Electrochemical Removal of Hydrocortisone from Aqueous Environments Using Aluminum Electrodes

HASHEM ALAANI[1]*, SHAHIR HASHEM[1] and FRANCOIS KARABET[1]

[1]Department of Chemistry, Faculty of Science, Damascus University, Damascus, Syria.
*Corresponding author E-mail: hashim.ani85@gmail.com

ABSTRACT

In this work, electrochemical removal of hydrocortisone, a steroid hormone, from water using aluminum electrodes was investigated. The effects of many experimental parameters such as current density, electrolysis time, initial concentration of hydrocortisone, initial pH, electrolyte type and concentration, and distance between electrodes were studied. Moreover, the sludge formed was characterized using high performance liquid chromatography (HPLC) and X-ray fluorescence (XRF). The electrical energy consumption was used to evaluate the economic feasibility of the electrochemical removal process. Results showed that the use of supporting electrolyte containing chloride ions had enhanced the removal efficiency due to the indirect electro oxidation by chlorine and hypochlorite generated electrochemically. Results demonstrated that the electrochemical treatment was simple, efficient, and cost effective method for removal of hydrocortisone from aqueous environments.

Keywords: Electrochemical removal, Hydrocortisone, Aluminum electrodes, Energy consumption, Aqueous environments.

INTRODUCTION

Hydrocortisone (See Fig. 1)[1] is a steroid hormone produced by the adrenal cortex[2]. Its synthetic counterpart is used as a medication for treating asthma, inflammation, allergy, multiple sclerosis, and skin conditions[3,4].

Steroid hormones are classified as Endocrine Disrupting Compounds (EDCs)[5,6]. EDCs may cause serious health effects in the organism[5,6,7] because they can mimic or block the normal hormones functions[5,6,7]. The exposure to these compounds may cause a decrease in male sperm count and increases in testicular, prostate, ovarian, and breast cancer[6,8,9]. Compared with all EDCs, steroid hormones have the greatest endocrine disrupting potency[6,8].

Humans and animals continuously introduce steroid hormones into the environment[6,9]. Concentrations of these hormones have been

detected in the fresh water bodies receiving effluent in North America, Europe, Japan, Brazil, and China[6,9]. The residues of the steroid hormones could find their way into the aquatic environment either by the excretions from humans and animals or by the remnants of the pharmaceutical industry.

During the past years, new methods have been developed for water purification. Electrochemical treatment is a simple, fast, efficient, and cost effective method for removal of pollutants from wastewater. Electrochemical treatment has been used for removal of various pollutants from aqueous solutions such as aromatic hydrocarbons[10], leachate[11], dyes[12,13,14,15], and other pollutants[16,17].
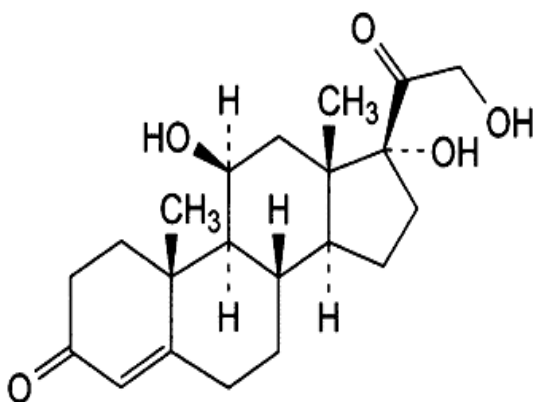

**Fig. 1. Chemical structure of hydrocortisone**

Generally, electrochemical treatment consists of many processes including electrooxidation, electrocoagulation, electroflocculation, and electro flotation. Electrooxidation of pollutants may be carried out directly (on the anode) or indirectly[18]. Indirect electrooxidation can occur, in the presence of high concentrations of chloride ions, by chlorine and hypochlorite generated due to the oxidation of chloride ions on the anode[11]. In the electro coagulation process, coagulants are *in-situ* generated by electro dissolution of a suitable sacrificial anode[10] usually made of iron or aluminum[14]. Coagulants neutralize the electrostatic charges of pollutants present in wastewater to become destabilized and separated from the aqueous phase[12,19]. In the electro flocculation, metallic hydroxide flocs are formed when metal ions, released from the metal electrodes, combine with hydroxide ions. These flocs have large surface

