Optimization of Coagulation-flocculation Process for Pre-treatment of Artisanal Tannery Wastewater Using Response Surface Methodology

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Optimization of coagulation-flocculation process for pre-treatment of artisanal tannery wastewater using response surface methodology

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Abstract

There is a dearth in knowledge on artisanal tannery wastewater treatment as most studies are focused on treatment of wastewater generated from modern-day leather manufacturing industries. The extensive use of plant materials in artisanal tanneries introduces high loads of polyphenolic

compounds in the wastewater rendering biological treatment of the wastewater ineffective. This study, therefore, employed coagulation-flocculation process to pre-treat artisanal tannery wastewater with the aim of applying the central composite design, a statistical approach in Response Surface Methodology (RSM) to model and optimize the removal of Chemical Oxygen Demand (COD), Total Suspended Solids (TSS) and turbidity and to minimize Sludge Volume Index (SVI). Optimization process focused on the two most important influencing parameters: dosage of aluminium sulphate and initial pH of wastewater. Results revealed that optimal pH and aluminium sulphate dosage of 6.09 and 11.6g/L respectively could yield maximum removal efficiencies of 38.51% of COD, 76.05% of TSS and 79.64% of turbidity from the wastewater with a minimum SVI of 29.57mL/g. Further experiments conducted to validate these results showed a good agreement between the experimental and predicted results signifying the suitability of RSM for optimization of the coagulation treatment process. This is the first reported study on optimization of coagulation-flocculation treatment of artisanal tannery wastewater. Results of this study can be used practically for efficient pre-treatment of artisanal tannery wastewater.

Keywords Aluminium sulphate, Central composite design, Colour, Chemical oxygen demand, Removal efficiency, Sludge volume index

Introduction

Wastewater originating from tanneries are toxic, malodourous, strongly coloured and heavily laden with dissolved and suspended matter, organic and inorganic contaminants (Zhao & Chen 2019). Discharge of the untreated wastewater is therefore, extremely harmful to both human and environmental health. As a result, numerous researches investigating into different treatment options for tannery wastewater have been conducted over the years. Different methods of treatment including coagulation, adsorption, reverse osmosis, electrocoagulation, ion exchange and

ultrafiltration have been proposed (Durmaz & Çiner 2017). However, a large number of these researches have been centered primarily on wastewater generated from modern-day tanneries with very little attention given to that originating from artisanal tanneries. Meanwhile, modern-day leather making (Thanikaivelan et al. 2005; Covington 1997) differs significantly from that of artisanal leather making (Appiah-Brempong et al. 2020; Wemegah 2014) in its manufacturing processes, type of process chemicals and equipment used and even the characteristics of the wastewater generated.

Although, it is estimated that 90% of tanneries world-wide engage in modern-day leather production practices (Dargo & Ayalew 2014), artisanal leather making is still an important source of livelihood for many people in most developing countries including Ghana (Wemegah 2014), Cameroon (Paltahe et al. 2019), Ethiopia (Gebremichael 2016), Nigeria (Zaruwa & Kwaghe 2014) and Sudan (Skinner 2007). Wastewater emanating from these artisanal tanneries is usually discarded into the environment without treatment. In Ghana, for instance, the untreated wastewater is discarded on the tannery grounds which is a potential source of pollution to soil, surface water, groundwater bodies and the surrounding atmosphere (Islam et al. 2014).

The predominant use of vegetative materials in the leather manufacturing process in artisanal tanneries generates wastewater composed of large quantities of polyphenolic compounds which are recalcitrant and toxic to microorganisms making biological treatment of the wastewater an inefficient option (Schrack et al. 2004). Coagulation-flocculation process, a physicochemical treatment method which is robust against wastewater toxicity and highly efficient in removal of both organic and suspended contaminants from wastewater (Aboulhassan et al. 2006) was, therefore, employed in this study. It is a commonly used wastewater pretreatment technology due to its efficiency and simplicity in its design and operation (Shewa & Dagne 2020). The

mechanism involved in the coagulation-flocculation treatment process is by the initial destabilization of colloidal particles in the wastewater during the coagulation phase and the subsequent aggregation of the destabilized colloids into floc particles during the flocculation phase. The floc particles are then separated through sedimentation processes as they settle under gravity (Maćczak et al. 2020).

