

## Organic pollutant removal from edible oil process wastewater using electrocoagulation

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**Abstract** Wastewaters generated from vegetable oil industries contain a high concentration of organic pollutants that are detrimental to the aquatic ecosystem. Electrochemical processes are gaining importance in the treatment of inorganic and resistant organic pollutants in wastewaters. In this study, electrocoagulation (EC) was applied to remove organic pollutants and oil and grease from canola oil wastewater using aluminum (Al) and iron (Fe) electrodes. The application of EC in the wastewater achieved more than 80% removal of organic carbon and nearly 100% removal of suspended solids (SS). The effectiveness of EC is influenced mainly by current density, pH, electrolyte (NaCl), electrode contact time and electrode type. It was observed that Al electrode combination yielded better removal at a lesser time compared to that of Fe electrodes. However, varying current densities had its significance in terms of coagulation time only. Increase in current density achieved decrease in coagulation time. Both Al and Fe could remove between 52-59% of oil and grease from canola oil wastewater

### 1. Introduction

The amount of wastewaters discharged from edible oil industries is high because of a large volume of water required during the processing steps. The compositions and characteristics of wastewaters from vegetable oil refinery facilities vary depending on the type of crop used to produce oil [1]. The biological oxygen demand (BOD)/chemical oxygen demand (COD) ratio of 0.2 – typical of vegetable oil effluent – is appropriate to destroy microbes required for biodegradation. Most of the times, the vegetable oil wastewater discharge, although supposedly treated, does not meet the environmentally acceptable level. A number of methods such as absorption, coagulation, anaerobic treatment, reverse osmosis, and ultrafiltration have been found useful for treatment of vegetable oil wastewaters [1].



Electrocoagulation (EC) has some advantages on the treatment of edible oil industry wastewaters compare to the currently adopted wastewater treatment methods. Biological treatment methods require a vast land and facility combined with long treatment duration [2,3]. An appropriate treatment system should provide efficient pollutant reduction, uses less treatment time, requires simple installation, maintenance, and operation with the addition of little or no chemical compounds [3].

EC method has proved to be promising and thus attracted the attention of researchers around the world. EC techniques involve metallic dissolution through anodic reaction for creation of metallic hydroxide [4]. The positive metallic ion react with negative charged particles in the wastewater forming complex molecules – flocs – that coagulate without the addition of chemical [1,5]. Many reports have shown that EC can reduce heavy metals [4], nutrients [2], natural organic matters [6], dissolved organic carbons [6], COD [3,7,8], dyes [9-11] and microorganisms [12,13] from various types of wastewaters. EC has been successfully applied to treat vegetable oil refinery [1], olive mill [9], slaughterhouse [14-16], baker's yeast [7,17,18], dairy and tannery [19-21], and restaurant wastewaters [22]. Aluminum (Al) and iron (Fe) electrodes have found extensive applications for the EC treatment process because of their abundant availability and low cost. The main objective of this study is to investigate the treatment performance of EC processes on canola oil process wastewater sources in the removal of total organic carbon, oil and grease and suspended solids.

