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OPTIMIZATION OF COAGULATION PARAMETERS IN THE REMOVAL OF TURBIDITY AND SUSPENDED SOLIDS FROM TANNERY EFFLUENTS USING THE BOX - BEHNKEN DESIGN

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Abstract

The present study evaluated the performance of tannery effluent treatments by coagulation processes. This was done by combining each of the organic coagulants L-1544, L-1541, and L-1700 with aluminium sulphate, respectively, as an inorganic coagulant in different mixing ratios. Subsequently, the response surface method optimized the coagulation conditions: agitation speed, time, and total coagulant concentration. The best results were obtained with the cationic coagulant based on L-1544; likewise, by superposition of contours plots, the conditions that maximize the percentages of simultaneous removal of turbidity and suspended solids were determined, the optimum coagulation values being time 4 minutes, agitation speed 169.7 rpm and total coagulant concentration 1354 ppm, obtaining 100 and 61.9 % removal of turbidity and suspended solids respectively. The R-Squared statistics show that the models explain 92.99 % and 93.94 % of the variabilities in turbidity and Suspended Solids Removal, respectively.

Keywords: Box-Behnken, Coagulation, Optimization, Suspended solids, Turbidity.

1. Introduction

The coagulation-flocculation process plays an indispensable role in the treatment of both domestic and industrial effluents, which consists in adding certain chemical additives such as aluminium sulphate and polymers to the wastewater, neutralizing and stabilizing the organic and inorganic colloids in suspension and favouring their sedimentation, as well as some dissolved substances which can be efficiently removed from the water during treatment [1-3]. The optimum dosage of a coagulant reflects the concentration that achieves maximum performance in removing turbidity with a minimum amount of chemical reagents, ensuring the best results at the lowest cost. The addition of coagulants favours the decrease of turbidity at the start of the coagulation process until an appropriate dose is found.

However, the subsequent addition can have the opposite effect by raising turbidity due to an excess of coagulant because too much coagulant can increase the turbidity of tannery effluents due to the formation of larger flocs and precipitates, particle regrouping and destabilisation of colloids. To minimise turbidity, it is essential to use the right amount of coagulant and to optimise water treatment processes for optimum efficiency [4, 5]. Optimization models are of immense importance in any process, as they improve performance; the Response Surface Method (RSM) consists of experimental design, analysis, and modelling by adapting the experimental factors [6]. The Box - Behnken design (BBD) allows working with fewer trials than a factorial design. This experimental design is widely used in scientific research to optimize the number of treatments and response variables [7, 8].

Some organic coagulants perform similarly to inorganic coagulants but under different optimum conditions [9]. However, little literature has been found on applying metal salts such as aluminium sulphate in combination with organic coagulants in treating tannery wastewater. This is precisely where its importance lies. Also, to meet the highly stringent requirements for tannery wastewater, scientists urgently need to devise new methods to control the quality of tannery wastewater [10]. In the case of tannery wastewater, 500 ppm for discharges to the sewer and 30 ppm in surface water [11].

In the local market, coagulants L-1541, L-1544 and L1700 are the most commonly used coagulants. Furthermore, mixing inorganic and organic coagulants has proven a high removal of turbidity and other effluent properties at a lower cost compared to coagulants used individually because they can work over a wide pH range (6-12) without having to adjust the pH for treatment [12-14]. Coagulant L-1700 is based on quaternary ammonium tannins, L-1541 is a cationic polymer based on polydiallyldimethylammonium chloride and L-1544 is a cationic polymer based on polyamine. Aluminium sulfate releases aluminium ions into the water that neutralize the negatively charged colloids causing their destabilization and precipitation in the form of hydroxides. Polyamines, whose amino functional group is positively charged, neutralize or help the formation of bridges between the flocs formed, also causing their precipitation. The efficiency of a hybrid formed from polyamine commercial with poly aluminium nitrate sulfate has been evaluated with other coagulants resulting in the hybrid coagulant being more efficient than the coagulants used individually [15].

In this sense, the present study had as its objective to evaluate the simultaneous removal of turbidity and suspended solids from tannery wastewater, using the application of aluminium sulphate in combination with organic coagulants optimizing the process variables such as agitation speed, time and total coagulant concentration. The novelty of the work is the application of the Box Behnken experimental design for the optimization of the coagulation conditions of this type of wastewater.

