



Wet air oxidation of leachate containing emulsified and solubilized hydrocarbons from crude oil-contaminated soil

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Abstract

The present research work is focussed on the treatment of leachate generated from crude oil-contaminated soil sites using wet air oxidation as an advanced oxidation process. The factors affecting the wet air oxidation (WAO) process, viz. temperature, pressure and time of treatment were optimized using central composite design and response surface methodology. The significant factors were optimized to maximize % COD removal from the leachate. The linear effects of pressure and temperature ($p=0.000$); the square effects of pressure ($p=0.019$) and time ($p=0.007$) and the interaction effect of temperature–pressure ($p=0.002$) were found to be significantly governing the % COD removal. The maximum COD removal of 76% was obtained at temperature = 244 °C, time = 30 min and pressure = 5 bar. Further, the biodegradability index (BOD_5/COD) increased from 0.14 ± 0.007 of the untreated leachate to 0.48 ± 0.02 of the wetox-treated leachate. Moreover, the degradation of recalcitrant hydrocarbons in initial leachate by WAO treatment was confirmed using GC–MS analysis.

Keywords Crude oil-contaminated soil · Leachate · Recalcitrant hydrocarbons · Wet air oxidation · Response surface methodology · Biodegradability index

Introduction

Crude oil has been widely used for the production of different products like gasoline, diesel and heavy oil. Crude oil is a complex mixture of aliphatic saturated hydrocarbons, cyclic saturated hydrocarbons, polycyclic aromatics hydrocarbons (PAH) and PAH containing nitrogen and sulphur compounds [1]. PAH are considered toxic, carcinogenic, and mutagenic [2]. Accumulation of long-chain saturated hydrocarbons, viz. nonacosane ($C_{29}H_{60}$), hentriacontane ($C_{31}H_{64}$), and tritriacontane ($C_{33}H_{68}$) are known to cause severe health problems in human [3] including skin irritation, eye irritation, respiratory irritation, drowsiness or dizziness, and possibly cancer. Worldwide average oil demand for the year 2016 was 96.1 mb/day, and it is estimated to reach up to 97.6 mb/day and 99 mb/day for the year 2017 and 2018 [4]. Increasing global demand for petroleum products leads to

increase in chances of crude oil spillage due to the transportation of oil, storage tank rupture, and pipeline leakage, thereby causing soil and water pollution [5].

Land treatment unit (LTU) has been reported as a potential bioremediation process for the treatment of crude oil contaminated soil [6]. In order to attain significant bioremediation using LTU the total petroleum hydrocarbon (TPH) concentration of contaminated soil should be below 8%. In addition, for an effective on-site bioremediation, (1) contaminated soil should contain less than 5% TPH; (2) proper irrigation system must be installed to maintain the soil moisture content for proper biodegradation and (3) the depth of the soil should not be more than 18 in. [7]. During the infiltration of water by irrigation and rainfall, water percolates through the contaminated soil and leaches out through LTU [8]. These leachates contain emulsified and solubilized non-biodegradable and partially degraded eco-toxic hydrocarbons which cause detrimental effects on the groundwater resources [9]. Scott and co-workers investigated the biodegradation of TPH in LTU leachate in California, USA [9]. They also reported a very low biodegradation (12%) of TPH owing to their recalcitrant nature due to the presence of long-chain hydrocarbons ($\geq C_{20}$) in the leachates. The safe

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disposal of leachate generated from LTU is a key issue and certain pretreatment is necessary.

In recent years, there has been an increasing interest in the use of advanced oxidation processes (AOPs) for the treatment of recalcitrant organic compounds in wastewater, and crude oil-contaminated soil. These AOP technologies include Fenton, Fenton-like process, ozonation, wet air oxidation, photo-catalysis, etc. Wet air oxidation (WAO) involves the aqueous phase oxidation of organic and some oxidizable inorganic components at elevated temperature 150–325 °C and pressures 5–200 bar [10]. It involves the formation of highly reactive hydroxyl radical which has a high oxidation potential, i.e., $E^0 = 2.8 \text{ V}$ [11]. WAO oxidizes recalcitrant organic component into biodegradable intermediates or mineralizes to carbon dioxide and water [12].

WAO has been widely reported for the treatment of oil sludge, dye degradation, municipal landfill leachate, and degradation of PAH in contaminated soil [13–16]. Jing et al. compared the wet air oxidation of oil sludge in presence of catalyst (Ni^{2+}) and without catalyst by keeping temperature, pressure and time constant. The oil sludge with an initial COD of $20,000 \text{ mg l}^{-1}$ showed 99.7% and 88.7% COD removal in presence of catalyst and without catalyst, respectively [13]. PAH degradation study was carried out using WAO in presence and absence of free radical promoter by Rivas et al. [17]. Four PAH namely acenaphthene, phenanthrene, anthracene and fluoranthene underwent 80–100% conversion at a temperature of 190 °C, a pressure of 50 bar and reaction time of 80 min while the addition of hydroxyl radical promoter reduced the reaction time up to 60 min and temperature up to 100–150 °C [17]. Some researchers have reported the applicability of WAO for the treatment of landfill leachate. Rivas et al. investigated the differential impact of sulphate radical and hydroxyl radical promoted WAO of landfill leachate with an initial COD of 2700–7000 mg l^{-1} . The temperature of 180–270 °C and pressure of 40–70 bar resulted in 20% COD conversion, while WAO using H_2O_2 provided 35% COD removal, and the addition of oxone resulted in 80% COD conversion [18]. In another study, factorial design methodology was used to optimize catalytic wet air oxidation (CWAO) conditions for the effective COD reduction of landfill leachate with an initial COD of 4920 mg l^{-1} and biodegradability index of 0.073. The temperature of 200 °C and time of 22 min had shown 78% COD reduction with $250 \text{ mg l}^{-1} \text{ Cu}^{2+}$ and $1500 \text{ mg l}^{-1} \text{ H}_2\text{O}_2$ loading at oxygen partial pressure of 25 bar [15]. However, to the best of our knowledge, no such study has been conducted previously for the WAO treatment of leachate generated from crude oil contaminated soil sites which further establishes the novelty of the present study.

