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PERFORMANCE OF ALUMINIUM SULPHATE AND POLYALUMINIUM CHOLORIDE IN BIODIESEL WASTEWATER

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ABSTRACT

The production of biodiesel through the transesterification method produces a large amount of wastewater that contains a high level of chemical oxygen demand (COD) and oil and grease (O&G). In this study, coagulation was adopted to treat the biodiesel wastewater. Two types of coagulation were examined using a standard jar test apparatus, i.e. polyaluminium chloride (PAC) and aluminium sulphate. 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 suspended solids (SS), colour, oil and grease (over 90%), and COD (over 80%) were achieved at pH 6. PAC was found to be superior to aluminium sulphate, yielding a lower amount of coagulation, i.e., 300 mg/L. The result indicated that the coagulation and flocculation process played bigger roles in the integrated treatment system.

Keywords: Coagulation-flocculation; coagulation dosage, biodiesel wastewater

INTRODUCTION

Biodiesel has significant promise as a potential replacement for petroleum-based diesel fuel [1]. Biodiesel is an alternative diesel fuel produced from the transesterification reaction of triglycerides from vegetables oils or fats with alcohols like methanol and ethanol in the presence of a homogeneous base catalyst like NaOH or KOH. Biodiesel is biodegradable, non-toxic, burns with a low sulphur, carbon monoxide, and aromatic-free emission profile, and is environmentally beneficial [2-7]. Although biodiesel generates low greenhouse gas emissions and has a very low toxicity, its production may cause some environmental problems. In the final process of biodiesel production, water is usually introduced into the biodiesel to remove impurities. This washing step is repeated 2–5 times, depending on the quantity of impurities in the methyl ester. A large amount of wastewater, 20–120 litres per 100 litres of biodiesel, is generated in this process [8-10]. Wastewater from the production processes is contaminated with water-insoluble methyl ester, methanol and by the product itself. It also contains a significantly higher content of COD of 170,000 mg/L and oil and grease of 9,000 mg/L [11]. The main component of the wastewater is the residual remaining oil, so such wastewater should not be discharged into public drainage because the oil causes plugging of drains and decreases biological activity in sewage treatment. The wastewater is basic (alkaline), with a high content of oil and grease, and a low content of nitrogen and phosphorus. As such, biological treatment of the biodiesel wastewater is difficult because the composition of the biodiesel wastewater is not suitable for microbial growth [8]. According to Sawin, Taweepreda [1], wastewater from the biodiesel production process contains white muddy particles like milk that are caused by the oil emulsified in water. However, most of the previous works on biodiesel have mainly focused on the technical processes of the production, while its environmental management aspect has usually been neglected [11].

A previous study showed that the biological treatment of biodiesel wastewater is difficult because the composition of biodiesel is not suitable for microbial growth [8]. For this reason, supportive physico-chemical methods are often used. One of the most frequently employed methods is coagulation. Coagulation and flocculation are widely used in water and wastewater treatment. The coagulation process is effective for removing high concentration organic pollutants [12, 13], heavy metal and some anions. Coagulation is the process where compounds such as metals salts are added to effluents in order to destabilize colloid material. As a result, the aggregation of small particles into larger and more easily removed floc takes place. Particles destabilized by charge neutralization are called primary floc or coagulation flocs, while flocs enlarged by bridging are sometimes termed as secondary flocs [14]. 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 organic compounds [13, 14]. The objectives of this study were to simulate coagulation/flocculation process efficiency for a biodiesel wastewater treatment plant with respect to removal of SS, colour, COD and oil and grease using aluminium sulphate [15] and polyaluminium chloride (PAC). We also investigate the optimum coagulant pH and optimum coagulant dosages on the coagulation process, and compare the effectiveness between aluminium sulphate and polyaluminium chloride as coagulant in biodiesel wastewater treatment.

