Lentil waste as novel natural coagulant for agricultural wastewater treatment

Siong-Chin Chua, Pau Loke Show, Fai-Kait Chong and Yeek-Chia Ho

ABSTRACT

Increasing agricultural irrigation to counteract a soil moisture deficit has resulted in the production of hazardous agricultural wastewater with high turbidity and chemical oxygen demand (COD). An innovative, sustainable, and effective solution is needed to overcome the pollution and water scarcity issues caused by the agricultural anthropogenic processes. This research focused on a sustainable solution that utilized a waste (broken lentil) as natural coagulant for turbidity and COD removal in agricultural wastewater treatment. The efficiency of the lentil extract (LE), grafted lentil extract (LE-g-DMC) and aluminium sulphate (alum) coagulants was optimized through the response surface methodology. Three-level Box–Behnken design was used to statistically visualize the complex interactions of pH, concentration of coagulants and settling time. LE achieved a significant 99.55% and 79.87% removal of turbidity and COD at pH 4, 88.46 mg/L of LE and 6.9 minutes of settling time, whereas LE-g-DMC achieved 99.83% and 80.32% removal of turbidity and COD at pH 6.7, 63.08 mg/L of LE-g-DMC and 5 minutes of settling time. As compared to alum, LE-g-DMC required approximately 30% less concentration. Moreover, LE and LE-g-DMC also required 75% and 65% less settling time as compared to the alum. Both LE and LE-g-DMC produced flocs with excellent settling ability (5.77 mg/L and 4.48 mL/g) and produced a significant less volume of sludge (10.60 mL/L and 8.23 mL/L) as compared with the alum. The economic analysis and assessments have proven the feasibility of both lentil-based coagulants in agricultural wastewater treatment.

Key words | alum, coagulation and flocculation, lentil extract, optimization, sludge, sludge volume index

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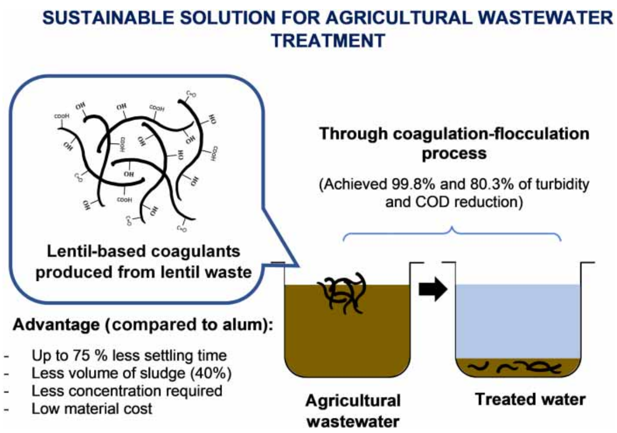
HIGHLIGHTS

- Sustainable utilization of lentil waste for wastewater treatment was studied.
- The two lentil-based coagulants achieved a significant turbidity and COD removal.
- Both lentil-based coagulants proved to significantly decrease the settling time.
- Grafted lentil extract produced excellent flocs and least volume of sludge.
- Lentil-based coagulants have advantages in material and sludge management costs.

doi: 10.2166/wst.2020.409

GRAPHICAL ABSTRACT



INTRODUCTION

All living organisms depend on adequate supplies of water for various activities including agriculture purposes, industrial input and, most importantly, domestic use. However, the overwhelming growth of the human population threatens the freshwater that is available on the earth (Brauman *et al.* 2016; Linares *et al.* 2017). To sustain sufficient food for human beings, the rapid growth of agricultural activities that require a large amount of water for irrigation has worsened the situation. According to Brauman *et al.* (2014), the irrigation process in the agricultural sector brought the largest impact to the depletion of the water as it consumes up to 85% of the global water supply. Apart from the water consumed, the wastewater produced at the end of the irrigation process is generally hazardous, as it is high in turbidity, heavy metals and chemical oxygen demand (COD) (Lim *et al.* 2018). In view of this, the World Wildlife Fund (WWF) estimated that by 2025, two-thirds of the world's population might experience water scarcity (López-Vinent *et al.* 2020).

Water recovery from the agricultural wastewater could be a sustainable solution for the water scarcity issue and has received more and more attention in recent years. Various treatment methods for the water recovery process have been discovered, including coagulation–flocculation (GilPavas *et al.* 2017; Webler *et al.* 2019; Ho *et al.* 2020; Wongcharee *et al.* 2020), advanced oxidation process (Zazou *et al.* 2019), membrane technology (Bae *et al.* 2017; Yu & Graham 2017; Park *et al.* 2020), biological treatment (Neoh *et al.* 2016; Min *et al.* 2018) and ion exchange technology (Wang *et al.* 2017). Coagulation–flocculation is one of the widely used, efficient and cost-effective technologies, which involves the addition of coagulants to the wastewater with the purpose of altering the physical state of the suspended solid (Long *et al.* 2017; Sillanpää *et al.* 2018; Ang & Mohammad 2020). This process is mainly used in removing natural organic matter and colloidal particles in the water and wastewater (Kakoi *et al.* 2016).

Coagulant plays a significant role in coagulation–flocculation technology and can be classified into two main categories, which are inorganic and organic coagulants. Inorganic coagulants, e.g. aluminium and iron salts, have been intensively studied and used in various kinds of wastewater due to its high efficiency properties (Parmar *et al.* 2011; Kang *et al.* 2017; Dotto *et al.* 2019). However, the sludges generated at the end of the process are large in quantity and have been classified as scheduled waste in some countries (Dotto *et al.* 2019). The residue in the treated water by using aluminium-based inorganic coagulant was found to link with neurodegenerative diseases (Alzheimer's disease) (Rondeau *et al.* 2000; Camacho *et al.* 2017; Asharuddin *et al.* 2019; Triques *et al.* 2020). Recently, natural coagulants have been given much attention as they generated less sludge and were safer to use, compared to inorganic coagulants (Choy *et al.* 2014; Yusoff *et al.* 2018). *Moringa oleifera* (Camacho *et al.* 2017; Teixeira *et al.* 2017), chitosan (Ang *et al.* 2016; Momeni *et al.* 2018), lentil extract (Chua *et al.* 2019), banana pith (Kakoi *et al.* 2016) and pectin (Kebaili *et al.* 2018) are the promising natural coagulants that have been studied recently.

In previous studies, lentil extract (LE) and grafted lentil extract (LE-g-DMC) were produced from broken lentils (waste from the lentil processing process) and found to be effective plant-based coagulants in turbidity removal from synthetic kaolin water, achieving up to 99% of removal (Chua et al. 2019; Chua et al. 2020). The utilization of the lentil-based coagulant could be a promising, sustainable and novel approach to treat agricultural wastewater for reuse purposes. In this study, both lentil-based coagulants, LE and LE-g-DMC, were used to remove turbidity and COD of the agricultural wastewater and the result was compared with the widely used inorganic coagulant alum.

MATERIALS AND METHODS

Materials

Hydrochloride acid (HCl), sodium hydroxide (NaOH), and kaolin powder of analytical-reagent grade were used. 2-methacryloyloxyethyl trimethyl ammonium chloride (DMC) with 75 wt.% in H_2O and ceric ammonium nitrate ($\geq$98%) were supplied by Sigma-Aldrich.

