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5 authors, including:

Nawel Adjeroud
Université de Béjaïa

Farid Dahmoune
Université de Bouira

Belkacem Merzouk
University of M'sila

J.-P. Leclerc
University of Lorraine

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Improvement of electrocoagulation–electroflotation treatment of effluent by addition of *Opuntia ficus indica* pad juice

Adjeroud Nawel [a], Dahmoune Farid [a], Merzouk Belkacem [a,b,*], Leclerc Jean-Pierre [c], Madani Khodir [a]

[a] Laboratoire de Biomathématiques, Biophysique, Biochimie, et Scientométrie, Faculté des Sciences de la Nature et de la Vie, Université de Bejaia, 06000 Bejaia, Algeria
[b] Département Hydraulique, Faculté de Technologie, Université Mohamed Boudiaf de M'sila, B.P. 166, Ichbilia, M'sila 28000, Algeria
[c] Laboratoire Réactions et Génie des Procédés, UMR 7274 CNRS, Université de Lorraine, 1 rue Grandville, B.P. 20451 Nancy, France

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A B S T R A C T

The aim of this study is the optimization of the effect of *Opuntia ficus indica* (OFI) pad juice on the electrocoagulation–electroflotation (EC–EF) water treatment process by response surface methodology (RSM). To estimate the efficiency of EC–EF technique assisted by *Opuntia ficus indica* pad juice, preliminary tests were conducted. The results obtained after RSM optimization for initial OFI pad juice volume, initial pH and initial conductivity were 0.016 mL/L, 8.2, and 3.04 mS/cm, respectively. Maximum predicted turbidity removal efficiency (TR %) under the optimized conditions was 87% ± 0.8, this predicted value was close to the experimental value of 86.9% ± 0.1. Compared to the conventional EC–EF (EC without OFI juice addition), which shows 71.9% of turbidity removal, the optimized cactus juice assisted EC–EF allows a turbidity removal enhancement of 15.1%. These results indicate suitability and validation of the employed model and the success of RSM in optimizing the EC–EF treatment conditions.

1. Introduction

Increase in urbanization, economic activity and industrialization created not only a rise in the volumes of related effluents, an ever increasing demand of drinking water supply but also resulted in a severe misuse of this natural resource. Treatment of wastewaters can be achieved by a wide range of techniques including biological processes, physicochemical processes, requiring chemical addition such as chemical precipitation and chemical oxidation [1], and electrochemical technologies including electrocoagulation–electroflotation (EC–EF) technique. This last process has been used successfully to treat a variety of industrial wastewaters [1–4], potable water [5] and urban wastewater [6]. EC–EF has the potential to extensively eliminate the disadvantages of the classical treatment techniques [1]. It is more efficient and more compact [2]. It includes simple equipment and easy operation, removes small colloidal particles compared with traditional coagulation and flocculation [7]. It is characterized by low capital and operating costs [3], short reaction time and low sludge production [6]. Another important benefit of EC–EF is the reduction in excessive amount of chemical coagulants [7]. However, bio-coagulants provide several environmental advantages [8], they are relatively cost-effective compared to chemical coagulants, can be easily processed in usable form and are biodegradable, when used for treatment of waters with low-to-medium turbidity range (50–500 NTU), they are comparable to their chemical counterparts in terms of treatment efficiency [9]. A large number and variety of natural substances, extracted from plant, have been examined for their coagulation properties [10]. Several authors reported the efficiency of *Opuntia ficus indica* mucilage for antimicrobial activity [11], for metals reduction (As, Cd, Cu and Fe) [12,13] as well as for turbidity removal [10,11,14–16], in the treatment of synthetic and real wastewaters by standard jar tests. Even if some authors consider that *Opuntia ficus indica* mucilage has potential to replace Fe or Al in the coagulation–flocculation process [15], and hence it can be used as coagulant–flocculant instead of using Fe or Al or other synthetic polymers. At the present time, this is not realistic from the industrial point of view because of the accessibility of Al and Fe around the world and the low cost of the metals. Nevertheless the use of *Opuntia ficus indica* as a natural adjuvant may intensify the treatment without notable additional cost. Similarly, Zhang et al. [17] found that the effect of cactus used with aluminum chloride synchronously to treat sewage water was better than that of cactus or aluminum chloride used solely.

Mucilage is produced in cells found both in the chlorenchyma and parenchyma and helps cactus to retain water. It produces unique surface-active properties in water, that give the mucilage the ability to precipitate particles and ions from aqueous solutions

* Corresponding author at: Département Hydraulique, Faculté de Technologie, Université Mohamed Boudiaf de M'sila, B.P. 166, Ichbilia, M'sila 28000, Algeria.
E-mail address: mbelka01@yahoo.fr (B. Merzouk).

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[18]. The mucilage is composed of 55 neutral sugars, mostly L-arabinose, D-galactose, L-rhamnose, D-xylose, and polygalacturonic acid [18–20], which are involved in the coagulation mechanism. *Opuntia* spp. mucilage extraction is amply reported in the bibliography. It is possible to obtain the pure mucilage using organic solvents, however, several studies confirmed the efficiency of the whole cactus cladode in wastewater turbidity removal. Diced *Opuntia* spp. cladodes have been used for centuries in Latin America as a primitive technology for the rapid flocculation of turbid natural spring waters [18]. The whole dried cladode gave the best COD and turbidity removals in comparison to heated mucilage, dry powder, and dry heated powder in a study of Torres Bustillos et al. [14]. Furthermore, Miller et al. [10] suggested that additional components of the *Opuntia* spp. pad beyond those found in the pure mucilage could contribute to the coagulation activity. The exploitation of the natural coagulation ability of *Opuntia ficus indica* can represent an appropriate solution to improve the treatment of wastewater or water by EC–EF technique. EC–EF efficiency depends on several parameters such as type, size, shape and distance between electrodes, current density, conductivity, pH, and reaction time [7], as well as coagulation–flocculation process that can be affected by several factors such as type and dose of coagulant–flocculant, pH and contact time [21]. However, there are no reports for the optimization of EC–EF parameters assisted by OFI pad juice using RSM.

