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Removal of turbidity and chemical oxygen demand using an eco-friendly coagulant/flocculent (optimization and modeling through the response surface methodology)

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ABSTRACT

The use of the cactus mucilage as a bio-coagulant/bio-flocculent in the treatment of wastewater is a real strategy for sustainable development of the environment, because of its abundance and the non-toxicity for the human health. In this research, the biomaterial was used to treat municipal wastewater plant by coagulation/flocculation process. To optimize two most important factors: dosage coagulant and initial pH, a central composite faced centered design, and response surface methodology were applied. The effect of the pH on the supernatant turbidity removal and the chemical oxygen demand (COD) reduction was very significant, whereas the coagulant dosage was insignificant on the COD removal efficiency, there is no interaction effect between coagulant dosage and initial pH on the responses studied. Experimental results revealed that the maximum reduction of turbidity and COD could be attained at optimal conditions, that is, coagulant dosage of 5.6 mL/L^{-1} and pH of 12 from which the removal of turbidity and COD were 99.39% and 80.03%, respectively. The study also showed that the quadratic regression model could be used as theoretical basis for coagulation/flocculation process of wastewater treatment based on the high coefficient of determination R^2 value of 0.93 obtained from the analysis of variances.

Keywords: Bio coagulant; Turbidity; COD; Central composite design; Analysis of variances

1. Introduction

Coagulation–flocculation is an important and critical process in municipal wastewater, surface water, and industrial wastewater including the elimination of dissolved organic, turbidity, and color. This also removes the microorganisms that are often attached to the particles [1]. Chemical coagulants based on synthetic polymers and inorganic salts such as ferric chloride and aluminum sulfate are actually used in water treatment all over the world. Aluminum sulfate (alum) which is common coagulant globally used in water and wastewater treatment can achieve 90%–99% microbial elimination under the optimal conditions.

However, these treatment strategies have many disadvantages over other treatment systems. It generates many problems; one problem associated with this methodology is the generation of high volume of toxic sludges, which contain large amount of metals Al and Fe. These metals make the sludge difficult to be treated by biological methods (biochemical oxygen demand to chemical oxygen demand ratios: BOD/COD could be low for these sludges) and that pose disposal challenges since they tend to accumulate in the environment. They also require corrosion-resistant

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storage and feed equipment. Synthetic coagulants have the inconvenience of toxicity, large dosage, and low effect [2,3]. Also other disadvantage associated with harmful effects on human health, the high level of residual aluminum (resulting from alum coagulation) has been linked to several medical disorders including osteomalacia, dialysis encephalopathy syndrome, Alzheimer's disease, and renal failure [4–6].

Conventional coagulants change the pH and water alkalinity after treatment; they react with natural alkalinity present in water leading to pH reduction, and prove low coagulation efficiency in cold waters [7].

They are also costly for developing countries and cause seeks economic growth [8]. Additionally, it is probable to increase aluminum concentrations in the treated water after application of the coagulant and create problems in distribution systems, interfering with the disinfection process, due to covering of microorganisms which join to the precipitated hydrated aluminum. Another problem is deposition of products from aluminum hydrolysis in the pipe walls, thus the transmission capacity decrease and generate corrosion problems [9]. So their application was limited.

Studies in the wastewater treatment strategies in recent years has been concentering regards on the use of biomaterials such as microorganisms, animals or plants to remove these issues and to combat pollutants including heavy metals, dyes, phosphates, nitrates, chlorides, phenolic compounds, pesticides, detergents, and particulates among others. This guides to the exploration of natural coagulants and flocculants that purify water through coagulation–flocculation processes [10,11].

These biomaterials are an alternative solution to many problems and the use of natural environmentally benign agents in the treatment of drinking water and wastewater have gained a global interest for their: low toxicity, low acquisition cost, relative abundance, renewability, biodegradability, safety for human health, and low sludge production at the end of the process. Also, they require no pH adjustment and they have a large number of charges on the surface that increase coagulation efficiency. Consequently, a lower environmental impact compared to inorganic and synthetic polymers [12].

Various researches have demonstrated the removal efficiency of turbidity in different types of water, using bio coagulants such as *Moringa oleifera*, bacterial isolates, and *Plantago psyllium* [13]. One of which is cactus (*Opuntia ficus indica*) commonly called nopal in Mexico, prickly pear or cactus leaf in USA which proved its competence in the coagulation process of drinking water and wastewater treatment including heavy metals removal, dyes and organic materials from aqueous environments. Further, it has the ability to remove bacteria [14,15].

Optimizing the significant parameters in the coagulation/flocculation process through the classical method includes the varying of a single factor while all other factors are kept fixed at a specific set of conditions. This is an extremely time-consuming (it requires many experiments runs), expensive, incapable of reaching the true optimum due to neglecting of the interaction among variables [16]. These limitations of the conventional method can be overcome by applying statistical experimental design techniques using the response surface methodology (RSM). This method has been applied successfully in various scientific and technical fields such as applied chemistry and physics, biochemistry and biology, chemical engineering, environmental protection, membrane science, and technology.

The main objectives of using RSM is developing models, improving, optimizing processes, and evaluating the relative significance of several affecting factors even in the presence of complex interactions. RSM uses an experimental design such as the central composite design (CCD) to fit a model by least squares techniques. Adequacy of the proposed model is then revealed using the diagnostic checking tests provided by analysis of variance (ANOVA) [17,18].

The work carried out concerns the treatment of municipal wastewater with a natural coagulant, the cactus, using the design of experiment by fixing two key factors (cactus concentration and pH) and two responses (turbidity and COD). For the study of coagulation/flocculation we used the design of experiment which is very interesting to take into account in order to produce reliable results as regards the evaluation of the optimum dose of coagulant and of pH for the treatment.

2. Materials and methods

2.1. Coagulant preparation

Opuntia ficus-indica (cactus) that belongs to the Cactaceae family and is a member of Opuntia kind was collected in a wild plantation near Constantine, east of Algeria, in February. It was immediately sorted, washed with running water to remove dirt particles, then with distilled water various times, and then air-dried.

The mucilage of cactus was prepared by cutting cactus into small pieces then they were pressed with a domestic centrifuge (Fig. 1). The liquid extract obtained was viscous with green color, its range of pH is of (3–4) and miscible with water. Its density is equal to 1.008 kg L^{-1}, and it can maintain its flocculation capacity for several days at room temperature, after 3 d two separate phases seem, that means the bio-coagulant has lost its physicochemical properties due to poor storage conditions. But, it can keep its flocculating capacity up to 7 d by keeping it at 5°C.

