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Modeling and optimization of experimental parameters in the treatment of effluents by coagulation-flocculation processes: Methodology of experimental design

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Abstract: The objective of this study is to determine the optimal conditions of the operational parameters: type of flocculant (chitosan(s) and ferrocryl®8723), dose of flocculant (0.1g/L at 0.5g/L) and pH (6 to 9) in the treatment of hot dip galvanizing effluents using coagulation/flocculation processes. The optimization of these parameters is done by the methodology of experimental design which allowed us to predict the optimal conditions. The concerned results, especially the theoretical operating parameters, allowed us to give a better reduction of the TSS, BOD_5 and COD in the optimal conditions namely: the pH of about 9, the type of flocculant is chitosan(s) with a dose of 0.2g/L.

Keywords: Flocculant, chitosan(s), ferrocryl®8723, COD, BOD_5, TSS, experimental design.

Introduction

The industrial effluents produced by hot-dip galvanizing techniques were mostly treated by physicochemical processes. These methods include several treatment methods from which there are mentioned: membrane processes [1], oxidation [2], adsorption on different adsorptive materials [3], electro coagulation [4] and also coagulation-flocculation processes [5,6]. The latter has wide use in the treatment of wastewater containing inorganic [7], organic [8] and organometallic micro pollutants [9]. However, these processes require huge quantities of products, chemical reagents and the results obtained through conventional methods do not give complete eliminations of the pollution level on the one hand. They require much time and also analysis on the other hand. In other ways, these processes are expensive and endless. To solve these problems, it was called for cheaper, cheaper and faster methods; one of its is the methodology of the planning of experiments. This methodology allowed us to evaluate several operating parameters (factors) at a time and the results obtained through this methodology were satisfied.

In this work, it was treated liquid effluents from hot-dip galvanizing by coagulation/flocculation processes using coagulant such as $Ca(OH)_2$ [10,11] and flocculants of ferrocryl®8723 [10,11] and chitosan(s) [11].

The objective of this work is to study the influence of the experimental factors (a type of flocculant, doses of flocculants and pH) on the studied responses that are in this work, the reduction rates of the TSS, BOD_5 and COD contents. To optimize these last factors, it was used the methodology of the experimental design based on a mathematical model of first degree which allowed us to find operating conditions allowing eliminate the maximums of the pollutants.

Materials and experimental methods

Flocculant(s)

The polyelectrolyte used for flocculation are ferrocryl®8723 powder with a purity of 98%, of the family of polyacrylamides whose chemical formula is $(C_3H_5NO.C_3H_4O_2)_n$ and the molecular weight between in range of 11.10^6 and 12.10^6 g/mol, ionic character is anionic and was provided by Henkel Metallochemistry and chitosan(s) is a cationic polymer that can be obtained by the acetylating of chitin [10-12,13] whose chemical formula $(C_6H_{11}NO_4)_n$.

Preparation of chitosan from chitin

Preparation of chitosan is simply deacetylation of chitin in alkaline medium. Figures 1 and 2 showed the necessary steps for obtaining chitosan.

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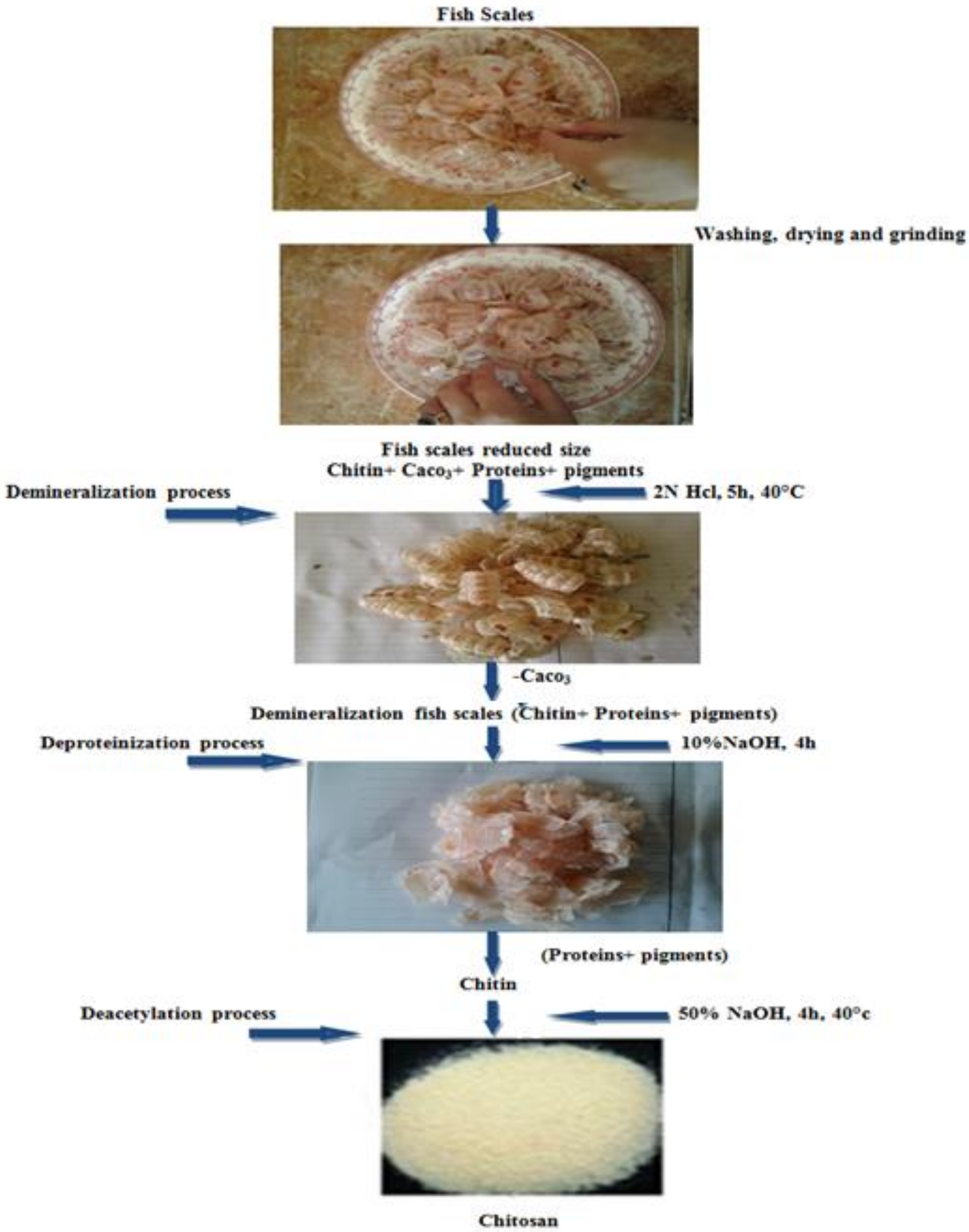

