

# Application of biopolymer in turbidity removal and sludge settling behaviour of travertine-processing wastewater: Performance optimization using response surface methodology (RSM)

Ebru Taş<sup>1</sup>, Emmanuel Ikechukwu Ugwu<sup>2</sup>, Eyüp Sabah<sup>1</sup>  and Zeyni Arsoy<sup>1</sup>

<sup>1</sup>Department of Mining Engineering, Faculty, Faculty of Engineering, Afyon Kocatepe University, 03200 Afyonkarahisar, Turkey

<sup>2</sup>Department of Civil Engineering, College of Engineering and Engineering Technology, Michael Okpara University of Agriculture Umudike, P.M.B. 7267, Umuhia Abia State, Nigeria

A flocculation process was performed to treat travertine-processing effluents with a high concentration of suspended solids using an eco-friendly biopolymer. The experiments were conducted through a standard jar test procedure to optimize the process parameters for sludge volume index (SVI) and turbidity removal. The effects of mixing time, suspension pH, and polymer dosage on treatment efficiency were investigated using central composite design, a standard technique in response surface methodology. The constructed response model was tested using the analysis of variance (ANOVA). Using the Design-Expert tool, the coefficients of regression models were computed. The Fischer value (F-value) was used to evaluate the significance and validity of the predicted model, while the coefficient of determination ( $R^2$ ) was applied to estimate the model significance by comparing the predicted data with the measured data. The optimized parameters obtained were polymer dose of 276.20 mg/L, suspension pH of 8.60, and mixing time of 4.20 min. The optimal SVI and turbidity values obtained were 1.36 mL/g and 2.99 NTU, respectively. Additionally,  $R^2$  values for SVI and turbidity were determined as 0.9337 and 0.8654, respectively. Also, the difference between adjusted  $R^2$  values and predicted  $R^2$  was less than 0.2. Validation tests showed that the response surface methodology is an effective method for optimizing the flocculation mechanism.

## INTRODUCTION

Natural stone processing/mining plants, such as for granite, travertine, marble, etc., generate a considerable amount of wastewater during cutting, washing, sizing, and polishing processes, which contains a high number of negatively charged colloidal-sized particles. Such effluents of high turbidity and low solids content are not easily removed by the pre-treatment process, constituting a severe environmental issue. Therefore, solid-liquid separation of wastewater across the natural stone processing industries is significant in terms of economic and ecological considerations.

The machines used in the natural stone processing stages have different speeds and water consumption depending on the manufacturer and model. Furthermore, the speeds at which the same machine is applied to stones with different physical properties vary. However, Mutlutürk (2017) observed that the amount of water used is always approximately the same regardless of the size and properties of the stone. It was further reported by Mutlutürk (2017) that the average amount of water consumed in gang saws used for cutting natural stones from dimension stone quarry is 2 650 L/m<sup>2</sup>. Furthermore, S/T installed in tile lines, machines used for caliber, honing, polishing, plate and tile slim, splitting machines, bridge cutting and sizing machines, and alternative surface treatments (brushing, sandblasting, hammering, edge-corner breaking) consume approximately 875, 6 300, 480, 390, and 5 L/m<sup>2</sup> of process water, respectively. That equates to 10 700 L of water per m<sup>2</sup> of natural stone. The processed/treated water is used to provide this large volume of water consumed in stone processing plants. There are two output parameters used in evaluating the treatment of travertine-processing wastewater. The first output parameter is the turbidity of water obtained from the upper flow of a thickener. The removal of suspended colloidal particles from the recycled water is necessary to avert their possible detrimental effects on life as well as the efficiencies of cutting and polishing equipment in the production of tiles or slabs and to prevent clogging of water pipes and pumps, etc. (Çelik and Sabah, 2008). The second output parameter used is the settled sludge volume of flocculated particles. Water content or solid concentration strongly affects the cost of sludge treatment (the filtration step followed by dewatering) and disposal operations.

Wastewater treatment is a process of treating sewage or wastewater to remove suspended solids and convert them into effluent that can be safely discharged into the environment. The coagulation/flocculation process is a type of physicochemical wastewater treatment method to reduce colloidal turbidity and suspended solids. It is a simple, efficient, and cost-effective method for natural stone processing wastewater treatment where inorganic salts of multivalent metals are mainly used as coagulants. In contrast, anionic or long-chain nonionic polymers are commonly used as flocculants. However, applying metal coagulants could constitute some significant environmental issues, such as the production of toxic sludge (large volumes of metal hydroxide). This causes an increase in concentrations of metals such as aluminum in the treated water as well as disposal problems, which may pose adverse health effects to humans (Rad et al., 2014; Okolo et al., 2017; Irfan et al., 2017).

