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Organic pollutants removal from olive mill wastewater by coagulation and electrocoagulation: application of Box-Behnken design (BBD)

Abeer El Shahawy[a,*], Shrouk Hassan[b], Ebrahiem Esmail Ebrahiem[c], Ibrahim El Kersh[d]

[a]*Department of Civil Engineering, Faculty of Engineering, Suez Canal University, PO Box 41522, Ismailia, Egypt, email: ahmedabeer12000@yahoo.com, abeer_shahawi@eng.suez.edu.eg (A.E. Shahawy), https://orcid.org/0000-0003-2331-5040*
[b]*Department of Civil Engineering, Faculty of Engineering, Suez Canal University, PO Box 41522, Ismailia, Egypt, email: shrouk_hassan17@yahoo.com (S. Hassan)*
[c]*Chemical Engineering Head Department Faculty of Engineering, El Minia University, Egypt, email: prof.ebrahiem@mu.edu.eg (E.E. Ebrahiem)*
[d]*Department of Civil Engineering, Faculty of Engineering, Suez Canal University, PO Box 41522, Ismailia, Egypt, email: himak2@hotmail.com (I.E. Kersh)*

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ABSTRACT

In this study, chemical coagulation and electrocoagulation (CC/EC) were evaluated as alternatives for olive mill wastewater (OMW) treatment. Jar test was used to determine the most favorable dosage of coagulant, pH of the process and proper flocculation time. CC experiments were carried out using coagulants (alum, lime, ferric chloride and cement dust). Coagulation efficiency was evaluated by measuring chemical oxygen demand (COD), color and turbidity removal ratio. From Tukey test, it was established that alum was more efficient than other coagulants. The maximum removal efficiency of COD and turbidity were 42%, 66%, respectively. The optimum condition was achieved at 0.5 g/100 ml of alum, pH = 6 and flocculation time ranging between 15 min to 25 min. This study used aluminum plates as anode and cathode in electrocoagulation to study COD removal from OMW. Its performance was optimized using Box-Behnken experimental Design and Response Surface Methodology. The following EC optimal conditions were found: current density = 60 mA/cm^2, pH = 4 and electrolysis time 20 min. At these conditions, the maximum COD removal ratio was 47% with an estimated operating cost of 1 USD/m^3.

Keywords: Chemical coagulation; Electrocoagulation; BBD; OMW; Optimization

1. Introduction

Wastewater treatment is a crucial environmental issue [1]. Extraction of oil from olive fruit is one of the important industries in the world especially in Mediterranean countries. Nowadays, nearly 900 million olive trees cover over 10 million ha worldwide, 98% of which are located in the countries of the Mediterranean basin [2,3]. As the demand of olive oil is quickly increasing worldwide, the environmental pollution created by olive mill wastes (OMW) is growing. This pollution is due to the fact that solid and liquid OMW are dark-colored wastes that contain high amounts of organic materials. Additionally, it contains many complex toxic substances that are not easily degradable. Another issue is that this waste has a high pollutant load. For example, it contains high levels of chemical oxygen demand (COD), biological oxygen demand (BOD), oil and grease Mediterranean (O&G), phenol and polysaccharides [4].

In Egypt, olive oil industry became the main agri-business activity in North Sinai governorate. An enormous amount of olive mill wastewater is produced, accounting for 0.5–1.5 m^3 of OMW per 1000 kg of olives (depending on the oil extraction process) [5]. OMW is characterized by extraordinary organic pollutants, which are difficult to deal with in conventional wastewater treatment processes [6]. Thus,

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*Corresponding author.

the direct discharge of OMW into the environment causes crucial hazard. Moreover, residential wastewater treatment plants (WWTPs), which receive discharges from OMW, are exposed to frequent failure. Thus, the treatment of OMW is one of the most essential environmental problems in North Sinai governorate, and there is a necessity for partial treatment of OMW before disposal into wastewater treatment plants or sewer pipes. Several techniques have been studied by many researchers for the treatment of OMW. The adopted techniques included chemical techniques (coagulation/flocculation/precipitation) [7,8], lumped action of electrochemical, physicochemical and hydrodynamic parameters [7–9] (electrocoagulation), biological (aerobic and anaerobic) [10,11] or combination of these methods [12]. Advanced methods, including adsorption [13], oxidation [14], Ozonation [15] and filtration through membranes [16] have also been researched for OMW treatment.

Coagulation-flocculation is a simple and efficient physico-chemical method for wastewater treatment that is widely used to treat palm oil mill effluents [17]. The removal mechanism of this process includes charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate through flocculation [18]. Coagulation–flocculation has always attracted considerable attention for yielding high removal efficiency in wastewater treatment. This process can be directly applied to wastewaters to remove organics together with suspended solids, without being affected by the toxicity in the wastewater [19]. The commonly used metal coagulants fall into two general categories: those based on aluminum and those based on iron. The aluminum coagulants include aluminum sulfate, aluminum chloride, sodium aluminate, aluminum chlorohydrate, polyaluminum chloride, polyaluminum sulfate chloride, polyaluminum silicate chloride, and forms of polyaluminum chloride with organic polymers. The iron coagulants include ferric sulfate, ferrous sulfate, ferric chloride, ferric chloride sulfate, polyferric sulfate, and ferric salts with organic polymers. Other chemicals used as coagulants include hydrated lime and magnesium carbonate. The popularity of aluminum and iron coagulants arises not only from their effectiveness as coagulants but also from their ready availability and relatively low cost. The efficacy of these coagulants arises principally from their ability to form multi-charged polynuclear complexes in solution with enhanced adsorption characteristics. The nature of the complexes formed may be controlled by the pH of the system [20]. Cement kiln dust (CKD) is a fine powdery material that is collected from kiln exhaust gasses during the manufacture of Portland cement. The generation of CKD is approximately 30 million ton/y worldwide. More than 2.5 million ton/y are generated in Egypt, and they are considered hazardous materials with high cost disposal. CKD greatly reduce organic matter and other pollutants in raw textile wastewater [21].

Electrocoagulation is an emerging prospect which offers an alternative to using chemical coagulants and has been successfully trialed to treat water and waste waters. Electrocoagulation involves electrolytic oxidation of anode material which results in in-situ generation of a coagulant. In recent years, electrocoagulation has generated a great deal of interest in treating water mainly because of its versatility and ease of operation [22]. Dissociation of water by electrocoagulation generates hydroxide ions, which are recognized as one of the most reactive aqueous radical specie [Eq. (1)]. The released ions neutralize the negatively charged particles leading to coagulation, and thus suspended solids could be removed by precipitation [23]. However, at the Al cathodes, reduction takes place which results in hydrogen bubbles and hydroxyl ions [Eq. (2)]. The hydrogen bubbles float, and hence drive the flotation process [24]. Furthermore, electrolytic dissociation of water molecules could produce tiny bubbles of hydrogen and oxygen gases [Eq. (3)]. Additionally, the generated hydroxides or polyhydroxides act as coagulant/flocculant for the dispersed particles converting them into flocs of enough density to be precipitated under gravity [7].

Anode (oxidation used for coagulation):

$$\mathrm{Al} \rightarrow \mathrm{Al}^{3+} + 3e^- \tag{1}$$

Cathode (reduction used for flotation):

$$2\mathrm{H_2O} + 2e^- \rightarrow \mathrm{H_2(g)} + 2\mathrm{OH}^- \tag{2}$$

$$2\mathrm{H_2O} \rightarrow 4\mathrm{H}^+ + \mathrm{O_2(g)} + 4e^- \tag{3}$$

Aluminum electrode was found to be more effective in reducing COD from the wastewater compared with iron electrode. Because iron hydroxides are relatively inefficient coagulants compared to aluminum hydroxides coupled to a higher faradaic yield with aluminum electrodes [25]. The advantages of electrocoagulation (EC) process such as simplicity of design and operation, low electrolysis time and sludge production, cost-effective treatment system without the need for added chemicals have led it to be considered an excellent alternative process to overcome the drawbacks of conventional technologies [25,26]. EC is a good pretreatment method because biological system needs a large area for separating sludge due to their high settling time, therefore there is no area for pretreatment unit. In evaluating the performance of electrocoagulation in OMW, it is important to study first what happens during the chemical coagulation of these effluent. This is because coagulation is a much simpler process than electrocoagulation and it can give us important information for understanding the electrochemical technology.

This study targets to evaluate OMW treatment using five types of coagulants considering different factors which influence the coagulation process to decrease OMW organic load. Moreover, to investigate organic load removal using electro-coagulation (EC) process to achieve better OMW management by using Box–Behnken response surface design to optimize and study the effect of the three operative factors, including pH, current density and EC time on COD removal.

2. Material and methods

2.1. Wastewater characteristics

Olive mill wastewater (OMW) was collected from Al-Fayrouze Olive Mill factory at El-Arish, North Sinai, Egypt. The sample was collected in containers at temperature 4°C. Table 1 shows the characteristics of OMW, which were collected from factory and analyzed in the laboratory.