## **2. Materials and Methods**

### *2.1. Sample collection and preparation*

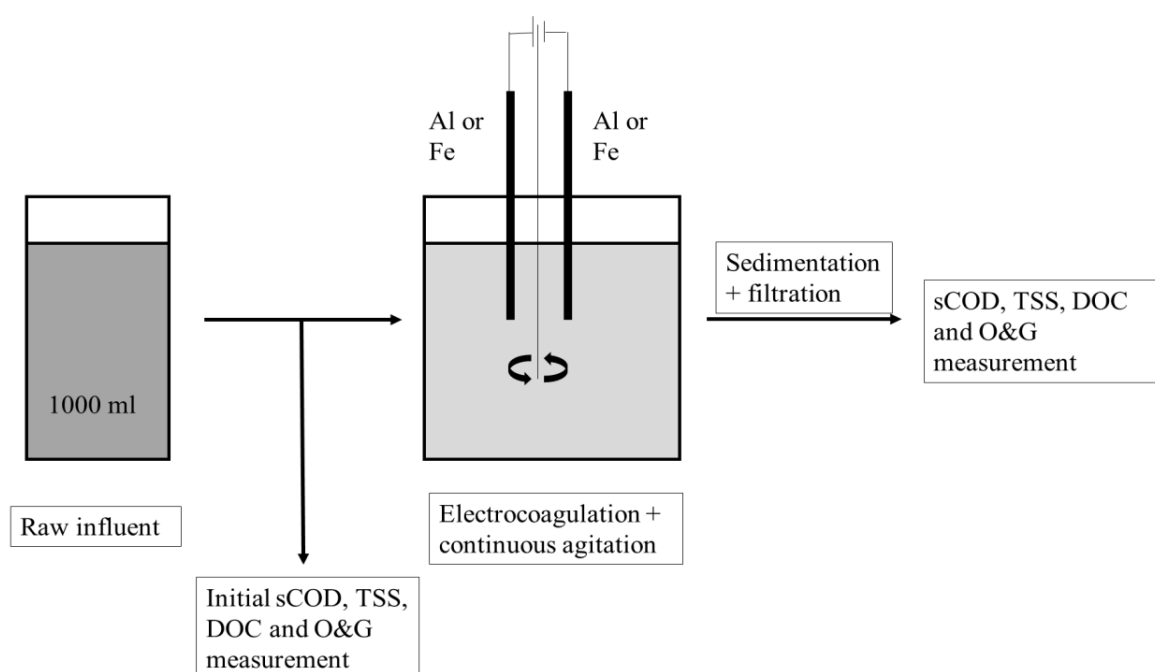
Canola oil process raw wastewater samples were collected using grab sampling method from Cargill West Fargo Oilseed Facility, West Fargo, ND. About one hour after collection, the samples were filtered through 1.2  $\mu\text{m}$  glass microfiber filter paper followed by 0.45  $\mu\text{m}$  pore size filter paper prior to determine initial parameters in the sample. The pollutant passing through a 0.45  $\mu\text{m}$  filter paper was considered to be soluble components. About 50 ml of raw wastewater sample was filtered and used to determine initial concentrations of soluble COD (sCOD), dissolved organic carbon (DOC), total suspended solids (TSS), and oil and grease (O&G). The sCOD was analyzed using Hach testing kits TNT 821 and TNT 822 with the detection limits of 0-150 mg/l and 2-1500 mg/L, respectively. The DOC was analyzed using Shimadzu TOC-L analyzer. TSS was measured using the standard methods [32].

The O&G was analyzed using an Infracal 2 Analyer (Wilks Enterprise, Norwalk, Connecticut, USA). This method complies with EPA methods of 413.1 and 418.1 correlating to EPA 1664A (EPA/821-R-00-003). The method is designed to measure oil and grease by infrared determination in wastewater using S-316 solvent for the extraction procedure.

### *2.2. EC application of the raw wastewater sample*

Raw wastewater sample was poured into a glass reactor for each set of batch EC experiments. The remaining samples were preserved at 4°C for the later usage. Every 3 or 4 days, any remaining wastewater samples were discarded and the fresh samples were collected from the facility. The working volume of 1 liter of raw wastewater sample was poured into glass reactor for the EC process. Al and Fe electrodes were used in two different combinations as AlAl and

Fe/Fe. The electrodes were placed at 1 cm apart, connected to a DC power supply and immersed into the sample in the reactor (Figure 1). The experiments were carried out at different current densities of 0.002, 0.01, 0.019, 0.029 A/cm<sup>2</sup>. The conductivity of the wastewater sample was 143  $\mu$ S/cm which was too low to initiate EC process. Two g/L sodium chloride (NaCl) was added to the sample to increase the conductivity to about 4.93 mS/cm [23]. The surface area of each electrode used in the experiments was 12 cm x 7 cm where the immersed effective surface area of 8 cm x 6.5 cm. The efficiency of the process also depends on the sample pH. The pH in the reactor was maintained between 6.0-6.5 for Al-Al electrodes and 8.0-8.5 for Fe-Fe electrodes [23]. Sample solution of 50 ml from each run were collected at contact times of 10, 20, 30, 40, 50, 60 and 70 minutes and tested for parametric analysis. The sample supernatant was filtered and analyzed for the presence of COD, DOC, TSS and O&G.



