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Treatment of landfill leachate by coagulation-flocculation with FeCl3: process optimization using Box–Behnken design

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Abstract

Landfill leachate is a complex mixture containing toxic and recalcitrant substances with considerably low BOD$_5$/COD indicating the necessity and difficulty of its treatment. Amongst treatment processes, integrated separating-destructive processes are promising gones. In this way, suspended and colloidal particles get separated in a separating process, while the soluble fraction under goes separating process; probably an coagulation-flocculation process. In this study, coagulation process using ferric chloride was employed as apre-treatment process for landfill leachate. Elimination of COD and turbidity was investigated using response surface method (RSM) with Box-Behnken design. Design experiments were modeled and analysed. In optimum conditions (7.2g/L FeCl$_3$ and 0.2mL/L flocculant) the average COD removals were occurred approximately 45%.

1. Introduction

Sanitary landfill has been introduced as an economical approach to dispose municipal solid waste in recent decades throughout the world. Leachates are often collected within the landfill system via collection reservoirs (or ponded onto the liner) and pumped outside of the landfill into holding ponds, then treated for discharge [1]. The most significant problem in landfills is the uncontrolled release of leachate which results in contamination of ground and surface water streams. Typically, leachates possess various characteristics in different zones of landfill sites due to several factors such as elapsed time, temperature, depth of landfill site, site hydrology, refuse composition and moisture content [2,3]. The leachate is a dark aqueous effluent generated as a consequence of rainwater percolation, inherent moisture content of the solid wastes, water production due to chemical and biochemical processes, and ground water entering into the waste [4]. Leachates are known for their high concentration of ammoniacal nitrogen, high strength of recalcitrant compounds and relatively low biochemical oxygen demand to chemical oxygen demand (BOD5/COD) ratios.

Therefore, the removal or reduction of contaminants to environmentally acceptable levels is necessary before discharging the leachate into natural waters. Leachate treatment methods can be classified as biological treatment and physical/chemical methods [5].

However, the leachates containing biologically recalcitrant compounds, with the ratio of BOD$_5$ to COD less than 0.5, are not efficiently treated with biological processes [6,7].

Compared to biological techniques, physicochemical treatment of leachate is typically cost-effective and can be completed in shorter time periods. The most common physicochemical treatment methods include coagulation-flocculation, adsorption, membrane processes, and oxidation [8,9].

Coagulation-flocculation (CF) is a relatively simple technique that has been employed successfully for the treatment of old and stabilized landfill leachates and pre-treatment of fresh leachates [10,11] and can remove

COD, turbidity, colour and metals with high efficiencies depending on contaminant and coagulant/flocculant type [12,13]. Aluminum sulfate (alum), ferrous sulfate, ferric chloride, and poly-aluminum chloride (PAC) are commonly used coagulants for leachate treatment [14]. Several researchers have studied the treatment of leachate by CF using different coagulants which and showed that ferric chloride is more effective for the removal of organic pollution [14-20].

The study of the CF process requires optimization of all parameters affecting it, in order to achieve high efficiency. The conventional experimental method of studying a process does not depict the combined effect of all the factors involved, it is time-consuming and requires a large number of experiments to determine optimum levels, which may or may not be reliable. These limitations can be eliminated by simultaneously varying all the parameters by using statistical designed experiments such as the response surface methodology (RSM) [22,23]. RSM is a collection of statistical and mathematical techniques that are useful for developing improving, and optimizing processes that can be used to evaluate the relative significance of all the factors involved in the process, even in the presence of complex interactions with reduced variations, time, and cost[10,24,25].

In the present study, in order to investigate coagulation- flocculation process as a pre-treatment, a high strength leachate sample was selected having high total suspended solids (TSS) and low biodegradability (low BOD_5/COD). Coagulation- flocculation process was optimized by RSM with tow responses of removal COD and turbidity. Particular attention is given to the response of removal COD.

2. Materials and methods

2.1. Sampling and characterization

The leachate samples used in this study were collected from The Mesbahiat landfill is located in the south-west of Mohammedia, about 5 km from the city and the Oued El Maleh. It covers an area of six hectares alongside the A3 and N1 roads. It’s an old quarry of limestone characterized by schists and representing fissures [26]. All samples were collected manually in 20-l plastic containers and then transferred to the laboratory, stored at 4◦C and analyzed within two days. The leachate analyses were conducted in accordance with the standard methods for the examination of water and wastewater [27] for the following parameters: pH, conductivity, total suspended matter (TSS), turbidity, COD, and BOD_5.

