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Landfill leachate pretreatment by biocoagulation/bioflocculation process using plant-based coagulant (optimization by response surface methodology)

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ABSTRACT

Landfill leachate contains persistent organic pollutants, and therefore, it must be treated before it is released into natural water courses. The present study, reports on investigations about the removal efficiencies of turbidity, chemical oxygen demand (COD) and phenols from leachate using a biocoagulant/bioflocculent (cactus cladode) as well as the volume of generated sludge. The experimental variables (pH and coagulant dosage) were optimized by applying response surface methodology (RSM) equipped with the central composite faced design. An empirical quadratic polynomial model can accurately model the surface response with R^2 values greater than 92% for all the responses. The results of confirmatory experiments correspond to the model predictions, which demonstrate that RSM can achieve good predictions with the least number of required experiments. Results showed that the reduction efficiencies for turbidity, COD and phenols at pH 2 and cactus dosage of 1.48 g L^{-1} were, respectively, 93.25%, 66.50% and 52.95%, to achieve final values of 8.1 NTU, 2,251.2 and 611.65 mg L^{-1} for turbidity, COD and phenols, respectively. Generated sludge volume was 200 mL at optimum conditions. Cactus dosage and pH variation have a significant effect on pollution reduction in leachate.

Keywords: Landfill leachate; cactus; Turbidity; Chemical oxygen demand; Phenols; Analysis of variance

1. Introduction

Sanitary landfilling is the most economic and significant traditional method that is accepted worldwide for municipal as well as industrial solid waste management in both developed and developing countries [1]. It helps minimize environmental impacts by permitting the waste to degrade under controlled conditions where it is eventually transformed into relatively inert and stabilized material [2]. However, in developed countries, it is used as a systematic and safe process while in developing countries, most solid wastes are disposed of in open dumping spaces. These dump-sites generate leachate with contaminants in the surface and groundwater resources [3].

Leachate properties vary as a function of a number of factors such as the time that elapses, variations in climate, landfill size, site hydrology, landfill age, moisture content, and the composition of the waste [4]. Generally, the composition of the leachate reflects variations within the waste composition. However, the composition plays a key role in developing remedial actions and in choosing the leachate treatment process [5]. Additionally, as the landfill site ages, more complex dissolved organic matter is made from the waste within the landfill's leachate which dramatically reduces the efficiency of biological treatments for chemical oxygen demand (COD) removal; thus, physicochemical methods have become necessary

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for the adequate removal of recalcitrant dissolved organic matter [4]. Various methods are currently in use to treat the landfill leachate. Most of these methods are adapted for wastewater treatment processing and may be divided into two main categories: biological treatments and physicochemical treatments [6]. An example of aerobic biological treatment is the aerated lagoons and activated sludge and for anaerobic biological treatment, there is an example of anaerobic lagoons reactors remain the most widely implemented type of biological process [5,7,8]. As for the physiochemical treatments, there is air stripping, pH adjustment, chemical precipitation, oxidation, and reduction, coagulation using lime, alum, ferric chloride, and land treatment. Advanced techniques like carbon adsorption, ion exchange [6]. The application of coagulation–flocculation in the stabilized landfill leachates has been studied to reduce impurities such as COD, heavy metals, suspended solids and color [9–11]. However, the effective process parameters studied were limited to physical contaminants removal (color, COD, suspended solids and turbidity) [12]. Other parameters such as biological oxygen demand (BOD_5), ammoniacal nitrogen, phenols and xenobiotic organic compounds were effectively been investigated with the combination of coagulation–flocculation process with various advanced treatment processes [10,13].

Considering the inconvenience of conventional coagulants, the use of natural coagulants and their derivatives has recently increased [14]. Much research has proven the potentiality of biomaterial to treat water and wastewater due to their inherently renewable character, low toxicity, lower sludge volume compared to alum, biodegradability, low commercial cost, relative abundance, high treatment efficiency, harmlessness to humans, unfound contamination by-product released into treated water, and overall smaller environmental impact compared to inorganic and synthetic polymers [15]. Cactus has shown great capabilities in wastewater treatment and as a factor for sustainable development of the environment. It has been used as a biosorbent [16], and as a biocoagulant for the elimination of heavy metals, dyes, organic materials, and bacteria [17–20].

The main objective of this work is to optimize the biocoagulation process of stabilized landfill leachate bio pretreatment by central composite faced design of response surface methodology. Performances reduction in turbidity, COD and phenols, and generated sludge volume were chosen as the dependent variables (output responses). Cactus dosage and initial pH were chosen as the influence factors (input variables).

2. Material and methods

2.1. Sample collection and characterization

The samples were collected on 11/04/2019, from Bougharb's Sanitary Landfill which is located in Ibn Badis, Constantine, East of Algeria. The site has been operational since 2010. It occupies 50 ha of land and receives 344.65-ton d^{-1} of waste. All samples used in the present study were collected from a single point source in a single site at different times (Fig. 1). After the identification of the sampling containers which are: the place, the points and the date of the sampling, we must prepare the necessary equipment: gloves, a pair of boots. According to the official procedure, the material (a sample filler and transport jerricans (flasks) were rinsed once with soapy water, three times with tap water and then twice with distilled water. During sampling, five rinses of the vials and sample are performed to ensure that all contaminants are removed.

The landfill leachate samples were measured for both temperature and pH, stored in jerricans and immediately delivered to the laboratory, kept at 4°C in refrigeration by placing a storage label on the bottles (which contains the necessary information), without adding any chemicals ahead of being used and analyzed (because there is a risk of affecting the results of the analysis). The main physical and chemical characteristics of raw landfill leachate samples are shown in Table 1.

2.2. Biocoagulant preparation

In this study, cactus cladodes (powder) were used as a biocoagulant/flocculent, it was prepared as follows: the cactus pads were collected from a wild plantation near Constantine, East of Algeria. They were immediately sorted, washed with running water to remove dirt particles, then with distilled water various times. They were dried at 45°C for 48 h and then crushed using a domestic grinder, finally, sieved to obtain solids with a diameter of 63 μm as shown in Fig. 2. The solids were used as a raw coagulant to treat leachate without any chemical pre-treatment [15].

2.3. Fourier-transform infrared spectroscopy analysis of cactus powder

A characterization study of the biocoagulant is carrying out using Fourier-transform infrared spectroscopy (FTIR), to identify functional groups. The FTIR spectroscopy analysis was performed by applying an infrared spectrometer in the range of 400–4000 cm^{-1}.

2.4. Experimental procedure

The experiment started by mixing the contents of the tank completely to confirm uniformed initial turbidity, temperature, and pH values. All the runs were carried out at a room temperature of 21°C ± 1°C. A standard jar test apparatus with a digital feedback control system (wise stir, JTM6C Model) was used to simulate the biocoagulation/flocculation process. Each beaker contained 500 mL of wastewater samples that were stirred at 180 rpm for 10 min and the biocoagulant was added into the samples at the beginning of the experiment, then the samples were stirred at 30 rpm for 30 min, the flocs formed were allowed to settle for 30 min. After settling, the supernatant turbidity, COD, phenols and produced sludge were determined. Turbidity measurements were determined by HANNA turbidimeter (HI88713), COD was determined according to the standard method [21], phenols concentration was measured using a spectrophotometer (UV-1601) at a wavelength of 270 nm and sludge volume was the volume occupied by the produced sludge during settling in half an hour using an Imhoff Cone of 1 L.