Methods

Lentil extract and grafted lentil extract

LE was produced as described by Chua et al. (2019). In brief, the lentil waste was powdered and mixed with distilled water at a lentil:water ratio of 1:15. The mixture was heated to 80 °C for 1 h. The mixture was then centrifuged and oven-dried to obtain dry LE.

The LE-g-DMC was produced following Chua et al. (2020). In brief, 1 g of LE and 2.8 g of DMC were dissolved into 40 and 10 mL distilled water, respectively. Both solutions and ceric ammonium nitrate were mixed in a Borosil beaker. The process was followed by irradiation of the solution at a known microwave power at 600 W for 2.6 minutes. Subsequently, ethanol was added, and the mixture was centrifuged at 3,500 rpm. The LE-g-DMC was then oven-dried, pulverized, and sieved to obtain dry LE-g-DMC.

Sampling of agricultural wastewater

The agricultural wastewater samples were collected at the paddy cultivation site at Seberang Perak (04° 4.783 N, 100° 52.01 E), Malaysia. The collected wastewater was produced by agriculture's irrigation activities. The turbidity and COD of the agricultural wastewater were reported as 890 ± 12 nephelometric turbidity units (NTU) and 372 ± 9 mg/L, respectively.

Assay of turbidity removal and COD removal

Jar tests were conducted to evaluate the coagulation–flocculation performance of LE, LE-g-DMC and alum in agricultural wastewater. Jar-test apparatus (VELP Scientifica srl-JLT6 flocculator) comprising six paddle rotors was used. Prior to the addition of coagulant, the pH value of the water sample was adjusted to the desired pH (ranging from pH 4 to pH 10) and the desired amount of coagulant (ranging from 1 to 100 mg/L) was added. The coagulation–flocculation process was started with 1 min of rapid mixing at 150 rpm, followed by 20 minutes of slow mixing at 30 rpm. The beakers were left undisturbed for 30 minutes for the settling process after that. Then 10 and 2 mL of the supernatants were withdrawn for the turbidity and COD measurement, respectively. The efficiency of turbidity and COD removal was calculated by using Equations (1) and (2). The COD of the water sample was measured in accordance to USEPA Reactor Digestion Method by using a Hach DR6000 UV Vis spectrophotometer.

$$\text{Turbidity removal (\%)} = \frac{\text{initial turbidity} - \text{final turbidity}}{\text{initial turbidity}} \times 100 \quad (1)$$

$$\text{Total COD removal (\%)} = \frac{\text{Initial COD} - \text{Final COD}}{\text{Initial COD}} \times 100 \quad (2)$$

Sludge volume and sludge volume index measurement

The amount of the sludge produced at the end of the coagulation–flocculation process was determined through the volumetric method by using Imhoff cones. The agricultural wastewater was transferred to a 1 L Imhoff cone and left undisturbed for 1 hour for sludge measurement. The sludge volume index (SVI) was calculated to determine the settling characteristic of produced sludge (floc) during the coagulation–flocculation process. SVI was determined using the standard method and calculated using Equation (3) (Rahmani et al. 2019).

$$\text{SVI}\left(\frac{\text{mL}}{\text{g}}\right) = \frac{\text{Settled sludge volume after 30 mins}\left(\frac{\text{mL}}{\text{L}}\right) \times 1{,}000}{\text{Total suspended solid}\left(\frac{\text{mg}}{\text{L}}\right)} \quad (3)$$

Experiment design and statistical analysis for optimization of coagulation–flocculation process

Experiment design. In the traditional approach, the optimization process was conducted by systematic variation of one parameter while other parameters were fixed constant. However, this method is time-consuming and the interaction between factors were unlikely to be determined. Hence, the optimum conditions of the designed factors were unable to be predicted precisely using the traditional method (Zarei *et al.* 2010). In recent years, response surface methodology (RSM), a statistical method, has been introduced as a promising alternative for the traditional optimization process. This statistical approach helps to quantify the relationship between the influencing factors with a limited number of experiment runs by varying all the influencing factors simultaneously (Huzir *et al.* 2019; Peng *et al.* 2019). The use of RSM consists of five steps: (1) selecting the influencing factors (independent factors); (2) choosing the experiment design; (3) conducting the experiment and processing the data; (4) evaluating the model adequacy and fitness; and (5) determining the optimum condition (Wu *et al.* 2015). In this research, a three-level Box–Behnken design (BBD) was used to investigate the relationship between designed influencing factors of the coagulation–flocculation process (pH, concentration of coagulant and settling time). The range of the designed influencing factors was ascertained through the preliminary experiments and each of the retained influencing factors was coded into three levels, low (−1), central point (0) and high (+1) as illustrated in Table 1 and Equation (4). The second-order polynomial model was fitted to the data by using Equation (4).

$$Y = b_o + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i<j}^{k} \cdot \sum_{j}^{k} b_{ij} X_i X_j + e \quad (4)$$

where Y and b_o are the predicted response and constant coefficient respectively; X_i and X_j are the coded level of the influencing factors (independent variable); b_i, b_{ii} and b_{ij} are known as the coefficients of the linear, interaction and quadratic terms, respectively; e is the random error; and lastly, k is the number of influencing factors (independent variables). Turbidity and COD removals were the responses for the designed model.

Table 1 | Box–Behnken design for optimization of turbidity and COD removal in agriculture wastewater treatment

Influencing factor	Unit	Coded symbol	Level and range −1	0	+1
pH	–	X_1	4	7	10
Concentration of coagulant	mg/L	X_2	1.0	50.5	100.0
Settling time	minute	X_3	1.0	10.5	20.0

Verification of the designed model. Verification is needed to ensure the accuracy of the predicted data. Hence, a validation experiment was conducted to examine the predicted value and the experimental value, for which a 95% confidence level needed to be achieved.

RESULTS AND DISCUSSION

Effect of influencing factors

Effect of concentration of coagulant and pH

The three-dimensional response surfaces for turbidity and COD removal as a function of pH and concentration of LE, LE-g-DMC and alum influencing factors are illustrated in Figures 1 and 2. Both pH and concentration of coagulant influencing factors showed a strong individual effect and interaction effect toward the turbidity removal and COD removal in agriculture wastewater treatment, which was evident from the *p*-value of each individual influencing factor. Contrastingly, in the case of LE-g-DMC as a coagulant, the pH influencing factor exhibited an insignificant effect with *p*-value of 0.7388 and 0.3953 toward turbidity removal and COD removal, respectively. Also, both pH and concentration of coagulant influencing factors do not interact with each other. This is attributed to the introduction of cationic functional groups originating from quaternary ammonium salts that reduced the sensitivity of the coagulant toward the pH in the water.

