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Treatment of Petroleum Refinery Wastewater by Activated Carbon Assisted Electrocoagulation Process

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ABSTRACT

The removal of COD from wastewater generated by petroleum refinery has been investigated by adopting electrocoagulation (EC) combined with adsorption using activated carbon (AC) derived from avocado seeds. The process variables influencing COD removal were studied: current density (2–10 mA/cm^2), pH (4–9), and AC dosage (0.2–1 g/L). Response surface methodology (RSM) based on Box–Behnken design (BBD) was used to construct a mathematical model of the EC/AC process. Results showed that current density has the major effect on the COD removal with a percent of contribution 32.78% followed by pH while AC dosage has not a remarkable effect due to the good characteristics of AC derived from avocado seeds. Increasing current density gives better results while neutral conditions are suitable for EC/AC. The optimized conditions for higher removal of COD adopting the combined process were a current density of 10 mA/cm^2, AC dosage of 0.2 g/L, and pH of 6.8 in which a removal efficiency of 81.6% was attained. The combining of EC with adsorption showed that adding a suitable amount of AC derived from avocado seeds resulted in enhancement of COD removal from 63.45% to 81.4%. Based on this high removal efficiency, the EC/AC could be adopted instead of traditional EC.

Keywords: avocado, adsorption, wastewater, COD removal, combined process, response surface methodology.

INTRODUCTION

The industry, specially the sector of petroleum refinery processes, generates a large amount of wastewaters that could be harmful for the environment if not treated by a suitable method [1]. These wastewaters consist of organic pollutants such as toluene, benzene, xylene and phenolic compounds besides the inorganic contaminants such as heavy metals, nitrates compounds [2]. Therefor treating these wastewaters are mandatory to discharge them at the standard limits [3]. Numerous approaches have been used to treat petroleum refinery wastewaters involving biological approach and physicochemical approaches such as coagulation, flocculation, and filtration [4–7]. Most of these methods could be in sometimes non-effective for complete removal of pollutants and may be suffered from high sludge production causing high implemental costs [8]. In general, these approaches proposed a spectrum of tradeoff between their costs and effectiveness [9]. Electrocoagulation (EC) method is a simple and cost-effective approach used for treating various types of wastewaters with no requiring for additional chemicals leading to no production of secondary pollutants [10, 11]. Additionally this approach has high removal efficiency for pollutants at a short operating period with possibility of operating at a complete automation in comparison with the other methods hence reducing the quantity of sludge that needs to dispose [12, 13].

EC is based on application a direct current between anode and cathode which are submerged partially in the wastewater. The applied current causes dissolving the anode into the solution as ions (Equation 1) and generating H_2 and hydroxide ions at the cathode (usually stainless steel) due to reduction of water (Equation 2). Two types of anodes were used AL and Fe in EC, however Al is preferred owing to the high coagulation efficiency of its ions [14]. The

produced Al ions react with hydroxyle ions to form amorphous $Al(OH)_3$ depending on the pH of solution as shown in Equation 3 [15]:
At the anode surface

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^{-} \quad (1)$$

At the cathode surface

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \quad (2)$$

In bulk

$$Al^{3+} + 3OH^{-} \rightarrow Al(OH)_{3(s)} \quad (3)$$

The flocs generated by $Al(OH)_3$ have large surface area causing rapid adsorption of soluble organic compounds with trapping the colloidal particles too [16]. The generated flocs after adsorption can be isolated from the treated water by flotation or sedimentation [17].

EC has been used as a successful wastewater treatment technology for various wastewaters from the textile [18], restaurants [19], paper [20], and metal plating industries [21], and petroleum refineries [22]. However, the main disadvantage of conventional EC represents by forming an impermeable oxide film on the cathode surface [23], causing a decline in the removal efficiency with an increase in the energy consumptions [24]. To overcome this issue for enhancing the traditional EC systems, a method apart from the changing polarity of electrodes [25] has been proposed by Narayanan and Ganesan, in which granular active carbon (GAC) was added to make the process faster and more efficient in separation comparing with traditional EC [26]. Similar researches have also been stated in which EC combined adsorption (AD) using GAC to treat various wastewaters [27–37]. To make the cost of the combined process (EC/AD) cheapest, further researches were performed to use agriculture wastes or AC derived from agriculture wastes for treating numerous sources of wastewaters [38–41] where good removal efficiencies were reported in comparison with traditional EC.

Recently, we utilized AC derived from avocado seeds for treating petroleum refinery by adsorption where could removal percent of COD was obtained at an optimized conditions [42]. However, coupling the EC with AC derived from avocado seeds to treat wastewater generated from petroleum refinery was not reported before. While application of EC/AC to treat petroleum wastewater is seldom reported before. Recently, a research conducted by Chabani et al. [37] on the application EC/AD for treating petroleum refinery wastewater from Algeria using Al electrodes with granular activated carbon as a hybrid system. They found that this system gives an economy treatment time with COD removal of 82% in comparison with conventional EC. Moreover, their hybrid system offers potential as applied tertiary treatment method that enhances the quality of treated wastewater from biological treatment unit. However, their study does not involved investigating the combined process in details.

