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# REDUCTION OF SOLUBLE ORGANIC CARBON AND REMOVAL OF TOTAL PHOSPHORUS AND METALS FROM SWINE WASTEWATER BY ELECTROCOAGULATION

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**Abstract** - In this study, the effects of operating time (t), current density (CD) and initial pH were investigated for soluble organic carbon (SOC) and total phosphorus (TP) removal from swine wastewater, pretreated in an UASB reactor, using an electrocoagulation process with aluminum (Al) and iron (Fe) electrodes. For the optimal conditions, Cu, Zn, Mn, Fe and Al removal, sludge production and energy consumption were evaluated. The removal efficiencies for the Al electrode were 78%, 96%, 84%, 99%, 65% and 84% for SOC, TP, Cu, Zn, Mn and Fe, respectively. For the Fe electrode the removal efficiencies were 57%, 96%, 81%, 99% and 61% for SOC, TP, Cu, Zn and Mn, respectively. The sludge generated, energy consumption, and theoretical hydrogen yields were 5 g/L, 1-18 kWh/L and 0.7-8.5 kWh, respectively. The electrocoagulation process can be used for soluble organic carbon, phosphorus and metals removal from swine wastewater. *Keywords*: Copper; Zinc; Manganese.

#### INTRODUCTION

Pollution from swine wastewater has received considerable attention because of high concentrations of organic matter, nitrogen, phosphorus, and hazardous heavy metals (Lee and Shoda, 2008; Amaral et al., 2014). Biological processes have been widely used to improve the treatment of swine effluents (Bernet andBéline, 2009).

Among the methods of biological swine wastewater treatment, the upflow anaerobic sludge blanket (UASB) is used for treating wastes with high soluble organic loads and works at low hydraulic retention times (Zhao et al., 2008). However, this system still does

not generate effluents that reach discharge standards according to Brazilian and international regulations (Foresti et al., 2006; Ramires and Oliveira, 2014).

Due to the complexity of this wastewater, treatment alternatives should be studied. Among the technologies of physical-chemical treatment, electrocoagulation (EC) is a viable alternative for the treatment of this effluent (Mores et al., 2016). EC is an emerging technology in water and wastewater treatment, as it combines the benefits of coagulation, flotation and electrochemistry (Moussa et al., 2017). The EC process is well known for its ability to remove metals, phosphorus and suspended solids (Dia, 2017). However, studies of metals, phosphorous and soluble

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organic carbon (SOC) removal in swine effluents using electrocoagulation are poorly reported in the literature.

Electrocoagulation technology involves applying an electric current to an aqueous solution through sacrificial metal electrodes such as aluminum (Al) and/or iron (Fe). This promotes the metal oxidation and dissolution, thus leading to the generation of ions and gases (oxygen and hydrogen), which at suitable pH generate reactions of coagulation/flocculation appropriate for wastewater treatment (Mollah et al., 2001; Chen, 2004; Jung et al., 2015. The major reactions that occur at Al and Fe electrodes during the EC process are presented below:

- Anode

$$Al_{(s)} \to Al^{3+}_{(aq)} + 3e^{-}$$
 (1)

$$Fe_{(s)} \to Fe^{2+}_{(aq)} + 2e^{-}$$
 (2)

$$Fe_{(s)} \to Fe^{3+}_{(aq)} + 3e^{-}$$
 (3)

- Cathode

$$2H_2O_{(1)} + 2e^- \rightarrow H_{2(g)} + 2OH_{(aq)}^-$$
 (4)

The hydrolysis products of Al and Fe destabilize/ neutralizing the repulsive forces that keep the particles suspended in wastewater, allowing their agglomeration and separation from the solution by sedimentation or flotation. The microbubbles (H<sub>2</sub> and O<sub>2</sub>) generated on the surfaces of the electrodes carry the agglomerated particles to the top of the solution (Mollah, 2001).

In this sense, the objective of this study was to establish optimal operating conditions for the parameters: operating time, initial pH and current density on the removal of soluble organic carbon (COS) and total phosphorus (TP) from swine wastewater pretreated by UASB using electrocoagulation with different electrode materials (Fe and Al). The best conditions were evaluated for the removal of Cu, Zn, Mn, Fe and Al.

### MATERIALS AND METHODS

#### Wastewater Characterization

Samples were collected of the UASB reactor effluent (URE) of a Swine Manure Treatment System (SMTS) in Concórdia, State of Santa Catarina, Brazil. The system received swine wastewater from Embrapa's experimental facilities (15 m³/d). The treatment system consisted of a solid–liquid separation step using a screen, an equalization tank, a settling tank,

**Table 1.** Characterization of URE used in this study.

Parameter	Value
Conductivity (mS/cm)	$6.06 \pm 0.62$
Total Alkalinity (mg CaCO <sub>3</sub> /L)	$3661.9 \pm 209.5$
pН	$7.5 \pm 0.53$
Turbidity (NTU)	$607.00 \pm 161.98$
SOC (mg/L)	$2425.00 \pm 521.07$
TP (mg/L)	$57.00 \pm 18.02$
Cu (mg/L)	$1.82 \pm 0.41$
Zn (mgL)	$6.27 \pm 1.14$
Mn (mg/L)	$1.58 \pm 0.30$
Fe (mg/L)	$9.21 \pm 2.38$
Al $(\mu g/g)$	-

an anaerobic reactor, an aerobic reactor and a second settling tank (Kunz et al., 2009). The characterization of the wastewater is shown in Table 1.

