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Statistical model for comparing the performance of four natural and chemical coagulants using polynomial model

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ABSTRACT

In this study, four coagulants were used to investigate their performances for the treatment of raw landfill leachate. Two inorganic coagulants, namely, ferric sulfate, $Fe_2(SO_4)_3$ and zinc sulfate, $ZnSO_4$ were compared to two types of palm date seeds, that is, khlas and sukkari as natural coagulants. Type of coagulant, dosage, pH and rapid mixing speed were designated as input variables, that is, operating conditions. In order to determine and compare the leachate treatment performances of the four coagulants, four responses were selected for this research, namely, chemical oxygen demand (COD), color, ammoniacal nitrogen (NH_3–N) or simply ammonia and total suspended solids (TSS). A response surface model (RSM) was developed for each selected response to find the optimum operating conditions for the input variable and for each coagulant that result in maximum removals. 72 experiments under different operating conditions were performed of which 18 runs were conducted for each type of coagulant wherein 100 mL of raw landfill leachate was the sample volume used for each run. The optimum operating conditions were found in the models and experimentally validated. The optimum dosage of ferric sulfate, zinc sulfate and khlas was found to be 6 mL. However, a lower dosage of 4.32 mL was found to be the optimum for sukkari. The optimal pH for ferric sulfate and sukkari was 5, whilst a pH of 9 was obtained for khlas and zinc sulfate. Finally, the optimum rapid mixing speeds for khlas and sukkari were rounded off to 195 and 200 rpm, respectively. Meanwhile, higher optimal rapid mixing speeds of 240 and 250 rpm were rounded out for ferric sulfate and zinc sulfate, correspondingly. Hence, the optimal reductions of COD, color, ammonia and TSS by (ferric sulfate–zinc sulfate) were rounded off to 55%–53%, 89%–73%, 15%–17% and 91%–89%, respectively. On the other hand, the optimum removals obtained by the natural coagulants (khlas–sukkari) were as the following: 12%–15% COD, 53%–56% color, 12%–14% ammonia and 78%–67% TSS. As regards the maximum removals of COD, color, ammonia and TSS by (ferric sulfate–zinc sulfate), they were found and rounded off to 60%–60%, 89%–84%, 18%–21% and 95%–96%, respectively. Contrariwise, the maximum reductions obtained by the natural coagulants (khlas–sukkari) were as the following: 16%–24% COD, 70%–74% color, 17%–17% ammonia and 91%–82% TSS. Thereupon, the natural coagulants showed effective removals, notably in terms of color, ammonia and TSS that could adequately replace the inorganic coagulants. A big margin of improvement in the removal of COD and other pollutants by khlas and sukkari could possibly be achieved in the upcoming studies by extensively investigating the preparation techniques of the natural coagulants.

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Keywords: Landfill; Leachate; Coagulants; Ferric sulfate, Zinc sulfate; Palm date seeds; Face-centered design; Response surface model; Removal; Pollutants; Chemical oxygen demand; Ammonia; Color; Total suspended solids

1. Introduction

The highly repulsive polluted liquid that seeps out from the landfill cells is called landfill leachate. Mainly, municipal solid waste (MSW) are dumped into those cells before being buried upon reaching full capacity. Hazardous waste could eventually be discarded into the landfill waste cells due to poor management of the landfill and deficient separation of incoming wastes. Hence, extremely hazardous leachate is produced resulting in dangerously threating the quality of the surrounding watercourses. Landfill leachate contains pollutants such as organic and inorganic material, heavy metals and other refractory substances that are more than many other industrial effluents [1]. Therefore, the necessity for effective landfill leachate treatment to be equipped within the site is essential. Biological treatments are commonly employed in almost all landfill leachate treatment facilities for their effective removal of pollutants particularly nutrients and biodegradable organic matter. However, in case of a lower ratio of biochemical oxygen demand to chemical oxygen demand, that is, BOD_5/COD biodegradability index, physicochemical treatments and/or combined with biological treatments are preferable [2].

Coagulation–flocculation process is generally used as a primary treatment in water and wastewater treatment plants. Typically, it involves the addition of coagulants and/or coagulant aids, that is, flocculants in order to remove the contaminants. Conventionally, suitable coagulants are added into the wastewater under specific operating conditions such as the dosage of the coagulant, pH of the wastewater and agitation speed. Charge neutralization of the suspended and colloidal particles are established followed by van der Waals attraction which cause the solids to aggregate. Slow mixing and/or flocculants are followed to enhance the agglomeration of the solids by developing larger flocs called macroflocs in order to improve and accelerate the settling process of these flocs hence it is separated and removed from the wastewater. The supernatant is then further filtered.

As far as coagulants are concerned, aluminium-coagulants and iron coagulants are classified as inorganic coagulants. In the meanwhile, the application of organic coagulants have recently been studied and practised. Inorganic trivalent coagulants such as aluminium sulfate, that is, alum and ferric sulfate are widely employed in the coagulation process. Chitosan and tannin are common examples of natural coagulants. For the high dense volume of sludge generated and the residuals of aluminium and iron in the treated effluent after the treatment which might jeopardize the aquatic life and human health, effective organic coagulants could replace the use of inorganic coagulants [3]. Tannin as in modified tannin for instance, it has been adequately studied and investigated as an organic amphoteric coagulant for the treatment of different wastewater such as landfill leachate [3] and anaerobically treated palm oil mill effluent [4]. Based on some reported removal efficiencies by several inorganic, organic and natural coagulants for the treatment of landfill leachate such as alum [3,5–7] and tannin [3,8,9], a general finding has concluded that organic and natural coagulants usually require lower dosage than inorganic for effective treatment of landfill leachate hence low capital and operational expenditures, that is, CapEx and OpEx. As a result, this has triggered and intrigued researches and scientists to further explore numerous organic and natural coagulants for different treatment applications such as moringa oleifera [10,11], okra and purple okra [11,12], chitosan, pine bark as coagulants/flocculants [13,14], longan seed [15] and red earth [6].

