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Optimization of the coagulation / flocculation of wastewater from oil refineries use of Response Surface Methodology

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Abstract

Spatial variation the degree of contamination in wastewater treatment plant of the refinery company SAMIR can create a fluctuation over time and therefore resulting in a negative effect on the biomass of the biological basin and the coagulation flocculation and subsequently poor degradation of pollutants. Optimization of coagulation flocculation process is necessary to improve the processing performance of the treatment plant. This study examines the evaluation and optimization of the physicochemical treatment by coagulation flocculation of wastewater from the company SAMIR, in the perspective of a compromise between efficiency and operational cost. The purpose of using the experimental design methodology and central composite response surface. The results showed that the best regression coefficients (R2) were obtained for the results showed that, the best regression coefficients (R2) were obtained for turbidity, DCO, BOD5, HC and Phenol, reaching values of 0.96, 0.95, 0.92, 0.92 and 0.95, respectively. Finally, the optimum values and resultants obtained were pH=6, 384 mg/ L of coagulant 14 mg / L of flocculant and , 78.52 % , 80.47% , 85.23% , 77.07 % and 75.75 % of Turbidity, COD, BOD5 , HC and Phenol removal, respectively

Keywords: Biological basin, coagulation/flocculation, Wastewater, Company SAMIR, Central composite, Regression coefficients.

1. Introduction

Wastewater of refineries and petrochemical plants belong to the ranks of industrial effluents mixed characteristics [1]. These waters contain high amounts of crude products of oil products, polycyclic and aromatic hydrocarbon, phenols, metal derivatives, surface active substances, sulfides, naphthalene acids and other chemical product [2]. The discharge of wastewater contains pollutants in the receiving environment without any treatment. This issue is a matter of increasing concern given the side effects that pollutants can cause and environmental and health problems [3]. Petroleum hydrocarbons pollutions, ranging from soil, ground water to marine environment, become an inevitable problem in modern life [4]. Many processing techniques have been tested in the fight against pollution in petroleum refinery effluents, only economically acceptable methods of low cost are solicited. A wide variety of physicochemical processes has been proposed (coagulation/flocculation, adsorption, photocatalysis, electrocoagulation, membrane filtration) [5].

In this case, the most used method is the physico-chemical treatment by coagulation-flocculation from where this method is applied directly to the raw water; thereby it is, with oxidation, one of the most important in water treatment processes [6]. The economic context makes inappropriate effective pathways such as activated sludge

treatment facilities, including investments and operating costs are prohibitive for the small scale sector. The need for a treatment solution, including the case of legislative pressure is necessary [7].
Many authors have used the response surface methodology and optimization to improve the process of coagulation/flocculation of wastewater from different origins [8]; [9]. These authors agree that the type and dosage of coagulant and flocculant reagents are critical to the success of the process of coagulation/flocculation.
The purpose of this study is to evaluate and optimize the physico-chemical treatment by coagulation flocculation of wastewater from the company SAMIR, from the perspective of a compromise between efficiency and operational cost. This work is a statistical analysis of experimental data to improve a real industrial process which is generally used to realize optimal conditions.

2. Materials and methods

2.1. Overview of the study area

Moroccan Refining Industry Company (SAMIR) extends over an area of 200 hectares to the west of the city Mohammedia near to the port, ideally situated with the objective to facilitate the reception of imported crude oil. It is connected by a network of oil pipeline port (remote 5km) and the storage depot distribution companies and the Central ONE (Office National electricity).

2.2. Sample collection

The sample was taken downstream of the primary clarifier (Fig.2), the upper catchment of coagulation/flocculation, the Step of wastewater Company SAMIR. Typical characteristics of this sample are shown in Table 1

Figure 2: SAMIR wastewater treatment station

Table 1: Physicochemical characterization of the sample

Settings	Units	Wastewater downstream primary clarifier
HC	mg/L	55
COD	mg O_2/L	1200
BOD_5	mg/L	380
COD/BOD_5	-----	3.15
NO_3^-	mg/L	22
pH	-----	7.06
Turbidity	NTU	420
Phenols	mg/L	43
TSS	mg/L	550

2.3. Characteristics of coagulation-flocculation

In this study, the Ferric chloride $FeCl_3$ (40 %) [10] Was among the coagulants most frequently used by the company SAMIR. The characteristics of this coagulant are shown in Table 2:

Table 2: Characteristics of Coagulant ($FeCl_3$ (40 %) and Flocculant (Polymers)

Appearance Milky	Value coagulant FeCl3 (40 %)	Value (flocculant = Polymers)
Aspect	Liquid	Liquid
Color	Brown	Off-White
Odour	Pungent	Neutral
Density Relative	1.42	1.03 g / cm^3
pH	<1	(20 ° C, 10 g / l): 6

Most flocculants [11] used by the company SAMIR in the physico-chemical treatment. In this study the flocculant used are synthetic polymers. The characteristics of this flocculant are given in table 2. The tested coagulation/flocculation have been realized in the laboratory at room temperature using a jar test ban (jar test flocculator FC-6S Velp scientifica) with six stirring blades connected to a motor that is adjustable .

3. Analytical Methods

The pH is a parameter that affects the process of coagulation/flocculation. It is advisable to control this parameter. According to the characteristics of water, there is an optimal pH for the best coagulation [12]. The initial pH of refining wastewater was adjusted by adding NaOH or H2SO4 to a desired value in the range of from 5 to 7.68. Dosage of coagulant ($FeCl_3$ of 40%) varied between 249 - 518.4 mg / L, whereas doses of the flocculant (Polymer of 1%) ranged between 8.9 to 19.04 mg / L.

