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Valorization of diatomaceous earth as a sustainable eco-coagulant for wastewater treatment: optimization by response surface methodology

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Abstract

The use of natural, eco-friendly coagulant-flocculants in wastewater treatment can help to reduce suspended particles in a way that includes less exhaustible materials with minimal adverse effects on the environment. Hence, this study is to investigate raw diatomaceous earth (diatomite) as a sustainable ecological coagulant to reduce colloids and suspended matter in wastewater and optimize the coagulation process parameters to improve efficiency, save energy consumption, and reduce costs in the urban sewage treatment plants. The Box-Behnken response surface design was applied to model the individual and combined interactions between four variable factors (initial pH, coagulant dose, coagulation speed, and coagulation time) and their effect on turbidity removal efficiency and final pH of water. Results showed that diatomite has excellent efficiency in reducing the turbidity of wastewater; Elimination reached a maximum of 85.74%. The optimal operating conditions for reducing energy consumption and cost of the operation while improving turbidity removal effectiveness and achieving a neutral final pH to avoid a post-adjustment are an initial pH of 7, a dose of diatomite of 0.5 g/L of effluent, and a coagulation speed of 100 rpm for 3 min. It results in 72.6% turbidity removal and a pH of 7.27. diatomaceous earth shows very usefully for reducing the turbidity of the sewage in the urban wastewater treatment plant.

Keywords: Wastewater; Process; Coagulation; Box-Behnken; Diatomite; Ecological; Environment.

1. Introduction

Water is one of the basic elements of sustainable development and its preservation is the protection of biodiversity on our planet. Growing urbanization and new modes of production and consumption in industrialized and developing countries create new challenges for managing the water cycle; wastewater sanitation is one of them [1]. It presents a dual challenge to public health and environmental protection; wastewater treatment plants are increasingly installed, and treatment technologies are being developed and improved [2]. The choice of technologies used depends essentially on the composition of the wastewater [3-8]. Nanotechnology, which deals with nanometre-sized objects (1-100 nm), has also been applied in a number of medical, biological, chemical, and wastewater treatment applications [9-14].

Aluminium and iron salts are the most frequently used coagulants **[15,16].** However, significant aluminium and iron concentrations can persist in the treated water and cause some undesirable toxicity [17,18]. One way to cut down on traditional chemical coagulants and flocculants is to use new natural biomaterials that are biodegradable, non-toxic, and more environmentally friendly [19]. Thus, researchers are interested in designing, developing, and evaluating new natural or biomaterials with coagulant and flocculent effects [55-60].

Diatomaceous earth is a naturally occurring material formed by the accumulation of Bacillariophyceae, composed of fossilized diatom shells (SiO₂ about 70%) characterized by highly complex surface porosity (80–90% voids) with highly symmetrical patterns [20-22]. It is characterized by interesting mechanical and optical properties thanks to

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the pores' arrangement, size, and shape on their surfaces [9-12]. Diatom shells can be equally effectively used for biological and biomedical applications such as drug carriers [23,24] and sensing devices [20,25]. The Food and Drug Administration of the United States has authorized some diatomaceous earth as food-grade and added it to the list of food additives as an inert carrier or anti-caking agent in animal feed [21]. Diatomaceous earth is also employed in water treatment as a filter media [22,26] and as an adsorbent [27-36], but few studies have investigated the coagulant flocculent effect of diatomite alone [37] or mixed with other coagulants [37-42].

The aims of this study were:

- To assess the viability of using raw diatomite as a sustainable ecological bio-coagulant to reduce the turbidity of the sewage in the urban wastewater treatment plant.
- To optimize the coagulation process parameters using response surface methodology (RSM), including the dosage of diatomite in order to reduce costs and energy consumption while increasing the efficiency of the process.

The RSM is widely used to optimize water treatment processes. It integrates several factors and examines their interactions while reducing the number of experimental tests.

2. Material and Methods

2.1. Collection of sewage samples.

The samples were collected from the clarification basin of the municipal wastewater treatment plant (MWTP) in Sidi Bel Abbès in northwest Algeria. The city is geographically located at 35°11'38"N and 0°38'29"W and covers an area of 9150.63 km2. The population of Sidi Bel Abbes is 681190, with an estimated density of 72 inhabitants/km2; most of them are concentrated in the state's northwestern region [43]. The city's geography occupies a strategic middle position. It extends approximately 15% of the northwestern region and is centered between 05 states and crossed by most national roads The MWTP receives urban wastewater and discharges from artisanal activities. The characteristics of the sewage are presented in Table 1.