2.2. Analytical method

The pH of the wastewater samples was determined using a portable calibrated pH meter (pHep®, HANNA, USA). Calibration was performed using pH 4.2 and pH 7 buffers. Adjustment of pH was conducted by NaOH and H_2SO_4 (98% m/m) solutions. Turbidity was determined using turbidimeter (HI98703-01 turbidity portable meter). True color (color of the filtrated sample) was determined spectrophotometrically at 410 nm against reference Pt-Co solutions COD was measured according to the standard method [27]. Coagulation was carried out using a six paddles stirrer using Jar test (IMASS) apparatus. All the chemicals and reagents were of analytical grade. For chemical coagulation four inorganic materials were used (alum, lime, ferric chloride, grey and white cement dust) in powder form. The coagulants used in this research were purchased from Chemproha Chemiepartner B.V. All experiments were conducted at around 25±2°C.

2.3. Chemical coagulation

The study consisted of two sets of experiments; the first set was used to study the effect of different coagulants (alum, lime, ferric chloride and cement dust); to determine the most efficient coagulant for reducing COD levels. The second one was used to illustrate the factors which may affect the coagulation process; such as dose from 0.25 to 2 g/100 ml, pH ranges from 2 to 7 and slow mixing time from 5 to 30 min. The coagulation-flocculation tests were carried out using the jar test in beakers of 250 ml volume were filled with 200 ml of olive mill wastewater. The studied coagulants with different doses stirred continuously for 1 min with rapid mixing 120 rpm, followed by slow mixing for 15 min at 30 rpm, beakers were allowed to settle for 3 h. Values of pH were adjusted by adding NaOH and/or H_2SO_4.

Table 1
Characteristics of olive mill wastewater compared with the allowable limits from Law No. 93 of 1962 regarding the discharge of industrial wastewater

Parameter	Concentration	Allowable limits
pH	4.6–5.1	6–9.5
Biological oxygen demand, mg L^{-1}	5,260	600
Chemical oxygen demand, mg L^{-1}	25,800–146,000	1,100
Total suspended solids, mg L^{-1}	12,760	800
Oil and grease, mg L^{-1}	4,230	100
Total phenols, mg L^{-1}	1,540	0.05
Color, TCU	1,400	Not defined
Turbidity, NTU	1,264	Not defined

2.4. Experimental procedures

A glass beaker with 1000 ml capacity, diameter 105 mm, height 145 mm have working volume of 800 ml was used to treat OMW with aluminum sheets (80 mm × 15 mm) as an electrode, as shown in Fig. 1. The beaker contains the cathodes and anodes (by six aluminum plates) immersed in OMW with effective dimensions of length 1.5 cm × height 6.5 cm × 2 faces with an effective surface area of 18 $cm^{2,}$ made of aluminum. The electrodes were connected to a DC power supply characterized by the ranges 0–5 A for current and 0–30 V for voltage. The electrodes were vertically installed and connected in monopolar parallel connection electrolytic cell with net spacing between electrodes was 15 mm [28]. Three alternate plates were linked to the positive pole and the other three were connected to negative pole of the DC power supply, thus acting as anode and cathode, respectively.

The IR-drop (resistance value) increases as the distance between electrodes increases. Thus, energy consumption decreases with decreasing the gap between electrodes. More electrochemically generated gas bubbles bring about turbulent hydrodynamics when the distance between electrodes is low. This leads to a high mass transfer as well as to a high reaction rate between the coagulant species and pollutants. In addition, inter-electrode gap defines the time of treatment for a batch reactor for reaching a desirable EC efficiency. Monopolar electrodes require a low voltage and a higher current contrary to the bipolar electrodes that oper-

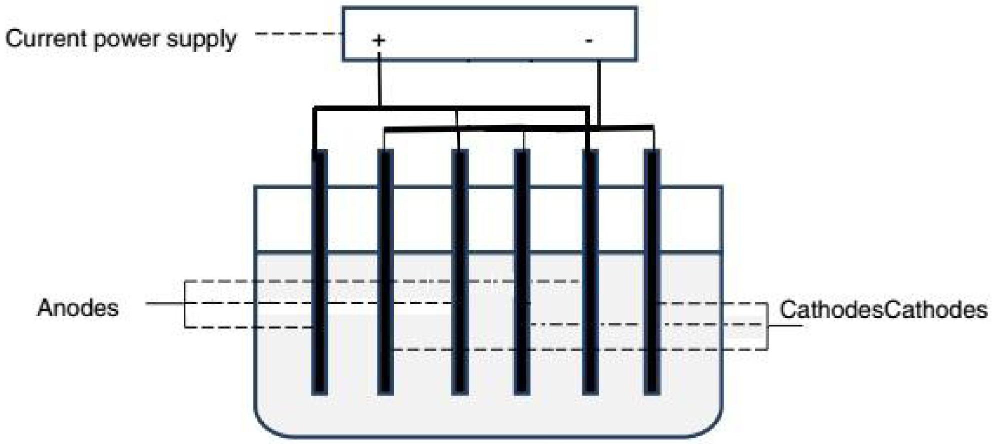

Fig. 1. Schematic diagram of the batch experimental set up treating olive mill wastewater.

ate under a high voltage and a lower current. Taking into account the ratio effectiveness-cost, monopolar electrodes may be deemed interesting because in many cases this electrodes arrangement offers a high pollutant removal with a lower energy consumption, knowing that bipolar electrode always consumes a high energy [29]. OMW was fed into the reactor in the beginning of each experiment. The Aluminum plates were cut from commercial grade sheet (95–99%) of 3 mm thickness. NaOH and H_2SO_4 were used to control the pH of the sample. A magnetic stirrer was used to stir the solution with 300 rpm stirring speed [30] to get a homogenous suspension. Treated solution was collected for an interval time from reactor and collected samples were filtered by a 0.45 µm filter before the analysis. The removal efficiency of COD for CC and EC was calculated using the following equation:

$$R\% = \frac{C_0 - C_t}{C_0} \tag{4}$$

where R is the removal efficiency of pollutant solid compound, C_0 is the initial concentration of COD and C_t is its concentration at time t.

2.5. Statistical analysis

The MINITAB 18.0 software was used for all statistical analysis. All statistical significance was considered when $p < 0.05$. Analysis of variance (ANOVA), with Tukey's test was carried out to verify the significance of differences among the means [31,32].

A multifactorial BBD was definite to found the synergetic effects of the operative factors and to adjust their conditions [33]. The BBD allows: (i) to estimate the parameters of the quadratic model; (ii) to build the sequential experimental designs; (iii) to detect the lack of fitting of the model; and (iv) to use the blocks. It is important to clarify that RSM was not used to appreciate the wastewater degradation mechanism but to determine the optimal operative conditions at certain operating specifications. Regression coefficients and their effects were analyzed using the analysis of variance (ANOVA), including the use of Pareto diagram and p-values (at probability levels lower than 0.05). Table 2 presents the operational factor at the evaluated levels. The proposed BBD, involving three independent variables (factors), required 15 experiments (including three central points), all experiments were carried out in duplicates. The average value of each measurement was used for data analysis.

The numerical data in this study using the single analysis of variance (ANOVA) and the simple correlation analysis. One-way ANOVA (at a significance level of 0.05) was applied to assess the removal efficiencies of EC.

Response surface methodology (RSM) incorporates a combination of statistical for designing experiments, generating models, and estimating the effects of variables. Recently, RSM has been utilized for demonstrating and streamlining an assortment of wastewater treatment innovations [34]. In the current study, the RSM was depend on a full-quadratic regression model Eq. (5) to fit the experimental results.

$$Y = \text{ß}_0 \sum_{1}^{3} \text{ßi}_i x_i + \sum_{1}^{3} \text{ßii} x^2{}_{ii} + \sum_{1}^{3} \sum_{1}^{3} \text{ßij} x_i x_j \tag{5}$$

Table 2
Coded and actual values of variables of the design of experiments for overall electrocoagulation

Variable	Unit	Factors	Coded factors (x)		
		x	–1	0	+1
EC time	min	X_1	10	20	30
pH		X_2	4	6.5	9
Current density	mA/cm^2	X_3	20	40	60

where ß_0, ß_i, ß_{ii}, and ßij are the regression coefficients for the intercept, linear, square, and interaction terms, respectively; and x_i and x_J are independent variables. The quality of the model and its prediction capacity were judged from the variation coefficient, R^2. From the developed mathematical model, the individual and synergetic effects of the operating factors on the response variables, using three-dimensional response surface plots, were mapped. Details of this methodology have already been reported elsewhere [35–37], where Y is the predicted response of COD removal efficiency (%); x_1 is electrolysis time 10–30 min; x_2 is pH 4–9; current density 20–60 mA/cm^2, respectively.