Therefore, the aim of present research is to investigate the removal of COD from petroleum refinery wastewater using EC coupled with AC derived from avocado seeds as a low-cost eco-friendly hybrid system. COD removal was chosen as a response and impact of current density, AC dosage, and pH on the COD removal were studied and optimized using RSM where a functional relationship that described the mathematical dependence of COD removal on the process variables was estimated.

EXPERIMENTAL WORK

Wastewater and chemical materials

All chemicals utilized in present work were analytical grade with no performing additional purification. H_3PO_4, NaOH, NaCl, and HCl were obtained from THOMA BAKER, India. Five liters of contaminated water was brought from the inlet tank prior to biological unit in Al-Diwanya petroleum refinery plant (Iraq) and stored in a closed container at 4 °C until use. Table 1 displays the characteristics of polluted water as getting from refinery plant administration.

AC preparation from avocados

The AC derived from avocado seeds was prepared according to the procedure outlined in our previous work [42], typically, a certain amount (50 g) of avocado seeds was rinsed thoroughly with water and dried at 70 °C for 24 h to get clean seeds followed by grinding for 15 min and sieving the powder between two sieves (700 µm and 350 µm). The cut hold on 350 µm sieve was mixed with 70% H_3PO_4 using an impregnated ratio (1:10) (W: V) at 50 °C for 6 h followed by calcination at 400 °C for 4h. More details can be found in [42]. The AC prepend from seeds has moisture content of 4%, Bulk density of 0.3932 g/cm^3 and specific surface area (BET) of 436.6 m^2/ g [42].

Table 1. Specifications of Al-Diwanya refinery plant wastewater

Property	Into treating system	Out treating system	Unit
Temperature	25	22	ºC
pH	6.6	7.3	–
Turbidity	33	7.29	NTU
TDS	5566	4898	mg/L
COD	550	102	mg/L
Phenol	18.5	0.05	mg/L

EC/AC system

The EC cell was a cylindrical vessel ended at the upper with a rectangular flange. It has dimensions (outside diameter of 90 mm, inside diameter of 80 mm, and length of 80 mm). Its cover has dimensions (130 × 130 mm) in which two slots for inserting the anode and cathode and a hole of 10 mm in diameter for feeding the solution and taking a sample. The cover was fixed with cell body by bolts and nets. Aluminum plate (50mm x 50mm x 2mm) was utilized as an anode and a stainless steel plate with the same dimensions was utilized as a cathode. Figure 1 displays the schematic diagram of the system.

Experiments were performed in twice at 25 ± 2 °C under galvanostatic conditions for a period of 60 min. First, 250 ml of the polluted water was discharged into a 0.5 L beaker. The beaker was then placed on a magnetic hot plate stirrer type-Heidolph,MR Hei-standard, Germany. The pH was adjusted to required value by adding 1M HCl or 1M NaOH then the required amount of NaCl was added at a concentration of 0.5 g/L for rising the solution conductivity leading to decrease the voltage requirement. The solution was then transfer to the cell which is also placed on a magnetic hot plate stirrer set at 750 rpm. The required amount of dosage was added followed by assembling the electrodes and starting to supply the current at certain value form a power supply type: UNI-T, UTP3315TFL-II, China. The solution was filtered after finishing the run then its COD value was determined. COD value was evaluated by digesting a sample of treated water (2 ml) with $KMnO_4$ (oxidizing