## CORRESPONDENCE

Eyüp Sabah

## EMAIL

[esabah@aku.edu.tr](mailto:esabah@aku.edu.tr)

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The polymeric flocculants are non-biodegradable; thus, their degraded products are toxic due to the emission of minute concentrations of monomeric acrylamide in water, which could permeate the food chain, causing cancer (Singh et al., 2010; Huppertsberg et al., 2020). Researchers worldwide are working toward developing biopolymer-based flocculants from natural sources that can substitute for synthetic polymeric flocculants, because of their accessibility, safety, and biodegradability, which have put them in high demand (Lee et al., 2014).

Although there are many publications on coagulation/flocculation of travertine-processing wastewater using inorganic coagulants and polymeric flocculants such as polyaluminum chloride, iron salts, alum, and anionic polyacrylamides (Alptekin, 2006; Ersoy et al., 2009; Sabah and Aciksoz, 2012; Taşdemir and Kurama, 2013; Onen et al., 2018) there is still a lack of data on the settling characteristics of the sludge of suspended travertine fines and the residual turbidity of water treated using environment-friendly biopolymers devoid of acrylamide monomers. This biopolymer is associated with an inorganic coagulant to form a new hybrid polymer that is non-toxic and biodegradable, making its application in wastewater treatment a promising possibility (Lee et al., 2012).

The main objective of the present study was to investigate the flocculation efficiency of an eco-friendly hybrid polymer consisting of biopolymer/inorganic metal salt, and the interactive effects of polymer dosage, mixing time, and pH, for minimizing sludge volume index (SVI) and turbidity. Central composite design (CCD), a response surface methodology (RSM)-based technique, was used to optimize the selected process parameters, which were aimed at obtaining the required responses.

## MATERIALS AND METHODS

### Sampling

The travertine-processing wastewater was used as the effluent, and was collected in suspension form according to TSE 5667-10 (2002). The effluent sample was collected from the outlet of the travertine-processing wastewater plant located in Afyonkarahisar, Turkey. The sample was transported to the laboratory in 100 L barrels, stored in a 200 L capacity stirring tank, and analysed within 48 h of collection. The samples were mixed to obtain a homogenous mixture before the characterization/flocculation test was carried out.

### Chemicals

The biopolymer used in this study is a blended biopolymer and polyaluminum chloride formulation free of acrylamide monomer (BHR-P50), supplied by Dober Chemical Company, USA. It is a whitish-yellowish-coloured opaque liquid with a viscosity and specific gravity of 500–1 300 cp and 0.95–1.15 cP, respectively. The suspension pH was adjusted using sodium hydroxide and hydrochloric acid (Merck grade) solutions.

### Preparation of solution

One mL liquid biopolymer was dissolved in distilled water of 100 mL volume (EC 0.2 S/cm) to make a primary stock solution of the polymer with a concentration of 10 000 mg/L. Before injecting the stock solution into the system for the flocculation tests, it was diluted with deionized water to achieve the desired concentrations of 50, 100, 200, and 400 mg/L standard biopolymer solutions.

### Experimental procedure

The flocculation experiments were carried out using a VELP Scientifica Srl (Velp JLT4) speed-controlled jar test. Firstly, 500 mL of travertine suspension of 1.0% w/w solids was put in a 600 mL glass beaker, which was vigorously agitated at 300 r/min for a period of 3 min, to achieve maximum dispersion as well as to regulate the

preset pH values of 6.0–10.0 by introducing sodium hydroxide/hydrochloric acid as required. The required quantities of the flocculant were injected into the travertine suspension and subjected to agitation for an extra 1 to 5 min at 200 r/min before being reduced to 30 r/min to allow the floc to mature at 4 min preset time.

After a 15 min settling period, 25 mL volume of supernatant sample was taken at 3 cm preset distance underneath the interface between air and liquid, using a unique framework consisting of a syringe with a pipe and a scale, which helped in preventing the turbidity measurements from being disrupted by the settled flocs.

