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Treatment of petroleum refinery wastewater by adsorption using activated carbon fixed bed column with batch recirculation mode

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ABSTRACT

Water pollution and the lack of access to clean water are general global problems that result from the expansion of industrial and agricultural activities. Petroleum refinery wastewaters consider as a major challenge to the environment and their treatment is mandatory. The present work concerns with the removal of chemical oxygen demand (COD) from petroleum refinery wastewater taken from Iraq's Al-Diwaniyah petroleum refinery plant by using an activated carb fixed-bed column operated at a batch recirculation mode. The fixed bed column used in this work was composed of three sections: upper, central, and bottom compartments. The bottom compartment serves as a feeding chamber to the central adsorption chamber while the upper compartment serves as a collecting effluent chamber. By adopting response surface methodology (RSM), in the pacts of various operational parameters such as packing level, pH, and time on the COD removal efficiency were investigated. The optimal conditions were an activated carbon packing level of 80%, pH of 5.7, and adsorption time of 73 min approximately, which resulted in a COD removal efficiency of 96.70%. The results indicated that the packing level of activated carbon had a major effect on COD elimination followed by pH, while time had a minor effect. The model equation's adequacy was demonstrated by its strong R^2 value (0.975). The present study demonstrates that the adsorption system by activated carbon is an effective method for removingcondomODom Al-Diwaniyah petroleum refinery wastewaters.

1. Introduction

One of the most serious environmental challenges nowadays is waste oil created by industrial sectors, particularly oil refineries and petroleum distribution businesses. [1–3]. Wastewaters of oil refinery have different organic substances with a high value of COD due to the variance in characteristics of crude oil and different processes that used for treating crude oil. Due to the presence of metal ions and organic hydrocarbon components in these wastewaters, their discharge without treatment can be extremely detrimental to the environment [4,5]. The importance of treating these wastes also resulted in the development of various cleaning methods, including biological treatment [5, 6], reverse osmosis [7], ion exchange resins [8,9], chemical precipitation [9], granular activated carbon adsorption [10-15], coagulation and coagulant aids [16], electro-coagulation [17,18], catalytic vacuum distillation [19], and electrochemical oxidation [20-23]. Petroleum Refinery wastewaters (PRWs) consider as refractory wastewaters which contain complex aromatics organic and inorganic compounds. Wastewaters generated from refineries have been recognized as extremely poisonous and more refractory to natural

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degradation compared to other types of wastewater generated from various industrial activities [24]. Coelho et al. [25] documented that, during the production stage in oil refinery processing, the amount of water consumed varies between 0.4 and 1.6 times the volume of processed oil, resulting in substantial environmental damage. Based on the complexity of the refinery, the generated wastewater in oil refineries comprises many different chemical compositions where typically COD value could be in the range of 300–600 mg/L; phenol concentration in the range of 20–200 mg/L; benzene in the range 1–100 mg/L; and heavy metals levels, for example, chromium (0.1–100 mg/L) and lead (0.2–10 mg/L) [24,26-28]. Adsorption is one of the most effective procedures for reducing organic and inorganic chemicals remaining in effluents following conventional treatment. The widest adsorption process is based on the adsorption by activated carbon [29]. Some of the relative advantages of adsorption over other advanced oxidation approaches include: (1) It has the capability in removing both organic and inorganic elements at extremely low concentrations, (2) There is no formation of sludge, (3) It is a simple and safe method of operation, and (4) The adsorbent is regenerable and reusable. Besides, the procedure is affordable because it utilizes readily available materials that can be employed as adsorbents after proper processing [30-32]. Using of adsorption contacting systems for PRWs treatment has become more prevalent in recent years. Activated carbon is the most frequently utilized adsorbent in adsorption applications [33]. Activated carbon (AC) adsorbents are complicated substances that are difficult to identify based on their behavior, surface qualities, properties, or utility. However, they are frequently categorized according to their particle shape and size, with around 55% of activated carbons produced as a powder, 40% as granular, and the remainder as pellets. Around 80% of the total output (powder, granular, and pellets) is used in liquid-phase applications, whereas 20% is used in gaseous-phase applications [34]. Activated carbon exhibits several unique qualities, including a high internal surface area, chemical properties, and excellent access to internal pores. There are three types of pores: macropores (diameter greater than 50nm), mesopores (diameter between 2 and 50 nm), and micropores (diameter less than 2 nm) [35]. Micropores typically account for a significant portion of the interior surface area. Macro and micropores can be thought of as entrances to the carbon particle. Combining the appropriate raw material and activation technique results in the desired pore shape for an activated carbon product [35]. Award. et al., [36] verified a matched pair method using activated carbon (AC) for refinery wastewater processing and accomplished a powerful COD elimination (90%). Many works have been conducted for the treatment of petroleum refinery process wastewater using activated carbon [10-15]. Most of these works adopted batch or continuous operation mode in the adsorption. However, many scientists have turned to use a reactor with a batch recirculation mode as a highly adaptable laboratory-scale reactor [37].