The pH was determined by a pH meter WTW pH 522 with combined electrode and the Conductivity was measured using a conductivity meter (HANNA EC 214). Turbidity was measured by nephelometry using a laboratory turbidimeter (2100P, HACH, USA) and expressed in NTU (Nephelometric Turbidity Unit). The chemical oxygen demand (COD) was determined using the ready-to-use closed tube method. The tube contains all the necessary reagents and it is enough to introduce a precise volume of sample and to follow the protocol described by the company (HACH LANGER).It is based on the same principle as the standardized tests (ISO 15705). To analyze BOD_5, we fill the samples in airtight bottles and we incubate them in a BOD meter at 20°C for 5 days.

2.2. Jar Test Procedure

To achieve the CF tests, we choose ferric chloride as coagulant and a cationic flocculantAN 934-SH poly-electrolytes manufactured by SNF Floerger were provided by ChemFlo-Hellas. The flocculation coagulation tests were carried out using a flocculator (jar test). The test material consists of a six-stirrer flocculator (Fisher 1198 flocculator) with an individual rotational speed ranging from 0 to 200 rpm [28]. This apparatus makes it possible to simultaneously agitate the liquid contained in a series of beakers filled each with 250 mL of leachate. Various concentrations of the selected coagulant were added to the leachate. The mixture is stirred rapidly at 200 rpm for 3 min. The speed is subsequently reduced to 60 rpm (10, 20 and 30 min). After 60 min of settling, the volume of the sludge is measured and then the supernatant is recovered to analyze the parameters such as turbidity, pH, and especially COD.

The experiments were carried out at pH = 6.3 as this was the natural pH value determined from the original landfill leachate. The optimum concentration of the coagulant was determined on the basis of turbidity, the volume of sludge produced and the visual appearance of the supernatant.

2.3. Calculation

The removal of the studied parameter from leachate was calculated based on the following formula:

$$Removal\ (\%) = 100 \times \frac{(C_0 - C_F)}{C_0} \qquad \text{Eq.1}$$

were C_0 and C_F are respectively the initial and final concentrations of the studied responses.

2.4. Experimental design

The Design Expert Software v9 was employed in this study for the statistical design of experiments and data analysis. The coagulation-flocculation process was designed and optimized using response surface method (RSM). Factorial experimental design was used to optimize the preparation conditions, COD and turbidity removal efficiency. RSM designs allow us to estimate interaction and even quadratic effects and hence give us the idea of the (local) shape of the response surface under investigation. Box-Behnken design is having the maximum efficiency for an RSM problem involving three factors (coagulant (X_1), flocculants (X_2) and time of stirring (X_3)), these variables with their respective domain are chosen on the basis of the literature data and preliminary experiments. With three levels Performance of the process was evaluated, by analyzing the COD and turbidity removal efficiencies. Independent factors, experimental range, and levels for landfill leachate are given in Table 1. The low, midpoint and high levels of each variable were designated as 1, 0, and +1, respectively. The variable ranges chosen were based on the preliminary experiment-trials conducted in our laboratory and literature information.

Table 1: Experimental range and levels of independent process factors.

	Levels of Box-Behnken		
Factors	Low (-1)	Middle (0)	High (+1)
Coagulant (g/L(X_1)	4.80	7.20	9.60
flocculants (mL/L) (X_2)	0.04	0.12	0.20
Time (min) (X_3)	10	20	30

The experimental design was conducted with 17 experiments with 5 replicates at the center point (0,0,0) to verify any change in the estimation procedure, as a measure of precision property. After testing increasingly complex models from linear to quadratic, a quadratic model was found to be suitable for studying the effects of the variables on the responses. A quadratic modelis given inEq. (2) [29,30]:

$$Y=b_0+b_1X_1+b_2X_2+b_3X_3+b_{12}X_1X_2+b_{13}X_1X_3+b_{23}X_2X_3+b_{11}X^2{}_1+ b_{22}X^2{}_3 \qquad (2)$$

Where Y is the response, b_0 is the constant, b_i is the linear coefficient, b_{ii} represents the quadratic coefficient, b_{ij} is the interaction coefficient, X_i is the coded variable level and *i or j* is the number of independent variables.

