

## ELECTROLYSIS OF SWINE MANURE EFFLUENTS USING THREE DIFFERENT ELECTRODES Fe-Fe, Al-Al AND Fe-Al

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### ABSTRACT

Swine effluent with high organic strength need to be treated to make it suitable for applying to crop/pasture fields, or discharging to any waterways. Electrocoagulation is a relatively simpler and cheaper technique over biological and chemical treatment methods currently used to treat high-strength industrial and municipal wastewater. The performance of an electrocoagulation system mainly depends on the pH, Electrical Conductivity (EC) of the medium, Chemical Oxygen Demand (COD) loading rates and catalytic activity of the electrodes used. In this research, a study was conducted to compare the pollutant removal efficiencies of three electrodes (Fe-Fe, Al-Al and Fe-Al) with three electric current levels (500, 1000 and 2000 mA) while treating swine manure effluents. The electrochemical cell consisted of two parallel rectangular plates (90×25×1.5 mm) of Iron (Fe-Fe), Aluminum (Al-Al) and Iron-Aluminum (Fe-Al, later on described as hybrid) electrodes; immersed in a beaker with 550 mL swine effluents and powered by a Direct Current (DC) supply. All studies were conducted in batches at room temperature. In general, removal efficiencies were increased with increasing current densities and electrolysis times for electrodes evaluated. Aluminum electrodes outperformed iron and hybrid (iron-aluminum electrodes) in removing Total Phosphorus (TP) at all current density levels tested. Overall, use of hybrid electrodes resulted in better COD removal. For the same treatment times (1200 s) at higher current density (21 mA cm<sup>-2</sup>), hybrid electrodes removed about 100% COD, which are about 1.9 and 1.3 times higher than those of aluminum and iron electrodes, respectively. Iron electrodes showed the highest removal efficiency (85%) for Total Organic Carbon (TOC) at 21 mA cm<sup>-2</sup> current density and 1200 s treatment time. Overall, lower Specific Electrical Energy Consumptions (SEECs) per kg of Pollutants (TP, COD and TOC) were estimated for the aluminum electrodes than the other electrodes combination.

**Keywords:** Total Phosphorus, Chemical Oxygen Demand, Total Organic Carbon, Manure Effluent, Electrode

### 1. INTRODUCTION

Nutrient management, especially phosphorus and nitrogen, of livestock liquid manure is a challenge due to their environmental impact potential on waters. If these nutrients from liquid manure can be removed and recovered, runoff potential of nutrients from livestock production facility or from land application of manure may be reduced. Also, recovered nutrients many be applied to crop later on. Phosphorus (P) is one of the essential

nutrients for life, however, phosphate rocks are limited in the world and around 80% of phosphate produced globally is used as fertilizers (Regy *et al.*, 2002; Udert *et al.*, 2006; Inan and Alaydin, 2014). Due to limited phosphate supply, efforts to reduce nutrient loading, especially phosphorus, from livestock manure and runoff are ongoing. The development of P removal and recovery may provide phosphorus sustainability (Morse *et al.*, 1998).

There are many options for nutrient removal such as evaporation, reverse osmosis, nitrification, precipitation,

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ammonia stripping, electro dialysis and advanced oxidation (Inan and Alaydin, 2014). However, P removal technologies are limited. Biological P removal, chemical precipitation and crystallization techniques are the most common methods used to remove P from wastewater (Morse *et al.*, 1998). Chemical precipitation is a flexible approach and can be applied at several stages of the wastewater treatment process as required (Morse *et al.*, 1998). This process, however, precipitates P-bound waste and the impact of disposing this waste to agricultural land is not well documented. In the biological process, the use of chemical may be avoided, but it requires complex plant configuration. In addition, some novel technologies such as ion exchange, struvite crystallization, magnetic attraction, electrolysis and sorption have been studied to remove P (Liang, 2011; Cho *et al.*, 2010). Electrolysis is a modern process of wastewater treatment and studied it to treat swine liquid manure in this study.

The electrolysis process works on the principal of oxidative or reductive chemistry and it needs relatively simple equipment at ambient temperature and pressure. The key process in electrolysis is the interchange of atoms and ions with addition or removal of electrons from an external source (Cho *et al.*, 2010). However, electrolysis efficiency depends on the electrode materials, electric current density, pH, etc. (Li and Liu, 2009; Liu *et al.*, 2009; Cho *et al.*, 2010). Researchers are using different electrode materials to optimize the system. In this study three different electrodes such as Iron (Fe-Fe), Aluminum (Al-Al) and Iron-Aluminum (Fe-Al) electrodes were tested to improve the quality of swine wastewater.

The main objective of the present study is to investigate the electrochemical oxidation of swine effluent obtained from a primary lagoon for reducing organic and inorganic pollutants. The specific objectives are (1) to compare the pollutants (TP, COD and TOC) removal efficiencies of Iron (Fe-Fe), Aluminum (Al-Al) and Hybrid (Fe-Al) electrodes from swine effluents at varying currents and treatment durations, (2) to estimate the Electrical Energy Consumption (EEC) per unit volume of effluents treated and (3) to determine constituents and characterize sludge formed after electrolysis process.

## 2. MATERIALS AND METHODS

### 2.1. Swine Effluents

Liquid swine manure effluent was obtained from a primary lagoon of swine research unit at North Dakota State University, Fargo, North Dakota and were stored

until analysis at 4°C. Before a batch experiment was initiated, the effluent was homogenized and characterized for the following parameters: Electrical Conductivity (EC), pH, Total Suspended Solids (TSS), Total Phosphorus (TP), Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC). Properties of tested swine effluents were presented in **Table 1**. In this study, no additives were used and no pH adjustment was made to swine manure effluent for enhancing electrolytic efficiency of the electrolyte. This study was aimed to treat the livestock wastewater in situ (at the generation and storage level) as an effective primary treating tool without any extra treatment cost.

