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Comparison of Alum and Poly Aluminium Chloride at Various Doses in Coagulation Process on Color Removal of Palm Oil Mill Effluent

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Abstract

The goal of this study was to investigate the effect of the type and dose of coagulants on the color removal of POME through the coagulation process. The coagulants used in this study were alum and poly aluminium chloride (PAC). The dose of coagulants was varied to 2, 4, 6, and 8 g/L. The results of this study showed that the optimum dose for coagulant of alum was 6 g/L and the optimum dose for coagulant of PAC was 8 g/L, in which these doses resulted in color removal efficiencies of 80.65±10.30% and 94.12±1.00%, respectively. The PAC coagulant was more effective than the alum coagulant. The kinetic models used to predict the color removal efficiencies were the first- and second-order kinetic models. Based on the kinetic analysis, the MAPE of the first and second-order kinetic models was 9.17-28.28% and 5.48-21.62%, respectively. It means that the second-order kinetic model can predict with higher accuracy than the first-order kinetic model. By the second order kinetic model, the reaction kinetic constant of the coagulation process at alum coagulant of 6/L and PAC coagulant of 0.021 and 0.057 /min, respectively.

INTRODUCTION

Palm oil mill effluent (POME) is a liquid wastewater resulting from the palm oil industries di Indonesia (Damayanti et al., 2019; Najafpour et al., 2006). The main product of the palm oil industries is crude palm oil (CPO) (Azis et al., 2018). Based on the statistical data released by Statista (2021), the CPO production increases from 26.02 million tons in the year of 2012 to 48.3 million tons in the year of 2020. In year of 2050, the Indonesian CPO production is predicted to reach 189.66 million tons (Gabungan Pengusaha Kelapa Sawit Indonesia (GAPKI), 2017). Because of the increase in the CPO production, the amount of POME will increase significantly in the future until the year of 2050. To produce 1 ton of CPO, the palm oil industries result in 2.5-3 m^3 of POME (Hasanudin & Haryanto, 2018). The POME has a color of dark brown (Rakhmania et al., 2022) and contains a high chemical oxygen demand (COD) content of 42,500-86,300 mg/L and a high biological oxygen demand (BOD) content of 21,500-55,200 mg/L (Najafpour et al., 2006; Singh et al., 2013; Wang et al., 2015) so it can pollute the water bodies if it is discharged directly.

One of the wastewater treatments that can be applied to treat organic waste liquid is coagulation (Tetteh & Rathilal, 2019). Some previous studies reported that the coagulation has the potential to be used in treating POME. The study of Huzir et al. (2019) reported that the chemical oxygen demand (COD) and total solid (TS) in POME can be removed using the coagulation process with a coagulant of rice husk ash and alum. Furthermore, the study of Bhatia et al. (2007) reported that the total suspended solid (TSS) was successfully removed using the

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coagulation process with a coagulant of *Moringa oleifera* extract seed. The study of Ismail et al. (2014) also studied the potency of the coagulation in decreasing the TSS concentration in POME with coagulant of alum. The study of Tan et al. (2006) examined the effect of coagulants of aluminium sulfate, ferric chloride, ferric sulfate, and ammonium sulfate on the changes in COD and turbidity of POME. The study of Ahmad et al. (2005) reported that the coagulation can decrease the turbidity of POME with coagulant of modified industrial grade alum. The study of Chung et al. (2018) found that the coagulation process can decrease the turbidity, COD, TSS of POME with coagulants of peanut and wheat germ.

Based on the information above, the coagulation successfully decreased the COD, TSS, TS, and turbidity of POME. However, the previous studies have not studied the effect of the coagulant on the color of POME. The common coagulants usually used are alum and poly aluminium chloride (PAC). Therefore, the purpose of this study was to examine the effect of types and doses of coagulants on the color removal of the local POME. Furthermore, kinetic analysis was also conducted in this study. The kinetic analysis in color removal of POME has not been conducted by the previous studies yet.

MATERIALS AND METHODS

Materials

The local POME was collected from PTPN VIII (Lebak, Banten Province, Indonesia). The local POME contained a total solid of 21,000 mg/L, a total suspended solid of 18,000 mg/L, and a pH level of 4.3. The technical NaOH was obtained from a local store.