The present research work aims to develop a WAO-based process for physico-chemical treatment of recalcitrant compounds in leachate obtained from crude oil contaminated

soil. In this study, significant parameters, viz. temperature, pressure, and time of WAO treatment was optimized by using response surface methodology (RSM) using central composite design (CCD). Further, the degradation of complex hydrocarbons present in the leachate by WAO was confirmed using GC–MS analysis. The specific objective of the study was to consider WAO as an advanced treatment process for enhancing the biodegradability index of the leachate generated from crude oil-contaminated soil sites.

Materials and methods

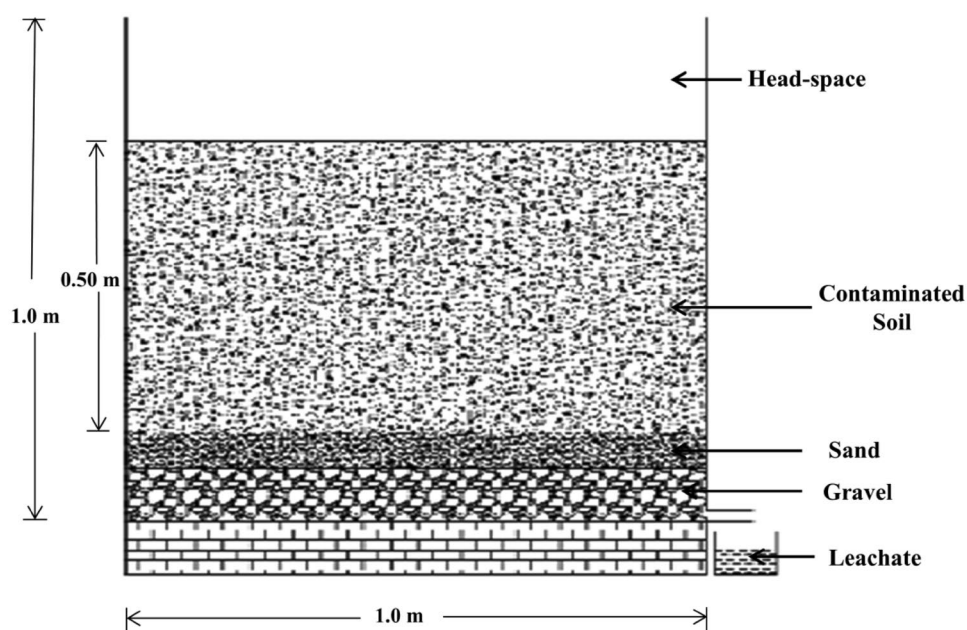
Leachate collection

Crude oil-contaminated soil was collected from the crude oil refinery industry situated in North India. The soil sample was collected from near composite well site, where several crude oil inlets merge and crude oil were processed for fractionation. Due to transportation and spillage of the crude oil, the soil was highly contaminated. The collected soil was analyzed for physico-chemical parameters, viz. particle size distribution, pH, electrical conductivity (EC), total petroleum hydrocarbons (TPH) concentration, total organic carbon (TOC), bulk density, porosity, maximum water holding capacity (MWHC), cation exchange capacity (CEC), etc.

Leachate was generated from the contaminated soil using a trough-shaped unit ($1 \text{ m} \times 1 \text{ m} \times 1 \text{ m}$). The unit was packed to the depth of 0.5 m with the contaminated soil leaving the head space above for holding water. The unit was divided into three 15-cm-long segments starting from the base of the unit by inserting annular rings between them. The annular rings acted as baffles to reduce sidewall flow condition so that water would pass evenly through the unit [19]. At the bottom of the unit, a layer of 10-cm gravels was placed followed by another layer of 5 cm sand for smooth percolation of leachate. The schematic diagram of the trough unit used for the leachate generation is represented in Fig. 1. A container was kept at the bottom of the unit for leachate collection. Leachate was collected in batches by passing a volume of water equal to the volume of soil in the unit. This process was continued until the COD of leachate reached a constant low level. The collected leachate and contaminated soil were stored in plastic barrels at 4 °C, to minimize any change in its physico-chemical and biological properties until the analysis and experiments were carried out.

The leachate was analyzed for different measurable parameters, viz. appearance, pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), color, biodegradability index (BI), total organic carbon (TOC). Further, the leachate sample was analyzed for GC–MS characterization.

Fig. 1 Schematic representation of the trough unit used for the collection of leachate from crude oil contaminated soil



Chemicals

C_8 – C_{40} hydrocarbon standard ($500 \mu\text{g ml}^{-1}$) and polycyclic aromatic hydrocarbons (PAH) standard ($1000 \mu\text{g ml}^{-1}$), were procured from Sigma Aldrich (USA) and was used for the preparation of calibration curve in GC–MS analysis. Dichloromethane (DCM), hexane, and cyclohexane (HPLC grade) were purchased from Finar (India) and used for the extraction of organic compounds from the contaminated soil and leachate. Reagents such as potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), silver sulphate (Ag_2SO_4), sulphuric acid (H_2SO_4), ferroin indicator, potassium dihydrogen phosphate (KH_2PO_4), magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), dipotassium hydrogen phosphate (K_2HPO_4), disodium hydrogen phosphate ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$), calcium chloride (CaCl_2), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ammonium chloride (NH_4Cl), sodium thio-sulphate ($\text{Na}_2\text{S}_2\text{O}_3$), sodium hydroxide (NaOH), etc., were of reagent grade and purchased from Fisher Scientific (India).

Wet air oxidation setup

The leachate was treated in a high pressure (HP) and high temperature (HT) wet air oxidation (WAO) reactor system (Parr, USA) made of stainless steel having total capacity of 1.8 L. The reactor could operate up to a maximum temperature of 350°C and the maximum pressure of 350 bars. The internal diameter of the reactor was 95 mm, and four-bladed turbine type impeller (I.D. 50 mm) was used for stirring. The stirring speed was kept constant at 400 rotations per minute (RPM) throughout the experiment which ensured adequate mass transfer from gas to the liquid phase. The reactor was provided with a pressure indicator gauge, a gas sparging

tube, a sampling port, a rupture disc as well as non-return valve at the gas inlet. The reactor was also equipped with a temperature controller unit and 2-kW electric heater was used to heat the reaction mixture to the desired temperature. The reactor was leakage proof and the valve of the reactor was tightly sealed with an end cap.