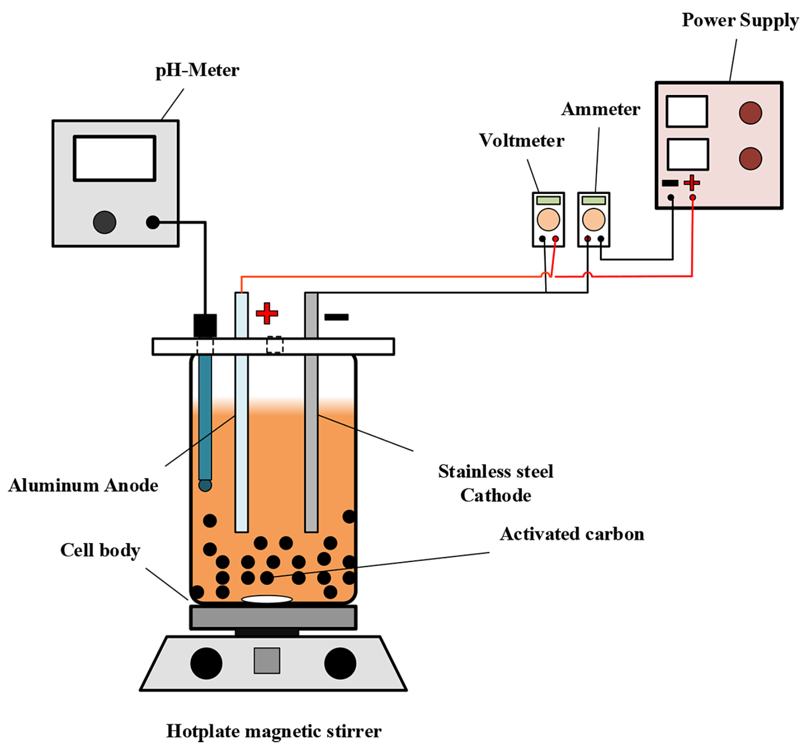


Figure 1. EC/AC system

agent) at a temperature of 150 °C for 120 min utilizing thermo-reactor (Lovibond, RD125). After completing the digesting,the sample allowed to cool then put inside the testing hole of a spectrophotometer (Lovibond, MD200)and recording its reading. pH was measured via pH meter with type ISOLAB Laborgerger GmbH, Germany. The conductivity was determined using HANNA type conductivity meter. The COD removal efficiency (RE%) was estimated using Equation 4 [43]:

$$RE\% = \frac{COD_i - COD_f}{COD_i} \times 100 \quad (4)$$

where: COD_f and COD_i represent the value of COD in mg/L (final and initial values).

Design of experiments

The traditional approach for studying effects of many variables on the object of any research is based on investigating the effect of only one variable making the other fixed at certain values which terms one-factor-at one time. However this approach suffers from a major defect represented by ignoring the interaction among the variables in the behavior during the process. Additionally, this approach claims large numbers of runs with consuming a huge amount of chemicals and longtime [44]. Many approaches that consider the interaction effect have been established, among them response surface methodology (RSM) is the preferred one which permits to obtain the responses of many factors simultaneously as they are changed [45]. RSM presents up to now the valuable approach to optimize many issues in the industry in spite of it could be not suitable for some cases such as highly nonlinear systems [46]. At the RSM based on Box–Behnken design (BBD), many assumptions were perused including the assumption of smooth-continuous

Table 2. Process parameters (Real and coded levels)

Process parameters		Range in Box–Behnken design	
Coded levels	Low(-1)	Middle(0)	High (+1)
Current density (mA/cm^2), X1	2.0	6.0	10
pH, X2	4.0	6.5	9.0
AC dosage(g/l), X3	0.2	0.6	1.0

Table 3. BBD array

Run order	Blocks	Coded value			Real value		
		x_1	x_2	x_3	Current density (mA/cm^2), X1	pH, X2	AC dosage (g/l), X3
1	1	1	1	0	10	9.0	0.6
2	1	-1	1	0	2.0	9.0	0.6
3	1	1	-1	0	10	4.0	0.6
4	1	0	-1	1	6.0	4.0	1.0
5	1	-1	0	1	2.0	6.5	1.0
6	1	1	0	-1	10	6.5	0.2
7	1	0	0	0	6.0	6.5	0.6
8	1	0	-1	-1	6.0	4.0	0.2
9	1	-1	0	-1	2.0	6.5	0.2
10	1	0	1	1	6.0	9.0	1.0
11	1	0	0	0	6.0	6.5	0.6
12	1	0	1	-1	6.0	9.0	0.2
13	1	1	0	1	10	6.5	1.0
14	1	0	0	0	6.0	6.5	0.6
15	1	-1	-1	0	2.0	4.0	0.6

surface with no multiple peaks or valleys could be existed [47]. The influences of three factors on the removal of COD (RE%) namely current density (X1), pH(X2) and AC dosage (X3) were investigated. Tables 2 displays the range of process factors while Table 3 represents the experimental array which has been designed using BBD via the software of Minitab-17.

For determining the relation among factors and a response, Analysis of variance (ANOVA) is used in which the significant this relation and their factor could be determined by estimating F-value and P-value (< 0.05). in RSM, a second order quadratic equation is adopted as shown in Equation 5 [44].

$$Y = a_0 + \sum a_i x_i + \sum a_{ii} x_i^2 + \sum a_{ij} x_i x_j \quad (5)$$

where: Y represents RE%,
$x_1, x_2 \ldots x_k$ indicate the process factors in coded value a_0,
a_0 denotes intercept term,
j and i indicate the index numbers for patterns,
a_i means the first-order (linear) main effect,
a_{ii} means second-order main effect,
a_{ij} denotes the interaction effect.