Based on the authors' knowledge, no previous work on the reduction of COD from petroleum refinery wastewater using granular activated carbon (AC) adsorption process operated at batch recirculation mode had been conducted. Therefore, this work aims to investigate the feasibility of COD removal from petroleum refinery wastewater using granular activated carbon adsorption technology in a batch recirculation mode of operation. Response surface methodology (RSM) combined with Box-Behnken design (BBD) was used to study and optimize the effects of main operating factors including packing level of activated carbon, pH, and time on the COD removal from wastewater produced by the Al-D**i**waniya**h** petroleum refinery.

2. Experimental work

From the Al-D**i**waniya**h** refinery plant, 50 liters of wastewater was taken from the feeding tank prior to the biological treatment unit and kept covered in containers at a temperature of 4 ºC until use. Table 1 provides the specifications of the raw effluent.

Table 1. Characteristics of the effluents in the Al-Diwaniyah petroleum refinery plant

Variable	value
COD	2455(mg/l)
pH	7.4
T.D.S	4267 (ppm)
Cl-	2128 (mg/l)
SO4-2	126 (mg/l)
Phenol	14.2(mg/l)
Turbidity	29.6 (NTU)
Conductivity	10.77 (mS/cm)

The adsorption system was composed of a cylindrical tank with a capacity (of 1.25L), an adsorbing column, a dosing pump (type-HYBL5LNPVF001, Italy,) with a maximum pressure of 10 bar, and a flow rate in the range of (1-3 L/h), a liquid flow meter (type-ZYIA,25-250 ml/min, china). The acrylic cylindrical reservoir has dimensions (20 cm in height, outer diameter of 10 cm, and thickness of 0.4cm) having a cover with dimensions (outside diameter of 12 cm and thickness of 1 cm). The reservoir has two outlets one at its bottom and the other at its lateral side located above its base at a distance of (3 cm). Each outlet was provided with a PVC valve. The cover was provided with two inlets; the first is for the recycle from the adsorbing column, while the second is for feeding the solution. Figure 1 shows the schematic diagrams for the adsorption system.

The adsorbing column is the backbone of the adsorption system. It is a new design adopted in the present work. It was made from transparent acrylic material, Perspex type. It was composed from tof compartments: upper, central, and bottom compartments. The bottom compartment serves as a feeding chamber for the adsorption process. It has a cylindrical shape with dimensions (outside diameter of 7 cm, total length of 5 cm, and thickness of 0.4 cm) ended at its upper face with a flange having dimensions (10 cm in diameter and thickness of 1cm) and contained four holes (0.5 cm in diameter) for fixing the compartment with the others via bolts and nets. The bottom compartment has an inlet pipe having a diameter of 1cm for entering the solution is located at the side of the compartment. Inside the cavity the of bottom compartment, a bed of spherical glass pellets was put which serves as a calming section. The diameter of the glass bead was 0.5 cm. The central compartment has a cylindrical shape with dimensions (outside diameter of 7 cm, total length of 7 cm, and thickness of 0.4 cm) ended at its upper and lower faces with flanges having dimensions (10 cm in diameter and thickness of 1 cm) and each one contained four holes. Upper flange was provided by perforated disc has dimensions (outside diameter of 6.8 cm, and thickness of 0.3cm) made from the same material of the compartment, while the lower flange was provided with the same disc as used at the upper flange. Both discs were perforated uniformly with hole of 1mm at equal distance among them. The upper compartment serves as a collecting chamber. It has a cylindrical shape with dimensions (outside diameter of 7 cm, total length of 5 cm, and thickness of 0.4 cm) ended at its lower face with a flange having dimensions (10 cm in diameter and thickness of 1 cm) and containing four holes. Figure 2 shows the schematic design of the adsorbing column.

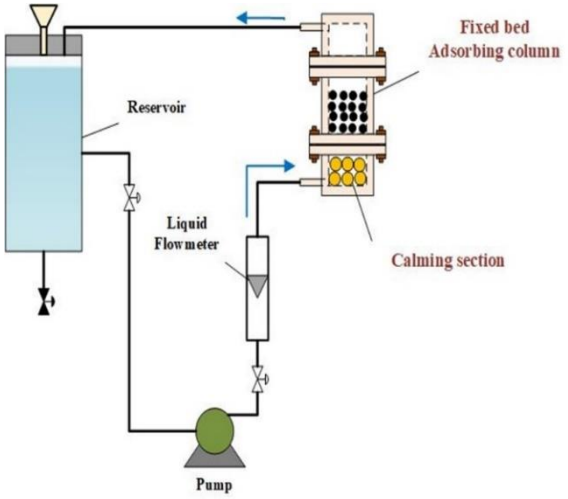
All chemicals used in the present work were analytical grade, H_2SO_4 (98%, Thomas baker, India) and NaOH (purity99%, BDH, England). Activated carbon (Zhengzhou Kelan Company, China). Table 2 shows the characteristics of the material as provided by the supplier (company).

Table 2 Granule activated carbon technical features.

