Pol. J. Environ. Stud. Vol. 30, No. 2 (2021), 1215-1225
DOI: 10.15244/pjoes/120515 ONLINE PUBLICATION DATE: 2020-09-28

Original Research

Response Surface Analysis for Sewage Wastewater Treatment Using Natural Coagulants

Arlene Abuda Joaquin[1]*, Gnanasundaram Nirmala[1], Panchanathan Kanakasabai[2]

[1]School of Chemical Engineering, Vellore Institute of Technology, Vellore, 632014, India
[2]Chemical Engineering Section, Salalah College of Technology, Salalah 211, Oman

Received: 29 February 2020
Accepted: 14 April 2020

Abstract

The studies on utilization of natural coagulants prepared from seeds of *Citrullus lanatus* (watermelon) and *Cucumis melo* (cantaloupe) provide insight on sewage wastewater treatment. The results were statistically analyzed by response surface methodology (RSM) based central composite design (CCD), and supported with results from Fourier Transform Infrared (FTIR) spectroscopy for functional groups present in coagulants. The batch coagulation studies were performed varying process parameters such as pH (5-7) and coagulant dosage (50-150 mg/L) at constant flocculant dosage of 10 mg/L using jar test. In jar test, coagulation was carried out with fast mixing (Mixing at 150 rpm for 1 min) followed by slow mixing (Mixing at 50 rpm for 30 min), and the final mixture was allowed to settle for 1 h at the temperature of 30±2ºC. Design-Expert® version 12 software was used to optimize pH and coagulant dosage for effective sewage wastewater treatment using natural coagulants with the objectives to maximize percentage reduction in turbidity, biological/biochemical oxygen demand (BOD), total suspended solids (TSS), and chemical oxygen demand (COD). The RSM results reveal that the optimum *C. lanatus* coagulant dosage of 72.3 mg/L at pH 5 achieved maximum efficacy removal of TSS and BOD by 92.8% and 92.1% respectively. The FTIR results show that the coagulants from plant seeds contain almost similar functional groups. Thus, it can be concluded that the coagulant prepared from *C. lanatus* would be more effective for treatment of sewage wastewater.

Keywords: coagulation-flocculation, sewage wastewater, natural coagulant, response surface methodology, FTIR analysis

Introduction

Nowadays, the treatment and disposal of sewage wastewater is gaining significance in order to protect the quality of terrestrial and aquatic life [1]. Discharging sewage wastewater without proper treatment contributes to pollution of the water resources and ecosystem [2]. The largest source of water pollution in terms of volume discharged is the sewage wastewater [3]. Sewage wastewater, the water generated from domestic, commercial and public buildings, is composed of bodily wastes (primarily feces and urine) along with the water utilized for toilet flushings, washing utensils, laundry preparation, and cleaning of other materials [4]. The wastewater can be destructive to public health because it contains high TSS, dissolved organic and

*e-mail: joaquin_arlene@yahoo.com

inorganic matter, biological substances and toxic materials [5].

The disposal of wastewater to groundwater or surface water without proper treatment causes risks to human health and environment. Therefore, it is important to identify the appropriate method of treating the wastewater for the welfare of the people and the community with maximum performance and low-cost [5, 6]. The efficiency of water and wastewater treatment is influenced by the number of stages. The three stages of wastewater treatment include primary, secondary and tertiary. The treatment methods involve water clarification processes such as coagulation, flocculation, sedimentation, disinfection, etc. [7]. One of the principal techniques for wastewater treatment is coagulation and flocculation, used mostly for the treatment of domestic, commercial and industrial wastewater in the world [6-8]. Coagulation is a process to destabilize charged particles to form a gelatinous mass to settle or to be trapped in the filter. On the other hand, flocculation is done by gentle mixing or agitation so that the particles agglomerate into floc [8].

The coagulation-flocculation process is affected by the type of coagulant, pH, coagulant dosage, flocculant dosage, mixing speed and time for fast and slow mixing in jar test, and the characteristics of wastewater [9]. Moreover, coagulation-flocculation process has been widely employed for potable water and wastewater treatment as a reliable and convenient technique to overcome the forces of stabilizing suspended particles and facilitating the collection and formation of flocs [10-11]. There are different types of coagulants such as natural/organic, inorganic and polymeric materials. Chemical coagulants such as alum [3, 12-14], ferric chloride [12, 14], polyaluminum chloride [13, 15], hydrated lime [3], and calcium carbonate [16] have been used in wastewater treatment to remove pollutants. Most municipal wastewater treatment plants use inorganic polymeric coagulants for turbidity and suspended solids removal [13, 15]. However, the most widely used coagulants for water and wastewater treatment is aluminium sulfate (alum) due to its effectiveness and low-cost although it has been found to cause some health effects to human and create problems to the environment upon long-term usage [3, 14].

On the other hand, biomass based organic polymeric flocculants prepared from *Moringa oleifera* seeds [17-19], nirmali (*Strychnos potatorum*) seeds [20-21], tannin [22] and cactus [22] have been the interest of many researchers as the viable alternative choice and tested over the years for different types of water and wastewater treatment due to its efficiency to flocculate with less dosage, high biodegradability, cost effective, abundant availability, eco-friendliness, production of biodegradable sludge, and not likely to produce extreme pH [23, 24]. The natural coagulants are generally produced from plant seeds which contain carboxyl, hydroxyl and amino groups that have significant affinity towards various pollutants from their aqueous solutions that enables the coagulation to work effectively [25-27]. In the present study, natural coagulants extracted from the seeds of *C. lanatus* and *C. melo* collected in the Dhofar Governorate of Sultanate of Oman was used. The climate and ecological diversity in the country offers an opportunity to grow off-season fruits and vegetables because of the mild winter climate. The farmers have selected and conserved landraces and local cultivars in a dynamic way.

The fruits of watermelon and cantaloupe are known for its high nutritional value and rich in vitamins and minerals. However, seeds from watermelon are known for its natural coagulant properties that removes the turbidity, BOD, TSS, and COD to greater extent [28, 29]. Furthermore, it is also effective to enhance the filtration process during water treatment with antimicrobial agents [30,31]. On the other hand, cantaloupe is one of the major fruits grown in the middle east. The peel of the fruit is naturally enriched with pectin, α-cellulose and non-essential amino acids [32, 33]. Furthermore, the seeds of watermelon and cantaloupe is a good replacement for inorganic and synthetic polyelectrolytes in treating water and wastewater since the natural coagulants are effective and cheaper. The functional goups in the seeds are generally characterized through FTIR. The presence of carboxyl, hydroxyl and amino groups in the coagulant accelerates the effectiveness of coagulation for the maximum removal of turbidity and TSS in municipal wastewater.