Other natural eco-friendly coagulants particularly the ones that are collected as by-products could in fact help treat wastewater effectively such as palm date seeds. The scientific name of date palm tree is *Phoenix dactylifera* L. which belongs to the Arecaceae family of flowering plants [16]. Date palms are substantially grown in dry regions that receive little precipitation such the Arabian Peninsula [17]. According to the latest accessible statics provided by the Food and Agricultural Organization (FAO), the global production of palm dates in 2020 are more than 9.4 million metric tons. From the data provided, a rising trend in palm dates production was observed annually. For example, the global production has increased around 16.8% from 2015 to 2020. FAOSTAT 2021 stated that Egypt is the world's largest dates producing country followed by Saudi Arabia and Iran with more than 17%, 16% and 13% of the global palm dates production, respectively. According to FAO, the Saudi palm dates production has grown more than 18% since 2014. Based on the Saudi National Center for Palms and Dates (NCPD), with an increase of 110% from 2016 to 2021, Saudi Arabia has become the largest exporter of palm dates exceeding 215 million kg to 113 countries in the world of a total export value of 1.2 billion SAR. The rarity of cultivation of date palm in Malaysia [18] mainly due to the tropical climate, has increased the degree of dependency on imports to cover the increasing local demands of dates for religious purposes as well as the awareness of its health benefits. Scientifically speaking, cultivation of date palms in Malaysia is quite possible [18] especially with the help of the current advanced agricultural technologies. Based on the available FAO figures from 2016 to 2020, the dates imported to Malaysia averaged more than 26 thousand metric tons per year. In 2019, the import volume of dates hit the ceiling at around 45 thousand metric tons. According to NCPD, around 5 thousand metric tons of dates were imported from Saudi Arabia in 2021.

Lately, the composition of several palm date seeds have been extensively studied. Generally, the seed consists highly of dietary fiber up to 74% mainly lignocellulosic material, that is, cellulose, hemicellulose and lignin in addition to other components such as carbohydrates, oil, moisture, proteins, tannins, polyphenols and other nutrients are also found to be contained in the palm date seeds [19]. The average weight percentage of the seed is 10% of the total palm date weight [20]. Hence, nearly 1 million metric tons of palm date seeds out of the global volume of palm dates produced in 2020 are generated. These seeds are considered to be the most wasted palm dates by-products. This huge amount of organic waste could cause adverse impact on the environment upon decomposition. Therefore, as 'an eloquent example of integrated sustainable use of renewable material resources', palm date by-products such as date seeds are recycled mainly for the use of animal feed [21]. For their antimicrobial, antioxidant and antiviral activities [22], the applications of palm date seeds not only has been used in animal feed but also invaded food, beverage and medicine industries. On the other hand, few number of studies were performed on the efficacy of palm date seeds on the treatment of wastewater hence their water and wastewater treatment applications are still ambiguous. Dependent on the desired application, palm date seeds might undergo certain preparation processes in which the end-product could serve as a coagulant, fertilizer (biochar), adsorbent (activated carbon) and metal scavenger (coke). According to NCPD, there are approximately 33 million date palms planted in Saudi Arabia in which khlas and sukkari contribute more than 40% of the total number of date palms, respectively. Response surface methodology (RSM) was used in various studies to optimize the results [23,24] The purpose of this research was to investigate the treatment performance of khlas and sukkari seeds as natural coagulants for the treatment of raw landfill leachate in comparison to two inorganic coagulants, that is, ferric sulfate and zinc sulfate. Moreover, optimization of the treatment using response surface methodology (RSM) was developed for each coagulant in order to find and validate the optimum operating conditions namely type and dosage of the coagulant, rapid mixing speed, and pH of the medium for the removals of COD, color, ammonia and total suspended solids (TSS).

2. Material and methods

2.1. Sampling

For the purpose of this study, a sample of 20 L of raw landfill leachate was collected in March 2022 from the 25 ha Sungai Udang Sanitary Landfill (SUSL), Malacca, Malaysia. The sample was kept in the laboratory fridge at 4°C so as to slow down any biological and chemical reaction.

2.2. Studied coagulants

Both inorganic coagulants namely; ferric sulfate, $Fe_2(SO_4)_3$ and zinc sulfate, $ZnSO_4$ were commercially purchased from a local supplier as analytical reagents. Technically, the ferric sulfate used in this research is known as iron(III) sulfate in a hydrated form of $Fe_2(SO_4)_3·xH_2O$ while zinc sulfate is heptahydrated, $ZnSO_4·7H_2O$. The ferric sulfate is a trivalent coagulant with a molecular weight of 399.88 g/mol. It is yellow and acidic crystal that is soluble in water with a purity of ≥98%. However, zinc sulfate is a bivalent coagulant with a molecular weight of 287.54 g/mol and a purity of 99%. It is white, water–soluble and acidic crystalline.

As for the natural coagulants, two common types of dates were selected. The palm date seeds (khlas and sukkari) were collected as a waste from Jeddah, Saudi Arabia. The physical appearance of khlas and sukkari powder are brown in color. Generally, they are made up of dietary fibre that is usually spectra-noticed in FTIR through the presence of hydroxyl and carbonyl groups. Additionally, other macro compounds such as carbohydrates, tannin and polyphenols which are highly believed to be the active ingredients that are responsible for the removal of contaminants from polluted water as well as some minerals. All coagulants involved in this study were used in liquid form of the same concentration based on preliminary experiments.

2.3. Preparation of natural coagulants

Khlas and sukkari seeds were collected and prepared separately in the same manner. The seeds were well-washed in order to remove any impurities including traces of pericarp (skin), mesocarp (pulp) and endocarp (membranous-like skin) surrounding the seeds. Then, the washed seeds were dried at room temperature for several weeks. If the time given so limited, this step could be shortened by using an oven-drying at 50°C for couple of hours. The dried seeds were further sieved to remove any impurities that might not have been washed away in the earlier step. Subsequently, a dual-stage grinding and sieving process was performed. First, the seeds were grinded to 500 micron in size and then sieved through 500 micron to ensure the size uniformity of the ground date seeds. The rejected portion was re-grinded and further sieved accordingly. Likewise, the 500 micron date seed powder was further grinded down to 250 micron. Lastly, the extraction process was executed in which the 250 micron date seed powder was stirred in water using magnetic stirrer at room temperature for about 30 min. The mixture was gravity-filtered through a qualitative filter paper. The filtrate was used as the coagulant and stored in the fridge at 4°C until needed.

2.4. Experimental design

A natural coagulant-based preliminary experiments were performed prior to the design of the experiments. Hence, the operating conditions and their levels in response to the selected parameters were determined in order to optimise the removal efficiencies. 72 experiments covering all possible combinations of various levels were conducted, wherein 18 runs were performed for each type of coagulant whether natural (khlas and sukkari palm date seeds) or inorganic (ferric sulfate and zinc sulfate). Incubator shaker BIOBASE (BJPX-103B) was used for simulating the coagulation–flocculation process. The temperature was held constant at room temperature for all runs. However, dosage, pH and rapid mixing speed were varied. The removal efficiencies for chemical oxygen demand (COD), color, ammoniacal nitrogen (NH_3–N) and total suspended solids (TSS) were investigated through the treatment of raw landfill leachate by the four natural and inorganic coagulants. The raw landfill leachate sample as well as the natural coagulants were warmed up to room temperature before commencing the experiments. For each run, a sample volume of 100 mL was transferred to a 250 mL-conical flask. The pH of the sample was adjusted accordingly, that is, 5.00, 7.00 and 9.00 prior to the addition of the coagulants. 5 M of sulfuric acid was used to adjust the pH of the sample for acidic medium while 5 M of sodium hydroxide was used if the desired medium was to be basic. Then, dosages of 1.00, 3.50 and 6.00 mL of 0.1 w/v of all coagulants were added to the respective flask. Three different rapid mixing speeds, that is, 100, 175 and 250 rpm were set accordingly. Each run was agitated rapidly for 15 min followed by a slow mixing at 60 rpm for 45 min. The liquor was settled for 60 min and then the supernatant was gravity-filtered through qualitative filter papers. Lastly, the removal efficiencies of the effluent from each run were determined.

