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Use of Recycled Aluminum - polyethylene Composite Films as Anodic Electrodes for Electrocoagulation of Wastewater

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This work evaluates the use of aluminum contained in the aluminum-polyethylene films as anodic electrodes using the electrocoagulation technique to reduce the pollutants contents of an industrial wastewater quickly and effectively. Two different current densities were applied 25 and 12.5 mA cm^{-2}. When the current density of 25 mA cm^{-2} is used, the aluminum electrodes reduce the COD of wastewater by about 65% and the aluminum-polyethylene films electrodes reduces the COD by 56%. The color and turbidity reductions are 87 and 90% respectively. The use of aluminum-polyethylene films as electrodes in the electrocoagulation process contributes to the pollutant removal without the addition of chemical reagents or changing the pH, so it is both effective and environmentally friendly.

Keywords: electrocoagulation, aluminum film, wastewater, COD.

1. INTRODUCTION

Flexible packages are becoming one of the largest segments of the packaging industry, since they can take the shape of the product such as bag, pouch, liner, or overwrap. This package material combines the best qualities of plastic, film, paper and aluminum foil that provides protective properties to the products. The Flexible Packaging industry had $25.4 billion in sales in the United States in 2011 [1]. Once that the food or beberage are consumed the flexible package is discarded. In developed economies one of the most common methods for final disposal of waste is the use of incinerator that produces energy [2]. However, in countries that do not have thermal systems for the final disposal or

recycling industries, the flexible packages represents environmental challenges related with the long times for degradation. Indeed, in México City is huge since every day is being produced 12,000 tons, and 1,000 tons are due to the different types of discarded packages [3, 4].

On the other hand, electrocoagulation is an electrochemical technique in which aluminum and iron "sacrificial" electrodes are dissolved, generating in situ coagulant agents, which will destabilize the colloidal particles. The objective of this process is to produce coagulants from the anodic dissolution of iron or aluminum electrodes, this leads to the formation of coagulants to destabilize colloidal pollutants and to remove them from wastewater [5, 6]. Electrochemical methods offer some advantages over traditional chemical treatments: less coagulant ion is required, less sludge is formed, and electrocoagulation equipment is very compact; thus, suitable for installation where the available space is rather limited. Furthermore, the convenience of dosing control only by adjusting current makes automation quite easy [7-10].

The aluminum-polyethylene films where obtained from a cellulose recover plant. In this facility the packages are processed in a mechanical centrifuge with water in which the cellulose is obtained with the water effluent and on the other hand, the aluminum-polyethylene films. Until now, the recovered cellulose is selling to the paper industry for producing tissue quality paper. However, the aluminum-polyethylene films represent an environmental problem since there is no use for this residue.

Thus, this study evaluates the pollutant removal capacity of an industrial wastewater using electrocoagualtion when aluminum-aluminum and aluminum-polyethylene films are used as electrodes. The effectiveness is evaluated in terms of color, turbidity and chemical oxygen demand (COD) reduction. The influence of operating parameters such as time of treatment and current density is also evaluated.

2. MATERIALS AND METHODS

2.1 Wastewater samples

Wastewater samples were collected from the exit of a biological reactor in a treatment plant of an industrial park, which receives the discharge of 144 different facilities. Therefore, the chemical composition of this effluent is rather complex. Samples were collected in plastic containers and cooled down to 4 °C, then transported to the laboratory for analysis and treatment. The pH of the raw wastewater is 7.8 and all treatment and testing was done at this value.

2.2. Electrochemical reactor

A batch cylindrical electrochemical reactor was set up for the electrochemical process. In the first case Al-Al electrodes of 10 by 10 cm were used; thus, the total anodic area was 200 cm^2. In the second test aluminum-polyethylene films with the same anodic area were employed as anode with the same area. The aluminum-polyethylene films where obtained from a cellulose recover plant. Batch

volumes of 125 mL were treated in the 250 mL reactor. A direct-current power source supplied the system with current densities of 12.5 and 25 mA cm^{-2}. Figure 1 shows a schematic diagram of the process.