A statistical experimental design, RSM, is used in the present study for better understanding of the experimental approach. It works by fitting experimental responses to quadratic function [34]. Also, RSM has successfully helped in the modeling and optimization of various experimental designs involving wastewater treatment process, extraction process, food preservation and other discipline of engineering [3, 15, 26, 32]. The stages involved in the RSM as an optimization tool include: selection of independent variables and their levels, selection of experimental design, generation and validation of model equation, graphical representation and searching for optimal region [35].

The main aim of the study is to investigate the efficacy of natural coagulants (*C. lanatus* and *C. melo*) for treatment of sewage wastewater using coagulation-flocculation process for the reduction of turbidity, BOD, TSS and COD.

Materials and Methods

Preparation of Natural Coagulants from *C. lanatus* (watermelon) and *C. melo* (cantaloupe) Seeds

The fresh fruits of watermelon and cantaloupe, grown locally, were procured from the local commercial market in Salalah, Oman. The natural plant seeds were collected from fresh fruits. The seeds were washed several times with double distilled water and dried in the hot air oven at 70ºC to drying. The seeds were sorted to remove debris, shelled and milled to obtain fine powder. The powdered seeds were extracted by means of Soxhlet extraction for about 6 hours using hexane as solvent to obtain a seed cake without oil [36]. The presence of oil in seed could reduce the efficiency of the coagulant. The cake seed is thoroughly washed with double distilled water in order to remove the excess n-hexane, and finally dried in oven at 60ºC until constant weight and screened through 255 microns and stored in air-tight containers for use as natural powder coagulant. The stock solution of natural coagulant was prepared by adding 1 g of processed seed cake in 100 mL of double distilled water.

Jar Test Method

The most widely applied technique in the sewage treatment plant is coagulation-flocculation due to its effectiveness [3, 37]. The study was performed using the jar test apparatus (Armfield Company, UK) for the evaluation and optimization of coagulation-flocculation. The jar test apparatus has stirrers with six blades each rotates with independent variable speed motors at a stirring speed of 0 to 200 rpm. The wastewater sample was well-shaken for the re-suspension of possible settling solids and the aliquot volume of sample transferred to the jar test beakers. The coagulant dosage (50-150 mg/L) and pH (5-7) were the input variables. However, turbidity, BOD, TSS and COD were the dependent variables for coagulation-flocculation performance. The pH of the wastewater sample was adjusted to the desired pH value of (5.0-7.0) by adding (1 N HCl) or (1 N NaOH) solution. The experimental process consists of 3 steps: fast mixing at 150 rpm for 1 min followed by slow mixing for 30 min at 50 rpm and finally settled for 1 h at the temperature of 30±2ºC. After the settling period time, the supernatant was withdrawn and transferred to the flask for subsequesnt analysis and the sludge (dense floc) was discarded. The characterization of supernatant was performed in quadrapulate and the mean value was taken as response, according to the standard operating procedures [38]. The coefficient of variance was found to be within 5%.

Experimental Design and Process Optimization Using RSM

Design-Expert® version 12 software from Statease Inc., USA was used in the present study for the statistical design of experiments and analysis of data. central composite design (CCD) and Box-Behnken design (BBD) are the two statistical experimental designs in RSM. CCD was selected in the present study to identify the optimal region for the factors affecting the performance of coagulation-flocculation process due to its efficiency [39].

The two most important operating variables in the study were coagulant dosage and pH. The coded values for pH (A) and coagulant dosage (B) were set at levels: pH (-1 ↔ 5.00) low, (+1 ↔ 7.00) high and coagulant dosage (-1 ↔ 50.00) low, (+1 ↔ 150.00) high. The response factors considered were percentage reduction in turbidity, TSS, BOD and COD. The number of trials performed in CCD is $2^f+2f+CP$ where f is the number of factors or variables and CP is the number of center points [40]. Trials performed as shown in Table 1 were thirteen (13) with 5 centre points for 2 variables as per the CCD matrix. The experimental data fitted to the quadratic equation was used to study the effect of factors on the response as represented in Equation (1) and model coefficients were evaluated using Equation (2). The coefficients in Equation (1) were analyzed for checking the similarity between experimental and predicted values based on the *p*-value with a 95% confidence level. The significance of the model was tested using analysis of variance (ANOVA). Regression coefficients R^2, adjusted R^2 and predicted R^2 values were assessed to find the fit between experimental and predicted values. The value between 0.9 and 1 reveals the best of fit between experimental and predicted values.

$$\mathrm{Y} = \beta_0 + \sum_{i=1}^{n}\beta_i X_i + \sum_{i=1}^{n}\beta_{ii} X_i^2 + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\beta_{ij} X_i X_j + \varepsilon \tag{1}$$

$$\beta = (X^T X)^{-1}(X^T Y) \tag{2}$$

...where: β_o is an intercept; β_i, β_{ii}, β_{ij} are linear, squared and interaction coefficients respectively, Y is the response; X_i and X_j are independent factors; and, ε is a random error.

FTIR Analysis

Fourier Transform Infrared (FTIR) spectrophotometer was used to detect functional groups. The samples *C. lanatus* and *C. melo* were grounded and then compressed and formed into pellets. The pellets formed were analyzed covering a frequency range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1} at room temperature [41].

Analytical Methods

The sewage wastewater sample was collected from *Salalah Sanitary Drainage Services Company* SAOC (SSDS) water reclamation plant where the flow rate is 35,000-40,000 m^3/day [42]. The sewage wastewater sample collected in an air-tight glass container was characterized for physiochemical parameters such as turbidity, TSS, BOD and COD. All experiments were performed to determine the physiochemical parameters in quadrapulate to ensure the results with minimum error. The pH of the solution was measured using a pH Meter (Hanna HI2211-02) with regular calibrations of 4.01, 7.0 and 10.0 standard pH buffer solutions (Thermo

Scientific Orion). The turbidity was measured using the ISO Turbidity Portable Meter (HI98713-01). However, the BOD was measured using 5-day DO test as per the APHA standard method and COD was measured using the dichromate open reflux method as per standard methods [43]. The TSS values were measured using gravimetric method.

