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Received on: 06/09/2018
Accepted on: 27/02/2019
Published online: 25/05/2019

Removal Oil from Produced Water by Using Adsorption Method with Adsorbent a Papyrus Reeds

Abstract- *A papyrus reed, as a type of unusable farming waste, was used as kind of low-cost biosorbent for elimination a crude oil from the produced water that was produced in an Al-Ahdab field, Iraq, in a batch stirred operation mode. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) were used to characterize the bio-sorbent before and after adsorption. Batch tests were employed as a function of the contact time, adsorbent dose, and the pH of the solution. The experimental results show that increases the amount adsorbent dosage, pH and contact times, the removal efficiencies were increases and optimum condition was obtained at pH value equal to 9, 5000 ppm adsorbent dose and 45 minutes contact time for removal about 94.5% of crude oil, for test sample initial crude oil concentration 257.06 ppm. Therefore, it can be disposed of without environmental damage. The better fitting for equilibrium sorption process data were satisfactorily by the Freundlich isotherm model with (R^2= 0.9665) and the adsorption kinetics best described by a pseudo-second-order kinetic model.*

Keywords- *Produced water, Papyrus reeds, crude oil removal, kinetic model, biosorption.*

How to cite this article: F.K. Al-Zuhairi, R.A. Azeez, S.A. Mahdi, W.A. Kadhim and M.Kh. Al-Naamee, "Removal oil from Produced Water by Using Adsorption Method with Adsorbent a Papyrus Reeds, Vol. 37, Part A, No. 05, pp. 157-165, 2019.

1. Introduction

Produced water is a water phase contained in a hydrocarbon reservoir and its comes to the external through oil or gas extraction [1,2], these water has a variable complex organic and inorganic compounds depending on the geographical site of the field, natures of produced hydrocarbon, geological formation, extraction methods and the lifetime of a reservoir [3], according to the different source, the compositions of produced water are differenced by order and magnitude [4], and its considered the largest source for environmental pollution associated with oil production activities [5].

The global generations of produced water to crude oil is about (3:1) and will increase in the near future with increasing lifetime of wells, that will boost the growth of the PW management techniques and marketing [6], to reused again in oil production field [7], or for further different purposes such as livestock watering, irrigation, municipal, aquifer storage and further industrial uses [8].

One of the harmful organic contaminants contained in produced water is dispersed oil that is a blend of hydrocarbons such as toluene, benzene, ethylbenzene, xylenes (BTEX), naphthalene, phenanthrene, dibenzothiophene (NPD), polyaromatic hydrocarbons (PAHs) and phenols, which not dissolve in the water [9], should be removed before disposal or reused [3].

Different available techniques were used to manage the produced water, such as micro-filtration and biological processes [10], variety of filters [11], ultrafiltration and nanofiltration membranes [12], membrane bioreactor [13], air flotation [14], electrocoagulation [15], adsorption [16]. The adsorption method is one of commonly applied technic to eliminate a dissolved organic

http://dx.doi.org/10.30684/etj.37.5A.2
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material in water, which is a physical adhesion of the contaminating material on the surface of a solid [17].

A wide range of bio-sorbent materials for removal oil from produced water actually has been used in the latest years, such as activated carbon, bentonite and deposited carbon [16], banana peel [18], Eggshell [19], rice husks ash [20] carbonized rice husks [21] anhydrous and hydrophobized vermiculite [22].

For the high cost of adsorbent material used for treating wastewater, many attempts have been done to satisfy the alternative material they are available easily throughout the world, Papyrus represents a low cost and more efficient material used as an adsorbent for treated water from contamination [23]. The crude oil content limitation varies with each country, but in general, for discarding of produced water, the monthly concentration of should be 29 ppm and the concentrated value of daily disposable is 42 ppm for reinjection in oil wells [٢٤].