Coagulation Process

The lab-scale coagulation reactor was a glass beaker with a volume 1 L. The local POME was put into the glass beaker. The coagulants (alum and PAC) were added at doses of 2, 4, 6, and 8 g/L. Furthermore, the technical NaOH was added to adjust the liquid pH to 7.0±0.1. The coagulation process was carried out with an agitation speed of 200 rpm for 120 min. Per 20 min, the liquid pH was measured using a digital pH meter and 25-mL liquid samples were taken and put into 50-mL measuring glasses. The liquid samples in the measuring glasses were settled for 24 h. After settling, the resulting supernatants were taken using a pipette and then analyzed for the color using a spectrophotometer.

Analysis

The liquid pH was measured using a digital pH meter with a model of PH-009(I)A, a pen-type pH meter. The color of the supernatants was measured using the spectrophotometer with a model of Genesys 10uv. The wavelength used for measuring the color supernatants was the optimum wavelength resulting in the highest absorbance value of the local POME sample. The absorbance values at various wavelengths using the local POME sample are shown in the Figure 1.

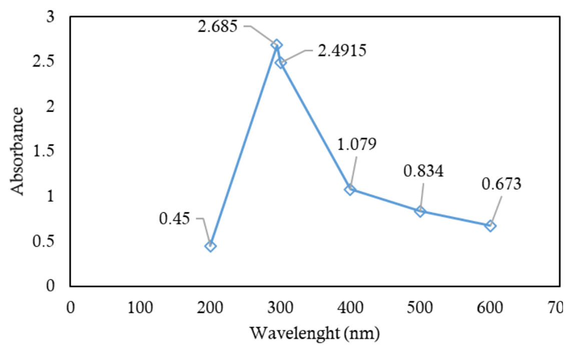


Figure 1. Absorbance value at various wavelengths using local POME liquid (dilution 10×).

Based on the Figure 1, the optimum wavelength was 295 nm which resulted in the highest absorbance value of 2.685. Therefore, the color of the supernatant samples was measured using the optimum wavelength. The efficiency of color removal was determined through Eq. (1).

$$C_r(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Where: C_r, color removal; C_0, color of the local POME; C_t, color of the supernatant at time of t.

Kinetics

The changes in liquid color can be modeled using the simple reaction rate equation shown in Eq. (2).

$$\frac{dC}{dt} = -kC^n \quad (2)$$

Where: C, color of the liquid; k, kinetic constant of coagulation reaction (/min); n, order of reaction; t, time of the process (min)

The reaction order can be 1 or 2. Therefore, kinetic models with reaction orders of 1 and 2 are shown in Eqs. (3) and (4).

$$\frac{dC}{dt} = -k_1 C \quad (3)$$

$$\frac{dC}{dt} = -k_2 C^2 \quad (4)$$

Eqs. (3) and (4) were integrated and arranged to find Eqs. (5) and (6).

$$C_t = \frac{C_0}{\exp(k_1 t)} \quad (5)$$

$$C_t = \frac{1}{k_2 t + \frac{1}{C_0}} \quad (6)$$

The modeled color removal was calculated using Eq. (1) in which the C_t used was the modeled C_t obtained through Eqs. (5) and (6). The kinetic constants of k_1 and k_2 was determined using the optimization using Ms.Excel with the objective function of Mean Average Percentage Error (MAPE) shown in Eq. (7).

$$MAPE = \frac{1}{n}\sum_{i=1}^{n} \frac{C_{r_i}(model) - C_{r_i}(experiment)}{C_{r_i}(experiment)} \times 100\% \quad (7)$$

