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Produced water treatment using olive leaves

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ABSTRACT

Olive leaves powder (OLP) was employed as a low cost adsorbent for the removal of hexane extractable crude oil from simulated produced water. The effect of contact time, adsorbent dosage, pH, salinity as well as temperature on the efficiency of oil removal was investigated. The optimum parameters for oil removal were determined to be pH = 7.0, adsorbent dose = 3.0 g/L, contact time = 80.0 min and salinity of 1,000 ppm in terms of NaCl at 25.0°C. The adsorption of crude oil by OLP was found to follow the Langmuir adsorption isotherm, with adsorption capacity of 143mg/g. The adsorption kinetics best described by pseudo-second-order with rate constant of 1.6×10^{-3} (g/mg.h). Heavy metal content of produced water and the ability of olive leaves to remove these heavy metals were also studies. The fraction of crude oil removed as well as the nature of olive leaves surface were characterized by thermal analysis, gas chromatography-mass spectrometry and infrared spectroscopy. The results render OLP as an excellent adsorbent for the removal of hexane extractable fraction of crude oil from produced water with an efficiency exceeding 80% in 80 min.

Keywords: Produced water; Olive leaves; Bio-sorbent; Equillibrium isotherms; Organic and inorganic pollutants

1. Introduction

In spite of its huge benefits and impacts on mankind, oil and gas industry has turned out to be one of the major risk on environment since it generates sheer volumes of produced water as byproduct along with the other valuable products [1–3]. There are various factors affecting the quantity of produced water generated where an average of 3–9 barrels of produced water per barrel of oil is generated. Such amount would amplify up to 98% of the material recovered from oil wells in the case of mature or aging fields [3–8]. Characteristics of the produced water depend on, but not limited to, several factors including geological location, type of hydrocarbon produced, geological formation, life time of the well including the fact that the constituents might vary over time in the same reservoir in addition to other factors such as operational, recovery and treatment chemicals [7,9,10]. Therefore, the constituents of produced water as well as its oil/water partition coefficient, oil fraction in the dissolved and suspended forms, toxicity, bioavailability, and biodegradability varies to a wide extent depending on a variety of interrelated factors [5,10–14]. Treatment of such large volumes of produced water with variable characteristics has been exigent and tricky for the industry as well as researchers especially with the enforcement of strict environmental policies by the environmental regulatory authorities associated with the potential toxic hazards of the discharge and water scarcity [5,15–19]. In view the above details, several techniques have

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been applied in industry for the removal of oil that includes filtration, de-emulsification, flocculation, coagulation and adsorption [20–26]. Among all, adsorption has been found to be the most effective in removal of matter from water; however, it involves higher economic costs [20–26]. In addition, various other methods including physical, chemical, and heat treatments have been employed to get the best results in terms of cost effectiveness, operation durability, and space requirements among which biological treatments have been sorted to be most cost effective and environment friendly. A milestone has been marked for the use and research on naturally abundant and inexpensive biosorbents. Various studies have been conducted on the effectiveness of biosorbents on the removal of oil from the produced water [27–39]. These include pomegranate peels [27], banana peels [29] and egg shells [30].

Olive (*Olea europaea*), evergreen tree covering an area of 10 million hectare with an approximated global production of 3 million metric tons of olive oil, is not only known internationally for its health, medical and nutritional benefits but also has been found effective in the removal of heavy metals from waste waters in the recent years using olive cake and leaves [40–45]. Italy, Portugal, Turkey, Greece, Syria and Spain are the main producers of olive worldwide, with Spain being the largest producer with an average production of 1.2 million metric tons [44]. Being quiet abundant in nature and with potential to be used as biological adsorbent, olive leaves may prove to be the best suitable alternative for the removal of oil from industrial waste waters.

In this paper, olive leaves powder (OLP) is examined as biosorbent for crude oil removal from produced water. The optimum adsorption parameters included in this study are sorption dosage, sorption time, pH, oil initial concentration, salinity and temperature. Moreover, kinetic parameters and adsorption isotherms have been deduced. The surface of OLP was characterized by Fourier transform infrared (FTIR), and thermal analysis (TGA). The nature of oil adsorbed on OLP was characterized using gas chromatography–mass spectrometry (GC-MS).

