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Comparative study between electrocoagulation used separately and coupled with adsorption for dairy wastewater treatment using response surface methodology design

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ABSTRACT

Dairy industrial wastewater is characterized by high chemical oxygen demand (COD) and other pollution loads. In this study, simulated dairy wastewater (SDW) was treated for turbidity and COD elimination via electrocoagulation (EC) with aluminum electrodes. COD concentration was not completely abated and exceeded allowable Algerian direct discharge limits. To enhance rate parameter pollution removal, electrocoagulation (EC) was combined with adsorption (AD) under the same operational electrocoagulation conditions. A full factorial design was employed to determine the optimum operating conditions for dairy wastewater treatment by electrocoagulation used separately or coupled with granular activated carbon (GAC). Current density, initial pH, and GAC mass were chosen as the controlling process parameters and examined at three levels. The results showed that EC reduced turbidity and COD from SDW to 98.75% and 78.09%, respectively, when pH = 4 and with current densities of 20.83–27.77 mA/cm^2. The EC/AD process enhanced turbidity reduction to 99.39% and COD removal to 87.12% when small masses of GAC (0.5 to 1.5 g) were used at the lowest applied current density level of 13.38 mA/cm^2. In comparison to classical electrocoagulation using aluminum electrodes in a batch system, coupling electrocoagulation to adsorption technique achieved faster removal of pollutants with lower operating costs. Operating costs of the EC/AD process for turbidity and COD removals were calculated as 0.360 €/m^3 and 0.746 €/m^3 vs. 0.494 €/m^3 and 0.692 €/m^3 for the EC process. Correlations with the experimental data for the EC process were R^2 = 95.78% for turbidity and R^2 = 96.22% for COD removal. For the coupled EC/AD they were R^2 = 96.61% for turbidity and R^2 = 95.48% for COD removal.

Keywords: Dairy wastewater; Chemical oxygen demand; Electrocoagulation; Adsorption; Operating cost; Full factorial design

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1. Introduction

Due to the steady rise in the demand for milk and milk products, the dairy industry is among the most highly polluting industries both in terms of volume of effluent generated [1] and its characteristic byproducts have high biological oxygen demands, high chemical oxygen demands (COD) and high turbidity [2]. Together these cause significant environmental problems when the effluent is discarded without treatment. Today, there are many technologies used to treat dairy wastewater, such as coagulation [3], anaerobic or/and aerobic reactors [4], adsorption [5], membrane separation [6], and others. Electrocoagulation (EC) is an efficient method that has been applied to treat a variety game of pollutants [7]. EC removal mechanisms include coagulation, adsorption, and precipitation and H_2 flotation [8–10]. Chezeau et al. [11] provided an overview of EC removal efficiencies for dairy wastewater. Typically, when EC was applied in a batch mode using parallel aluminum electrodes, high CODs were not completely alleviated and remained above discharge limits, thereby requiring additional treatment. Coupling electrocoagulation with adsorption to enhance dairy wastewater treatment is a relatively new approach [12].

The present work investigates in the first part the optimization of operating parameters for electrocoagulation batch treatment of simulated dairy wastewater (SDW) using aluminum electrodes. COD concentration in the treated SDW was not completely abated and was above the permitted Algerian direct discharge limits. In the attempt to enhance the electrocoagulation process in terms of turbidity and COD abatements and energy consumption, we opted in the second part to couple EC with the absorption process by introducing different masses of granular activated carbon (GAC) into the electrocoagulation reactor containing the wastewater influent. In the classical method of optimization, one parameter is varied at a time while the other being constant which stymies the ability to understand complex interactions between the variables and the response. In contrast, response surface methodology (RSM) is a collection of mathematical and statistical techniques for modeling and analysis of problems in which a response of interest is influenced by a set of independent variables [13]. In recent years, RSM has been successfully tested to optimize the efficiency of processes like electrocoagulation [14]. However, using it to compare EC when employed as a single treatment process and coupled with adsorption into GAC has yet to be done. That is the approach adopted herein.

2. Material and methods

2.1. Material and experimental procedure

Wastewater was generated in the laboratory by dissolving 2.5 g of milk powder (LOYA, Algeria) per liter of potable water to create a constant wastewater composition to experimentally simulate real dairy wastewater. The main characteristics of the SDW were as follows: pH_0 = 6, 66, conductivity = 3 ms/cm, COD = 2,300 mg/L, turbidity = 1,000 NTU and $DB0_5$ = 1,270 mg O_2/L. The SDW was prepared freshly, and these characteristics were maintained uniformly throughout the study.

Electrocoagulation of SDW effluent was conducted in a 1 L beaker in a batch mode (Fig. 1). 1.5 g of NaCl was added to the SDW to adjust conductivity, and the pH was adjusted to desirable values (3, pH_{reel} = 6.66 and 10) using HCl and NaOH solutions. In the testing, a pair of aluminum electrodes (12 cm × 3 cm × 0.5 cm) was separated by 1 cm and dipped in the wastewater. The current was provided by a GW GPR3030D, 3 A–30 VDC power supply. The effluent under treatment was homogenized by gentle magnetic stirring at 300 rpm, which allowed the separation of gasses formed from the solution, thus avoiding the formation of foam, which can affect the course of the batch processing. The electrochemical cell and electrodes were cleaned with detergent and acetone and then rinsed with distilled water, after each experiment. All experiments were conducted at room temperature at 25°C ± 2°C.