The pH of the collected leachate was considered as initial pH for the WAO pretreatment, therefore the pH of leachate was not adjusted during the pretreatment. For each experimental run, the reaction vessel was loaded with 500 ml of leachate having initial COD of $2000 \pm 10.64 \text{ mg l}^{-1}$. All lines were properly closed, ensuring the absence of any leakage from the reactor. Oxygen was supplied at the initial stage of the reaction and the stirring speed was fixed at 400 RPM for all the reaction conditions. Preliminary experiments were performed to investigate the effect of pH and stirring speed on % COD removal. The results of the preliminary experiments were described in detail under the “Result” and “Discussion” sections. WAO parameters were optimized by varying temperature in the range of 150 – 220°C , the oxygen pressure in the range of 10–25 bar and reaction time in the range of 10–25 min. The WAO pre-treated samples were analyzed for pH, COD, BOD, BOD_5/COD ratio after each experimental run.

Statistical design of experiments

Temperature, pressure, and time are the important parameters influencing the WAO treatment. These factors were optimized using two-level three-factor central composite design (CCD) [20–22]. Minitab software version 16.1 was used for the design of experiment. A total of 20 experimental



runs were carried out in order to maximize the response, i.e., % COD removal from crude oil leachate. A model was constructed based on the effect of independent variables on % COD removal for which the quadratic equation is generated as follows:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{1,1} X_1^2 + \beta_{2,2} X_2^2 + \beta_{3,3} X_3^2 + \beta_{1,2} X_1 X_2 + \beta_{1,3} X_1 X_3 + \beta_{2,3} X_2 X_3 \quad (1)$$

where Y (% COD removal) is the predicted response; X_1 , X_2 , X_3 are independent variables corresponding to temperature, pressure and time, respectively; X_1^2 , X_2^2 , X_3^2 are the squared effects of independent variables; $X_1 X_2$, $X_1 X_3$, $X_2 X_3$ are interaction effects; β_0 is the constant term; β_1 , β_2 , β_3 are the linear regression coefficients for individual factors; $\beta_{1,1}$, $\beta_{2,2}$, $\beta_{3,3}$ are the coefficients for squared effect; $\beta_{1,2}$, $\beta_{1,3}$, $\beta_{2,3}$ are the regression coefficients corresponding to interaction effects. All the quadratic coefficients in the equation (Eq. 1) were calculated by regression analysis of the experimental responses. In the CCD RSM design, lower and higher values corresponding to each independent variable were fixed based on the previously reported WAO studies (Table 1) [15]. The experiments were performed in the randomized order in duplicate. In order to minimize block effect on the predicted response, all the experimental runs were performed within a week by the same individual [23]. The GC–MS analysis of WAO optimized leachate was carried out to determine the degree of degradation of leachate components.

Analytical methods

The pH and electrical conductivity of all the samples were checked using a pH meter (Cyberscan Eutech 510, US) and an EC meter (HI 8730, Hanna instrument, US). Particle size distribution was analyzed by the Hydrometer method (IS 2720 Part 4). Bulk density, porosity, maximum water holding capacity (MWHC) were measured using K-R box method (USDA Gravimetric method). Cation exchange capacity (CEC) was determined by the acetate extract technique (IS 2720 part 24). TPH in soil was gravimetrically analyzed by the EPA method 9071 B. Total organic carbon (TOC) was measured by means of Shimadzu TOC-L instrument equipped with an ASI-V autosampler. The color of leachate sample was measured using the spectrophotometric

multi-wavelength method as per APHA 2120 D method. The sample analysis was performed at two pHs, one at original pH and other adjusted at pH 7 using sulphuric acid or sodium hydroxide. The sample was filtered using 0.22- μm filter in order to prevent the interference by particulate matter during spectrophotometric method. The readings were taken for the 10 ordinates and calculations were performed as per APHA guideline. COD and BOD were determined according to APHA standard protocols. The % COD removal of leachate from WAO treatment was calculated using the following formula:

$$\% \text{COD removal} = \frac{X_i - X_f}{X_i} \times 100 \quad (2)$$

where X_i and X_f represent COD of initial and WAO-treated leachate, respectively.

For BOD analysis, the seed was isolated from crude oil contaminated soil. In this process, contaminated soil suspension was incubated in Bushnell Haas medium containing 0.5% crude oil as the sole carbon source and incubated at ambient temperature for 1 week. The culture was enriched further by sub-culturing in medium containing a higher concentration of crude oil up to 1%. The final enriched culture was used as the seed.

Biodegradability index (BI) is the ratio of BOD_5 : COD, which is also a measure of the extent to which leachate is amenable to biodegradation. The COD and BOD of WAO treated leachate were analyzed as per the standard protocol provided by APHA, and compared with the initial leachate without WAO treatment.

TPH was extracted from the contaminated soil by means of soxhlet extraction (EPA method 3540 C) with dichloromethane as extracting solvent. 10 g of soil was blended with 10 g of anhydrous sodium sulphate and placed in an extraction thimble. After extraction, the collected extract was passed through anhydrous sodium sulphate column and concentrated in a rotary evaporator at a temperature of 35 °C. The final volume of the extract was around 2 ml. A 1 μl of the sample was analyzed by GC MS. Organic compound from leachate were extracted by liquid–liquid extraction (EPA method 3510C). The aqueous leachate solution was extracted 3 times with DCM. The organic fraction was passed through a packed sodium sulphate column to remove moisture content and then concentrated up to 2 ml using a

Table 1 Experimental factors and levels for RSM design

Variables	Factors	Levels				
		$-\alpha$	-1	0	$+1$	$+\alpha$
Temperature (°C)	X_1	126	150	185	220	244
Pressure (bar)	X_2	5	10	17.5	25	30
Time (min)	X_3	5	10	17.5	25	30



rotary evaporator. Finally, the sample was syringe filtered through 0.22 μ filter and analyzed using GC–MS instrument.