2. Materials and methods

2.1. Materials and instrumentations

The olive leaves were brought from Palestine. Crude oil was obtained from Abu-Dhabi National Oil Company (ADNOC), UAE. Analytical grade n-hexane (95% pure, J.T. Baker), oil surfactant (ENDCOR OCC9783, General Electric Water, UAE) and double distilled water (Water Still Aquatron A4000D, UK) were used. Fluidized bed dryer (Sherwood Scientific, UK) with precise vacuum oven (Model WOV-30, DAIHAN Scientific Co. Ltd., Korea) fitted with a vacuum pump (Model G-50DA,Ulvac Kiko, Japan) was used to dry the powdered sorbent. Separation and classification into different sizes (500–150 microns) were done following ASTM C136 for sieving (stainless steel; Aperture 150–500 micro meter (Pascal Engineering Company, UK). A fuzzy control system was used as digital reciprocating shaker (Model SHR-2D, DAIHAN Scientific Co. Ltd., Korea). For temperature control, hot plate stirrer (Model MSH-20D, DAIHAN Scientific Co. Ltd., Korea) was used. The samples were mixed using mechanical shaker. The oil was analyzed using UV-VIS spectrophotometer (Model DR-5000, HACH, USA) at wavelength 275 nm. pH measurement were done by a pH meter (3320, JENNWAY Ltd., UK). The pH of all solutions was adjusted using either 0.1–1 M HCl or 0.1–1 M NaOH. FTIR spectroscopy (Bomem MB-3000 equipped with ZnSe optics and a DTGS detector) was used to obtain spectra for olive leaves before and after treatment. Total Metals was determined using Varian Liberty axial sequential inductively coupled plasma-optical emission spectrometer (ICP-OES: Varian, Australia). Thermogravimetric (TG) and differential thermogravimetric (DTG) curves were obtained by measuring the change in the mass of sample with temperature using thermal analyzer (TA: Perkin-Elmer thermal analyzer, USA). A QP2010 Ultra Thermal Desorption-Gas Chromatography-Mass Spectrometry (TD-GC-MS: Shimadzu, Japan) was used to identify the volatile and semi-volatile organic compounds present in the samples included in this study. Accurately weighed samples, around 50 mg in mass, were places in a clean desorption tubes. The desorption temperature was set to 300°C at which the samples were desorbed for 10 min at 50 mL/min and collected in a secondary trap prior to purging into the GC column. Split injection mode of 30:1 was used with injection temperature equivalent to 280°C. The initial temperature of the oven was maintained at 40°C for 3 min, and then increased at a rate of 5°C/min to 300°C where it was held constant for 15 min. The column flow was set at 41.6 ml/min. A 30-meter Rtx-5MS column (crossbond 100% dimethyl polysiloxane) was used from Restek, USA.

2.2. Bio-sorbent preparation

Olive leaves was thoroughly washed with doubled distilled water and then air-dried for 24 h. The olive leaves were ground to particle sizes between 2 and 3 mm and it was further dried using fluidized bed drier at 70°C. The shredded leaves was then refluxed for 3 h in n-hexane (after that the leaves were kept and a new batch of n-hexane was introduced and refluxed again for 3 h) in order to remove hydrophobic soluble organic matter and colored pigments. The treated olive leaves were then washed thoroughly with doubled distilled water for several times and dried in fluidized bed dryer. A grinder was used to obtain fine OLP and it was sieved through 500–150 micron sieve. Finally the fine powder of olive leaves was washed with double distilled water and dried in a vacuum oven at 76°C for 24 h. The treated adsorbent (OLP) was homogenized and then stored in air tight glass containers.

2.3. Emulsified simulated produced water (SPW) preparation

Known mass of crude oil, with American Petroleum Institute (API) quality grade of less than 22.3, was dispersed in water-surfactant mixture (60:40 w/w) to obtain the required concentration of oil in produced water. Water-surfactant mixture instead of deionized or distilled water was preferred for oil-in-water-surfactant mixtures (SPW) preparation since deionized or distilled water is rarely a constituent of industrial produced water while surfactants are normally an intrinsic part of such industrial waste streams.

