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Effect of dual flocculant by unmodified *manihot esculenta* starch and aluminium sulphate on the removal of chemical oxygen demand optimized by response surface methodology

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Abstract. Applying inorganic metal salt-based aluminium sulphate ($Al_2(SO_4)_3$) or alum in wastewater treatment has gained many concerns regarding the impact on health and environmental implications. Due to the negative consequences, incorporating inorganic and natural flocculants in the coagulation-flocculation process is the alternative way to reduce undesirable effects. In this study, an evaluation performance of *Manihot esculenta* (ME) starch and alum as a dual flocculant was conducted to remove chemical oxygen demand (COD) in the optimum weight ratio of alum/starch = 0.06. The optimization of coagulation-flocculation by the optimal (custom) design, response surface methodology (RSM) presented that applying a dual flocculant improved the COD removal efficiency by up to 93% compared to a single coagulant (alum) of 85%. Besides the performance of COD removal increased, the dosage of the chemical coagulant was reduced by up to 64% at the optimum condition of 18 mg/L alum dosage, 307 mg/L starch dosage, pH 9, and 27 mins settling time. The analysis of variance (ANOVA) indicated that the quadratic model was significantly developed with a p-value < 0.05. The results were justified by a high coefficient of determination (R^2_{alum} = 0.9641) and ($R^2_{\text{dual flocculants}}$ = 0.9335) using single and dual flocculants, respectively. The findings supported ME starch as an alternative approach in minimizing chemical coagulants in wastewater treatment.

1. Introduction

Clean water is a precious resource all over the world. Globally 44% of municipal wastewater is not adequately treated, especially in middle and low-income countries [1]. In Malaysia, there are seven thousand sewage treatment plants, covering approximately 27 million population equivalents, which dominantly discharge the effluent to surface water [2]. By 2030, United Nations expressed in the Sustainable Development Goals (SDG) target to improve water quality by eliminating and minimizing the proportion of untreated wastewater [3]. Consequently, wastewater must be completely managed and treated before it is released into the natural environment or utilized for various purposes.

Various types of physical, chemical, and biological technologies have been designed to remove organic and inorganic contaminants for wastewater treatment. Certain treatment processes require high maintenance costs, high energy consumption, and high-skilled operators, making wastewater treatment a burden work [4]. The coagulation-flocculation process is a chemical technique predominantly applied in wastewater treatment. The coagulation-flocculation method is used in wastewater treatment because of its low maintenance, easy operation, and produce high-quality effluent discharge compared to other chemical treatments. Through these processes, the formation of flocs happens through charge neutralization and destabilization of particles by coagulants. The flocculants are commonly applied to achieve high pollutant removal and high performance of the flocculation process through a bridging mechanism that attached and interconnected the suspension, resulting in larger and denser settleable flocs. Chemical oxygen demand (COD) commonly signifies all organic and inorganic matter forms, including biodegradable and nonbiodegradable in wastewater. Therefore, COD is an important parameter for assessing the effectiveness of the coagulation-flocculation process [5].

Aluminium sulphate ($Al_2(SO_4)_3$) or alum is commonly used in the wastewater industry for the coagulation process to enhance the removal efficiency of COD [6]. In spite of their superior efficacy in treating wastewater, chemical coagulants have detrimental effects on human health and the environment in long-term applications. Aluminium has been found to be a neurotoxic chemical substance that can trigger Alzheimer's disease. Furthermore, the excessive usage of aluminium in wastewater processes generates toxic sludge that might contaminate groundwater quality [7].