The mucilage collected was diluted to 10% in distilled water and stored in a glass bottle for further utilization.

2.2. Composition of cactus mucilage

Table 1
Composition of cactus mucilage

	Stintzing and Carle [19]	Malainine et al. [20]	Batista et al. [21]
Minerals (g/100 g)	–	20	23.5
Protein (g/100 g)	4–10	–	10
Carbohydrates (g/100 g)	64–71	48	71
Lipids (g/100 g)	1–4	7.2	4
Fiber (g/100 g)	18	25	30
Ash (g/100 g)	19–23	–	–

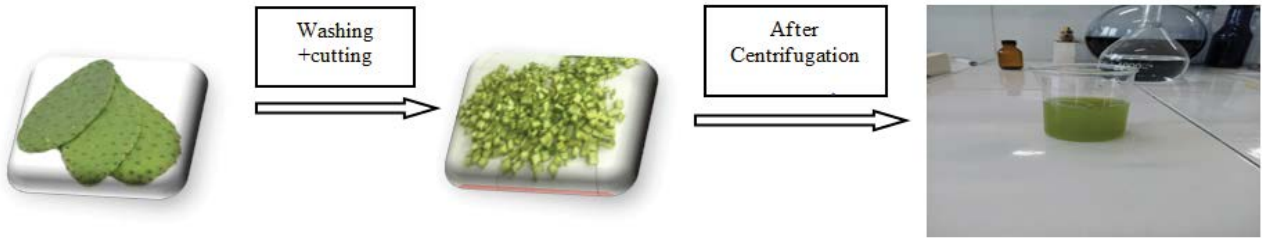

Fig. 1. Cactus mucilage.

2.3. FTIR analysis of cactus

A characterization study of cactus mucilage is carrying out using FTIR, to identify functional groups. The Fourier transform infrared (FTIR) spectroscopy analysis was performed by applying an infrared spectrometer in the range of 400–4,000 cm^{-1}.

2.4. Jar-test assay

A standard jar test apparatus with digital feedback control system (JTM6C Model) was used in the coagulation/flocculation tests. Samples of wastewater (500 mL) were stirred at a high speed of 160 rpm for 2 min and during this time the coagulant was added from a pipette to give the required dose. The stirring speed was then lowered to 45 rpm for 20 min after which the samples were allowed to settle for 30 min.

The pH value was adjusted to the desired value with HCl and NaOH before the coagulant/flocculent was added.

2.5. Analytical methods

Two parameters were kept in this study: turbidity and COD. Their elimination efficiency was calculated as follows:

$$Y \text{ removal}(\%) = \frac{C_0 - C_f}{C_0} \times 100 \tag{1}$$

where Y is response removal efficiency for turbidity or COD. C_0 is the initial value and C_f is the final value of turbidity or COD.

Measurements of turbidity, pH, temperature, conductivity, and dissolved oxygen were made, respectively using a turbidity meter HACH 2100, pH meter, thermometer, and conduct meter JENWAY 3505 and oximeter HACH HQ440d multi.

The physico–chemical analyses of water examined as part of this work were: COD, BOD_5, PO_4^-, $N–NO_3^-$, $N–NH_4^+$, and TSS. They were determined in laboratory according to the methods given in the series of standard methods for the examination of water and wastewater [22].

Each experiment is carried out in triplicate and the average results are presented.

2.6. Urban wastewater sampling

Municipal wastewater samples used in this study were obtained from Ferjiwa's wastewater plant located in the municipality of Mila, Algeria in 08/03/2019. The station is intended for the treatment of wastewater from this commune and that of Ferjiwa, with 9,600 $m^3 d^{-1}$ of capacity. It was designed some years ago (in 2013) to receive municipal wastewater; which will help to fight the various forms of water-borne diseases, will also be used for the irrigation of agricultural land and intended for the protection of the BENI HAROUN dam.

Samples were kept in washed HDPE bottles at a temperature of 4°C without adding any chemicals until use in order to minimize the changes in their characteristics and to decelerate bacterial activity.

2.7. Experimental design

In order to obtain the optimum and the relationship between factors affecting the output responses of the bio coagulation/flocculation process, the statistical design of experiments (DoE) is structured and systematized in which all factors are varied simultaneously over a set of experimental runs.

RMS used in the present research was a central composite faced design (CCFD) implying two independent variables; coagulant dosage (*A*) and initial pH (*B*), each controllable variable (factors) had three levels: –1, 0, and +1. Factors with coded and actual values are represented in Table 2. The output responses chosen in this study were turbidity and COD removal efficiencies determined by Eq. (1).

CCFD contains 13 runs as shown in Fig. 2, with 2^2 full factional design points: four cubic points, four axial points, and five central points for replication. The experimental design matrix is summarized in Table 3.

In this work experimental data was evaluated using Minitab16, analyzer of variances (ANOVA) was used to provide the diagnostic checking test to reveal the adequacy of the proposed model. The coefficient of determination R^2 expressed the quality of the fit polynomial model. It provides a measure of how much variability in the observed response values can be explained by the experimental factors

Table 2
Experimental range and levels of independent variables

Variables	Coded and actual values		
	–1	0	+1
A: coagulant dosage (mL L^{-1})	0.4	5.2	10
B: pH	2	7	12

and their interactions. These analyses are done by means of Fisher's test and p-value (probability).

Three and two-dimensional contour plots were used to illustrate the interactive effects of the independent variables on the dependent ones. For statistical calculations, the variables X_i were coded as x_i according to Eq. (2).

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

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

3. Results and discussion

3.1. FTIR analysis of cactus mucilage

In contrast (Fig. 3), FTIR has been implemented to identify the presence of functional groups on the cactus mucilage. Peaks in the wave number 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 cactus spectrum.

3.2. Wastewater effluent characteristics

The main parameters analyzed of wastewater sampled are shown in Table 5. The pH and temperature values are acceptable according to the standards norms. The TSS values show that the wastewater studied is characterized by a high concentration. This result is often linked to the high load of organic and mineral matter. A high charge expressed in BOD_5 and COD, corresponding to 602 mg L^{-1}, it should be noted that these average values are high compared to domestic wastewater in Algeria and can be classified as highly polluted urban wastewater.

Based on the effluent biodegradability coefficient, 6.02 larger than 4, which presents a low degree of biodegradability (not easily biodegradable effluent, even no biodegradable) what means that this effluent is of industrials predominance with hardly biodegradable organic matters. So, this ratio helps us to make a good decision to carry out a physicochemical treatment such as coagulation flocculation which helps to eliminate inorganic particles obtained from synthetic chemistry followed by a biological treatment.