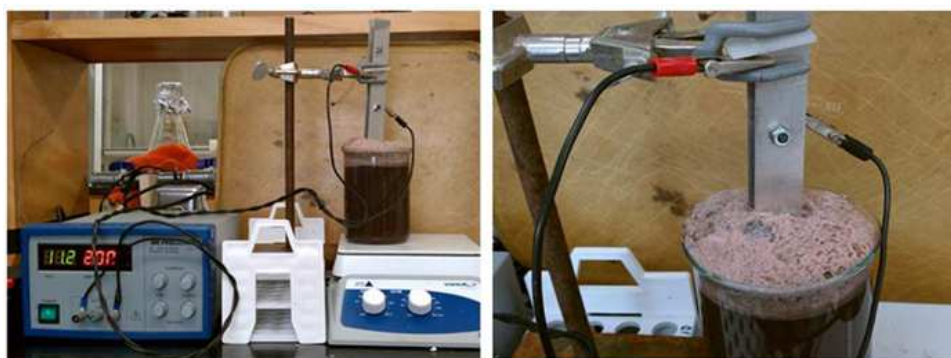
### 2.2. System Description and Operation

In this experiment, a pair of parallel plate of three different electrodes such as Iron (Fe-Fe), Aluminum (Al-Al) and Hybrid (Fe-Al) were (wired as mono-polar connection) tested in batches at room temperature around  $25\pm 2^\circ\text{C}$ . The electrochemical cell was consisted of two parallel rectangular plate electrodes ( $200\times 25\times 1.5$  mm) immersed to a depth of 90 mm in a 550 mL swine effluents contained in cylindrical glass beaker (**Fig. 1**). The total effective area of anode and cathode electrodes under wastewater in the beaker was  $96\text{ cm}^2$ . The gap between anode and cathode plates was maintained at 8 mm using Teflon spacers and mounted vertically with the help of clamp. At the beginning of a run, the electrodes were placed into the swine effluent and electrodes were powered by a regulated DC powered supply (Model BK-1621 A, 0-18;0-5 A; BK Precision, Yorba Linda, CA) equipped with both ammeter and voltmeter displaying the current passing through the circuit and the cell voltage, respectively. To avoid electrode passivation and any contamination, electrodes were cleaned at the end of each treatment run by rinsing in diluted HCl (5% v/v) solution. The polarity of electrodes was reversed every 300 s to prevent the formation of a passive layer on the electrode surface that reduces the efficiency of the electrolysis system. Polarity reversing also increases the longevity of the electrodes by ensuring equal wearing of anodes and cathodes. During electrolysis, the effluent under treatment was homogenized by gentle magnetic stirring at 200-300 rpm. A stirring intensity of 200-300 rpm was used in order to get a correct homogenization of the wastewater-flocs mixture.

**Table 1.** Characteristics of swine effluents used in the experiments

Parameters	Measured concentrations	NDPDES discharge permit limit
pH	8.3±0.1	6.0-9.0
Electrical Conductivity (mS cm <sup>-1</sup> )	6.7±0.1	0.9
TSS (mg L <sup>-1</sup> )	980±50	100(50)
TP (mg L <sup>-1</sup> )	35.3±3.1	2.0
TOC (mg L <sup>-1</sup> )	490±13	-
COD (mg L <sup>-1</sup> )	1577±110	120
Copper (mg L <sup>-1</sup> )	DM*	0.1685
Arsenic (mg L <sup>-1</sup> )	DM	0.0636
Zinc (mg L <sup>-1</sup> )	DM	0.117

- NDPDES (2009) discharge limit for storm water from industrial activity (NDR09-0000); - \*DM = didn't measured in manure



**Fig. 1.** Photograph of the laboratory scale electrolysis experiment set up taken from this research

### 2.3. Treatment

The overall performance and economy of an electrocoagulation process mainly depends on applied energy. Based on the EC of swine manure effluent used in this study, the maximum possible current that could be applied was 2000 mA. Therefore, three current levels (500, 1000 and 2000 mA) were tested with three replicates to investigate the effect of applied current on the efficiency of electrocoagulation process for treating swine effluent. The current density levels were about 5, 10 and 21 mA cm<sup>-2</sup>, which was calculated by dividing applied currents with effective electrodes area immersed under wastewater. Electrolysis process was continued for a period of 3600 s at each current density.

### 2.4. Sampling and Analysis

Electrolyzed wastewater samples were sampled at five predetermined intervals (300, 1200, 1800, 2400 and 3600 s) to investigate electrolysis duration on nutrients removal. At the end of each time interval, about 10 mL of supernatant sample was removed using a pipette and stored in test tubes to settle

suspended particles overnight before analysis was initiated. No centrifuging or filtration of samples was carried out followed by the electrolysis. Supernatant of the wastewater samples before and after electrolysis treatments were analyzed for TP, COD, TOC, pH and EC using Standard method of water and wastewater analysis (APHA, 2005). The pH and EC were analyzed using a hand held Orion pH and EC meter (Model, 990). Hach methods 10127, 8000 and 10173 were followed to determine TP, COD and TOC contents, respectively, in the sample before and after the electrolytic treatments. All analyses were performed calorimetrically using a HACH Model DR/2800 spectrophotometer (HACH Company, USA). All chemical used in the analyses were analytic grade. Analyses were performed in Waste Management Laboratory of North Dakota State University.

### 2.5. Sludge Characterization

At the end of electrocoagulation period, the floating scum buildup at the surface of electrolysis water was scraped and removed. The remaining treated (electrolyzed) wastewater was allowed to settle

overnight. Then, settled sludge was filtered (Whatman, 11  $\mu\text{m}$  pore size) and oven dried at  $103\pm 2^\circ\text{C}$  until the weight of the sludge samples were stabilized. A composite sample was made using the sludge from three replicates for each current density and electrodes type. The dried sludge was stored in a desiccators until analysis was completed. The sludge formed during electrolysis process was characterized by Inductively Coupled Plasma spectroscopy (ICP) using a 2010-11-15 Standard Method in the Wet Ecosystem Lab at North Dakota State University.

### 2.6. Removal Efficiency (RE)

The REs for TP, COD and TOC concentrations were calculated using the following relationship (Equation 1):

$$RE = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where, RE,  $C_i$  and  $C_f$  are removal efficiency (%), initial and final concentrations (ppm) of the pollutant under investigation.