2. Prediction of Aerodynamic Coefficients

The methodology followed to optimize the coagulation conditions of tannery wastewater, using the Box Behnken experimental design, was carried out in the following stages:

2.1. Composite sample collection and preparation

The wastewater samples were collected from the company Junior S.A.C., Trujillo-Peru. Once the samples were collected, they were left to settle for four hours, then 75% of the top was taken; 20 L of the sample was taken from the middle zone of the sedimentation pond every 30 minutes, obtaining a 200 L composite sample. The composite sample was characterized by analysing pH, turbidity and suspended solids [16] at the National University of Trujillo Water Research Laboratory, using a 2100Q Thermo Scientific Orion Star A3295 portable water quality multi-parameter equipment and a Hach 2100Q Portable Turbidimeter with Tungsten filament lamp respectively.

2.2. Coagulation test

The coagulation and flocculation tests were carried out in a six-unit Phipps & Bird Jar Test with 2 L square jars.

In order to evaluate the removal of turbidity and suspended solids, the following were mixed aluminium sulphate (AS) as an inorganic coagulant with organic coagulants L-1541, L-1544, and L-1700 as follows: AS/L-1541, AS/L-1544 y AS/L-1700 in the percentage ratios of 80%-20%, 60%-40%, 40%-60% and 20%-80%. These ratios were based on research where inorganic coagulants (salts) are mixed with organic coagulants (polyelectrolytes) in a 95%-5% ratio [12] and another where the inorganic coagulant (aluminium sulphate) is mixed with the organic coagulant (polydimethyldiallylammonium chloride) in the proportion 17%-83% [17]. The total concentration of both coagulants in the effluent was maintained at 1000 ppm.

All initial tests (before optimization) were carried out at ambient conditions, and the agitation speed and coagulation time were kept constant at 150 rpm and 5 minutes, respectively; agitation speed and flocculation time at 40 rpm and 10 minutes, respectively; and sedimentation time at 30 minutes based on values close to the references [11, 18-20]. The results of this jar test at the indicated conditions are shown in Table 1.

2.3. Optimization of factors in the coagulation process

The best coagulant mixture obtained was AS/L-1544 in the 80%-20% ratio as shown in Table 1. With this mixture ratio selected, the coagulation conditions (total coagulant concentration, time, and agitation speed) were optimized using the Box Behnken experimental design. Sixteen treatments were performed, including four replicates of the central levels. The concentrations used were 1000 ppm as the central level, with 1400 ppm and 600 ppm as the extreme levels. The coagulation process times were 2, 5, and 8 min and the agitation speed was 80, 150, and 220 rpm [6]. The results obtained under these conditions are reported in Table 2.

The independent variables were compound coagulant concentration, agitation time, and the speed of agitation, and as dependent variables, the removal of turbidity and suspended solids, as shown in Table 2. Using the contour plot overlay method shown in Figs. 1 and 2, the best conditions for the simultaneous removal of turbidity and suspended solids were sought by changing the three-dimensional surface-response plots to two-dimensional planes. The optimal removal conditions are shown individually (for turbidity and suspended solids) and simultaneously in Table 4. The Design Expert software version 11.1.2.0 was used, and contour plot overlays were made using Statgraphics centurion XVI.

3. Results and Discussion

3.1. Simultaneous removal of coagulants at different percentage rates

Table 1 shows the turbidity removal percentages for the ratios of selected mixtures of aluminium sulphate and organic coagulants; also, pure organic coagulants have been evaluated. For selecting the best mixing ratio of aluminium sulphate with an organic coagulant, the jar tests were carried out considering only turbidity as a suitable variable since it neutralizes the negative charges of the small particles dispersed in the water, causing their agglomeration, flocculation and subsequent sedimentation. However, suspended solids are composed of particles of different sizes and densities, making their removal difficult [21, 22].

Table 1. Turbidity removal, using a combination of inorganic and organic coagulants.

