Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.28378

256 (2022) 125–138
April

Statistical model for comparing the performance of two coagulants using response surface model

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Received 5 September 2021; Accepted 2 March 2022

ABSTRACT

In this research, the performances of modified tannin and aluminium sulfate (alum) for stabilized leachate treatment were investigated and compared using coagulant dosage, pH, and rapid mixing speed as the input variables. Four different responses were used to compare the treatment performances; the responses are, chemical oxygen demand (COD), color, ammoniacal nitrogen (NH_3–N) and total suspended solids (TSS). The results of the analysis for 36 experiments showed that the optimum operating conditions for 1% modified tannin and 10% alum are a coagulant dosage of 6 mL, a pH of 9 and a rapid mixing speed of 100 rpm. The optimum removal efficiencies of COD, color, NH_3–N and TSS using 1% modified tannin were 42.86%, 54.38%, 39.39% and 60.33% respectively, and using 10% alum were 60.71%, 63.09%, 42.42% and 60.33%, respectively. The findings revealed that the effectiveness of modified tannin for the treatment of landfill leachate was significant using a ten-time lower dosage concentration than alum. This study will help better understanding the behaviour of organic and inorganic coagulants for wastewater treatments using the same polynomial model.

Keywords: Tannin; Alum; Coagulation; Face-centered design; Polynomial model; Removal

1. Introduction

Landfill leachate is simply defined as a contaminated liquid that oozes out of the landfill. It is mainly originating from rain, melted snow and/or from the waste that has been dumped into the landfill cells. The generation of landfill leachate very much depends on the amount of municipal solid waste (MSW) that is being discarded into the landfills. Poor recycling and segregation of MSW affects the quality and quantity of landfill leachate. Based on the statement released by the Solid Waste Management and Public Cleansing Corporation (SWCorp), about 38,000 tonnes of domestic waste is generated daily in Malaysia. Almost half of that is daily food waste where 24% could be avoided which quantitatively means that more than 4,000 tonnes of the wasted food is edible [1]. Including but not limited to, two factors that directly affect the landfill leachate generation the most in Malaysia are annual heavy rain in such a

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1944-3994/1944-3986

tropical country as well as a yearly increase of population according to the United Nation world population statistics. With regard to the Peninsular Malaysia, the Malaysian Meteorological Department (MET) has stated in their latest available annual report that the annual total rainfall ranges from 1,800 and 3,900 mm [2]. It is approximately 3 million L/d and counting of highly polluted landfill leachate is generated in the country [3] with a total reported landfills of 166 that are still in service [4] in which most of them could cause severe environmental pollution for not being fitted out with effective leachate treatment plants.

Landfill leachate consists of large amount of versatile pollutants. It could contain large amount of biodegradable and non-biodegradable organic matter, inorganic macro-components such as ammonia, heavy metals and other xenobiotics in addition to its repulsive color and foul odor [5]. In a statement released by the United States Environmental Protection Agency (USEPA), landfill leachate may also contain household hazardous contaminants originated from paints, batteries, cosmetics, pharmaceuticals and cleaning chemicals as well as bulky wastes such as household appliances and construction sites [6]. Regardless the age of the landfill, the strength or in other words, the complexity of leachate mixture generated of varying molecular weight fractions as low as 2,000 up to 100,000 Da highly contributes to the difficulty of treatment which may result in exceeding the environmental threshold discharge limits [7]. Thus, discharging untreated and/or partially treated landfill leachate exerts a potential threat that could cause a damaging impact and severe harm on the environment and human health. Therefore, effective landfill leachate treatment is required. Generally, the volume, quality and complexity of the landfill leachate generated along with the environmental compliance discharge limit are the main factors in which the selection of treatment technologies to be used is determined upon. More often than not, landfill leachate requires a series of physicochemical and biological treatments for the effluent to comply with the corresponding discharged limits. Biological treatments such as up-flow anaerobic sludge blanket (UASB) and sequencing batch reactor (SBR) are extremely effective for the removal of biodegradable organic matter and ammonia [8]. However, the older and more hazardous landfill leachate, the more constraints of the current technology where it typically relies solely on the conventional biological treatment technologies [7], that is, the older and more complex the leachate, the less effective the biological treatments. This arises as the time passes by, the mixture of non-biodegradable, refractory organic matter and inorganic waste are accumulated in mature leachate an old landfill develops. Therefore, the need for physicochemical treatment technologies that are either implemented pre- or post-biological treatments or both together are crucial. Coagulation–flocculation process is commonly used as a physicochemical treatment technology that is generally followed by sedimentation or a dissolved air floatation (DAF) system, chemical precipitation, oxidation, and activated carbon filtration. Coagulation–flocculation is a chemical water and wastewater treatment technology to remove contaminates via either charge neutralization, bridging and/or absorption dependent on the type of coagulant and flocculant used as well as agitation/mixing conditions. This treatment technique consists of the addition of a substance that is either inorganic or organic, through a specific chemical reaction, forms an insoluble end product that serves to remove pollutants from the wastewater in which polyvalent metals are commonly used [9]. Coagulation end product is usually called as microfloc where the end product of the flocculation process is often termed as pinfloc and/or macrofloc.

Coagulants are generally classified as an organic and inorganic substances. In wastewater treatment, inorganic coagulants are widely used for their effectiveness in removing contaminants and cost effective. Inorganic coagulants are commonly categorized as aluminium (Al) and iron (Fe) based coagulants. Al-coagulants that have been abundantly used in wastewater treatment such as aluminium sulfate, $Al_2(SO_4)_3$ which is commercially known as alum and poly-aluminium chloride (PAC) all of which are trivalent cations. Whereas Fe-coagulants which are the second widely used inorganic coagulants after Al-coagulants could either be trivalent cations such as ferric sulfate, $Fe_2(SO_4)_3$ and ferric chloride, $FeCl_3$ or bivalent such as ferrous sulfate, $FeSO_4$. Alum is considered to be the most widely used inorganic coagulant in wastewater treatment plants. It is inexpensive and effective for the removal of pollutants such as suspended solids. Similar to all metal coagulants, alum produces aluminium precipitates in the midst of the coagulation process so as to remove pollutants. Being a trivalent cationic coagulant, alum is more preferable than many other bivalent coagulants in treating wastewater. Alum usually comes in a hydrated crystalline form $[Al_2(SO_4)_3{\cdot}xH_2O]$ in which the degree of hydration, x ranges from 14–21 [10]. For being cheap and effective, the most common hydrated form of alum in wastewater treatment plants is decaoctahydrated where $x = 18$ [11]. The main drawback about alum besides its sludge volume after treatment is the add-up of Al-content into the sludge that would have to be further treated. Above and beyond, it would eventually end up in the effluent if no further treatment to be employed such as chemical precipitation and activated carbon filtration. As a result, it would destructively affect the quality of the discharge and possess a threat to the ecosystem and human health. It is reported that beyond certain concentrations of aluminium in water could cause dementia and Alzheimer's [12].

