Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.26017

198 (2020) 396–406
September

Application of experimental design methodology to optimize dye removal by *Mucuna sloanei* induced coagulation of dye-based wastewater

Patrick Nnaji[a,*], Chika Anadebe[b], Okechukwu Dominic Onukwuli[c]

[a]*Department of Chemical Engineering, Michael Okpara University, Umudike, Nigeria, Tel. +2348038679175; email: pc.nnaji@mouau.edu.ng/nnaji_pat@yahoo.com (P.C. Nnaji)*
[b]*Department of Chemical Engineering, Federal University Ndufu-Alike, Nigeria, Tel. +2348034142042; email: anadebechika@gmail.com (V.C. Anadebe)*
[c]*Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Nigeria, Tel. +2348063635864; email: onukwuliod@yahoo.com (O.D. Onukwuli)*

Received 23 December 2019; Accepted 17 April 2020

ABSTRACT

A Box–Behnken design implementing response surface methodology was employed to investigate the sludge generation and removal of pollutants from dye-based wastewater using *Mucuna sloanei* seed powder (MSSP) in their natural form as biomass in the coagulation process. With color/total suspended solids (CTSS) removal, chemical oxygen demand (COD) removal and sludge volume index as the three responses, the three quadratic models of three variables including MSSP dosage, solution pH and stirring time were developed. At the optimal conditions, the response recorded for CTSS removal was 87.7% with 1.8 g/L dosage at solution pH 2 and 15 mins stirring time. While COD removal was 91.69% with 1.8 g/L dosage at solution pH 6 and stirring time of 30 mins, and maximum sludge of 104.3 mL/g was generated with 1.4 g/L dosage at pH 2 and stirring time of 30mins. The use of MSSP thus exhibited great potential for dye-based wastewater treatment and thus, contributes to the green environment.

Keyword: Experimental design; Colour/total suspended solids removal; *Mucuna sloanei*; Sludge volume index; Dye-based wastewater

1. Introduction

The increasing population and consequent industrial explosion are at its peak throughout the globe, particularly in developing countries such as Nigeria. Increased dye manufacturing has led to the proliferation of industrial wastewater generation, particularly from textile industries, to satisfy the textile requirements of the population. The primary cause of this wastewater generation is the use of a large volume of water during processing, which is accompanied by chemical complexes and particulate elements in the effluent streams [1,2]. This large amount of wastewater generally finds its way into our waterways like the Aba River in Abia State, Nigeria, with little or no treatment. Local inhabitants rely on this river because of their water source, and the treatment facilities are highly restricted. Textile wastewater pollutants are usually produced from caustic soda, detergents, starch, wax, urea, ammonia, pigments, and dyes that boost its biochemical oxygen demand (BOD), chemical oxygen demand (COD), solid content and toxicity [3]. The decomposition of organic pollutants from dye materials can generate toxic substances that are known to have mutagenic effects and are not biodegradable due to their high molecular mass and complex molecular structures [2,4,5].

---

* Corresponding author.

Removal of these pollutants requires the implementation of multiple treatment techniques, including membranes separation, aerobic and anaerobic degradation with different microorganisms, chemical oxidation, coagulation, flocculation and reverse osmosis [6], chromatography, lime precipitation and modified bleaching sequence [7]. Coagulation stands out as the most feasible primary treatment alternative for removing pollutants from dye-based wastewater despite the development of these techniques. This is due to its simple application on-site, high efficiency of treatment, simplicity as well as low cost of assembly and operation [1].

The coagulation process is achieved by adding a coagulant to the wastewater in order to destabilize and neutralize the color/colloid dispersion and the subsequent agglomeration of the resulting individual particles [1]. Chemical coagulants such as ferric chloride; aluminum sulfate etc. have been commonly used to remove a broad variety of wastewater pollutants [8]. However, there is an intrinsic disadvantage in the brownish coloring of machinery by iron salts and secondary contamination issues connected with aluminum salts [2,9]. Associated health issues such as human Alzheimer's disease [1,9], generation of large sludge volumes resulting in enormous disposal costs and inefficiency of aluminum salt in low-temperature waters [10] have been reported.

The search and use of biomass for wastewater treatment have gained importance in reducing these established hazards and increasing concern for environmental issues associated with the use of conventional coagulants. Natural biomass used for wastewater treatment is easily accessible, environmentally friendly, efficient, secure for both humans and animals and contributes to the green environment [1,2]. Natural materials such as *Moringa oleifera*, tannins, *Detarium microcarpum*, etc. have been explored for the removal of pollutants [1,11]. Wastewater treated with natural biomass using a coagulation method does not pose a danger to biological organisms as opposed to synthetic coagulants. The generated sludge can be treated through biological means and used as a soil conditioner [2].

The coagulation process is influenced by temperature, solution pH, quality of wastewater, the concentration of coagulants, and type of coagulant among other variables. Optimizing these factors can significantly enhance the effectiveness of the method. Apart from the time-consuming nature of the conventional one factor at one time experiments, it is not possible to obtain the exact option since the interactions between variables are ignored. In developing the response surface methodology (RSM) jar test, a three-factor Box–Behnken design (BBD) implementing RSM using Design Expert 10.0 was used. The suggested RSM will determine the effects and interactive impacts of individual factors.

RSM, a collection of statistical principles was suggested for developing experiment design models, assessing the impacts of different factors and looking for optimum variables' conditions. RSM also quantifies the relationship between different measured responses and the essential variables of input [2]. In the literature [1,2,9] there are reports on the implementation of RSM for wastewater treatment through coagulation with natural biomass. However, less attention has been paid to optimizing the method of coagulation using *Mucuna sloanei* seed powder (MSSP), in its natural form as biomass for removing pollutants from dye-based wastewater.

Mucuna sloanei is cultivated as a food crop in Nigeria. *Mucuna* extract was used as bio-coagulant mainly in non-dye-based wastewater and the shell as adsorbent [12] but has little use in dye-based wastewater treatment, especially in its natural form. The objective of this study is to optimize the process of coagulation and to investigate the interactive influences of the experimental variables, including solution pH, the dosage of MSSP and stirring time. To this end, dye-based wastewater was selected as the target wastewater to be treated using RSM-optimized coagulation technique. COD, color/total suspended solids (CTSS) removal from wastewater and sludge volume index (SVI) have been selected as responses.

2. Materials and methods

The raw dye-based wastewater was gathered from the textile plant in Aba, Nigeria. The grab sampling method was used for wastewater collection. A plastic container of 25 L was used to collect the samples and stored in the laboratory at 4°C. The analytical grade was used for all reagents.