When LE alone was used as a coagulant, the increase of concentration of LE at low pH aided both turbidity and COD removal in agriculture wastewater: ∼99% of turbidity removal and ∼80% of COD removal when the concentration of LE was in the range 80 to 100 mg/L. However, a very low turbidity removal (20–35%) and COD (∼10–20%) removal were achieved at pH range from pH 8 to 10. This was attributed to the nature of the LE as an anionic polymer and its governing mechanism, bridging mechanism (Chua *et al.* 2019). For coagulant with bridging mechanism, sufficient hydrogen ions are required to assist LE in binding the particles through its polymer chain. Hence, an insufficient amount of hydrogen

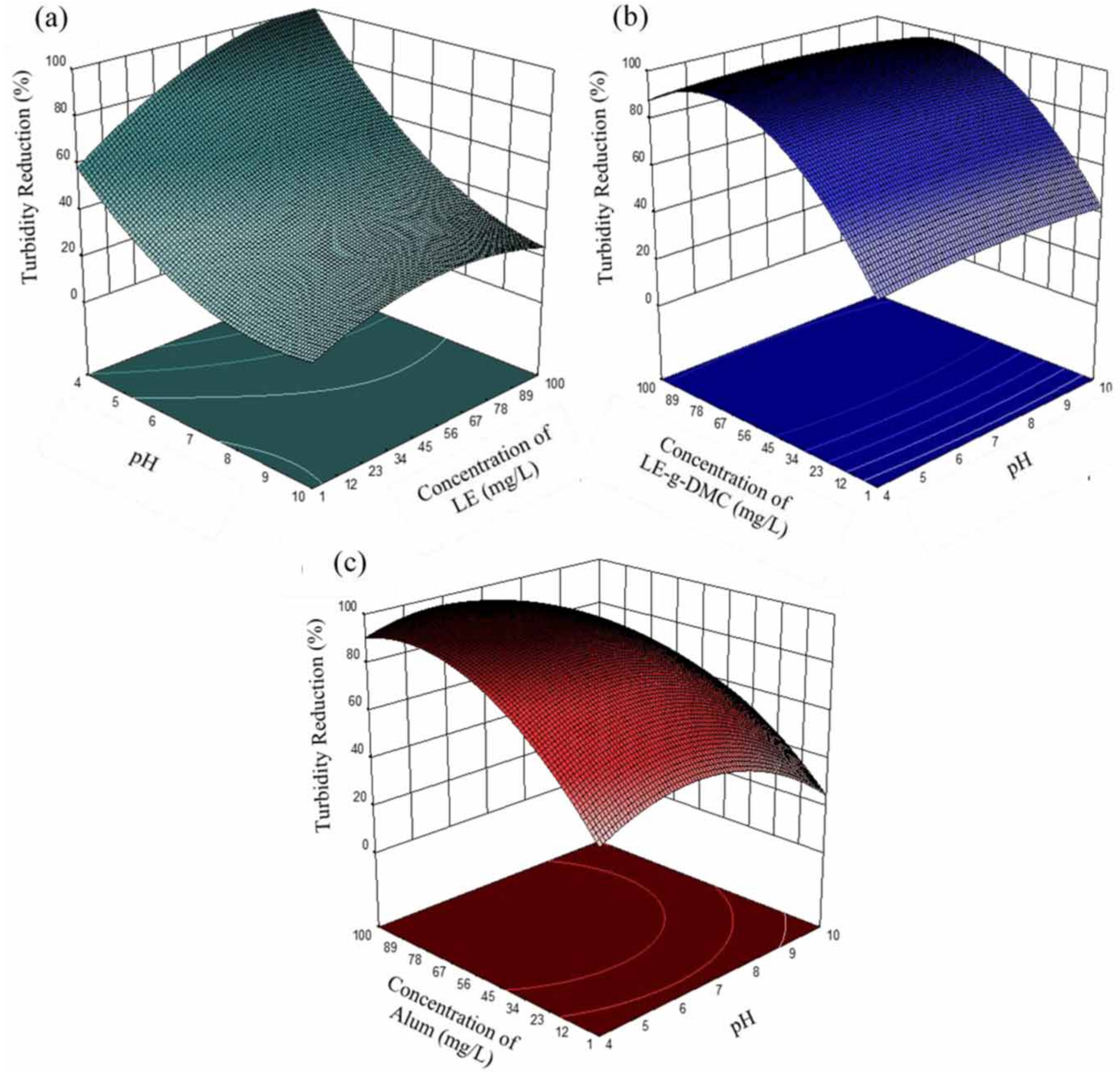


Figure 1 | Three-dimensional response surface plots of the effect of pH and concentration of coagulants for turbidity removal (%) using (a) LE, (b) LE-g-DMC and (c) alum as coagulants in agriculture wastewater treatment.

ions in high pH water significantly reduced the efficiency of LE.

When LE-g-DMC was used as a coagulant, a consistent trend was observed across all pH values, as illustrated in Figures 1(b) and 2(b). LE-g-DMC is less sensitive toward the change in pH. Instead, both turbidity and COD removal were mainly affected by the concentration of LE-g-DMC in agricultural wastewater treatment. Maximum turbidity (~99.5%) and COD removal (~80%) were achieved at concentration range from 60 to 70 mg/L. When alum was used, high turbidity and COD removal were only achieved at the pH range from 5.5 to 7 as alum is a highly pH-dependent coagulant. This is attributed to the OH^- ion that competes with organic compounds for metal adsorption sites at the alkaline conditions. On the other hand, the attraction of the coagulant toward anionic pollutants in the water reduced due to the insufficient positively charged in the coagulant (Freitas *et al.* 2015).

Effect of pH and settling time

pH showed a strong individual effect on the turbidity and COD removal when LE and alum were used. Contrastingly, settling time only showed a strong individual effect toward the turbidity and COD removal when alum was used as a coagulant. This is due to the long-chain properties of