RESULTS AND DISCUSSION

Experimental design results

According to RSM, 15 runs should be performed to find the optimum levels of variable and their interactions. Table 4 shows the experimental values of RE% in addition to predicted values based on the quadratic model. It can be seen that the removal efficiency was ranged between 67 to 78%. A comparison between run1 and 2 reveals that increasing current density results in a rise in the removal efficiency. While the comparison between run 1 and 3 confirm that the removal efficiency at the acidic condition is lower than basic condition. Increasing dosage of AC results in decreasing the removal efficiency as shown in the comparison between run 5 and 6. However the interaction effect could be estimated according to the analysis of the model results based on the response surface figures. Equation 6 shows the quadratic model that obtained from the software of Minitab 17 in term of real values of factors.

$$\text{RE\%} = 44.53 + 0.939\,X1 + 8.44\,\text{pH}\,X2 - 9.02\,X3 - 0.0284\,X1^2 - 0.6087\,X2^2 + 3.72\,X3^2 - 0.0175\,X1{\cdot}X2 + 0.141\,X1{\cdot}X3 + 0.225\,X2{\cdot}X3 \quad (6)$$

Table 5 displays the ANOVA results of the system. It can be seen that current density has the

Table 4. Experimental results of COD removal using Box–Behnken design

Run order	Pt type	Blocks	X1	X2	X3	RE%	
						Actual	Predicted
1	2	1	10	9.0	0.6	74.00	74.18
2	2	1	2.0	9.0	0.6	69.70	69.98
3	2	1	10	4.0	0.6	72.00	71.73
4	2	1	6.0	4.0	1.0	69.00	69.20
5	2	1	2.0	6.5	1.0	71.70	71.68
6	2	1	10	6.5	0.2	78.00	78.03
7	0	1	6.0	6.5	0.6	74.00	74.93
8	2	1	6.0	4.0	0.2	71.20	71.45
9	2	1	2.0	6.5	0.2	74.00	73.93
10	2	1	6.0	9.0	1.0	72.70	72.45
11	0	1	6.0	6.5	0.6	76.80	74.93
12	2	1	6.0	9.0	0.2	74.00	73.80
13	2	1	10	6.5	1.0	76.60	76.68
14	0	1	6.0	6.5	0.6	74.0	74.93
15	2	1	2.0	4.0	0.6	67.0	66.83

Table 5. ANOVA for COD removal

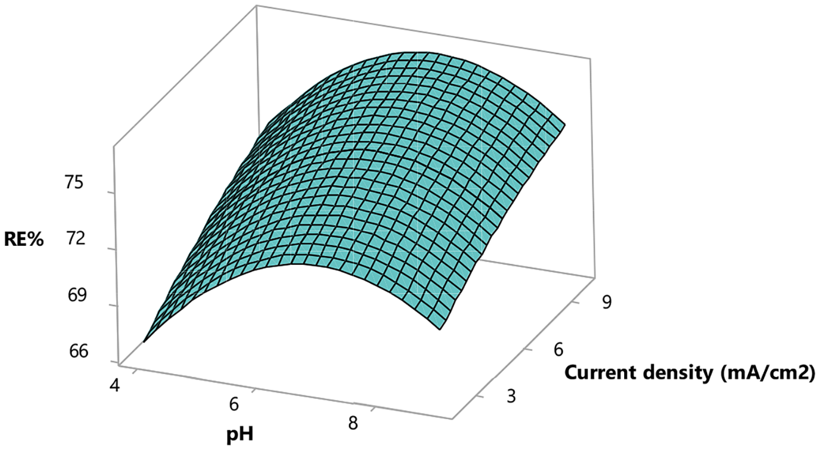
Source	DF	Seq. ss	Contr.%	Adj. ss	Adj. Ms	F-value	P-value
Model	9	120.647	95.52%	120.647	13.4053	11.85	0.007
Linear	3	63.565	50.33%	63.565	21.1883	18.73	0.004
(X1)	1	41.405	32.78%	41.405	41.4050	36.60	0.002
(X2)	1	15.680	12.41%	15.680	15.6800	13.86	0.014
(X3)	1	6.480	5.13%	6.480	6.4800	5.73	0.062
Square	3	56.555	44.78%	56.555	18.8516	16.66	0.005
X1*X1	1	0.189	0.15%	0.762	0.7616	0.67	0.449
X2*X2	1	55.055	43.59%	53.434	53.4339	47.23	0.001
X3*X3	1	1.311	1.04%	1.311	1.3108	1.16	0.331
2-Way inter.	3	0.527	0.42%	0.527	0.1758	0.16	0.922
X1*X2	1	0.122	0.10%	0.122	0.1225	0.11	0.755
X1*X3	1	0.202	0.16%	0.202	0.2025	0.18	0.690
X2*X3	1	0.203	0.16%	0.203	0.2025	0.18	0.690
Error	5	5.657	4.48%	5.657	1.1313		
Lack of fit	3	0.430	0.34%	0.430	0.1433	0.05	0.979
Pure-error	2	5.227	4.14%	5.227	2.6133		
Total	14	126.304	100.00%				
Model-summary		S.	R^2	R^2(adj.)	PRESS	R^2(pred.)	
		1.06364	95.52%	87.46%	18.64	85.24%	

major impact on the removal efficiency with a contribution of 32.78% followed by pH then AC dosage. The P-value of the model is 0.007 lower than 0.05 confirms that the model is significant and has a good fit with the experimental data. It's R^2 (95.52%) also confirms the good fitting of predicted and experimental data. Beside the difference between adj.R^2 and pred.R^2 is lower than 20% that confirms the effectiveness of model terms to describe the experimental results [42]. The linear portion of model has the major contribution of 50.33% while the square term has the second contribution with 44.78% while 2-way interactions have no significant effect with P-value of 0.92. All the terms of linear portion of the model are approximately significant in addition to the square term of pH while other terms are non-significant and their effect can be neglected. The P-value of lack of Fit is 0.979 conferring it is not significant in comparison with pure error approving that the model is active and significant in performing the removal of contaminants using the combined process [42].