Approximately 5 mL of sample were taken at 6-time intervals (5, 10, 15, 30, 45 and 60 min). The samples were allowed to settle, filtrated by means of Whatman 0.45 mm filters, and then measured for COD and turbidity. COD levels were determined using the standardized calorimetric technique with an excess of hexavalent chromium and subsequent measurement of the optical density. Turbidity was measured with a Hanna Instrument LP 2000 turbidimeter.

The coupling process experiments involved adding commercially available GAC masses to the 1 L of prepared SDW. The GAC used (Chemviron-F400) is a mineral coal of less than 1 mm in size. It is mesoporous, with a specific surface area of 1,200 m^2/g, of porous volume 0.9 cm^3/g, and with the use of successive surface oxides much more acidic than basic: 1.29 and 0.27 meq/g [15]. Then the solution was placed in the EC reactor under the fixed temperature of 25°C± 2°C and under an agitation speed of 300 rpm (round per minute). The variable parameters tested in a conventional EC process (current density and initial pH values) were kept the same.

The percentage removal of both turbidity and COD were calculated using Eq. (1):

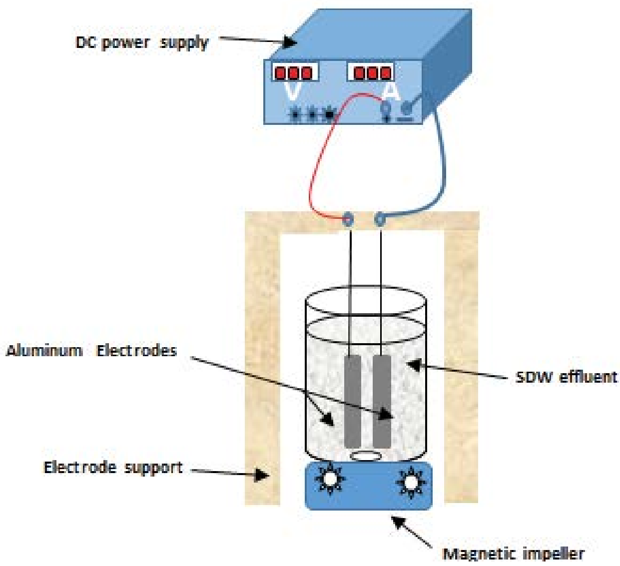

Fig. 1. Electrocoagulation apparatus.

$$\%\text{removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0: initial turbidity (NTU)/COD concentration (mg O_2/L); C_e: the equilibrium turbidity (NTU)/COD concentration (mg O_2/L).

2.2. Operational costs

A cost analysis (€/m^3 of wastewater treated) was performed to determine whether electrocoagulation used alone or coupled with GAC adsorption was more economical. The operational cost includes materials (mainly electrodes), electrical energy, and chemicals. In this study, specific energy consumption was calculated for all monitored runs but the calculation of operating costs was done only for the optimal operating conditions via this formula [16]:

$$\text{Operating cost} = A\ \text{Energy}_{\text{consumption}} + B\ \text{Electrode}_{\text{consumption}} + C\ \text{Chemical}_{\text{consumption}} \quad (2)$$

Energy and electrode consumption (Eqs. (3) and (4)) are reported as per cubic meter of wastewater treated. The terms *A*, *B*, *C*, are unit prices given for the Algerian market in December 2020: electrical energy price 0.01479 €/kWh for the first 125 kWh and 0.03473 € beyond that. The electrode material price was 1.53 €/kg for aluminum, and chemical costs were 0.492 €/L for HCl, 1.11 €/kg for NaOH, and 1.11 €/kg for KCl and 81.33 €/kg for commercial granular activated carbon.

Specific electrical energy consumption (kWh/m^3) and electrode consumption (kg Al/m^3) were calculated from the following equations [16]:

$$\text{Energy}_{\text{consumption}}\left(\frac{\text{KWh}}{\text{m}^3}\right) = \frac{IUt_{\text{EC}}}{v} \quad (3)$$

$$\text{Electrode}_{\text{consumption}} = \frac{It_{\text{EC}}M}{nFv} \quad (4)$$

where U is the cell voltage (V), I is the current (Ampers), t_{EC} is the operating time (s), v is the volume (m^3) of the wastewater, M is the molecular weight of the metal (g/mol), z is the number of electrons involved in the reaction ($z = 2$), and F is Faraday's constant (96.485 C/mol).

2.3. Experimental design

The software Minitab 18 design was used for the optimization of turbidity reduction and determination of COD removal efficiency. A total of 36 experiments were conducted: 9 with the EC process with the 2 continuous factors X_1 (pH_0) and X_2 (current density) and 27 experiments coupling the EC/GAC absorption process with the 3 factors X_1 (GAC), X_2 (pH_0), and X_3 (current density). Selected parameter levels are shown in Table 1. Each of these independent variables was coded in 3 levels (–1, 0 and +1):

$$X_i = \frac{x_1 - x_0}{\Delta_x} \quad i = 1,2,3 \quad (5)$$

Table 1
Process parameters and their levels for EC and EC/AD treatment of SDW

Process		EC		
Parameter	X	Levels		
		–1	0	+1
pH_0	X_1	4	6.66	10
Current density (mA/cm^2)	X_2	13.88	20.83	20.77
Process		EC + AD		
Parameter	X	Levels		
		–1	0	+1
GAC mass (g)	X_1	0.5	1.5	3
pH_0	X_2	4	6.66	10
Current density (mA/cm^2)	X_3	13.38	20.83	27.77

where x_0 is the initial value of the parameter, x_1 is the final value of the parameter, Δ_x is the variation interval of the parameter's value.