On the other hand, organic coagulants are characterised into two main groups either as polyamines and polydadmacs or melamine formaldehydes and tannins [13]. These organic coagulants could be natural, synthetic or modified organic coagulants. In comparison to inorganic coagulants, organic ones usually require lower dosage, generate lower volume and density of the sludge and flocs as well as they barely have an effect on the pH. What makes organic coagulants tannin in particular superior to metal coagulants is the nontoxicity and biodegradability of the sludge generated as well as no additional metal contents are discharged with the effluent. However, it is highly believed that organic coagulants have not generally been as applicable for an extensive variety of wastewater particularly with raw water of low turbidity as compared to inorganic coagulants. Tannin is the second most abundant natural aromatic biomolecule extracted from the biomass after lignocellulose [14]. The chemical structure of tannin is quite complex and difficult to confirm due to its versatility. Tannins are generally defined as complex compounds of polyphenols in which their reactivity and complexity are mainly due to its functional groups of phenols and aliphatic hydroxyls. Tannins by nature are amphiphilic compounds and they are generally classified as hydrolysable, complex and condensed tannins. These complex substances could possess molecular weights between 500 and 3,000 Da [15]. In short, condensed tannins are more attractive commercially for their availability and low cost. More than 90% of commercial tannins worldwide are condensed tannins which are made up of 3–8 repeated units of flavonoid each of which has two different phenolic rings of distinct reactivity [14]. In water and wastewater treatment technologies, this type of tannin has lately been investigated as biocoagulant-flocculant. Therefore, tannin is simply defined as a biodegradable anionic polymer in the corresponding discipline. Recently, several studies evaluated the performance of different types of coagulants for removing pollutants from different types of wastewater. Their findings for comparing the performance between different coagulants was reported using individual experimental approach. In this research, the performance of aluminium sulfate decaoctahydrate, [$Al_2(SO_4)_3 \cdot 18H_2O$] as an inorganic and tannin as an organic coagulants for leachate treatment was evaluated and compared using one response experimental model. The statistical relationship between all factors and responses was evaluated simultaneously in the same experimental model using response surface methodology (RSM). Response surface has been used for finding the best operating conditions in various fields [16–18].

2. Material and methods

2.1. Sampling area and technique

Sungai Udang Sanitary Landfill (SUSL) site is located in the sea-side city of Sungai Udang, Central Malacca district, about 3 km to the northeast of Sungai Udang town and around 9 km west to the Straits of Malacca, Malaysia. A recent study conducted in Sungai Udang found out that the average annual rainfall was about 2,000 mm with temperature ranging from 21°C to 32°C [19]. After the recent closure of the landfill site at Krubong at the end of 2014, SUSL has been operating ever since which makes it the only sanitary landfill that is still operating in Malacca with a land area of 26 ha. It has been receiving more or less 25,000 tonnes of garbage each month [20]. SUSL is equipped with a landfill leachate treatment facility which has lately been operated by GreenViro Solutions Sdn. Bhd. According to the available information provided by SWM Environment Sdn. Bhd., the ex-operator, SUSL has a landfill capacity of more than 700,000 tonnes of waste and a capacity of leachate treatment plant of about 200 m^3/d with a gas venting system. The Malaysian Ministry of Housing and Local Government has announced earlier that SUSL would be going to be one of its kind to adopt and develop the waste-to-energy (WtE) project by 2021 [21].

The raw leachate samples were collected manually from the equalization pond (EqP) in SUSL treatment plant. In March 2021, individual samples of 25 L were manually collected over a period of time not more than 15 min intervals. They were collected by a sampling rod at a depth of 0.3 m and then transferred into high density polyethylene (HDPE) containers which had been washed with detergent, rinsed with deionized water (DIW) several times, and fully ambient air dried in the laboratory prior to the collection time. All of the samples were immediately stored into approximately 5°C–4°C in a styrofoam ice box, transported to the designated laboratory, and kept in the fridge at 4°C in order to minimize any further biological and chemical reactions.

2.2. Investigated coagulants

For the purpose of this study, tannin as an organic coagulant and alum as inorganic were both used in liquid form of certain concentrations. Tannin used in this study was commercially provide by a local supplier as a modified tannin that was said to be extracted from Acacia mearnsii, universally known as black acacia or wattle in Brazil. As for alum, it was locally supplied as a commonly commercial product of aluminium sulfate decaoctahydrate, [$Al_2(SO_4)_3 \cdot 18H_2O$]. This commercial alum contains around 15% w/w alumina, Al_2O_3 while in terms of aluminium, it has about 8% w/w Al.

2.3. Tannin characterization

Modification of tannin in order to further increase its removal efficiency for pollutants from wastewater was successfully accomplished via Mannich reaction in which tannin is cationized by the reaction between aldehyde and amine compounds. This Mannich reaction has given tannin its amphoteric character by the addition of amine, and it is thus commercially named as modified tannin. According to literatures, the possible products of the modification of tannin extracted from Acasia via Mannich reaction dependent on the amine compound used as a reactant. To further investigate the existence of the main possible functional groups in modified tannin, the corresponding infrared (IR) spectrum using Fourier-transform infrared (FTIR) spectroscopy was generated as shown in Fig. 1. To begin with, FTIR analysis alone is not meant to confirm the nature of the compound that is being studied in which other analysis such as nuclear magnetic resonance (NMR) is needed yet, it could predict the compound by determining the presence of its functional groups. Knowing that the tannin used in this study was commercially supplied as modified tannin, FTIR analysis was adequately done to identify and possibly spotlight its main functional groups. To ease the analysis of the IR spectrum obtained for modified tannin, the bands range- where its functional groups could possibly present within- were highlighted in different colors. In the blue region of (3,500–2,600) cm^{-1}, the observed two peaks could indicate the existence of amine and hydroxyl groups that probably overlapping each other. Due to that, some suggestions could be made. The sharper peak shows secondary amine while the other shows a hydroxyl group. Another approach is that these two well-noticed lumpy peaks could

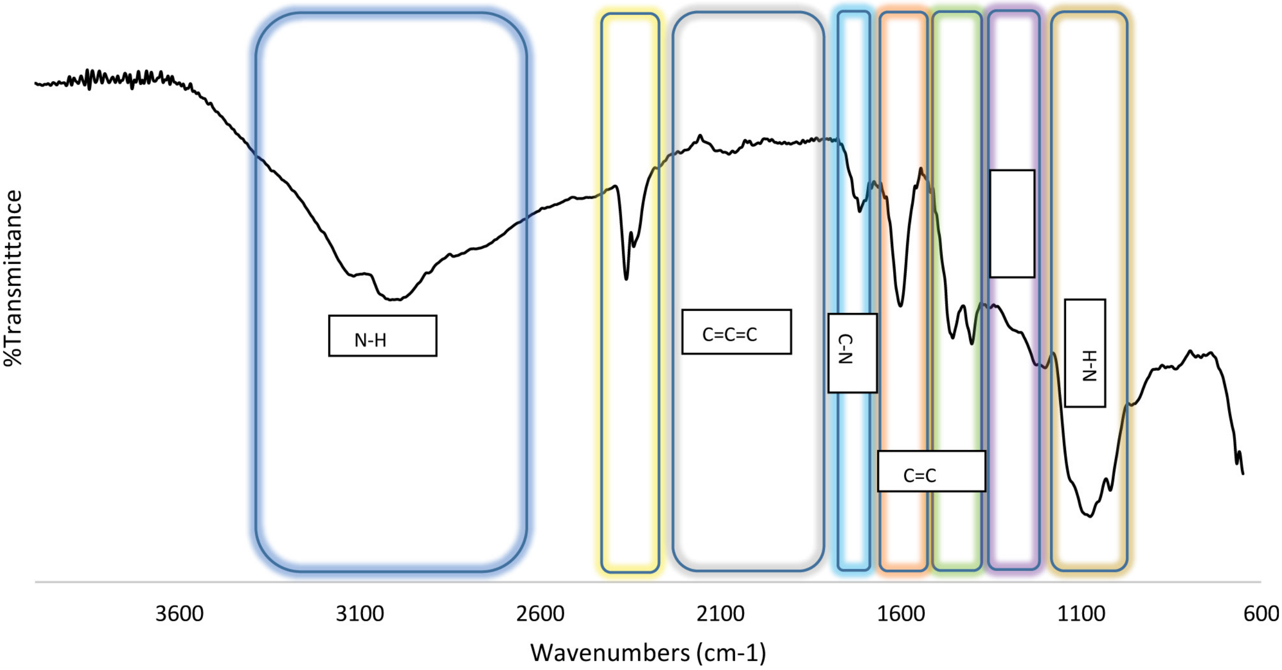

Fig. 1. IR spectrum of the modified tannin utilized in this study using ATR-FTIR.

also imply the existence of primary amine. The broadness of this band may highly indicate the presence of amine salt. All of which are possible for the proposed chemical structures of modified tannin. Whereas tertiary amine never shows any peak in this region. For the next region, however, it is not expected to observe any band in the yellow region as they usually indicate the presence of triple bonds containing compounds which is not applicable to modified tannin. The peak in this region could be due to the intrusion of carbon dioxide from the environment as the FTIR technique used here was attenuated total reflectance (ATR) technique which is prone to such interference. As for the possible overtone in the grey region, it shows an aromatic compound. The peaks and shoulders in the light blue region of 1,750–1,650 cm^{-1} shows the C–N link where the ones from 1,650 to 1,550 cm^{-1} in the orange region either confirms a primary amine N–H or the aromatic C=C. In the green region of 1,500–1,350 cm^{-1} the peaks are also associated with aromatic rings as well as the presence of phenol. The shoulder in the purple region between 1,300–1,250 cm^{-1} 1indicates an aromatic ester C–O bond. The brown region of 1,200–1,000 cm^{-1} shows the N–H aliphatic amine.