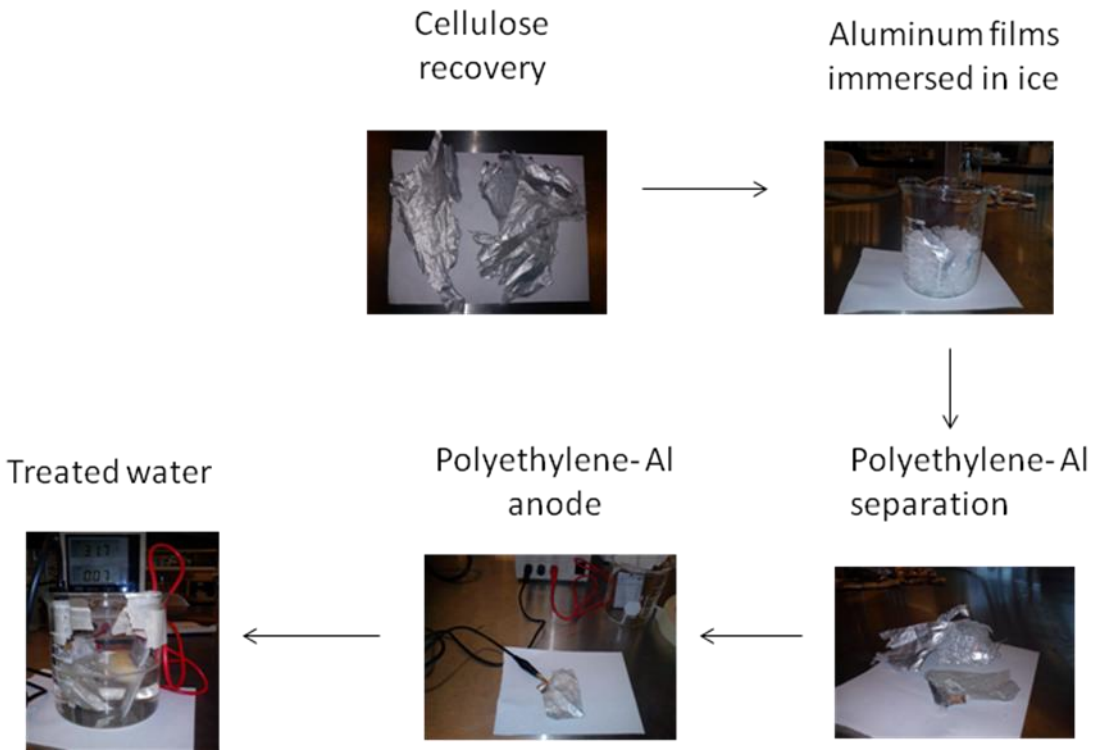

Figure 1. Schematic diagram of the use of aluminum-polyethylene films as anodes for water treatment

2.3 Methods of analysis

The initial evaluations were determined by analysis of the COD (mg/L), color (Pt-Co scale), and turbidity (NTU scale) COD was determined by the open reflux method according to the American Public Health Association (APHA). Following this method, samples are refluxed with potassium dichromate and sulfuric acid for 2 hours. Once the optimal conditions were found the raw and treated wastewater samples were analyzed for the Solids, Coliforms and Biological Oxygen Demand (BOD_5) using the Standard Methods for the Examination of Water and Wastewater Procedures [11].

2.4 UV–vis spectrometry

UV–vis spectra were obtained from samples of raw and treated wastewater using a double beam Perkin-Elmer 25 spectrophotometer. The scan rate was 960 nm s^{-1} within a 900–200 nm wavelength range. The samples were scanned in quartz cells with a 1 cm optical path [12].

2.5 Zeta Potential measurements

The Z-potential determination of wastewater was obtained using a Zetasizer Nano-Z series (Malvern Instrument GmbH, UK). This equipment measures the Z-potential as an indirect reading of electrophoretic mobility and using Laser Doppler Velocimetry (LDV). Wastewater samples are injected into a folded capillary cell and introduced into the equipment. The output from the instrument includes the average ζ-potential and its standard deviation. The ζ-potentials reported here were calculated from the average of three separate injections per sample. [13]

2.6 Cyclic voltammetry

Cyclic voltammetry of crude and treated wastewater were performed using a standard three-electrode cell. The waveforms were generated by an EpsilonTM Electrochemistry Basi Cell Stand C-3 Potentiostat; using a round carbon paste electrode (CPE) as working electrode, prepared from a 1:1 mix of 99.99% pure single-crystal graphite (Alfa Aesar) and nujol oil (Aldrich). The paste was transferred into a PVC tube and compacted to eliminate trapped air then a copper conductor was back-inserted before the paste set. The surface of the electrode was renewed through light polishing after each potential scan. The scan rate was 100 mVs^{-1} with an Ag/AgCl reference electrode and a carbon rod counter electrode.