Turbidity reduction, COD removal efficiency were the response according to Eq. (6):

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} X_i^2 + \sum_{i=1}^{n}\sum_{j=i+1}^{n} b_{ij} X_{ij} \quad (6)$$

where b_0 is the constant coefficient; b_i is the regression coefficients for linear effects; b_{ii} is the quadratic coefficients; b_{ij} is the interaction coefficients and X_i, X_j are the coded values of parameters (–1, 0 or +1).

3. Results and discussion

As mentioned above, the regression and graphical analysis of the obtained experimental data were done using Minitab 18. The accuracy of the model was justified through the design of experiments (DOE), the high percentage of the coefficient of correlation R^2, and the F-values.

3.1. Effect of various parameters on electrocoagulation process

The response (Y) of turbidity reduction and COD removal from SDW by EC experiments and the corresponding predicted values are shown in Table 2. Experimental data were fitted to quadratic models. The quadratic Eqs. (7) and (8) were obtained in terms of coded factors as given below:

$$Y_{\text{Turbidity}} = 1881.1 + 35.1X_1 - 23.49X_2 - 2.394X_1X_1 + 0.449X_2X_2 + 0.242X_1X_2 \quad (7)$$

$$Y_{\text{COD}} = -324.4 + 33.3X_1 + 26.00X_2 - 1.332X_1X_1 - 0.606X_2X_2 - 0.37X_1X_2 \quad (8)$$

The concordance of the experimental and predicted value of turbidity and COD is shown in Fig. 2, and the

Table 2
Full factorial design used for the turbidity and COD removal from SDW by EC process

Run	pH (X_1)	Current density (X_2)	Turbidity removal (%)		COD removal (%)	
			Y_{exp}	Y_{pred}	Y_{exp}	Y_{pred}
1	–1	–1	60.01	64.1078	11.45	10.8514
2	–1	0	97.85	98.6372	51.43	48.0271
3	–1	+1	98.75	93.8650	63.78	67.7815
4	0	–1	26.93	15.8543	25.8	34.9391
5	0	0	51.28	54.8832	72.75	65.2525
6	0	+1	48.25	55.7225	78.09	76.4484
7	+1	–1	3.95	10.9279	9.07	0.5295
8	+1	0	58.84	54.4496	13.09	23.9904
9	+1	+1	63.48	60.8925	29.00	26.6401

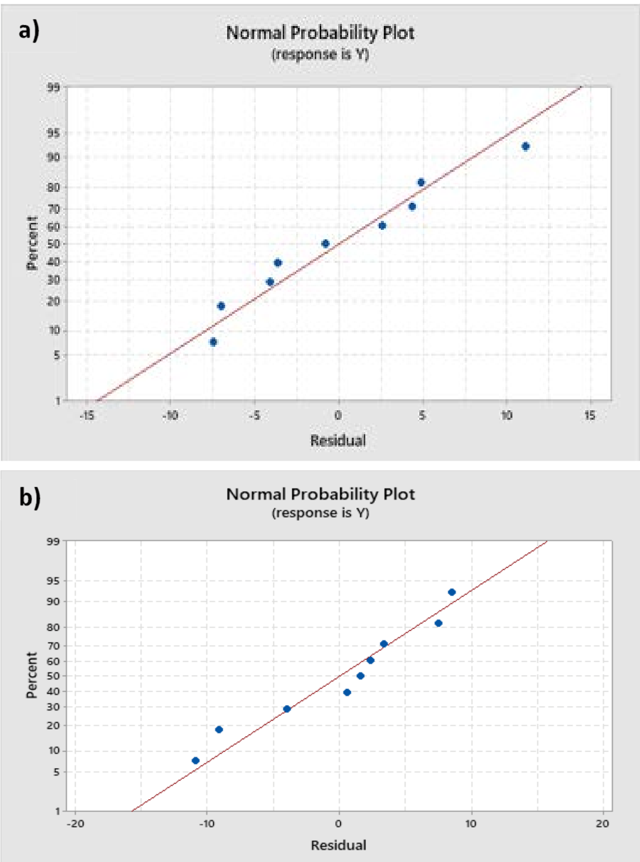

Fig. 2. Normal probability plot of: (a) turbidity removal response and (b) COD removal response obtained by EC treatment.

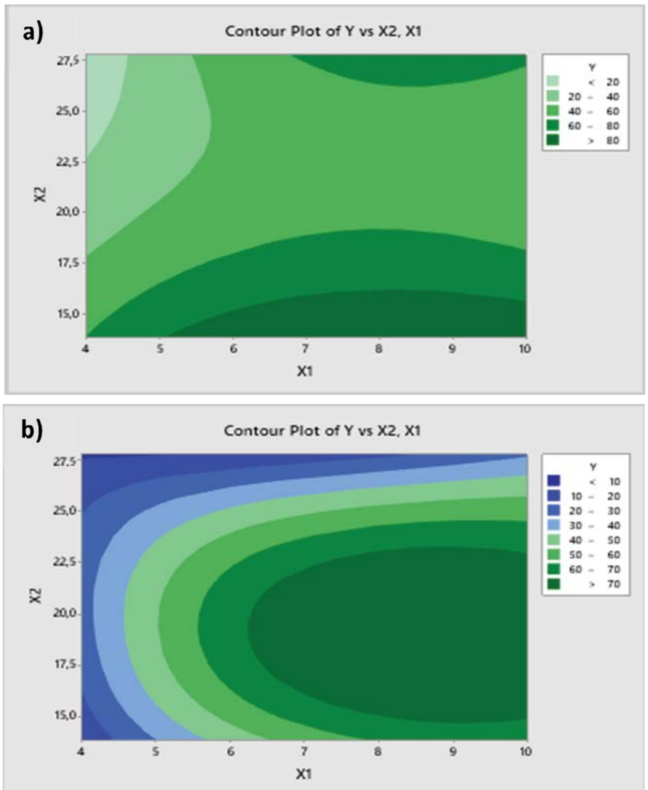

Fig. 3. Contour plot of the predicted data of the effect of pH (X_1) and current density (X_2): (a) turbidity reduction and (b) COD removal by EC.

high R^2 values of 95.78% and R^2 = 93.91% validate the statistical significance of the model. More details about these models are expressed by Eqs. (7) and (8) are given in Appendix A.