### Physical, mineralogical, and physicochemical analysis

The travertine fines' particle size distribution (PSD) was determined using the Malvern Mastersizer 2000 laser diffraction technique. X-ray diffraction (XRD) was used to determine the mineral constituents of the travertine (Shimadzu XRD-6000). The conductivity and pH of the effluent samples were determined with the aid of a pH meter (WTW InoLab Multi 720), whereas turbidity was determined using a turbidimeter (WTW Turb 550) based on a nephelometric turbidity unit (NTU) for the supernatant of all samples, including samples with and without the biopolymer. Total suspended solids (TSS) and total solids (TS) concentrations were measured according to the Standard Methods for the Examination of Water and Wastewater, 2540 (APHA, 2005). The total dissolved solids (TDS) were determined as the difference between the TSS and TS. Titration with a chelating agent, ethylene diamine tetraacetic acid (EDTA), was used to determine the ions and hardness in water  $Mg^{2+}(aq)$  and  $Ca^{2+}(aq)$ . SVI is an indicator of the settling behaviour of sludge. To experimentally determine SVI, 1 L of wastewater is poured into a graduated cylinder of 1 000 mL volume (Imhoff cone); after waiting 30 min for settling of solids, the volume occupied by the sludge is reported in milliliters. The SVI is calculated by dividing the result of the settling test in mL/L by the TSS concentration in mg/L, as shown in Eq. 1.

$$SVI \left( \frac{mL}{g} \right) = \frac{\text{Settled sludge volume} \left( \frac{mL}{L} \right)}{\text{Total suspended solids} \left( \frac{mg}{L} \right)} \times 1000 \quad (1)$$

### Experimental design

In optimizing process parameters for turbidity removal and sludge settling behaviour of travertine-processing wastewater, the central composite design (CCD), based on the conventional response surface methodology (RSM), was chosen. Since various parameters are often represented in multiple units and also have different levels of variance, the relevance of their influence on responses could only be correlated after they had been coded. The parameters were coded, as can be seen in Eq. 2, for statistical analysis.

$$X_i = \frac{X_i - X_0}{\Delta X} \quad (2)$$

where  $X_i$  is the un-coded function of the  $i^{\text{th}}$  variable,  $X_0$  is the  $X_i$  value at the center of the field under investigation, while  $\Delta X$  is the phase shift. Three parameters in the optimization technique were selected as  $X_1$ ,  $X_2$ , and  $X_3$  for polymer dosage, suspension pH, and mixing time, respectively. The range and levels of the coded and actual values are presented in Table 1.

**Table 1.** The coded and actual values of the parameters analysed

Variables	Symbols	Coded and actual values				
		1	α	0	+α	+1
Polymer dosage, mg/L	$X_1$	20	50	100	200	400
Suspension pH	$X_2$	6	7	8	9	10
Mixing time, min	$X_3$	1	2	3	4	5

The responses were identified as turbidity and SVI. A polynomial function was used to connect the dependent with the independent variables, as seen in Eq. 3.

$$Y_i = \beta_0 + \sum_{i=1}^5 \beta_i X_i + \sum_{i=1}^5 \beta_{ii} X_i^2 + \sum_{i=1}^5 \sum_{j=i+1}^5 \beta_{ij} X_i X_j + \varepsilon \quad (3)$$

where  $Y$  represents the dependent variable (turbidity and SVI),  $X_i$  and  $X_j$  are the independent variables influencing  $y$ ; and  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$ , and  $\beta_{ij}$  are the offset terms, the  $i^{\text{th}}$  linear coefficient, the  $ii^{\text{th}}$  quadratic coefficient, the  $ij^{\text{th}}$  interaction coefficient, and  $\varepsilon$  the error term, respectively (Onukwuli et al., 2021; Nnaji et al., 2022). The experimental design of this study and the responses are presented in Table 2.

Using the Design-Expert Tool 13 free trial version, the coefficients of regression models were computed. The Fischer value (F-value) was used to evaluate the significance and validity of the predicted model (Kumar et al., 2009), while the coefficient of determination ( $R^2$ ) was applied to estimate the model significance by comparing the predicted data with the measured data (Anilkumar et al., 2016).

## RESULTS AND DISCUSSION

### Characterization of travertine fines and suspensions

Powder X-ray diffraction (XRD) of travertine fines in wastewater showed that they were composed of calcite. Their particle size and distributions determined by laser light scattering are closely related to the settling characteristics of the travertine-processing wastewater. As Table 3 indicates, almost 94% of travertine fines are less than 40  $\mu\text{m}$ , with a mean particle size  $d_{50}$  of 9.32  $\mu\text{m}$ . So travertine-processing wastewater has both the properties of a suspension and the nature of a colloid. Therefore, it is challenging to clarify naturally. Furthermore, Brownian motion is significant to maintain the travertine fines in a dispersed phase because of high

(to 94%) content of finely dispersed (less than 40  $\mu\text{m}$ ) fractions of travertine fines, fairly low (1.0%) solid ratio of the suspension, very high TSS (9.722 mg/L) and turbidity (>1 085 NTU) at natural pH, and weak electronegativity on the surface of particles caused by high-valence cations like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . This suggests that the effect of particle-particle interactions in travertine suspension was insignificant and, therefore, zeta potential would not be expected to influence sedimentation stability significantly.