3. RESULTS AND DISCUSSION

3.1 Aluminum and aluminum-polyethylene electrocoagulation treatment

The COD reduction (%) as function of electrochemical treatment time using 25 $mAcm^{-2}$ with aluminum - aluminum electrodes and aluminum - polyethylene films as electrodes on the raw industrial wastewater is shown in Figure 2. When the pure Al electrodes are used the maximum COD reduction of 65% was observed at 25 min of treatment, whereas the COD efficiency aluminum - polyethylene films is 56 %. This difference can be explained by the fact that during the treatment time there is a variation of the current density when using the aluminum - polyethylene films as electrodes. When the aluminum electrodes are used there is no current density variation. Nevertheless, in both cases no more COD reduction can be reached after 25 minutes.

The COD reduction (%) as function of electrochemical treatment time on the raw wastewater when using 12.5 $mAcm^{-2}$ is shown in Figure 3. The maximum COD reduction for both types of electrodes is around 50% observed at 25 min of treatment. Note, that in this case very similar results can be obtained with both kinds of electrodes. Indeed, at this case no current density variations where observed.

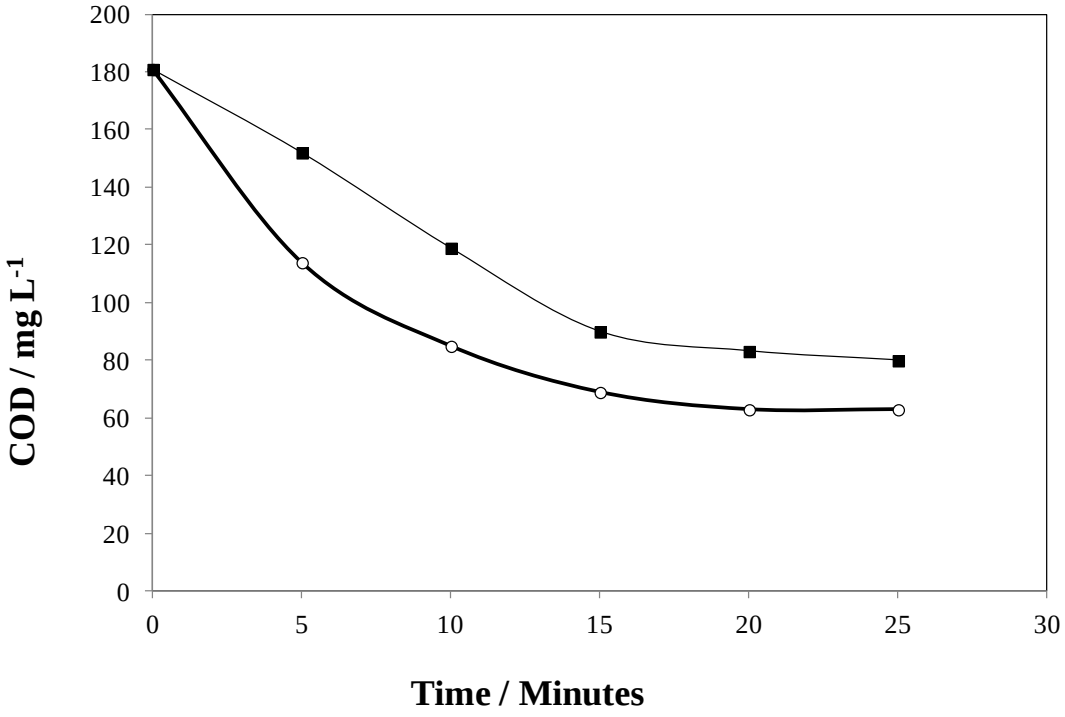

Figure 2. COD removal as a function of electrocoagulation treatment time at 25 mA cm^{-2}. Using aluminum electrodes (○) and aluminum - polyethylene films as electrodes (■)