The objective of this publication is to report a removal efficiency of crude oil by papyrus reeds as a biosorbent for real produced water obtained from Al-Ahdab field, Iraq, moreover, the factors affecting their adsorptive nature such as (contact time, the dosage of adsorbent and pH) have been studied

2. Materials and Methods

I. Materials

Papyrus reeds were collected from agro-land at Al-Dujail city (Iraq). The leaves were separated from stems, washed, dried overnight at 105˚C and minced with a chopper, then sieved to particle sizes 300 µm, because of the small size of adsorbent increases the surface area for adsorption will be increased that allowable to more contact with activates group [٢٥].

Real Produced water was used obtained from Al-Ahdab field, Iraq with crude oil concentration (257.06 ppm) and pH 6.18.

II. Bio-sorption studies

Pyrex bottle sizes 250 ml, with a working volume of 200 mL, were used for batch tests. The bottles were filled with produced water, dosage with different (w/v%) of biosorbent / produced water, the pH of a solution was confirmed to the desired value by using (0.1 N HCl and 0.1 N NaOH) after that the bottle was placed on a magnetic stirrer at 250 rpm and 25ºC. Samples were taken at different intervals (15, 30, 45, 60, 75 and 90 min). Then, the biosorbent was separated from the produced water by normal settling.

III Analytical methods

The calibration curve relating a mixture of crude oil in n-hexane was made by dissolving a specific weight from crude oil in n-hexane to obtained concentration 1000 ppm then diluted many times by n-hexane (to obtaining a different concentration 500, 250, 125, 62.5 and 31.25 ppm), the optical density for each concentration was measured using spectrophotometer (Cary 300 UV-Vis) at wavelength 450 nm.

The remaining crude oil content in produced water was extracted by a solvent (n-hexane) and the concentration determined by using spectrophotometer (Cary 300 UV-Vis) at wavelength 450 nm. The quantity of adsorbed and removal percentages at a given time were calculated by using Equations (1&2) [15].

$$q_t = \frac{V_s\ (C_i - C_t)}{m} \qquad (1)$$

$$\%R = \frac{(C_i - C_t)}{C_i} \times 100 \qquad (2)$$

Where:

q_t = Adsorbed crude oil (mg crude oil/g biosorbent) at a given time

V_s = Volume of total solution (L)

C_i= Initial concentration (ppm)

C_t= concentration at a given time (ppm)

m = Weight of dry biosorbent (g)

%R=Removal percentage

IV. Characterization of adsorbent

The functional groups presented in the papyrus reeds before and after adsorption were characterized by Fourier transform-infrared (FTIR) spectroscopy (Bruker Tensor 27 instrument, Germany).

The microstructure of adsorbent before and after adsorption was characterized by Scanning Electron Microscope (SEM) (Silicon Drift Detector (SDD) - X-Max, Oxford Instruments Group).

V. Adsorption isotherm

Investigation of adsorption isotherm data at the equilibrium is a significant key for a description of an adsorbate molecules distribution between two phases (liquid and solid) at the interface [٢٦]. Therefore the result was found from isothermal experiments, was verified with most commonly two adsorption isotherms Freundlich and Langmuir models [2٧, 2٨].

The Freundlich isotherm is an experimental model described multilayer adsorption not limited only to monolayer coverage, the mathematical expression for Freundlich isotherm given by Equation (3) [2٧].

$$log\, q_e = log\, k + \frac{1}{n} log\, C_e \qquad (3)$$

The mathematical expression for Langmuir isotherm in the linear form given by Equation (4) [2٨]

$$\frac{1}{q_e} = \frac{1}{bq_oC_e} + \frac{1}{q_o} \qquad (4)$$

Where:

q_e = quantity of adsorbed crude oil per mass of a dry biosorbent (mg/g) at equilibrium.