### 2.7. Electrical Energy Consumption (EEC)

The EEC (kWh) per unit volume ( $Q$ ) was calculated using following relationship (Equation 2):

$$EEC = \frac{VIt}{3600 \times Q_{\text{influent}}} \quad (2)$$

Where:

$I$  = Operating current (mA)

$t$  = Electrolysis time (s)

$V$  = Applied cell volt

$Q$  = Volume (L) of manure effluent treated

### 2.8. Statistical Data Analysis

Measured pollutants (EC, pH, P, COD and TOC concentrations) concentrations and calculated REs in each treatment (current level) run were compared using Analysis Of Variance (ANOVA). The null hypothesis tested was that mean measured pollutant concentrations and RE among various current levels (treatments) were equal. All statistical analyses were performed in the SAS environment using the PROC Means procedures (SAS, 1999). Mean concentrations and RE were then separated using Duncan's Multiple Range Test (Steel *et al.*, 1997) at 5% significance level ( $p \leq 0.05$ ) if the main effect (month) was significant using F test at  $p \leq 0.05$ .

## 3. RESULTS

**Table 1** shows the initial characteristics of the swine manure effluent used in this research. The effluent had high organic strength (COD  $> 1,000 \text{ mg L}^{-1}$ ), TP ( $> 35 \text{ mg L}^{-1}$ ) and TOC ( $> 490 \text{ mg L}^{-1}$ ) according to NDPDES (2009) discharge limit. Therefore, the swine effluent must be treated before applying to crop/pasture fields or discharging to any water streams. Removal of nutrients using the electro-coagulation method is strongly dependent on the EC of the aqueous medium. In addition, pH, particle size, COD loading rates, electrodes nature and area and catalytic activity of the anodes also affect the process. In this study, pH and EC were measured twice; just before applying the power to the system and after 3600 s of electrolysis treatment time. Measured initial pH and EC were  $8.3 \pm 0.1$  and  $6.7 \pm 0.1 \text{ mS cm}^{-1}$ , respectively.

### 3.1. Effect of Treatment Duration on Pollutants Removal Efficiency

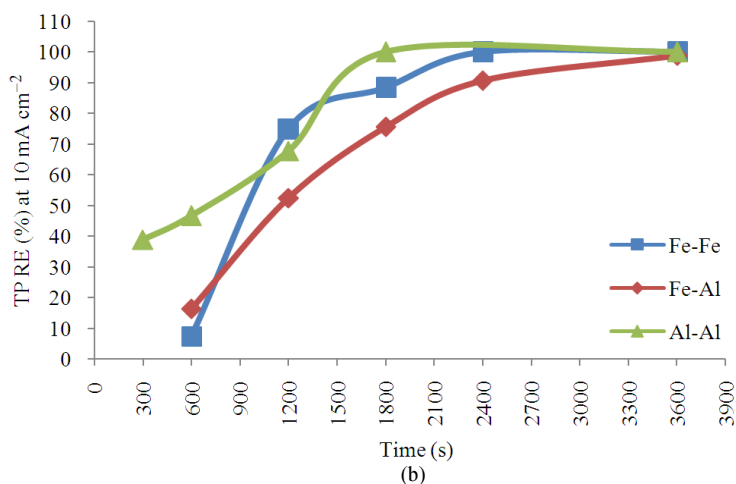
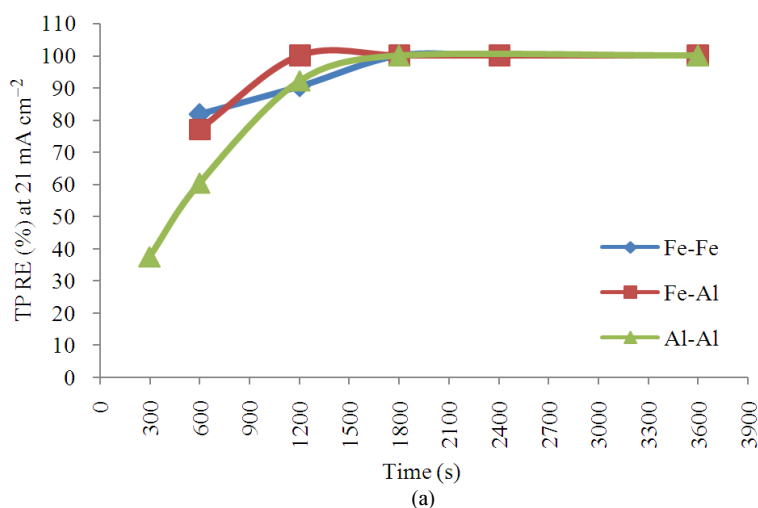
The removal efficiencies of all pollutants (TP, COD and TOC) under investigation at different current densities, treatment times and electrode types were presented (**Fig. 2 to 4**). The REs of TP increased with all electrode combinations at varying current densities ( $5\text{-}21 \text{ mA cm}^{-2}$ ) as treatment times progressed. At higher current density ( $21 \text{ mA cm}^{-2}$ ), Fe-Al electrodes had shown better TP removal efficiency than other electrodes within 1200 s of treatment initiation (**Fig. 2a**), but at lower current densities ( $5$  and  $10 \text{ mA cm}^{-2}$ ) Al-Al electrodes outperformed the other electrodes for TP removal (**Fig. 2b and c**). TP removal progressed overtime, maximum TP removal occurred within 1800 s from the start of each experiment. Overall, Al-Al electrodes resulted in better TP removal over all current densities during the experimental period. Similarly, at  $21 \text{ mA cm}^{-2}$  current density, Fe-Al electrodes removed about 100% of COD within 1200 s of the process began (**Fig. 3a**), but at  $5$  and  $10 \text{ mA cm}^{-2}$  current densities COD removal efficiency for Fe-AL electrodes reached  $\sim 80\%$  in 3600 s (**Fig. 3b and c**). At  $10 \text{ mA cm}^{-2}$  current density, Fe-Fe electrodes showed better COD removal efficiency than other electrodes combination. Overall, the Fe-Al electrodes resulted in better COD removal (**Fig. 3**).

