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The Effect of pH on the Stability of Grease and Oil in Wastewater from Biodiesel Production Process

Aneak SAWAIN¹, Wirach TAWEEPREDÁ², Udomphon PUETPAIBOON³, Chaisri SUKSAROJ*⁴

Abstract

This research investigated the effect of pH by acids adjustment and using coagulant and coagulant aid in combination with pH control on grease and oil removal in wastewater from biodiesel process. This wastewater contains the emulsion particle, could not be treated by conventional process. The effect of pH on the reduction of emulsion property by adding acids, coagulant, coagulant aid and coagulant aid were studied and compared. The formation by coalesce of oil drop in wastewater occurred when the pH was reduced. But only use of acid adjustment was not appropriate in this case. The practical means for oil and grease removal from biodiesel wastewater were use of ferric chloride or ferric chloride with cationic polymer and controlled pH in rage of 5-6. The contaminated organics in term of COD and grease and oil removal efficiencies obtained in this study was up to 97%.

Keywords] biodiesel, emulsion, coagulant, grease and oil

I Introduction

The biodiesel production process with tranesterification reaction uses a large amount of water for product rinsing, to remove undesirable substances like soap and others residual initial substances (Gerpen et. al. 2004, and Tonggurai et. al. 2001). The wastewater from this process contained oily substances that appeared in emulsion form, was difficult to remove by conventional grease and oil trap. The cause of emulsion in biodiesel wastewater is soap produced from saponification reaction occurred during the tranesterification, the carboxylic group from fatty acid would react with alkalinity that used as catalyst in tranesterification (Gerpen et. al. 2004). As soap is a surfactant, it can form complex with oil to be micelle and could be oil emulsified in water (O/W) (Jones, 2005 and Sawain et. al. 2008). A stable O/W emulsion in wastewater from biodiesel process is a colloidal system of electrically charged oil droplets surrounded by an ionic environment, suspended in water (Kemmer and McCallion, 1979).

The wastewater from biodiesel production process contains the white muddy particle like milk caused by the oil emulsified in water. Many researchers (Sawain et. al. 2008, Suehara et. al. 2005 and Ruengkong et. al. 2008) have been reported this wastewater characteristics, for example the pH was 8.5-10.5, the suspended solid was in the range of 1,500 – 28,790 mg/L, the COD was in the range of 60,000 – 545,000 mg/L, BOD was in the range of 105,000 – 300,000 mg/L and Grease & Oil was in the range of 7,000 – 44,330 mg/L. According to high impurity loading that was low biodegradable material, this wastewater somewhat difficultly to treat directly with conventional wastewater treatment plant. In addition, the wastewater from biodiesel production process contained nutrient insufficient for microorganism (Ruengkong et. al. 2008). In this case, the pre-treatment to remove oil and grease in wastewater before treating in conventional treatment unit was necessary (Suehara et. al. 2000 and Fujii et. al. 2007).

While the emulsion was stabilized itself, it may due to the friction between the oil and water phases created by vigorous mechanical or physical agitation. Static electric charges developed by this action tend to collect at the O/W interface. An emulsifier is usually a complex molecule, frequently having a hydrophilic group at one end and a lyophilic (oil-loving) group at the other. Therefore they have an affinity for both water and oil that enables them to overcome the natural forces of coalescence, the result is emulsifiers disperse oil droplets in the water phase. Most natural particle in water and emulsifier are surfactants which have either anionic or nonionic polar group (Kemmer and McCallion, 1979). Sulfonated fatty acids and protein is common anionic emulsifier. Protein contains amino group (-NH₂) and