Sixteen trials were performed. After addition of the coagulant, the wastewaters obtained downstream of the primary clarifier was stirred at 170 rpm for 10 min (fast stirring), thereby to ensure a good dispersion and homogenization of the reactants and a good chemical destabilization the colloids. The flocculant was then added and stirred at 30 rpm for 20 min (slow agitation). After stirring, the Samples were then poured into Imhoff cones where they undergo settling for two hours.

The samples was then obtained from the supernatant siphoned using a pipette to avoid disturbing the floc formed to complies with analyses [Turbidity [13] (Determined by turbidimeter Model HACH 2100N),Color (Determined using a UV/Visible spectrophotometer Model 7800 UV/VIS), COD (Determined by potassium dichromate titrimetric to standard method AFNOR [16]), BOD_5 [12] (Determined by BOD meter) ,Hydrocarbon (Analyzed by IR after extraction with tetrachlorethylene , this parameter analyzed by method AFNOUR [14] , Phenol (The principle of this assay is adapted by Singleton and Ross (1965) with the Folin - Ciocalteu [15]). The percentage of COD, BOD_5, Hydrocarbon, phenol and turbidity were obtained using to the given formula below:

$$\textbf{Reduction}\ \% = \left(\mathbf{1} - \frac{\mathbf{C}}{\mathbf{C0}}\right) \times \mathbf{100} \quad (1)$$

Were C0 and C are the initial and final COD values, BOD5 values , Hydrocarbon values ,Phenol values or turbidity values of wastewaters obtained downstream of the primary clarifier , after treatment by coagulation ($FeCl_3$ of 40%) and flocculation (polymer of 1%) , respectively.

4. Design of Experiment

Essentially, an optimization process involves three main steps that are the coefficients in a mathematical model, the statistically designed experiments and the checking adequacy of the model [16].

Central Composite Design (CCD, rotatable) and Response Surface Methodology (RSM) were used to optimize extraction parameters [17]. The CCD consists of a 2n factorial or fraction (coded to the usual ±1 notation) augmented by 2n axial points (± α, 0... 0), (0, ± α, 0,..,0), (0, 0,..., ± α), and n_c centre points (0, 0,.. ,0) [16]. The value of α for rotatability depends on the number of experimental runs in the factorial portion of the central composite design, which is given in Eq (2):

$$\alpha = [\text{number of factorial runs}]1/4 \qquad (2)$$

If the factorial is a full factorial, then : α= [2K] 1/4
Table 3 illustrates some typical value of α as a function of the number of factors.

Table 3: Determining α for Rotatability

Number of Factors	Factorial Portion	Scaled Value for α Relative to ± 1
2	22	22/4=1.414
3	23	23/4=1.682
4	23	24/4=2.000
5	25-1	24/4=2.000
5	25	25/4=2.378
6	26-1	25/4=2.378
6	26	26/4=2.828

In this study, three variables X_1 (pH), X_2 (coagulant dosage) and X_3 (flocculent dosage) were used, so reponses were Turbidity removal (Y_{Tub}), COD removal (Y_{COD}), BOD_5 removal (Y_{BOD}), Hydrocarbon removal (Y_{HC}) and Phenol removal (Y_{Phenol}) of the wastewaters downstream primary clarifier. Each response was used to develop an empirical model that correlated the response to the coagulation processes activated variables using a second-degree polynomial equation as given by Eq. (3) [18] :

$$\hat{Y} = \beta o + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_{12} + \beta_{22} X_{22} + \beta_{33} X_{32} \quad (3)$$

Where Y is the predicted response, β_o the constant coefficient, β_i the linear coefficients, β_{ij} the cross-product coefficients and βii the quadratic coefficients. In this study the software “JMP 10” (Version 10) was used for data analysis and graph plotting

5. Results and discussion

5.1 .Development of the regression model equation

Test experiments were carried out to screen to allow parameters and to determine the experimental domain.
From these experiments, the effects of initial pH of the wastewater downstream primary clarifier (X_1), coagulant dosage in ml/L (X_2) and flocculant dosage in ml/L were investigated on five responses: Turbidity removal, COD removal, BOD_5 removal, Hydrocarbon removal and Phenol removal. The parameter levels are shown in Table 4. The experimental design matrix, the corresponding experimental parameters and response value were shown in Table 5. JMP 10 computer software was used to model and optimize the experimental results.

* The coded values Xj = ± 1 are obtained by equation: Xj = (x j- xj)/Δ

Table 4: Independent variables process and their corresponding levels

Independent variables (X_j)	Unit	Coded variables X_1,X_2,X_3*				
		a	-	0	+	A
X_1=pH	-	4.32	5	6	7	7.68
X_2= Coagulant Dosage	mg/L	249.6	304	384	464	518.4
X_3=Flocculant dosage	mg/L	8.96	11	14	17	19.04

The results of the experimental design for wastewater downstream primary clarifier removal are show in Table 5:

Table 5: Experimental design and results for wastewater downstream primary clarifier removal