## **Experimental Setup and Procedure**

The experiments were performed in batch mode in an open reactor with a useful volume of 1.8 L. Fe and Al electrodes with 130 mm of height and 70 mm of width were used. An orifice in the center of 12 mm diameter for passage of the electrode nylon screw and another orifice at the top of 4 mm to couple the electrode connections power supply to a power source of direct current (DC Power Supply FA-3005 Intrutherm). The electrodes were vertically installed with a distance of 2 cm between them. The system was operated under stirring using a magnetic stirrer (Fisher Scientific). The cleaning of the electrodes was conducted with steel wool and rinsed with distilled water. Before each batch experiment, swine wastewater pH was adjusted according to the matrix of experimental design (Table 2) using sulfuric acid and sodium hydroxide (Vetec) as required.

# **Experimental Design**

In this study, a central composite rotatable design (CCRD)  $2^3$  was used to verify the performance of the electrode materials (Al and Fe) on the operating time (9.60 to 110.04 min), current density (20.22 to 57.56 mA/cm) and initial pH (0.96 to 11.04).

#### **Analytical Methods**

The SOC was analyzed by burning at 950°C and CO<sub>2</sub> measured by a NDIR infrared detector for elemental analysis equipment, Multi Elemental Analitic®Multi C/N 2100 brand Analytik Jena. The elements Cu, Zn, Mn, Fe and Al were determined by flame atomic absorption spectrophotometry (AAS) according to the AOAC Official Method 975.03 described by AOAC (1995). Total phosphorus (TP) was performed by spectrophotometry in the ultraviolet-visible region using the AOAC Official Method 958.01 described by AOAC (1995).

\*CD **SOC (%)** TP (%) Final pH pН (min) (mA.cm<sup>-2</sup>) Run  $(X_3)$ Al Fe Al Fe Al Fe  $(X_1)$  $(X_2)$ -1 (27.8) -1 (30.0) -1 (3.0) 54.7 1 11.8 4.3 77.2 4.3 5.0 1 (90.0) -1 (27.8) -1(3.0)93.7 73.5 5.0 52.1 3.8 7.6 3 -1(30.0)-1(3.0)50.3 15.8 68.2 1 (50.0) 58.6 4.8 7.0 4 1 (90.0) 1 (50.0) -1(3.0)47.7 18.4 92.3 3.9 8.8 8.3 5 -1 (30.0) -1 (27.8) 1 (9.0) 33.7 0.0 50.7 30.9 9.1 9.3 6 34.0 1 (90.0) -1(27.8)1(9.0)23.2 91.4 100.0 9.4 9.8 7 1 (50.0) -1(30.0)1(9.0)43.4 5.8 92.9 41.0 9.5 9.6 1 (90.0) 1 (50.0) 1(9.0)40.5 0.0 93.9 10.0 10.8 86.0 9 -1.68 (9.60) 36.2 5.1 29.0 0(38.9)0(6.0)78.1 6.3 7.5 10 1.68 (110.04) 0(38.9)0(6.0)36.9 57.0 96.3 95.8 8.8 9.4 96.8 11 0(60.0)-1.68 (20.2) 0(6.0)63.6 13.1 89.6 7.4 7.6 8.5 12 1.68 (57.6) 0(6.0)54.4 15.4 96.7 95.8 8.7 0(60.0)13 0(60.0)0(38.9)-1.68 (0.96) 10.2 11.5 2.3 0.0 1.1 1.2 14 0(60.0)0(38.9)1.68 (11.0) 22.6 12.5 65.4 72.6 10.9 11.9 15 0(60.0)0(38.9)0(6.0)78.6 30.4 96.6 75.4 8.6 8.4 16 0(60.0)0(38.9)0(6.0)26.3 96.4 80.7 8.5 8.4 76.6 17 0(60.0)0(38.9)0(6.0)78.6 25.7 95.6 76.9 8.5 8.9

**Table 2.** Experimental matrix of CCRD (2<sup>3</sup>) design and results for the electrodes of Al and Fe.

The pH was determined using a Marconi PA200 pHmeter and the conductivity using a Hanna HI 255conductivimeter. The sludge after the EC treatment was filtered using a filter paper (Quanty 25  $\mu$ m) and dried in an oven (Marconi MA035) at 103-105 C for 24 h. The dry sludge was pulverized in a mortar and pestle.

The SOC and TP removal concentration was calculated (RC) by Eq. (5)

$$RC(\%) = \frac{C_0 - C_t}{C_0} 100 \tag{5}$$

where  $C_0$  is the initial concentration of the constituents and C is the final concentration of the constituents (after EC).

# **Energy Consumption**

The energy consumption was calculated (Eq. 6) according to Kobya et al. (2015):

$$C_{\text{energy}} = \frac{U \cdot i \cdot t_{\text{EC}}}{V_{\text{ef}}}$$
 (6)

where U is the voltage (V), i is the current (A),  $t_{EC}$  is the electrocoagulation operating time (h) and  $V_{ef}$  is the volume of the wastewater treated (L).