Travertine-processing wastewater with an alkaline nature (8.24) contains high amounts of various inorganic substances such as  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , at 424 mg/L and 699 mg/L, respectively, which leads to high water hardness with 1 746 mg/L  $\text{CaCO}_3$  ( $\approx 175^\circ\text{F}$ ). This is well above the proposed limiting value and falls within the class of very hard waters. Besides, the high bivalent ion concentration of the wastewater seems to decrease the specific resistance and increase the conductivity. The conductivity of the wastewater, which contained travertine fines and was measured at a natural pH, was high (2 360  $\mu\text{S}/\text{cm}$ ). Changes in the composition and ionic strength of water, together with the colloidal behaviour of solid particles in wastewater, significantly affect the flocculation process and the floc structure. The presence of cationic compounds alters the interactions between the colloidal particles and the polymer molecules, which causes a more coiled form of the polymer chain. This implies that not only an inferior settling rate but also increased turbidity is observed (Sabah and Erkan, 2006).

### Regression models for SVI and turbidity

Statistical identification of the relationship between the operational and settling parameters and turbidity for the travertine-processing wastewater experiment is described in Table 2. The regression equations for SVI and turbidity are shown as Eqs 4 and 5:

$$\text{SVI} = +3.85 + 1.30 X_1 + 0.92 X_2 - 0.52 X_3 + 0.24 X_1 X_2 - 0.09 X_1 X_3 - 0.35 X_2 X_3 \quad (4)$$

$$\text{Turbidity} = -449.10 - 138.01 X_1 - 163.85 X_2 + 220.36 X_3 - 28.48 X_1 X_2 + 22.05 X_1 X_3 + 26.25 X_2 X_3 + 6.49 X_1^2 - 19.78 X_2^2 - 29.89 X_3^2 \quad (5)$$

where  $X_1$ ,  $X_2$ , and  $X_3$  are polymer dosage, suspension pH, and mixing time, respectively. The effect of a single variable is defined by the coefficient of one factor, while the interaction between the two variables and the quadratic effect is defined by the coefficient of two factors and those with a second-order term. A positive sign before the words indicates a synergistic effect, while a negative sign indicates an antagonistic effect (Kim, 2016).

**Table 2.** Experimental design and responses

Std	Run	$X_1$ (mg/L)	$X_2$	$X_3$ (min)	Turbidity (NTU)	SVI (mL/g)
22	1	20	6	1	21.6	1.34
8	2	20	7	2	40.4	1.54
19	3	20	8	3	74.8	1.77
6	4	20	9	4	77.5	1.85
17	5	20	10	5	41.6	1.95
21	6	50	7	1	11.8	2.06
18	7	50	8	2	20.5	2.26
10	8	50	9	3	25.4	2.37
16	9	50	10	4	13.1	2.08
23	10	50	6	5	17.2	1.85
7	11	100	8	1	8.71	2.28
11	12	100	9	2	14.4	2.35
13	13	100	10	3	7.25	2.67
15	14	100	6	4	11.7	1.65
24	15	100	7	5	19.9	2.16
14	16	200	9	1	8.36	2.67
2	17	200	10	2	4.78	2.88
3	18	200	6	3	7.38	2.06
25	19	200	7	4	11.2	2.47
4	20	200	8	5	19.1	2.57
5	21	400	10	1	2.95	3.29
12	22	400	6	2	3.68	2.26
9	23	400	7	3	4.68	2.88
1	24	400	8	4	6.37	2.98
20	25	400	9	5	13.1	3.09

**Table 3.** Characteristics of the travertine-processing wastewater and fines

Parameter	Value
<b>Suspension</b>	
Natural pH	8.24
Solid content (%)	1.0
Total suspended solids (mg/L)	9 722
Turbidity (NTU)	>1 095
Conductivity ( $\mu\text{S}/\text{cm}$ )	2 360
Total hardness (mg/L $\text{CaCO}_3$ )	1 746
$\text{Mg}^{2+}$ concentration (mg/L)	424
$\text{Ca}^{2+}$ concentration (mg/L)	699
<b>Solid</b>	
Particle size less than 40 $\mu\text{m}$ (%)	94
Mean particle size, $d_{50}$ ( $\mu\text{m}$ )	9.32
Mineral component	Calcite