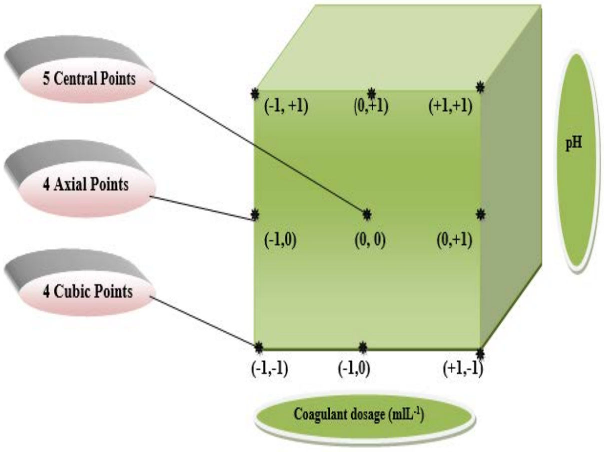

Fig. 2. Study domain.

3.3. Fitting the models

3.3.1. Removal turbidity

Based on the CCFD experimental design results presented in Table 3, the RSM was applied to develop a regression polynomial equation and find a relationship between the output (the responses) and the input (factors independent) where predicted results of turbidity removal (%) was evaluated as a function of bio coagulant dosage (A) and pH (B). Significant model terms are needed to obtain an adequate fit in a particular model. The regression response surface obtained in terms of coded parameters of turbidity removal efficiency is determined and written in general form as shown in Eq. (3).

$$\mathrm{TUR}(\%) = 64.67 - 4.88 \times A + 25.64 \times B - 6.23 \times A^2 + 8.93 \times B^2 + 6.17 \times A \times B \qquad (3)$$

To verify and confirm the significance of each of the coefficients, it is recommended to use p-values or Student's t-student as a tool in order to understand the mutual interaction motif among the factors. The larger the Student's t-test and the smaller p-value are the more significant is the corresponding coefficient [23]. If the coefficient probability value (p) was greater than 0.05, it can be concluded that the term did not have a significant effect on the predicted response [24].

Table 3
Experimental matrix design and results for turbidity and COD removal efficiencies (experimental and predicted values)

Run	A	B	Turbidity removal (%)		COD removal (%)	
			Exp.	Pred.	Exp.	Pred.
1	–1	–1	52.30	53.34	27.75	32.92
2	1	–1	30.50	30.14	45.20	45.83
3	–1	1	92.46	91.21	67.50	69.33
4	1	1	97.50	94.85	75.25	72.55
5	–1	0	63.12	63.34	61.25	54.24
6	+1	0	50.55	53.56	60.25	62.30
7	0	–1	48.64	47.97	54.20	48.39
8	0	1	95.36	99.26	79.10	79.95
9	0	0	65.34	64.67	66.40	67.29
10	0	0	65.34	64.67	66.01	67.29
11	0	0	65.34	64.67	66.01	67.29
12	0	0	65.30	64.67	66.30	67.29
13	0	0	65.30	64.67	66.79	67.29

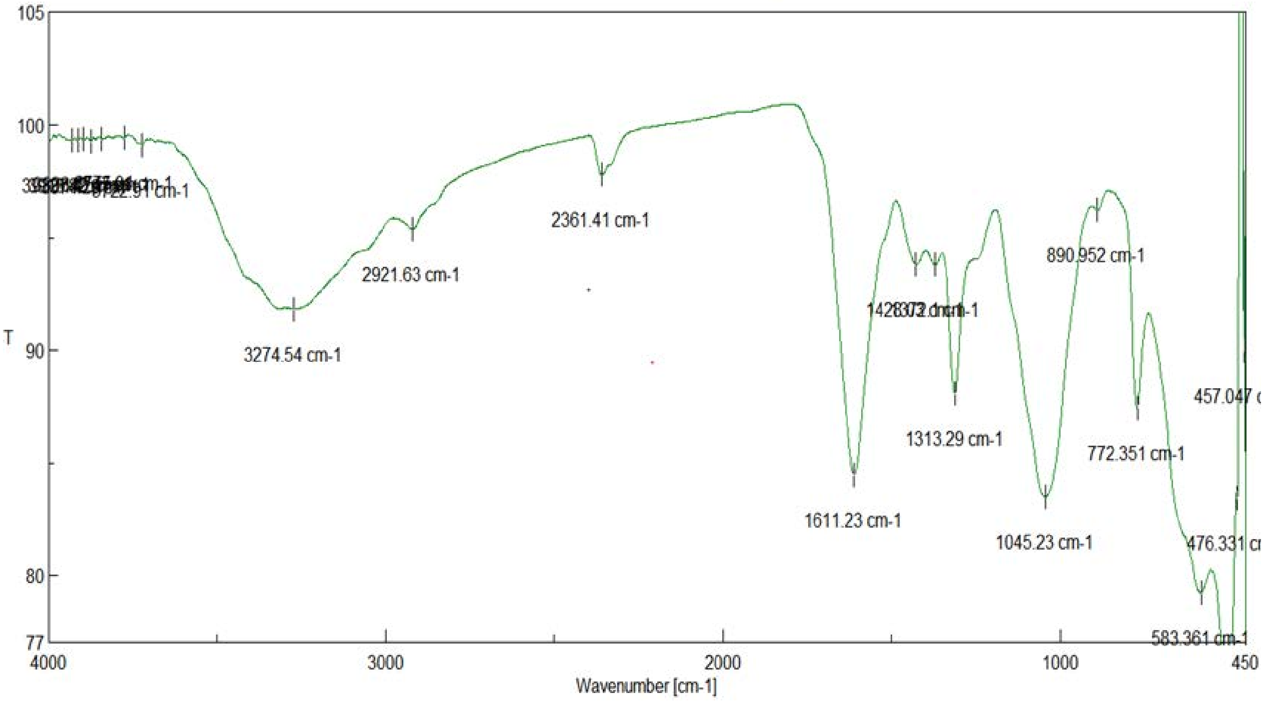

Fig. 3. FTIR analysis of cactus mucilage.