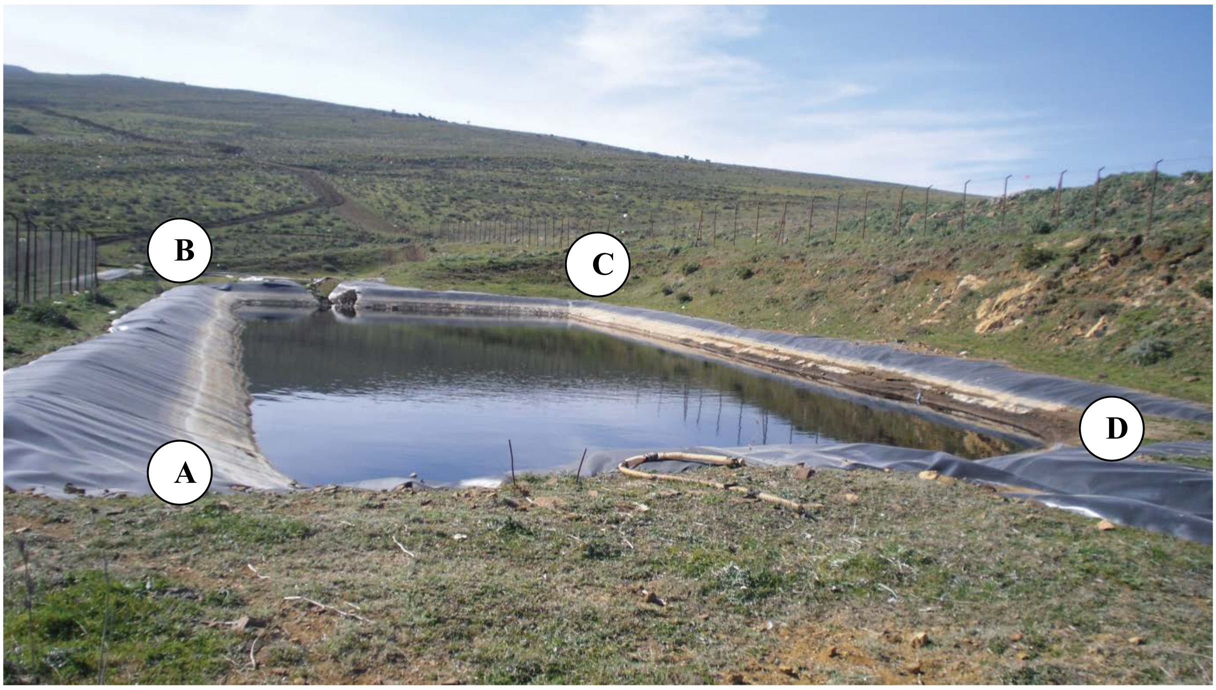


Fig. 1. Sampling collection points.

Table 1
Characteristics of the raw leachate (11/04/2019)

Parameter	Average values	LLD[a] [23]
pH	8.19	6.5–8.5
Temperature, °C	14.6	30
Electrical conductivity, mS cm^{-1}	10.08	/
Color	Blackish brown	/
Turbidity, NTU	120	/
Dissolved oxygen, mg L^{-1}	7.31	/
Potential redox, mV	–91.6	/
Chemical oxygen demand, mg L^{-1} O_2	6,720	130
Biological oxygen demand, mg L^{-1} O_2	450	40
BOD_5/COD	0.066	/
Nitrates (NO_3^-), mg L^{-1}	1.64	/
Ammonium (NH_4^+), mg L^{-1}	10.08	/
Orthophosphate (PO_4^{3-}), mg L^{-1}	1.31	/
Phenols, mg L^{-1}	1,300	0.5
Chlorides, mg L^{-1}	6,850	7

[a] legal limits for discharge into urbanized streams.

The turbidity, COD and phenols removal efficiencies (turbidity %, COD % and phenols %) were calculated using Eq. (1).

$$Y(\%) = \frac{Y_0 - Y}{Y_0} \times 100 \quad (1)$$

where Y_0 and Y represent the initial and final values of turbidity, COD and phenols of landfill leachate, respectively.

The pHs of the samples were adjusted from 2 to 12 using 1 M H_2SO_4 and 1 M NaOH solutions and measured with pH meter JENWAY 3505.

2.5. Experimental design and data analysis

The design of experiments is used to highlight and quantify the influence of the parameters taken into account. The steps in carrying out this study are as follows:

Step 1: Formalize the problem (identify the problem, quantify the objective to be reached by defining one or more responses);

Step 2: Select the parameters, fix their modalities (level of parameter variations) and select their interactions;

Step 3: Build the plan according to the Taguchi tables (Table 5);

Step 4: Carry out the tests;

Step 5: Analyze the results; there are two complementary analyzes;

Graphic analysis: It gives a simple representation of the results. It makes it possible to visualize the influence of the parameters and their interactions.

Statistical analysis: The analysis of variance aims to distinguish, in the overall variations of the response, the part due to the real influence of the parameters from the part due to chance. This analysis:

Step 6: Conclude after choosing the setting of the parameters which can be mastered and confirmation test;

A central composite faced design (CCFD) with two independent variables was used. Thirteen runs were

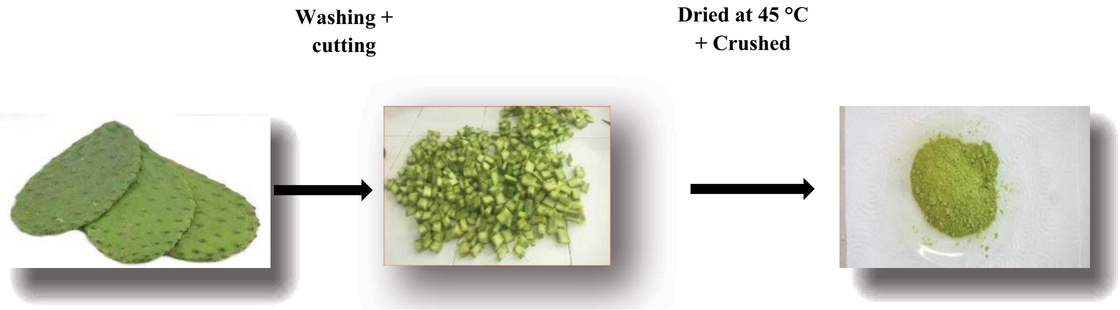


Fig. 2. Biocoagulant preparation.

required to cover all possible combinations of factor levels. Data was collected as a 2^2 factorial design (four cubic points) augmented by five center points and four axial points. The order, in which the experiments were run, was randomized to avoid the influence of unexpected variability in the observed responses.

The influence of the two selected factors: The mass of biocoagulant (cactus powder), (*A*) and the initial pH (*B*), on the yield of the four important responses which are the removal of turbidity: Turbidity (%), the reduction of the chemical oxygen demand: COD (%) and the elimination of aromaticity: phenols (%) and volume of generated sludge (mL) were studied. All the experiments are conducted in triplicate for each test to dampen uncontrollable variation (noise) [15,22].