An analysis of variance (ANOVA) was used to determine whether the developed models were statistically significant and to identify the interactions between the process variables and responses [10]. The quality of the fit polynomial model was expressed by the value of correlation coefficient (R^2), and its statistical significance was checked by the F test in the same program. Model terms were evaluated by the P value (probability) with 95 % confidence level.

3. Results and discussion

3.1. Characterization of landfill leachate

To evaluate the impact of a landfill on the environment, it is necessary to characterize the effluent that it generates. Its composition depends on many factors: waste composition, water balance, landfill method, climatic conditions, and thickness of waste layer, nature of cover and age of leachate [31-33]**.** The physicochemical characteristics of the leachate are presented in Table 2.

Referring to table 2, the leachate has a neutral pH, this value is lower than that reported by [34] in the Fez leachate (7.66) and by [35] in the Essaouira leachate (8.44). The value of the electrical conductivity for the leachates analyzed is 26.900 mS/cm, and is higher than that recorded in the Kenitra landfill (22792µs/cm) [36]. Its turbidity reached 3160 NTU and is higher than the value reported by [20] in the Rabat landfill (222 NTU). It is loaded with suspended matter with a concentration about 1666 mg/L. and is considerably higher than 2.7 mS/cm, considered as the limit value for direct rejection in the receiving environment [37], this value and much lower than that recorded in the Agadir landfill (64.650 ms/cm)**.**

The leachate is also loaded with organic matter, represented by a COD about 25300mg/L and BOD_5 about 7630mg/L. These values are higher than those reported by [20] in Rabat city's landfill and [21] in Tangier landfill which reached 11520 mg/L and 2397 mg/L for COD, 6710mg/L and 166.78 mg/L for BOD_5 respectively. These values exceed the Moroccan standards, which are set at 500mg/L for COD and 100mg/L for BOD_5 [37]. The BOD_5/COD ratio allows determining the age of leachate and its biodegradability. According to [9], BOD_5/COD ratios which are higher than 0.3 characterize the young biodegradable leachate, while older or stabilized leachates are distinguished by ratios less than 0.1. For the leachate studied, the BOD_5/COD ratio varies around 0.3 (= 0.297), revealing that it is a young - intermediate leachate with a very important biodegradability.

Table2: Leachate characteristics

Composition of studied leachate		Moroccan standards Limit values for direct discharges
Variable	Value	
pH	6.34	6.5 – 8.5
electrical conductivity (mS/cm)	26.9	2.7
turbidity (NTU)	3160	-
Total SuspendedSolids (mg/L)	1666	200
COD (mg/L)	25344	500
BOD_5 (mg/L)	7630	100
BOD_5 / COD	0.297	-

3.2. Factorial experimental design

In a first step, tests were carried out to evaluate the optimal quantity of the coagulant. $FeCl_3$ dosage was varied from 4.8 g/L to 9.6 g/L which was supplemented with 0.04 mg/L to 0.2 mg/L of a cationic polymer as flocculant for all the experiments at pH 6.3. The results are presented in Figure 1.