areas[11,12,13] and can adsorb pollutants[19]. Flocs are removed from the aqueous phase by sedimentation or electro flotation[12] (flotation of flocculated particles and pollutants by hydrogen and oxygen bubbles generated electrochemically)[10]. The main reactions occurring when using aluminum electrodes are[10,11,12,13,14,20]:
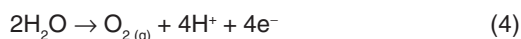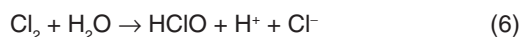
At the anode

$$Al \rightarrow Al^{3+} + 3e^- \tag{1}$$

At the cathode

$$3H_2O + 3e^- \rightarrow 3/2H_{2(g)} + 3OH^- \tag{2}$$
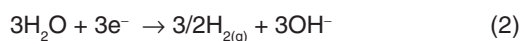
In the solution (at alkaline conditions)

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \tag{3}$$

Oxygen evolution reaction

$$2H_2O \rightarrow O_{2\,(g)} + 4H^+ + 4e^- \tag{4}$$

Chlorine and hypochlorite formation

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{5}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{6}$$

$$HClO \rightarrow ClO^- + H^+ \tag{7}$$

The aim of the present work is to evaluate the removal of hydrocortisone, a steroid hormone, from water by the electrochemical treatment using aluminum electrodes and to study the experimental parameters affecting the removal efficiency and the energy consumption.

MATERIALS AND METHODS

Chemicals

Hydrocortisone sample was obtained from Symbiotica, Malaysia, and used as received without further purification. Sodium chloride was purchased from Fisher Scientific, United Kingdom. Potassium chloride was purchased from SHAMLAB, Syria. Methanol and acetonitrile were of HPLC grade. Other reagents were of analytical grade. Water for injections[21] (WFI), that has a conductivity less than 1 µs/cm, was used for the preparation of solutions.

Electrochemical experiments

The electrochemical system consisted of 1 L glass beaker as a reactor and a locally made direct current (DC) power supply unit (220 V input, 0–40 V output). An appropriate mixing was provided by a magnetic stirrer (Cole-Parmer, Malaysia). Aluminum rectangular plates with dimensions of (6.5 cm height, 3 cm width, and 0.35 mm thickness) were used as electrodes and placed vertically in the reactor. The total active surface area of the electrodes was 24 cm². Fig. 2 shows the schematic diagram of the electrochemical system.
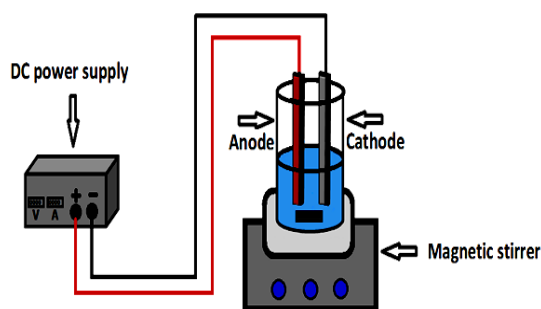

Fig. 2. The schematic diagram of the electrochemical system

Experiments were performed in batches[19] at room temperature. In each experiment, 600 mL of hydrocortisone solution (with a specific concentration) was placed in the electrochemical reactor. Concentrations of NaCl or KCl were added to the hydrocortisone solution in order to investigate the effect of electrolyte type and concentration on the removal efficiency and energy consumption. Initial pH of the solution was adjusted with 0.1 M NaOH and 0.1 M HCl solutions using calibrated pH meter (Orion 320, USA). During the experiments, the hydrocortisone solution was continuously mixed by the magnetic stirrer at about 200 rpm.

After each electrochemical experiment, the electrodes were washed, with the aid of ultrasound, first with 0.1M HCl solution and then with WFI. This process could overcome the electrode passivation[17] that caused by the oxide film formed on the electrodes during the electrochemical treatment [17,19].

At the end of each run, the solution was kept without mixing for about 20 min to let the flocs settling down[10]. Then the supernatant was filtered using filter paper (MN713, Macherey-Nagel, Germany) and prepared for the analysis.

