



## TREATMENT OF BIODIESEL WASTEWATER BY COAGULATION-FLOCCULATION PROCESS USING POLYALUMINIUM CHLORIDE (PAC) AND POLYELECTROLYTE ANIONIC

Zawawi Daud<sup>1</sup>, Nazlizan Nasir<sup>1</sup>, Ab. Aziz Abdul Latiff<sup>1</sup>, Mohd Baharudin Ridzuan<sup>1</sup> and Halizah Awang<sup>2</sup>

<sup>1</sup>Team of Research in Integrated Solid Waste Management, Faculty of Civil and Environment Engineering, Universiti Tun Hussein Onn Malaysia, Parit Raja, Batu Pahat, Johor, Malaysia

<sup>2</sup>Faculty of Technical and Vocational Education, Universiti Tun Hussein Onn Malaysia, Parit Raja, Batu Pahat, Johor, Malaysia  
E-Mail: [zawawi@uthm.edu.my](mailto:zawawi@uthm.edu.my)

### ABSTRACT

In this study, coagulation and flocculation process was used to treat a biodiesel wastewater with polyaluminium chloride as a coagulant. The improvement of the process by using anionic as coagulant aids was also investigated. Optimum condition for the coagulation/flocculation process, such as pH, coagulant dosage and polyelectrolyte dosage of the solution were investigated using a jar test experiment. The result showed that in the optimal pH is 6. The percentage removal of 97%, 95%, 75% and 97% for SS, colour, COD and O&G respectively, were achieved at an optimum dosage value; 300 mg/L. While, 89.9%, 91%, 69.4, 81.5% removal of SS, colour, COD, O&G respectively, were achieved with the addition 10 mg/L anionic to 150 mg/L polyaluminium chloride. It can be concluded from this study that coagulation/flocculation may be a useful as a pre-treatment process for biodiesel wastewater.

**Keywords:** coagulation-flocculation, biodiesel wastewater, polyaluminium chloride.

### INTRODUCTION

Biodiesel process uses large amounts of water for product rising, to remove undesirable substances like soap and other residual initial substances [1]. For 100 L of biodiesel produced, about 20 L of raw wastewater is discharged [2]. Wastewater from biodiesel production contained the white muddy particle like milk cause by the oil emulsified in water. Biodiesel wastewater basic (alkaline), with a high content of oil and grease, and a low content of nitrogen and phosphorus. Thus, biodiesel wastewater is unfavourable for microbial growth. Biological treatment of biodiesel wastewater is expected to very difficult [3]. For this reason supportive physico-chemical methods are often used. Although one of the most frequently employed method is coagulation.

The coagulation is widely used in wastewater treatment and the operating cost is low [4]. The coagulation was the process whereby destabilization of a given suspension or solution is affected. That is, the function of the coagulation is to overcome the factors that stimulate the stability of a given system. Flocculation was the process whereby destabilized particles formed as an effect of destabilization, are induced to come together, make contact, and thereby form larger agglomerates [5].

Aluminum sulphate (alum), ferric chloride and ferric sulphate were usually used as coagulants. However, in recent years, much attention has been paid to hydrolysing metal salt coagulants namely polyaluminum chloride (PAC) due to its higher coagulant competence and relative low cost compared to the conventional coagulants [6,7].

Besides, PAC poses a good structure and higher charge density, which leads to decrease in dosage requirements and hence lesser sludge production. The application of PAC as a coagulant for the removal of colour, COD and ammonia from water and wastewater [8]

According Zouboulis & Tzoupanos [9] polyaluminium chloride has become one of the most effective coagulant agents in water and wastewater treatment facilities with numerous applications, including the removal of colloids and suspended particles, organic matter, metal ions, phosphates, toxic metals and colour.

The objective of this study was the efficiency of the coagulation/flocculation process for the removal of suspended solids (SS), colour, COD and oil and grease (O&G) from biodiesel wastewater using polyaluminium chloride. This study also investigates optimum pH, optimum coagulant dosage on and polyelectrolytes dosage optimum on the coagulant process. The optimization of these features may significantly increase the process competence.