**Figure 1.** Schematic diagram of the electrocoagulation process in canola oil process wastewater.

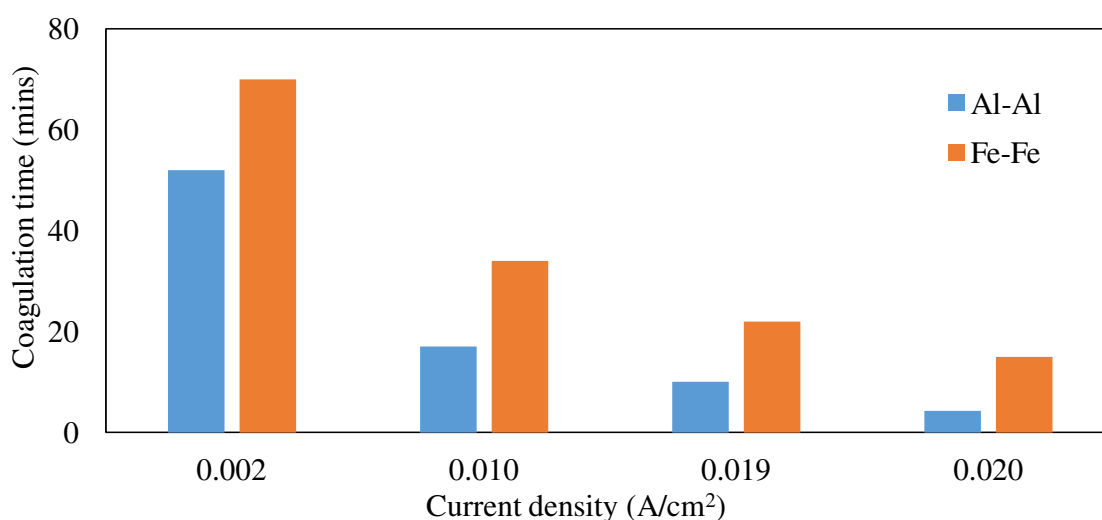
### 3. Results and Discussion

#### 3.1. Effect of current density on Al-Al and Fe-Fe electrodes

During the EC process, the samples were introduced to various current densities ranging between 0.002 to 0.029 A/cm<sup>2</sup>. Figure 2 shows that effect of current density to coagulate colloidal particles depended on the electrode combination. It was observed that higher the current density, faster the process of coagulation. However, Al-Al electrode combination achieved coagulation at a time lesser than Fe-Fe combination. It can be deduced that the amount of Al<sup>3+</sup> and Fe<sup>2+</sup> ions produced for the applied current density are not sufficient to form enough flocs for complete removal of pollutants. El-Taweel et al., (2015) studied the removal of hexavalent chromium ions

from wastewater through EC using iron electrodes. The study found that as the initial concentration of Cr(VI) ions increased, removal of these ions required increase in current density as well as electrocoagulation time for complete removal [4].

In our study, the reactor was run for 70 mins and samples were collected every 10 mins. The reactor was run even after coagulation was completed and flocs formed at the surface. At current density of  $0.002 \text{ A/cm}^2$ , coagulation was formed at Al/Al electrodes at a time interval of 25 mins, whereas, for iron electrodes, no coagulation was observed until 70 minutes. At higher current densities of  $0.019$  and  $0.029 \text{ A/cm}^2$ , time required to form coagulation was as low as 6 and 10 mins/L respectively.