In this respect, our objectives through this work were to:

- Scrutinize the effect of OFI pad juice on turbidity removal efficiency as coagulant aid in combination with EC–EF technique.
- Investigate the effect of some EC–EF operating parameters, such as initial pH and initial conductivity, on the turbidity removal efficiency.
- Optimize initial OFI pad juice volume, pH and conductivity using response surface methodology in order to enhance the turbidity removal efficiency of simulated wastewater model treated by batch EC–EF process.

2. Materials and methods

The EC–EF unit shown in Fig. 1 consisted of an 4 L electrochemical reactor with two aluminum electrodes of rectangular shape (27 mm × 17 mm × 1 mm), corresponding to $S = 4.59\ cm^2$ electrode surface area, installed vertically in the middle of the reactor. The electrodes were connected to a DC power supply (Statron Typ 3217, Germany) providing 0–30 V (0–10 A). The distance between electrodes was 1 cm. All the runs were performed at room temperature. In each run 2000 mL of the synthetic wastewater was decanted into the electrolytic cell and samples were taken at 4.5 cm above the bottom of the reactor and measured over time after sedimentation. Neither centrifuging nor filtration was performed. All experiments were repeated three times. The synthetic wastewater was prepared using 2000 mL of tap water to cover the aluminum electrodes in the EC–EF unit, and 300 mg/L of silica gel (Woelm Pharma) to simulate highly turbid industrial discharges [22].

2.1. Chemical analysis

Samples turbidity was determined by UV–VIS spectrophotometer (Spectro Scan 50, Japan). pH and conductivity of the solution were measured using EC 211 pH meter and EC 215 conductivity meter (HANNA instruments, Italy), respectively. Silica gel concentration was estimated from its absorbance characteristics at maximum wavelength (λ_{max}) of 740 nm. The calculation of turbidity removal efficiency (TR %) after electrochemical cactus juice free treatment or cactus juice assisted treatment was performed using the following formula:

$$TR\ (\%) = \frac{C_0 - C}{C_0}.100 \quad (1)$$

C_0 and C are concentrations of silica gel before and after EC–EF process in mg/L.

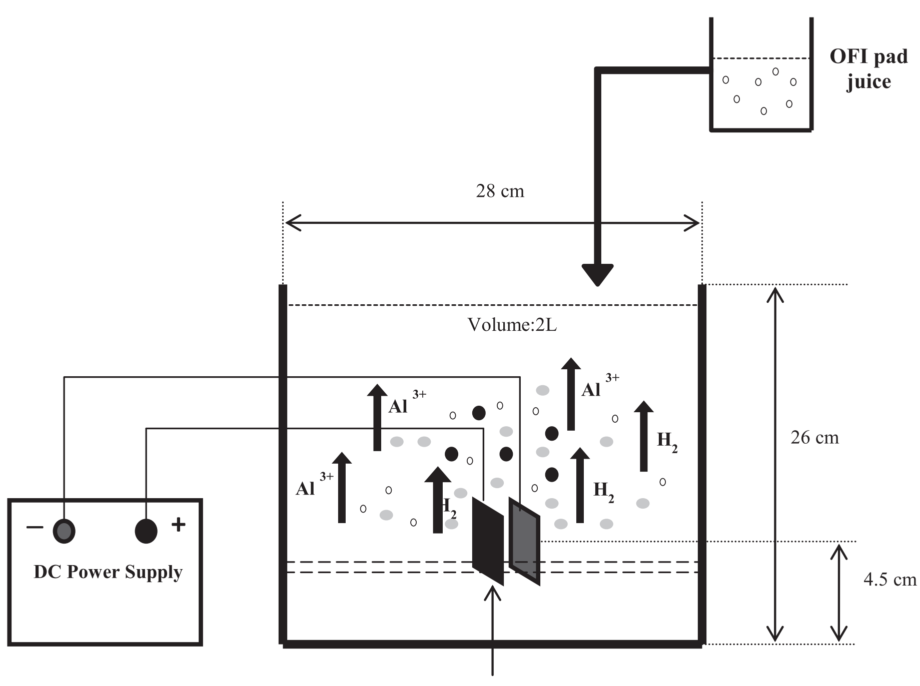

Fig. 1. Batch electrocoagulation–electroflotation unit assisted by *Opuntia ficus indica* pad juice.

2.2. Natural coagulant extraction

Opuntia spp. pads without spines were collected from the area of Ziama Mansouriah in Jijel in the North east of Algeria. Fresh *Opuntia* spp. was used within two days of collect and was stored in a refrigerator at 4 °C when not in use. Pads were rinsed carefully with tap water followed by distilled water and cut into small pieces with a kitchen knife. The skin (the waxy covering on the upper surface of the stem), was peeled from the pads before dissection [10]. Cactus pieces were grounded using a domestic blender, 10 g of the mashed cactus pieces was added to 100 mL distilled water (10% dilution) followed by agitation for homogenization. Finally, the aqueous viscous extract was filtered through a sieve (diameter > 0.5 mm) to remove large particles. The output was 90 mL of liquid extract for 10 g of fresh pads. The final product is a relatively stable viscous liquid of slight green color, of pH 6.14, and conductivity of 1.75 mS/cm.

2.3. Experimental optimization

2.3.1. Preliminary trials

Before optimization of the OFI pad juice assisted EC–EF, the influences of the process parameters were initially separately investigated in single-factor experiments to limit the total experimental work (Table 1). When one variable was not studied, it was kept constant. The major objective of the paper is to study the benefits of using natural adjuvant to intensify the treatment by electrocoagulation. The current density (43.6 mA/cm^2) value using a set of small electrodes was chosen higher that the optimal range of values from the energetic point of view in order to exhibit a strong effect on EC. At high current density, the extent of anodic dissolution of aluminum increases, resulting in a greater amount of precipitate for the removal of pollutants. Moreover, bubble generation rate increases and the bubble size decreases with increasing current density.

To investigate the influence of OFI pad juice volume, pH and conductivity were set at 7.7, and 1.4 mS/cm, respectively. To investigate the effect of pH, OFI pad juice volume and conductivity were fixed at 0.015 mL/L and 1.4 mS/cm, respectively. To investigate the effect of conductivity, OFI pad juice volume and pH were fixed at 0.015 mL/L and 8.7, respectively. During all the trials, the constant values for the interelectrode distance, current density (j) and initial synthetic wastewater concentration were 1 cm, 43.6 mA/cm^2 (measured potential U = 20 V), and 300 mg/L, respectively [23].