The percentage removal efficiencies of turbidity, TSS, COD and BOD was determined according to Equation (3):

$$\% \text{ Removal} = (C\mathit{influent} - C\mathit{effluent}) \div (C\mathit{influent}) \times 100 \quad (3)$$

...where: C*influent* and C*effluent* are the concentrations of TSS, COD and BOD in the influent and effluent respectively.

Results and Discussion

Characteristics of Sewage Wastewater Collected

The sewage wastewater was characterized and pH, turbidity, TSS, BOD and COD were found to be 7.25, 225 mg/L, 500 mg/L, 60 mg/L and 575 mg/L respectively.

Assessment of Statistical Modeling and Optimization through RSM

Tables 1 and 2 show the results of the CCD matrix designed for input variables with percentage reduction in turbidity, COD, TSS and BOD using *C. lanatus and C. melo* as natural coagulants. The independent variables (inputs) used in this experiment were pH (5-7) and coagulant dosage (50-150 mg/L). The reduction percentage in turbidity, TSS, BOD and COD were the responses or dependent variables. Optimization was carried out for thirteen experiments to compare the corresponding experimental and predicted results for both coagulants for removal efficiencies of responses as given in Table 3. From the results obtained in the experiments, quadratic model was recommended to represent the performance of coagulation-flocculation process for each coagulant used in the experiments. The pH and dosage are both significant terms to yield higher percentage removal of TSS [43]. The TSS response surface indicates 92.8% removal efficiency, which agrees with findings using conventional coagulants found to be the same in *C. lanatus* natural coagulant.

Tables 4 and 5 show the analysis of variance (ANOVA) results of the quadratic models. The results were assessed with various descriptive statistics such as; *p* value, lack of fit test, coefficients of determination R^2 and adequate precision. The *p-value* is used to estimate whether the F value is large enough to indicate statistical significance [44]. The higher Fishers's *F*-test values and low of *p*-values (<0.05) imply that the quadratic model terms are significant [45]. However, *p*-values ≥ 0.05 indicate the insignificant model terms. Thus, results in quadratic models predicted in *C. lanatus* are higher in *F*-test and *p*-value less than 0.05 (Table 4). For *C. melo*, F-value is lower than *C. lanatus* with *p*-value less than 0.05 (Table 5) which means that both results were

Table 1. CCD matrix for reduction of Turbidity, TSS, BOD and COD by coagulation using citrullus lanatus coagulant.

		Factor 1	Factor 2	Response 1	Response 2	Response 3	Response 4
Std	Run	A:pH	B:Coagulant dosage	Reduction in Turbidity	Reduction in TSS	Reduction in BOD	Reduction in COD
			mg/L	%	%	%	%
11	1	6	100	37.6	87.7	95.5	71.4
5	2	5	100	37.6	92.2	97.7	71.4
7	3	6	50	96.6	86.7	76.1	10
13	4	6	100	37.6	87.7	95.5	71.4
8	5	6	150	35.6	76.7	95.5	78.6
4	6	7	150	40	77.2	88.1	71.4
1	7	5	50	95.5	93.3	86.4	14.3
6	8	7	100	34.1	87.7	85.2	71.4
9	9	6	100	37.6	87.7	95.5	71.4
2	10	7	50	92.8	85.5	50	34.3
10	11	6	100	37.6	87.7	95.5	71.4
12	12	6	100	37.6	87.7	95.5	71.4
3	13	5	150	36.5	79.5	96.6	81.4

Table 2. CCD matrix for reduction of Turbidity, TSS, BOD and COD by coagulation using cucumis melo coagulant.

		Factor 1	Factor 2	Response 1	Response 2	Response 3	Response 4
Std	Run	A:pH	B:Coagulant dosage	Reduction in Turbidity	Reduction in TSS	Reduction in BOD	Reduction in COD
			mg/L	%	%	%	%
11	1	6	100	53.2	91.1	95.4	28.6
5	2	5	100	30.1	88.9	88.6	11.4
7	3	6	50	59.5	87.7	39.8	88.6
13	4	6	100	53.2	91.1	95.4	28.6
8	5	6	150	46.7	89.4	96	50
4	6	7	150	69.1	77.7	93.3	69.9
1	7	5	50	41.8	64.4	44	22.9
6	8	7	100	88.2	87.7	94.3	57.1
9	9	6	100	53.2	91.1	95.4	28.6
2	10	7	50	68.1	87.7	65.9	71.4
10	11	6	100	53.2	91.1	95.4	28.6
12	12	6	100	53.2	91.1	95.4	28.6
3	13	5	150	32.1	88.4	92	48.6

significant. Therefore, the model developed in the study was statistically significant in (±5%).

The adequate precision ratios obtained as shown in Table 6 (*C. lanatus*) and Table 7 (*C. melo*) were greater than 4, indicating that the adequate signal for all models could be used to navigate the design space. The lack of fit test describes the variation of data around the fitted model. If the quadratic models fit the data, the lack-of-fit test will be insignificant [46]. Table 4 and 5 indicate that the lack-of-fit values in all models are insignificant. The ANOVA of regression model (R^2) greater than 0.98 values indicates the aptness of the model. R^2 values in *C. lanatus* (Table 6) are all greater than 0.81 while in *C. melo* (Table 7) all values were reduced. Moreover, R^2 values close to 1 denote a satisfactory adjustment of the quadratic models to the experimental data. This phenomenon justified the high treatment efficiency removal in *C. lanatus* rather than *C. melo* coagulant.

