Biodiesel wastewater treatment by coagulation process for chemical oxygen demand reduction

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Abstract. Biodiesel wastewater contained residual of alkali catalyst, soap and glycerol which causing in high chemical oxygen demand (COD). The optimum conditions of aluminium sulphate (alum), poly-aluminium chloride (PAC) and laterite soil (silifloc) in the coagulation of biodiesel wastewater for COD reduction were explored through a sequence of studies including the effects of pH and dosage of coagulants. Coagulation process were conducted in the fixed conditions of mixing rate, mixing time, settling time and anionic polymer aid as flocculant. Silifloc could treat acidified biodiesel wastewater with 32.35\% at pH 2 and dosage of 4000ppm, the highest among these three coagulants. This was due to the silifloc rich in silica component had a higher rate law at sufficient dosage and had an effective range of at around pH 2. Whereas, PAC had a highest efficiency with 61.58\% at pH 6 and dosage of 1100ppm in coagulation of raw biodiesel wastewater due to its solubility and elements of higher ions content. On other hand, alum had a moderate performance in acidified and raw wastewater with 26.42\% at pH 6 and 57.63\% at pH 4, respectively.

1. Introduction
Biodiesel is an alternative renewable resource of fossil diesel that made from vegetable oil and it produced lower pollutant emission compared to fossil fuel. Currently, transesterification is the most common method used to produce biodiesel with low oil viscosity compared to pyrolysis, blending and micro-emulsions. However, purification after transesterification by using a traditional and widely used method, wet washing process with water to take out the impurities will be produced above 20 liter of wastewater per 100 liter of biodiesel generated. This biodiesel wastewater containing residual methanol, glycerol, oil, free fatty acids, salt, and mono, di and triglycerides [1]. If it discharged without the treatment, the wastewater with high chemical oxygen demand (COD) due to the high concentrations of organic carbon, oil and grease will impact to the aquatic life and environment.

Coagulation is often used in integrated process as a pretreatment method due to its economical, simple and effective in metal and toxic waste removal prior to the biological treatment. Aluminium sulphate (alum) and poly-aluminium chloride (PAC) are the most extensive conventional aluminium-based coagulant that provide positive charge Al species to neutralize the negative charged particles and flocculate into settleable flocs. Presently, biodiesel industry in Malaysia has been applied the integrated process of coagulation and aerobic process. However, the COD removal
efficiency failed to reach the expectation. This may be due to the condition in the treatment process are not optimized. Overdosing of these coagulants also produced sludge that containing high amount of residual aluminium and aluminium salt that may cause Alzheimer’s disease [2]. Therefore, alum, PAC and silifloc, a silicon (Si)-rich laterite soil as a natural coagulant were used in the treatment of biodiesel wastewater from the washing process. The aim of this study was to optimize the pH and dosage of coagulant in order to achieve the maximum removal efficiency of COD in biodiesel wastewater. The comparison of effectiveness under the optimum condition of coagulants was observed.

2. Materials and methodology

2.1. Experimental materials

Raw biodiesel wastewater and acidified biodiesel wastewater were collected from a palm oil biodiesel plant in Perak. Before the samples were used in coagulation, they were raised to room temperature after moved out from chiller. PAC and alum powders were diluted with distilled water according to the concentration needed. Filtered and decolorized silifloc paste was blended with distilled water according to concentration needed. 500 ppm of anionic polymer stock solution was prepared as a flocculants. 1.0 M of hydrochloric acid (HCl) and 1.0 M of sodium hydroxide (NaOH) were prepared for pH adjustment.

2.2. Coagulation experiment

Coagulation was conducted by using jar tester (JLT6 VELP Scientifica) to obtain the optimum pH and dosage for COD removal. The initial pH of biodiesel wastewater was measured by HI 9125 (HANNA) and then followed by the pH adjustment. Each beaker for coagulation was filled in 250 ml of mixture of sample and coagulant at various pH (2, 4, 6, 8, 10 and 12) with final concentration of 500 ppm for PAC, alum and 4000 ppm for silifloc. Optimization of dosage was conducted at optimal pH and various dosage (100, 300, 500, 700, 900, 1100 ppm and further increased if needed) for PAC and alum while various dosage (4000, 8000 12000 and 16000 ppm) for silifloc. Mixture of wastewater sample and coagulant was stirred rapidly at 200 rpm for 2 minutes for coagulation, then the stirring speed was decreased to 100 rpm for 15 minutes for flocculation. Flocculant was added at 5 minutes before end of jar test. 20 mL of the samples was collected from the top of the settling beaker (2 cm beneath the water surface). The collected sample was filtered through ALBET standard ashless filter paper and used in COD analysis by DRB 200 COD reactor (HACH) and read by DR 2800 spectrophotometer (HACH).

3. Results and discussion

3.1. Effect of pH on coagulation of biodiesel wastewater

The effect of pH was analysed by varying the pH of biodiesel wastewater with fixed mixing rate and time. Figure 1 demonstrated the COD removal in biodiesel wastewater. The optimum pH of PAC for acidified and raw biodiesel wastewater was achieved with a pH 6 which had 58.72 % and 79.70 % of COD removal efficiency, respectively. For alum, the optimum pH for acidified and raw biodiesel wastewater were pH 6 with 79.62 % of COD removal efficiency and pH 4 with 55.30 % of COD removal efficiency, respectively. Both acidified and raw biodiesel wastewater coagulated by silifloc had a maximum efficiency at pH 2 which gave 32.35 % and 35.23 % removal efficiency, respectively. At the optimum pH, aluminium-based coagulant PAC and alum provided multivalent aluminium ions Al(OH)2+, Al(OH)3+ and Al3+, that can used in neutralization of particle charges and the hydrolysed aluminium flocs aggregated the colloids [3]. Meanwhile, silifloc had zero charge when it was in acidic condition around pH 2. At this point, silica in the forms of [SiOH]2− and [SiO3]2− which can be applied as a coagulant to improve the rate of neutralization in the system [2]. In this case, PAC had a highest removal efficiency due to its wider pH condition and in good controlling of OH/Al compared to alum and silifloc.