### 3.2. Effect of Current Densities, Treatment Times and Electrode Types on Pollutants Removal Efficiency

Current density is one of the most crucial and steerable factors that control electrolytic treatment. In this study, electrode spacing was fixed at 8 mm, but current densities were varied at three preselected levels using a DC power source equipped with ammeter and voltmeter displays. The voltage level fluctuated, which was obvious due to oxidation and ionization at the anode surfaces and minimized by reversing the polarity every 300 s. For each current level, voltages were recorded at 300 s intervals during the 3600 s electrolysis period; an average of 12 voltage values was used to calculate the energy requirement. As with increased treatment duration, increased current densities demonstrated

similar proportional effects on the RE sand Electrical Energy Consumption (EEC) described as follows.

The removal efficiencies of TP, COD and TOC were positively correlated with increasing treatment times and three levels of current densities (5, 10 and 21 mA cm<sup>-2</sup>) and treatment times for each electrode type (Fig. 2 to 4). Removal efficiencies of TP for all three electrodes (Fe-Fe, Fe-Al and Al-Al) were similar (90 to 100%) at 21 mA cm<sup>-2</sup> current densities for a 1200 s treatment time (Fig. 2a). Removal efficiencies of TP during 1800s treatment time for all three electrodes at 21mA cm<sup>-2</sup> current density were about 100%. The TP removal efficiency with Al-Al electrodes was about 100% at 1800s treatment time for all three levels of applied current densities (Fig. 2). Even at lower current density (5 mA cm<sup>-2</sup>), removal efficiencies of TP with Al-Al electrodes was higher than those of Fe-Fe and Fe-Al electrodes (Fig. 2b and c).



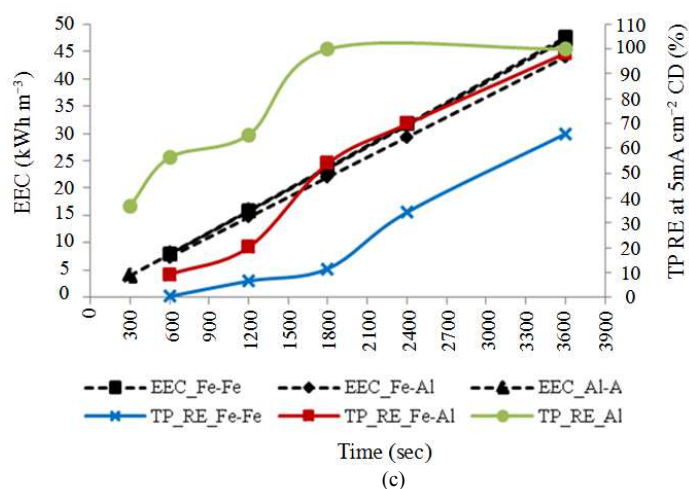
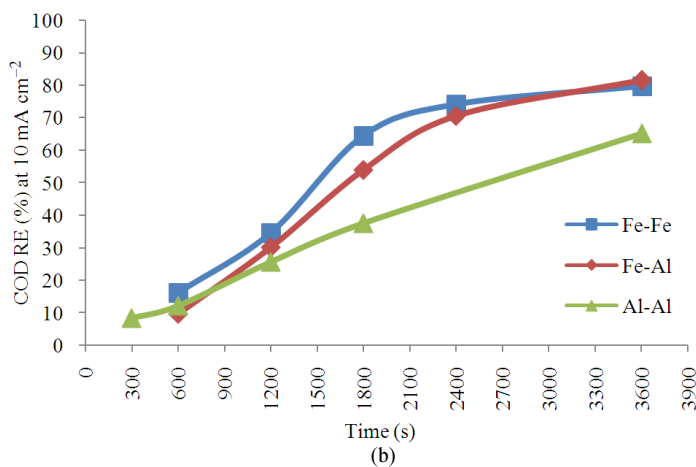
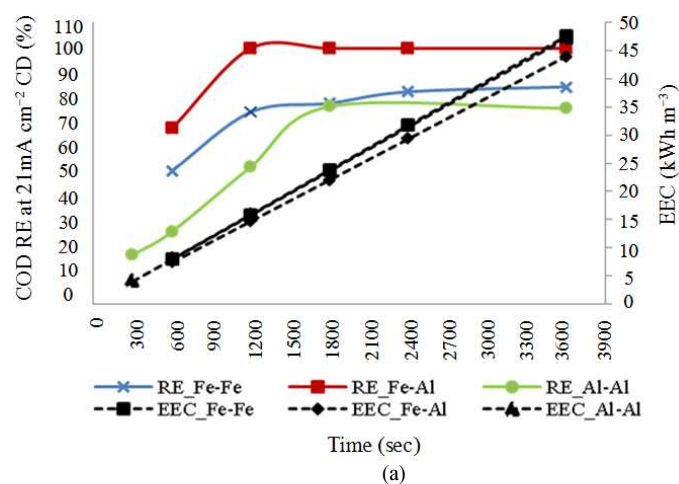
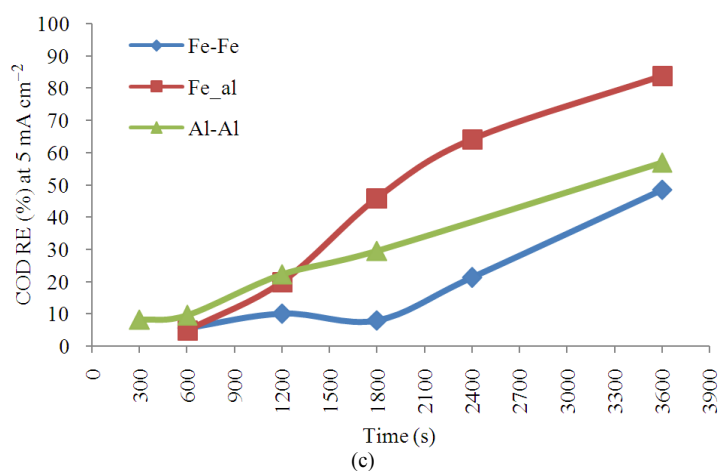
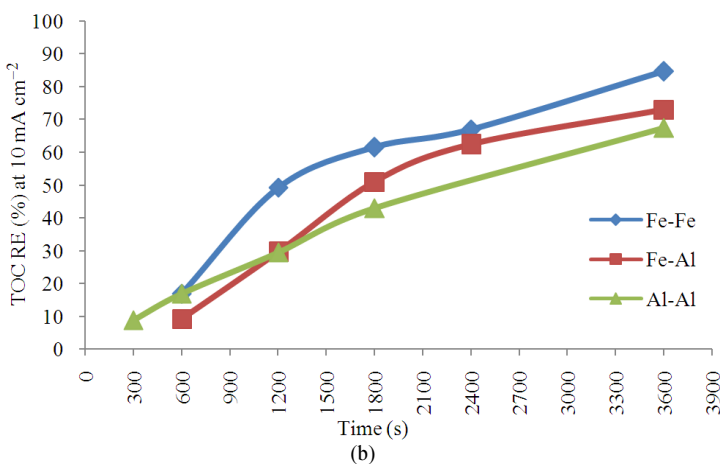
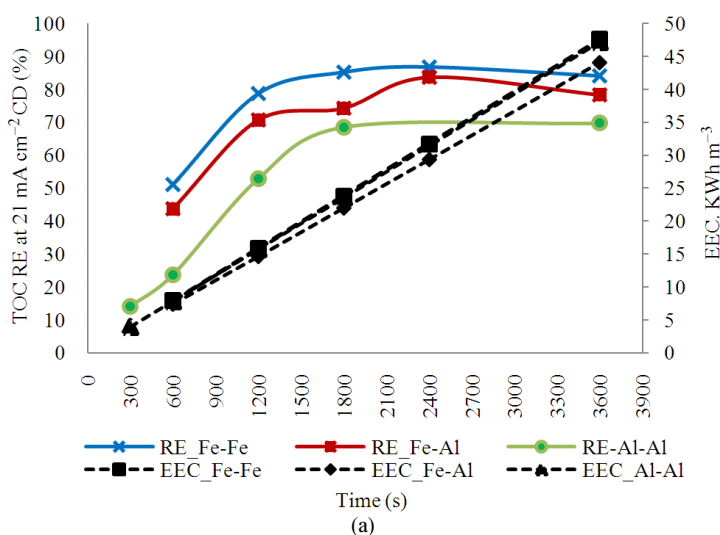