Total concentration of coagulants (1000ppm)		Turbidity removal (%)		
aluminium sulphate (AS) (%)	Organic coagulant (%)	L-1541	L-1544	L-1700
80	20	96.25	99.18	94.97
60	40	96.81	99.00	93.96
40	60	96.29	99.02	94.22
20	80	93.78	98.22	93.54
0	100	90.50	97.00	92.00

The combinations of aluminium sulphate and L-1544 showed the best results in Turbidity Removal (TR), reaching percentages > 98% in all combinations, being the 80%-20% ratio the highest value with 99.18% TR followed by the combinations of aluminium sulphate and L-1541 with a TR of 96.81% at a 60%-40% ratio, this being their highest value (See Table 1).

The combinations of aluminium sulphate and organic coagulants decreased the concentrations of aluminium sulphate needed, resulting in heavier sludge, which is why they sediment faster [5, 23].

Comparatively, reference [13] mentions that effluents from newsprint mills treated with PANS-PA (polyaluminum nitrate sulfate - mixture of polyamines) mixture, without specifying the ratio, obtained a turbidity removal of 90% while reference [17] mentions that raw water from Yangtze River treated with AS-

PDAMC (aluminium sulphate - polydimethyl diallyl ammonium chloride) mixture with the mass ratio 10:1 obtained a removal, without filtering, of 88.96% of the same parameter. The removal values obtained in the present investigation were higher; however, the characteristics of the effluents are very different.

3.2. Simultaneous optimization for the removal of turbidity and suspended solids

After selecting the best ratio of aluminium sulphate with coagulant L-1544 at 80%-20% according to the tests performed in 3.1, we proceeded to vary the stirring speed and time as well as the concentration in ppm of the mixture from 80%-20%.

Table 2 shows the results for turbidity, suspended solids (SS), and their respective removal percentages. As indicated in Table 2, the initial parameters are initial turbidity of 2423 NTU, initial suspended solids of 4432 ppm, and initial pH of 8.4.

Figure 1(a) reveals a moderate interaction between time and TR since any change in its value along its axis does not lead to any significant change in TR. It also shows a strong interaction between stirring speed and TR since any change in rate above or below 150 rpm leads to a decrease in TR; increasing its value prevents giving the coagulant the necessary time to perform its function while decreasing it prevents the coagulant from reacting with the whole sample homogeneously. Figures 1(b) and (c) reveal that high concentrations of compound coagulant significantly increase TR and that time has no significant change on TR [6, 20].

It is essential to mention that the activity of coagulants is the neutralization of the colloids present in the effluent and can be constituted by a variety of substances, acids, alkalis, solvents, proteins, salts, oils and residues of chemicals (tannin and chromium based) used in the tanning process. It should be noted that the exact composition may vary depending on the industry and the specific practices used [23, 24].

Table 2. Experimental design Box Behnken for the mixture of 80%-20% aluminium sulphate and L-1544.

Experimental design				Initial turbidity: 2423 NTU, SSi: 4432 ppm, pH: 8,4			
N°	Velocity (rpm)	Time (min)	Concentration (ppm)	T_f (NTU)	Removal (%)	SS_f (ppm)	Removal (%)
1	150	2	600	199.00	91.79	4075	8.06
2	150	8	600	155.00	93.60	3625	18.21
3	150	2	1400	11.10	99.54	1765	60.18
4	150	8	1400	11.17	99.54	1865	57.92
5	80	5	600	127.00	94.76	2705	38.97
6	220	5	600	113.00	95.34	3030	31.63
7	80	5	1400	12.23	99.50	1690	61.87
8	220	5	1400	8.27	99.66	1735	60.85
9	80	2	1000	28.53	98.82	2225	49.80
10	220	2	1000	20.57	99.15	1980	55.32
11	80	8	1000	64.90	97.32	1810	59.16
12	220	8	1000	75.13	96.90	1905	57.02
13	150	5	1000	14.47	99.40	2140	51.71
14	150	5	1000	14.30	99.41	2325	47.54
15	150	5	1000	11.60	99.52	2130	51.94
16	150	5	1000	18.93	99.22	2120	52.17