2.4. Adsorption experiments

To find the equilibrium time, 16 samples of 100 mL SPW solution with oil concentrations of 250 ppm and 0.3 g of OLP were placed in 250 mL conical flasks. The solutions were agitated at 150 rpm for different time intervals using mechanical shaker at ambient conditions and initial pH of 7.25. Then the bio-sorbent and sorbate were separated using a centrifuge. Oil content remaining in the treated water was extracted twice using 9 mL of n-hexane solvent each time. The absorbance of the n-hexane extract at wavelength of 275 nm was then recorded using Hack spectrophotometer. The amount of oil removed by the OLP was determined from a calibration curve. Similar experiments were performed using SPW concentrations of 150 ppm, 250 ppm, 300 ppm and 400 ppm.

2.5. Effect of pH, salinity, temperature and OLP dosage

The effect of pH, OLP dosage, temperature and salinity on oil removal efficiency was investigated. The pH values were varied between 3 and 10. In this experiment, oil content of 250 ppm and contact time for 80 min. Similarly, the bio-sorbent dosage was varied between 1 and 7 g/l. Furthermore, the effect of temperature was determined by varying the solution temperature in the range of 25°C–50°C. Finally, the salinity was varied between 0 and 2,000 ppm using NaCl and adjusting the initial pH to 7.25.

3. Results and discussions

3.1. Effect of pH

The significance of pH in adsorption processes using biosorbents is implicit due to its effects on available binding sites as well as on biosorbent surface properties [46]. Fig. 1 shows the variation of the percent removal of oil from SPW by OLP with pH. At lower pH, the efficiency of OLP in removing oil from produced water increases until the mixture become neutral. The increase in the removal efficiency in this region with increasing pH can be attributed to the hydrophobic nature of OLP in this pH region and the destabilization of produce water mixture [35,47]. At pH 4.5, the removal efficiency of OLP was 28% which increased to 57.9% at neutral conditions. Inspection of Fig. 1 reveals that further increase in the alkalinity was not favorable for the adsorption process as the removal efficiency started to show slight decrease as the pH of the medium increased from neutral to highly alkaline medium. The pH in this region seems to stabilize the SPW and therefore negatively impact the adsorption process.

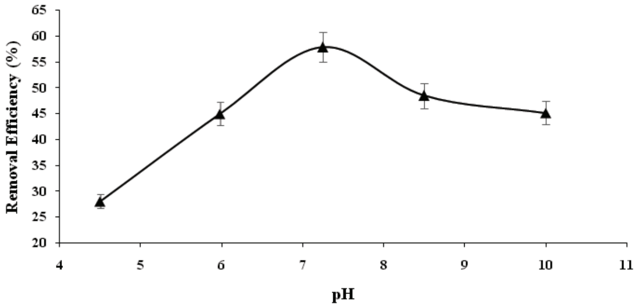

Fig. 1. Effect of pH on the percent removal of oil from SPW by OLP.
Note: The stirring speed was 150 rpm, stirring time was 80 min, adsorbent dosage was 3 g/L, T = 25.0°C, and SPW initial concentration was 250 ppm.

3.2. Effect of OLP dosage

The removal efficiency of oil from SPW by OLP was studied by varying the initial biosorbent concentration in SPW from 1.0 to 7.0 g/L. The mixture was stirred for 80 min with neutral pH and at ambient temperature (Fig. 2).

The efficiency increased appreciably as the biosorbent concentration increased from 1.0 to 3 g/L after which no appreciable change in the removal of oil from the produced water was observed. The results clearly indicate that the 3 g/L is the optimum biosorbent concentration to be used.

3.3. Effect of contact time

To study the effect of contact time on adsorption efficiency of oil from SPW by OLP and to determine the equilibrium time, the removal efficiency of oil from SPW by OLP was measured at room temperature with varying time interval from 10 to 150 min. Fig. 3 shows that the removal efficiency increased to 58% within 80 min after which no appreciable change was observed. Hence, it can be concluded that the optimum equilibrium time is 80 min. Further experiments were carried out at this optimum time to assure that the system reached equilibrium prior to any further measurements.