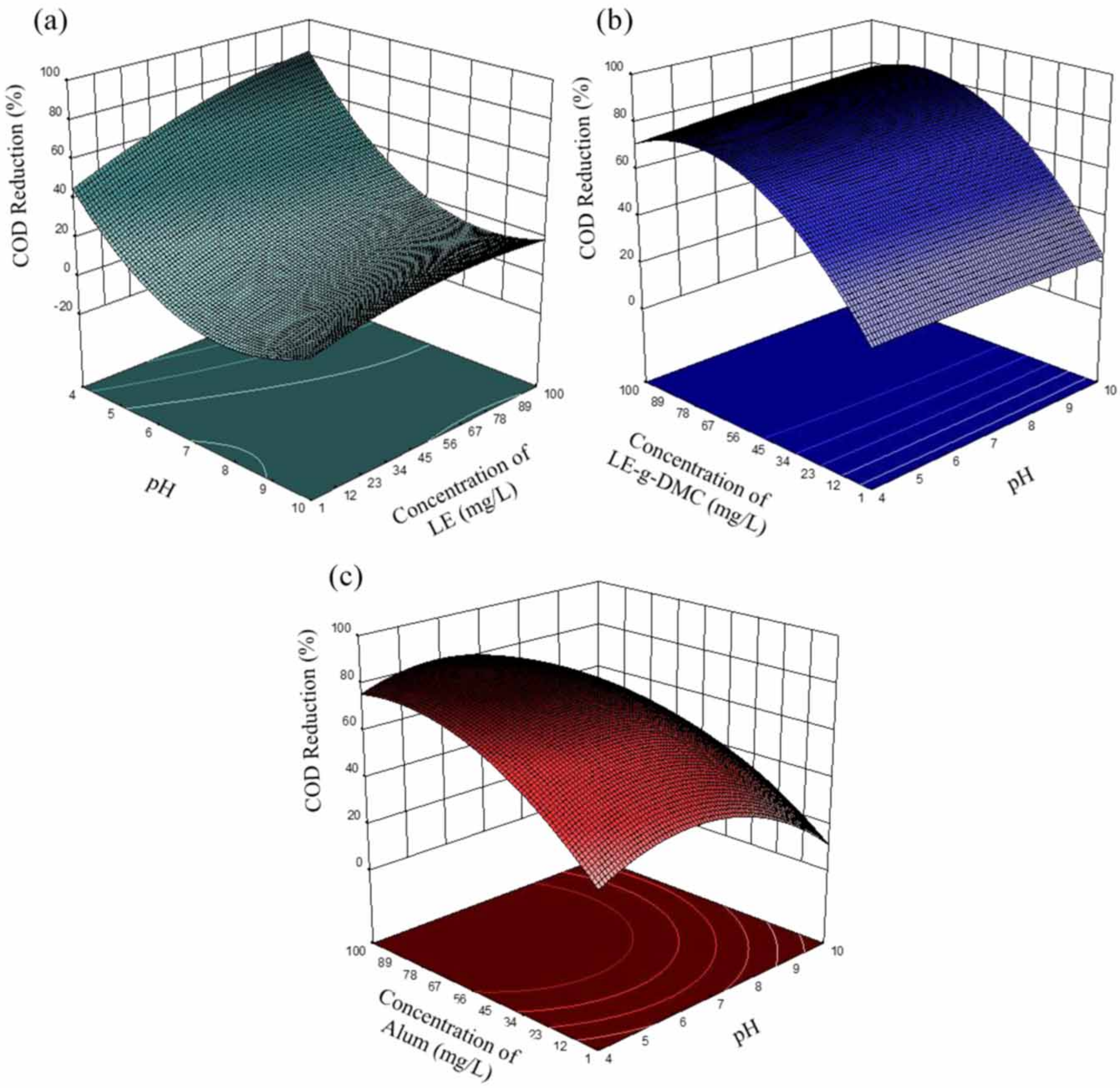


Figure 2 | Three-dimensional response surface plots of the effect of pH and concentration of coagulants for COD removal (%) using (a) LE, (b) LE-g-DMC and (c) alum as coagulants in agriculture wastewater treatment.

polymers that enhance the formation of a more compact and denser floc. Consequently, the floc required less time to settle down and thus was less sensitive toward the settling time, which is evidently shown in the three-dimensional response surface of the LE and LE-g-DMC (Figure 3). When LE was used as a coagulant, approximately 95% of turbidity removal and 75% of COD removal were achieved in 1 minute at pH 4. Also, prolonging settling time to more than 1 minute gave a minimum effect to the turbidity removal. This is because the flocs formed during the process were compact and dense, and settled within 1 minute. A similar trend was found, where settling time had a minimum effect toward turbidity removal, when LE-g-DMC was used. However, the settling time influencing factor significantly affected the turbidity and COD removal when alum was adopted in the agricultural treatment process. The increase in settling time enhanced the turbidity and COD removal, until they reached an optimum point (turbidity ~99% and COD ~80%); further increase in settling time did not significantly impact both turbidity and COD removal as illustrated in Figures 3(c) and 4(c). The high sensitivity of alum toward settling time was attributed to the nature of the alum and its respective governing mechanism during the treatment process. Being different from a polymeric coagulant, alum is a

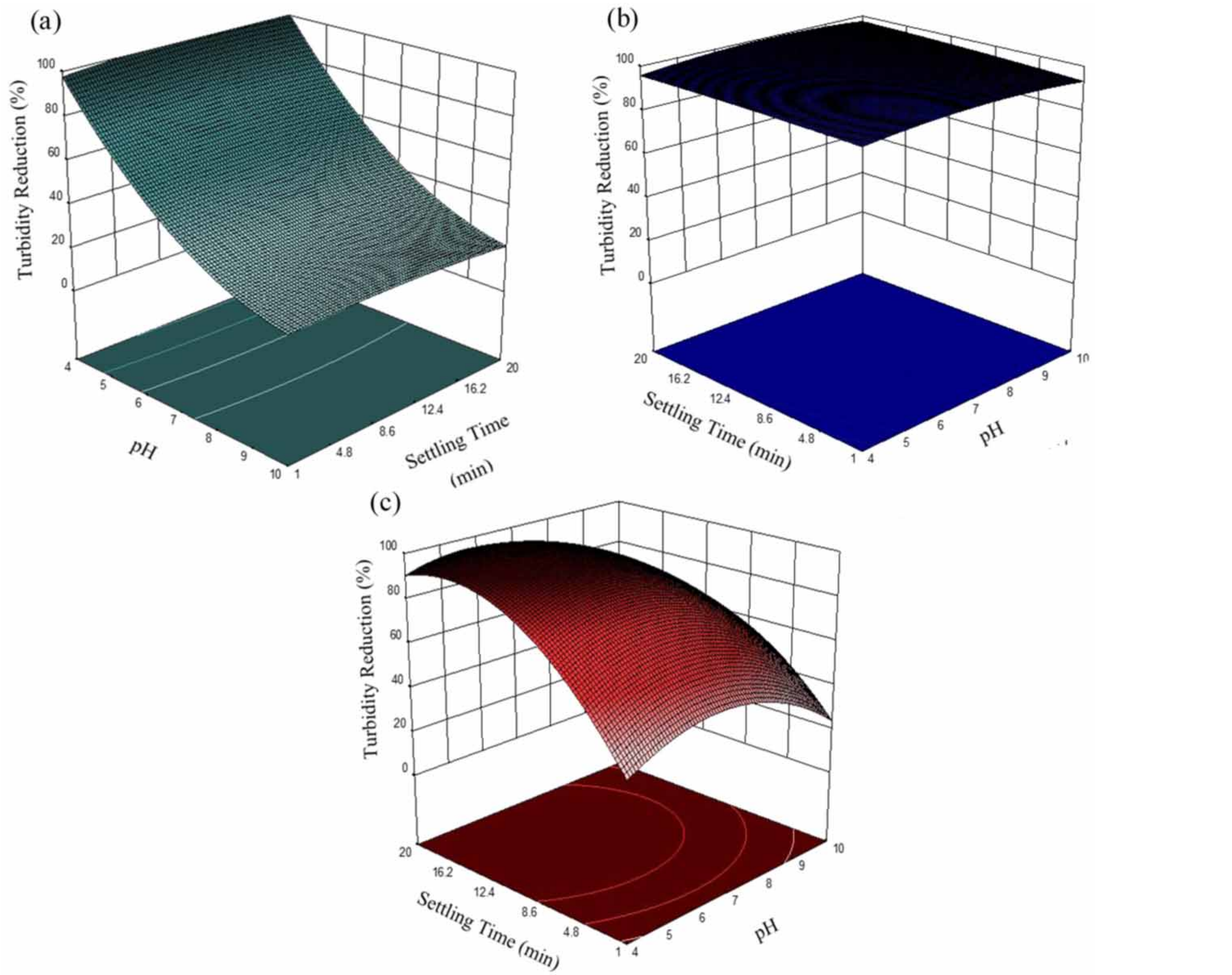


Figure 3 | Three-dimensional response surface respond plots of the effect of pH and settling time for turbidity removal (%) using (a) LE, (b) LE-g-DMC and (c) alum as coagulants in agriculture wastewater treatment.

hydrolyzing metallic salt without a long chain, in which the governing coagulation–flocculation mechanism is mainly the charge neutralization instead of bridging. Consequently, less compact and lighter flocs were formed as compared to polymeric coagulant, which required longer settling time (Sanghi *et al.* 2002).