Applying natural flocculants from plants has received positive feedback in minimizing the health effect and environmental contamination due to their nontoxic characteristics and biodegradability [8]. Among natural flocculant substituents, starch-based flocculants have been proven to perform well in flocculation tests. In previous years, researchers have dedicated a growing interest in unmodified starch for water and wastewater treatment [9]. Starch has polysaccharides, namely amylose and amylopectin. The linear polymer amylose consists of poly-α-1,4-D-glucopyranoside units, and branch polymer amylopectin consists of poly-α-1,6-glucopyranoside units [10]. The high weight of glucose polymer, glycosidic and multiple hydroxyls in starch have the ability to bind a small particle during the flocculation process. Hamidi *et al.* [11] investigated *Orchis mascula* tuber starch to remove COD in wastewater treatment. They proved that the existence of divalent ions such as Ca^{2+} and Mg^{2+} in natural coagulants has a beneficial impact on the bridging mechanism in the coagulation-flocculation process. However, recent findings demonstrated that applying unmodified starch as a single flocculant requires a greater dosage to achieve high removal performance [12]. Yusof *et al.* [13] employed unmodified *Dioscorea hispida* starch through a coagulation process and discovered that the maximum COD reduction was only 22% using a large dosage of 2500 mg/L in wastewater treatment.

Combining chemical and natural coagulants is an alternative way to minimize the dosage of chemical application coagulants while increasing treatment efficiency [14]. This approach possibly decreases the aluminium residual amounts in treated wastewater before being discharged to water bodies. Lapointe *et al.* [15] investigated the combined chemical polymer polyacrylamide and natural starch as a dual polymer system, successfully removing pollutants up to 70% in industrial wastewater. The performance of pollutant removal in wastewater treatment usually depends on the pollution concentration, pH of the solution, coagulant-flocculant dosage, and settling time [16]. Therefore, the optimal condition that influences the treatment process should be studied.

This study aimed to explore the application of dual flocculants from natural *Manihot esculenta* starch and chemical coagulant (alum) for treating COD from wastewater. The single treatment by alum was also carried out using the same wastewater source as a comparison study. The optimum COD removal was explored in the coagulation-flocculation process based on alum dosages, starch dosage, pH condition, and settling time. The optimal (custom) design RSM was used to develop a quadratic model to predict COD removal efficiency. This study would contribute as a reference for researchers and engineers working in the wastewater field in understanding the role of ME starch for COD removal in wastewater treatment.

2. Materials and Methods

2.1. Sample collection and characteristics of municipal wastewater

The municipal wastewater samples were collected from Taman Universiti Sewage Treatment Plant, Batu Pahat, Malaysia. The sewage treatment plant served 10,000 population equivalents (PE). The raw wastewater was contained in a 10 L container, transported to a laboratory within 5 mins, and stored at 4 °C. The COD analysis was carried out according to the United States Environmental Protection Agency (USEPA) reactor digestion method 8000 for water and wastewater. A preheated reactor power DRB200 was used to heat COD samples for 2 hours. The analysis was performed using a HACH DR6000 spectrophotometer with high-speed wavelength scanning across the UV and visible spectrum with 435 COD high-range code programmed. The pH of wastewater was tested using a pH meter by Eutech Cyberscan pH 510 Bench. The pH was adjusted by adding HCl and NaOH, obtained from Sigma-Aldrich (M) Sdn Bhd in Malaysia. The alum was provided by Melaka Water Company that was used in a water treatment plant. It was a commercial water-soluble alum containing a minimum of Al_2O_3 8% w/w. All materials were analytical grade. The COD values of the raw wastewater were measured between 280 and 336 mg/L, which exceeds the standard A permissible effluent discharge limit of 120 mg/L set by the Malaysia Environmental Law, Environmental Quality 1974 (Sewage Regulation) [17]. The pH values were between 6.7 and 7.4, which was slightly neutral.

2.2. Preparation of starch

For this study, raw *Manihot esculenta* (ME) was collected and proceeded for starch preparation. The outermost layers (brownish tint) were removed with a fruit scrapper. The starch was washed and rinsed to remove any surface contaminants. The starch (200g) was suspended in 400 mL distilled water and blended for 10 mins to a fine paste and thin slurry in a blender, as shown in Figure 1(a). After that, the suspension sample was mixed with distilled water and stirred for 5 mins. A double-folded muslin cloth was used to filter the starch slurry for 5 hours. The supernatant was discarded after decanting. The starch sediment was collected and sun-dried for at least 48 hours to eliminate the moisture content. This method was modified based on a previous study by Asharuddin *et al.* [18]. For future usage, the dry cassava peel starch was stored in a securely sealed container, as seen in Figure 1(b).