2.1. Characterization and chemical analysis of MSSP

Mucuna sloanei pods were purchased from Nduoru Market in Ikwuano L.G.A of Abia State, Nigeria. The *Mucuna sloanei* pods were cracked and seed removed. The seeds were ground into a powder and sieved to obtain particle size in the range of 60–500 nm for homogeneity and placed in a container that was airtight. The proximate MSSP analysis was based on standard methods [13] and presented in Table 1. Using an infrared spectrometer (Agilent Technologies, USA) with a resolution range of 4,000–650 cm^{-1} and 30 scans at 8 cm^{-1} with 16 background scans, Fourier-transform infrared spectroscopy (FTIR) spectra were acquired. A scanning electron microscope (Phenom-World, MVE 016477830, Netherlands) acquired the sample's morphological features.

2.2. Characterization of dye-based wastewater

By standard methods [14], the characterization of dye-based wastewater has been determined. The characterization was carried out and presented in Table 2 at the National Soil,

Table 1
Proximate analysis results of biomass

S/no.	Parameters	MSSP
1.	Moisture content (%)	8.46
2.	Ash content (%)	2.84
3.	Fat content (%)	10.40
4.	Crude protein (%)	36.90
5.	Carbohydrate (%)	35.28
6.	Crude fibre (%)	14.60
7.	Calorific value (KJ/Kg)	382.24
8.	Dried moisture (%)	91.54

Table 2
Characterization results of textile wastewater

S/no.	Parameters	Textile wastewater
1.	pH	6.45
2.	EC (μohms/cm)	392.16
3.	SDP (mg/L)	5638.2
4.	BOD (mg/L)	491.4
5.	COD (mg/L)	920.15
6.	TOC (mg/L)	588.10
7.	Lead (mg/L)	0.049
8.	Nickel (mg/L)	0.014
9.	Chromium (mg/L)	0.0027

EC – electrical conductivity; SDP – solid/dissolved particle; TOC – total organic carbon

Plant, Fertilizer and Water Laboratory, Umudike, Nigeria. Mettler Toledo Delta 320 pH meter (UK), DDS-307 conductivity meter (UK), and UNICO 1100 spectrophotometer (China) were used to determine the solution pH, electrical conductivity and CTSS.

2.3. Coagulation process

The coagulation process was performed using MSSP 0.2, 0.28 and 0.36 g in 200 mL dye-based wastewater at pH 2, 6 and 10 to give a concentration of 1.0, 1.4, and 1.8 g/L of MSSP. Using 0.1 M sulphuric acid and 0.1 M sodium hydroxide, respectively, pH adjustment was accomplished. A modified jar test method (using a magnetic stirrer, D-91126 Schwabach, MR Hei-Standard) was used with a fast stirring of 2 min at 150 rpm and a slow agitation of 5, 15, and 30 min at 25 rpm. Before the agitation, the biomass was added. The solution was carefully poured into a 250 mL cylinder at the end of the slow stirring and allowed to settle for 300 min. After settling, each cylinder's supernatant was used to evaluate CTSS and COD to determine their level of removal. The rest of the supernatant was used by conventional techniques to achieve SVI [14].

2.4. BBD of experiment

In developing the RSM jar test, BBD implementing RSM from Design Expert 10.0 was used. BBD is a three-level design of quantitative variables with all factors. The layout varied over three levels each of the numerical variables; a high (+ 1), low (–1) and mid (0). The experiment needed a total of 17 runs (Table 3). The response factors represented as Y were CTSS removal percentage, COD removal percentage, and SVI (mL/g). The chosen variables for the study were the dosage of MSSP (X_1), solution pH (X_2) and stirring time (X_3). The range and concentrations used in the research are provided in Table 4. This strategy is to fit a quadratic polynomial equation model [2,9,15]:

$$y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i}^{k} \sum_{j} b_{ij} X_i X_j \tag{1}$$

where y is the variable response to be modeled; X_i, and X_j are the independent variables influencing y, b_0, b_i, b_{ii} and b_{ij} the offset terms, the ith linear coefficient, the iith quadratic coefficient and the ijth interaction coefficient, respectively.

Table 3
BBD for COD, CTSS removal and SVI for textile wastewater

Run	Coded			Uncoded			Responses		
	X_1	X_2	X_3	Dosage (g/L)	pH	Stirring time (min)	CTSS removal	COD removal	SVI
1.	1	0	1	1.8	6	30.0	44.8	91.69	47.55
2.	0	0	0	1.4	6	15.0	42.3	78.5	60.5
3.	1	0	–1	1.8	6	5.0	72.1	89.6	48.55
4.	–1	1	0	1.0	10	15.0	11.9	57.68	37.5
5.	0	0	0	1.4	6	15.0	42.3	75.8	60.91
6.	0	–1	1	1.4	2	30.0	76.7	87.2	104.3
7.	–1	0	1	1.0	6	30.0	47.9	80.6	45.4
8.	–1	–1	0	1.0	2	15.0	28.0	67.89	88.4
9.	1	1	0	1.8	10	15.0	10.4	56.83	36.1
10.	0	0	0	1.4	6	15.0	51.1	77.4	61.5
11.	0	–1	–1	1.4	2	5.0	59.0	64.81	101.22
12.	1	–1	0	1.8	2	15.0	87.7	86.6	101
13.	–1	0	–1	1.0	6	5.0	44.1	74.08	37.4
14.	0	0	0	1.4	6	15.0	40.5	76.8	62.11
15.	0	1	1	1.4	10	30.0	11.1	50.2	36.8
16.	0	1	–1	1.4	10	5.0	18.5	63.5	36.5
17.	1	0	1	1.8	6	30.0	44.2	76.8	61.09

Table 4
Experimental design levels of chosen variables

Variables	Coded values levels		
Coded level	Lower limit (-1)	Middle (0)	Up Limit (+1)
Biomass dosage, X_1 (g/L)	1.0	1.4	1.8
pH, X_2	2	6	10
Stirring time, X_3 (min)	5.0	15.0	30.0

3. Results and discussion

3.1. Characterization of MSSP

The results presented in Table 1 show a fairly high level of crude protein that is similar to the literature accessible. The literature available indicates that MSSP has crude protein of 25.65% [16], 22.7% [12], and while defatted MSSP contains crude protein of 60.5% [17]. It has been noted that crude protein is the active element for coagulation.

To make the greatest use of this biomass, it is essential to understand the nature and property of the biomass. For the prediction of chemical interactions, peak shift and intensity are essential in FTIR absorbance spectroscopy. While peak shift indicates a change in a functional group's chemical environment, bandwidth appearance and disappearance point at reactions involving the relevant functional groups [2]. Fig. 1a shows the existence of the polymeric-OH functional group at 3,268.9 cm^{-1}, methyl C–H and methylene C–H asymmetric stretching group at 2,918.5 and 2,091.0 cm^{-1} respectively. 1,986.7 cm^{-1} could be an indication of carboxylic ketone stretching [10,18], while 1,636.3; 1,543.1; 1,438.8 and 1,405.2 cm^{-1} could be attributed respectively to olefin, aromatic ring stretch, and methyl asymmetric bends. It was possible to assign spectra 1,364.2; 1,252.4 and strong 1,002.7 cm^{-1} to skeletal C–C vibration and primary C–N stretch amine. For the attachment of colloidal particles and some dissolved ions, the presence of OH, carboxyl stretching and other groups could serve as active sites [2]. Fig. 1b, the sludge spectrum (biomass and coagulated CTSS) showing peak shift around 2,800–3,300 cm^{-1} bandwidth may be due to shifts in the polymeric-OH group's chemical environment. Perhaps due to reactions involving carboxylic, olefin and aromatic groups could be the presence of more bandwidth points between 0–1,800 cm^{-1}. The result could not have been unconnected with the presence of coagulated sludge-settling CTSS.