C_e = residual crude oil concentration (ppm) at equilibrium.

k and *n* = Freundlich constants concerning to capability and intensity of adsorption respectively determined from, the linear plot of $\log q_e$ against $\log C_e$ with intercept and slope $\log k$ and $\frac{1}{n}$ respectively.

b = adsorption coefficient.

q_o= quantity of adsorbed crude oil per mass of the bio-sorbent (mg/g) conforming to the broad coverage of accessible sites (i.e., monolayer saturation capacity), the values of b and $q_o$were calculated from the slope and intercept of the linear plot of $^1/_{q_e}$ against $^1/_{C_e}$ respectively.

VI. Kinetic models of adsorption

In order to study a dynamics of the adsorption that represent a significant phenomenon clarifies the adsorption rate that describes an interaction time between two phases (solid and liquid) at an interface, three kinetic models, pseudo-first-order, pseudo-second order adsorption, and intraparticle diffusion [2٩,٣٠,٣١] were tested.

The linear form of the mathematical expression for pseudo-first-order (Lagergren model) given by Equation (5) [2٩].

$$ln(q_e - q_t) = ln\, q_e - k_1 t \qquad (5)$$

Where:

q_t = quantity of adsorbed crude oil per mass of a dry biosorbent (mg/g) at time *t* and k_1 is the first-order adsorption rate constant of (min^{-1}), that was determined from linthe ear plot of $\ln(q_e - q_t)$ against t with slope k_1.

The linear form of the mathematical expression for pseudo-second-order (Lagergren model) given by Equation (6) [٣٠].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

Where:

k_2 (mg/g min) is the rate constant of second-order adsorption. The intercepts k_2 and slope q_e were determined from linethe ar plot of $\frac{t}{q}$ against t.

Intraparticle diffusion describes the transport process that including a movement of species from the bulk to the solid phase and adsorbed on it porous. The intraparticle diffusion model was stated mathematically by Equation (7) [٣١]

$$q_t = k_p t^{1/2} + C \qquad (7)$$

Where:

C is the intercept, and k_p is the intraparticle diffusion rate constant (mg/ g $min^{1/2}$), that were found from lithe near plot of q_t against $t^{1/2}$.

3. Results and Discussion

I. Characterization of adsorbent

Toward investigate types of effective functional groups for removal a crude oil, FTIR spectra of a biosorbent, before and after removal of crude oil, were investigated as shown in Figure 1. The absorption spectrum of the biosorbent material was recorded at a wave range of 600-4000 cm^{-1}.

FTIR spectrum of papyrus reeds before and after adsorption showed a broad peak at 3338.10 and 3331.12 cm^{-1} respectively which was connected to the O-H stretching vibrations of absorbed water cellulose, hemicellulose, pectin and lignin [٣٢]. The peaks were observed in the range 2918.64 - 2852.39cm^{-1} can be indicating to the C-H stretching vibrations of methyl, methylene and methoxy groups [3٣]. The peaks observed at 1733.42, and 1717.28cm^{-1} were attributed to stretching vibration of the carboxyl groups (C=O) of pectin, hemicellulose, and lignin [٣٢]. The peaks in the range 1647.29 - 1508.22 cm^{-1} indicates the presence of aromatic or benzene rings in lignin(C=C) [3٤]. The peaks located in the range 1457.16 - 1315.43 cm^{-1} may be because of aliphatic and aromatic (C-H) groups related to deformation vibrations of methyl, methylene and methoxy groups [٣٢]. The peaks in the range 1242.01-1034.14cm^{-1} could be related to the (C-O) stretching vibrations of alcohols, ethers, esters, carboxylic acids and anhydrides groups [3٥]. The peaks in the range 898.84-831.32 cm^{-1} could be ascribed stretch (C-C) related to the deformation of a carbonate group [3٣], while, the peaks in the range 796.09-608.46 cm^{-1} related to aliphatic chlorides [3٦]. After the papyrus reeds were loaded with crude oil, some differences in the peaks absorbance were shown due to the interaction between crude oil and different functional groups.

