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Research Article

Performance Optimization of Chemical and Green Coagulants in Tannery Wastewater Treatment: A Response Surface Methodology Approach

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Vegetable tannery wastewater, highly laden with recalcitrant organics, is not easily treatable through biological processes. This study focuses on the use of response surface methodology in optimizing a coagulation-flocculation process for pretreatment of vegetable tannery wastewater. This study also assessed the possibility of replacing chemical coagulants such as aluminum sulphate with green alternatives such as cassava starch and orange peel powder. The effects of coagulant dosage and pH on three key wastewater quality parameters (chemical oxygen demand (COD) and total suspended solids (TSS)'s removal efficiencies as well as sludge volume index (SVI)) were also assessed. Quadratic models developed for all the three responses were adequate. The optimal conditions were attained at a pH of 3.17 and a dosage of 2.76 g/L for cassava starch coagulant, pH of 3.74 and a dosage of 5.16 g/L for orange peel powder coagulant, and pH of 6.09 and a dosage of 11.60 g/L for aluminum sulphate. The COD and TSS removal efficiencies as well as SVI achieved under these optimal conditions were 37.25%, 73.95%, and 14.80 mL/g, respectively, for cassava starch coagulant; 17.97%, 66.08%, and 19.87 mL/g, respectively, for orange peel powder coagulant; and 38.51%, 76.06%, and 29.57 mL/g, respectively, for aluminum sulphate. The outperformance of cassava starch over orange peel powder and its comparable results with aluminum sulphate makes the former a more environment-friendly alternative to aluminum sulphate for treatment of tannery wastewater.

1. Introduction

Tannery wastewater is toxic, malodourous, and heavily laden with organic and suspended contaminants [1]. Indiscriminate discharge of the untreated wastewater is extremely deleterious to public and environmental health [2]. Vegetable tanning, one of the primary techniques in leather making, employs natural tannins generated from vegetal matter [3] in converting animal skins into strong, heavy leathers purposefully used for making wallets, belts, soles of shoes, leather furniture, and baggage [4]. This form of tanning technique releases huge quantities of polyphenolic compounds contained in the plant materials into the resulting wastewater. Polyphenolic compounds are recalcitrant and toxic in nature and renders biological treatment of the wastewater ineffective [5]. Hence, a physicochemical wastewater pretreatment method, coagulation-flocculation process, highly effective for

removal of suspended and colloidal matter and also insensitive to wastewater toxicity [6] was adopted in this study. Aside its efficiency, coagulation-flocculation treatment is widely used in pretreatment of wastewater due to the simplicity and faciliness in its design and operation [7]. The treatment process encompasses an initial stage which involves destabilization of the colloidal matter in the wastewater under rapid mixing in the coagulation phase followed by agglomeration of the destabilized colloids into large floc particles under slow mixing in the flocculation phase. The floc particles which settle out of the wastewater under gravity are then separated through a sedimentation process [8].

Chemical coagulants, such as aluminum sulphate, are popularly used in the coagulation process due to their high efficiency [9]. The major drawback with these coagulants pertains to their toxicity, high sludge generation, and nonbiodegradability [10]. As a result, recent research studies are being focused on the application of natural organic polymeric coagulants such as chitosan, moringa, mucilage, starch, and fruit peels [11] as green alternatives in wastewater treatment because of their ecological-friendliness, availability, renewability, biodegradability, low sludge production, nontoxicity, and low cost [10].

In line with this, this study centred on the use of cassava starch and orange peel powder for pretreatment of vegetable tannery wastewater. Cassava (*Manihot esculenta*), a widely grown perennial root crop is an essential food crop in Ghana and in many other countries in Africa, Asia, and Latin America [12]. In Ghana alone, about 15×10^6 tonnes of cassava is produced yearly making the nation the sixth largest producer globally [13]. Cassava starch, making up approximately 88% of the root crop [14], is therefore readily and cheaply available [12]. Oranges (*Citrus sinensis*) are other widely cultivated crops in the world with the global production estimated at 79×10^6 tonnes in 2019. The estimated production in Ghana alone was 78×10^4 tonnes in the same year [15]. According to Rezzadori et al. [16], oranges are principally cultivated for industrial production of orange juices resulting in the generation of about 8 to 20 million tonnes of waste per year globally. The waste products which are abundantly available are, however, underutilized. From the literature, starch from cassava peels has been applied in the treatment of river water [17], semiconductor wastewater [18], and dam water [19] while orange peel powder has been utilized in dairy wastewater [20] and lake water [21] treatment. However, their efficiencies in the treatment of vegetable tannery wastewater have not been investigated.

To enhance coagulation efficiency, optimization of operating parameters which include coagulant type and dosage, wastewater pH, and mixing speed [22] is essential. Among these factors, the two most significant parameters are pH and coagulant dosage [9]. The conventional method of optimizing the coagulation-flocculation process by altering only one factor at a time and maintaining all other factors constantly is arduous, time-consuming, and costly as lots of experiments are conducted and may be inaccurate in yielding the actual optimal conditions since the effect of interaction among factors is ignored [23]. Response surface methodology (RSM), a statistical approach which utilizes design of experiments, overcomes these shortcomings. RSM is used in developing regression models for a process, assessing the statistical significance of process parameters, determining the interaction effect among the factors, and defining the optimal process conditions through fewer numbers of experiments [24].

The principal objective of this study was, therefore, to assess the efficiency of orange peel powder, cassava starch, and aluminum sulphate in pretreatment of vegetable tannery wastewater through coagulation-flocculation processes. Operation parameters: pH and coagulant dosage, were optimized using RSM to maximize removal of chemical oxygen demand (COD) and total suspended solids (TSS) from the wastewater whilst minimizing sludge volume index (SVI). It is worth mentioning that this is the first study investigating into the optimization of coagulation-flocculation treatment of vegetable tannery wastewater using natural polymers as coagulants in comparison to aluminum sulphate.

2. Materials and Methods

2.1. Wastewater Sampling and Characterization. The vegetable tannery wastewater was obtained from the Aboabo Tannery in Kumasi (Ashanti Region, Ghana) located at 6°41′50.57″N 1°36′7.02″W. For characterization purposes, wastewater samples were collected on five different occasions during the study period. The samples were preserved and analyzed following the Standard Methods for Examination of Water and Wastewater [25]. pH was measured with the aid of a Milwaukee MW 101 pH meter. TSS and turbidity were analyzed using the gravimetric method and the HANNA turbidimeter (HI 93414), respectively. Colour, COD, and total nitrogen (TN) were determined using the Hach methods with the aid of the Hach DR 3900 spectrophotometer. Biochemical oxygen demand (BOD_5) was determined by employing the dilution method in combination with dissolved oxygen measurement. The argentometric method was used to analyze the chloride (Cl^-) concentrations in the wastewater.

2.2. Coagulants and Characterization. Laboratory grade aluminum sulphate hexadecahydrate ($Al_2(SO_4)_3.16H_2O$) reagent commonly referred as alum of 98% purity with a molar mass of 630.4 g/mol was purchased from Qualikems Fine Chem Pvt. Ltd. The orange peels and cassava starch were obtained from local markets in Kumasi. The orange peel powder was prepared according to a procedure proposed by Anju and Mophin-Kani [20]. The peels were initially washed thoroughly with tap water and then with distilled water. They were then sun-dried for 2 hours and oven-dried at 110°C for 24 hours. The dried peels were then ground into powder using a blender, passed through a sieve with a mesh size <600 μm, and afterwards oven-dried for 30 minutes at a temperature of 80°C before being used in the experiments. The cassava starch and orange peel powder were used in the experiments in their unmodified state.

The natural coagulants were characterized using Fourier transform infrared (FTIR) spectrometer (IR Tracer-100, Shimadzu Co., Japan) together with a GATR10 attenuated total reflectance (Shimadzu Co., Japan) to study the surface functional groups within a wavenumber range of 4000 and 600 cm^{-1}. The surface morphology was examined using the JEOL JSM-6060S scanning electron microscope (SEM).

2.3. Experimental Procedure. A 100 g/L stock solution of cassava starch, orange peel powder, and aluminum sulphate was prepared separately in three 1 L volumetric flasks. Appropriate volumes of each coagulant were measured and used in the experiments. Freshly prepared stock solutions of the natural coagulants were always used in these series of experiments.

Coagulation-flocculation experiments were run at room temperature in a jar test apparatus (Stuart® SW6 flocculator). One [1] L beaker was filled to the 500 mL mark with the tannery wastewater. The initial pH of the wastewater was changed to the required pH by adding 0.1 M H_2SO_4 or 100 g/L $Ca(OH)_2$ before pouring in the appropriate volumes of the coagulants. The mixtures were then rapidly mixed at a speed of 250 rpm for 1 minute followed by a slow-mix at 30 rpm for 30 minutes [26]. After allowing a settling time of 30 minutes, samples of the supernatant were collected from about 3 cm below the surface for COD and TSS analyses. The volume of the sludge in each beaker was noted for the computation of the sludge volume index (SVI) according to equation (1). The removal efficiency of COD and TSS were calculated according to equation (2). All experiments were performed in the Environmental Quality Engineering Laboratory of the Kwame Nkrumah University of Science and Technology (Ghana).

$$\mathrm{SVI}\left(\frac{mL}{g}\right) = \frac{\text{volume of sludge } (mL/L)}{\mathrm{TSS}\,(g/L)}, \tag{1}$$

$$\text{removal efficiency } (\%) = \frac{C_i - C_f}{C_i} \times 100\%, \tag{2}$$

where C_i and C_f are the initial and final concentrations of the measured COD (mg/L) and TSS (mg/L) of the wastewater.

2.4. Experimental Design for Coagulation Experiments at Different Coagulant Dosages and Wastewater pH. Central composite design (CCD), an experimental design tool in response surface methodology, well-known for its efficiency in building quadratic models was applied in assessing the effect of the two most relevant independent variables ($n = 2$), namely, coagulant dosage (X_1) and initial pH of wastewater (X_2) on three [3] response variables (Y) in the coagulation-flocculation process. The three responses were removal efficiencies in COD (Y_{COD}) and TSS (Y_{TSS}) as well as SVI (Y_{SVI}).