Biomass surface morphology was observed using scanning electron microscopy (SEM) assessment. The aggregated porous nature of MSSP with tender sought of tissues was revealed by two magnifications of 200 and 1,000 μm described in Fig. 2a. The surface morphology is similar to those presented in the literature [12,19]. The observed nature presents a potentially active site for the sticking of particles during coagulation [20]. The sludge (biomass and coagulated CTSS) morphology in two magnifications of 200 and 1,000 μm obtained after coagulation shown in Fig. 2b shows rough and irregular texture, which could be attributed to the process of coagulation involving certain chemical reactions, which breakdown the existing structure to allow floc formation.

3.2. Response surface fitting by BBD

The three responses, Y_1 for CTSS removal (%), Y_2 for COD removal (%) and Y_3 for SVI (mL/g) were associated with three variables, MSSP dosage (X_1), solution pH (X_2) and stirring time (X_3), using the quadratic polynomial equation as described in Eq. (1). The models of second-order regression from the experimental data were displayed in Eqs. (2)–(4).

$$Y_1\left(\text{CTS Sremoval}\right) = 44.080 + 12.600X_1 - 13.590X_2 + 4.990X_3 - 19.730X_1X_2 - 7.780X_1X_3 - 19.550X_2X_3 + 2.580X_1^2 - 21.590X_2^2 + 5.560X_3^2 \quad (2)$$

$$Y_2\left(\text{COD removal}\right) = 77.060 + 5.560X_1 - 9.790X_2 + 2.210X_3 - 4.890X_1X_2 - 1.110X_1X_3 - 8.920X_{23} + 3.880X_1^2 - 13.690X_2^2 + 3.050X_3^2 \quad (3)$$

$$Y_3\left(\text{SVI}\right) = 61.220 + 3.060X_1 - 31.000X_2 + 1.300X_3 - 3.500X_{12} - 2.250X_1X_3 - 0.700X_2X_3 - 10.230X_1^2 + 14.750X_2^2 - 6.270X_3^2 \quad (4)$$

where X_1, X_2, and X_3 are the dosage of MSSP, solution pH, and stirring time. The one-factor coefficient represents the effect of the specific variable, whereas the two-factor coefficient and the second-order coefficient represent the interaction between the two variables and the quadratic impact. A positive sign before the conditions is synergistic, while a negative sign is an antagonistic effect [2,15]. Following removal of non-significant interaction terms as shown in Table 5, Eqs. (5)–(7) have been produced.

$$Y_1\left(\text{CTS Sremoval}\right) = 44.080 + 12.600X_1 - 13.590X_2 - 19.730\ X_1X_2 - 21.590X_2^2 \quad (5)$$

$$Y_2\left(\text{COD removal}\right) = 77.060 + 5.560\ X_1 - 9.790X_2 + 2.210X_3 - 4.890X_1X_2 - 1.110X_1X_3 + 3.880X_1^2 - 13.690X_2^2 + 3.050X_3^2 \quad (6)$$

$$Y_3\left(\text{SVI}\right) = 61.220 + 3.060X_1 - 31.000X_2 - 3.500X_1X_2 - 10.230X_1^2 + 14.750X_2^2 - 6.270X_3^2 \quad (7)$$

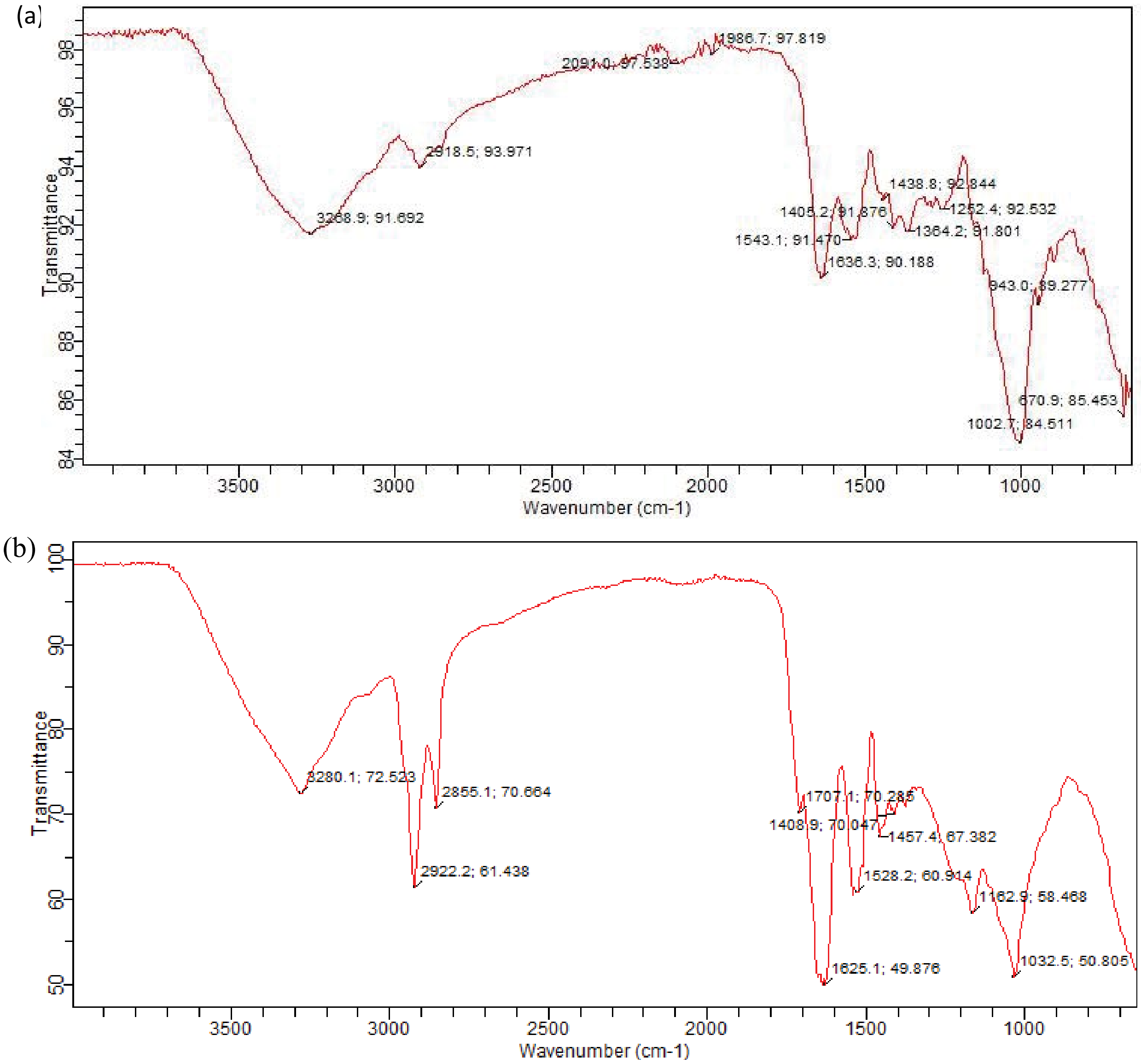


Fig. 1. FTIR spectra of (a) *Luffa cylindrica* seed powder and (b) sludge (biomass and coagulated CTSS).