2.3.2. Experimental design (RSM optimization)

On the basis of the single-factor experimental results, the factor levels corresponding to each independent variable (OFI pad juice volume, pH, and conductivity) were chosen. The turbidity removal was the dependent variable response. Then, a response surface methodology based on a Box–Behnken Design (BBD) for cactus pad juice assisted EC–EF treatment was conducted to optimize the process (Table 2). The factor levels were coded as −1 (low), 0 (central point or middle) and 1 (high), respectively. Maximum information using minimum trials is obtained by experimental design based on mathematical rules. The RSM is a set of mathematical techniques in which a response of interest is influenced by several variables [24]. It can help in investigating the interactive effect of process variables and in building a mathematical model that accurately describes the overall process, allowing process optimization to be conducted effectively [25].

Regression analysis of the data to fit a second-order polynomial equation (quadratic model) was carried out according to the following general equation (Eq. (2)), which was then used to predict the optimum conditions of cactus juice assisted EC–EF treatment.

$$Y = B_0 + \sum_{i=1}^{k} B_i X_i + \sum_{i=1}^{k} B_{ii} X^2 + \sum_{i>1}^{k} B_{ij} X_i X_j + E \quad (2)$$

where Y represents the response function (in our case turbidity removal); B_0 is a constant coefficient; B_i, B_{ii} and B_{ij} are the coefficients of the linear, quadratic and interactive terms, respectively, and X_i and X_j represent the coded independent variables. According to the analysis of variance, the regression coefficients of individual linear, quadratic and interaction terms were determined. In order to visualize the relationship between the response and experimental levels of each factor and to deduce the optimum conditions, the regression coefficients were used to generate 3-D surface plots from the fitted polynomial equation. The variables were coded according to the following equation (Eq. (3)):

$$X_i = \frac{x_i - x_0}{\Delta x} \quad (3)$$

Table 1
Results of single-factor experiments for OFI pad juice assisted EC–EF water treatment.

OFI pad juice (mL/L)	TR (%)	pH	TR (%)	Conductivity (mS/cm)	TR (%)
0.0	71.85 ± 0.12	5.0	41.36 ± 1.73	1.5	64.05 ± 0.09
0.005	75.91 ± 1.01	6.0	65.89 ± 0.71	1.6	63.72 ± 0.49
0.010	80.18 ± 1.49	6.6	66.92 ± 0.72	1.8	73.57 ± 0.90
0.0125	80.43 ± 1.69	7.4	70.52 ± 1.72	2.2	73.34 ± 1.30
0.015	83.93 ± 1.26	7.6	73.79 ± 1.85	2.5	79.83 ± 1.21
0.0175	82.17 ± 0.23	8.0	74.55 ± 1.33	2.7	85.63 ± 0.12
0.02	72.32 ± 0.24	8.2	76.30 ± 0.79	3.1	84.34 ± 1.02
0.025	72.96 ± 1.53	8.4	76.69 ± 1.56	3.4	79.79 ± 0.67
0.03	78.27 ± 1.59	8.7	80.92 ± 0.93	3.8	65.23 ± 0.55
		9.0	75.97 ± 0.24		
		10.2	75.00 ± 0.41		

Table 2
Factors and levels for RSM Box–Behnken Design (in coded and uncoded level of three variables) with the observed and predicted response values for turbidity removals (%).

Run	OFI pad juice (mL/L)	pH	Conductivity (mS/cm)	TR efficiencies (%)	
				Experimental	Predicted
1	0.01 (−1)	8.35 (0)	3.4 (+1)	84.35 ± 1.37	84.62
2	0.015 (0)	8.35 (0)	2.8 (0)	86.51 ± 0.60	86.93
3	0.015 (0)	8.35 (0)	2.8 (0)	87.21 ± 0.32	86.93
4	0.015 (0)	9.00 (+1)	2.2 (−1)	85.42 ± 0.78	85.81
5	0.01 (−1)	9.00 (+1)	2.8 (0)	86.37 ± 0.90	85.81
6	0.02 (+1)	8.35 (0)	2.2 (−1)	83.26 ± 1.47	82.98
7	0.015 (0)	7.70 (−1)	2.2 (−1)	82.85 ± 1.54	82.56
8	0.01 (−1)	8.35 (0)	2.2 (−1)	85.45 ± 0.63	85.61
9	0.015 (0)	9.00 (+1)	3.4 (+1)	83.84 ± 0.93	84.12
10	0.02 (+1)	7.70 (−1)	2.8 (0)	84.38 ± 0.53	84.93
11	0.02 (+1)	8.35 (0)	3.4 (+1)	86.46 ± 1.54	86.29
12	0.015 (0)	8.35 (0)	2.8 (0)	87.08 ± 0.23	86.93
13	0.02 (+1)	9.00 (+1)	2.8 (0)	85.34 ± 1.25	85.22
14	0.015 (0)	7.70 (−1)	3.4 (+1)	86.98 ± 1.13	86.58
15	0.01 (−1)	7.70 (−1)	2.8 (0)	85.19 ± 1.06	85.30

where X_i is the (dimensionless) coded value of the variable x_i, x_0 is the value of x at the center point and Δx is the step change. Analysis of variance was performed for the response variable using the full model where p-value (partitioned into linear and interaction factors) indicated whether the terms were significant or not. To verify the adequacy of the models, additional cactus juice assisted EC–EF treatment trials were carried out at the optimal conditions predicted by the RSM and the obtained experimental data were compared to the values predicted by the regression model.

Efficiency of the cactus juice assisted EC–EF treatment was evaluated based on the turbidity (TR) measured after the EC–EF process run under the optimum conditions selected by RSM.

2.4. Statistical analysis

Data obtained from the BBD was statistically analyzed using ANOVA for the response variable in order to test the model significance and suitability. $p < 0.05$ and $p < 0.01$ were taken as significant and highly significant levels, respectively. The JMP (Trial Version 10, SAS, USA) software was used to construct the BBD and to analyze all the results.