The contour plot for estimation of the turbidity reduction and COD removal efficiencies (Y) over the independent variables pH (X_1) and current density (X_2) are shown in Fig. 3; these graphical representations are derived from the model of Eqs. (9) and (10).

As shown in Fig. 3a, the turbidity removal efficiency (Y) is high with all the tested pH values but increases when pH > 5. In EC treatments, phenomenon occurring in the acidic medium is the neutralization of colloids negatively charged Al^{+3} provided from anode dissolution. For higher pH values, the adsorption phenomena into $Al(OH)_3$ dominates [17] and enhances COD removal. Notably, dairy wastewater has an electric point pH (pH_{iso}) around 4.5 [9]. The response surface of turbidity removals shows that its maximum is achieved without requiring high current density values (I < 20.83 mA/cm^2). Increasing the current density beyond 20.83 mA/cm^2 produced no significant improvement in turbidity reduction.

As observed in Fig. 3b, COD removal efficiency (Y) has a distinct behavior from turbidity reduction (Fig. 3a). Even with small current densities all along the axis X_1 (pH), turbidity removal tends to cancel out. Notably, COD removal takes its maximal values from pH (X_1) pH ≈ 6. This yield could be improved with higher current densities and more aluminum species available in solution for this pH zone, as previously observed by Tchamango et al. [13].

3.2. Coupled electrocoagulation/adsorption process

3.2.1. Effects of various parameters on the coupled EC/adsorption process

The results of the Y (response) on turbidity reduction and COD removal with the coupled EC/GAC process are presented in Table 3. The quadratic regression model in terms of coded factors is given by Eqs. (9) and (10). The coefficients of correlation of the two models are R^2 = 92.22% for turbidity and and R^2 = 95.48% COD removal.

$$Y_{\text{Turbidity}} = 237.1 + 11.7X_1 - 65.97X_2 + 4.65X_3 + 1.45X_1X_1 + 3.34X_2X_2 - 0.127X_3X_3 - 0.039X_1X_2 - 0.56X_1X_3 + 0.33X_2X_3 \quad (9)$$

$$Y_{\text{COD}} = 153.5 - 0.52X_1 + 44.74X_2 - 26.12X_3 - 0.10X_1X_1 - 1.914X_2X_2 + 0.746X_3X_3 + 0.143X_1X_2 + 0.291X_1X_3 - 0.82X_2X_3 \quad (10)$$

As all values from the models should be inside the interval [0,100], there were initially three values without physical significance (Table 3): 2 values exceeded 100, and 1 was negative. These required modification of the model's expression. After a series of adjustments to Eq. (9), the equation that generated values closest to the experimental ones was Eq. (11):

$$Y_{\text{Turbidity}} = 32015 - 117X_1 - 7916X_2 + 88.8X_3 + 335X_1X_1 + 462.1X_2X_2 - 35.5X_1X_3 \quad (11)$$

Table 3
Full factorial design used for the turbidity and COD removal from SDW by coupled EC/AD process

Run	GAC mass (X_1)	pH (X_2)	Current density (X_3)	Turbidity removal (%)		COD removal (%)	
				Y_{exp} (%)	Y_{pred} (%)	Y_{exp} (%)	Y_{pred} (%)
1	–1	–1	–1	98.92	87.428	43.25	39.50
2	–1	–1	0	98.46	96.36	13.25	16.18
3	–1	–1	+1	99.39	93.015	62.87	64.83
4	–1	0	–1	1.93	18.79	75.16	74.21
5	–1	0	0	39.43	33.91	29.55	35.67
6	–1	0	+1	21	36.74	74.69	69.12
7	–1	+1	–1	3.6	–0.055	86.2	79.25
8	–1	+1	0	21.76	22.78	16.43	21.72
9	–1	+1	+1	38.38	33.32	35.34	36.22
10	0	–1	–1	89	93.99	31.87	43.40
11	0	–1	0	90.98	98.98	26.26	22.10
12	0	–1	+1	99.36	91.7	76.76	72.77
13	0	0	–1	39.24	25.25	87.12	78.50
14	0	0	0	28.3	36.43	39.24	41.97
15	0	0	+1	25.27	35.32	80.5	77.44
16	0	+1	–1	5.2	6.28	79.28	84.02
17	0	+1	0	22	25.17	27.54	28.51
18	0	+1	+1	45.58	31.77	45.21	45.02
19	+1	–1	–1	99.35	109.28	43.76	48.90
20	+1	–1	0	99.84	108.36	39.12	30.63
21	+1	–1	+1	99.04	95.17	79.54	84.33
22	+1	0	–1	58.36	40.38	84.19	84.56
23	+1	0	0	57.53	45.65	49.05	51.07
24	+1	0	+1	40.62	38.64	82.66	89.57
25	+1	+1	–1	7.53	21.22	86.35	90.80
26	+1	+1	0	43.56	34.2	45.78	38.33
27	+1	+1	+1	22	34.9	59.65	57.87

The model modification was followed by deletion of terms with a non-signification, as shown in the pareto chart of the standardized effects (Fig. 4). The predicted values from the new model and experimental ones are given in Table 4.