## Theoretical Hydrogen Yields

The amount of H<sub>2</sub> gas emitted from an EC unit could be estimated by Eq. 7 (Phalakornkule et al., 2010; Lakshmi et al., 2013; Hashim et al., 2017).

$$Q_{H_2} = \frac{CD \cdot A \cdot t \cdot H}{F} \tag{7}$$

where,  $Q_{H2}$ , CD, A, t, H, and F are the quantity of the emitted amount of  $H_2$  gas (mole), applied current density (A/m<sup>2</sup>), effective surface area of electrodes (m<sup>2</sup>), treatment time (s), number of hydrogen molecules (1/2), and Faraday's constant (96,500), respectively. The amount of  $H_2$  produced could be expressed in volumetric units using the ideal gas law (Eq. 8):

$$P \cdot V = n \cdot R \cdot T \tag{8}$$

where P, V, n, R, and T represent pressure (kPa), volume (L), moles of gas, gas constant (8.314 J/kmole, at atmospheric pressure), and gas temperature (K), respectively. The yieldable energy from the H<sub>2</sub> gas could be estimated by Eq. 9. (Phalakornkule et al., 2010):

$$E_{H_2} = m \left( 0.244_{\text{mole}}^{MJ} \right) \tag{9}$$

where  $E_{H2}$  is the yieldable energy (MJ) and m is the amount of  $H_2$  gas (mole), respectively. It is noteworthy to highlight that each 3.6 MJ is enough to produce 1.0 kWh (Phalakornkule et al., 2010).

#### RESULTS AND DISCUSSION

Table 2 shows the matrix of the CCRD 2<sup>3</sup> and experimental response related to removal of SOC and TP and the monitored parameter final pH for the electrodes of Al and Fe.

When evaluating the operating conditions and the values of removal of COS and TP, it can be observed

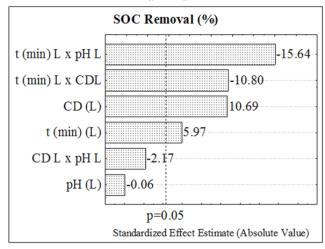
<sup>\*</sup>t - Operating time; \*CD - Current density.

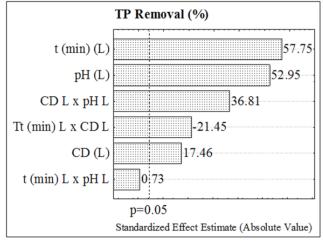
that only TP did not show removal above 50% at acidic initial pH and at times below 30 min for both electrodes. Regarding the COS, for the aluminum electrode only the tests 2, 3, 11, 12 and 15-17 showed removal above 50%, and with the iron electrode only the test 10. Due to the great difficulty of removal of the COS, (COS presented high variability of its organic components in terms of molecular and electrical propertiesmaking it difficult to adsorb the soluble particles) we opted for consider this parameter to determine the optimal operating conditions in the EC process.

For better visualization a Pareto chart was constructed (Fig. 1) showing the effect of the independent variables (t, CD and pH) on the responses of SOC and TP during the treatment process using EC for the electrodes Al and Fe (Table 2). The magnitude of each effect is indicated by the horizontal bars and the vertical line corresponding to p<0.05, which indicate how huge the effect is statistically significant.

For the Al electrode the interaction between time and pH and between time and CD had a negative effect and the variables CD and time a positive effect. For the Fe electrode, the time presented a positive effect, the

Aluminium





interaction between pH and CD and time and CD had a negative effect on SOC removal.

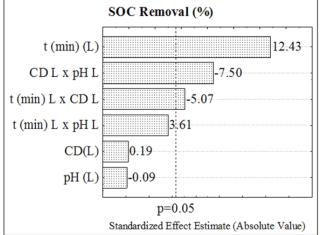
For the removal of TP using Al electrode it was observed that the time exerted greater influence and for the Fe electrode the interaction time and pH.

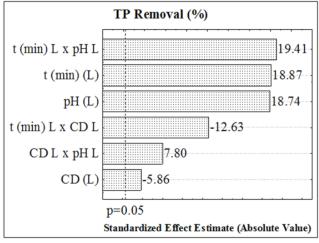
The removal is favored when t values are higher, since the concentration of hydroxides of Al and Fe dissolved in the EC system is high. These hydroxides neutralize electrostatic charges on the dispersed particles, reducing the electrostatic repulsion between the particles to the point where van der Waals attractions become predominant and thereby facilitate the agglomeration and adsorption of the pollutants (Kobya et al., 2015).

The positive effects for the iron electrode (Fig. 1) show that increasing the operational time of treatment enhances the SOC and TP removal efficiency. Studies found that Fe (II) is a weak coagulant if compared to Fe (III) due to its lower positive charge. A lower positive charge indicates that the ion's ability to compress the electrical double layer/destabilize colloids is weaker (Moussa et al., 2017).

This phenomenon was observed during the treatment process with Fe electrodes. The color of the







**Figure 1.** Pareto chart for Al and Fe electrodes for SOC and TP removal.

treated effluent and sludge became greenish, due to the dissolution of the Fe electrode to Fe<sup>2+</sup> and then became brown color due to oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> (Lakshmi and Sivashanmugam, 2013).

It is important to note that the time for the EC process is related with CD. The CD is an important parameter to control the speed of reactions (Akyol et al., 2013; Thirugnanasambandham et al., 2015) since it determines the coagulant dosage rate, the rate of bubble generation, and the size and growth of the flocs (Kobya et al., 2003; Chen et al., 2002).