3. Results and discussions

Aluminum and iron electrode are the most widely used materials in EC–EF process [26]. EC–EF produces coagulants in situ by electrical dissolution of either aluminum or iron ions. The metal ions generation occurs at the anode by oxidation reaction, at an appropriate pH they can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants. Hydrogen gas, that would help to float the flocculated particles, is released from the cathode where reduction reaction occurs [2,4,27]. In the case of aluminum, main reactions are as follows (reactions 4 and 5):

$$\text{Anode}: Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \quad (4)$$

$$\text{Cathode}: 3H_2O_{(l)} + 3e^- \rightarrow 3/2H_{2(g)} + 3OH^-_{(aq)} \quad (5)$$

Al^{3+} and OH^- ions generated by electrode reactions (4) and (5) react to form various monomeric species such as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(OH)_4^-$, and polymeric species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$, which transform finally into $Al(OH)_{3(s)}$ according to complex precipitation kinetics (reaction 6) [1,28,29]:

$$Al^{3+}_{(aq)} + 3H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + 3H^+_{(aq)} \quad (6)$$

3.1. Preliminary study

Table 1 shows the results of the single-factor experiments carried out for preliminary optimization of the EC–EF technique and the turbidity removal efficiency values. The effect of each parameter is discussed below.

3.1.1. Effect of initial volumes of OFI pad juice on turbidity removal efficiency

To investigate the effect of OFI pad juice on turbidity removal efficiency various OFI pad juice volumes ranging from 0.005 to 0.03 mL/L, were tested. EC–EF was carried out under preselected experimental conditions of: initial pH 7.7, distance between electrodes 1 cm, conductivity was set at 1.4 mS/cm, initial synthetic wastewater concentration and current density were fixed at 300 mg/L and 43.6 mA/cm^2, respectively. The results are shown in Figs. 2–4. When OFI pad juice volume increased from 0.005 to 0.015 mL/L, turbidity removal efficiency increased until it reached up to 83% at 0.015 mL/L juice volume (Fig. 2) (Table 1). It was observed for all tested cactus volumes that turbidity removal efficiencies increase steadily over time and do not change after 20 min run time (Fig. 3). The EC–EF performance attained its maximum levels using 0.015 mL/L cactus dose when compared to the other tested volumes (Fig. 3). According to this result, optimum OFI pad juice concentration and run time for simulated wastewater treatment were considered to be: 0.015 mL/L and 20 min, respectively. Miller et al. [10] found that only 0.005 g/L to 0.015 g/L (approximatively 0.05–0.015 mL/L) of *Opuntia* spp. cladode powder was efficient to treat 0–125 NTU of synthetic wastewater.

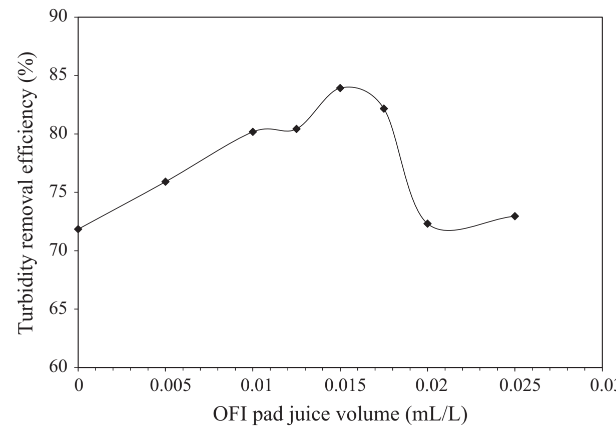

Fig. 2. Effect of initial volumes of OFI pad juice on turbidity removal efficiency: initial silica gel concentration C_0 = 300 mg/L, initial pH 7.7, interelectrode distance d = 1 cm, conductivity κ = 1.4 mS/cm, run time t = 20 mn, current density j = 43.6 mA/cm^2.

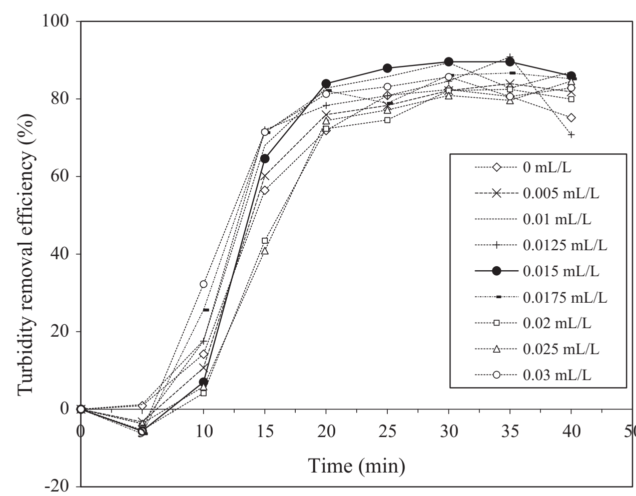

Fig. 3. Effect of OFI pad juice volume on the turbidity removal efficiencies: initial silica gel concentration C_0 = 300 mg/L, interelectrode distance d = 1 cm, initial pH 7.7, conductivity κ = 1.4 mS/cm, current density j = 43.6 mA/cm^2.

The negative removal efficiencies of the turbidity occasionally observed at initial times in Fig. 3 can be explained by the polymerization of dissolved aluminum in the shape of aluminum hydroxide, thus increasing turbidity [30]. However, residual turbidity levels at 30 min ranged from 30 to 58 mg/L depending on initial cactus pad juice dose used (30 mg/L in the case of 0.3 mL dose), which means that initial turbidity was reduced by 5–10-fold.

It is important to highlight that very small amount of OFI pad juice (0.03 mL) is required to enhance EC–EF turbidity removal efficiency of 2 L synthetic wastewater volume by 12.1% when compared to EC free OFI pad juice (Table 1), on a large scale application this may resolve the problem of increasing microbial activity, since the use of natural coagulants may increase the organic load in waters [31]. In addition, this could be very interesting, since the lower the coagulant dose, the lower the wastewater treatment total cost [15]. *Opuntia ficus indica* is largely widespread all over the world and grows wild and spontaneously, it requires only to be planted and to let it grow on itself, without fertilizer or watering. The high efficiency of converting water in nopal biomass produces a high productivity value. For example a nopal fruit crop can generate production of 20 tons per hectare annually and produce up to 50 tons of dry material with the potential use as a natural coagulant. Cost of the extraction process is low. OFI fresh juice is directly extracted from the *Opuntia* cladodes without boiling or heating the cladodes before, thus reducing energy consumption (even though the cladodes were mixed in a blender but for a short time, for only 45–50 s).