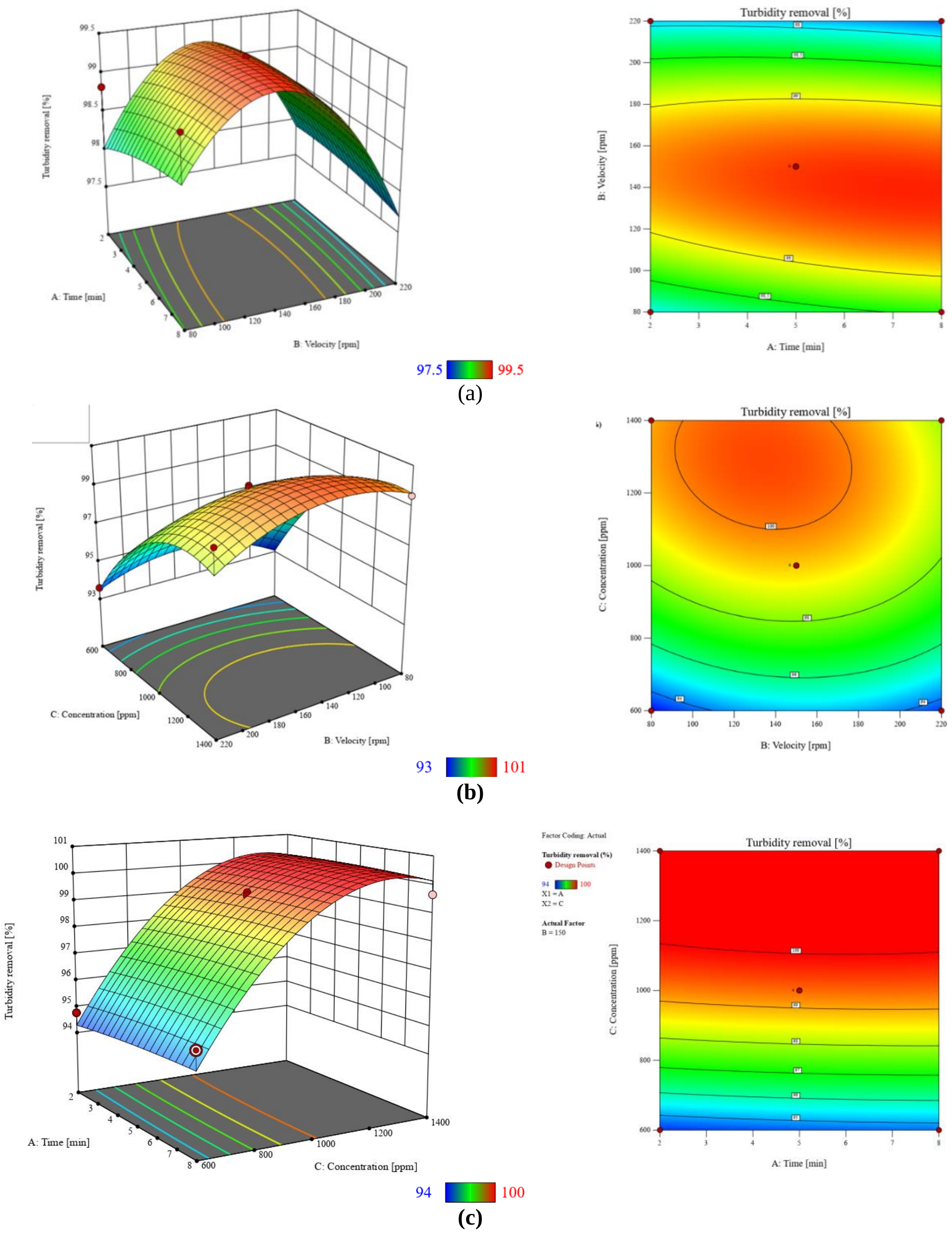

Fig. 1. 3D surface-response and 2D contour plots for turbidity removal, evaluating different conditions (a)Velocity-Time; (b) Concentration-Velocity, and (c) Concentration-Time