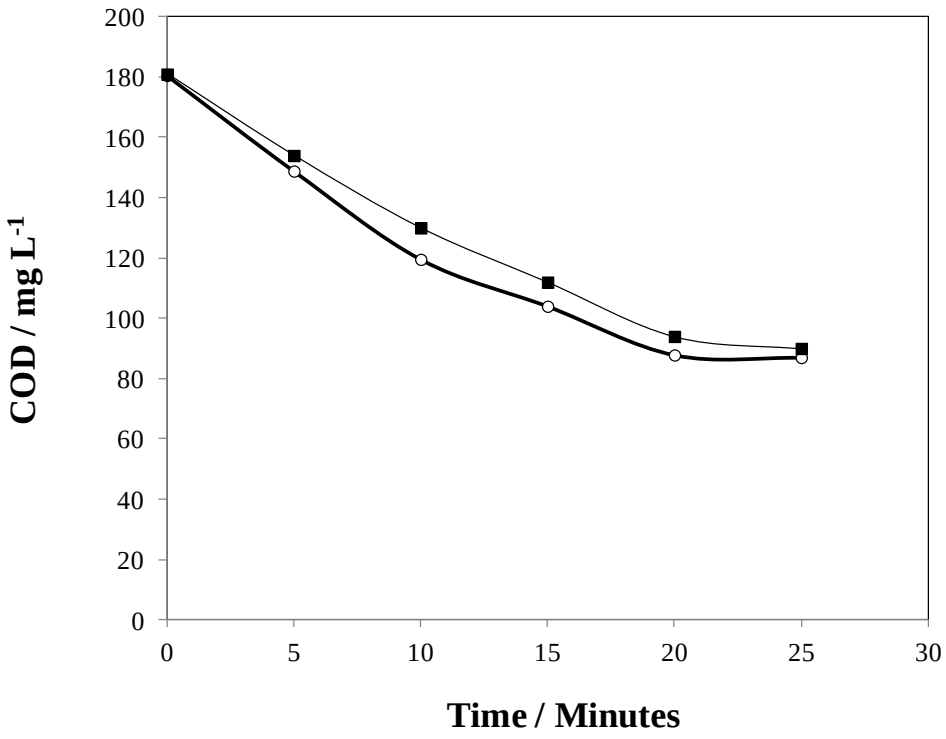

Figure 3. COD removal as a function of electrocoagulation treatment time at 12.5 mA cm^{-2}. Using aluminum electrodes (○) and aluminum - polyethylene films as electrodes (■)

Table 1 indicates the results for the Color and Turbidity reduction when the aluminum-aluminum electrodes are used (Al) and for the aluminum - polyethylene (Al-P) films for both current densities applied. As expected grater reduction values are reached when 25 $mAcm^{-2}$ of current density are applied. Color can be reduced by 87 % whereas the turbidity removal rate is around 90 %.On the other hand when using 12.5 $mAcm^{-2}$ of current density, the color reduction is 75 % and the turbidity is 80 %.

Table 1. Color and Turbidity of the treated wastewater using both current densities

	Al 25 mA cm^{-2}		Al 12.5 mA cm^{-2}		Al-P 25 mA cm^{-2}		Al-P 12.5 mA cm^{-2}	
Time / Min	Color	Turbidity	Color	Turbidity	Color	Turbidity	Color	Turbidity
0	146	30	146	30	146	30	146	30
5	100	15	113	20	108	16	116	21
10	70	7	90	10	81	9	96	12
15	34	5	60	8	51	7	65	10
20	18	3	40	6	22	3	43	8
25	18	3	36	6	22	3	32	8

In the electrolytic dissolution of the aluminum anode or the aluminum-polyethylene films the production of cationic monomeric species such as Al^{3+} takes places as shown in reactions (1-2), the cathodic reaction is presented in equation 3.

Anode:

$$Al \rightarrow Al^{3+} + 3e^{-} \quad (1)$$

$$2H_2O \rightarrow 4H^{+} + O_2 + 4e^{-} \quad (2)$$

Cathode:

$$2H_2O + 2e^{-} \rightarrow 2OH^{-} + H_2 \quad (3)$$

The generated metal ions in equation 1 are hydrolyzed in the electrochemical cell to produce metal hydroxide ions and the solubility of the formed metal hydroxide complexes depends on pH and ionic strength of the solution. For instance:

$$Al_3^{+}(aq) + 3(OH^{-}) \rightarrow Al(OH)_3(s) \quad (4)$$

According to literature, in the electrocoagulation treatment the species can interact in solution in several stages: a) electrophoresis and aggregation due to charge neutralization, b) the cation or hydroxyl ion (OH^{-}) forms a precipitate with the pollutant, c) the aluminum cation interacts with OH^{-} to form a hydroxide, d) the hydroxides form larger lattice-like structures and sweep through the water (coagulation) [14-15].