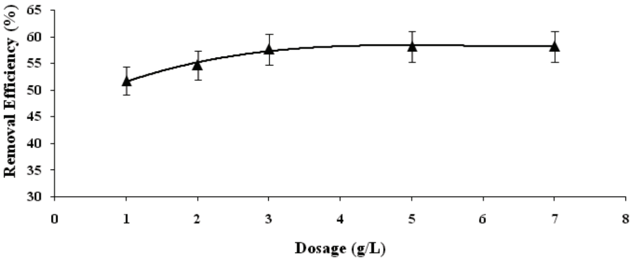

Fig. 2. Effect of OLP dosage on the percent removal of oil from SPW.
Note: The stirring speed was 150 rpm, stirring time was 80 min, pH was 7.25, T = 25.0°C, and SPW initial concentration was 250 ppm.

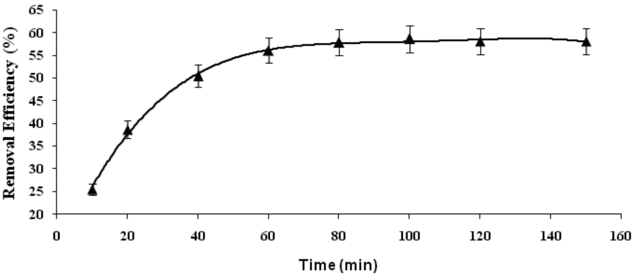

Fig. 3. Effect of contact time on the percent removal of oil from SPW.
Note: The stirring speed was 150 rpm, pH was 7.25, OLP dosage was 3.0 g/L, T = 25.0°C, and SPW initial concentration was 250 ppm.

3.4. Effect of temperature

To study the effect of temperature, the efficiency of oil removal from SPW by OLP was carried out at three different temperatures ranging from 25, 40 and 50°C while keeping other parameters at optimum conditions (Fig. 4). The variations in the removal efficiency of OLP with temperature are quite pronounced. Inspection of Fig. 4 reveals that as temperature increases, a sharp decrease in the removal efficiency is observed. Furthermore, Fig. 4 reveals that 25°C is the optimum temperature for oil removal from SPW using OLP. An increase in temperature from 25 to 50°C resulted in decrease of the removal efficiency from 80% to 40%. This is not surprising since adsorption processes are usually exothermic in nature.

3.5. Effect of salinity

The variations in the removal efficiency of biosorption process by salinity are of prime importance. Fig. 5 displays the effect of salinity on the percent removal of oil from SPW by OLP. It is evident that the involvement of NaCl, saline medium, seems to support the oil removal from the samples. The increased oil removal efficiency by OLP can be attributed to the fact that the emulsion (produced water) became unstable with the introduction of NaCl in the medium. Any instability in the emulsion would result in the separation of oil and the surfactant molecules thus increasing the possibility of oil particles to be retained on the surface of OLP. The optimum NaCl dosage was chosen experimentally to be 1,000 ppm.

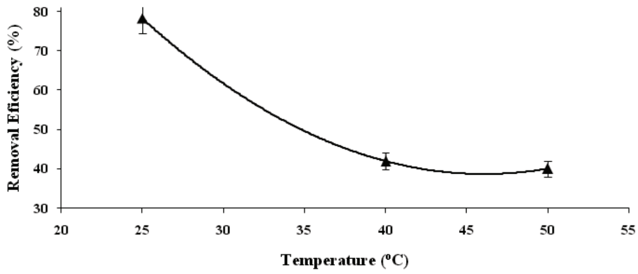

Fig. 4. Effect of temperature on the percent removal of oil from SPW. Note: The stirring speed was 150 rpm, stirring time was 80 min, pH was 7.25, OLP dosage was 3.0 g/L, and SPW initial concentration was 250 ppm.

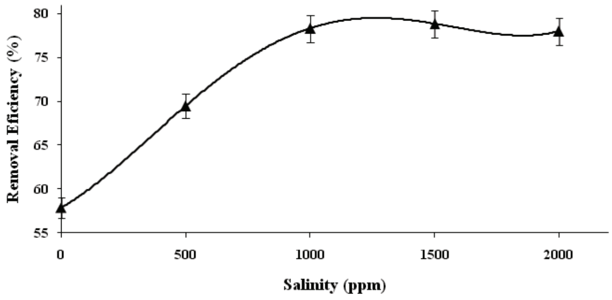

Fig. 5. Effect of salinity on the percent removal of oil from SPW. Note: The stirring speed was 150 rpm, stirring time was 80 min, pH was 7.25, OLP dosage was 3.0 g/L, T = 25.0°C, and SPW initial concentration was 250 ppm.