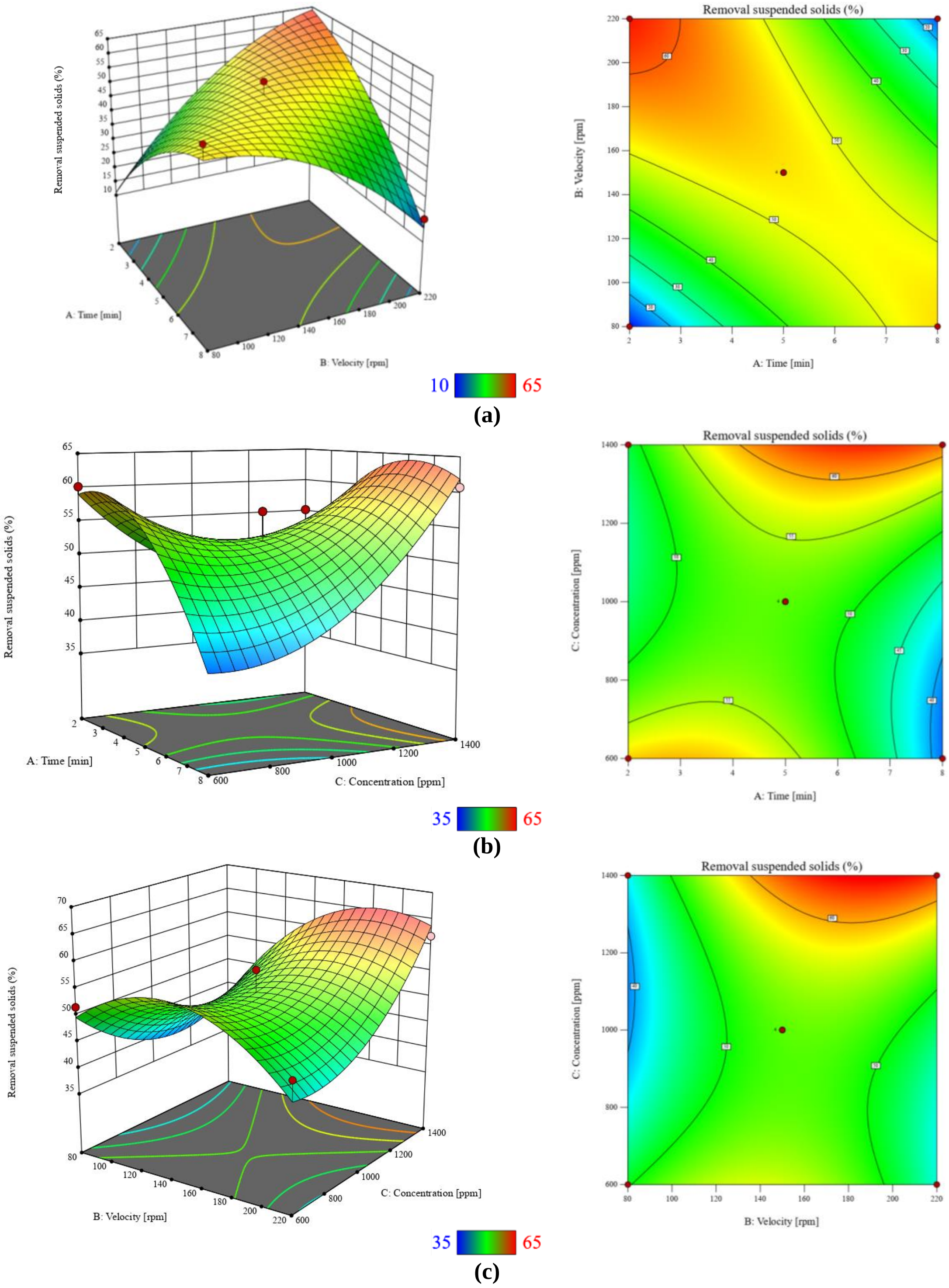

Fig. 2. 3D surface-response and 2D contour plots for suspended solids removal, evaluating different conditions (a) Velocity-Time, (b) Concentration-Time, and (c) Concentration-Velocity.

Figure 2(a) shows the mutual interaction between operating time and stirring speed; the best suspended solids removal occurred at low times and high stirring speed, while at slow stirring speed, a high time is necessary to achieve considerable suspended solids removal. Figures 2(b) and (c) show similar results at concentrations higher than 1200 ppm of coagulant, where the best suspended solids removal results can be seen at an operating time higher than 4 min and an agitation speed higher than 160 rpm, respectively [6, 25].