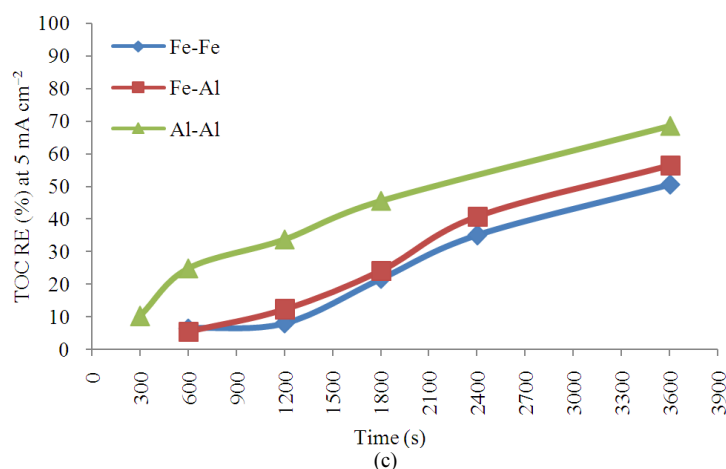
Fig. 2. The variations of TP Removal Efficiencies (REs) and Electrical Energy Consumptions (EEC) with electrode types at (a) 21, (b) 10 and (c) 5 mA cm<sup>-2</sup> current densities





**Fig. 3.** The variations of COD Removal Efficiencies (REs) and Electrical Energy Consumptions (EEC) with electrode types at (a) 21, (b) 10 and (c) 5 mA cm<sup>-2</sup> current densities





**Fig. 4.** The variations of TOC Removal Efficiencies (REs) and Electrical Energy Consumptions (EEC) with electrode types at (a) 21, (b) 10 and (c) 5 mA cm<sup>-2</sup> current densities

In this study, it was observed that the electrode types responded differently with increased treatment times and levels of applied current densities. At low current density (5 mA cm<sup>-2</sup>), removal efficiencies of COD for all electrode types were  $\leq 20\%$  up to 1200 s treatment time, but removal efficiencies increased as treatment time progressed (Fig. 3c). With longer treatment times (1800 to 3600 s), Fe-Al electrodes removed the highest amount of COD (46 to 80%) followed by Al-Al (30 to 57%) and Fe-Fe (8 to 49%) electrodes. Similarly, at 10 mA cm<sup>-2</sup> current density, Fe-Fe electrodes removed the highest COD (60 to 80%) followed by Fe-Al (54 to 82%) and Al-Al (38 to 65%) (Fig. 3b).

A previous study reported a maximum 80% COD removal with an electrolytic system that consisted of alternate Al and Fe electrodes (Fe-Al) using treated sludge from textile wastewater (Ciardelli and Ranieri, 2001). In this study, Electrodes Fe-Fe at 10 and 21 mA cm<sup>-2</sup> current densities, removed higher TOC (17 to 85% and 51 to 100%, respectively) than those of Fe-Al (9 to 73% and 44 to 84%, respectively) and Al-Al (9 to 67% and 14 to 70%, respectively) (Fig. 4a and b). On the contrary, Al-Al electrodes removed higher TOC (10 to 69%) than those of Fe-Fe and Fe-Al electrodes at lower current density (5 mA cm<sup>-2</sup>) for all treatment times (600 to 3600s) (Fig. 4c). The performance of Fe-Fe and Fe-Al electrodes at 5 mA cm<sup>-2</sup> current density were close (~6 to 50%) for all treatment times. The high removal efficiency for TOC (85%) was achieved at 1800 s treatment time at 21 mA cm<sup>-2</sup> current density with Fe-Fe electrodes (Fig. 4a). Previously, Al electrodes showed higher removal efficiency (56%) than of Fe (35%) based on COD removal for 1800s time while treating landfill leachate effluents (Ilhan *et al.*, 2008).