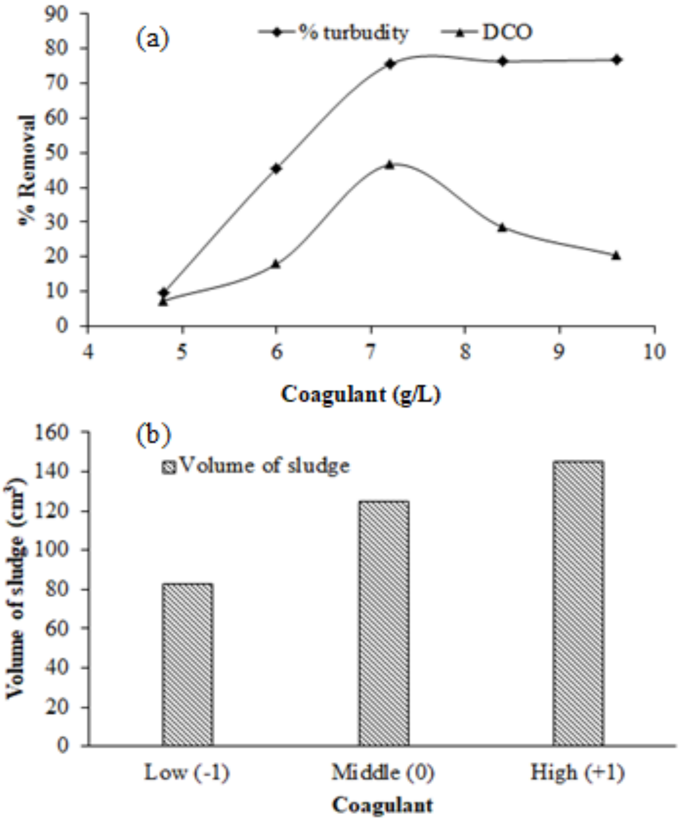

Figure1: (a) Percentage of removal COD and turbidity, (b) volume of sludge.

These results show that the percentage of elimination of turbidity and COD increased with increasing coagulant. The optimal dose obtained under these conditions is estimated at 7.2 g/L with a removal efficiency of 75%, 45% for turbidity and COD, with a sludge volume of 94.25cm^2. Leachate is subject to significant discoloration.

Coagulation with iron(III) chloride was optimized using RSM to determine optimum values of $FeCl_3$, flocculant concentration and time, to enable desirable removal efficiencies of the responses (COD and turbidity removals) to be achieved. Experimental results showing the coded and un-coded value of the variables together with the % COD and the turbidity reduction efficiency for landfill leachate are given in Table 3. The % COD and turbidity reduction were calculated by using Equation 1.

Table 3: Factorial experimental design matrix coded, real values and experimental results of the response

Run	Coded values			Actual values			Responses	
	X1	X2	X3	X1	X2	X3	%COD	Turbidity (NTU)
1	0	0	0	7.2	0.12	20	36.51	3020
2	0	0	0	7.20	0.12	20	33.19	2730
3	-1	0	+1	4.8	0.12	30	3.98	384
4	0	0	0	7.2	0.12	20	33.20	2420
5	0	+1	0	7.2	0.20	20	45.14	3030
6	+1	0	-1	9.6	0.12	10	35.18	3070
7	0	0	0	7.2	0.12	20	39.17	2810
8	+1	-1	0	9.6	0.04	20	36.51	1970
9	-1	+1	0	4.8	0.20	20	7.30	333
10	0	-1	+1	7.2	0.04	30	31.86	1930
11	0	-1	-1	7.2	0.04	10	21.91	2470
12	0	0	0	7.2	0.12	20	38.50	3020
13	0	+1	+1	7.2	0.20	30	35.18	2180
14	-1	-1	0	4.8	0.04	20	7.30	921
15	+1	0	0	9.6	0.20	20	2.62	2280
16	+1	0	+1	9.6	0.12	30	1.05	2130
17	-1	0	0	4.8	0.12	10	9.29	935

Table 3 listed the experimental conditions and values for the two responses. The data show that the highest COD removal efficiency of 45.14%, was achieved for the amount of coagulant 7.2 g/L respectively, for 0.2 mL/L and 20 minutes. As a result, the COD concentration of the leachate was reduced from about 25334 mg/L to 11400 mg/L in these conditions. However, at a certain concentration, reagent addition does not improve the removal efficiency. This can be explained by the breakage of flocs due to the excess of reagents, which causes an inversion of the charge and a dispersion of the agglomerated particles [38]**.** Moreover, optimal turbidity removal of about 89.5% was found at $FeCl_3$ = 4.8 g/L, flocculant = 0.2 mL/L and 20 minutes. The turbidity varied between 333 and 3070 NTU. The COD removal efficiency was higher in run 5, but the turbidity reduction efficiency was lower (4%). The removal efficiency of turbidity increases by increasing the concentration of the coagulant until it reaches a maximum value of 89.5% in run 9 and tends to decrease due to an excess of coagulant. This phenomenon could be caused by the stabilization of colloidal particulates when the coagulants were used at dosages in excess of the optimum value [39].