The aberrant values –0.055, 109.28, and 108.36 (Table 3) became 8.96, 100.83, and 100.21, respectively (Table 4), from which 8.96, 100.83, and 100.21 are considered to be in agreement with the experimental ones.

Concerning the model summary for transformed response, the correlation coefficient R^2 increased to 96.61% from R^2 = 92.22%, and the difference between R^2 (Adj.) = 95.9% and R^2 (Pred.) = 93.43% was also reduced, thereby showing its improved performance with respect to the experimental results (Fig. 5). More details about these models (Eqs. (10) and (11)) are given in Appendix B.

Figs. 6 and 7 show the contour plots obtained from the predicted data of turbidity reduction and COD removal respectively: (a) Y vs. X_1, X_2; (b) Y vs. X_1, X_3; (c) Y vs. X_2, X_3.

In Fig. 6a, the interactions between GAC dose (X_1) and pH (X_2) are shown, in which higher values of Y appear in low pH environments compared to when EC was used alone where adsorption of aluminum hydroxides was needed. That is recompensed by adsorption on GAC. The maximum yield was achieved using only small masses of carbon. The same behavior was observed in Fig. 6c when minimal current density at lower pH levels had positive effects on the Y response. Fig. 6b shows the interactions between GAC dose (X_1) and current density (X_3). Higher current densities and higher GAC doses were required to obtain higher turbidity removal. This might be explained by the fact that in a conventional EC process, the flow of ions is not perturbed [18]. Fig. 7 shows that statistically Y maximizes when X_1 (GAC dose) and X_3 (current density) are at their maximal values for the reasons discussed below. The positive effects of pH (X_2) is in the range of (6 < pH < 8) when the form of $Al(OH)_3$ dominates. COD removal efficiency (Y) increases when GAC (X_1) is at its maximum.

When the dairy wastewater was only treated with EC using aluminum electrodes in a batch mode [10,19], COD abatement did not exceed 61% (Table 5). Linares-Hernández et al. [20] found that when adsorption is coupled with electrocoagulation the removal rate increases. Specifically, Linares-Hernández et al. [20] demonstrated that using *Ectodemis* of *Opuntia* as a bio-sorbent for the electrocoagulation treatment of industrial wastewater reduced COD from 66.66% to 84%. According to [16], 2 g/L of activated carbon introduced to an electrocoagulation unit was sufficient to improve COD abatement to 67.9% instead of the 42.2%

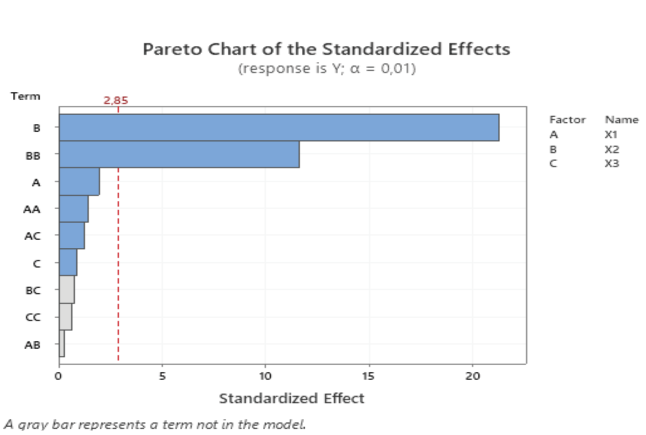

Fig. 4. Pareto chart of the standardized effects.

Table 4
Experimental and predicted values of turbidity removal from SDW by coupled EC/AD process

Run	Y_{exp}	Y_{pred}	Run	Y_{exp}	Y_{pred}
1	98.920	93.575	15	25.270	36.616
2	98.460	96.176	16	5.200	11.890
3	99.360	98.705	17	22.000	19.700
4	1,390	28.045	18	45.580	25.189
5	39.430	35.778	19	99.350	100.830
6	21.000	42.106	20	99.840	100.215
7	3.600	8.960	21	99.040	99.598
8	21.760	23.955	22	58.360	46.871
9	38.380	32.660	23	57.530	45.534
10	89.000	93.901	24	40.620	44.159
11	90.980	95.206	25	7.530	38.609
12	99.360	96.491	26	43.560	36.974
13	39.240	29.114	27	22.000	35.267
14	28.300	33.081	/	/	/

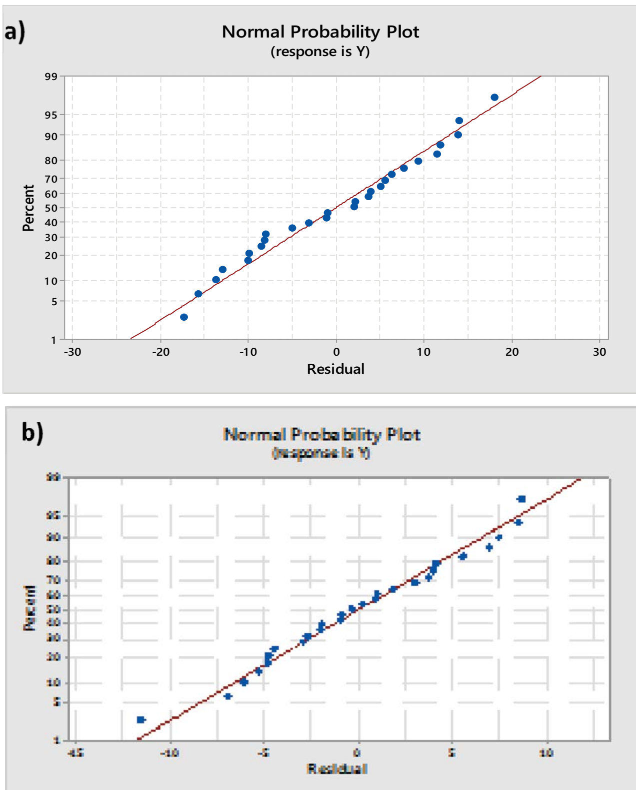

Fig. 5. Normal probability plot of (a) turbidity reduction and (b) COD removal responses obtained by coupled EC/AD treatment.