As expected OFI pad juice reduces turbidity and hence interacts with suspended solids. Its natural coagulation capacity is attributed to the action of mucilage. Contrary to synthetic coagulants as metallic salts [32] and to another well-known natural coagulant *Moringa oleifera* [33], which operates through charge neutralization, it was suggested using zeta potential measurements and electron microscopy images of formed flocs that the coagulation mechanisms of *Opuntia* spp. functions predominantly through adsorption. This process can be achieved by natural *Opuntia* spp. electrolytes, particularly the divalent cations, and bridging in which clay particles are bound to a polymer-like material from *Opuntia* spp. [10]. In addition, Majdoub et al. [34] isolated the free proteins mucilage fraction and showed that it contains about 20% charged sugars that can potentially interact with divalent cations [18]. Moreover, to better elucidate coagulation mechanism Miller et al. [10] tested mucilage sugars independently or in combination and showed that the coagulation activity is predominantly due to galacturonic acid alone or in combination either with arabinose, galactose, or rhamnose.

It can be supposed that turbidity removal occurs through physical scavenging of the suspended solids by the dispersed mucilage in water, but the colloidal solids can only be removed by charge neutralization achieved by the electrolysis of aluminum plaques during the electrochemical process. However, it is probable that the metal ions generated at the anode interact with suspended particles forming small flocs, which could attach to the cactus mucilage increasing its coagulation capacity. The inverse mechanism could also occur.

When pH evolution was monitored during investigation of OFI pad juice volume effect on EC–EF, using increasing cactus dosages, there was no significant effect on the final pH. Yang et al. [16] found that cactus powder did not cause a significant effect on final pH of waters when compared to chemical coagulants.

3.1.2. Effect of initial pH on turbidity removal efficiency

pH is an important operating factor that influence the performance of the electrochemical process [3,29,35]. Even if it is all the time preferable to keep the initial pH of the solution to avoid addition of chemicals, influence of the initial pH is sometime very sensitive on the efficiency in particular on the kinetic rate, despite the buffer effect during the EC treatment. Because of this initial pH was varied from 5 to 10.2. The effect of the initial pH on turbidity removal efficiency for the EC–EF assisted with 0.015 mL/L of OFI pad juice volume is shown in Fig. 4. The sample was adjusted to the desired pH by adding the appropriate amount of 0.1 M NaOH or HCl. The maximum removal of turbidity (80.9%) (Table 2) was observed at pH 8.7.

It is desirable that final pH values are near neutrality after EC–EF process. Fig. 5 demonstrates pH changes during EC–EF.

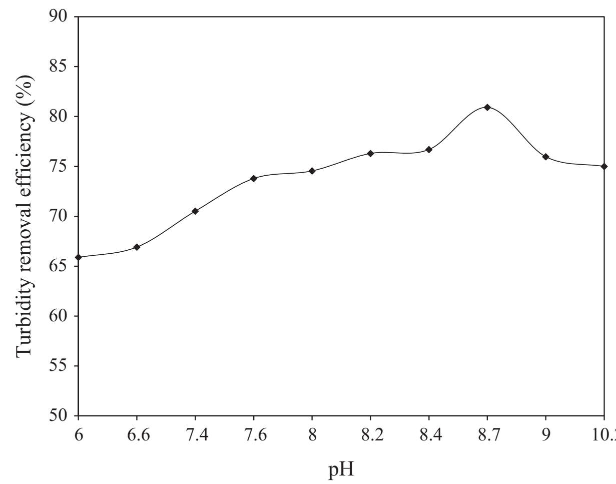

Fig. 4. Effect of initial pH on turbidity removal efficiency: initial OFI pad juice volume V_0 = 0.015 mL/L, initial silica gel concentration C_0 = 300 mg/L, interelectrode distance d = 1 cm, conductivity κ = 1.4 mS/cm, current density j = 43.6 mA/cm^2, run time t = 20 mn.

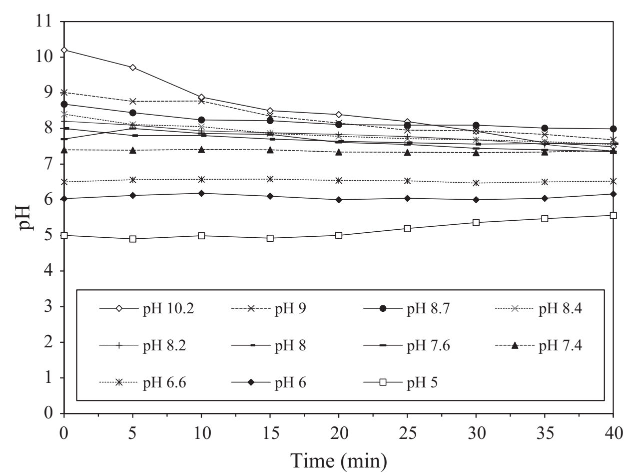

Fig. 5. Evolution of pH values during EC–EF for different values of initial pH: initial OFI pad juice volume V_0 = 0.015 mL/L, initial silica gel concentration C_0 = 300 mg/L, interelectrode distance d = 1 cm, conductivity κ = 1.4 mS/cm, current density j = 43.6 mA/cm^2.

This was observed by several authors [3,22,27]. Its evolution depends on initial pH: whatever the initial pH values, acidic or basic, there is an EC–EF buffering trend toward pH around 7. This is explained by a balance between OH^- production and consumption, preventing high changes in pH [2,4], which is advantageous for wastewater treatments.