3.6. Heavy metal removal

Real produced water samples were analyzed, before and after adsorption, for heavy metal content. Table 1 summarizes the results obtained from ICP analysis. The analyzed samples were found to contain Al, Cr, Cu, Fe and Ni. Other elements were not identified simply because they are either absent or present in amounts below the detection limit of the instrument. Table 1 reveals that Al and Cr were efficiently adsorbed by OLP, whereas Cu was not adsorbed at all and Fe was found to increase in concentration due to possible leaching from OLP. Table 1 also includes heavy metal content of crude oil from the field for comparison.

3.7. Adsorption isotherms

Being of prime importance, the study of sorption equilibrium of oil from SPW by OLP was studied. Freundlich and Langmuir are the most commonly used isotherms in liquid applications [48]. The experimental data were correlated using Freundlich (Eq. (1)), Langmuir (Eq. (2)) and Temkin (Eq. (3)) adsorption isotherms.

$$Inq_e = InK_f + \frac{1}{n}InC_e \tag{1}$$

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{C_e}{q_m} \tag{2}$$

$$q_e = BInK_T + BInC_e \tag{3}$$

where C_e and q_e represents equilibrium concentration and equilibrium mass of adsorbate adsorbed per gram of adsorbent, K_f and q_m is adsorption capacity, whereas n and K_a refers to adsorption constants for Freundlich isotherm. B and K_T are constants and are biosorbent related.

Regression coefficient (R^2) for the above generated plots provided values of 0.965, 0.996 and 0.990 in case of Freundlich, Langmuir and Temkin isotherms, respectively. Thus, the best fit of 0.996 is presented by Langmuir isotherm thus suggesting the applicability of this isotherm for the adsorption process of oil on OLP with adsorption capacity of 143 mg/g (Fig. 6). The parameters of these isotherms are presented in Table 2.

Table 1
Heavy metals concentration in crude oil, produced water before and after treatment with olive leaves.

Heavy metal	Concentration (ppm)		
	Crude oil	Produced water before treatment with OLP	Produced water after treatment with OLP
Al	55.6	5.62	1.20
Cr	56.2	1.32	1.03
Cu	19.8	0.400	0.40
Fe	272	1.60	4.00
Ni	230.	4.60	4.40

Note: SPW initial concentration was 250 ppm; olive leave dosage was 3.0 g/L; T = 25.0°C.

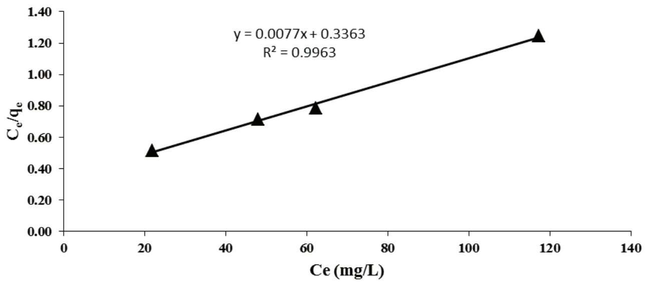

Fig. 6. Linearized Langmuir isotherm for the removal of oil in SPW by OLP at room temperature, 3 g/L biosorbent dosage, 1000 ppm salinity, stirring time of 80 min and pH of 7.25.

Table 2
Equilibrium adsorption isotherm parameters

Isotherm model	Parameters		R^2
Langmuir	q_m (mg/g)	143	0.996
	K_a (L/mg)	2.00 × 10⁻²	
Freundlich	K_f	10.1	0.965
	n	2.08	
Temkin	K_T	2.00 × 10⁻²	0.990
	B (L/g)	31.3	

3.8. Adsorption kinetics

To investigate the biosorption mechanism, kinetic models were applied at optimum conditions. Pseudo-first-order and pseudo-second-order kinetics are claimed to be most suitable for biosorption studies [49]. In this study, experimental data were fitted to linearized forms of pseudo-first-order (Eq. (4)), and pseudo-second-order (Eq. (5)) kinetic models.

$$In(q_e - q_t) = -k_I t + Inq_e \tag{4}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_{II} q_e^2} \tag{5}$$

where q_t represents sorbate amount at given time, while k_I, k_{II}, refers to the rate constant for pseudo-first-order and pseudo-second-order reactions, respectively.