Configuration	pH	Coagulant	Polymer	Turbidity %	COD %	BOD_5 %	HC %	Phenol %
−−−	5	304	11	57.71	45	62.59	55.81	44.18
−−+	5	304	17	65.21	32	60.26	49.81	37.2
−+−	5	464	11	60	49	65.22	56.54	51.16
−++	5	464	17	73.14	43	62.36	50.9	41.86
+−−	7	304	11	63.4	52	65.63	62.72	53.48
+−+	7	304	17	64.07	65	75.26	70	63.25
++−	7	464	11	82.73	56	68.27	63.09	58.13
+++	7	464	17	81.1	85	87.06	80.18	79.06
a00	4.31	384	14	44.69	28	50.97	40	30.23
A00	7.68	384	14	50.96	60	70.79	66	60.46
0a0	6	249.45	14	80.9	30	55.26	45.54	34.88
0A0	6	518.54	14	87.5	75	85.22	75.09	72.09
00a	6	384	8.954	79.75	62	75.22	69.45	61.62
00A	6	384	19.04	80.88	73	79.15	73.45	69.76
000	6	384	14	77.19	80	85.22	76.36	74.41
000	6	384	14	79.5	81	85.22	77.81	76.74

Table 6: The regression coefficient R^2 and adjusted R^2

	Turbidity removal (%)	COD removal (%)	BOD_5 removal (%)	Hydrocarbon removal (%)	Phenol removal (%)
R^2	0.96	0.95	0.92	0.92	0.95
R^2adj	0.88897	0.874973	0.791429	0.796012	0.86796

The coefficients of the model equation which are used to foretell the optimum degree of wastewater downstream primary clarifier are shown below. The R^2 values in this study were relatively high, indicating a good agreement between the model predicted and the experimental values. When R^2 and adjusted R^2 differ dramatically, there is a good chance that insignificant terms have been included in the model [19]; [20]. As shown in Table 6, the two R^2 values were not significantly different.

5.2. Turbidity removal

The regression equation for turbidity removal was obtained as follows:

$$Y = 78.52+ 3.35\ X_1+ 4.22\ X_2 + 1.58\ X_3 -11.23\ (X_1^2) + 1.62\ (X_2^2) + 0.25\ (X_3^2) + 3.26\ (X_1\ X_2) - 2.7\ (X_1\ X_3) + 0.41\ (X_2X_3).$$

The results of experimental values versus predicted values for the Turbidity removal are shown in Fig 3. From this figure we observe that the actual values were distributed near a straight line, denoting that the model fits well with the measured values. [20]. The coefficient of determination R2 is a measure of the global fit of the model. The adjusted coefficient of determination (adj.R^2) is used to compare the models with different numbers of independent variables. [21]. Form this figure we see that with the coefficients of determination (R^2) as 0.96 of turbidity removal. The result for response Turbidity analyzed by analysis of variance ANOVA has been abstracted in Table 7. Data in this table stated that pH, coagulant and pH*pH resulting from ANOVA analysis in terms of defined variables were significant at 95% confidence level, with p-values of regression <0.05 [22]. The comparative study showed that the results of the analysis of variance (ANOVA) obtained are close to the results reported by Taşkın et al (2016), during wastewater treatment tested by the domestic response surface methodology using $FeCl_3$ coagulant, which values high R-squared ($R^2 = 0.93$) models confirm their agreements [23] .The factors influence of the elimination of Turbidity are pH and dosage coagulant. At pH equal to 6, coagulant dosage equal to 384 mg/L and flocculant dosage equal to 14 mg/L there is a high value of percentage removal of Turbidity (78.52 %). (Fig. 3(b)). Vimalashanmugam et al (2012) reported that response surface plots as a function of two factors at a time, maintaining all other factors at fixed levels are more helpful in understanding both the main and the interaction effects of these two factors. Figure 3(c) shows 3D response surface plots for turbidity removal. The best results for turbidity removal were obtained at very high coagulant dosage and at pH near to neutrality [20], as can be observed by the wastewater obtained downstream primary clarifier at dosage flocculent fixed at 14 mg/L.