Figure 1. Overall Processes for the preparation of chitin from fish scales

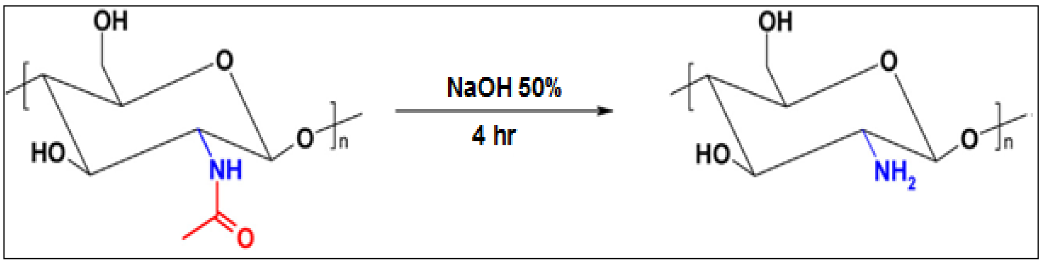

Figure 2. Deacetylation reaction of chitin for obtaining chitosan

Experimental Section

To determine the effects of the factors and their interactions on the responses we studied, there were used the experimental design methodology by using the Nemrodw software that allows the development of planning of experiments and analysis of experimental results by analyzing statistical indicators and other specific tools to achieve the proposed objective.

Experimental Planning Methodology (EPM)

The classical method used to study the influence of parameters on a studied response is to change one of these operating parameters while the others are now fixedx[14]. On the other hand, the methodology of the experimental designx[15,16] allowed us to simplify the exploitation of the results of the experimental study while minimizing the number of tests carried out [17]. Through a multidimensional experimental field, it can determine the main effects, and their interactions on the responses studied.

Description of the experimental study

The flocculant dose optimization depends on three factors (type of flocculant, dose of flocculant and pH) that influence the responses (TSS, COD and BOD_5). It was chosen a factorial matrix that could find the optimal qualities predicting or conforming the calculated response to all experimental study field points. Its various factors, experimental responses, matrix of experiments, experimental design and characteristics of the problems have been summarized in the Tables (1- 4).

Table 1. Experimental domain of the factors studied.

	Factors	levels
X_1	type of flocculants	ferrocryl®8723
		chitosan(s)
X_2	dose of flocculants	0.1g/L
		0.5g/L
X_3	pH	6
		9

Table 2. Experimental Response(s) Studied.

	Responses	Unit
Y1	TSS	mg/L
Y2	COD	mg O2/L
Y3	BOD_5	mg O2/L

Table 3. Experiment Matrix.

N° Exp	X_1	X_2	X_3
1	-1	-1	-1
2	1	-1	-1
3	-1	1	-1
4	1	1	-1
5	-1	-1	1
6	1	-1	1
7	-1	1	1
8	1	1	1
9	-1	-1	-1
10	1	-1	-1
11	-1	1	-1
12	1	1	-1
13	-1	-1	1
14	1	-1	1
15	-1	1	1
16	1	1	1

Table 4. Experimental Plan.

N° Exp	Type of flocculants	Dose of flocculants	pH	TSS mg/L	COD mg/L	BOD_5 mg/L
1	Ferrocryl®8723	0.1	6	375.00	1455.00	352.00
2	Chitosan(s)	0.1	6	341.00	1405.00	316.00
3	Ferrocryl®8723	0.5	6	393.00	1500.00	397.00
4	Chitosan(s)	0.5	6	363.00	1467.00	367.00
5	Ferrocryl®8723	0.1	9	346.00	694.00	258.00
6	Chitosan(s)	0.1	9	329.00	662.00	215.00
7	Ferrocryl®8723	0.5	9	354.00	730.00	310.00
8	Chitosan(s)	0.5	9	332.00	715.00	234.00
9	Ferrocryl®8723	0.1	6	352.00	1370.00	392.00
10	Chitosan(s)	0.1	6	325.00	1312.50	457.00
11	Ferrocryl®8723	0.5	6	377.50	1430.00	456.00
12	Chitosan(s)	0.5	6	338.00	1400.00	401.00
13	Ferrocryl®8723	0.1	9	327.00	689.00	275.00
14	Chitosan(s)	0.1	9	326.50	661.00	220.00
15	Ferrocryl®8723	0.5	9	336.00	736.00	308.00
16	Chitosan(s)	0.5	9	332.00	706.00	229.00

Results and Discussion

Characteristic of the physical-chemical parameters of the hot-dip galvanizing rejects

Table 5 summarizes the average values the effluent physical-chemical parameters used in this study.

Table 5. The average values of the physical-chemical parameters of the liquid effluents taken at two different points [11] and limit values retained.

Analyzed Parameters	Measured values downstream of the neutralization station	Measured values upstream of the neutralization station	Limit values retained [18]
pH	4.01	3.56	**6-9**
COD (mg O2/l)	2862	2075	**500**
BOD_5 (mg O2/l)	602	546	**100**
TSS (mg/l)	**570**	**515**	**50**

From the Table 5 we noticed that:
The liquid effluents of hot-dip galvanizing provide values of major physical-chemical parameters that relatively exceed the general values limits for the "hot-dip galvanizing" branch [18].

Characterization of chitosan(s)
Metallographic microscopy

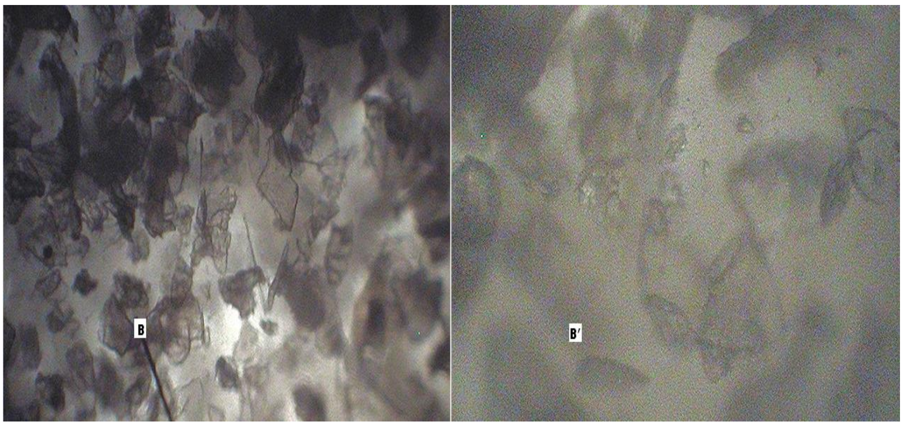

Figure 3. Morphology of chitosan(s) (B, B') seen by metallographic microscopy at 40x (B) and 100x (B')

According to this figure, it was noticed that extracted chitosan exhibited flake layers, and in the same sense, it was observed an increase in pores density in some areas, as in the studies of Kucukgulmezand al [19] which simulated this work.