2.4. Experimental design

A set of preliminary experiments were performed in order to optimize the experimental design for this study. Based on that, the experimental treatment conditions and variables were determined in response to the selected parameters. Orbital shaker was employed to simulate the coagulation-flocculation process for the treatment of raw landfill leachate samples. Total of 36 runs were performed in which 18 runs were conducted for each type of coagulant. Three different operating conditions which are dosage, pH and rapid mixing speed were examined for the removal efficiencies for the selected parameters; chemical oxygen demand (COD), color, ammoniacal nitrogen (NH_3–N) and total suspended solids (TSS). The raw landfill leachate samples were brought to room temperature and well-shaken before transferring 100 mL of the sample into a 250 mL-conical flask for each run. The pH of each sample was adjusted to the required value, ranging from 5.00 to 9.00, prior to the addition of coagulants. The pH adjustment of the sample was done by adding 5 M of sodium hydroxide for basic medium while 5 M of sulfuric acid for acidic medium. For the high alkalinity of the sample, such concentrations were preferably used in order to avoid diluting the sample. Subsequently, dosages of 0.01 w/v tannin including 1.00, 3.50 and 6.00 mL were separately added to each sample accordingly. In the same manner, 0.1 w/v alum dosages were used. Three different speeds of rapid mixing were set to include 100, 175 and 250 rpm. A total of 60 min of the treatment agitation process was set for each run in which the rapid mixing was conducted for 15 min followed by a slow agitation at 60 rpm for 45 min. Then, the liquor was settled for 60 min to develop sedimentation and separation. The effluent was gravity-filtered and the supernatant was thoroughly shaken for further quantitative post-analysis to determine the removal efficiencies of each coagulant under the corresponding set of conditions for the selected parameters after each run.

2.5. Analytical study

All parameters in this study were analyzed according to the standard methods for the examination of water and wastewater (APHA) and methods for chemical analysis of water and wastes (USEPA). Five parameters; including pH, the concentrations of COD, color, NH_3–N and TSS were tested before and after each run. Four parameters; COD, color, NH_3–N and TSS signified the investigated treatment responses. Prior to each analysis and designated treatment, leachate samples were ensured to be brought to room temperature and well-homogenized before each run. The initial pH of the raw leachate was measured via portable digital pH meter in situ. HACH DR/2800 (Loveland, Colorado, United States) was used to help determine COD, color, NH_3–N and TSS. COD was measured by method 8000, a reactor digestion method at wavelength of 620 nm. Apparent color was determined by method 8025 at 455 nm. NH_3–N was tested by method 8155 and method 10031 used for high range (HR), a salicylate method at 655 nm. TSS was measured by method 8006, a photometric method at 810 nm. Furthermore, total dissolved solids (TDS), electrical conductivity (EC) and salinity were determined by portable electric conductivity meter, Mettler Toledo FE30 FiveEasy benchtop conductivity meter. Alkalinity in terms of $CaCO_3$ was determined by titration. Flame atomic absorption spectrometer (FAAS) was utilized for the analysis of metals and heavy metals by method 200.2 [22]. Concentrated nitric acid HNO_3, was used in this method to meet the compatibility of the instrument and the high solubility of their nitrate salts in the sample.

3. Statistical analysis

Face-centered composite design was employed [23,24] to investigate the effect of four factors, namely dosage of coagulant (*A*), mixing speed (*B*), pH (*C*) and type of coagulants, on four parameters COD, color, ammonia and TSS removals from landfill leachate, in order to find the optimum operating conditions for the input variable and for each coagulant that result maximum removals. The selected levels for the input variable are presented in Table 1. The total number of experiments was 36 experiments (18 experiments for each type of coagulant) (Table 2). A mathematical model was developed to optimize the process by finding the best operating conditions for the selected input variables so as to maximize the four removals.

4. Results and discussion

The characteristics of the raw landfill leachate sample that was collected for this research are presented in Table 2. The treatment responses selected for this research are COD, color, ammonia and TSS. The pH, COD and ammonia of the landfill leachate are considered to be among the most common indicators used to characterize the landfill. Based on that, the analysed sample of the landfill leachate presumes that the landfill cells where the leachate is generated from is in the methanogenic phase. The average pH was found to be basic at 8.52 and the mean COD and ammonia concentrations were 4,550 and 2,650 mg/L, respectively. The pH usually increases till steady when transitioning from early stages of aerobic and anaerobic acid phases to methanogenic where all carboxylic acids and other end-products accumulated are consumed and converted mainly to methane. In this phase of methanogenesis compared to early stages, the COD concentration plumps as time passes compared to early phases in which the highest COD concentration could be measured at about more than 10,000 mg/L, depending on the composition of the landfill, as organic matter did not undergo further decomposition yet. The COD would eventually reach to a steady pool concentration as only refractory matter exists. Unlike ammonia, it keeps to mount up as the decay of organic matter and mineralization process takes place where the highest concentration is usually detected in the methanogenic phase. The maximum ammonia concentration of this sample was found to be 3,300 mg/L which is considered to be high when compared to younger landfills reading around by far less than 1,000 mg/L.

The treatment mechanism of both tannin and alum differs from each other. Tannin as a natural organic coagulant works on bringing the particles into flocs through two main principles namely, hydrophobic and hydrophilic interactions. Once natural tannin is added into the wastewater, the hydrophobic-ends of the poly-phenolic compound colloid and clump together triggering its phenolic-ends to be more opened and exposed to further colloid with the particles within the wastewater via Van der Walls interactions resulting in the development of flocs that precipitate and settle. The resultant flocs are usually fragile, loose and tiny that require longer time to settle. However, modified tannin exerts another interaction principle of neutralizing the particles through its cat-ionized-end contributing to further removal of contaminates and much better coherent flocs. While alum as an inorganic coagulant, as it is added to wastewater, there are mainly two possible mechanisms to remove pollutants. In case the wastewater to be treated of high alkalinity such as leachate, that is, the sample used in this research, alum would hydrolyse to form Al-hydroxide precipitates and carbon dioxide causing a slight decrease in pH. In the absence of alkalinity in such industrial wastewater, alum would dissociate to form Al ions and sulfuric acid resulting in a higher drop in pH. As far as leachate is

Table 1
The levels for the selected input variables

Input variable	Natural levels			Coded levels		
	Low	Centre	High	Low	Centre	High
Dosage of coagulant	1	3.5	6	–1	0	1
Speed of mixing	100	175	250	–1	0	1
pH	5	7	9	–1	0	1
Type of coagulant				–1 (Tannin)		1 (Alum)