3.3. Analysis of variance (ANOVA)

The COD and turbidity removal efficiencies were subjected to ANOVA to determine the degree of removal of organics. Obtained results were shown in Tables 4 and 5. The lack of fit should be insignificant if the equation fits well. For a good fit of model, the correlation coefficient should be at a minimum of 0.80. A high R^2 value close to 1 illustrates good agreement between the calculated and observed results within the range of experiment and shows that a desirable and reasonable agreement with adjusted R^2 is necessary [40,41].

According to the ANOVA (Tables 4 and 5), the associated values of p lower than 0.01 indicate that the model is statistically significant [42]. The model developed to explain the relationship between the factors and the response has very good agreement with the experimental value.

Fitting of the data to various models and their ANOVA showed that the COD reduction was most suitably described with a quadratic polynomial model. The equation of the model in terms of coded factors is as follows:

$$\text{COD removal (\%)} = -35.43 - 5.93(X_1) - 0.39(X_2) - 4.19(X_3) - 22.52(X_1X_1) - 8.47(X_1X_2) - 7.21(X_1X_3)$$

The model F-value 5.64 (Table 4) with a p-value less than 0.05 implied that the model was significant. The coefficient of determination (R^2= 0.78) also showed the suitability of the developed model for representing the real relationship among the parameters [43]. The significance of each term in the model was determined by testing the null hypothesis. The variables X_1, X_2, and X_3 represented $FeCl_3$, flocculant concentrations, and time contact. In this case, X_1^2 was the significant model terms. The obtained results indicated that the $FeCl_3$ concentration would affect the COD removal efficiency.

Table 5 indicate, according to ANOVA, that a quadratic polynomial model was statistically significant to represent the real relationship between the turbidity removal efficiency and the variables, with a very small *p*-value (<0.0001), and a high coefficient of determination (R^2= 0.9202). The R^2 value of 0.9202 was in reasonable agreement with the Adj R^2 value of 0.8723. In addition, the R^2 value of 0.9202 indicated that the model was able to fit at least 92.02% of the variability in turbidity removal efficiencies obtained from experimental data.

The equation of the model in terms of coded factors is given below:

Turbidity (NTU) = -2665,07–859,63 (X1) – 0.39(X2) –113,46 (X3) −375,65 (X1X2) – 97,25 (X1X3)−7.21(X1X3)- 1162,20(X1X1)

The $FeCl_3$ and time contact were found to have significant effects on the turbidity removal while the flocculant was not a significant parameter.

Table 4: ANOVA for analysis of variance for COD removal

Source	sum of squares	df	mean square	F-Value	P-Value prob>F	
Model	2963.1	6	493.85	5.64	0.0085	significant
X_1	281.77	1	281.77	3.22	0.1031	
X_2	1.22	1	1.22	0.014	0.9085	
X_3	118.86	1	118.86	1.36	0.2710	
X_1X_2	287.19	1	287.19	3.28	0.1002	
X_1X_3	207.74	1	207.74	2.37	0.1545	
X_1^2	2132.26	1	2132.26	24.35	0.0006	
Residual	875.68	10	87.57			
Cor Total	3838.78	16				

R^2= 0.78 . Adj R^2=0.64

Table 5: ANOVA for analysis of variance for Turbidity removal

Source	sum of squares	df	mean square	F-Value	P-Value prob>F	
Model	1.246E+007	6	2.076E-006	19.22	< 0.0001	
X_1	5.91E+06	1	5.91E+06	54.72	< 0.0001	significant
X_2	1.01E+05	1	1.01E+05	0.94	0.3561	
X_3	9.55E+05	1	9.55E+05	8.83	0.0140	
X_1X_2	2.02E+05	1	2.02E+05	1.87	0.2019	
X_1X_3	37630.25	1	37630.25	0.35	0.5672	
X_1^2	5.68E+06	1	5.68E+06	52.55	< 0.0001	
Residual	1.080E+006	10	1.080E+005			
Cor Total	1.354E+007	16				

R^2= 0.9202. Adj R^2=0.8723

3.4. Normal probability plot of residuals

To confirm if the selected model provides an adequate approximation of the real system, the normal probability plots of the studentized residuals and diagnostics are provided by the Design Expert 6.0. Software,the normal probability plots that helped us judge the models (Figure2a–b) demonstrate the normal probability plots of the standardized residuals for COD and turbidity removal. A normal probability plot indicates that if the residuals follow a normal distribution, as shown in Figure2, the points will follow a straight line for each case. However, some scattering is expected even with the normal data. Accordingly, the data indicates that the experiments can be considered as normally distributed in the responses.