The experimental range for each independent variable was based on a preliminary study, biocoagulant dosage range was [1–3] g L^{-1} and the pH range was [2–12]. The ranges and levels of the investigated variables; are presented in Table 2. For statistical calculations of Table 2, the variables X_i were coded as x_i according to the following equation:

$$X_i = \frac{X_i - X_0}{\delta X} \tag{2}$$

where X_i is the uncoded value of the independent variable, x_0 is the value at the center point of the investigated area and δX is the step change.

In this study, experimental data is evaluated using the software Minitab 17. Analysis of variances (ANOVA) was applied to provide the diagnostic checking test to assess the adequacy of the fitted model [11]. The coefficient of determination R^2 expressed the quality of the fitted polynomial model. It provides a measure of how much variability in the observed response values can be explained by the experimental factors and their interactions [14]. These analyses are done by means of Fisher's test and *p*-value (probability) [15]. Three and two-dimensional contour plots were used to illustrate the interactive effects of the independent variables on the dependent ones. 3D plots were drawn using MATLAB 7.9.0 (R2009b).

The fitting model should be of a second-order polynomial equation [Eq. (3)] which correlates the independent variables and the responses.

$$Y_m = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k}\sum_{j=1}^{k} b_{ij} X_i X_j + \sum_{i=1}^{k} b_{ij} X_i^2 + \varepsilon \tag{3}$$

Table 2
Independent variables levels for the central composite faced design

Variables	Coded variables levels[a]		
	–1	0	1
	Actual variables levels		
A: [cactus] (g L^{-1})	1	2	3
B: pH	2	7	12

[a] for the passage from actual variables level to coded variable level, the following equations were used: *A* = [cactus]–2; *B* = (pH–7)/5.

where Y_m is the response variable to be modeled, X_i and X_j the independent variables which influence Y_m, b_0, b_i, b_{ii} and b_{ij} are the offset terms, the *i*th linear coefficient, the quadratic coefficient and *ij*th interaction coefficient, respectively.

To remove insignificant terms from the predicted model, it is necessary to re-analyze the surface response designs without insignificant coefficients.

3. Results and discussion

3.1. Characteristics of the raw leachate

The chemical composition of the leachate is specific to each landfill. Indeed, it varies closely depending on the nature and age of the landfill, the type of waste and its degree of decomposition, the method of the landfill, the nature of the landfill site and climatic conditions.

The leachate from Bougherb's landfill center is blackish-brown in color due probably to the presence of humic substances [24] and fecal-like odor. Examination of the average values of the physicochemical parameters collected in Table 1 shows that the leachate studied shows a diversified and high pollutant load.

Indeed, the average electrical conductivity is 10.08 mS cm^{-1}, indicating the strong mineralization of the leachate. This mineralization is mainly attributable to the following parameters: chlorides (6,850 mg L^{-1}), orthophosphates (1.31 mg L^{-1}), ammonium (10.08 mg L^{-1}) and nitrates (1.64 mg L^{-1}). The average values of the parameters pH and turbidity are respectively 8.19 and 120 NTU. This shows, on the one hand, the basic character of the leachate from the landfill studied and on the other hand, their high mineral and organic load [25].

Table 3
Physicochemical composition of cactus pads

Parameters	Méndez et al. (Spain)[29]	Mounir et al. (Morocco)[30]
Ash (g/100 g)	1.05 ± 0.11	13.22 ± 0.31
Dry matter	5.7 ± 0.31	8.91 ± 0.25
Protein	0.34 ± 0.05	2.49 ± 0.08
Total sugar		41.20 ± 0.82
Brix degree	3.93 ± 0.76	/
pH	4.57 ± 0.07	3.93 ± 0.03
Ascorbic acid	1.75 ± 0.31	/
Phenolic compounds	143.3 ± 24.2	/
P	18.92 ± 5.23	/
Na	1.24 ± 0.5	/
K	226 ± 39	/
Ca	181 ± 28	/
Fe	151 ± 56	/

With regard to the organic load, the contents mean of COD and BOD_5 are respectively 6,720 mg L^{-1} (O_2) and 450 mg L^{-1} (O_2), with a BOD_5/COD ratio of 0.066. This indicates that the leachate and the landfill studied are in an intermediate phase, or even at its end [26]. Furthermore rising presence of high molecular weight contaminants, that is, bio-recalcitrant compounds, is associated with a very low biodegradability ($BOD_5/COD < 0.1$). Furthermore, the redox potential is also an important parameter to measure because it conditions the development of certain reactions, in particular the establishment of the various degradation phases which mostly take place in a reducing medium. The process of biodegradation and physicochemical reactions will allow the degradation of organic substances and immobilize non-degradable metals. With regard to metals and inorganic substances, these are either retained in their original state or adsorbed on surfaces or else present in the form of precipitates. Thus, the maturation phase reflects the end of biodegradation phenomena, with a transformation of internal metabolites into CH_4 and CO_2 by methanogenesis. The pH rises under the control of the buffering capacity of the carbonates. The redox potential is at its minimum value, the metallic species precipitate. In general, the complexation of metal spikes takes place during acidogenesis and this precipitates during methanogenesis [27].

In Algeria, standards have not yet been established for landfill leachate, but we referred to the current standard for industrial liquid effluent discharges [23] given that landfill juices or leachate are comparable to complex industrial discharges [28]. From the analysis of all the physicochemical results of the leachate from the Boughereb's landfill, these characteristics classify these leachates in the stabilized, given its BOD_5/COD ratio of 0.066 [5]. Other parameters confirm this evolution over time, namely: basic pH (8.19).

3.2. Physicochemical composition of cactus pads

As presented in Table 3, the chemical composition of cactus cladodes varies considerably among species and cultivars. It is also influenced by cladode age, seasonal temperature and rainfall conditions, and various agronomic factors, such as soil type and growing conditions [30].

3.3. FTIR analysis of cactus powder

FTIR has been implemented to identify the presence of functional groups on cactus powder. Peaks in the wavenumber region below 800 cm^{-1} could be attributed to nitrogen-containing bio ligands. These results indicate that the dried cactus contain various functional groups such as carboxyl, hydroxyl, sulfate, phosphate, aldehydes, ketones, and other charged groups. Table 4 shows the band assignments associated with the cactus spectrum.

3.4. Modeling the biocoagulation/bioflocculation process, statistical analysis and validation

The relationship between four criteria of pollutant removal (turbidity, COD, aromaticity and generated sludge volume) and two controllable factors (biocoagulant dosage and pH) was studied. A CCFD shown in Table 5 allows the development of mathematical models where each response variable y is assessed as a function of biocoagulant dosage (cactus powder) (A) and pH (B) and calculated as the sum of a constant, two first-order effects (terms in A and B), two second-order effects (A^2 and B^2) and one interaction effect (terms in $A \times B$) according to Eq. (3).

A total of 13 sets of batch runs were realized according to the CCFD matrix for experimental design (coded values of the two factors, that is, biocoagulant dosage and pH), experimental and predicted responses for removal efficiencies of turbidity, COD and phenols, and generated sludge volume have been summarized in Table 5.

