

Removal of organic matter contained in slaughterhouse  
wastewater using a combination of anaerobic digestion and solar  
photoelectro-Fenton processes

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**Abstract**

Here, the mineralization of organic matter present in slaughterhouse wastewater from a Chilean meat company was achieved by a combination of anaerobic digestion followed by the solar photoelectro-Fenton (SPEF) process. The first step was the biological treatment, during which 90% of COD removal was achieved, producing 90 mL of CH<sub>4</sub>. Further, the post-biological effluent showed lower color, odor, amount of solids and turbidity but higher conductivity due to an increase in the concentration of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>. This was followed by different electrochemical advanced oxidation processes (EAOPs): electro-oxidation (EO), electro-Fenton (EF) and SPEF. With SPEF, almost complete mineralization was achieved with a high efficiency. With SPEF, the fast mineralization rate is due to hydroxyl radicals (<sup>•</sup>OH) that are generated in the bulk, on the anode surface, by solar radiation, and most importantly, by the direct photolysis of complexes formed between Fe<sup>3+</sup> and some organic intermediates.

The combination of both processes, biological digestion and SPEF, produces a totally clarified effluent, with a COD removal greater than the separate processes and better than the final effluent from industrial wastewater plants at comparable reaction times.

Keywords: slaughterhouse wastewater; anaerobic digestion; solar photoelectro-Fenton process; hydroxyl radical.

## 1. Introduction

The industries involving the production, harvest, distribution, and marketing of chicken, pork, turkey, salmon, and processed foods are steadily growing in the world and particularly, in developing countries. The production of meat from animals in Chile has shown remarkable growth since the 1990s, with annual production increases of 9.3% for the period 1996-2014 [1,2].

In Chile, different laws and decrees set standards stating that these waters must be returned to the natural effluent state, and increasingly stringent laws are being imposed because water resources are increasingly scarce and the scenario may worsen in coming years [3]. Therefore, it is necessary to promote new and effective alternatives for the treatment of wastewater. Among them, biological treatment is highlighted due to its characteristic of producing fully biodegradable organic matter [4-6].

In Chile, the vast majority of water treatment plants use aerobic biological treatment. For the process to be effective, microorganisms require oxygen for the removal of organic matter. This is responsible for the main operational cost in the complete wastewater treatment process. Thus, in recent years, anaerobic biological treatment is being used in larger plants due to its advantages of lower operating costs and the production of methane [7-10], which can be used as a fuel to supply energy for other plant processes. This fuel production is characterized by the conversion of organic matter to 70% CH<sub>4</sub> and 30% CO<sub>2</sub>, without any oxygen and through the interaction of different bacterial populations [11-13]. Anaerobic processes are suitable for the treatment of wastewater with very high concentrations of organic substances [14, 15]. However, this treatment is not capable of degrading residual bio-resistant organic matter in the wastewater. For this reason, new alternatives have been investigated for the treatment of wastewater. Among these, the following advanced oxidation processes (AOPs), are highlighted: (i) ozone-based processes (O<sub>3</sub>, O<sub>3</sub>/UV, O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub>) [16]; (ii) catalysis with titanium dioxide (TiO<sub>2</sub>), or TiO<sub>2</sub> combined with H<sub>2</sub>O<sub>2</sub> (TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>) and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (TiO<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) [17]; and (iii) the Fenton reaction, including the photo-Fenton (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV)

[18,19] and Solar Photo-Fenton ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV-Vis}$ ) [20-23] processes. Nevertheless, these AOPs present a series of disadvantages, such as high operating costs, the requirement for constant addition of reactants to the process, high sludge formation and safety concerns arising from the direct manipulation of strong oxidizing agents [23-25].

During the last decade, other alternative treatment strategies have been investigated, such as electrochemical advanced oxidation processes (EAOPs). These technologies present an excellent alternative for wastewater treatment and the removal of persistent contaminants from wastewater. These methods are based on the use of oxidizing agents and electricity to degrade organic contaminants, resulting in complete mineralization to produce  $\text{CO}_2$ , water and inorganic ions, or at least to achieve mostly innocuous and/or biodegradable transformation products [26, 27]. The main advantages of these methods are: (i) the quick breakdown of organic compounds, (ii) low cost of reagents, (iii) environmental compatibility, (iv) safe working conditions, (v) high efficiency in the degradation of pollutants [28-30]. The hydroxyl radical ( $\bullet\text{OH}$ ), which is the strongest oxidant free radical due to its high standard potential ( $E^\circ = 2.87$  vs. SHE), is the main oxidizing agent in this process. Additionally, it is not selective towards organic contaminants, reacting principally by dehydrogenation or abstracting a hydrogen atom to form water; or by hydroxylation or electrophilic addition to an unsaturated bond [30-32]. Many EAOPs involve methods based on the Fenton reaction, allowing the treatment of wastewater containing organic pollutants [29, 31, 33]. These methods are described below.

The electro Fenton (EF) reaction is based on the continuous electro-generation of  $\text{H}_2\text{O}_2$  from oxygen, in the presence of a carbon cathode (graphite, carbon felt, air diffusion) [34-36] by the following reaction:



The addition of a small amount of  $\text{Fe}^{2+}$  enhances the oxidizing power of  $\text{H}_2\text{O}_2$  by producing hydroxyl radicals *in situ* by the Fenton reaction [32-35].



Reaction (2) may occur again due to the reduction of  $\text{Fe}^{3+}$  at the cathode according to the following reaction [34-37].

