Coagulation and Flocculation Treatment of Biodiesel Wastewater Using Ferric Chloride

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Abstract. Attempts were made this study to examine of coagulation and flocculation process using ferric chloride and polyelectrolyte (cationic) for the treatment biodiesel wastewater. Removal of SS (suspended solid), color, COD (Chemical Oxygen Demand) and Oil and Grease (O&G) using ferric chloride and organic polyelectrolyte during coagulation/flocculation process were investigated. Also the optimum condition for coagulation/flocculation process, such as pH, coagulant dosage and polyelectrolyte dosage of solution were investigated using jar test experiment. The effect of different dosage of polyelectrolyte in combination with coagulant was also studied. The result revealed that in the range of pH tested, the optimal pH is 6. Percentage removal of 95%, 93%, 63%, 97% for SS, color, COD and O&G respectively, were achieved at optimum dosage value; 350 mg/L. While, 86.3%, 86.7%, 57.2, 81% removal of SS, color, COD, O&G respectively, were achieved with the addition 10 mg/L cationic to 125 mg/L ferric chloride. It can be conclude from this study that coagulation/flocculation may be a useful as a pre-treatment process for biodiesel wastewater.

1. Introduction
Wastewater from biodiesel production is a main problem in biodiesel production. About 20 l of wastewater is discharge per 100 L of biodiesel production. The principal component in waste water remaining residual oil, consequently such waste water really should not be drained through public drains because the oil induces drains plugging and decreasing biological activities in the treatment of sewage [1]. Biodiesel wastewater is dark yellowish cream in colour, highly turbid, pungent smelling and has high organic load as seeds are used as chief raw material in the production, with high levels of chemical oxygen demand, biological demand, oil, high suspended and dissolved solids, high amount of sodium, nitrogen, phosphorus and potassium content[1]. Mostly from the past analysis it has been
shown that wastewater from biodiesel treated by biological process is very complicated because composition of wastewater from biodiesel are not suited for microbial growing [1]. The physico-chemical method much favorable and supportive for this purpose. Though the coagulant is one the most common and widely utilized method. Coagulant and Flucculant are commonly utilized in treating water and wastewater. Coagulation techniques useful and efficient in removal of heavy metals, and some ions from highly concentrated organic pollutant [2]. Coagulant is phase thorough which the effluent is applied to substances namely metal salt to destabilized colloid content. As the consequence, tiny particle is aggregated into bigger size, easier-to-remove flocks. Un-stabilized particle are referred as to primary flocks neutralizing charge (coagulation flocks and flocks expanded are often referred to as secondary flocks [3]. The efficacy of the cycle is determined coagulant factor, the coagulant dose, pH and ionic strength and also the organic compounds nature and concentration [3].

The aim of this present research work to examine the effectiveness of coagulant/flocculant for reduction of suspended solid (SS), COD, Color, and Oil and Grease (O&G) obtained from the biodiesel wastewater by utilizing ferric chlorides. This research also examines optimal coagulant pH, optimal dose of the coagulant and optimal dose of polyelectrolytes to the coagulant cycle. The optimizing certain factor will significantly improve the system efficiency.

2. Materials and Methods

2.1. Wastewater

For this research analysis biodiesel wastewater was utilized as raw sample. The sampling were done manually UTHM biodiesel pilot plant located in Universiti Tun Hussein Onn Malaysia. This plant produces palm oil as raw material and alkali catalyzed transesterification method. The collected samples placed in chiller at room temperature. Table 1, show the characterization of raw biodiesel wastewater based on the standard method for examination of water and wastewater [4].

| Characteristics       | Unit  | Value |
|-----------------------|-------|-------|
| COD                   | mg/L  | 15500 |
| SS                    | mg/L  | 348   |
| Color                 | Pt-Co | 88    |
| Oil and Grease        | mg/L  | 2700  |
| pH                    | -     | 4.5-5.5 |

2.2. Experimental set-up

The research was carried out to determine the removal of coagulation and flocculation. The coagulation and flocculation were analyzed in regular jar-testing equipment, it consists of six paddle motor (24.5 mm x 63.5 mm), fitted with 6-beaker of 1L volume. The 12 number of beaker mounted on a magnetic stir, and coagulant dose stated. The value of pH of biodiesel wastewater samples was modified to pH in ranges 2-12 using 1.0M H2SO4 or 1.0M NaOH respectively after applying 100 mg/L of ferric chlorides to biodiesel wastewater samples. While magnetic stir at 150 rpm for 4 min and slow mixed at 20 rpm for 20 min, the liquid was described 30min, the supernatant was then withdraw from a points around 2 cm below the top of the beaker liquid surface, utilizing standardized methods for determining COD, SS, color, and oil and grease (O&G) [4] even though the impact of pH be study.

50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550 and 600 mg/L ferric chlorides were applied to 1L biodiesel wastewater samples. The supernatant was removed while stirring and clarifying as mentioned above to evaluate COD, SS, color and oil and grease in order to test the effects of coagulant dosage. Ferric chlorides were applied to biodiesel wastewater at a rate of 175 mg/L (half optimal dosage value). While magnetic stir at 150 rpm for 4 min and varying polyelectrolyte concentrations (2,
4, 6, 8, and 10 mg/L) was applied and the liquid was gradually mixed at 20 rpm for 20 minutes, the supernatant was withdrawn as previously mentioned to determine the optimal polyelectrolyte that enhances coagulation.