2.5. Analytical study

Four parameters signified as the investigated treatment responses; including the concentrations of COD, color, NH_3–N and TSS were tested before and after each run. 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 and adjusted pH of the raw leachate sample were measured via Fisher Scientific accumet Basic (AB150) pH-mV/temp bench-top meter. HACH DR/2800 (Loveland,Colorado, United States) was used to measure the initial and final 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 10031 high range (HR) Test 'N Tube Vials, a salicylate method at 655 nm. TSS was measured by method 8006, a photometric method at 810 nm. All parameters in this study were analyzed according to the standard methods for the examination of water and wastewater (APHA).

2.6. Statistical analysis

The effect of four factors, namely dosage of coagulant (A), rapid mixing speed (B), pH (C) and type of coagulants (D), on four parameters COD, color, ammonia and TSS removals from landfill leachate was studied using face-centered composite design [3,25]. A response surface model was developed for each selected response 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. 72-experiments were used (18 experiments for each type of coagulant) (Table 2). A response surface model was fitted to describe the behavior of selected input variables towards the four responses and then find the optimum operating condition that maximize the outputs.

Table 1
Actual and coded levels for the selected variables

Actual levels			Coded	Type of coagulant	Coded
Dosage of coagulant	Mixing speed	pH			
1	100	5	–1	Khlas	1
3.5	175	7	0	Sukkari	2
6	250	9	1	Ferric sulfate	3
				Zinc sulfate	4

3. Results and discussion

The physicochemical characteristics of the raw landfill leachate for the selected responses are shown in Table 3. The average concentrations of COD, color, ammonia and TSS of the leachate were 3,722 mg/L, 8,068 Pt-Co, 1,821 mg/L and 663 mg/L, respectively. It is demonstrated that the amount of contaminates exceed the discharge limits stipulated by the Malaysian Environmental Quality Act (MEQA) 1974, Department of Environment (DoE). The biodegradability index, BOD_5/COD is one of the main indicator of the nature of the leachate. The leachate nature highly depends on the activity and age of the waste cells given by the biodegradability index. For instance, the BOD_5/COD index of the raw landfill leachate used was monitored from September 2020 to December 2022 along with the pH. The minimum biodegradability index recorded was 0.04 with a pH more than 8 – which is the latest – in comparison to 0.15 right after the newly third cell was opened. This indicates that the current raw landfill leachate of Sungai Udang dealt with is stabilized leachate. The main challenge in treating such mature leachate is mainly the refractory COD and high concentration of ammonia which contributes to black leachate. Therefore, physiochemical methods are required for an effective treatment.

The effect of four variables (dosage of coagulant, rapid mixing speed, pH, and type of coagulant). Face-centered composite design with 72-experiments was used to cover all possible combinations of the studied variables. The collected data produced from face-centered design were analysed using analysis of variance (ANOVA) [8,26] to test the influence of the selected input variables on the selected responses. The results of ANOVA are presented in Table 4. Response surface model that shows the influence of selected variables on COD, color, ammonia and TSS are presented in Eqs. (1)–(4).

$$\begin{aligned}\text{COD} = {} & +30.01+1.63A+0.45B-3.45C-16.26D[1] \\ & -12.13D[2]+9.64D[3]-1.08A2-2.38B2 \\ & -2.14C2+0.26AB+1.48AC-1.99AD[1] \\ & -8.06AD[2]+4.95AD[3]+0.14BC \\ & -0.43BD[1]+0.66BD[2]-0.52BD[3] \\ & +3.77CD[1]+1.72CD[2]-7.80CD[3]\end{aligned} \tag{1}$$

$$\begin{aligned}\text{Color} = {} & +55.69+7.85A-0.22B-6.07C-10.62D[1] \\ & -8.47D[2]+12.35D[3]-0.064AB \\ & +4.73AC-3.36AD[1]-0.20AD[2] \\ & +1.73AD[3]-1.03BC+0.53BD[1] \\ & -3.15BD[2]+1.00BD[3]+6.48CD[1] \\ & -4.24CD[2]-8.82CD[3]\end{aligned} \tag{2}$$

$$\begin{aligned}\text{Ammonia} = {} & 13.25+1.23A+1.08B-0.67C-1.90D[1] \\ & -0.068D[2]+0.92D[3]\end{aligned} \tag{3}$$

Table 2
Design with the measured responses (COD, color, ammonia, and TSS)