3. Results and discussion

3.1. Coagulants performance and selection

In the first set, four types of coagulants were studied (alum, lime, ferric chloride, white and grey cement dust) to select the best coagulant. The treatment performance was determined mainly according to chemical oxygen demand (COD) and turbidity removal ratio from olive mill wastewater. Experiments were performed at initial pH (original pH) of raw OMW at room temperature. All coagulants at concentration 0.5, 1, 1.5, 2 g/100 ml, respectively. The initial rapid mixing speed was at 120 rpm for 60 s, the initial slow mixing speed was at 30 rpm for 15 min and settling time was 3 h. Coagulation and flocculation tests were achieved to examine the effects of alum dosage on COD and turbidity removals from OMW. As shown in Figs. 2, 3, COD removal was 47% at 2.0 g/100 ml of alum with r 0.934, p 0.66, and turbidity removal was 64% at concentration 1.5 g/100 ml with r 0.765, p 0.235. While, maximum color R.R with r 0.921, p 0.079 was 44% at 2g/100 ml alum dose. Lime tests for OMW treatment were performed to determine the lime dosage effect on COD, color and turbidity removals. Experiments were conducted at the same conditions for alum. As shown in Fig. 4, COD removal ratio reached 35% at concentration 1.5 g/100 ml of lime with r 0.826, p 0.174 and turbidity reached 13% at 1 g/100 ml with r 0.386, p 0.614. This results were in agreement with Chiavola et al. [38] who reported that using 2.0 g/100 ml of lime was the optimal reagent in OMW treatment to remove around 64% for TS and about 51% of COD. In addition to, Aktas et al. [39] reported that after addition 1.0–2.5 g/100 ml of lime, COD reduction values in samples of the wastewater could be by 65.7% and 27% TSS. When lime dose increased from 2.5 to 4.0 g/100 ml, the reduction was 41.5% for COD and 29.3% for total solids. No color removal was recorded with lime. It must be noted that although lime had a good

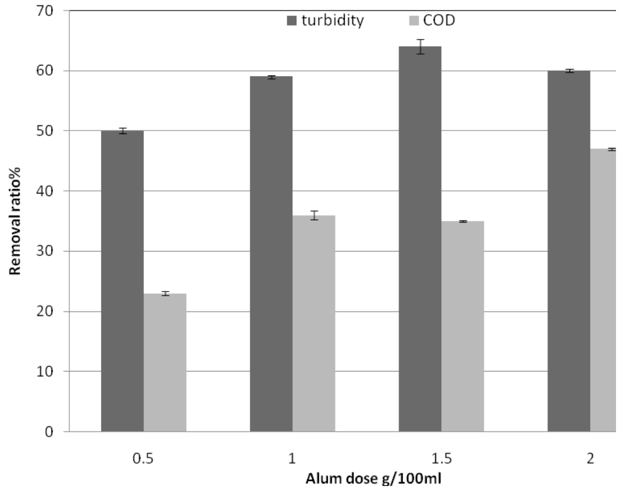

Fig. 2. The effect of alum dose on COD and turbidity removal ratio.

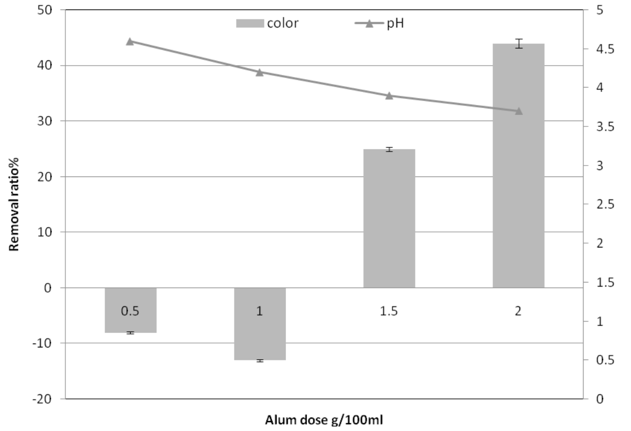

Fig. 3. The effect of alum dose on pH and color removal ratio.

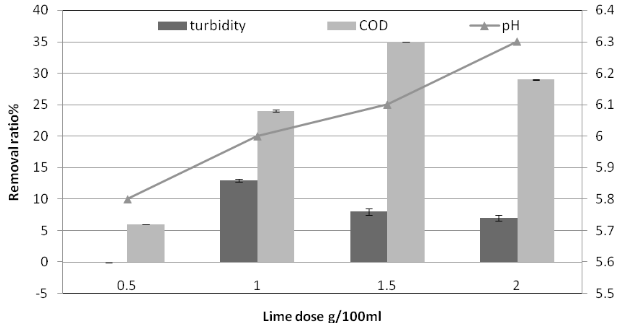

Fig. 4. The effect of lime dose on COD and turbidity removal ratio with pH.

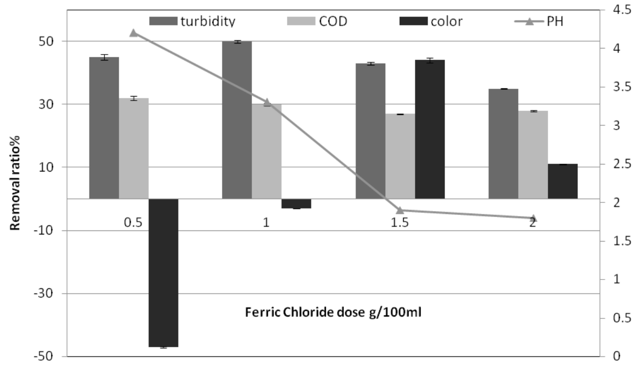

Fig. 5. The effect of ferric chloride dose on COD, turbidity and color removal ratio.

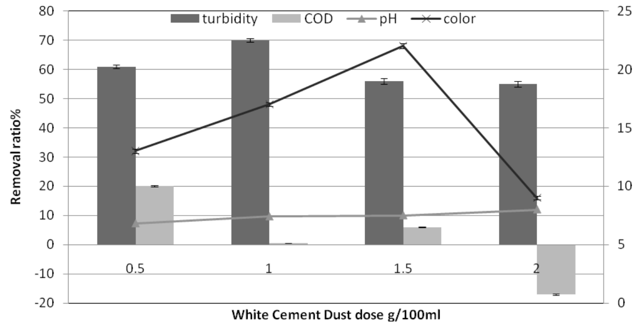

Fig. 6. The effect of white cement dust dose on COD, turbidity and color removal ratio with pH.

performance in reducing pollutants such as oil, COD, and odors, it has some disadvantages. The major disadvantage is the production of big amount of sludge, leading to disposal problems because of their high pollution load [40]. As shown in Fig. 5, the turbidity removal ratio increased from 45% to 50% by using 0.5 and 1 g/100 ml ferric chloride, respectively with r - 0.766, p 0.234. The best result of removing COD was 31% by using 0.5 g/100 ml of ferric chloride r - 0.873, p 0.127. Similar studies on OMW found that, the increasing of ferric chloride dose from 0.1 to 0.3 g/100 ml enhances the performance of coagulation especially in case of turbidity and COD removal, which reached 99.2% and 91.2%, respectively. While further addition of coagulant dose between 0.4 and 0.6 g/100 mL does not markedly influence the organic pollutants removals [41]. Chiavola et al. [38] found that using $FeCl_3$ in OMW treatment at a 0.3 g/100 ml dosage led to a COD removal 19 % (average value). Fig. 6 shows the results of using different doses of white cement dust for removing COD (r - 0.89, p 0.11) and turbidity (r - 0.603, p 0.397). The results showed that; by using 1 g/100 ml cement dust, the removal ratio was 70% for turbidity. On the other hand, the results showed an adverse effect of cement dust on removing COD. Although cement dust achieved better performance in the removal of turbidity, the pollutants in the OMW increased, which happened in the COD levels. Cement dust is one of the sources of environmental pollution [42,43], it contains high amounts of heavy metals and hazardous organic and inorganic compounds (F, As, Cd, Ca, Mg, Hg, Al, Be, Co, Cr, Cu, Ni, Pb, Zn, CaO, K_2O and Na_2O) [44–46] as it has a bad effect on the soil, plants and human healthy [47–49]. This could explained the poor performance in removing COD and also might explain why few researches used cement dust in wastewater treatment [41]. After studying the effect of four coagulants (alum, lime, ferric chloride and cement dust) on the removal ratio of COD and turbidity from olive mill wastewater, a comparison was approved to attain the best coagulant which decreases the COD and turbidity levels. Regarding to the obtained results of the four coagulants, it was found that; Ferric chloride also had a good result in COD and turbidity removal, which reached 32% and 50% at concentration 0.5 and 1 g/100 ml, respectively. But it had insignificant effect on the color with r 0.756, p 0.244 as shown in Fig. 5, as the color of OMW turned from brown to dark black. OMW has a very high color concentration. This dark-colored wastewater includes poly-aromatic compounds, which are difficult to remove. The removal of color from OMW was experimentally investigated by using CC process. The color removal yield was examined as the result of using different coagulant doses, for 5 coagulants, but all these changes have inconsiderable effect on the color removal percentage. Iron hydroxides (Fe^{2+} and Fe^{3+} ions, correspondingly) dissolve and combine with hydroxyl ions in the water. They form metal hydroxyls, which are partly soluble in the water under definite pH values. This caused the dark black color [50].