The number of experimental runs for a CCD is obtained from the sum of the 2^n factorial points, $2n$ axial points, and the number of replicates (c), as shown in equation (3). n which represents the number of independent variables being considered was 2 in this study. Hence, for a 2^2 full factorial central composite design, thirteen [13] experiments were conducted. Five [5] replications at the centre point were performed to ensure repeatability of the results. The four axial points in the central composite design are located at a distance, α from the centre with designations: $(0, \pm\alpha)$ and $(\pm\alpha, 0)$. The value of α is computed from the expression $(2^n)^{1/4}$. Hence, for two independent variables, $\alpha = 1.414$.

$$\begin{aligned} N_{\mathrm{total}} &= 2^n + 2n + c \\ &= 4 + 4 + 5 \\ &= 13, \end{aligned} \tag{3}$$

where N_{total} is the total number of experiments, n is the number of independent variables, and c is the number of replications at the centre point.

Preliminary experiments were performed to determine the range within which the dosage of each coagulant and the initial pH of the wastewater operated effectively (Table 1). It was noted that cassava starch and orange peel powder operated effectively within a dosage range of 3 to 11 g/L and an initial pH range of 3 to 9. For alum, the effective range for the dosage was within 7 and 17 g/L and within 6 and 9 for pH. The coagulant concentrations applied were relatively high due to the large contaminant loads in the tannery wastewater [27]. Similar observations in high coagulant dosages were made by Muruganandam et al. [28] and Ghafari et al. [29]. After the definition of the range of values for coagulant dosage and pH, codes were given to these values such that ±1 denoted the upper and lower levels of the factorial points, 0 denoted the centre points, and $\pm\alpha$ denoted the lower and upper axial points. The ranges and levels of the independent factors (coagulant dosage and initial pH) are presented in Table 1. The experimental runs were randomized to reduce the effect of residual error.

2.5. Statistical Analysis and Modelling of Response Surfaces. The experimental results for each of the responses were fitted to second-order polynomial models. Equation (4) shows the general formula for a polynomial.

$$Y = \beta_O + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n} \sum_{j=1}^{n} \beta_{ij} X_i X_j + \varepsilon, \tag{4}$$

where Y denotes the predicted response; β_O, β_i, and β_{ij} are collectively referred to as model coefficients; β_O represents the constant coefficient; and β_i, β_{ii}, and β_{ij} are the linear, quadratic, and interaction coefficients, respectively. The error associated with the model is represented by ε. X_i and X_j are the codes given to the two independent variables—coagulant dosage and pH, respectively [30]. Statistical significance of the regression models was evaluated through the analysis of variance (ANOVA) test. The significance of the model coefficients was determined using Fisher's test in which the p value was set at a confidence interval of 95%. The adequacy of the quadratic models was assessed using the

Table 1: Range and levels of the independent variables.

Coagulants	Code	Variables	Ranges and levels				
			$-\alpha$	-1	0	$+1$	$+\alpha$
Cassava starch	X_1	Dosage (g/L)	2.76	4	7	10	11.24
	X_2	pH	3.17	4	6	8	8.83
Orange peel powder	X_1	Dosage (g/L)	2.76	4	7	10	11.24
	X_2	pH	3.17	4	6	8	8.83
Aluminum sulphate	X_1	Dosage (g/L)	6.34	8	12	16	17.66
	X_2	pH	6.09	6.5	7.5	8.5	8.91

coefficient of determination (R^2) and lack-of-fit tests. Based on the regression models, response surface and contour plots illustrating the interaction effect of the two process parameters as well as the optimal regions of the coagulation-flocculation process were derived for each response. The optimal process parameters predicted by the models were authenticated experimentally. The Minitab statistical software package version 16 was used in executing the experimental design matrices, statistical analyses, and optimization processes.

3. Results and Discussion

3.1. Vegetable Tannery Wastewater Characteristics. The physicochemical characteristics of the tannery wastewater are presented in Table 2. The wastewater is slightly acidic and its average pH value of 6.29 falls within the limits of the Ghana Environmental Protection Agency (EPA) standards for wastewater discharge. The wastewater is dark-red in colour (22400 Pt-Co) resulting from the tannins and dyes applied in the leather production process [32]. Its total dissolved solid (4585.25 mg/L) and suspended solid (3441.25 mg/L) contents as well as its high turbidity (1380 NTU) levels originating from the plant materials used in the leather making process [33] also surpassed the Ghana EPA set limits of 1000 mg/L, 50 mg/L, and 75 NTU, respectively. The average COD (9459.34 mg/L) and BOD_5 (2639 mg/L) concentrations of the tannery wastewater exceeded the permissible limits of 250 mg/L and 50 mg/L, respectively, by nearly 38 and 21 times, respectively. The biodegradability index (BOD_5/COD) of the vegetable tannery wastewater was averagely 0.11 which correlates to the nonbiodegradability characteristic of the wastewater [34]. This is as a result of the occurrence of the phenolic compounds such as tannins and natural dyes in the wastewater [35]. It is worth mentioning that the levels of COD, TSS, and the BOD_5/COD ratio obtained in this study are in agreement with those reported by Balakrishnan et al. [5]. The concentration of total nitrogen (36.70 mg/L) may be due to the presence of vegetal matter as well as the small pieces of flesh and adipose tissues released from the animal skins into the wastewater [33]. The chloride ions (722 mg/L) in the wastewater could be resulting from the salts used in preserving the animal skins [30].

Table 2: Characteristics of vegetable tannery wastewater.

Parameters	SI unit	Values	Ghana EPA [31]
pH	—	6.29 ± 0.35	6.0–9.0
Colour	Pt-Co	22400 ± 5931.86	100
TSS	mg/L	3441.25 ± 621.63	50
Turbidity	NTU	1380 ± 399.53	75
COD	mg/L	24928 ± 327.26	250
BOD_5	mg/L	2639 ± 25.56	50
BOD_5: COD	—	0.11 ± 0.01	—
TN-N	mg/L	36.70 ± 5.45	50
Cl^-	mg/L	722 ± 56	—

3.2. Characteristics of Natural Coagulants

3.2.1. Fourier Transform Infrared Spectroscopy. FTIR spectra for cassava starch and powdered orange peels are illustrated in Figure 1. The principal components of cassava starch are cellulose, lignin, amylose, amylopectin, proteins, and fats [36, 37] while that of orange peels are cellulose, pectin, lignin, fats, proteins, and soluble sugars [38]. These constituents have distinct functional groups which correspond to the different wavenumbers and broadband widths as seen in the FTIR spectra. From Figure 1, the similarity in the shape of the FTIR spectra of both cassava starch and powdered orange peels indicates that they have similar functional groups as was ascertained by Mohd-Asharuddin et al. [36].

The broadband width occurring between 3500 and 3200 cm^{-1} corresponds to O-H bonds of polymeric compounds (mostly alcohols, carboxylic acids, and phenols) and hydroxyl functional groups. There is also C-H stretch of alkyne (3320–3310 cm^{-1}) as well as alkane and alkene functional groups (2970–2850 cm^{-1}). The peaks between 1750 and 1705 cm^{-1} also depict the presence of the carbonyl functional group ($C=O$) of ketones, aldehydes, carboxylic acids, and esters. The absorption band ranges from 1680 to 1600 cm^{-1} indicates $C=C$ stretch in the alkenyl functional group. The $C=O$ stretch within the range of 1420 and 1380 cm^{-1} may be assigned to the presence of carboxylic acid salt. The wide absorption band ranging from 1420 to 900 cm^{-1} comprises O-H stretch of tertiary alcohol or phenol (1410–1310 cm^{-1}), C-N stretch of the amine functional group (1360–1310 cm^{-1}), C-O stretch of alcohol and ether (1150–1050 cm^{-1}), silicate ion (1100–900 cm^{-1}), and C-OH stretch of alcohol (1040–960 cm^{-1}) [39]. FTIR of cassava peel starch presented by Mohd-Asharuddin et al. [36] is similar to that of cassava starch studied in this work. Similar FTIR results of orange peel powder were also obtained by Vinay et al. [40] who looked into orange peel extracts.

3.2.2. Surface Morphology. The surface morphology of cassava starch and powdered orange peels illustrated in Figure 2 is obtained from the SEM micrographs. Cassava starch was observed to have granules which were smooth, spherical, and tightly packed together [30]. This observation is in agreement with that described by Xia et al. [41].

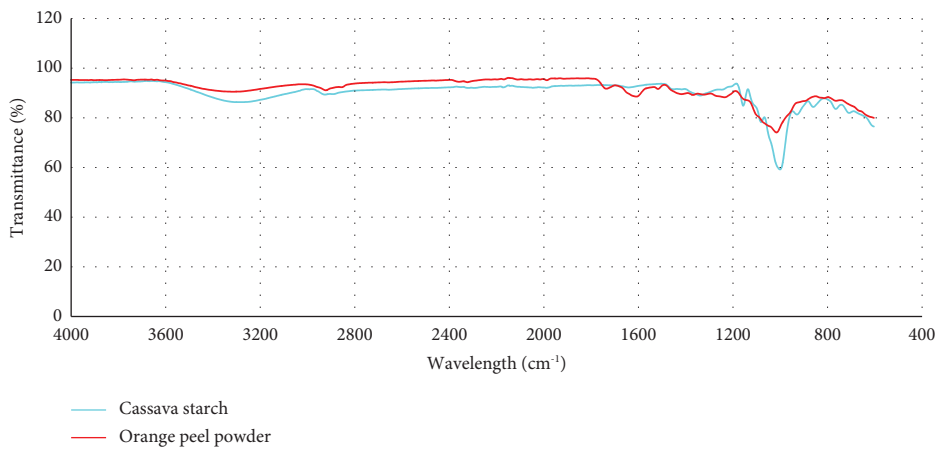


Figure 1: FTIR spectra of cassava starch and orange peel powder.

Mohd-Asharuddin et al. [36] also gave a similar description for starch extracted from cassava peels. The morphology of powdered orange peels was of irregular-sized polygonal-shaped particles with a layered structure as was also observed by Romero-Cano et al. [42] who investigated into the adsorption properties of orange peels.

3.3. Development of Regression Models. Pretreatment of the tannery wastewater through coagulation-flocculation process using the three different coagulants, cassava starch, orange peel powder, and aluminum sulphate, was optimized based on the central composite design to maximize removal of COD and TSS and minimize SVI. Experimental design matrices consisting of thirteen experimental runs displaying the experimental results and predicted values of the three responses are presented in Tables 3 and 4. Quadratic regression models obtained after correlating the independent variables (coagulant dosage (X_1) and pH (X_2)) with the three different responses which were COD removal efficiency (Y_{COD}), TSS removal efficiency (Y_{TSS}), and SVI (Y_{SVI}) are presented in equations (6)–(13) for each coagulant.