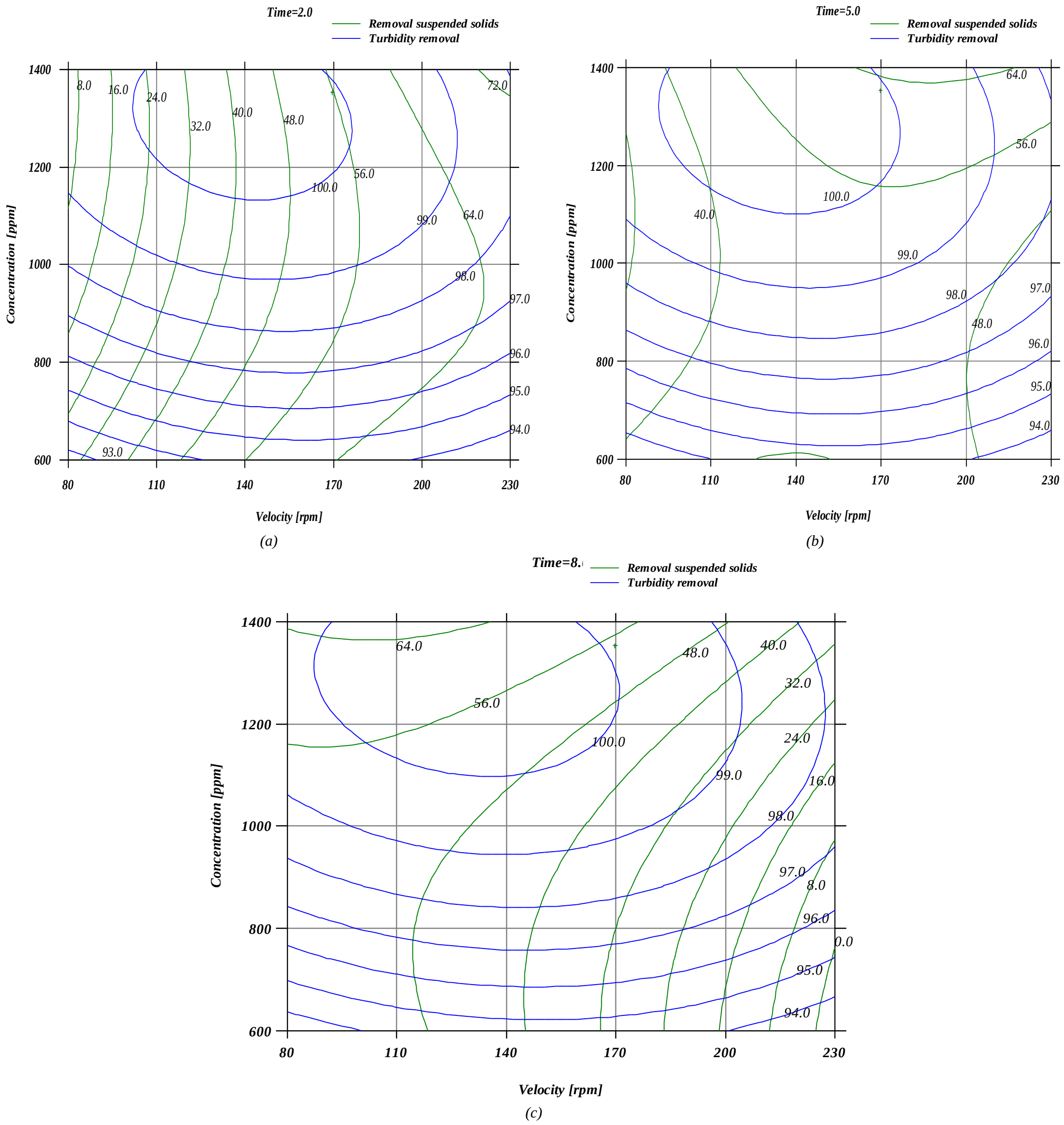

Fig. 3. 2D contour overlay plots evaluated at different conditions (a) 2 minutes, (b) 5 minutes, and (c) 8 minutes.

Using Statgraphics software and overlapping the 2D contour plots, simultaneous optimization was achieved by identifying the conditions that mutually maximize the turbidity and suspended solids removal rates. This can be seen in Fig. 3.