Table 2
Characteristics of the raw landfill leachate sample

Parameter	Unit	Readings			Std. Limit, (MEQA), 1974
		Minimum	Maximum	Mean	
pH	–	8.43	8.61	8.52	6–9
COD[a]	mg/L	4,200	4,900	4,550	400
Color[a]	Pt-Co	8,000	8,900	8,450	100
NH_3–N[a]	mg/L	2,100	3,300	2,650	5
TSS[a]	mg/L	274	300	287	50
TDS	mg/L	9,390	9,390	9,390	–
EC	µS/cm	20,900	20,900	20,900	–
Salinity	PSU	12.27	12.27	12.27	–
Alkalinity	mg/L as $CaCO_3$	7,507	8,257	7,882	–
Na	mg/L	–	–	9.15[b]	–
Ca	mg/L	–	–	48.9[b]	–
Mg	mg/L	–	–	4.32[b]	–
Fe	mg/L	–	–	13.61[b]	5.0
Cu	mg/L	–	–	0.22[b]	0.20
Cd	mg/L	–	–	0.12[b]	0.01
Pb	mg/L	–	–	0.17[b]	0.10
Mn	mg/L	–	–	0.51[b]	0.20
Ni	mg/L	–	–	3.73[b]	0.20
Zn	mg/L	–	–	0.51[b]	2.0

[a]Selected treatment responses;
[b]Average of five readings obtained by FAAS.

concerned, Al-hydroxide precipitates, $Al(OH)_3$ develop a sweep-floc coagulation producing short polymer chains which help coagulate the particles and settle the flocs as they fall down. Two major observations were recorded in the midst of the research experiments. Modified tannin developed small and less dense flocs that took longer to settle out of the leachate. Alum, on the other hand, established a slightly larger and dense flocs which took less time to settle. The gelatinous $Al(OH)_3$ precipitates, however, formed viscous effluent that took longer time to be filtered. On the contrary, the modified tannin effluent was rapidly filtered.

The results of 36 experiments using face-centered design (Table 3) were analyzed using analysis of variance (ANOVA) [25] to study the effect of input variables (dosage of coagulant (A), rapid mixing speed (B), pH (C) and type of coagulants) on COD, color, ammonia and TSS removals as selected responses. The results of ANOVA are presented in Table 4, the selected input variables showed a strong significant effect on the selected responses which indicates that the input variables are influential variable on the selected removals. Furthermore, quadratic and some interaction effect showed a significant effect on ammonia and TSS.

The data was further analyzed and modelled using a regression equation. A model that best describes the obtained results was built, first-order model for COD and color removals was developed [Eqs. (1) and (2)] and a second-order model was developed for ammonia and TSS [Eqs. (3) and (4)].

$$\text{COD} = +48.07 + 1.8A - 2.3B - 2.99C + 5.77D \tag{1}$$

$$\text{Color} = +60.92 + 2.30A - 3.54B - 4.82C + 9.45D \tag{2}$$

$$\begin{aligned}\text{Ammonia} = {} & +34.00 + 2.73A + 3.33B + 2.73C \\ & + 1.60D - 0.96A^2 - 3.99B^2 + 3.59C^2 \\ & - 1.14AB + 3.03AC - 0.30AD - 1.89BC \\ & - 0.91BD + 0.61CD\end{aligned} \tag{3}$$

$$\begin{aligned}\text{Total suspended} = {} & +32.62 + 8.13A - 6.12B + 4.18C \\ & - 2.06D + 3.09A^2 + 11.01B^2 - 2.99C^2 \\ & - 0.69AB - 3.65AC + 1.37AD - 1.23BC \\ & + 1.12BD + 0.050CD\end{aligned} \tag{4}$$

The results of the analysis showed that the coefficient of determination (R^2) for the first-order models are adequately fitted the data for COD and color. The value of R^2 for COD and color are 88.25% and 90.89% for COD and color removals respectively. Whereas the second-order models are adequately fitted the data for ammonia and TSS. The value of R^2 for ammonia and TSS are 79.89% and 90.16% for ammonia and TSS removals respectively.

The relative contribution of each input variable to each response was directly measured by the regression coefficient in the fitted model in Eqs. (1)–(4). A positive sign for the regression coefficient in the fitted model indicates the ability of the input variable to increase the response, whilst a negative sign indicates the ability of an input variable to decrease the response.

Table 3
Showing the design and the results of the selected responses

Dosage	Mixing speed	pH	Coagulant	COD	Color	Ammonia	Total suspended solids
1.00	250.00	9.00	Al	45.14	57.00	36.36	35.33
3.50	175.00	9.00	Al	49.57	63.00	42.42	35.33
3.50	175.00	5.00	Al	50.00	74.00	33.33	18.00
1.00	100.00	5.00	Al	55.71	74.66	27.27	23.00
3.50	100.00	7.00	Tannin	40.00	51.24	24.24	57.33
1.00	175.00	7.00	Al	53.57	68.37	30.30	30.33
3.50	175.00	7.00	Al	56.00	72.00	36.36	30.33
1.00	250.00	9.00	Tannin	32.86	40.22	30.30	36.33
6.00	175.00	7.00	Tannin	45.71	55.17	33.33	42.33
6.00	250.00	9.00	Tannin	37.14	44.94	39.39	48.00
3.50	100.00	7.00	Al	57.14	74.00	36.36	43.33
1.00	100.00	9.00	Al	51.14	68.80	27.27	47.33
1.00	250.00	5.00	Tannin	44.29	48.09	36.36	24.00
6.00	250.00	5.00	Al	55.43	78.46	36.36	52.67
1.00	100.00	5.00	Tannin	45.71	57.53	21.21	39.67
3.50	175.00	7.00	Tannin	41.43	45.00	30.30	41.33
6.00	250.00	5.00	Tannin	45.71	58.31	36.36	41.67
3.50	175.00	7.00	Tannin	45.71	55.00	36.36	35.00
3.50	175.00	7.00	Tannin	45.71	57.00	27.27	35.67
6.00	175.00	7.00	Al	55.00	71.52	36.36	38.33
3.50	250.00	7.00	Al	51.43	67.00	30.30	30.33
1.00	175.00	7.00	Tannin	41.43	49.00	33.33	29.33
6.00	100.00	5.00	Tannin	51.43	66.18	24.24	55.33
6.00	100.00	5.00	Al	61.43	75.46	24.24	61.00
6.00	100.00	9.00	Tannin	42.86	54.38	39.39	60.33
3.50	175.00	5.00	Tannin	41.43	47.30	33.33	28.00
3.50	175.00	7.00	Al	56.43	73.00	39.39	28.00
1.00	250.00	5.00	Al	53.00	73.09	36.36	24.00
1.00	100.00	9.00	Tannin	41.43	53.00	21.21	50.67
6.00	250.00	9.00	Al	52.86	62.22	42.42	42.67
3.50	175.00	7.00	Al	56.71	73.00	33.33	32.00
3.50	175.00	7.00	Al	56.00	72.00	36.36	29.00
6.00	100.00	9.00	Al	52.71	69.09	42.42	60.33
3.50	250.00	7.00	Tannin	35.71	44.16	30.30	41.00
3.50	175.00	7.00	Tannin	44.29	56.00	30.30	34.67
3.50	175.00	9.00	Tannin	38.57	44.00	42.42	34.67

The effect of various variables on the selected responses are presented in pictorial form using three-dimensional response surface plot (Figs. 2–9), showing the effect of one variable in the presence of other variables.