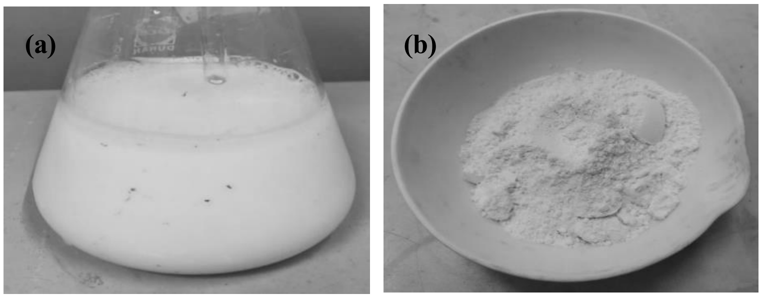

Figure 1. (a) Starch slurry and (b) Dried starch.

2.3. Coagulation and flocculation studies

The coagulation-flocculation studies of COD removal were carried out in a conventional 1000 mL jar test equipped with six beakers by Velp, Italy. The various dosages of alum (5-55 mg/L), starch (100-500mg/L), pH (2-11), and settling times (10-120 mins) were adapted according to the experimental design. Preliminary studies were done to determine the range of different variables. Afterwards, the optimal (custom) design was selected in RSM to develop the experimental design. By implementing custom design, specific points for certain independent variables could be obtained and generate more accurate results. After adding the alum coagulant, the solution was mixed rapidly at 200 rpm for 5 mins. Then, starch flocculant was added and continued by slow mixing at 200 rpm for 30 mins. After the samples settled in different sedimentation ranges, the supernatant was collected 2 cm below the surface water. The samples were directly analyzed for COD removal. The coagulation-flocculation studies were done for two batches of treatment: single coagulant alum and dual flocculants (alum and starch), as shown in Figure 2. The removal efficiency was calculated manually according to equation (1). The experiments were replicated, and an average value was recorded.

$$COD\ Removal\ (\%) = \frac{N\,i - N\,e}{N\,i} \times 100 \tag{1}$$

where N_i is the influent COD value, and N_e is the effluent COD value in mg/L.

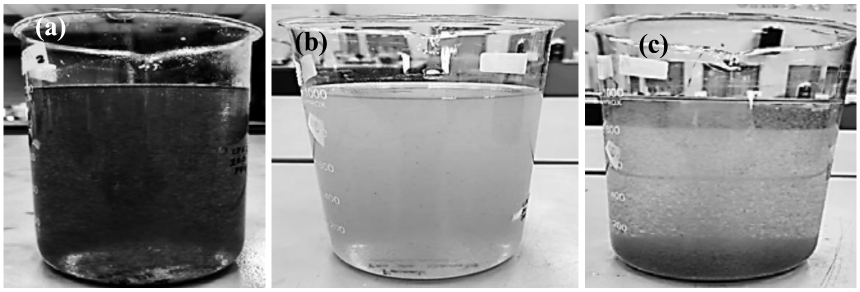

Figure 2. Observation of samples during the coagulation-flocculation process using (a) raw wastewater (control); (b) alum; and (c) dual flocculants (alum and starch).

2.4. *Response Surface Methodology (RSM)*

In this experiment, an optimal (custom) RSM design was implemented to optimize the coagulation-flocculation process. The total number of experiments from the software was designed 40 for each set of tests with no replicates. The experiments were then triplicated, and the average value was presented. The analysis was conducted with alum dosage from 5 to 55 mg/L, starch dosage from 100 to 500 mg/L, pH from 2 to 11, and settling time from 10 to 120 mins. The design of the experiments is summarized in Table 1.