The micrographs of papyrus reeds surface were analyzed by SEM before and after crude oil adsorption as shows Figure 2.
The microstructure of this material can facilitate the adsorption of crude oil, because of an irregular surface condition that a great region for ion-surface interaction (Figure 2a), a substantial change in the surface of biosorbent was detected after the adsorption of crude oil (Figure 2b). A roughing effect was observed in Figure 2b might be as a result of the adsorption of crude oil over bio-
sorbent surface makes it's rougher than the original form.

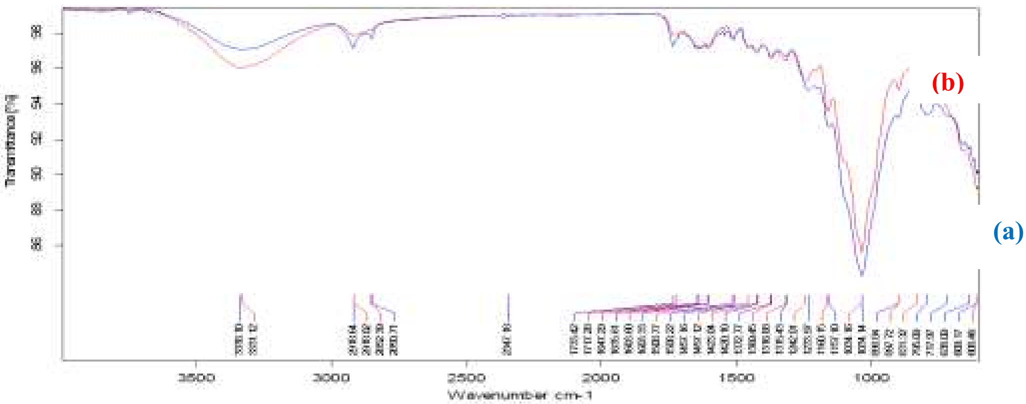

Figure 1: Fourier transform infrared (FTIR) spectra investigation of papyrus reeds before (a) and after (b) crude oil adsorption.

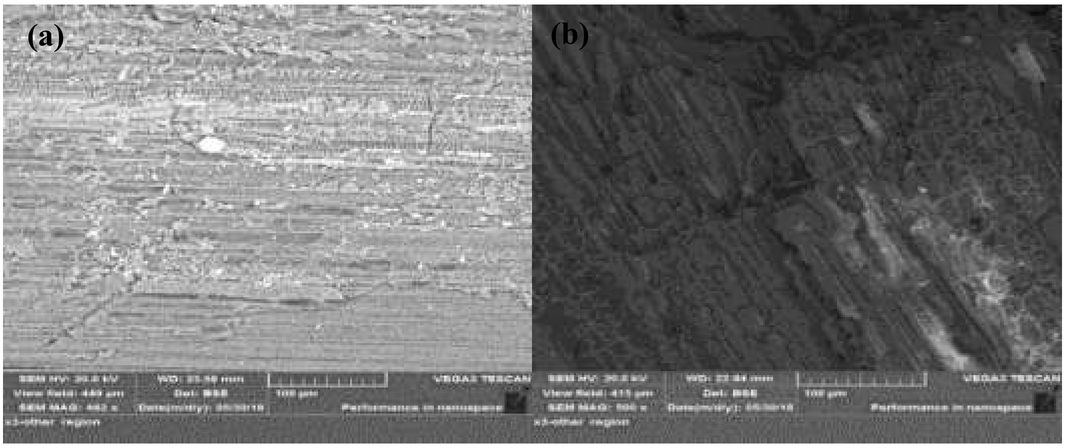

Figure 2: Scanning Electron Microscopy (SEM) analysis of papyrus reeds (a) before and (b) after crude oil adsorption

