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# Double aluminum recovery and its reuse in wastewater treatment

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**Abstract** This work evaluates the use of aluminum contained in the aluminum–polyethylene films as anodic electrodes using the electrocoagulation technique to reduce the pollutant contents of industrial wastewater quickly and effectively. Thermal treatment at 500 °C produces pure aluminum (according to TGA and SEM/EDS analysis) which is used to construct aluminum disks (applying 6 tons/cm$^2$ of pressure). Aluminum disks are used as cathodes and anodes in an electrochemical cell. The current density applied in the recovered Al electrodes was 12 mA cm$^{-2}$, and the maximum COD reduction of wastewater was 77 % at 25 min of treatment. The color and turbidity reductions are 87 and 90 %, respectively. The resulting sludge of wastewater treatment was thermally treated and a second aluminum recovery was reached; since the organic material present in the sludge was removed by the high temperature, the obtained aluminum was pure enough for its reuse. 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 · Material recuperation · Tetra pak · Waste management

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## Introduction

Aluminum production is based on the extraction from bauxite ores and by recycling from aluminum scrap. In 2010, the aluminum production from ore extraction was 38 million tonnes, whereas aluminum recovered from recycling processes reached 18 million tonnes, which indicates that 32 % of the Al is currently produced from recycling scrap. Furthermore, it is estimated that in 2020, more than 31 million tonnes of Al could be obtained from recycling aluminum scrap (IAI 2009; Tenorio and Espinosa 2002; Tsakiridis et al. 2013).

Aluminum recycling processes provide important energy savings, as well as ecological benefits (Azom 2002; Macaskie et al. 2010; Shinzato and Hypolito 2005). For example, 1 kg of recovered aluminum cans save 4 kg of bauxite, 2 kg of chemicals, and 7.5 kWh of electricity (Ilyas et al. 2010; Kim et al. 2009; Momade and Sraku-Lartey 2010).

Flexible packages are becoming one of the largest segments in the packaging industry, since they can take a lot of different shapes, such as bag, pouch, liner, or overwrap. This package material combines the best qualities of plastic film, paper, and aluminum foil and provides great protection to the packaged products. The flexible packaging industry had $25.4 billion in sales in the USA in 2011 (http://flexpack.org/buyers_guide/Buyers_Guide.pdf). Once the food or beverage is 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, which have the advantage of energy production (Rogoff and Screve 2011). However, in countries that do not have thermal systems for the final disposal of residues, or even better with recycling industries, the flexible packages constitute environmental challenges

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regarding the long times for degradation. Indeed, in Mexico City, it is a huge problem, since every day is being produced 12,000 tons of trash and 1,000 tons is due to the different types of discarded packages (http://www.sma.df.gob.mx/rsolidos/02/03clave.pdf).

Tetra pak is being used as aseptic packaging material for the distribution of liquids, such as juice, soy beverages, and milk. However, once the product is consumed, the package is discarded. Indeed, it has been reported that 137 billion tetra pak packages were used in 2007, and this residue is one of the most important components of the municipal solid wastes. The main composition of the tetra pak is cellulose (75 %), low-density polyethylene (20 %), and aluminum (5 %). For the recycling purposes, cellulosic fibers are separated from the other components using hydro-pulping process. Until now, the aluminum–polyethylene layers have been thermally treated using incineration or pyrolysis (Korkmaz et al. 2009; Lopes and Felisberti 2006).

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 particle making them to precipitate. The objective of this process is to produce coagulants from the anodic dissolution of iron or aluminum electrodes, which leads to the formation of coagulants to destabilize colloidal pollutants to remove them from wastewater (Barrera-Díaz et al. 2003; Cañizares et al. 2009). 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 (Barrera-Díaz et al. 2011; Bernal-Martínez et al. 2013, 2010; Linares-Hernández et al. 2009).

The aluminum–polyethylene films are obtained from a cellulose recovery plant located in Central Mexico during 2013. In this facility, the packages are mixed with water and processed in a mechanical centrifuge; after this process, the cellulose is obtained within the water effluent, and on the other side, the aluminum–polyethylene films are separated. Until now, the recovered cellulose is sold 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 presents the aluminum recovery from the residue of tetra pak and evaluates its pollutant removal capacity of mixed industrial wastewater obtained from a treatment plant that provides service to 144 different industrial facilities, such as pharmaceutical, food, electric, textile, and many others, by means of electrocoagulation technique, using disks of the recovered aluminum as electrodes. The effectiveness of the process is evaluated in terms of the reduction of color, turbidity, and chemical oxygen demand (COD). The influence of operating parameters, such as time of treatment and current density, is also evaluated. Then, the generated sludge of the wastewater treatment is thermally treated for re-recover the aluminum allowing a closed-loop technology.