For cassava starch coagulant, the regression models obtained for the three responses were

$$Y_{COD}(\%) = 38.5 - 4.27X_1 + 0.1933\,X_1^2 \cdot \left(R^2 = 89.75\%, R^2_{adj} = 82.43\%\right), \tag{5}$$

$$Y_{TSS}(\%) = 95.8 - 7.72\,X_2 + 0.438\,X_2^2 \cdot \left(R^2 = 87.83\%, R^2_{adj} = 79.14\%\right), \tag{6}$$

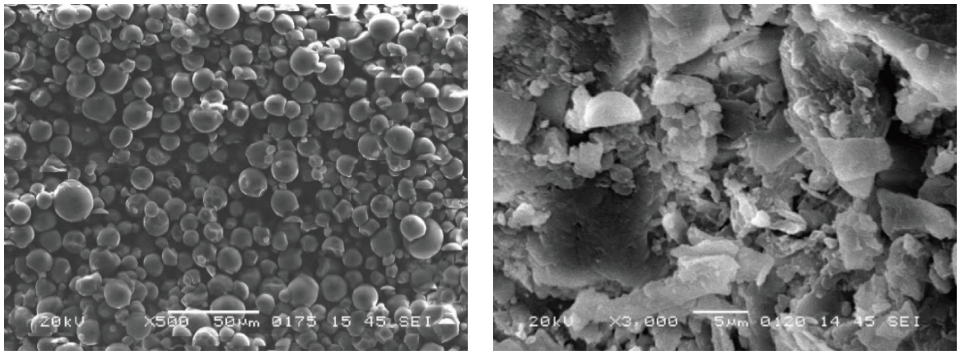
$$Y_{SVI}\left(\frac{mL}{g}\right) = 3.14 + 2.564X_1 + 2.951X_2 + 0.406X_1^2 + 0.3224X_2^2 - 1.2693X_1X_2 \cdot \left(R^2 = 98.04\%, R^2_{adj} = 97.63\%\right). \tag{7}$$

For orange peel powder coagulants, the regression models attained for each response were

$$Y_{COD}(\%) = -13.2 + 7.98\,X_1 - 0.7045\,X_1^2 + 0.503X_1X_2 \cdot \left(R^2 = 91.73\%, R^2_{adj} = 85.83\%\right), \tag{8}$$

$$Y_{TSS}(\%) = 94.6 - 1.33\,X_2 - 0.82\,X_2^2 + 1.306X_1X_2 \cdot \left(R^2 = 92.55\%, R^2_{adj} = 87.23\%\right), \tag{9}$$

$$Y_{SVI}\left(\frac{mL}{g}\right) = 14.21 - 5.245X_1 + 4.177X_2 + 0.8885X_1^2 + 0.186X_2^2 - 0.475X_1X_2 \cdot \left(R^2 = 98.89\%, R^2_{adj} = 97.81\%\right). \tag{10}$$



(a) (b)

Figure 2: SEM of (a) cassava starch and (b) orange peel powder.

Table 3: CCD matrix for coagulation experiments using cassava starch orange peel powder coagulants.

Run order	Independent variables		Responses					
			Cassava starch			Orange peel powder		
	Dosage X_1 (g/L)	pH, X_2	COD removal, Y_{COD} (%)	TSS removal, Y_{TSS} (%)	SVI, Y_{SVI} (mL/g)	COD removal, Y_{COD} (%)	TSS removal, Y_{TSS} (%)	SVI, Y_{SVI} (mL/g)
1	10	4	24.89	68.48	35.12	14.49	53.37	51.47
2	7	6	30.19	64.15	16.90	19.71	61.99	32.89
3	10	8	27.77	61.22	11.36	15.83	58.10	58.53
4	7	6	33.02	64.85	17.27	24.35	59.61	32.35
5	7	6	31.94	61.88	16.34	20.87	57.24	33.59
6	7	3.17	28.03	74.42	25.36	17.97	57.67	25.57
7	4	4	36.11	68.21	16.97	15.94	68.68	19.60
8	11.24	6	31.07	65.66	27.74	15.65	56.16	66.89
9	2.76	6	38.93	65.15	21.13	2.90	61.12	30.17
10	7	6	31.25	64.65	16.63	22.32	60.91	33.13
11	7	8.83	30.56	61.45	14.05	18.55	50.08	42.48
12	7	6	30.19	61.02	17.76	20.29	60.69	32.30
13	4	8	38.19	59.79	23.68	5.22	42.07	38.05

Table 4: Central composite design matrix for coagulation experiments with aluminum sulphate coagulants.

Run order	Independent variables		Responses		
	Alum dosage (X_1) (g/L)	pH, X_2	COD removal, Y_{COD} (%)	TSS removal, Y_{TSS} (%)	SVI, Y_{SVI} (mL/g)
1	16	8.5	36.91	71.07	35.09
2	17.66	7.5	32.30	69.52	27.97
3	12	6.09	39.22	76.03	29.26
4	12	7.5	32.34	73.89	30.23
5	12	7.5	30.18	72.78	29.84
6	12	7.5	31.97	73.01	30.39
7	12	7.5	32.22	72.94	30.03
8	16	6.5	33.47	71.59	27.41
9	12	7.5	30.29	73.78	29.95
10	6.34	7.5	20.81	73.32	35.95
11	12	8.91	34.10	74.05	45.46
12	8	6.5	30.92	75.53	31.05
13	8	8.5	21.97	73.12	45.04

For aluminum sulphate, the regression models obtained for each response were

$$Y_{\mathrm{COD}}(\%) = 213.6 - 0.83X_1 - 47.36X_2 - 0.1637X_1^2 + 2.431X_2^2 + 0.775X_1X_2 \cdot \left(R^2 = 97.92\%, R^2_{\mathrm{adj}} = 96.43\%\right), \tag{11}$$

$$Y_{\mathrm{TSS}}(\%) = 128.1 + 0.305X_1 - 13.839X_2 - 0.0644X_1^2 + 0.78X_2^2 \cdot \left(R^2 = 96.00\%, R^2_{\mathrm{adj}} = 93.15\%\right), \tag{12}$$

$$Y_{\mathrm{SVI}}\left(\frac{mL}{g}\right) = 174.82 + 0.78X_1 - 44.17X_2 + 0.05828X_1^2 + 3.632X_2^2 - 0.3942X_1X_2 \cdot \left(R^2 = 98.69\%, R^2_{\mathrm{adj}} = 97.76\%\right). \tag{13}$$

From the quadratic models, the coefficients of the individual variables (coagulant dosage (X_1) and initial pH (X_2)) show the linear effects of these factors on the coagulation-flocculation process. On the other hand, the coefficients of X_1^2 and X_2^2 depict the quadratic or squared effect of the factors while those of X_1X_2 indicate the effect of the interaction between the two factors (X_1 and X_2) on the coagulation-flocculation process. The occurrence of a positive sign (+) before a term connotes a synergistic effect on the coagulation-flocculation process whilst a minus sign (−) defines an antagonistic effect of that factor [26] on the treatment process.

3.4. Validity of Regression Models. The adequacy of the regression models was validated before the optimization process to ascertain that they are adequately approximate to the actual coagulation-flocculation process. The model adequacy was checked through a diagnostic plot of the predicted and the actual values of the responses for each coagulant (Figures 3–5). Observation of the figures indicated that the predicted values are a good approximation of the experimental data.

The precision of the models was assessed from the coefficient of determination (R^2). R^2 values greater than 75% [43] and also very close to the adjusted R^2 values are usually considered satisfactory [44]. The R^2 values obtained for COD and TSS removal efficiencies as well as for SVI were 89.75%, 87.83%, and 98.04%, respectively, for cassava starch; 91.73%, 92.55%, and 98.89%, respectively, for orange peel powder; and 97.92%, 96%, and 98.69% respectively, for alum (Figures 3–5) which were all greater than 75% signifying good predictive models [30].

Furthermore, the precision of the models was also judged through ANOVA using Fisher's test (F-test) to evaluate their statistical significance. The results are given in Tables 5 and 6. The statistical significance of the regression models was evaluated from the F and p values. As can be observed from the tables, the p values for COD and TSS removal efficiencies as well as for SVI were 0.002, 0.004, and ≤0.001, respectively, for cassava starch; ≤0.001, ≤0.001, and ≤0.001, respectively, for orange peel powder; and ≤0.001, ≤0.001, and ≤0.001, respectively, for alum. The very low p values evidently indicate that all the models were highly statistically significant.

Lastly, the lack-of-fit of a regression model can also be used to evaluate the validity of the regression models. From the F-test, the lack-of-fit becomes statistically significant if the model is not a good fit to the experimental data. The large p values greater than 0.05 obtained for lack-of-fit of the three models shown in Tables 5 and 6 for COD and TSS removals as well as for SVI which were 0.139, 0.413, and 0.262, respectively, for cassava starch; 0.213, 0.202, and 0.388, respectively, for orange peel powder; and 0.688, 0.720, and 0.062, respectively, for alum highlight the adequacy of the models in representing the experimental data.

3.5. Effect of Process Parameter on SVI, TSS, and COD Removal Efficiencies Using Cassava Starch and Orange Peel Powder. The effect of process parameters, coagulant dosage and initial pH of wastewater, on SVI, removal of COD, and TSS from the tannery wastewater are illustrated in the 2D contour and 3D response surface plots (Figures 6–11) [30]. In addition, the statistical significance of each of the model coefficients (linear, quadratic, and interaction terms) using the F-test and p values is presented in Table 5. Generally, a model coefficient becomes increasingly statistically significant when its F-value increases and its p value decreases [44].