The concentration of hydrocortisone before and after the electrochemical treatment was determined using UV/Vis. Spectrophotometer (CECIL, CE 7200, United Kingdom) at 248 nm as λ_{max}. A calibration curve was plotted between absorbance and hydrocortisone concentration and the linearity was found to be satisfactory ($R^2 = 0.9998$). Additional dilutions of the hydrocortisone solution were performed when needed. Fig. 3 shows the UV spectra of hydrocortisone before and after an electrochemical treatment.
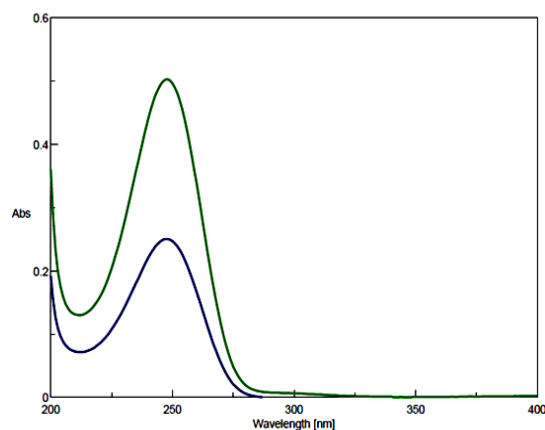

Fig. 3. The UV spectra of hydrocortisone before and after an electrochemical treatment

The removal efficiency (%) of the electrochemical treatment was estimated using the formula

$$Removal\ \% = [(C_0-C)/C_0] \times 100 \qquad (8)$$

In which, C_0 and C are the hydrocortisone concentrations (mg/L) before and after the electrochemical treatment, respectively.

The amount of hydrocortisone removed (µg) in each electrochemical experiment was determined using the formula

$$Amount\ removed\ (µg) = Removal\ \% \times C_0 \times V \times 1000 \qquad (9)$$

In which, Removal % is the removal efficiency (%), C_0 is the initial concentration of hydrocortisone (mg/L) before the electrochemical treatment, and V is the volume, (L) of the treated solution.

In order to evaluate the economic feasibility of the electrochemical removal process, the electrical energy consumption per mass (KWh g^{-1}) was calculated using the following formula[11,22,23]

Electrical energy consumption (KWh g^{-1}) = [I.U.T]/[(C$_0$-C)V]   (10)

In which, I is the current (A), U is the voltage (V), T is the time (h), C$_0$ and C are the hydrocortisone concentrations (mg/L) before and after the electrochemical treatment, respectively, and V is the volume, (L) for the treated solution.

The electro dissolution (g/L) of the aluminum anode was calculated according to Faraday's law using the following formula[10]

Anode electro dissolution (g/L) = (I.t.M)/(z.F.V)   (11)

In which[10], I is the current (A), t is the electrolysis time (s), M (26.98 g mol^{-1}) is the anode material atomic weight, z (z$_{Al}$ = 3) is the number of transferred electrons, F (96500 C mol^{-1}) is Faraday's constant, and V is the volume of treated solution (L).

In addition, the electrodes were weighed before and after the electrochemical experiments to determine the practical dissolution of the electrodes.

Further experiments were performed to evaluate the influence of several experimental parameters on the removal efficiency and energy consumption.

The sludge formed at the end of the electrochemical treatment was dried in the oven (Raven 2 Oven, LTE Scientific, United Kingdom) at 100 °C for about 4 hours. After grinding the dried mass, a pale pink fine powder was obtained. This powder was analyzed using high performance liquid chromatography (HPLC) (LA Chrom ELITE, VWR Hitachi, Germany) and X-ray fluorescence (XRF). In addition, the loss on ignition (LOI) of the dried powder was determined using muffle furnace (Nabertherm, Germany).

RESULTS AND DISCUSSION

Effect of current density

In order to investigate the influence of the current density on the electrochemical treatment, electrochemical experiments at current densities ranged (from 15 to 35 mA/cm^2) were performed. The other parameters were (electrolysis time: 120 min, initial concentration of hydrocortisone: 10 mg/L, electrolyte: 2.5 g/L NaCl, initial pH: 6.0, and the distance between electrodes: 4 cm). The results shown in (Table. 1 and Fig. 4) demonstrated that the removal efficiency increased with increasing current density. The increase of the current density may increase the formation of aluminum hydroxide flocs[10,15,19], the electro generation of bubbles[10], and the formation of chlorine and hypochlorite[10]. That could enhance the electro flocculation, electro flotation, and indirect electro oxidation.