Test standard	ASTMD
Total surface area	950-1200 m2/g
Iodine number	900-1150 mg/g
Total ash content	Max.5%
Hardness	Min. 97%
Apparent density	460 kg/m3
Moisture content	8%(as packed)
Particle size	8x30 mesh

The BET surface area of AC was measured using ISO-9277-2010 method at petroleum R &D center, ministry of oil in Iraq using BET surface area analyzer model-No. Qsurf9600, Thermo Finnegan Co. USA. The IR spectra of the AC samples were obtained using a Model Perkin Elmer 1100 series FT-IR operating in the range 4000–400 cm^{-1} and utilizing KBr pellets with a resolution of 1 cm^{-1}. A pellet was created for infrared research by combining a specific sample with KBr crystals and pressing it into a pellet.

Figure 1. Schematic diagram of the chemical system by adsorption process.



Before starting each experiment, activated carbon was sieved between 1.7mm and 0.85 mm then 200 g of AC was rinsed with 0.5 L of distilled water several times until its pH became 7, after that the washed AC was separated from water by filtration then dried at 100 ºC for 1hr using the oven (Type-LA MER, GERMANY). 1L of wastewater was taken and poured inside a 2liters beaker mounted on a magnetic hot plate stirrer (Hieroglyph, MR Hei-standard, Germany) then Its pH was modified to get the desired value by 1M H_2SO_4 or 1M NaOH, then transferred to the reservoir of the adsorption system. A certain amount of activated carbon that corresponds to the required packing level was placed in the central compartment of adsorbing column. The dosing pump was turned on for circulating the solution through the adsorbing column at a Liquid flow rate of 200 ml/min and the adsorption process was continued for some time at a constant temperature of 25±2 ºC. At the end of each run and before carrying out COD tests, the sample of treated wastewater was taken and filtered then tested for its COD value. A digital pH meter was used to measure the electrolyte pH (HNNA Instrument Inc.PH211, Romania), whereas conductivity and TDS were determined by utilizing a conductivity meter model COM-100 from HM Digital Inc. in Korea. Solution turbidity was measured by Jenway-6035, Germany. SO_4^{-2} and Cl^{-1} were analyzed by using Photo Flex. Series, WTW model no 14541, Germany.

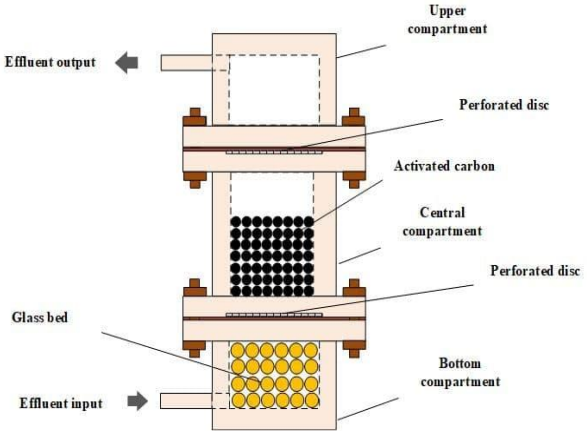


Figure 2 Schematic diagram of the chemical reactor

Effluent COD was used to measure the number of organic compounds in the waste stream. the quantity of COD in the petroleum refinery effluents was determined by taking a sample (0.2 ml) of effluent digested for 120 minutes at 150 ºC with $K_2Cr_2O_7$ as an oxidizing agent using a Thermos reactor (RD125, Lovibond). To analyze the digested sample, it had to be cooled down to room temperature first then COD was measured by spectrophotometer (MD200, Lovibond). Method 8047 of the Hach Company/Hach Lange GmbH, USA, was used to measure phenol concentration. The COD was measured three times, with the averages used in this study. The effectiveness of COD removal was determined using eq.1[38]

$$RE\% = \frac{COD_i - COD_f}{COD_i} \times 100 \quad (1)$$

Where The removal efficiency (RE%), the initial COD (mg L1), and the final COD (mg L1) are all represented by the letters COD in the formula. When digesting a kg of COD.

Design of experiments

Response surface methodology (RSM) is summarized as a collection of mathematical and statistical tools for determining a regression model equation that correlates an objective function with its independent variables [39]. Box–Behnken design (BBD) was adopted to examine the impact of process variables on COD removal. The removal effectiveness of COD (RE %) was considered as a response, while the packing level (X1), time (X2), and pH (X3) were taken as process parameters [39]. The scales of the process components were designated as follows: low (-1), middle or center

point (0), and high level (1). Table 3 shows the process parameters with their selected levels while Table 4 shows the experiments array provided by BBD for the current work, which was obtained by the Minitab-17 program. The amount of AC for each packing level corresponds to 10 g for 20%, 25 g for 50%, and 40 g for 80%, which results in a dose of adsorbent 10g/l, 25g/l, and 40g/l respectively.

Table 3. Process variables with their level for refinery wastewater treatment

Process parameters	**Box– Behnken** level		
Levels that are coded	Low (-1)	Middle (0)	High (+1)
X1- Packing level (%)	20	50	80
X2- Time (min)	60	70	80
X3- PH	3	5	7

In this work, the following second-order model with the least-squares approach was used to determine the correlation between COD removal and its independent variables. [40,41]:

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

a_0 is referred to as the intercept term., x_1 is the first process variable, x_2 is the second process variable, and x_k is the last process variable. Main effects a_i, a_{ii}, and a_{ij} all reflect the first order (linear) effects; the interaction effects are represented by a_{ij}. Analyzing variability and then calculating a correlation coefficient (R^2) confirmed the model's suitability.