Table 1. Design of experiments in optimal (custom) design RSM.

Variables	Symbol	Factor level	
		Min.	Max.
Alum			
Dosage (mg/L)	χ_1	5	55
pH	χ_2	2	11
Settling time (min)	χ_3	10	120
Alum and starch			
Alum dosage (mg/L)	χ_1	5	55
Starch dosage (mg/L)	χ_2	100	500
pH	χ_3	2	11
Settling time (min)	χ_4	10	120

The analysis of variance (ANOVA) was implemented to determine the significance of each variable. The response of dependent variables presented for the COD removal rate was fitted by a second-order model in the quadratic polynomial equation, as mentioned in equation (2) [19].

$$Y = \beta_{\circ} + \sum_{i=1} \beta_i\, \chi_i + \sum_{i=1} \beta_{ii}\, \chi_i^2 + \sum_{i=1} \sum_{i \neq j=1} \beta_{ij}\, \chi_i\, \chi_{ij} + \varepsilon \tag{2}$$

where Υ is the observed responses, χ_i is the independent variables, β_o is the constant variables; β_i, $\beta_{ii,}$ and β_{ij} represent the coefficients for interaction effects and quadratic, while ε refers to the random error. Model performance and verification using the multivariate regression approach were determined by the coefficient of determination (R^2). The R^2 values were calculated using experimental and predicted model values, as presented in equation (3) [20].

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(y_i^* - y_p^{(i)})}{\sum_{i=1}^{\eta}(y_i^* - \bar{y})^2} \tag{3}$$

where ȳ is the average of y over η data, the *i*th target and predicted responses are y_i^* and $y_p^{*(i)}$, respectively. Regression analysis and ANOVA were employed in Design-Expert (Version 13.0, Stat-Ease Inc., Minneapolis, USA) software to assess the statistical fitness of the projected value at a 95% confidence level.

3. Results

3.1 ANOVA analysis

The relationship between the independent variables (alum dosage, starch dosage, pH, and settling time) and the dependent variable (COD removal) for coagulation-flocculation was determined using RSM. The ANOVA results for a quadratic model using alum are presented in Table 2. Meanwhile, the ANOVA results for a quadratic model using the dual flocculant alum and starch are demonstrated in Table 3. The results showed that both models were significant, with a *p*-value <0.05, and revealed that the model is suitable for predicting COD reduction within the design range. The F-value was identified at 29.80 and 5.01 for single and dual flocculants, respectively, which was larger than the *p*-value, meaning that the model was significant.

Based on the analysis, pH condition and settling time were the two significant parameters in the quadratic model using a single coagulant (alum). In the dual flocculant model, two parameters were statistically significant: starch dosage and pH, while other parameters were insignificant. Both batches of treatment proved that increasing and decreasing the pH condition significantly affects the coagulation-flocculation process. Arris *et al.* [21] agreed that pH was the most important parameter influencing COD removal. Another study using an organic flocculant by Guo *et al.* [22] also supported that pH conditions and dosage affect the COD removal mechanism. The effect of all variables is presented in section 3.2.

The coefficient determination (R^2) of the single coagulant and dual flocculant models were 0.9641 and 0.9335, respectively. The R^2 indicated that 96% and 93% of the model variance were completely expressed. The results revealed a lower error in the predicted models; only 4% and 7% of the total variances could not be expressed by the COD model. If the coefficient of variance is not more than 10%, the model can be considered reliable. A high R^2 value closer to 1 indicates a good fit of the model between the observed and estimated results [23]. However, the model fitness not just be determined by the R^2 value obtained by the error sum of squares. Adeq Precision measures the signal-to-noise ratio, and if the ratio is greater than 4, the model can be used to navigate the design parameters [24]. In this study, the Adeq. Precision for the single and dual flocculant model was higher than 4, meaning the output was sufficient and acceptable. The model was applicable to be used. After coagulation-flocculation treatment of single and dual flocculants, the average COD value was 48.89 mg/L and 41.43 mg/L, respectively. The average COD value was below the Malaysian effluent wastewater standard for COD standard, which is 120 mg/L.