### EXPERIMENTAL

#### Wastewater

Biodiesel wastewater collected from UTHM Biodiesel Pilot Plant was used as feed in this study. Biodiesel Pilot Plant which is located in University Tun Hussein Onn Malaysia. Alkali-catalysed transesterification process and palm oil as a feedstock was used in this plant. For avoid further biodegradation, the sample, then kept in a cold room at temperature of 4°C. The characteristic of this biodiesel wastewater was analyzed according to the standard methods for examination of water and wastewaters [10] are shown in Table-1.

**Table-1.** Biodiesel wastewater characteristics.

Characteristic	Unit	Value
COD	mg/L	5900
SS	mg/L	348
Colour	Pt-Co	95
Oil and Grease	mg/L	2680
pH	-	4.5 -5.5

### Experimental procedure

Standard jar-test apparatus is used to performed coagulation and flocculation studied, Jar Tester Model CZ150 comprises of six paddle motors (24.5mm x 63.5mm), equipped with 6 beakers of 1 litre volume. Twelve beakers positioned on magnetic stirrer and definite dosage of coagulant. The pH value of 500 millilitre biodiesel wastewater sample was adjusted to pH in the range 2-12 respectively, by using 1.0 M H<sub>2</sub>SO<sub>4</sub> or 1.0 M NaOH, after the addition 100 mg/L polyaluminium chloride to biodiesel wastewater 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 2cm below the top of the liquid level of the beaker to determine COD, SS, colour, and oil and grease (O&G) by using 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 polyaluminium chloride was added to 1 litre biodiesel wastewater sample. After stirring and clarifying as described in above, the supernatant was withdrawn to define the COD, SS, colour and oil and grease, so that the effect of coagulant dosage could be studied. 150 mg/L (half optimum dosage value) polyaluminium chloride was added to biodiesel wastewater. After rapid mixing for 4 min at 150 rpm different concentrations (2, 4, 6, 8 and 10 mg/L) of polyelectrolyte were added and the liquid was mixed slowly for 20 min at 20 rpm, the supernatant was withdrawn as prior described to determine the optimum polyelectrolyte that enhance coagulation.

### Sampling and analysis

Analyses undertaken in triplicates. pH meter (Cyberscan 20) used to measure pH, while oil and grease measured according standard method 1164, EPA. Suspended solid, colour and COD measured by DR 5000 HACH spectrophotometer that is adapted from Standard Method for Water and wastewater. The platinum-cobalt (Pt-Co) method has been used to measure water colour described in this work report as true colour values, the unit of colour being that produced by 1 mg platinum/L in the form of the chloroplatinate ion [10]. The samples were filtered using 0.45µm filter paper before colours were measured.

## RESULT AND DISCUSSION

### Effect of pH on coagulation

In the coagulation–flocculation process, pH is significant since the coagulation occurs within a specific pH range for each coagulant. In this study, a varied range of pH between 2-12 was selected.

The effect of pH was analysed at 100 mg/L polyaluminium chloride, with 150 rpm of mixing rate for 4 minutes and 20 rpm of mixing rate for 20 minutes and settling time in 30 minutes for a range of pH which varied from pH 2 to pH 12. The extent of pH range is affected by the types of the coagulant used and by the chemical composition of water as well by the concentration of coagulant.

Figure-1 showed the optimum pH value of 6 enhanced substantial removals of the contaminants. It can be noted from these figures that, relatively higher removals of SS, colour, COD and oil and grease (O&G) were observed at range pH 5 to pH 7. Referring to Figure-1, at pH 6 shows the highest percentage removal of SS, colour, COD and oil and grease are 77%, 80%, 52% and 63% respectively.

Rattanapan *et al.*, [3] investigated pH control affected the concentration using polyaluminium chloride, ferric chloride and alum sulphate. Coagulation pH as a factor that influences coagulation is important because the addition of metallic cation (in this case Fe<sup>3+</sup>) automatically lower pH, which may cause further reduction in the removal of the contaminants [11]. The need to employed higher dose of coagulant may pose a health hazard as a result of residual quantities of excess chemical additives.