The 3-D response surface plots of the regression equation (1) are presented in Figs 1 and 2. The effect of natural coagulant dosage and pH and their interactions on a percentage reduction in turbidity, BOD, TSS, and COD are shown in Figs 1(a-d) and 2 (a-d) for watermelon (*C. lanatus*) and cantaloupe (*C. melo*) respectively. The results of the experiments conducted for the effect of pH and dosage on turbidity and TSS removal are presented in Fig. 1(a-b) and Fig. 2(a-b). Results from Fig. 1(a-b) showed that at pH 5 and coagulant dosage of 50 mg/L, the removal of turbidity and TSS were high at 95.5 and 93.3% respectively. When coagulant dosage was increased to 100 mg/L, the removal of turbidity and TSS were reduced to 37.6 and 92.2% respectively. On the other

Table 3. Optimal values for reduction of Turbidity, TSS, BOD and COD by coagulation using *Citrullus lantus* and *Cucumis melo* *c*oagulant.

Natural Coagulant	pH	Natural Coagulant Dosage mg/L	% Turbidity Reduction	% TSS Reduction	% BOD Reduction	% COD Reduction
Citrullus lanatus	5	72.3	66.5 (Experimental)	92.8 (Experimental)	92.1 (Experimental)	42.9 (Experimental)
			62.8 (Predicted)	94.2 (Predicted)	94.9 (Predicted)	44.3(Predicted)
Cucumis Melo	7	76.7	78.2 (Experimental)	87.7 (Experimental)	80.1 (Experimental)	64.3 (Experimental)
			77.0 (Predcted)	89.6 (Predicted)	86.9 (Predicted)	56.9 (Predicted)

Table 4. ANOVA result of the quadratic models for reduction in Turbidity, TSS, COD and BOD coagulation-flocculation using *C. lanatus*.

Source	df	% Turbidity Reduction				% TSS Reduction				% BOD Reduction				% COD Reduction			
		Sum of Squares	Mean Square	F-value	p-value	Sum of Squares	Mean Square	F-value	p-value	Sum of Squares	Mean Square	F-value	p-value	Sum of Squares	Mean Square	F-value	p-value
Model	5	7719.08	1543.82	671.21	< 0.0001	315.48	63.10	935.32	< 0.0001	2053.18	410.64	68.40	< 0.0001	6960.87	1392.17	78.38	< 0.0001
A-pH	1	1.22	1.22	0.5282	0.4909	35.53	35.53	526.64	< 0.0001	549.13	549.13	91.47	< 0.0001	16.67	16.67	0.9384	0.3650
B-Coagulant dosage	1	4976.64	4976.64	2163.71	< 0.0001	171.74	171.74	2545.77	< 0.0001	763.88	763.88	127.25	< 0.0001	4976.64	4976.64	280.20	< 0.0001
AB	1	9.61	9.61	4.18	0.0802	7.56	7.56	112.11	< 0.0001	194.60	194.60	32.42	0.0007	225.00	225.00	12.67	0.0092
A^2	1	2.03	2.03	0.8817	0.3790	13.54	13.54	200.65	< 0.0001	62.63	62.63	10.43	0.0145	23.56	23.56	1.33	0.2872
B^2	1	2386.16	2386.16	1037.44	< 0.0001	100.63	100.63	1491.75	< 0.0001	299.42	299.42	49.88	0.0002	1614.72	1614.72	90.91	< 0.0001
Residual	7	16.10	2.30			0.4722	0.0675			42.02	6.00			124.33	17.76		
Lack of Fit	3	16.10	5.37			0.4722	0.1574			42.02	14.01			124.33	41.44		
Pure Error	4	0.0000	0.0000			0.0000	0.0000			0.0000	0.0000			0.0000	0.0000		
Cor Total	12	7735.18				315.95				2095.20				7085.19			

Table 5. ANOVA result of the quadratic models for reduction in Turbidity, TSS, COD and BOD coagulation-flocculation using *C. melo*.

Source	df	% Turbidity Reduction				% TSS Reduction				% BOD Reduction				% COD Reduction			
		Sum of Squares	Mean Square	F-value	p-value	Sum of Squares	Mean Square	F-value	p-value	Sum of Squares	Mean Square	F-value	p-value	Sum of Squares	Mean Square	F-value	p-value
Model	5	2598.69	519.74	12.80	0.0021	638.48	127.70	16.36	0.0010	4760.10	952.02	34.60	< 0.0001	5104.94	1020.99	5.85	0.0193
A-pH	1	2456.33	2456.33	60.51	0.0001	21.66	21.66	2.78	0.1396	139.20	139.20	5.06	0.0593	2223.38	2223.38	12.74	0.0091
B-Coagulant dosage	1	77.04	77.04	1.90	0.2107	41.08	41.08	5.26	0.0554	2886.43	2886.43	104.91	< 0.0001	34.56	34.56	0.1980	0.6698
AB	1	28.62	28.62	0.7051	0.4288	289.00	289.00	37.04	0.0005	106.09	106.09	3.86	0.0903	184.96	184.96	1.06	0.3376
A^2	1	23.56	23.56	0.5804	0.4710	92.69	92.69	11.88	0.0107	1.79	1.79	0.0651	0.8060	64.97	64.97	0.3722	0.5611
B^2	1	27.05	27.05	0.6663	0.4412	84.86	84.86	10.88	0.0132	1428.81	1428.81	51.93	0.0002	2518.97	2518.97	14.43	0.0067
Residual	7	284.16	40.59			54.62	7.80			192.60	27.51			1221.96	174.57		
Lack of Fit	3	284.16	94.72			54.62	18.21			192.60	64.20			1221.96	407.32		
Pure Error	4	0.0000	0.0000			0.0000	0.0000			0.0000	0.0000			0.0000	0.0000		
Cor Total	12	2882.85				693.10				4952.70				6326.90			

Table 6. Regression analysis and model coefficients for reduction in Turbidity, TSS, BOD and COD by coagulation-flocculation using C. lanatus coagulant

Coagulant	Response	Regression Analysis				Model Coefficient					
		R^2	Adj. R^2	Pred. R^2	Adeq Precision	Intercept	A	B	AB	A²	B²
Citrullus Lanatus	% Turbidity reduction	0.9979	0.9964	0.9798	58.9137	37.3448	-0.45	-28.8	1.55	-0.856897	29.3931
	% TSS reduction	0.9985	0.9974	0.9848	94.7693	87.7103	-2.43333	-5.35	1.375	2.21379	-6.03621
	% BOD reduction	0.9799	0.9656	0.7982	28.7189	95.7034	-9.56667	11.2833	6.975	-4.76207	-10.4121
	% COD reduction	0.9825	0.9699	0.8333	25.3571	70.5655	1.66667	28.8	-7.5	2.92069	-24.1793

Table 7. Regression analysis and model coefficients for reduction in Turbidity, TSS, BOD and COD by coagulation-flocculation using *C. melo* coagulant.