Infrared spectroscopy

Fourier transform infrared spectroscopy analysis of chitosan, and the main bands are shown in Figure 4:

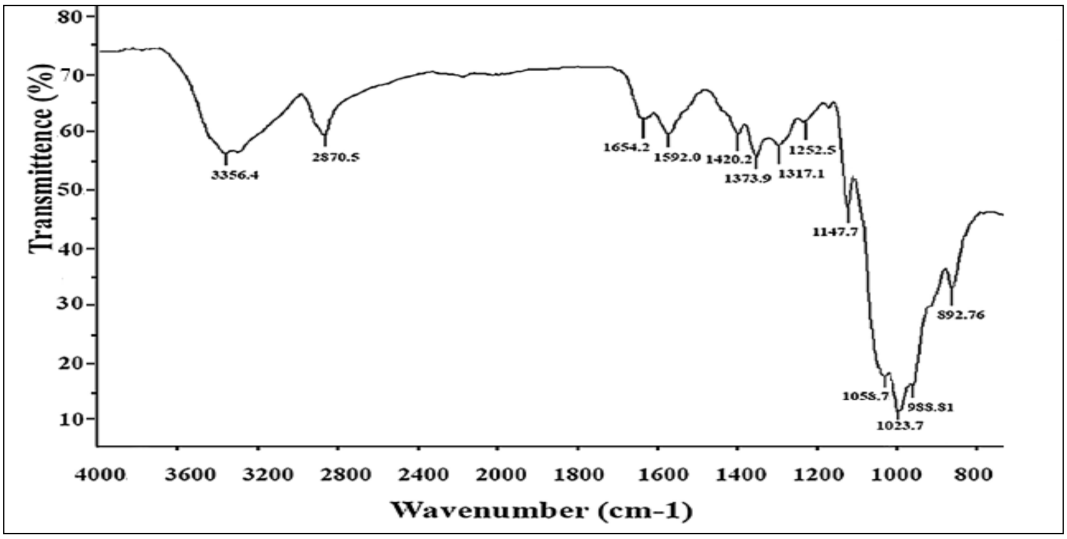

Figure 4. IRTF Spectrum of Chitosan(s)

From Figure 4, we found that the main peaks found at 3356.4 cm^{-1} for chitosan beads were assigned to the stretching vibration of OH and NH groups. The peak at 2870.5 cm^{-1} was due to stretching of the CH vibration. $-CONH_2$ stretching in the secondary amide groups was observed at 1654.2 cm^{-1} while the peak at 1592cm^{-1} was attributed to NH bending in the primary amine (NH_2) groups. The deformation vibration of NH in NH_2 was represented by the peak at 1420.2 cm^{-1}. Other peaks observed chitosan beads were found at 1373.9 cm^{-1} stretching vibration of (-CN), 1147.7 cm^{-1} asymmetric stretching vibration of (COC), 1058.7 cm^{-1} vibration of symmetric stretching (COC) and 1023.7 cm^{-1} stretching vibration (CO in COH). The 892.76 cm^{-1} band was assigned to the absorption peaks of α-(1, 4) glycoside in chitosan. These results confirm that the experimentally prepared chitosan was identical to that of the chitosan structure [20-22].

Statistical analyzes

Model equation

The mathematical model used in work is a polynomial model of a first degree. It includes linear effects, interaction effects and quadratic effects of factors.

$$Y = b_0 + b_1X_1 + b_2 X_2 + b_3 X_3 + b_{12}(X_1X_2) + b_{13}(X_1X_3) + b_{23}(X_2X_3) + \varepsilon \quad (1)$$

Where:

Y: Response function

X_i: is the coded independent variable, meaning

X_1: Level attributed to the factor 1 (type of flocculant);

X_2: Level attributed to the factor 2 (dose of flocculant);

X_3:Level attributed to the factor 3 (pH);

b_i: defines the model coefficients

b_0:Value of the response of the center of experimental fields;

b_1: Effect of factor 1;

b_2: Effect factor 2;

b_3: Effect factor 3;

b_{12}: Interaction between factors 1 and 2;

b_{13}: Interaction between factors 1 and 3;

b_{23}: Interaction between factors 2 and 3;

ε: Residues.

Estimation and statistical coefficients

All the coefficient factors studied as well as their effects, as well as the observed probability (significance), are grouped in Table 6. The values of t-student are used to determine the significance of the coefficients of each factor, whereas the signals are defined as the smallest significance level. In general, the larger t-student size, the smallest of significance, and the more significant of the coefficient term [23,24].

Table 6. Analysis of the coefficients.

	Coefficient	Coefficient value	F. Inflation	Standard deviation	t exp.	Significance, %
TSS	b0	346.688	1.00	2.851	121.59	***
	b1	-10.875	1.00	2.851	-3.81	**
	b2	6.500	1.00	2.851	2.28	*
	b3	-11.375	1.00	2.851	-3.99	**
	b12	-1.063	1.00	2.851	-0.37	71.7%
	b13	5.438	1.00	2.851	1.91	8.6%
	b23	-3.313	1.00	2.851	-1.16	27.5%
COD	b0	1058.281	1.00	9.395	112.64	***
	b1	-17.219	1.00	9.395	-1.83	9.7%
	b2	27.219	1.00	9.395	2.90	*
	b3	-359.156	1.00	9.395	-38.23	***
	b12	3.719	1.00	9.395	0.40	70.2%
	b13	4.094	1.00	9.395	0.44	67.5%
	b23	-4.594	1.00	9.395	-0.49	64.0%
BOD_5	b0	317.938	1.00	5.430	58.55	***
	b1	-25.563	1.00	5.430	-4.71	**
	b2	19.813	1.00	5.430	3.65	**
	b3	-61.813	1.00	5.430	-11.3	***
	b12	-4.438	1.00	5.430	-0.82	44.0 %
	b13	-6.063	1.00	5.430	-1.12	29.4%
	b23	-5.688	1.00	5.430	-1.05	32.4%
***significant at 0.1%, **significant at 1% and *significant at 5% [25]						

From the results obtained in Table 6, it was found that there are small significant values indicating that the model has a good significance of the coefficient.

