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Treatment of Biodiesel Wastewater using Ferric Chloride and Ferric Sulfate

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Abstract: The production of biodiesel through the transesterification method produces a large amount of wastewater that contains high level of chemical oxygen demand (COD) and oil and grease. In this study, coagulation was adopted to treat the biodiesel wastewater. Two types of coagulants were examined using standard jar test apparatus, i.e. ferric chloride and ferric sulfate. The effects of pH and coagulant dosage were examined at 150 rpm of rapid mixing and 20 rpm slow mixing and 30 min settling time, higher removal of SS (over 80%), colour (over 80%), COD (over 50%) and Oil and Grease (over 90%) were achieved at pH 6. Ferric Chloride was found to be superior was observed at reasonable lower amount of coagulant i.e. 300 mg/L. The result indicated that coagulation and flocculation process had contributed bigger roles in integrated treatment system.

Keywords; Coagulation, Biodiesel Wastewater, Optimum coagulant dosage

1. Introduction

Biodiesel produce from transesterification method produce a large amount of wastewater that contains high levels chemical oxygen demand (COD), suspended solids (SS), colour and oil and grease [1–4]. The wastewater is basic (alkaline), with a high content of oil and grease, and a low content of nitrogen and phosphorus. Srirangsan et al., [5] investigated therefore; a large amount of wastewater is generated by approximately of 20 to 120 liter/100 liter of biodiesel fuel being produced. The generated wastewater is strong basic (alkaline), contains a high content of hexane extracted oil, but a less nitrogen and phosphorus content; thus, it is unfavorable for the growth of microorganism.

The production of biodiesel through a transesterification method produces a large amount of wastewater that contains high levels of chemical oxygen demand (COD) and oil and grease [6]. Many researchers [1,5] have been reported the following wastewater characteristics that pH was 8.5 to 10.5, the suspended solid (SS) was 1,500 to 28,790 mg/L, the chemical oxygen demand (COD) was 60,000 to 545,000 mg/L, the biological oxygen demand (BOD_5) was 105,000 to 300,000 mg/L and oil and grease was 7,000 to 44,300 mg/L [1,5]. Biological treatment of the biodiesel wastewater is expected to be very difficult [1,7].

In this study, coagulation and flocculation was employed for biodiesel wastewater treatment. Usually, in wastewater treatment coagulation and flocculation process mainly used for the removal of colloid material, which cause colour and turbidity. An essential feature of wastewater flocculation is the elimination of suspended solids (SS) and as much material as well [2,3,8,9]. Coagulation process is effective for removing high concentration organic pollutants [3,8,9] heavy metal and some anions.

Coagulation is the processes where compounds such as metal salts are added to effluents in order to destabilize colloid material [10]. As the result, aggregation of small particle into larger, more easily removed floc takes place. Unstabilized particles by charge neutralization are called primary floc or coagulation flocs and flocs enlarged by bridging is sometimes termed as secondary flocs [2,11]. The effectiveness of the process is influenced by the coagulating agent, the coagulant dosage, the pH and ionic strength as well as the concentration and the nature of the organic compounds [2,5,8,12].

The aim of this work were to simulate coagulation/flocculation process efficiency for biodiesel wastewater treatment plant with respect to removal of SS, colour, COD and oil and grease using ferric chloride and ferric sulfate, also investigate optimum coagulant pH,

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optimum coagulant dosages on the coagulation process and compare the effectiveness between ferric chloride and ferric sulfate as coagulant in biodiesel wastewater treatment.

2. Materials And Method

2.1 Sample Colection And Materials

Sample of biodiesel wastewater was collected from UTHM Biodiesel Pilot Plan which is situated in University Tun Hussein Onn Malaysia. This plant uses palm oil as a feedstock and alkali-catalyzed tranesterification process. The characteristic of this biodiesel wastewater were analyzed according to the standard methods for examination of water and wastewater [13] and are shown in Table 1. The sample had been store in the refrigerator in order to minimize the the charges in the characteristics of wastewater since it may vary from the day to day. Two types of coagulants were considered, namely ferric chloride and ferric sulfate.

Table 1 Characteristic of Biodiesel Wastewater

Parameter	Value
Suspended solids (SS)	348 mg/L
COD	1,5500 mg/L
colour	88 mg/L
Oil and Grease	2700 mg/L
pH	4.5-5.5

2.2 Experimental

Coagulation and flocculation studied were performed in standard jar-test apparatus (Jar Tester Model CZ150 comprises of six paddle rotors (24.5mm x 63.5mm), equipped with 6 beakers of 1 liter volume.. Twelve beakers positioned on magnetic stirrer and a specified dosage of coagulant. The pH value of 1 liter biodiesel wastewater sample was adjusted to pH in range 2 to 12 respectively, by using 1.0 M H_2SO_4 or 1.0 M NaOH, after the addition 100 mg/l ferric chloride or ferric sulfate to biodiesel wastewater sample. After rapid mixing for 3 min at 150 rpm and slow mixing for 20 min at 20 rpm, the liquid was clarified for 30 min, then the supernatant was withdrawn from a point located about 2 cm below the top of the liquid level of the beaker to determined COD, SS, colour and oil and grease by using standard methods [13] so that the effect of pH could be studied.