Table 1: The characteristics of the sewage

parameter	pН	Electric conductivity ((µs/cm)	TDS (mg/L)	Turbidity NTU
value	7.01	950	440	288

The raw effluent undergoes four stages of treatment before being returned to the receiving environment (Mekerra valley): desanding, coagulationflocculation, biological filtration, and disinfection. Using 1000 mL HDPE bottles, wastewater samples were taken at the inlet of the treatment plant's clarification tank. The water samples were stored and transported to the laboratory for analysis. The turbidity and pH of the wastewater were measured using an model infrared AQUALYTIC AL250T-IR turbidimeter and a HI-2211 benchtop pH and mV meter.

2.2. *Experimental procedure of coagulationflocculation.*

The coagulation-flocculation tests were performed in a Jar Test apparatus (model AOUA / UTC) equipped with four stainless steel blades; the stirring speed varies from 0 to 200 rpm, while the stirring time is from 0 to 30 min.

A 600 ml beaker was filled with 400 ml of wastewater for each test. First, the wastewater's initial pH (pH_i) was adjusted to the desired value using two solutions of 0.1N HCl and 0.1N NaOH. Then, a dose of diatomite varying between 0.5 and 3 g/L was added. Coagulation speed and time varied depending on the design (50, 150, and 200 rpm for 3, 5, and 7 min). Then, the speed of stirring was reduced to 20 rpm for 20 min to promote the formation of flocs (flocculation). After flocculation, the samples were left to stand for 60 minutes. Then, 300 ml of the supernatant was removed using a dipstick for analysis. equation (1) was used to calculate the rate of turbidity removal, which was expressed as a percentage.

Turbidity removal efficiency (%)= [1-(final turbidity/initial turbidity)]*100 (1)

2.3. Experimental design.

A statistical optimization was carried out to minimize the energy consumed during the coagulation operation while improving the rate of elimination of turbidity and making the final pH of the water tend towards neutrality to avoid a possible post pH adjustment. Response surface methodology (RMS) was employed to study mutual interaction effects among the selected operating parameters using the Box-Behnken design (BBD) Design-Expert® software. The impact of four variable factors: initial pH (X_1), the dose of diatomite (X_2), the coagulation speed (X_3), and the coagulation time (X_4) on the efficiency of turbidity removal (Y_1) and the final pH (Y_2) was studied.

Ranges of the variables have been set according to experiments previously carried out. The values are presented in Table 2.

	Coded levels				
Coded factors	Factors	Unit	-1	0	+1
X_1	Initial pH	4	7	10	
X_2	Dose of diatomite	g/L	0.5	1.75	3
X_3	Coagulation speed	rpm	100	150	200
X_4	Coagulation time	mn	3	5	7

Table 2: Experimental range and levels of variables

The number of tests (n) required to generate Box Behnken Design is specified as follows:

$$n = 2f(f-1) + Cp \tag{2}$$

f and *Cp* denote the number of factors and the number of central points, respectively.

Experiments were carried out randomly to reduce systematic error; furthermore, three center replicates were inserted to evaluate the pure experimental error and improve the model's design. A total of 27 experiments were performed, and the obtained and predicted responses achieved are shown in Table 3. The relationships between responses and independent variables and predict the optimal coagulationflocculation process conditions were established using an empirical second-order polynomial model (equation 3).

$$Y = a_0 + \sum_{i=1}^{k} a_i X_i + \sum_{i=1}^{k} a_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} a_{ij} X_i X_j + e$$
(3)

Design-Expert software was used for the design of the experiment, estimation of the coefficients, analysis of data, and plotting of graphs.

3. Results and Discussion

3.1. Characterization of the raw diatomite.

The diatomite used in this study was collected from the TAHLAIT ENOF deposit, located 5 km from the Sig area in Algeria. It is a light, powdery rock that is brilliantly white. The raw diatomite sample was crushed, air-dried, finely ground, and finally sieved. The sample's chemical composition was identified using x-ray fluorescence spectrometer (model Rigaku ZSX Primus II). SiO₂ has been identified as the most predominant constituent, and the main minor components are calcium oxide and metal oxides (CaO, Al_2O_3 , and Fe_2O_3) (Table 4).