The third column of the coefficient analysis table gives the inflation factor which is an absolute measure of the independence of the coefficients [26,27], that it measures the degree of orthogonality of the matrix experiments. This shows that the quality of information decreases with the increase of the inflation factor. It can be said that an experience matrix provides the desired information if the inflation factor remains closest to 1.

Stick-attracted scheme medium effects

The stick-attracted diagram is to supplement the results obtained by the statistic which estimates the systems of previously obtained coefficients. Figures (5-7) represent stick-attracted diagrams that would release the most influential factors on the elimination of the rate of responses (TSS, BOD_5 and COD) by the coagulation/ flocculation process.

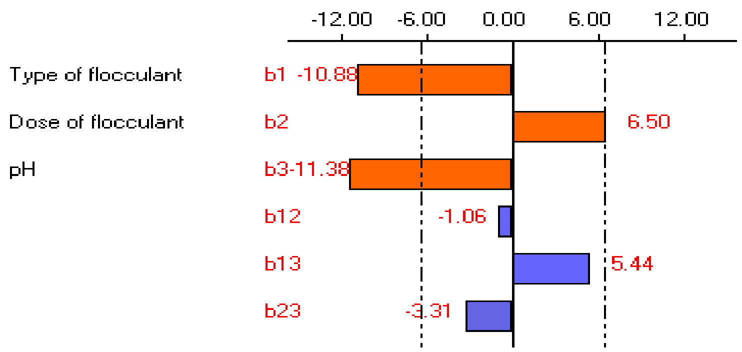

Figure 5: Study of the effects of the factors (X_i) on the TSS

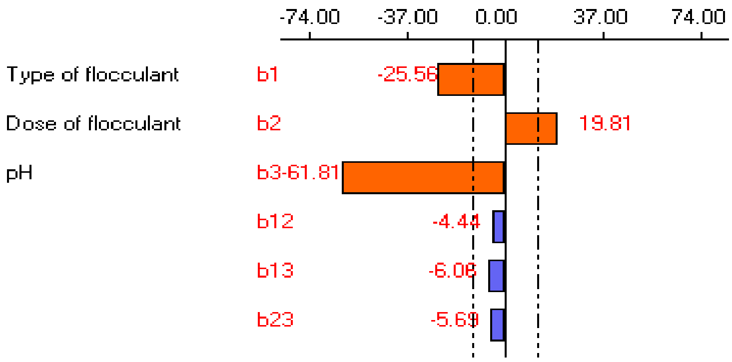

Figure 6: Study of the effects of the factors (X_i) on the BOD_5

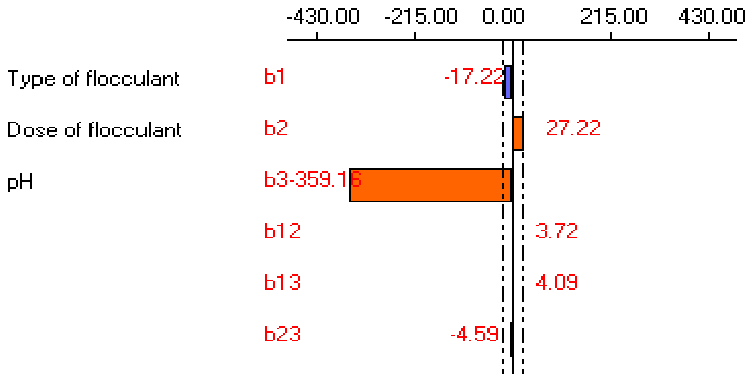

Figure 7: Study of the effects of the factors (X_i) on the COD

From the Figures (5-7) it is noticed that previously studied factors type of flocculant (b_1), dose of flocculant (b_2), pH (b_3), give a significant improvement and effect on the elimination of the responses, thus a greater effect between the interaction (b_{12}, b_{13} and b_{23}).

Results analysis

Analysis of variance

Variance analysis makes it possible to show if the variables used for modelling as a whole have a significant effect on the response.

Table 7 shows the results of the analysis of variance, significant and the level of confidence of the model obtained.

Table 7. Analysis of the variance of the model obtained.

	Source of variation	Sum of Squares	Degrees of freedom	Average Square	Report	Significance
TSS	Regression	5.30519	6	8.84198	6.7972	**
	Residues	1.17075	9	1.30083		
	Total	6.47594	15			
COD	Regression	8.18654	6	1.36442	1.1666	40.1%
	Residues	1.05259	9	1.16955		
	Total	1.87125	15			
BOD_5	Regression	7.92889	6	1.32148	28.0103	***
	Residues	4.24606	9	4.71785		
	Total	8.35349	15			

The results presented in Table 7 indicate that the main effect of the regression is significant since the probability of the importance of the p-value risk is less than 5%, so the model is statistically significant, especially since it has a higher level of confidence [28].

Statistical analysis of the results

In order to judge the quality of the chosen model, it was limited only to using the multiple linear correlation coefficient R^2. It is well known that this coefficient must be handled with care. It is, therefore, more prudent to accompany it in practice by calculating another coefficient such as the adjusted multiple linear correlation coefficient R^{2a} [29-30] Table 8 presents the description coefficient of quality of the different models obtained.

Table 8. Estimates and statistics of the coefficients of the model applied.

	TSS (mg/L)	BOD$_5$(mg O2/L)	COD(mg O2/L)
Standard deviation of response	10.630	21.721	37.581
R^2	0.974	0.949	0.994
R^{2a}	0.970	0.915	0.990
R^2pred	0.962	0.839	0.981
PRESS	4657.680	13419.654	40173.086
Number of degrees of freedom	9	9	9
PRESS = Predicted Residual Sum of Squares			

From the results presented in the Table 8 due to the estimation and the statistics of the coefficients of the postulated models, it was observed that all answers of the three models obtained have a satisfactory descriptive quality because their correlation coefficients (R^2 = 0.974, 0.949 and 0.994) and coefficients of determination (R^{2a} = 0.970, 0.915 and 0.990) have values closer to1.

Statistical analysis of residues

To confirm that the model describes well the variations of the responses, it is necessary to ensure that, locally, the residues are not abnormally high. The normality of the distribution of residues is an important assumption of the least squares method. Given the number of N tests presented in experimental design, Henry's graphical method is generally used as in Figures 8-10.