The results shown in Table 2 indicate that the removal efficiencies of SOC and TP are proportional to the CD and time. Current density, which is the current per area of electrode, determines the amount of metal ions released from the electrodes. In general, metal ion dissociation is directly proportional to the applied current density. However, when too large a current is used there is high chance of wasting electrical energy in heating the water and even a decrease in current efficiency, expressed as the ratio of the current consumed to produce a certain product to the total current consumption (Moussa et al., 2017).

Thus, the time interaction effect and CD are negative, since the increase in time is unnecessary when the CD level is high +1 (50.0 mA/cm²) and +1.68 (57.6 mA/cm²). Very high current values may negatively affect the EC efficiency. Hakizimana et al., (2017) suggested secondary reactions may occur, and overdosing can reverse the charge of the colloids and redisperse them, leading thereby to a decrease of the coagulant efficiency and to a reduction of the electrode lifetime. Thus, CD values above 50.0 mA/cm² are at the critical point, not favoring a significant improvement in the quality of treated water.

Regarding the interaction of time and pH and the interaction CD and pH, the time and CD determine the forms of the hydroxides present during the EC process, since the pH of the treated water changes during the EC process (Kobya et al., 2003; Daneshvar, 2006). In the initial acid pH conditions, hydrolysis products ( $Al^{3+}$ ) are soluble aluminum hydroxides, and are not able to remove pollutants (Gomes et al., 2007). The aqueous  $Al(H_2O)_6^{3+}$  complex predominates at pH <4.0. As the pH increases during the EC operating time, trivalent aluminum ion is subjected to hydrolysis, initially forming  $Al(OH)_1(H_2O)_5^{2+}$  and then hydroxy aluminum species, such as:  $Al(OH)_2^{4+}$ ,  $Al(OH)_3^{4-}$  (insoluble),  $Al(OH)_4^{4-}$ ,  $Al_2(OH)_2^{4+}$  e  $Al(OH)_5^{2-}$ , and, possibly, polymers, such as: hydroxy  $Al_{13}(OH)_{32}^{7+}$ .

In conditions of pH 5 and 6, the hydrolysis products are Al(OH)<sup>2+</sup> and Al(OH)<sub>2</sub><sup>+</sup>, and between pH 5.2 and 8.8 solid Al(OH)<sub>3</sub> is the most prevalent. However, the main species responsible of the flocules and aggregates formation is Al(OH)<sub>3</sub>, which is formed by complex precipitation mechanisms from the soluble

monomeric and polymeric cations (Garcia-Segura, 2017); with pH values above 9.0, the soluble species Al(OH)<sub>4</sub><sup>-</sup> is prevalent, becoming the only species present above pH 10 (Gomes et al., 2007).

The electrochemical dissolution of the Fe anode is much more complex if compared to Al, because there are two oxidation states of Fe (Fe<sup>2+</sup> and Fe<sup>3+</sup>) (Panizza and Cerisola, 2010). According to the pH of the solution and dissolved oxygen, Fe<sup>2+</sup> species can potentially be oxidized to Fe<sup>3+</sup> and by hydrolysis generate monomeric Fe(OH)<sub>3</sub> and Fe(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> complex, Fe(H<sub>2</sub>O)<sub>5</sub>(OH)<sub>2</sub><sup>+</sup>, Fe(H<sub>2</sub>O)<sub>4</sub>(OH)<sub>2</sub><sup>+</sup>, Fe<sub>2</sub>(H<sub>2</sub>O)<sub>8</sub>(OH)<sub>2</sub><sup>4+</sup> and Fe<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(OH)<sub>4</sub><sup>2+</sup> (Panizza and Cerisola, 2010; Chen, 2004). These hydroxides, poly-hydroxides and metal hydroxides have a strong affinity with the dispersed particles that act as counterions, occasioning coagulation (Mollah et al., 2004).

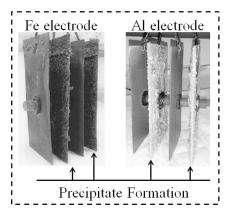
Thus, the EC experiments with initial low pH values (0.96 and 3.0) presented soluble hydroxide forms and, with the passage of operational time, pH values increased and reached the optimal value of formation of solid hydroxide (Al(OH)<sub>3</sub>) and/or Fe(OH)<sub>3</sub>, responsible for removal of SOC. At initial pH 9.0, precipitate formation around the cathode was observed (Fig. 2), which according to Zhao et al (2014) is the precipitation of calcium sulfate Eq. (10-12).

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O$$
 (10)

$$CO_3^{2-} + Ca^{2-} \leftrightarrow CaCO_3 \tag{11}$$

$$SO_4^{2-} + Ca^{2+} + 2H_2O \leftrightarrow CaSO_4 \cdot H_2O$$
 (12)

During the treatment process by EC, the pH of all experiments using Fe and Al electrodes increased (Table 2). The pH increased as a result of the generation of aluminum and iron hydroxides. This is due to the oxidation-reduction reaction of the water, which is more prevalent than the anodic oxidation of water (Canizares et al., 2005).