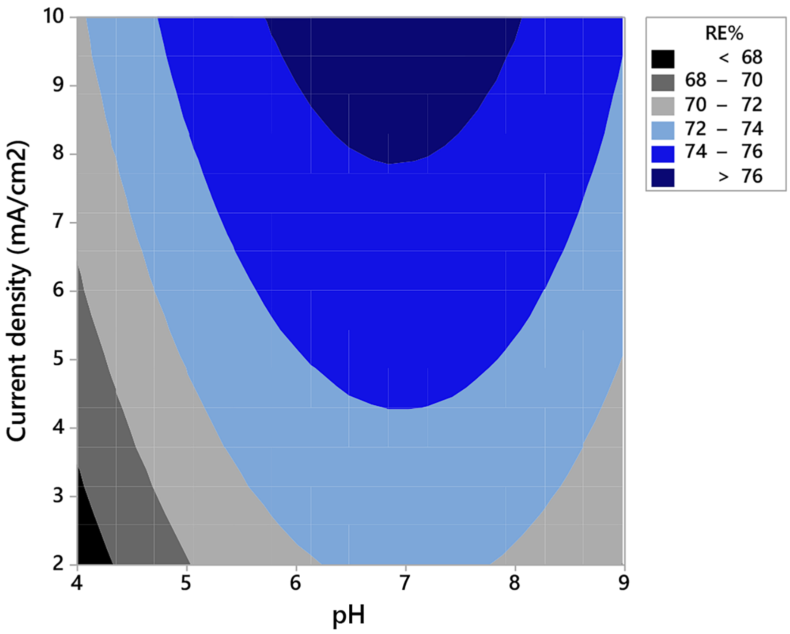
Influence of process variables on RE%

Figure 2 shows the response surface plot combined with contour plot for the effect of current density and pH on the removal efficiency at fixed value of AC dosage of 0.6 g/L. It can be seen that an increase in the current density results in an enhancement in the removal of COD. The relation was found to be almost linear. At EC, increasing current density results in increasing the current applied on the anode hence more releasing of Al^{3+} ions according to faraday's law [37]. These ions are subsequently hydrolyzed to form $Al(OH)_3$ and its polymeric compounds which act as an active adsorbent for organic and inorganic contaminants leading to decrease the COD level. At the same time increasing current results in increasing the rate of bubbles formation (H_2 gas) on the cathode as well as the their size [48] while in the combined process, additional effect can be happened via the adsorption by AC. Similar observations were noted by previous works for treating aqueous solutions containing dyes [39, 41] and removal of sulphate from mine wastewaters [40].

The effect of pH on the removal of COD has different behavior. As shown in Figure 2, the removal efficiency of COD increases with increasing the pH as going from the acidic conditions to the neutral conditions to reach a maximum then start to decrease as the pH going from neutral to basic conditions. The impact of pH is vital in both EC



(a)



(b)

Figure 2. Impact of current density and pH on the removal efficiency of COD a) surface plot, b) contour plot

and AD because it effect the solubility of $Al(OH)_3$ and surface characteristic of AC[42]. Figure 3 shows the relation between Al^{3+} and $Al(OH)_3$ at equilibrium where different forms of $Al(OH)_3$ can be observed based on pH and concentration of aluminum ions [49]. at acidic or basic media $Al(OH)_3$ would be in its charged form and soluble in water while at neutral media,it would be stable and insoluble in water so it can be functioned as adsorbent [50]. On the other hand, the mechanism of EC depends on the nature of pollutant in the wastewater [22]. Similar results were observed in various EC + AD processes [38–40] in which the preferred pH is 6.5 to7. Figure b shows that the preferred range of pH in present work is in the range of 6–8 while the preferred current density is in the range of 8–10 mA/cm^2 in which a highest removal could be attained.