3. Results and discussion

3.1 Characteristics of Activated carbon

The results of the BET surface area analysis were a BET Surface Area of 1204.2337 ± 39.5518 m²/g which is a desirable quality in wastewater treatment applications. The average pore volume and diameter were found to be 0.636180 cm³/g and 2.11314 nm, respectively. These are the properties of a mesoporous substance. The adsorption-desorption plot for AC was presented in Fig. 3. Nitrogen uptakes rose as the relative pressure increased across the whole pressure range. AC exhibited type I features with a hysteresis loop at 0.4≤ p/p≤0 0.9, which is consistent with the

categorization of the International Union of Pure and Applied Chemistry (IUPAC). As a result, the presence of mesopores with highly absorbent surfaces were confirmed, as has been previously reported in similar investigations [42, 43].

3.2 Results of experimental design

According to BBD design, fifteen runs were performed to investigate the optimum conditions for COD removal. Table 5 summarizes experimental findings regarding COD removal effectiveness (RE percent). Results showed that the efficiency of COD removal was in the range of 84% - 96.26%. As a preliminary inspection, a comparison between run(1) and run(15) showed that the packing level of activated carbon has a considerable impact on the efficiency of COD removal where RE% increased from 87 to 95.9% making a difference of 8.6% as packing level of activated carbon increased from 20%to 80% at pH 5 and time of 60 min, while the comparison between run (5) and (6) showed that pH followed the packing level in its effect on the COD removal efficiency where

Table 4. Box- Behnken experimental design

Run	Blk	Coded levels			Real value		
		x_1	x_2	x_3	Packing level %, X1	Time (min), X2	PH , X3
1	1	0	-1	1	20	60	5
2	1	-1	1	0	20	80	5
3	1	1	0	0	80	70	3
4	1	-1	1	0	50	80	3
5	1	-1	-1	1	20	70	7
6	1	0	0	1	20	70	3
7	1	1	0	1	50	70	5
8	1	1	0	-1	50	70	5
9	1	0	1	0	80	70	7
10	1	0	-1	0	50	60	3
11	1	0	1	-1	80	80	5
12	1	-1	0	-1	50	60	7
13	1	1	0	0	50	70	5
14	1	0	0	0	50	80	7
15	1	0	-1	-1	80	60	5

Table 5. Experimental results of Box–Behnken design for COD removal

Run Order	Blocks	Parameters			RE%	
		Packing level (%)	Time (min)	pH	Actual	Predicted
1	1	20	60	5	87	87.088
2	1	20	80	5	90.24	90.688
3	1	80	70	3	91	91.663
4	1	50	80	3	89.71	89.135
5	1	20	70	7	90	89.338
6	1	20	70	3	84	84.1285
7	1	50	70	5	93.57	93.597
8	1	50	70	5	92.53	93.597
9	1	80	70	7	95.78	95.653
10	1	50	60	3	87	86.785
11	1	80	80	5	96.26	96.173
12	1	50	60	7	91	91.575
13	1	50	70	5	94.69	93.597
14	1	50	80	7	93.33	93.545
15	1	80	60	5	95.9	95.453

RE% increased from 84 to 90% making a difference of 6% as the pH increased from 3 to 7 at packing level of 20% and time of 70min. However, the precise effect of these parameters can be observed via ANOVA results. By using Minitab-17 software, results of COD removal efficiency were analyzed and a quadratic model for the effectiveness of COD elimination (RE percent) expressed in terms of real process parameters was formulated as follows:

$$RE\% = 15.2 + 0.382\,X1 + 1.079\,X2 + 8.60\,X3 - 0.000729\,X1*X1 - 0.00591\,X2*X2 - 0.686\,X3*X3 - 0.00240\,X1*X2 - 0.00508\,X1*X3 - 0.0048\,X2*X3 \quad (3)$$

Where:

- X1X2, X1X3., and X2X3. denote the effect of model parameters on one another.
- (X1)2, (X2)2, and (X3)2 all reflect a measure of the model parameters' major effect.

The expected values of COD removal efficiency were computed and summarized in Table 4 using equation 3.

In eq.3, the positive coefficient in front of any parameter reveals that RE% increases with its increase and vice versa. The acceptability of BBD was identified by the use of analysis of variance (ANOVA).