Table 4
FTIR structural elucidation of cactus

Wave number (cm^{-1})	Vibration and liaisons	
890.94	Sulfoxides	S–O
1,045.23	Chloro alcanes	C–Cl
1,313.29	Polysacharides	C–O–C– or –OH
1,428.02	Phenol	C–OH
1,611.23	Aromatic	C=C
1,740.44	Carboxylic acid, esters	C–O
2,361.41	Nitrile	C≡N
2,921.63	Aliphatic	CH$_3$, CH$_2$, and CH
3,274.54	Alcohols, phenol, acid, and amine	O–H, H–N

It can be deducted from the findings in Table 6, that the bio coagulant dosage (A) and initial pH (B) have p-values equal to 0.001 and 0.000, respectively, suggesting that these terms are important in the model (significant) with a confidence level of 95%.

Furthermore, with regard to the effect of quadratic terms, it can be observed that A^2 (p-value 0.003) and B^2 (p-value 0.000) mean significant. Also, the interaction term: bio coagulant dosage (A) with pH (B) has had a major effect on the process of coagulation flocculation using cactus mucilage and its p-value is 0.001.

Statistical testing of the model was performed with Fisher's statistical test for ANOVA, was performed to evaluate the quality of the adjustment and to examine the efficiency and the statistically significance of the model; Fisher variation ratio (F-value) is the ratio between the mean square of the model and of residual error, which is a statistical measure utilized to know how well the factors represent the variation in the data with respect to its mean [25]. The model is suitable and good predictor of the experimental results, when the F-value is greater than the tabulated value of F-distribution for a certain freedom degrees number in the model at a level of significance α [26].

From the analysis (ANOVA from Table 6), the empirical regression model is highly significant as the F-test, in this case F_{model} equal to 172.57 greater than $F_{\text{tabulated}}$ ($F_{(5,7)}$) equal to 3.97 with a very low probability value $p_{\text{model}} < 0.005$. This means that the acquired response model is validated from a statistical standpoint and is a good predictor of the experimental data. All terms are significant terms ($p < 0.005$), it indicates that bio coagulant dosage and pH are the key factors for turbidity reduction.

Table 5
Average values of wastewater effluent characteristics

Parameters	Average values
Turbidity, NTU	45
pH	7.60
Temperature, °C	14.7
Conductivity, μs cm^{-1}	1,961
Dissolved oxygen, mg L^{-1}	9.17
Ortho-phosphate (PO_4^{2-}), mg L^{-1}	0.626
Nitrate ($N–NO_3^-$), mg L^{-1}	0.91
Ammonium ($N–NH_4^+$), mg L^{-1}	2.7
Total suspended solids, mg L^{-1}	338
COD, mg L^{-1} (O^2)	602
BOD_5, mg L^{-1} (O^2)	100
COD/BOD_5	6.02

Table 6
Analysis of variance (ANOVA) for turbidity removal regression model

Source	DF	SS	MS	*F*-value	*p*-value
Regression	5	4,516.28	903.26	172.57	0.000
Linear	2	4,089.88	2,044.94	390.69	0.000
A	1	143.37	143.37	27.39	0.001
B	1	3,946.51	3,946.51	753.99	0.000
A^2	2	25.81	107.20	20.48	0.003
B^2	1	220.49	220.49	42.12	0.000
$A \times B$	1	180.10	180.10	34.41	0.001
Residual error	7	36.64	5.23		
Lack of fit	3	36.64	12.21	25,442.51	0.000
Pure error	4	0.00	0.00		
Total	12	4,552.92			

$R^2 = 0.992$, $R^2_{adj} = 0.986$.
DF: degree of freedom; SS: sum of squares; MS: mean square.

Since all the coefficients have an important effect on the turbidity removal efficiency, no term will be eliminated from the developed empirical model presented in Eq. (5) and so the model will be written in actual terms as presented in Eq. (4):

$$\text{TUR}(\%) = 54.45 - 0.16 \times [\text{bio coagulant dose}] - 1.33 \times \text{pH} - 0.27 \times [\text{bio coagulant dose}]^2 + 0.36 \times \text{pH}^2 + 0.28 \times [\text{bio coagulant dose}] \times \text{pH} \quad (4)$$

Moreover, the R^2-value is 0.992, close to 1 is desirable and it ensures a satisfactory fit of the quadratic model to the experimental data which confirms the model's accuracy. Also, it implies that more than 99.2% of the data deviation can be explained by the developed empirical models. Also, a higher value of the correlation coefficient justifies an excellent correlation between the independent variables. Furthermore, the predicted R^2 value is in agreement with the adjusted statistic $R^2_{adj} = 0.986$, this means that significant terms have been included in the empirical model.

Applying a diagnostic graph, the predicted vs. actual plot for turbidity is shown in Fig. 4a, The spotted points of this plot reveal that the actual values are distributed relatively near to the straight.

3.3.2. Removal COD

The results shown in Table 7 can provide us the regression model of the second studied response shown in Eq. (5).

$$\text{COD}(\%) = 67.29 - 4.03 \times A + 15.78 \times B - 9.01 \times A^2 - 3.11 \times B^2 - 2.42 \times A \times B \quad (5)$$

The results of ANOVA for COD reduction are regrouped in Table 7.

The results of F_{model} equal to 21.17 greater than $F_{(5,7)}$ equal to 3.97 for the COD removal efficiency show that the second-order polynomial model was significant and fitted well the experimental results.

The value of the correlation coefficient ($R^2 = 0.938$) indicates that only 6.2% of the total variation could not be explained by the empirical model. While the R^2 value of the quadratic model ($R^2 = 93.8\%$) is not as high as that of the model for turbidity. The *p*-value (*p*-value < 0.0001) of Eq. (5) also indicates that the polynomial quadratic model fitted the experimental results well. B, A^2 are significant terms (*p*-value < 0.05), it indicates that pH and bio coagulant dosage are the key variables for COD elimination. Thus, all other terms will be eliminated from the regression model as shown in Eq. (6).

$$\text{COD}(\%) = 66.41 + .03 \times A + 15.78 \times B - 10.21 \times A^2 \quad (6)$$

Eq. (7) is the quadratic model of the COD reduction efficiency in actual (incoded) terms:

$$\text{COD}(\%) = 27.96 + 5.45 \times [\text{bio coagulant dose}] + 3.16 \times \text{pH} - 0.44 \times [\text{bio coagulant dose}]^2 \quad (7)$$

Fig. 4b shows that the measured vs. predicted plot values were distributed evenly near to the straight line.