2.3. Sampling and analysis

Analysis were carried out in triplicate. The pH measured by using (pH meter CyberScan 20), thus oil and grease measure by standard 1164, EPA. SS, color, and COD determined by DR 5000 HACH spectrophotometer according to Standard Water and Wastewater Method. Water colored measurements mentioned for this research report that use the platinum-cobalt (Pt-Co) methods as real color value, the unit of color is that of the chloroplatinate ion formed by 1 mg platinum/L [4]. The sample were filtered using filter paper of 0.45 μm before measuring color.

3. Results and discussion

3.1. Effect of pH on coagulation

The pH effects were measured at 100 mg/L ferric chloride, with mixed rate of 150 rpm for 4 minutes and mixed rate of 20 rpm for 20 minutes, and settling time of 30 minutes for a range of pH ranging from pH2 to pH12. The pH range of the spectrum influenced by coagulant form and chemical properties of water, and also the coagulant concentration [5, 6, 7, 8]. As shown in figure 1, optimal pH6 was observed to facilitate significant removal of the pollutants. From these figures it could be observed that comparatively higher removal rates of SS, colour, COD, and oil and grease (O&G) recorded level of pH5 to pH7. Based on figure 1, higher removal of SS, color, COD and oil and grease at pH6 is 70%, 75%, 47% and 65% respectively. The pH regulation studied by author [9] influenced the concentration of ferric chlorides, polyaluminium chlorides, and alum sulphates. Coagulant pH as a factor influencing coagulations is essential since the application of metallic cation (in this case Fe3+) immediately reduces the pH that might result in further decrease with in removal of pollutants [10]. Because of the residual amounts of excessive chemical additives, the essential to use high dosage of coagulation might present a health danger.

![Figure 1](image.png)

**Figure 1.** Removal percentage in SS, Color, COD and Oil and Grease for pH by using 100 mg/L ferric chloride.
3.2. Effect of coagulant dose on coagulation

Dose was one of the key imperative parameter considered to assess the optimal condition for the coagulation and flocculation of ferric chloride performance. Essentially, inadequate dosage or over dosage contributes to poor results in flocculation [5]. Dosage effect was evaluated at pH 6, 150 rpm of mixed rate for 4 minutes and 20rpm of mixed rate for 20 minutes, and 30 minutes of settling time for a spectrum of ferric chloride dosage varying from 50 mg/L to 600 mg/L, the experiment was performed at optimum pH6. Result of the impact of various dosages of ferric chlorides as single coagulation on the removals of SS, colour, COD and oil and grease (O&G) from the wastewater area of biodiesel shown in Figure 2. Following figure 2 shows clearly the ferric chloride extracts the strongest 95%, 93%, 63% and 97% respectively from SS, colour, COD and O&G grease. When ferric chlorides dosage became increasing above 350 mg/L the efficiency of removal decreased. From the findings, that was clearly indicates that removal of SS, colour, COD and O&G significantly increased as the amount of dosage of ferric chlorides increased. Whenever the dose reached the optimal dosage, the efficiency of removal of all parameter decreased. Each coagulation has optimal range of dosages. Coagulation can support destabilize the colloids particle, help the forming of a floc and thus accelerate the process of settling [11].

![Image of graph showing removal percentage of SS, Color, COD and Oil and Grease for dosage Ferric Chlorides in pH6.](image)

**Figure 2.** Removal percentage of in SS, Color, COD and Oil and Grease for dosage Ferric Chlorides in pH6.

3.3. Effect of polyelectrolyte dose on coagulation

Polyelectrolytes are used as coagulation aid in water and wastewater treatment and can also be utilized primary coagulation [10]. The addition to neutralizing the positively charged in water, causes the formation of flocks and increases the amount of sedimentation by connecting and linking the already produced flocks as then they takes other small particles with the system characterized through sedimentation which cannot create flocks among them and allowing them sediment amongst themselves[12]. Most polyelectrolyte are advantage over chemical coagulants due to their safer handling and easier biodegradation [10]. As shown in figure 3, the removal rate of SS, colour, COD, and oil & grease as functioning of various polyelectrolyte dosage. The polyelectrolytes dosage has been ranges from 0 to 10 mg/L, and dosage of ferric chlorides at 175 mg/L was kept constant. For increasing dosage of polyelectrolytes, the removal rate of SS, colour, COD, and O&G increased. Figure 3, illustrated that the rate of removal of SS with the use of 175 mg/L ferric chloride and 2mg/L polyelectrolyte exceeded 80%. Once the polyelectrolyte dosage was raised to 4 mg/L, the SS rate of removal increases about 82%. Color removal percentage achieved full 86.7% utilizing ferric chlorides
175 mg/L and polyelectrolyte dosage 10 mg/L. Total reduction of 57.2% and 81% with the use of 125 mg/L ferric chlorides and 10 mg/L was achieved for the COD removal and oil and grease.

![Figure 3](image)

**Figure 3.** Removal percentage of SS, Colour, COD and O&G for cationic dosage pH6 utilizing 175mg/L ferric chlorides.

4. Conclusions
This research study work shown that coagulation and flocculation are suitable in treating wastewater from biodiesel. Coagulation and flocculation are very efficient in the reduction of SS, Colour, O&G and appropriately efficient in reduction of COD from biodiesel wastewater. The potential of the study should be able to reducing pollutant produced from biodiesel wastewater before releasing into waterbodies. Therefore, it is expected that in the future this treatment method has become one of the alternative of treating biodiesel wastewater in Malaysia.

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