The analysis of residuals was illustrated in (Figure 2, 3 and Table 6), difference between the predicted and experimental responses, is another important diagnostic tool for judging adequacy of the fitted model for predicting the response. Figure 2 shows the residual values for each experiment. It shows that the residue does not exceed the amount removal,which is ofthe order of magnitude of the variety of experimental results due to handling. This residue is evenly distributed in space. The model was accepted. Moreover, this illustrates that this model describes the phenomenon under study.

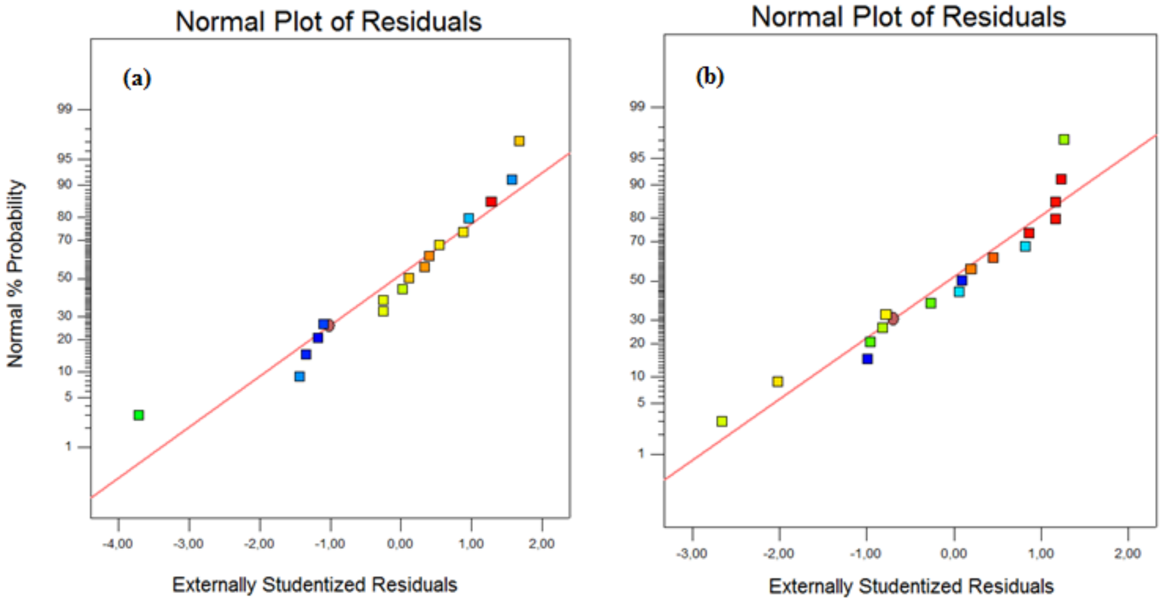

Figure 2: Normal probability plots of residuals for (a) COD and (b) turbidity.