### Fit statistics for SVI and turbidity

The fit statistics for SVI are shown in Table 4, while that for turbidity is shown in Table 5. The values obtained for the coefficients of determination ( $R^2$  of 0.9337 and 0.8654 for SVI and turbidity, respectively) are indications that the empirical model could only account for 10.2% of the overall variation (Ahamad et al., 2015). The findings also revealed F-values of 42.23 and 5.44 for SVI and turbidity (Tables 6 and 7). The F-value is a metric that indicates how well empirical models are suited to describing the statistical variance. The lower the value of  $p$  and the higher the value of F, the higher the level of significance of the coefficient terms and the model's ability to explain data variation (Chowdhury, 2013). All the individual terms for SVI and turbidity were significant in the models. In the case of interaction terms,  $X_1X_2$  and  $X_2X_3$  were substantial in the models for SVI and turbidity, while  $X_1X_3$  was not important in the models (Tables 6 and 7). The quadratic terms  $X_2^2$  ( $p = 0.0350$ ) and  $X_3^2$  ( $p = 0.0032$ ) for turbidity were significant in the model, whereas  $X_1^2$  ( $p = 0.4950$ ) was not significant (significance is determined by comparing the F-value and  $p$ -value results) (Table 7). The lack of fit was ineffective in any of the scenarios, confirming the accuracy of the developed models (Mondal et al., 2020). The polymer dosage ( $X_1$ ) had the most significant impact on SVI (Table 6), whereas the mixing time ( $X_3$ ) had the most significant effect on turbidity removal (Table 7), according to the F values.

**Table 4.** Fit statistics for SVI

Statistic	Value
Standard deviation	0.1492
Mean	2.29
Coefficient of variation (%)	6.50
Coefficient of determination ( $R^2$ )	0.9337
Adjusted coefficient of determination	0.9116
Predicted coefficient of determination	0.8626
Adequate precision	23.9586

### Analysis of variance (ANOVA) for SVI and turbidity

At 95% confidence level, the models for the responses were checked for validity, as presented in Tables 6 and 7. In ANOVA, the model and parameters are significant when  $p < 0.05$ ; therefore, the models were statistically significant, as shown by  $p$  values of  $<0.05$  (Aravind et al., 2015). The findings also revealed F-values of 42.23 and 5.44 for SVI and turbidity (Tables 6 and 7). The F-value is a metric that indicates how well empirical models are suited to describing the statistical variance. The lower the value of  $p$  and the higher the value of F, the higher the level of significance of the coefficient terms and the model's ability to explain data variation (Chowdhury, 2013). All the individual terms for SVI and turbidity were significant in the models. In the case of interaction terms,  $X_1X_2$  and  $X_2X_3$  were substantial in the models for SVI and turbidity, while  $X_1X_3$  was not important in the models (Tables 6 and 7). The quadratic terms  $X_2^2$  ( $p = 0.0350$ ) and  $X_3^2$  ( $p = 0.0032$ ) for turbidity were significant in the model, whereas  $X_1^2$  ( $p = 0.4950$ ) was not significant (significance is determined by comparing the F-value and  $p$ -value results) (Table 7). The lack of fit was ineffective in any of the scenarios, confirming the accuracy of the developed models (Mondal et al., 2020). The polymer dosage ( $X_1$ ) had the most significant impact on SVI (Table 6), whereas the mixing time ( $X_3$ ) had the most significant effect on turbidity removal (Table 7), according to the F values.

**Table 5.** Fit statistics for residual turbidity

Statistic	Value
Standard deviation	2.10
Mean	9.50
Coefficient of variation (%)	12.06
Coefficient of determination ( $R^2$ )	0.8654
Adjusted coefficient of determination	0.7346
Predicted coefficient of determination	0.7265
Adequate precision	18.2066

**Table 6.** Analysis of variance for SVI

Source	Sum of squares	df	Mean squared	F-value	$p$ -value	Lack-of-fit
Model	5.64	6	0.9396	42.23	$< 0.0001$	Significant
$X_1$	0.4081	1	0.4081	18.34	0.0004	Significant
$X_2$	0.4071	1	0.4071	18.30	0.0005	Significant
$X_3$	0.1308	1	0.1308	5.88	0.0261	Significant
$X_1X_2$	0.2366	1	0.2366	10.63	0.0043	Significant
$X_1X_3$	0.0339	1	0.0339	1.52	0.2328	Not significant
$X_2X_3$	0.4101	1	0.4101	18.43	0.0004	Significant
Residual	0.4005	18	0.0223			
Corrected total	6.04	24				