**Figure 2.** Coagulation time needed for electro-coagulation using aluminum and iron electrodes

### 3.2. Effect of electrode combination on removal of pollutants

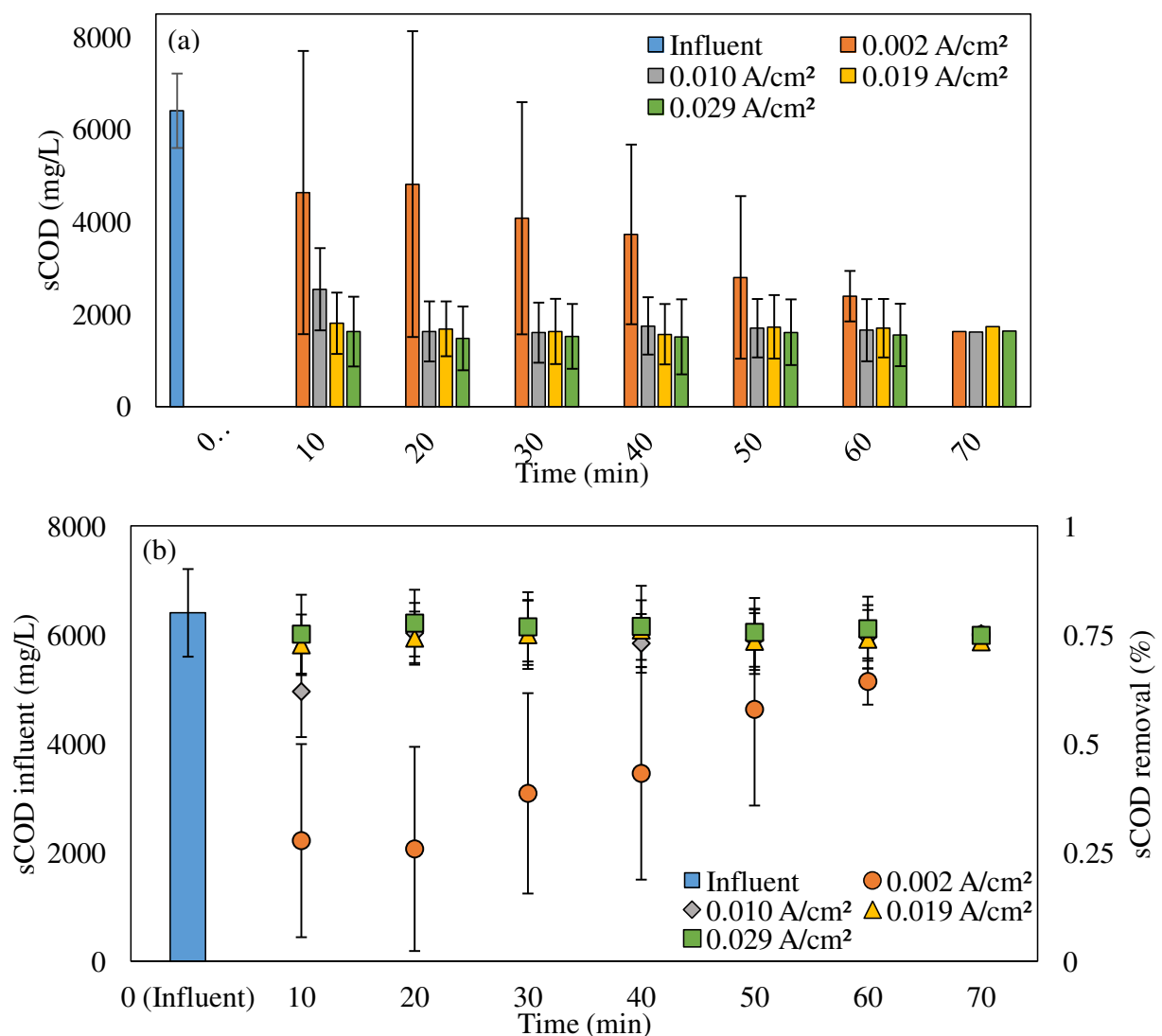
#### 3.2.1. Removal of sCOD

The impact of Al/Al and Fe/Fe electrode combinations with various current densities on the removal of sCOD was investigated (Figure 3 and 4). Samples were collected every 10 mins during the operation and initial and final concentration of sCOD was measured. The analysis was carried out both before and after coagulation was achieved in the reactor. Al/Al electrode combination could remove 75% at  $0.002 \text{ A/cm}^2$  and upto 78% at  $0.029 \text{ A/cm}^2$  (Figure 3a and 3b). However, at  $0.002 \text{ A/cm}^2$ , time required to achieve 75% removal was 70 mins compared to that of 10 mins at  $0.029 \text{ A/cm}^2$ . Fe/Fe achieved a removal efficiency of maximum 78% at the current density  $0.029 \text{ A/cm}^2$  after 60 mins (Figure 4a and 4b). Removal efficiency depended on the contact time as well. Aluminum electrodes achieved higher removal efficiency at lower contact time than that of iron electrodes. It was also observed that iron electrodes took longer time of operation than aluminum electrode to attain the same amount of removal. From Figure 3 and 4, it can be concluded that aluminum electrodes achieved optimal removal of 78% at contact time of 10 mins at current density of  $0.029 \text{ A/cm}^2$  and achieved steady state condition once the coagulation was formed. It was established in various studies that the current determines the dosage rate and