EXPERIMENTAL SET-UP

Sample Collection and Material

A sample of biodiesel wastewater was collected from UTHM Biodiesel Pilot Plant which is situated in University Tun Hussein Onn Malaysia. This plant uses palm oil as a feedstock and an alkali-catalyzed transesterification process. The characteristics of this biodiesel wastewater were analysed according to the standard methods for examination of water and wastewaters [16], as shown in Table 1. The sample was stored in a refrigerator in order to minimize changes in the characteristics of the wastewater, since it may vary from day to day. Two types of coagulants were considered, namely aluminium sulphate and polyaluminium chloride.

Table 1. Characteristics of biodiesel wastewater.

Parameters	Value
Suspended solids (SS)	348 mg/L
COD	15,500 mg/L
Colour	88 PtCo
Oil and grease	2,700 mg/L
pH	4.5 – 5.5

Experimental Procedure

Coagulation and flocculation studies were performed in standard jar-test apparatus, with Jar Tester Model CZ150 comprising 6 paddle motors (24.5 mm x 63.5 mm), equipped with 6 beakers of 1 litre volume. Twelve beakers were positioned on a magnetic stirrer with the specified dosage of coagulant. The pH value of 1 litre of biodiesel wastewater sample was adjusted to pH values in the range 2–12, by using 1.0 M H_2SO_4 or 1.0 M NaOH, after the addition of 100 mg/L alum or PAC to the sample. After rapid mixing for 4 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 determine the COD, SS, colour, and oil and grease (O&G) using the standard methods [10] so that the effect of pH could be studied. 50,100,150, 200, 250, 300, 350, 400, 450, 500, 550 and 600 mg/L alum or PAC was added to 1 litre of the biodiesel wastewater sample. After stirring and clarifying as described above, the supernatant was withdrawn to determine the COD, SS, colour and oil and grease, so that the effect of coagulant dosage could be studied.

Analytical Analysis

Analyses were undertaken in triplicate. The pH was measured by a pH meter (Cyberscan 20), while oil and grease were measured according to standard method 1164, EPA. Suspended solids, colour and COD were measured by a DR 5000 HACH spectrophotometer, adapted from the Standard Method for Water and Wastewater. All water colour measures described in this work are 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 [16]. The samples were filtered using 0.45µm filter paper before colours were measured.

RESULTS AND DISCUSSION

Effect of pH on Coagulation

The pH affects not only the surface charge of coagulants, but also the stabilization of the suspension; it is the most important variable in the coagulation process for water treatment [17, 18]. A suitable pH will help to neutralize the negative charge of colloidal particles and to form linkages between colloid particles, thus effectively helping with floc formation and reaching the expected settlement [19].

Therefore, the study of pH was essential to determine the optimum pH condition for the treatment system. The effect of pH was analysed at 100 mg/L dosages, with a 150 rpm mixing rate for 4 minutes and 20 rpm mixing rate for 20 minutes, plus 30 minutes of settling time for a pH range from 2 to 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.