Aluminium sulphate is one of the most widely used coagulants due to its availability, relatively low cost and high coagulation performance (Shewa & Dagne 2020). Nevertheless, it suffers a major drawback of releasing toxic aluminium ions into the environment, particularly when applied in excess. Long-term exposure to aluminium can result in bioaccumulation of the ions in humans, nervous breakdown and Alzheimer's diseases. Aluminium ions in the soil can also hamper plant growth and restrict nutrient uptake (Jaishankar et al. 2014). Thus, it is imperative to optimize the amount of aluminium sulphate used in wastewater treatment to protect human and environmental health.

Various factors influence the coagulation-flocculation process. These include temperature, pH, coagulant type and dosage as well as mixing speed (Wang et al. 2014). Among these factors, pH and coagulant dosage have been identified as the most important parameters influencing the coagulation-flocculation process (Verma et al. 2012). Optimization of these factors enhances coagulation efficiency and maximizes removal efficiency of contaminants from the wastewater. Conventionally, optimization of the coagulation process has been performed by varying one factor at a time whilst maintaining all other variables constant. This method is not only laborious and time-consuming but also expensive as it demands the performance of lots of experiments to define the optimal conditions. Additionally, the actual optimal conditions may not be attained using the conventional method since it ignores the effect of the interaction between the factors (Kumar et al.

2018). The Response Surface Methodology (RSM), a statistical method makes use of design of experiments to overcome these limitations of the conventional method. Through RSM, regression models which describe the coagulation process can be developed, the statistical significance of the various factors influencing the process can be determined, the interaction effect among the factors can be assessed and the optimal process conditions can be defined (Bas & Ismail 2007).

In light of this, this study aimed at using RSM to optimize the pH and the dosage of aluminium sulphate required to maximize chemical oxygen demand, total suspended solids and turbidity removal from artisanal tannery wastewater whilst minimizing the sludge volume index.

Materials and Methods

Wastewater sampling and characterisation

The wastewater was sampled from the Aboabo Tannery in Kumasi (Ashanti Region, Ghana) located at 6°41'50.57"N 1°36'7.02"W. The leather making process encompasses different activities which include curing, soaking, liming, unhairing, deliming and bating, fleshing, vegetable tanning, oiling, red, brown and black dyeing and drying. Detailed information on each of the production stages have been reported by Appiah-Brempong et al. (2020). The wastewater generated is primarily composed of the spent liquors arising from the vegetable tanning and red dyeing processes as other liquors used in the production processes are rarely discarded. A composite wastewater was formed by combining the spent liquors from the red dyeing and tanning processes in a 1:3.33 ratio according to their generation rates.

Wastewater samples were collected on five occasions from the tannery during the study period. The preservation and laboratory analyses of the samples were performed following the Standard Methods for Examination of Water and Wastewater (APHA 1999). Parameters including pH,

Electrical Conductivity (EC), Total Dissolved Solids (TDS) were tested using a portable multipurpose meter. Turbidity and Total Suspended Solids (TSS) were also measured using HANNA turbidimeter (HI 93414) and the gravimetric method respectively. The HACH methods were employed in determining colour, Chemical Oxygen Demand (COD), ammonia ($\text{NH}_3\text{-N}$) and Total Nitrogen (TN) with the aid of the HACH DR 3900 spectrophotometer. The dilution method in combination with dissolved oxygen measurement was used in determining the Biochemical Oxygen Demand (BOD_5). Chloride (Cl^-) concentration was determined using the argentometric method.

Experimental procedure

Laboratory grade aluminium sulphate hexadecahydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$) reagent also termed as alum (98% purity; molar mass of 630.4g/mol) obtained from QUALIKEMS Fine Chem Pvt. Ltd was the coagulant used in the experiments. A 100g/L stock solution of aluminium sulphate was prepared out of which appropriate volumes were measured and used in the experiments.

Coagulation experiments were performed at room temperature using the jar test apparatus (Stuart® SW6 flocculator). Each 1L beaker was filled with 500mL of the tannery wastewater. The initial pH of the wastewater was altered using 0.1M H_2SO_4 and 100g/L $\text{Ca}(\text{OH})_2$. Different volumes of the stock solution of the aluminium sulphate were poured into the beakers. The different adjustment in pH and coagulant dosage have been presented in Table 1. The mixtures were initially mixed rapidly at a speed of 250rpm for 1 minute and then slowly at 30rpm for 30 minutes (Kim 2016). After a settling time of 30 minutes, samples of the supernatant were taken from about 3cm below the surface for turbidity, COD, total suspended solids and pH tests. The volume of sludge in each beaker was measured to compute the Sludge Volume Index (SVI) as shown in Equation (1). The removal efficiency for turbidity, COD and TSS were computed according to Equation (2).