3.4. Process analysis

From the analysis of the models, it reveals that the models can be considered adequate for the predictions and optimization. As shown in Fig. 5 which indicates the scatterplot of turbidity removal efficiency vs. COD removal efficiency for the bio coagulation/flocculation process, a clear correlation between the two responses is noticeable. The optimum turbidity removal might impact on COD removal and vice versa. Consequently, the removal mechanisms of turbidity and COD were close and the optimum conditions for the removal of each substance would also be the same. Precedent studies also mentioned that optimum

Table 7
Analysis of variance (ANOVA) for COD removal regression model

Source	DF	SS	MS	*F*-value	*p*-value
Regression	5	1,978.83	395.77	21.17	0.000
Linear	2	1,592.29	796.14	42.58	0.000
A	1	97.61	97.61	5.22	0.056
B	1	1,494.68	1,494.68	79.94	0.000
A^2	2	336.22	224.45	12.00	0.010
B^2	1	26.80	26.80	1.43	0.270
$A \times B$	1	23.52	23.52	1.26	0.299
Residual error	7	130.89	18.70		
Lack of fit	3	130.47	130.47	415.90	0.000
Pure error	4	0.42	0.42		
Total	12	2,109.72			

$R^2 = 0.938$, $R^2_{\text{adj}} = 0.893$.

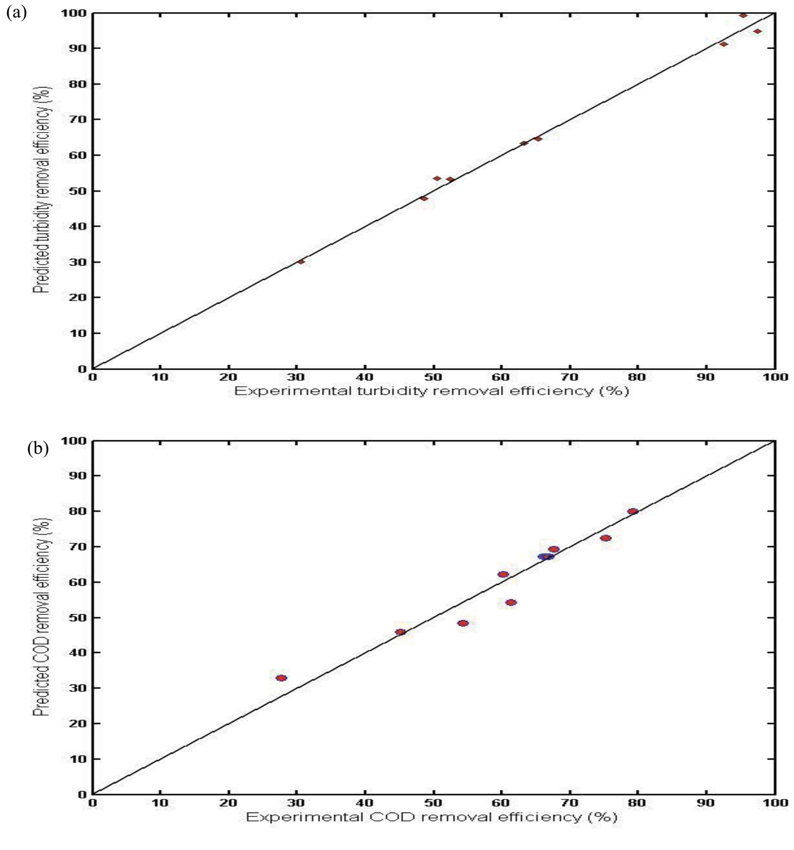

Fig. 4. Experimental vs. predicted values for turbidity (a) and COD (b) removal efficiencies.

conditions for turbidity removal are practically always the same as those for COD removal [27].

The Minitab optimizer of the considered RSM design gave the results of the mono objective optimization of turbidity and COD removal efficiencies shown in Fig. 6.

By specifying the desirable limits of 99% turbidity removal and 80% COD removal, the optimum condition can be visualized graphically by superimposing the contours for the two responses in an overlain plot, as shown in the Fig. 6.

Graphical optimization visualizes the area of feasible response values in the factor space and the regions that fit the optimization criteria were whiten. Base on the white area of overlain contour in Fig. 7, a compromise of (80%–90%) for turbidity removal and (70%–80%) for COD removal can be met at (3–10 mL L^{-1}) of cactus jus dose and pH from 10 to 11.

The 3D response surface plots and 2D contour plots of the quadratic models were illustrated in Fig. 8.

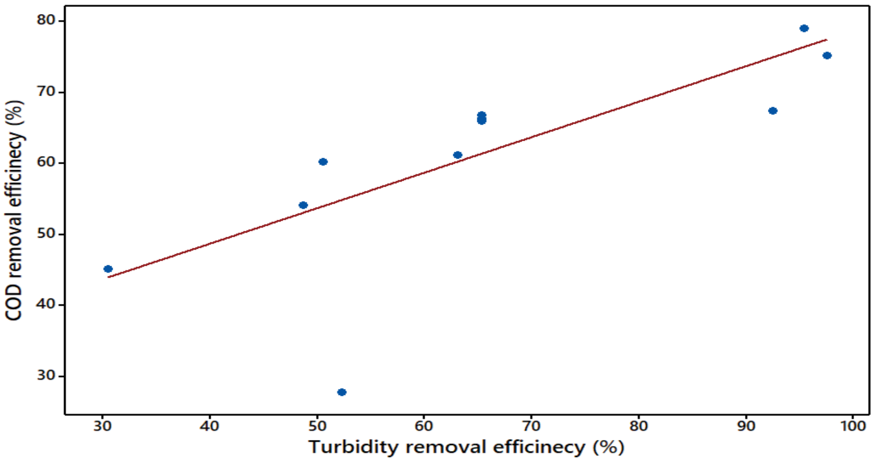

Fig. 5. Scatterplot of COD removal efficiency (%) vs. turbidity removal efficiency (%).

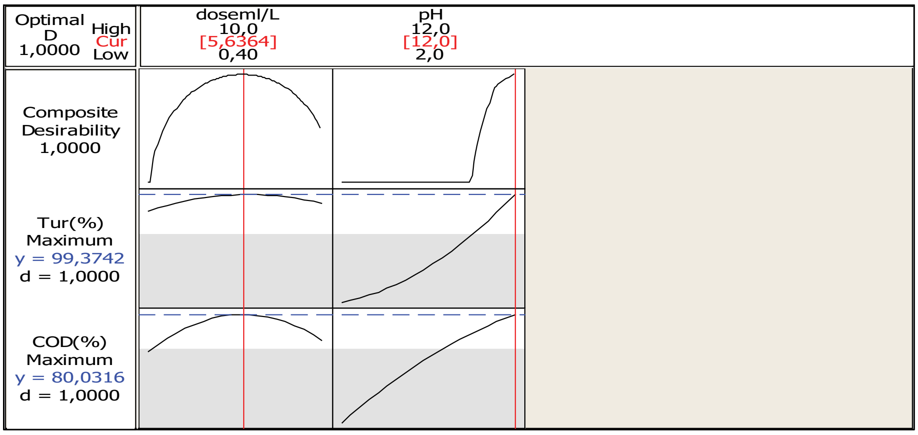

Fig. 6. Minitab results from the optimizer for the turbidity removal efficiency (%), COD reduction efficiency (%).