a Corresponding author, Tel.: 0-7428-7116; Fax: 0-7445-9396; E-mail address: schaisri@eng.psu.ac.th
1, 3, 4 Department of Civil Engineering, Faculty of Engineering, Prince of Songkla University, Songkhla, 90112, Thailand
2 Faculty of Science, Prince of Songkhla University, University, Songkhla, 90112, Thailand.
carboxylic group (COOH), that their dissociation depend on the pH of solution. The destabilization or demulsification can be achieved with reducing electric forces or destroys electrical double layer (Tuntoolavest, 1999. and Reynolds and Richards, 1996) by pH adjustment. The pH adjustment can change chemical structure of functional group, result in the change of stability. For example if pH was equal pK (4-6.5 for carboxylic group), -COO⁻ equivalent to -COOH and then the system was close to the isoelectric points (iep), the zeta potential that was indicator of the stability of colloid was close to zero, the coalesce of oil drop was occurred (Reynolds and Richards, 1996). In addition the demulsification and destabilization of emulsion can be achieved with the coagulation-flocculation by adding inorganic salts as Alum or FeCl₃, following with the sedimentation or the floatation (depend on their density), that have been widely used in water and wastewater treatment processes as solid-liquid separation aids. Fine particulates are coagulated or flocculated to form so much coarser size of flocs that settle or float more rapidly and leave the overflow clear. This phenomenon was due to the reduction of charge in the electrical double layer by depress the electrical double layer, made the electrical double layer to collapse and adsorption of hydroxo complexes on particle (Tuntoolavest, 1999. and Reynolds and Richards, 1996). Furthermore, the pH control can enhance the efficiency of coagulation by inorganic salt (Reynolds and Richards, 1996) such as, at low pH, Fe ion is surrounded with water molecule [Fe(H₂O)₆]³⁺ then was difficult to contact with colloid but at the optimum pH range (4 – 10) or high dosage, the Fe ion can form complex to be Fe(OH)₃ that is solid form. This solid form will enmesh suspended particles and sweep down (up) slowly to the bottom (top) of the container as know Sweep Coagulation, as found in the case of Al(OH)₃ from alum coagulation (Tuntoolavest, 1999) in this case the alkalinity control was necessary by adding NaOH or KOH. Sweep coagulation can enhance by using some organic polymer to improve the floc size and characteristics even polymer use as a coagulant or use as a coagulant Aid (Tuntoolavest, 1999. and Reynolds and Richards, 1996)

The aim of this research then be emphasized the effect of pH on the oil emulsified in biodiesel wastewater, contained mainly grease, oil and soap. The coagulation process using FeCl₃ and cationic polymer, including pH influent was also conducted. Finally, the consideration guide line for scale up approach, operating system and economic determination was reported.

II Materials and Methods

Biodiesel wastewater sample was taken from Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, Faculty of engineering, Prince of Songkla University.

The studies of pH effect on grease and oil removal was conducted by using analytical grade of 1 N hydrochloric acid (HCl) and 1 N Sulfuric acid (H₂SO₄) for 1 lite of wastewater sample. The experiments were conducted with the jar test apparatus (PHIPPS & BRD). The wastewater was mixed of 30 rpm for 20 min then measured the oil layer by the time.

The studies of coagulant use for grease and oil removal were investigated with the reagent grade ferric chloride (Ajax) at difference concentration with and without pH controlled. The 20% by weight of cationic polymer solution (INNOLYMER CO., LTD) was also studied. The experiments were conducted by using jar test apparatus (PHIPPS & BRD). The wastewater coagulated was mixed rapidly at 100 rpm for 1 min and following by slow mixing at 30 rpm for 20 min (Udomsinrrot, 1999).

The wastewater characteristics were analyzed by following Standard method (APHA, AWWA and WEF. 1998). The grease and oil was analyzed by Soxhlet Extraction Method, total Suspended Solid was analyzed by Dried at 103 – 105 °C, the COD was analyzed by Open Reflux Method, the pH value was measured by pH meter HACH (Sensions 1) and the turbidity was measured by turbid meter (HACH 2100N).

III Results and Discussions

1. General characteristic of biodiesel wastewater

This wastewater appears as the high concentration of white muddy particle, looks like milk, due to the oil emulsified in water. The pH was 8.5-10.5, the suspended solid was in the range 1,500 – 5,000 mg/L, the COD was in the range 60,000 – 150,000 mg/L and Grease & Oil was in the range 7,000–15,000mg/L.