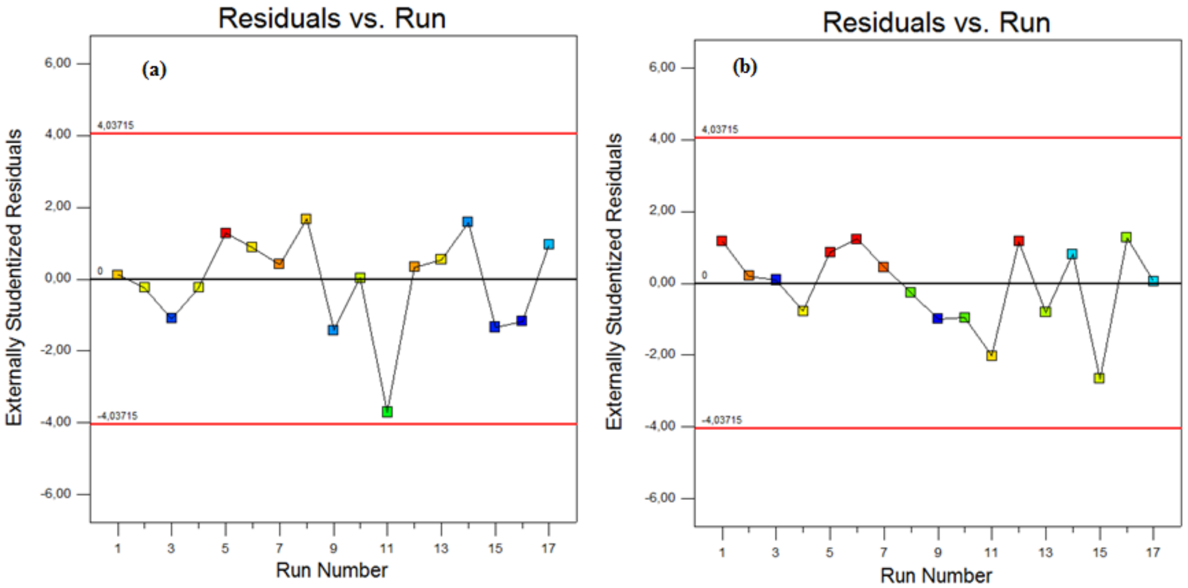

Figure 3: Analysis of residual for the responsefor (a) COD and (b) turbidity.

3.5. Response surface analysis and optimization process

The mathematical models for the COD and turbidity removal were used to build response surfaces as well as to determine the optimal conditions of this process. Optimal dosages are defined as the value above where there is no improvement of removal efficiency even if we add more coagulant or flocculant [44]. It is possible to optimize each response separately from the others. Figure 4 present the 3D response surfaces plots for the obtained interactions. For the COD removal, the most significant interactions are the coagulant/time, and the interaction between the flocculant/coagulant. For turbidity removal, the best significant interaction was time /coagulant in the removal of turbidity.

Figure 4 shows the effect of the coagulant mass, the volume of the flocculant and the contact time on the removal of COD and turbidity. The maximum removal of COD was 39.5% at coagulant mass 7.2 g/L, flocculant volume 0.2 mL/L and 18min reaction time. The 3D plot for turbidity achieved an efficiency of 89.45% in reducing turbidity by adding an optimal dose of 4.8 g/L of $FeCl_3$, 0.2 mL/L of flocculant and 20min reaction time.

Table 6: Factorial design matrix of two variables along with experimental and predicted responses for COD and turbidity.

		COD			Turbidity	
Run	Actual Value	Predicted Value	Residual	Actual Value	Predicted Value	Residual
1	36.51	35.43	1.08	3020	2665.07	354.93
2	33.19	35.43	-2.24	2730	2665.07	64.93
3	3.98	9.98	-6	384	364.85	19.15
4	33.2	35.43	-2.23	2420	2665.07	-245.07
5	45.14	35.04	10.11	3030	2778.53	251.47
6	35.18	30.24	4.95	3070	2835.4	234.6
7	39.17	35.43	3.74	2810	2665.07	144.93
8	36.51	27.71	8.8	1970	2024.54	-54.54
9	7.3	15.05	-7.75	333	532.21	-199.21
10	31.86	31.63	0.23	1930	2175.97	-245.97
11	21.91	40.02	-18.11	2470	2927.26	-457.26
12	38.5	35.43	3.07	3020	2665.07	354.93
13	35.18	30.84	4.34	2180	2402.88	-222.88
14	7.3	-1.11	8.41	921	754.29	166.71
15	2.62	9.97	-7.35	2280	2700.46	-420.46
16	1.05	7.44	-6.39	2130	1889.6	240.4
17	9.29	3.96	5.34	935	921.65	1335