The GC–MS analysis was performed using Perkin Elmer Clarus 600 C Quadrupole gas chromatograph equipped with mass spectrophotometer detector. A DB-5 MS capillary column (30 m \times 0.25 mm ID \times 0.25 μ m) was used for the analysis of TPH in extracted samples, while, DB 624 Ultra inert (UI) capillary column (30 m \times 0.32 mm ID \times 1.80 μ m) was used for the detection of acetic acid in the aqueous leachate sample after WAO treatment. Helium was used as the carrier gas with a flow rate of 1 ml min⁻¹. The GC injection temperature was set at 250 °C. For TPH analysis, the column temperature was fixed at 60 °C, for 1 min, followed by heating at a rate of 6 °C min⁻¹ to 300 °C and hold for 20 min. For acetic acid analysis, the initial column temperature was maintained at 110 °C and then it was increased at the rate of 8 °C min⁻¹ to 150 °C with 1 min hold time. Afterwards, the column was heated at a rate of 8 °C min⁻¹ to 190 °C. The MS detector was operated in the EI mode (70 eV) and scanned from 40 to 500 amu for TPH and 40 to 200 amu for acid analysis.

The calibration curves for C₈–C₄₀ hydrocarbons and PAHs were prepared using varying concentration ranges, viz. 5, 10, 15, 20 and 25 ng μ l⁻¹ and their respective peak areas. All the standard solutions were prepared in DCM from the stock solution. The concentration of compounds present in untreated and WAO treated samples were determined on the basis of respective calibration curves. Further, the % degradation of compound was calculated using the formula:

$$\% \text{degradation of compound} = \frac{Z_i - Z_f}{Z_i} \times 100,$$

where Z_i and Z_f represent the initial and final concentration of compounds before and after WAO, respectively.

Results and discussion

Characterization of crude oil-contaminated soil and leachate

The physico-chemical characteristics of crude oil-contaminated soil and leachate are presented in Tables 2 and 3, respectively. The particle size distribution showed that percentage of sand was found to be around 98% in comparison to clay (2%) on the soil texture triangle diagram. The electrical conductivity of contaminated soil was found to be 206.5 μ s cm⁻¹ because of the high TPH percentage. The contaminated soil showed the pH of 7.04 \pm 0.15 and cation exchange capacity (CEC) of 5.37 \pm 0.26 meq/100 g. The higher CEC indicates the presence of a large amount of organic matter in soil. Further, the presence of long-chain hydrocarbons was confirmed from the GC–MS analysis.

Table 2 Physico-chemical characterization of the crude oil-contaminated soil

Parameters	Value
Particle size distribution	
Sand %	98
Clay %	2
Texture class	Sand
pH	7.04 \pm 0.15
EC	206.5 \pm 2.48 μ s cm ⁻¹
TPH	3.22 \pm 0.18%
TOC	6.64 \pm 0.16%
Bulk density	1334 \pm 14.64 kg m ⁻³
Porosity	4.733 \pm 0.12%
MWHC	2.979 \pm 0.24%
CEC	5.37 \pm 0.26 meq/100 gm

Table 3 Physico-chemical characterization of the leachate before and after wet air oxidation at optimized conditions (temperature = 244 °C, pressure = 5 bar, and time = 30 min)

Parameters	Before WAO	After optimized WAO
pH	7.12 \pm 0.08	6.98 \pm 0.12
COD	2000 \pm 10.64 mg l ⁻¹	480 \pm 9.63 mg l ⁻¹
BOD ₅	280 \pm 18.43 mg l ⁻¹	230 \pm 11.68 mg l ⁻¹
TOC	678 \pm 15.83 mg l ⁻¹	250 \pm 8.96 mg l ⁻¹
Color (at original pH)	Greenish yellow	Pale yellow
Color (at pH 7)	Greenish yellow	Pale yellow
BI	0.14 \pm 0.007	0.48 \pm 0.02

BI, biodegradability index

The pH of collected leachate was found to be 7.12 \pm 0.08. The recalcitrant nature of leachate is evident from high COD = 2000 \pm 10.64 mg l⁻¹, BOD₅ = 280 \pm 18.43 mg l⁻¹ and TOC content ~ 678 mg l⁻¹. The initial leachate has a biodegradability index (BI) of 0.14 which indicates its non-biodegradable nature. On the other hand, it is clear from the characterization data (Table 3) that the COD drastically reduced to 480 \pm 9.63 mg l⁻¹ after WAO treatment. The degradation of organic matter present in the leachate was confirmed from the TOC data, showing an overall TOC reduction of 63% after wet air oxidation (Table 3). Further, the BOD changes from 280 \pm 18.43 to 230 \pm 11.68 mg l⁻¹ after WAO and the biodegradability index (BI) was increased up to 0.48 \pm 0.02 after WAO corresponding to 71% increase in the BI.

The improvement in the biodegradability index (BI) after WAO may be attributed by the degradation of recalcitrant compounds present in leachate and getting transformed into the smaller organic compound like acetic acid, carbon dioxide, etc., making the leachate amenable to further biological



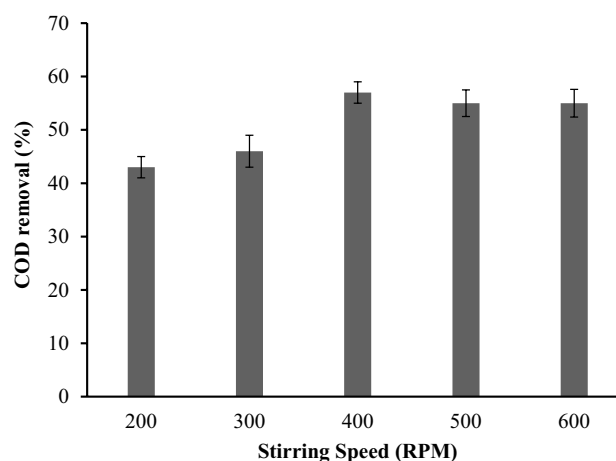
treatment. The effect of WAO was also reflected in color of the leachate which changed from greenish yellow to pale yellow (Table 3).