## Materials and methods

Figure 1 displays a flow diagram for the proposed technology, in which the material recovery in each treatment is shown. The process starts with the tetra pak residue, which is submitted to a hydro-treatment process, in which all the cellulose is removed and polyethylene–aluminum (P–A) films are obtained as a residue. The P–A films are thermally treated in the conditions indicated in the thermogravimetric analysis (TGA), and then, a high-quality aluminum is obtained, which is compressed and converted into aluminum disks (see Fig. 2). The disks are used as anodes in an electrochemical wastewater treatment, which gives treated water and sludge. The sludge produced is introduced into the thermal treatment, and then, the aluminum recovered is again used to make the aluminum disks.

### Aluminum recuperation

The P–A films were obtained from a cellulose recovery plant, in which the cellulosic fibers are separated from the other components using hydro-pulping process. The cellulose can be directly used in the paper recycling industry, but the P–A films that constitute vast quantities of residues

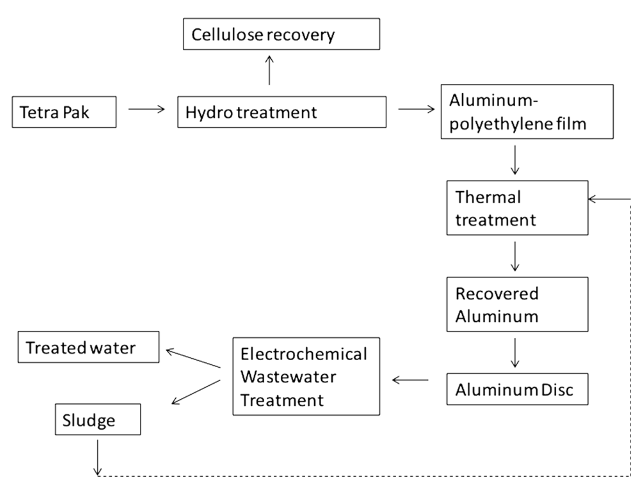


**Fig. 1** Flow diagram for the aluminum recovery process and its reuse in wastewater treatment


**Fig. 2** Diagram for the aluminum recuperation and reuse

are a major problem for the industry since there is no easy final disposal. Figure 2 shows the P–A films obtained from the industry, and then, these films were cut and sieved to obtain a homogenous size, after thermal treatment under the conditions mentioned in the TGA section, and were compacted as described in the Al electrode section. Finally, the Al disk was used as anodic material for wastewater treatment.

## Thermogravimetric analysis (TGA)

This analysis was performed on a TGA 51 TA thermogravimetric analyzer, which was operated in nitrogen atmosphere at 10 °C $min^{-1}$ heating rate, in temperature range from 25 to 800 °C (Barrera-Díaz et al. 2005).

## Electrode preparation

The P–A films were cut and sieved and then thermally treated at 500 °C (this condition was used as a result of the TGA). The electrode disk was prepared by mixing 1.75 g of <20 µm recovered aluminum powder collected from the P–A films. The mixture was compacted in a 22-mm-diameter stainless steel holder applying 6 tons/$cm^2$ of pressure. The disk was kept at room temperature until it was used in the electrochemical reactor (Guerrero et al. 2010; Lai et al. 2004).

## Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)

Surface topography was evaluated in a JEOL JSM 6510LV at 15 kV, using both secondary and backscattered electron signals. Samples were sputtered with a thin layer of about 15 nm of gold using a Denton Vacuum DESK IV system. In order to determine the elemental composition and distribution of the samples, EDS analysis was performed with an Oxford PentaFetx5 probe on the SEM. The probe was calibrated prior to analysis with a copper standard, and the data were analyzed with the INCA software included with the equipment.

## 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, cooled down to 4 °C, and then transported to the laboratory for analysis and treatment. The pH of the raw wastewater is 7.8, and all treatment and testing were done at this value.

## Electrochemical reactor

A batch cylindrical electrochemical reactor was set up for the electrochemical process. The anode and cathode were used from the Al recovered material. The electrodes have 2.2 cm of diameter; thus, the total anodic area was 7.6 $cm^2$. Batch volumes of 60 mL were treated in a 125-mL reactor. A direct-current power source supplied the system with current densities of 8 and 12 mA $cm^{-2}$.