136 All experiments were carried out in the Environmental Quality Engineering Laboratory of the
137 Kwame Nkrumah University of Science and Technology (Kumasi, Ghana).

$$\text{SVI (mL/g)} = \frac{\text{Volume of sludge (mL/L)}}{\text{TSS (g/L)}} \quad (1)$$

$$\text{Removal Efficiency (\%)} = \frac{C_0 - C_f}{C_0} \times 100\% \quad (2)$$

138

139 where, C_0 and C_f are the initial and final concentrations of the measured COD (mg/L), TSS (mg/L)
140 and turbidity (NTU) of the wastewater.

141 **Experimental design**

142 A statistical design tool in RSM, Central Composite Design (CCD) which is very efficient in
143 developing quadratic models was used in determining the influence of the two most important
144 independent variables ($n=2$), coagulant dosage (X_1) and initial wastewater pH (X_2) on four (4)
145 response variables (Y) in the coagulation process. These responses are efficiencies of COD
146 removal (Y_1), TSS removal (Y_2), turbidity removal (Y_3) and SVI (Y_4).

147 For n number of factors, the total number of experiments to be conducted for a central composite
148 design is based on $2n$ axial points, 2^n factorial points and the number of replications. Therefore,
149 for two (2) independent variables in a 2^2 full factorial central composite design, a total number of
150 thirteen (13) experiments made up of four (4) axial points, four (4) factorial points and five (5)
151 replicates at the centre points as shown in Equation (3) are required. The effect of residual error
152 was reduced by randomizing the experimental runs.

$$N_{\text{expt}} = 2^n + 2n + c = 4 + 4 + 5 = 13 \quad (3)$$

where, N_{expt} is the total number of experimental runs, n is number of independent variables, c is the number of replications at the centre point.

The axial points are fixed at a distance, α from the centre with coordinates of $(0, \pm\alpha)$ and $(\pm\alpha, 0)$ for two (2) independent variables in a central composite design. The value of α is computed from the expression $(2^n)^{0.25}$ and this value is 1.414 for two independent variable, $n=2$.

Preliminary experiments were conducted to set the range for the alum concentrations and wastewater pH. It was observed that alum was effective within the dosages of 7 to 17g/L and a pH range from 6 to 9. The levels for each independent variable were given the codes +1, 0 and -1 designating the high, medium and low levels of the factorial points respectively. The ranges and levels of the independent factors are shown in Table 1.

Table 1 Range and levels of independent variables.

Variables	Code	Range and levels				
		$-\alpha^a$	-1	0	+1	$+\alpha$
Dosage (g/L)	X_1	6.34	8	12	16	17.66
pH (-)	X_2	6.09	6.5	7.5	8.5	8.91

Statistical analysis and modelling of response surfaces

Based on the experimental results, second-order polynomial models were developed for each of the responses. A general formula for the polynomial is shown in Equation (4).

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i=1}^n \sum_{j=1}^n \beta_{ij} X_i X_j + \varepsilon \quad (4)$$

where Y represents the predicted response; β_0, β_i and β_{ij} are collectively termed as the model coefficients, β_0 is the constant coefficient, β_i, β_{ii} and β_{ij} are the linear, quadratic and interaction coefficients respectively. ε is the error associated with the model. X_i and X_j are the codes given to the two independent variables (coagulant dosage and pH). Statistical significance of the regression models was evaluated by conducting Analysis of Variance (ANOVA) test. The significance of the model coefficients was assessed using Fisher's F-test with the p -value at the confidence interval of 95%. The model adequacy was assessed using the coefficient of determination (R^2) and lack-of-fit test. From the models, surface and contour plots showing the interaction effect of the process parameters and the optimum regions of the coagulation process were obtained for each of the responses. The optimum process parameters defined by the models were verified experimentally (Hamid et al. 2014). The experimental design matrices, statistical analyses and optimization processes were performed using the Minitab statistical software package version 17.

Results and Discussion

Artisanal tannery wastewater characteristics

The physicochemical characteristics of artisanal tannery wastewater are presented in Table 2. The wastewater is slightly acidic with an average pH value of 6.29 which falls within the acceptable range of the Ghana Environmental Protection Agency (2016) standards. It is dark-red in appearance (22400PtCo) due to the use of tannins and dyes in the production process. The electrical conductivity (9370 μ S) and total dissolved solids (4585.25 mg/L) exceeded the stipulated standard of 1500 μ S and 1000mg/L respectively.