As shown from the results, the obtained values were reasonably close to the predicted experimental values, specifying the efficiency of the developed model to describing the correlation between the controlling parameters on treatment efficiency of landfill leachate. Within the chosen range of the experiment, the observed removal efficiencies varied between 45.25% and 92.13% for turbidity (average is 69.06%), 5.46% and 65.83% for COD (average 31.19%), 2.50%–64.81% for aromaticity (average 19.75%) and 84–201 mL for generated sludge volume (average 132.13 mL).

The results of the fitted models in coded terms for turbidity elimination, COD removal and phenols reduction, and volume of generated sludge are given in Eqs. (4)–(7) and presented in Table 6.

The significance of each term in the model was determined by the student test and the probability values (p-value. The regression coefficients values, t-student and significance level p-values of all the studied responses are regrouped in Table 7.

According to the t-test, the constants and the two first-order effects (terms in A and B) for all the studied responses are significant since their p-values were smaller than 0.05. Furthermore, t-values were greater than t_{crit} (0.05, 7) equal to 2.37, indicating meaningful corresponding terms which are cactus dosage and pH effects. The same case for the two second-order effects (terms in A^2 and B^2), their p-values were <0.001 [31]. It is important to

Table 4
FTIR structural elucidation of cactus

Wave number (cm^{-1})	Vibration and liaisons	Chemical grouping
890.94	S–O	Sulfoxides
1,045.23	C–Cl	Chloro-alkanes
1,313.29	C–O–C– or –OH	Polysaccharides
1,428.02	C–OH	Phenol
1,611.23	C=C	Aromatic
1,740.44	C–O	Carboxylic acid, esters
2,361.41	C≡N	Nitrile
2,921.63	CH_3, CH_2 and CH	Aliphatic
3,274.54	O–H, H–N	Alcohols, phenol, acid, and amine

Table 5
Experimental conditions and results of the CCFD design

Run	*A* [cactus]	*B* pH	Turbidity (%)		COD (%)		Phenols (%)		Sludge volume (mL)	
			Exp.	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.
1	–1	–1	82.25	79.01	65.45	64.04	54.81	53.53	180.5	180.8
2	1	–1	74.50	73.77	56.34	55.37	18.62	22.11	155	159.36
3	–1	1	55.45	52.79	10.50	10.94	4.12	0.25	120.20	114.66
4	1	1	45.25	45.10	05.46	6.34	2.50	2.90	84	83.25
5	–1	0	52.18	58.07	22.50	23.46	12.91	18.56	101	115.94
6	1	0	50.75	51.61	16.75	16.83	8.33	4.43	93.5	89.88
7	0	–1	92.13	96.09	65.83	68.19	48.45	46.23	201	197.04
8	0	1	65.85	68.65	18.45	17.12	5.76	9.73	120	126.28
9	0	0	77.55	74.54	28.65	28.63	20.74	19.91	131	130.23
10	0	0	76.25	74.54	28.91	28.63	20.74	19.91	130.25	130.23
11	0	0	75.75	74.54	29.55	28.63	20.28	19.91	130.25	130.23
12	0	0	75.00	74.54	28.46	28.63	19.45	19.91	131	130.23
13	0	0	74.95	74.54	28.64	28.63	20.10	19.91	131	130.23

Exp.: experimental values, Pred.: predicted values.

Table 6
Empirical second-order polynomial equations in coded an actual terms

Equations in coded terms		Equations
Turbidity (%)	$\text{Tur }(\%) = 74.55 - 3.23A - 13.74B - 19.7A^2 + 7.82B^2 - 0.61AB$	(4)
COD (%)	$\text{COD }(\%) = 28.63 - 3.31A - 25.53B - 8.48A^2 + 14.02B^2 + 1.01AB$	(5)
Phenols (%)	$\text{Phenols }(\%) = 19.91 - 7.07A - 18.25B - 8.41A^2 + 8.07B^2 + 8.64AB$	(6)
Sludge (mL)	$\text{Sludge (mL)} = 130.23 - 13.03A - 35.38B - 27.32A^2 + 31.43B^2 - 2.68AB$	(7)
Equations in actual terms		
Turbidity (%)	$\text{Tur }(\%) = 35.04 + 76.43[\text{cactus}] - 6.88\text{pH} - 19.7[\text{cactus}]^2 + 0.31\text{pH}^2 - 0.12[\text{cactus}]\text{pH}$	(8)
COD (%)	$\text{COD }(\%) = 67.42 + 29.20[\text{cactus}] - 13.37\text{pH} - 8.48[\text{cactus}]^2 + 0.56\text{pH}^2 + 0.2[\text{cactus}]\text{pH}$	(9)
Phenols (%)	$\text{Phenols }(\%) = 66 + 14.48[\text{cactus}] - 11.63\text{pH} - 8.41[\text{cactus}]^2 + 0.32\text{pH}^2 + 1.72[\text{cactus}]\text{pH}$	(10)
Sludge (mL)	$\text{Sludge (mL)} = 150.7 + 100[\text{cactus}] - 23.61\text{pH} - 27.32[\text{cactus}]^2 + 1.25\text{pH}^2 - 0.53[\text{cactus}]\text{pH}$	(11)

note that the pH term was the most significant component of all the regression models for the present study. The interaction effect was insignificant for turbidity, COD removal efficiencies, and the generated sludge volume since their *p*-values were: 0.744, 0.181 and 0.294, respectively. They, therefore, can be removed from their quadratic models. The interaction effect ([cactus] × pH) of the phenol removal performance response was very strong

Table 7
Coefficients, *t*-values and *p*-values for all the studied responses

Studied responses	Coded coefficients				*t*-values				*p*-values			
	Turbidity (%)	COD (%)	Phenols (%)	Sludge (mL)	Turbidity (%)	COD (%)	Phenols (%)	Sludge (mL)	Turbidity (%)	COD (%)	Phenols (%)	Sludge (mL)
Constants	74.55	28.63	19.91	130.23	79.82	50.39	12.51	66.50	0.000[a]	0.000[a]	0.000[a]	0.000[a]
A: [cactus]	−3.23	−3.31	−7.07	−13.03	−2.20	−5.94	−4.52	−6.77	0.064[b]	0.001[a]	0.003[a]	0.000[a]
B: pH	−13.72	−25.53	−18.25	−35.38	−9.33	−45.71	−11.67	−18.38	0.000[a]	0.000[a]	0.000[a]	0.000[a]
A^2: [cactus]^2	−19.70	−8.48	−8.41	−27.32	−9.09	−10.31	−3.65	−9.63	0.000[a]	0.000[a]	0.008[a]	0.000[a]
B^2: pH^2	7.85	14.02	8.07	31.43	3.61	17.04	3.50	11.07	0.009[a]	0.000[a]	0.010[a]	0.000[a]
$A \times B$: [cactus] × pH	−0.61	1.01	8.64	−2.68	−0.34	1.49	4.51	−1.13	0.744[b]	0.181[b]	0.003[a]	0.294[b]

[a]significant; [b]insignificant.

since its *p*-value is equal to 0.004, indicates that there is an interactive effect between pH and mass of cactus in the elimination of aromaticity. Positive term values in the developed models have positive effects while negative values have negative effects on the response variable.