Effect of stirring speed

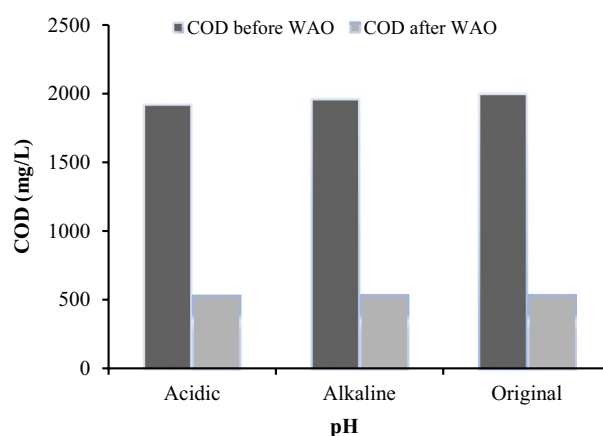
Wet air oxidation involves two significant stages; first one is the mass transfer of oxygen from the gas phase to the liquid phase and second is a chemical reaction between the transferred oxygen and organic compound present in the medium. Mass transfer of oxygen from gas to liquid phase plays a crucial role for the oxidation of long chain/complex organic compounds into smaller compounds which further enhances the % COD removal [24]. However, for good mass transfer of oxygen from gas to liquid phase, a turbulence has been required in the aqueous phase which was generated using a controlled agitation process. Further, in order to visualize the effects of agitation on % COD removal, the experiments were conducted at varying speed of agitation in the range of 200–600 rpm, and fixing the other variables as constant (temperature = 200 °C, pressure = 10 bar, time = 30 min) [24, 25]. The results depicts an increase in % COD removal with agitation speed with a maximum % COD removal of $57 \pm 2\%$ at 400 rpm as evident from Fig. 2a. Nevertheless, there is no significant effect in % COD removal by enhancing the agitation speed beyond 400 rpm (Fig. 2a). Therefore, all the optimization experiments were conducted at fixed agitation speed of 400 rpm.

Effect of pH

The experiments were performed at three different pH, viz. acidic (3.5 ± 0.08), original (7.12 ± 0.08), and alkaline (9.5 ± 0.12) to determine the effect of pH on COD of pre- and post-WAO-treated leachate. The experiments for studying the effect of pH on COD were conducted at temperature = 200 °C, pressure = 10 bar and time = 30 min. The initial COD of untreated leachate was found to be $2000 \pm 10.64 \text{ mg l}^{-1}$ at original pH, $1940 \pm 12.55 \text{ mg l}^{-1}$ at acidic pH and $1960 \pm 10.83 \text{ mg l}^{-1}$ at alkaline pH, respectively. From Fig. 2b, COD after WAO at acidic, original, and alkaline pH were found to be $535 \pm 8.75 \text{ mg l}^{-1}$, $540 \pm 7.68 \text{ mg l}^{-1}$ and $538 \pm 9.24 \text{ mg l}^{-1}$, respectively, which shows that no significant changes were observed in COD values. This may be due to the complex nature of leachate which was generated from crude oil contaminated soil. This leachate contains solubilized and emulsified hydrocarbon resistant to oxidation so that COD were not remarkably reduced before WAO. After this experiment, the conclusion was drawn that there is no need of pH adjustment of leachate before WAO. All the optimization experiments were performed at original pH without adjustment of pH.



(a) Effect of stirring speed on % COD removal



(b) Effect of pH on COD of Initial and after WAO of leachate

Fig. 2 a Effect of stirring speed on % COD removal. b Effect of pH on COD of initial and after WAO of leachate

Optimization and validation of optimized conditions

Response surface methodology was used to evaluate the correlation between independent variables and their effect on the dependent variable (% COD removal). The results from individual runs were analyzed by regression in order to optimize the significant factors influencing WAO conditions (Table 4). A quadratic polynomial equation was predicted as follows:

$$Y = 52.32 - 0.003X_1 + 0.923X_2 - 1.388X_3 + 0.0004X_1^2 + 0.019X_2^2 + 0.023X_3^2 - 0.008X_1X_2 + 0.003X_1X_3 + 0.008X_2X_3 \quad (3)$$

where X_1 = temperature, X_2 = pressure, X_3 = time.

The experimental- and model-predicted values were found to be in close accordance with each other as evident

Table 4 Central composite design (CCD) showing experimental run conditions and results

Std. order	Independent variables			Experimental (% COD removal) <i>Y</i>	Predicted (% COD removal) <i>Y</i>
	<i>X</i> ₁	<i>X</i> ₂	<i>X</i> ₃		
1	150	10	10	56.30	55.47
2	220	10	10	62.63	64.08
3	150	10	25	52.64	54.09
4	220	10	25	64.73	65.70
5	150	25	10	62.63	62.92
6	220	25	10	63.64	63.46
7	150	25	25	63.48	63.31
8	220	25	25	64.74	66.84
9	126	17.5	17.5	55.45	55.62
10	244	17.5	17.5	67.80	65.83
11	185	17.5	5	61.66	61.84
12	185	17.5	30	65.50	63.52
13	185	5	17.5	59.63	58.44
14	185	30	17.5	66.27	65.67
15	185	17.5	17.5	59.12	59.09
16	185	17.5	17.5	59.36	59.09
17	185	17.5	17.5	59.06	59.09
18	185	17.5	17.5	58.86	59.09
19	185	17.5	17.5	58.80	59.09
20	185	17.5	17.5	59.06	59.09

*X*₁ = temperature, *X*₂ = pressure, *X*₃ = time

from Fig. 3. Table 5 represents the results of analysis of variance (ANOVA). It was apparent from the ANOVA that the main effects of temperature and pressure ($p = 0.000$); the square effects of pressure ($p = 0.019$), time ($p = 0.007$) and the interaction effects of temperature and pressure ($p = 0.002$) significantly affected the COD removal (p values < 0.05). Further, the coefficient of determination was found to be $R^2 = 0.93$ which reveals that 93% of the variance in COD removal has been predicted accurately by using the independent variables. Figure 4a depicts the normal % probability and Studentized residuals plot which indicates satisfaction of the normality. The data point indicates the linearity with observed and model predicted values. The Studentized residual and predicted % COD removal of leachate plot is shown in Fig. 4b. The plot depicts the random scattering of data points around the central line in the range of ± 2 and resembles the data were accurate and trustworthy. The plot showed no abnormality.