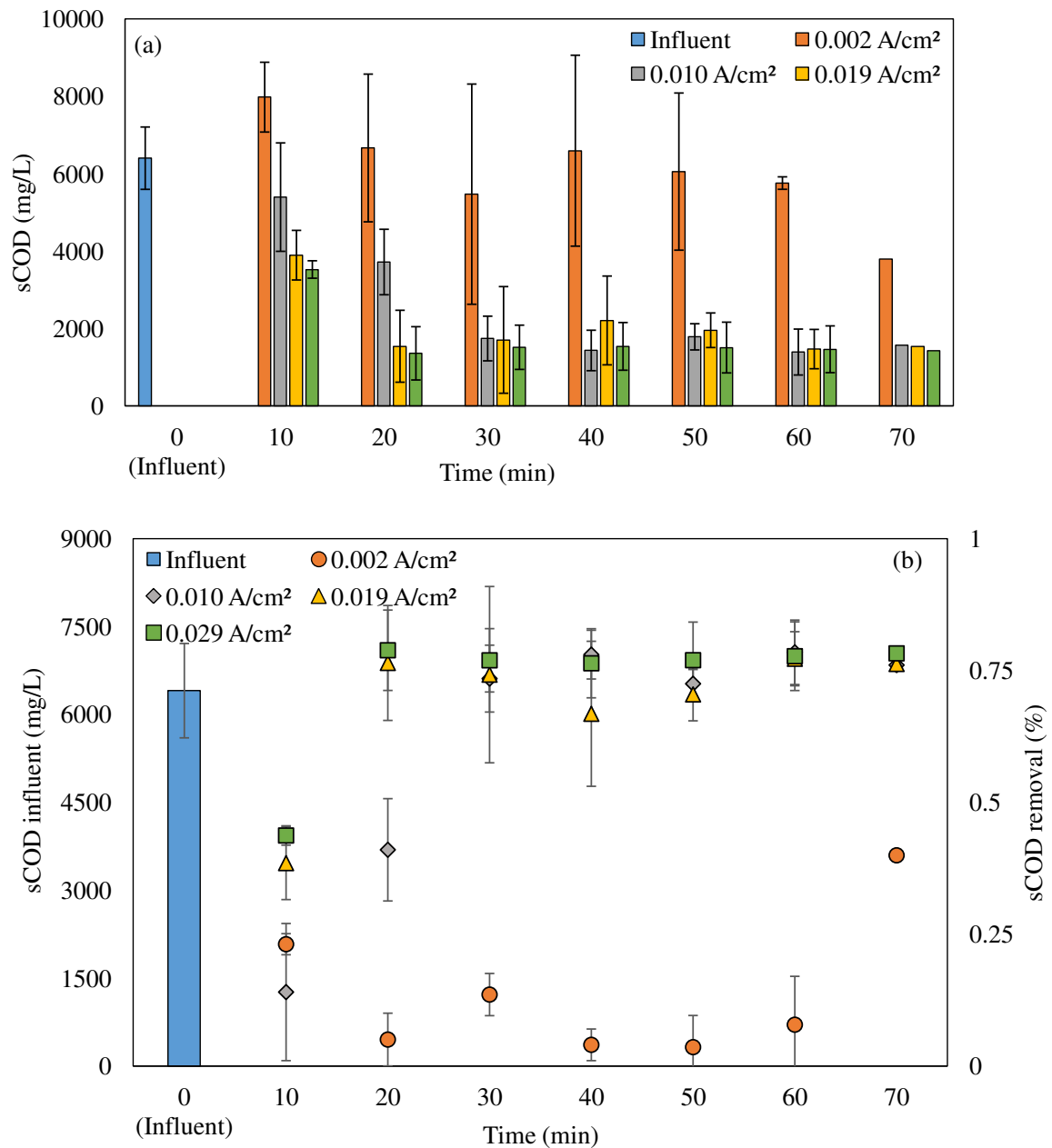
size of flocs which in turn determines the removal efficiency of coagulation. Previous studies also stated that after 30 mins of coagulation at various current densities, the removal efficiencies tend to constant values in industrial and paper mill wastewater [24,25]. The removal of sCOD achieved stable concentration once coagulation was formed. The percentage removal of COD after EC was calculated as:

$$\text{Removal (\%)} = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

Where  $C_0$  and  $C_f$  are initial and final concentration measured in mg/L, respectively.