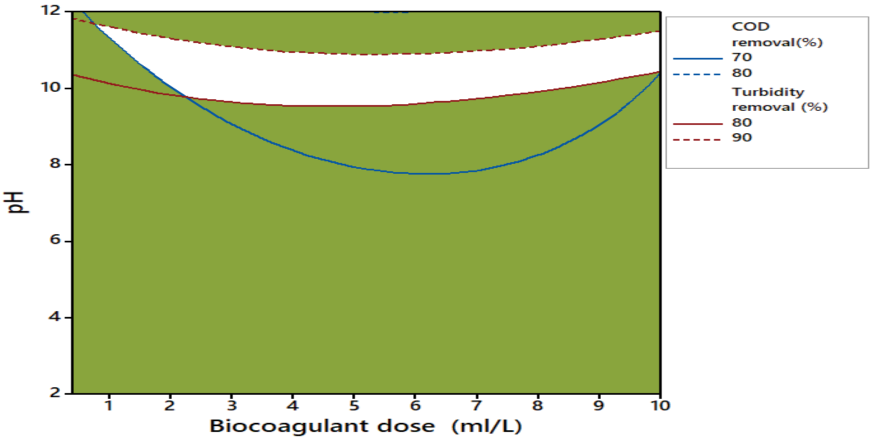

Fig. 7. Overlain contour plots of turbidity removal and DOC removal for mucilage of cactus.

As shown in Figs. 8a and c, increased turbidity removal was observed with increasing pH values, and elimination efficiency higher than 95% was obtained at pH value of 12. However, an increase of bio coagulant dose beyond the optimum region result a decrease in the removal efficiency. At a dose higher than 5.634 mL L^{-1} (optimum bio coagulant dosage), the removal efficiency began to decrease at all of the coagulation pHs. This implies that overdosing occurred

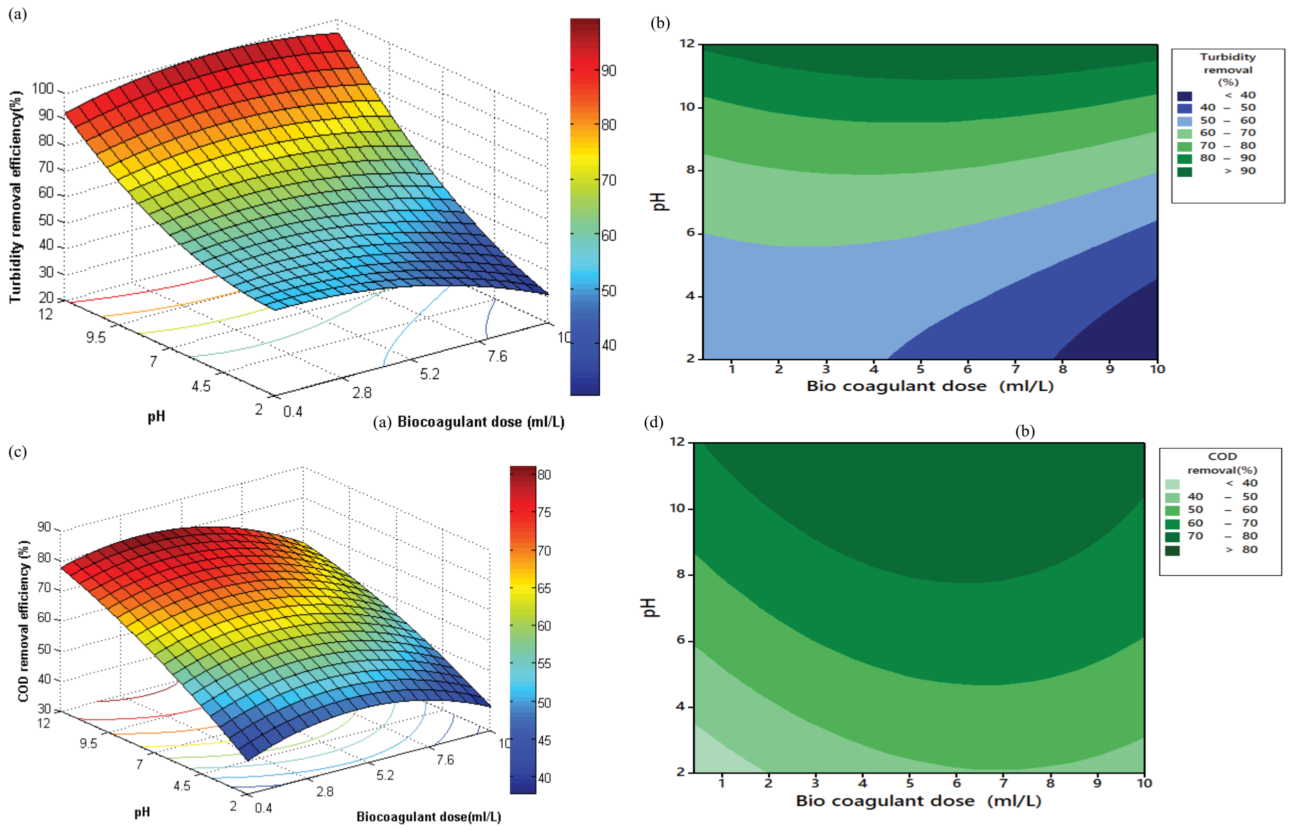

Fig. 8. Response surface plots (a, c) and contour plots (b, d) of predicted turbidity and COD removal efficiencies factor as function of the operating bio coagulant dose and initial pH.

in the reaction solution. Overdosing damaged supernatant quality, referring to the "restabilization" of the colloidal particles, and thus the particles could not be coagulated well.

The results in [13] support the hypothesis that the predominant coagulation mechanism for cactus is "adsorption and bridging" where by clay particles do not directly contact one another but are bound to a polymer-like material from cactus.

In this study, it was concluded that the greatest coagulation activity of cactus occurs in basic waters (coagulant molecules are mainly extracted at basic pHs), this result was in accordance with the results of Bouaouine et al. [28]. They were able to demonstrate experimentally that the alkaline pH of the flocculation (pH = 10) really suggests an adsorption mechanism with bridging between the particles by the extracted molecules soluble in water.