191 **Table 2** Characteristics of artisanal tannery wastewater.

Parameter	Unit	Average	Ghana EPA (2016)
pH	-	6.29 ± 0.35	6.0 – 9.0
Colour	PtCo	22400 ± 5931.86	10
EC	μS	9370 ± 0.99	1500
TDS	mg/L	4585.25 ± 473.92	1000
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	-
NH ₃ -N	mg/L	10.15 ± 3.32	1
TN-N	mg/L	36.70 ± 5.45	50
Cl ⁻	mg/L	722 ± 56	-

192

193 The wastewater is also heavily laden with suspended matter with a mean concentration of

194 3441.25mg/L which contributes to its high turbidity value of 1380NTU. The suspended matter

195 originates from the use of crushed pods of *Acacia nilotica* and sorghum leaf sheaths in the leather

196 making process. The total suspended solids and turbidity also exceeded the limits (50mg/L and

197 75NTU respectively) set by Ghana Environmental Protection Agency (2016). The organic

198 component of the wastewater measured as COD (24928mg/L) and BOD₅ (2639mg/L) was also

199 very high exceeding the limits of 250mg/L and 50mg/L respectively by approximately 38 and 21

200 times respectively. The biodegradability index (BOD₅/COD) of the wastewater was 0.11

signifying its high non-biodegradability nature (Andrio et al. 2019) due to the presence of tannins and natural dyes (Schrank et al. 2004). The nitrogenous component with average values of 36.70TNmg/L and 10.15NH₃-Nmg/L could be coming from the plant materials used as well as the traces of flesh and fatty tissues on the animal skins after the fleshing process. The chloride ions with an average concentration of 722mg/L were sourced from the salts applied on the skins to preserve them.

Development and validation of response surface models

An experimental design matrix displaying the coded and uncoded factors, the experimental results and predicted values of the four responses are shown in Table 3. Quadratic regression models were developed by correlating the independent variables: alum dosage (X_1) and pH (X_2) with the four responses: COD removal (Y_1), TSS removal (Y_2), turbidity removal (Y_3) and SVI (Y_4). The models for the responses are given in Equations (5) to (8).

$$Y_1(\%) = 213.6 - 0.83X_1 - 47.36X_2 - 0.1637X_1^2 + 2.431X_2^2 + 0.775X_1X_2 \quad (5)$$

$$(R^2 = 97.92\%, R_{adj}^2 = 96.43\%)$$

$$Y_2(\%) = 128.1 + 0.305X_1 - 13.839X_2 - 0.0644X_1^2 + 0.78X_2^2 + 0.1182X_1X_2 \quad (6)$$

$$(R^2 = 96.00\%, R_{adj}^2 = 93.15\%)$$

$$Y_3(\%) = 57.20 + 1.537X_1 + 3.65X_2 - 0.1021X_1^2 - 0.420X_2^2 + 0.161X_1X_2 \quad (7)$$

$$(R^2 = 91.69\%, R_{adj}^2 = 85.76\%)$$

$$Y_4(\text{mL/g}) = 174.82 + 0.78X_1 - 44.17X_2 + 0.05828X_1^2 + 3.632X_2^2 - 0.3942X_1X_2 \quad (8)$$

$$(R^2 = 98.69\%, R_{adj}^2 = 97.76\%)$$

From the regression models, the coefficients of the individual factors, namely, alum dosage (X_1) and pH (X_2) depict the linear effects of the factors on the coagulation process. Whilst the coefficients of X_1^2 and X_2^2 reveal the quadratic effect of the factors and that of X_1X_2 shows the

effect of the interaction between X_1 and X_2 on the process. The presence of a positive sign before a term denotes a synergistic effect on the coagulation process whilst the occurrence of a minus sign signifies an antagonistic effect (Kim 2016).

To ensure accuracy, the adequacy of the regression models was checked before the optimization process to ensure they give a good approximation of the actual coagulation process. The adequacy of the model was assessed by comparing the predicted and the actual values of the responses (Fig. 1). As can be observed from Fig. 1 the predicted values are in close agreement with the experimental data indicating good fits.