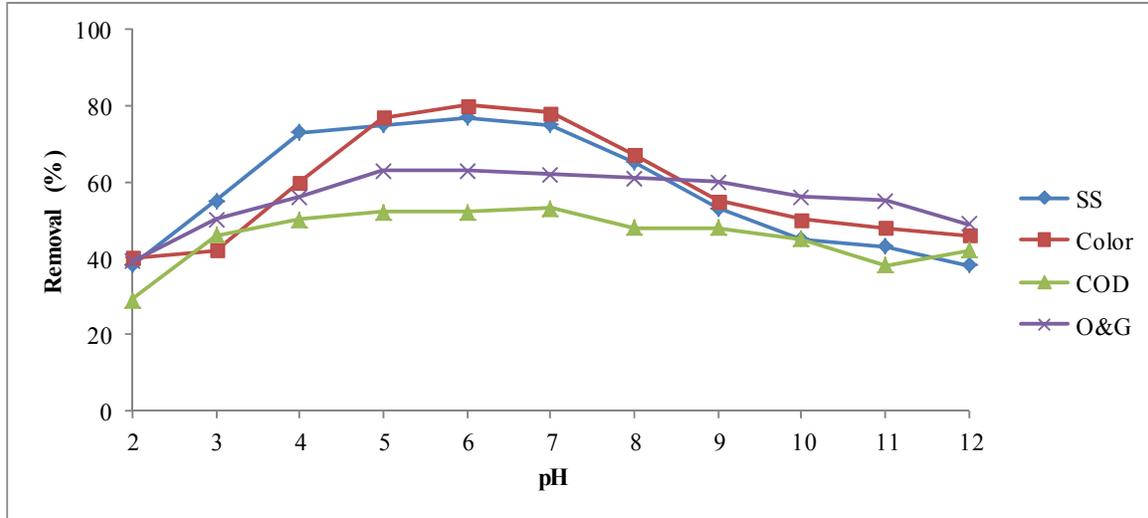
### Effect of coagulant dosage on coagulation

The dosage was of the most important parameters that been considered to determine the optimum condition for the performance of polyaluminium chloride in coagulation and flocculation. Basically, insufficient dosage or overdosing would result in poorer performance in flocculation [12]. The effect of dosage was analysed at pH 6, 150 rpm of mixing rate for 4 minutes and 20 rpm of mixing rate for 20 minutes, settling time in 30 minutes and the test was conducted at optimum pH of 6 for a range dosage polyaluminium chloride which varied from 50 mg/L to 600 mg/L

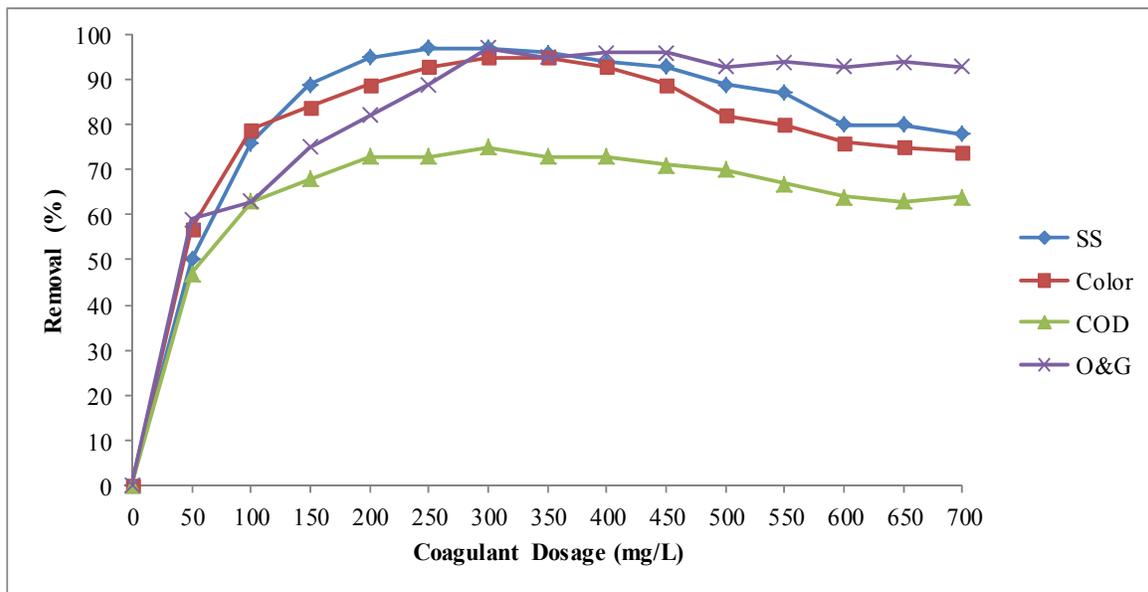
The results of the effects of different dosage of polyaluminium chloride as coagulant on the removal of SS, colour, COD and oil and grease (OG) from the biodiesel wastewater areas present in Figure-2. From the Figure-2 clearly show that polyaluminium chloride removes SS, colour, COD and O&G grease the best 97%, 95%, 75% and 97% respectively. When the dosage of polyaluminium chloride was increased beyond 350 mg/L, the removal efficiency decreased. It is clear from the results that SS, colour, COD and O&G removals increased substantially as the dosage of polyaluminium chloride increases. When the dosage was beyond the optimum dosage, there was a decrease in the removal efficiency for all the parameters. Each coagulant has its own optimal



