cost associated with EC process. Therefore, it is important to optimize this parameter in order to reduce economic and environmental impacts [34]. The electrical energy consumption (EEC) was calculated regarding $kWh.m^{-3}$ using Eq. (2) [35].

$$EEC = U.I.t / V \qquad \text{Eq. (2)}$$

Where U is the potential difference (V), I is the current intensity applied to the process (A), t is the reaction time (h) and V is the volume of treated effluent (m^3).

2.3. Mass Spectrometry Analysis

Mass spectrometry (MS) analysis was carried out in a mass spectrometer microTOF III (Brucker Daltonics, Bremen, Germany) equipped with a commercial electrospray ionization (ESI) source (Brucker Daltonics, Bremen, Germany). Samples were methanol-diluted to a (1:1000) ratio, followed by acidification with 0.1% formic acid. The resulting solution was directly injected with a flow rate of $4\mu L.min^{-1}$; all analyses were performed in the positive full scan mode (m/z 100–1000). ESI(+) source conditions were as follows: nebulizer nitrogen gas temperature and pressure of 2.0 bar and 200 °C, capillary voltage of −4 kV, transfer capillary temperature of 200°C; drying gas of $4L.min^{-1}$; end plate offset of −500V; skimmer of 35V and collision voltage of −1.5V. Each spectrum was acquired using 2 microscans per second during one minute.

The resolving power (m/Δm50%) was of 16.500,00, where Δm50% is the peak full width at half-maximum peak height). Mass spectra were acquired and processed with Data Analysis software (Brucker Daltonics, Bremen, Germany).

A quantification method by MS was also designed focusing the assessment of industrial scale treatment system efficiency. To avoid matrix effect, the method of standard addition was used to construct the calibration curves of algestone acetophenide and gestodene. Briefly, 1 mg.mL^{-1} algestone acetophenide and gestodene methanolic stock solutions were prepared and subsequently diluted to concentrations: 0.5; 2.0; 3.5; 5.0; 6.5 mg.L^{-1} in effluent water sample. Finally, 0.1% formic acid was added to 500μL of each analytical solutions, in order to improve the ionization process.

Chemicals used were all of ACS grade and purchased from Sigma-Aldrich, they were used without any further purification. MS and HPLC (High Performance Liquid Chromatography) grade solvents were purchased from J.T. Baker

3. RESULTS AND DISCUSSION

3.1. Physicochemical data and removal efficiency

The test was performed at ambient temperature, with a system connected directly to the local power grid. The electric conditions in the treatment system are displayed in Table 2.

Table 2. Electrical conditions during the test with the industrial system.

Time (Min)	Temperature (°C)	Voltage (V)	Current (A)
0	28	26.2	15.4
60	30	26.5	28.0

Table 3. Physicochemical parameters evaluated during the industrial test.

Parameter	Treatment time (min)		Units
	0	60	
Electrical conductivity	515	417	μS.cm^{-1}
Color	1110	345	mg.L^{-1} $CaCO_3$
BOD	4111	1158	mg.L^{-1} O_2
COD	7125	3395	mg.L^{-1} O_2
pH	5.95	10.68	–
Turbidity	837	7.7	NTU

In an EC experiment, the electrode or electrode array is generally connected to an external source of energy. The amount of dissolved or deposited metal is dependent on the amount of electricity passing through the electrolytic solution. Using Eq. (1), the amount of coagulant delivered to the solution varied between 16.04–29.17 g of Fe^{2+} and 10.69–19.45 g of Fe^{3+}. A variation of voltage and current was observed, which occurred due to a variation on the composition of effluent during the assay, as shown in Table 3. In addition, these parameters were monitored to assess the EC process.

Due to the constant flow and the hydraulic retention time were obtained good results concerning the removal efficiency of COD and BOD (71.80% and 52.30% respectively). In the same sense, good removal efficiency was achieved through color and turbidity (68.92% and 99.08% respectively). With the more current application, the efficiency BOD and COD removal increases. This is attributed to the fact that at high current densities, the dissolution of Fe^{2+} and Fe^{3+} ions increases according to Faraday's Law.

Carbon steel electrodes release iron ions that have a valence load higher than others ions (i.e. Al^{3+}, Zn^{2+}, Mg^{2+}), favoring the coagulation process with lower concentration of coagulant [20]. Steel electrodes are also among the preferred for EC because they are more cost-effective and are the type marketed by the company Aqua ETE, partner of this research.