The optimized conditions from RSM were found to be temperature = 244 °C, pressure = 5 bar, time = 30 min resulting in maximum predicted COD removal of 76% with the desirability of 1. In order to further validate and re-check the predicted optimum conditions and its effect on the response, additional experimental trials were run only at the optimized conditions and % COD removal was evaluated. The % COD removal thus obtained after the final experimental run was found to be 75%, which is in close accordance with the model-predicted values under optimized conditions.

Fig. 3 Experimental and predicted values for % COD removal

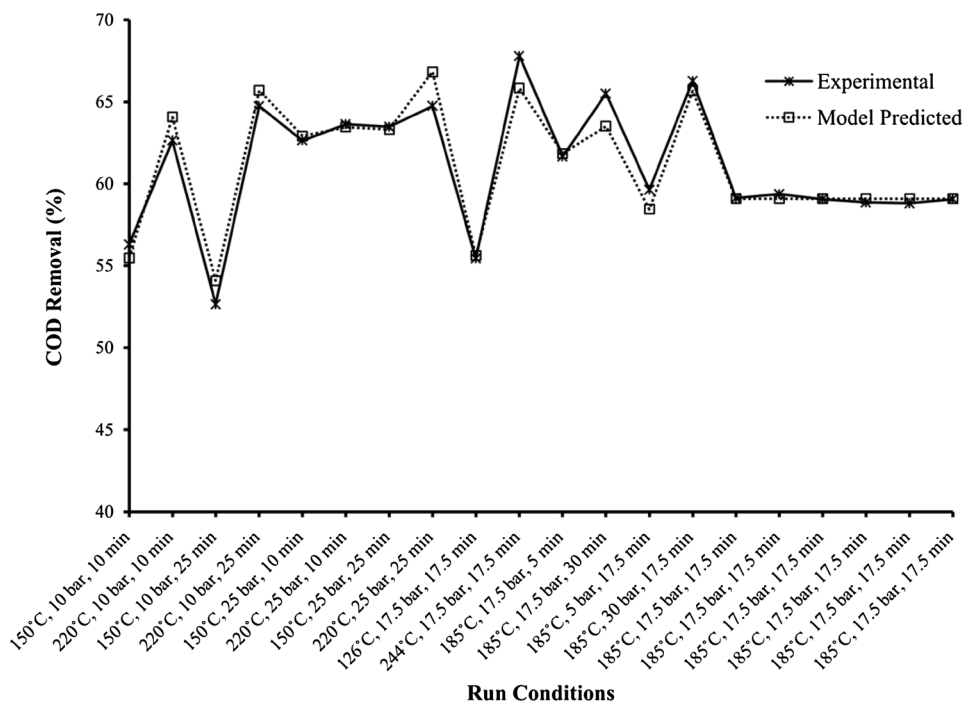
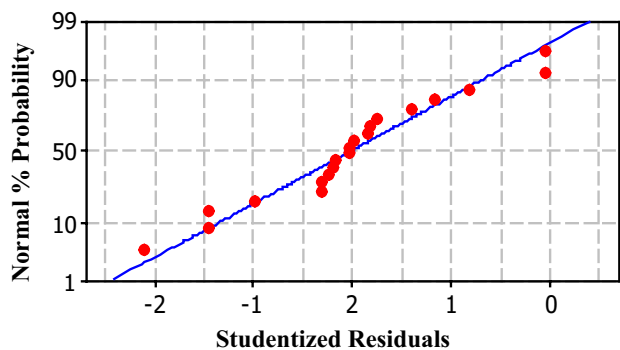
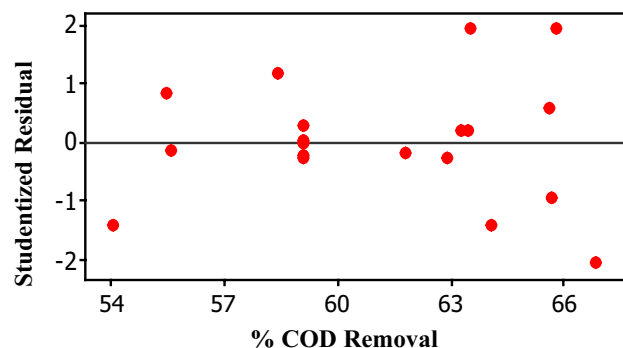


Table 5 Analysis of variance (ANOVA) data for % COD removal

Source	Degree of freedom	Adj MS	F	p
Regression	9	29.835	14.73	0.000
Linear	3	64.136	31.67	0.000
X_1	1	125.867	62.15	0.000
X_2	1	63.107	31.16	0.000
X_3	1	3.434	1.70	0.222
Square	3	12.484	6.16	0.012
$X_1 * X_1$	1	4.793	2.37	0.155
$X_2 * X_2$	1	15.742	7.77	0.019
$X_3 * X_3$	1	23.167	11.44	0.007
Interaction	3	12.886	6.36	0.011
$X_1 * X_2$	1	32.603	16.10	0.002
$X_1 * X_3$	1	4.515	2.23	0.166
$X_2 * X_3$	1	1.540	0.76	0.404
Residual error	10	2.025	–	–
Lack-of-fit	5	4.011	100.51	0.000
Pure error	5	0.040	–	–
Total	19			

$R^2 = 93\%$, X_1 = temperature, X_2 = pressure, X_3 = time

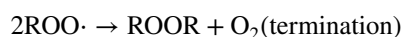
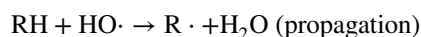
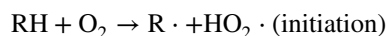
**(a)** Studentized residuals and normal % probability plot**(b)** % COD removal and Studentized residuals plot**Fig. 4** **a** Studentized residuals and normal % probability plot. **b** % COD removal and Studentized residuals plot

Study of the interaction effects

The effect of interaction between different independent variables and its impact on COD removal has been the key feature of the present study and was visualized by using contour plots.