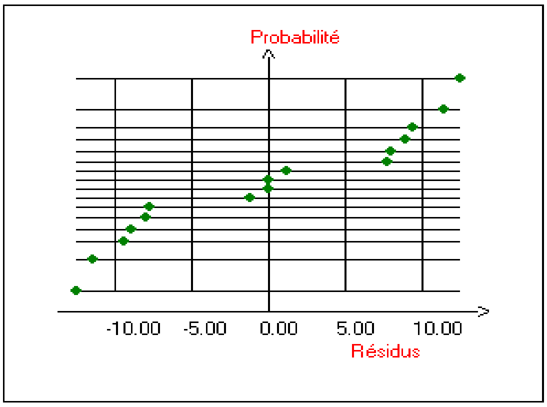

Figure 8. Henry's Right of Response (TSS)

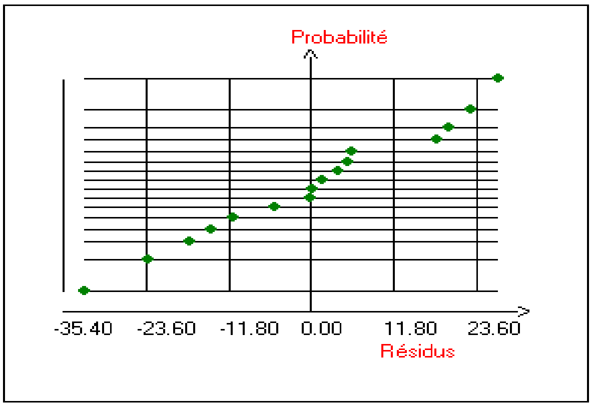

Figure 9. Henry's Right of Response (BOD$_5$)

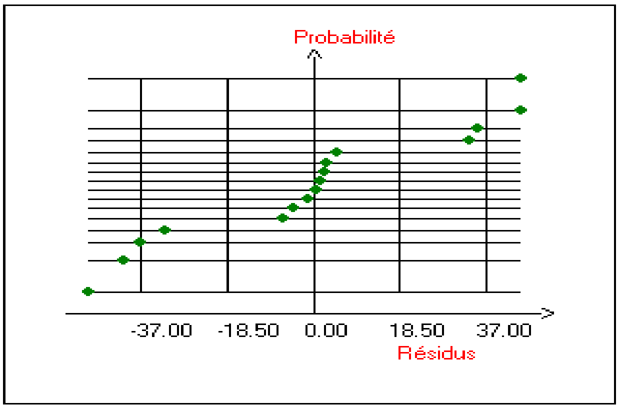

Figure 10. Henry's Right of Response (COD)

According to Figures 8-10, which show the distributions of residues, it is observed that each point on the Henry line has a residual value at one point of the experimental design.

Graphical study of interactions between factors [31]

Interaction pH/dose of flocculant

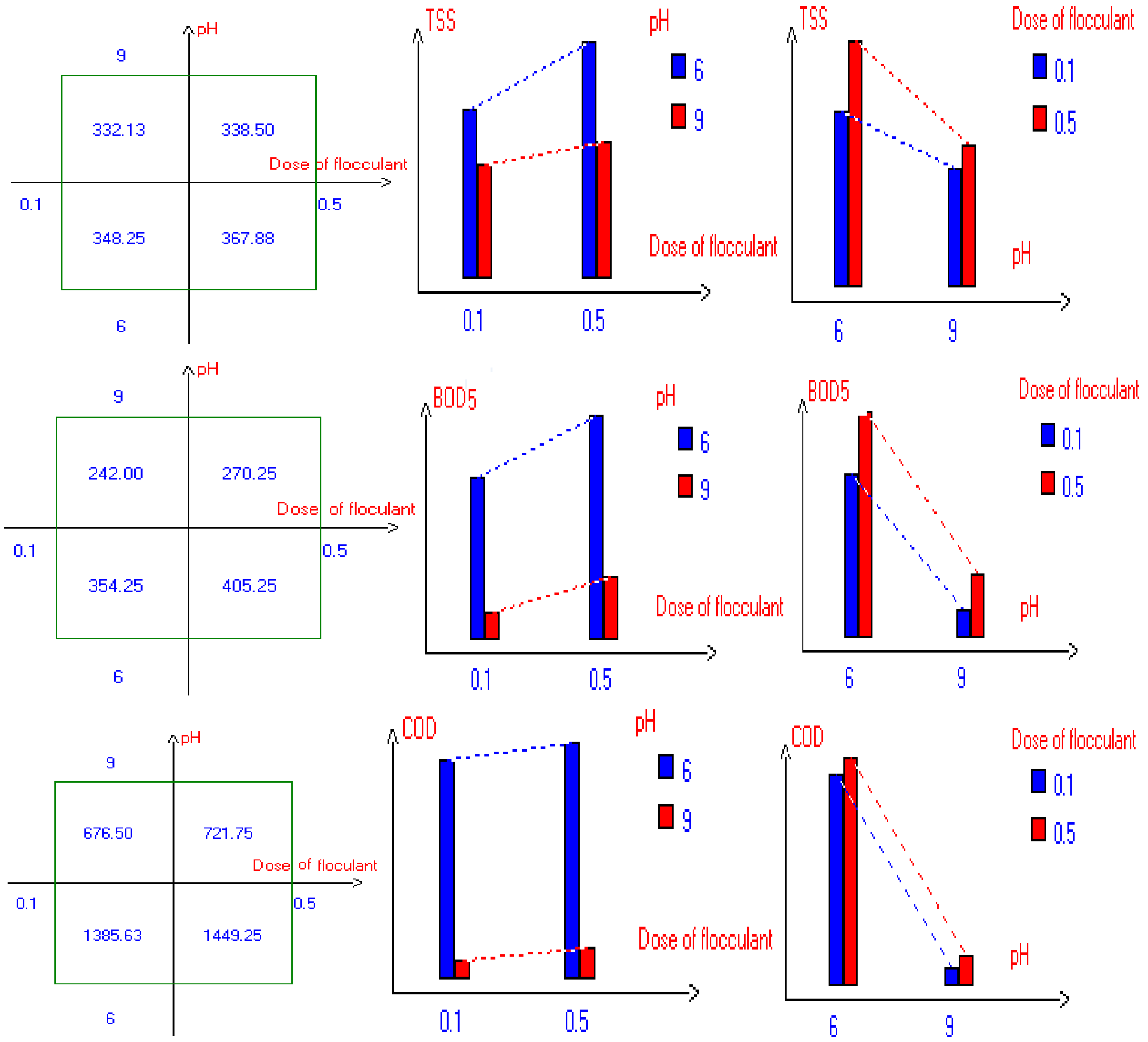

Figure 11. Graphic Study of the interaction pH/dose of flocculant

From Figure 11 it can notice that the interaction of two factors (pH and dose of flocculant) has a significant effect on the responses. Since the TSS, BOD_5 and COD decreases when the pH increased from 6 to 9 (TSS increases from 348.25 to 332.13 mg/L, BOD_5 increases from 354.25 to 242 mg O2/L and COD from 1385.63 to 676.50 mg O2/L) and flocculant doses increase from 0.1 to 0.5 g/L (TSS increases from 338.50 to 332.13 mg/L, BOD_5 increases from 270.25 to 242 mg O2/L and COD from 721.75 to 676.50 mg O2/L).