RESULTS AND DISCUSSION

Experimental Analysis

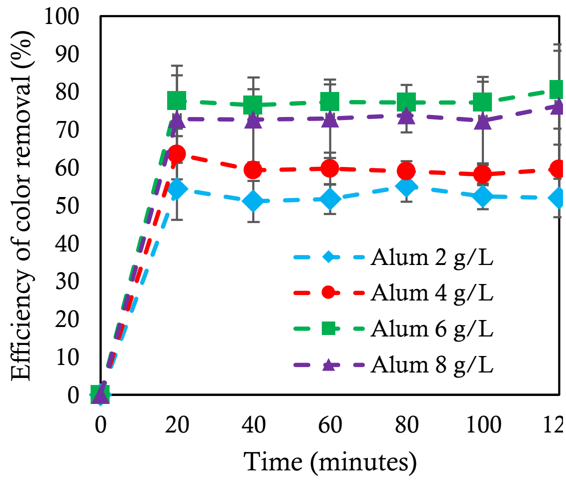
Coagulant of Alum

The color removal efficiency at various alum doses is shown in Figure 2(a). Based on the Figure 2(a), after process time of 120 min, the optimum alum dose was 6 g/L resulting in the color removal of 80.65±10.30%. An increase in alum dose from 2 g/L to 6 g/L successfully increased the color removal from 52.07±5.06% to 80.65±10.30%. However, a further increase in alum dose to 8 g/L increased the color removal to 76.37±16.14%.

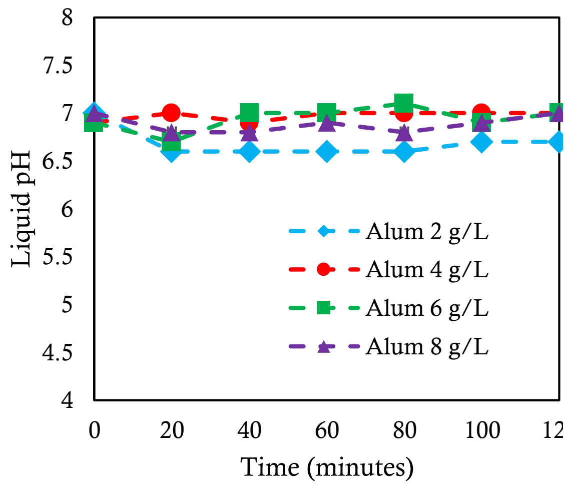
When alum is added to the waste liquid, the coagulants of $Al(OH)_3$ are formed. The coagulants have the characteristic of gelatinous so they can adsorb the organic compounds to form flocs. The flocs will react with each other to form sludge. The coagulation reaction with the coagulant of alum can be written in Eqs. (8) and (9).

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2SO_4 \quad (8)$$

$$Al(OH)_3 + impurities \rightarrow flocs \rightarrow sludge \quad (9)$$



(a)



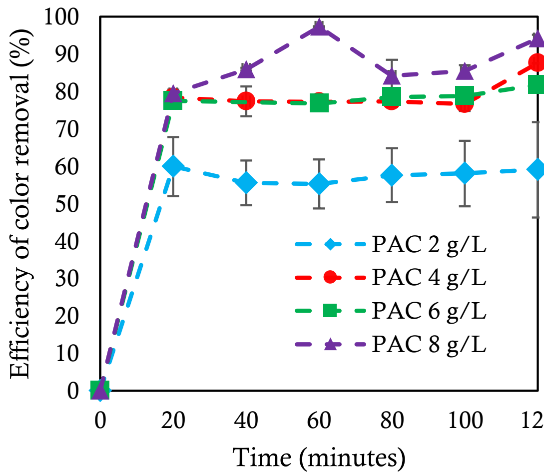
(b)

Figure 2. Effect of alum doses on the profiles of (A) color removal efficiency, (B) liquid pH.

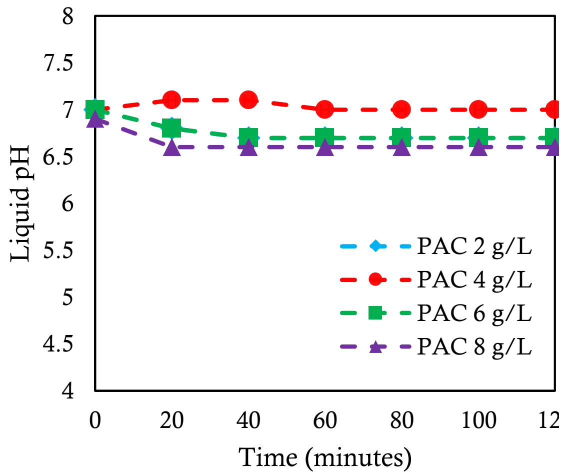
Based on the Eqs. (8) and (9), the more the alum dose, the more the impurities can be removed, so the more the color can be removed. These phenomena were shown by the increase in alum dose from 2 to 6 g/L. However, an alum dose of 8 g/L resulted in less color removal than an alum dose of 6 g/L. It might be caused by that too many flocs were formed in the liquid and the flocs were still dispersed in the liquid. A previous study also reported that too much coagulant (watermelon seed) dose was not effective to remove total dissolved solid, turbidity and color of the river water (Ernest et al., 2017). Furthermore, the profiles of liquid pH during the coagulation process are shown in Figure 2(b). The pH profiles tended to be constants.