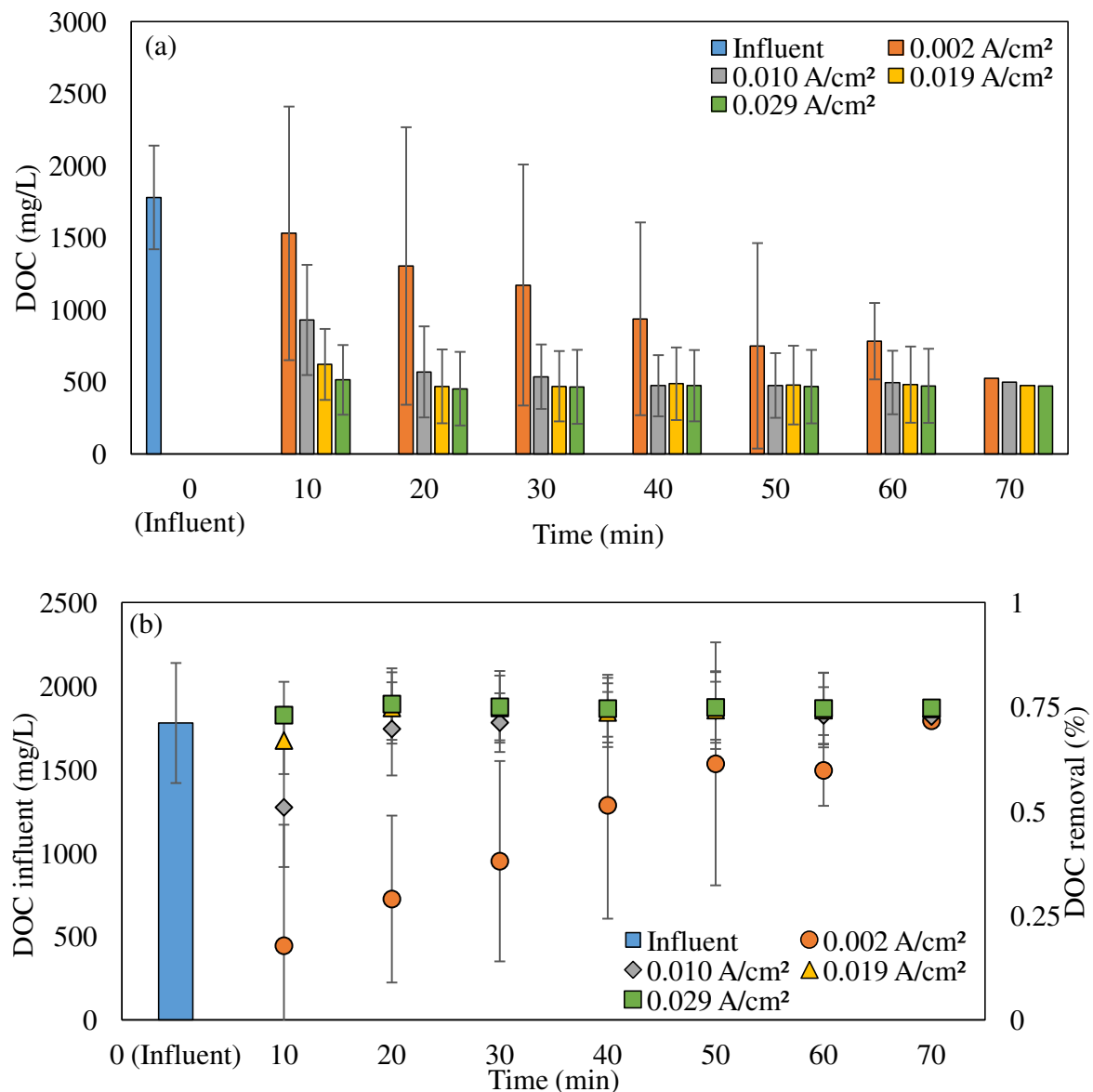
**Figure 3.** sCOD removal using electrocoagulation on canola oil wastewater using aluminum electrodes at various current densities a) concentration of sCOD in mg/L b) sCOD removal in percentage (%).



**Figure 4.** sCOD removal using electrocoagulation on canola oil wastewater using iron electrodes at various current densities a) concentration of sCOD in mg/L b) sCOD removal in percentage (%).

### 3.2.2. Removal of DOC

Removal of DOC using aluminum electrodes has yielded better performance compared to that of iron electrodes (Figure 5 and 6). Al-Al electrode combination was able to achieve more than 75% of DOC at all current densities that were applied (Figure 5a and 5b). On the other hand, Fe-Fe electrodes achieved maximum removal of 75% at  $0.029 \text{ A/cm}^2$  at the end of 40 mins. Fe/Fe electrodes achieved not more than 16% removal in the concentration of DOC at current density of  $0.002 \text{ A/cm}^2$  (Figure 6a and 6b). For Fe/Fe electrodes, removal efficiency was slower



**Figure 5.** DOC removal using electrocoagulation on canola oil wastewater using aluminum electrodes at various current densities a) concentration of DOC in mg/L b) DOC removal in percentage (%).

compared to Al/Al electrodes at all current densities applied. Similar results were obtained in the study conducted by Un et al., (2009a) on vegetable oil refinery wastewater using EC in a batch mode by adding poly aluminum chloride. The study was conducted to investigate the effect of pH and current density on wastewater using aluminum electrodes, which was proved to be the superior combination compared to that of iron electrodes. El-Nas et al (2009) evaluated the removal efficiency of sulfate and COD on petroleum refinery wastewater using three types of electrode materials, which were stainless steel, aluminum, and iron. The study concluded that aluminum had better removal performance compared to the other two electrode materials.