Dosage of coagulant	Mixing speed	pH	Type of coagulant	COD	Color	Ammonia	TSS
1	100	5	Khlas	11.33	45.92	13.21	64.84
6	100	5	Khlas	9.16	46.94	12.95	71.21
1	250	5	Khlas	11.57	48.98	14.25	63.57
6	250	5	Khlas	10.12	44.90	13.73	67.52
1	100	9	Khlas	10.36	35.71	9.33	67.77
6	100	9	Khlas	15.90	70.41	12.18	91.46
1	250	9	Khlas	12.29	38.78	9.33	68.92
6	250	9	Khlas	11.57	55.10	17.36	82.29
1	175	7	Khlas	7.95	50.00	4.66	66.11
6	175	7	Khlas	3.13	46.94	9.59	67.52
3.5	100	7	Khlas	8.19	35.71	5.70	70.06
3.5	250	7	Khlas	9.64	50.00	9.59	70.32
3.5	175	5	Khlas	8.92	43.88	11.92	65.86
3.5	175	9	Khlas	4.10	34.69	8.81	67.52
3.5	175	7	Khlas	13.25	39.80	16.32	67.13
3.5	175	7	Khlas	14.46	40.82	11.92	66.24
3.5	175	7	Khlas	14.70	40.82	12.69	67.90
3.5	175	7	Khlas	14.94	41.84	10.88	65.73
1	100	5	Sukkari	21.69	45.92	10.62	54.65
6	100	5	Sukkari	11.81	72.45	13.99	82.29
1	250	5	Sukkari	24.10	48.98	17.10	57.20
6	250	5	Sukkari	12.29	74.49	16.06	81.27
1	100	9	Sukkari	18.55	44.90	9.84	62.29
6	100	9	Sukkari	6.02	52.04	14.77	75.92
1	250	9	Sukkari	21.45	27.55	12.69	62.29
6	250	9	Sukkari	8.92	39.80	14.51	81.15
1	175	7	Sukkari	22.41	46.94	11.40	62.04
6	175	7	Sukkari	4.82	52.04	16.58	72.61
3.5	100	7	Sukkari	10.36	45.92	10.62	67.77
3.5	250	7	Sukkari	12.77	36.73	5.44	66.75
3.5	175	5	Sukkari	16.63	57.14	16.58	66.37
3.5	175	9	Sukkari	14.22	31.63	13.99	71.59
3.5	175	7	Sukkari	13.49	42.86	11.92	69.94
3.5	175	7	Sukkari	15.66	43.88	13.99	69.55
3.5	175	7	Sukkari	15.90	42.86	13.47	68.28
3.5	175	7	Sukkari	14.70	43.88	13.73	67.77
1	100	5	Ferric sulfate	42.89	88.57	11.40	91.85
6	100	5	Ferric sulfate	47.23	81.43	10.36	95.29
1	250	5	Ferric sulfate	40.96	86.22	16.06	89.04
6	250	5	Ferric sulfate	46.02	81.53	18.39	94.90
1	100	9	Ferric sulfate	16.14	34.69	11.40	72.61
6	100	9	Ferric sulfate	27.23	69.90	13.47	81.40
1	250	9	Ferric sulfate	13.01	41.84	13.21	73.25
6	250	9	Ferric sulfate	31.57	73.57	17.10	83.57
1	175	7	Ferric sulfate	27.23	42.86	13.99	62.55
6	175	7	Ferric sulfate	53.98	83.57	17.62	87.64
3.5	100	7	Ferric sulfate	29.64	70.00	8.81	81.91
3.5	250	7	Ferric sulfate	30.84	69.18	17.62	80.13
3.5	175	5	Ferric sulfate	59.52	84.18	10.62	94.65
3.5	175	9	Ferric sulfate	36.14	53.06	13.99	67.13

Table 2 (Continued)

Table 2

Dosage of coagulant	Mixing speed	pH	Type of coagulant	COD	Color	Ammonia	TSS
3.5	175	7	Ferric sulfate	38.07	64.39	16.84	74.52
3.5	175	7	Ferric sulfate	38.55	65.82	14.51	76.43
3.5	175	7	Ferric sulfate	38.80	65.92	15.80	75.29
3.5	175	7	Ferric sulfate	39.76	67.86	13.99	77.32
1	100	5	Zinc sulfate	35.18	50.00	18.91	62.55
6	100	5	Zinc sulfate	40.96	52.04	20.73	64.46
1	250	5	Zinc sulfate	35.42	46.94	17.10	59.62
6	250	5	Zinc sulfate	44.58	62.24	16.84	72.36
1	100	9	Zinc sulfate	28.43	35.71	11.14	61.78
6	100	9	Zinc sulfate	44.82	67.35	12.95	84.20
1	250	9	Zinc sulfate	28.67	37.76	13.21	61.40
6	250	9	Zinc sulfate	49.16	74.49	17.62	94.14
1	175	7	Zinc sulfate	44.10	62.24	11.66	85.35
6	175	7	Zinc sulfate	59.52	73.47	12.95	63.57
3.5	100	7	Zinc sulfate	56.14	84.49	13.99	95.67
3.5	250	7	Zinc sulfate	55.18	82.14	12.44	91.46
3.5	175	5	Zinc sulfate	40.72	50.00	10.88	64.97
3.5	175	9	Zinc sulfate	34.46	51.02	17.88	73.63
3.5	175	7	Zinc sulfate	56.14	71.94	11.14	71.46
3.5	175	7	Zinc sulfate	54.70	73.06	12.95	71.08
3.5	175	7	Zinc sulfate	57.11	74.80	13.47	68.92
3.5	175	7	Zinc sulfate	56.39	73.98	11.40	72.74

Table 3
Physico-chemical characteristics of the raw landfill leachate samples for the selected parameters

Parameter	Unit	Readings			Std. limit, (MEQA), 1974
		Minimum	Maximum	Mean[a]	
COD	mg/L	3,300	4,150	3,722	400
Color	Pt-Co	6,700	9,800	8,068	100
NH_3–N	mg/L	1,710	1,930	1,821	5
TSS	mg/L	548	785	663	50

[a] Average of four samples taken from March to August 2022.

$$\begin{aligned}\text{TSS} = {} & 73.20 + 6.13A + 0.029B + 0.50C - 3.65D[1] \\ & - 4.33D[2] + 7.88D[3] + 0.44AB + 1.81AC \\ & - 1.25AD[1] + 3.35AD[2] - 0.78AD[3] \\ & + 0.35BC - 1.30BD[1] + 0.54BD[2] - 0.25BD[3] \\ & + 4.00CD[1] + 0.65CD[2] - 9.27CD[3] \end{aligned} \tag{4}$$

(Note: Subscripts 1, 2, 3 and 4 denote codes of "dummy variables" where coagulant type 1, $D[1] = 1$; $D[2] = 0$; $D[3] = 0$ (khlas), type 2, $D[1] = 0$; $D[2] = 1$; $D[3] = 0$ (sukkari), type 3, $D[1] = 0$; $D[2] = 0$; $D[3] = 1$ (ferric sulfate), and type 4, $D[1] = 0$; $D[2] = 0$; $D[3] = 0$ (zinc sulfate)).

The coefficient of determination (R-square) for the mathematical Eqs. (1)–(4) are 0.91, 0.74, 0.31 and 0.63 for COD, color, ammonia and TSS, respectively. The value of R-square fluctuate from 0.63 to 0.91, which indicates that most of the variance in the data is captured by the models and fitted the collected data adequately except for ammonia model, the R-square reported is 0.31. The very low R-square for ammonia may be attributed to its limited removal efficiency (15%–15%) using natural coagulants. COD, color and TSS could be any bulk of organic and inorganic pollutants that contribute to their concentrations, unlike ammonia is one of inorganic macro-components in landfill leachate. Generally, coagulants alone could amply remove COD, color and TSS but limitedly reduce ammonia, in particular, from highly polluted raw landfill leachate. Righetto et al. [27] reported only 20% removal for ammonia from landfill leachate by optimizing the performance of tannin as a natural coagulant. Moreover, a large-scale treatment figure was presented by Ayash et al [1] in which the removal efficiency of ammonia was 16.48% via chemical coagulation-flocculation process that was employed as a primary treatment in the facility.