Effect of concentration of coagulant and settling time

When LE was used for the treatment of agriculture wastewater, the increasing concentration of LE enhanced the turbidity removal in settling time ranging from 1 minute to 20 minutes. However, the turbidity and COD removal reduced after the optimum point at the concentration ranging from 65 to 80 mg/L. This was attributed to the insufficient absorption sites of the particle surface. The excessive dosage of LE had fully occupied the surface of the particles (Bolto & Gregory 2007). A similar finding was reported when LE-g-DMC was dosed for the treatment. The optimum concentration and settling time to achieve ~99% of turbidity removal and ~80% of COD removal are approximately 65–75 mg/L and 5–6 minutes, as shown in Figures 5(b) and 6(b).

Multiple responses optimization for turbidity removal

Based on the sum of squares when LE was used as a coagulant, the total contribution of linear, quadratic and interaction terms in turbidity removal are 83.05% (70.80%

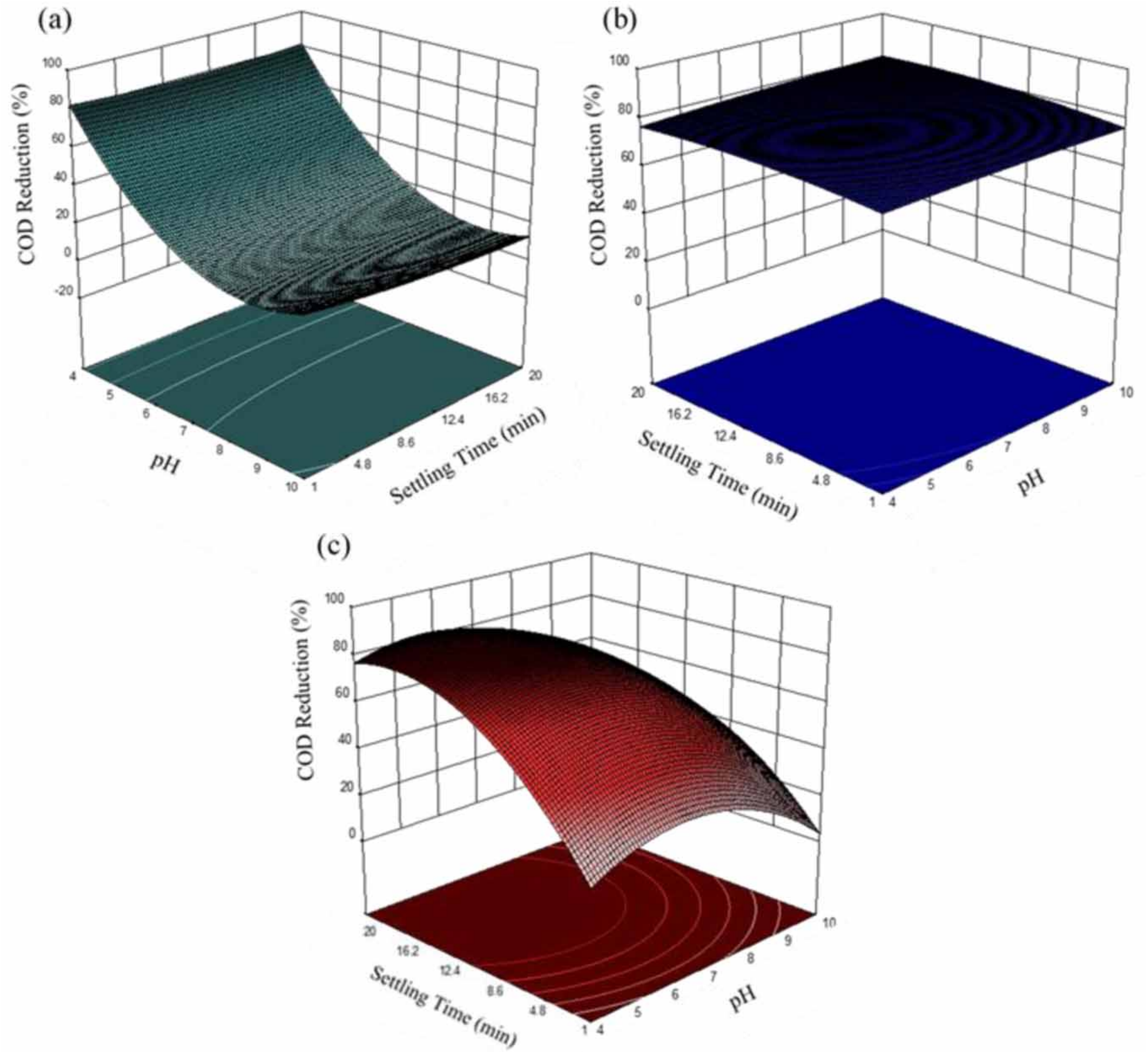


Figure 4 | Three-dimensional response surface plots of the effect of pH and settling time for COD removal (%) using (a) LE, (b) LE-g-DMC and (c) alum as coagulants in agriculture wastewater treatment.

pH, 12.51% concentration and 3.4% time), 12.50% (8.27% pH^2, 4.09% $concentration^2$, 0.14% $time^2$) and 3.40% (3.28% pH and concentration, 0.07% pH and time and 0.05% concentration and time), respectively. In the case where LE-g-DMC was used as coagulant, the total contribution effects of the linear, interaction and quadratic terms were found to be 58.75% (0.01% pH, 58.53% concentration and 0.21% time), 0.13% (0.06% pH and concentration, 0.02% pH and time and 0.05% concentration and time) and 41.32% (0.38% pH^2, 40.93 $concentration^2$, 0.01% $time^2$) respectively. This result shows a good agreement with the three-dimensional response surface result, where the pH and settling time had limited effect on turbidity removal when LE-g-DMC was used as a coagulant.

When alum was used as coagulant for turbidity removal, linear terms (8.55% pH, 22.48% concentration and 22.79% time) had the highest contribution effect, followed by quadratic terms (11.08% pH^2, 13.74% $concentration^2$, 17.53% $time^2$) and interaction terms (0.60% pH and concentration, 1.23% pH and time and 7.53% concentration and time). A similar trend was observed for the COD removal when alum was used as a coagulant. The highest contribution effect was found for linear terms, followed by quadratic terms and interaction terms, with total contribution of 66.37% (0.15% pH, 65.95% concentration and 0.26% time), 33.44% (0.02% pH^2, 33.18% $concentration^2$, 0.25% $time^2$) and 0.34% (0.21% pH and concentration, 0.01% pH and time and 0.11% concentration and time), respectively.