Table 4 shows other results obtained in the treatment of effluents of different origins by EC.

Table 4. Different EC study results (best conditions).

Wastewater	**Parameter**	***Initial Concentration**	**Electrodes**	**Removal eff. %**	**Reference**
Pharmaceutical Industry	COD	7125	Carbon steel	52.3	This study
	BOD	4111		71.8	
	Color	1110		68.9	
	Turbidity	837		99.1	
Industrial Estate	COD	873	Iron anode	91.7	[36]
Industrial Park	COD	231,8	Copper anode	89.0	[37]
	Color	-		97.0	
	Turbidity	203		91.0	
	COD	2202	Aluminum anode	50.0	[38]
	BOD	1030		46.0	
	COD	2202	Iron anode	70.0	
	BOD	1030		70.0	
	COD	2202	Aluminum–Iron anode	69.0	
	BOD	1030		71.0	
Petroleum Refinery	COD	590	Iron anode	6.8	[39]
	COD	596	Aluminum electrode	63.0	[40]
	COD	3600–5300	Aluminum (anode & cathode)	97.0	[41]
Leachate of Oil-drilling Mud	COD	303	Aluminum electrode	95.0	[42]
Gas Refinery	COD	4000	Aluminum electrode	97.0	[43]

Drilling Fluids	COD	5000	Aluminum anode	89.0-100.0	[44]
Phenolic	COD	1118	Zn Anode / Stainless steel cathode	40.3	[34]
Metal Processing	COD	17312	Iron electrode	92.0	[45]
Pulp and Paper Mill	COD	2000	Iron anode	80.0	[46]
Tannery & Textile Industry	COD	-	Aluminum (anode & cathode)	82.2	[47]
	COD	-	Iron (anode & cathode)	67.4	
	Turbidity	-	Iron (anode & cathode)	96.0	[48]
Textile	COD	1970	Fe-Al composite	90.0	[49]
	Color	200		100.0	
Palm Oil Mill	COD	50000	Aluminum electrode	57.6	[50]
Almond Industry	COD	5300	Aluminum & iron (Alternating anode/cathode)	81.0	[29]
	BOD	1000		80.0	
	Color	18000		99.6	
	Turbidity	3200		99.4	
Dairy	COD	6114	Aluminum anode	98.8	[51]
	BOD	2919		97.9	
	COD	7560	Aluminum electrode	80.0	[52]
	COD	780	Aluminum electrode	80.0	[28]
	Fosfate	28.6		98.0	
	SST	198		100.0	
	Turbidity	440		100.0	
Food Industry	COD	-	Aluminum (anode & cathode)	98.8	[53]
	BOD	-		97.9	

* Unit: COD, BOD, Color, Fosfate and SST = mg.L^{-1}; Turbidity = NTU.

From the physicochemical point of view, these results show that the industrial prototype marketed by Aqua ETE is very promising in the removal of synthetic hormones from industrial effluent. This fact could be supported by mass spectrometry analysis of Algestone Acetophenide and Estradiol Enanthate degradation, where were obtained good efficiency, 88.9% and 91.8% respectively, being crude effluent (dark gray) and treated effluent (light gray) (Fig. 3).