**Table 7.** Analysis of variance for residual turbidity

Source	Sum of squares	df	Mean square	F-value	$p$ -value	Lack-of-fit
Model	7 164.10	9	796.01	5.44	0.0021	Significant
$X_1$	1 236.67	1	1 236.67	8.45	0.0109	Significant
$X_2$	878.52	1	878.52	6.00	0.0271	Significant
$X_3$	1 589.06	1	1 589.06	10.85	0.0049	Significant
$X_1X_2$	1 092.21	1	1 092.21	7.46	0.0155	Significant
$X_1X_3$	654.23	1	654.23	4.47	0.0517	Not significant
$X_2X_3$	691.70	1	691.70	4.72	0.0462	Significant
$X_1^2$	71.61	1	71.61	0.4891	0.4950	Not significant
$X_2^2$	786.30	1	786.30	5.37	0.0350	Significant
$X_3^2$	1 796.23	1	1 796.23	12.27	0.0032	Significant
Residual	2 196.35	15	146.42			
Corrected total	9 360.45	24				

## Effect of process parameters on SVI and turbidity

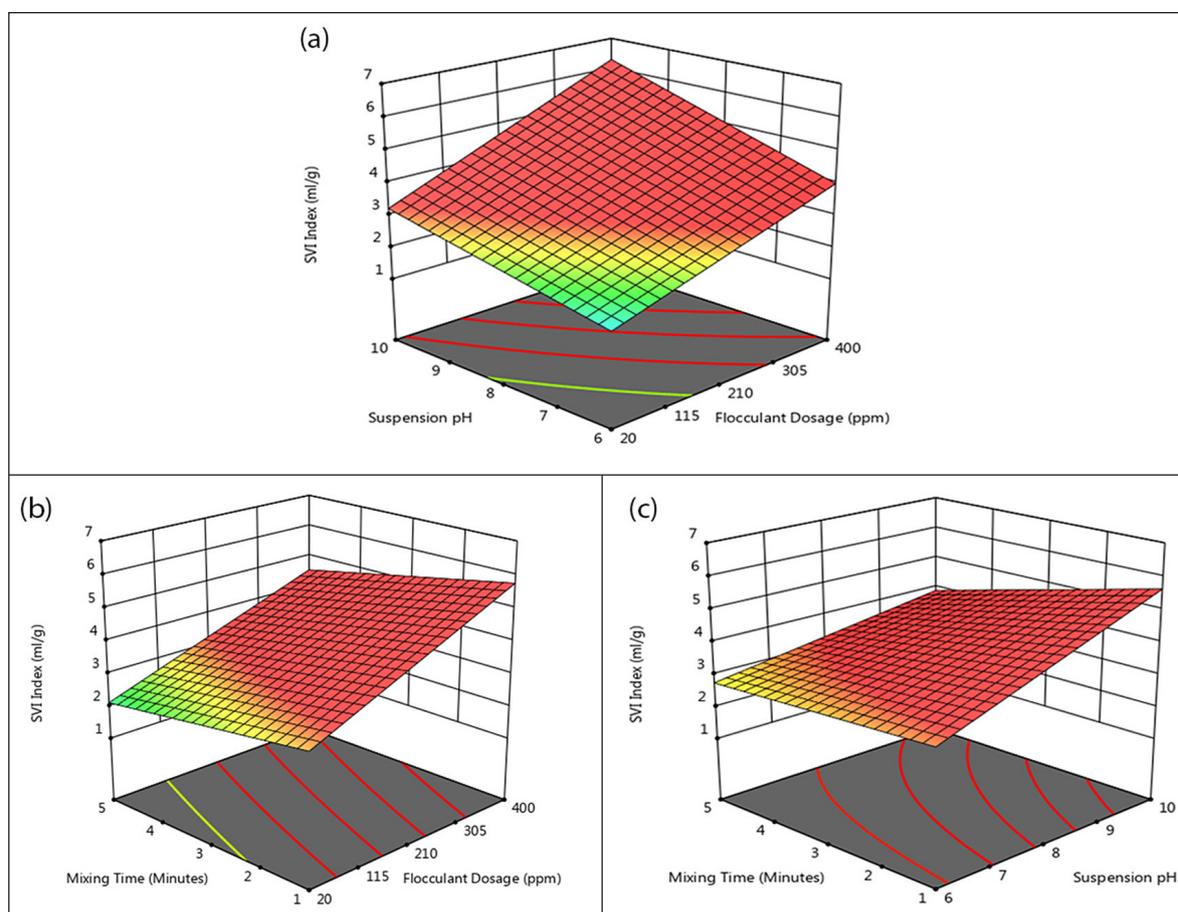
The plots showing the response surface for SVI are presented in Fig. 1. The result indicated that the SVI increased as the suspension pH and polymer dosage increased (Fig. 1a). Fig. 1b shows that the SVI is at the lowest when the polymer dosage decreases, irrespective of the mixing time value. In the case of mixing time and suspension pH, as the suspension pH increased and the mixing time decreased, SVI increased (Fig. 1c). SVI is guided by three variables in the coagulation-flocculation technique, i.e., hydration, high polymer, and osmotic pressure effects (Ives, 1978). The hybrid polymer used in this study was a blended biopolymer and polyaluminum chloride (PAC) formulation carrying highly positive polymer charges. When the polymer was positively charged, the osmotic effect could be reduced, and the high polymer effect could be ignored (Wang et al., 2007). Therefore, a hybrid polymer with cationic nature was favourable for minimizing the SVI under neutral and slightly acidic conditions.