Table. 1: The effect of current density on the electrochemical treatment

Current density (mA/cm^2)	15	20	25	30	35
Removal %	8.9%	15.6%	40.9%	46.7%	58.3%
Electrical energy consumption (KWh g^{-1})	14.56	14.97	8.26	10.23	10.71
Electro dissolution of anode (predicted) (g)	0.242	0.322	0.403	0.483	0.564
Practical dissolution of anode (g)	0.308	0.401	0.522	0.586	0.710
Practical dissolution of cathode (g)	0.132	0.137	0.211	0.252	0.310

Table. 2: The effect of electrolysis time on the electrochemical treatment

Electrolysis time (min)	30	60	90	120	150
Removal %	0.9%	12.3%	30.8%	46.7%	58.3%
Electrical energy consumption (KWh g^{-1})	146.00	19.61	12.39	10.23	10.34
Electro dissolution of anode (predicted) (g)	0.121	0.242	0.362	0.483	0.604
Practical dissolution of anode (g)	0.187	0.294	0.451	0.586	0.734

Fig. 4. The effect of current density on the removal efficiency
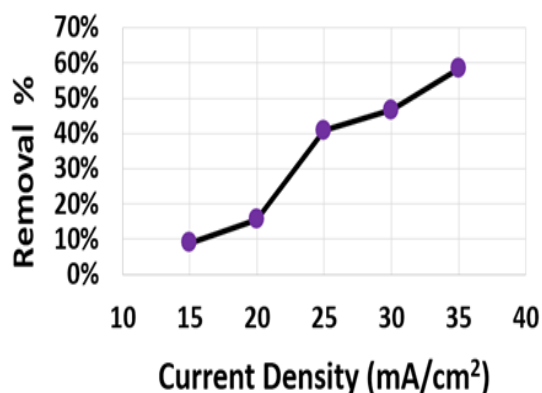

Fig. 5. The effect of electrolysis time on the removal efficiency

Although it is expected that the increase of the current density will increase the electrical energy consumption[24], the highest energy consumption was at current density of 20 mA/cm². That because the amount removed of hydrocortisone affects the value of electrical energy consumption per mass according to equation (10).

According to Faraday's law, the electro dissolution of the anode increases with increasing current density. That was clearly demonstrated in Table 1. However, the practical dissolution of the anode was found to be higher than the predicted values by the Faraday's law[22]. This difference may be due to the chemical dissolution of the anode[22,25].

The cathode dissolution may be explained by the chemical attack[11,19,26] by hydroxide ions, generated during water reduction (equation 2), at high pH[19]:

$$2Al + 6H_2O + 2OH^- \rightarrow 2Al(OH)_4^- + 3H_2 \qquad (12)$$

Effect of electrolysis time

To study the effect of electrolysis time on the electrochemical treatment, electrochemical experiments were performed with electrolysis times 30, 60, 90, 120, and 150 min. The other parameters were (current density: 30 mA/cm², initial concentration of hydrocortisone: 10 mg/L, electrolyte: 2.5 g/L NaCl, initial pH: 6.0, and distance between electrodes: 4 cm). Results are summarized in (Table. 2 and Fig. 5).
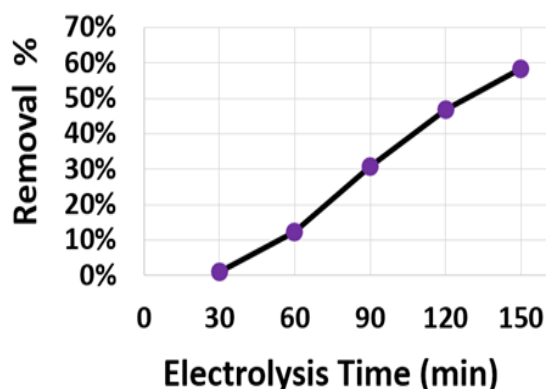
The removal efficiency increased with increasing electrolysis time due to the increase of generation of metal ions and flocs[10,14,19]. The dissolution of electrodes increased with increasing electrolysis time according to Faraday's law[10]. The highest energy consumption was at electrolysis time of 30 min as a result of the extremely small amount of hydrocortisone removed after 30 min. While the lowest energy consumption was at electrolysis time of 120 min due to the huge amount of hydrocortisone removed after this time.