## 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 were refluxed with potassium dichromate and sulfuric acid for 2 h. 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 (APHA-AWWA-WPCF 1989).

## UV–Vis spectrometry

UV–Vis spectra were obtained from samples of raw and treated wastewater using a double-beam PerkinElmer 25 spectrophotometer. The scan rate was 960 nm $s^{-1}$ within a

900- to 200-nm wavelength range. The samples were scanned in quartz cells with a 1-cm optical path.

Zeta potential measurements

The Z potential determination of wastewater was carried out 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 (Narong and James 2006).

## Results and discussion

Samples of aluminum–polyethylene layers obtained from the cellulose recovery plant were used as raw materials. A thermal treatment was provided using the conditions obtained in the TGA, and the recovered Al was conditioned in order to obtain a disk. Then, the disk was used as anodic material for wastewater treatment.

TGA results

The decomposition profile of the aluminum–polyethylene is given in Fig. 3. It can be seen in Fig. 3a that the polyethylene is evaporated at lower temperature than aluminum layer. Separate peaks of degradation are clearly observed for the plastic and the metal. Following the mass loss corresponding to loss of moisture (below 105 °C), the first devolatilization took place between 300 and 400 °C with maximum peak temperature at 360 °C, showing a sharp weight decrease. The second devolatilization occurred between 480 and 510 °C with a maximum peak temperature at 500 °C. There are two main components in the decomposition of polyethylene: char and aluminum. These results agree with the previous studies (Korkmaz et al. 2009; Wu and Chang 2001). TGA results showed that weight loss of aluminum–polyethylene was over at the temperature of 500 °C. In Fig. 3b, the TGA for the recovered aluminum is shown, indicating that this residue is quite stable since only 2 % of the weight loss is registered.

SEM/EDS results

As shown in Fig. 4, there are noticeable changes in both morphology and elemental composition on the films. A 100× image of the surface shows that the aluminum–polyethylene films consisted in Al plates covered with the

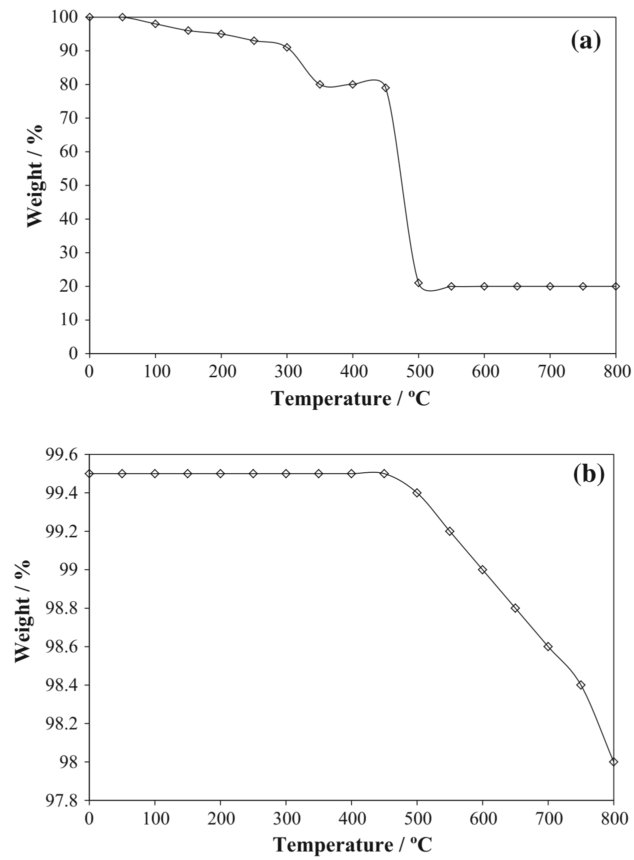


**Fig. 3** Weight loss as a function of temperature of **a** aluminum–polyethylene films and **b** recovered aluminum

polyethylene films over the surface, while the aluminum thermally treated shown in Fig. 4b has an homogenous surface. The surface compositions of both materials are shown in the EDS spectra. The EDS spectrum indicates the presence of Al, C, and O in the aluminum–polyethylene film. The EDS spectrum of the thermally treated films only shows the presence of Al. There are noticeable changes in both morphology and elemental composition.