Actually, the dominant aluminum species are different according to the solution pH: at low pH, such as 2–3 (pH lower than 4), where precipitation mechanism occurs, cationic monomeric species Al^{3+} and $Al(OH)_2^+$ predominate. For higher pH, pH between 4 and 9, adsorption occurs, the Al^{3+} and OH^- ions generated by the electrodes react to form various monomeric species such as $Al(OH)_2^+$, $Al(OH)_2^{2+}$, and polymeric species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_{13}(OH)_{34}^{5+}$ that finally transform into insoluble amorphous $Al(OH)_{3(s)}$ through complex polymerization/precipitation kinetics [22,27]. When pH is higher than 10, the monomeric $Al(OH)_4^-$ anion concentration increases at the expense of amphoteric $Al(OH)_{3(s)}$ according to the following reaction (Eq. (7)), which causes a slight decrease in final pH by consuming OH^- ions.

$$Al(OH)_3 + OH^- \leftrightarrow Al(OH)_4^- \quad (7)$$

In addition, the cathode may be chemically attacked by OH^- ions generated together with H_2 at high pH values (reaction 8) [7]:

$$2Al + 6H_2O + 2OH^- \rightarrow 2Al(OH)_4^- + 3H_2 \quad (8)$$

Thus, the majority of aluminum complexes and the precipitates responsible for adsorption are optimally formed in the pH range investigated in this work. Besides, Vial et al. [36] reported that hydrogen bubbles are known to be the smallest about neutral pH. Thus, pH may be adjusted in a range that allows equilibrium between best coagulation and best flotation [22].

There is a relationship between pH and *Opuntia ficus indica* coagulation activity. Its coagulation ability increases at alkaline pH [10,37]. Torres [15] observed that *Opuntia ficus indica* mucilage is efficient in removing COD at pH 10. Similarly, Zhang et al. [17] have reported that *Opuntia* spp. is most effective at pH 10 and is least effective at pH 6. However, electrolytes affect also basic operating pH; in the treatment of a turbid water model containing background electrolytes, *Opuntia* spp. was very effective at pH 8–10, operating with highly efficacious range at pH around 10 in the absence of electrolytes. These electrolytes decrease repulsion between particles, and facilitate coagulation that occurs at pH 8 [10].

According to Torres [15], sludge production was lower for *Opuntia's* coagulant than that of $FeCl_3$ used as chemical coagulant. In the present case, we did not observe a notable effect on the sludge production.

The OFI pad juice pH was slightly acidic (6.14), regarding the small added volume there was no effect on the initial pH values. In the following section, initial pH was fixed at 8.7 to maximize turbidity removal efficiency.

3.1.3. Effect of initial conductivity on turbidity removal efficiency

The conductivity of the wastewater model was adjusted by adding appropriate volumes of 1 M NaCl solution. The conductivity effect was investigated between 1.5 and 3.8 mS/cm. 87.7% of turbidity removal efficiency was attained at 2.7 mS/cm (Fig. 6), during OFI pad juice assisted EC–EF using the following experimental conditions: 0.015 mL/L pad juice volume, initial pH 8.7, current density $j = 43.6\ mA/cm^2$, EC–EF run time of 20 mn, interelectrode distance 1 cm. The maximum turbidity removal efficiency was observed at 2.1 mS/cm in the EC–EF parameter optimization study of Merzouk et al. [22]. The turbidity removal raise is proportional

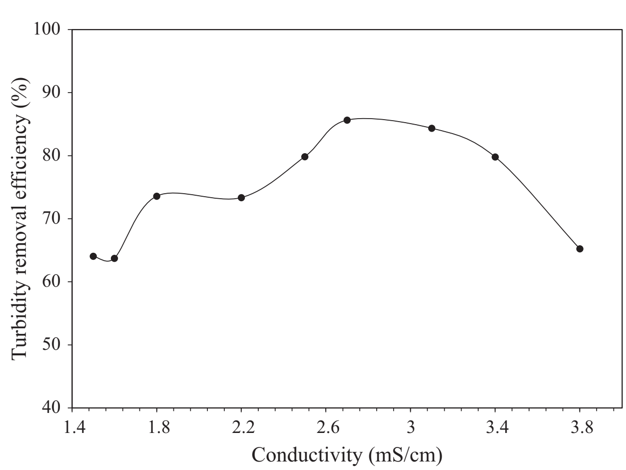

Fig. 6. Effect of initial conductivity on turbidity removal efficiency: initial OFI pad juice volume $V_0 = 0.015$ mL/L, initial pH 8.7, initial silica gel concentration $C_0 = 300$ mg/L, interelectrode distance $d = 1$ cm, current density $j = 43.6\ mA/cm^2$, run time $t = 20$ mn.

to the conductivity until the inverse effect is observed as conductivity value reached 2.7 mS/cm (Fig. 6).

Conductivity affects the cell voltage U and consumption of electrical energy. Electrolyte addition employed to increase the conductivity is known to reduce the ohmic resistance of the wastewater to be treated and hence the cell voltage U at constant current density [26,27,35]. The energy consumption will decrease since it depends on cell voltage U and current intensity I.

The use of NaCl to increase conductivity has other benefits; chloride ions could significantly reduce the adverse effects of other anions, such as HCO_3^- and SO_4^{2-} [2], carbonate ions cause the precipitation of Ca^{2+} ion that forms an insulating layer on the surface of the cathode increasing the ohmic resistance of the electrochemical cell [26,38].

3.2. Optimization using Box–Behnken Design (BBD)

3.2.1. Modeling and fitting the model using response surface methodology (RSM)

Based on the preliminary results reported in Table 1, the following parameter ranges: 0.01–0.02 mL/L, 7.7–9, and 2.2–3.4 mS/cm were selected for initial OFI pad juice volume, initial pH and initial conductivity respectively, in order to achieve RSM optimization tests. Table 2 presents the experimental design and the corresponding turbidity removal efficiencies obtained in the trials of the BBD. Confirming the results of the preliminary trials, the turbidity removal efficiency reached a maximum level when OFI pad juice volume, pH and conductivity were set at medium levels (0 coded values) (Table 2). The regression coefficients of the intercept, linear, quadratic and interaction terms of the model were calculated using the least square technique [39] and are shown in Table 3. It was evident that the linear (X_3) parameter was significant at the level of $p < 0.05$ and its quadratic parameter was highly significant at the level of $p < 0.01$, while only the quadratic parameter of (X_2) was significant at the level of $p < 0.05$. The interaction parameters (X_1X_3) and (X_2X_3) were significant ($p < 0.05$) and highly significant

Table 3
Estimated regression coefficients for the quadratic polynomial model and the analysis of variance (ANOVA) for the experimental results.