Figure 3 shows the behaviour of the turbidity and suspended solids removals throughout the change of values of the agitation speed and the concentration composed in the three levels of time (2, 5, and 8 min), showing that the best conditions at all three times occur at a composite concentration greater than 1300 ppm. Looking directly at Figs. 3(a) and (b) show that the best conditions are found at an agitation speed close to 170 rpm [6, 12], achieving 100% turbidity and 56% suspended solids removal in (a), while (b) shows 100% turbidity and 64% suspended solids removal; however, in (c) the best conditions occur at speed between 80-110 rpm because low agitation speeds need high operating time to improve their effect on turbidity removal. It should be noted that the Statgraphs software models and optimizes the best turbidity and suspended solids removal values, indicating that the best conditions occur at an agitation time of 3.8 min, agitation speed of 169.7 rpm and coagulant mixture concentration of 1354 ppm, as shown in Table 3.

Other research reports that with a mixture of cationic and anionic polyacrylamide polymers with ferric chloride or aluminium chloride at pH < 3 resulted in 95% removal of TSS and 95% removal of colour from pulp mill wastewater effluent (turbidity was not evaluated) [12]. Similarly, the most effective product for removing suspended solids from effluents from newsprint mills was PAC-HB, a polyaluminum chloride coagulant of intermediate aluminium content and high basicity, which achieved a removal rate of total suspended solids (TSS) of 85% and a 90% removal of turbidity with pH values of 6.5-6.8 [13].

Although the removals of total suspended solids were higher than the research presented, the characteristics of the effluents and the coagulants used were different. From the results obtained in the optimization (Table 3), under the appropriate conditions, turbidity can be completely removed.

3.3. Statistical analysis

The statistical analysis focused on optimizing the parameters (time, agitation speed and coagulant concentration) with Statgraphs software, which models and reports the best values. These parameters were optimized for the best 80:20 ratio of inorganic coagulant aluminium sulfate (AS) and organic coagulant L-1544.

The R-Squared statistics show that the models explain 92.99% and 93.94% of the variabilities in turbidity and Suspended Solids Removal, respectively. The results of the optimization of the factors time, agitation speed, and coagulant concentration are shown in Table 3.

The optimization analysis reports the best turbidity and suspended solids removal values individually after modelling between high and low agitation speed and time and coagulant concentration levels. The results are reported in Table 3. In the same way and simultaneously, the best removal of turbidity and suspended solids. It should be noted that in the ranges used, the suspended solids removal does not exceed 72.2%.

Table 3. Optimization of turbidity and suspended solids removal levels.

Factor	Low level	High level	Optimum Value, Turbidity Removal, TR	Optimum Value, Removal of Suspended Solids, RSS	The optimum value for the simultaneous removal of turbidity and Suspended Solids
Time, min	2.0	8.0	6.1	2.0	3.8
Stirring rate, rpm	80.0	220.0	132.2	220.0	169.7
Coagulant concentration, ppm	600.0	1400.0	1291.7	1400.0	1354.0
Removal percentage			100 % TR	72.2 % RSS	100 % TR y 61.9 % RSS

4. Conclusions

The present study showed the effectiveness in the removal of turbidity and suspended solids when using combinations of organic and inorganic coagulants, obtaining the best results at 80% of aluminium sulphate and 20% of L-1544, achieving simultaneous removal of 100% turbidity, and 61.9% suspended solids present in tannery effluents, under optimized operating conditions at a time of 4 min, 170 rpm agitation speed and a total coagulant concentration of 1354 ppm. The R-Squared statistics show that the models explain 92.99% and 93.94% of the variabilities in turbidity and suspended solids removal, respectively. It is recommended to experiment with other inorganic coagulants, such as ferric chloride and ferric sulphate, with the same or different Polyamine organic coagulants to verify for synergistic effects and cost reduction.

Nomenclatures

AS	Aluminum sulphate
RSS	Removal of suspended solids, %
SS	Suspended solids, ppm
SSf	Final suspended solids, ppm
SSi	Initial suspended solids, ppm
Tf	Final Turbidity, NTU
TR	Turbidity removal, %

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