Effect of temperature and pressure

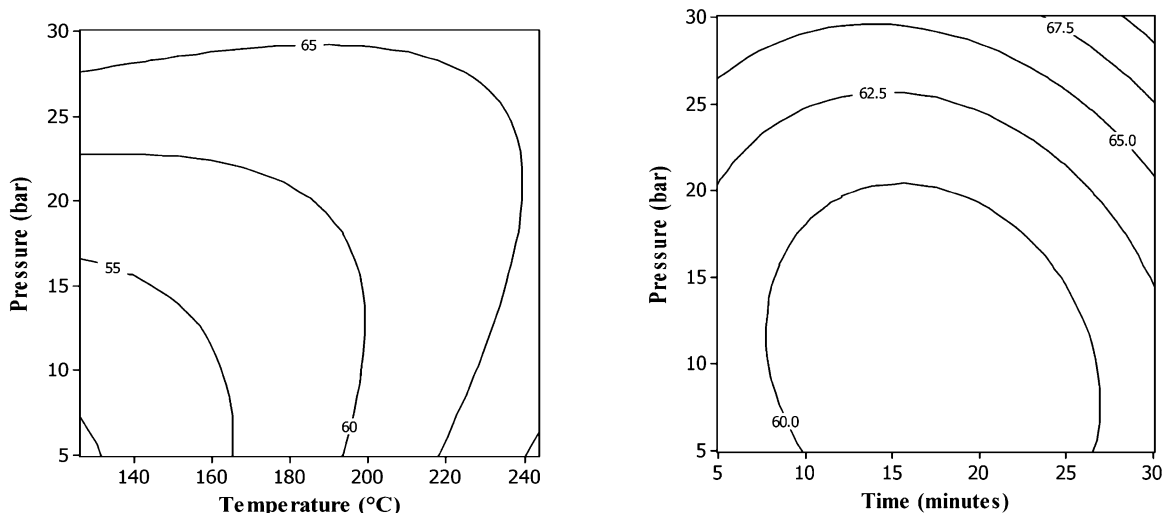
From Fig. 5a, it is evident that both temperature and pressure significantly affect the response. % COD removal increases with increase in temperature and pressure. A high COD removal of 65–70% has been observed as the temperature reaches above 220 °C and pressure increases to 27 bars with a hold time of 17.5 min. These experimental results were found to be in accordance with previous studies conducted by different researchers around the world, as reported by Luck [26]. The possible explanation behind the enhanced COD removal is as temperature and pressure increase inside the reactor, hydroxyl radicals are generated in presence of an O_2 -rich environment, which in turn react with the hydrocarbon C–H bond and enhance the rate of decomposition [27]. Furthermore, the addition of molecular O_2 initiates a chain reaction (initiation, propagation, and termination) as described below [27–29]:



These reactions generate organic radicals, hydroxyl radicals and free radicals which may be the reason for higher % COD removal. Generally, the WAO reaction involves the breakdown of complex organic molecules into intermediates with lower carbon atoms under high temperature and pressure. These molecular breakdown reactions leads to the formation of carboxylic acids, viz. acetic acid or formic acid which are eventually converted into CO_2 and H_2O as the final product [30].

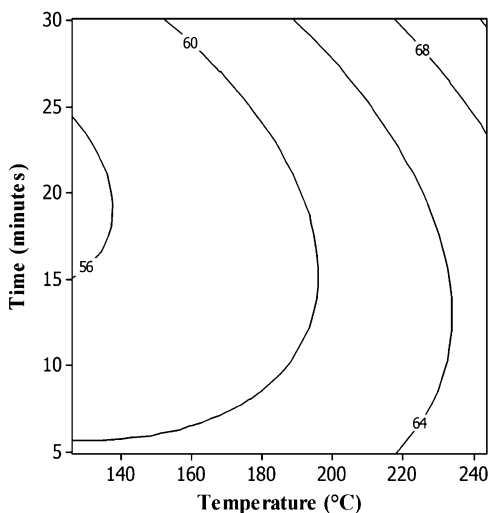
Effect of time and pressure

Figure 5b presents the effects of pressure and time on % COD removal. From the figure, it is significant that % COD removal increased with increase in pressure and time which is also evident from the ANOVA results (Table 5) which reveals that both the individual effect ($p = 0.000$) and square



(a) Contour plot showing the effect of temperature and pressure on % COD removal at a given time (17.5 minute)

(b) Contour plot showing the effect of time and pressure on % COD removal at a given temperature (185 °C)



(c) Contour plot showing the effect of temperature and time on % COD removal at a given pressure (17.5 bar)

Fig. 5 **a** Contour plot showing the effect of temperature and pressure on % COD removal at a given time (17.5 min). **b** Contour plot showing the effect of time and pressure on % COD removal at a given tem-

perature (185 °C). **c** Contour plot showing the effect of temperature and time on % COD removal at a given pressure (17.5 bar)

effects of pressure ($p=0.019$) and the square effect of time ($p=0.007$) are significant. Further, at lower pressure (5 bar, time = 30 min) % COD removal was found to be in the range of 60–62%, which is lower than the % COD removal at high pressure (30 bar, time = 30 min) which was 67–70%. The plausible reason behind this may be explained on the basis of the fact that the organic compounds are degraded to recalcitrant organic compounds, i.e., low-molecular weight carboxylic acid with time which are resistant to further oxidation [30].

Effect of temperature and time

Figure 5c represents the interaction effect of temperature and time at a given pressure. A COD removal of 72% was obtained at a temperature of 240–245 °C and time of 30 min with pressure hold value of 17.5 bars. It is evident from Fig. 5c that no significant effect on % COD removal was observed if only reaction time is raised at any given temperature. However, the vice versa is not necessary the same. This is because when the temperature was