50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550 and 600 mg/l ferric chloride or ferric sulfate was added to 1 liter biodiesel wastewater sample. After stirring and clarifying as described in above, the supernatant was withdrawn to determine the COD , SS, colour and oil and grease, so that the effect of pH on coagulant could be studied.

2.3 Analytical Analysis

Analyses will be undertaken in triplicates. The pH will be measured by pH meter (CyberScan 20), while oil and grease will be measure according standard method 1164, EPA. Suspended Solid, colour and COD will be measured by DR 6000 HACH spectrophotometer that is adapted from Standard Method for Water and wastewater. All water colour measures described in this work report as true colour values using the platinum-cobalt (Pt-Co) method, the unit of colour being that produced by 1 mg platinum/L in the form of the chloroplatinate ion [13]. The sample will be filtered using 0.45μm filter paper before colour will be measured.

3. Results and Discussion

3.1 Effect of pH on Coagulation

Coagulation and flocculation process depends on the pH of the water system to be treated [1,3,11]. It is the main factor affecting the ion exchange reaction process for the destabilization of colloid particles during the coagulation and flocculation. The appropriate pH will help to neutralize the negative charge colloidal particles and form linkages between colloidal particles more effectively thus helping the formation flocs and achieve the characteristics required of precipitation [1,11].

The influence of different pH was further investigated as the pH is an important factor in the coagulation process [14]. The use of coagulant at its optimum pH displays maximum pollutant removal with the highest performance of wastewater treatment. Nasir & Daud [3] suggest the optimum range for ferric chloride is from about 4 to 12. The operating region for ferric hydroxide precipitation is from a pH range of 7 9, with minimum solubility occurring at pH of 8 [2,8].

Therefore, the study of pH was essential to determine the optimum pH condition of the treatment system. The effect of pH was analysed at 100 mg/l dosage, with 150 rpm of mixing rate for 3 minutes and 20 rpm of mixing rate for 20 minutes and 30 minutes of settling time for a range pH 2 to pH 12. The efficiencies based on the removal and reduction of SS, colour, COD and oil and grease in the biodiesel wastewater were used to determine the optimum pH. Results showed at pH 6, the percentage removal of SS, COD, colour and oil and grease gives the highest for both coagulants.

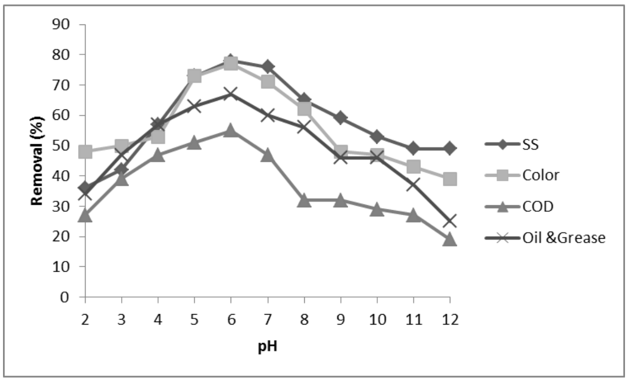

Fig. 1 Percentage of SS, colour, COD and oil and grease removal against pH using 100 mg/L ferric chloride.

At optimum pH of ferric chloride, the removal of SS, colour, COD and oil and grease are 78%, 77%, 55% and 67% respectively as compared 69%, 67%, 43% and 57% were removed respectively at optimum pH of ferric sulfate as shown in Fig. 1 and Fig. 2. The optimum pH, large flocs hydroxide will settle easily. After pH 6, contribution of charge neutralization decreased while contribution of the adsorption and entrapment or sweep coagulation predominated until pH 12.

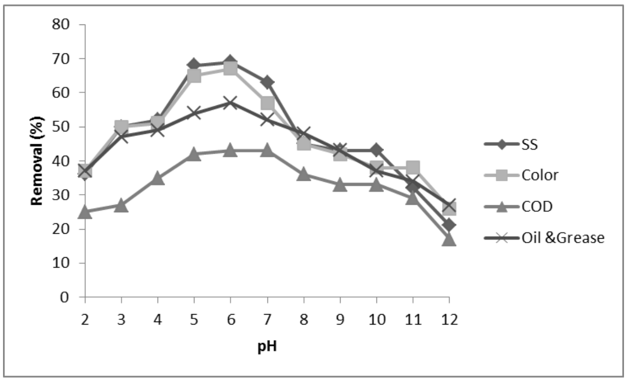

Fig. 2 Percentage of SS, colour, COD and oil and grease removal against pH using 100 mg/L ferric sulfate.