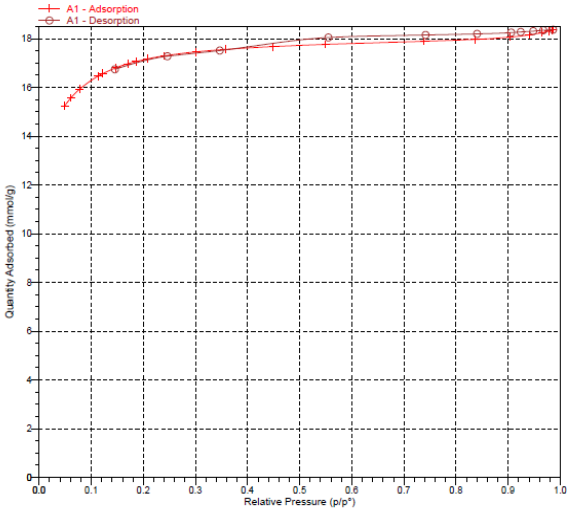


Figure 3. N2 adsorption-desorption isotherm of AC Results of experimental design

It is an analytical technique that utilizes Fisher's F- and P-tests to determine the model's and its parameters' significance [44]. In general, bigger F-values and smaller p-values indicate that the coefficient terms are more important [45]. The response surface model is illustrated in Table 6 using ANOVA. This table contains, Contr.% denotes the percentage of contribution of each variable, DF represents the degree of freedom of the model and its parameters, and the statistical terms are represented by the sum of the square (Seq. SS), the adjusted sum of the square (Adj. SS), and adjusted mean of the square (Adj. MS) respectively. P-values of (0.002) and F-value of (22.54) were obtained which elucidate that the regression model is highly significant. The model's coefficient of multiple correlations was 0.9759, indicating that the regression is statistically significant and that the model confirms only (0.0241) of the total variations. The adjusted multiple correlation coefficient (adj. R^2) equals 0.9326, while the predictable multiple correlation coefficient (pred. R^2) equals 0.790 in this model was well-matched since the difference between them is less than 0.2[46].

Results of table 5 showed that packing level has the major effect with a contribution of 52.27% followed by pH with a contribution of 23.06%. While time has a lower effect with a contribution of 5.09%. These results confirm that adsorption is governed by two operating parameters (packing level and pH). These results are expected because during the adsorption process, with increasing pH, the negative surface charge of the adsorbents decreases, resulting in a strengthening of the electrostatic adsorption force between the adsorbent and contaminants with a positive charge, hence boosting the removal of pollutants [47]. Besides increasing packing level means increasing adsorbent dosage hence more active sites with the AC are available for adsorbing more organic materials resulting in high removal of COD. The interactions among the variables are non-significant except for the highly significant double interaction of pH. In the present study, the lack-of-fit P-value (0.677 > 0.05) indicates that the lack of model fit was not statistically significant in comparison to the pure error [48]. As a result, the model can generate an adequate prediction that corresponds to the response values. The contribution of the linear term was 80.42% while the square and 2-way interactions were 15.82% and 1.35% respectively. Hence the interaction effect generally is significant.

Table 6. Analysis of variance for COD removal.

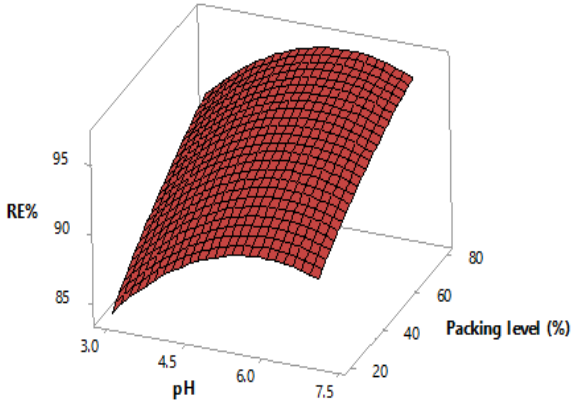
Source	DF	Seq. ss	Contr. %	Adj. ss	Adj. Ms	F-value	P-value
Model	9	179.069	97.59	179.069	19.8965	22.54	0.002
Linear	3	147.562	80.42	147.562	49.1875	55.72	0.002
(X1)	1	95.911	52.27	95.911	95.9112	108.65	0.001
(X2)	1	9.331	5.09	9.331	9.3312	10.57	0.023
(X3)	1	42.320	23.06	42.320	42.3200	47.94	0.001
Square	3	29.025	15.82	29.025	9.6748	10.96	0.012
"X1 * X1"	1	0.651	0.35	0.651	1.5881	1.80	0.238
"X2 * X2"	1	0.535	0.29	0.535	1.2889	1.46	0.281
"X3 * X3"	1	27.839	15.17	27.839	27.8385	31.54	0.002
2-Way lnter.	3	2.482	1.35	2.482	0.8273	0.94	0.488
X1 * X2	1	2.074	1.13	2.074	2.0736	2.35	0.186
X1 * X3	1	0.372	0.20	0.372	0.3721	2.35	0.545
X2 * X3	1	0.036	0.02	0.036	0.0361	0.42	0.848
Error	5	4.414	2.41	4.414	0.8827	0.04	
Lack of Fit	3	2.080	1.13	2.080	0.6933		0.677
"Pure-Error"	2	2.334	1.27	2.334	1.1669	0.59	
Total	14	183.482	100				

Model-summary	S.	R^2	R^2(adj.)	PRESS	R^2(pred.)
	0.939544	97.59%	93.26%	93.26%	79.00%