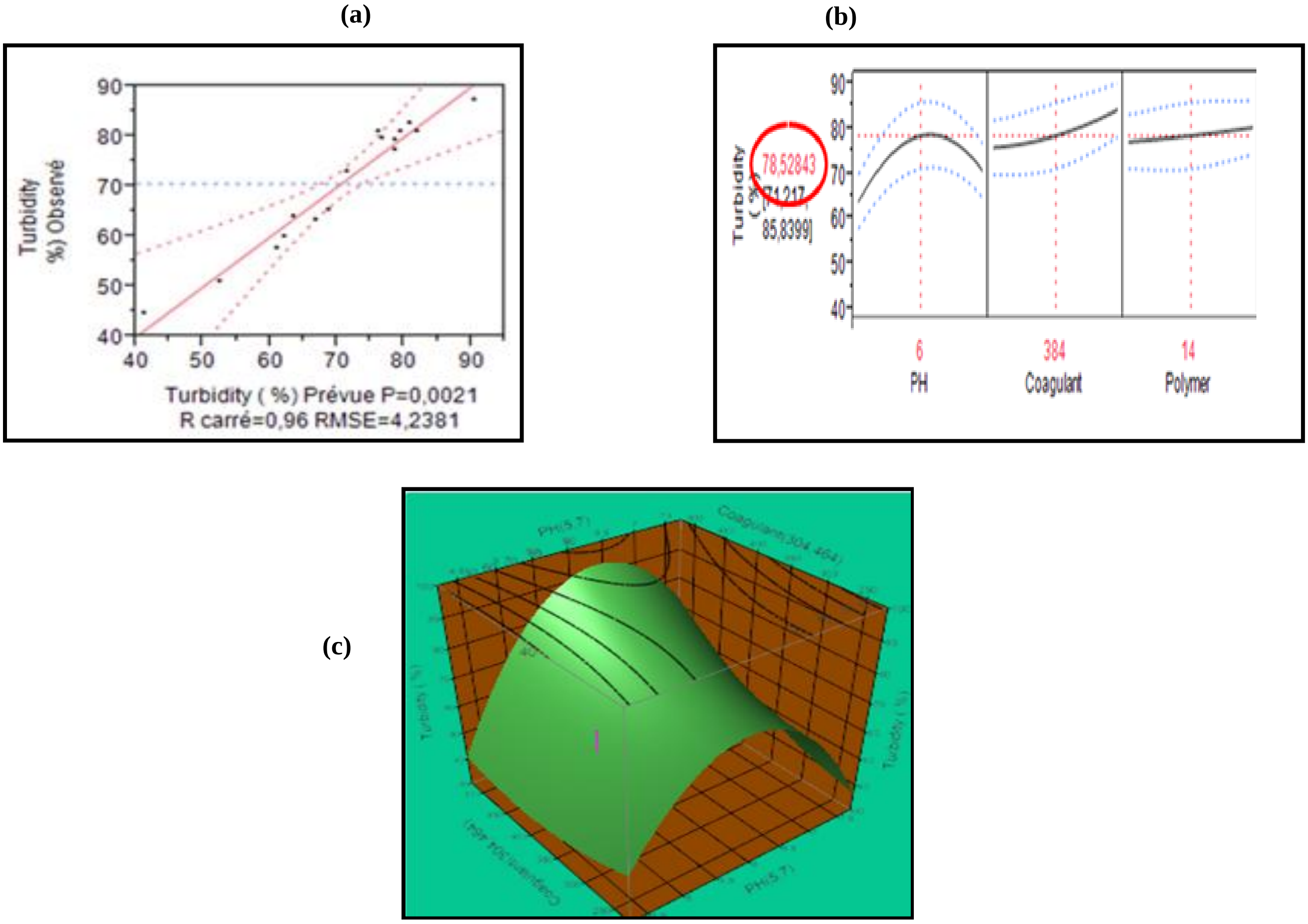


Figure 3: (a) Experimental values versus predicted values for the Turbidity removal model. (b) Profiler for Turbidity removal. (c) Response surface plots for Turbidity removal as a function of pH and coagulant dosage at Polymer dosage equal at 14 mg/L.

Table 7 : ANOVA for Turbidity removal response surface models (JMP10)

Source	Degree of freedrom	Sum of squares	Mean square	Rapport t	P-Value
pH (5.7)	1	153.4945	153.494	8.5456	0.0265*****
Coagulant (304.464)	1	243.6112	243.611	13.5627	0.0103*
Polymer(11.17)	1	34.1012	34.101	1.8985	0.2174
PH*Coagulant	1	85.4124	85.412	4.7552	0.0720
PH*Polymer	1	58.3200	58.320	3.2469	0.1216
Coagulant*Polymer	1	1.3945	1.394	0.0776	0.7899
PH*PH	1	1169.0137	1169.013	65.0830	0.0002*
Coagulant*Coagulant	1	24.5296	24.529	1.3656	0.2869
Polymer*Polymer	1	0.5960	0.596	0.0332	0.8615

*: Significant at the 92% confidence level

-Degrees of freedom: an estimate of the number of independent categories in a particular statistical test or experiment

- Sum of squares: sum of squares is a mathematical approach to determining the dispersion of data points. The sum of squares is used as a mathematical way to find the function which best fits (varies least) from the data.

-Mean square: the mean square of a set of values is the arithmetic mean of the squares of their differences from some given value, namely their second moment about that value.
- p-Value: p value is associated with a test statistic. It is the probability, if the test statistic really were distributed as it would be under the null hypothesis, of observing a test statistic [as extreme as, or more extreme than] the one actually observed.

5.3.COD removal

We obtained the following regression equation (in coded factors) for the COD removal:
$Y = 80.47 + 10.45\ X_1 + 8.39\ X_2 + 3.03\ X3 - 12.84\ (X_1^2) – 9.83\ (X_2^2) – 4.53\ (X_3^2) + 1.12\ (X_1\ X_2) + 7.62\ (X_1\ X_3) + 2.87\ (X_2X_3)$.
The experimental values are distributed relatively close to the straight line. The result for COD response analyzed by ANOVA to assess “the goodness of fit” are shown in Table 8. The values of p > F, unless 0.05 indicates that the model is considered to be statistically significant [24] . As can be observed in this table for the significant terms in the model were pH, Coagulant, pH*Polymer, pH*pH, coagulant*coagulant. Other model terms were not significant. The interaction between pH, coagulant and Polymer for COD removal are shown in Figure 4 (b) ,form this figure we see at pH equal to 6, coagulant dosage equal to 384 mg/L and flocculant dosage equal to 14 mg/L there is a high value of percentage removal of COD (80.47%). Results of these evaluations show that the coagulation/flocculation mechanism determined by pH value and dosage of coagulant. After studying the effect of the independent variables on the response, the levels of the variables that give the optimum response were determined [24]. Thirugnanasambandham et al (2016), studied the performance evaluation of the chemical coagulation process to treat bagasse wastewater by the response surface methodology using the coagulant $FeCl_3$ a good reduction of COD has been realized (67 %) [25] .Figure 4 (c) , shows 3D response surface plots for COD removal. The best resultant for COD removal were obtained at high coagulant dosage and at pH near to neutrality as can be observed by the wastewater downstream primary clarifier at flocculant dosage fixed at 14 mg/L. The optimum removal point (82.21 %) obtained at around coagulant dose of 450 mg/L and initial pH 7.20. Lower yields of elimination are observed when one moves away from that point, which means that an increase or decrease in one of the tested variables is desired [20].