3.2 Effect Of Coagulant Dosage on Coagulation

Dosage was the most important parameters that been considered to determine the optimum condition for the performance of coagulation and flocculation. Each type of the coagulants has its own characteristic optimum dosage range. Basically, insufficient dosage or overdosing would result in the poor performance in flocculation [3,8]. Therefore, it was crucial to determine the optimum dosage to order to minimize the dosing cost and obtain the optimum performance in treatment.

The effect of dosage was analyzed at 150 rpm of mixing rate for 3 minute and 20 rpm of mixing rate for 20 minutes and 30 minutes of settling time for a range dosage which varied from 50 mg/l to 600 mg/l. Figure 3 to 4 present the result of the effect of coagulation dosage on suspended solids, colour, COD and oil and grease respectively.

From the Fig. 3 and Fig. 4, all the residual parameters were decreased while their removal efficiencies were improved substantially as the dosage of ferric chloride or ferric sulfate was increasing until reached optimum dosage. When the dosages were exceeding the optimum dosage for both coagulants, there was a decrease in the removal efficiency for all the parameters. Each type of coagulant has its own optimal dose range. Coagulant is a compound that helps coagulation. Coagulation with help destabilize the colloidal particles, helping the formation floc and consequently accelerate the settling process [3].

Optimum coagulant dose of ferric chloride and ferric sulfate were 300 mg/L and 450 mg/L respectively. At optimum coagulant dose of ferric chloride, the removal of SS, colour, COD and oil and grease are 95%, 93%, 68% and 99% respectively as compared 86%, 83%, 59% and 90% were removed respectively at optimum dose of ferric sulfate.

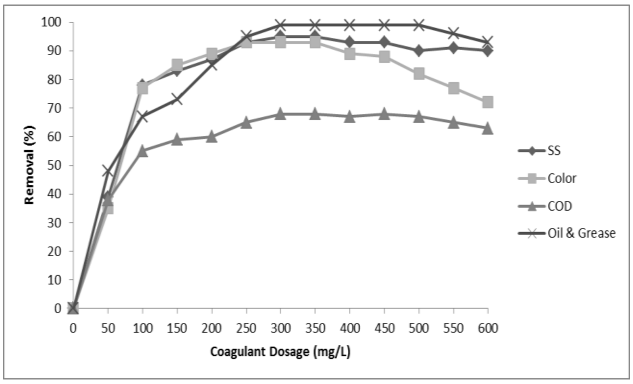

Fig. 3 Percentage of SS, colour, COD and oil and grease removal against ferric chloride dose at pH 6.

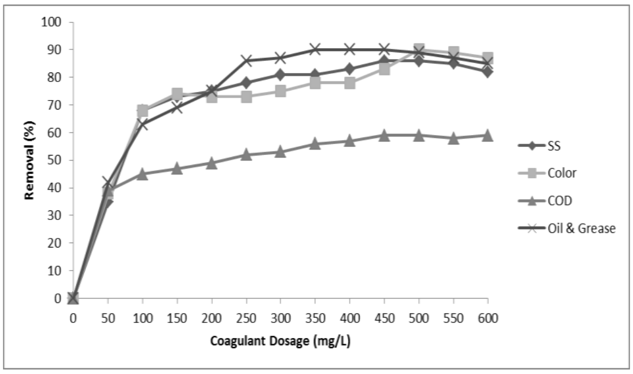

Fig. 4 Percentage of SS, colour, COD and oil and grease removal against ferric sulfate dose at pH 6.

4. Conclusions

In this study, two coagulant ferric chloride and ferric sulfate has been used to study the effectiveness on removal of SS, COD, colour and oil and grease in the biodiesel wastewater for the determine the optimum conditions based on the dose and pH for coagulation and flocculation process. The result showed that optimum pH for both coagulant is 6 and optimum coagulant dose of ferric chloride and ferric sulfate were 300 mg/l, and 450 mg/l respectively.

Here, the coagulation process and all parameter removal was considerably affected by pH, coagulant dosage, as well as initial characteristics of biodiesel wastewater for both ferric chloride and ferric sulfate Investigating the influence of rapid mixing parameters, time and intensity of mixing, as well as slow mixing parameters on turbidity removal by ferric chloride and ferric sulfate is also suggested for future studies.

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