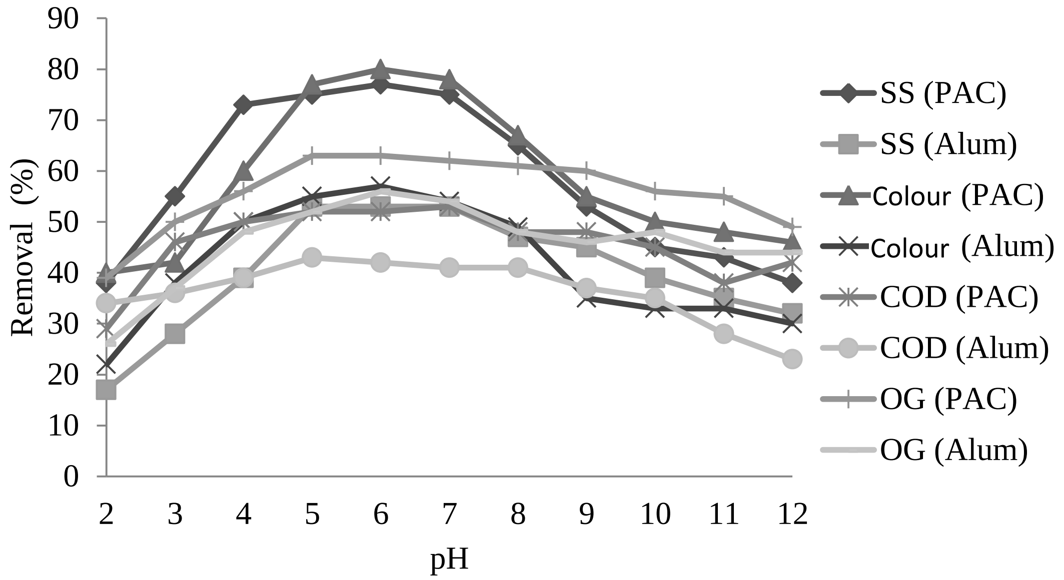

Figure 1. Percentage of SS, colour, COD and oil and grease removal against pH using 100 mg/L PAC and alum.

Figure 1 presents the results of the effect of pH on SS, colour, COD and oil and grease removal by using alum and PAC as coagulant. The figure shows that the optimum pH for both coagulants is in the range 5 to 8. PAC gives a greater range of pH and better removal percentage compared to alum due its solubility and elements of higher ions in the PAC [13, 20]. At lower pH, most of the organic substance has no charge or is neutral at its surface, while hydrolysis salts such as PAC and alum have a lot of positive charge in their hydrolysis chains [19]. According to Figure 1, pH 6 shows the highest percentage removal of SS, colour, COD and oil and grease for both alum and PAC. The percentages of removal of SS, colour, COD and oil and grease for alum are 53%, 57%, 42% and 56%, while for PAC the highest removal percentages of SS, colour, COD and oil and grease are 77%, 80%, 62% and 63% respectively. The study shows that pH control affected the concentration of polyaluminium chloride and alum used [21]. The efficiency of grease and oil removal using both coagulants at pH values of 6–7 was greater than 90%. A decrease in the removal efficiency of polyaluminium chloride occurred when the pH tended towards acidic or basic values and this is in accordance with the amphoteric character of aluminium hydroxide, which precipitates at pH 6–7, while its solubility increases as the solution becomes either more acidic or alkaline [13, 19, 22]. The pH of biodiesel wastewater is found to have a tremendous effect on SS, colour, COD and oil and grease removal through the coagulation process.

Effect of Coagulant Dose on Coagulation

Dosage was the most important parameter that was considered to determine the optimum condition for the performance of coagulation and flocculation. Each type of coagulant has its own characteristic optimum dosage range. Basically, insufficient dosage or overdosing will result in poor performance in flocculation [17, 18]. Therefore, it was crucial to determine the optimum dosage in order to minimize the dosing cost and obtain the optimum performance in treatment. The effect of dosage was analysed at a 150 rpm mixing rate for 4 minutes and 20 rpm mixing rate for 20 minutes, followed by 30 minutes of settling time for a dosage range which varied from 50 mg/L to 600 mg/L.