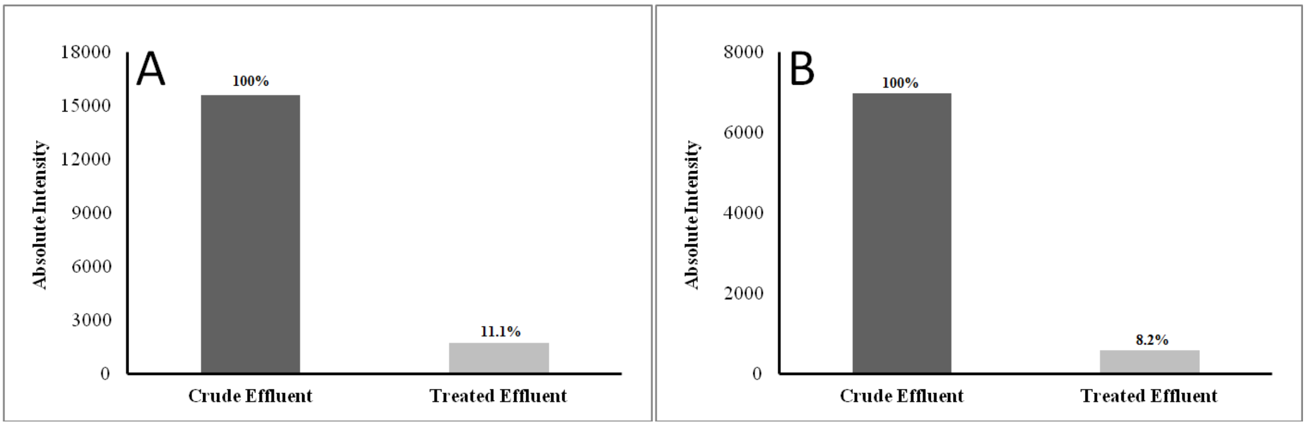


Figure 3. The removal efficiency of Algestone Acetophenide (88.9%) **(A)** and Estradiol Enanthate (91.8%) **(B)**. Crude effluent (dark gray) and treated effluent (light gray).

Table 5. EC studies for drug removal (best conditions).

Compound	**Removal eff. %**	**Electrodes**	**Time (min)**	**Voltage, Density or Intensity of Current**	**Reference**
Algestone Acetophenide Estradiol Enanthate	88.9 91.8	Carbon steel	60	26.5 V	This study
Estrone 17β-Estradiol 17α-Ethinylestradiol Estriol	61.0 63.0 64.0 56.0	Aluminium	6	98.0 V	[55]
Oxytetracycline Hyd.	93.2 87.7	Iron Aluminium	120	20.0 mA.cm^{-2}	[56]
Diclofenac Carbamazepine Amoxicillin	90.0 70.0 77.0	Aluminium	15	0.5 mA.cm^{-2}	[57]
Tetraciclina	>99.0	Aluminium	15	0.1 A	[58]
17α-Ethinylestradiol	22.74	Aluminium	40	5.0 V	[59]
Ampicillin Doxycycline Sulfathiazole Tylosin	3.6 ± 3.2 ~100.0 3.3 ± 0.4 3.1 ± 0.3	Low-carbon steel	36	10.0 ± 0.2 mA	[60]
Ciprofloxacin	~100.0	Iron	20	15.0 mA.cm^{-2}	[61]

These results can be corroborated with the quantification method by MS. The initial and final concentrations were calculated, and were 4.58 ppm ($y = 0.0758x + 0.3487$; $r^2 > 0.93$) and 0.98 ppm ($y = 0.064x + 0.0063$; $r^2 > 0.97$), respectively.

Their physicochemical properties can explain the high removal efficiency of the hormones. The octanol-water partition coefficient (K_{ow}) describes the partitioning behavior of a compound between the aqueous and organic phases. Higher K_{ow} values implicate in a higher probability of being removed from the solution [54-55].

Most synthetic sex hormones are hydrophobic and have similar log K_{ow} values (> 3.0). Since these hydrophobic compounds are readily adsorbed to the sludge, sorption plays a vital role in their removal from aqueous phase. The two compounds herein studied have high log K_{ow} (5.53 and 7.40), and in this sense, they are prone to bind to the flocculant produced during EC treatment.

In literature, there are few reports of medicines remediation via EC and to our knowledge, this is the first study to test the removal of synthetic hormones in industrial scale. Table 5 shows the results of this and other EC drug removal work.

A result between 0.403 and 0.742 $kWh.m^{-3}$ was obtained for this process, which is within the range of values referred in the literature for the energy consumption with EC systems lying between 0.002 and 58 $kW\ h.m^{-3}$ [34-35].

The EEC can be reduced by a proper design that takes into account the solution conductivity, the distance between the electrodes, the current and the electrode surface area. With a minimal distance between the electrodes, the potential required for the process is expected to reduce, therefore minimizing energy consumption. Furthermore, electrode incrustation is reduced by alternating the polarity [62].

4. CONCLUSION

In this work, the real scale electrochemical removal of two synthetic sex hormones was conducted. After 60 minutes of EC, 88.9% of Algestone Acetophenide, 91.8% of Estradiol Enanthate, 68.9% of color, 71.8% of BOD, 52.3% of COD and 99.1% of turbidity of the pharmaceutical effluent were removed. In this sense, EC on an industrial scale is an effective, cheap treatment process and may be applicable in the degradation of other compounds. Nonetheless, this is the first study of the removal of synthetic hormones on industrial scale and the protocol herein used may provide a basis to further investigations.

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