### 3.3. Electrical Energy Consumption (EEC)

Figure 2 to 4 and Table 2 show the effect of current densities and treatment times on EEC per unit volume of treated wastewater (kWh m<sup>-3</sup>) coupled with pollutant removal efficiencies. Energy consumption was directly proportional to the current densities applied to the electrolysis system.

At a current density of 21 mA cm<sup>-2</sup>, Fe-Al electrodes removed higher COD (~100%) from wastewater than Al-Al (~54%) and Fe-Fe (~75%) electrodes at a similar EEC (14.7 to 15.9 kWh cm<sup>-3</sup>) and treatment time (1200 s) (Fig. 3a). If 70% COD reduction was considered reasonable, then a 1800 s treatment time could be used with similar energy consumptions for all three electrodes (Table 2). On the contrary, TOC removal was higher using the Fe-Fe electrodes (~80%) with identical energy consumption, treatment time and current density (21 mA m<sup>-2</sup>, 1200 s EEC 14.7 to 15.9 kWh m<sup>-3</sup>), compared to the Al-Al (~51%) and Fe-Al (~71%) electrodes (Fig. 4a).

All three electrodes achieved TP removal efficiencies >90% when treating swine liquid manure under identical conditions (21 mA cm<sup>-2</sup>, EEC 14.7 to 15.9 kWh m<sup>-3</sup>, 1200 s). Electrodes Al-Al with 1800 s treatment time showed about 100% removal of TP at a low current density level (5 mA cm<sup>-2</sup>) and thus indicated low energy consumption (2.45 kWh m<sup>-3</sup>) by the Al-Al electrodes (Fig. 2c). In contrast, Al-Al electrodes consumed 23.6 kWh m<sup>-3</sup> energies at 21 mA cm<sup>-2</sup> current density to remove 90% of TP in 1200 s treatment time



**Table 2.** Comparison of removal efficiencies, sludge collected and energy consumptions at three current densities for 1800s treatment time

Current density (mA cm <sup>-2</sup> )	EC	pH	Removal efficiency (%)			Electrical Energy Consumption (EEC) (kWh m <sup>-3</sup> )	Sludge (kg m <sup>-3</sup> )	Specific energy (kWh kg-sludge <sup>-1</sup> )	Specific Electrical Energy Consumption (SEEC) (kWh kg-pollutants <sup>-1</sup> removed)		
			TP	COD	TOC				TP	COD	TOC
<b>Fe-Fe electrode</b>											
5	5.9	8.4	12	8	22	2.1	2.80	0.75	287	9	11
10	5.9	8.7	88	74	62	6.8	3.20	2.13	121	4	12
21	5.8	8.4	100	79	85	23.8	7.50	3.17	374	11	31
<b>Fe-Al electrode</b>											
5	5.5	8.9	54	46	24	1.9	1.62	1.17	55	1	9
10	5.5	8.9	76	54	51	6.6	3.38	1.95	137	4	14
21	5.6	8.8	100	100	74	22.0	7.30	3.01	346	8	33
<b>Al-Al electrode</b>											
5	6.7	8.4	100	30	46	2.5	2.43	1.03	39	3	6
10	6.6	8.3	100	38	43	6.8	3.22	2.11	106	6	17
21	6.6	8.4	100	77	69	23.6	4.70	5.02	371	11	38

Specific Electric Energy Consumption (SEEC) per unit mass of sludge removed (kWh kg-sludge<sup>-1</sup>) were close between Iron (Fe-Fe) and Iron-Aluminum (Fe-Al) based electrodes (**Table 2**). However, SEEC for Aluminum (Al-Al) electrode was slightly higher than those of Fe-Fe and Fe-Al for all current density levels. The SEEC based on per unit mass of TP removed (kWh kg-TP<sup>-1</sup>) were ranged from 121-374, 55-346 and 39-371 kWh kg-TP<sup>-1</sup> for Fe-Fe, Fe-Al and Al-Al electrode, respectively, for all three levels of applied current densities. Similarly, SEEC per kg of COD removed (kWh kg-COD<sup>-1</sup>) were ranged from 4 to 11, 1 to 8 and 5 to 10 kWh kg-COD<sup>-1</sup> for Fe-Fe, Fe-Al and Al-Al electrodes, respectively, with the same levels of applied current densities. The SEEC per kg of TOC removed (kWh kg-TOC<sup>-1</sup>) removed were ranged from 12 to 31, 9 to 33 and 6 to 38 kWh kg-TOC<sup>-1</sup> for Fe-Fe, Fe-Al and Al-Al electrodes, respectively.

### 3.4. Sludge Characterization

In this study, the residual Iron (Fe<sup>2+</sup> and Fe<sup>+3</sup>) and Aluminum (Al<sup>3+</sup>) ion concentrations in swine manure were not determined. However, the elemental contents of sludge residues was analyzed and quantified. In electro-coagulation process, the coagulant is generated in situ by electrolytic oxidation of an appropriate anode material which was either Fe or Al or hybrid (combined Fe-Al) in this study. At the beginning of the electrolysis process, Al and Fe ions were produced by anodic dissolution and reacted immediately with hydroxide ions in aqueous medium to produce aluminum hydroxide (Al(OH)<sub>2</sub><sup>+</sup> and Al(OH)<sub>3</sub><sup>-</sup>) or iron hydroxide (Fe(OH)<sub>2</sub> and Fe(OH)<sub>3</sub>), respectively. Subsequently, this process initiated polymerization reactions when metallic hydroxide particles produced had reached

sufficient concentration and deposited as sediment (Laridi *et al.*, 2005; Ilhan *et al.*, 2008).

Elemental analyses of electrolysis sludge are listed in **Table 3**. All electrolysis sludge contains a significant quantity of heavy metals. When Al-Al or Fe-Al electrodes were used, it deposited significantly higher Al content in the sludge, but lower Al content in Fe-Fe electrolysis sludge. Similarly, the opposite trend was observed for Fe content. For the Fe-Fe and Fe-Al electrodes, significantly higher Fe content was observed in electrolysis treated sludge than in the Al-Al electrode treated sludge. In contrast, when Fe-Fe electrodes were used, significantly lower Al content was measured. Although these elements were not measured for the raw swine manure, but when compared with published literature Cu, Zn, Mn, Ca, Mg, K, Na content were significantly higher in the electrolysis treated sludge than in the raw manure (Overcash *et al.*, 1978). Total Copper (Cu) and Zn concentrations in sludge are higher than the North Dakota Pollutant Discharge Elimination Systems (NDPDES) discharge limits (**Table 1**). Higher element content in sludge is likely due to precipitation of element during electrolysis process.