2. Influence of pH on grease and oil removal

The result of the experiments showed that the change of emulsion and coalesce of oil was observed when the pH value decrease to about 5. It may be due to the environment changed to close to the isoelectric point (iep), the result in zeta potential was nearly zero, and then the demulsification was occurred. The separation of oil droplet could be observed obviously when pH was lower than 3 (Fujiia et. al. 2007, Reynolds and Richards, 1996 and Eckenfelder, 2000). The Figure 1 presented the coalescence of oil drop occurred at pH 1 and 3. It could be seem that the accumulation of oil drop coalescence at pH 1 was higher than that obtained at pH 3 and
density was lower than water. The increase of oil drop coalescence made more grease and oil removed when they floated to the water surface that enhanced higher grease and oil removal efficiency as showed in Figure 2. But this reaction took a long time, the Figure 3 showed the oil floating after 24 h. It was found that the most partial grease and oil and emulsion still suspended in water, it need a few days for demulsification and floating to water surface both in the case of Hydrochloric acid and sulfuric acid use. Although the higher grease and oil removal efficiency could be enhanced at low pH, but the partial grease and COD were still leaved that needed to be treated by following conventional biological wastewater unit. Therefore the pH of wastewater after grease and oil removal which had low pH was not suitable to treat in following by biological process. In addition, it would introduce corrosive problem also, the study of pH effect on grease and oil removal used ferric chloride was examined.

![Figure 1 Coalescence of oil drop at pH 1 and 3 with 20 times microscope enlargement; HCl (a: pH1, b: pH3), H₂SO₄ (c: pH 1, d: pH 3)](image)

3. The pH effect on grease and oil removal by ferric chloride coagulation

The use of ferric chloride in the range of 0.5 – 10.0 g/L with uncontrolled pH showed an ineffective grease and oil demulsification. But when the ferric chloride was increased into the range of 1-1.5 g/L and pH was controlled at 5, the oil layer at water surface could be observed. The rust color grease and oil floc were formed and gathered to be floating floc as presented in Figure 4. The rust color of these floating floc may caused by the red color of oxide Iron. In this case, the grease and oil separation mechanism may be different from that use only pH adjustment approach. The use of ferric chloride with pH control may depress the electrical double layer and introduce the adsorption of hydroxo complexes on colloids surface (Tuntoolavest, 1999. and Reynolds and Richards, 1996). But when the ferric chloride was up to 2 g/L and higher, the quantity of ferric hydroxo complexes that would agglomerate with grease and oil was increased. This led the increasing of the rust color floc mass and density and sunk to the bottom whereas the partial of them still floated to the water surface. The ferric chloride since 2.0 mg/L and more, therefore, were not suitable to be used because the grease and oil separated would be more difficulty removed.

The effect of pH on grease and oil removal used ferric chloride (1.5-2.5 g/L) coagulation and pH controlled at 5, 6 and 7 was presented in Figure 5. At 0.5 mg/L of ferric chloride used, the highest grease and oil removal efficiency was found at pH 6. This due to pH 6 was the optimal for ferric hydroxide (Fe(OH)₃) formation. But when the ferric chloride concentration was increase to be 1.0, 1.5, 2.0 and 2.5 g/L, their remove efficiency were not different. Furthermore, the sedimentation could be observed in all pH values tested with 2.0 and 2.5 mg/L of ferric chloride as described in above.

![Figure 2 Grease and oil removal efficiency by using pH adjustment at pH 1 and 3 with HCl and H₂SO₄](image)

![Figure 3 Floatation of grease and oil layer at pH 1 and 3 for HCl (a, b) and H₂SO₄ (c, d)](image)

![Figure 1 Coalescence of oil drop at pH 1 and 3 with 20 times microscope enlargement; HCl (a: pH1, b: pH3), H₂SO₄ (c: pH 1, d: pH 3)](image)
Figure 4 Floatation/sedimentation of grease and oil floc by ferric chloride coagulation at pH 5 and detention time 1 h.