**Figure 2.** Precipitate formation around the cathodes of iron and aluminum electrodes.

The EC with alkaline initial pH exhibited little pH increase during the operational time. This increase was limited due to low OH formation at the cathode. pHs above 9.0 act negatively on the EC system due to the formation of soluble species of aluminum hydroxide which are ineffective during the treatment process (Kobya and Delipinar, 2008). Thus, the initial optimum pH to perform electrocoagulation with Al and Fe electrode is close to 6.0 (Gatsios et al., 2015; Kobya et al., 2011).

The statistical analysis of data from Table 3 was used to estimate the effects of the independent variables on removal of SOC and TP. These effects are related to the terms of a quadratic models, which are presented in Eq. (13 and 14):

SOC = 
$$77.14 + 1.85x_1 - 13.97x_1^2 + 3.34x_2 -$$
  
-  $6.03x_2^2 - 0.02x_3 - 21.08x_3^2 - 4.41x_1x_2 -$  (13)  
-  $6.37x_1x_3 - 0.89x_2x_3$ 

$$TP = 78.12 + 13.94x_1 - 6.92x_1^2 - 4.34x_2 + + 3.78x_2^2 + 13.86x_3 - 16.19x_3^2 - 12.20x_1x_2 + + 18.75x_1x_3 + 7.71x_2x_3$$
 (14)

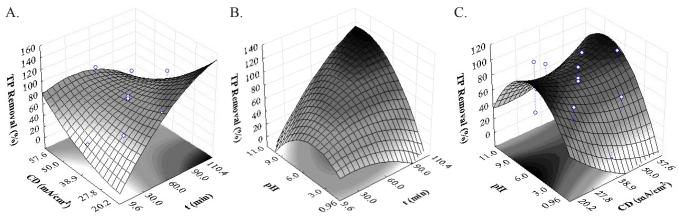
where  $x_1$  is the t,  $x_2$  is the CD and  $x_3$  is the initial pH.

This model was validated by analysis of variance used in a confidence interval of 95%. Calculated F for the removal of SOC with the Al electrode was 1.58 times greater than the tabulated one and for removal of TP with the Fe electrode was 1.69 times greater, validating the model, while SOC presented  $r^2 = 0.882$  and TP  $r^2 = 0.889$ , respectively.

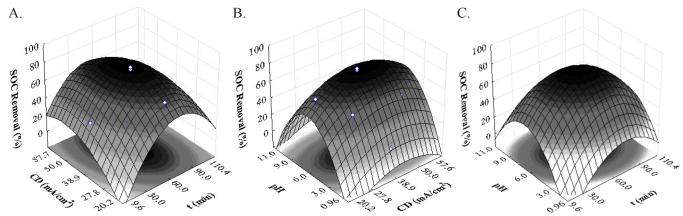
The empirical models allowed the construction of the response surfaces (Fig. 3 and 4), which are used to demonstrate the interactive effect of independent variables on the TP and SOC responses. It can be verified that, to maximize TP removal, the pH should be maintained between 3.0 and 9.0 and t above 30 min (Figure 3).

The best results (78%) were achieved at level 0 (center point), corresponding to an operational time of 60 min, CD 3.5 and pH 6.0. In extreme conditions de t, CD and pH of EC, was not possible to obtain good SOC removal results; at most extreme levels of CCRD, the independent variables CD, pH and t do not present a synergism for the generation of flocs, which are responsible for the removal of pollutants.

The optimal region of SOC removal, for the Al electrode was 60 min, CD 38.89 mA/cm<sup>2</sup> and pH



**Figure 3.** Response surfaces for TP removal (%) a) Effect of current density (CD) and operational time, b) Effect of initial pH and current density (CD), c) Effect of initial pH and operational time.



**Figure 4.** Response surfaces for SOC removal a) Effect of current density (CD) and operational time, b) Effect of initial pH and current density (CD), c) Effect of initial pH and operational time.

6.0 and for Fe electrode was 110.04 min, CD 38.89 mA/cm² and pH 6.0. These were evaluated for the removal of Cu, Zn, Mn, Fe and Al, which are present in swine wastewater and are considered harmful when discarded without treatment, mainly because of their non-degradability, toxicity and/or carcinogenicity (Hahladakis et al., 2013).

EC using Al electrodes removed 84% of Cu, 99% of Zn, 65% of Mn and 84% of Fe and the Fe electrode removed 81% of Cu, 99% of Zn, 61% of Mn, and Al was below the detection limit in wastewater (Table 3). As expected, treatment by EC is efficient for removal of Cu, Zn, Mn and Fe, and this removal was performed by adsorption of metal ions on the particle surface of aluminum or iron produced in the EC system and/or by the precipitation of metal ions, such as the corresponding hydroxides (Cu(OH)<sub>2</sub>, Zn(OH)<sub>2</sub>, Mn(OH)<sub>2</sub> and Fe(OH)<sub>2</sub>,) when the pH is higher, due to the formation of hydroxide ions (Mollah et al., 2004).

The amount of sludge generated in the optimal operational conditions for the Al electrode (60 min, CD 38.89 mA/cm<sup>2</sup> and pH 6.0) was 5.10 g/L¹where the concentration of Al in the sludge was 76.05 mg/kg. For

the Fe electrode in the optimal operational conditions (110.04 min, CD 38.89 mA/cm²and pH 6.0) the amount of sludge was 5.47 g/L and Fe concentration in the sludge was 213 g/kg. The high concentration of Fe is explained by the phenomenon "pitting corrosion" that causes holes in the electrodes and which provides a greater loss of the Fe electrode surface for the system (Dermentzis et al., 2011).