An extraction water at pH = 10 (flocculation optimum) was performed to confirm this process and the solution was acidified (pH = 7) to permit precipitation of the active flocculant molecules so considered. This extract's strong flocculant property was validated, and the titration of this solution showed at least pKa of 9.0 ± 0.6 corresponding to groups of phenols which may be assigned to lignin and tannin.

Monitoring the zeta potential allows us to propose a reaction mechanism for the process. The zeta potential of the colloids and the solution of the cactus are the both negative, therefore the neutralization of the charge of the colloids is impossible. This result indicates that colloids and suspended solid cactus material do not interact by colloidal neutralization of particles in water, but by adsorption and bridging between particles.

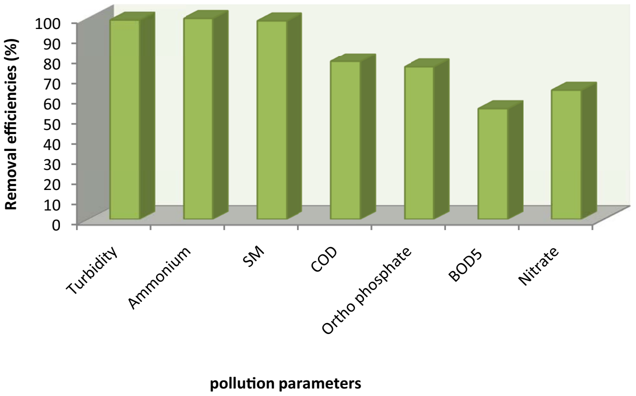

Fig. 9. Effectiveness of bio coagulation to eliminate the other pollution parameters

The surface and contour plots of the quadratic models for COD removal are presented in Figs. 8b and d.

Fig. 8d shows an optimum of 80% of COD removal obtained with cactus liquid dose range from 3.5 to 9 mL L^{-1}, corresponding to the pH range from 9 to 12. Elimination efficiencies are found to reduce when moving away from

Table 8
Confirmation experiments at optimum conditions

	pH	Dose (mL L^{-1})	Predicted values	Experimental values	Error
Turbidity removal (%)	12	5.6	99.37	98.85	0.52
COD removal (%)	12	5.6	80.03	78.25	1.78

Table 9
Actual optimization values

pH	Optimal dose of cactus mucilage (mL L^{-1})	Final COD		Final turbidity	
		Final value (mg L^{-1}) (O_2)	Removal efficiency (%)	Final value (NTU)	Removal efficiency (%)
7	3	165.13	67.31	15.5	64.68
10	5.8	138.5	75.83	5.9	83.08
12	5.6	131	78.25	0.27	98.85

Table 10
Cost estimates for coagulation/flocculation process

Coagulant/flocculent	Bio coagulant dosage	Cost Algerian Dinar/m^3 of wastewater effluent	Cost American dollar/m^3 of wastewater effluent
Cactus mucilage at pH = 10	5.8 mL L^{-1}	1.39	0.011
$FeCl_3$ at pH = 6.72	22.12 mg L^{-1}	16.96	0.16

these ranges, significance that either increase or decrease in any of the factors resulted in decline of the response.

3.5. Confirmation experimental results

Confirming the validity of statistical experimental strategies by repeating additional runs was expert; in which carried out the bio coagulant dosage and pH that were determined as the optimum conditions in this study. As presented in Table 8, the COD and turbidity removal efficiencies obtained experimentally were very close to those evaluated using the models. This indicates that RMS approach used in this work was appropriate to optimize the conditions of the bio coagulation/flocculation process.

Optimization by the experimental design allows us to have the maximum yield of turbidity and COD by approaching the performance limits of the process involved. According to Table 9, a coagulation treatment with a pH of 10 already leads to a satisfactory COD (138.5 mg L^{-1}) which meets the Algerian discharge standards. So in practice it makes more sense to consider pH 10 as the actual optimum value.

From an economic point of view coagulation/flocculation process cost of biomaterials is influenced by production costs of cactus and coagulation/flocculation process energy. A comparative study was done between coagulation flocculation using biomaterials and conventional coagulant ($FeCl_3$) in term of this process prices. Table 10 represents the results; it is clearly shown that treatment using chemical agents was greater than natural process with equal performance.

3.6. Control of the other parameter of pollution

According to Fig. 9, we noted a significant lowering of the parameters of pollution, a reduction yield of o-phosphate which exceeds 75% to reach a final value of 0.153 mg L^{-1}. The elimination of total suspended solids has experienced a higher yield which exceeds 95% and remains only 5.2 mg L^{-1}. After treatment, the nitrates have been reduced to a value of 0.327 mg L^{-1}. While the ammonium remains only in the trace state 0.009 mg L^{-1} and BOD_5 was reduced from 100 to 45 mg L^{-1} with efficiency removal of 55%. The Fig. 9 shows a decrease in the biodegradability coefficient from 6.02 to 2.67, making biological treatment possible. Therefore, the treatment with the cactus has significantly removed the hard COD.

4. Conclusion

In this research, cactus mucilage as a biomaterial has proven its ability to retain suspended solids and COD through the coagulation/flocculation process of the wastewater plant treatment. RSM using CCFD was used to optimize operational conditions for the maximum turbidity removal (99.39%) to reach 0.27 NTU and COD elimination (80.03%) to obtain 131 mg $L^{-1}(O_2)$ at the end of treatment, which is conform to Algerian norm (125 mg L^{-1}). An optimal condition of coagulant dosage 5.6 mL L^{-1} and pH 12 was obtained from the compromise of the two desirable responses (TUR % and COD %) a considerable decreasing of the pollution parameters (O–PO_4^{-2}, N–NO_3^-, and N–NH_4^+)

was demonstrated more than 64% of the elimination efficiency.

In practice it makes more sense to consider pH 10 and bio coagulant dose equal to 5.8 mL L^{-1} as the actual optimum values, since we reach significant removal efficiencies of turbidity and COD to 83.08% (5.9 NTU) and 75.83% (138.5 mg L^{-1}), respectively.

Coagulant dosage and initial pH are both significant terms to yield higher removal of turbidity. On the contrary, coagulant dosage is not an important factor influencing COD removal efficiency. The interaction effect between coagulant dosage and pH is negligible. ANOVA showed high R^2 values of the regressions models equations $R^2 = 0.9992$ (TUR %) and $R^2 = 0.938$ (COD %), thus ensuring a statistical adjustment of the second-order regression model with the experimental data.