Based on the observed trend of the data in Table 2, the treatment performances of tannin and alum in response to the removal efficiencies of COD, color, ammonia and TSS had shown an increased tendency as the dosage of the corresponding coagulant was desirably adequate for the treatment. The less or more dosage of a coagulant than the optimum, the less removal of contaminants. For instance, taking tannin as the type of coagulant, at pH 9 and rapid mixing speed of 100 rpm, the removal efficiency of ammonia increased from 21% up to 39% as the dosage of 1% tannin increased from 1 to 6 mL. For rapid mixing speed, the effect on the removal efficiencies of all selected parameters was observed. At 100 rpm, the treatment performances of tannin and alum were optimal in general. It is believed that a reversal reaction leading to lower removals would occur upon the increase of both dosage and agitation speed. Excess or dearth of coagulant dosages beyond the desired amount might lead to the formation of reversed charged particles and hindered active sites. Whereas, beyond optimal agitation speed would probably cause the coagulated particles to be sheared off and disrupting the development of microflocs to further aggregate and stick together resulting in scattered flocs pertaining to a non-desired degree of particles collision. As a good example, at pH 9 and a dosage

Table 4
Showing the results of analysis of variance

Source	Sum of squares	DF	Mean square	F-value	Prob. > F
COD					
Model	1,549.71	4	387.43	58.2	<0.0001
A	64.85	1	64.85	9.74	0.0039
B	105.73	1	105.73	15.88	0.0004
C	179.19	1	179.19	26.92	<0.0001
D	1,199.95	1	1,199.95	180.27	<0.0001
Residual	206.34	31	6.66		
Lack of fit	193.74	25	7.75	3.69	0.0548
Pure error	12.61	6	2.1		
Total	1,756.05	35			
Color					
Model	4,035.26	4	1,008.81	77.30	<0.0001
A	105.69	1	105.69	8.1	0.0078
B	250.88	1	250.88	19.22	0.0001
C	464.89	1	464.89	35.62	<0.0001
D	3,213.79	1	3,213.79	246.24	<0.0001
Residual	404.59	31	13.05		
Lack of fit	310.84	25	12.43	0.8	0.6876
Pure error	93.75	6	15.63		
Total	4,439.85	35			
Ammonia					
Model	990.02	13	76.16	6.72	<0.0001
A	148.73	1	148.73	13.13	0.0015
B	222.18	1	222.18	19.62	0.0002
C	148.73	1	148.73	13.13	0.0015
D	92.06	1	92.06	8.13	0.0093
A^2	4.95	1	4.95	0.44	0.5153
B^2	86.1	1	86.1	7.6	0.0115
C^2	69.81	1	69.81	6.16	0.0211
AB	20.66	1	20.66	1.82	0.1906
AC	***146.89***	***1***	***146.89***	***12.97***	***0.0016***
AD	1.84	1	1.84	0.16	0.6911
BC	***57.38***	***1***	***57.38***	***5.07***	***0.0347***
BD	16.53	1	16.53	1.46	0.2399
CD	7.34	1	7.34	0.65	0.4293
Residual	249.15	22	11.32		
Lack of fit	187.18	16	11.7	1.13	0.4706
Pure error	61.97	6	10.33		
Total	1,239.17	35			

Continued

Table 4 Continued

Source	Sum of squares	DF	Mean square	*F*-value	Prob. > *F*
Total suspended solids					
Model	4,043.47	13	311.04	15.50	<0.0001
A	1,323.08	1	1,323.08	65.93	<0.0001
B	748.11	1	748.11	37.28	<0.0001
C	349.87	1	349.87	17.43	0.0004
D	152.19	1	152.19	7.58	0.0116
A^2	51.88	1	51.88	2.59	0.1221
B^2	657.12	1	657.12	32.74	<0.0001
C^2	48.32	1	48.32	2.41	0.135
AB	7.52	1	7.52	0.37	0.5467
AC	***212.65***	***1***	***212.65***	***10.6***	***0.0036***
AD	37.4	1	37.4	1.86	0.186
BC	24.18	1	24.18	1.2	0.2842
BD	24.95	1	24.95	1.24	0.2768
CD	0.049	1	0.049	#######	0.961
Residual	441.5	22	20.07		
Lack of fit	403	16	25.19	3.93	0.0499
Pure error	38.5	6	6.42		
Total	4,484.97	35			

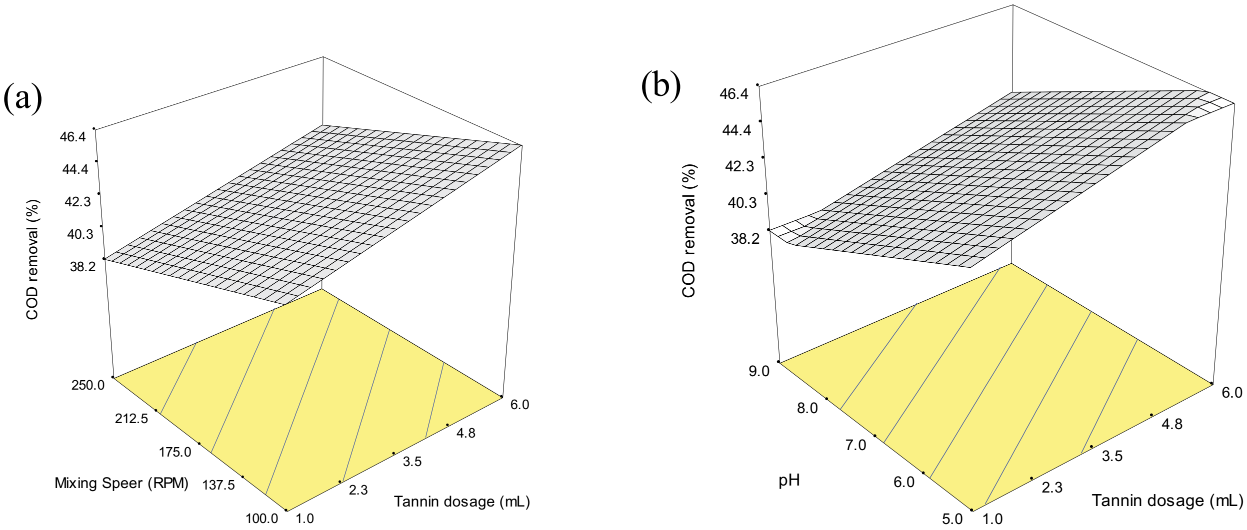

Fig. 2. Effect of tannin dosage, mixing speed and pH on COD removal.

of 6 mL of 10% alum, the removal efficiency of TSS dropped from 60% down to about 43% as the rapid mixing speed increased from 100 to 250 rpm, respectively. However, the pH highly depends on the type of coagulant used in relation to the selected parameter. On the subject of the removal efficiencies of ammonia and TSS as one segment and COD and color as another, tannin and alum were found to generally perform better at basic condition in terms of the removal of the first segment (consider revise sentence). On the other hand, tannin and alum performed better at acidic-neutral medium for the removal of the second segment. When the pH of the sample is more than 7, the ammoniacal nitrogen equilibrium of both ammonia, NH_3 and ammonium, NH_4^+ to some extent shifts towards the non-ionized form, NH_3 which contributes for a better removal of ammonia concentration. Moreover, considering most of the polluted particles are negatively charged, the removal of TSS enhanced at basic medium as the Brownian motion, that is, random movement of the particles in suspension increased caused by the collision and random spatial positions of these particles thus better removal. In comparison to the treatment performances of tannin and alum in terms of the removal efficiencies of ammonia and TSS, the highest removals were achieved at pH 9 where the lowest were by large recorded in acidic media. For the second segment of COD and color removals, it is greatly believed that the presence of