Aluminum electrocoagulation treatment of wastewater

The obtained recovered aluminum disks shown in Fig. 2 were used as anode material in an electrochemical cell, in which raw wastewater was introduced. Samples of treated water were taken at elapsed times and analyzed for testing the treatment effectiveness. The COD reduction (%) as function of electrochemical treatment time using different current densities on the raw industrial wastewater is shown in Fig. 5. When the recovered Al electrodes were used at 12 mA cm$^{-2}$, the maximum COD reduction of 77 % was observed at 25 min of treatment, whereas the COD efficiency using 8 mA cm$^{-2}$ is 56 %. This difference can be explained by the fact that during the treatment time, there is

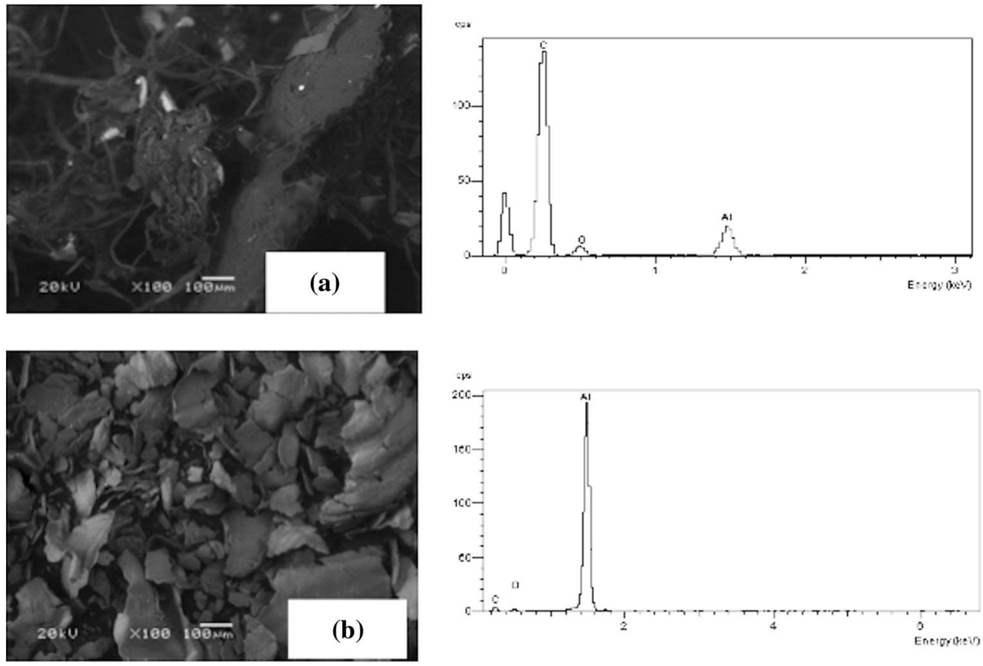


**Fig. 4** SEM images (100×) and EDS spectra of the **a** aluminum–polyethylene surface and **b** aluminum

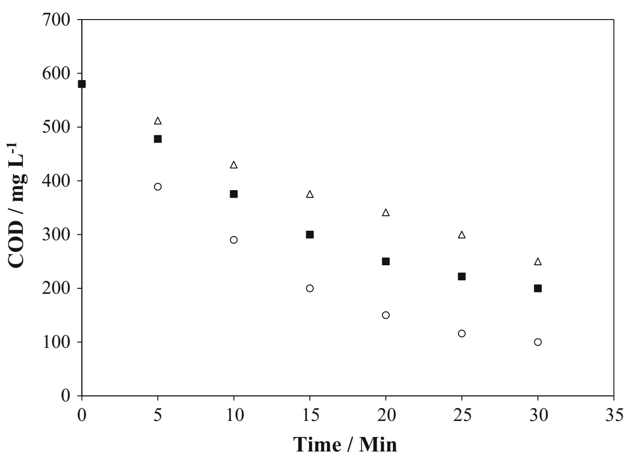


**Fig. 5** COD removal as a function of electrocoagulation treatment time at (*open circle*) 12, (*filled square*) 10, and (*open triangle*) 8 mA cm$^{-2}$