The UV-Vis spectra of the raw and treated wastewater are shown in Figure 4. The raw wastewater shows considerable absorbance in the visible range of 200 to 900 nm which confirms that

it is highly colored as presented in Table 1. However, this color is effectively reduced by the electrocoagulation treatment using aluminum - polyethylene film as anode.

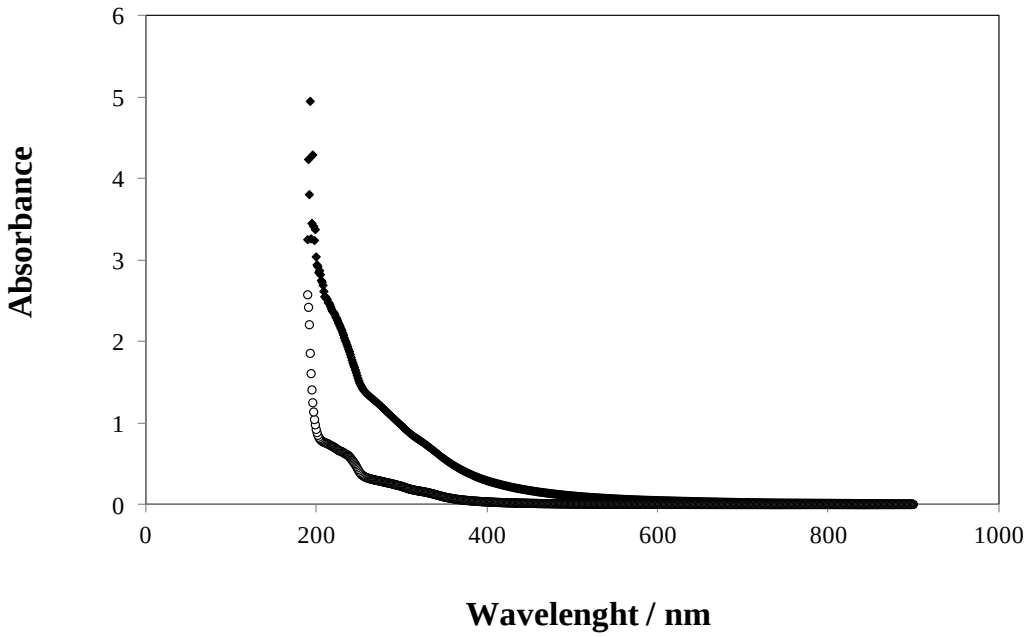

Figure 4. UV-Vis spectra of the (♦) raw and (○) treated industrial wastewater. The parameters of the electrocoagulation treatment were 12.5 $mAcm^{-2}$, initial pH 7.8 and aluminum-polyethylene film electrode

3.2 Zeta potential

Colloids suspension is maintained by electrostatic repulsion between particles. The zeta potential provides an effective measurement of the particles charge. The addition of aluminium ions into solution decreases the electric double layer around colloidal particles, thus encouraging aggregation of the pollutant [15, 16].

Figure 5 shows the zeta potential of wastewater as a function of the electrochemical treatment time for the natural pH of 7.8. The colloidal system is stable, with the particles being negatively charged. When the aluminium is electrochemically added the zeta potential is increased, although it remained below zero. Although, the zeta potential decreases monotonically close to an isoelectric point at this conditions is not reached. Gao and Yue 2005 indicates that the isoelectric point indicates that the positive aluminium hydrolysis products can destabilize negatively charged colloids by charge neutralization, the availability of positively charged aluminum polymers is an important consideration for coagulation of negatively charged colloids [17].

Figure 6 shows the voltammograms of the raw and treated wastewater obtained by starting the potential scan in the positive direction, where the results show an oxidation process and a reduction process in the raw wastewater detectable at potentials lower than those corresponding to oxidation due to pollutants present.