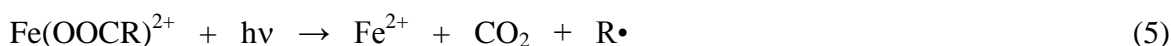


The solar photoelectro-Fenton (SPEF) reaction is presented as a clean, renewable and inexpensive alternative because this method uses UV radiation coming directly from the sun [38, 39]. This process has a higher efficiency compared to that of EF, which may be due to:

(i) increased regeneration of homogeneous  $\text{Fe}^{2+}$  and production of the  $\bullet\text{OH}$  radical from the photo-reduction of  $\text{Fe}(\text{OH})^{2+}$  by the following reaction [37-41]:



(ii) photodecarboxylation of complexes of Fe (III) with carboxylic acids and of the intermediates generated by the action of the hydroxyl radical on organic pollutants by the following reaction [37-42]:



If the SPEF process is complemented by the method of electro-oxidation (EO), the water decontamination process becomes even more effective because the organic contaminants can undergo two simultaneous oxidation processes: (i) oxidation by the  $\bullet\text{OH}$  formed in the solution according to the Fenton reaction (2) and (ii) oxidation action of the OH generated at the anode surface (M) by the discharge or oxidation of water through reaction (6) [38-43]. In EF-based processes, the chemical nature of the anode is a key factor which can increase the efficiency of the electrochemical process [44, 45]. The boron-doped diamond (BDD) electrode has been identified as an excellent non-active anode for application in the electrochemical treatment of several organic pollutants [37, 39, 41]. An important feature of the BDD surface is that it interacts weakly with the  $\bullet\text{OH}$  due to its inert surface and low adsorption properties, allowing for the easy reaction of

physisorbed hydroxyl radicals (BDD( $\bullet$ OH)) (reaction 6) with the organics (represented as R) in the solution, resulting in non-selective and complete mineralization to carbon dioxide (reaction 7).



The aim of this study was to evaluate the degradation of organic matter in wastewater coming from a slaughterhouse by a treatment comprising (i) a biological process of anaerobic digestion in batch reactors to remove the biodegradable fraction with the concomitant production of methane and (ii) a subsequent SPEF treatment to degrade the bio-resistant matter in a short time by electrolysis using an Air Diffusion Electrode/Boron-Doped Diamond system (ADE/BDD).

## 2. Experimental

### 2.1. Chemicals

Analytical grade anhydrous sodium sulfate, used as the background electrolyte, and Iron (II) sulfate heptahydrate, used as the catalyst in EF and SPEF, were obtained from Merck. Concentrated sulfuric acid and sodium hydroxide, both of analytical grade, were used for pH adjustment and were supplied by Merck.

### 2.2. Slaughterhouse wastewater and anaerobic sludge

The slaughterhouse wastewater samples were supplied in August 2015 by a slaughterhouse located in the town of Puente Alto, Santiago, Chile.

This company provides a full-service slaughterhouse and roughing of pork and beef. It also has plants for the chemical and biological treatment of effluents generated from the production, to fulfill the requirements of community safety. The effluents are used as an irrigation system on their

facility. Samples were collected after coagulation (chemical treatment) and prior to their aerobic biological treatment.

The inoculum was obtained from an anaerobic reactor of the La Farfana Water Treatment Plant of Aguas Andinas in Santiago, Chile.

### 2.3. Biological oxidation anaerobic treatment

Anaerobic digestion assays were carried out in 34 bioreactors of 500 mL capacity (ILMABOR bottles) over 30 days. In each bioreactor, a 320 mL of the slaughterhouse sample was mixed with 80 mL anaerobic sludge (to obtain a total volume of 400 mL). The bioreactors were stoppered with rubber stoppers and sealed with white silicone to ensure anaerobiosis, and they were covered with aluminum foil to prevent the growth of photosynthetic organisms. All test runs were performed in duplicate. The pH of the assays was adjusted to 7.2 and the temperature was regulated with a thermostat at 35 °C. Three times a week, two bottles were opened, to monitor the slurry by COD, UV-Vis and pH tests. Manual stirring was performed once or twice per day before reading the volume displaced by methane.

Methane production was measured by volumetric displacement, connecting an inverted falcon tube containing a 3% w/w NaOH solution to eliminate CO<sub>2</sub> and H<sub>2</sub>S as main impurities from the biogas, displacing only the methane volume. The resulting biogas travels through the flexible tubing to the Falcon tube, where it comes in contact with the NaOH solution, forming sodium carbonate and only bubbling methane. The methane collected in the Falcon tube is sucked with a syringe and released in a flame to confirm the presence of methane [42].

The methane volume was normalized and expressed as dry gas according to the following equation:

$$V_N = V_m \cdot \frac{(P_0 - P_{v,H_2O}) \cdot T_0}{P_m \cdot T_m} \quad (8)$$

where  $V_N$  is the normalized CH<sub>4</sub> volume (NmL),  $V_m$  is the measured volume,  $P_0$  is the normal pressure (1 atm),  $P_{v,H_2O}$  is the water vapor pressure at  $T_m$ ,  $T_0$  is the normal temperature (273° K),  $P_m$

is the pressure in the assays (1 atm) and  $T_m$  is the temperature in the assays (308 °K).

#### 2.4. Electrochemical treatments

A volume of 100 mL of biologically treated slaughterhouse wastewater, containing 0.05 M  $\text{Na}_2\text{SO}_4$  and 1.0 mM  $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ , was electrolyzed. The solution was adjusted to pH 3.0 using a concentrated solution of  $\text{H}_2\text{SO}_4$ .

The electrolysis was carried out in a 100 mL open-cell compartment under applied current densities of 30-50  $\text{mA cm}^{-2}$  and with constant stirring to ensure mass transport. The temperature of the solution was adjusted to 35 °C with a WiseCircu® WCB-11 bath. A Si/BDD thin-film electrode ( $2.5 \text{ cm}^2$ ) from Adamant® (500 ppm B) was used as the anode and a  $2.5 \text{ cm}^2$  carbon-PTFE air-diffusion electrode from Electrocell® was used as the cathode. The cathode was fed with compressed air flowing at  $1.0 \text{ L min}^{-1}$  for  $\text{H}_2\text{O}_2$  generation. The trials were performed at constant current provided by an MCP M10-QD305 power supply. In SPEF, the solution was irradiated directly by sunlight.