The effect of each selected variable on the measured response can be measured by the regression coefficient associated with each variable 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.

The results of ANOVA (Table 4) showed that the effect of dosage of coagulants, pH and type of coagulant or interaction with other variables was highly significant on COD, color and ammonia (P-value < 0.05) whilst rapid mixing speed showed a significant effect only on ammonia. It is highly believed that the removal of ammonia requires a

Table 4
Results of analysis of variance

Source	Sum of squares	DF	Mean square	*F*-value	Prob. > *F*
			COD		
Model	18,503.43	21	881.12	24.44	<0.0001
A	105.82	1	105.82	2.94	0.0928
B	8.17	1	8.17	0.23	0.6362
C	**476.60**	**1**	**476.60**	**13.22**	**0.0007**
D	**15,405.66**	**3**	**5,135.22**	**142.46**	**<0.0001**
A^2	12.69	1	12.69	0.35	0.5556
B^2	61.26	1	61.26	1.70	0.1983
C^2	49.47	1	49.47	1.37	0.2470
AB	2.10	1	2.10	0.058	0.8104
AC	69.71	1	69.71	1.93	0.1705
AD	**1,194.13**	**3**	**398.04**	**11.04**	**<0.0001**
BC	0.59	1	0.59	0.016	0.8989
BD	9.76	3	3.25	0.090	0.9651
CD	**833.61**	**3**	**277.87**	**7.71**	**0.0002**
Residual	1,802.39				
Total	20,305.81	71			
R-squared	0.9112				
			Color		
Model	13,696.92	18	760.94	8.25	<0.0001
A	**2,467.78**	**1**	**2,467.78**	**26.75**	**<0.0001**
B	1.97	1	1.97	0.021	0.8844
C	**1,473.25**	**1**	**1,473.25**	**15.97**	**0.0002**
D	**6,880.57**	**3**	**2,293.52**	**24.86**	**<0.0001**
AB	0.13	1	0.13	1.411E-003	0.9702
AC	**714.65**	**1**	**714.65**	**7.75**	**0.0074**
AD	177.28	3	59.09	0.64	0.5923
BC	33.74	1	33.74	0.37	0.5479
BD	137.91	3	45.97	0.50	0.6850
CD	**1,809.63**	**3**	**603.21**	**6.54**	**0.0008**
Residual	4,889.16	53	92.25		
Total	18,586.09	71			
R-squared	0.7369				
			Ammonia		
Model	225.18	6	37.53	4.94	0.0003
A	**60.57**	**1**	**60.57**	**7.97**	**0.0063**
B	**46.79**	**1**	**46.79**	**6.16**	**0.0157**
C	18.15	1	18.15	2.39	0.1270
D	**99.66**	**3**	**33.22**	**4.37**	**0.0072**
Residual	493.72	65	7.60		
Total	718.90	71			
R-squared	0.3132				
			TSS		
Model	4,741.08	18	263.39	5.09	<0.0001
A	**1,501.80**	**1**	**1,501.80**	**29.01**	**<0.0001**
B	0.033	1	0.033	6.348E-004	0.9800
C	9.87	1	9.87	0.19	0.6641
D	**1,694.67**	**3**	**564.89**	**10.91**	**<0.0001**

Table 4 (Continued)

Table 4

Source	Sum of squares	DF	Mean square	*F*-value	Prob. > *F*
			TSS		
AB	6.14	1	6.14	0.12	0.7320
AC	104.53	1	104.53	2.02	0.1612
AD	151.42	3	50.47	0.98	0.4115
BC	3.93	1	3.93	0.076	0.7841
BD	30.60	3	10.20	0.20	0.8980
CD	**1.238.10**	**3**	**412.70**	**7.97**	**0.0002**
Residual	2.743.53	53	51.76		
Total	7.484.61	71			
R-squared	0.6334				

complex condition of medium and coagulant at the same time. In particular, the kinetic energy thus entropy that is required to form an adduct covalent bonds in order to form a precipitate with the selected coagulant at specific pH which determines whether the ammoniacal nitrogen equilibrium shifts towards the ionized form (ammonium), NH_4^+ or towards the unionized aqueous form (ammonia/ammonium hydroxide), NH_3/NH_4OH. Hence, the degree of the dispersion of a certain type and dosage of coagulant at specific pH of the medium are significant factors for the removal of ammonia. Unlike COD and color, the selected range of rapid mixing speed was insignificant in which the required minimal rapid agitation for their removals were achieved employing a definite type and dosage of a coagulant and pH of the medium.

Significant interaction refers to the dependency of the variables on each other and produce another effect which is different from the direct interaction. This means that not all types of coagulants generate the optimum/maximum removals of pollutants at the same dosage, rapid mixing speed and pH of the medium. Therefore, the comprehension of the correlation among all the selected operating conditions, that is, how they work collectively is significant in order to achieve the desired removals of pollutants from the wastewater.

Three-dimensional response surface plot is used to show the effect of various selected variables on the responses pictorially (Figs. 1–4), showing the effect of one variable in the presence of other variables. The region of maximum effect is well defined with the selected boundaries of selected input variables.

4. Optimization of leachate treatment

Maximum removals for the COD, color, ammonia and TSS was found as long as a mathematical model was developed and analysed. The highest removals are summarized and presented in Table 5. The optimum operation conditions for the input variables were calculated using the models in Eqs. (1)–(4). While the optimum setting with the results of COD, color, ammonia and TSS are given in Table 6 for the four types of coagulants.

In regard to the raw landfill leachate treatment efficiencies of both natural coagulants (khlas and sukkari) and inorganic coagulants (ferric sulfate and zinc sulfate), it is observed that each type worked better under different operating conditions. Despite the fact that the natural coagulants are both palm date seeds but distinct types, each performed independently. Khlas achieved the highest removals of 16% COD, 70% color, 17% ammonia and 91% TSS at pH 9 with a dosage of 6 mL. Whereas, at pH 5, sukkari accomplished the highest removals, that is, 24% COD, 74% color, 17% ammonia and 82% TSS. 1 mL of dosage was enough for the removals of COD and ammonia where 6 mL was required for the color and TSS removals. In regard to inorganic coagulants, trivalent ferric sulfate reached the highest removals of 60% COD, 89% color, 18% ammonia and 95% TSS with a dosage of 3.5 mL, 1 mL for COD and color, respectively and 6 mL for ammonia and TSS at pH 5. In the meanwhile, the highest removals of COD, color and TSS attained by the bivalent zinc sulfate at pH 7 were 60%, 84% and 96%, respectively. However, the highest removal of 21% ammonia was reached at pH 5. 6 mL was utilized for the removals of COD and ammonia while 3.5 mL for color and TSS.