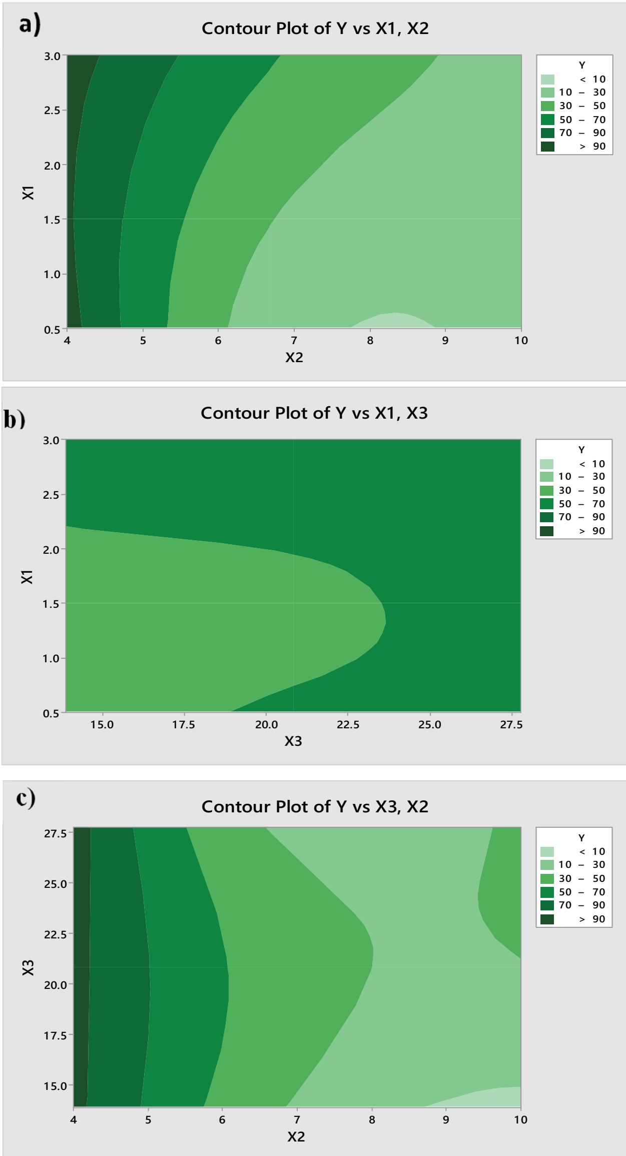

Fig. 6. Contour plot obtained from the predicted data of turbidity reduction by coupled EC/AD (a) Y vs. X_1, X_2; (b) Y vs. X_1, X_3; (c) Y vs. X_2, X_3.

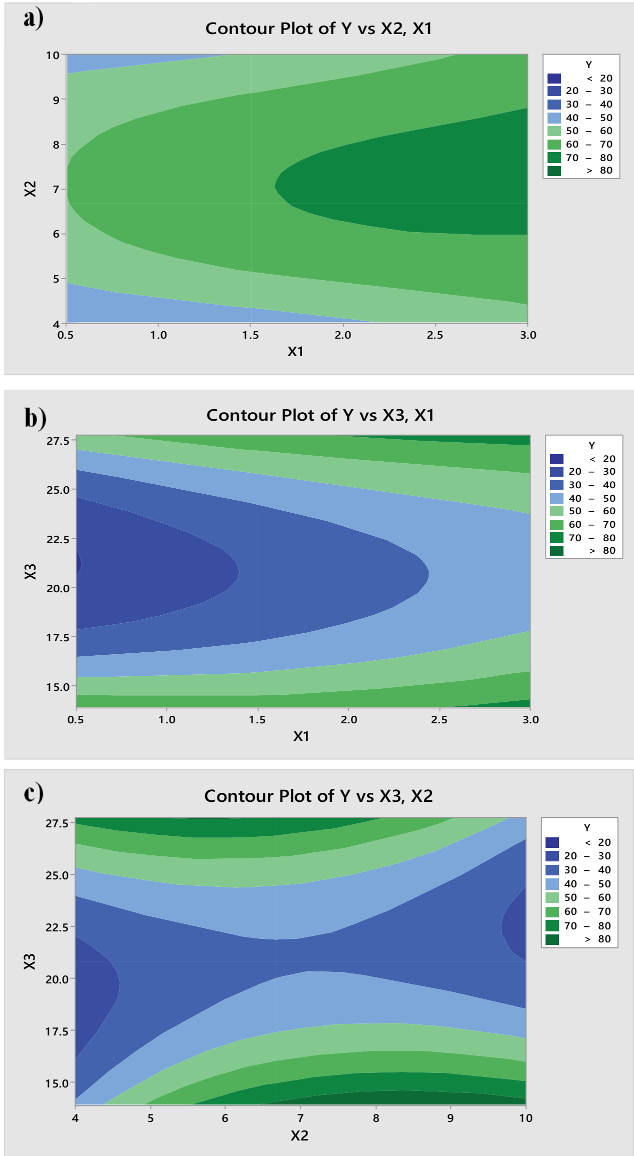

Fig. 7. Contour plot obtained from the predicted data of COD removal by EC/AD (a) Y vs. X_1, X_2; (b) Y vs. X_1, X_3; (c) Y vs. X_2, X_3.