Figure 4 illustrates the response surface plot combined with contour plot for the effect of current density and AC dosage on the removal efficiency at fixed value of pH 6.5. It can be seen that increasing the dosage of AC has an adverse effect on the removal of COD. This outcome suggests that COD is not decline effectively with increasing AC dosage in the combined process due to the interaction between the two adsorbents AC and $Al(OH)_3$. This behavior may be resulted due to the interference between binding sites, the electrostatic interactions, and reduced many of the adsorption sites. However, the decline in COD removal with increasing AC

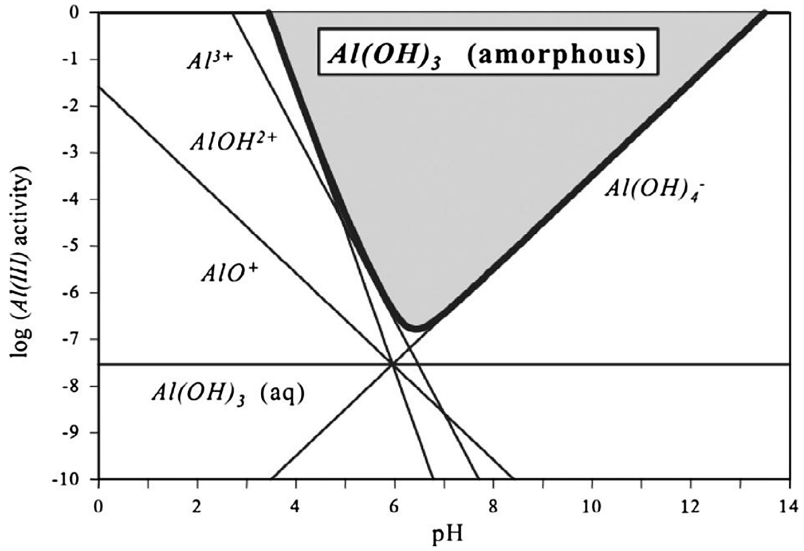


Figure 3. pH-diagram for Al^{3+} in equilibrium with $Al(OH)_3$

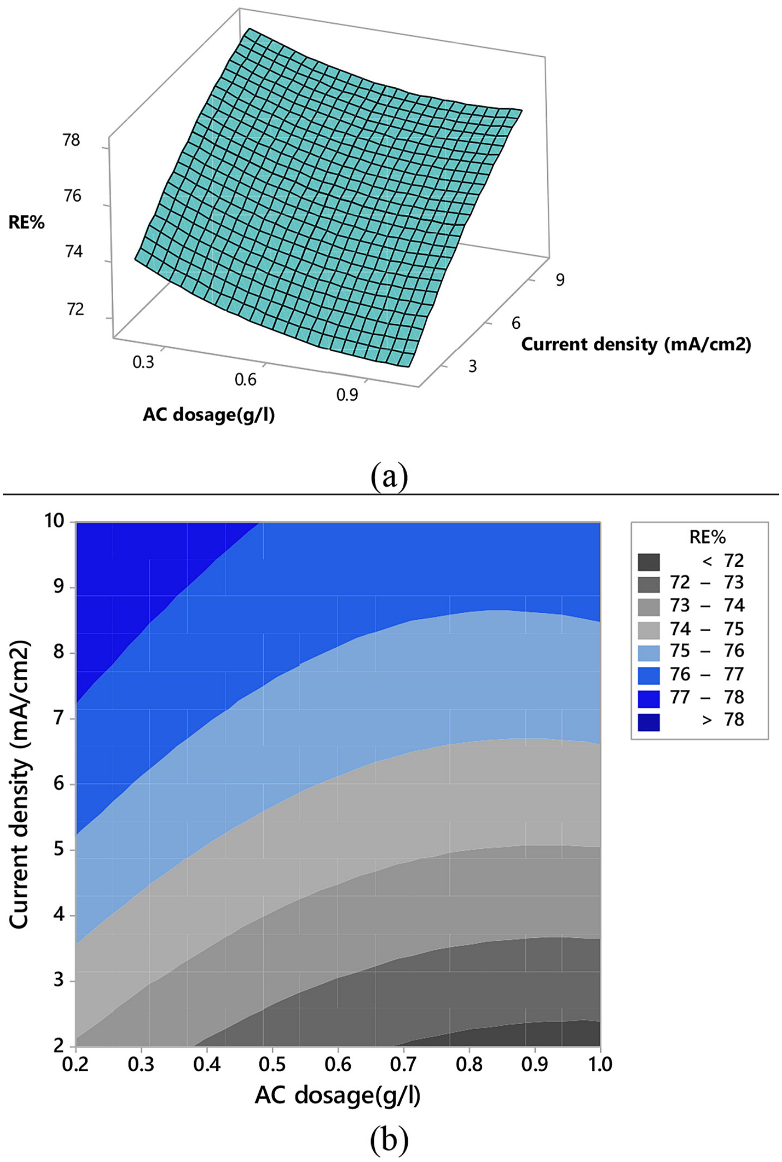


Figure 4. Impact of AC dosage and current density on COD removal efficiency (a) surface plot, (b) contour plot

dosage is not significant according to Table 5 and it could be considered similarly as a plateau in its effect as revealed by Figure 4b in which for all range of AC dosage the removal efficiency lays between 76–78% at higher current density hence the lower value of dose would be preferred. This is an indication of the high activity of AC derived from avocado seeds. Similar results found by Jalil et al in removal of fluorine from semiconductors wastewaters [51]. While removal of pollutants was found in other studies to be increased to a certain dosage value then stay constant with further increasing in the adsorbent dosage was [39, 40].