3.3. Model adequacy

Model summary statistics and analysis of variance (ANOVA) were used to determine the adequacy of the model to identify the factors influencing the variables of response and thus to determine the most significant parameters. In Tables 5 and 6, these are presented. Table 6 *p*-value for CTSS removal was 0.0248, while for the selected model the COD removal and SVI value were lower than 0.001. Considering the CTSS removal response (Y_1), it is clear that the linear terms for MSSP dosage (X_1) and solution pH (X_2) have a moderate effect on the removal of the dye as indicated by their *F*-values of 6.64 and 7.72 respectively, while the stirring time factor (X_3) has a negligible effect due to the low *F*-value of 1.04. Given the negligible effect of (X_3), the quadratic term (X_3^2) showed an insignificant effect, while that of pH (X_2^2) revealed its dominance with an *F*-value of 10.27. The interaction terms X_1X_2 and X_1X_3 showed a relatively high impact on the removal of dye with *F*-values of 8.14 and 7.99, respectively.

Likewise, for the COD removal response, the solution pH factor (X_2) for linear, quadratic (X_2^2) and the interaction term (X_2X_3) showed a dominant effect with very high *F*-values of 386.96, 398.41 and 160.83, respectively. Furthermore, the linear term for MSSP dosage (X_1), the quadratic term of stirring time (X_3^2) and the interaction term (X_1X_3) suggested significant effects. Similarly, the linear terms (X_1) and (X_2) suggested significant effects for SVI response, while (X_3) showed relatively no effect with a *p*-value above 0.34. The interaction terms X_1X_3 and X_2X_3 have a negligible impact on sludge generation.

The model summary statistics showed determination coefficient R^2, 0.8616, 0.9941 and 0.9960 respectively for CTSS, COD removal and SVI. This means that the independent variables explained 88.29%, 99.12% and 99.46% of the variation for CTSS, COD removal and SVI and also implied that the

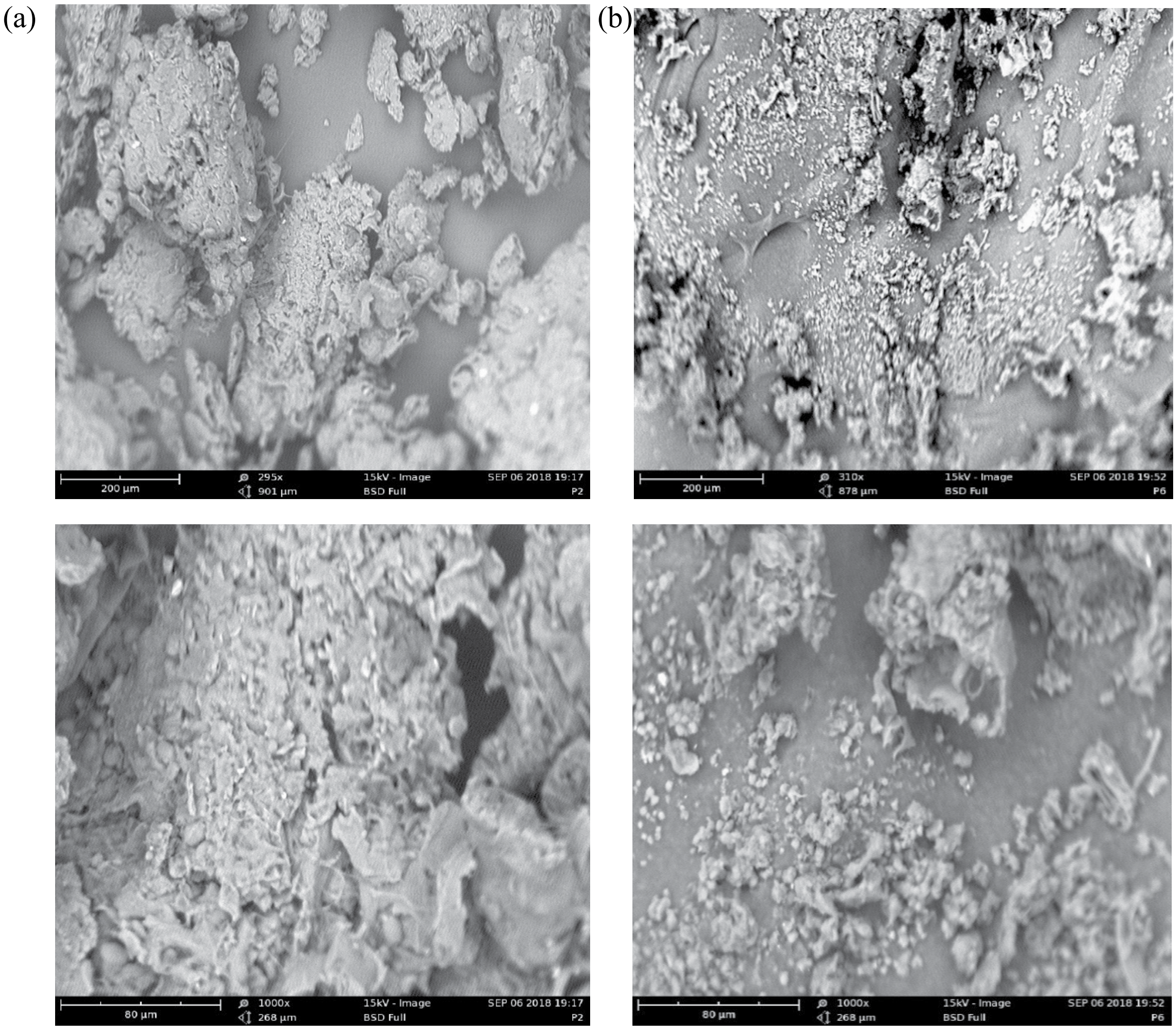


Fig. 2. SEM micrograph of the (a) biomass and, (b) sludge (biomass and coagulated CTSS) (magnification 200×, top and 1,000×, bottom).

empirical models could not explain 13.84%, 0.59%, and 0.40% of their variations respectively. The elevated R^2 values stated that the model was well fitted to the response [9]. From the results, it can also be seen that the experimental data shows a desirable and acceptable agreement with the proximity of the R^2 to the adjusted R^2. This proximity suggests that the quadratic models were modified satisfactorily to experimental data as observed with COD removal and SVI responses with the difference between R^2 and the adjusted R^2 reported respectively as 0.0076 and 0.0052 [9,15]. However, a significant gap between R^2 and the adjusted R^2 shows the presence of insignificant terms and/or moderate effects of factors on the response variables as observed with CTSS response with a difference between R^2 and the adjusted R^2 recorded as 0.1780 [21,22].