Alum was better than ferric chloride in the treatment although ferric chloride has less human health risks than the aluminum-based coagulants in an overdose condition [51,52]. White and grey cement dust have a great result on turbidity removal 70, 45% at concentration 1, 2 g/100 ml, respectively. But, white cement dust had very bad effect on COD removal ratio with increase in cement dose. While, increase in grey cement dose did not make significant change in COD R.R with r - 0.730, p 0.27, maximum COD R.R was 29% at 0.5 g/100 ml as shown in Fig. 7. No removal in color recorded with increase in cement dose, while, white cement dust recorded 22% color R.R at 1.5 g/100 ml, with r 0.998, p 0.041 from 0.5 to 1.5 g/100 ml. Lime ($Ca(OH)_2$) also has a significant effect on OMW treatment special in removing COD but alum and ferric chloride were better than it. From above results, alum was the superior coagulant and the subsequent experiments were carried out on alum. On the other hand, there was a study conducted by Ref. [27] and disagreed with the present study. Yazdanbakhsh et al. favored ferric chloride due to its high efficiency compared with the other coagulants such as alum, where the removal efficiency of COD and turbidity for alum were 88% and 99% and for ferric chloride 91.2% and 99.2%, respectively. Additionally, it was noted that the cost of $FeCl_3$ in market is 5 times less than the costs of alum. Furthermore, results of settleable solids test showed that $FeCl_3$ had the lowest value (516 ml/l) compared to alum (583 ml/l), which justifies selection of $FeCl_3$ as the superior coagulant. Running Tukey test for studied coagulants was done to confirm the proper coagulant selection at doses 0.5, 1, 1.5, 2 ppm. The results displayed in Tables 3 and 4, there was weighty difference between alum and cement dust. Alum has the biggest mean COD R.R and the second order in mean turbidity R.R after white cement dust.

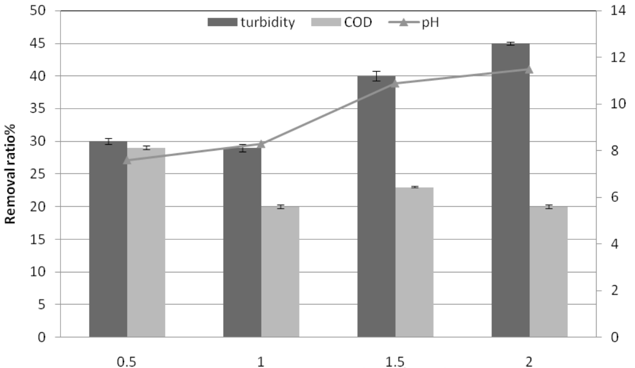

Fig. 7. The effect of grey cement dust dose on COD and turbidity removal ratio with pH.

From Tukey test it was found that COD removal ratio at alum > ferric chloride > lime > cement dust.

The difference in COD R.R, turbidity R.R and color R.R in CC among the five coagulants, may be attributed to different factors such as PH, coagulant dose, the characteristics of floc and alkalinity. The proper dosage must be determined through actual use. Destabilization begins after addition of a dose of coagulant that exceeds the operational solubility limit of aluminum (or the other tested coagulants) hydroxide. In the over-dosing region of each coagulant type, no increase in the pollutants removal ratio was observed due to charge reversal. It is important to mention that the appearance of H^+ necessarily causes a drop in pH and alkalinity consumption. The rate of the hydrolysis reaction and the nature of formed species depend strongly on the concentration of aluminum salts in solution and their pH. The hydrolysis products contain cationic monomers, complex cationic polymers, microcrystals, and a precipitate of the hydroxide of the metal ion. The characteristics of floc (size, density, structure and strength) are very important which affect solid/liquid separation and then the efficiency of coagulation. Flocs must resist the stresses if they are to prevent being broken into smaller particles which will generally settle more slowly than larger particles of similar density [53–55].

Table 3
Grouping information using the Tukey method for turbidity R.R and 95% confidence

Factor	N	Mean	Grouping		
Turbidity R.R White cement dust	4	60.50	A		
Turbidity R.R alum	4	58.25	A		
Turbidity R.R Ferric chloride	4	43.25		B	
Turbidity R.R grey cement dust	4	36.00		B	
Turbidity R.R lime	4	7.00			C

Table 4
Grouping information using the Tukey method for COD R.R and 95% confidence

Factor	N	Mean	Grouping	
COD R.R alum	4	35.25	A	
COD R.R Ferric chloride	4	29.25	A	
COD R.R lime	4	23.50	A	B
COD R.R grey cement dust	4	23.00	A	B
COD R.R White cement dust	4	2.38		B

3.2. Factors affecting coagulation with alum

3.2.1. Dosage effect

Fig. 8 shows the effect of alum doses on COD removal with r 0.027, p 0.959 and turbidity with r -0.836, p 0.038. COD and turbidity removal ratio were 46% and 56% at 0.5 g/100 ml of alum, respectively. This concentration was suitable to increase the floc growth rate and strength of the linkage between the primary particles in the floc by increasing the $Al(OH)_3$ surface coverage, making it more resistance to breakage [56]. A similar study by [38] found that using alum in OMW treatment achieved COD removal average 19% at a 0.4 g/100 ml dosage. On the other hand, Yazdanbakhsh et al. [41] achieved great results in removing COD and turbidity 88% and 99%,respectively by using 0.2 g/100 ml of alum. This difference in results between the current study and the study by [27] might be due to different operating conditions such as pH, where Yazdanbakhsh et al. adjusted pH of the OMW samples to 10.

3.2.2. pH effect

pH is a key factor for proper coagulation performance. For studying the effect of PH, the optimal dose of the coagulant (0.5 g/100 ml of alum) was first added to the wastewater sample. The pH was varied from 2 to 7 through the addition of sulfuric acid and/or sodium hydroxide. As shown in Fig. 9, increasing the pH achieved gradual increase in COD removal ratio with r 0.788, p 0.063 and turbidity with r 0.968, p 0.002. Turbidity removal ratio increased from 62.7% to 82.5% when pH increased from 5 to 6. The corresponding COD removal recorded a good result 40% at pH 6. AWWA [57] reported that, the best coagulation performance of alum is generally seen at pH values that are close to the pH of minimum solubility of the coagulant. This limits dissolved Al residuals, also strengthening the presence of floc particles. Also, they reported that the minimum solubility pH of alum is 6 at 20°C. This could explain the above results, from pH 6 up to 7, the strong coagulating power of the trivalent aluminum ion acting on negatively charged colloidal, forming flocs. Additionally, when the pH values decreased from 5 to 2, coagulant species dissolved in water causing high turbidity. Similar results were reported by Yazdanbakhsh et al. [41], who showed that when the pH increased, the treatment efficiency increased, where, at pH 10 and 0.2 g/100 ml alum dose, the COD, phenol, TSS and turbidity removals were at the highest levels and the removal efficiencies were 88, 88.7, 98.3 and 99%, respectively. Chiavola et al. [38] achieved COD removal average 19% at a 0.4 g/100 ml dosage of alum and pH was adjusted to 8. These results also were in agreement with Lafi et al. [58] who found that, at pH 6, the alum provided 14% COD removal ratio, while, at pH 9, the COD removal ratio was 54%.

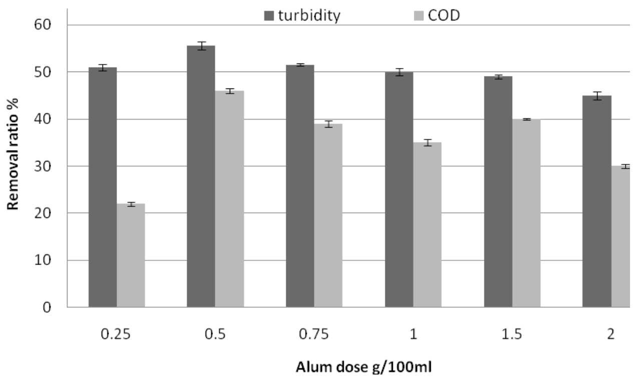

Fig. 8. The effect of alum dose on COD and turbidity removal ratio.