Coagulant	Response	Regression Analysis				Model Coefficient					
		R^2	Adj. R^2	Pred. R^2	Adeq Precision	Intercept	A	B	AB	A²	B²
Cucumis melo	% Turbidity reduction	0.9014	0.8310	0.0281	11.5178	54.0655	20.2333	-3.58333	2.675	2.92069	-3.12931
	% TSS reduction	0.9212	0.8649	0.3263	12.8323	91.9552	1.9	2.61667	-8.5	-5.7931	-5.5431
	% BOD reduction	0.9611	0.9333	0.6495	16.6861	94.0414	4.81667	21.9333	-5.15	0.805172	-22.7448
	% COD reduction	0.8069	0.6689	-0.7929	8.6787	31.6	19.25	-2.4	-6.8	-4.85	30.2

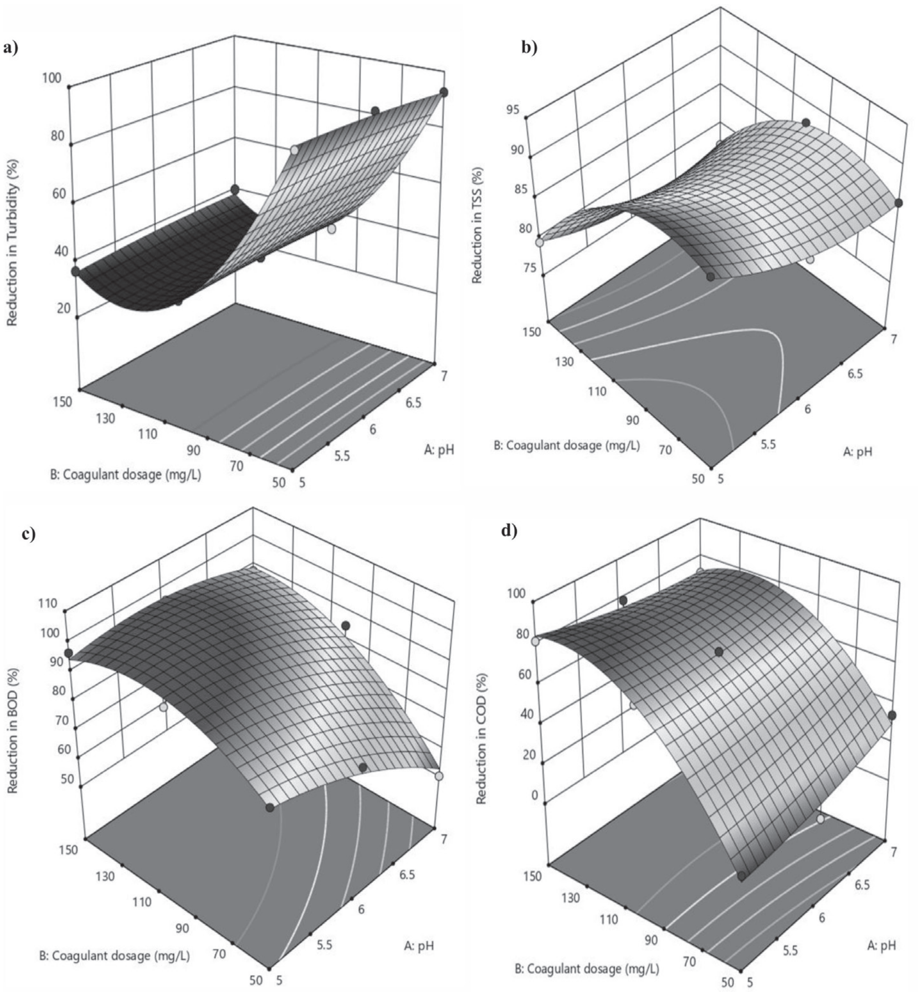

Fig. 1. Three dimensional response surface plots showing the effect of pH and coagulant dosage on reduction of a) Turbidity, b) TSS, c) BOD (d) COD by coagulation using watermelon (citrullus lanatus) coagulant.

hand, a dosage of 150 mg/L was also decreased in turbidity to 36.5 and TSS to 79.5%. However, in Fig. 2(a-b), it is clear that at pH 5 and coagulant dosage of 50 mg/L, the removal of turbidity and TSS were only 41.8 and 64.4 % respectively. When the coagulant dosage was increased to 100 mg/L and 150 mg/L, the percentage removal of turbidity was reduced more to (30.1 and 32.1%) while TSS increased to (88.9 and 88.4%) respectively. The natural coagulant is more effective in turbidity at lower pH and dosage. Thus, TSS was found to be efficient regardless of dosage and pH.

The results of the experiments conducted for the effect of pH and dosage on the BOD and COD removal are presented in Fig. 1(c-d) and 2(c-d). The results from Fig. 1(c-d) showed that at pH 5 and coagulant dosage of 50 mg/L, the removal of BOD was 86.4% and COD removal was very low at 14.3%. When coagulant dosage was increased to 100 mg/L, the percentage removal of BOD and COD increased to 97.7 and 71.4% respectively. Again, after the coagulant dosage was increased to 150 mg L^-, the removal were remained high of 96.6 for BOD and 81.4 % for COD. Further, Fig. 2(c-d) resulted in lower BOD (44%) and COD (22.9%) in 50 mg/L at pH 5. When dosage increased to 100 mg L^- and 150 mg L^-, the percentage removal of BOD increased to 88.6 and 92% respectively. Thus, as pH increases to 6 and 7 and dosage of 100 and 150 mg/L in both natural coagulants the percentage removal of BOD remains high. However, the percentage removal of COD remains low in 100 mg/L (11.4%) and 150 mg/L (48.6%). The study showed that the response surface method was very effective to obtain the optimum condition and maximizing the removal of turbidity, BOD and COD.