The verification experiments demonstrate that a combination of the RSM and CCFD is an effective and powerful approach for the optimization of the coagulation/flocculation process for wastewater plant treatment using cactus mucilage which can be considered as an appropriate alternative for conventional costly coagulants.

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References

[1] Z. Abidin, N. Shamsudin, Optimisation of a method to extract the active coagulant agent from Jatrophacurcas seeds for use in turbidity removal, Ind. Crops Prod., 41 (2013) 319–323.

[2] T. Nharingo, M.T. Zivurawa, U. Guyo, Exploring the use of cactus *Opuntia ficus indica* in the biocoagulation–flocculation of Pb(II) ions from wastewaters, Int. J. Environ. Sci. Technol., 12 (2015) 3791–3802.

[3] N.H.A. Al-Saati, E.H. Hwaidi, S.H. Jassam, Comparing cactus (*Opuntia* spp.) and alum as coagulants for water treatment at Al-Mashroo Canal: a case study, Int. J. Environ. Sci. Technol., 13 (2016) 2875–2882.

[4] S.C. Bondy, The neurotoxicity of environmental aluminum is still an issue, Neurotoxicology, 31 (2010) 575–581.

[5] F. Trond, Aluminium as a risk factor in Alzheimer's disease, with emphasis on drinking water, Brain Res. Bull., 55 (2001) 187–196.

[6] J.M. Sieliechi, G.J. Kayem, I. Sandu, Effect of water treatment residuals (aluminum and iron ions) on humanhealth and drinking water distribution systems, Int. J. Conserv. Sci., 1 (2010) 175–182.

[7] M. Sciban, M. Klasnja, M. Antov, B. Skrbic, Removal of water turbidity by natural coagulants obtained from chestnut and acorn, Bioresour. Technol., 100 (2009) 6639–6643.

[8] A.A. Abia, M. Harsfall, O. Didi, The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from aqueous solution, Bioresour. Technol., 90 (2003) 345–348.

[9] A. Fernández, F. Herrera, M. Mas y Rubí, D. Mejías, A. Diaz, Evaluación delexudadogomoso de Acacia siameacomo coagulante en la clarificación de las aguas para consumo humano, Rev. Téc. Ing. Univ. Zulia, 31 (2008) 32–40.

[10] Z. Li, N. Li, H. Zhang, Studies and application processes on flocculant in water treatment in China, Electron. J. Geotech. Eng., 14 (2009) 134–138.

[11] P.M. Armenante, Coagulation and Flocculation. Available at: cpe.njit.edu/dlnotes/che685/cls07-1.pdf (accessed November 22, 2014)

[12] B. Mounir, Z. Abdeljalil, A. Abdellah, Comparison of the efficacy of two bioflocculants in water treatment, Int. J. Eng. Sci., 3 (2014) 734–737.

[13] S.M. Miller, E.J. Fugate, V.O. Craver, Toward understanding the efficacy and mechanism of *Opuntia* spp. as a natural coagulant for potential application in water treatment, Environ. Sci. Technol., 42 (2008) 4274–4279.

[14] L. Gomes, E.P. Troiani, Opuntiaficus as a polyelectrolyte source for the treatment of tannery wastewater, Desal. Water Treat., 57 (2016) 10181–10187.

[15] S. Vishali, R. Karthikeyan, Cactus *opuntia* (*ficus-indica*): an eco-friendly alternative coagulant in the treatment of paint effluent, Desal. Water Treat., 56 (2015) 1489–1497.

[16] A.L. Ahmad, S.S. Wong, T.T. Teng, A. Zuhairi, Optimization of coagulation–flocculation process for pulp and paper mill effluent by response surface methodological analysis, J. Hazard. Mater., 145 (2007) 162–168.

[17] M. Khayet, A.Y. Zahrim, N. Hilal, Modelling and optimization of coagulation of highly concentrated industrial grade leather dye by response surface methodology, Chem. Eng. J., 167 (2011) 77–83.

[18] D.C. Montgomery, Design and Analysis of Experiments, 5th ed., John Wiley & Sons, New York, NY, 2001.

[19] F.C. Stintzing, R. Carle, Cactus stems (*Opuntia* spp): a review on their chemistry, technology and uses, Mol. Nutr. Food Res., 49 (2005) 175–194.

[20] M.E. Malainine, A. Dufresne, D. Dupeyre, M. Mahrouz, R. Vuong, M.R. Vignon, Structure and morphology of cladodes and spines of *Opuntia ficus-indica*. Cellulose extraction and characterisation, Carbohydr. Polym., 51 (2003) 77–83.

[21] M.V. Batista, A.F. Mustafa, G.R.A. Santos, F.F.R. de Carvalho, J.C.B. Dubeuxjr, M.A. Lira, S.B.P. Barbosa, Chemical composition and ruminal dry matter and crude protein degradability of spineless cactus, J. Agron. Crop Sci., 189 (2003) 123–126.

[22] APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, 1998.

[23] A. Aleboyeh, N. Daneshvar, M.B. Kasiri, Optimization of C.I. Acid Red 14 azo dye removal by electrocoagulation batch process with response surface methodology, Chem. Eng. Process., 47 (2008) 827–832.

[24] W. Jiang, J.A. Joens, D.D. Dionysiou, K.E. O'Shea, Optimization of photocatalytic performance of TiO_2 coated glass microspheres using response surface methodology and the application for degradation of dimethyl phthalate, J. Photochem. Photobiol., A, 262 (2013) 7–13.

[25] A. Rabahi, D. Hauchard, S. Arris, M. Berkani, W. Achouri, A. Meniai, M. Bencheikh-Lehocine, Leachate effluent COD removal using electrocoagulation: a response surface methodology (RSM) optimization and modelling, Desal. Water Treat., 114 (2018) 81–92.

[26] M. Elibol, Response surface methodological approach for inclusion of perfluorocarbon in actinorhodin fermentation medium, Process. Biochem., 38 (2002) 667–673.

[27] L. Gomes, E.P. Troiani, G.R. Malpass, J. Nozaki, *Opuntia ficus indica* as a polyelectrolyte source for the treatment of tannery wastewater, Desal. Water Treat., 57 (2016) 10181–10187.

[28] O. Bouaouine, I. Bourven, F. Khalil, M. Baudu, Identification of functional groups of *Opuntia ficus-indica* involved in coagulation process after its active part extraction, Environ. Sci. Pollut. Res., 25 (2018) 11111–11119.