3.5.1. Effect of Process Parameters on TSS Removal. TSS removal using cassava starch and orange peel powder was highly influenced by the initial pH of the wastewater (X_2) with p values ≤0.001 and 0.002 for cassava starch and orange peel powder, respectively. However, the high p values (>0.05) obtained for cassava starch dosage X_1 ($p = 0.653$) and orange peel powder dosage X_1 ($p = 0.365$) signify that these parameters were not statistically significant in the removal of TSS from the wastewater (Table 5). TSS removal efficiency decreased with increase in pH for both cassava

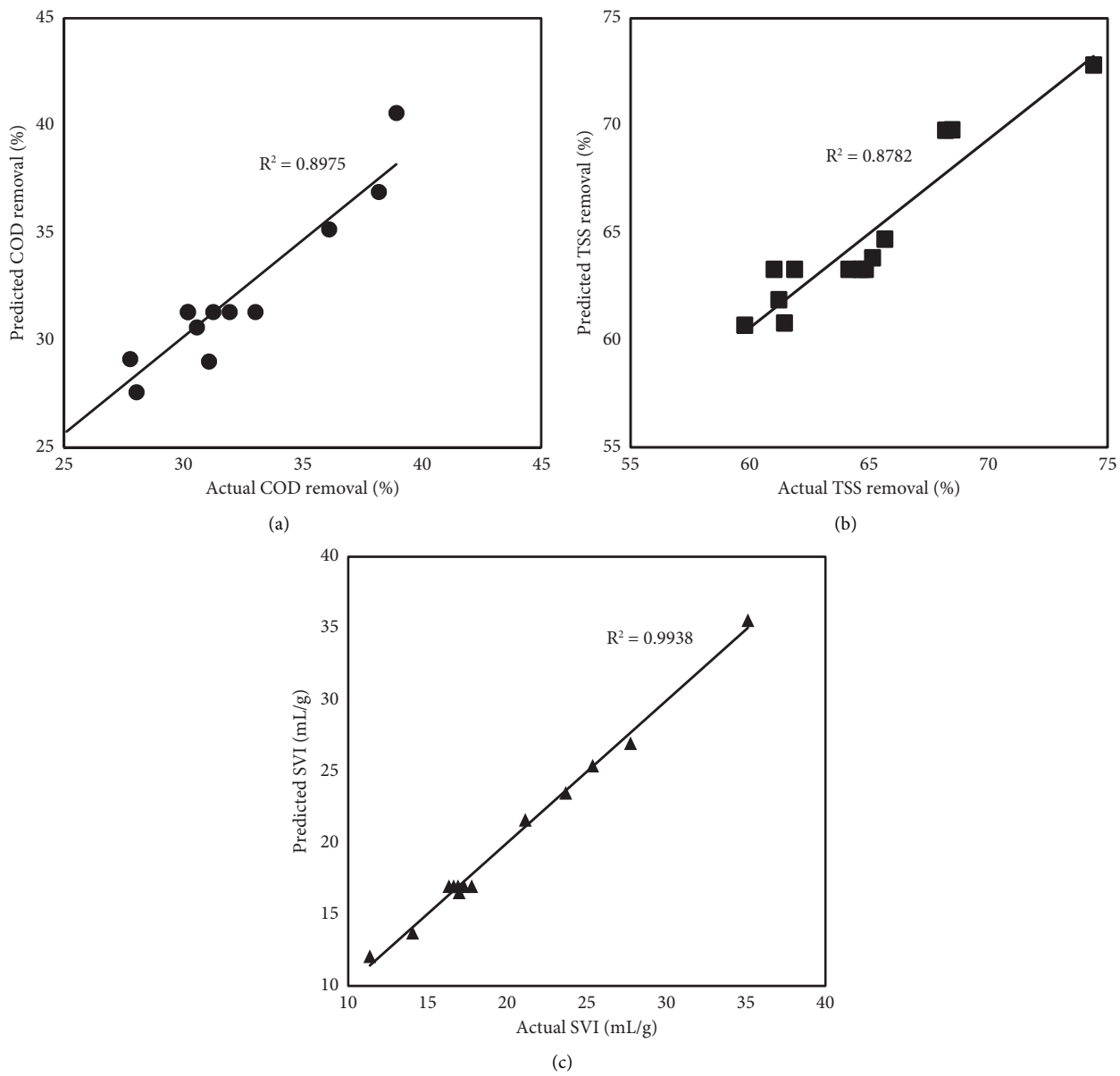


Figure 3: Predicted versus actual results for (a) % COD removal, (b) % TSS removal, and (c) SVI (mL/g) using cassava starch coagulants.

starch and orange peel powder (Figures 6 and 9) [30]. A maximum TSS removal efficiency above 70% and 60% was attained with cassava starch and orange peel powder coagulant, respectively. These occurred within an optimum pH range of 3.17 and 4 and a dosage range within 2.76 and 11.2 g/L for cassava starch coagulant. For orange peel powder coagulant, the optimal pH range fell within 3.17 and 5.8 and a dosage range within 2.76 and 8 g/L. Thus, TSS removal efficiency was maximized within the acidic region for both types of coagulants. A similar trend was observed by Teh et al. [45] who reported a maximum TSS removal of 88.9% from a palm oil mill effluent at an optimum pH of 3 and rice starch dosage of 2 g/L.

The principal coagulation mechanisms by which cassava starch and orange peel powder removed contaminants from the wastewater were via adsorption, bridging, and charge neutralization [27]. Cassava starch contains two glucose polymers with large molecular weights, namely, amylose and amylopectin. Amylose, which forms about 10 to 20% of the starch, is a linear polysaccharide while amylopectin, constituting about 80 to 90%, is a branched polymer [46]. The natural polymers in orange peels, on the other hand, are cellulose, pectin, hemicellulose, proteins, lignin, flavonoids, and pigments [38]. The functional groups occurring along these polymer chains in cassava starch and orange peel powder are principally the carboxyl (-COOH) and hydroxyl (−OH) groups as were observed in the FTIR spectra (Figure 1) [47]. These functional groups are known to have coagulating properties and are involved in the adsorption and bridging mechanism of coagulation [48].

In addition to the bridging mechanism, the colloidal particles were destabilized through adsorption and charge

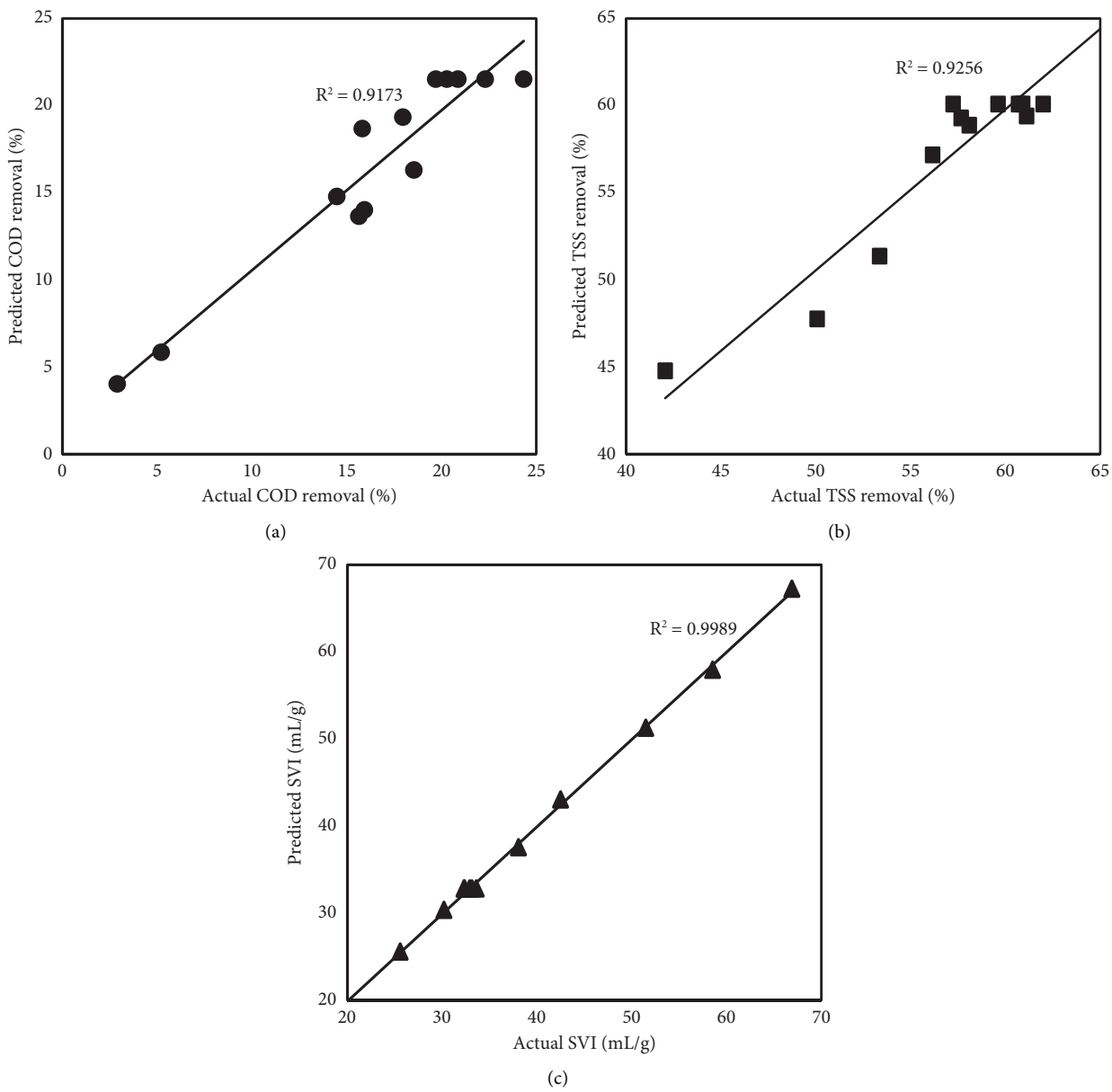


Figure 4: Predicted versus actual results for (a) % COD removal, (b) % TSS removal, and (c) SVI (mL/g) using orange peel powder coagulants.

neutralization mechanism. At low pH, the amino functional groups of the crude proteins in the cassava starch and powdered orange peels (Figure 1) became protonated resulting in the increase in the density of the positively charged hydrogen ions of the coagulants [49]. This created a strong affinity between the positively charged coagulants and the negatively charged colloidal pollutants in the wastewater resulting in the adsorption of the coagulant granules onto the colloids, neutralization of charges, and their subsequent removal through settling [45]. A study by Abd Rahim et al. [50] also recorded a maximum TSS removal of 77.78% from dam water using cassava peel starch coagulant at an optimum pH of 2.

At high pH range, the intensity of negative charges on the protein molecules of the coagulants is increased resulting in a reduction of the positively charged density on the coagulants. As a result, the electrostatic force of attraction between the negatively charged colloids and the coagulants is weakened at high pH leading to insufficient charge neutralization [43] and a lower removal efficiency of TSS. Similar observations at high pH were also made by Teh et al. [45].