Parameter[a]	Estimated coefficients	Standard error	DF[b]	Sum of squares	*F*-value	Prob > *F*
Model	86.9333	0.3273	9	25.9865	8.9794	0.0132
Intercept						
B_0	86.9333	0.3273		25.9865	8.9794	<0.0001
Linear						
X_1	−0.2400	0.2004	1	0.4608	1.4330	0.2849
X_2	0.1962	0.2004	1	0.3081	0.9582	0.3726
X_3	0.5812	0.2004	1	2.7028	8.4054	0.0338
Quadratic						
X_1^2	−0.7529	0.2951	1	2.0931	6.5093	0.0512
X_2^2	−0.8604	0.2951	1	2.7334	8.5007	0.0332
X_3^2	−1.3004	0.2951	1	6.244	19.4179	0.0070
Interaction						
X_1X_2	−0.0550	0.2835	1	0.0121	0.0376	0.8538
X_1X_3	1.0750	0.2835	1	4.6225	14.3753	0.0127
X_2X_3	−1.4275	0.2835	1	8.1510	25.3485	0.0040
Lack of fit			3	1.3305	3.2000	0.2472
Pure error			2	0.2772		
Residual			5	1.6100		
R^2					0.9417	
$R^2_{adjusted}$					0.8368	
C.V.%	0.66					
RMSE	0.5670					
Cor total			14	27.5942		

X_1 = OFI pad juice volume, X_2 = pH, X_3 = conductivity.
[a] Coefficients refer to the general model.
[b] Degree of freedom.

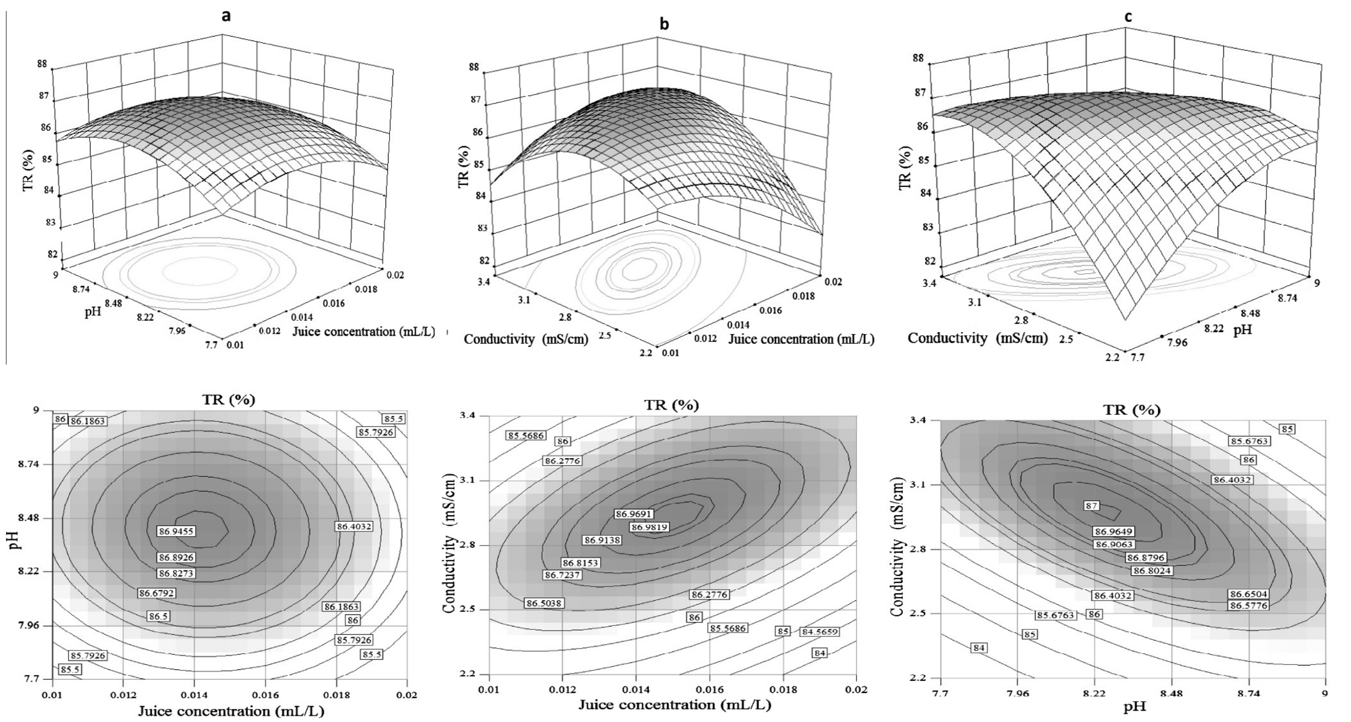

Fig. 7. Response surface plots (a–c) and their contour plots showing the interactive effects of pH and OFI pad juice volume (a), conductivity and juice volume (b), conductivity and pH (c) on the turbidity removal efficiency. Experimental data and conditions are shown in Table 2.

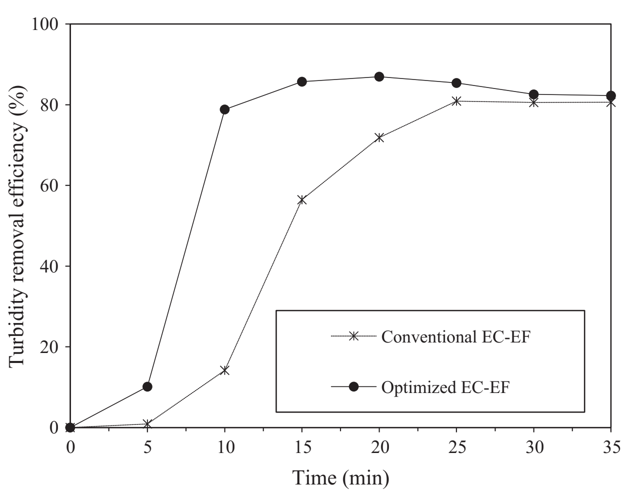

Fig. 8. Effect of RSM optimization on turbidity removal efficiency. Conventional EC–EF: initial OFI pad juice volume $V_0 = 0$ mL, pH 7.7, conductivity $\kappa = 1.4$ mS/cm. Optimized EC–EF: initial OFI pad juice volume $V_0 = 0.016$ mL/L, pH 8.7, conductivity $\kappa = 3.04$ mS/cm. Both EC–EF were performed at initial silica gel concentration $C_0 = 300$ mg/L, interelectrode distance $d = 1$ cm, current density $j = 43.6$ mA/cm^2.