The amount of sludge produced is related to amount of removed pollutants (suspended solids, minerals and metals) (Kobya et al., 2006). The sludge generation is an important parameter in the EC treatment process because the amount of sludge produced during electrocoagulation presents an environmental relevance (Kobya et al., 2014).

# Estimating the Produced Hydrogen Gas and the Yieldable Energy from this Gas

The harvesting of  $H_2$  gas is one of the most important advantages of the EC technology because the hydrogen gas ( $H_2$ ) is an eco-friendly and high energy fuel (Hashim et al., 2017). Table 4 presents

**Table 3.** Metal concentration in the wastewater before and after the electrocoagulation process, and percentage of removal.

Parameter	Electrocoagulation						
	Before		A	fter	Removal (%)		
	Al	Fe	Al	Fe	Al	Fe	
Cu (mg/L)	$1.90 \pm 0.19$	$1.76 \pm 0.08$	$0.30 \pm 0.01$	$0.33 \pm 0.05$	84.2	81.5	
Zn (mg/L)	$7.32 \pm 0.90$	$5.57 \pm 0.56$	$0.01 \pm 0.00$	$0.01 \pm 0.01$	99.9	99.9	
Mn (mg/L)	$1.73 \pm 0.11$	$1.49 \pm 0.30$	$0.60 \pm 0.01$	$0.73 \pm 0.16$	65.2	51.2	
Fe (mg/L)	$9.36 \pm 0.40$	$9.47 \pm 0.33$	.33 $1.46 \pm 0.50$ $63.01 \pm 1.73$		84.5	-	
*Al (µg/g)	-	-	-	-	-	-	

<sup>\*</sup>Detection limit Al - 1 µg/g.

**Table 4.** Comparison of theoretical energy yield from the harvested hydrogen product and energy required for the electrocoagulation process.

Run	*t (min)	*CD (mA/cm²)	рН	Theoretical amount of H <sub>2</sub>	Theoretical H <sub>2</sub> volume	Theoretical amount energy of H <sub>2</sub>	Energy yield by experimentally produced H <sub>2</sub>	Experimental energy requirement (kWh/L)	
	$(X_1)$	$(X_2)$	$(X_3)$	Q <sub>H</sub> , (Mole)	(L)	$E_{H}$ , $(MJ)$	(kWh)	Al	Fe
1	-1 (30.0)	-1 (27.8)	-1 (3.0)	23.3	560.6	5.7	1.6	1.7	1.7
2	1 (90.0)	-1 (27.8)	-1 (3.0)	69.9	1681.7	17.1	4.7	5.2	5.2
3	-1 (30.0)	1 (50.0)	-1 (3.0)	42.0	1009.0	10.2	2.8	6.0	6.0
4	1 (90.0)	1 (50.0)	-1 (3.0)	125.9	3027.0	30.7	8.5	18.4	18.4
5	-1 (30.0)	-1 (27.8)	1 (9.0)	23.3	560.6	5.7	1.6	1.8	1.8
6	1 (90.0)	-1 (27.8)	1 (9.0)	69.9	1681.7	17.1	4.7	5.2	5.2
7	-1 (30.0)	1 (50.0)	1 (9.0)	42.0	1009.0	10.2	2.8	6.1	6.1
8	1 (90.0)	1 (50.0)	1 (9.0)	125.9	3027.0	30.7	8.5	18.0	18.0
9	-1.68 (9.60)	0 (38.9)	0 (6.0)	10.4	251.1	2.5	0.7	1.0	1.1
10	1.68 (110.04)	0 (38.9)	0 (6.0)	120.1	2888.0	29.3	8.1	11.8	12.9
11	0 (60.0)	-1.68 (20.2)	0 (6.0)	33.9	816.2	8.3	2.3	1.8	1.8
12	0 (60.0)	1.68 (57.6)	0 (6.0)	96.6	2322.9	23.6	6.5	14.7	14.7
13	0 (60.0)	0 (38.9)	-1.68 (0.96)	65.3	1569.5	15.9	4.4	6.2	7.0
14	0 (60.0)	0 (38.9)	1,68 (11.0)	65.3	1569.5	15.9	4.4	6.4	6.8
15	0 (60.0)	0 (38.9)	0 (6.0)	65.3	1569.5	15.9	4.4	6.6	6.6
16	0 (60.0)	0 (38.9)	0 (6.0)	65.3	1569.5	15.9	4.4	6.4	6.6
17	0 (60.0)	0 (38.9)	0 (6.0)	65.3	1569.5	15.9	4.4	6.2	6.8

T= 283k; P= 101.325kPa.

the theoretical amount and volume of H<sub>2</sub>, theoretical amount energy of H<sub>2</sub> energy yield of H<sub>2</sub> experimentally produced (kWh) and experimental energy requirement (kWh.L<sup>-1</sup>).

Comparing the energy gained by hydrogen generation and energy consumption for an electrocoagulation process, the results show that the energy yield of generated hydrogen can reduce the electrical energy demand of the electrocoagulation process. With the reduction of the net energy demand, electrocoagulation may become a useful method for reducing environmental problems associated with power production (Lakshmi et al., 2013).