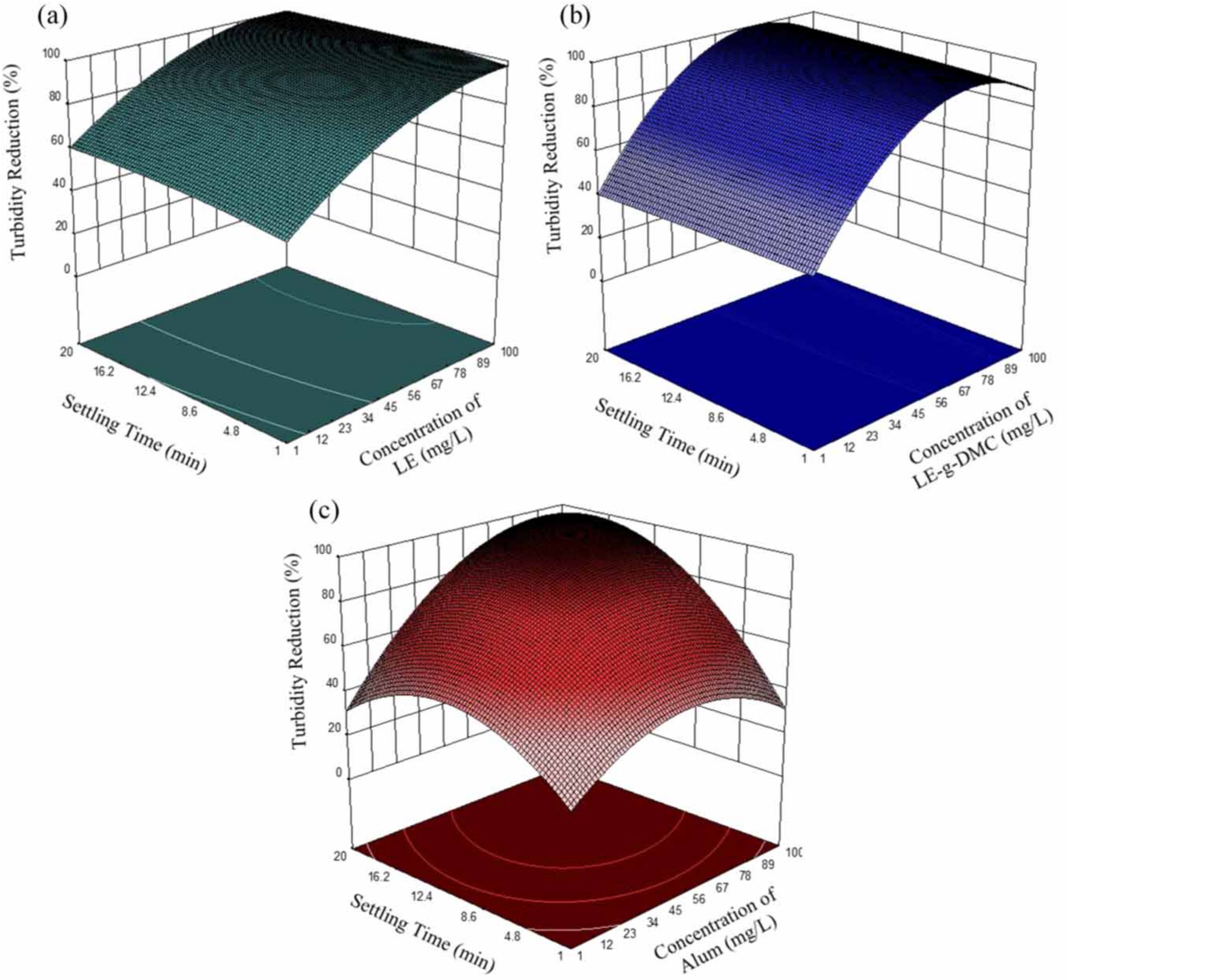


Figure 5 | Three-dimensional response surface plots of the effect of concentration of coagulants and settling time for turbidity removal (%) by using (a) LE, (b) LE-g-DMC and (c) alum as coagulants in agriculture wastewater treatment.

The operational parameters of the turbidity and COD removal are required to be further optimized. The coded regression equations of the turbidity and COD removal for LE, LE-g-DMC and alum as coagulant are illustrated in Equations (5)–(10) in Table 2.

The aforementioned equations were used to determine the value of optimum influencing factors to achieve the maximum turbidity and COD removal when LE, LE-g-DMC and alum were used as a coagulant. In the case where LE was used as a coagulant, the optimum conditions to achieved maximum turbidity of 98.55% and maximum COD removal of 79.87% were found to be pH 4.0, 88.46 mg/L concentration of LE and 6.9 minutes settling time. When LE-g-DMC was used as a coagulant, the optimum conditions were with pH 6.7, 63.08 mg/L concentration of LE and 5 minutes settling time to achieve 99.83% turbidity removal and 80.32% COD removal. Contrastingly, the optimum conditions to achieve maximum turbidity removal (99.27%) and COD removal (79.95%) for alum were pH 6.7, 89.30 mg/L concentration of alum and 19.8 minutes of settling time.

In agriculture wastewater treatment, both synthesized coagulants work effectively for both turbidity and COD removal, and achieved up to 99% of turbidity removal and 80% of COD removal. Also, LE-g-DMC works effectively across pH ranges from pH 4 to pH 10, unlike LE which only works effectively at acidic pH while alum only works effectively in near-neutral pH. Moreover, LE-g-DMC