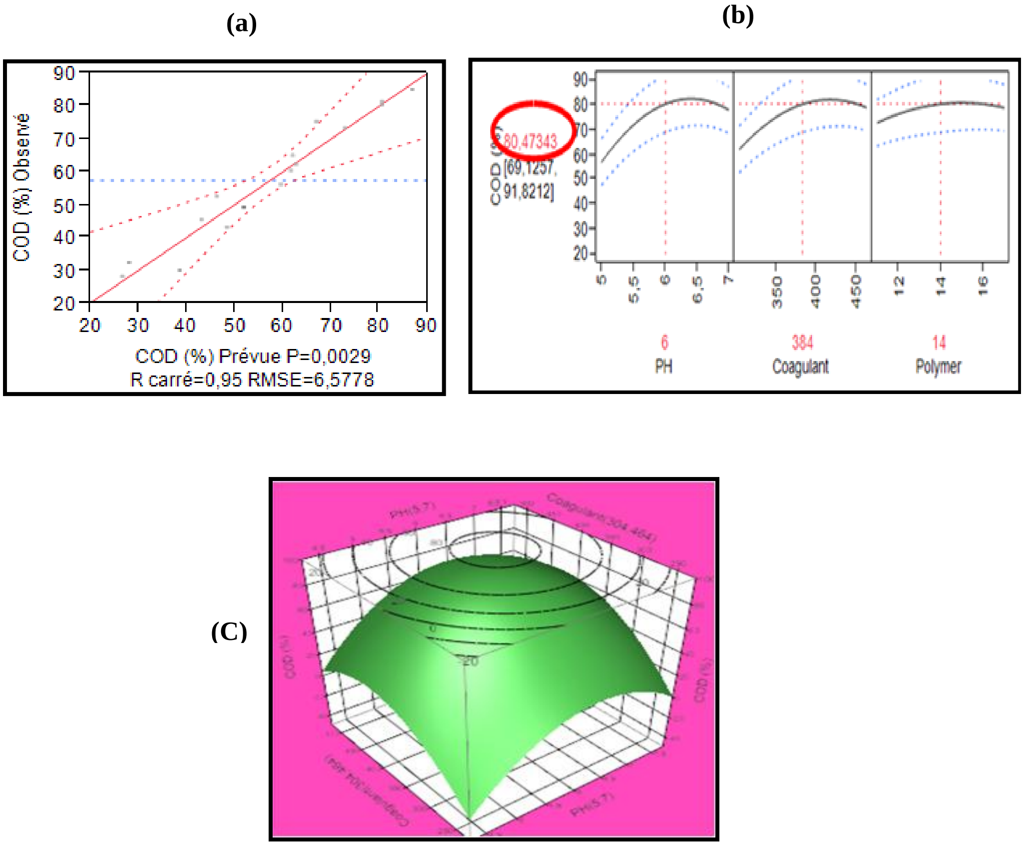


Figure 4: (a) Experimental values versus predicted values for the DCO removal model. (b) Profiler for DCO removal. (c) Response surface plots for DCO removal as a function of pH and coagulant dosage at Polymer

Table 8: ANOVA for COD removal response surface models (JMP10)

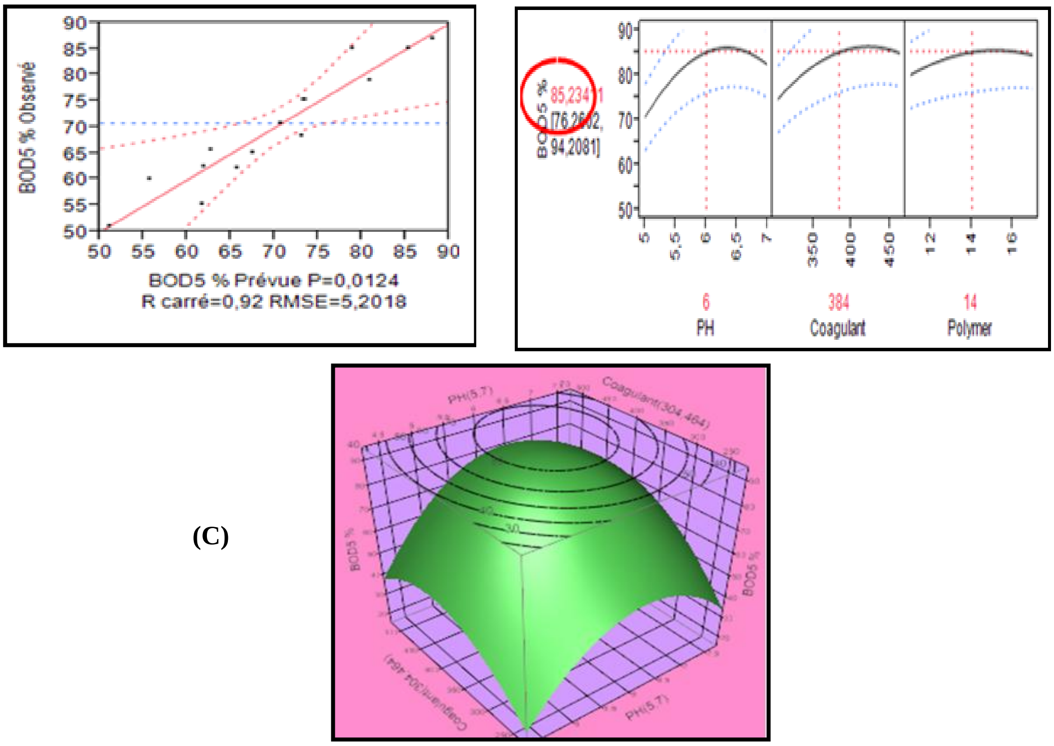
Source	Degree of freedrom	Sum of squares	Mean square	Rapport t	P-Value
pH (5.7)	1	1493.5212	1493.521	34.5183	0.0011*
Coagulant (304.464)	1	963.0078	963.008	22.2571	0.0033*
Polymer(11.17)	1	126.1071	126.107	2.9146	0.1387
PH*Coagulant	1	10.1250	10.125	0.2340	0.6457
PH*Polymer	1	465.1250	465.125	10.7500	0.0168*
Coagulant*Polymer	1	66.1250	66.125	1.5283	0.2626
PH*PH	1	1527.4682	1527.468	35.3029	0.0010*
Coagulant*Coagulant	1	896.1572	896.157	20.7120	0.0039
Polymer*Polymer	1	190.2801	190.280	4.3978	0.0808