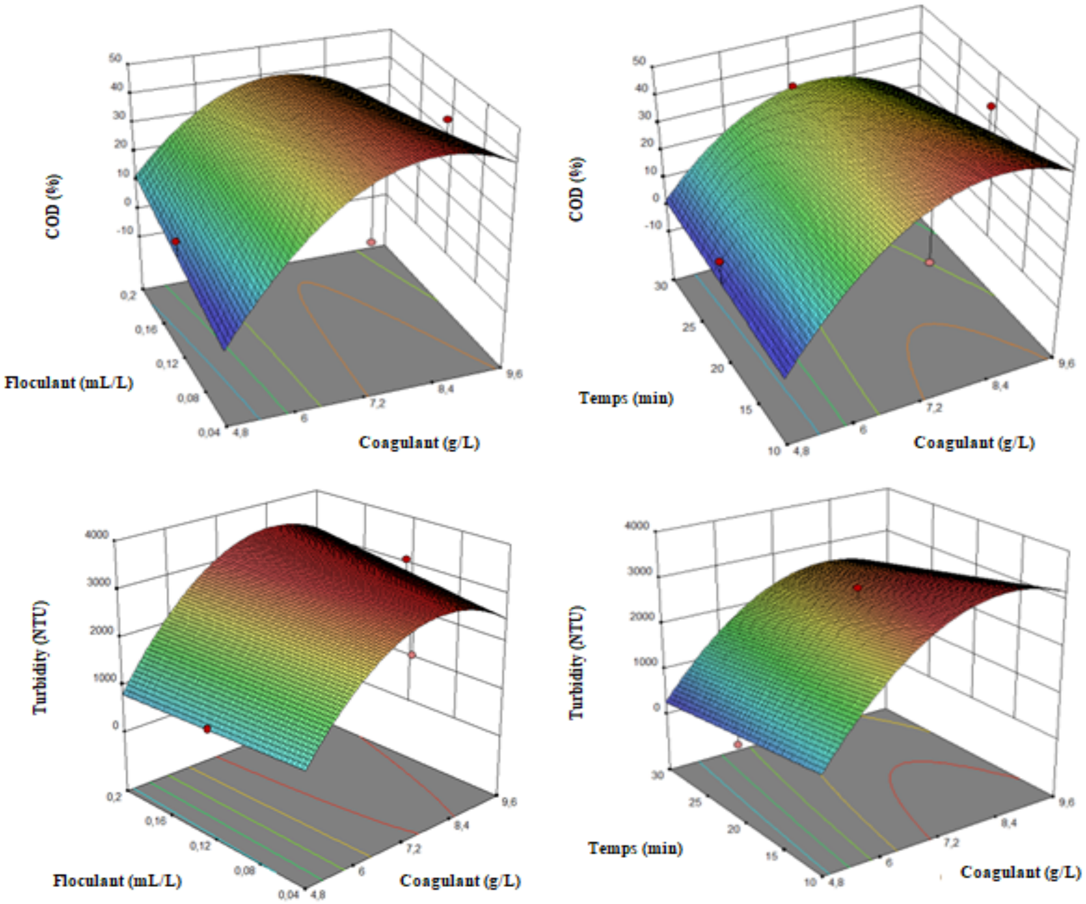

Figure4: Representation surface for removal of COD and turbidity.

As shown in Table 7, the COD removal efficiency under our optimal conditions was higher than those of the few other articles that have explored this issue.

Table 7: Comparative overview with prior researches

Conditions		Initial COD (mg/L)	COD removal efficiency (%)	Reference
Coagulant	Flocculant			
1.4 g/L $FeCl_3$	-------	3500	32.5	[45]
5 g/L $FeCl_3$	0.07 g/l PAM	4135	82	[46]
4.4 g/L $FeCl_3$	9.9 mL/L PAM	11520	80	[20]
7,2 g/l $FeCl_3$	0.2 mL/L PAM	25344	45	*This study*

Conclusion

In this study, a methodology of experimental design was used to optimize the COD and turbidity removal by coagulation-flocculation process and to determine the influence of the parameters (coagulant. flocculants dose and time of stirring) on the treatment of landfill leachate by coagulation-flocculation. We were more interested in the removal of COD. The main conclusions that can be drawn from this work are given below, the effect of the coagulation dose showed a positive impact on the amount of COD and turbidity removal. However, the model designed for the optimal design well fitted the experimental data with a coefficient of determination. R^2 of 0.92 and an Adj-R^2 of 0.88. The p-value of this model was less than 0.05. This indicates that the model is adequate and significant. Experimental design and response surface methodology were applied to determine the optimal conditions of removal of COD and turbidity. It shows that the maximum COD removal at masse of coagulant 7.2g/L, 0.2 mL/L of flocculants and temps=20min. The average COD removals, in optimum conditions, were occurred approximately 45%.

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