3.5.2. Effect of Process Parameters on COD Removal. From Table 5, cassava starch dosage, X_1 ($p \leq 0.001$), played the most influential role in COD removal. This was followed by the squared effect of dosage, X_1^2 ($p = 0.031$). However, the initial pH of the wastewater, X_2 ($p = 0.119$), and its squared effect, X_1^2 ($p = 0.127$), did not significantly influence COD

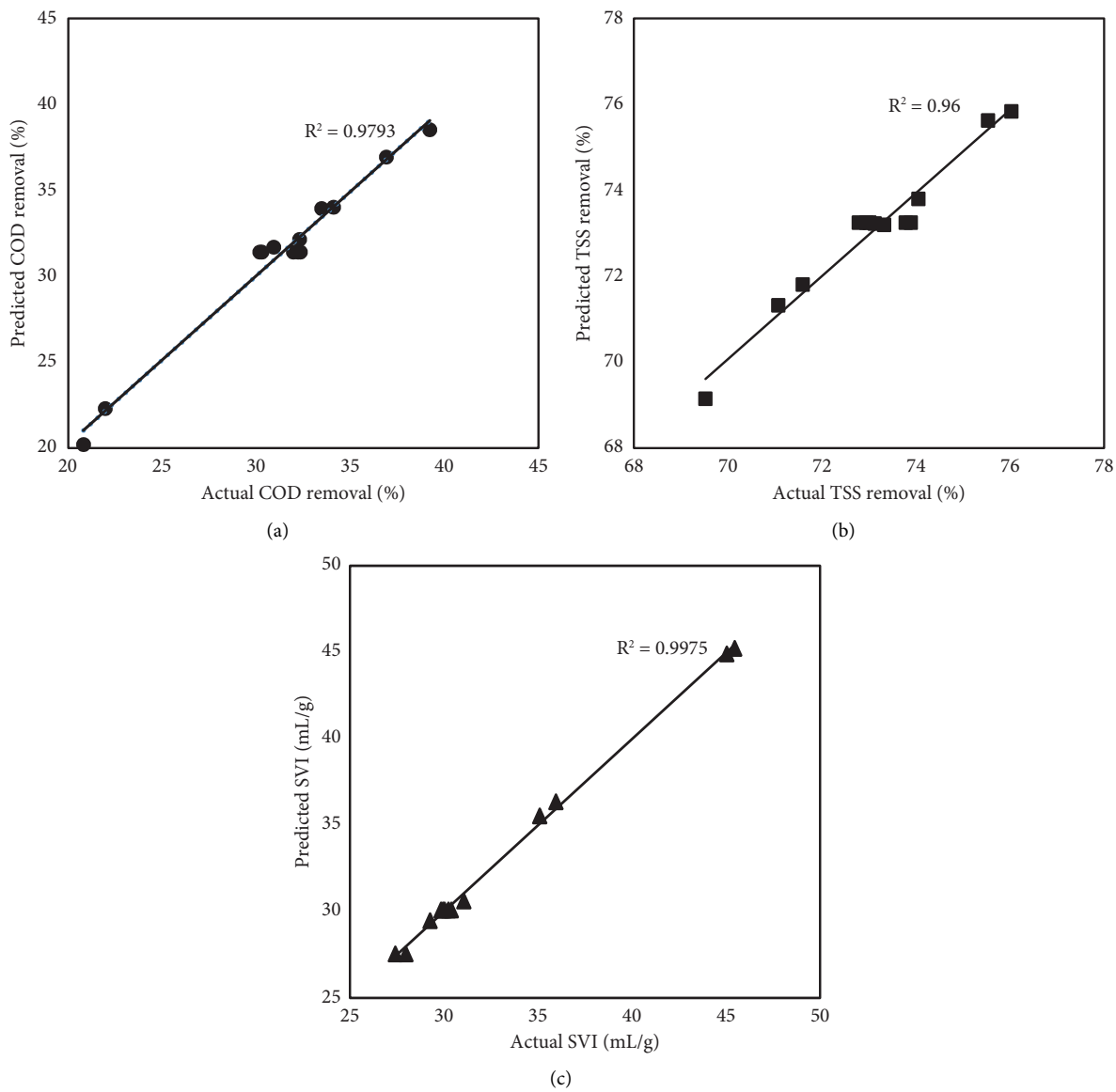


Figure 5: Predicted versus actual for (a) % COD removal, (b) % TSS removal, and (c) SVI (mL/g) using aluminum sulphate as coagulant.

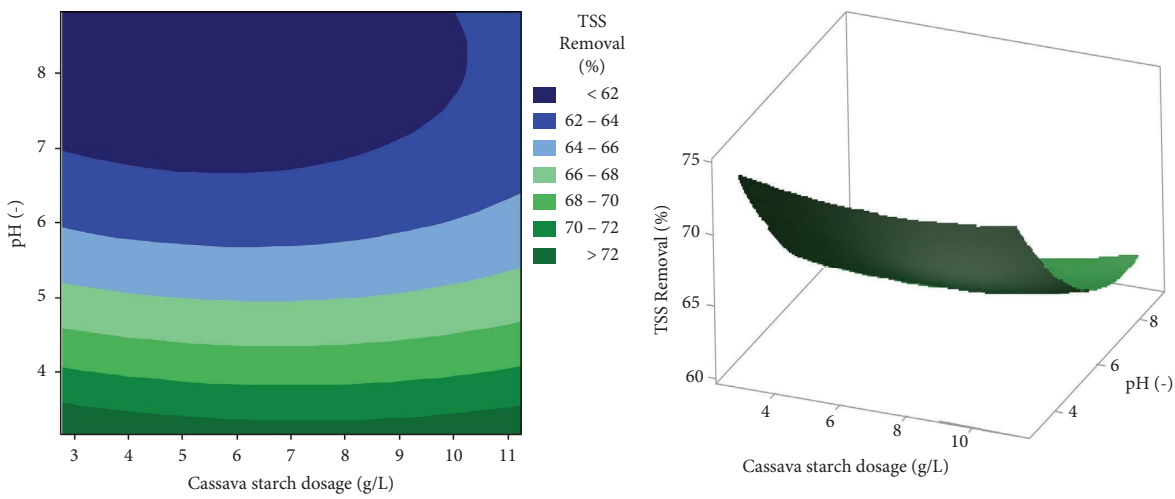
Table 5: Analysis of variance for response surface model of %COD removal (Y_{COD}), %TSS removal (Y_{TSS}), and SVI (Y_{SVI}) with cassava starch and orange peel powder coagulants.

Term	d.f	Cassava starch						Orange peel powder					
		F-value			*p* value			*F*-value			*p* value		
		Y_{COD}	Y_{TSS}	Y_{SVI}	Y_{COD}	Y_{TSS}	Y_{SVI}	Y_{COD}	Y_{TSS}	Y_{SVI}	Y_{COD}	Y_{TSS}	Y_{SVI}
Model	5	12.3	10.1	223	0.002	0.004	≤0.001	15.5	17.4	1288	≤0.001	≤0.001	≤0.001
X_1	1	46.4	0.22	64.9	≤0.001	0.653	≤0.001	16.9	0.94	4085	0.005	0.365	≤0.001
X_2	1	3.15	43.6	308	0.119	≤0.001	≤0.001	1.68	25.1	918	0.237	0.002	≤0.001
X_1^2	1	7.28	0.49	209	0.031	0.505	<0.001	51.1	1.06	1336	≤0.001	0.337	≤0.001
X_2^2	1	2.99	6.44	26.1	0.127	0.039	≤0.001	4.34	14.2	11.6	0.076	0.007	0.011
X_1X_2	1	0.06	0.10	523	0.821	0.760	≤0.001	6.65	46.4	97.5	0.037	≤0.001	≤0.001
Lack-of-fit	3	3.31	1.21	1.96	0.139	0.413	0.262	2.36	2.46	1.31	0.213	0.202	0.388

removal. COD removal efficiency decreased with increasing cassava starch dosage with maximum removal efficiency above 37.5% occurring at an optimum dosage from 2.76 to 4 g/L and a pH range within 3.17 and 9 (Figure 7). At the optimum dosage, good coagulation efficiency via adsorption, bridging, and charge neutralization resulted in high

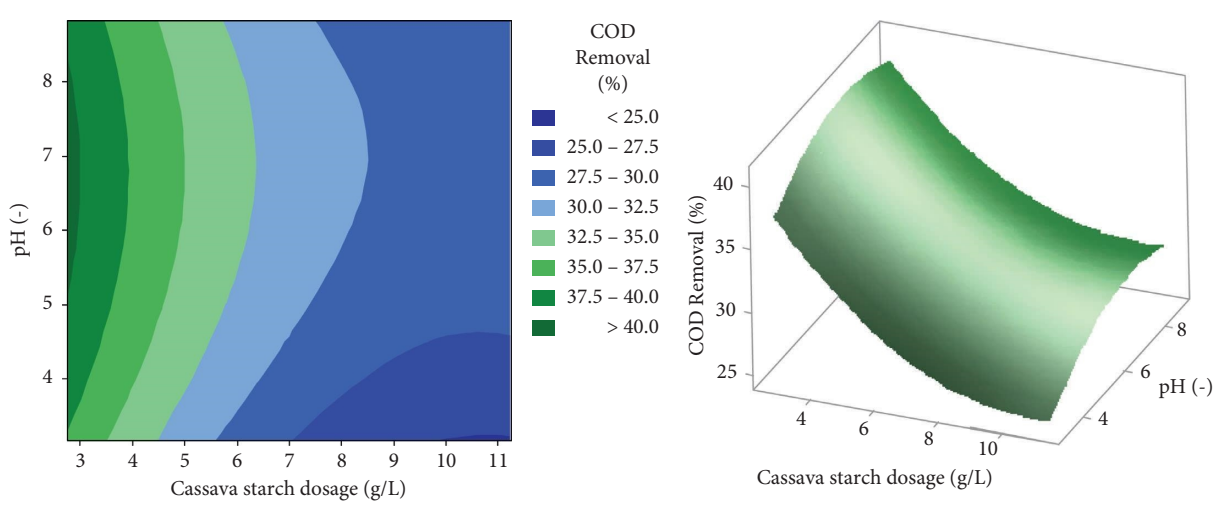
Table 6: Analysis of variance for response surface model for %COD removal (Y_{COD}), %TSS removal (Y_{TSS}), and SVI (Y_{SVI}) with aluminum sulphate.

Term	d.f	*F*-value			*p* value		
		Y_{COD}	Y_{TSS}	Y_{SVI}	Y_{COD}	Y_{TSS}	Y_{SVI}
Model	5	66.2	33.6	572	≤0.001	≤0.001	≤0.001
X_1	1	112	9.63	164	≤0.001	0.017	≤0.001
X_2	1	61.8	14.4	611	≤0.001	0.007	≤0.001
X_1^2	1	55.7	36.1	40.3	≤0.001	≤0.001	≤0.001
X_2^2	1	52.1	20.7	612	≤0.001	0.003	≤0.001
X_1X_2	1	41.9	4.36	66.3	≤0.001	0.075	≤0.001
Lack-of-fit	3	0.53	0.47	5.77	0.688	0.720	0.062



(a) (b)

Figure 6: (a) Contour and (b) response surface plots showing the combined effect of cassava starch dosage and pH on TSS removal efficiency.