3.2.3. Flocculation time

After determining the suitable coagulant, the suitable dose and the ideal pH, it was time to study the effect of slow mixing time on olive mill wastewater treatment. Fig. 10 shows the effect of application different times of slow mixing on COD with r 0.44, p 0.383 and turbidity with r -0.288, p 0.579. As shown, the suitable time for COD and turbidity reduction ranged from 10 min to 25 min. This time seems to be suitable to allow alum species interacting with colloids in water and promote orthokinetic collisions of particles and hence floc growth. A similar study by [24] reported 19% enhancement in the removal ratio of COD with slow mixing time of 30 min. Another study by [27] used 40 min for the slow mixing time and achieved 88 and 99% for COD and turbidity, respectively. This difference in the results may

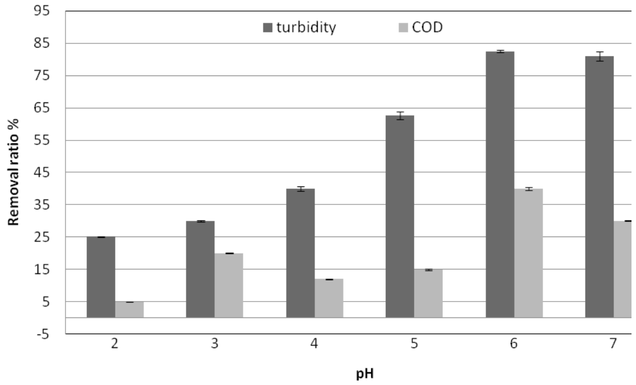

Fig. 9. The effect of pH on COD and turbidity removal ratio.

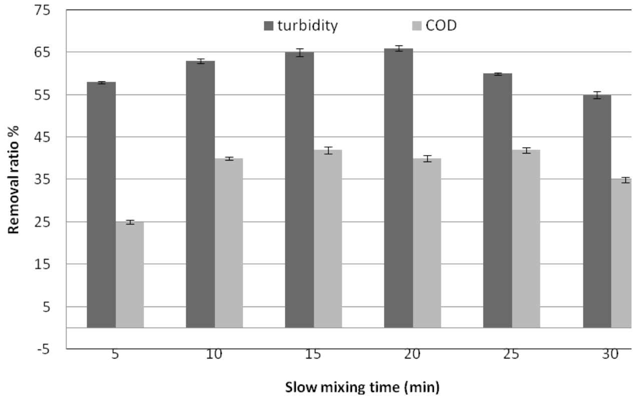

Fig. 10. The effect of flocculation time on COD and turbidity removal ratio.

be due to changing water properties from place to place due to different methods of olive cultivation and olive oil extraction process.

3.3. Electrocoagulation

3.3.1. Analysis of variances

From the response surface regression analysis, the Box-Behnken design suggested that the quadratic model was fit for the three responses. The regression analysis is used to solve multivariable equations simultaneously [59]. The quadratic equations used to depict the removal of parameter COD (*y*) is depicted in Eq. (6). The coefficient of determination between measured data and simulated results (r^2), adjusted r^2, and predicted r^2 were 0.986, 0.9596 and 0.7689 for COD R.R. The high r^2-value suggested the reliability of the proposed model. This analysis involved the reduction of model to ensure the models were fit for the responses. As listed in Table 5, negative linear effects of the independent variables “current density” and “pH” on COD removal ratio were observed to be significant ($p < 0.05$). Additionally, a significant positive effect ($p < 0.05$) was noticed for the quadratic term of “pH”. However, insignificant positive effects ($p > 0.05$) were determined for the linear and quadratic terms of “electrolysis time”, as well as quadratic terms of “current density”, for the two-way interaction terms “pH × electrolysis time”. However, significant positive effects ($p < 0.05$) were determined for the two-way terms of “electrolysis time× current density”, and also significant negative effects for the two-way interaction terms of “pH × current density”. For simplicity, the insignificant factors were excluded, and a new regression model was obtained in Eq. (7):

$$\text{COD R.R} = 83.8 - 1.003\ \text{Time} - 11.00\ \text{pH} - 0.173\ \text{Current Density} + 0.0035\ \text{Time*Time} + 0.683\ \text{pH*pH} + 0.00536\ \text{Current Density*Current Density} + 0.0016\ \text{Time*pH} + 0.02161\ \text{Time*Current Density} - 0.0867\ \text{pH*Current Density} \tag{6}$$

$$\text{COD R.R} = 73.8 - 0.854\ \text{Time} - 10.60\ \text{pH} + 0.256\ \text{Current Density} + 0.654\ \text{pH*pH} + 0.02161\ \text{Time*Current Density} - 0.0867\ \text{pH*Current Density} \tag{7}$$

Statistical testing of the model was done with the Fisher’s statistical test for analysis of variance (ANOVA), which was piloted to determine the suitability of the second-order polynomial equation with the experimental results. The results of the ANOVA for COD, removal is shown in Table 6. The ANOVA result for the COD removal showed a high F-value of 54.94. The huge values of F show that most of the variation in the response can be elucidated by the regression equation, and the terms in the model have a significant effect on the response. R^2 values of 0.976, which expresses a high correlation between the observed and the predicted values. A low P value 0.05 indicates that the model is statistically significant, and that the model terms are significant at high probability level. In addition, this implies that 97.63% of the variations for percent COD removal is explained by the independent variables, and this also means that the model does not explain only about 2.37% of variation. Predicted R^2 is a measure of how good the model predicts a response value. The adjusted R^2 and predicted R^2 should be within 0.20 of each other to be in reasonable agreement. If they are not, there may be a problem with either the data or the model. In our case, the predicted R^2 of 0.959 is in reasonable agreement with

Table 5
ANOVA results of the predicted response surface quadratic model

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	1823.85	202.65	37.90	0.000
Linear	3	1594.48	531.49	99.41	0.000
Time	1	0.09	0.09	0.02	0.902
pH	1	1544.29	1544.29	288.85	0.000
Current density	1	50.10	50.10	9.37	0.028
Square	3	79.55	26.52	4.96	0.059
Time*Time	1	0.45	0.45	0.08	0.784
pH*pH	1	67.24	67.24	12.58	0.016
Current density*Current density	1	16.99	16.99	3.18	0.135
2-Way interaction	3	149.82	49.94	9.34	0.017
Time*pH	1	0.01	0.01	0.00	0.974
Time*Current density	1	74.74	74.74	13.98	0.013
pH*Current density	1	75.08	75.08	14.04	0.013
Error	5	26.73	5.35		
Lack-of-Fit	3	26.73	8.91	*	*
Pure error	2	0.00	0.00		
Total	14	1850.58			
Model summary		R-sq	R-sq(adj)	R-sq(pred)	R-sq
98.56%		95.96%	76.89%	98.56%	

Table 6
ANOVA results of the predicted response surface quadratic model

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	6	1806.73	301.12	54.94	0.000
Linear	3	1594.48	531.49	96.97	0.000
Time	1	0.09	0.09	0.02	0.901
pH	1	1544.29	1544.29	281.74	0.000
Current density	1	50.10	50.10	9.14	0.016
Square	1	62.44	62.44	11.39	0.010
pH*pH	1	62.44	62.44	11.39	0.010
2-Way interaction	2	149.82	74.91	13.67	0.003
Time*Current density	1	74.74	74.74	13.63	0.006
pH*Current density	1	75.08	75.08	13.70	0.006
Error	8	43.85	5.48		
Lack-of-Fit	6	43.85	7.31	*	*
Pure error	2	0.00	0.00		
Total	14	1850.58			
Model summary		S	R-sq	R-sq(adj)	R-sq(pred)
2.34121		97.63%	95.85%	88.14%	

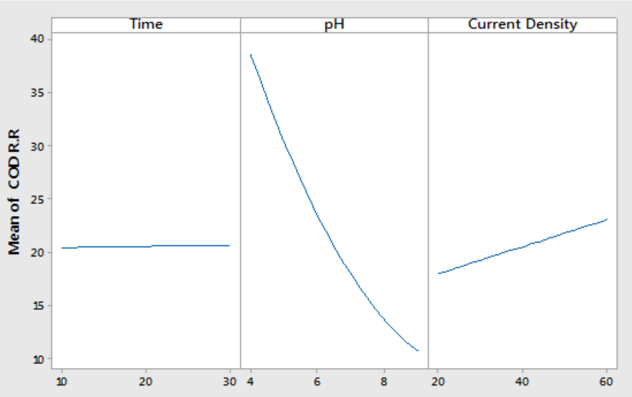

Fig. 11. The main effects plot of COD removal ratio.

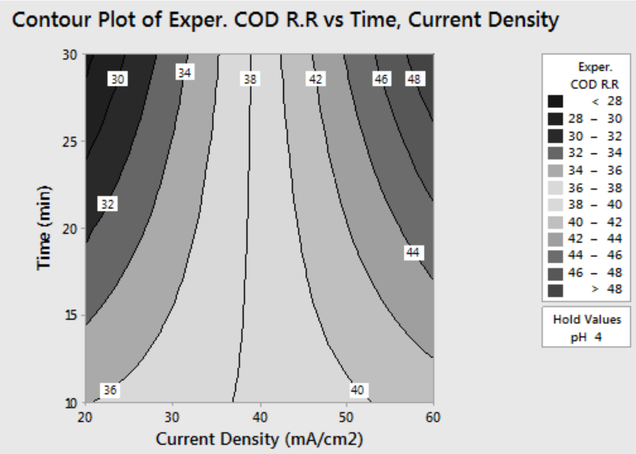

Fig. 12. The contour plot of COD removal ratio at pH = 4.

the adjusted R^2 of 0.881. The COD removal (P = 0.000) was found statistically more significant. The ANOVA revealed that the equation adequately characterized the relationship between the response (the percentage COD removal) and the significant variables. The models have high R^2 value, significant F-value, an insignificant lack-of-fit P-value and low standard deviation and coefficient of variance.