The SPEF method, electro-Fenton method (SPEF without sunlight, in the dark), electro-oxidation in the presence of  $\text{H}_2\text{O}_2$  (same conditions as EF, without  $\text{Fe}^{2+}$  catalyst) and solar radiation (photolysis without applied current) were applied for the removal of organics.

A total of 11.62 mM  $\text{H}_2\text{O}_2$  was accumulated after 3 h of electrolysis of 0.1 L of 0.1 M  $\text{Na}_2\text{SO}_4$  at pH 3.0, under an applied current of 50  $\text{mA cm}^{-2}$  at 35 °C, by the EF and SPEF processes.  $\text{H}_2\text{O}_2$  was quantified using the light absorption of its Ti(IV)– $\text{H}_2\text{O}_2$  colored complex at  $\lambda = 409 \text{ nm}$  [44].

The average UV sunlight photoionization energy was  $19 \text{ W/m}^2$ . Solar radiation data were measured on a GigaHertz-Optics X11 p/n 103929 radiometer during the experiments and confirmed from the weather station of the Department of Physics of the Universidad de Santiago de Chile ( $33^\circ 26' 51.6''$  south latitude,  $70^\circ 40' 53.5''$  west longitude). The photolysis and SPEF assays, carried out between



the months of November and December 2015, involved the exposure of solutions to direct solar radiation.

## 2.5. Apparatus and analytical procedures

The total organic carbon (TOC) and dissolved inorganic carbon (DIC) were separately determined by catalytic combustion at 850 °C and acidification, respectively, both using a nondispersive infrared detector (NDIR) in a Vario TOC Select Elementar analyzer. The total dissolved nitrogen (TN<sub>d</sub>) was determined in the same analyzer coupled with an electrochemical nitrogen detector.

The pH was measured with a pH-meter, pH/ORP HANNA HI 8424 model. The conductivity was measured by a HANNA Instruments HI 98312 Multiparameter Meter. The turbidity was measured by a HANNA Instruments portable turbidity meter HI 98703. The chemical oxygen demand (COD) was determined by digestion with reactive HANNA for 2 h at 150 °C in a HANNA Instruments HI 839800. After the complete time of digestion, the samples were cooled and analyzed in a photometer HANNA Instruments HI 83099. The 5-day biochemical oxygen demand (BOD<sub>5</sub>) was determined by a dissolved oxygen meter analyzer, HANNA Instruments HI 98186, according to the Standard Methods for the Examination of Water and Wastewater [47]. The total suspended solids (TSS) and volatile suspended solids (VSS) were measured according to the Standard Methods for the Examination of Water and Wastewater [47].

The decolorization of cattle slurry solutions was monitored from the absorbance (A) decay at the maximum visible wavelength ( $\lambda_{\max}$ ) of 418 nm, measured by a 8453 model Agilent spectrophotometer.

Inorganic ions were analyzed in a HANNA Instruments HI 83099 photometer, using ammonia MR reagent HI 93715-01 to determine the concentration of ammonium ions, nitrate reagent HI 93728-0 to determine the concentration of nitrate ions, total chloride reagent HI 93711-01 to determine the

concentration of chloride ions and iron high reagent HI 93721-01 to determine the concentration of  $\text{Fe}^{2+}$ .

COD data were also used to calculate the current efficiency at a given electrolysis time in the batch operation mode at constant current, as follows:

$$\text{Current efficiency (\%)} = \frac{(\Delta\text{COD})F V_s}{8 I t} \times 100 \quad (9)$$

where  $\Delta\text{COD}$  is the decay in COD ( $\text{g dm}^{-3}$ ) at time  $t$  (s),  $V_s$  is the solution volume ( $\text{dm}^3$ ),  $F$  is the Faraday constant ( $96,487 \text{ C mol}^{-1}$ ),  $I$  is the applied current (A) and the constant 8 is the oxygen equivalent mass ( $\text{g equiv}^{-1}$ ).

### 3. Results and discussion

#### 3.1. Characterization of slaughterhouse wastewater

Different analyses were performed to determine the characteristics and composition of slaughterhouse wastewater. The results are shown in Table 1. The slaughterhouse wastewater presented a strong, dark red coloration, consistent with the high absorbance value observed for the initial sample. The spectrum displays a band at 418 nm (Figure 1) that might correspond to different compounds that absorb in this region of wavelengths. Hemoglobin, which absorbs at 410 nm and at a pH close to 8.0, shows a bathochromic effect towards 418 nm, was one of the compounds found in the wastewater [48]. The slaughterhouse wastewater also presented a strong odor of "fecal decomposition", which may be due to the presence of compounds present in the digestive tracts of animals, such as proteins, fats, carbohydrates and other nutrients. All of these compounds undergo microbial decomposition under aerobic conditions. The main group of compounds responsible for the odors in wastewater from livestock includes ammonia, sulfur compounds, amines, volatile fatty acids, scatoles, indoles, phenols, mercaptans, alcohols and carbonyls [49].

The wastewater was found to have a pH of 7.8. As mentioned in section 2.2, the wastewater used in this work was obtained from the slaughterhouse treatment plant after the step of chemical coagulation and prior to its aerobic biological treatment. This pH is optimum for the formation of the coagulant  $\text{Fe}(\text{OH})_3$ , according to reaction (10). During the water treatment, specifically in the coagulation step,  $\text{FeCl}_3$  and  $\text{NaOH}$  are added for the production of  $\text{Fe}(\text{OH})_3$  as the main coagulant, resulting in the removal of a large amount of organics [50 – 52].



The presence of organic matter was quantified by the COD ( $1494 \text{ mg L}^{-1}$ ), BOD<sub>5</sub> ( $658 \text{ mg L}^{-1}$ ), TOC ( $513 \text{ mg L}^{-1}$ ) and TID ( $21 \text{ mg L}^{-1}$ ). These values indicate that the wastewater has a moderate concentration of organic and inorganic matter in solution.