The models were also validated by conducting ANOVA using the Fisher's test (F-test) to determine their statistical significance. The results are given in Table 4. The statistical significance of the model was judged from the F and p -values. Generally, large F values and small p values (<0.05) signify a significant difference at a confidence interval of 95%. As can be observed from the table, the p -values for COD, TSS, turbidity removal efficiencies and SVI were 0.00, 0.00, 0.001 and 0.00 respectively depicting the statistical significance of all the four models. Additionally, the lack-of-fit of a regression model which indicates the differences in the experimental results around the fitted quadratic model can be used to assess the validity of the model. From the F-test, the lack-of-fit becomes statistically significant (for $p<0.05$) if the model is not well fitted to the data.

234 **Table 3** Central Composite Design matrix for coagulation experiments with alum coagulant.

Std order	Run order	Independent Variables				Responses							
		Alum dosage (X_1) (g/L)		pH, X_2		COD removal, Y_1 (%)		TSS Removal, Y_2 (%)		Turbidity Removal, Y_3 (%)		SVI, Y_4 (mL/g)	
		Coded	Uncoded	Coded	Uncoded	Expt ^a	Pred ^b	Expt ^a	Pred ^b	Expt ^a	Pred ^b	Expt ^a	Pred ^b
4	1	+1	16	+1	8.5	36.91	36.93	71.07	71.37	78.93	78.56	35.09	35.54
6	2	+ α	17.66	0	7.5	32.30	32.13	69.52	69.21	78.06	77.90	27.97	27.55
7	3	0	12	- α	6.09	39.22	38.52	76.03	75.85	80.46	79.68	29.26	29.47
12	4	0	12	0	7.5	32.34	31.40	73.89	73.28	79.05	79.51	30.23	30.09
13	5	0	12	0	7.5	30.18	31.40	72.78	73.28	80.01	79.51	29.84	30.09
9	6	0	12	0	7.5	31.97	31.40	73.01	73.28	80.13	79.51	30.39	30.09
10	7	0	12	0	7.5	32.22	31.40	72.94	73.28	79.32	79.51	30.03	30.09
2	8	+1	16	-1	6.5	33.47	33.93	71.59	71.85	78.06	78.70	27.41	27.55
11	9	0	12	0	7.5	30.29	31.40	73.78	73.28	79.03	79.51	29.95	30.09
5	10	- α	6.34	0	7.5	20.81	20.20	73.32	73.23	74.54	74.58	35.95	36.35
8	11	0	12	+ α	8.91	34.10	34.01	74.05	73.83	77.00	77.65	45.46	45.23
1	12	-1	8	-1	6.5	30.92	31.69	75.53	75.64	77.14	77.64	31.05	30.61
3	13	-1	8	+1	8.5	21.97	22.30	73.12	73.26	75.43	74.92	45.04	44.91

235 ^a Expt= experimental values ^b Pred = predicted values

However, from Table 4, the large p -values for lack-of-fit of the four models which were 0.688 for COD removal, 0.72 for TSS removal, 0.194 for turbidity removal and 0.062 for SVI reveal the high precision of the models.

Furthermore, the precision of the model can be judged from the coefficient of determination (R^2). An R^2 value above 75% which is also close to the adjusted R^2 values is usually desired (Hamid et al. 2014). The R^2 values obtained for COD, TSS and turbidity removal efficiencies as well as for SVI were 97.92%, 96%, 91.69 and 98.69% respectively. Hence, only about 2.07%, 4%, 8.31% and 1.31% of the total variation in the respective models could not be explained by the regression models. The values of the adjusted R^2 for all the four models were also near to the respective R^2 values which also indicates that the quadratic models give a good prediction of the experimental data.

Fig. 1 Predicted versus actual (a) % COD removal, Y_1 (b) % TSS removal, Y_2 (c) % turbidity removal, Y_3 (d) SVI, Y_4 (mL/g) with alum as coagulant

Optimization of coagulation-flocculation process

Effect of process parameters on removal of COD, TSS and turbidity from artisanal tannery wastewater

The effect of alum dosage and initial pH of wastewater on removal of COD, TSS and turbidity from the artisanal tannery wastewater can be evaluated by observing the combined effect of both parameters on the removal efficiencies as shown in the 2D contour and 3D response surface plots illustrated from Fig. 2 to Fig. 5 and by assessing the statistical significance of each of the model coefficients (linear, quadratic and interaction terms) using the Fisher's test and p -values as shown in Table 4. Generally, as the F -value increases, the corresponding p -value decreases and the associated model coefficient becomes increasingly significant (Hamid et al. 2014).