If manure is treated by any of these electrolysis processes, significant amounts of heavy metals, anion and cations may be deposited as sludge from the swine manure before applying to crop land or any other alternative disposal options. Thus, an electrolysis process would likely improve wastewater quality. Some of the elements (Al, B, Ca, Cu, Fe, K, Mg, Na, P, Pb, S, Si and Zn) concentrations in sludge are very high and they can be treated separately to reduce environmental impact.

**Table 3.** Elemental analysis of electrolysis sludge

Parameters	ppm		
	Al-Al	Fe-Fe	Fe-Al
Ag	0.15c±0.00	1.42a*±0.32	0.85b±0.13
Al	148888a±381787	130c±164	83377b±234644
As	1.23c±0.00	80.74a±21.37	34.75b±6.19
B	31.53a±2.42	30.50a±2.24	26.08a±4.97
Ba	2.27b±1.13	5.56a±1.12	3.94ab±1.17
Ca	12422a±5501	13740a±8522	12969a±5620
Cd	1.44b±0.34	19.44a±7.20	6.16b±2.21
Ce	1.27c±0.83	5.42a±0.22	3.11b±0.347
Co	1.28c±0.24	7.95a±0.98	4.45b±0.30
Cu	33.76b±14.05	58.16a±7.31	54.53a±2.92
Fe	4142c±1234	337640a±81923	172416b±23751
K	6853a±93.57	3720b±595	4236b±617
Li	4.02b±1.24	1.15b±0.23	14.16a±5.00
Mg	6648ab±945	5419b±1317	10224a±3416
Mn	95.83c±26.48	506.60a±56.57	287.29b±9.92
Na	2469a±74	1566b±252	1726b±210
Ni	9.01c±1.93	49.23a±4.55	32.40b±1.45
P	6839a±3738	6917a±6795	11539a±6998
Pb	150.97a±113	1.83b±1.34	49.33ab±12.38
S	5020a±1757	2766a±1515	4144a±1757
Sb	1.51a±0.001	1.51a±0.001	1.51a±0.001
Se	5.84a±0.60	1.56b±0.003	2.48b±0.79
Si	39.23ab±1.84	50.64a±12.02	28.06b±8.13
Sn	2.57a±1.27	4.93a±1.68	3.29a±1.12
Sr	23.64a±11.51	25.81a±12.68	26.20a±11.51
Ti	9.75a±0.45	5.47b±2.18	7.66ab±0.52
Tl	2.36a±0.47	2.65a±0.60	3.33a±1.00
V	8.15a±3.35	7.35a±0.53	8.93a±1.52
Zn	414.13a±454	168.13a±104	267.05a±168

\*Averages within a column followed by different letters are significantly different at  $p < 0.05$  according to Duncan multiple range tests

#### 4. DISCUSSION

The EC contents of the liquid manure were decreased during electrolysis process which was also perceived by other researchers (Hong *et al.*, 2013; Kim *et al.*, 2013). The decrease in EC contents during electrolysis was possibly due to the loss of electrolyte ions in the wastewater, transformation of chlorine ion into chlorine gas after playing the role of electron donor and after converting anodically to chlorine which is further converted to hypochlorous acid in the aqueous solution (Costaz *et al.*, 1983; Krstajić *et al.*, 1987). A pH 6.0 is optimal for both Al and Fe based electrodes (Inan *et al.*, 2004). In a neutral and slightly acidic solution (treating medium), Aluminum (Al-Al) based electrodes performed better in removing COD than that of Iron (Fe-Fe) electrodes. In contrast, iron based electrodes performed better in alkaline solutions (Inan *et al.*, 2004; Kobya *et al.*, 2003).

In general, removal efficiencies of pollutants (TP, COD and TOC) from this research showed an increasing trend with treatment duration for all three pollutants and electrodes types under investigation. Generally, the organic concentration in wastewater reduces with the increase in electrolytic time. Previous results reported that at a particular voltage and current density, removal of TP (Kim *et al.*, 2013; Hong *et al.*, 2013; Bensadok *et al.*, 2011; Tchamango *et al.*, 2010), COD (Bensadok *et al.*, 2011; Merzouk *et al.*, 2011; Naïm *et al.*, 2007; Inan *et al.*, 2004; Laridi *et al.*, 2005; Capunitan *et al.*, 2008) and TOC (Merzouk *et al.*, 2011; Cho *et al.*, 2010) increased with increased process/treatment time. In this study, maximum reduction occurred within 1800 s of treatment began.

The electrodes Al-Al outperformed Fe-Fe and Fe-Al electrodes in removing TP for the same current density levels tested. This was likely because the highest amounts of dissolved aluminum were produced when both anode and cathode were made of aluminum (Al-Al electrodes system) even at a low current density of 5 mA

$\text{cm}^{-2}$  (Bensadok *et al.*, 2011). With Al-Al electrodes, pollutant reductions was enhanced through excess active ionization, where aluminum ion combined with the Hydroxyl Ion ( $\text{OH}^-$ ) contributed to the generation of higher amounts of aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ) (Hong *et al.*, 2013; Sposito, 1996). At high current density ( $21 \text{ mA cm}^{-2}$ ), TP removal was comparable among all three electrode types, but at low current density ( $5 \text{ mA cm}^{-2}$ ), the Al-Al electrodes outperformed Fe-Fe and Fe-Al electrodes. This indicated that applied current densities have an effect on the response of electrode materials.