Table 5
Summary of the results obtained by the two methods: EC and coupled EC/AD applied to dairy and other effluents

Effluent	EC		EC/AD		References
	Removal efficiency	Cost	Removal efficiency	Cost	
Dairy	COD (61%)	/	Not done	/	[10]
Dairy	COD (57%)	3.48R$/m^3	Not done	/	[19]
Dairy	COD (78.09%)	0.692 €/m^3	87.12%	0.476 €/m^3	This study
Cr(VI)	75%	/	94%	/	[21]
Cr(VI)	78%	/	97%	/	[22]
Industrial wastewater	COD (66.66%)	8.181 kWh = 68.6 cents (USA)	84.53%	/	[20]
Textile wastewater	COD (42.2%)	1.52 €/m^3	67.9%	1.64 €/m^3	[16]

obtained with a conventional EC approach. Researchers [21,22] observed that the addition of conventional adsorbent (GAC) or non-conventional adsorbent (red onion skin) to an electrocoagulation treatment has been shown to enhance chromium removal, from 75% to 94% in the former and from 78% to 97% in the latter.

3.2.2. Results of optimum operational conditions and operation cost

Specific electrical energy consumption (SEEC) was calculated according to Eq. (3). Data of experimental SEEC values obtained after both EC and EC/AD treatment are presented in Table 6.

According to experimental data shown previously, the maximum turbidity reduction from SDW by EC demonstrated that the optimum value of current density is 20.83 mA/cm^2 at $pH_{solution}$ = 4. The associated electrical energy consumed was 8.46 kWh/m^3 which corresponds to 0.494 €/m^3 operational costs including those of electrode material consumption (0.25 kg/m^3) and chemicals (negligible). Adding small masses of GAC (0.5 g) gave the best turbidity reduction, even with lower applied current density values, which resulted in lower energy consumption – not exceeding 5.75 kWh/m^3. That corresponds to 0.360 €/m^3 in operational costs including the costs affiliated with electrode material consumption (0.15 kg/m^3), granular activated carbon (0/04 €), and negligible chemicals fee. For the COD removal, the highest percentage removal, which was 78.09% (current density = 27.17 mA/cm^2, pH = 6.66) was obtained with an energy consumption of 13.74 kWh/m^3 costing 0.692 €/m^3 when the EC was applied alone. The percentage COD removal improved to 87.12%, with the addition of adsorbent, even at lower current density values (I = 13.88 mA/cm^2), hence reducing the SEEC of the system to a maximum of 4.99 kWh/m^3 and thus the operation cost (0.476 €/m^3).

Thus, we concluded that the coupling of electrocoagulation and adsorption processes using different absorptive material types might prove a judicious choice for treating wastewater influent polluted by a variety range of pollutants. Studies found in the literature are also shown in Table 5.

Table 6
Data of experimental SEEC values for EC and EC + AD processes

SEEC (kWh/m^3)						
EC			EC/AD			
X_1	X_2	Y_{exp}	X_1	X_2	X_3	Y_{exp}
–1	–1	4.005	–1	–1	–1	4.05
–1	0	8.46	–1	–1	0	7.72
–1	+1	14.74	–1	–1	+1	13.96
0	–1	3.91	–1	0	–1	4.66
0	0	8.19	–1	0	0	7.59
0	+1	13.37	–1	0	+1	14.43
+1	–1	3.67	–1	+1	–1	4.45
+1	0	6.78	–1	+1	0	7.35
+1	+1	12.28	–1	+1	+1	12.44
			0	–1	–1	4.56
			0	–1	0	9.09
			0	–1	+1	14.61
			0	0	–1	4.65
			0	0	0	8.31
			0	0	+1	12.89
			0	+1	–1	4.06
			0	+1	0	7.76
			0	+1	+1	13.12
			+1	–1	–1	5.75
			+1	–1	0	10.11
			+1	–1	+1	15.64
			+1	0	–1	4.99
			+1	0	0	9.09
			+1	0	+1	13.54
			+1	+1	–1	4.6
			+1	+1	0	8.4
			+1	+1	+1	13.6

4. Conclusions

This study investigated the possibility of improved turbidity and COD removal from SDW by an EC process using granulator commercial activated carbon. Minitab 18.1 was used to achieve a better understanding of the effects of the contributing parameters and their interactions on the performance of EC used separately and in a coupled EC/GAC process. Turbidity and COD removal efficiencies at optimum conditions (4 ≤ pH ≤ 6 and 20, 83 mA/cm^2 ≤ I ≤ 27, 77 mA/cm^2) were found to be 98.75% and 78.09%, respectively, when EC was employed by itself. The addition of moderate masses of GAC (0.5–1.5 g) as an adsorbent increased the removal rate of turbidity and COD at lowest current density (I = 13.88 mA/cm^2) than the conventional EC process, thus reducing specific energy consumption of the system and thus minimizing the operation cost. Also, when there is an elevated pH (pH ≥ 6), the approach was even more effective due to simultaneous adsorption by the GAC and also by aluminum hydroxides. Minitab18 was successfully employed for experimental design and analysis of results. Highly significant of the models via analysis of the F-values and the obtained coefficients of correlation for the EC and EC/AD processes confirm design of the accomplishment experiments done in this study. Consequently, this demonstrated a satisfactory fit of the second order regression model with the experimental data.