When cyclic voltammetry was applied to the wastewater treated after the process of electrocoagulation, the peaks do not appear, indicating that pollutants in the raw wastewater have already been eliminated. Zhang *et al.* present the cyclic voltammogram of high discoloration efficiency of methyl red in synthetic water when electrocoagulation was applied, they report that the Acid Red 2 can be removed and the oxidation peak in the voltammogram disappeared after the treatment [18]. This agrees with the voltammogram that we present in Figure 6. In early works we have pointed out that pollutants in wastewater are eliminated due to the action of the in situ coagulant generation (see eq. 4) and enmeshment processes and then the corresponding oxidation peaks in the cyclic voltammograms which originally correspond to raw wastewater are no longer present in the treated water [19-20].

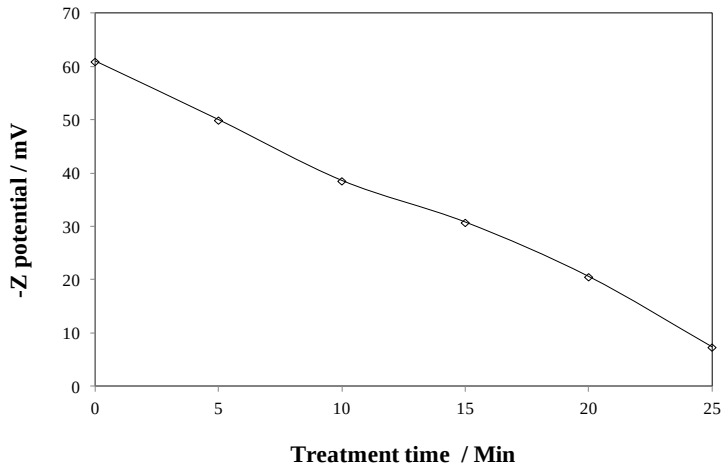

Figure 5. Z-potential raw and treated industrial wastewater as a function of treatment time. The parameters of the electrocoagulation treatment were 12.5 mAcm^{-2}, initial pH 7.8 and aluminum-polyethylene film electrode.

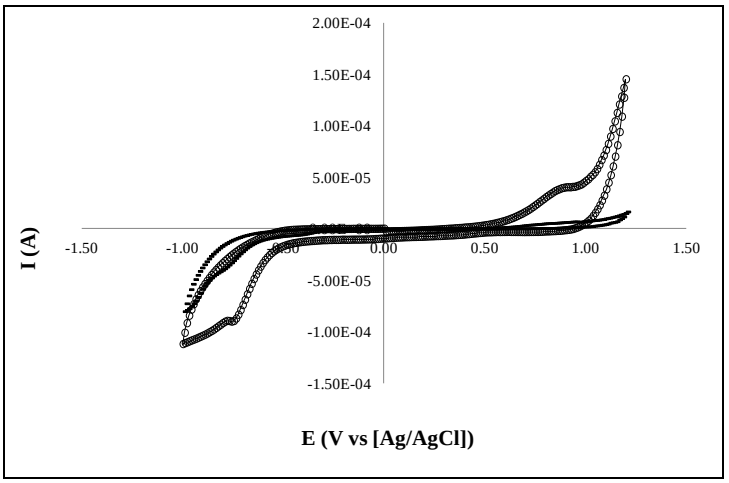

Figure 6. Cyclic voltammogram the (♦) raw and (○) treated industrial wastewater. The parameters of the electrocoagulation treatment were 12.5 mAcm^{-2}, initial pH 7.8 and aluminum-polyethylene film electrode

4. CONCLUSIONS

The use of electrocoagulation process greatly enhances the rate and extent of removal of COD, color, and turbidity from a chemically complex industrial effluent. While electrocoagulation efficiency usually increases with increasing current density, this process is more efficient at a relatively low (12.5 mA cm^{-2}) current density when using aluminum –polyethylene electrodes. Electrocoagulation using aluminum - aluminum electrodes present best results when used at current density of 25 $mAcm^{-2}$, since no variation in the current is detected in the system. However, at a current density of 12.5 $mAcm^{-2}$, the pollutant removal using aluminum - polyethylene electrodes is quite similar that the obtained with aluminum electrodes. In both cases, the addition of further chemical reagents is not required making the process quite sustainable.

ACKNOWLEDGMENTS
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