Table 2. ANOVA results for a quadratic model using alum.

Source	*df*	Sum of Squares	Mean Square	F-value	*p*-value	Std. Dev	Mean	R^2	Adjusted R^2	Adeq. Precision
Model	9	13563.43	1507.05	29.8	< 0.0001	7.11	48.89	0.9641	0.9317	14.4435
A-Alum	1	30.47	30.47	0.6025	0.4556					
B-pH	1	6543.27	6543.27	129.39	< 0.0001					
C-Time	1	320.71	320.71	6.34	0.0305					
AB	1	357.18	357.18	7.06	0.024					
AC	1	2006.69	2006.69	39.68	< 0.0001					
BC	1	327.75	327.75	6.48	0.0291					
A^2	1	97.89	97.89	1.94	0.1943					
B^2	1	3853.39	3853.39	76.2	< 0.0001					
C^2	1	109.86	109.86	2.17	0.1713					

Table 3. ANOVA results for a quadratic model using dual flocculant.

Source	*df*	Sum of Squares	Mean Square	F-value	*p*-value	Std. Dev	Mean	R^2	Adjusted R^2	Adeq. Precision
Model	14	19553.87	1396.70	5.01	0.0426	16.69	41.43	0.9335	0.7472	5.9396
A-alum	1	1286.67	1286.67	4.62	0.0844					
B-Starch	1	2029.24	2029.24	7.28	0.0429					
C-pH	1	5356.14	5356.14	19.22	0.0071					
D-Time	1	1076.76	1076.76	3.86	0.1065					
AB	1	1420.49	1420.49	5.10	0.0736					
AC	1	174.38	174.38	0.6258	0.4648					
AD	1	205.72	205.72	0.7383	0.4295					
BC	1	34.51	34.51	0.1238	0.7393					
BD	1	220.22	220.22	0.7903	0.4147					
CD	1	850.50	850.50	3.05	0.1411					
A^2	1	2730.10	2730.1	9.80	0.0260					
B^2	1	949.15	949.15	3.41	0.1243					
C^2	1	225.23	225.23	0.8083	0.4098					
D^2	1	260.89	260.89	0.9362	0.3777					

The results were then analyzed to develop a mathematical quadratic equation for COD removal by alum, presented in equation (4). While the quadratic equation for COD removal by dual flocculant is presented in equation (5). The predicted results were analyzed and calculated as the sum of a constant for dosage, pH and settling time, including first-order effects (A, B, C, and D), one interaction effect (AB, AC, and BC) and second-order effects (A^2, B^2, C^2, and D^2). Figures 3(a) and 3(b) show the residual value and experiment run number for single and dual flocculant. The residual value was distributed less than 4.1% and 6.7% for single and dual flocculant. The residual proves that the lower the error, the higher the predictability of the model.

$$\text{COD removal by alum} = 72.25 - 1.80\,A + 26.61\,B - 5.91\,C + 8.02\,AB - 20.55\,AC + 8.00\,BC - 4.99\,A^2 - 34.62\,B^2 - 5.30\,C^2 \tag{4}$$

$$\text{COD removal by dual flocculants} = 74.74 + 10.95\,A + 13.90\,B + 24.56\,C - 11.23\,D - 14.17\,AB - 5.47\,AC + 5.65\,AD - 2.45\,BC + 6.51\,BD + 12.75\,CD - 34.66\,A^2 - 19.69\,B^2 + 10.08\,C^2 + 10.03\,D^2 \tag{5}$$