Figure 5 illustrates the response surface plot combined with contour plot for the effect of pH and AC dosage on the removal efficiency at fixed value of current density of 6 mA/cm^2 where the preferred range of pH in present work is in the range of 6–8 while the preferred AC dosage is in the range of 0.2–0.3 g/L in which a highest removal could be attained.

Since the removal of COD is owing to the combined effect of both AD and EC, the isotherms based on Langmuir and frenudlich models cannot be obtained [26].

Optimized conditions with confirmation runs

Numerical optimization for the combined process (EC/AC) was applied to find the best solution with the targeting of getting the maximum removal of COD based on the

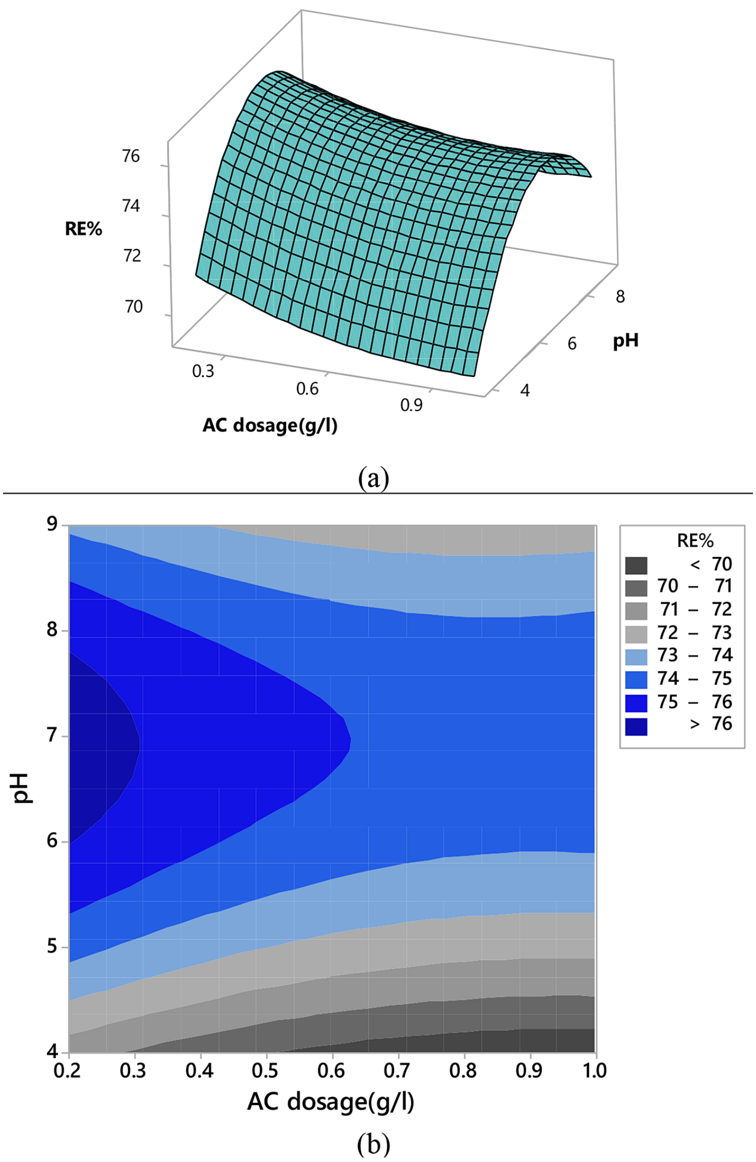


Figure 5. Impact of pH and AC dosage on the removal efficiency of COD a) surface plot, b) contour plot

Table 6. Optimization of COD removal

Response	Goal	Lower	Target		Upper	Weight	Importance
RE (%)	Maximum	67	Maximum		78	1	1
Solution: Parameters			Results				
Current density (mA/cm^2),	pH	AC dosage (g/l)	RE (%) Fit	D_F	SE Fit	95% CI	95% PI
10	6.8	0.2	78.091	1	0.925	(75.713,80.469)	(74.467,81.714)

desirability function. Results of the response optimizer /Minitab-17 are shown in Table 6. It was cleared that the optimum conditions to get a maximum theoretical COD removal of 78.091 were a current density of 10 mA/cm^2, pH = 6.8, and AC dosage of 0.2 g/L. Two confirmative runs were performed to check the feasibly of model results as shown in Table 7 where an actual removal of COD of 81.6% was achieved confirming the good compatibility of model prediction with experimental value. A further experiment was conducted to illustrate the impact of addition AC to EC as shown in Table 7 where a reduction the COD removal from 81.6% to 63.45% was happened if AC is not added to EC confirming the activity of the combined process in treating the wastewater with high efficiency. A comparison of the properties of the treated wastewater by EC/AC with the raw one has been shown in Table 8 where in addition to high removal of COD a significant removal of phenol (99.46%) was happened too with reduction in the turbidity at a removal percent of 95.15%.

