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Experimental Investigations of the Effects of Current Density during the Electrocoagulation of Bio-Treated Distillery Wastewater using Aluminum-Aluminum Electrode Pair

Chompey Den, Lawrence P. Belo, Elaine G. Mission, Hirofumi Hinode, Leonila C. Abella and Pag-asa D. Gaspillo*
De La Salle University
pag-asa.gaspillo@dlsu.edu.ph

Abstract: Bio-treated distillery wastewater (BTDW) has found to have a good application as fertilizer and irrigation to increase the yield of agriculture production because it contains high nutrients such as nitrates and phosphates. However, the land application with high concentration of nutrients in BTDW is not suitable in view of the fact that it would affect the plant growth, the physico-chemical properties of the soil and it would be contaminated to the ground and surface water which is harmful to aquatic life. This study investigated the use of Electrocoagulation (EC) technology as post treatment for BTDW using an upflow semi-batch reactor with Aluminum/Aluminum (Al/Al) electrode pair. The BTDW has a chemical oxygen demand (COD) ranging from 14,112 mg/L to 32,928 mg/L, nitrate (NO_3^-) from 5.15mg/L to 8.41 mg/L, and phosphate (PO_4^{3-}) from 22.1 mg/L to 52.18 mg/L. Literature stated that current density has a pronounced effect on removal during EC. In this paper, the effects of current density on the removal of COD, NO_3^-, and PO_4^{3-} were investigated. With the current density of 35.92 A/m^2, flow rate of 0.4 L/min and initial pH of 3, the average percentage removal of COD, nitrate, and phosphate from BTDW were 50 %, 26 % and 61 % respectively. pH profiling was also monitored.

Key Words: Electrocoagulation, aluminum, BTDW,

1. INTRODUCTION

Bio-treated distillery wastewater (BTDW) has found application as fertilizer to increase the yield of agriculture production because it contains high amount of nutrients such as total nitrogen (900 mg/L), ammonia-nitrogen (714.2 - 743.86 mg/L) and phosphate (30.26 - 32.8 mg/L) (Nandy et al. 2002, Chidankumar et al. 2010; Ansari et al. 2012; Sankaran et al. 2014). However, the land application with high concentration of nutrients in BTDW is not suitable in view of the fact that it would delay the seed germination, seedling growth and chlorophyll content in the plant; as a result it decreases the yield of the production. In addition, long term use of BTDW could affect the physico-chemical properties of the soil as well as the crop growth due to increase in soil salinity (Gahlot et al. 2011). Apart from that, excessive use of BTDW in agriculture as fertilizers on soil increases the quantity of nitrates and phosphates in ground and surface water, mainly during the rainy season. In addition, discharge of BTDW with an excess level of nitrates, phosphates, and COD cause serious problem to aquatic life. When nitrates, phosphates and COD dissolve in ground and surface water, the dissolved oxygen gets depleted, and leads to the eutrophication of lakes, streams and rivers which give the negative impacts to the water bodies such as algal bloom (Domagalski et al. 2007).

Several techniques such as aerobic treatment, anaerobic treatment and chemical coagulation have been applied as post-treatment methods to reduce nitrates, phosphates and COD concentration in BTDW (Chaudhari et al. 2007). However, the effluent still exceeds the DENR limits standard. Hence, there remains a need for a suitable post treatment method to address the adverse potential environmental impacts to both soil and water environment. The Department of Environmental and Natural Resources (DENR) Administrative Order number 35 (DAO 35) in the Philippines have set a limit standard of discharged effluent into water class C for river, stream, fishery water for growth fish and propagation with the level of nitrate (NO_3^- N) at 10 mg/L, phosphate at 0.4 mg/L and COD at 100mg/L.

Electrocoagulation (EC) is known as a reliable, fast and cost effective wastewater treatment technique. EC is easy to operate, takes short operation time, requires no addition of chemicals and produces less amount of sludge which is better than the conventional method chemical coagulation (Berktas et al. 2004). EC involves generation of H_2 gas which is formed at cathode, and promotes the separation of flocs by floatation process. In the recent years, EC has been applied as an effective method in the treatment of COD, nitrate and phosphate of various wastewaters such as black liquor from paper industry (Zaied & Bellakhal, 2009), textile wastewater (Can et al. 2006), abattoir wastewater (Drogui et al. 2008), landfill leachate (Li et al. 2011), groundwater (Lacasa et al. 2011b) and municipal wastewater (Tran et al. 2012).