Additionally, volatile suspended solids (VSS), which are organic compounds that volatilize at temperatures above  $550 \text{ }^\circ\text{C}$ , and total suspended solids (TSS), representing the sum of the organic and inorganic suspended solids that are found in solution at  $105 \text{ }^\circ\text{C}$ , were measured. All of these tests were carried out to quantify the amount of solid organic and inorganic matter in suspension. The obtained concentrations of VSS and TSS were  $395 \text{ mg L}^{-1}$  and  $19717 \text{ mg L}^{-1}$ , respectively. According to these results, the solids contribute a higher concentration of contaminants to water (both organic and/or inorganic compounds) compared to the amount of contaminants in solution. In the same way, the wastewater was found to have a turbidity of 89 NTU (Table 1). This value is consistent with the concentration of suspended solids.

The total chlorine and  $\text{Fe}^{2+}$  were quantified and these results are shown in Table 1. The total chlorine includes all chlorine species, but can be mainly attributed to the presence of chloride ions from the coagulation step.

One of the main components of the slaughterhouse wastewater is nitrogen in various forms. The solution showed dissolved organic nitrogen (DON) of  $95 \text{ mg L}^{-1}$ . The main compounds that could contribute to these DON concentrations are urea, proteins, amino acids and nucleic acids, while the content of inorganic nitrogen is quite variable. Finally, a higher concentration of ammonium ions ( $\text{NH}_4^+$ ) was found compared to nitrate anions, in agreement with E. Marañón (1998) [53], as shown in Table 1. The presence of these and other inorganics contributes directly to the conductivity of the wastewater.

### *3.2. Anaerobic Biological Treatment*

The wastewater was first treated by the anaerobic biological process. The decay of organic matter

was followed by tracking the COD. Figure 2 shows the change of COD during the assay. The slaughterhouse solution had an initial COD of 1494 mg L<sup>-1</sup>. During the first six days, the COD increased to 1980 mg L<sup>-1</sup>, which could be attributed to processes of hydrolysis or liquefaction that occur in the first step of anaerobic digestion [54]. Hydrolysis is the conversion of polymers to their respective monomers, which contribute to an increase in soluble COD. This also explains the increase in the concentration of ammonia (Table 1). Between days 6 and 15, the decrease of COD is more pronounced, which is typical in anaerobic treatment [54]. After the 15<sup>th</sup> day, the COD decay was much slower because the amount of biodegradable COD was significantly lower and therefore, the rate of biodegradation decreased [54]. The COD after 30 days of the anaerobic process was 137 mg/L, which is still higher than the value allowed by Chilean environmental legislation. Further, several non-biodegradable compounds were not removed by the biological process. Therefore, to reuse the wastewater, it is necessary to reduce the concentration of bio-resistant pollutants.

Figure 3 shows the accumulated methane production over 30 days of anaerobic treatment. The continuous production of methane indicates that the methanogenic archaea degraded organic matter during the process. The production of CH<sub>4</sub> reached a value of 90 mL by the 22<sup>nd</sup> day, after which there was no methane generation. This is consistent with the results shown in Figure 2, which show no decay of COD after the 22<sup>nd</sup> day. The methane production is low compared to previously reported values. Jensen et al. (2014) [56] reported a high amount of obtained biogas (between 776.5 m<sup>3</sup> d<sup>-1</sup> - 12739 m<sup>3</sup> d<sup>-1</sup>), which depends on the composition and nature of the waste used, the carbon/nitrogen ratio of 30:1 being optimal for further degradation and methane generation. According to the authors, carbon and nitrogen are the main food sources of methanogenic archaea; carbon constitutes the energy source and nitrogen is required for the formation of new cells. Thus, the growth of methanobacteria could be severely inhibited by a lack of nutrients if the nutrients are not present in the optimal ratio. Other authors, such as Ornet et al. (2014) [57] have reported that the methane yield (up to 310 Nm<sup>3</sup>/t COD) is influenced by the amount of ammonia, temperature

and trace elements. However, the results obtained in this work can be explained because the wastewater used was the effluent of a primary step, and most of the particulate volatile solids had been removed. Therefore, the organic matter present in wastewater was mainly soluble organic matter and its concentration was low in comparison with the values reported in other studies.

The color, odor and turbidity of the wastewater were also reduced during anaerobic digestion. The post-biological water has a pale yellow color, is odorless and shows low turbidity. Better removal of organics (TOC, COD, BOD<sub>5</sub>), TSS and VSS was observed by applying anaerobic digestion to the final industry effluent (Table 1). Finally, an increase in the concentration of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> was observed, significantly increasing the conductivity.

### 3.3. Electrochemical Treatments

Photolysis, electro-oxidation in the presence of hydrogen peroxide (EO-H<sub>2</sub>O<sub>2</sub>), EF and SPEF treatments were applied to the degradation of slaughterhouse wastewater after the anaerobic process described above. In the abovementioned electrochemical processes, •OH is formed at the anode surface and/or in the bulk, and this reacts with organics, leading to their mineralization to form CO<sub>2</sub>, water and inorganic ions. The combination of EF processes and electro-oxidation using a BDD anode increases the amount of oxidant •OH produced from reactions (2), (4) and (6), thus increasing the rate of mineralization of organic pollutants present in the aqueous medium. For each experiment, a 0.05 M sodium sulfate was added to the solution, and the pH was adjusted to 3.0. Additionally, an initial concentration of 1.0 mM of Fe<sup>2+</sup> was added for the EF and SPEF experiments. Two current densities (*j*) were applied: 30 mA cm<sup>-2</sup> and 50 mA cm<sup>-2</sup>. The results are shown in Figure 4.