The plots showing the response surface for turbidity are presented in Fig. 2. The significant decrease in the response surface plots suggests that the best conditions were precisely within the model boundaries (Fig. 2). The effect of mixing time and suspension pH indicates that as the mixing time increased and the suspension pH decreased, the turbidity removal increased (Fig. 2a). The optimal conditions were found in the region where the mixing time increased from 1 to 5 min while the polymer dosage decreased from 400 to 20 mg/L on the response surface plot for mixing time versus polymer dosage (Fig. 2b). Conversely, the polymer dosage, suspension pH, and mixing time all had noticeable interactive effects on residual turbidity. This is due to the internal interactions of the variables. The destabilization capacity of mono-component

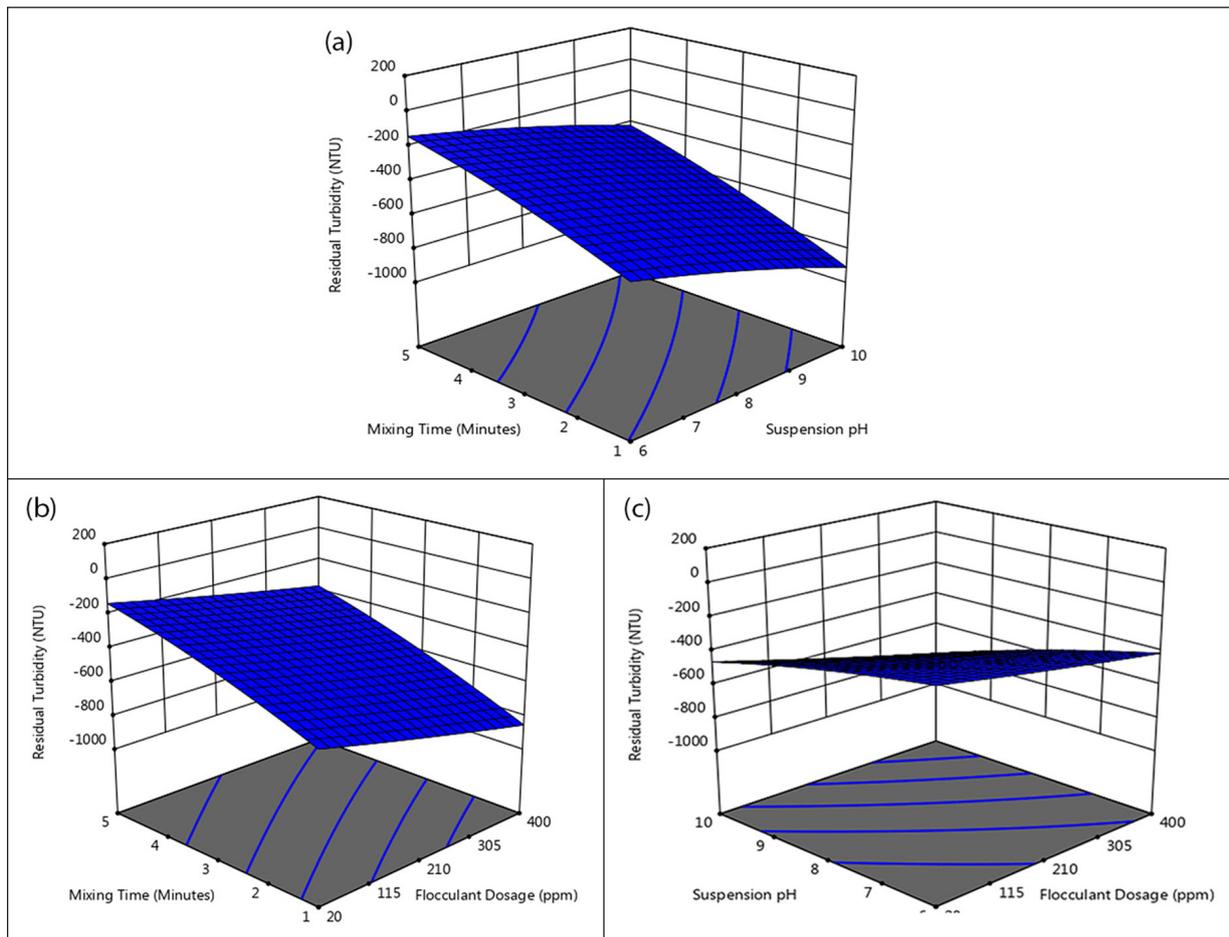
travertine-processing wastewater increases in alkaline and neutral media due to charge neutralization between Al species contained in the hybrid polymer and negatively charged travertine-processing wastewater fines (Sabah and Aciksoz, 2012). Also, more mixing time is required to ensure adequate contact between the polymer molecules and colloidal particles to create stable flocs, in the case of low polymer concentrations. The optimal conditions were found in the zone where the polymer dosage increased from 200 to 400 mg/L while the pH decreased from 10.0 to 6.0, according to the response surface plot for mixing time versus suspension pH (Fig. 2c). The sphere-like shape, with the highest response at the central curvature (Fig. 2c) implies that polymer dosage, as well as suspension pH, had a strong effect on turbidity removal (Wang et al., 2007).