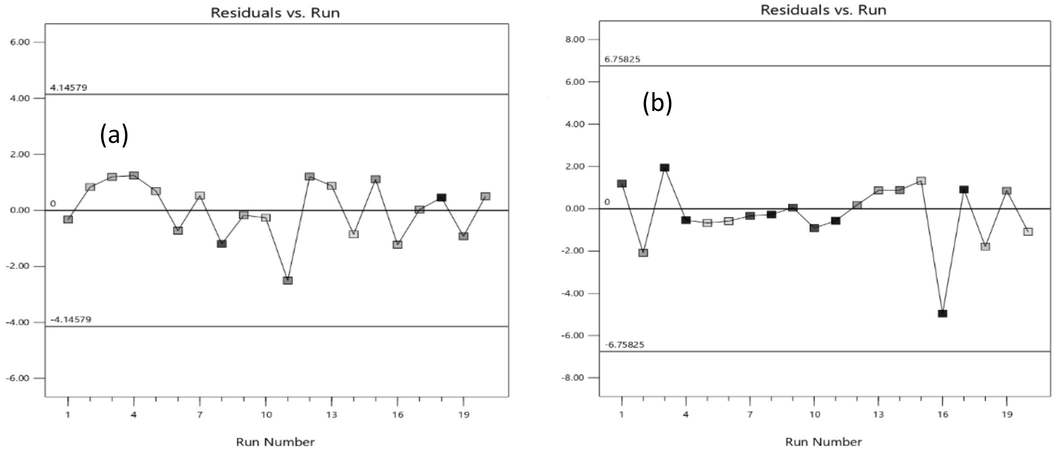

Figure 3. Residual vs. run number of (a) alum and (b) dual flocculant model.

3.2 Effect of dosage, pH, and settling time

The effect of dual flocculant was presented in four independent variables: alum dosage, starch dosage, pH, and settling time on COD removal. Figure 4(a) shows the response surface 3D plots for the effect of dosage. The COD removal was increased when the alum and starch dosage was increased. From the graph, the COD removal rapidly increased to 77% when alum dosage increased from 5 to 30 mg/L and starch dosage increased from 100 to 350 mg/L. However, after this point, the removal efficiency was decreased to 36% after the alum dosage exceeded 35 mg/L. At the same time, COD removal was reduced to 41% after the starch dosage exceeded 400 mg/L. Overdosing after the optimum level impacted the effluent quality, which could not be coagulated-flocculated well, referring to the restabilization of the colloidal particles. Due to restabilization, the repulsive forces between colloids increased and reduced the Van de Waals force, diminishing Brownian motion and weakening the zeta potential [25]. As a result, the COD removal decreased, and previous researchers expressed the same finding [26]. Sometimes, the overdose could give the same results as the optimum level but require a high cost [27]. Therefore, selecting the minimum dosage of coagulant-flocculant with the maximum removal efficiency was the best way to practice. Based on this hypothetical, the optimal dosage for alum and starch should be below the restabilization level. The result was similar to Barros *et al.* [28], which observed that COD removal efficiency depended on dosage. Another study by Sibiya *et al.* [29] also agreed that optimum starch dosage caused a better COD removal performance.

Figure 4(b) shows the response surface 3D plots for pH conditions. In this study, the combined use of starch and alum at higher pH resulted in higher COD removal efficiency than at lower pH. The graph clearly shows that in 100 mg/L starch dosage at pH 2, the COD removal only achieved 20%. The COD removal was increased to 45% in pH 7 at 100 mg/L starch. The COD removal keeps increasing to 78% at pH 11 with a 100 mg/L of starch dosage. The pollutant removal was increased to more than 80% in pH 7 and above when increasing the dosage to 300mg/L. The present study evaluated a pH range between 2 and 11, and it was found that the high efficiency of COD removal (>80%) started from pH 7 and above. The coagulation-flocculation process worked well in neutral to alkaline conditions for COD removal in municipal wastewater. A study by El-Bied *et al.* [30] agreed the optimum pH for COD removal was around 7.5, which could reach COD removal to 88%. The finding also revealed that pH was the dominant factor in COD removal. ME starch has a negative charge, and the wastewater was in a neutral condition. Practically, the COD removal could be reduced by more than 80% without adjusting the pH condition. In low pH conditions with high concentrations of hydrogen ions (H^+), it seems that charge neutralization of the negatively charged surface particles of wastewater improved COD removal [31]. However, in alkaline conditions, the removal of COD increased significantly due to the sweep and bridging mechanism rather than charge neutralization. During the bridging mechanism, the connecting particles played a prominent role in the flocculation process in which the pollutant was trapped and bound together, forming larger flocs. Starch polymers possessing a high molecular weight and a prolonged chain structure are beneficial for promoting intra-particles binding [32]. If the initial reading of the pollutant is in higher concentration, makes the bridging mechanism improves and reacts rapidly [33].