1.0 mM Fe<sup>2+</sup> was added to the solutions from the post-anaerobic biological treatment in 0.05 M Na<sub>2</sub>SO<sub>4</sub> at pH 3.0, and the resulting solutions were directly exposed to sunlight. When the solution was exposed to direct radiation, a slight decline in the absorbance (Figure 4A) and a poor COD decay was observed after 50 min (Figure 4B). When electrochemical methods were, complete

decolorization was achieved before 50 min of electrolysis. On the other hand, if the experiment was performed without a catalyst (EO-H<sub>2</sub>O<sub>2</sub>), the COD decay reached 67% after 180 min under an applied current density of 50 mA cm<sup>-2</sup>, due to the action of hydroxyl radicals generated on the BDD surface and the oxidative capacity of the electro-generated hydrogen peroxide. Through EF, a COD abatement of 80% occurred under an applied current density of 30 mA cm<sup>-2</sup> because in EF, hydroxyl radicals are formed at the BDD anode and in the bulk of the solution. At a current density of 50 mA cm<sup>-2</sup>, no difference in the COD decay was observed, but this method caused progressive consumption of electric charge, decreasing the current efficiency (CE) values from 17% at 30 mA cm<sup>-2</sup> to 9% using 50 mA cm<sup>-2</sup>, which is close to the CE values obtained for EO-H<sub>2</sub>O<sub>2</sub> (Figure 5). It is known that a series of parasite reactions occurs in Na<sub>2</sub>SO<sub>4</sub> media, increasing the electric charge consumption,  $q$ , with loss in CE at higher current densities. In other words, the occurrence of non-organic oxidizing reactions involving hydroxyl radicals yields a relatively lower amount of organic oxidation events [29]. When the solution is treated by SPEF at 30 and 50 mA cm<sup>-2</sup>, practically complete mineralization (~90–95 %) is achieved. This is reflected in the greater efficiency of the solar process, compared to EF and EO-H<sub>2</sub>O<sub>2</sub> (Figure 5). For the same applied current at the end of the duration of electrolysis, the electro-Fenton process increases the efficiency of mineralization 1.6 times compared to the electro-oxidation process. On the other hand, the SPEF process increases the efficiency 1.3 times compared to EF and 2.1 times compared to EO. Thus, the SPEF process shows the synergistic use of (i) ultra violet radiation coming directly from the sun which allows photo-reduction and decarboxylation of Fe<sup>3+</sup> complexes, (ii) the presence of catalyst, and (iii) a non-active electrode such as BDD.

Another important result is related to the concentrations of nitrate and ammonium ions. The mineralization of organic compounds includes the loss of their nitrogen in the form of inorganic ions such as NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions. The formation of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions may be due to mineralization of urea, proteins, amino acids and nucleic acids present in the slaughterhouse

wastewater. The increase of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions after biological and electrochemical treatments suggests the inability of both processes to degrade dissolved organic N-compounds until they are transformed to ions.

#### *3.4. Evaluation of the combined Anaerobic Digestion/Solar photoelectro-Fenton process*

It was possible to remove > 90% of COD through anaerobic treatment after 22 days of incubation, based on the steady state observed in degradation and in methane production during the process over 30 days, as shown in Figure 2. The  $\text{CH}_4$  production was close to 90 mL. Further, the final water showed a very low turbidity, a decrease of 65% in total solids and the complete removal of volatile suspended solids (Table 1). Immediately following the anaerobic biological treatment, the water was treated by the SPEF process. The results of both processes are shown in Figure 6. The same pattern was observed in the decay of COD shown in Figure 6, with a decay of 83%. Before this process, the water presented a strong red color while after incubation for 20 days, it acquired a pale yellow color. The resulting water (post-anaerobic digestion) was treated by the SPEF process under an applied current density of  $30 \text{ mA cm}^{-2}$ , to obtain colorless water with an organic matter content of  $10 \text{ mg L}^{-1}$ , equivalent to 99% COD removal after 3 h of electrolysis (Figure 6). Additionally, complete reduction of the turbidity of the solution and solids present was also achieved (Table 1). Thus, the combined treatment increased the COD removal. This high reduction in COD is explained by the degradation of compounds of high molecular mass by methanogenic bacteria to short-chain (monomers), which are easier to oxidize by hydroxyl radicals during the SPEF process.



#### 4. Conclusions

Slaughterhouse wastewater was treated by anaerobic biological oxidation, electrochemical advanced oxidation processes and the combination of both treatments. The biological oxidation treatment resulted in high COD removals >90%, indicating that the water has high biodegradability. Further, an accumulation of 90 mL of CH<sub>4</sub> was observed over 30 days of the reaction.

The relative oxidative capacity of EAOPs increased in the order EO-H<sub>2</sub>O<sub>2</sub> < EF < SPEF, with COD removals of 63%, 79% and > 95%, respectively, after 180 min of reaction. In the SPEF process, hydroxyl radicals are generated in the bulk, and additional •OH-production is induced by solar radiation. In addition, the direct photolysis of complexes between Fe<sup>3+</sup> and some organic intermediates led to the fastest reaction rates.

Finally, the combination of both processes produced a totally clarified, odorless effluent, without solids in suspension and with a COD removal of 97%, compared to the separate processes producing an accumulation of a specific CH<sub>4</sub> volume of 90 mL.

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**Figure Captions.**

Figure 1. UV-Vis spectra of the initial and final samples of industrial wastewater from the slaughterhouse.

Figure 2. Decay of COD during anaerobic bio-digestion of 400 mL of cattle slurry in water for 30 days at 35 °C.

Figure 3. Specific volume of methane, normalized and expressed as dry gas per total COD over 30 days of anaerobic digestion at 35 °C.

Figure 4. (A) Absorbance and (B) COD decay of slaughterhouse wastewater after the anaerobic process. Experimental conditions: 0.05 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, pH = 3.0, T = 35 °C, [Fe<sup>2+</sup>] = 1.0 mM. (▶) Photolysis, (◀) EO-H<sub>2</sub>O<sub>2</sub> j = 50 mA cm<sup>-2</sup>, (▼) EF j = 30 mA cm<sup>-2</sup>, (▲) EF j = 50 mA cm<sup>-1</sup>, (●) SPEF j = 30 mA cm<sup>-2</sup>, (■) SPEF j = 50 mA cm<sup>-2</sup>.