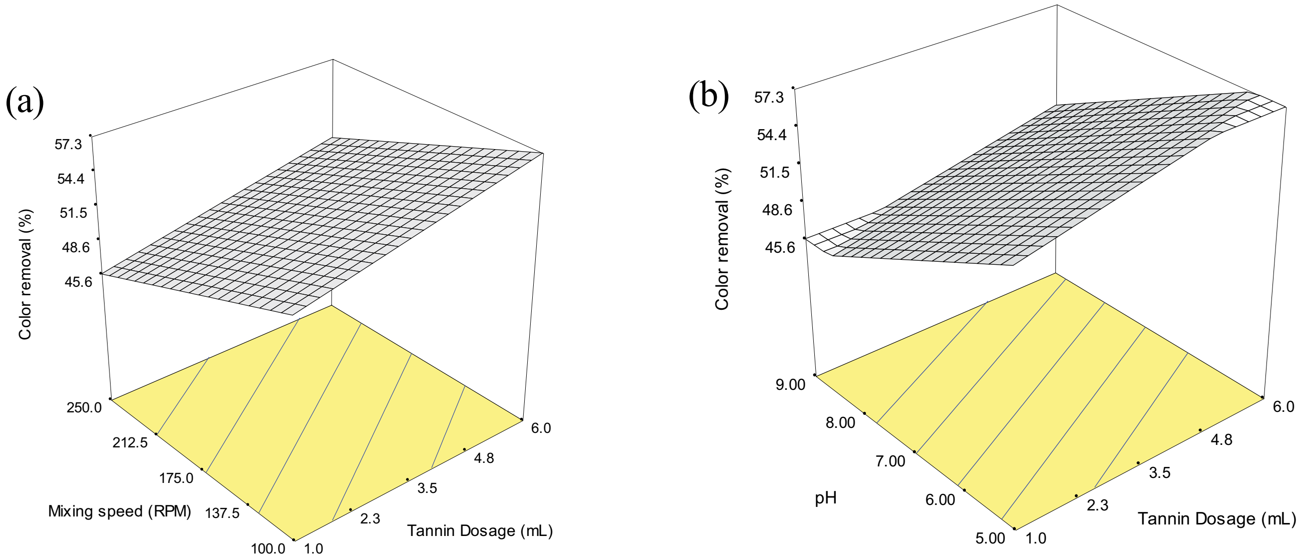

Fig. 3. Effect of tannin dosage, mixing speed and pH on color removal.

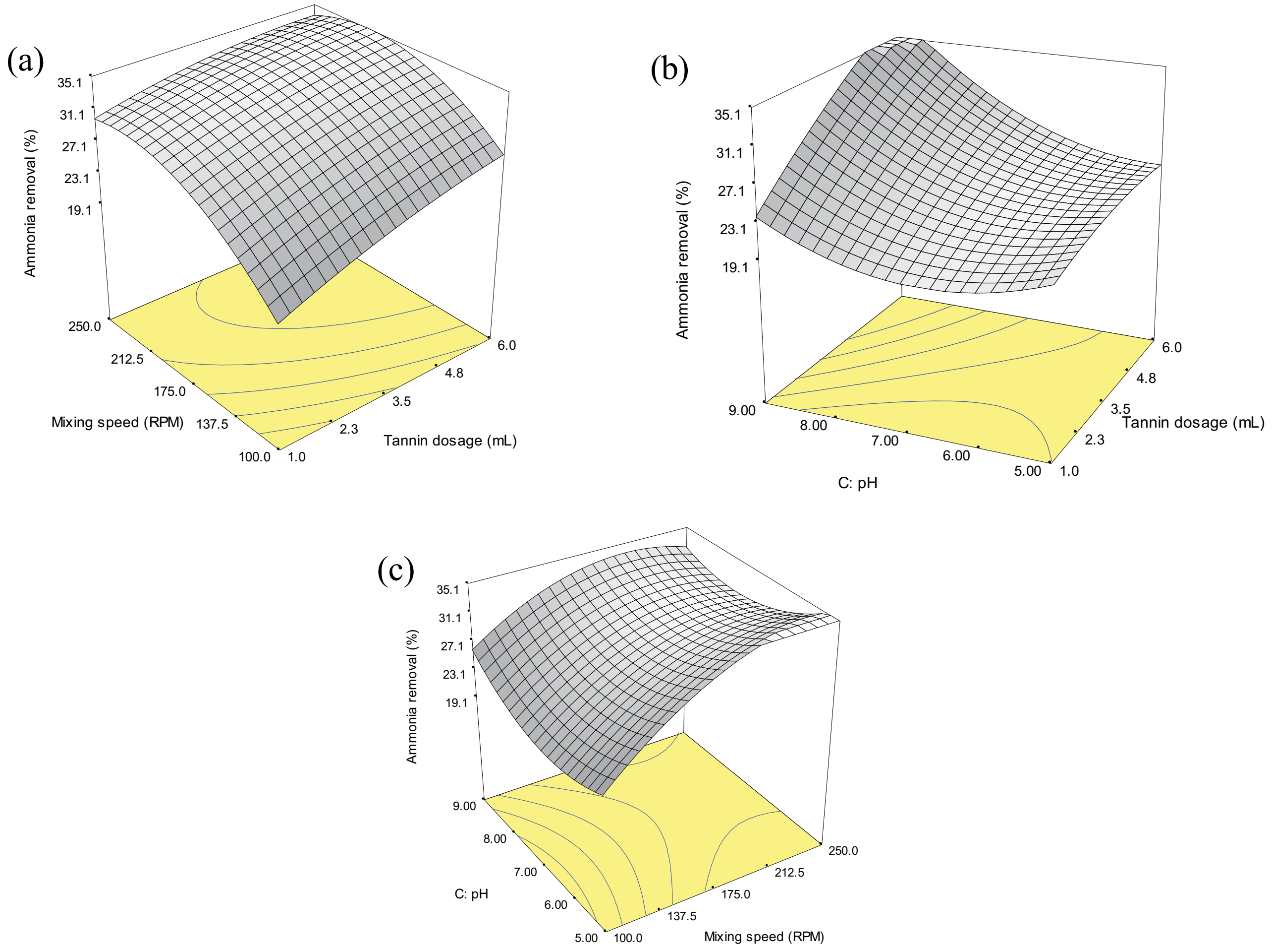

Fig. 4. Effect of tannin dosage, mixing speed and pH on ammonia removal.

recalcitrant compounds, that is, humic substance (HS) contributes to the COD and color concentrations especially for such moderate to old leachate [26]. In such landfill leachate, most of the COD concentration is linked to the presence of humic matter which results in the dark-brown to black leachate sample that most of its fractions are soluble at high

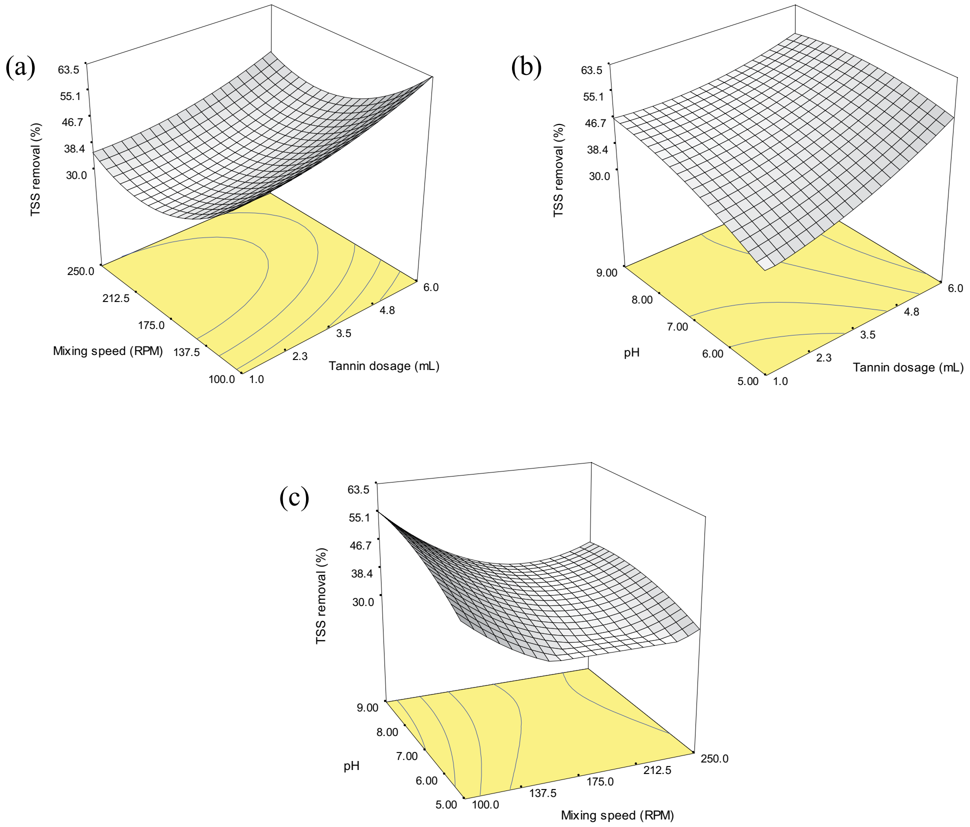

Fig. 5. Effect of tannin dosage, mixing speed and pH on TSS removal.