From the table, all model terms; alum dosage (X_1), initial pH of the tannery wastewater (X_2), the square of both factors (X_1^2 and X_2^2) as well as their interaction effect (X_1X_2) had significant

264 **Table 4** Analysis of variance for response surface model for %COD removal (Y_1), %TSS removal (Y_2)), %turbidity removal (Y_3)
 265 and SVI (Y_4) with alum.

Source	d. f	Adj SS				Adj. MS				<i>F</i> -value				<i>p</i> -value			
		Y_1	Y_2	Y_3	Y_4	Y_1	Y_2	Y_3	Y_4	Y_1	Y_2	Y_3	Y_4	Y_1	Y_2	Y_3	Y_4
Model	5	303	34.4	35.7	429	60.6	6.88	7.14	85.8	66.2	33.6	15.5	572	0.000	0.000	0.001	0.000
X_1	1	103	2.00	26.0	24.6	103	2.00	26.0	24.6	112	9.63	56.4	164	0.000	0.017	0.000	0.000
X_2	1	56.7	3.00	4.12	91.6	56.7	3.00	4.12	91.6	61.8	14.4	8.92	611	0.000	0.007	0.020	0.000
X_1^2	1	47.7	7.39	18.6	6.05	47.7	7.39	18.6	6.05	55.7	36.1	40.2	40.3	0.000	0.001	0.000	0.000
X_2^2	1	41.1	4.23	1.23	91.7	41.1	4.23	1.23	91.7	52.1	20.7	2.65	612	0.000	0.003	0.147	0.000
X_1X_2	1	38.4	0.89	1.66	9.43	38.4	0.89	1.66	9.94	41.9	4.36	3.59	66.3	0.000	0.075	0.100	0.000
Total error	7	6.41	1.43	3.23	1.05	0.92	0.21	0.46	0.15								
Lack of fit	3	1.81	0.37	2.12	0.85	0.60	0.12	0.71	0.28	0.53	0.47	2.55	5.77	0.688	0.72	0.194	0.062
Pure error	4	4.60	1.06	1.11	0.20	1.15	0.27	0.28	0.05								

influence on COD removal efficiency with each having a p -value of 0.00. Observation of the contour and response surface plots in Fig. 2 shows that removal efficiency of COD generally decreased with increasing pH but increased with increasing alum concentration until a dosage of 16.2gAlum/L. The optimum range for a maximum COD removal efficiency above 35% occurred within two regions: a pH range of 6 to 6.5 and alum dosage range of 7.8 to 16.2g/L and also from pH 8.2 to 9 and an alum dosage range of 16 to 18g/L. Outside these optimal regions, COD removal efficiency declined. The percentage COD removal is quite low depicting that most of the COD exist in the soluble form. The removal efficiency obtained agrees with that reported by Shewa & Dagnew (2020).

For TSS, the square of alum dosage, X_1^2 ($p=0.001$) had the greatest influence in 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 the TSS removal efficiency ($p=0.075$) (Table 4). From the plots shown in Figure 3, the removal efficiency of TSS decreased with increasing pH. It, however, increased with alum dosage from 6 to 11.8g/L and then decreased with further increase in alum concentration. A maximum TSS removal efficiency above 76% can be attained at the optimal ranges of 6 to 6.3 for pH and 6.6 to 11.8g/L for alum dosage.

With regards to turbidity, the alum dosage, X_1 and its square, X_1^2 were the most significant parameters in the removal efficiency at $p=0.00$. The pH, X_2 ($p=0.02$) also played a significant role in the removal efficiency. However, both the square of pH, X_2^2 ($p=0.147$) and the interaction of both factors, X_1X_2 ($p=0.1$) were statistically insignificant in the turbidity removal from the wastewater. Observing Fig. 4, there was a general decrease in the turbidity removal with increasing pH and an increase with increasing alum dosage up to 13.8g/L. Beyond this concentration, the

removal efficiency decreased. The optimum range to achieve a turbidity removal efficiency above 79.5% lies between 6 and 7.7 for pH and 11 to 13.8g/L for alum dosage.