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3.2. Effect of dosage on coagulation of biodiesel wastewater

The optimum dosage was obtained by conducting the coagulation with variation of dosage and selected optimum pH. Silifloc was a natural coagulant, natural soil that had a high plasticity when water content reduced. The accuracy of volume measurement affected and limited by the plasticity. Hence, the dosage of silifloc was varied below 16000 ppm. As shown in figure 2, the optimum dosage of PAC for acidified biodiesel wastewater was 900 ppm which has 30.49 % of COD removal efficiency while for raw biodiesel wastewater was 1100 ppm which has 61.58 % of COD removal efficiency, respectively. The optimum dosage for both acidified and raw biodiesel wastewater that using alum were 700 ppm which can treat for 28.42 % and 57.63 % of COD, respectively. Acidified and raw biodiesel wastewater coagulation by using silifloc gave a highest efficiency at 4000 ppm with 32.35 % and 16000 ppm with 39.06 %, respectively.

Based on figure 2, the overall results obtained clearly showed a similar trend. The COD removal efficiency increased as the dosage of coagulant increased until it reached a maximum efficiency at optimum value, the results started to decrease or maintained at the same efficiency. When there was a further increased in coagulant dosage after the optimum dosage would initiated the restabilization of colloidal particulates [4]. With the large amount of extra coagulant dosage, the opposite charge formed on the surface particles due to continue adsorption of mononuclear and polynuclear hydrolysis species of coagulant. Hence, the positively charged colloidal particles failed to remove by perikineti flocculation and decreased in the efficiency [5].

Figure 1. COD removal after coagulation by PAC, alum and silifloc at various initial pH.
Figure 2. COD removal after coagulation by PAC, alum and silifloc at various dosage.

3.3. Comparison of effectiveness of PAC, Alum and Silifloc

Table 1 showed that PAC was most effective in raw biodiesel wastewater. This might due to the solubility of PAC and elements of higher ions content which can increased the efficiency [6]. Whereas, silifloc had a highest COD removal efficiency in treating the acidified biodiesel wastewater. Silifloc had a higher rate law at sufficient dosage and had a greater efficiency at the range that same with the effective range of acidification at pH 2 [7]. Overall, the results of coagulation process by using PAC, alum and silifloc presented in study were showing the trend was tend to the acidic condition. This can achieved by the H⁺ ions to react with residual alkali catalyst and soap molecule to form fatty acids and free FAME prior the coagulation process [8].

| Parameter                  | Value |
|----------------------------|-------|
| **Biodiesel Wastewater**   |       |
| Coagulant                  | PAC   | Alum  | Silifloc | PAC | Alum  | Silifloc |
| Optimum pH                 | 6     | 4     | 2        | 6   | 6     | 2        |
| Optimum Dosage (ppm)       | 1100  | 700   | 16000    | 900 | 700   | 4000     |
| COD Removal Efficiency (%) | 61.58 | 57.63 | 39.06    | 30.49 | 28.42  | 32.35    |
4. Conclusion
This study showed that the COD removal efficiency of PAC, alum and silifloc in treating the biodiesel wastewater were pH and dosage dependent. These coagulants used in biodiesel wastewater had an effective range that tend to the acidic condition due to the residual alkali catalyst and soap. Silifloc showed a greatest removal efficiency of 32.35% at the optimum condition in treating the acidified biodiesel wastewater compared to PAC and alum. Although PAC had a highest efficiency of 61.58% in raw biodiesel wastewater, further research should conducted to determine the optimum dosage for silifloc, since the dosage of silifloc in this study was limited by the volume measurement caused by high plasticity. Oil and grease removal and sludge production also should be studied to investigate the cost effective of PAC, alum and silifloc in coagulation of biodiesel wastewater since silifloc was reusable and effective to oil absorption.

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References
[1] Daud N M, Sheikh Abdullah S R, Abu Hasan H and Yaakob Z 2015 Process Saf. Environ. Prot. 94 487–508
[2] Lau Y Y, Wong Y S, Teng T T, Morad N, Rafatullah M and Ong S A 2014 Chem. Eng. J. 246 383–390
[3] Srivastava V C, Mall I D and Mishra I M 2005 Colloids Surf. A Physicochem. Eng. Asp. 260 17–28
[4] Aguilar M I, Sáez J, Lloréns M, Soler A, Ortuño J F, Meseguer V and Fuentes A 2005 Chemosphere 58(1) 47–56
[5] Verma S, Prasad B and Mishra I M 2010 J. Hazard. Mater. 178(1-3) 1055–1064
[6] Rui L M, Daud Z and Latif A A A 2012 Int. J. Adv. Sci. Eng. Inf. Technol. 2(2) 114
[7] Elaziouti A, Laouedj N and Ahmed B 2011 J. Chem. Eng. Process Technol. 24
[8] Kumjadpai S, Ngamlerdpokin K, Chatanon P, Lertsathitphongs P and Hunsom M 2011 Canadian J. Chem. Eng. 89(2) 369–376