Interaction pH/type of flocculant

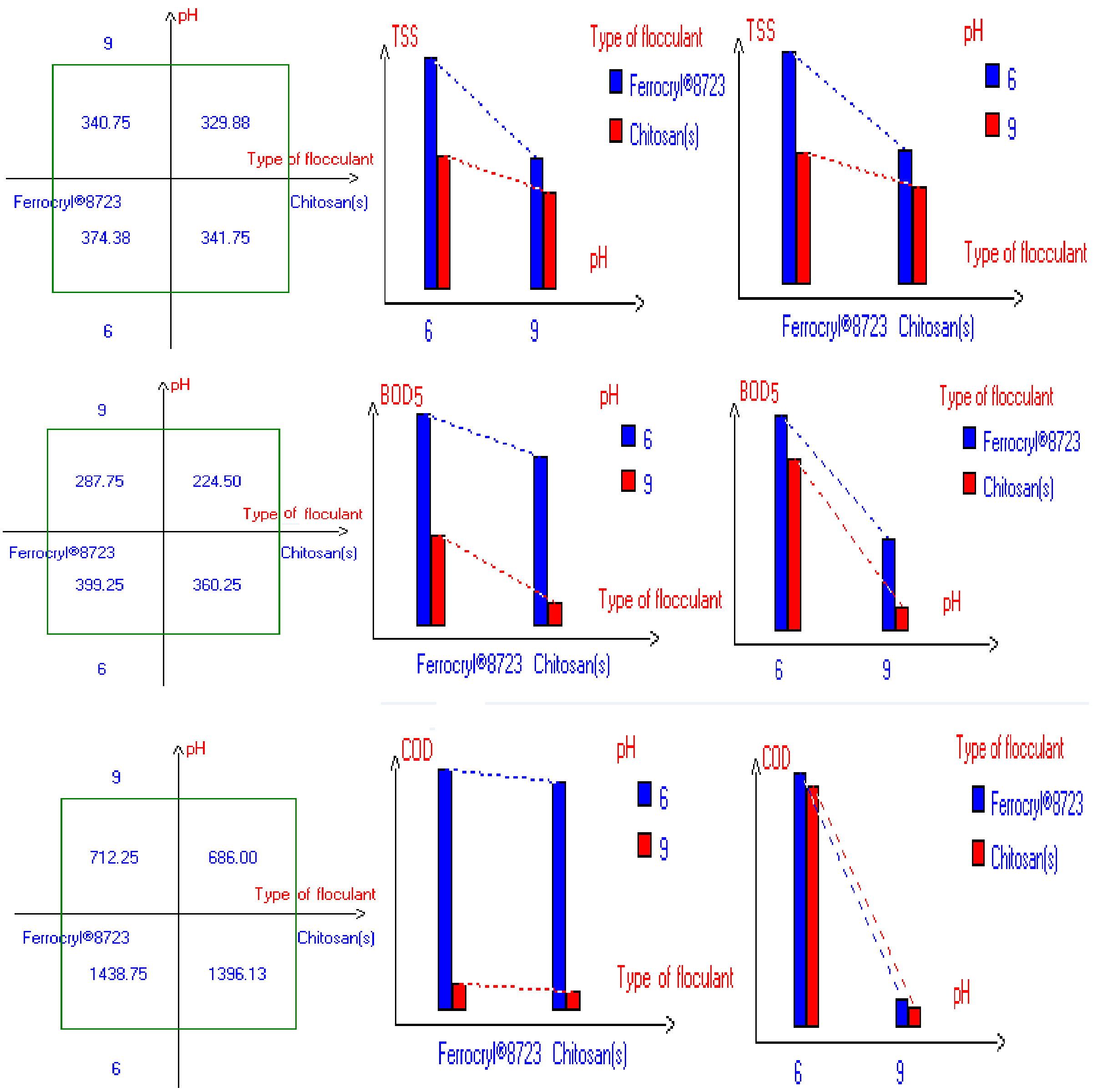

Figure 12. Graphic Study of the interaction pH/type of flocculant

From Figure 12 it can notice that the interaction of two factors (pH and type of flocculant) has a significant effect on TSS, BOD_5 and COD. The content of these latter factors are decreased when the pH increases (TSS goes from 341.75 to 329.88 mg/L, BOD_5 goes from 360.25 to 224.50 mg O2/L and COD goes from 1396.13 to 686 mg O2/L) and the best type of flocculant is chitosan(s) in this case the TSS goes from 340.75 to 329.88 mg/L, the BOD_5 goes from 287.75 to 224.50 mg O2/L, and the COD goes from 712.25 to 686 mg O2/L).