The main effects of each parameter on COD removal ratio are shown in Fig. 12. From the graphs discussion and the coefficients of Eq. (7), we can conclude that pH is the most important variable on COD R.R since its coefficient is the largest in absolute value (11). The negative sign of this coefficient means that the intensification of this parameter decreases COD R.R. However, the effects of current density (CD) is positive since an increase in COD R.R is observed when these factors change from low to high. With an increase in CD, the quantity of dissolved aluminum in solution increases, therefore the amount of aluminum hydroxide $Al(OH)_3$ formed is important, which facilitates an increase in the percentage removal of COD. The electrolysis time is the least significant variable since its coefficient is the lowest in absolute value (0.183). The interaction term in our model causes the curvature of the contour lines in the graph. Straight contour lines mean no interaction between factors. The parallel lines in this figure indicate that there are no significant interactions between studied time and pH. However, the most vital interaction is observed between pH and CD. This indicates that decreasing pH from 9 to 4 enhances COD R.R at CD (60 mA/cm^2). This interaction is significant since the pH of the solution has significant effect in the range of the experimental values of the present study. For a better understanding of the relationship between factors and a response, a cube plot was produced as shown in Fig. 18. The cube plot shows that increasing electrolysis time from 10 to 30 did not have a significant effect on COD R.R (from 35.88% to 27.45% only 8.43% reduction) at low current density (20 mA/cm^2), while at higher CD (60 mA/

cm^2), changes in electrolysis time do not have a greater effect (an increase of only 8.86%). Increasing electrolysis time can cause secondary reactions and overdosing can reverse the charge of the colloids and redisperse them leading thereby to a decrease of the coagulant efficiency and to a reduction of the electrode lifetime [29].

Also, another study by [60] emphasized that there with two possible reasons. First, the excessive addition of counter ions from coagulant (iron) may result in restabilization by a charge reversal; the net charge on the particles may be reversed by the adsorption of an excess of counter ions. Second, the particles restabilization, if there was an insufficient number of a colloidal particle available for bridging or due to surface saturation or sterical stabilization [60].

On the anode, aluminum dissolution and oxygen evolution can compete. On the cathode, hydrogen evolution is the main expected reaction. On the other hand, high current densities lead to less efficient processes. This fact can be explained in terms of the competition between aluminum dissolution and oxygen evolution. At low values of current density, only the aluminum dissolution exists, while at high values, both processes compete and, as a consequence, the aluminum generation efficiency decreases. In the anode, the water oxidation process (oxygen evolution) generates a high concentration of protons and, thus, a lower pH must be obtained. In the cathode, the water reduction process results in the formation of hydroxyl ions and a higher pH must appear in this zone [61]. In addition, increasing pH from 4 to 9, at higher electrolysis time (30 min), diminishes the percentage removal from 27.45% to 8.32% at lower CD (20 mA/cm^2). A significant decrease in COD R.R from 49.76% to 13.31% was observed at higher CD (60 mA/cm^2) with pH increase from 4 to 9. This means that both the effect of variation of pH and current density have the highest effect on COD R.R. The highest percentage removal in this study was 49.76%, obtained at pH (4), current density60 mA/cm^2.

3.3.2. Process variables effect on responses

Significant interaction factors deduced in the new simplified fitted model were chosen for the axes of the response surface plots. So that, from the developed regression models, response surface contour plots were plotted to assess the effects of the independent variables on the responses.

3.3.2.1. Significant linear terms - pH effect

pH is a central parameter [62] which affects the performance of the treatment efficiency. To investigate the effect of pH on responses, electrocoagulation treatment was achieved at various pH ranges from 4 to 9. Figs. 12 and 13 illustrate the contour lines and the response surface at pH 4. From the results, it was found that COD R.R was increased with the decrease in pH from 9 to 4. It is evident that there is a noticeable interaction between the initial pH and the current density on COD removal. Whereas, pH shows negligible effect on electrolysis time.

COD R.R extremely diverse from max. to min. value according to pH change. In acidic condition, at pH 4 relying on the current density and EC time, the maximum values of COD R.R was obtained. This study agree with the previous studies [63,64]. In acidic condition, Al^{3+} is altered into soluble monomeric kinds such as $Al(OH)_2^+$ and $Al(OH)^{2+}$. These monomeric cations can alter to hydroxy-polymeric kinds such as $Al_2(OH)_2^{4+}$ and $Al_6(OH)_{15}^{3+}$ [65]. Great efficiency achieved with pH value of 4, results from efficient sedimentation of pollutant molecules, according to the mechanism outlined by Eqs. (8) and (9). In addition, the superior coagulant is $Al(OH)_3$ in this pH [66]. Thus, maximum COD R.R was 47% at pH of 4. The influence of pH on the solubility of $Al(OH)_3$ was clearly identified in the solubility diagram of aluminum hydroxide. Additionally, in acidic conditions, oxidation of aluminum plates with simultaneous reduction of water result in formation of Al^{3+}[67]. Hanafi et al. [68] suggested that the optimum pH for treatment of OMW wastewater by electrocoagulation is below 6.

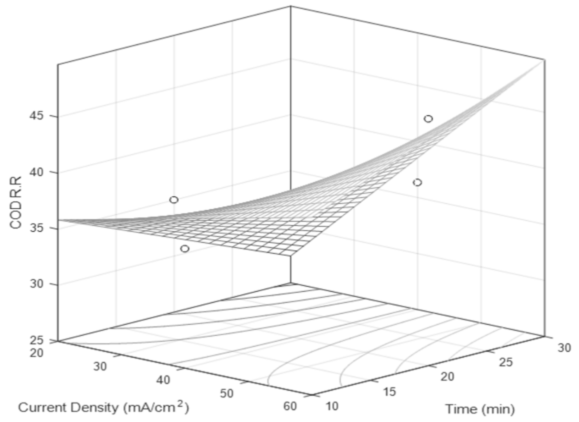

Fig. 13. Response surface plot shows the effect of current density and time on COD removal efficiency at pH = 4.

$$\text{COD} + \text{monomeric Al} \rightarrow [\text{COD-monomeric Al}]\ (s)\ (\text{pH: 4–5}) \quad (8)$$

$$\text{COD} + \text{polymeric Al} \rightarrow [\text{COD-polymeric Al}]\ (s)\ (\text{pH: 5–6}) \quad (9)$$

3.3.2.2. Significant linear terms - current density effect

Current density is a significant operating parameter in EC treatment process, which greatly affects the efficiency of treatment process and the economy of the process. The study was carried out at different current densities (20–60 mA cm^{-2}) and the contour lines and RSM at current density = 60 mA cm^{-2} are shown in Figs. 14 and 15. As shown in the figures, COD removal increased with increasing current density at 60 mA cm^{-2}. Because of the rise in the current density yields metal hydroxides, that has high affinity towards dispersed and colloidal particles in the wastewater and results in coagulation, which effectively removes COD. Thereafter, there is almost constant removal efficiencies beyond current density of 60 mA cm^{-2}. This could be due to the very high current values that may negatively affect the EC efficiency. For instance, secondary reactions may occur chiefly, and overdosing can reverse the charge of the colloids and redisperse them leading thereby to a decrease of the coagulant efficiency and to a reduction of the electrode lifetime [29]. Anyway, current density exhibits strong effect on electrical energy consumption that is to say EC linearly rises with increasing current density throughout the experiment. Current density determines

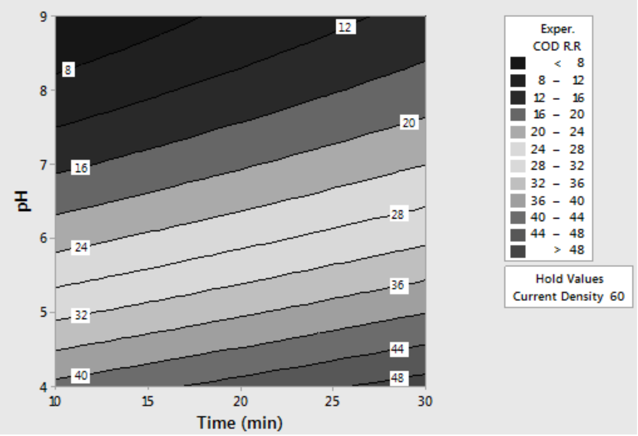

Fig. 14. The contour plot of COD removal ratio at CD = 60 mA/cm².