Due to the moderate and high F-value of 4.84 and 130.7 for CTSS and COD removal, and 193.36 for SVI, the second-order regression for CTSS and COD removal efficiency shows that the models were significant. Similarly, for quadratic regression models, the p-value that provides an indication of the significance of a model in relation to the F-value was less than 0.05. This indicated that for a confidence level of 95%, the models were statistically significant, meaning that there is only a 5% chance that the F-value was due to noise. The model is not significant if the p-value is above 0.1 [9].

3.4. Process analysis

Table 5 explains the linear (X_1, X_2, X_3), quadratic (X_1^2, X_2^2, X_3^2) and interaction (X_1X_2, X_2X_3, X_1X_3) effects of the parameters. The response, Y_1, revealed that X_1, X_2, X_2^2, and X_1X_2 are meaningful terms with $p < 0.05$, whereas X_3, X_1^2, X_3^2 and X_2X_3 are not meaningful terms. Similarly, Y_2 and Y_3 responses to contain significant terms of X_1, X_2, X_3, X_1^2, X_2^2, X_3^2, X_1X_2, X_1X_3, and X_1, X_2, X_1^2, X_2^2, X_3^2, X_1X_2. Although non-significant terms are X_2X_3 and X_3, X_2X_3, X_1X_3, respectively. For Y_1, Y_2, and Y_3, respectively, the lack of fit F-values of 0.1148, 0.1345 and 0.1130 implies that the lack of fits is not significant compared to the pure error. Only 13.84%, 0.59% and 0.40% respectively for Y_1, Y_2, and Y_3, are likely to occur due to noise for the lack

Table 5
ANOVA results for three responses (Y_1, Y_2, and Y_3)

Response	Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob > F	Remark
Y_1 (CTSS) %	Model	8,331.64	9	925.74	4.84	0.0248	Suggested
Linear	X_1	1,270.58	1	1,270.6	6.64	0.0366	
	X_2	1,476.42	1	1,476.4	7.72	0.0274	
	X_3	199.00	1	199.00	1.04	0.3416	
Pure quadratic	X_1^2	28.08	1	28.08	0.15	0.7129	
	X_2^2	1,963.10	1	1,963.1	10.27	0.0150	
	X_3^2	130.28	1	130.28	0.68	0.4364	
Interaction	X_1X_2	1,557.09	1	1,557.1	8.14	0.0246	
	X_2X_3	241.80	1	241.80	1.26	0.2979	
	X_1X_3	1,528.81	1	1,528.8	7.99	0.0255	
	Residual	1,338.68	7	191.24			
	Lack of fit	1,270.23	3	423.41	24.74	0.1148	Not significant
	Pure error	68.45	4	17.11			
	Cor. Total	9,670.32	16				
Y_2 (COD) %	Model	2,329.12	9	258.79	130.71	<0.0001	Suggested
Linear	X_1	247.20	1	247.20	124.85	<0.0001	
	X_2	766.17	1	766.17	386.96	<0.0001	
	X_3	39.16	1	39.16	19.78	0.0030	
Pure quadratic	X_1^2	63.31	1	63.31	31.97	0.0008	
	X_2^2	788.83	1	788.83	398.41	<0.0001	
	X_3^2	89.30	1	39.30	19.85	0.0030	
Interaction	X_1X_2	95.65	1	95.65	48.31	0.0002	
	X_2X_3	4.91	1	4.91	2.48	0.1595	
	X_1X_3	318.44	1	318.44	160.83	<0.0001	
	Residual	13.86	7	1.98			
	Lack of fit	9.95	3	3.32	3.39	0.1345	Not significant
	Pure error	3.91	4	0.98			
	Cor. Total	2,342.98	16				
Y_3 (SVI)	Model	9,295.94	9	1,032.9	193.36	<0.0001	Suggested
Linear	X_1	75.03	1	75.03	14.05	0.0072	
	X_2	7,689.24	1	7,689.2	1,439.42	<0.0001	
	X_3	13.47	1	13.47	2.52	0.1563	
Pure quadratic	X_1^2	440.30	1	440.30	82.42	<0.0001	
	X_2^2	916.55	1	916.55	171.58	<0.0001	
	X_3^2	165.58	1	165.58	31.00	0.0008	
Interaction	X_1X_2	49.00	1	49.00	9.17	0.0192	
	X_2X_3	20.25	1	20.25	3.79	0.0926	
	X_1X_3	1.93	1	1.93	0.36	0.5665	
	Residual	37.39	7	5.34			
	Lack of fit	35.89	3	11.96	31.86	0.1130	Not significant
	Pure error	1.50	4	0.38			
	Cor. Total	9,333.34	16				

of fit F-values this large. There is a good non-significant lack of fit, the model must fit.

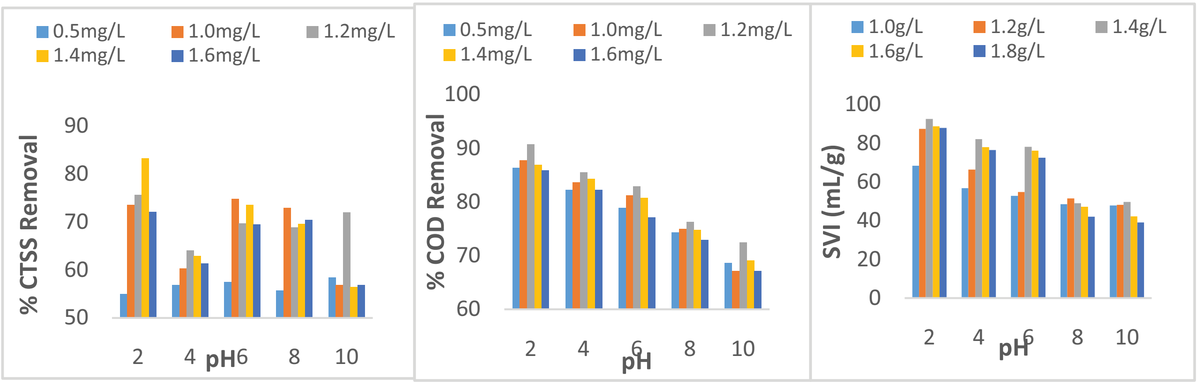
3.5. Effect of variables on CTSS removal efficiency (Y_1)

Fig. 3a shows the effect of MSSP dosage and solution pH factors on removing CTSS applying one factor at a time method. The plot in Fig. 4 shows the individual effect on the percentage of CTSS removal of MSSP dosage, solution pH and stirring time applying a total of 17 BBD of three variables; MSSP dosage (X_1), solution pH (X_2) and stirring time (X_3) as shown in Table 3.