Figure 5. Effect of current efficiency on the degradation of slaughterhouse wastewater vs. the electrolysis time for the treatment to 0.1 L of solution. Experimental conditions: 0.05 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, pH = 3.0, T = 35 °C, [Fe<sup>2+</sup>] = 1.0 mM. (◀) EO-H<sub>2</sub>O<sub>2</sub> j = 50 mA cm<sup>-2</sup>, (▼) EF j = 30 mA cm<sup>-2</sup>, (▲) EF j = 50 mA cm<sup>-1</sup>, (●) SPEF j = 30 mA cm<sup>-2</sup>, (■) SPEF j = 50 mA cm<sup>-2</sup>.

Figure 6. COD decay under a combination of anaerobic digestion and solar photoelectron-Fenton treatments, with 30 days of anaerobic digestion followed by 180 min of treatment through the SPEF process. SPEF experimental conditions: 0.05 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, pH = 3.0, T = 35 °C, j = 30 mA cm<sup>-2</sup> [Fe<sup>2+</sup>] = 1.0 mM. The inset shows an enlargement of the SPEF treatment.

Table 1. Characterization of slaughterhouse wastewater obtained in this study.

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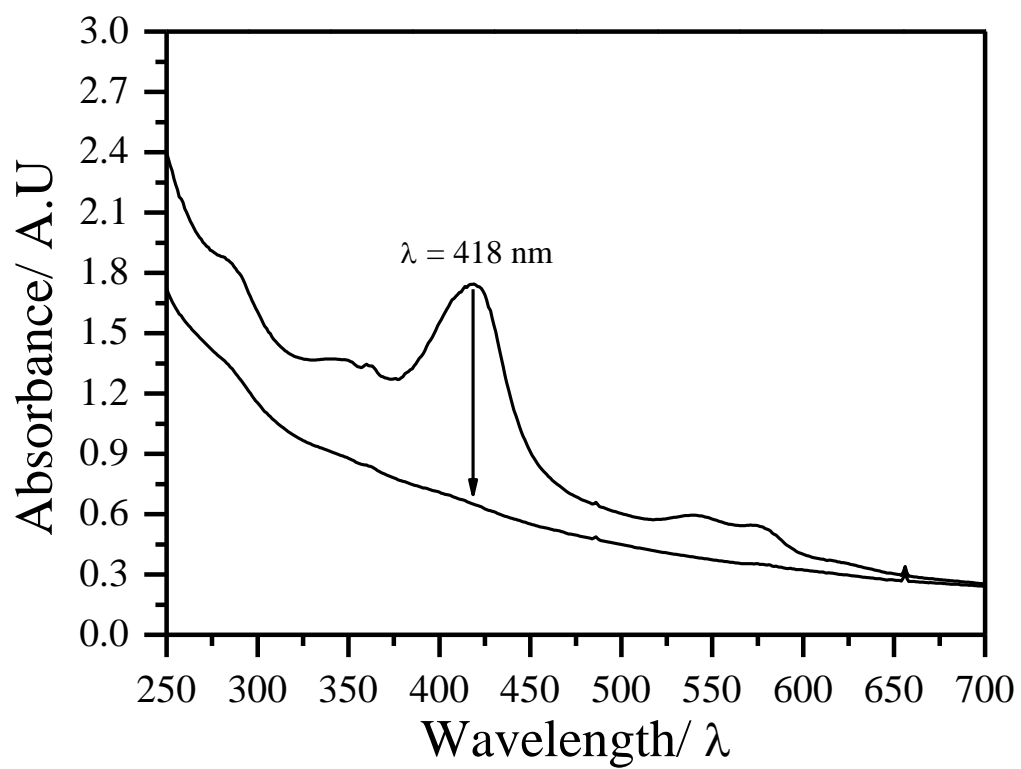


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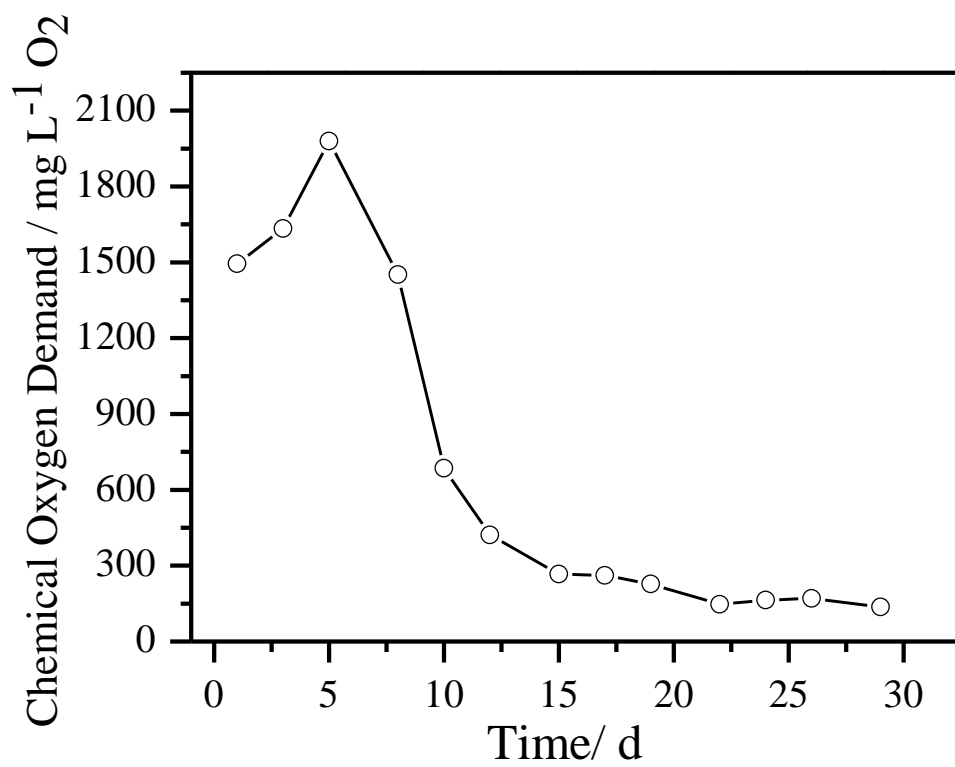
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**Figure 1.**