Table 7 presents some reported coagulation–flocculation treatments of landfill leachate using inorganic (chemical) such as ferric chloride [28,29], organic and natural coagulants such as tannin [3,8,9]. The main optimum removal efficiencies and operating conditions are summarized and compared to the findings of the current research. It is observed that organic and natural coagulants have the ability to effectively treat landfill leachate with lower dosages and without toxic residuals unlike chemical coagulants. Combination treatment systems of organic and natural coagulants are potentially recommended for more effective removal of pollutants.

For the purpose of overall observations, the following remarks are significant in order to comprehend the general performance of each coagulant within the selected range of pH and dosage in response to all parameters. In terms of the dosage of coagulants, it was found out that khlas, sukkari, ferric sulfate and zinc sulfate worked better with a high dosage. However, sukkari required by far a lower dosage for the removal of COD. This could be due to the high load of oxidizing agents of both organic and other inorganic constituents found in the sukkari extract with an increase in the dosage. It was experimentally proven that the COD of sukkari was around 2.5 times that of khlas. With respect to

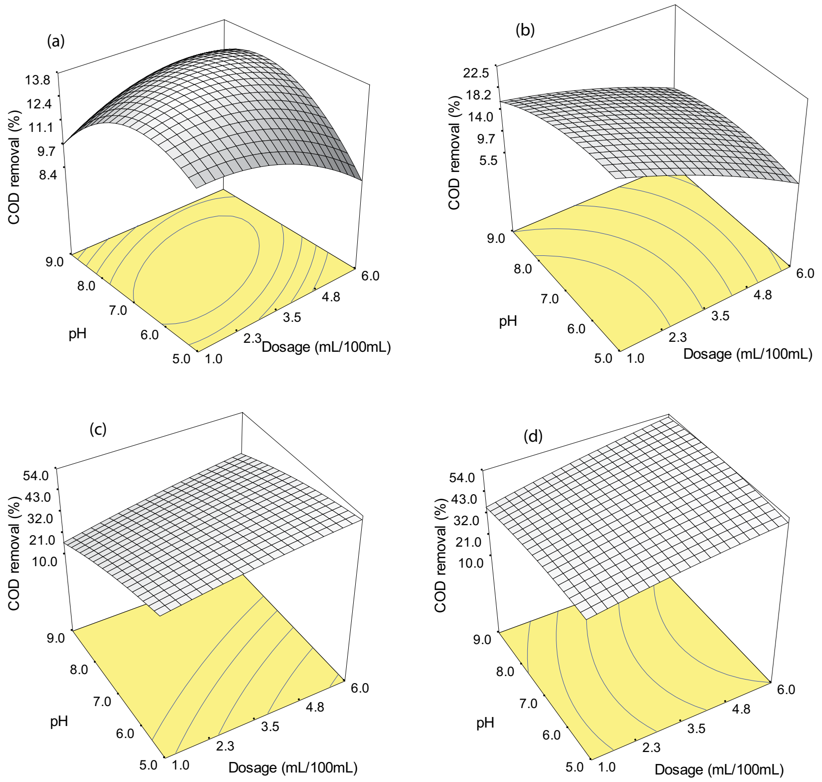

Fig. 1. Effect of dosage of coagulant and pH on COD removal. (a) Mixing speed = 175 and type of coagulant = khlas, (b) mixing speed = 175 and type of coagulant = sukkari, (c) mixing speed = 175 and type of coagulant = ferric sulfate and (d) mixing speed = 175 and type of coagulant = zinc sulfate.

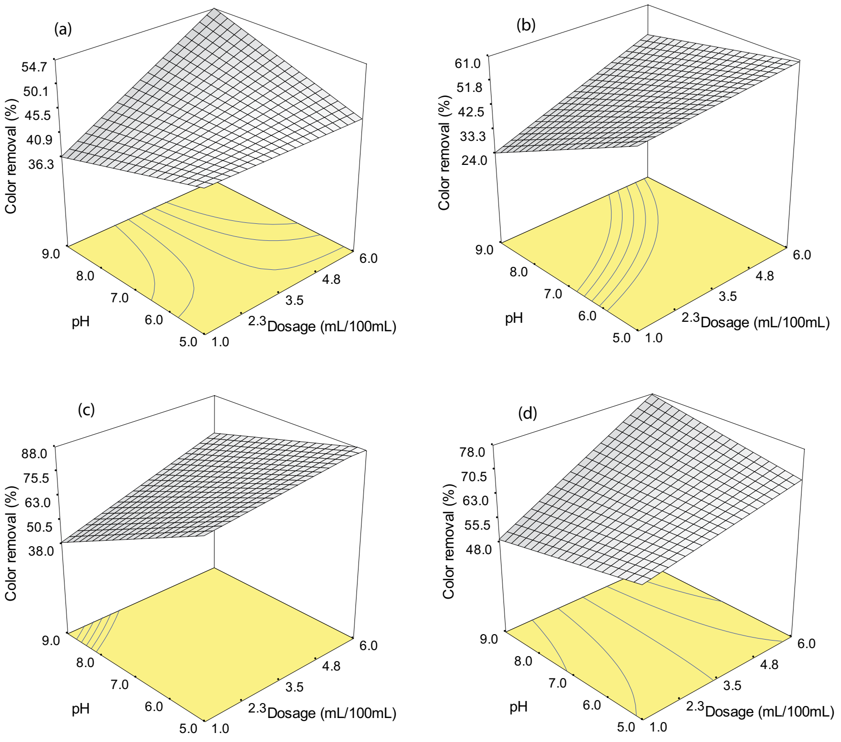

Fig. 2. Effect of dosage of coagulant and pH on color removal. (a) Mixing speed = 175 and type of coagulant = khlas, (b) mixing speed = 175 and type of coagulant = sukkari, (c) mixing speed = 175 and type of coagulant = ferric sulfate and (d) mixing speed = 175 and type of coagulant = zinc sulfate.