Interaction dose of flocculant/type of flocculant

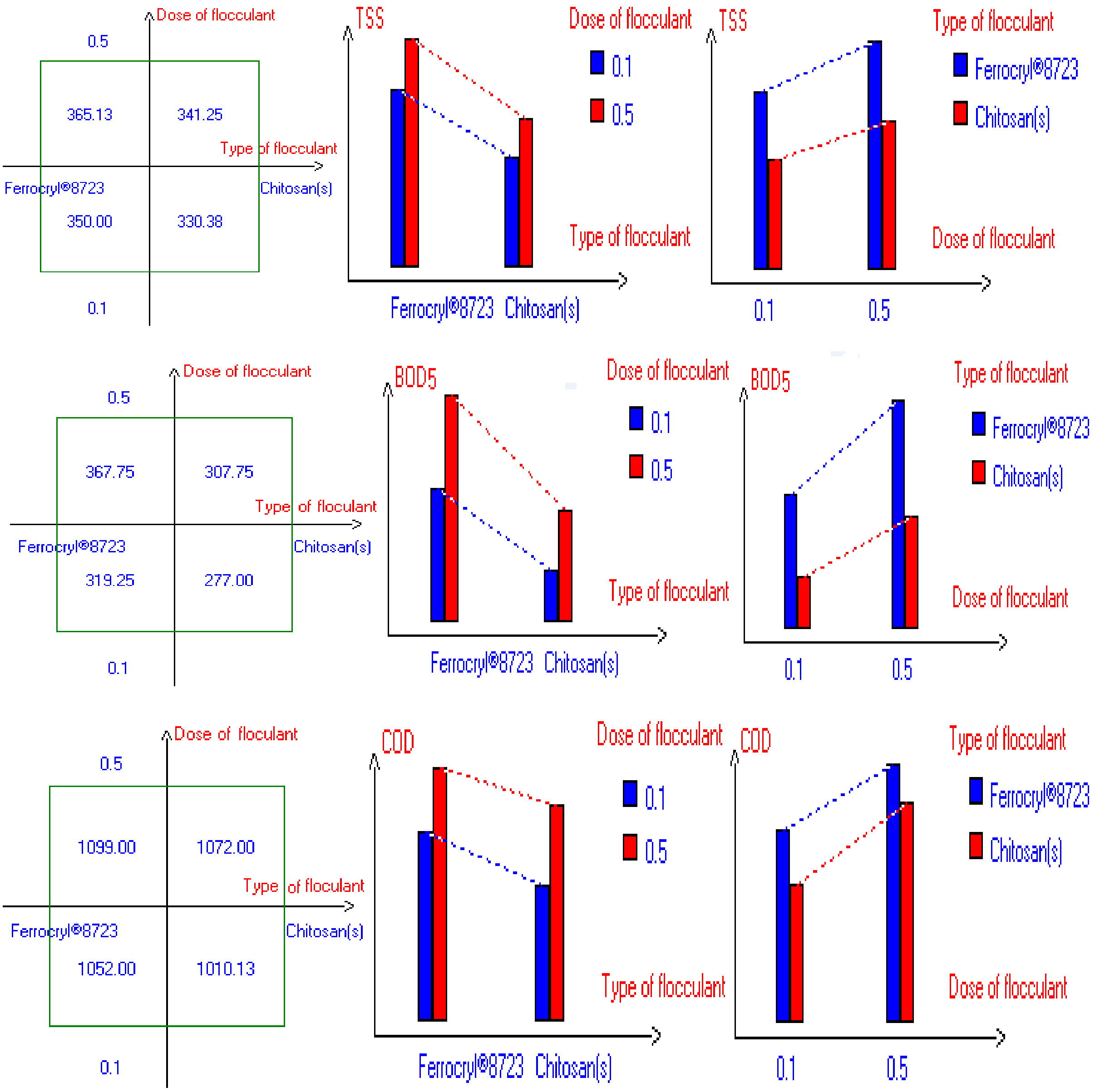

Figure 13. Graphic Study of the interaction dose of flocculant/type of flocculant

From Figure 13 it can notice that the interaction of two factors (type of flocculant and dose of flocculant) has a significant effect on the responses. These last factors decrease when flocculant doses are of 0.2 g/L (TSS increases from 341.25 to 330.38 mg/L, BOD_5 increases from 307.75 to 277 mg O2/L and COD increase from 1072 to 1010.13 mg O2/L) and flocculant of chitosan(s) type (TSS increases fr mg O2/L om 350 at 330.38 mg/L, BOD_5 increases from 319.25 to 277 mg O2/L and COD increases from 1052 to 1010.13).

At the end of this section, we extracted the optimal conditions, which will be necessary to have a maximum reduction of the TSS, BOD_5 and COD on the one hand and the economic and environmental requests on the other hand. Table 9 extracts the optimal conditions.

Table 9. The optimal conditions.

Factor name	type of flocculant(X_1)	dose of flocculant(X_2)	pH(X_3)
Content	chitosan(s)	0.2	9

Search for the optimum

The terms are easily calculated by substituting the data values in the expressions for the least squares which estimates the coefficients (Table 6). The mathematical models adapted to the answers are written in equation (3-5):

TSS: $346.688-10.875X_1+6.500X_2-11.375X_3-1.063X_1X_2+5.438X_1X_3-3.313X_2X_3$ (3)

COD: $1058.281-17.219X_1+27.219X_2-359.156X_3+3.719X_1X_2+4.094X_1X_3-4.594X_2X_3$ (4)

BOD_5: $317.938-25.563X_1+19.813X_2-61.813X_3-4.438X_1X_2-6.063X_1X_3-5.688X_2X_3$ (5)

Selected mathematical models

From equations (3-5), it is possible to calculate the estimated value of dependent response ($\hat{Y}$) and the corresponding residual values as in equation 6.

$$\varepsilon = Yi - \hat{Y} \quad (6)$$

From Table 6, the three mathematical models selected are as follows (7-9):

TSS: $346.688-10.875X_1+6.500X_2-11.375X_3$ (7)

COD: $1058.281+27.219X_2-359.156X_3$ (8)

BOD_5: $317.938-25.563X_1 +19.813X_2-61.813X_3$ (9)

From equations (7-9), it is found that the responses calculated by the three models selected are adequate to the results found experimentally.

Validation of the model

The model validation is to ensure that the responses calculated (predicted response by model) for experimental variation field are roughly the same as the measured responses. Table 10 gathers the experimental results and the results calculated using the NEMRODW software.

Table 10. Comparison between experimental results and values calculated from the model.

	TSS			BOD_5			COD		
N° Exp	**Yexp**	**Ycalc**	**Residue**	**Yexp**	**Ycalc**	**Residue**	**Yexp**	**Ycalc**	**Residue**
1	375.00	363.50	11.50	352.00	369.31	-17.31	1415.00	1410.65	4.35
2	341.00	333.00	8.00	316.00	339.18	-23.18	1375.00	1360.59	14.41
3	393.00	385.25	7.75	397.00	429.18	-32.18	1460.00	1466.84	-6.84
4	363.00	350.50	12.50	367.00	381.31	-14.31	1442.00	1431.65	10.35
5	346.00	336.50	9.50	258.00	269.18	-11.18	694.00	693.34	0.65
6	329.00	327.75	1.25	215.00	214.81	0.18	662.00	659.65	2.34
7	354.00	345.00	9.00	310.00	306.31	3.68	730.00	731.15	-1.15
8	332.00	332.00	00	234.00	234.18	-0.18	715.00	712.34	2.65
9	352.00	363.50	-11.50	392.00	369.31	22.68	1389.64	1410.65	-21.01
10	325.00	333.00	-8.00	357.00	339.18	17.81	1342.50	1360.59	-18.59
11	377.50	385.25	-7.75	456.00	429.18	26.81	1457.00	1466.84	-9.84
12	338.00	350.50	12.50	401.00	381.31	19.68	1420.00	1431.65	-11.65
13	327.00	336.50	-9.50	275.00	269.18	5.81	689.00	693.34	-4.34
14	326.50	327.75	-1.25	220.00	214.81	5.18	661.00	659.65	1.34
15	336.00	345.00	-9.00	308.00	306.31	1.68	736.00	731.15	4.84
16	332.00	332.00	0.00	229.00	234.18	-5.18	706.00	712.34	-6.34
exp : experimental calc : calculated Yexp - Ycalc = Residue									