Effect of initial concentration of hydrocortisone

The influence of the initial concentration of hydrocortisone on the electrochemical treatment was studied with concentrations from 5 to 30 mg/L. The other parameters were (current density: 30 mA/cm², electrolysis time: 120 min, electrolyte: 2.5 g/L NaCl, initial pH: 6.0, and distance between electrodes: 4 cm). Results shown in (Fig. 6a, 6b, and 6c) demonstrated that the removal efficiency decreased slightly with increasing initial concentration. However, the amount of hydrocortisone removed increased with increasing initial concentration. This behavior was also observed in the removal of organic pollutants by photocatalysis[27]. The electrical energy consumption decreased with increasing initial concentration as a result of the increase of the amount removed of hydrocortisone, since the amount removed of hydrocortisone affects the value of electrical energy consumption per mass according to equation (10)[11,22,23].
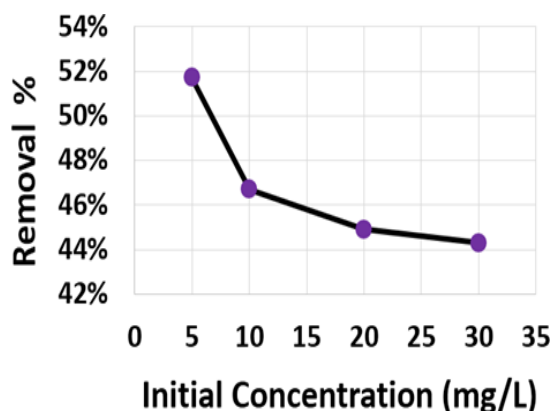
Fig. 6a. The effect of initial concentration on the removal efficiency
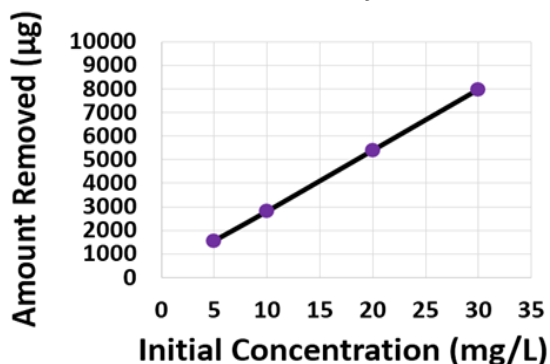

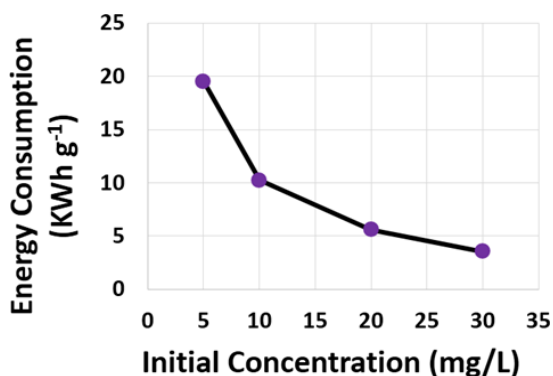**Fig. 6b. The effect of initial concentration on the amount removed of hydrocortisone**

Fig. 6c. The effect of initial concentration on the energy consumption

Effect of distance between electrodes

The effect of the distance between electrodes on the electrochemical treatment was studied with distances ranged from 2 to 8 cm. The other parameters were (current density: 30 mA/cm², electrolysis time: 120 min, electrolyte: 2.5 g/L NaCl, initial pH: 6.0, and initial concentration of hydrocortisone: 10 mg/L). It was found that the

removal efficiency and the energy consumption increased with increasing the distance. These results correspond well with other published articles[15,16,19]. Results are summarized in Tabel.3.