Figure 4(c) presents the response surface 3D for the effect of settling time. The results show that when the settling time was 10 mins with a starch dosage of 300 mg/L, gives a COD removal efficiency of 80%. When the settling time increased to 120 mins, the removal efficiency achieved 75%. The removal efficiency remains the same or decreases slightly (from 80 to 75%) by increasing the settling time to 120 mins longer. This is due to the restabilization of particles after the optimum conditions. The flocs formed in the flocculation process were easily broken after a certain period. According to Alnawajha *et al.* [34] who studied the effect of settling time using a plant-based coagulant and found that macro flocs have bigger sizes, which assist them in settling faster and higher efficiency up to 93% within the first 5 mins and reduce a little slow to 90% after that. Heiderscheidt *et al.* [35] found that the removal efficiency was highest within 5 mins and decreased after 8 mins using inorganic and organic coagulants in aquaculture wastewater treatment.

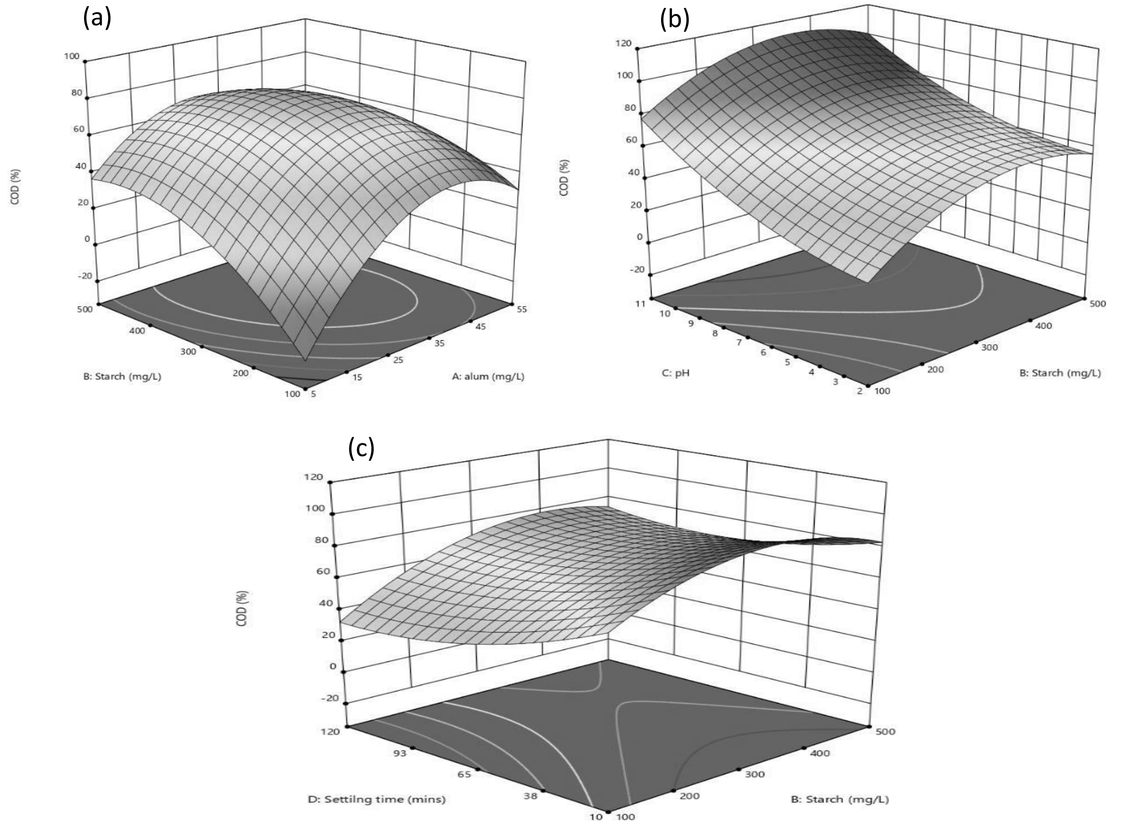

Figure 4. Response surface 3D plots of (a) alum and ME starch dosage; (b) ME starch dosage and pH; and (c) ME starch dosage and settling time.

3.3 Validation and optimization of coagulation-flocculation

The model was validated by performing additional experiments in which alum dosage, starch dosage, pH, and settling time were at optimum conditions. The optimal condition for single and dual flocculant for COD removal is presented in Table 4. The optimum weight ratio of dual flocculant was alum/starch = (18 mg/307 mg) = 0.06. The COD removal by dual flocculant was achieved at 93% compared to 85% for single coagulant. The optimal conditions for dual flocculant revealed 18 mg/L of alum dosage, 307 mg/L of starch dosage, pH 9, and 27 mins settling time. In comparison, the optimal condition for the single coagulant was found at 50 mg/L of alum dosage, pH 7, and 22 mins settling time. After the alum coagulation process, the COD values were between 40.3 and 48.0 mg/L. The COD values using dual flocculant were between 19.6 and 23.5 mg/L, which is far below the permissible limit set by Malaysia wastewater effluent discharge EQA 1974. Besides increased