(a) (b)

Figure 7: (a) Contour and (b) response surface plots showing the combined effect of cassava starch dosage and pH on COD removal efficiency.

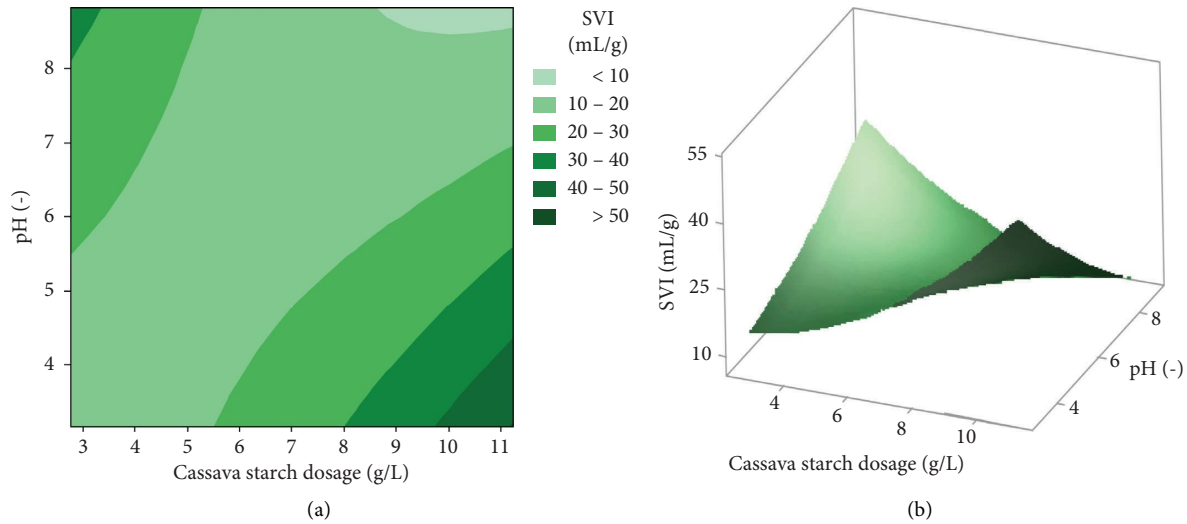


Figure 8: (a) Contour and (b) response surface plots showing the combined effect of cassava starch dosage and pH on SVI.

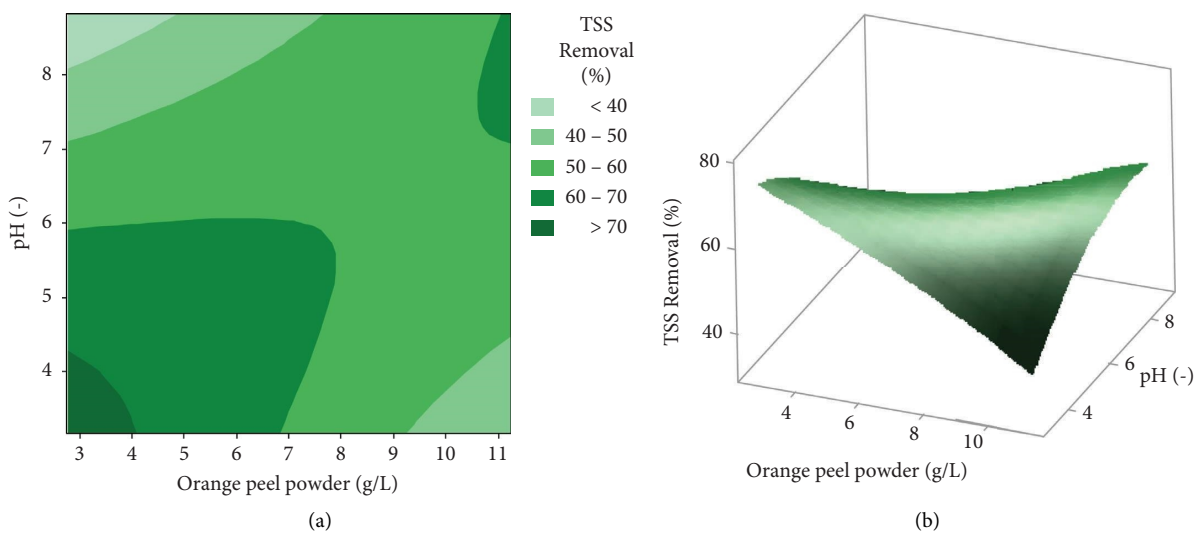
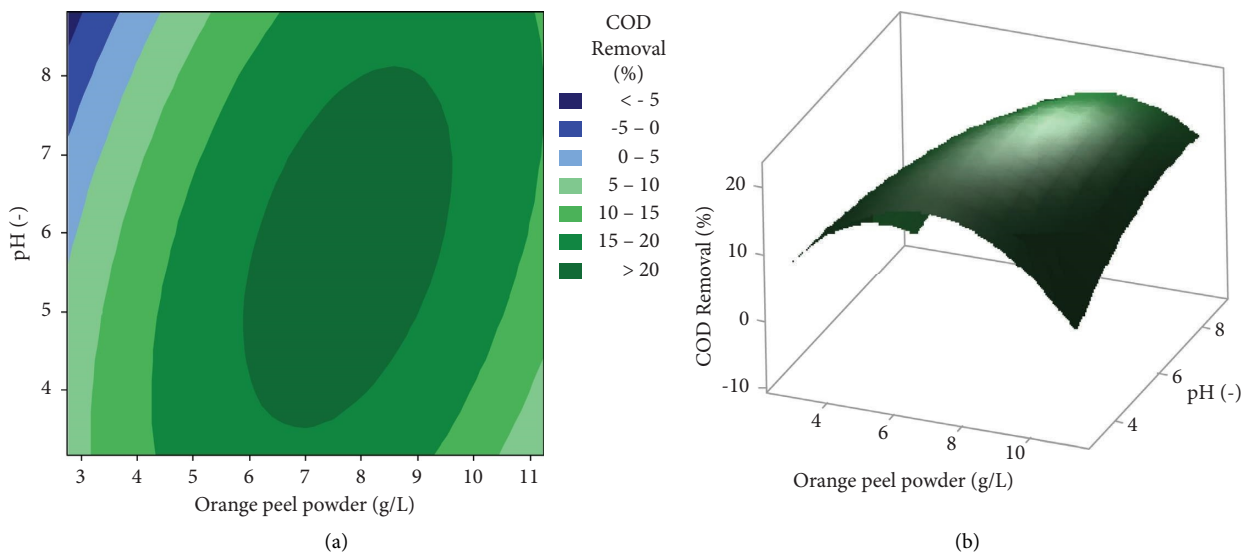


Figure 9: (a) Contour and (b) response surface plots showing the combined effect of orange peel powder dosage and pH on TSS removal efficiency.

contaminant removal efficiency. However, excessive dosage above the optimum might have caused charge reversal leading to restabilization of the colloids in the wastewater [51] and hence a reduced COD removal efficiency. In treating dam water with cassava peel starch, Abd Rahim et al. [50] and Othman et al. [52] made similar observations at high coagulant dosages.

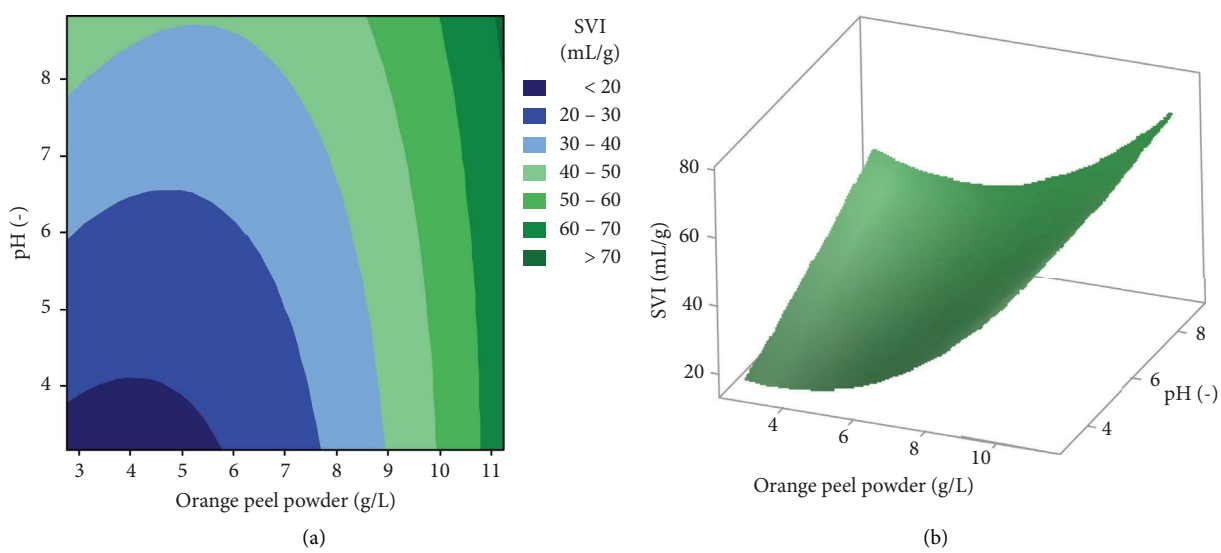
Similarly, COD removal with orange peel powder was highly affected by the quadratic, X_1^2 ($p \leq 0.001$), and the linear, X_1 ($p = 0.005$), effects of dosage, whilst the linear ($p = 0.237$) and the quadratic ($p = 0.076$) effects of pH were negligible. From Figure 10, COD removal efficiency with orange peel powder increased sharply with increasing dosage up to 8 g/L and then declined. A maximum COD removal efficiency above 20% can be achieved at an optimum dosage range within 5.7 and 8 g/L and a pH range from 3.5 to 8. Dosages below this optimum region caused a reduction in the COD removal efficiency as a result of insufficient polymer chains for adsorption and bridging as well as for charge neutralization of the colloidal particles [30]. The removal efficiency of the COD, however, enhanced with increments in dosage up to the optimum range. Above the optimum regions, the removal efficiencies declined due to the overdose of the orange peel powder resulting in charge reversal and the subsequent restabilization of the colloids in the wastewater [53]. The removal efficiencies obtained by both coagulants agree with that reported by Shewa and Dagnew [7] who explained that the low COD removal efficiencies could be probably due to a high proportion of the COD in the wastewater being in a soluble form.