Coagulant of PAC

The color removal efficiency at various PAC doses is shown in Figure 3(a). Based on the Figure 3(a), after a process time of 120 min, the optimum alum dose was 8 g/L resulting in the color removal of 94.12±1.00%. An increase in PAC dose from 2 g/L to 8 g/L successfully increased the color removal from 59.09±12.72% to 94.12±1.00%.



(a)



(b)

Figure 3. Effect of PAC doses on the profiles of (a) color removal efficiency, (b) liquid pH

When PAC is added to the waste liquid, the coagulants of $Al(OH)_3$ are also formed. The coagulation reaction with the coagulant of alum can be written in Eqs. (10) and (11).

$$Al_2Cl(OH)_5 + H_2O \rightarrow 2Al(OH)_3 + HCl \quad (10)$$

$$Al(OH)_3 + impurities \rightarrow flocs \rightarrow sludge \quad (11)$$

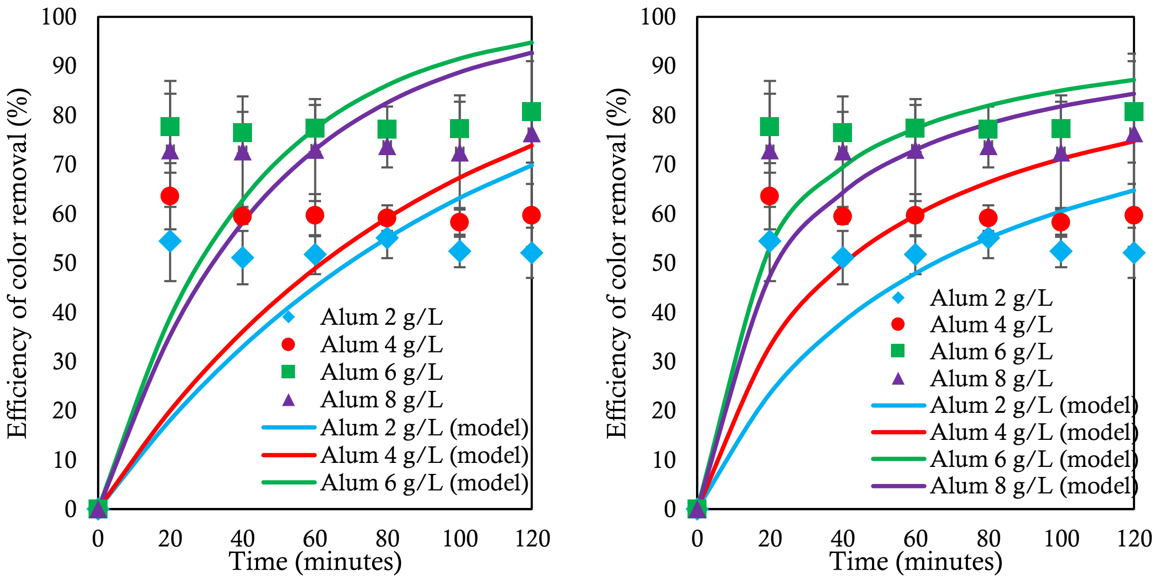
Based on the Eqs. (10) and (11), the more the alum dose, the more the impurities can be removed, so the more the color can be removed. These phenomena were shown by the increase in alum dose from 2 to 8 g/L. Furthermore, the profiles of liquid pH during the coagulation process are shown in Figure 3(b). The pH profiles tended to be constants.