Regression coefficients (R^2) for the two models were determined to be 0.976 and 0.997, respectively; thus, demonstrating that the biosorption of crude oil onto OLP is obeying pseudo-second-order reaction kinetics with reaction rate constant of 1.6 × 10⁻³ (g/mg.h) (Fig. 7). The parameters of pseudo-first-order and pseudo-second-order kinetics are mentioned in Table 3.

3.9. OLP characterization

3.9.1. FTIR spectroscopy

OLP was refluxed with n-hexane for 6 h and dried. The FTIR spectra were collected for untreated OLP, treated OLP with n-hexane and treated OLP after adsorption of oil from SPW (Fig. 8). The results points out that there are no measurable differences between the spectra of the olive before and after hexane treatment even though some decolorization was observed experimentally. Fig. 8 reveals a major enhancement in the intensity of the absorption peaks of the OLP spectra after loading with oil which provides evidence, that OLP has retained oil fractions that contains aromatic, carboxylic and aliphatic in nature.

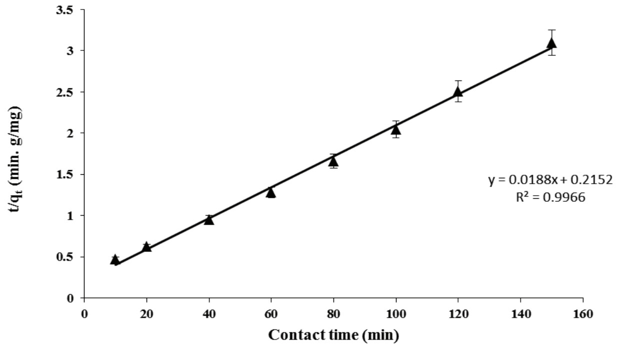

Fig. 7. Linearized pseudo-second-order fit for the removal of oil in SPW by OLP at room temperature, 3 g/L biosorbent dosage, 1,000 ppm salinity, SPW initial concentration of 250 ppm and pH of 7.25.

Table 3
Kinetic model parameters for biosorption of oil onto the surface of OLP

Kinetic model	Parameters	Value
Pseudo-first-order	k_I (g/mg h)	6.47 × 10⁻³
	R^2	0.976
Pseudo-second-order	k_{II} (g/mg h)	1.64 × 10⁻³
	R^2	0.997

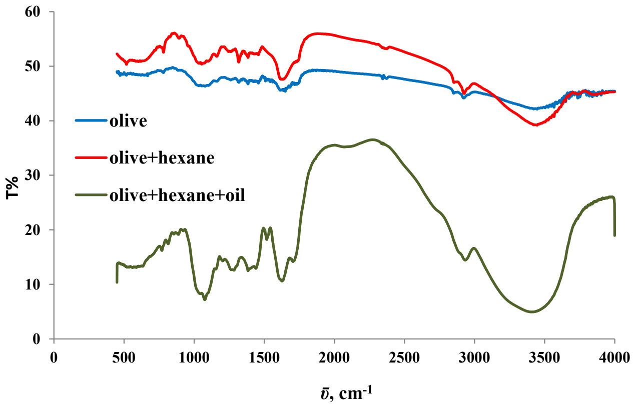

Fig. 8. FTIR spectra of olive without treatment, olive treated with n-hexane (OLP) and OLP after oil loading.

3.9.2. Thermal analysis

Thermal Analysis was carried out using PerkinElmer thermal analyzer. A method adapted for this analysis based on the following settings: heating rate 10°C/min under flow of nitrogen gas at flow rate of 100 mL/min. About 8–15 mg sample was used for each measurement where TG and DTG curves were obtained by measuring the change in the mass of sample with temperature. The TG curves (Fig. 9) present the % weight loss caused by the decomposition of surface functional groups or as a result of desorption of adsorbed compounds with heating.

The TGA analysis of the three samples revealed very interesting results (Fig. 9). The initial weight loss (<110°C) is most likely due to evaporation of any residual water since most of the highly volatile compounds are assumed to be removed by the initial treatment. TG curves show that washing the olive with hexane cleaned the surface of the olive by removing compounds of higher boiling points than water. It is evident that the main weight loss after hexane treatment is in the temperature range of110°C–300°C. Such compounds would have possible interference with the adsorption of oil on the OLP sample. Adsorption of oil from SPW on the hexane-treated olive samples showed noticeable removal of a wide range of oil compounds as it appears from the difference in the weight loss of the treated olive sample before and after oil adsorption. It is worth noting the noticeable weight loss is in the temperature range 350°C–550°C which indicates the removal of high boiling point compounds from oil.