It must be stated here that increments in dosage of orange peel powder increased the colouration of the treated



(a) (b)

Figure 10: (a) Contour and (b) response surface plots showing the combined effect of orange peel powder dosage and pH on COD removal efficiency.



(a) (b)

Figure 11: (a) Contour and (b) response surface plots showing the combined effect of orange peel powder dosage and pH on SVI.

wastewater due to the release of orange colour pigments from the peels into the wastewater. These pigments composed of phenolic compounds and carotenoids [54] could also have added to the COD levels of the wastewater [27] resulting in a low COD removal efficiency. The increase in colour and organic components in the wastewater with increasing powdered orange peel dosage has also been reported by Klančnik [55] who treated printing ink wastewater with orange peel powder.

3.5.3. Effect of Process Parameters on SVI. Sludge volume index (SVI) is generally used to assess the compressibility of sludge [56]. It depends on the degree of compaction of the sludge [57], and it is defined as the volume occupied by 1 g of sludge after a sedimentation time of 30 minutes [58]. The volume of sludge produced and characteristics of the floc particles such as floc size, its density, and surface charge are reliant on process conditions such as type of coagulant, pH, and coagulant dosage [56].

Observing Table 5, the influence of both dosages (X_1) and pH (X_2) on the sludge volume index was statistically significant at p values ≤0.001 for both cassava starch and orange peel powder. The contour and response surface plots illustrating the quadratic model for SVI for use of cassava starch (Figure 9) and orange peel powder (Figure 11) revealed that SVI increased with increasing pH and coagulant dosage [30]. An SVI below 100 mg/L is generally acceptable since it is an indicator of sludge with good settleability [26]. Thus, the highest SVI of 35.12 and

66.89 mL/g obtained for treatments with cassava starch and orange peel powder coagulants, respectively, is satisfactory. The least SVI which was below 20 mL/g was attained within an optimum pH range of 3.17 to 5.6 and a dosage range of 2.76 and 5.60 g/L for cassava starch and at a pH range of 3.17 to 4 and a dosage range within 2.76 and 5.80 g/L for orange peel powder.

Sludge volume index was lower within the acidic region because of the high coagulation efficiency via charge neutralization and bridging mechanisms which resulted in the formation of macrosized, dense floc particles with good settleability, and lower sludge volume [30]. Contrarily, at high pH, the decrease in coagulation efficiency due to electrostatic repulsion between the contaminants and the coagulants could have led to the formation of microsized flocs with low densities and poor settleability. In addition, at high pH, the flocs became negatively charged and created repulsive forces which reduced the interaction among the floc particles and thus kept them apart leaving them in an expanded state [56]. Consequently, a loosely packed sludge with high volume and SVI was generated at high pH [30].

The good coagulation efficiency attained at the optimum dosages favoured the production of large, dense flocs which settled to form a well-compacted sludge with low sludge volume and SVI [59]. However, at increased dosages of the coagulants, poor coagulation efficiency resulting from the reversal of charges on the colloidal particles reduced the flocculating ability of the colloids leading to the formation of weakly bonded flocs with low densities and poor settling characteristics [56, 59]. Hence, the high SVI is observed at increased dosages of the cassava starch and orange peel powder coagulants.

3.6. Effect of Process Parameters on SVI, TSS, and COD Removal Efficiencies Using Aluminum Sulphate as Coagulants. The results of Fisher's test for alum are presented in Table 6 and the 2D contour and 3D response surface plots are illustrated in Figures 12–14.

3.6.1. Effect of Process Parameters on TSS and COD Removal. With regards to TSS, the square of alum dosage, X_1^2 ($p \leq 0.001$), had the greatest influence on its removal, followed by the square of pH, X_2^2 ($p = 0.003$), the pH of the wastewater, X_2 ($p = 0.007$), and then the alum dosage, X_1 ($p = 0.017$). The interaction of the factors (X_1X_2) was, however, statistically insignificant in TSS removal efficiency ($p = 0.075$) (Table 6) [30]. From Figure 12, TSS removal efficiency decreased with increasing pH. It, however, increased with alum dosage from 6.3 to 11.8 g/L and then decreased with further addition of alum. A maximum TSS removal efficiency above 76% was obtained at the optimal ranges within 6 and 6.3 for pH and 6.3 and 11.8 g/L of alum.

Regarding COD, all the model terms, alum dosage (X_1), initial pH of the tannery wastewater (X_2), and the square of both factors (X_1^2 and X_2^2), as well as the interaction effect (X_1X_2), had significant influence on the COD removal efficiency with each having a p value ≤ 0.001 (Figure 13). Observation of the contour and response surface plots (Figure 13) [30] showed that removal efficiency of COD decreased with increasing pH but increased with increasing alum concentration until a dosage of 16.2 gAlum/L which is similar to that observed with TSS removal using alum. The optimum range for a maximum COD removal efficiency above 35% occurred at a pH range between 6 and 6.5 and alum dosage range between 7.5 and 16.2 gAlum/L. Outside this optimal region, COD removal efficiency is declined.

The high removal efficiency achieved at the optimum pH range within 6 and 6.3 for TSS and 6 and 6.5 for COD can be explained by the adsorption and neutralization of the negatively charged colloidal particles in the wastewater by positively charged aluminum hydroxide ions (Al^{3+}, $Al(OH)_2^+$, $Al(OH)^{2+}$, $Al(OH)_{3(s)}$, and $Al(OH)_4^-$) which were produced in the wastewater through hydrolytic reactions between $Al_2(SO_4)_3$ and water [60] (equations (14)–(17)). Subsequently, aluminum hydroxide-colloid complexes were formed which aggregated into large floc particles capable of settling out of solution to form sludge [61].

$$Al^{3+} + H_2O \leftrightarrow Al(OH)^{2+} + H^+, \tag{14}$$

$$Al(OH)^{2+} + H_2O \leftrightarrow Al(OH)_2^+ + H^+, \tag{15}$$

$$Al(OH)_2^+ + H_2O \leftrightarrow Al(OH)_3 + H^+, \tag{16}$$

$$Al(OH)_3 + H_2O \leftrightarrow Al(OH)_4^- + H^+. \tag{17}$$

Furthermore, additional colloids could have been removed via sweep flocculation mechanism in which the colloids were entrapped in the nuclei of aluminum hydroxide precipitates ($Al(OH)_{3(s)}$) during their formation. When these precipitates were settling, they could also have swept other colloids along with them [51]. With increasing pH, the different species of the positively charged aluminum hydroxide ions (Al^{3+}, $Al(OH)_2^+$, $Al(OH)^{2+}$, and $Al(OH)_3$) were transformed into the negatively charged aluminum tetrahydroxide $Al(OH)_4^-$) resulting in the unavailability of precipitates and positively charged ions to adsorb, neutralize, and "sweep" out the colloidal particles [61]. This led to the lower removal efficiencies of COD and TSS. Decrease in coagulation efficiency of alum at high pH was also reported by Asharuddin et al. [62].

From the response surface and contour plots, lower dosages of alum below 7.5 g/L was associated with low COD removal efficiency due to inadequate aluminum ions to produce enough positively charged aluminum hydroxide species. Thus, the adsorption sites available to adsorb the colloids and neutralize them were inadequate [63]. Hence, the poor coagulation efficiency is observed at low dosages. At the optimum dosage for TSS (6.3 and 11.8 g/L) and COD (7.5 to 16.2 g/L) removal efficiencies, there were more positively charged aluminum hydroxide ions to adsorp and neutralize the colloids resulting in a high coagulation efficiency. The production of $Al(OH)_3$ precipitates at high alum concentrations also removed a large quantity of the suspended solids through the mechanism of sweep flocculation [51]. The removal efficiencies of COD and TSS decreased

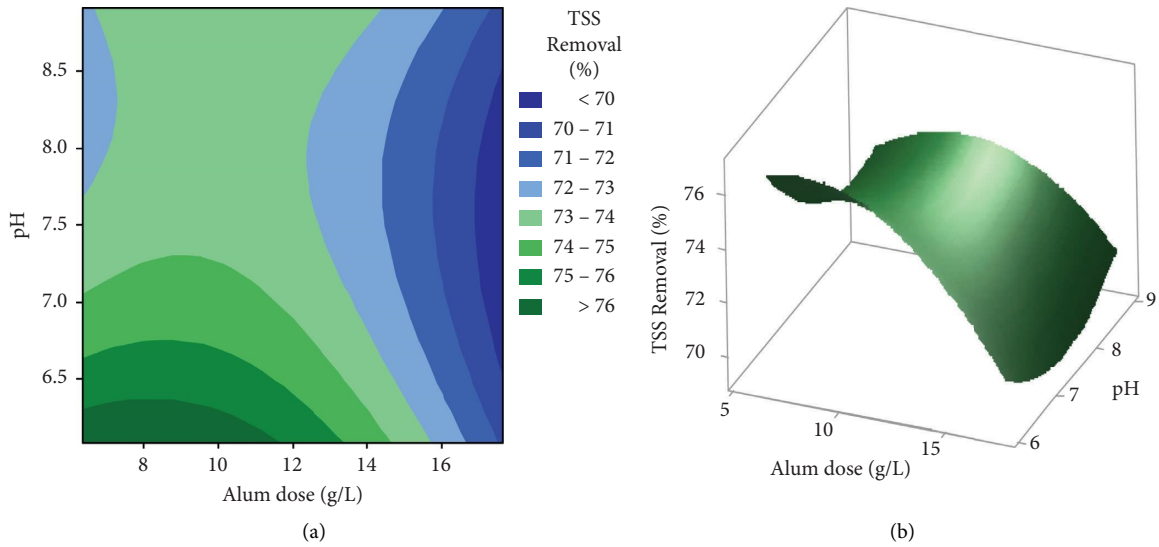


Figure 12: (a) Contour and (b) response surface plots showing the combined effect of alum dosage and pH on TSS removal efficiency.