Table 8 provides the ANOVA of variables fitted to quadratic polynomial models as well as other statistical parameters for turbidity, COD and aromaticity removal efficiencies and volume of generated sludge. A closer analysis of the table reveals that all the models were significant at a 95% confidence level and in most of the cases *p*-values were less than 0.05. In order to evaluate the adjustment quality and to examine the efficiency and the statistical significance of the polynomial regression models, statistical testing of the models was performed with Fisher's test.

The fitted model was suitable and was a good predictor of the experimental results when the *F*-value is larger than the tabulated value of F ($F_{(5,7)}$) equal to 3.97 for a certain freedom degrees number in the model at a level of significance α [14]. In Table 2, four fitted models have *F*-values of 34.09, 486.78, 39.08 and 108.3 with a very low probability value ($P < 0.005$) implied that terms were significant in all models. The ANOVA results showed high R^2 values varied from 0.9614 to 0.9971. The correlation coefficient needs to be at a minimum of 0.80 for a good fit of the model [32]. These high R^2 coefficients (closer to 1) reveals good accordance between the quadratic models and the experimental data [33]. The values of the adjusted R^2 of 0.9339, 0.9951, 0.9407 and 0.9781 respectively, for turbidity, COD, phenols removal efficiencies, and for generated sludge volume were also high to advocate the high significance of the models within the range of experiment. Therefore, the empirical models were accurately employed for predicting the variation percentage of the study's responses [34,35].

By applying a diagnostic graph, such as the one of predicted vs. actual values of turbidity reduction efficiency in Fig. 3a, the COD removal efficiency in Fig. 3b, the aromaticity elimination efficiency in Fig. 3c and the generated sludge volume in Fig. 3d, the data points are closely spread around the first bisector and indicate a good agreement between predicted and experimental values of all the chosen responses [8].

Fitting of the data to various models (such as linear, two factorial, quadratic, partial quadratic) and their subsequent ANOVA showed that the turbidity removal efficiency, COD reduction efficiency and generated sludge volume were most suitably described with quadratic polynomial models. The reduced quadratic models contain linear terms and include pure quadratic terms but didn't contain partial interaction quadratic terms. Table 9 illustrates the reduced quadratic models in terms of coded and actual factors with significant terms with their new correlation and adjusted coefficients.

3.5. Process analysis

Fig. 4a, c, e and g represent the surfaces plots (3D plots) determined by regression models equations of the turbidity, COD and phenols removal efficiencies and generated sludge volume with the independent variables.

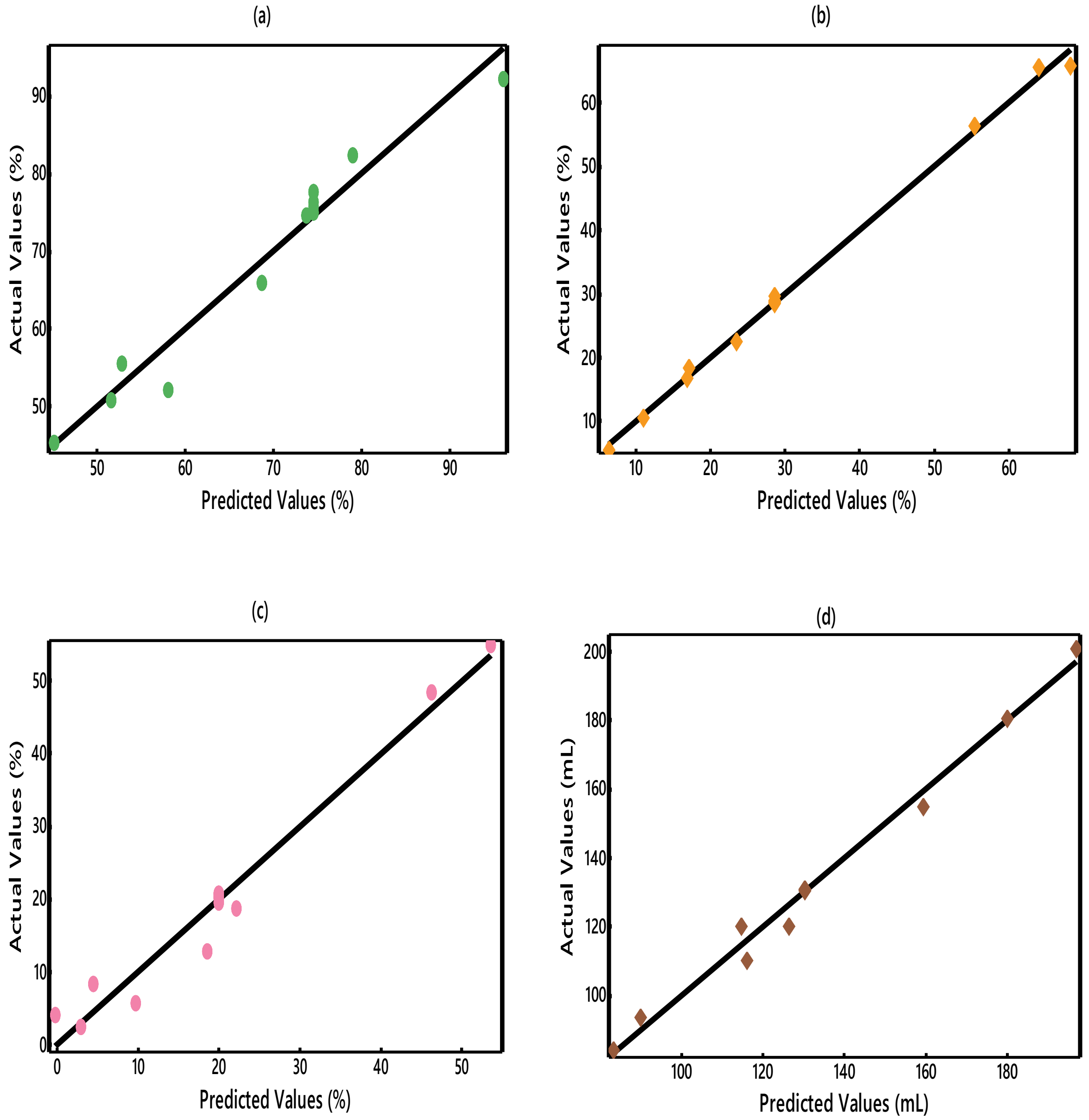
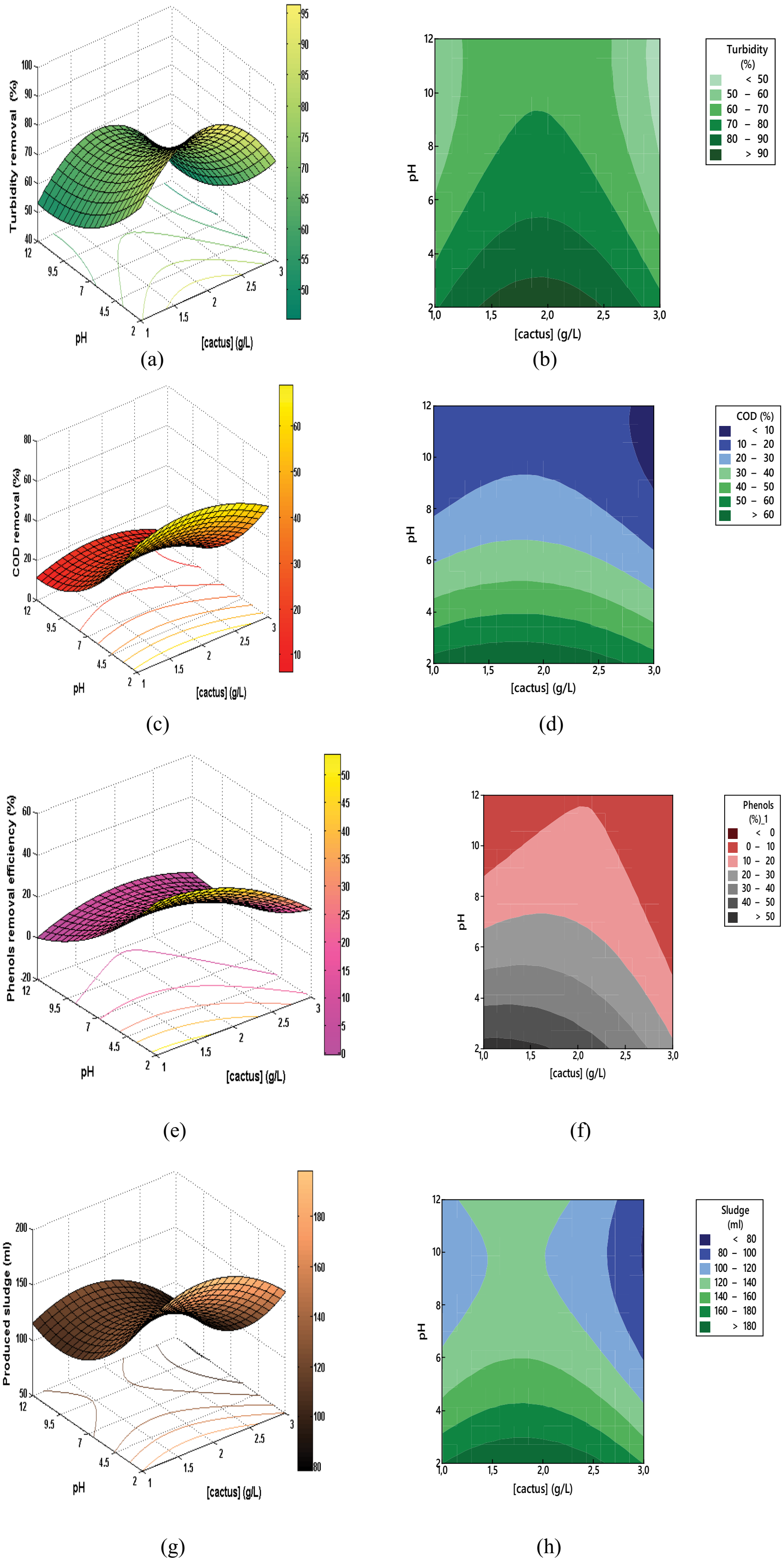