The present study aimed to investigate the effects of current density on the removal of COD, nitrates and phosphates from BTDW using two pairs of aluminum-aluminum electrodes. The study presented in this paper is a part of a research project which investigated the effect of current density, pH and flow rate on the removal nutrients, Total Suspended Solids (TSS), Chemical Oxygen Demand (COD) and color.

2. METHODOLOGY

Distillery wastewater after biological process was collected from a distillery plant in the Philippines. The wastewater was adjusted to pH below 2 with H_2SO_4 and stored at 4°C (U. S. Environmental Protection Agency. 1983). This is to ensure that the storage conditions will not change the composition of the wastewater. The procedure flow of the experiment is described in **Fig.1**.

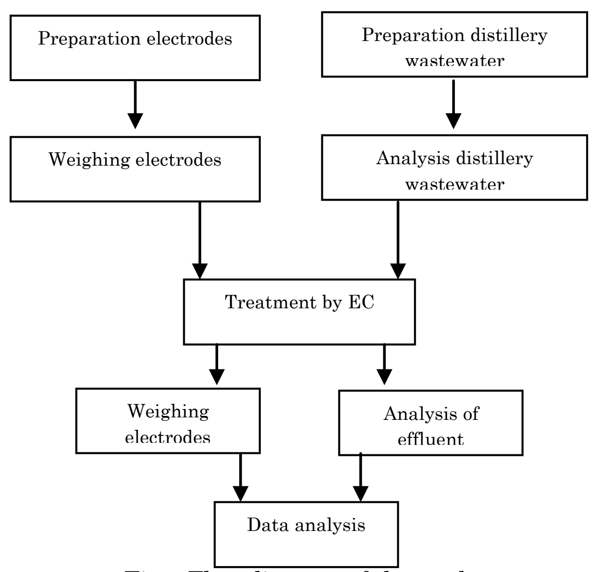

Fig.1 Flow diagram of the study

Aluminum electrodes were sourced from Sancedra Engineering Enterprises. The SEM-EDX analysis showed 73% purity, and other impurities were carbon and oxygen. The dimensions of the electrodes are 45.72 cm × 7.62 cm and 2 cm thick. The effective electrode area is 0.1394 m^2. Before each experiment, the electrodes were cleaned with sand paper, washed with nitric acid 3M HNO_3 to remove scale and oxide layer on the electrode surfaces; then rinsed with water and air dried in order to remove the coating that present on the surface of the electrodes (Golder et al. 2007). **Fig. 2** shows the Al electrodes after cleaning with sand paper.

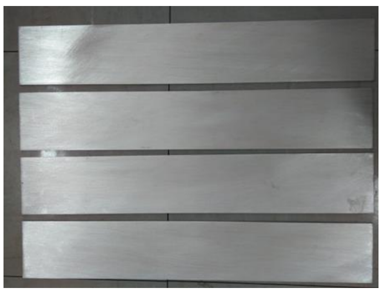

Fig. 2 Al electrodes after cleaning with sand paper

The EC system in this study was adapted from the work of Lieu (2012). The schematic diagram and the actual photograph of EC system are shown in **Fig. 3** and **4**.

The four aluminum electrodes were put vertically upright in the reactor and arranged in parallel connection. The feed tank was filled with 5 litres of wastewater and was recirculated in upflow mode to the EC reactor by a submersible pump. The reactor maintains 13 litres of wastewater via an overflow to the feed tank.

The experiment was conducted with replicate runs (2 runs) in a semi-batch up flow for 90 minutes at a fixed pH of 3, flow rate 0.4 L/min and current 3, 5A. Samples were collected at 2 to 3 minutes intervals in the first 10 minute, then 5, 10 and 20 minutes intervals afterwards. COD was analysed by Closed Reflux Titrimetric method, nitrate was measured by Cadmium Reduction Method and phosphate was analysed by Ascorbic Acid Method (APHA, 1990).