### 3.2.3. Removal of oil and grease (O&G)

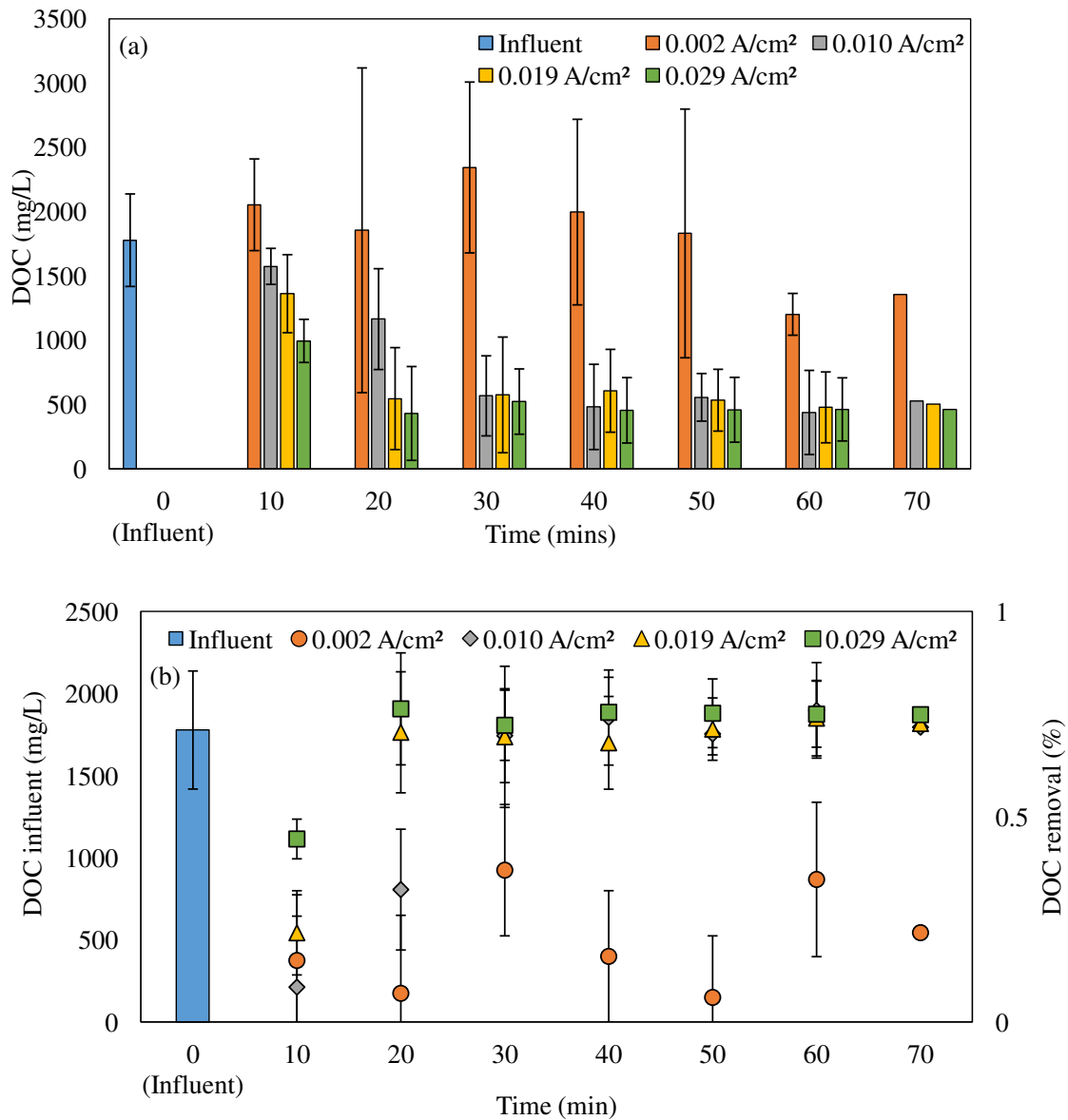
There was no significant difference in the removal efficiency of O&G (Figure 5) between the two electrode combinations (aluminum and iron). Both the electrodes could remove O&G between 52% and 59% from the canola oil wastewaters. Previous studies have also concluded that EC can remove more than 80% of O&G in vegetable oil wastewater sample [26-29]. This study observed that oil removal efficiency in both electrodes was nearly equal. However, at current density of  $0.002 \text{ A/cm}^2$ , iron electrodes could remove not more than 26% of O&G.