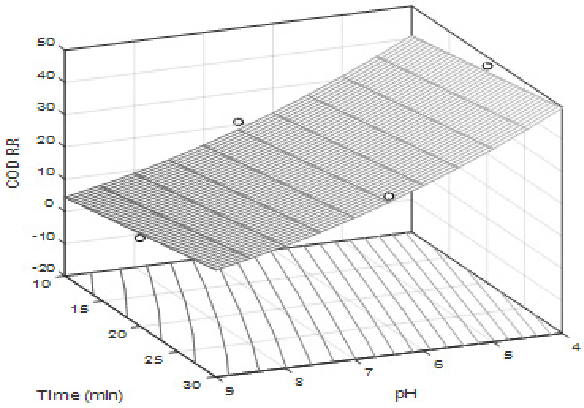

Fig. 15. Response surface plot shows the effect of time and pH on COD removal efficiency at current density = 60 mA/cm².

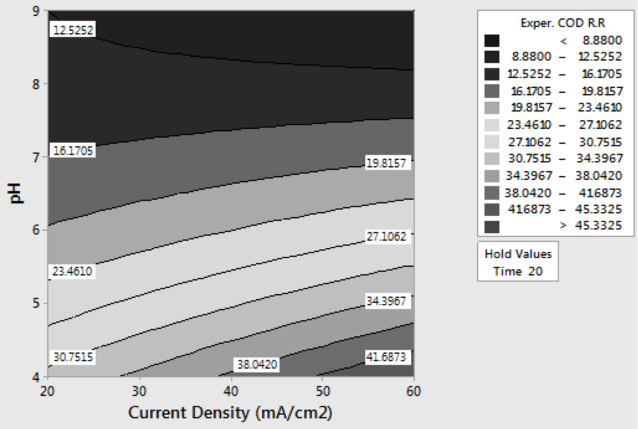

Fig. 16. The contour plot of COD removal ratio at time = 20 min.

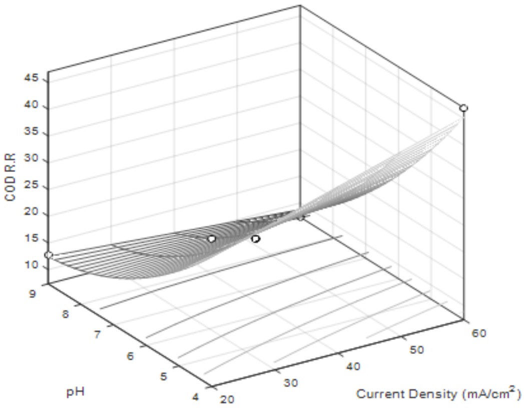

Fig. 17. Response surface plot shows the effect of current density and pH on COD removal efficiency at time = 20 min.

the dissolution rate of metal ions and size of created bubble directly influencing the growth of flocs, which controls the rate of COD removal [69]. By increasing CD, degradation of anodized aluminum plates and organic pollutants removal improved [70]. The concentration of metal in the EC cell was attained from Faraday's law [Eq. (10)] [71]. In this study, the effect of CD to the EC cell was tested by varying the current density level from 20 to 60 mA/cm² at the studied pH and EC time. When the current density increases from 20 to 60 mA/cm², COD R.R increases.

3.3.2.3. Significant two-way interaction terms - current density effect × pH

There is a deep interaction between the initial pH and the current density on COD R.R (p-value $0.006 < 0.05$). In Figs. 16 and 17, at a low limit of current density, COD R.R was reduced by increasing the pH, the same trend at a high limit of current density. In acidic pH and a higher limit of current density, the COD removal efficiency was improved. At high constant current density, the coagulant dosage will be produced due to Faraday's law [Eq. (10)] and in a pH of 4, COD R.R of the solubility of $Al(OH)_3$ is in its minimum value and the adsorption process [Eqs. (11), (12)] is predominant [72,73]. Consequently, efficiency increased, but at a lower limit of current density and acidic initial pH, the bubble production will be also augmented, results in disturbing flocs, which diminished the removal ratio. Faraday's low is expressed as [71]:

$$C = \frac{It_{EC}M}{ZFW} \tag{10}$$

Adsorption process:

$$\text{COD pollutants} + Al(OH)_3 \rightarrow \text{sludge } (pH > 6.5) \tag{11}$$

$$\text{COD pollutants-polymeric Al} + Al(OH)_3 \rightarrow \text{sludge} \tag{12}$$

$$Al(OH)_3 + OH^- \rightarrow Al(OH)^-_4 \, (pH > 9) \tag{13}$$

where C is AL concentrationin the EC cell, M the molecular weight of anode (Al), Z the chemical equivalence, F the Faraday's constant and W is the electrolytic cell volume. In alkaline pH and a lower limit of current density, by increasing pH, COD R.R was decreased. In alkaline pH, the main reaction is given in Eq. (13).

At constant current density of 60 mA/cm^2, the amount of Al^{3+} and $Al(OH)_3$ is released. Consequently, the amount of $Al(OH)_3$ overcomes the amount of OH^-, then more sedimentation will be created, resulting in more removal efficiency. Generally, in a pH range of 6.5–9, COD R.R is not significantly changed at current densities 20, 40 mA/cm^2. The reason is that the solubility of $Al(OH)_3$ is in its minimum value at this pH range, and the adsorption process [Eqs. (11), (12)] is predominant [72,73]. However, at pH from 6.5 to 4 and a higher limit of current density 60 mA/cm^2, decreasing pH, COD R.R is significantly changed.

3.3.2.4. Significant two-way interaction terms - current density effect × electrolysis time

EC time affects the efficiency of EC process. Electrolysis time determined the creation of Al^{3+} ions from aluminum electrodes. Figs. 12 and13 show the influence of EC time on COD R.R of OMW when it changed from 10 to 30 min at constant pH 4 and constant current density 60 mA/cm^2. When the EC time increased from 10 min to 30 min, the amount of COD decreased, but COD R.R became constant with increase in time from 10 to 20 min. This is due to changes in the amounts of coagulant species generated during the EC at different times. However, these changes will have narrow effect, unlike pH. Fig. 16 shows gradual increase in COD removal efficiency from 32% to 44% at 20 min at current density 20 and 60 mA/cm^2, respectively. At a higher time range from 20 to 30 min, the maximum of more than 44% COD R.R is detected. The results of this study agree well with other studies, indicating that the optimum amount of COD removal occurred at around 20 min [74]Considering the treatment cost and efficiency, the optimal reaction time was 20–30 min normally in literatures [75–77]. This is due to the fact that, as the time of electrolysis increased, the mixing and reaction time also increased [78]. This is also attributed to the fact as the time increased, more hydrogen bubbles were generated at the cathode; these bubbles improved the degree of mixing and enhanced the flotation ability of the cell with a consequential improved in the percentage removal [79]. pH values in the range of 4–9 and at electrolysis time from 10 to 30 min is insignificant and very less change in COD removals as deduced from model statistics.

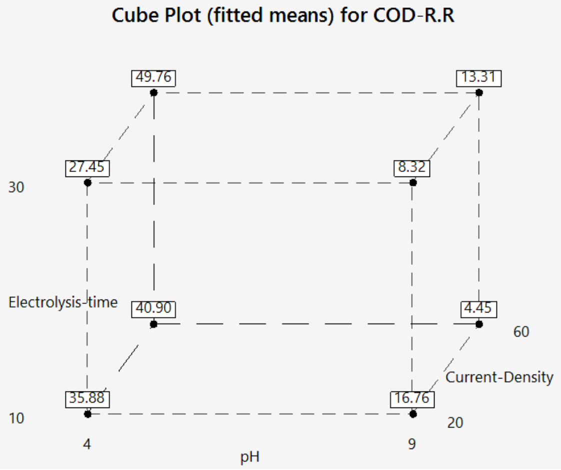

Fig. 18. Cube plot for COD removal efficiency.

3.4. Optimization of operating conditions

The optimization plot for estimation of the industrial removal efficiency COD removal over independent variables current density and electrolysis time is shown in Fig. 19. These graphical representations are derived from the models of Eq. (7). Based on the overlay plot, the optimum conditions for current density and electrolysis time are, respectively, 60 mA cm^{-2} and 20 min at pH = 4 for a large percentage of COD removal of more than 49.76%.