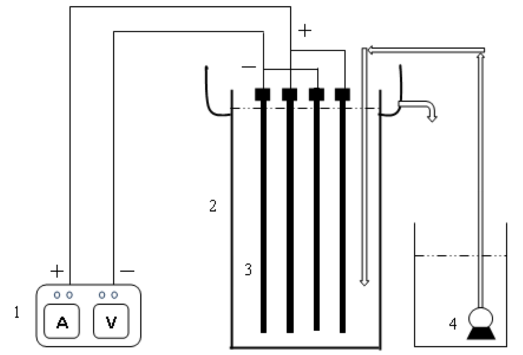

Fig.3 Schematic diagram of EC set up, (1) DC power, (2) EC reactor (13L), (3) Electrodes, (4) Submersible pump, (5) Feed tank (5L)

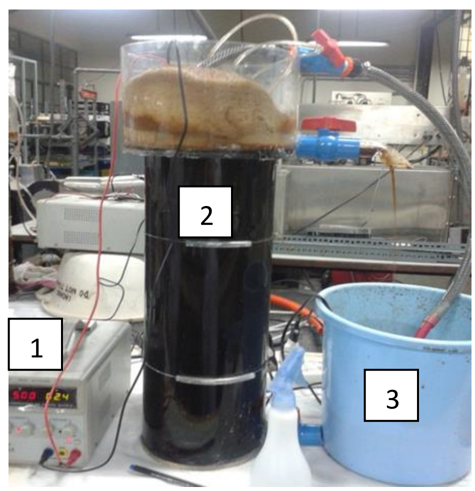

Fig.4 Actual photograph of EC system, (1) DC power, (2) EC Reactor (13L), and (3) Feed tank (5L)

3. RESULTS AND DISCUSSION

3.1 Effect of Current Density on the Removal of COD

Current density is a very important parameter in electrocoagulation processes which determines the coagulation dosage rate, bubble production rate, size and growth of the flocs. **Fig. 5** illustrated the effect of the current density on COD

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removal at pH 3 and flow rate 0.4 L/min. As can be seen in the figure, the highest average percentage removal of COD 60 % was obtained at high current density 36 A/m^2 at the first 20 minutes of electrolysis time.

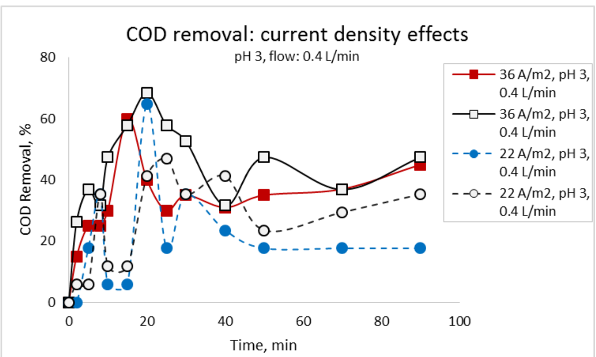

Fig. 5 Effect of current density on COD removal (pH 3, flow rate 0.4 L/min)

This result could be attributed to the dissolution of the fresh Al anode which generated high aluminium ions, and the high production of H_2 gas bubble and hydroxide ions (OH^-) at cathode in accordance to Eq.3.1 and 3.2, respectively. After 20 minutes, the average percentage of COD value dropped and levelled at 50 % towards the end of the electrolysis time (90 minutes). Shorter of electrolysis time is required when high current applied. High current generates H_2 bubbles rapidly which inhibits the formation of floc, results to decrease in percentage removal of the pollutants.

Anode Al $\rightarrow Al^{3+}{}_{(aq)} + 3e^-$ Eq.3.1

Cathode $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ Eq. 3.2

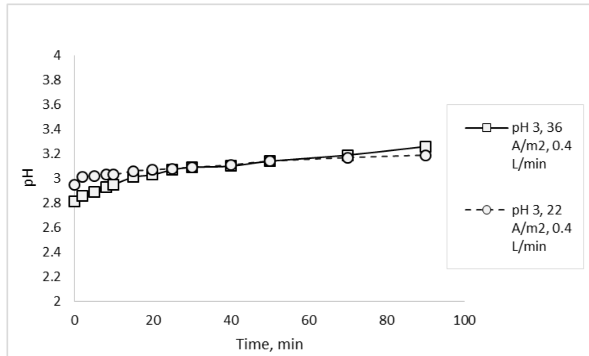

Fig. 6 pH profiles at different applied current density

pH profiling is shown in **Fig.6**. It was observed that the final pH was always to be higher than its initial pH. The increase in pH is attributed to the hydroxide ions (OH^-) production at the cathode in accordance to Eq.3.2. Also, the high current density (36 A/m2) promoted the generation of hydroxide ions (OH^-). The final pH reached to 3.26, higher when compared to pH at low current density (22 A/m2).