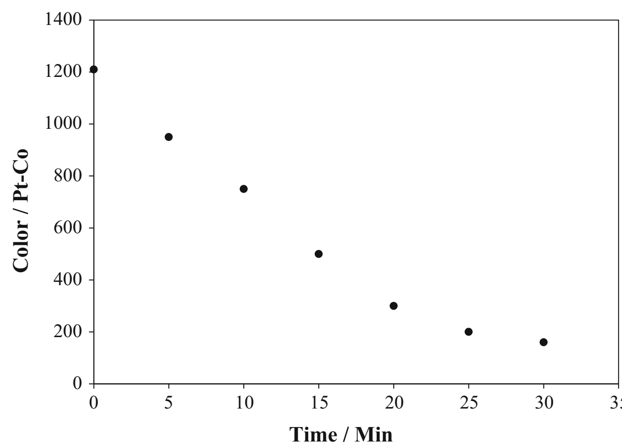


**Fig. 6** Color removal as a function of electrocoagulation treatment time at (*filled circle*) 12 mA cm$^{-2}$

a variation on the aluminum released into the solution. Nevertheless, in both cases, no more COD reduction can be reached after 30 min.

The color reduction (%) as function of electrochemical treatment time on the raw wastewater when using 12 mA cm$^{-2}$ is shown in Fig. 6. The maximum color reduction is around 88 % observed at 25 min of treatment.

## UV–Vis spectra

The UV–Vis spectra of the raw and electrochemically treated wastewater are shown in Fig. 7. There are no peaks in the spectra corresponding to components of the raw and treated wastewater; it is only a continuous curve that has the higher absorbance in the zone of 200–400 nm. However, it is interesting to note that the absorbance of the curve decreases when the electrochemical treatment is applied.

## Z potential

Figure 8 shows the zeta potential of wastewater as a function of the electrochemical treatment time for the natural pH of 7.8. At initial conditions, the colloidal system is stable, with the particles being negatively charged.

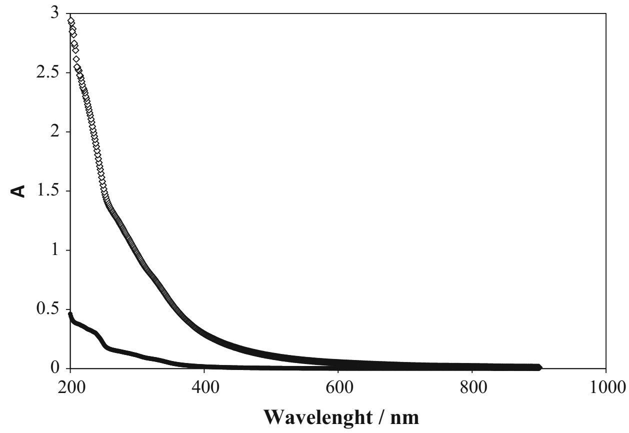


**Fig. 7** UV–Vis spectrum of treated water, before and after the electrochemical treatment at 12 mA cm$^{-2}$

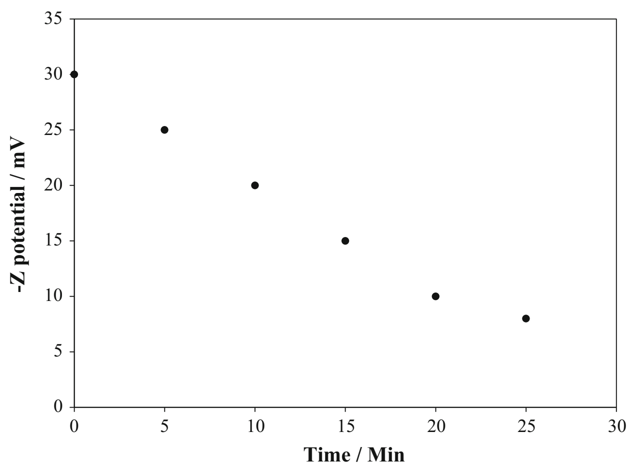


**Fig. 8** Z potential behavior as a function of electrocoagulation treatment time at (*filled circle*) 12 mA cm$^{-2}$

Colloid suspension is maintained by electrostatic repulsion between particles. The zeta potential provides an effective measurement of the particle charge. The addition of aluminum ions into solution decreases the electric double layer around colloidal particles, thus causing aggregation of the pollutant. When the aluminum is electrochemically added, the zeta potential is increased, although it remained below zero. Although the zeta potential decreases monotonically getting close to an isoelectric point, at these conditions, it is not reached. The isoelectric point indicates that the positive aluminum hydrolysis products can destabilize negatively charged colloids by charge neutralization, and the availability of positively charged aluminum polymers is an important consideration for coagulation of negatively charged colloids (Barrera-Díaz et al. 2011). Table 1 summarizes the characteristics of the treated wastewater prior to treatment and after aluminum electrocoagulation process treatment.