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Appendix A

The analysis of variance for the second-order equation for the response (Y) of turbidity reduction, Eq. (11), and chemical oxygen demand (COD) removal from SDW, Eq. (12), for the corresponding predicted values are given in Tables A1 and A2, respectively.

According to the table of Fischer's F law, for $\alpha = 0.95$, we found that for the value DF of the model = 5 and Error = 3 the corresponding value between them. This corresponding value is (9.01) defining the limit when the model is considered significant. For all values of column $F \geq 9.01$ meaning that the model's terms are significant. Also, all values of the column $P \leq 0.05$ mean that model's terms are significant. Consequently, the P-value of this model of turbidity reduction is 0.028, so the model is significant.

In the same manner, for Table A2, the corresponding value is (9.01). All values of column $F \geq 9.01$ meaning model's terms are significant. Also, all values of column $P \leq 0.05$ mean that the model's terms are significant. The P-value

Table A1
Analysis of variance for the turbidity reduction

Source	DF	Adj. SS	Adj. MS	F-value	P-value	
Model	5	6,985.1	1,397.0	13.63	0.028	Significant
Linear	2	5,161.0	2,580.5	25.18	0.013	
X_1	1	2,383.3	2,383.3	23.26	0.017	Significant
X_2	1	2,777.8	2,777.8	27.11	0.014	Highly Significant
Square	2	1,839.6	919.8	8.98	0.054	
X_1X_1	1	902.7	902.7	8.81	0.059	
X_2X_2	1	937.0	937.0	9.14	0.057	Significant
2-way Interactions	1	102.5	102.5	1.00	0.391	
X_1X_2	1	102.5	102.5	1.00	0.391	
Error	3	307.4	102.5			
Total	8	7,292.5				

Table A2
Analysis of variance for the COD removal from SDW

Source	DF	Adj. SS	Adj. MS	*F*-value	*P*-value	
Model	5	5,667.0	1,133.4	9.25	0.048	Significant
Linear	2	3,577.1	1,788.5	14.59	0.028	
X_1	1	2,585.9	2,585.9	21.10	0.019	Highly Significant
X_2	1	991.2	991.2	8.09	0.065	
Square	2	1,990.7	995.4	8.12	0.062	
X_1X_1	1	279.3	279.3	2.28	0.228	
X_2X_2	1	1,711.4	1,711.4	13.96	0.033	Significant
2-way Interactions	1	238.4	238.4	1.95	0.257	
X_1X_2	1	238.4	238.4	1.95	0.257	
Error	3	367.7	122.6			
Total	8	6,034.7				

of this model of COD removal is 0.048. Thus, the model is significant.

Appendix B

The analysis of variance for the second-order equation for the response (Y) of COD removal with coupled electrocoagulation (EC)/GAC, Eq. (14), and turbidity reduction, Eq. (15), for the corresponding predicted values are given in Tables A3 and A4, respectively.

The corresponding value for Table A3 is (2.49). All values of column $F \geq 2.49$ meaning that the model's terms are significant. Similarly, all values of column $P \leq 0.05$ mean that the model's terms are significant. The P-value of this model of COD removal is $0.00 < 0.05$. Thus, in this case, the model is highly significant.

The corresponding value for Table A4 is 2.6. All values of column $F \geq 2.6$ meaning that the model's terms are significant. Similarly, all values of column $P \leq 0.05$ mean that the model's terms are significant. The P-value of this model of turbidity reduction is $0.00 < 0.05$. So the model is highly significant.

Consequently, all quadratic models presented in this study can be used to optimize the operational parameters and obtain the predicted value by the highly significant model, without further experimentation.

Table A3
Analysis of variance for the COD removal with coupled EC/GAC

Source	DF	Adj. SS	Adj. MS	*F*-value	*P*-value	
Model	9	14,363.2	1,595.91	39.90	0.000	Highly Significant
Linear	3	1,340.8	446.93	11.17	0.000	
X_1	1	1,082.1	1,082.14	27.05	0.000	Highly Significant
X_2	1	197.5	197.50	4.94	0.040	Significant
X_3	1	64.5	64.46	1.61	0.221	
Square	3	9,505.8	3,168.61	79.21	0.000	
X_1X_1	1	0.1	0.12	0.00	0.956	
X_2X_2	1	1,731.1	1,731.11	43.28	0.000	Highly Significant
X_3X_3	1	7,774.6	7,774.59	194.36	0.000	Highly Significant
2-way Interactions	3	3,600.8	1,200.26	30.01	0.000	
X_1X_2	1	3.5	3.53	0.09	0.770	
X_1X_3	1	77.6	77.56	1.94	0.182	
X_2X_3	1	3,519.7	3,519.70	87.99	0.000	Highly Significant
Error	17	680.0	40.00			
Total	26	15,043.2				

Table A4
Analysis of variance for the turbidity reduction

Source	DF	Adj. SS	Adj. MS	*F*-value	*P*-value	
Model	6	424,649,014	70,774,836	94.88	0.000	Highly Significant
Linear	3	342,173,327	114,057,776	152.90	0.000	
X_1	1	2,834,869	2,834,869	3.80	0.065	Significant
X_2	1	338,727,129	338,727,129	454.07	0.000	Highly Significant
X_3	1	611,267	611,267	0.82	0.376	
Square	2	102,390,803	51,195,401	68.63	0.000	
X_1X_1	1	1,498,287	1,498,287	2.01	0.172	
$X_2 X_2$	1	100,892,516	100,892,516	135.25	0.000	Highly Significant
2-way	1	1,155,950	1,155,950	1.55	0.228	
Interactions						
X_1X_3	1	1,155,950	1,155,950	1.55	0.228	
Error	20	14,919,573	745,979			
Total	26	439,568,587				