DTG curves were then calculated from TG curves and are presented in Fig. 10. The position of the peaks on DTG curves is related to the thermal stability of the surface groups [50]. The shape and position of the peaks refers to the type and thermal stability/ binding energy of the decomposed/ desorbed groups. Hexane treatment results in the removal of volatiles mainly those of thermal stability/ binding energy below 300°C. However, it is noticeable that the hexane treatment has shifted the thermal stability of other species to higher temperature assuming no direct chemical reaction has occurred between hexane and the surface of the olive. In addition, it is evident that OLP sample is efficient in adsorption of compounds of boiling points below 300°C.

More quantitative details were extrapolated from the TG curves and summarized in Table 4. The change in the olive sample as a result of hexane treatment is evident where significant amount of species were removed from the surface of olive. That is clear in the changes in the percent weight loss from the olive sample as a result of such treatment. Hexane treatment resulted in the removal of 0.93, 9.75 and 10.12% wt in the temperature range 30°C–120°C, 120°C–300°C and 300°C–800°C indicating that 20.8% by weight of the surface compounds were removed by the hexane treatment.

Adsorption of oil on the hexane-treated olive showed that the olive have high affinity for the oil compounds mainly those of boiling points higher than 110°C where a noticeable change in the percent weight loss after oil adsorption were calculated from the thermal desorption profiles. The amount of oil desorbed from the surface of olive are 14.22% and 4.20% wt in the temperature ranges below 120°C–300°C and 300°C–800°C, respectively. Accounting for the slight initial change in weight, the results indicate that the olive was capable of removing about 16.74% of oil by weight which is equivalent to 167.4 mg/g. Such results are very close to the adsorption capacity predicted by Langmuir model (143 mg/g) and support the validity of the isotherm.

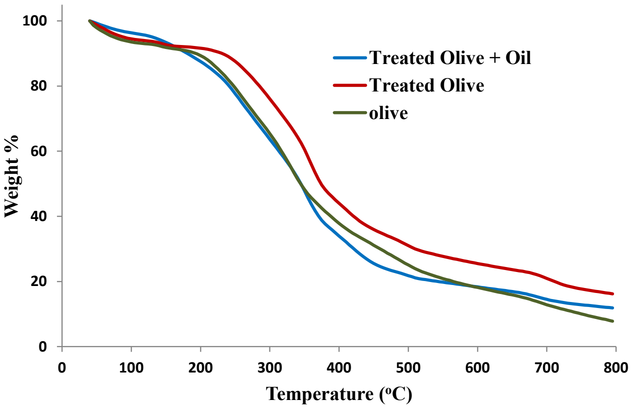

Fig. 9. TG curves of olive without treatment, olive treated with n-hexane (OLP) and OLP after oil loading.

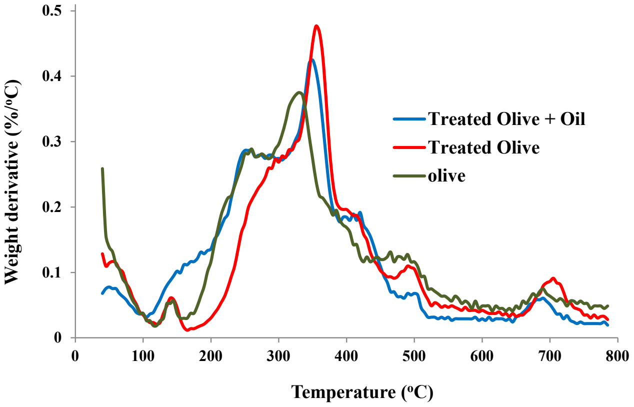

Fig. 10. DTG curves of olive without treatment, olive treated with n-hexane (OLP) and OLP after oil loading.