Fig. 3. Predicted vs. actual for (a) turbidity, (b) COD and (c) phenols removal efficiencies and (d) for generated sludge volume.

Corresponding contour plots (2D plots) of all the responses were illustrated in Fig. 4b, d, f and h.

Coagulant dosage is a critical factor to be assessed when determining the optimum conditions of pollutant reduction during the coagulation–flocculation process because overdosage or insufficient dosage may result in poor removal efficiency. As shown in Fig. 4a, increased turbidity removal was observed with increasing cactus dose and decreasing pH values. However, an increase in cactus dose beyond the optimum region resulted in a decrease in the removal efficiency. This trend can be observed for all the other studied responses COD and phenols removal efficiencies Fig. 4c and e. This implies that overdosing happened in the reaction solution. Overdosing deteriorated supernatant quality, referring to the "re-stabilization" of the colloidal particles, and therefore the particles could not be coagulated well [36]. Also beyond the optimal dose, the excess of the coagulant itself increases the concentration of suspended matter and consequently turbidity, COD and phenols since it is based on organic matter and contains phenols.

The pH is an extremely essential variable in the coagulation/flocculation process that affects cactus flocculation. The variation of pH may ultimately alter the surface characteristics of colloids of the pollutant and flocculent charge status, which results in the variation of flocculation capability [37]. The contour plots and 3D response surfaces showed that the elimination efficiencies of turbidity, COD and phenols enhanced at initial acidic pHs of landfill leachate. The maximum reduction percentages of all the responses were obtained at optimum pH values



(a) (b)

(c) (d)

(e) (f)

(g) (h)

Fig. 4. Response surface plots (a, c, e and g) and contour plots (b, d, f and h) of predicted turbidity, COD and phenols removal efficiencies, and generated sludge volume as a function of the operating biocoagulant dose and initial pH.

Table 8
ANOVA results for responses parameters

Source	Sum of squares	Freedom degree	Mean of square	F-value	p-value
Turbidity removal efficiency (%)			$R^2 = 96.14\%$, $R^2_{\text{adj}} = 93.39\%$		
Model	2,266.04	5	453.21	34.90	0.000
Residual error	90.91	7	12.99		
Lack of fit	86.33	3	28.78	25.13	0.005
Total	2,356.94	12			
COD reduction efficiency (%)			$R^2 = 99.71\%$, $R^2_{\text{adj}} = 99.51\%$		
Model	4,557.83	5	911.57	486.78	0.000
Residual error	13.11	7	1.87		
Lack of fit	12.38	3	4.13	22.63	0.006
Total	4,570.94	12			
Phenols elimination efficiency (%)			$R^2 = 96.54\%$, $R^2_{\text{adj}} = 94.07\%$		
Model	2,868.64	5	573.73	39.08	0.000
Residual error	102.76	7	14.68		
Lack of fit	101.62	3	33.87	118.56	0.000
Total	2,971.41	12			
Produced sludge (mL)			$R^2 = 98.72\%$, $R^2_{\text{adj}} = 97.81\%$		
Model	12,048.9	5	2,409.79	108.33	0.000
Residual error	155.7	7	22.24		
Lack of fit	155.0	3	51.68	306.25	0.000
Total	12,204.6	12			

Table 9
Reduced polynomial regression models

Reduced equations in coded terms		Equations
Turbidity (%)	$\text{Tur}\ (\%) = 74.55 - 3.23A - 13.74B - 19.7A^2 + 15.65B^2$; $R^2 = 96.08\%$, $R^2_{\text{adj}} = 94.12\%$	(4)′
COD (%)	$\text{COD}\ (\%) = 28.63 - 3.31A - 25.53B - 8.48A^2 + 14.02B^2$; $R^2 = 99.62\%$, $R^2_{\text{adj}} = 99.43\%$	(5)′
Phenols (%)	$\text{Phenols}\ (\%) = 19.91 - 7.07\text{A} - 18.25B - 8.41A^2 + 8.07B^2 + 8.64AB$; $R^2 = 96.54\%$, $R^2_{\text{adj}} = 94.07\%$	(6)′
Sludge (mL)	$\text{Sludge}\ (\text{mL}) = 130.23 - 13.03A - 35.38B - 27.32A^2 + 31.43B^2$; $R^2 = 98.49\%$, $R^2_{\text{adj}} = 97.73\%$	(7)′
Reduced equations in actual terms		
Turbidity (%)	$\text{Tur}\ (\%) = 36.75 + 75.57[\text{cactus}] - 7.13\text{pH} - 19.7[\text{cactus}]^2 + 0.31\text{pH}^2$	(8)′
COD (%)	$\text{COD}\ (\%) = 64.57 + 30.63[\text{cactus}] - 12.96\text{pH} - 8.48[\text{cactus}]^2 + 0.56\text{pH}^2$	(9)′
Phenols (%)	$\text{Phenols}\ (\%) = 66 + 14.48[\text{cactus}] - 11.63\text{pH} - 8.41[\text{cactus}]^2 + 0.32\text{pH}^2 + 1.72[\text{cactus}]\text{pH}$	(10)′
Sludge (mL)	$\text{Sludge}\ (\text{mL}) = 158.2 + 96.2[\text{cactus}] - 24.68\text{pH} - 27.32[\text{cactus}]^2 + 1.25\text{pH}^2$	(11)′

In Eqs. (4)′, (5)′ and (7)′, it was observed a small changes in the reduced models terms values.