**Figure 2.**

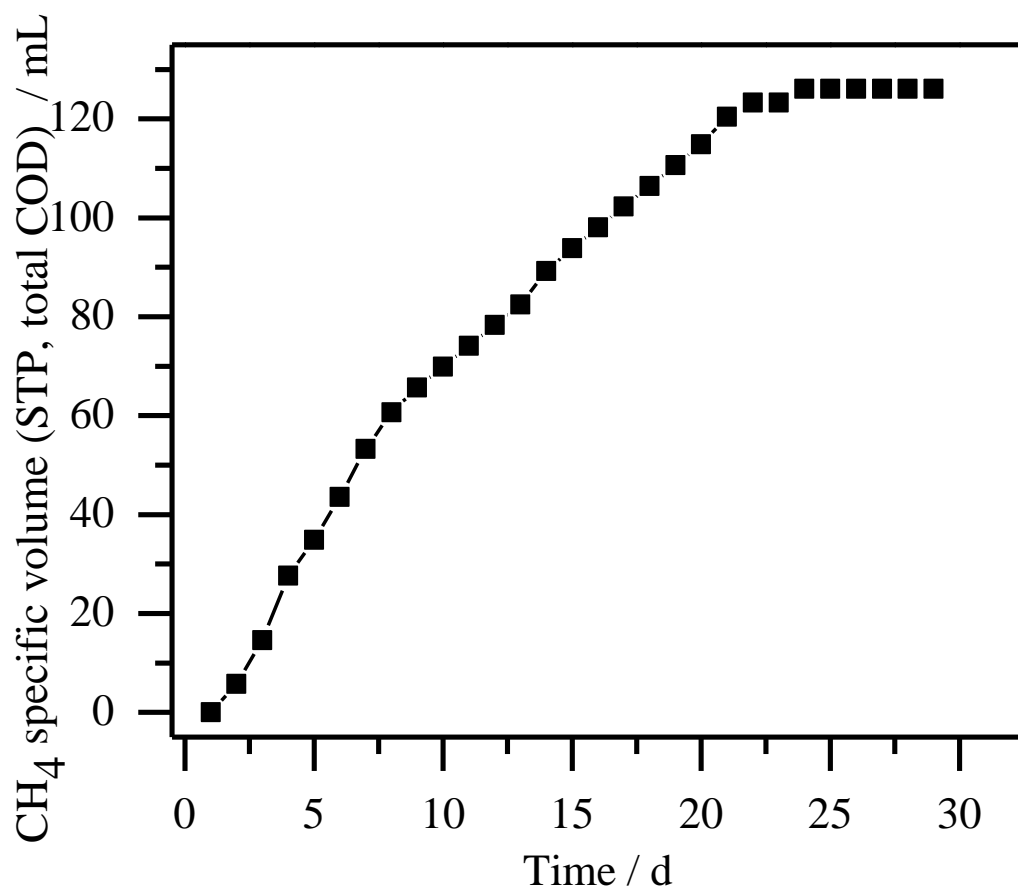


Figure 3.

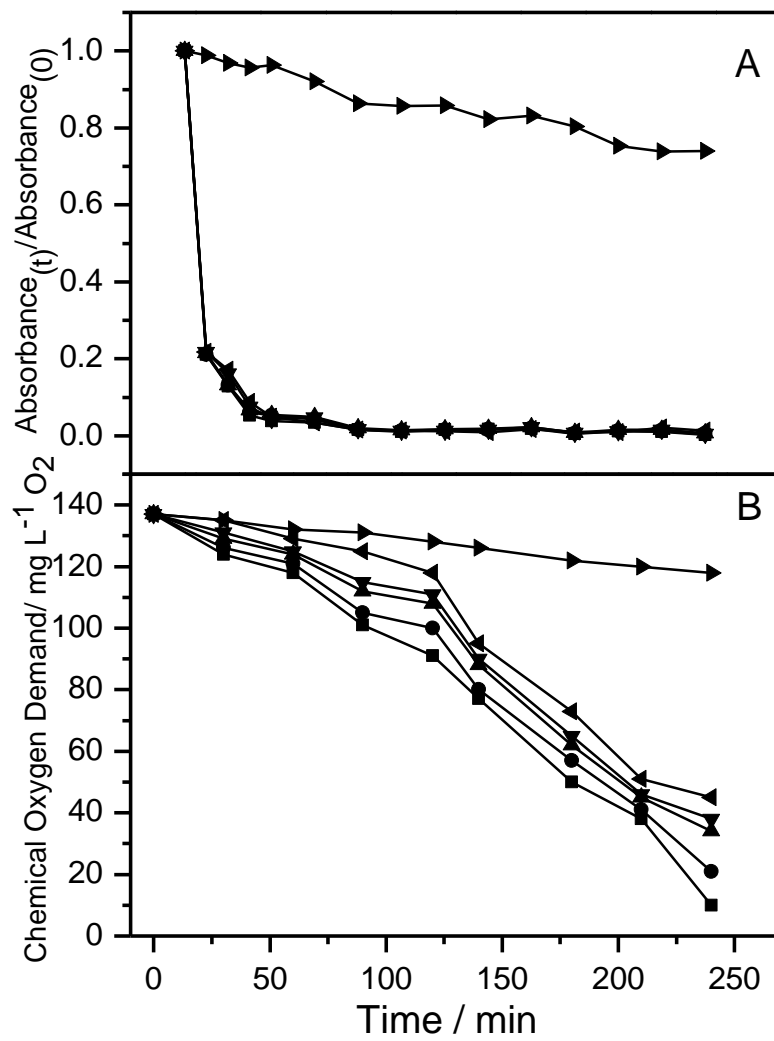


Figure 4.