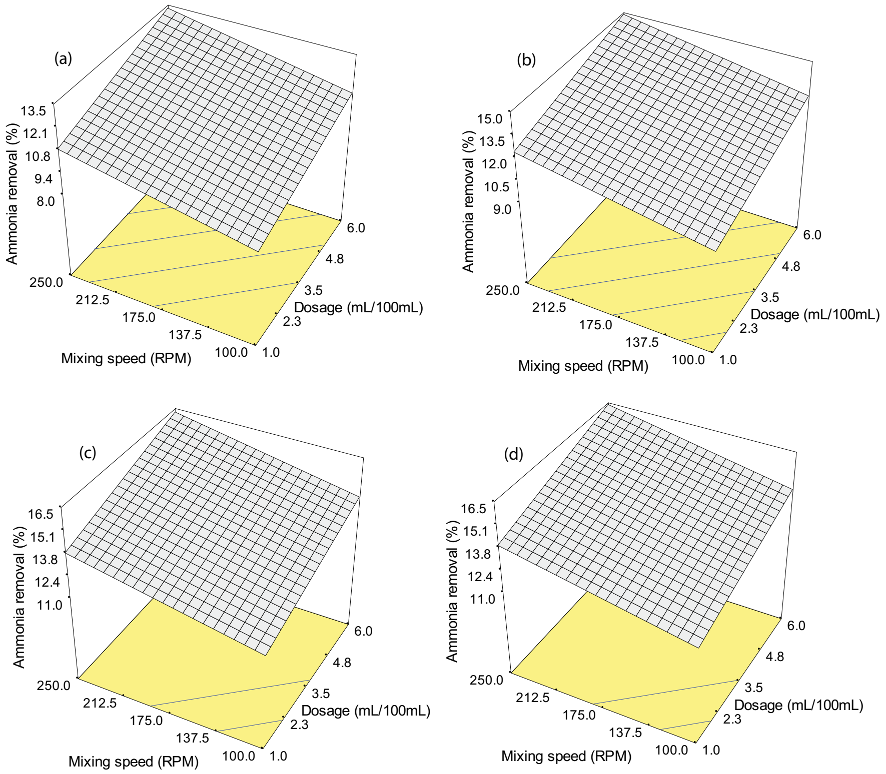

Fig. 3. Effect of dosage of coagulant and pH on ammonia removal. (a) Mixing speed = 175 and type of coagulant = khlas, (b) mixing speed = 175 and type of coagulant = sukkari, (c) mixing speed = 175 and type of coagulant = ferric sulfate and (d) mixing speed = 175 and type of coagulant = zinc sulfate.

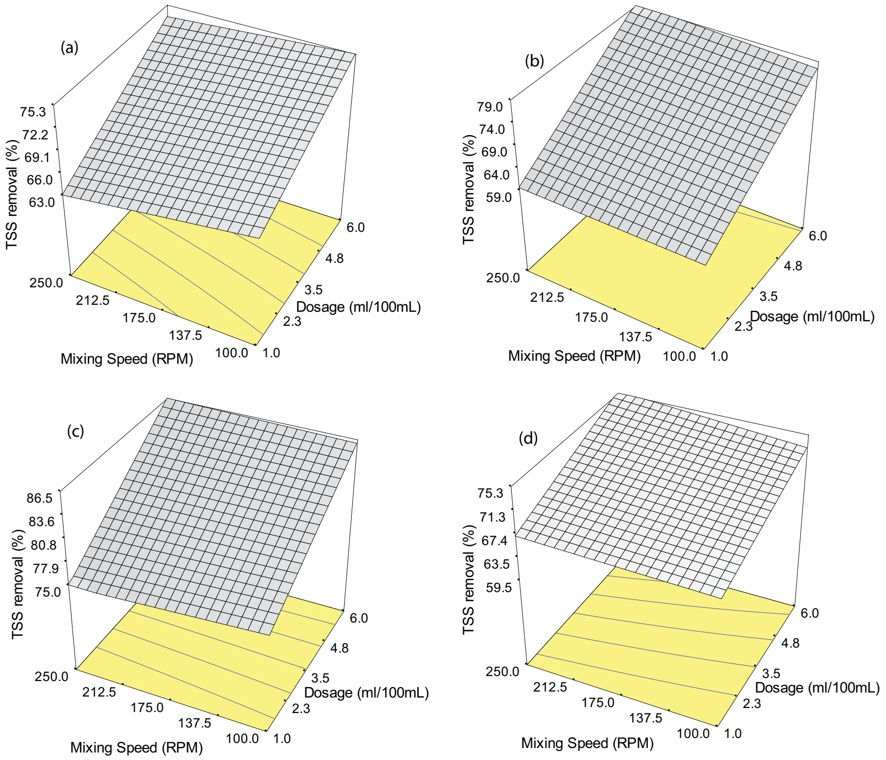

Fig. 4. Effect of dosage of coagulant and pH on TSS removal. (a) Mixing speed = 175 and type of coagulant = khlas, (b) mixing speed = 175 and type of coagulant = sukkari, (c) mixing speed = 175 and type of coagulant = ferric sulfate and (d) mixing speed = 175 and type of coagulant = zinc sulfate.

Table 5
Maximum removals of COD, color, ammonia and TSS

Type of coagulant	Removal, %				Operating condition				
	COD	Color	Ammonia	TSS	pH		Dosage, mL		
Khlas	16	70	17	91	9		6		
Sukkari	24	74	17	82	5		$1^{a,c}$	$6^{b,d}$	
Ferric sulfate	60	89	18	95	5		1^{b}	3.5^{a}	$6^{c,d}$
Zinc sulfate	60	84	21	96	7	5^{c}	$3.5^{b,d}$	$6^{a,c}$	

[a]Chemical oxygen demand (COD) removal, %; [b]Color removal, %; [c]Ammonia removal, %; [d]Total suspended solid (TSS) removal, %

Table 6
Validation of the optimum operating conditions

Run				Ferric sulfate							
Dosage, mL	Rapid mixing speed, rpm	pH	Type of coagulant	Experiment				Model			
				COD, %	Color, %	Ammonia, %	TSS, %	COD, %	Color, %	Ammonia, %	TSS, %
6.00	238.43	5.00	Ferric sulfate	55.34	89.39	15.28	91.07	51.1187	89.2467	16.9956	93.2937
				Zinc sulfate							
6.00	250.00	9.00	Zinc sulfate	53.13	73.00	16.58	88.79	51.3672	77.6634	15.9304	86.8487
				Khlas							
6.00	194.66	9.00	Khlas	11.61	53.06	12.22	78.20	11.9063	54.4858	12.1964	80.6096
				Sukkari							
4.32	201.42	5.04	Sukkari	14.75	56.12	13.99	67.11	14.9015	57.465	14.628	70.4142

Table 7
Reported performances of inorganic, organic and natural coagulants for the treatment of landfill leachate in comparison to the current study