Fig. 3a indicates that CTSS removal efficiency has greater performance at pH 2 with 1.4 g/L optimum dosage

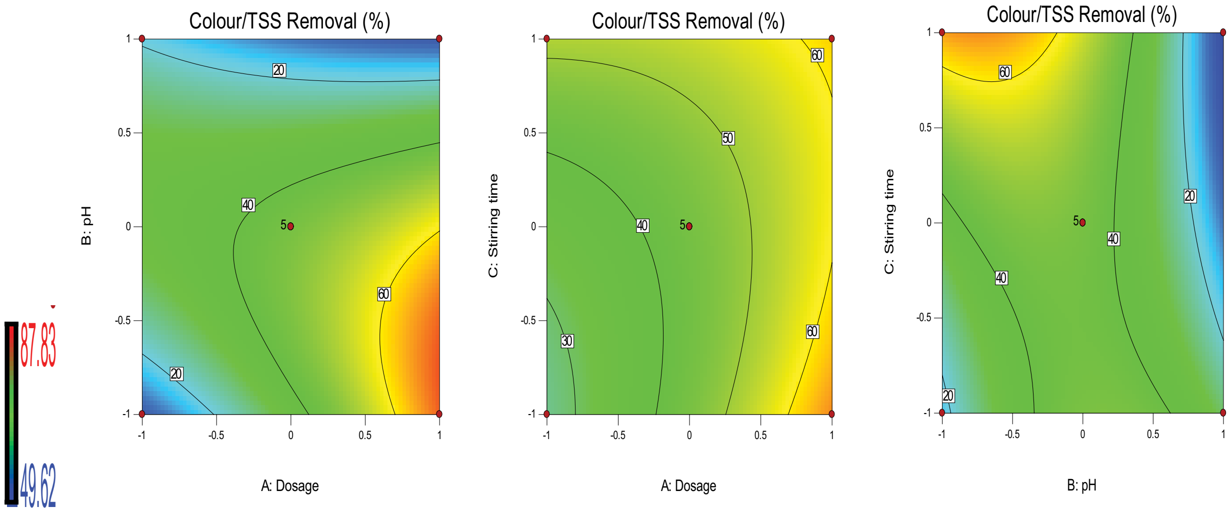
Table 6
Model summary statistics for three responses (Y_1, Y_2, and Y_3)

Response	Source	*F*-value	Prob > *F*	Standard deviation	R^2	Adj. R^2	Press	Remark
Y_1 (CTSS) %	Linear	1.90	0.1797	22.74	0.3046	0.1442	13,816.6	
	2FI	3.27	0.0676	18.43	0.6488	0.4380	16,373.9	
	Quadratic	3.59	0.0744	13.83	0.8616	0.6836	20,430.6	Suggested
	Cubic	24.74	0.0048	4.14	0.9929	0.9717		Aliased
Y_2 (COD) %	Linear	3.53	0.0454	9.96	0.4492	0.3221	2,648.76	
	2FI	1.63	0.2500	9.34	0.6281	0.4049	4,259.13	
	Quadratic	144.38	<0.0001	1.41	0.9941	0.9865	165.28	Suggested
	Cubic	3.39	0.1345	0.99	0.9983	0.9933		Aliased
Y_3 (SVI)	Linear	21.67	<0.0001	10.94	0.8333	0.7949	3,251.57	
	2FI	0.16	0.9209	12.18	0.8410	0.7455	7,607.09	
	Quadratic	90.29	<0.0001	2.31	0.9960	0.9908	576.61	Suggested
	Cubic	31.86	0.0030	0.61	0.9998	0.9994		Aliased



a) b) c)

Fig. 3. One factor at a time plots of (a) % CTSS removal, (b) % COD removal, and (c) SVI (mL/g) vs. pH.



a) b) c)

Fig. 4. Contour plots of CTSS removal from dye-based wastewater (a) dosage vs. pH, (b) stirring time vs. dosage, and (c) stirring time vs. pH.

yielding >80% CTSS removal, pH 6 and 8 showed high performance giving >70% CTSS removal at 1.0 g/L and 1.4 g/L MSSP dosage, respectively. It's clear from the figure that MSSP performed better at lower pH values. This is consistent with some coagulation research, which showed improved natural coagulant efficiency at lower pH values [1,9,11,23]. This could be due to better reaction conditions at lower pH levels for specific coagulation reactions involving the bio-coagulant natural polymer and dye-based wastewater. The reaction gave rise to the rapid coagulation in solution pH 2 occasioned by instant charge destabilization and neutralization [1,9,23]. The contour plot (2D) in Fig. 4 shows the optimum pH 2, 1.8 g/L dosage and 30 min stirring time. These optimum points are clearly shown by the orange to red shades as indicated by the legend. The considerable curvature in the contour curves implies the interdependence of these three factors [24]. For the contour plot of solution pH and MSSP dosage, however, the curvature is more pronounced, indicating them as dominant factors.

3.6. Effect of variables on COD removal efficiency (Y_2)

Fig. 3b shows the effect of two individual factors; MSSP dosage and solution pH on COD removal applying one factor at a time. From the figure, a drop in COD removal from pH 2 to pH 10 was observed with an optimal condition at 1.2 g/L MSSP dosage yielding >90% COD removal. Fig. 5 shows the individual effect of MSSP dosage, solution pH, and stirring time on COD removal applying a total of 17 BB-design of these three variables. After 30 min of stirring time, the contour chart stated optimum points at pH 6 and dosage 1.8 g/L. This is indicated by the red shade in the contour plot. The fair curvature in the contour curve shows the interdependence of the three factors. Furthermore, in order to clearly see the interpretation of the effects of independent variables, the Pareto analysis is conducted on the basis of Eq. (8) and is graphically illustrated in Fig. 6 [24].

$$P_i = \left(\frac{b_i^2}{\sum b_i^2} \right) \times 100 \left(i \neq 0 \right) \tag{8}$$