Correlation of theoretical and experimental results

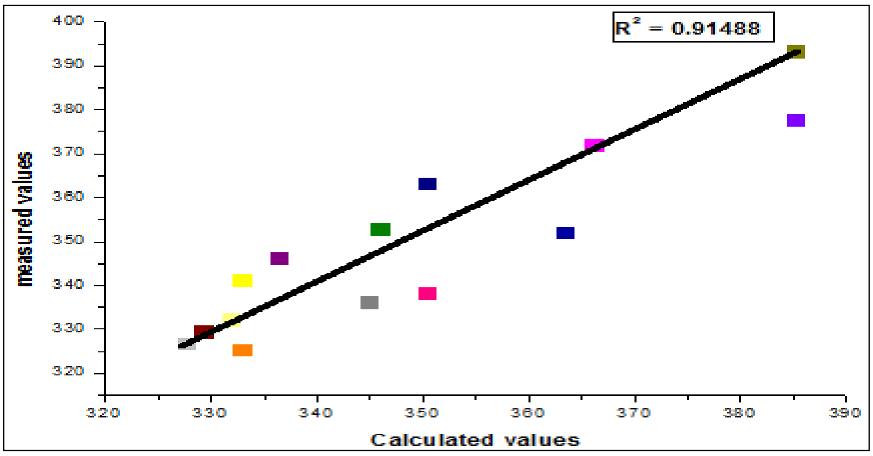

Figure 14. Observed values according to the calculated values (TSS)

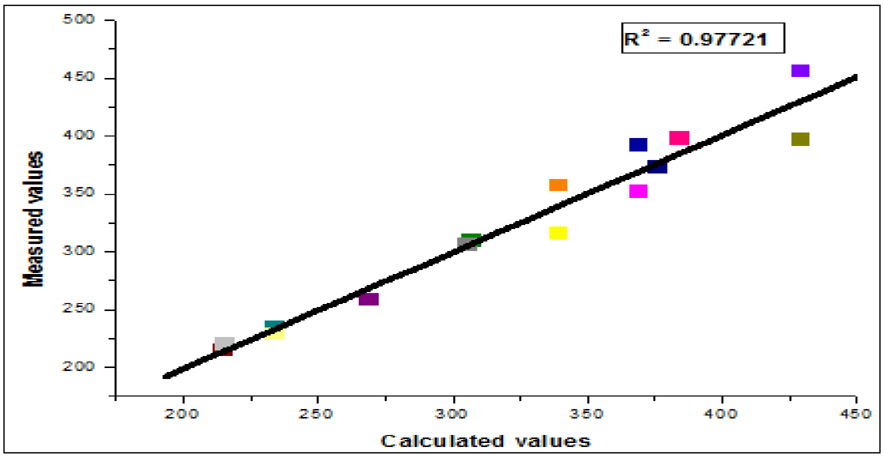

Figure 15. Observed values as a function of calculated values (BOD_5)

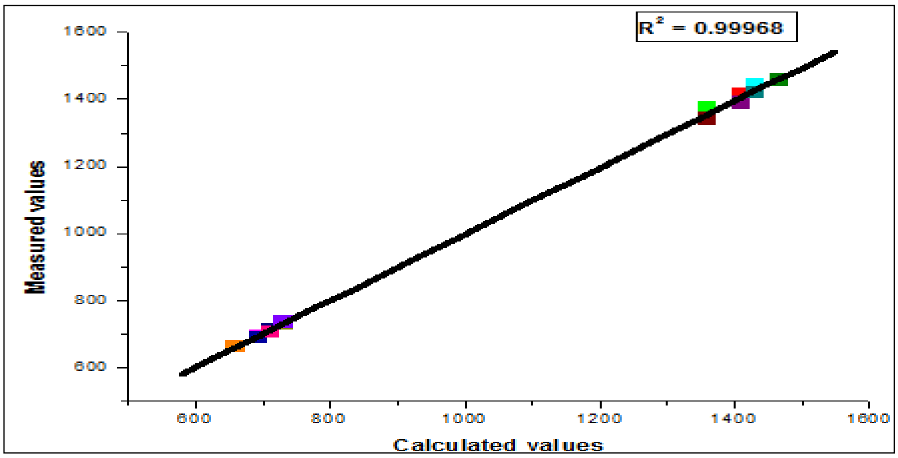

Figure 16. Observed values versus calculated values (COD)

According to Figures 14-16, which illustrate the correlations of the experimental and modelled results, it was found that the theoretical results coincide with the experimental results. This made possible to say that the three models obtained are adequate for our study.

At the end of this work, it was realized a test, which considered the optimum operating conditions. The coordinates were: X_1 = chitosan(s), X_2 = 0.2 g/L and X_3 = 9. Table 11 displays the results of the predicted and experimental values.

Table 11. Predicted and experimental values for the optimum test points.

Response	TSS (mg/L)		BOD_5 (mg O2/L)		COD (mg O2/L)	
Optimum conditions	PR	ER	PR	ER	PR	ER
X_1= chitosan(s) X_2 = 0.2 X_3 = 9	332.13	329.98	224.50	230.26	676.50	679.17
PR: Predicted response ER: Experimental response						

The mentioned results in Table 11 show that there is no significant difference between the experimental and predicted responses, which show that the approach used in this study gave us satisfactory results.

Conclusion

In this work, we studied the modelling and the optimization of physical-chemical operating variables or operating factors (TSS, BOD_5 and COD) by the methodology of the experimental design in order to find the mathematical model which allowed us to predict the results obtained physical-chemical values of selected operating parameters. Through the optimization studies, it was found that the results of the responses calculated by the three modules selected are close to those found by experimentation.

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