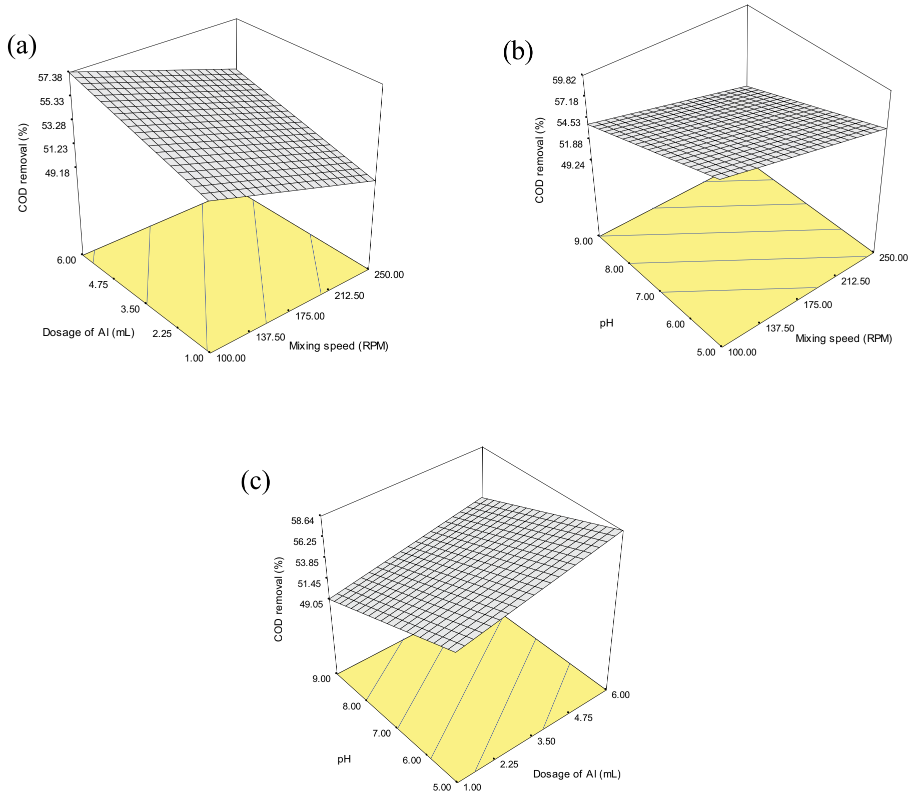

Fig. 6. Effect of Al dosage, mixing speed and pH on COD removal.

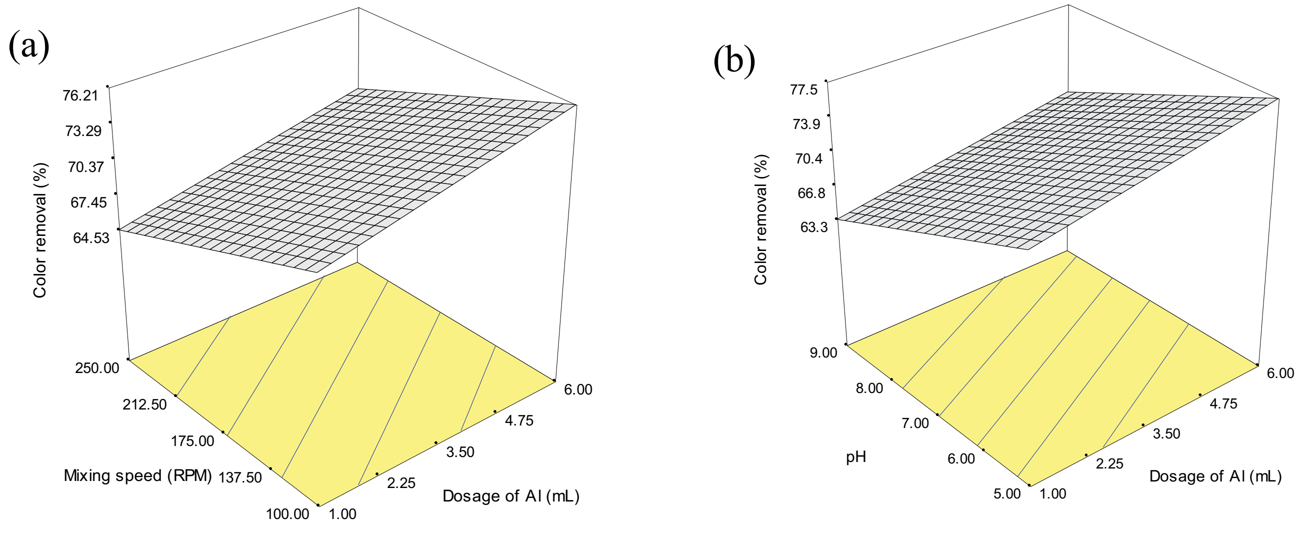

Fig. 7. Effect of Al dosage, mixing speed and pH on color removal.