II. Effect of contact time

Figures 3a & 3b presents the concentration and percentage of removal for crude oil respectively, as functions of contact time on the surface of papyrus reeds material, which varied from 15 to 90 minutes, using initial oil concentration of 257.06 ppm, different dosage concentration of biosorbent, initial pH value 6.18, 250 rpm and 25 ºC. It can be noticed in the figures that the concentration of crude oil decreased and the removal efficiency increase with increasing contact time, because of at increasing the contact time acceptable to more crude oil contact with the active groups contained in the structure of adsorbent. However, it became almost constants when equilibriums were reached after about 45 minutes for (4000 and 5000 ppm) and 60 minutes for (1000, 2000 and 3000 ppm) dosage concentration were used. The higher removal percentage for (4000 and 5000 ppm) dosage concentration were used it's about 81.5 and 87.6 % with a residual concentration (48 ppm and 32.2 ppm) respectively could be attributed to obtainable adsorbing sites on the surface of the sorbent material.

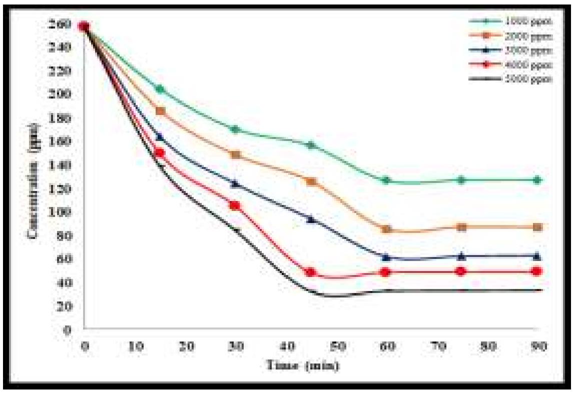

Figure 3a: Effect of contact time on the concentration of crude oil at different adsorbent dosage concentration, pH 6.18, 250 rpm, 25 ºC and initial crude oil concentration 257.06 ppm

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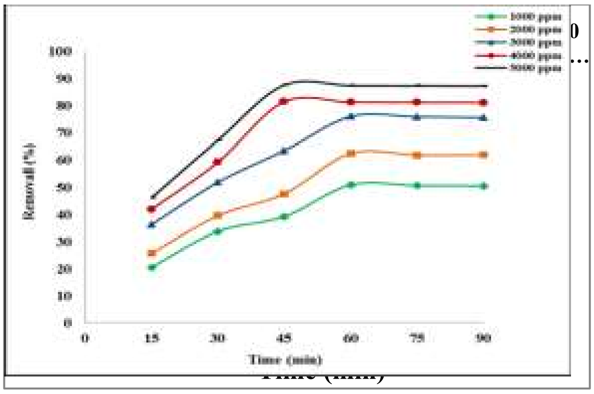

Figure 3b: Effect of contact time on removal percentage of crude oil at different adsorbent dosage concentration, pH 6.18, 250 rpm, 25 ºC and initial crude oil concentration 257.06 ppm

III. Effectdosage of biosorbent

The dosages concentration is an essential factor in biosorption studies since it locates the competency of the adsorbent for a certain initial concentration of crude oil in a solution. The result of different adsorbent dosage concatenation on the crude oil removal percentage at an initial concentration of 257.06 ppm was studied and it is presented in Figure 4. It is clear that when the dose concentrations were increased from 1000 to 5000 ppm, the crude oil removal percentage will be increased from about 50.8 to 87.6 % respectively. An increase of adsorption efficiency with increase in a biosorbent dosage recognized to the obtainability of more surface area and additional adsorption sites that will be improved the removal percentage. Besides, this result suggests that the higher adsorption efficiency at 5000 ppm was used.