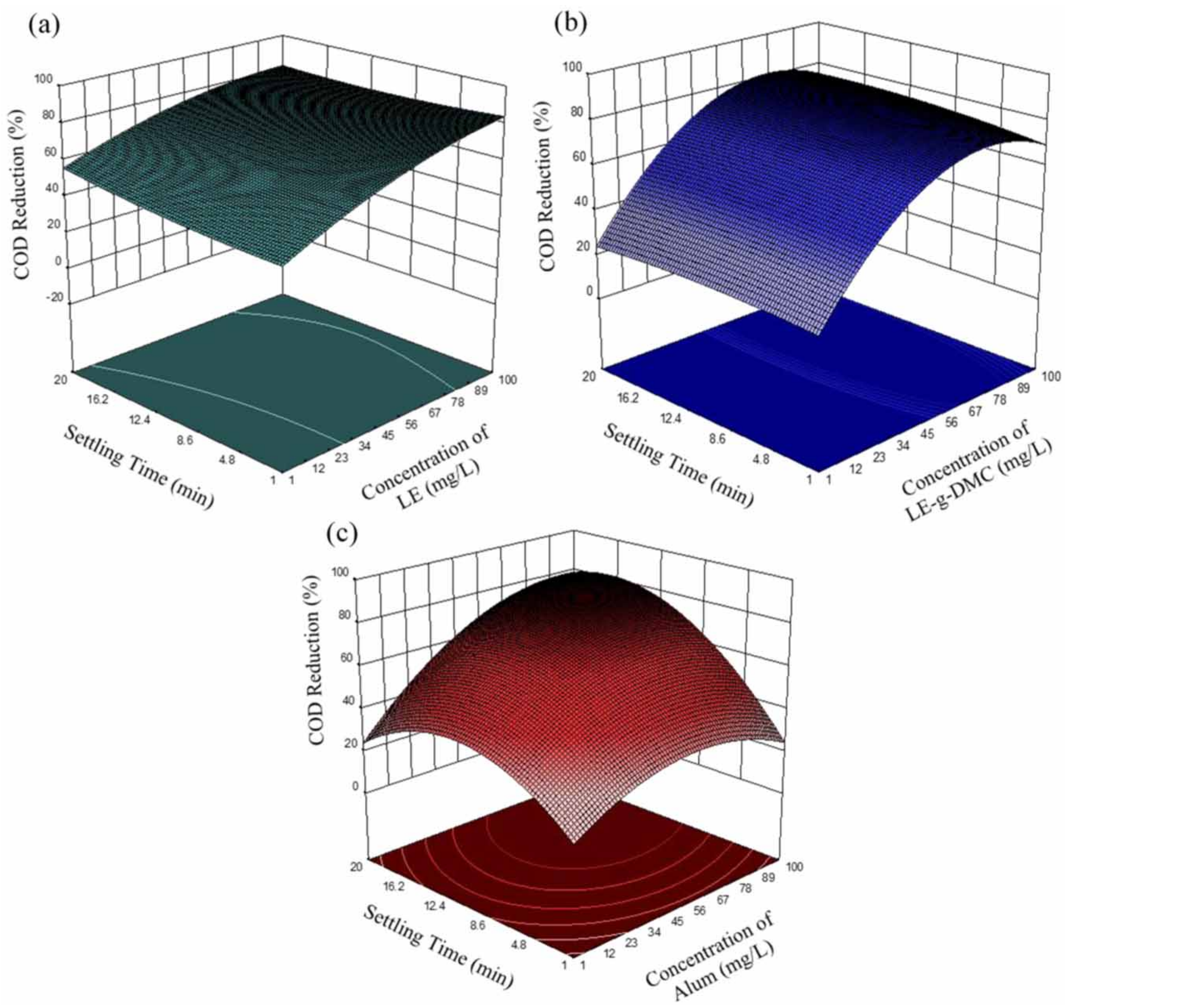


Figure 6 | Three-dimensional response surface plots of the effect of concentration of coagulants and settling time for COD removal (%) by using (a) LE, (b) LE-g-DMC and (c) alum as coagulants in agriculture wastewater treatment.

required an approximately 30% lower concentration as compared to LE and alum at their optimum conditions. In terms of settling time, LE and LE-g-DMC required 75% and 65% less settling time as compared to the alum. In a nutshell, both LE-g-DMC and LE are promising and effective green coagulants for agriculture wastewater to replace the current chemical coagulants.

Validation

To confirm the validity of the statistical experimental strategies, four confirmation experiments for each design model were conducted. All chosen conditions are listed in Table 3, along with the predicted and experimental results. The predicted values were in agreement with the experimental values, at a 95% confidence interval (<5%), indicating that the three designed models for LE, LE-g-DMC and alum, including the predicted optimum conditions, were accurate and reliable. This also testifies that the RSM approach was appropriate for optimizing the influencing factors of the coagulation–flocculation process for agricultural wastewater treatment.

Sludge produced and sludge volume index

The sludges produced by using different coagulants under optimum conditions were evaluated and the results are illustrated in Figure 7. The agriculture wastewater treatment

Table 2 | Final reduced quadratic model for agriculture wastewater treatment

Coagulants	Response	Coded regression equation	Eqn no.
LE	Turbidity removal	$46.41 - 29.34\mathbf{D}_1 + 12.13\mathbf{D}_2 + 1.35\mathbf{D}_3 - 8.93\mathbf{D}_1\mathbf{D}_2 - 1.36\mathbf{D}_1\mathbf{D}_3 - 1.15\mathbf{D}_2\mathbf{D}_3 + 14.76\mathbf{D}_1^2 - 10.38\mathbf{D}_2^2 - 1.95\mathbf{D}_3^2$	(5)
	COD removal	$16.41 - 26.54\mathbf{D}_1 + 9.23\mathbf{D}_2 + 0.20\mathbf{D}_3 - 6.91\mathbf{D}_1\mathbf{D}_2 - 2.10\mathbf{D}_1\mathbf{D}_3 - 3.10\mathbf{D}_2\mathbf{D}_3 + 27.57\mathbf{D}_1^2 - 5.72\mathbf{D}_2^2 + 2.16\mathbf{D}_3^2$	(6)
LE-g-DMC	Turbidity removal	$97.07 + 0.25\mathbf{E}_1 + 23.05\mathbf{E}_2 + 1.39\mathbf{E}_3 - 1.06\mathbf{E}_1\mathbf{E}_2 + 0.55\mathbf{E}_1\mathbf{E}_3 + 0.97\mathbf{E}_2\mathbf{E}_3 - 2.74\mathbf{E}_1^2 - 28.38\mathbf{E}_2^2 - 0.46\mathbf{E}_3^2$	(7)
	COD removal	$75.79 + 1.17\mathbf{E}_1 + 24.25\mathbf{E}_2 + 1.53\mathbf{E}_3 + 1.94\mathbf{E}_1\mathbf{E}_2 + 0.51\mathbf{E}_1\mathbf{E}_3 + 1.43\mathbf{E}_2\mathbf{E}_3 - 0.59\mathbf{E}_1^2 - 25.32\mathbf{E}_2^2 - 2.19\mathbf{E}_3^2$	(8)
Alum	Turbidity removal	$89.77 - 10.95\mathbf{F}_1 + 17.75\mathbf{F}_2 + 17.87\mathbf{F}_3 - 4.12\mathbf{F}_1\mathbf{F}_2 - 5.89\mathbf{F}_1\mathbf{F}_3 + 14.53\mathbf{F}_2\mathbf{F}_3 - 18.34\mathbf{F}_1^2 - 20.34\mathbf{F}_2^2 - 23.08\mathbf{F}_3^2$	(9)
	COD removal	$72.93 - 11.50\mathbf{F}_1 + 15.38\mathbf{F}_2 + 15.15\mathbf{F}_3 - 3.16\mathbf{F}_1\mathbf{F}_2 - 4.98\mathbf{F}_1\mathbf{F}_3 + 11.73\mathbf{F}_2\mathbf{F}_3 - 19.37\mathbf{F}_1^2 - 15.73\mathbf{F}_2^2 - 21.62\mathbf{F}_3^2$	(10)

$\mathbf{D}_1$ $\mathbf{E}_1$, $\mathbf{F}_1$ = pH; $\mathbf{D}_2$ $\mathbf{E}_2$, $\mathbf{F}_2$ = concentration of coagulant; $\mathbf{D}_3$, $\mathbf{E}_3$ $\mathbf{F}_3$ = settling time.

using alum produced the highest amount of the sludge (13.8 mL/L), followed by LE with an average 10.6 ml/L of sludge produced. Among all the tested coagulants, LE-g-DMC produced the least sludge with an average of 8.23 mL/L. This result demonstrates the feasibility of the LE-g-DMC for agriculture wastewater treatment as it produces 40% and 22.3% less sludge, as compared to alum and LE, respectively.