Table 10
Confirmatory experiments at optimum conditions

	pH	Dose (g L^{-1})	Predicted	Experimental	Error
TUR (%)	2	1.48	92.17	93.25	1.08
COD (%)			67.54	66.50	1.04
Phenols (%)			52.23	52.95	0.72
Sludge volume (mL)			198.02	200	1.98

of 2. Moreover, in acidic media at low pH, protonation may occur, resulting in reduced charge density, which leads to self-aggregation of COD and phenols where less coagulant is required. For instance, at fixed pH, an increase of the cactus dose leads to greater phenols removal until the optimum dose which decreases gradually as the cactus dose increases further.

Based on Fig. 4b, the turbidity removal was optimum at a higher dosage of 1.5 to 2.5 g L^{-1} of cactus, with pH between 2 and 3. At this condition, the percentage removal of turbidity was greater than 90%. Previous studies have shown that high turbidity removal efficiency was found at 160 mg L^{-1} of $FeCl_3$ and pH of 3 [25]. Yusoff et al. [38] have reported that the application of crosslinking modification for *Durio zibethinus* seed waste starch flocculants showed good improvement (more than 90% of turbidity removal using 400 mg L^{-1} of natural flocculent). According to Kakoi et al. [31], the optimum conditions for the removal of turbidity were 1.2 g L^{-1} and pH of 5 using Maerua Decumbent as a biocoagulant to achieve more than 99% of turbidity removal efficiency. Although the treatment achieved significant removal of COD of up to 60% it did not achieve the recommended limit for COD in wastewater before disposal to the environment of 130 mg L^{-1} [23]. Therefore, the application of cactus as a coagulant for COD removal would be recommended for pre-treatment purposes. According to the results, maximum removal efficiency can be obtained at pH 2 and dosage between 1 and 2.5 (Fig. 4d). This result confirms the results found by Zainol et al. [20], in which cactus opuntia was able to remove 66.8% of turbidity and 42% of COD at optimal pH 2 with a favorable dose of 8 g L^{-1}. A study performed by Rasool et al. on the combined use of *Ocimum basilicum* L and PAC for leachate pretreatment showed that more than 60% of COD removal efficiency was obtained at ratio 1:1 [39]. Also, recent works clearly reveal that iron salts which are the most efficient coagulant, are resulting in COD reductions up to 70% [11,40–42]. A similar result was observed by Luo et al. [43] they have observed that achieving 50.40% of COD removal was at pH 3 and coagulant dosage of 0.50 g PAC/g COD_0 (initial COD). Raw landfill leachate recorded a total average concentration of phenols at 1,300 mg L^{-1}. Phenol usually comes from resins, paints, plastics, sand casting foundry. Furthermore, phenol is the most important derivative of benzene, after styrene. Given its toxic nature, several methods have been developed for its treatment, namely: ozonation, chlorination, coagulation/flocculation and also adsorption on activated carbon. Biological processes are less commonly used because of the inhibition of anaerobic and aerobic bacteria caused by phenol [8,44,45]. For this study, the effective reduction of phenol from leachate was evaluated by using cactus dosage varying from 1 to 1.5 g L^{-1}. At pH 2, the cactus exhibited a maximum phenol reduction efficiency of 52.23% (Fig. 4f). Several studies have demonstrated the effectiveness of coagulation–flocculation for the removal of phenol. About 76% of bisphenol A removal was achieved with an initial concentration of 37.05 mg L^{-1} at pH 7.5 by using 0.5 g L^{-1} of locust bean gum [36]. Bakraouy et al. [8] have found more than 98% of phenol removal efficiency using 4.2 g L^{-1} of ferric chloride and 11.5 mL L^{-1} of flocculent at a pH of 8.

Fig. 5. Leachate before and after pretreatment.

In addition to pollutant removal, sludge production was considered in this work. We obtained significantly high removal efficiency values with the biocoagulant used during the pretreatment of leachate through coagulation. However, as the cactus dose increased, the sludge volume amount increased as well. The quantity of sludge produced should also be taken into account along with removal efficiency. Sludge volume in this study was measured and is presented in Fig. 4g and h. The produced sludge amount was observed to be increased due to coagulant dose studies. Characterization of the produced sludge was brown in flocculated form. The quantity of sludge generated by cactus significantly increased as the coagulant dose increased. At the optimum conditions generated sludge volume was 200 mL L^{-1}. the comparison of sludge volumes generated at equal efficiencies pretreatment for stabilized leachate using cactus (200 mL L^{-1}) and alum (338 mL L^{-1}) [46], it is shown that biocoagulant generate less and safe sludge.

Considering that the produced sludge has a 150 $/ton disposal cost, it should be evaluated with the costs of chemicals. Comparison of cost and efficiency values revealed that optimum treatment can be achieved by cactus with a suitable cost and low sludge quantity.

The coagulation may be due to anyone or a combination of the following mechanism: double layer compression, sweep flocculation or enmeshment within colloidal floc, adsorption and charge neutralization by oppositely charged ions, adsorption and interparticle bridging in case of polymeric coagulant [36]. Bouaouine et al. [19] have reported that the biocoagulation/bioflocculation mechanism takes place by entrainment and sweeping during slow settling. The adsorption and interparticle bridging mechanism can lead to gel formation minimizing the amount of sludge.

The main factor behind the possibility of using cactus as a material for wastewater treatment is its biochemical composition. Cactus is composed of proteins of cationic, anionic and non-ionic nature, lipid contents, and polysaccharide which is considered as the main ingredient (biopolymeric structure). Many research showed that proteins work like cationic polyelectrolytes once they are added to raw water. Proteins cause colloids destabilization and neutralize suspended particles [47], this confirmed our belief that protein can be the responsible bioactive coagulating agent in cactus. Since cactus contains 4.8% of crude protein. Aziz et al. [36] had demonstrated that the zeta potential in landfill leachate was slightly increased with the decrease of pH, which showed that the static repulsive energy among the flocculants and suspended particulates and the biomaterial did not completely exert in the coagulation/flocculation process. This led to exclude the charge neutralization mechanism in the biocoagulation process and even if it exists, it will be insignificant. Under such conditions, many researchers had proven that most of the natural coagulants are biopolymers with high molecular weight and consist of long-chain structures that provide many unoccupied adsorption sites. These biopolymers can be polysaccharides [18,36,47]. In this context, it was reported that galacturonic acid is significantly implicated as the main active coagulant agent, based on its polymeric structure. This biopolymeric structure provides a bridge for particles to adsorb. Moreover, the functional groups of cactus polysaccharides included carboxyl (–COOH), hydroxyl (–OH) and amino or amine ($-NH_2$) groups, as well as hydrogen bonds. These functional groups are considered as preferred groups for the flocculation process [17]. As mentioned above, over-dosage resulted in surface saturation and induced re-stabilization of colloidal particles due to the excess adsorption of polymer species that occupied excessive binding sites, which inhibited the intraparticle bridging between neighboring particles. Moreover, Vijayaraghavan et al. [48] indicated that natural coagulants generated small quantities of sludge due to their physical properties and bridging mechanism.