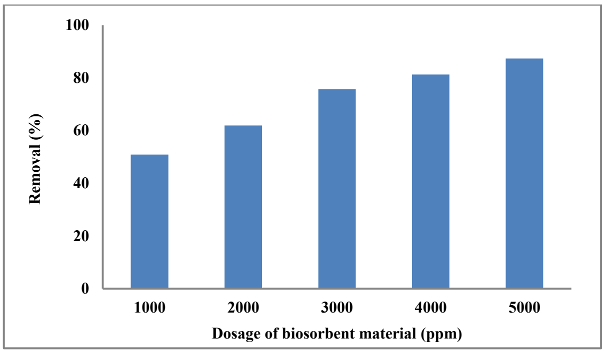

Figure 4: Effect of adsorbent dosage on removal percentage of crude oil at different adsorbent dosage, pH 6.18,250 rpm, 25 ºC, initial crude oil concentration 257.06 ppm and contact time 90 minutes

IV. Effect of initial pH

The pH value of the solution has a considerable effect on the adsorption process since it influences the chemical speciation of functional groups on the adsorbent surfaces [3٧]. This test focuses the effect of the initial pH on the removal percentage by used papyrus reeds at 45 minutes contact time, 250 rpm, initial crude-oil concentration 257.06 ppm, 25 ºC and adsorbent dosage (5000 ppm). Figure 5 explains as the pH increases the adsorption efficiency of crude oil increases and inclines to be constant at pH value more or equal to eight. So, the highest removal efficiency was about 94.6 % with a residual concentration (14 ppm) at pH 9. This result can be attributed by the electrostatic interaction of the basic cationic species with the negatively charged surface of the adsorbent [3٨], according to this statement the electrostatic attraction force of the crude oil compounds were increased when the pH values were increases.

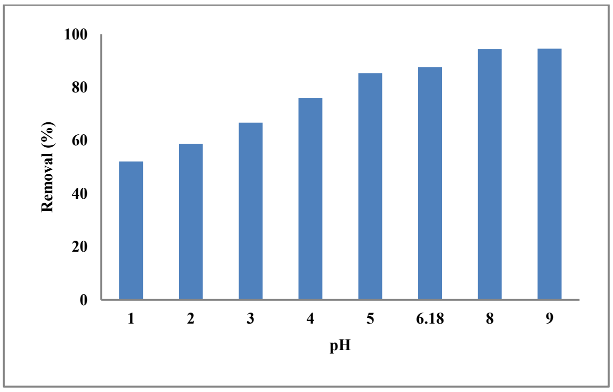

Figure 5: Effect of pH on removal percentage of crude oil at adsorbent dosage 5000 ppm, initial crude oil concentrations 257.06 ppm, 250 rpm, 25 ºC and contact time 45 minutes

V. Adsorption isotherms

Adsorption isotherms investigated using a sample of produced water with initial oil concentrations 257.06 ppm, pH 6.18, adsorbent dosage 1000, 2000, 3000, 4000, 5000 ppm, 25 ºC and 250 rpm to reach equilibrium. The linearized plots of Freundlich and Langmuir isotherms were obtained presented in Figures 6 and 7 respectively, and the comparison between them were listed in Table 1, *n* value for Freundlich isotherm more than unity which a sign on a favorable adsorption [31], for the Langmuir isotherm model the maximum monolayer saturation capacity (q_o) was specified to be 229.726 mg/g, b is Langmuir constant associated with the adsorption energy [3٩] was found to be 0.007 L/g, the values of obtained a regression coefficient (R^2) were about a unity which equal to 0.9665 and 0.9329 for Freundlich and Langmuir respectively. Obviously, the better fitting for sorption of crude oil from produced water by a papyrus reed is accessible by the Freundlich isotherm.