dose range. Coagulation will help destabilize the colloidal particles, helps the formation floc and consequently accelerate the settling process [13].



**Figure-1.** Percentage of removal in SS, Colour, COD and Oil and Grease for pH by using 100 mg/L Polyaluminium chloride.



**Figure-2.** Percentage of removal in SS, Colour, COD and Grease for dose polyaluminium chloride at pH 6.

#### Effect of polyelectrolyte dosage on coagulation

Polyelectrolyte may act as coagulant aids or primary coagulant in the treatment of water and wastewater [11]. The addition polyelectrolyte to neutralize the positive charges in water, causes the formation of flocks more quickly and increase the rate of sedimentation by bridging and connecting the already-formed flocks so that with the network formed during sedimentation, they take other small particles which couldn't form flocks

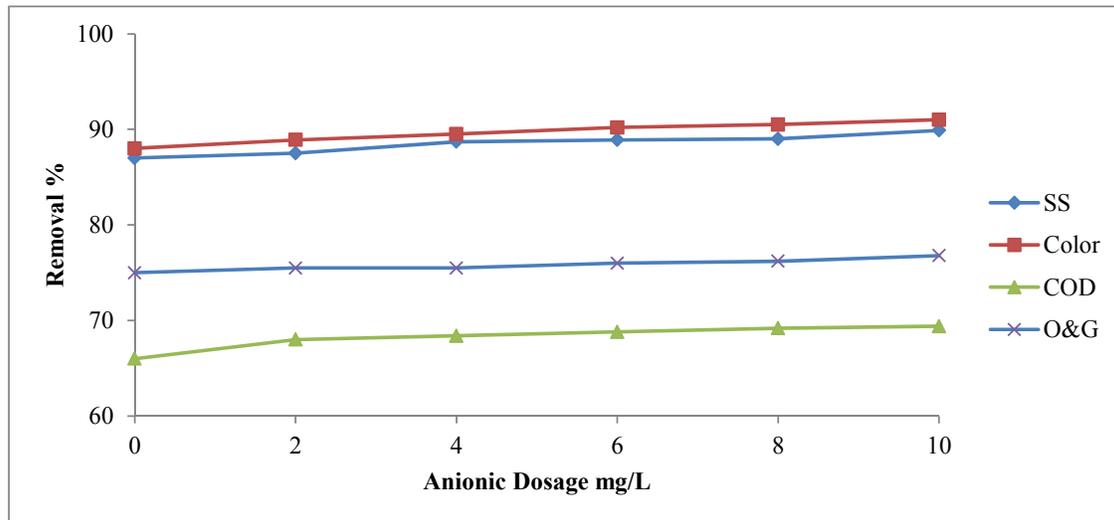
inside them and make them sediment among with themselves [13]. Many polyelectrolytes are advantages over chemical coagulants because they are safer to handle and easily biodegraded [11].