FT-IR analyses in the 400-4000 cm⁻¹ range were performed using an Alpha Bruker FT-IR spectrometer to investigate the surface characteristics of the raw diatomite. The infrared spectra illustrated in Figure 1 show the prominent absorption bands. The bands at 998, 872, 792, 689, 521, and 460 cm⁻¹ were particularly noticeable. The band at 998 cm⁻¹ corresponds to the siloxane group's (-Si-O-Si-) elongation, whereas the band at 872 cm⁻¹ corresponds to the silanol group's Si-O elongation. The bands at 792 and 689 cm⁻¹ are assigned to the vibrations of the SiO-H bonding, and Absorption peaks at 521 and 460 cm⁻¹ are attributed to Si–O–Si bending vibrations [44,45].X-ray analysis identified the crystalline phases using a Siemens D5000 diffractometer utilizing g CuKal radiation in the Bragg Brentano configuration. The XR- diffractogram of diatomite is shown in Figure 2. The prominent peaks correspond to quartz, calcite, cristobalite, and a mixture of kaolinite, smectite, and hematite [46-48].

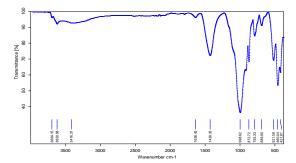
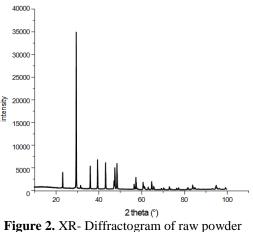


Figure 1. FT-IR spectra of the raw powder diatomite



diatomite

Run			Factors		Responses			
-	X_1 X_2		X3	X_4		Y1		Y ₂
	Initial	Dose of	Coagulation speed	Coagulation time	Turibidi	ity removal	Fii	nal pH
	pН	diatomite (g/L)	(rpm)	(min)	((%)		
					Actual	predicted	Actual	predicted
1	7	1.75	150	5	75.55	74.13	7.19	7.20
2	7	1.75	200	3	72.96	73.43	7.21	7.31
3	7	1.75	100	3	74.07	73.41	7.27	7.32
4	4	3.00	150	5	66.66	66.26	6.62	6.74
5	10	3.00	150	5	83.33	83.78	9.60	9.44
6	7	1.75	100	7	73.7	73.78	7.32	7.31
7	7	0,50	150	7	74.44	72.75	7.17	7.17
8	10	0.50	150	5	84.26	85.20	9.63	9.60
9	10	1.75	150	7	85.74	85.79	9.65	9.60
10	4	1.75	150	3	62.96	64.38	6.7	6.68
11	10	1.75	150	3	82.4	83.01	9.65	9.61
12	7	1.75	200	7	72.22	73.43	7.28	7.32
13	10	1.75	100	5	84.72	84.08	9.52	9.67
14	7	1.75	150	5	72.77	74.13	7.21	7.20
15	4	1.75	200	5	64.07	62.69	6.93	6.76
16	7	3.00	150	7	75.55	75.03	7.23	7.28
17	10	1.75	200	5	85.74	84.33	9.43	9.56
18	7	3.0	100	5	73.51	74.09	7.25	7.27
19	4	1.75	100	5	63.88	63.27	6.8	6.65
20	7	1.75	150	5	74.07	74.13	7.21	7.20
21	4	1.75	150	7	61.11	61.97	6.74	6.71
22	7	0.50	200	5	70.74	71.64	7.30	7.21
23	7	3.0	150	3	75.18	74.85	7.24	7.22
24	4	0.50	150	5	60.18	60.28	6.21	6.47
25	7	0.50	150	3	74.07	72.57	7.29	7.22
26	7	0.50	100	5	72.03	73.28	7.25	7.19
27	7	3	200	5	75.18	75.40	7.25	7.24

Table 3: Experimental conditions of Variables and response

Table 4: C	Themical	composition	of the raw	v diatomite p	owder
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Oxide	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	TiO ₂	Fire losses
Wt %	69.07	15.42	6.14	2.73	1.70	1.18	0.14	0.085	3.5