Comparison between Alum and PAC on the Color Removal Efficiency

The color of treated POME after the coagulation process for 120 min at alum doses of 2, 4, 6, and 8 g/L was 52.07±5.06%, 59.66±6.43%, 80.65±10.30%, and 76.37±16.14%, respectively. Meanwhile, the color of treated POME after the coagulation process at PAC doses of 2, 4, 6, and 8 g/L was 59.09±12.72%, 87.60±0.11%, 81.79±0.47%, and 94.12±1.00%, respectively. Based on these data, the PAC was more effective than the alum in reducing the color of the local POME. The molecular weight of alum ($Al_2(SO_4)_3$) and PAC ($Al_2Cl(OH)_5$) was 342.15 g/mol and 174.45 g/mol. Based on Eqs. (8) and (10), 1 mol of $Al_2(SO_4)_3$ or $Al_2Cl(OH)_5$ is equal to 2 moles of $Al(OH)_3$. Because the molecular weight of $Al_2(SO_4)_3$ was bigger than $Al_2Cl(OH)_5$, the amount of moles of $Al(OH)_3$ at addition of $Al_2(SO_4)_3$ was less than at addition of $Al_2Cl(OH)_5$ with the same dose level. For example, the addition of 6 g/L of alum and PAC resulted in the moles of $Al(OH)_3$ of 0.0175 mol/L and 0.0344 mol/L. It means that, at the same doses, the addition PAC resulted in more moles of $Al(OH)_3$ than the addition of alum. Therefore, the addition of the PAC was more effective than the alum. A previous study also found the same results as this study. Study of Zouboulis et al. (2008) reported that the PAC resulted in better performance than the alum in treating the drinking water.

Kinetic Analysis

In this study, the first order kinetic model and the second order kinetic model were used to simulate the color removal of the local POME through the coagulation process with coagulant types of alum and PAC at various doses of 2, 4, 6, and 8 g/L. The two kinetic models were successfully used to predict the color removal efficiency profiles as a function of process time in coagulation with alum and PAC. The plotting between the experimental color removal and modeled color removal in coagulation with alum and PAC is shown in Figures 4 and 5. Furthermore,



(a) (b)

Figure 4. Simulation of color removal efficiency as function of time during coagulation with coagulant of alum using (a) first order kinetic model, (b) second order kinetic model

Table 1. Kinetic constant values resulted from simulation in coagulation with alum

Parameters	Alum doses (g/L)			
	2	4	6	8
First order kinetic model				
k_1 (/min)	0.010	0.011	0.025	0.022
MAPE (%)	28.28	27.54	19.24	21.19
Second order kinetic model				
k_2 (/min)	0.006	0.009	0.021	0.017
MAPE (%)	21.62	20.70	10.85	12.68

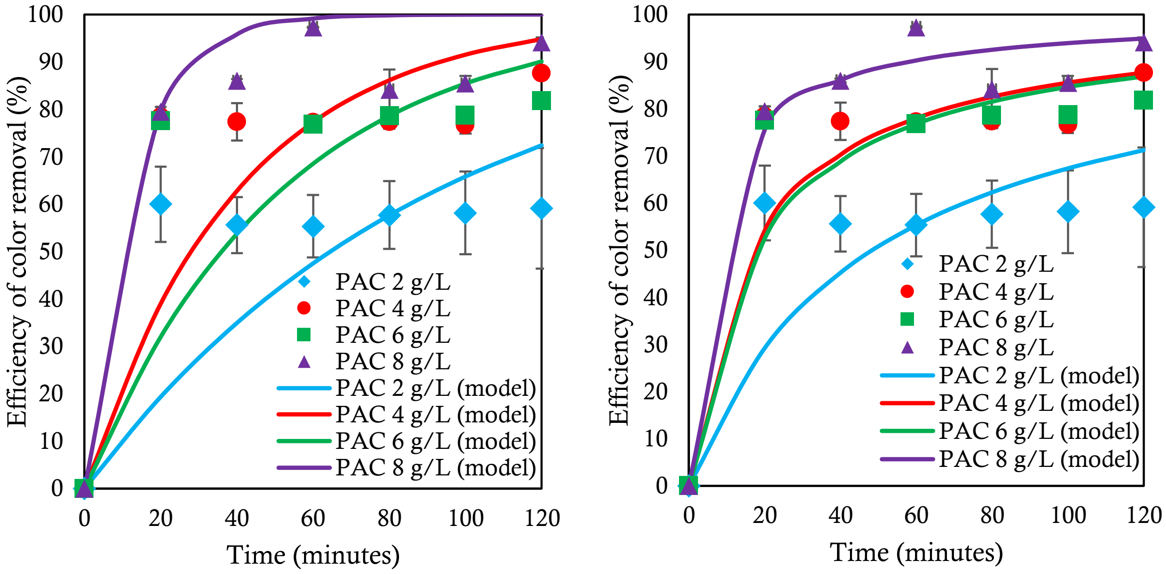
the kinetic constant values are shown in Tables 1 and 2.