5.4.BOD_5 removal

We obtained the following regression equation (in coded factors) for the BOD5 removal

$Y = 85.23 + 5.79X_1 + 5.09\ X_2 + 2.18\ X_3 - 8.63\ (X_1^2) - 5.33\ (X_2^2) - 2.87\ (X_3^2) + 1.21\ (X_1\ X_2) + 4.20\ (X_1\ X_3) + 1.07\ (X_2X_3)$.

The results from the central composite experimental design (CCD) and response surface model (RSM) in the form of analysis of variance for BOD_5 are shown in Table 9. When the p-value derived from ANOVA is generally less than 0.05 a statistical significant regression is obtained [26] .As one can see in Table 9, the significant terms in the model were pH , Coagulant, pH*pH and coagulant*coagulant. The factors influencing the removal of BOD_5 are pH and dosage coagulant. Figure 5(b) illustrates profiler for COD removal, form this figure we see at pH equal to 6, coagulant dosage equal to 384 mg/L and Flocculant dosage equal to 14 mg/L there is great value of percentage removal of BOD_5 (85.23%) (Fig. 5(b)). The 3D (Fig. 5(c)) representation of the response on the dose and initial pH upper surface present concentrically closed curves whose centers represent the optimum conditions. Figure 5(c), demonstrate that the optimum removal point (86.47%) obtained at around dose Coagulant 458 mg/L and initial pH 7.5.



(a) **(b)** **(C)**

Figure 5: (a) Experimental values versus predicted values for the BOD_5 removal model. (b) Profiler for BOD5 removal. (c) Response surface plots for BOD_5 removal as a function of pH and coagulant dosage at Polymer dosage equal at 14 mg/L

Table 9: ANOVA for BOD5 removal response surface models (JMP10)

Source	Degree of freedrom	Sum of squares	Mean square	Rapport t	P-Value
pH (5.7)	1	458.41233	458.4123	16.9413	0.0062*
Coagulant (304.464)	1	354.26229	354.2623	13.0923	0.0111*
Polymer(11.17)	1	65.19748	65.1975	2.4095	0.1716
PH*Coagulant	1	11.78551	11.7855	0.4356	0.53338
PH*Polymer	1	141.20401	141.2040	5.2184	0.0624
Coagulant*Polymer	1	9.30961	9.3096	0.3441	0.5789
PH*PH	1	691.49252	691.4925	25.5551	0.0023*
Coagulant*Coagulant	1	263.21287	263.2129	9.7274	0.0206
Polymer*Polymer	1	76.56667	76.5667	2.8296	0.1435

5.5. Hydrocarbon removal

We obtained the following regression equation (in coded factors) for the Hydrocarbon removal
$Y = 77.03 + 7.80\ X_1 + 4.54\ X_2 + 1.42\ \ X_3 - 8.40\ \ (X_1^2) - 5.81\ (X_2^2) - 1.87\ (X_3^2) + 1.09\ (X_1\ X_2) - 4.50\ (X_1\ X_3) + 1.27\ (X_2X_3)$.

Table 10 shows the ANOVA results for Hydrocarbon removal efficiency. Data listed in this table showed that the significant terms in the model were pH, Coagulant, pH*pH and coagulant*coagulant. These analyses as the p-value were lower than 0.05 and the selected variables at a 95% confidence level. [26]

A different way to assess the quality of fit of the model is by plotting the experimental values compared to predicted values for the elimination of Hydrocarbon. As can be seen in Figure 6, the overall model approximately represents the experimental data over the interval studied. The graph shows that the best fit can also be observed by the regression coefficient [20]. We observed in figure 6 (b) profiler for Hydrocarbon removal, from this figure we see at pH equal to 6, coagulant dosage equal to 384 mg/L and flocculant dosage equal to 14 mg/L there is great value of percentage removal of HC (77.03 %).Figure 6 (c) below shows the response surface plots for Hydrocarbon removal as a function of pH and coagulant dosage at flocculent dosage equal 14 mg/L. Form this figure we observed that the optimum Hydrocarbon removal point (80.19%) obtained at around dose 450 mg/L and pH = 6.5