3.2. Statistical analysis

Analysis of variance (ANOVA) was utilized to examine the relationships among factors, their possible interactions, and their impacts on responses and validate and determine the significance of the developed models. ANOVA analysis indicated that the linear model was highly significant for the response Y_1 , while the quadratic was selected to be more appropriate for the response Y_2 . Summary statistics for the models are summarized in Table 5. The first statistical analysis is by the F and p values. The model F-value of 159.58 and 109.01 and the model p-values of under 0.0001 for the linear and quadratic models are less than 0.05, implying that the models were significant (Tables 6 and 7). The factors significantly impacting turbidity removal and final pH are also given in tables 6 and 7. For the turbidity removal, initial pH (X₁) and the mass of diatomite (X₂) were significant terms (p < 0.05). For the final pH of the effluent, its initial pH (X₁) and quadratic initial pH (X₁²) were significant terms. The linear and quadratic equations used to explain the removal of turbidity (Y₁) and the final pH of water (Y₂) are represented in equations 4 and 5, respectively. Equations were adjusted by removing terms that were judged to be statistically insignificant. The mathematical equations obtained were used to analyze the goodness of fit. $Y_1 = 51.33626 + 3.31635 X_1 + 0.220452 X_2$ (4) $Y_2 = 8.60766 - 0.807461 X_1 + 0.099352 X_1^2$ (5)

The predicted and experimental values of Y_1 and Y_2 presented in Figure 3 are in close agreement. In addition, the data points are well dispensed along the 45° axis, indicating that the models developed for the turbidity removal and the final pH were well-suited for forming a relationship between independent and dependent variables.

The coefficient of determination Regression (R2) responses Y_1 and Y_2 was found to be 0.9667 and 0.9922, respectively (Table 8), which means that the total variation explained by the developed models was 96.67 and 99.22 %; this indicates that the dependent and independent variables were in a reliable relationship. On the other hand, there might be 3.33 and 0.78 % of the total variation, which could not be explicated by the models developed. Compared to prior research adopting Response Surface Methodology to improve the coagulation step in wastewater treatment, the high correlations between experimental and predicted data indicated that our models could be judged highly significant [49-54,61-66].

The predicted R^2 values for responses Y_1 and Y_2 were 0.9490 and 0.9551, respectively (Table 7), which were close to the R^2 values (0.9667 and 0.9922, respectively). They are also in good agreement with the RMS adjusted R^2 values of 0,9606 and 0,9831 for turbidity removal (Y_1) and final pH (Y_2), respectively; the difference is less than 0.2.

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Adequate Precision (A.P) measures the experimental signal-to-noise ratio. It is preferable to have a ratio that exceeds four. The AP score was 37.326 and 30.288 for Y_1 and Y_2 , respectively. That reflected an adequate signal and indicated that the model would perform admirably (table 8). The standard deviation (S.D) and coefficient of variation (C.V) indicate the degree of precision the experiments are compared. The lower values of S.D (1.46 and 0.1419 for Y_1 and Y_2 , respectively) and C.V (1.98% and 1.86% for Y_1 and Y_2 , respectively) imply good precision and reliability of the experiments and indicate that the models are reasonably reproducible (Table 8).

 Table 5: Model Summary Statistics

Statistics				D 1	D 2	
	source	p-value	R ²	$\mathbf{R}^{2}_{\mathrm{adj}}$	R ² pred	
al lit	Linear	< 0.0001	0.9667	0.9606	0.9490	Suggested
ibic v	2FI	0.0660	0.9828	0.9721	0.9494	
Turbidit y removal	Quadratic	0.9730	0.9835	0.9642	0.9146	
L n	Cubic	0.9786	0.9880	0.9219	-0.3422	Aliased
	Linear	< 0.0001	0.8223	0.7900	0.7287	
ïnal pH	2FI	0.9998	0.8244	0.7146	0.4525	
Final pH	Quadratic	< 0.0001	0.9922	0.9831	0.9551	Suggested
	Cubic	0.1086	0.9991	0.9940	0.8691	Aliased

Tables 6: ANOVA for linear model (Response Y1)

source	df*	SS*	MS*	F-value	p-value	
Model	4	1366.70	341.67	159.58	< 0.0001	sign**
X ₁ -initial pH	1	1350.87	1350.87	630.93	< 0.0001	sign **
X ₂ - dose of diatomite	1	15.64	15.64	7.31	0.0130	sign**
X ₃ - coagulation speed	1	0.0867	0.0867	0.0405	0.8424	no sign**
X ₄ -coagulation time	1	0.1045	0.1045	0.0488	0.8272	no sign**
Residual	22	47.10	2.14			
Cor Total	26	1413.80				