FTIR Results from Watermelon (*Citrullus lanatus*) and Cantaloupe (*Cucumis melo*) Seeds

The Fourier transform infrared spectroscopy (FTIR) technique was an important tool to identify some functional groups present in the natural coagulant of watermelon *(C. lanatus)* and cantaloupe *(C. melo)* as shown in Fig. 3. The spectrum shows the plot of absorption intensity versus the wavelength frequencies of the compound. Two similar strong peak patterns observed both in *C. lanatus* and *C. melo* at

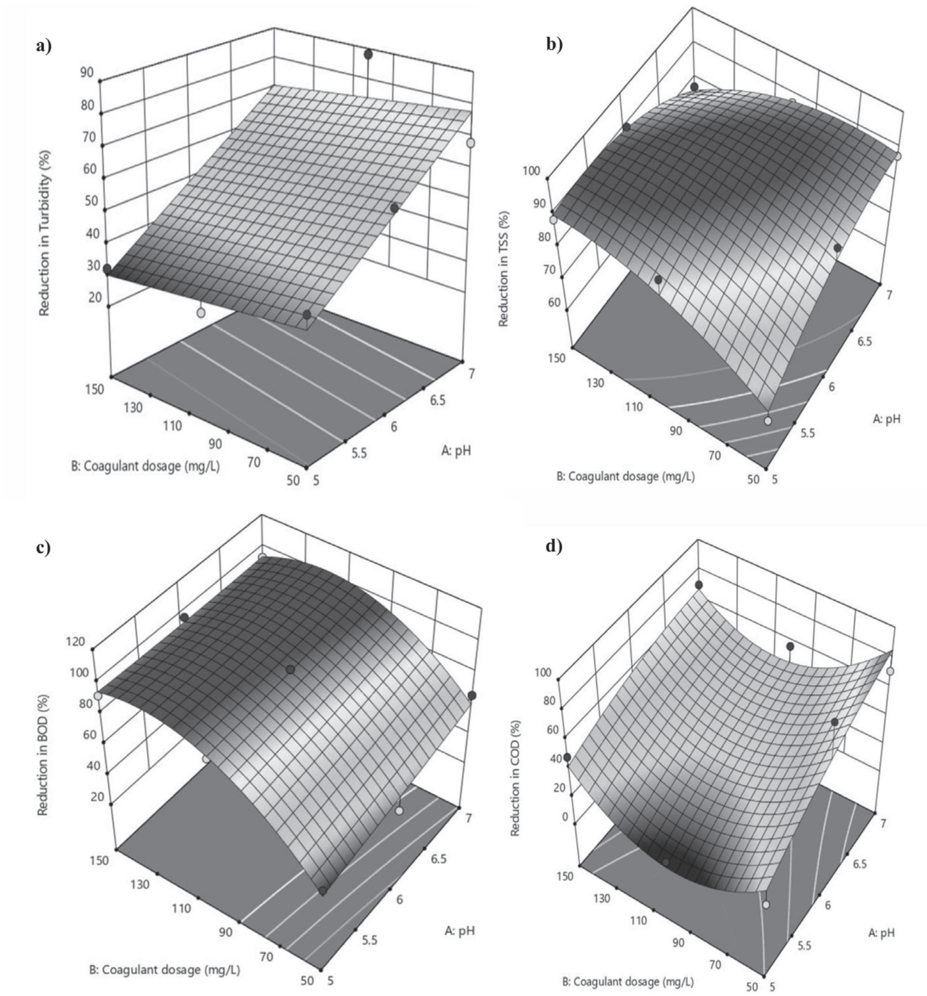

Fig. 2. Three dimensional response surface plots showing the effect of pH and coagulant dosage on reduction of a) Turbidity, b) TSS, c) BOD (d) COD by coagulation using cantaloupe (cucumsis melo) coagulant.

3269.34 cm^{-1} which signify the presence of strong bands of O-H bond that indicates the presence of water. In addition, stretching was observed in the region between 2500 and 3000 cm^{-1} indicates the presence of C-H bond. These two main functional groups found in *C. lanatus* and *C. melo* could be attributed to the contents of protein [47]. These results are in agreement obtained in the high percentage removal of turbidity in the study.

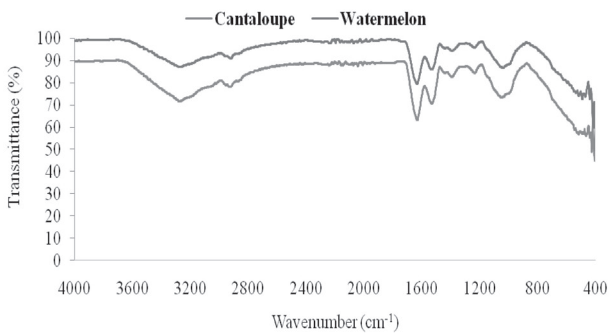

Fig. 3. FTIR spectra of extracting seeds from watermelon *(C. lanatus)* and cantaloupe *(C. melo)* seeds.

Thus, some studies show that natural coagulant from *M. oleifera* seeds have greater effectiveness for the removal of high turbidity in wastewater [48]. Moreover, the region between 1400 and 1700 cm^{-1} corresponds to the carbonyl, C=O-NHR, amine, NH_2 and ammonium, NH^{+3} bands. As it can be seen in the result strong bands similarity of C=O stretching was observed in the region between 1500 and 1750 cm^{-1}. Also, free amino acids aggravate the catalytic property, thus improving charge neutralization of suspended solids and bridging the flocculation [49]. One comparable bending band observed at 1000 and 1500 which verified the presence of amino group in both natural coagulants (*C. lanatus* and *C. melo*) which reduce the TSS and COD levels after the treatment [50]. Moreover, it was observed that the two plant species seeds obtained almost similar spectra.

Conclusion

Application and optimization of natural coagulants from watermelon *(C. lanatus)* and cantaloupe *(C. melo)* in the coagulation-flocculation process were investigated in this study. The response surface methodology design using CCD was applied to determine the operating conditions of turbidity, total suspended solids, BOD, and COD. Based on the results demonstrated, the removal efficiency of both natural coagulants was highly effective. The natural coagulants of *C. lanatus* and *C. melo* achieved the maximum treatment performance of TSS (92.8% and 87.7%) and BOD (92.1% and 80.1%) under the dosage of 72 mg/L and 76.7 mg/L in pH (5 and 7) respectively. Instead of discarding or simply thrown away the seeds, a possible option is to convert into a natural coagulant to purify water and wastewater. The ability of natural plant seeds from *C. lanatus and C. melo* to act as a natural coagulant for treatment of municipal wastewater can be a suitable and effective pre-treatment option instead of conventional coagulants.