**Table 1** Physicochemical and microbiological parameters of wastewater under study prior to treatment and after treatment

| Parameters | Wastewater from industrial treatment plant | After electrochemical treatment |
|---|---|---|
| COD (mg/L) | 580 | 190 |
| $BOD_5$ (mg/L) | 297 | 58 |
| Color (Pt–Co) | 1,200 | 200 |
| Turbidity (NTU) | 70 | 8 |
| Total solids (mg/L) | 970 | 95 |
| Fecal coliforms (MPN/100 mL) | 59,000 | >3 |

## Aluminum recovered in the sludge

The electrochemical aluminum dissolution corresponds to the oxidation of the aluminum disk with the simultaneous reduction of water to form hydrogen, and the electrochemical processes that occur on the anode and on the cathode surfaces are represented by Eqs. (1)–(2). On the anode, aluminum dissolution takes place. On the cathode, hydrogen evolution is the main reaction. In the electrochemical processes, hydrogen is generated as shown:

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

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \quad (2)$$

As a result of the reactions (1) and (2), the formation of $Al(OH)_{3(s)}$ in aqueous solution is expected. The pollutants present in wastewater are removed by enmeshment of the flocs formation. After some time, the sludge sediment of treated water is separated via decantation.

The SEM and EDS results for sludge generated by the electrochemical process are reported here. Figure 9 shows the morphology and the characteristic of the chemical sludge produced during the electrochemical process, and it can be observed that the generated sludge appears to be heterogeneous in both shape and size. Its elemental composition determined by EDS (Fig. 9a) has shown that the sludge was mainly constituted by aluminum, carbon, and oxygen.

## Introducing the method into the industrial sector

Today, the industry only recovers the cellulose layer from the flexible packages, and this results in the accumulation of large amounts of P–A films. The proposed method consists in giving to this waste a thermal treatment in which the aluminum recovery could be done. The recovered Al can be compressed, and then, the aluminum in this form can be used to treat industrial wastewater.

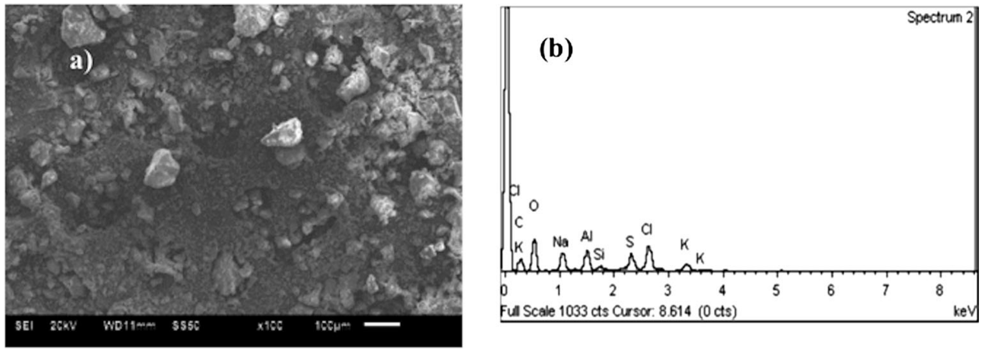


**Fig. 9** **a** Scanning electron micrographs (×100 magnification) of the chemical sludge from the electrochemical process and **b** microanalysis image (EDS) of dry sludge from the electrochemical process

## Conclusion

The research described here showed that waste generated by the discarding of flexible packages used as liquid containers may be converted into innovative upgraded products. Thermal processes can be used in the recycling of aluminum–polyethylene films that now are considered wastes with a good cost−value relationship. In this case, the obtained aluminum was used in an environmentally friendly process for wastewater treatment. Moreover, the reduction of the costs related to the final correct disposal of the wastes generated by flexible packages containers must be considered. The obtained results showed that the aluminum is easily recovered and converted into aluminum disks, which are used as anode for wastewater treatment. The electrochemical method presented in this study reduces the concentration of organic pollutants in wastewater. The wastewater quality is greatly improved in terms of the COD, $BOD_5$, color, and fecal coliforms. UV–Vis and Z potential confirm the upgrading in the wastewater quality after the electrochemical treatment. The aluminum present in the sludge generated in wastewater treatment was recovered with a thermal treatment and returned to the disks elaboration step. SEM analysis on the P–A surface, Al, and sludge showed the morphology, while EDS analysis evidenced the presence of aluminum in all cases.

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