Table 7: ANOVA for quadratic model (Response Y2)

source	df*	SS*	MS*	F-value	p-value	
Model	14	30.74	2.20	109.01	< 0.0001	sign**
X ₁ -initial pH	1	25.46	25.46	1264.30	< 0.0001	sign**
X ₂ - dose of diatomite	1	0.0096	0.0096	0.4783	0.5023	no sign**
X ₃ - coagulation speed	1	8.333E-06	8.333E-06	0.0004	0.9841	no sign**
X ₄ -coagulation time	1	0.0001	0.0001	0.0037	0.9523	no sign**
$X_1 X_2$	1	0.0484	0.0484	2.40	0.1470	no sign**
$X_1 X_3$	1	0.0121	0.0121	0.6008	0.4533	no sign**
$X_1 X_4$	1	0.0004	0.0004	0.0199	0.8903	no sign**
$X_2 X_3$	1	0.0006	0.0006	0.0310	0.8631	no sign**
$X_2 X_4$	1	0.0030	0.0030	0.1502	0.7051	no sign**
$X_3 X_4$	1	0.0001	0.0001	0.0050	0.9450	no sign**
X_1^2	1	4.26	4.26	211.73	< 0.0001	sign**
X_2^2	1	0.0068	0.0068	0.3400	0.5706	no sign**
X3 ²	1	0.0195	0.0195	0.9666	0.3449	no sign**
X_{4^2}	1	0.0149	0.0149	0.7415	0.4060	no sign**
Residual	12	0.2417	0.0201			
Cor Total	26	30.98				



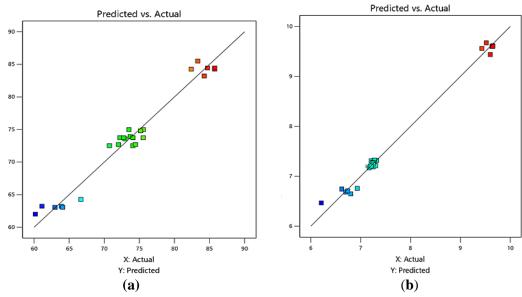


Figure 3. Predicted vs. actual plot for turbidity removal (a); final pH (b)

Table 8: Statistical parameters for responses Y_1 and Y_2							
	Y1	Y ₂					
	Turbidity removal (%)	Final pH					
R ²	0.9667	0.9922					
Adjusted R ²	0.9606	0.9831					
Predicted R ²	0.9490	0.9551					
Adequate Precision A.P	37.3261	30.2879					
Standard Deviation S.D	1.46	0.1419					
Coefficient of Variation C.V. %	1.98	1.86					

3.3. Process optimization.

A numerical optimization analysis was performed using BBD. The objective was to minimize the energy consumed and the cost of coagulation treatment while ensuring good turbidity removal efficiency. The objectives and limitations of the optimization are reported in Table 9.

The initial and final pH levels were targeted to 7 to avoid a pH adjustment step before or after coagulation treatment. Speed and time of coagulation and the dose of diatomite were minimized throughout the range of variation of each factor to reduce energy consumption. The selected optimal conditions were: an initial pH of 7, a dose of diatomite of 0.5g/L, coagulation speed of 100 rpm, and coagulation time of 3 min (Figure 4).

At these optimal conditions, the predicted removal of turbidity obtained is 72.60%, and the final pH is 7.27, a pH close to neutral, which does not require post adjustment. The desirability of these optimal conditions is 0.992 (Figure 5). The 3D graph of this desirability is shown in Figure 6.

In order to explain the independent variables' effects and interactions, 2D contour and 3D response surface plots were made as a function of two variables with the remaining variables held constant at optimal conditions. The behavior of turbidity removal and final pH is illustrated in the graphs shown in Figures 7 and 8. Parallel and well-spaced curvatures are observed, which affirm a positive relationship between the two variables, initial pH (X₁) and the dose of the diatomite (X₂), of linear profile for the turbidity removal efficiency (Y₁) and quadratic for the final pH (Y₂) (Figures 7).

The 3D response surface plots of Y_1 and Y_2 at the optimum condition (X_3 : 100 rpm and X_4 : 3 min) are shown in Figure 8. The initial pH was the

most influential and effective parameter on diatomite performance. The maximum reduction in turbidity was observed at high pH and the low mass of diatomite. The turbidity removal rate has increased to reach its maximum (85.74%) at pH 10 and a diatomite dose of 3 g/L (figure 8a). The optimal point was not observed at the highest reduction rate due to the objectives set for the optimization. The optimum point was reached at 72.60% turbidity removal for a pH_i of 7 and a diatomite dose of 0.5g/L.

The final pH of wastewater strongly depended on its initial pH; an increase in pH_i induced an increase in pH_f. Independent of diatomite mass, minimum and maximum pH_f were reached at the lowest and highest pH_i. The pH_f range was minimal, with an increase in diatomite mass as shown in Figure 8b.