### 3.2.4. Removal of suspended solids

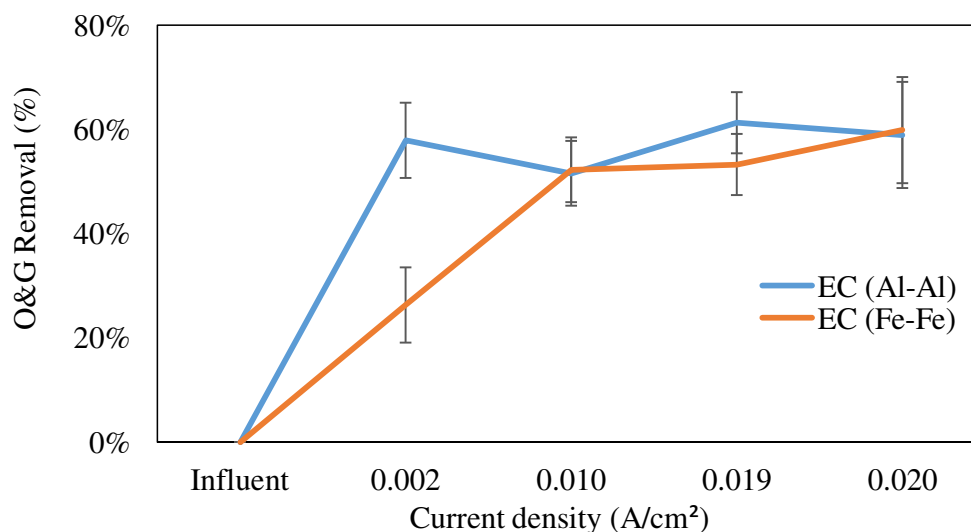
The results (Figure 8) showed that aluminum electrodes achieved almost 100% removal of total suspended solids at the end of each operation time compared to that of iron electrodes. Both electrode combinations achieved 100% removal of TSS and the results were significant in terms of contact time. Iron electrodes consumed longer time to achieved 100% removal compared to aluminum electrodes. However, it is important to mention that maintaining the pH of the electrolyte solution determines the time required to coagulate. Other studies that was conducted in textile, dairy and tannery wastewaters found similar results in the removal of suspended solids using EC [5,30,31].

Thus, comparing the removal rates and capability to remove organic carbon and suspended solids along with O&G, Al-Al electrodes combination was chosen to be superior compared to that of iron electrodes combination.

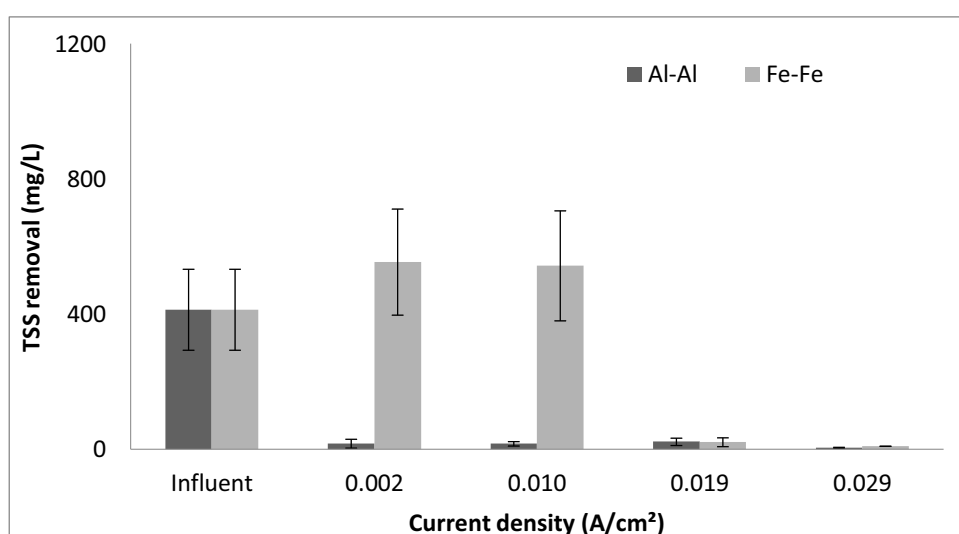




**Figure 6.** DOC removal using electrocoagulation on canola oil wastewater using iron electrodes at various current densities a) concentration of DOC in mg/L b) DOC removal in percentage (%).



**Figure 7.** Oil and grease removal using combined electrocoagulation in canola oil wastewater



**Figure 8.** TSS removal by EC using Al-Al and Fe-Fe and EF process on Canola oil wastewater

#### 4. Conclusion

The main conclusions that can be drawn from this study are, varying current density effects the coagulation time in edible oil wastewater. The higher the current density, lower time it takes to coagulate. Al-Al electrode combination achieved higher removal efficiency of organic pollutants at a lesser time compared to that of Fe-Fe electrode combination. The aluminum electrodes achieved more than 80% removal of DOC at all current densities under observation. Whereas, at

low current densities, iron electrode combination could not yield more than 16% removal of DOC. Both Al-Al and Fe-Fe electrode combination could remove O&G between 52% and 59% showing that the removal efficiency was statistically insignificant for both electrode combinations. The EC process successfully removes nearly 100% of suspended solids using both Al-Al and Fe-Fe electrodes.

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