Acknowledgement

The authors would like to acknowledge the support of Salalah Sanitary Drainage and Services (SSDS) and Salalah College of Technology (SCT), Engineering Department, Sultanate of Oman, for the opportunity to perform the various stages of research. Also, to the School of Chemical Engineering, Vellore Institute of Technology (VIT), India, for the guidance and evaluation of the research.

Conflict of Interest

The authors declare no conflict of interest.

References

1. YANG G., ZHANG G., WANG H. Current state of sludge production, management, treatment and disposal in China. Water Research, **78**, 60, **2015**.
2. MORRISON G., FATOKI O.S., PERSSON L., EKBERG A. Assessment of the impact of point source pollution from the Keiskammahoek Sewage Treatment Plant on the Keiskamma River-pH, electrical conductivity, oxygen-demanding substance (COD) and nutrients. Water SA, **27** (4), 475, **2001**.
3. JOAQUIN A.A., NIRMALA G. Statistical modeling and process optimization of coagulation–flocculation for treatment of municipal wastewater. Desalination and Water Treatment, **157**, 90, **2019**.
4. EDZWALD J.K. Rapid-Mixing Tanks for Coagulation: Are They Needed?. Journal of the New England Water Works Association, **128** (1), 1, **2014**.
5. SIVARANJANI S., RAKSHIT A. Study on removal efficiency of blended coagulants on different types of wastewater. Nature Environment and Pollution Technology **16** (1), 107, 2017**.**
6. NAIDOO S., OLANIRAN A.O. Treated wastewater effluent as a source of microbial pollution of surface water resources. International Journal of Environmental Research and Public Health, **11** (1), 249, **2014**.
7. SPILLER M., VREEBURG J.H., LEUSBROCK I., ZEEMAN G. Flexible design in water and wastewater engineering - definitions, literature and decision guide. Journal of Environmental Management, **149**, 271, **2015.**
8. BINTI SAHARUDIN N.F.A., NITHYANANDAM R. Wastewater treatment by using natural coagulant. 2nd Eureca, **4**, 213, **2013**.
9. AGUNBIADE M.O., POHL C.H., ASHAFA A.O. A review of the application of biofloccualnts in wastewater treatment. Polish Journal of Environmental Studies, **25** (4). 1381, **2016**.
10. GOLOB V., VINDER A., SIMONIČ M. Efficiency of the coagulation/flocculation method for the treatment of dyebath effluents. Dyes and Pigments, **67** (2), 93, **2005**.
11. TEH C.Y., BUDIMAN P.M., SHAK K.P.Y., WU T.Y. Recent advancement of coagulation–flocculation and its application in wastewater treatment. Industrial & Engineering Chemistry Research, **55** (16), 4363, **2016**.
12. JOHNSON P.N., AMIRTHARAJAH A. Ferric chloride and alum as single and dual coagulants. Journal-American Water Works Association, **75** (5), 232, **1983**.
13. MCCURDY K., CARLSON K., GREGORY D. Floc morphology and cyclic shearing recovery: comparison of alum and polyaluminum chloride coagulants. Water Research, **38** (2), 486, **2004**.
14. DAUD Z., AZIZ A., LATIF A., MAO L. Coagulation-flocculation in leachate treatment by using ferric chloride and alum as coagulant. International Journal of Engineering Research and Applications, **2** (4), 1929, **2012**.
15. NG M., LIANA A.E., LIU S., LIM M., CHOW C.W.K, WANG D., DRIKAS M., AMAL, R. Preparation and characterisation of new-polyaluminum chloride-chitosan composite coagulant. Water Research, **46** (15), 4614, **(2012)**.
16. WU C., WANG Y., GAO B., ZHAO Y., YUE Q. Coagulation performance and floc characteristics of aluminum sulfate using sodium alginate as coagulant aid for synthetic dying wastewater treatment. Separation and Purification Technology, **95**, 180, **2012**.
17. NDABIGENGESERE A., NARASIAH K.S. Use of *Moringa oleifera* seeds as a primary coagulant in wastewater treatment. Environmental Technology, **19** (8), 789, **1998**.
18. BHUPTAWAT H., FOLKARD G.K., CHAUDHARI, S. Innovative physico-chemical treatment of wastewater incorporating *Moringa oleifera* seed coagulant. Journal of Hazardous Materials, **142** (1-2), 477, **2007**.
19. CAMACHO F.P., SOUSA V.S., BERGAMASCO R., TEIXEIRA M.R. The use of *Moringa oleifera* as a natural coagulant in surface water treatment. Chemical Engineering Journal, **313**, 226, **2017**.
20. ADINOLFI M., CORSARO M.M., LANZETTA R., PARRILLI M., FOLKARD G., GRANT W., SUTHERLAND J. Composition of the coagulant polysaccharide fraction from *Strychnos potatorum* seeds. Carbohydrate Research, **263** (1), 103, **1994**.
21. RANI C.N., JADHAV, M.V. Enhancing filtrate quality of turbid water incorporating seeds of *Strychnos potatorum*, pads of *Cactus opuntia* and mucilage extracted from the fruits of *Coccinia indica* as coagulants. Journal of Environmental Research and Development, **7** (2), 668, **2012**.
22. ABOULHASSAN M.A., SOUABI S., YAACOUBI A., BAUDU M. Coagulation efficacy of a tannin coagulant