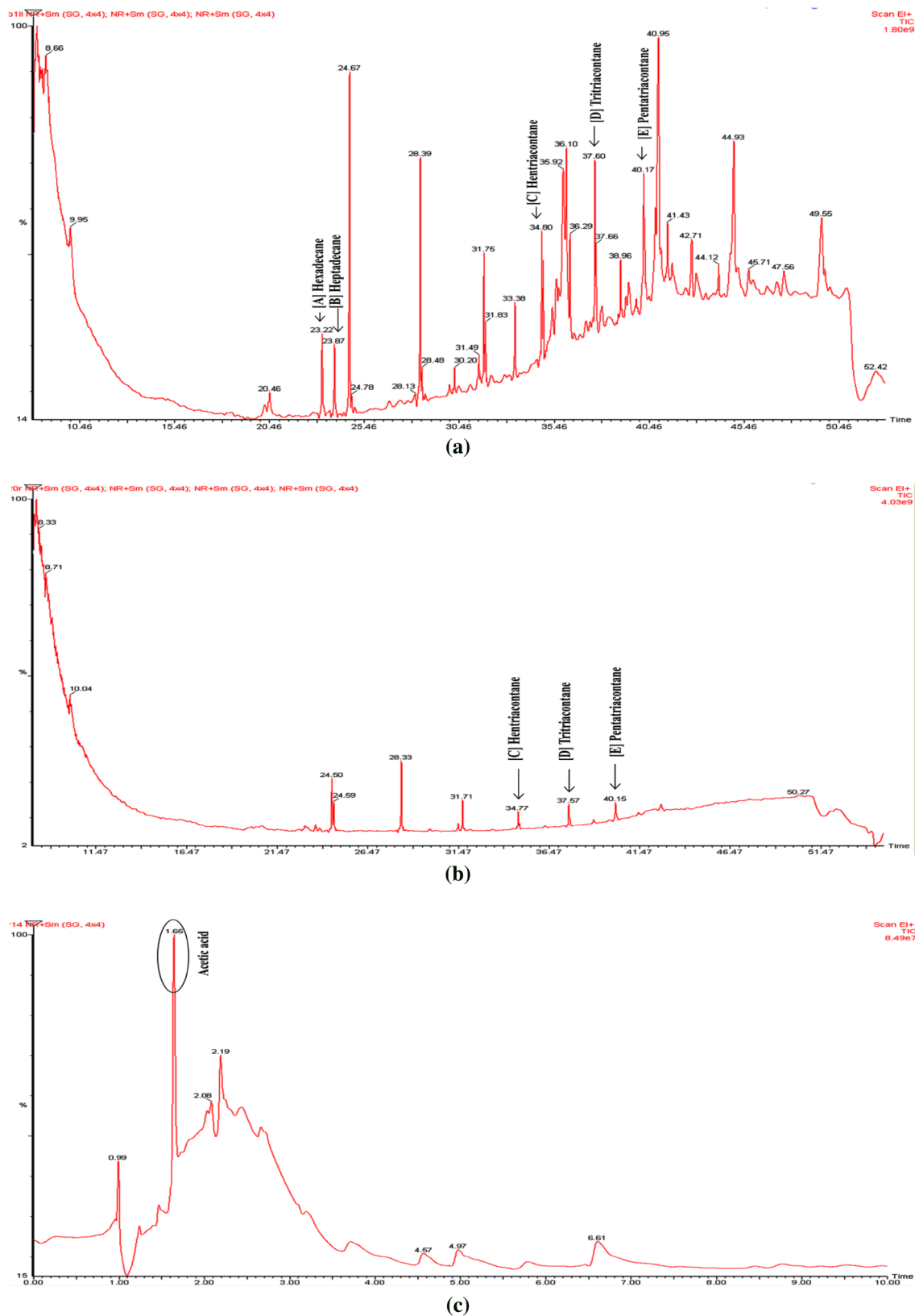


Fig. 6 GC–MS chromatogram of **a** initial leachate, **b** WAO-treated leachate and **c** WAO-treated leachate showing peak of acetic acid

Table 6 % degradation of long-chain hydrocarbon compounds

Peak	Compound	Chemical formula	Molecular weight (g mol ⁻¹)	% degradation
A	Hexadecane	C ₁₆ H ₃₄	226	96 ± 1.24
B	Heptadecane	C ₁₇ H ₃₆	238	93 ± 1.68
C	Hentriacontane	C ₃₁ H ₆₄	436	68 ± 1.88
D	Trtriacontane	C ₃₃ H ₆₈	464	66 ± 2.09
E	Pentatriacontane	C ₃₅ H ₇₂	492	55 ± 1.98

increased and time was kept constant (for e.g., 10 min), the maximum % COD removal was increased to 64–68% (refer to Fig. 5c). This finding was further supported by the ANOVA results (Table 5), which also shows that the temperature has been a significant factor ($p = 0.000$).

However, most of the results of the present study could not be compared with the available literature, because there are no data available for the treatment of leachate containing solubilized and emulsified hydrocarbons generated from crude oil-contaminated soil sites which further adds to the novelty of this work.

GC–MS analysis

The GC–MS chromatogram of initial and WAO-treated leachate is shown in Fig. 6a, b. The analysis of initial leachate showed the presence of long-chain aliphatic hydrocarbons, viz. hexadecane (C₁₆H₃₄), heptadecane (C₁₇H₃₆), hentriacontane (C₃₁H₆₄), trtriacontane (C₃₃H₆₈), and pentatriacontane (C₃₅H₇₂). The leachate was treated by WAO under the operating conditions optimized by RSM. The intensity of peaks in WAO-treated leachate chromatogram was lower than the initial leachate indicating degradation of compounds. Few residual peaks in the treated leachate may correspond to relatively recalcitrant compounds. The percentage degradation of the above-mentioned compounds is shown in Table 6.

The GC–MS analysis confirmed the presence of carboxylic acid like acetic acid in the WAO-treated leachate which is shown in Fig. 6c. It has been widely reported that, acetic acid is recalcitrant to further oxidation [30] and contributes to residual COD at the end of WAO process.

Conclusions

The current study addresses the issue of safe disposal of leachate generated during bioremediation of crude oil-contaminated soil. These leachates contain emulsified and solubilized non-biodegradable and partially degraded eco-toxic hydrocarbons. As these hydrocarbons have already escaped bioremediation, a stronger treatment is necessary for their removal. This study establishes wet air oxidation (WAO) to be a promising technique for treatment of leachate generated

from crude oil-contaminated soil for the first time. The optimization of WAO process was found to result in removal of 75% COD and 3.4-fold increase in biodegradability index (BOD5/COD) of the crude oil leachate. The degradation of crude oil leachate components was corroborated by GC–MS analysis. Thus, we propose WAO to be an effective pretreatment step for crude oil leachate, making it amenable to subsequent biological treatment.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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