Among the electrode types, the Fe-Al electrodes outperformed Fe-Fe and Al-Al electrodes for removing COD at 5 and  $21 \text{ mA cm}^{-2}$  current densities (**Fig. 3a and c**), but Fe-Fe electrodes resulted in better COD removal at  $10 \text{ mA cm}^{-2}$  than the other electrodes (**Fig. 3b**). For the same treatment times (1200 s) at a high current density ( $21 \text{ mA cm}^{-2}$ ), COD removal efficiency of Fe-Al electrodes was about 100%, which were about 1.9 and 1.3 times higher than those of Al-Al and Fe-Fe electrodes, respectively (**Fig. 3a**). The Fe-Fe electrodes performed the best in removing COD followed by Hybrid (Fe-Al) and Al-Al electrodes at high current density levels. The COD removal efficiencies of hybrid electrodes were in-between Fe-Fe and Al-Al. Laridi *et al.* (2005) stated that at 1500 and 2000 mA current levels iron electrodes resulted in significantly greater COD reductions than that of aluminum using swine liquid manure for a 1800s treatment time. It was demonstrated in a bench scale study using neutral and alkaline textile wastewater that the Fe-Fe was more efficient than Al-Al electrodes in removing COD and electrode's efficiency was reversed when wastewater medium was acidic (Kobyia *et al.*, 2003). In our study, the final pH recorded for all electrodes types were ranged from 9-9.5. Thus, slightly basic swine liquid manure with iron based electrodes (Fe-Fe and Fe-Al) electrodes resulted higher COD reduction than Al-Al electrodes. This research indicated that Al-Al electrodes at low current density ( $5 \text{ mA cm}^{-2}$ ) were sufficient in removing TP from swine manure tested. Similarly, Bensadok *et al.* (2011) reported that Al-Al electrode reduced 80% COD and 60% phosphate ( $\text{PO}_4^{3-}$ , 60%) from dairy wastewater when current density, treatment time, pH and Sodium Chloride (NaCl) concentration were  $5 \text{ mA cm}^{-2}$ , 120 s, 6.6 and  $1.5 \text{ gL}^{-1}$ , respectively. They reported that the energy consumption for these conditions was found to be near  $0.03 \text{ kWh/kg}$  of COD removal.

Similar to pollutants removal efficiencies and EECs, sludge productions ( $\text{kg m}^{-3}$ ) were increased with increasing applied current density levels (**Table 2**). The highest amount of sludge was produced at an applied current level of  $21 \text{ mA cm}^{-2}$  for all electrode types. Sludge productions were 7.5, 7.3 and  $4.7 \text{ kg m}^{-3}$  for Fe-Fe, Fe-Al and Al-Al electrodes, respectively. It is well known that for an electro-coagulation process using sacrificial electrodes, the sludge amount and the energy consumption increase with the treatment time increases. Our results also showed a good agreement with a previous study that reported a higher amount of sludge with Fe electrodes than that of Al while treating swine liquid manure obtained from bio-filtration process when treated for 1800 s (Laridi *et al.*, 2005). The Fe-Fe electrodes transfer higher numbers of Fe ions into solution and they produce a higher amount of sludge (Ilhan *et al.*, 2008). However, higher amounts of sludge may accrue higher disposal cost.

Overall low SEECs per kg of pollutants (TP, COD and TOC) were estimated for Al-Al electrodes. The lowest SEEC per kg of TP were estimated for Al-Al electrodes at a current density of  $7 \text{ mA cm}^{-2}$  ( $39 \text{ kWh kg-TP}^{-1}$ ) followed by  $106 \text{ kWh kg-TP}^{-1}$  using same electrodes at a current density of  $10 \text{ mA cm}^{-2}$ . Similarly, low SEEC per kg of  $\text{COD}^{-1}$  and per kg of  $\text{TOC}^{-1}$  removal were also calculated for Al-Al. Calculated SEECs were 3 and  $6 \text{ kWh kg-COD}^{-1}$  and 6 and  $17 \text{ kWh kg-TOC}^{-1}$  for 5 and  $10 \text{ mA cm}^{-2}$  current density, respectively, with Al-Al electrodes. With Al-Al electrodes, the pollutants reductions were enhanced through excess active ionization, where aluminum ion combined with the hydroxyl ion ( $\text{OH}^-$ ) and contributed to the generation of higher amounts of Aluminum Hydroxide ( $\text{Al}(\text{OH})_3$ ) (Hong *et al.*, 2013; Sposito, 1996). The elemental analysis indicated sedimentation of metal residue in a sludge from runoff wastewater during an electrolysis process. However, residues were rich with respective metal of the electrodes tested with the electrolysis process. Therefore, this study clearly indicated the effect electrolysis in removing metals presented in the swine wastewater.

## 5. CONCLUSION

This research investigated the effects of current density levels on the electrolysis of swine liquid manure with electrodes consisting of either Fe-Fe, Fe-Al, or Al-Al electrode materials. We obtained the following results in this study.

- The removal efficiencies of TP, COD and TOC were positively correlated with increasing treatment times and applied current densities (5, 10 and 21 mA cm<sup>-2</sup>) for each electrode materials
- The current densities applied to the electrolysis system were directly proportional to the energy consumption and sludge generated
- Aluminum (Al-Al) electrode consumed low energy at a low current density level with high TP removal efficiency (100%)
- Hybrid electrode (Fe-Al) outperformed Al-Al and Fe-Fe electrodes in treating COD at similar EEC level
- Iron Electrode (Fe-Fe) outperformed hybrid and Al electrodes in treating TOC at similar EEC
- The aluminum electrodes showed low SEEC per kg of TP (39 kWh kg-TP<sup>-1</sup>, 5 mA cm<sup>-2</sup>) followed by 106 kWh kg-TP<sup>-1</sup> at a current density of 10 mA cm<sup>-2</sup>. The SEEC per kg of COD<sup>-1</sup> and per kg of TOC<sup>-1</sup> removal were similar among electrodes tested
- Electrolysis process deposited significant amount of elements in the sludge, thus likely to improve wastewater quality

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### 6.1. Authors Contribution

Both authors have contributed equally. Md. Borhan has conducted the experiment and data analysis. Shafiqur Rahman has designed the experiment, written the manuscript and interpreted the data.

### 6.2. Ethics

This manuscript has neither been published, nor under consideration for publication or in press elsewhere concurrently.

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