Table 4
Percent weight loss at different temperature zones using thermal analysis

Experimental sample ID	Weight loss (%)		
	110°C	110°C–300°C	300°C–800°C
Olive	6.75	27.85	57.56
Treated olive	5.82	18.10	47.44
Treated olive + oil	4.00	32.32	51.78

3.9.3. TD-GC-MS

TD-GC-MS analysis was done and the chromatograms for the olive sample before and after hexane treatment are shown in Fig. 11. The thermal desorption temperature was adjusted to 300°C based on the limitation of the technique and the thermal analysis results presented in Figs. 9 and 10. The presence of peaks in the chromatograms reflects that different type of compounds were desorbed or decomposed as a result of heating in the inert environment. The area under the peaks give indication of the amount of each of the chemical compounds removed.

The results of the GC-MS chromatogram clearly support the information obtained from the thermal analysis. It is evident that hexane washing resulted in decreasing the amounts of compounds on the olive sample surface where the number and the intensity of the peaks decreased after hexane treatment. Also, the effectiveness of the OLP for oil removal is evident in Fig. 11 where significant number of peaks of large intensities was introduced after oil adsorption. It is interesting to see the introduction of the oil compounds to the hexane-treated olive revealing that high affinity of the olive surface for such applications. To better understand the chemistry associated with such changes, NIST mass spectral libraries were used to identify the organic compounds. Prior to the library search, the mass spectrum for each peak was processed separately to reduce background interferences and minimize any overlap between peaks.

The peaks in Fig. 11 associated with the olive sample prior to hexane treatment were diverse in chemistry and included derivatives of hydrocarbons, fatty acids, fatty acid methyl ester, phthalates and to fewer extents derivatives of alcohols, aldehydes and ketones. Hexane treatment seems to remove most of the hydrocarbons, fatty acids, fatty acid methyl ester and phthalates. A wide range of organic compounds were adsorbed from SPW by OLP. The chemistry of the removed organic compounds varies where hydrocarbons presence on the surface of OLP was distinct after oil adsorption. Among many others, the presence of hydrocarbons such as pentadecane, hexadecane, 2-methyloctacosane, 2-methylhexacosane, Tetratetracontane and Eicosane were distinct on the surface of OLP after oil removal. Most of these compounds have boiling points in the range 300°C–500°C which is aligned with the results presented in TG curves. In addition, compounds that belong to fatty acids, fatty acid methyl esters and ketones were also removed and their peaks were present in Fig. 11.

3.10. Desorption studies

The regeneration of the adsorbent material was evaluated at the optimum adsorption capacity using hexane as a solvent. The regeneration process showed high efficiency (87%) where the adsorption capacity of the adsorbent material dropped from 80% to 70% after hexane regeneration.

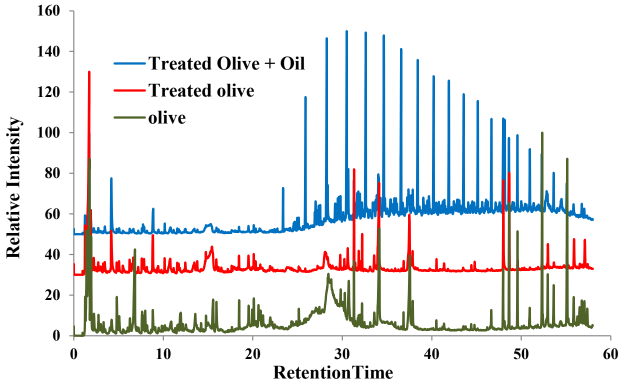

Fig. 11. GC-MS of olive without treatment, olive treated with n-hexane (OLP) and OLP after oil loading.

4. Conclusions

This work provides a new approach of treating produced water using natural materials. A SPW model was developed. Olive leaves were treated effectively with hexane and characterized. The optimum conditions for oil removal from produced water were found to be pH = 7.0, adsorbent dose = 3.0 g/L, contact time = 80.0 min, salinity of 1,000 ppm in terms of NaCl, and adsorption temperature = 25.0°C. Langmuir model best described the removal of oil from produced water on treated olive leaves. Olive leaves showed high efficiency toward oil removal from produced water with adsorption capacity of 143 mg/g. The capacity was confirmed via thermal analysis (167 mg/g). The majority of the compounds removed from olive leaves were desorbed in the temperature range 110°C–500°C. Olive leaves removed organic compounds of wide range of chemical backgrounds among which high molecular weight alkanes and fatty acids methyl esters were distinct.

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