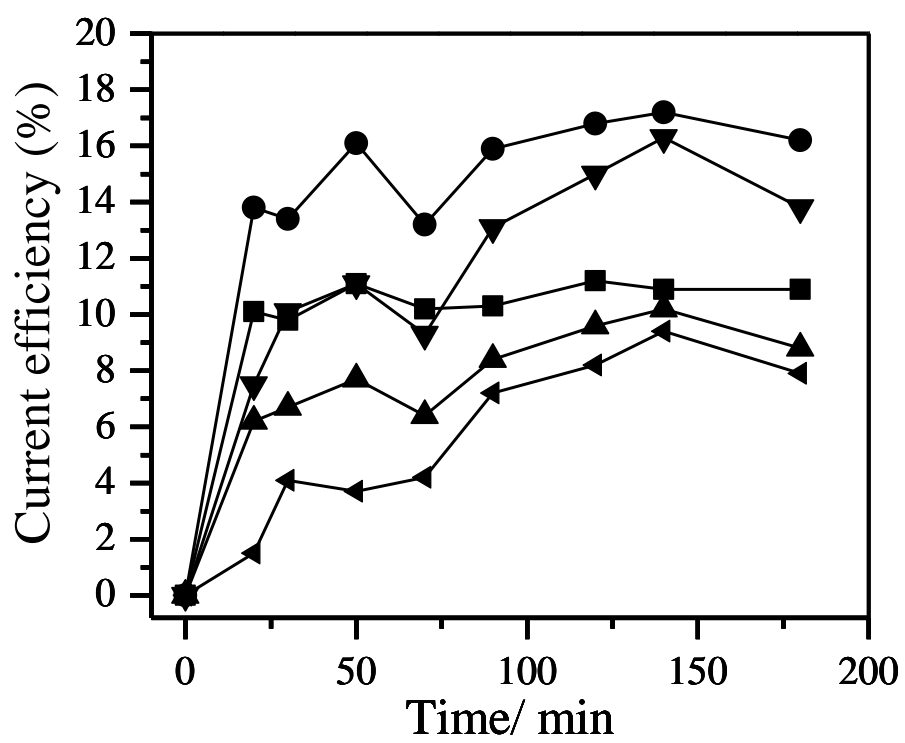


Figure 5

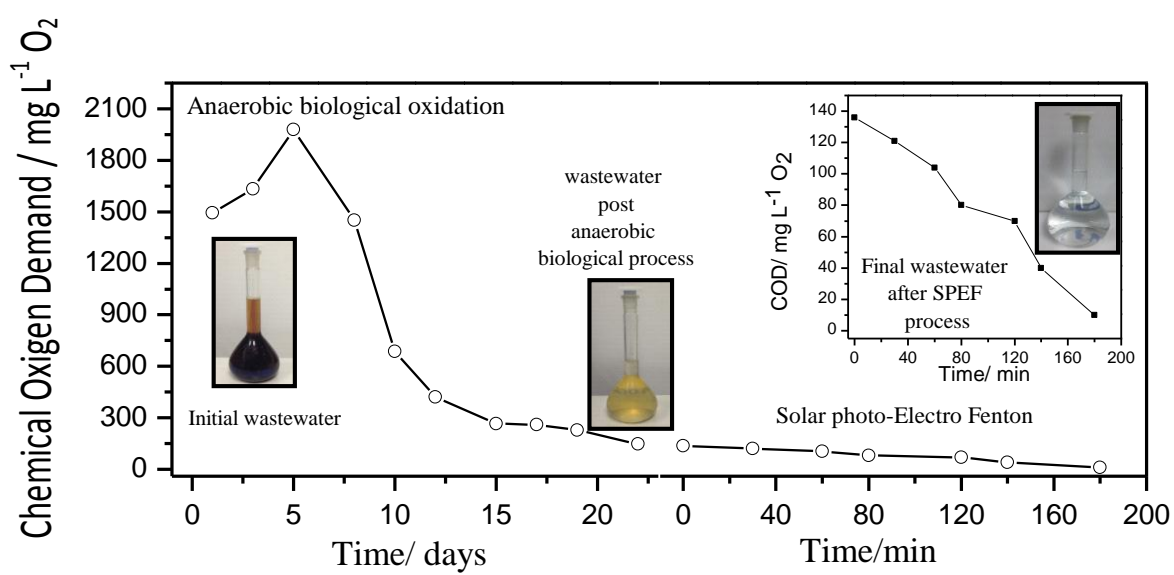


Figure 6

Parameters	Slaughterhouse wastewater			
	Initial Sample	Final industry effluent	After anaerobic biological oxidation	After SPEF
Color	Dark red	Light yellow	Light yellow	Uncolored
Odor	Intense	without smell	without smell	without smell
pH	7.8	7.6	8.3	3.4
Conductivity (mS)	2.2	2.1	5.4	12.3
Turbidity (NTU)	89	22	15	0.35
Total Carbon Organic (mg L <sup>-1</sup> )	513	132	52	4
Dissolved Inorganic Carbon (mg L <sup>-1</sup> )	21	10	8	2
Chemical Oxygen Demand (mg L <sup>-1</sup> )	1494	480	137	10
5-day Biochemical Oxygen Demand (mg L <sup>-1</sup> )	658	267	183	6
Absorbance at 418 nm (U.A)	1.91	0.30	0.25	0.0018
Total Suspended Solids (mg L <sup>-1</sup> )	19717	12725	890	n.d
Volatile Suspended Solids (mg L <sup>-1</sup> )	395	165	14	n.d
Dissolved Organic Nitrogen (mg L <sup>-1</sup> )	95	79	58	36
Ammonium NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	181	142	430	435
Nitrate NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	50	125	251	125
Dissolved Fe <sup>2+</sup> (mg L <sup>-1</sup> )	0.12	0.14	0.15	3.7
Total Chlorine (mg L <sup>-1</sup> )	0.27	0.30	0.29	0.15

**Table 1. Characterization of slaughterhouse wastewater obtained in this study.**