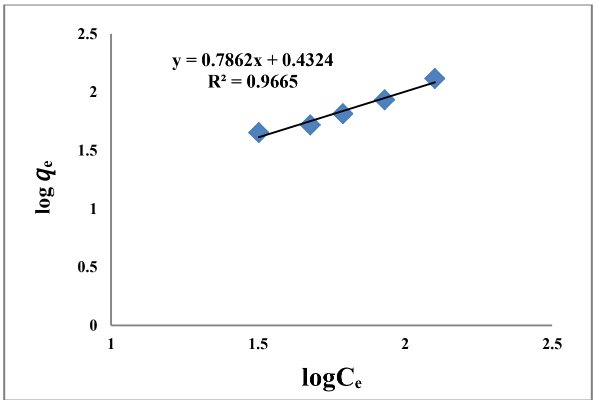

Figure 6: Linearized Freundlich isotherm model plot for biosorption of crude oil at pH 6.18, initial crude oil concentration 257.06 ppm, 250 rpm and 25 ºC.

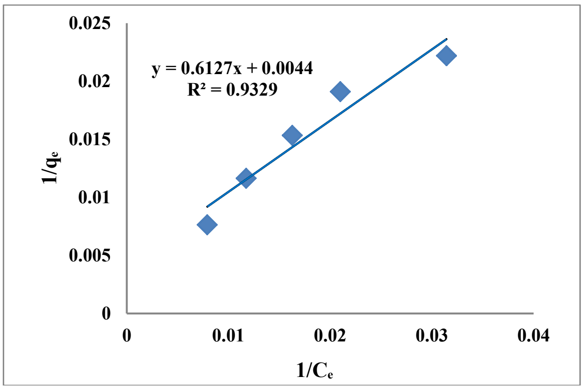

Figure 7: Linearized Langmuir isotherm model plot for biosorption of crude oil at pH 6.18, initial crude oil concentration 257.06 ppm, 250 rpm and 25 ºC

Table 1: Parameters for plotting Freundlich and Langmuir adsorption isotherms.

Freundlich		Langmuir	
n	1.272	q_o *(mg/g)*	229.726
k *(mg/g)(mg/L)*	2.723	*b* *(L/mg)*	0.007
R^2	0.9665	R^2	0.9329

VI. Kinetic studies

The kinetic parameters were investigated by using a sample of produced water with oil concentrations 257.06 ppm, pH 6.18, adsorbent dosage 1000, 2000, 3000, 4000, 5000 ppm, 25 ºC and 150 rpm to reach equilibrium. The linear plots of kinetics adsorption models for pseudo first order, pseudo-second order and intraparticle diffusion models were used to evaluate the kinetics process of adsorption a crude oil from produced water by papyrus reeds, the obtained kinetic parameters for fitting were taken from Figures (8,9, and 10) and Equations (5,6,7) respectively, are listed in Table (2). As stated in the table, the regression coefficient R^2, for pseudo-second order was greater and closer to unity than the pseudo first order and intraparticle diffusion models. For occasion, for a sample with adsorbent dosage (1000 ppm), the regression coefficient of pseudo-second order could better describe to the kinetics of oil adsorption on the papyrus reeds.

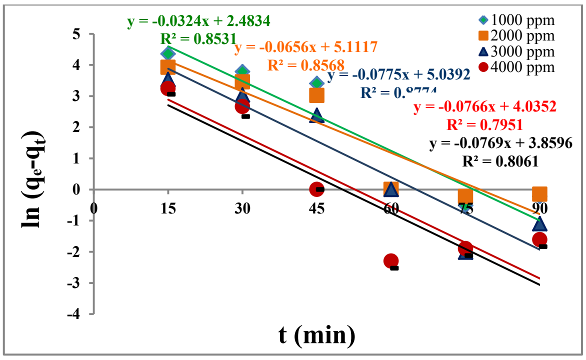

Figure 8: Pseudo-first-order kinetic model plot for different adsorbent dosage addition on biosorption of crude oil at pH 6.18, initial crude oil concentration 257.06 ppm, 250 rpm and 25 ºC.