Effect of initial pH

To evaluate the effect of the initial pH of the treated solution on the electrochemical treatment, pH values have been varied from 4 to 10. The other parameters were (current density: 30 mA/cm², electrolysis time: 120 min, electrolyte: 2.5 g/L NaCl, distance between electrodes: 4 cm, and initial concentration of hydrocortisone: 10 mg/L). Results shown in Fig. 7 demonstrated that the optimal pH value was 6. Although the literature survey revealed that the initial pH was one of the important factors affecting the electrochemical treatment[19,28,29], our findings showed that the initial pH has no significant impact on the removal efficiency.
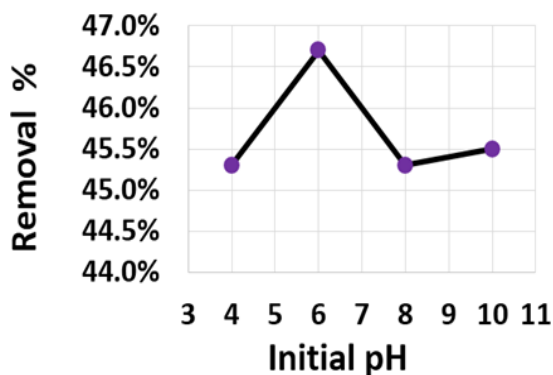

Fig. 7. The effect of initial pH on the removal efficiency

Effect of electrolyte type and concentration

To investigate this factor, NaCL (at concentrations of 1.5, 2, and 2.5 g/L) and KCl (at a concentration of 2 g/L) were used as supporting electrolytes. The other parameters were (current density: 30 mA/cm², electrolysis time: 120 min, distance between electrodes: 4 cm, initial pH: 6.0, and initial concentration of hydrocortisone: 10 mg/L). Results are summarized in Fig. 8a, 8b, 8c, and 8d. The optimal NaCl concentration was 2 g/L that achieved higher removal efficiency and less electrical energy consumption. Comparing between NaCl and KCl at a constant concentration of 2 g/L, It was found that NaCl was the most favorable electrolyte.
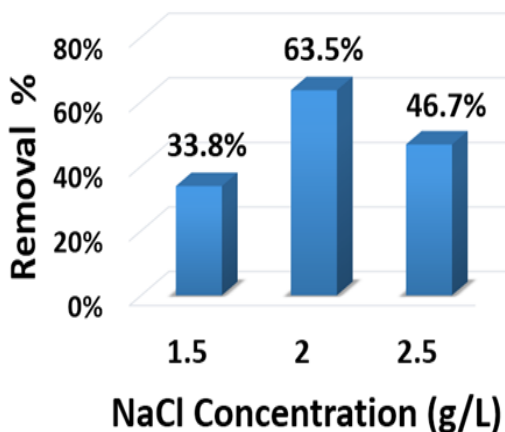
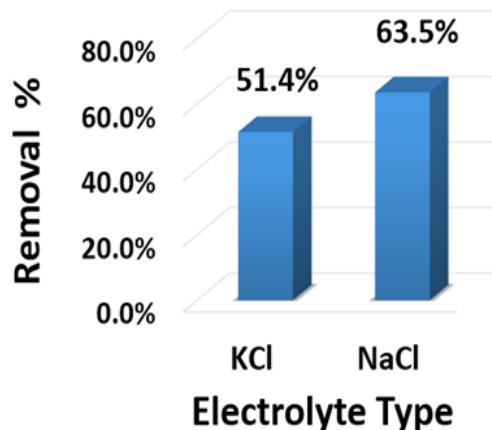**Fig. 8a. The effect of NaCl concentration on the removal efficiency**

Fig. 8c. The effect of electrolyte type on the removal efficiency (at a constant electrolyte concentration of 2 g/L)
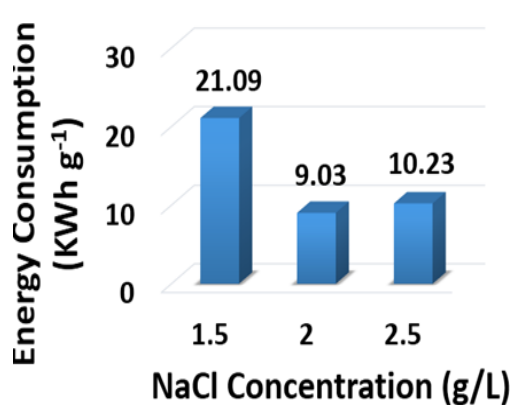