Fig. 2 (a) Contour and (b) response surface plots showing the combined effect of alum dosage and pH on COD removal efficiency

Figure 3 (a) Contour and (b) response surface plots showing the combined effect of alum dosage and pH on TSS removal efficiency

Fig. 4 (a) Contour and (b) response surface plots showing the combined effect of alum dosage and pH on turbidity removal efficiency

Fig. 5 (a) Contour and (b) response surface plots showing the combined effect of alum dosage and pH on SVI

The results indicate the essential roles of pH and alum dosage in the efficiency of the coagulation process. At pH range between 6 and 7, the addition of aluminium sulphate to the wastewater releases aluminium ions (Al^{3+}) which undergo hydrolytic reactions with hydroxide ions (OH^-) in the wastewater to form hydrogen ions and different species of aluminium hydroxide compounds:

308 Al^{3+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_{3(s)}$ and $\text{Al}(\text{OH})_4^-$ (Pernitsky & Edzwald 2006) as shown in
 309 Equation (9) to (12) (Nowacka et al. 2014). These compounds coexist in solution at different
 310 concentrations depending on the pH. The negatively charged colloidal particles in the wastewater
 311 get adsorbed onto these positively charged aluminium hydroxide species leading to neutralisation
 312 of surface charges on the colloidal particles. The repulsion energy of the colloids diminishes and
 313 the colloids are destabilised through the adsorption and neutralisation mechanism. Subsequently,
 314 aluminium hydroxide-colloid complexes are formed which aggregate into large floc particles
 315 capable of settling easily out of solution to form sludge (Gheraout et al. 2009).

316

317 Sweep flocculation is another coagulation mechanism which could have occurred simultaneously
 318 with the adsorption and charge neutralisation mechanism in destabilising the colloidal particles.
 319 This phenomenon occurs when the aluminium sulphate concentration is high enough and it
 320 involves the entrapment of colloidal particles into the aluminium hydroxide precipitates
 321 $[\text{Al}(\text{OH})_{3(s)}]$. The entrapment usually happens either during the formation of the $\text{Al}(\text{OH})_3$
 322 precipitates or afterwards when some of the colloids are adsorbed onto the amorphous, large
 323 surface area of the precipitates. The process results in the formation of dense, stable flocs and as
 324 they fall to the bottom of the jar, they ‘sweep’ most of the colloidal particles alongside with them
 325 (Gheraout & Gheraout 2012).

Thus, the major pathways by which TSS, COD and turbidity were removed from the wastewater were adsorption, charge neutralisation and sweep flocculation mechanisms. According to Ghernaout & Ghernaout (2012), highly turbid wastewaters such as tannery wastewater are best treated within the optimum pH range of 5 to 7 which agrees with the optimum pH range within 6 and 7 obtained in this study. Other authors such as Malik (2018) reported that maximum turbidity removal from muddy water using alum occurred at an optimum pH of 6. Mehmood et al. (2019) also observed maximum reduction in COD, TSS, turbidity and colour from pulp and paper mill wastewater at an optimum pH of 6.

Beyond pH 7, the different species of the positively charged aluminium hydroxide (Al^{3+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_2^{2+}$) are transformed into the negatively charged aluminium tetrahydroxide $\text{Al}(\text{OH})_4^-$. The concentration of aluminium hydroxide $[\text{Al}(\text{OH})_3]$ precipitates also decreases in solution by dissolution resulting in the unavailability of precipitates for adsorption of the colloidal particles. Hence, the extent of charge neutralisation and sweep flocculation mechanisms diminishes resulting in lower removal efficiencies of COD, TSS and turbidity (Ghernaout et al. 2009). Decrease in low coagulation efficiency of alum at high pH was also reported by Asharuddin et al. (2019).

The hydrogen ions produced during the hydrolytic reactions leads to a decline in the wastewater pH (Krupińska 2020). This drop in pH was observed in the coagulation experiment when the initial pH range between 6.09 and 8.91 dropped to ranges between 2.58 and 3.37 after the experiments.

From the response surface and contour plots, lower dosages of alum generally below 6.5g/L could not yield maximum removal of the pollutants even at a pH range within 6 and 7. This depicts that the alum concentrations were too low to produce adequate concentrations of the aluminium hydroxide species capable of providing enough surface for adsorption of the colloidal substances in the wastewater (Gregory & Duan 2001). Hence, the poor coagulation efficiency observed at low

dosages. However, above this dosage to 13.4g/L, optimum removal of the pollutants was achieved probably because the aluminium hydroxide species produced were sufficient enough to cause destabilisation of the colloids through charge neutralisation and sweep flocculation mechanisms (Bratby 2006). The coagulation efficiency, however, decreased at concentrations above 13.4g/L of alum due to excess dosage above the optimum which may have caused charge reversal of the colloidal particles. Thus, the negatively charged colloids became positively charged resulting in restabilisation of the colloidal particles in the wastewater (Gregory & Duan 2001).