3.6. Process optimization

With multiple responses, the optimum conditions where all variables simultaneously meet the desirable reduction criteria (Fig. 5) could be visualized graphically by superimposing the contours of the response surfaces in an overlay plot presented in Fig. 6. Graphical optimization displays the area of feasible response values in the factor space and the regions that do fit the optimization criteria would be white. The multi-objective optimization has been effected using the Minitab Optimizer option. The results of the optimization multi-objective are shown in Fig. 7.

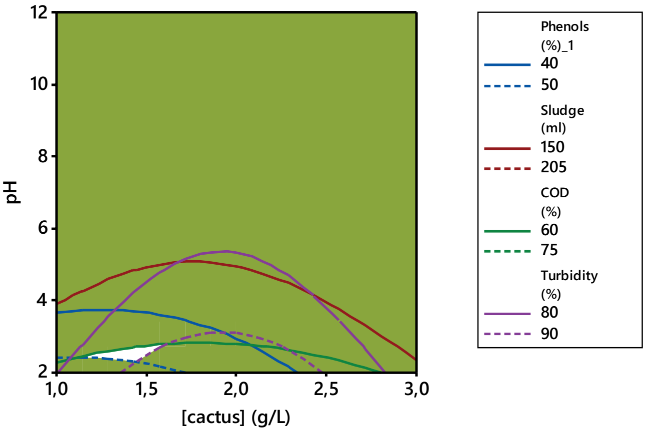


Fig. 6. Overlain contour plots of turbidity, COD and phenols removal performances with sludge volume generated by the coagulation/flocculation process.

Three additional runs were conducted applying the optimal conditions to confirm the validity of the results achieved from models and experiments for cactus as biocoagulant. As shown in Table 10, the removal efficiencies for all response parameters obtained from the experiments and as estimated by models were in close agreement. The estimated errors for turbidity, COD and phenols removal efficiencies, and generated sludge volume are acceptable.

3.7. Characterization of treated supernatant

In order to evaluate the impact of the use of the biocoagulant, it was judicious to examine the quality of the pretreated landfill leachate, in addition to the parameters

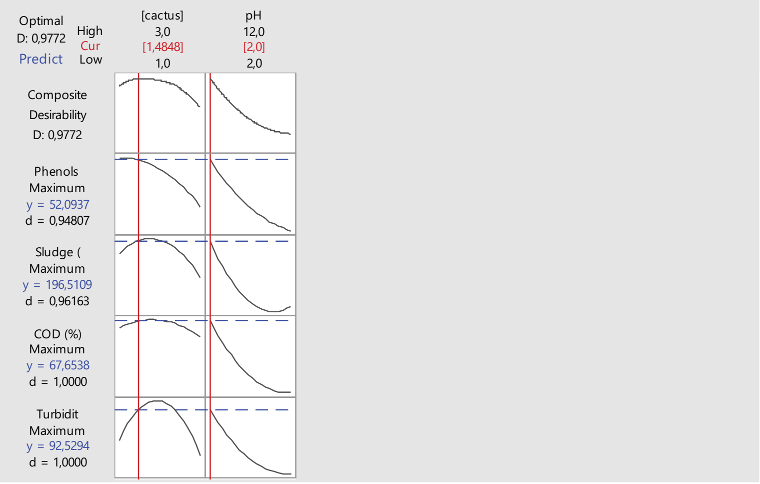


Fig. 7. Optimizer plot for the pretreatment of leachate.

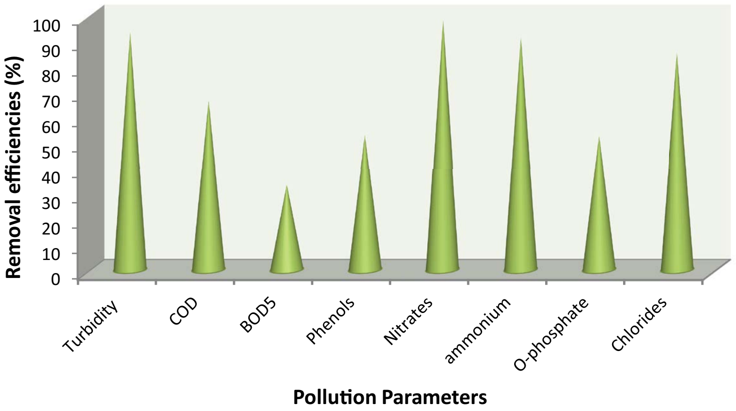


Fig. 8. Characterization of pretreated landfill leachate supernatant.

followed during this study which are turbidity, COD and phenols, and the volume of generated sludge, the values of the other parameters were determined such as BOD_5, nitrates, ammonium, o-phosphates and chlorides.

The optimal values (dose of biocoagulant = 1.48 g L^{-1} and pH = 2) were used to test the ability of the biocoagulant to remove pollution and to have an idea about the second process to treat the leachate. Fig. 8 shows a significant decrease lowering of the pollution parameters using the cactus powder in the biocoagulation/flocculation process, a reduction yield of the turbidity that exceeded 93% to reach a final value of 8.1 NTU. The final value of COD was 2251.2 mg L^{-1} with an efficiency of 66.5%. The phenols were reduced to 0.611 mg L^{-1} (52.95%), while the chlorides (Cl^-) only remained 0.993 mg L^{-1} (more than 85% of reduction efficiency). Ammonium and nitrates have exceeded an efficient removal of 90%. In conclusion, the cactus can replace conventional coagulants that generate toxic products and can be used to reduce the pollution of leachates in landfills.

4. Conclusion

The objective of the present work is to explore the optimum process conditions, using response surface methodology (RSM), required while using cactus as a biocoagulant to remove turbidity, COD and phenols, and to evaluate the volume of generated sludge from landfill leachate pretreatment. It was established that pH and coagulant dosage has a considerable effect on the removal of the selected parameters. Maximum removal of turbidity, COD and phenols was observed more than 93.25%, 66.5% and 52.95%, respectively at a pH of 2 and a biocoagulant dose of 1.48 g L^{-1}. ANOVA showed high R^2 values (>90%) of the regressions models equations for all the responses, thus ensuring a statistical adjustment of the second-order regression model with the experimental data.

The combination of the RSM and CCFD was an effective and powerful approach for the optimization of the coagulation/flocculation process for landfill leachate pretreatment, as well as cactus can be significantly employed as a coagulant for pre-treatment or post-treatment of landfill leachate having a high concentration of recalcitrant compounds rendering biological processes inefficient.

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