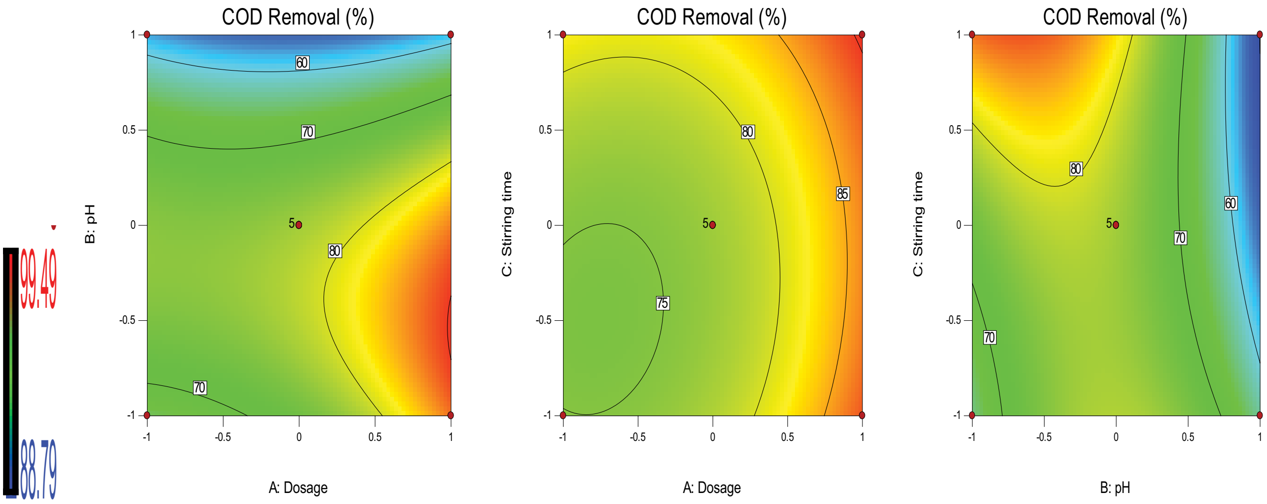
From the graph, pH is the most critical variable for removing COD from dye-based wastewater with an effect of 90.7%. The dominant effect of solution pH is further demonstrated by the 98.11% interactive effect of pH × pH, while the dosage × stirring time is 91.7%. Dominant solution pH effect may be attributed to better coagulation reactions induced by lower pH value, while high dosage × stirring time interaction is due to higher charge neutralization and destabilization, and consequent aggregation.

3.7. Effect of variables on SVI (Y_3)

Similarly, the effect of two individual MSSP dosage and solution pH variables on SVI applying standard one factor at a time shown in Fig. 3c shows comparable trends as in the removal of COD. The contour plot applying 17 BBD of three variables; MSSP dosage, solution pH and stirring time shown in Fig. 7 show sensible quadratic curvature in the contour curve of pH-dosage and pH-stirring time as reflected by the red shades. This is a clear sign of the variables' interdependence and positive interaction [25]. However, though the contour curve of dosage-stirring time showed a sensible curve, it does not reflect the positive interaction of the variables as indicated by blue shades based on the contour legend.

4. Conclusion

The MSSP spectrum disclosed waveform with peaks of complicated polysaccharides features. Further assessment



a) b) c)

Fig. 5. Contour plots of COD removal from dye-based wastewater (a) dosage vs. pH, (b) stirring time vs. dosage, and (c) stirring time vs. pH.

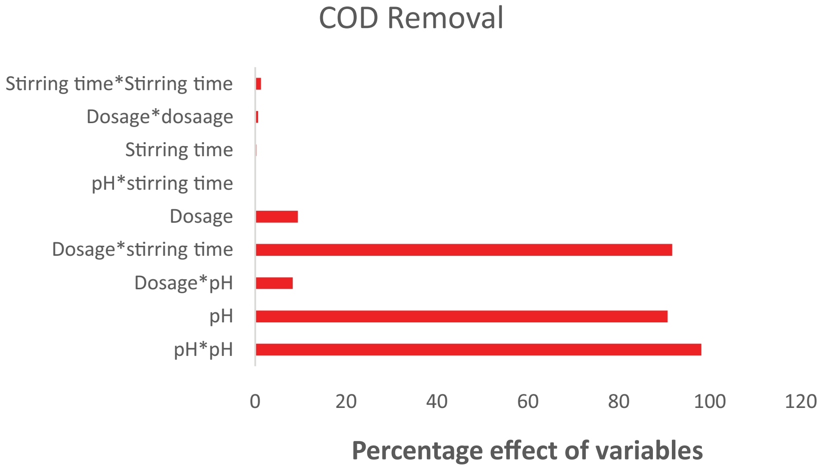
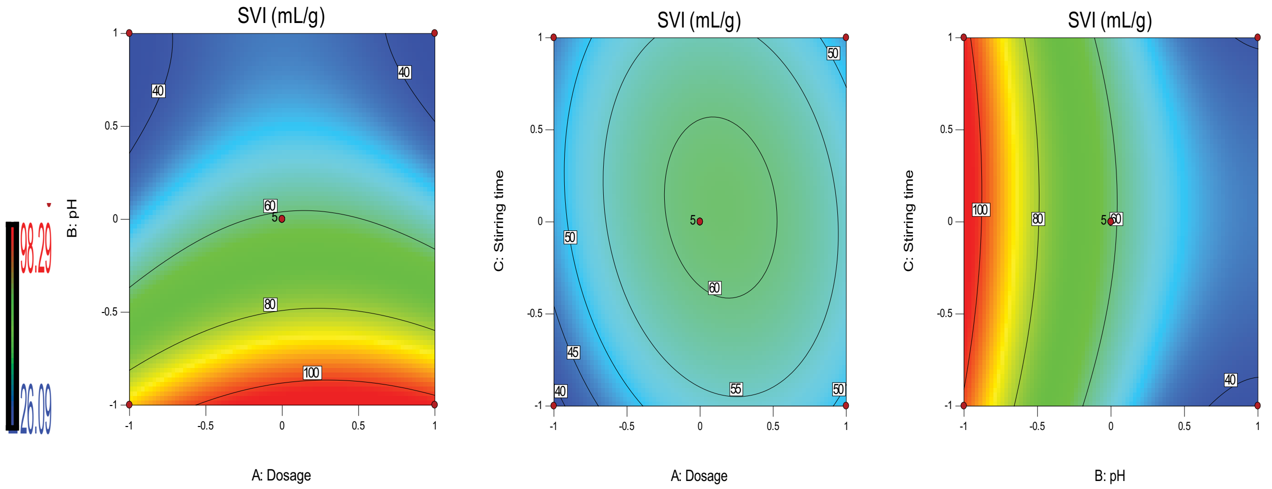


Fig. 6. Pareto graph of coagulation of dye-based wastewater indicating the percentage effect of each factor.



a) b) c)

Fig. 7. Contour plots of SVI for dye-based wastewater (a) dosage vs. pH, (b) stirring time vs. dosage, and (c) stirring time vs. pH.

showed a compound with aggregated porous nature with tender sought of tissues. To study the real applicability of MSSP as natural biomass, BBD implementing RSM optimization was conducted. ANOVA disclosed the data fit the quadratic model and the concentration of MSSP showed important effectiveness in removing CTSS and COD. The effect of MSSP dosage in sludge generation was also stated by ANOVA.