Effect of process parameters on SVI

From the results of the Fisher's test shown in Table 4, all the parameters, alum dosage (X_1), initial pH of the wastewater (X_2), 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 p - values of 0.00. The response surface and contour plots (Fig. 5) revealed that SVI increased with increasing pH and decreased with increasing alum dosage. The lowest sludge volume index that was attained was below 30mL/g and it occurred within a pH range from 6 to 7.7 and an alum dosage range between 9 and 18g/L.

At pH ranges within 6 and 7, formation of dense, macro-flocs through charge neutralisation and sweep flocculation mechanisms produced well-compacted sludge of low sludge volumes and SVI. However, above pH 7, the reduction in coagulation efficiency due to the decreasing levels of the aluminium 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 higher 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 (Jin et al. 2003).

The high SVI recorded at low dosages could be attributed to the poor coagulation efficiency (weak neutralisation of the colloids) due to insufficient alum dosage (Wei et al. 2018). Hence, the formation of less dense, micro-sized flocs resulting in poorly compacted sludge with higher sludge volume and SVI. However, with increased alum concentration, coagulation efficiency was enhanced which promoted the formation of macro-sized floc particles, dense enough to produce tightly packed sludge with low sludge volume and SVI. Mehmood et al. (2019) in treating pulp and paper mill wastewater also reported a decrease in SVI with increasing alum dosage.

Optimization and verification of process parameters

Optimization of the coagulation-flocculation process was targeted at obtaining an optimal condition at which maximization of COD, TSS and turbidity removal efficiencies and minimization of SVI can occur simultaneously. The response optimizer function of Minitab 16 was used to optimize the coagulation process. The optimum levels for pH and alum dosage as given by the optimizer were verified through coagulation experiments. The results are detailed out in Table 5. These results are in close agreement to those given by the regression models confirming the accuracy of the models developed.

Table 5 Predicted and experimental values at optimal process conditions

Variables		Responses							
Alum dosage X_1 (g/L)	pH X_2 (-)	COD removal, Y_1 (%)	TSS Removal, Y_2 (%)	Turbidity Removal, Y_3 (%)		SVI, Y_4 (mL/g)			
		Pred ^a	Expt ^b	Pred ^a	Expt ^b	Pred ^a	Expt ^b	Pred ^a	Expt ^b
11.6	6.09	38.51	38.95	76.05	77.16	79.64	79.81	29.57	30.14

^a pred = predicted ^b Expt = experimental

Conclusion

This is the first study conducted to optimize coagulation-flocculation treatment of artisanal tannery wastewater. Response surface methodology using the central composite design was applied to assess the effect of varying pH and dosage of aluminium sulphate on the treatment efficiency. It was also used to develop quadratic models and to define the optimal process conditions required to maximize removal efficiencies of COD, TSS and turbidity from the wastewater whilst minimizing the SVI. The results proved that at an optimal pH of 6.09 and aluminium sulphate dosage of 11.60g/L a maximum COD removal of 38.51%, TSS removal of 76.05% and turbidity removal of 79.64% with a minimum SVI of 29.57mL/g can be achieved. These results indicate that coagulation-flocculation is a good pre-treatment option for artisanal tannery wastewater. Further treatment to meet permissible discharge limit is required for this high-strength wastewater. Experiments conducted to validate these optimum results also demonstrated that RSM is an efficient optimization tool for the coagulation-flocculation treatment process. It is however, recommended that further studies assessing the efficiency of natural coagulants in the treatment of artisanal tannery wastewater should be conducted.

411 **Declarations**

412 **Ethics approval**

413 Not applicable.

414 **Consent to participate**

415 Not applicable.

416 **Consent for publication**

417 Not applicable.

418 **Availability of data**

419 All data generated and analysed during this study are included in this published article.

420 **Competing interests**

421 The authors declare that they have no competing interests.

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428 **Author contributions**

429 Miriam Appiah-Brempong, Francis Momade, Helen Essandoh, Nana Asiedu: Conceptualization,
430 Visualization. Miriam Appiah-Brempong: Writing-original draft, Methodology, Formal analysis,
431 Data Curation. Miriam Appiah-Brempong, Samuel Dadzie: Investigation, Validation. Helen
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