In terms of SVI, LE-g-DMC produced the lowest SVI (4.48 mL/g) as compared to the LE (5.77 mL/g) and alum (7.51 mL/g). Theoretically, the low SVI of LE-g-DMC indicated the good settling characteristic of the flocs/sludge produced. The low SVI in LE-g-DMC was caused by the ability of the grafted polymer to produce a stronger and denser floc through effective charge neutralization and bridging mechanism, as discussed earlier. The good settling properties of the flocs produced by LE-g-DMC further showed its economic feasibility in agriculture wastewater treatment as it significantly reduces the settling time of the flocs produced.

Cost analysis of lentil-based coagulant in agricultural wastewater treatment

Economic feasibility analysis is extremely important as it affects the commercialization potential of a product in industrial applications. The major cost in the coagulation–flocculation process is made up from material cost and sludge management costs. Cost analysis to valorize LE and LE-g-DMC in turbidity and COD removal was performed based on these two aspects. Table 4 shows the material costs of using different coagulants in the treatment process (LE, LE-g-DMC and alum). LE was the best treatment option in agriculture wastewater treatment, as it had the lowest material cost (USD0.0265) as compared to LE-g-DMC and alum, with USD0.0277 and USD0.0384/m^3 of water treated. This finding revealed that LE and LE-g-DMC could reduce by up to 30.9% and 27.9% the material cost, which demonstrates the high feasibility of LE and LE-g-DMC as a plant-based coagulant for turbidity and COD removal in agriculture wastewater treatment.

Apart from the material cost, the sludge management costs of using LE, LE-g-DMC and alum as coagulants were evaluated. Based on the data from the US Environmental Protection Agency, the sludge's management cost ranged from USD35 to USD38 per dry ton. The use of LE and LE-g-DMC as coagulants in agriculture wastewater generated 22.2% and 40.4% less sludge, which could save up to USD15.2 per ton of the sludge produced. Contrastingly, the sludges generated using plant-based coagulant are

Table 3 | Confirmation experiment for agricultural wastewater treatment

			Turbidity removal (%)			COD removal (%)		
pH	**Concentration of coagulant (mg/L)**	**Settling time (min)**	**Predicted**	**Actual**	**Error**	**Predicted**	**Actual**	**Error**
LE as coagulant								
7.7	25.75	8.0	32.00	35.12	3.12	6.19	8.45	2.26
6.6	56.84	4.4	50.80	52.17	1.37	22.83	24.16	1.33
4.4	53.60	12.0	83.86	84.39	0.53	60.57	63.96	3.39
4.0	88.46	6.9	99.55	99.43	0.12	79.87	80.54	0.67
LE-g-DMC as coagulant								
6.1	10.06	3.3	58.12	54.73	3.39	37.74	32.95	4.79
8.1	28.13	4.1	69.00	66.43	2.57	47.49	46.01	1.48
4.6	45.48	3.7	84.50	82.82	1.68	63.61	65.26	1.65
6.7	63.08	5.0	99.83	99.72	0.11	80.32	81.78	1.46
Alum as coagulant								
9.3	71.36	1.0	30.00	30.74	0.74	16.91	13.63	3.28
5.0	29.60	3.1	50.17	52.83	2.66	37.91	37.23	0.68
6.4	63.14	5.35	75.52	74.85	0.67	60.79	62.85	2.06
6.7	89.30	19.8	99.27	99.59	0.32	79.95	80.36	0.41

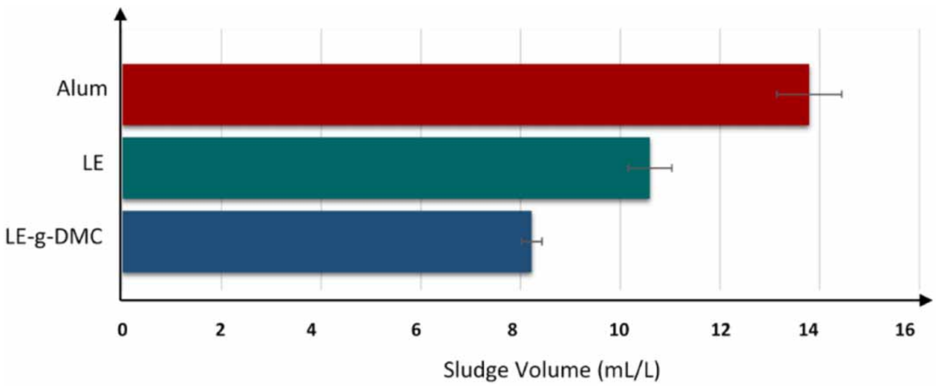


Figure 7 | Sludge generated after the agriculture wastewater treatment.

Table 4 | Cost of LE, LE-g-DMC and alum in agricultural wastewater treatment

Coagulants	**Unit price (USD/kg)**	**Optimum concentration, $\times 10^{-3}$ (kg/m^3)**	**Total material cost, $\times 10^{-3}$ (USD/m^3)**
Alum	0.43	89.30	38.39
LE	0.30	88.46	26.53
LE-g-DMC	0.434	63.08	27.68

generally biodegradable organics which may be reused for other purposes. Hence, valorization of lentil-based coagulants in potable water treatment offers a few significant advantages in terms of material and sludge disposal cost reduction.

CONCLUSION

The use of lentil-based natural coagulants in agricultural wastewater treatment was successfully evaluated in this experiment. A few significant findings are concluded as follows.

- The high correlation of the designed model for the optimization process revealed the suitability of the second-order polynomial model using three-level BBD as an optimization tool. The quadratic terms of pH, concentration of coagulant, and settling time were found to have a positive effect on the turbidity and COD removal.

- The optimum conditions for LE to achieve 99.55% and 79.87% of turbidity and COD removal were pH 4, 88.46 mg/L of LE and 6.9 minutes of settling time, whereas the optimum conditions for LE-g-DMC to achieve 99.83% and 80.32% of turbidity and COD removal were pH 6.7, 63.08 mg/L of LE-g-DMC and 5 minutes of settling time.
- LE-g-DMC required approximately 30% lower concentration as compared to LE and alum, at their optimum conditions. LE and LE-g-DMC also required 75 and 65% less settling time as compared to the alum.
- LE-g-DMC produced flocs with excellent settling ability (4.48 mL/g) and produced the least volume of sludge (8.23 mL/L) as compared to LE and alum.
- The use of lentil-based coagulants reduced by up to 30.9% the material cost and 40% the sludge management cost in agricultural wastewater treatment.

Both LE and LE-g-DMC surprisingly outperformed alum in all aspects. They reveal a high potential as a sustainable choice for turbidity and COD removal in agricultural wastewater treatment to replace the current chemical coagulants. The treated water may be reused for irrigation purposes to resolve the water scarcity issue and future research in this area is needed. This study not only successfully provides a detailed insight into the performance of both lentil-based coagulants in agricultural wastewater treatment, but also provides valuable information on the optimization study for other applications in related fields.

ACKNOWLEDGEMENT

This research was funded by PETRONAS through YUTP grant (015LC0-169). The authors would like to express deepest gratitude to Mdm. Norhayama Bt Ramli for technical assistance and Universiti Teknologi PETRONAS for providing laboratory facilities.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 30 May 2020; accepted in revised form 12 August 2020. Available online 27 August 2020