#### **CONCLUSION**

This study evaluated the method of treatment by electrocoagulation for SOC and TP removal of UASB swine wastewater.

The optimum condition for the Al electrode was an operational time of 60 min, CD 38.89 mAcm<sup>2</sup> and pH 6.0 that removed 78 % of SOC, 96% of TP, 84% of Cu, 100% of Zn, 65% of Mn and 84% of Fe, and the amount of sludge generated was 5.10 g/L. The optimum condition for the Fe electrode was an operational time of 110 min, CD 38.89 mA/cm<sup>2</sup>and pH 6.0 that removed 57% of SOC, 96% of TP, 81% of Cu, 100% of Zn, 61% of Mn, and the amount of sludge generated was 5.47 g/L.

Electrocoagulation is an efficient system to remove SOC, TP, copper, zinc and manganese, for both the aluminum and iron electrodes for swine wastewater. The Al electrode is the most efficient in terms of removal and operational time, and also did not present Al in the final effluent.

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#### **REFERENCES**

- Akyol, A., Can, O.T., Demirbas, E., Kobya, M., A comparative study of electrocoagulation and electro-fenton for treatment of wastewater from liquid organic fertilizer plant. Separation and Purification Technology, 112, 11–19 (2013).
- Amaral, A.C., Kunz, A., Steinmetz, R.L.R., Justi, K.C., Zinc and copper distribution in swine wastewater treated by anaerobic digestion. Journal of Environmental Management, 141, 132-137 (2014).

- Association of Official Analytical Chemists. Official methods of analysis of the Association of Official Analytical Chemists. 16th ed. 1995. Metals in plants. Atomic absorption spectrophotometric method. (b) wetashing (AOAC 975.03).
- Bernet, N., Béline, F., Challenges and innovations on biological treatment of livestock effluents. Bioresource Technology, 100, 5431–5436 (2009).
- Canizares, P., Carmona, M., Martinez, F., Rodrigo, M.A., Electrodissolution of Al electrodes in electrocoagulation process. Industrial & Engineering Chemistry Research, (44), 4178–4185 (2005).
- Chen, G., Electrochemical technologies in wastewater treatment. Separation and Purification Technology, 38, 11–41 (2004).
- Chen, X., Chen, G., Yue, P.L., Investigation on the electrolysis voltage of electrocoagulation, Chemical Engineering Science, 57, 2449-2455 (2002).
- Dia, O., Drogui, P., Buelna, Dubé, G., R., Strategical approach to prevent ammonia formation during electrocoagulation of landfill leachate obtained from a biofiltration process. Separation and Purification Technology, 189, 253-259 (2017).
- Daneshvar, N., Oladegaragoze, A., Djafarzadeh, N., Decolorization of basic dye solutions by electrocoagulation: An investigation of the effect of operational parameters. Journal of Hazardous Materials, 129, 116–122 (2006).
- Dermentzis, K., Christoforidis, A., Valsamidou, E., Removal of nickel copper, zinc and chromium from synthetic and industrial wastewater by electrocoagulation. International Journal of Environmental Science and Technology, 1, 697–710 (2011).
- Foresti, E., Zaiat, M., Vallero, M., Anaerobic processes as the core technology for sustainable domestic wastewater treatment: Consolidated applications, new trends, perspectives, and challenges. Environmental Science and Bio/Technology, 5, 3–19 (2006).
- Garcia-Segura, S., Eiband, M.M.S.G., de Melo, J.V., Martínez-Huitle, C.A., Electrocoagulation and advanced electrocoagulation processes: A general review about the fundamentals, emerging applications and its association with other Technologies. Journal of Electroanalytical Chemistry 801, 267-299 (2017).
- Gatsios, E., Hahladakis, J.N., Gidarakos, E., Optimization of electrocoagulation (EC) process for the purification of a real industrial wastewater from toxic metals. Journal of Environmental Management, 154, 117–127 (2015).
- Gomes, J.A.G., Daida, P., Kesmez, M., Weir, M., Moreno, H., Parga, J. R., Irwin, G., Whinney, H., Grady, T., Peterson, E., Cocke, D.L., Arsenic removal by electrocoagulation using combined Al–Fe electrode system and characterization of products. Journal of Hazardous Materials, 139, 220–231 (2007).