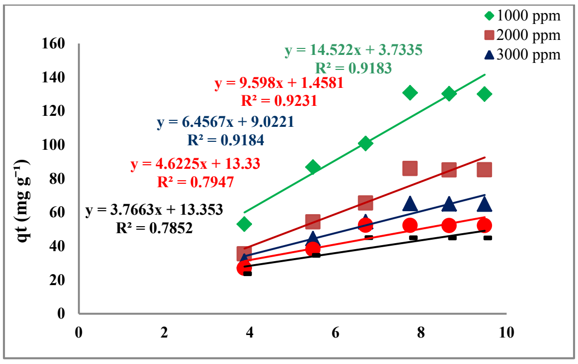

Figure 9: Pseudo-second -order kinetic model plot for different adsorbent dosage addition on biosorption of crude oil at pH 6.18, initial crude oil concentration 257.06 ppm, 250 rpm and 25 ºC.

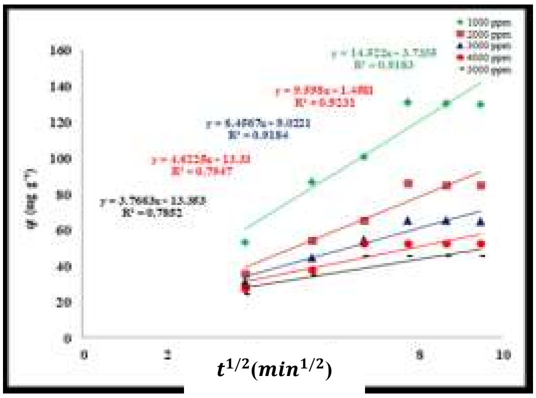

Figure 10: Intraparticle diffusion model plot for different adsorbent dosage addition on biosorption of crude oil at pH 6.18, initial crude oil concentration 257.06 ppm, 250 rpm and 25 ºC 257.06 ppm, 250 rpm

Table 2: Parameters for plotting pseudo-first-order, pseudo-second-order and intra- particle diffusion models.

	Adsorbent dosage (ppm)				
	1000	2000	3000	4000	5000
Pseudo-first-order					
k_1 (min^{-1})	-74.6 ×10^{-3}	-65.6×10^{-3}	-77.5×10^{-3}	-76.6×10^{-3}	-76.9×10^{-3}
q_e ($mg.g^{-1}$)	304.3546	165.9442	154.3513	56.5535	47.4453
R^2	0.8531	0.8568	0.8774	0.7951	0.8061
Pseudo-second-order					
k_2 ($g.mg^{-1}.\ min^{-1}$)	0.1×10^{-3}	0.2×10^{-3}	0.4×10^{-3}	0.8×10^{-3}	1.2×10^{-3}
q_e ($mg.g^{-1}$)	190.9108	126.1716	86.8178	65.0186	54.6419
R^2	0.9806	0.9751	0.9835	0.9644	0.967
Intraparticle diffusion					
k_p($mg.g^{-1}.min^{-1/2}$)	14.522	9.598	6.457	4.623	3.766
C	3.734	1.458	9.022	13.330	13.353
R^2	0.9183	0.9231	0.9184	0.7947	0.7852

3.Conclusion

This study recognized papyrus reeds as a beneficial material that may be used for the after crude oil biosorption, they have shown different types of functional groups and irregular surface condition involved on the surface of papyrus reeds that indicated its well biosorbent material. Adsorption equilibriums were achieved within 45 min for 4000 and 5000 ppm of adsorbent dose were used. The best result for removal percentage was about 94.5% obtained at pH value equal to 9, 5000 ppm adsorbent dose and contact time equal to 45 minutes. The adsorption isotherm studies presented that Freundlich isotherm model fitted well with the experimental data with n value more than unity and regression coefficient was about a unity. The rate of kinetics by the papyrus reed biosorbent was best described by the pseudo-second-order model. Additionally, Batch studies for crude oil removal of crude oil from produced water. The FTIR and SEM characterizing of a biosorbent material, before and

removal using papyrus reeds particle indicate that papyrus reeds particle is effective and efficient for oil removal and it can be expressively used as a low-cost and environmentally friendly adsorbent for produced water treatment.

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