Comparison with similar works

Table 9 represents results of present work in comparison with related previous works that used

Table 7. Confirmative runs

Run	Current density (mA/cm^2),	pH	AC dosage (g/l)	COD (ppm)		RE (%)	
				Initial	Final	Actual	Average
1	10	6.8	0.2	550	101	81.6	80.8
2	10	6.8	0.2	550	110	80	
3	10	6.8	0	550	201	63.45	

Table 8. Properties of the treated water and wastewater

Property	COD (ppm)	Phenol (ppm)	Turbidity (NTU)
Raw effluent	550	18.5	33
Treated effluent	101	0.1	1.6

Table 9. Comparison of COD removal from different wastewaters using EC combined with AC

Wastewater	Adsorbent	Anodes	Operating conditions	Removal (% COD)	Ref.
Beverage industry wastewater	Activated carbon	Al	COD initial = 2779 mg/L; dose = 10 g/L;12 voltage; EC =120 min/AD = 240 min.	98.66	29
Automobile wastewater	Activated carbon	Al	COD initial = 750 mg/L, dose = 1.81 mg/L. 465 rpm; 25 min	71.58	30
Paper mill effluent	Activated carbon	Al/Fe	COD initial = 586 mg/L, dose = 0.7g/L. pH = 3.21; 300 rpm;120 min	98.97	32
Diary wastewater	Activated carbon	Al	dose = 1.5 g/L; pH = 4; 13.38 mA/cm^2	87.12	33
car wash wastewater	Activated carbon	Al	Current density: 10.5 mA/cm2; reaction time: 60minutes.pH = 7.8	94	36
Petroleum refinery	Powder-activated charcoal	Al	COD initial = 350 mg/L, dose = 0.5 g/L. 465 rpm; 60 min; 8 mA/cm^2, pHi = 9	82	37
Petroleum refinery	Coconut activated carbon	Al	COD initial = 50 mg(O_2)/L(residual), dose = 0.5 g/L; 120 min; 7.5 mA/cm^2, pHi = 7.7–8.1	52	52
Petroleum refinery	AC derived from Avocado seeds	Al	COD initial = 550 mg/L, dose = 0.2 g/L. 750 rpm; 60 min; 10 mA/cm^2, pHi = 6.8	81.6	Present work

the combined process with different sources of activated carbon for treating different sources of wastewater. In comparison with previous work used for treating different sources of wastewaters (excluding petroleum refinery type), the present work has preferable results at low time and dosage with a good removal efficiency in spite of higher removal efficiencies reported by these studies. From environmental and economic viewpoints, present results are acceptable due to the good properties of AC derived from avocado seeds and the synergetic effect of combining with EC. In comparison with similar studies used the combined processes for treating wastewater generated from petroleum refineries, the present results are promising where staring from high initial value of COD, high removal efficiency at lower operating time with lower dose of AC hence reducing the energy and material requirement. This is an indication of the good activity of AC derived from avocado seeds and the combined process has high the synergetic effect.

CONCLUSIONS

The present work confirms that application of combined process (EC/AC) for treating wastewater generated from petroleum refineries is a feasible process. RSM based on Box–Behnken design was successfully adopted to optimize the effect of three operating variables namely current density, pH, and AC dosage on the removal of COD from petroleum refinery wastewater. The regression analysis confirms that a good fitting between the experimental and predicted values with $R^2 = 0.9552$. Results revealed that current density has the major impact on the removal efficiency with a contribution of 32.78% followed by pH with a contribution of 12.4% while effect of dosage in not significant within the studied range. The square term in the model has a major impact with contribution of 44.78% while 2-way interactions has no significant in the model Equation. The optimum conditions for higher removal of COD in the combined process were a current density of 10 mA/cm^2, AC dosage of 0.2 g/L, and pH of 6.8 in which a removal efficiency was 81.6%.

Basic or acidic conditions are not favorable for the combined process while neutral media is the best solution. Addition of AC derived from avocados seeds which has high surface area (436.6 m^2/g) to the EC resulted in remarkable increase in the COD removal from 63.45% to 81.6% in case of adding 0.2 g/LAC. Hence, the success of EC/AC process could be linked to the specific characteristic of the AC derived from avocado seeds. Additionally, adding access of AC higher than 0.2 g/l might defeat the purpose and increase the sludge volume.

Hence combining of different mechanisms for developing a hybrid approach to remove the COD from petroleum refinery effluents like performed by Chabani et al. [37] and present work may pave way for a new dimension in the field of wastewater treatment for industrial sectors. Furthermore, the adopting of this hybrid approach would be enhanced the reuse of treated water again in the refinery plant at large amount with enhancement in the environmental sustainability.

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