## Optimization of SVI and turbidity

For model validation, the experiments were performed with the predicted values. The process optimization solution was chosen on the basis of its proximity to one of the highest desirability (Araromi et al., 2017). The target for optimization of SVI and turbidity was set at the minimum for all the operating conditions studied. The following were the optimal conditions for SVI and turbidity: polymer dosage of 276.20 mg/L, suspension pH of 8.60, and mixing time of 4.20 min, with the minimum turbidity and SVI determined to be 2.99 NTU and 1.36 mL/g, respectively, within the optimal conditions (Table 8). Based on the results obtained, the experimental values of turbidity, as well as SVI, were very close to the predicted values. This implies that the RSM method was very efficient in optimizing the coagulation-flocculation technique (Wang et al., 2007).



**Figure 1.** Plots for SVI: effects of (a) suspension pH and flocculant dosage pH, (b) mixing time and flocculant dosage, (c) mixing time and suspension pH



**Figure 2.** Plots for turbidity: effects of (a) mixing time and suspension pH, (b) flocculant dosage and mixing time, (c) suspension pH and flocculant dosage

**Table 8.** Optimization of SVI and residual turbidity

Response	Flocculant dosage (mg/L)	Suspension pH	Mixing time (min)	Predicted values (%)	Experimental values (%)	Error (%)
SVI (mL/g)	276.20	8.61	4.20	1.34	1.36	0.02
Turbidity (NTU)	276.20	8.61	4.20	2.95	2.99	0.04

## CONCLUSIONS

Considering the high volume of wastewater containing a large amount of suspended solids generated from natural stone mining/processing plants (marble, travertine, granite, etc.), the practical and economical treatment of travertine-processing wastewater to meet water quality objectives for wastewater reclamation and reuse and to protect public health is an important topic. Obtaining treated travertine-processing wastewater with low turbidity and low SVI is the essential objective to be achieved through the flocculation process using an eco-friendly biopolymer derived from chitosan and plants. In this study, the flocculation technique was applied in turbidity removal and sludge settling behaviour of travertine-processing wastewater using a biopolymer as a flocculant. A total of 20 CCD-based experimental runs were generated to optimize the polymer dosage, suspension pH, and mixing time. A desirability function technique was used to obtain equilibrium between the different responses of SVI and turbidity. The optimization study was aimed at minimizing SVI and turbidity, and the results indicated that the optimum values of mixing time, suspension pH, and polymer dosage to achieve the minimum SVI, as well as turbidity, were 276.20 mg/L, 8.60,

and 4.20 min, respectively. The optimal SVI and turbidity values obtained were 1.36 mL/g and 2.99 NTU. The RSM approach was found to be efficient in optimizing the flocculation process in validation experiments.

## AUTHOR CONTRIBUTIONS

Mr Sabah supervised the investigation; Mrs Taş applied the experiments; Mr Ugwu developed the methodology; Mr Arsoy prepared the tables; Mrs Taş, Mr Ugwu, Mr Sabah and Mr Arsoy discussed the method and the main text.

## ORCID

Eyüp Sabah

<http://orcid.org/0000-0002-5225-0891>

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