agent compared to metal salts for paint manufacturing wastewater treatment. Desalination and Water Treatment, **57** (41), 19199, **2016**.
23. YIN C.Y. Emerging usage of plant-based coagulants for water and wastewater treatment. Process Biochemistry, **45** (9), 1437, **2010**.
24. SIEVÄNEN K., KAVAKKA J., HIRSILÄ P., VAINIO P., KARISALMI K., FISKARI J., KILPELÄINEN I. Cationic cellulose betainate for wastewater treatment. Cellulose, **22** (3), 1861, **2015**.
25. IMRAN Q., HANIF M.A., RIAZ M.S., NOUREEN S., ANSARI T.M., BHATTI H.N. Coagulation/flocculation of tannery wastewater using immobilized chemical coagulants. Journal of Applied Research and Technology, **10** (2), 79, **2012**.
26. VISHALI S., ROSHINI S.K., SAMYUKTHA M.R. Towards zero waste production in the paint industry wastewater using an agro-based material in the treatment train. Environmental Monitoring and Assessment, **190** (10), 587, **2018**.
27. VERMA A.K., DASH R.R., BHUNIA P. A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. Journal of Environmental Management, **93** (1), 154, **2012**.
28. UGWU S.N., UMUOKORO A.F., ECHIEGU E.A., UGWUISHIWU B.O., ENWEREMADU C.C. Comparative study of the use of natural and artificial coagulants for the treatment of sullage (domestic wastewater). Cogent Engineering, **4** (1), 1365676, **2017**.
29. VIJAYARAGHAVAN G., SIVAKUMAR T., KUMAR A.V. Application of plant based coagulants for waste water treatment. International Journal of Advanced Engineering Research and Studies, **1** (1), 88, **2011**.
30. SATHISH S., VIKRAM S., SURAJ R. Effectiveness of turbidity removal from synthetic and tannery wastewater by using seeds of a natural coagulant *Citrullus lanatus*. Nature Environment and Pollution Technology, **17** (2), 551, **2018**.
31. BANERJEE K., RAMESH S.T., GANDHIMATHI R., NIDHEESH P.V., BHARATHI, K.S. A novel agricultural waste adsorbent, watermelon shell for the removal of copper from aqueous solutions. Iranica Journal of Energy & Environment, **3** (2), 143, **2012**.
32. CRINI G. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Progress in polymer science, **30** (1), 38, **2005**.
33. KERMET-SAID H., MOULAI-MOSTEFA N. Optimization of turbidity and COD removal from pharmaceutical wastewater by electrocoagulation> Isotherm modeling and cost analysis. Polish Journal of Environmental Studies, **24** (3), **2015**.
34. NAIR A.T., MAKWANA A.R., AHAMMED M.M. The use of response surface methodology for modelling and analysis of water and wastewater treatment processes: a review. Water Science and Technology, **69** (3), 464, **2014**.
35. SAID K.A.M., AMIN M.A.M. Overview on the response surface methodology (RSM) in extraction processes. Journal of Applied Science & Process Engineering, **2** (1), **2015**.
36. MUHAMMAD I.M., ABDULSALAM S., ABDULKARIM A., BELLO, A.A. Water melon seed as a potential coagulant for water treatment. Global Journal of Research In Engineering, **15** (1), 17, **2015**.
37. RAMAVANDI B. Treatment of water turbidity and bacteria by using a coagulant extracted from *Plantago ovata*. Water Resources and Industry, **6**, 36, **2014**.
38. SIVAMANI S., BASKAR R. Process design and optimization of bioethanol production from cassava bagasse using statistical design and genetic algorithm. Preparative Biochemistry and Biotechnology, **48** (9), 834, **2018**.
39. MINER G. Standard methods for the examination of water and wastewater. American Water Works Association. Journal, **98** (1), 130, **2006**.
40. NWABUEZE, T.U. Basic steps in adapting response surface methodology as mathematical modelling for bioprocess optimisation in the food systems. International Journal of Food Science & Technology, **45** (9), 1768, **2010**.
41. DOS SANTOS J.D., VEIT, M.T., PALÁCIO, S.M., GONCALVES G.D.C., FAGUNDES-KLEN M.R. Evaluation of the combined process of coagulation/ flocculation and microfiltration of cassava starch wastewater: Removal efficiency and membrane fouling. Water, Air, & Soil Pollution, **228,** 238, **2017**.
42. BAAWAIN M.S., AL-FUTAISI A.M., AL-OMAIRI A., AL-JABRI M. Investigating municipal wastewater treatment in the sultanate of Oman. WIT Transactions on Ecology and the Environment, **145**, 711, **2011**.
43. ALMEIDA I.L., DE ASSUNCAO R.M., TARLEY C.R., SEGATELLI M.G., COELHO N.M.M. Characterization and use of *Moringa oleifera* seeds as biosorbent for removing metal ions from aqueous effluents. **62** (9), 2198, **2010**.
44. MATEUS G.A.P., FORMENTINI-SCHMITT D.M., NISHI L., FAGUNDES-KLEN M.R., GOMES R.G., BERGAMASCO R. Coagulation/flocculation with *Moringa oleifera* and membrane filtration for dairy wastewater treatment. Water, Air, & Soil Pollution, **228** (9), 342, **2017**.
45. ADNAN O., ABIDIN Z.Z., IDRIS A., KAMARUDIN S., AL-QUBAISI M.S. A novel biocoagulant agent from mushroom chitosan as water and wastewater therapy. Environmental Science and Pollution Research, **24** (24), 20104, **2017**.
46. SHAK K.P.Y., WU, T.Y. Coagulation–flocculation treatment of high-strength agro-industrial wastewater using natural *Cassia obtusifolia* seed gum: Treatment efficiencies and flocs characterization. Chemical Engineering Journal, **256**, 293, **2014**.
47. AHMAD A.L., WONG S.S., TENG T.T., ZUHAIRI A. Optimization of coagulation–flocculation process for pulp and paper mill effluent by response surface methodological analysis. Journal of Hazardous Materials, **145** (1-2), 162, **2007**.
48. SRIDHAR R., SIVAKUMAR V., MARAN J.P., THIRUGNANASAMBANDHAM, K. Influence of operating parameters on treatment of egg processing effluent by electrocoagulation process. International Journal of Environmental Science and Technology, **11** (6), 1619, **2014**.
49. BASKAN M.B., PALA, A. A statistical experiment design approach for arsenic removal by coagulation process using aluminum sulfate. Desalination, **254** (1-3), 42, **2010**.
50. MUHAMAD M.H., ABDULLAH S.R.S., MOHAMAD A.B., RAHMAN R.A., KADHUM, A.A.H. Application of response surface methodology (RSM) for optimisation of COD, $NH_{3-}N$ and 2,4-DCP removal from recycled paper wastewater in a pilot-scale granular activated carbon sequencing batch biofilm reactor (GAC-SBBR). Journal of Environmental Management, **121**, 179, **2013**.