The best condition for dye-based wastewater treatment was 1.8 g/L MSSP, solution pH 2 and 15 min, yielding 87.7% removal of CTSS; 1.8 g/L MSSP, pH 6 and 30 min yielding 91.69% removal of COD; and 1.4 g/L MSSP, pH 2 and 30 min yielding 104.3 mL/g SVI. In conclusion, the results obtained indicated that MSSP has a strong potential for the treatment of dye-based wastewater via the coagulation technique. This treatment will be achieved at low-cost and will contribute to the green environment.

References

[1] B.I. Okolo, P.C. Nnaji, O.D. Onukwuli, Nephelometric approach to study coagulation–flocculation of brewery effluent medium using *Detarium microcarpum* seed powder by response surface methodology, Environ. Chem. Eng., 4 (2016) 992–1001.

[2] M.T.F. de Souza, C.A. de Almeida, E. Ambrosio, L.B. Santos, T.K.F. de Souza Freitas, D.D. Manholer, G.M. de Carvalho, J.C. Garcia, Extraction and use of *Cereus peruviamus cactus* mucilage in the treatment of textile effluents, J. Taiwan Inst. Chem. Eng., 10 (2016) 1–10.

[3] N. Muralimohan, T. Palanisamy, Treatment of textile effluent by natural coagulants in Erode district, Asian J. Chem., 26 (2014) 911–914.

[4] S.M. Hadi, M.K.H. Al-Mashhadani, M.Y. Eisa, Optimization of dye adsorption process for *Albizia lebbeck* pods as a biomass using central composite rotatable design model, Chem. Ind. Chem. Eng. Q., 25 (2019) 39–46.

[5] S.S. Konstantinovic, M.G. Kodric, R. Nicic, D.M. Djordjevic, Decolorization of model wastewater by adsorbent obtained

from waste hemp fibers, Chem. Ind. Chem. Eng. Q., 25 (2019) 11–19.

[6] S.B. Olugbenga, M.L. Bukola, J.A. Olamide, E. Vunain, Scavenging rhodamine B dye using *Moringa oleifera* seed pod, Chem. Speciation Bioavailability, 29 (2017) 120–134.

[7] I. Muhammad, B. Tahir, I. Naz, A. Naeem, A.K. Ruaf, S. Aamir, The removal of COD, TSS and colour of black liquor by coagulation–flocculation process at optimized pH, settling and dosing rate, Arabian J. Chem., 10 (2017) S2307–S2318.

[8] W.W. Pei, T.T. Tjoon, A.R. Nik, N. Nik, Efficiency of the coagulation-flocculation method for the treatment of dye mixtures containing disperse and reactive dye, Water Qual. Res. J. Can., 42 (2007) 54–62.

[9] B.I. Okolo, P.C. Nnaji, E.O. Oke, K.F. Adekunle, C.S. Ume, O.D. Onukwuli, Optimizing bio-coagulants for brewery wastewater treatment using response surface methodology, Nigerian J. Technol., 36 (2017) 1104–1113.

[10] C.O. Aniagor, M.C. Menkiti, Kinetics and mechanistic description of adsorptive uptake of crystal violet dye by lignified elephant grass complexed isolate, J. Environ. Chem. Eng., 6 (2018) 2105–2118.

[11] J.U. Ani, N.J.N. Nnaji, O.D. Onukwuli, C.O.B. Okoye, Nephelometric and functional parameters response of coagulation for the purification of industrial wastewater using *Detarium microcarpum*, J. Hazard. Mater., 243 (2012) 59–66.

[12] M.C. Menkiti, I. Ezemagu, B. Okolo, Perikinetics and sludge study for the decontamination of petroleum produced water (PW) using novel mucuna seed extract, Pet. Sci., 13 (2016) 328–339.

[13] AOAC, Official Methods of Analysis, 16th ed., Association of Official Analytical Chemist, Gaitherburg, 2005.

[14] AWWA, APHA, WEF, Standard Method for the Examination of Water and Wastewater, 22nd ed., American Water Works Association, American Public Health Association, World Economic Forum, New York, 2012.

[15] S.-C. Kim, Application of response surface method as an experimental design to optimize coagulation–flocculation process for pre-treating paper wastewater, J. Ind. Eng. Chem., 38 (2016) 93–102.

[16] I.O. Balogun, O.P. Olatidoye, Chemical composition and nutritional evaluation of velvet bean seeds (*Mucuna utilis*) for domestic consumption and industrial utilization in Nigeria, Pak. J. Nutr., 11 (2012) 116–122.

[17] F.Y. Oladipo, C.E. Chigbundu, V.N. Atasie, I. Iyeimo, Extraction, purification and analysis of *Mucuna sloanei* seed gum, Int. J Appl. Res. Technol., 2 (2013) 94–100.

[18] N.H. Azmi, U.F.M. Ali, F.M. Ridwan, K.M. Isa, N.Z. Zulkurnai, M.K. Aroua, Preparation of activated carbon using sea mango (*Cerbera odollam*) with microwave-assisted technique for the removal of methyl orange from textile wastewater, Desal. Water Treat., 54 (2016) 1–10.

[19] C.A. Igwegbe, P.C. Onyechi, O.D. Onukwuli, I.C. Nwokedi, Adsorptive treatment of textile wastewater using activated carbon produced from *Mucuna pruriens* seed shell, World J. Eng. Technol., 4 (2016) 21–37.

[20] R. Ahma, S. Haseeb, Competitive adsorption of Cu^{2+} and Ni^{2+} on *Luffa acutangula* modified tetra ethoxy silane (LAP-TS) from the aqueous solution: thermodynamics and isotherm studies, Groundwater Sustainable Dev., 1 (2015) 146–154.

[21] V.K. Sangal, V. Kumar, I.M. Mishra, Optimization of structural and operational variables for the energy efficiency of a divided wall distillation column, Comput. Chem. Eng., 40 (2012) 33–40.

[22] A. Baharlouei, E. Jalilnejad, M. Sirousazar, Fixed-bed column performance of methylene blue biosorption by *Luffa cylindrica*: statistical and mathematical modeling, Chem. Eng. Commun., 205 (2018) 1537–1554.

[23] M.C. Menkiti, O.D. Onukwuli, Coag-flocculation of mucuna seed coag-flocculant (MSC) in coal washery effluent (CWE) using light scattering effect, AlChE J., 156(2012)303–313.

[24] M. Ahmadi, F. Ghanbari, S. Madihi-Bidgoli, Photoperoxi-coagulation using activated carbon fibre cathode as an efficient method for benzotriazole removal from aqueous solutions: modelling, optimization and mechanism, J. Photochem. Photobiol., A, 322 (2016) 85–94.

[25] I. Fendri, L. Khannous, A. Timoumi, N. Gharsallah, R. Gdoura, Optimization of coagulation-flocculation process for printing ink industrial wastewater treatment using response surface methodology, Afr. J. Biotechnol., 12 (2013) 4819–4826.