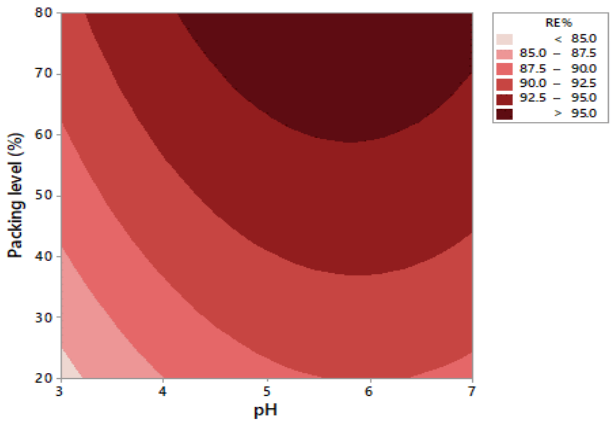
3.3 The Influence of process factors on the efficiency of COD removal

Graphical representations of RSM can be used to illustrate the interactive effects of the selected variables and their effect on the response. The figures, (4-a, b) illustrate the influence of pH on various packing levels (20% -80%) over a constant period (70 min.). The response surface plot is shown in Figure 4-a, as well as the contour plot is shown in Figure 4-b. The shape of the control plot indicates the nature and extent of the interactions. From the layout of the surface, it was observed that, at any pH value, as the packing level is increased from 20% to 80%, the efficiency of COD elimination increases. The increase in RE% seems to be linear. A similar observation was identified by previous works [14]. This behavior is in agreement with the fact that adsorption occurs via the production of carbon-oxygen surface complexes. The nature and quantity of carbon
oxygen bonds are determined by the carbon surface, the oxidative treatment, the surface area, temperature, and pressure [49]. At any value of packing level, RE% increases with increasing of pH 3-7 then start to be approximately constant at higher pH values. The related contour map demonstrates that the 96 percent COD removal efficiency value happened Figures (5-a,b) show the impact of time on the RE% for various values of packing level (20%-80%) at constant pH(5). Figure 5-a demonstrates that the efficiency of COD removal increases exponentially with increasing time at low packing levels. While at a high value of packing level the effect of time is little with no significant effect. The results showed that the reaction time has a positive effect on the progress of the adsorption process only at low packing levels. This is explained by the fact that there are initially a large number of vacant surface sites accessible for adsorption. Additionally, it was hypothesized that there was a strong attraction between the pollutants and the sorbent and that as contact time grew, the remaining unoccupied surface locations became harder to occupy due to saturation.

This could also be a result of a shortage of suitable sorption sites after the sorption process resulting in nearly constant removal efficiency. This outcome validates by prior research [50].
The related contour map fig.(5-b) reveals that the COD removal efficiency of 96 percent is concentrated in a narrow area with packing levels ranging vinside a limited area with a pH range of 5-7 and a packing level in the range (of 60%-80%).

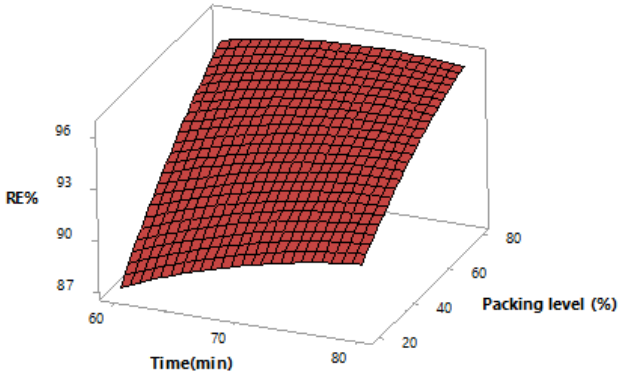


(a)

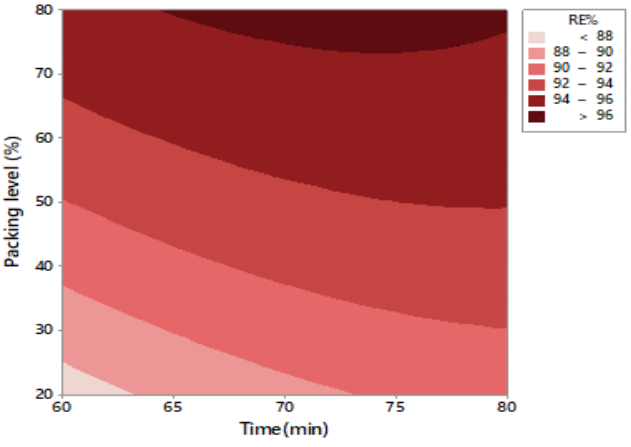


(b)

Figure 4. Impact of activated carbon ratio (packing level) and pH on the RE %, (a) Response surface plot, (b) Contour plot. (Hold values: time =70 min)



(a)



(b)

Figure 5. Effect of time and activated carbon ratio on the RE%, (a) Response surface plot, (b) Contour plot (Hold value: pH =5).

from 70% to 80% and time frames ranging from 60 to 80 minutes. As a result, the implementation of RSM will enable the identification of feasible optimum values for the researched parameters, as well as its function in providing valuable information about the interactions between the variables.