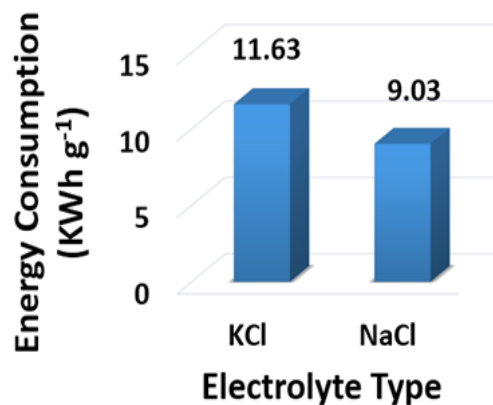**Fig. 8b. The effect of NaCl concentration on the electrical energy consumption**

Fig. 8d. The effect of electrolyte type on the electrical energy consumption (at a constant electrolyte concentration of 2 g/L)

Table. 3: The effect of distance between electrodes on the electrochemical treatment

Distance between electrodes (cm)	2	4	6	8
Removal %	43.4%	46.7%	49.3%	53.5%
Electrical energy consumption (KWh g^{-1})	7.69	10.23	12.90	14.09

Generally, the presence of the electrolyte increases the ionic strength[30] and the conductivity. That causes a reduction of the cell voltage at constant current density[19,31] and minimizes the electrical energy consumption[19].

The increase of the removal efficiency in the presence of electrolyte contains chloride ions could be caused by the indirect electro oxidation by chlorine and hypochlorite generated electrochemically[32] (reactions 5, 6, and 7).

Characterization of the sludge

After drying and grinding the sludge, a pale pink fine powder was obtained. The loss on ignition (LOI) of the dried powder, determined at 550 °C until constant weight, was found to be 26.7%. This value equates to the organic matter and volatile solids content[33].

In addition to Al_2O_3, the detected by-products formed after electrochemical treatment[33] were elements like Fe, Ni, Mn, and Zn as XRF analysis showed (Table. 4).
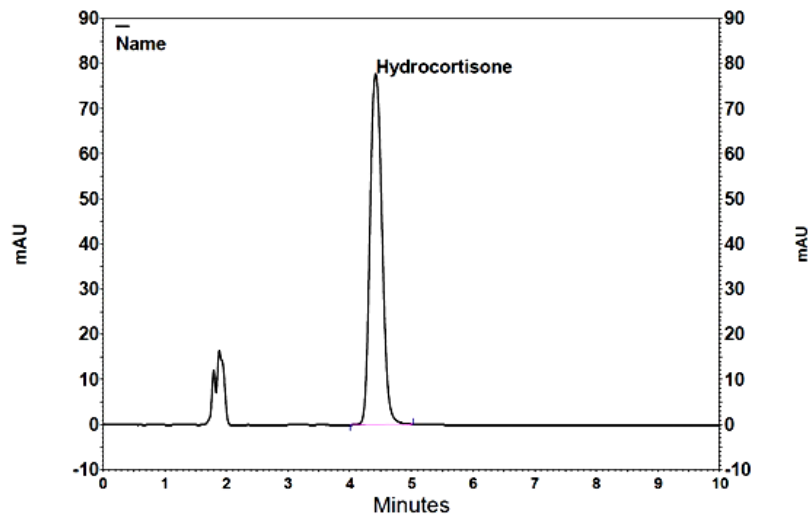
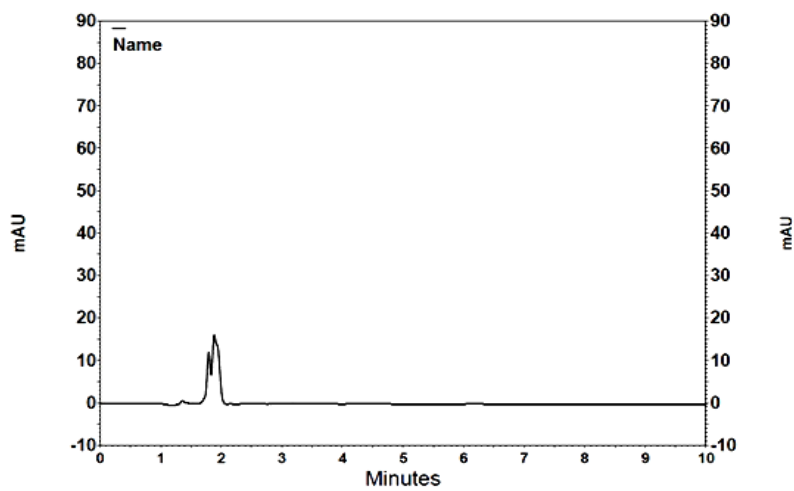**Fig. 9a. The representative chromatogram of hydrocortisone standard solution**