3.2 Effect of Current Density on the Removal of Nitrate

The effect of the current density on nitrate removal is shown in **Fig. 7**. The average percentage of nitrate values removal of 26 % was obtained at high current density 36 A/m^2, while at low current density 22 A/m^2, the average percentage of nitrate values removal was 20 %. This finding was contributed by high formation of $Al(OH)_3$ and hydrogen gas bubbles generation at high current density in accordance to Faraday's law (**Eq.3.3**). High formation of $Al(OH)_3$ allowed more nitrate absorbed on their surface which increased the removal efficiency.

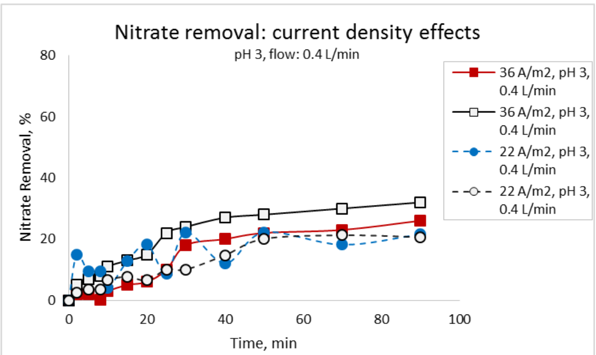

Fig. 7 Effect of current density on nitrate removal (pH 3, flow rate 0.4 L/min)

$$m_{Faraday} = \frac{ItM}{zF} \qquad \text{Eq.3.3}$$

m : theoretical of mass Al anode (g), I : current (A)

t: time (s), M: molar mass of electrode (g/mol)

z: number of electrons transferred in the anodic dissolution and F: Faraday's constant (96,486C/mol).

3.3 Effect of Current Density on the Removal of Phosphate

The effect of current density on phosphate removal was significant. As can be seen in **Fig. 8**, at 90 minutes of electrolysis time, the percentage removal of phosphate was 61 % at high current density value of 36 A/m^2 which is higher than the percentage removal of phosphate of 18 % at current density 22 A/m^2. According to Faraday's law, high applied current density produces greater amount of metal ions. The generation of Al^{3+} into the aqueous solution is very important to coagulate with PO_4^{3-}. At low pH, phosphates ions can be removed by precipitation through the formation of $AlPO_4$ insoluble (Eq. 3.4).

$$Al^{3+} + PO_4^{3+} \rightarrow AlPO_4 \qquad \text{Eq. 3.4}$$

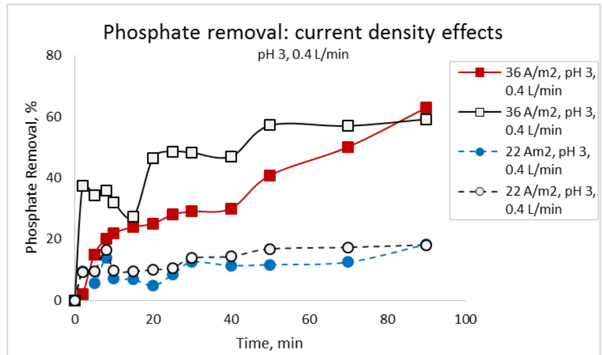

Fig. 8 Effect of current density on phosphate removal (pH3, flow rate 0.4 L/min)

4. CONCLUSIONS

In the present study, the average percentage removal of COD, nitrate, and phosphate from BTDW were 50 %, 26 % and 61 % respectively.

In all three cases, the highest percentages of COD, nitrate and phosphate removal were observed at high applied current density. This means that the current density is a significant factor in BTDW removal using EC.

5. ACKNOWLEDGMENTS

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