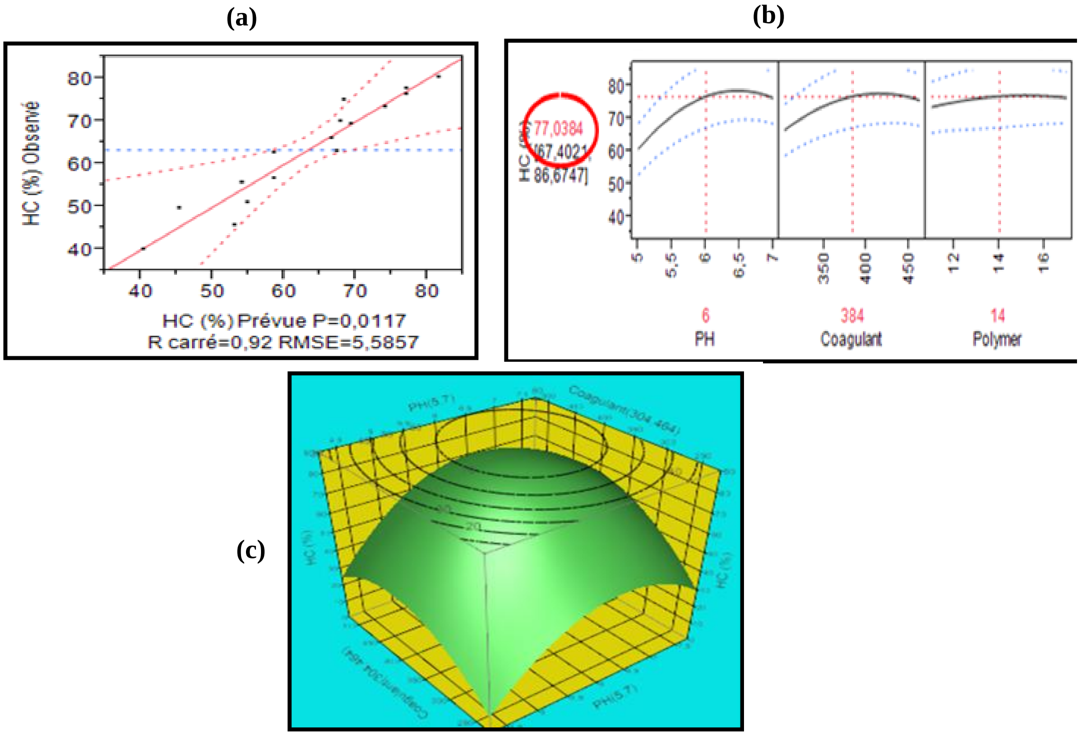


Figure 6: (a) Experimental values versus predicted values for the HC removal model. (b) Profiler for HC removal. (c) Response surface plots for HC removal as a function of pH and coagulant dosage at Polymer dosage equal at 14 mg/L

Table 10: ANOVA for HC removal response surface models

Source	Degree of freedrom	Sum of squares	Mean square	Rapport t	P-Value
pH (5.7)	1	832.96146	832.9615	26.6971	0.0021*
Coagulant (304.464)	1	282.07885	282.0789	9.0409	0.0238*
Polymer(11.17)	1	27.72099	27.7210	0.8885	0.3823
PH*Coagulant	1	9.52661	9.5266	0.3053	0.6005
PH*Polymer	1	162.09001	162.0900	5.1951	0.0629
Coagulant*Polymer	1	12.92861	12.9286	0.4144	0.5436
PH*PH	1	654.11870	654.1187	20.9650	0.0038*
Coagulant*Coagulant	1	313.43108	313.4311	10.0457	0.0193*
Polymer*Polymer	1	32.73530	32.7353	1.0492	0.3452

