Electrochemical Removal of Hydrocortisone from Aqueous Environments Using Aluminum Electrodes

HASHEM ALAANI*, SHAHIR HASHEM1 and FRANCOIS KARABET1

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

http://dx.doi.org/10.13005/ojc/340123

(Received: September 03, 2017; Accepted: November 05, 2017)

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) is a steroid hormone produced by the adrenal cortex. Its synthetic counterpart is used as a medication for treating asthma, inflammation, allergy, multiple sclerosis, and skin conditions.

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

Humans and animals continuously introduce steroid hormones into the environment. Concentrations of these hormones have been...
detected in the fresh water bodies receiving effluent in North America, Europe, Japan, Brazil, and China. 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, leachate, dyes, and other pollutants.

Areas can adsorb pollutants and can adsorb pollutants. Flocs are removed from the aqueous phase by sedimentation or electro flotation (flotation of flocculated particles and pollutants by hydrogen and oxygen bubbles generated electrochemically). The main reactions occurring when using aluminum electrodes are:

**At the anode**
$$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^- \tag{1}$$

**At the cathode**
$$3\text{H}_2\text{O} + 3\text{e}^- \rightarrow \frac{3}{2}\text{H}_2(\text{g}) + 3\text{OH}^- \tag{2}$$

**In the solution (at alkaline conditions)**
$$\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 \tag{3}$$

**Oxygen evolution reaction**
$$2\text{H}_2\text{O} \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \tag{4}$$

**Chlorine and hypochlorite formation**
$$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \tag{5}$$
$$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{H}^+ + \text{Cl}^- \tag{6}$$
$$\text{HClO} \rightarrow \text{ClO}^- + \text{H}^+ \tag{7}$$

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 (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.

Experiments were performed in batches 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 0.1 M HCl solution and then with WFI. This process could overcome the electrode passivation that caused by the oxide film formed on the electrodes during the electrochemical treatment.

At the end of each run, the solution was kept without mixing for about 20 min to let the flocs settling down. 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 λmax. A calibration curve was plotted between absorbance and hydrocortisone concentration and the linearity was found to be satisfactory (R² = 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.

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

$$\text{Removal} \% = \left(1 - \frac{C}{C_0}\right) \times 100 \quad (8)$$

In which, C₀ 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

$$\text{Amount removed (µg)} = \text{Removal} \% \times C_0 \times V \times 1000 \quad (9)$$

In which, Removal % is the removal efficiency (%), C₀ 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\textsuperscript{11,22,23}

\[
\text{Electrical energy consumption (KWh g}^{-1}) = \frac{[I\cdot U\cdot T]/[(C_0-C)\cdot V]}{10}
\]  

(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\textsuperscript{10}

\[
\text{Anode electro dissolution (g/L)} = \frac{(I\cdot t\cdot M)/(z\cdot F \cdot V)}{10}
\]  

(11)

In which\textsuperscript{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, 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\textsuperscript{10,15,19}, the electro generation of bubbles\textsuperscript{10}, and the formation of chlorine and hypochlorite\textsuperscript{10}. That could enhance the electro flocculation, electro flotation, and indirect electro oxidation.

![Table 1: The effect of current density on the electrochemical treatment](image1)

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

![Table 2: The effect of electrolysis time on the electrochemical treatment](image2)

<table>
<thead>
<tr>
<th>Electrolysis time (min)</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal %</td>
<td>0.9</td>
<td>12.3</td>
<td>30.8</td>
<td>46.7</td>
<td>58.3</td>
</tr>
<tr>
<td>Electrical energy consumption (KWh g(^{-1}))</td>
<td>146.00</td>
<td>19.61</td>
<td>12.39</td>
<td>10.23</td>
<td>10.34</td>
</tr>
<tr>
<td>Electro dissolution of anode (predicted) (g)</td>
<td>0.121</td>
<td>0.242</td>
<td>0.362</td>
<td>0.483</td>
<td>0.604</td>
</tr>
<tr>
<td>Practical dissolution of anode (g)</td>
<td>0.187</td>
<td>0.294</td>
<td>0.451</td>
<td>0.586</td>
<td>0.734</td>
</tr>
</tbody>
</table>
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/cm\(^2\). 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\(^19\):

\[
2\text{Al} + 6\text{H}_2\text{O} + 2\text{OH}^- \rightarrow 2\text{Al(OH)}_4^- + 3\text{H}_2 \quad (12)
\]

**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/cm\(^2\), 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/cm\(^2\), 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)\(^11,22,23\).
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, distance between electrodes: 4 cm, 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. Results are summarized in Table 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, our findings showed that the initial pH has no significant impact 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. 8b. The effect of NaCl concentration on the electrical energy consumption

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

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

<table>
<thead>
<tr>
<th>Distance between electrodes (cm)</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal %</td>
<td>43.4%</td>
<td>46.7%</td>
<td>49.3%</td>
<td>53.5%</td>
</tr>
<tr>
<td>Electrical energy consumption (KWh g⁻¹)</td>
<td>7.69</td>
<td>10.23</td>
<td>12.90</td>
<td>14.09</td>
</tr>
</tbody>
</table>

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

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 (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.

In addition to Al₂O₃, the detected by-products formed after electrochemical treatment 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*

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

* Results are valid for sample of Al₂O₃ 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 (Cl₂, 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

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

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/cm², 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.

ACKNOWLEDGMENT

The authors would like to thank the quality control team in Diamond Pharma for pharmaceutical industries, Syria, especially Ms. Douaa Almoukdad for the support.

The authors would also like to thank the Central Laboratory in Damascus University, Faculty of Science, Department of Chemistry, for providing the XRF analysis.

REFERENCES


22. Secula, M. S.; Creşescu, I.; Petrescu, S. Electrocoagulation treatment of sulfide wastewater in a batch reactor: effect of