- Hahladakis, J., Smaragdaki, E., Vasilaki, G., Gidarakos, E., Use of sediment quality guidelines and pollution indicators for the assessment of heavy metal and pah contamination in greek surficial sea and lake sediments. Environmental Monitoring and Assessment, 185, 2843-2853 (2013).
- Hakizimana, J. N., Gourich, B., Chafi, M., Stiriba, Y., Vial, C., Drogui, P., Naja, J., Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. Desalination, 404, 1–21 (2017).
- Hashim, K. S., Shaw, A., Khaddar, Ra. A., Pedrola, M. O., Phipps, D., Iron removal, energy consumption and operating cost of electrocoagulation of drinking water using a new flow column reactor. Environmental Management, 189, 98-108 (2017).
- Jung, K., Hwang, M., Park, D., Ahn, K., Combining fluidized metal-impregnated granular activated carbon in three-dimensional electrocoagulation system: Feasibility and optimization test of color and COD removal from real cotton textile wastewater. Separation and Purification Technology, 146, 154– 167 (2015).
- Kobya, M., Can, O.T., Bayramoglu, M., Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, Journal of Hazardous Materials, B100, 163–178 (2003).
- Kobya, M., Can, O.T., Bayramoglu, M., Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. Journal of Hazardous Materials, B100, 163–178 (2003).
- Kobya, M., Delipinar, S., Treatment of the baker's yeast wastewater by electrocoagulation. Journal of Hazardous Materials, 154, 1133-1140 (2008).
- Kobya, M., Gebologlu, U., Ulu, F., Öncel, S., Demirbas, E., Removal of arsenic from drinking water by the electrocoagulation using Fe and Al electrodes. ElectrochimicaActa, 56, 5060–5070 (2011).
- Kobya, M., Hiz, H., Senturk, E., Aydiner, C., Demirbas, E., Treatment of potato chips manufacturing wastewater by electrocoagulation. Desalination, 190, 201–211 (2006).
- Kobya, M., Oncel, M.S., Demirbas, E., Şik, E., Akyol, A., Ince, M., The application of electrocoagulation process for treatment of the red mud dam wastewater from bayer's process. Journal of Environmental Chemical Engineering, 2, 2211–2220 (2014).
- Kobya, M., Ozyonar, F., Demirbas, E., Sik, E., Oncel, M.S., Arsenic removal from groundwater of Sivas-Şarkişla Plain, Turkey by electrocoagulation process: Comparing with iron plate and ball electrodes. Journal of Environmental Chemical Engineering, 3, 1096–1106 (2015).
- Kunz, A., Miele, M., Steinmetz, L.R.L., Advanced swine manure treatment and utilization in Brazil. Bioresource Technology, 100, 5485-5489 (2009).

- Lakshmi, J., Sozhan, G., Vasudevan, S., Recovery of hydrogen and removal of nitrate from water by electrocoagulation process. Environmental Science and Pollution Research, 20, 2184–2192 (2013).
- Lakshmi, P.M., Sivashanmugam, P., Treatment of oil tanning effluent by electrocoagulation: Influence of ultrasound and hybrid electrode on COD removal. Separation and Purification Technology, 116, 378–384 (2013).
- Lee, H., Shoda. M., Removal of COD and color from livestock wastewater by the Fenton method. Journal of Hazardous Materials, 153, 1314-1319 (2008).
- Lu, J., Li, Y., Yin, M., Ma, X., Lin, S., Removing heavy metal ions with continuous aluminum electrocoagulation: A study on back mixing and utilization rate of electro-generated Al ions. Chemical Engineering Journal, 267, 86-92 (2015).
- Mollah, M.Y., Schennach, R., Cocke, D.L., Electrocoagulation (EC)—Science and applications. Journal of Hazardous Materials, 84, (1), 29–41 (2001).
- Mollah, M.Y.A., Morkovsky, P., Gomes, J.A.G., Kesmez, M., Cocke, J.P.D.L., Fundamentals, present and future perspectives of electrocoagulation. Journal of Hazardous Materials, 114, 199-210 (2004).
- Mores,R., Treichel, H., A. Z., Claudio, Kunz, A., Steffens, J., Dallago, R. M.,Remove of phosphorous and turbidity of swine wastewater using electrocoagulation under continuous flow. Separation and Purification Technology, 171, 112-117 (2016).
- Moussa, D. T., El-Naas, M. H., Nasser, M., Al-Marri, M. J., A comprehensive review of electrocoagulation for water treatment: Potentials and challenges Review. Journal of Environmental Management, 1861, 24–41 (2017).
- Ndegwa, P. M., Zhu, J., Luo, A., Effects of solid levels and chemical additives on removal of solids and phosphorus in swine manure. Journal of Environmental Engineering, 127(12), 1111-1115 (2001).
- Panizza, M., Cerisola, G., Applicability of electrochemical methods to carwash wastewaters for reuse. Part 2: Electrocoagulation and anodic oxidation integrated process. Journal of Electroanalytical Chemistry, 638, 236-240 (2010).
- Phalakornkule, C., Sukkasem, P., Mutchimsattha, C., Hydrogen recovery from the electrocoagulation treatment of dye-containing wastewater. International Journal of Hydrogen Energy, 35, 10934-10943 (2010).
- Ramires, R.D., Oliveira, R.A., COS, TSS, Nutrients and coliforms removals in UASB reactors in two stages treating swine wastewater. Engenharia Agrícola, 34, 1256-1269 (2014).

Thirugnanasambandham, K., Sivakumar, V., Maran, J. P., Optimization of process parameters in electrocoagulation treating chicken industry wastewater to recover hydrogen gas with pollutant reduction. Renewable Energy, 80, 101–108 (2015).

- Zhao, B.H., Yue, Z.B., Zhao, Q.B., Mu, Y., Yu, H.Q., Harada, H., Li, Y.Y., Optimization of hydrogen
- production in a granule-based UASB reactor. International Journal of Hydrogen Energy, 33, 2454-2461 (2008).
- Zhao, S., Huang, G., Cheng, G., Wang, Y., Fu, H., Hardness, COD and turbidity removals from produced water by electrocoagulation pretreatment prior to reverse osmosis membranes. Desalination, 344, 454–462 (2014).