($p < 0.01$), respectively, whereas (X_1X_2) was insignificant ($p > 0.05$) [40]. The mathematical (Eq. (9)) correlating the turbidity removal efficiency with EC–EF treatment parameters is given below including significant and non-significant terms:

$$Y(\mathrm{TR}) = 86.93 - 0.24\,X_1 + 0.19\,X_2 + 0.58\,X_3 - 0.05\,X_1X_2 + 1.07\,X_1X_3 - 1.42\,X_2X_3 - 0.75\,X_1^2 - 0.86\,X_2^2 - 1.30\,X_3^2 \quad (9)$$

The analysis of variance (ANOVA) for the experimental results is given in Table 3, the model fitted F-value of 8.98% implies that the model is significant. There is only a 1.32% chance that a "Model F-Value" this large could occur due to noise, the determination coefficient (R^2) was 0.94, indicating that the sample variations of 94.1% for the cactus juice assisted EC–EF efficiency were attributed to the independent variables, and only 5.9% of the total variations cannot be explained by the model. However, a large value of R^2 does not always mean that the regression model is a good one [41]. For a good statistical model, R^2 adjusted should be close to R^2 [39]. As shown in Table 3, R^2 and R^2 adjusted values for the model did not differ greatly. The "Lack of Fit F-value" of 3.20 implies that the Lack of Fit is not significant relative to the pure error ($p > 0.05$), thereby confirming the validity of the model. The value of coefficient of variation (C.V.%) of 0.66% and "Adequate Precision" ratio of 9.43 were lower than 10 and higher than 4, respectively suggesting that the model was reliable and reproducible [42]. The results indicated an adequate signal for the model suggesting that it could work well for water treatment by OFI pad juice assisted EC–EF technique used in this study.

3.2.2. Analysis of the response surface model and contour plots

The interactive effects of the independent variables and their mutual interaction on the efficiency of the EC–EF treatment process can also be seen on three dimensional response surface profiles of multiple non-linear regression models. The 3-D plots and their respective contour plots are shown in Fig. 7. The 3-D plots were generated by plotting the response using the z-axis against two independent variables while keeping the other independent variable at its zero level [43]. Consequently, the quadratic experimental model had a stationary point, and the predictive turbidity removal efficiency was the maximal value in the stationary point [44]. Fig. 7a shows the 3-D response surfaces and the contour plot of the integrated effect of the pH and OFI pad juice volume on EC treatment. The turbidity removal efficiency (%) was maximal at high levels of pH and at low OFI pad juice volumes. Fig. 7b depicts the interactions between conductivity and OFI pad juice volume on the turbidity removal efficiency. Decreasing values of OFI pad juice volume and conductivity lead to an increase in turbidity removal resulting in a parabolic shape design. Fig. 7c presents the combined effect of conductivity and pH. The turbidity removal efficiency increased gradually to reach its maximal value with increasing conductivity and pH values. Turbidity removal decreases at the higher pH and conductivity values and drops more at the lower pH and conductivity values.

As shown in Table 3, the turbidity removal efficiency mainly depends on the conductivity as its linear and quadratic effects were significant ($p < 0.05$) and highly significant ($p < 0.01$), respectively. Since the quadratic effect of pH was significant ($p < 0.05$) the interaction effect of conductivity and pH had a pronounced influence on the turbidity removal efficiency (Fig. 7c) as the synergetic effect was highly significant ($p < 0.01$) (Table 3).

Globally, these results are in accordance with those obtained in the preliminary study whereby increasing pH and conductivity values to a certain limit lead to an increase in the turbidity removal efficiency, whereas increasing levels of OFI pad juice volume (>0.015 mL/L) decreases the turbidity removal efficiency.

3.2.3. Validation and verification of predictive model

The stationary point giving a maximum turbidity removal efficiency of EC–EF obtained using RSM had the following critical values: OFI pad juice volume 0.016 mL/L, pH 8.2, and conductivity 3.04 mS/cm. The appropriateness of the model equation for predicting the optimum response values was tested using the selected optimal conditions. The predicted turbidity removal efficiency value was 87.0% ± 0.8 which was consistent with the practical turbidity removal value of 86.9% ± 0.1. The predicted values were in close agreement with the experimental values (Table 2) and were found to be not significantly different at $p > 0.05$ using a paired *t*-test [45]. The predicted response values are nearly equal to the experimental data. The normal probability at residuals indicated no abnormality in the methodology adopted. The strong agreement between the real and predicted results confirmed that the response of regression model was adequate to reflect the expected optimization [39].

Finally, the comparison of the turbidity removal efficiency value of the RSM optimized EC–EF assisted by OFI pad juice (86.9%) with that of the conventional EC–EF (71.9%) shows that the optimized process by RSM allows an enhancement of the electrochemical process by 15.1% (Fig. 8).

4. Conclusions

The results obtained through this work suggest an opportunity for the use of the OFI pad juice as a natural coagulant aid to improve the turbidity removal efficiency of the EC–EF technique. OFI pad juice constitutes a possible bio-coagulant to promote the application of clean technologies which reduce damaging environmental impact. The wide cactus sub products uses around the word make it a low cost bio-coagulant. Moreover the extraction processes are easy to handle and the raw material is available in many countries all over the year.

The response surface methodology allowed the successful optimization of the EC–EF process. Under the optimal operating conditions (initial OFI pad juice volume V_0 = 0.016 mL/L, initial pH 8.2, conductivity κ = 3.04 mS/cm) the turbidity removal was enhanced by 15.1% at current density j = 43.6 mA/cm^2, run time t = 20 min, initial silica gel concentration C_0 = 300 mg/L and interelectrode distance d = 1 cm. From an industrial application point of view since numerous laboratory and scale studies are showing that the use of eco-friendly plant coagulants is technically feasible, mathematical models are required to optimize and predict the process in order to modify the classical EC–EF process. However, the standardized equations used in RSM have no methodological background. Consequently, the designed model can only be used within the experimental range and cannot be used for extrapolation. Furthermore, the RSM was useful to investigate the effect of the three studied parameters (OFI pad juice volume, pH, and conductivity) on the turbidity removal response. The applied second-order polynomial model gave a satisfactory description of the experimental data, it showed that turbidity removal efficiency was mostly affected by conductivity followed by pH and OFI pad juice volume.

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