3.4 The optimization and confirmation test

Optimizing process conditions is critical and should be accomplished. Numerous standards have been identified for optimizing the system by maximizing the desired function (DF) by varying the importance or weight, which may alter the objective's characteristics. The variable's target fields have five options: maximizing, objective, minimizing, within the range, and none. The target of removal of COD was selected as 'maximum' with corresponding 'weight'1.0. The independent parameters examined in the study have been specified in a range of designed levels (activated carbon ratio "packing level" from (20%-80%) time: (60-80min.) and pH (3-7). The lower limit value of the efficiency of COD removal was assigned to be 87%, whereas the upper limit value was assigned to be 96.26%. The optimization procedure was carried out within those constraints and the outcomes are reported in Table (7) with the function of desirability (1). Two confirmatory experiments with expanded parameters were conducted to validate them; the results are shown in Table (8). After 72.7 minutes of adsorption and packing at an 80 percent level, an average COD removal efficiency of 96.8 percent was obtained at pH=5.7, which is within the range of the ideal value obtained through optimization analysis using the desirability function of (1) Table (7). As a result, combining the Box–Behnken design with the functional desirableness is effective and efficient in maximizing COD removal. Table (9) compares the parameters of wastewater effluent and treated effluent based on the results of the current work in AC. As can be observed, treated wastewater has improved characteristics and conforms to the standard limitations for effluent discharge Tabula (9). The present study established the efficacy of adsorption activated carbon in the treatment of wastewater generated by the Al-Diwaniyah petroleum refinery plant by achieving a COD removal efficiency of 96.8 percent, a phenol removal efficiency of 93.2 percent, and a turbidity removal efficiency of 95.87 percent based on the raw effluent properties.

Results of the present work reveal that adsorption using an activated carbon system can be applied successfully for the treatment of the Al-D**i**waniya**h** petroleum refinery. Starting from an initial COD of 2428 ppm, it could be achieved a COD removal efficiency of 96.70% at 73 min with a packing level of 80%. These results prove that the adsorption process absorbs the refractory natural or organic compounds that exist in petroleum refinery wastewater more proficiently.

3.5 FTIR spectral analysis

To investigate the effect of adsorbed organic compounds during the adsorption process in the removal of COD from petroleum refinery wastewater, the FTIR spectrum was obtained for the activated carbon before and after adsorption at the optimum conditions as shown in figure 6. The FTIR spectrum of material can provide valuable information about its chemical composition. during adsorption where shifting in the spectra, as well as disappearance or reduction of the peaks, can indicate the efficiency of the adsorption process[51].

Table 7: Optimum of process parameters for maximum COD removal efficiency (RE%)

Response	Goal	Lower	Target	Upper	Weight	Importance
RE (%)	*maximum*	84	Maximum	96.62	1	1

Solution:

Parameters			Results					
pH	Packing (%)	level	Time (min)	R E (%) Fit	D_F	SE Fit	95% CI	95% PI
5.7	80		72.72	96.811	1	0.61	(95.244,98.377)	(93.932,99.689)

Table 8: Optimum of process parameters for maximum COD removal

.

Run	pH	Packing level (%)	Time (min)	COD (ppm)		R E (%)	
				Initial	Final	Actual	Average
1	5.7	80	72.72	2428	80	96.70	96.69
2	5.7	80	72.72	2460	84	96.68	

Table 9. Comparison between the wastewater effluent and the treated effluent

Parameter	COD	Phenol	Turbidity	SO_4^{-2}	Cl^-
Effluent	(ppm)	(ppm)	(NTU)	(ppm)	(g/l)
Raw effluent	2428	17.6	31.6	137	2.207
Treated effluent	80(96.70%)	1.196(93.87%)	1.305(95.87%)	210	1.874

The peaks 3845.45,3830.02, 3780.07, and 3737.84$cm^{-1}$are assigned to stretching vibration of the O–H bond caused by the presence of chemisorbed water and surface hydroxyl groups, which may be responsible for the organic adsorption interaction [51,52,53]. Peak at 3391.07cm^{-1} corresponds to O-H stretches in hydroxyl, carboxylic, and phenolic groups [54]. This peak is not found in activated carbon before treatment. The peak at 3031.45 cm^{-1} corresponds to the aromatic C-H groups [55,51]. This peak is disappeared in the activated carbon after treatment. The peaks 2435.8, 2355.02, and 2319.4 cm^{-1} are assigned to C≡C stretching vibrations in alkyne groups [56, 57]. The peak at 1684.9 cm^{-1} is due to the C=O stretching vibrations of ketones, aldehydes, lactones, and carboxyl groups. [58, 51, 55]. This peak is not found at activated carbon before treatment. The peaks 1582.98 and 1533.14 cm^{-1} could be due to C=C stretching in the monosubstituted and para-disubstituted benzene rings [59, 56, 53, 57].

Peaks of 1152.66 and 1185.14 cm^{-1} correspond to the C-O stretching vibrations in alcohols, phenols, or ether [60, 56]. Finally, peak 675.89 cm^{-1} corresponding to C-C stretching is found in activated carbon after treatment [61].

3.6 Comparison with previous works

Most of the previous works were conducted at either batch or once through the continuous mode of operation. Table 10 shows a comparison between our results and the results of familiar works. As can be observed, the current system performed better in terms of COD, turbidity, and phenol removal. the reason behind these results could be the higher turbulence promotion observed by using the batch recirculation mode of operation. Therefore adopting batch recirculation in the removal of COD considers a promising step in the application of such a mode of operation for the treatment of different types of wastewater generated from different industrial activities.