Symbol	Factor	Unit	Aim	Minimum level	Maximum level
X1	Initial pH	-	target to 7	4	10
X_2	dose of diatomite	g/L	minimize	0.5	3
X3	coagulation Speed	rpm	minimize	100	200
X_4	coagulation Time	min	minimize	3	7
Y1	turbidity removal	%	in range	70	100
Y ₂	final pH	-	target to 7	0	14

Table 9: Objectives and ranges of optimization

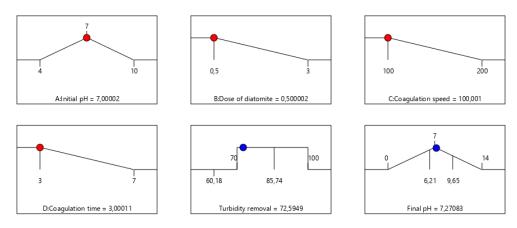
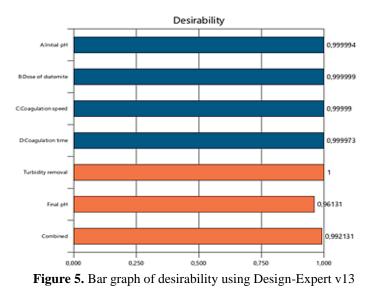


Figure 4. predicted solution obtained by numerical optimization



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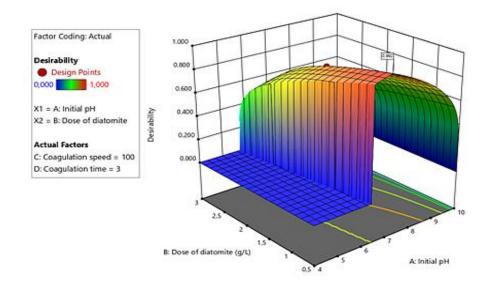


Figure 6. Desirability surface for optimal conditions using Design-Expert v13 software. The three-dimension response surface plots (3D).

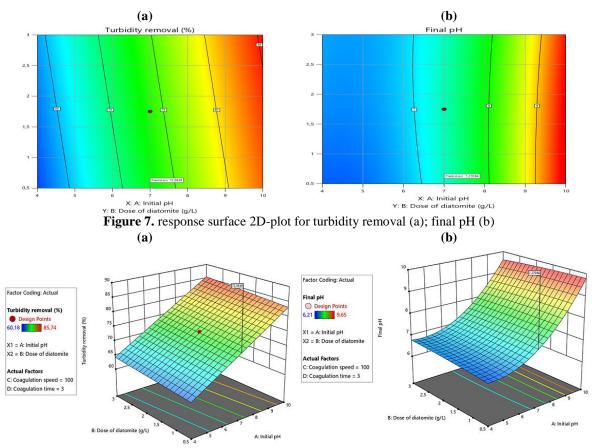


Figure 8. response surface 3D-plot for (a) turbidity removal; (b) final pH

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4. Conclusions

This study exploited the experimental design methodology to evaluate the performance of crude diatomaceous earth as a natural ecological coagulating agent and optimize process parameters to reduce energy consumption in the municipal water treatment plant. As a result, it was possible to achieve optimum efficiency of 85.74% turbidity removal using diatomite coagulant. Under optimum conditions, 72.60 was reached, and the final pH of the water tended to be 7.27. Furthermore, no initial pH adjustment was necessary to achieve these results. In addition, the dose of diatomite used and the speed and time of agitation during the coagulation phase were the lowest, which made it possible to save as much energy and cost of treatment as possible while still getting rid of more than 70% of suspended solids expressed in terms of turbidity. The application of this inexpensive natural agent can overcome the challenges related to suspended solids and colloidal particles responsible for the turbidity of wastewater. The recorded correlation between experimental and predicted responses was perfect. In addition, The BBD models developed presented high correlation coefficient (R^2) values, 96% for turbidity reduction efficiency and 99% for final water pH, respectively, indicating the excellent adequacy of both quadratic and linear models and correctly describing the interaction between all the factors involved.

These results showed that the response surface methodology could be successfully used to simulate and optimize the coagulation process in the step of the clarification of wastewater. Furthermore, it is economical and provides the most accuracy and information in the shortest time with the fewest experiments. Using natural materials and limiting energy consumption in the wastewater treatment plant reduces the pollution generated, allows the installation's proper operation, and increases its lifespan while improving the process's performance.

5. Conflicts of interest

"There are no conflicts to declare".

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