Coagulants	Operating dosage	Operating pH	Removal efficiencies[a]	References
Poly-aluminium chloride (PACl)	1.9 g/L	7.5	57% COD 97% Color	[5]
	5.0 g/L	6.0	67% COD 98% Color 99% SS	[15]
Aluminium sulfate (Alum)	9.4 g/L	7.0	84% COD 92% Color	[5]
	9.0 g/L	5.0	67% COD 43% Ammonia	[6]
	5.0 g/L	7.0	64% COD 87% Color	[7]
	6.0 g/L	9.0	53% COD 69% Color 42% Ammonia 60% TSS	[3]
Ferric chloride, $FeCl_3$	COD:$FeCl_3$ 1:1.3	6.0	77% COD	[28]
	2.0 g/L	5.0	68% COD 97% Color	[7]
	12 g/L	7.6	50% COD 90% Turbidity 80% Color	[29]

Table 7 (Continued)

Table 7

Coagulants	Operating dosage	Operating pH	Removal efficiencies[a]	References
Tannin	1.46 g/L	6.0	53% COD 91% Color 66% Ammonia 61% TSS	[8][b]
			50% COD 91% Color 65% Ammonia 69% TSS	[9]
	0.6 g/L	9.0	43% COD 54% Color 39% Ammonia 60% TSS	[3]
Dimocarpus longan seed	2.0 g/L	4.0	39% COD 28% Color 22% SS	[15]
Red earth	8.0 g/L	2.0	54% COD 47% Ammonia	[6]
Ferric sulfate, $Fe_2(SO_4)_3$[c]	6.0 g/L	5.0	55% COD 89% Color 15% Ammonia 91% TSS	Current research
Ferric sulfate, $Fe_2(SO_4)_3$[d]	–	–	60% COD 89% Color 18% Ammonia 95% TSS	
Zinc sulfate, $ZnSO_4$[c]	6.0 g/L	9.0	53% COD 73% Color 17% Ammonia 89% TSS	
Zinc sulfate, $ZnSO_4$[d]	–	–	60% COD 84% Color 21% Ammonia 96% TSS	
Date palm seed, Khlas[c]	6.0 g/L	9.0	12% COD 53% Color 12% Ammonia 78% TSS	
Date palm seed, Khlas[d]	–	–	16% COD 70% Color 17% Ammonia 91% TSS	
Date palm seed, Sukkari[c]	4.32 g/L	5.0	15% COD 56% Color 14% Ammonia 67% TSS	
Date palm seed, Sukkari[d]	–	–	24% COD 74% Color 17% Ammonia 82% TSS	

[a]All values were rounded off, [b]Confirmatory laboratory experiments, [c]Optimum values, [d]Maximum values.

the pH of the medium, it was observed that khlas performed better at an alkaline medium yet it could work well at acidic medium, too. On the contrary, sukkari and the trivalent ferric sulfate coagulants were shown to work better at acidic medium. In the meanwhile, the bivalent zinc sulfate performed greater at neutral medium.

Therefore, the highest removals of the selected parameters that were summarized in Table 5 demonstrated that the treatment performance of the natural coagulant sukkari was found to be better than khlas particularly in terms of the COD removal. This might be due to the intermolecular forces exerted by the higher amount of various organic material and/or due to the higher content of phenolic compounds including total phenolics, flavonoids and tannins found within the aqueous extract of sukkari in comparison with that of khlas [30]. In the meantime, in spite of ferric sulfate being a trivalent compared to the bivalent zinc sulfate hence a denser ferric hydroxide-flocs formed in contrast to zinc hydroxide-flocs, the highest removals achieved by both inorganic coagulants were quite similar. This might be attributed to that zinc sulfate in fact is bigger in atomic size thus more electropositive than ferric sulfate. As a result, the tendency for zinc sulfate to ionize is higher hence more reactive.

Given earlier that there was an effect produced from significant interaction- that was different from the direct interaction- driven by the dependency of the variables on one another, the optimum operating conditions were necessarily vital in order to apprehend the correlation among all settings and yield optimum removals. A good example of the newly produced effect, considering the COD removal as the parameter, for instance, khlas was found to remove 16% COD at pH of 9 with a dosage of 6 mL while the removal declined down to 9% when the pH was 5 using the same dosage. Another example, sukkari could remove 24% of COD at pH 5 with a dosage of 1 mL yet the COD removal dropped dramatically by half down to 12% at the same pH but with an increased dosage of 6 mL.

5. Validation of the optimization conditions

Confirmation experiments were carried out using the optimum operation conditions found from the models for the khlas, sukkari, ferric sulfate, and zinc sulfate. Two experiments were run for each type of coagulant and the average results are also presented in Table 6. The rapid mixing speeds were rounded off for the compatibility of the orbital shaker in which khlas, sukkari, ferric sulfate and zinc sulfate were rapidly agitated at 195 rpm, 200 rpm, 240 rpm and 250 rpm, respectively. It is shown that the experimental results validated the predicted outcomes based on the optimum operating conditions generated by the models.

6. Conclusion

With the aid of RSM, the treatment performances of khlas, sukkari, ferric sulfate and zinc sulfate were determined and compared in response to the removals of COD, color, ammonia and TSS under different operating conditions, that is, type of coagulant, dosage, pH and rapid mixing speed. Per 100 mL sample of raw landfill leachate, the optimum dosage of khlas, ferric and zinc sulfates was 6 mL, while sukkari's was found to be 4.32 mL. At pH 5, ferric sulfate and sukkari performed optimally, whereas 9 was the optimum pH for khlas and zinc sulfate. The optimum rapid mixing speeds for khlas and sukkari were rounded off to 195 rpm and 200 rpm, respectively. Meanwhile, 240 rpm and 250 rpm were rounded out for ferric sulfate and zinc sulfate, correspondingly. Therefore, the optimal removals of COD, color, ammonia and TSS by (ferric sulfate–zinc sulfate) were rounded off to 55%–53%, 89%–73%, 15%–17% and 91%–89%, respectively, in comparison to the natural coagulants (khlas–sukkari) where the optimum removals obtained were as the following: 12%–15%, 53%–56%, 12%–14% and 78%–67%, subsequently. In regard to the maximum reduction of COD, color, ammonia and TSS, the maximum removals of 60%, 89%, 18% and 95% were achieved by ferric sulfate, respectively. Zinc sulfate, on the other hand, could remove 60% COD, 84% color, 21% ammonia and 96% TSS. As for the natural palm date seed coagulants, khlas maximally removed 16% COD, 70% color, 17% ammonia and 91% TSS. On the contrary, the maximum removals accomplished by sukkari were 24% COD, 74% color, 17% ammonia and 82% TSS. Hence, khlas and sukkari were proven to be effective natural coagulants that might replace the conventional coagulants for the removal of color, ammonia and TSS. On the other hand, enhancing the preparation of the natural coagulants and employing combined treatment systems need to be further investigated in order to improve the removal of COD and other possible pollutants.

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