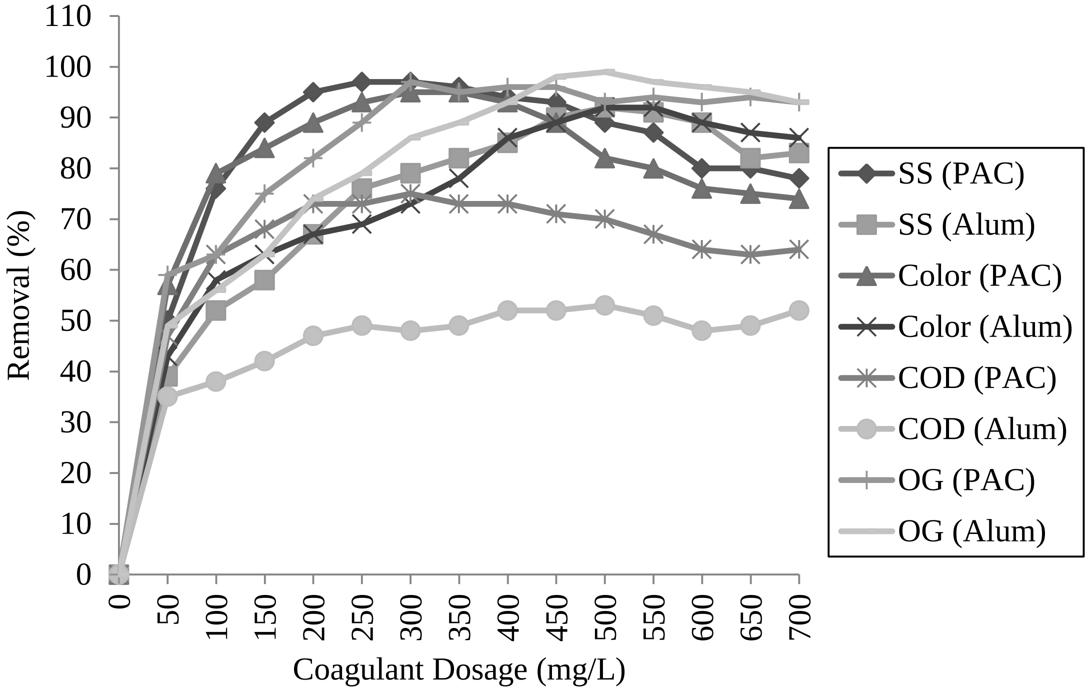

Figure 2. Percentage SS, colour, COD and oil and grease removal against PAC and alum dosage at pH 6.

The effect of dosage coagulants on SS, colour, COD and oil and grease are shown in Figure 2. It is clearly shown that PAC removed SS, colour, COD and oil and grease the best at 97%, 95%, 81% and 97% with 300 mg/L, while alum removal of SS, colour, COD and oil and grease was the highest at 92%, 92%, 53% and 99% with 500 mg/L. COD removal efficiency decreased with increasing coagulant concentration. At high coagulant doses, metal hydroxides are produced and organic substances are removed by incorporation into sorption onto hydroxide flocs [12, 13]. When the concentrations were higher than necessary, the efficiency of COD removal decreased because the flocs formed by coagulation were smaller and less compact, which was not favourable for sludge [18]. The findings show the comparison of oil and grease removal between alum and PAC. For alum, the maximum removal of oil and grease increase stated decreased at a dosage of 550 mg/L. The PAC's maximum reduction of oil and grease (97%) which started at a dosage of 100 mg/L, began to decrease at a dosage of 450 mg/L. Rattanapan, Sawain [21] investigation of three coagulants, namely, alum, PAC and ferric chloride, for removing oil and grease in biodiesel wastewater found them to be equally effective. Hence, alum was found to provide the best removal compared to other coagulants. From the figures, all the residual parameters decreased while their removal efficiencies improved substantially as the dosage of aluminium sulphate or polyaluminium chloride increased until reaching the optimum dosage. When the dosage exceeded 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. A coagulant is a compound that helps coagulation, which helps destabilize the colloidal particles, so helping the formation of floc and consequently accelerating the settling process [13, 19, 22].

CONCLUSIONS

The results showed that polyaluminium chloride (PAC) was more effective in biodiesel wastewater treatment compared to alum. However, alum achieved a higher percentage removal of oil and grease. The percentage of removal of suspended solids, colour, COD and oil and grease increased until the optimum value of pH or dosage was achieved, after which the percentage slowly decreased. The result showed that the optimum pH for both coagulants is 6 and the optimum coagulant doses of aluminium sulphate and polyaluminium chloride were 500 mg/L, and 300 mg/L respectively. At optimum pH, the percentages of SS, colour, COD and oil and grease removal by alum are 53% , 57%, 42%, and 56%, while by PAC they are 77% , 80%, 62%, and 63% respectively. At optimum coagulant dose, the percentages of SS, colour, COD and oil and grease removal by alum are 92%, 92%, 53%, and 99%, and by PAC are 97%, 95%, 81%, and 97% respectively. The coagulation process and all the removal parameters were considerably affected by pH, coagulant dosage, and the initial characteristics of the biodiesel wastewater for both alum and PAC. Investigating the influence of the rapid mixing parameters, the time and intensity of mixing, as well as slow mixing parameters on turbidity removal by alum and PAC is also suggested for future studies.

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