The percentage removal of SS, colour, COD and O&G as functions of different doses of polyelectrolytes is as shown in Figure-3. The dose of polyelectrolyte varied from 0 to 10 mg/L and the polyaluminium chloride dose was made constant at 150 mg/L. The removal of SS,



colour, COD and O&G increased with increasing dose of polyelectrolyte. From Figure-3, it can be seen that the removal of SS reached 87% during the use of 150 mg/L polyaluminium chloride and 2 mg/L polyelectrolyte. The SS percentage removal increased to 82% when the dose of the polyelectrolyte was increased to 4 mg/L. The percentage removal of colour reached maximum 91% and

with the use of 150 mg/L polyaluminium chloride and 10 mg/L dose of the polyelectrolyte. For the removal of COD and oil and grease, maximum removal of 69.4% and 81.5% was achieved with the use of 150 mg/L polyaluminium chloride and 10 mg/L.



**Figure-3.** Percentage of removal SS, Colour, COD and Oil and Grease for anionic dosage pH 6 using 150 mg/L polyaluminium chloride.

## CONCLUSIONS

This study has shown that coagulation and flocculation is a useful method as a pre-treatment of biodiesel wastewater. Coagulation and Flocculation is very effective in the suspended solids, colour, and Oil and Grease removal and moderately effective in the COD removal of the biodiesel wastewater. In order to achieve better percentage removal for COD, suspended solids, colour and oil and grease, further treatment is needed.

## ACKNOWLEDGEMENTS

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## REFERENCES

- [1] Sawain, W. Taweepreda, U. Puetpaiboon and C. Suksaroj. 2009. The effect of pH on the stability of grease and oil in wastewater from biodiesel production process. *Renewable Energy*. 0-4.
- [2] J. A. Siles, M. C. Gutiérrez, M. A. Martín and A. Martín. 2011. Physical-chemical and biomethanization treatments of wastewater from biodiesel manufacturing. *Bioresource Technology*. 102(10): 6348-635.
- [3] Rattanapan, A. Sawain, T. Suksaroj and C. Suksaroj. 2011. Enhanced efficiency of dissolved air flotation for biodiesel wastewater treatment by acidification and coagulation processes. *Desalination*. 280(1-3) : 370-377.
- [4] X. J. Wang, S. Chen, X. Y. Gu and K. Y. Wang. 2009. Pilot study on the advanced treatment of landfill leachate using a combined coagulation, fenton oxidation and biological aerated filter process. *Waste Management*. 29: 1354-1358.
- [5] L. Semerjian and G. M. Ayoub. 2003. High-pH-magnesium coagulation-flocculation in wastewater treatment. *Advances in Environmental Research*. 7: 389-403.
- [6] N. A. Zainol, H. A., Aziz, M. S. Yusoff and M. Umar. 2011. The use of polyaluminium chloride for the treatment of landfill leachate via coagulation and flocculation processes. *Journal of Chemical Sciences*. 1(3) : 35-39.
- [7] Z. Daud, H. A. Aziz, M. N. Adlan and Y. T. Hung. 2009. Application of combined filtration and coagulation for semi-aerobic leachate treatment. *International Journal of Environment and Waste Management*. 4(3-4): 457-469.



- [8] H. Aziz, Z. Daud, M. N. Adlan and Y. T. Hung. 2009. The use of polyaluminum chloride for removing colour, COD and ammonia from semi-aerobic leachate. *International Journal of Environmental Engineering*. 1 (1): 20-35.
- [9] A. I. Zouboulis and N. Tzoupanos. 2010. Alternative cost-effective preparation method of polyaluminium chloride (PAC) coagulant agent: Characterization and comparative application for water/wastewater treatment. *Desalination*. 250(1): 339–344.
- [10] APHA, AWWA and WEF. (2012). *Standard Methods for the Examination of Water & Wastewater*. 22nd Ed. Washington DC: American Public Health Association
- [11] O. S. Amuda and A. Alade. (2006). Coagulation - flocculation process in the treatment of abattoir wastewater. *Desalination*. 196(1-3): 22–31.
- [12] M. A. Hassan, P. L. Tan and N. Z. Zainon. 2009. Coagulation and flocculation treatment of wastewater in textile industry using chitosan. *Journal of Chemical and Natural Resources Engineering*. 4(1): 43–53.
- [13] A. Koohestanian, M. Hosseini and Z. Abbasian. 2008. The separation method for removing of colloidal particles from raw water. *Euras. J. Agric. & Environ. Sci*. 4(2): 266–273.