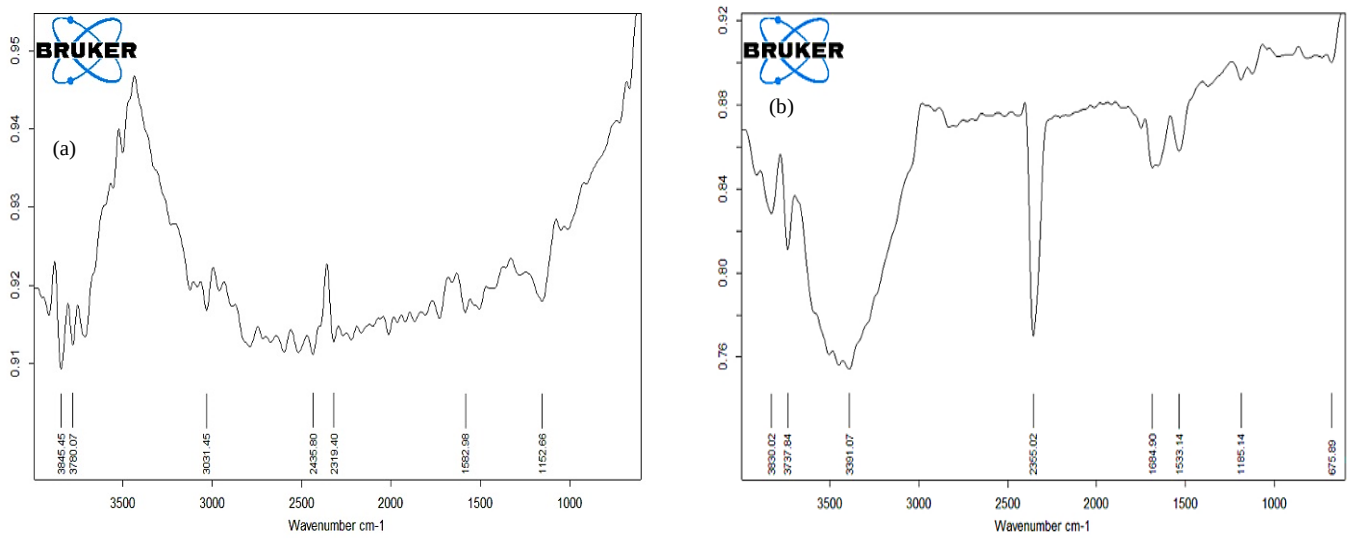


Figure 6. FTIR spectra of activated carbon (a) before treatment (b) after treatment

Table 10. Comparison of petroleum refinery wastewater treatments by Ac adsorption using various mode of operation under several operating conditions

Type of wastewater	Mode of operation	Characterization of wastewater	Optimum conditions	Efficiency	Ref.
Local petroleum refinery in UAE	Batch	COD:3490 ppm, pH=7.9	pH=6 dosage=20g/l Time =60 min.	COD%=87	[10]
Tehran refinery wastewater	Continuous	COD:420 ppm, pH=7.9	pH=6 dosage=06.5g flow rate= 0.185cm3/s	COD%=78	[11]
Leading refinery in S. Oman	Batch	COD:900ppm, pH=7.2	pH=6 dosage=0.6g/500ml Time(min)=120	COD%=79, NTU%=43of	[13]
Oman.					
Tabriz refinery	Batch	COD:622ppm, pH=7.9	pH=5.5 dosage=0.5g/100ml Time(min)=90	COD%=89.87	[14]
Synthetic produced water	Batch	COD:2508 ppm, Turbidity:53NTU , pH=7	pH=5.5 dosage=0.5g/100ml Time(min)=90	COD%=95.87 NTU%=99.65	[15]
Al-Diwaniyah petroleum refinery wastewater	Batch Recirculation	COD:2428 ppm, Turbidity:31.6NTU , pH=7.4	pH=5.7 Packing level(%)= 80Time(min)=72.72	COD%=96.70 NTU%=95.87, Phenol%=93.2	**Present work**

4. Conclusions

This study was concerned with COD removal from petroleum refinery effluent using an activated carbon-adsorption process operated in a batch recirculation mode. The response surface approach was used to conduct experiments to determine the influence of operating parameters such as packing level of activated carbon, pH, and time on the removal of COD from petroleum refinery effluent generated by the Al-D**i**waniya**h** refinery plant in Iraq. Based on BBD, the best conditions were achieved at a packing level of 80%, a pH of 5.7, and a time of 73 minutes, in which COD removal of 96.7% was obtained. The high R^2, adj.$R^{2,}$ and pred. R^2 values indicate that the model fitted very well to the experimental data the results indicate that RSM can be successfully used to analyze the impact of various operating factors and develop the required optimum conditions thus reducing the number of runs, time, and cost of experiments.

The efficiency of the activated carbon- adsorption process was found to be dependent on two main parameters (packing level and pH). Time was found to have the least effect. The batch recirculation mode was able to operate the system without operational problems (experimental observations), and attain good COD removal during a circulation time of 73 min. From this study, the activated carbon- adsorption process seems to be an environmentally friendly process to remove COD from petroleum refinery wastewater.

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