Based on Table 1, by using the first-order kinetic model, the alum dose of 6 g/L resulted in a higher k_1 than the other doses, in which it was 0.025 /min. The higher the k_1 value, the faster the color was adsorption by coagulants. It means the fastest coagulation reaction occurred at the alum addition of 6 g/L. By using the second-order kinetic model, the alum dose of 6 g/L also resulted in a higher k_2 than the other doses, in which it was 0.021 /min.

Furthermore, Based on Table 2, by using the first-order kinetic model, the PAC dose of 8 g/L resulted in a higher k_1 than the other doses, in which it was 0.079 /min. It means the fastest coagulation reaction occurred at the PAC addition of 8 g/L. By using the second-order kinetic model, the PAC of 8 g/L also resulted in a higher k_2 than the other doses, in which it was 0.057 /min.

At the alum coagulant, the second-order kinetic model resulted in fewer MAPE values (12.68-21.62%) than the first-order kinetic model (21.19-28.28%). Also, at the PAC coagulant, the second-order kinetic model resulted in fewer MAPE values (5.48-19.06%) than the first-order kinetic model (9.17-25.82%). Overall, the MAPE of the first and second-order kinetic models was 9.17-28.28% and 5.48-21.62%, respectively. It means that the second-order kinetic model can predict with higher accuracy than the first-order kinetic model either at the alum coagulant or the PAC coagulant.

Based on Tables 1 and 2, by using second-order kinetic model, the MAPE value at coagulant dose of 2 g/L was higher than that at other coagulant doses, which was 21.62% and 19.06% for alum and PAC, respectively. It might be caused by the complex organic compounds in POME. However, these MAPE values were below 25%. The model resulting in MAPE value below 25% shows the excellent prediction (Estévez et al., 2020). Therefore, in this study, the second-order kinetic model was still good in predicting the color removal



(a) (b)

Figure 5. Simulation of color removal efficiency as a function of time during coagulation with coagulant of PAC using (A) first-order kinetic model, (B) second-order kinetic model.

Table 2. Kinetic constant values resulted from simulation in coagulation with PAC

Parameters	PAC doses (g/L)			
	2	4	6	8
First-order kinetic model				
k_1 (/min)	0.011	0.025	0.019	0.079
MAPE (%)	25.82	18.04	17.64	9.17
Second-order kinetic model				
k_2 (/min)	0.008	0.022	0.021	0.057
MAPE (%)	19.06	9.89	9.97	5.48

efficiency at various coagulant doses with coagulant type of alum and PAC.

CONCLUSION

By using alum as a coagulant, the optimum dose resulting in the highest color removal efficiency of 80.65±10.30% was 6 g/L. Furthermore, the optimum dose resulting in the highest color removal efficiency of 94.12±1.00% was 8 g/L. Hence, the PAC coagulant was more effective than the alum coagulant because the amount of moles of $Al(OH)_3$ at addition of $Al_2(SO_4)_3$ was less than at addition of $Al_2Cl(OH)_5$ with the same dose level. Based on the kinetic analysis, the MAPE of the first and second-order kinetic models was 9.17-28.28% and 5.48-21.62%, respectively, so the second order kinetic model resulted in better prediction than the first order kinetic model. The k_2 of coagulation process at alum coagulant of 6/L and PAC coagulant of 0.021 and 0.057 /min, respectively.

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