COD removal efficiency, the alum dosage was reduced by up to 64%. Optimization using RSM has facilitated the present research by providing the flexibility to achieve the highest removal of COD efficiency by approaching the process performance limit. From an economic perspective, the optimum process of coagulation-flocculation indirectly influences the cost of wastewater treatment and produces better and equal performance as required.

Table 4. Summary of optimal condition for COD removal.

Coagulant / Flocculant	Independent factors	Optimized	Removal performance (%)
Alum	Alum dosage pH Settling time	50 mg/L 7 22 mins	85.62
Alum and ME starch	Alum dosage Starch dosage pH Settling time	18 mg/L 307 mg/L 9 27 mins	93.00

4. Conclusion

The current study revealed that the dual flocculant has excellent potential for wastewater treatment. The optimum alum/starch weight ratio = 0.06 was achieved to obtain higher COD removal percentages compared to a single coagulant. The coagulation-flocculation process using dual flocculant showed that the COD removal was up to 93% at 18 mg/L alum dosage, 307 mg/L ME starch dosage, pH 9, and 27 mins settling time. The coagulation process using a single coagulant was carried out on the same wastewater samples for comparative analysis. The optimum condition for a single coagulant was removed COD up to 85% using an alum dosage of 50 mg/L, pH 7, and 22 mins of settling time. When inserting a specific starch dosage after the coagulation process using alum, it can reduce the use of alum by up to 64%. At the same time, the removal performance increased by 7%. The optimal (custom) design from RSM developed the quadratic models to predict the COD removal efficiency based on experimental value. Both ANOVA analyses for single and dual flocculant showed that the models were significant, with a p-value < 0.05. The high value of the coefficient of determination (R^2) for single and dual flocculants was determined, which were 0.9641 and 0.9335, respectively, to ensure the satisfactory fit of the models. For further study, it is suggested to analyze the zeta potential of the particles to understand the flocculation mechanism when implemented in high pollutant concentrations.

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