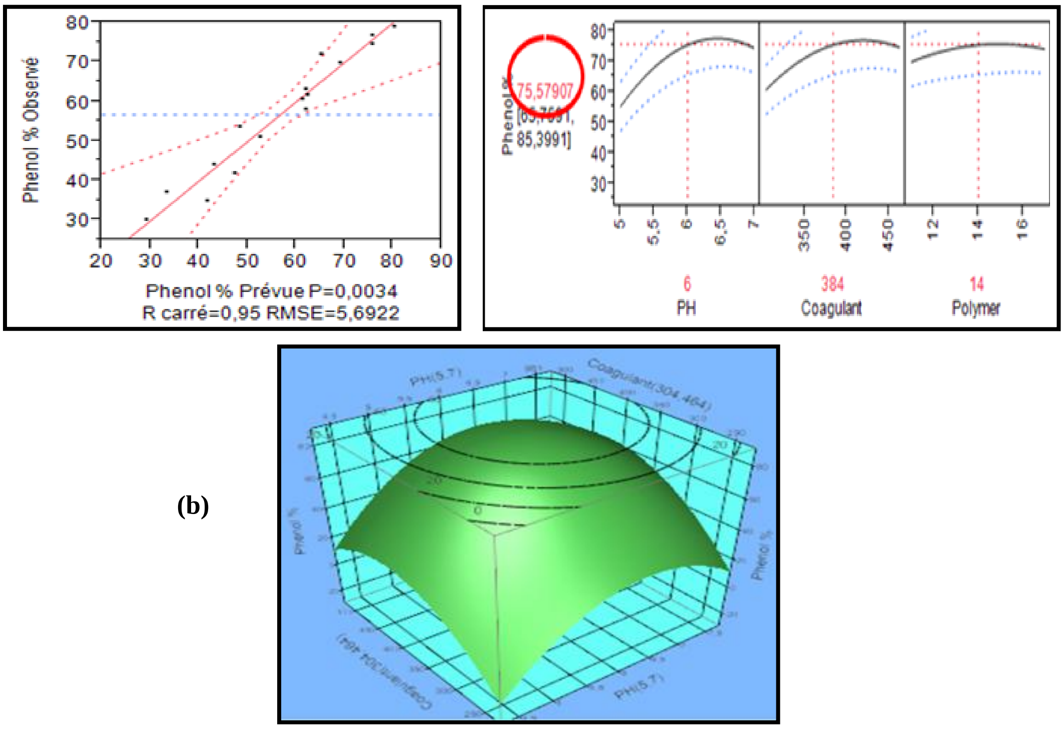
6.6. Phenol removal

We obtained the following regression equation (in coded factors) for the phenol removal
$Y = 75.57 + 9.54\ X_1 + 6.93\ X_2 + 2.05\ \ X_3 - 10.69\ \ (X_1^2) - 7.81\ (X_2^2) - 3.50\ (X_3^2) + 1.10\ (X_1\ X_2) + 5.87\ (X_1\ X_3) + 1.10\ (X_2X_3)$.

The ANOVA analysis indicates a linear relationship between the main effects, quadratic effect and interaction effect of X_1, X_2 and X_3 respectively [26] .Table 11 shows the result of the ANOVA analysis for the model. The model equation adequately describes the response surfaces of Phenol removal in the interval of investigation. In fact, the R2 value was high (0.95). For Phenol reduction, it can be seen that linear effects of coagulant dosage and pH are significant [22].

Figure 7(b) illustrates profiler for phenol removal, such as can be seen in this figure. We observed that at pH equal to 6, coagulant dosage equal to 384 mg/L and flocculant dosage equal to 14 mg/L there is great value of percentage removal of Phenol (75.57%).The 3D representation of dose response and the pH of this upper surface of concentric closed curves whose centers represent the optimum conditions. Figure 7(C) show that the optimum Phenol removal point (80.60 %) obtained at around dose coagulant at 452 mg/L and pH at 7.4.

(a) **(b)**



(b)

Figure 7: (a) Experimental values versus predicted values for the phenol removal model. (b) Profiler for phenol removal. (c) Response surface plots for phenol removal as a function of pH and coagulant dosage at Polymer dosage equal at 14 mg/L

Table 11: ANOVA for Phenol removal response surface models (JMP10)

Source	Degree of freedrom	Sum of squares	Mean square	Rapport t	P-Value
pH (5.7)	1	1244.3484	1244.348	38.4041	0.0008*
Coagulant (304.464)	1	656.3891	656.389	20.2580	0.0041*
Polymer(11.17)	1	57.8582	57.858	1.7857	0.2299
PH*Coagulant	1	9.7241	9.724	0.3001	0.6036
PH*Polymer	1	275.8901	275.890	8.5147	0.0267
Coagulant*Polymer	1	9.7682	9.768	0.3015	0.6028
PH*PH	1	1060.2054	1060.205	32.7209	0.0012*
Coagulant*Coagulant	1	566.4992	566.499	17.4838	0.0058*
Polymer*Polymer	1	113.7912	113.791	3.5119	0.1101

6. Optimization the response

Models obtained in this study were utilized for each response in order to determine the specified optimum, at pH = 6, coagulant dosage of 384 mg/l and polymer fixed at dosage of 14 mg/l respectively, as tabulated in Table 12. Form this table we see that the experimental results are very similar to the expected results when the models at higher levels of factors. Consequently, one can conclude that the models represent faithfully Turbidity, COD, BOD5, HC and Phenol removal on the experimental field study. In this study the optimal values of factors and responses were pH=6, 384 mg/ L of coagulant 14 mg / L of polymer and 78.52%, 80.47%, 85.23 %,77.07% and 75.75% of Turbidity, COD, BOD5 , HC and Phenol removal, respectively.

Table 12: Optimization the response

pH	7	7.20	7.50	6.5	7.4
Coagulant (mg/L)	464	450	458	450	452
	Turbidity (%)	DCO (%)	BOD_5 (%)	HC (%)	Phenol (%)
Optimum response predicted	83.01	82.21	86.47	80.19	80.60
Validation of model at: PH=6 , Coagulant =384 mg/L and Polymer = 14 mg/L					
Optimum response	78.52	80.47	85.23	77.07	75.57

Conclusion

We used in this work a methodology for the experimental design and response surface to optimize coagulation/flocculation process of wastewater society SAMIR, for reducing the number and cost of experiments and improving the process at industrial scale. The best regression coefficients (R2) were obtained for turbidity, COD,BOD_5, HC and Phenol, reaching values of 0.96, 0.95 ,0.92 ,0.92 and 0.95 ,respectively. Coagulant dosage and pH seems to be the most significant factors in the soluble removal of COD, BOD5 and turbidity.

The validation of this model show the optimal values of factors and responses were pH=6, 384 mg/ L of coagulant 14 mg / L of Flocculant and , 78.52%, 80.47%, 85.23%, 77.07% and 75.75% of Turbidity, COD, BOD_5, HC and Phenol removal, respectively.

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