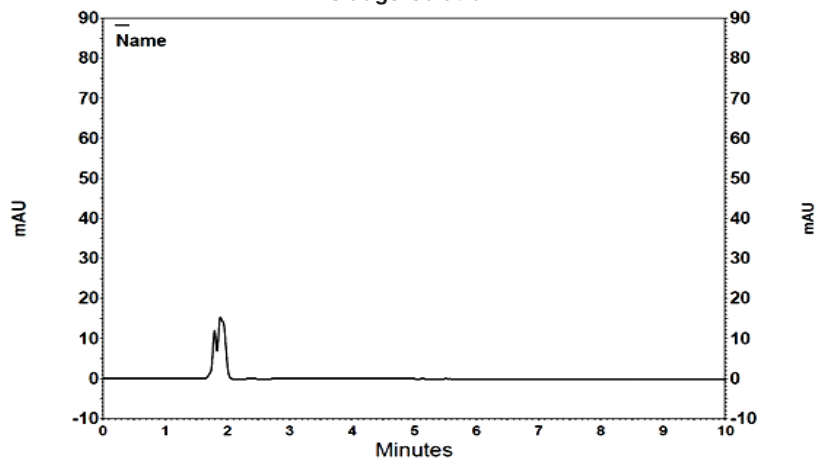**Fig. 9b. The representative chromatogram of the studied sludge solution**

Fig. 9c. The representative chromatogram of ethanol

Table. 4: XRF results of the dried sludge*

Element	Concentration (μg/g)
Cr	31.1 ± 6.6
Mn	821 ± 68
Fe	525 ± 32
Ni	4.81 ± 0.96
Cu	97.4 ± 5.8
Zn	15.6 ± 1.3
Ga	6.74 ± 0.70
Pb	1.97 ± 0.30

* Results are valid for sample of Al_2O_3 matrix

In order to determine the residual amount of hydrocortisone in the sludge, a portion of the dried powder was transferred to a volumetric flask containing ethanol (a suitable solvent for hydrocortisone extraction), and shaken by mechanical means and with the aid of ultrasound for about one hour to extract the hydrocortisone.

Then the solution was filtered and analyzed using HPLC. Table. 5 shows the chromatographic conditions of the analytical procedure. Fig 9a, 9b, and 9c show the representative chromatograms of the hydrocortisone standard solution, the solution of the studied sludge, and the solvent used in the extraction process (Ethanol), respectively. It was found that no traces of hydrocortisone were detected in the dried sludge. That may be explained by the destruction of hydrocortisone by the oxidants (Cl_2, ClO^-) generated during the electrochemical treatment. The chromatograms also showed that the peaks obtained at the retention times (between 1.6 - 2.1 min) were ascribed to the ethanol. The recovery of the extraction process was determined by adding a known quantity of hydrocortisone to the sludge and then extract this quantity. The recovery (%) of the extraction process was found to be 99.4%.

Table. 5: The chromatographic conditions of the analytical procedure

Column	C18 (150 mm, 4.6 mm i.d., 5 μm)
Mobile phase	50% water, 25% Methanol, 25% Acetonitrile
Flow rate	1 mL/min
Column temperature	40 °C
Detection wavelength	248 nm
Injection volume	10 μL
Standard solution	Hydrocortisone, 0.04 mg/mL (in ethanol)

CONCLUSION

These findings indicated that the electrochemical treatment using aluminum electrodes was an appropriate choice for removal of hydrocortisone from water. The optimal values of experimental parameters that achieved the suitable electrical energy consumption, removal efficiency, and electrode consumption were: current density: 30 mA/cm^2, electrolysis time: 120 min, distance between electrodes: 4 cm, initial pH: 6.0, electrolyte: 2 g/L NaCl, and initial concentration of hydrocortisone: 30 mg/L. Indirect electro oxidation, by chlorine and hypochlorite, played a major role in the destruction of hydrocortisone.

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