3.5. Comparison with phenomenological conclusions

Wastewater treatment by electrocoagulation is a very intricate process and few models are reachable for the elucidation. With aluminum electrodes, an initial pH of 4 have already been found to be suitable since the pH increased during the treatment up to 9, and thus it is not necessary to adjust it initially. Finally, treatability study is important step before deciding the type of treatment process. As illustrated in Table 7, authors as [9,30,80–113] reported studies on electrocoagulation for COD removal from water. Due to wastewater characteristics in addition to initial COD concentration. Chemical oxygen demand (COD) is a major parameter, as it indicates the overall reduction in OMW pol-

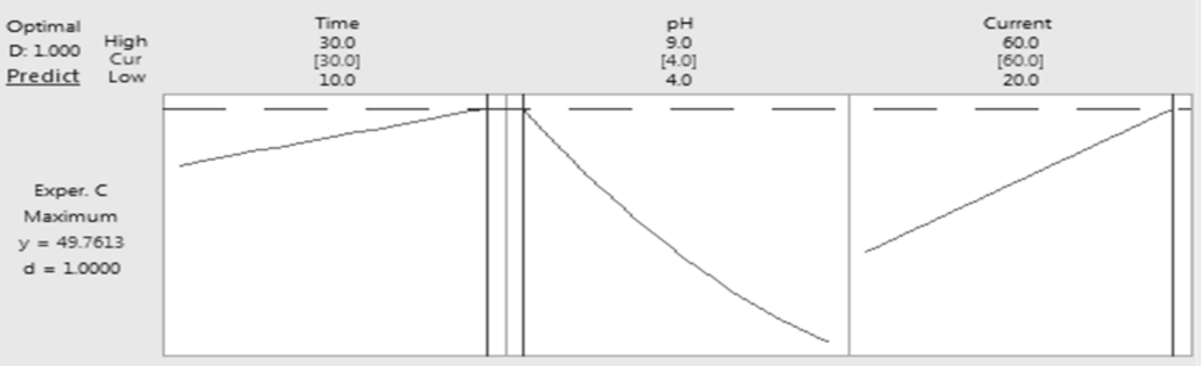

Fig. 19. Optimization plot of COD removal efficiency.

Table 7
Summary of electrocoagulation treatment performance of various oily wastewater treatment systems, compared to the present study

Oily water source	Oil conc. mg/l	Electrode	Current density (A/m^2)	Reaction time (min), pH	Removal efficiency (%)	Energy and cost analysis (kWh/m^3)	References
Biodiesel wastewater	6,412	Iron	100	25–7	82	0.43 kWh/g oil and grease	[80]
Slaughterhouse wastewater	720–950	Iron	13.63	60–(6–9.5)	99	0.00015 kWh/m^3	[81]
Oilfield wastewater	50–100	Aluminum	18.5	40–4.72	>90	0.17–2.25	[82]
Slaughterhouse wastewater	1500–1800	Iron	100–150	25–3	98	0.015 \$/kg COD removed	[83]
Slaughterhouse wastewater	143.1	Aluminum	10	20–3	85 (COD)	2.14 kWh/m^3	[84]
Metal processing wastewater	60,282–116,128(COD)	Aluminum	100–200	60–7	60–90	/	[85]
Dairy wastewater	7560 (COD)	Aluminum	50	2–6.6	80 (COD)	0.03 kWh/kg of COD	[9]
Biodiesel wastewater	6,020	Aluminum, graphite	124.8	23.54–6.06	97.77	5.57 kWh/m^3	[86]
Restaurant wastewater	120–1500	Aluminum	30–80	15–7	>94	< 1.5 kWh/m^3	[87]
Restaurant wastewater	1,300	Aluminum, graphite	12.12	90–7	98	3.35 kWh/m^3	[88]
Petrochemical wastewater	1.96	Iron and aluminum	150	10–7.6	80	2.2 kWh/m^3	[89]
Slaughterhouse wastewater	853	Aluminum	50	90–(7.8–8.9)	86.3 (COD)	11.3 kWh/m^3	[90]
Petroleum refinery wastewater	596 (COD)	Aluminum	130	60–8	63	/	[91]
Petroleum refinery wastewater	3600–5300(COD)	Aluminum	30	10 ml/min–7.5	46	/	[92]
Produced water	> 2400	Aluminum and iron	1,343	6.8 l/min–9.5	0–60%	/	[93]
Leachate of oil-drilling mud	303 (COD)	Aluminum	286	60–8	95	/	[94]
Restaurant wastewater	180–280	Aluminum and iron	43	34–(5–6)	99	/	[95]
Slaughterhouse wastewater	1500–1800	Iron	150	25–(2–3)	98	> 0.3 kWh/m^3	[96]
Metal processing wastewater	17,312 (COD)	Iron	60	25–7	92	0.497 \$/m^3	[97]
Tannery wastewater	638–780	Iron	22.4	20–7	99	0.13 kWh/m^3	[98]
Bilge water	2,000	Pt/Ir	128	240–(7.8–8.2)	93.2	33.25 kWh/kg COD removed	[99]
Oil tanning wastewater	4,340	Iron	200	15–6.74	90 (COD)	1.279 kWh/m^3 and 6.28 \$/m^3	[100]
Oil petroleum wastewater	700 (COD)	Aluminum and iron	90	39–not mentioned	85	0.74 kWh/m^3	[101]
Palm oil mill wastewater	50,000 (COD)	Aluminum	35.8	480–4	57.66 (COD)	0.3 kWh/kg COD removed	[102]
Slaughterhouse wastewater	275–376	Aluminum	100	20–4	94.7	25.02 kWh/m^3	[103]
Vehicle cleaning wastewater	572 (COD)	Iron, boron–doped diamond	20	6–6.4	75	0.14 kWh/m^3	[104]
Palm oil mill wastewater	3,000	Aluminum	20	5–5	72	0.1 kWh/m^3	[105]
Bilge water	5,000	Iron and aluminum	6	1 l/min–not mentioned	> 99	/	[106]
Gas refinery wastewater	4000 (COD)	Aluminum	400	90–7	97	11.057 kWh/kg COD removed	[107]
Metal processing wastewater	9,600	Aluminum	60–180	120–6.5	>97	/	[108]
Bilge water	39–736	Aluminum	120	20–6.7	81	/	[109]
Dairy wastewater	4,750	Iron	6	1–7	99	0.003 kWh/kg COD	[110]
Tannery liming drum wastewater	185	Iron	35	10–3	96	0.00015 kWh/m^3 of oil and grease	[111]
Tannery wastewater	1,574	Iron	200	40–9	95	6 KWh/m^3	[30]
Bilge water	338	Aluminum	30–150	12–6.95	90.31 COD–81.7 oil&grease	/	[112]
Restaurant wastewater	100–250	Iron	10–14	30–(3–10)	>95	0.60–0.84 kWh/m^3	[113]
The present study	(70000–100000) (COD)	Aluminum	600	20–4	47	18.525 kWh/m^3	

lutants. The Electrocoagulation efficiently removed COD (47% removal ratio). Though that was markedly lower than those reported in Table 7, it may be owed to using diluted OMW, that the later were achieved. Thus, the current results prove suitability of electrocoagulation to mitigate excessive COD as a post treatment.

4. Operating cost

The estimated running cost for treating olive mill wastewater using chemical coagulation, was calculated to be 1.5 US$/m^3, which corresponds to an alum dose of 5 kg/m^3. There was a direct relationship between amount of coagulant dose and operating cost. Indicating that the coagulation/flocculation process for the treatment of OMW under optimum conditions is quite economical.

Electrical energy consumption of EC process was calculated based on Eq. (14), as the most important parameter of economical assessment. Where U is the cell voltage (V), i is the electrical current (A), t is the electrolysis time (h) and v is the volume of solution in the reactor (m^3). Regarding Eq. (14), increasing the electrical current and electrolysis time increases energy consumption [114].

$$EEC = \frac{U * i * t}{V} \tag{14}$$

The running cost for treating 0.8 L of OMW using electrocoagulation was estimated as 0.05$/kWh at optimum condition, where Current Density = 60 mA /cm^2, electrodes effective area = 78 cm^2, electric potential = 9.5 V, electric current = 4.68 A, aluminum concentration in EC cell at the optimum conditions is 200 g/m^3, and contact time = 20 min. The consumed power and energy were 44.46 W and 0.01482 kWh, respectively. It can be deduced that, the required energy for 1 m^3 of treated water is 18.525 kWh with an estimated operating cost of 1 USD/m^3.

5. Conclusion

Four types of coagulants were studied (alum, lime, ferric chloride, white and grey cement dust) to select the best coagulant. Tukey test for the studied coagulants was done to confirm the proper coagulant selection at doses 0.5, 1, 1.5, 2 ppm. There was weighty difference between alum and cement dust. Alum has the biggest mean COD R.R and the second order in mean turbidity R.R after white cement dust. It was found that the COD removal ratio foralum > ferric chloride > lime > cement dust. The COD removal was 47% at 2.0 g/100 ml of alum with r 0.934, p 0.66, and turbidity removal was 64% at concentration 1.5 g/100 ml with r 0.765, p 0.235. While, maximum color R.R with r 0.921, p 0.079 was 44% at 2 g/100 ml alum dose.

A Box–Behnken design was successfully employed in the present study for experimental design, analysis of results, and optimization of electrocoagulation processes by the operating parameters for maximizing the COD removal of OMW effluent using aluminum electrodes. Regression analysis exhibited a high coefficient of determination value more than ($R^2 = 0.98$), high accuracy model. COD removal efficiencies 47%, from OMW effluent by EC process observed at the common optimum CD, pH, and time were 60 mA cm^{-2}, 4.0, and 20 min, respectively. COD removal was optimized by RSM. Optimum values attained in the present study are consistent with phenomenological elucidation of the experimental data. The estimated running cost for OMW treatment using chemical coagulation and electrocoagulation was approximately 1.5 USD/m^3 and 1USD/m^3 for treatment of 1 m^3 of OMW, respectively.

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