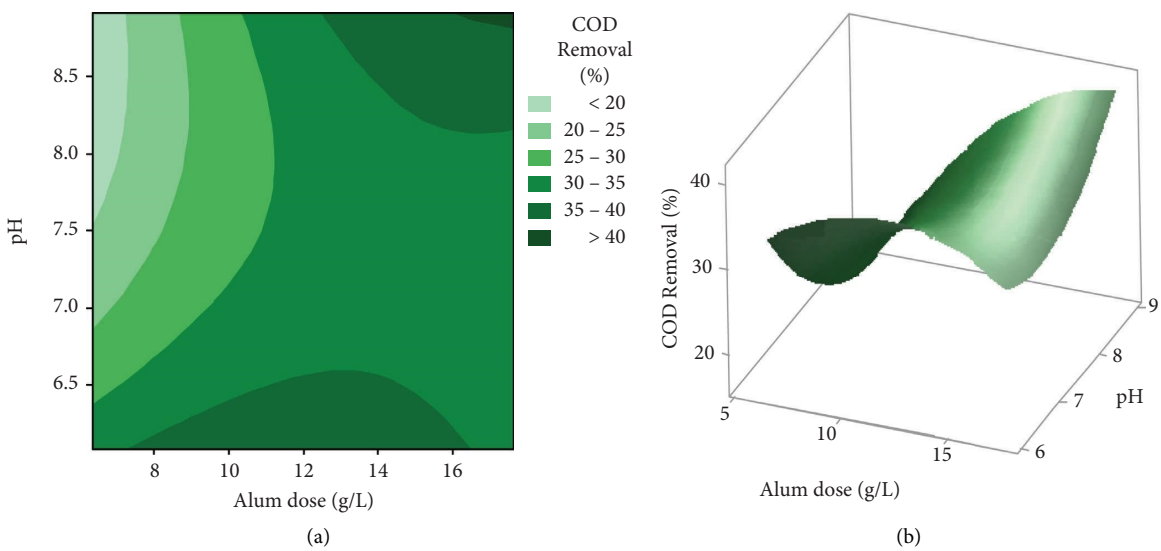


Figure 13: (a) Contour and (b) response surface plots showing the combined effect of alum dosage and pH on COD removal efficiency.

above the optimal dosages due to charge reversal and the subsequent restabilization of the colloidal materials [63].

3.6.2. Effect of Process Parameters on SVI. From the results of Fisher's test shown in Table 6, all parameters, alum dosage (X_1), initial pH of the wastewater (X_2), and square of both factors (X_1^2 and X_2^2), as well as their interaction effect (X_1X_2) had significant effect on the sludge volume index with each having a p value of 0.00. The response surface and contour plots (Figure 14) revealed that SVI increased with increasing pH and decreased with increasing alum dosage. The lowest sludge volume index that was attained was below 30 mL/g, and it occurred within a pH range from 6 to 7.7 and an alum dosage range between 9 and 18 g/L.

At the optimal pH ranges within 6 and 7.7, formation of dense, macroflocs through charge neutralization and sweep flocculation mechanisms produced well-compacted sludge with low sludge volumes and SVI. However, above pH 7.7, the reduction in coagulation efficiency due to the decreasing levels of the positively charged aluminum hydroxide precipitates could have resulted in the formation of few flocs with low densities and hence the generation of a loosely packed sludge with a high sludge volume. The attainment of negative charges on the flocs at high pH leading to repulsion among flocs and the subsequent production of loosely packed sludge can also explain the high SVI occurring at high pH [56].

The high SVI recorded at low dosages could be attributed to a lower coagulation efficiency due to insufficient alum dosage [64]. Hence, the formation of less dense, microsized flocs resulting in poorly compacted sludge with a higher sludge volume and SVI. However, with increased alum concentration, coagulation efficiency was enhanced which

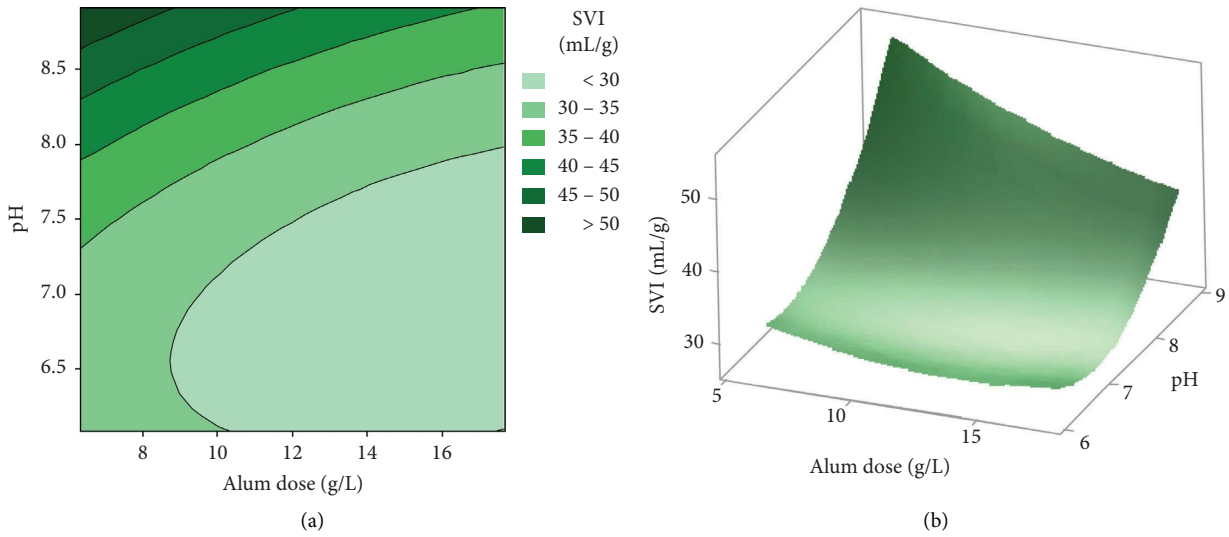


Figure 14: (a) Contour and (b) response surface plots showing the combined effect of alum dosage and pH on SVI.

Table 7: Predicted and experimental values at optimal process conditions.

Variables		Responses					
Dosage, X_1 (g/L)	pH, X_2	COD removal, Y_{COD} (%)		TSS removal, Y_{TSS} (%)		SVI, Y_{SVI} (mL/g)	
		Predicted	Experimental	Predicted	Experimental	Predicted	Experimental
Cassava starch							
2.76	3.17	37.25	37.01	73.95	73.61	14.80	15.01
Orange peel powder							
5.16	3.74	17.97	17.72	66.08	65.79	19.87	19.44
Alum							
11.6	6.09	38.51	38.85	76.05	76.36	29.57	29.24

Table 8: Comparison of different coagulants in the removal of TSS and COD from vegetable tannery wastewater.

Coagulant	Type of coagulant	Initial concentration	Coagulant dosage (mg/L)	pH	Removal efficiency (%)	Reference
TSS removal						
Chemical coagulant	PACl	18500	600	4	45	[66]
	PACl + CA-3130 (coagulant aid)	18500	600 + 65	4	80	[66]
	Alum	3441	11600	6.09	76.36	Present study
Green coagulant	Cassava starch	3441	2760	3.17	73.61	Present study
	Orange peel powder	3441	5160	3.74	65.79	Present study
COD removal						
Chemical coagulant	PACl	27000	600	4	20	[66]
	PACl + CA-3130 (coagulant aid)	27000	600 + 65	4	42	[66]
	Alum	24928	11600	6.09	38.85	Present study
Green coagulant	Cassava starch	24928	2760	3.17	37.01	Present study
	Orange peel powder	24928	5160	3.74	17.72	Present study

Initial concentrations of TSS and COD are measured in mg/L and mgO_2/L.

promoted the formation of macrosized floc particles, dense enough to produce tightly packed sludge with low sludge volume and SVI. Mehmood et al. [65] in treating pulp and paper mill wastewater also reported a decrease in SVI with increasing alum dosage.

3.7. Optimization and Verification of Process Parameters. Optimization of the coagulation-flocculation process was targeted at obtaining an optimal condition at which maximization of COD and TSS removal efficiencies and minimization of SVI occurred simultaneously. The response

optimizer function of Minitab 16 was used to optimize the coagulation-flocculation process. The optimal levels for pH and dosages of cassava starch, orange peel powder, and aluminum sulphate as given by the optimizer were verified through coagulation experiments. The results are detailed out in Table 7. The experimental results obtained were in close agreement to those given by the regression models confirming the accuracy of the models developed. From Table 7, aluminum sulphate yielded the best performance in the removal of TSS and COD. However, the use of cassava starch gave very comparable results to that of alum as the removal efficiencies of TSS and COD were only 2.1% and 1.26%, respectively, lower than those of alum. Furthermore, the cassava starch coagulant produced the least SVI of 14.80 mL/g with that of alum being more than twice that of cassava starch. Comparison made between the results of this study and that of other studies from literature adequately confirms that the performance of cassava starch is close to the chemical coagulants used in the removal of TSS and COD from vegetable tannery wastewater (Table 8).

4. Limitation of the Study

The cassava starch and orange peel powder coagulants were not characterized after being used in the treatment process. Hence, a comparison of the coagulants before and after use could not be made. Further studies carried out on this study should incorporate characterization studies of the coagulants.

5. Conclusions

In this study, vegetable tannery wastewater was treated through the coagulation-flocculation process using cassava starch, orange peel powder, and aluminum sulphate as coagulants. The treatment process was optimized by applying the response surface methodology. The effects of coagulant dosage and initial pH of wastewater on COD and TSS removal as well as on sludge volume index were investigated. All quadratic models developed were statistically adequate. The optimal operation conditions obtained were a dosage of 2.76 g/L and pH of 3.17 for treatment with cassava starch coagulant, an optimal dosage of 5.16 g/L and pH of 3.74 for orange peel powder coagulant and 11.6 g/L and pH of 6.09 for aluminum sulphate. The COD and TSS removal efficiencies as well as SVI at these optimal conditions were 37.25%, 73.95%, and 14.80 mL/g, respectively, for cassava starch coagulant; 17.97%, 66.08%, and 19.87 mL/g, respectively, for orange peel powder coagulant; and 38.51%, 76.09%, and 29.57 mL/g, respectively, for aluminum sulphate. Verification of these predicted results through further coagulation-flocculation experiments proved the accuracy and reliability of the models. Among the three coagulants, the highest sludge volume recorded was with the application of alum and the least was with cassava starch coagulant. Even though, alum yielded the best removal efficiency of COD and TSS, its performance was comparable to cassava starch coagulant. Cassava starch can, therefore, be considered as a green alternative to aluminum sulphate in the pretreatment of tannery wastewater to ensure a sustainable environment.

Data Availability

The data used to support the findings of this study are included within this article.

Disclosure

This article has initially been presented as a preprint article with reference to Appiah-Brempong M, Essandoh HMK, Asiedu NY, Dadzie SK, and Momade FWY.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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