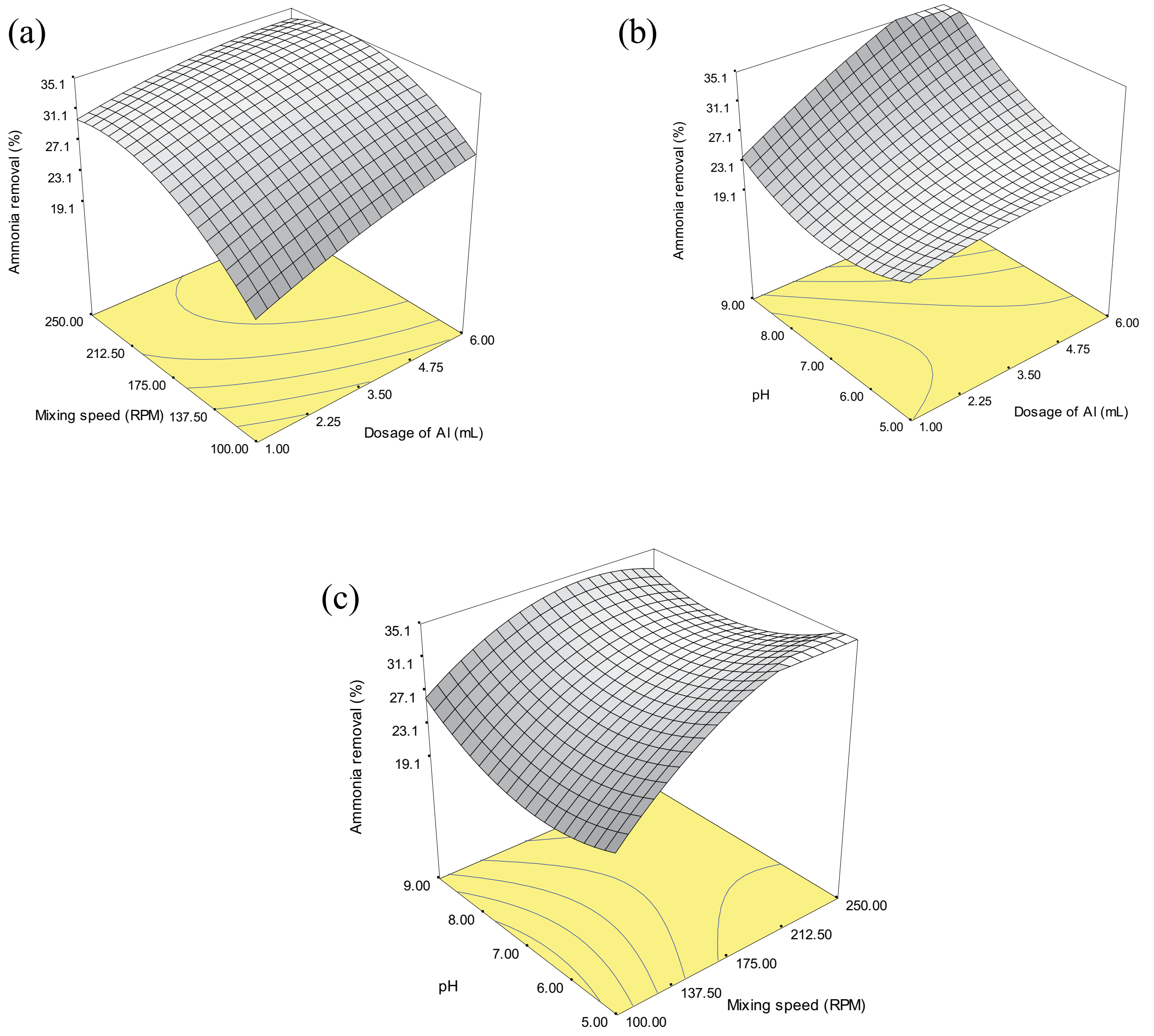

Fig. 8. Effect of Al dosage, mixing speed and pH on ammonia removal.

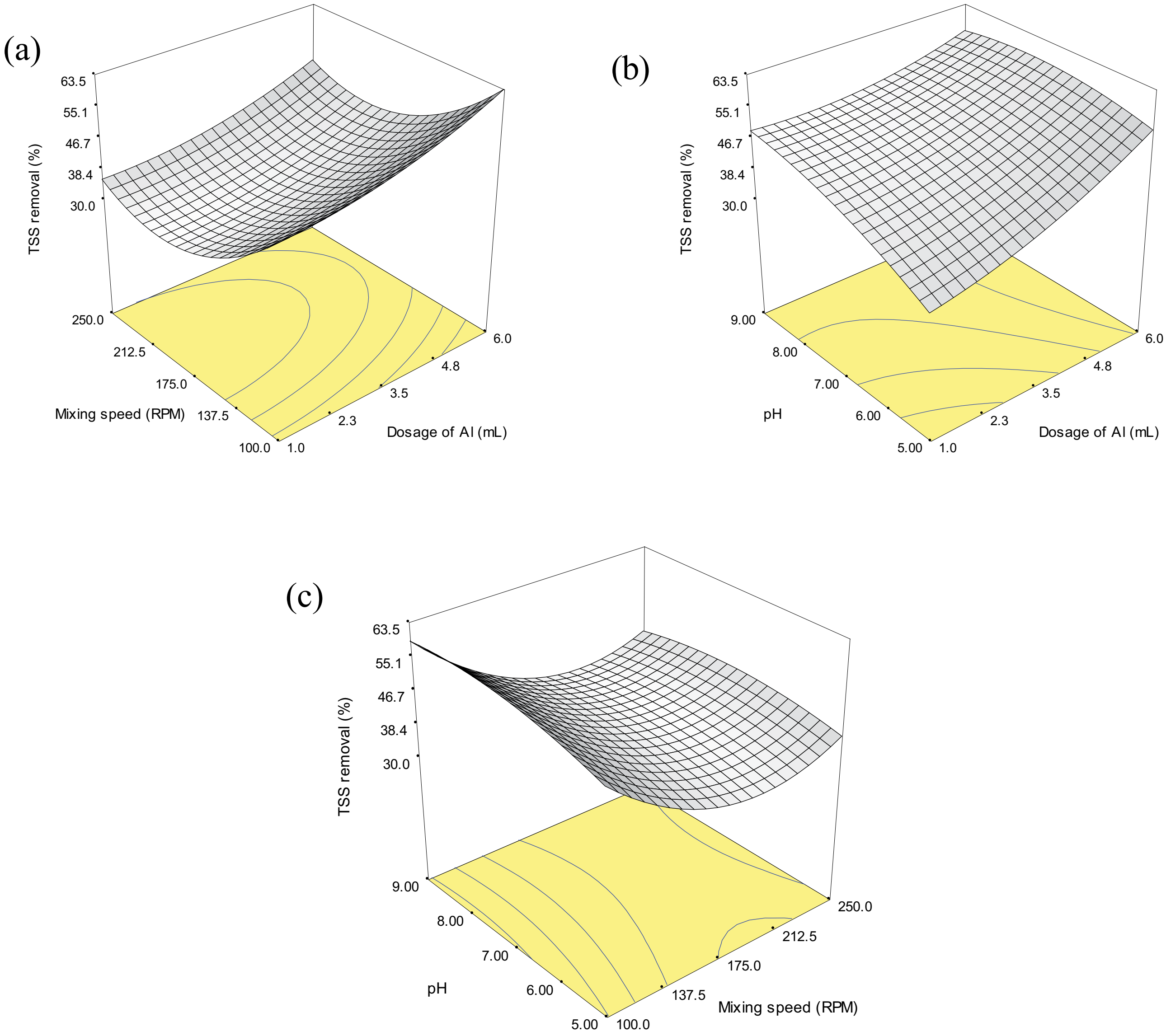

Fig. 9. Effect of Al dosage, mixing speed and pH on TSS removal.

Table 5
Validation of the optimum operating conditions

Run	Tannin											
	Dosage 1%, mL	Rapid mixing speed, rpm	pH	Coagulant type	Experiment				Model			
					COD, %	Color, %	Ammonia, %	TSS, %	COD, %	Color, %	Ammonia, %	TSS, %
	6.00	100.00	9.00	Tannin	42.86	54.38	39.39	60.33	43.56	52.73	37.32	62.40
	Alum											
	Dosage 10%, mL	Rapid mixing speed, rpm	pH	Coagulant type	Experiment				Model			
					COD, %	Color, %	Ammonia, %	TSS, %	COD, %	Color, %	Ammonia, %	TSS, %
	6.00	100.00	9.00	Alum	52.71	69.09	42.42	60.33	55.20	71.78	42.42	59.00

pH. Therefore, in acidic medium to neutral, the removals of COD and color were found to be the highest while the lowest removals were observed in basic media.

5. Validation of the optimization conditions

Two confirmation experiments were carried out with optimum operation conditions for the tannin and Al, to validate the regression models used to describe the relationship between input variables and selected removals. The results of the two experiments with the predicted results are presented in Table 5.

6. Conclusion

The treatment performances of modified tannin as an organic coagulant and alum as an inorganic coagulant were determined and compared using RSM. With 1% modified tannin dosage of 6 mL, pH of 9 and a rapid mixing speed at 100 rpm, the optimum removal efficiencies of COD, color, NH_3–N and TSS were 42.86%, 54.38%, 39.39% and 60.33%, respectively. In contrast, employing the same operating conditions, 10% alum could remove 60.71% COD, 63.09% color, 42.42% NH_3–N and 60.33% TSS. Although the performance of alum was reported higher efficiency than tannin for organic removals (COD and color), however, tannin reported significant removals of ammonia and TSS.

Acknowledgments

This work was supported by the FRGS Research grant Scheme (Ref: FRGS/1/2019/SSI12/UNIKL/02/1), distributed by the Ministry of Higher Eduction (MOHE), Malaysia, to the Universiti Kuala Lumpur.

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