Figure 5 Effect of pH on grease and oil removal by ferric chloride coagulation

However, ferric chloride adding can decrease the pH value in water also. It could be noted that the grease and oil removal efficiency with pH control at 5, 6 and 7 was quite different (97% grease and oil reduction, 60% COD reduction and 97% suspended solids reduction) therefore the pH control at 5-6 may be more appropriated with economic consideration.

Since the turbidity value varies with the colloid concentration in water, it could be used as the indicator of grease and oil residual in water (Yang, 2007 and Rios, et al. 1998). Actually, the original wastewater from biodiesel process contained high concentration of colloid that was over than turbid meter measureable range but after treatment with coagulation and flocculation, the residual turbidity was in the range that could be measured by turbidity meter. The result was corresponded with the result of grease and oil removal and turbidity decrease with the increasing of ferric chloride concentration as showed in Figure 6. The value of turbidity was closely after 6 h. and ferric chloride beyond 1.5 g/L.

Figure 6 Turbidity removals by different concentration of ferric chloride coagulation in function of time (pH=5)

It could be noted that when the turbidity of wastewater was less than 20 NTU then the grease and oil was less than 200 mg/L, so it was still some oil emulsified in water even the grease and oil removal was over 97%. With the reason of residual oil remained and problem of the combine sediment and float of floc, the coagulation with cationic polyamine normally used as a coagulant aid was also studied to enhance grease and oil removal efficiency. And in this case, the problem of floc sedimentation would be considered.

4. Grease and oil removal by ferric chloride and cationic polymer coagulation and their pH effect

In case of using cationic polymer as a coagulant aid after 0.5 mg/L of ferric chloride coagulant was added, the use of 20 % by weight cationic polymer yielded the high efficiency of grease and oil removal at neutral pH value. The bigger floc was occurred than that used only ferric chloride. Using 0.5-0.75 ml/L of polymer could yielded the high efficiency of grease and oil removal (97%), the lower turbidity (<20 NTU) remained and the sedimentation of floc was not observed, it may be due to the low density of floc when using polymer and the ferric chloride concentration used was reduced. This can enhance the floatation of grease and oil floc from wastewater in the operation process and the organic polymer floc can easily to degrade than ferric floc and contains lower water in waste sludge. (Reynolds and Richards, 1996 and Metcalf and Eddy, 2004)

5. The tentative list of chemical estimate cost.

The application of chemicals mentioned as above depends on many factor requirements such as the effluent quality and the operation system etc. However, this will depend on the reagent cost as show in Table 1.
### Table 1 The list of chemical cost using in this study

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Baht/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Hydrochloric acid</td>
<td>3 – 4</td>
</tr>
<tr>
<td>2. Sulfuric acid</td>
<td>12 – 16</td>
</tr>
<tr>
<td>3. Ferric chloride*</td>
<td>16.5 – 22.5</td>
</tr>
<tr>
<td>4. Ferric chloride + polymer*</td>
<td>46.5 – 52.5</td>
</tr>
</tbody>
</table>

**Remark** *: Include adjustment pH reagent

### IV Conclusions

The wastewater from biodiesel process requires pre-treatment to remove their before treatment by conventional biological treatment unit. The pH could affect the oil emulsion in this wastewater. To enhance the grease and oil removal efficiency, the pH of wastewater should be adjusted to be low. But only pH adjustment may be not appropriate because it made effluent was strong acid. The use of coagulant such as ferric chloride in combination with pH adjustment may be more practical. In this case, the grease and oil, COD and suspended solids removal efficiencies obtained were high with 97% of total removal efficiency at pH in range of 5-7 and these efficiencies could be enhanced by using cationic polymer as coagulant aid.

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### References


