

Cane Papyrus as Sustainable and Natural Bio-sorbent for Polluted Oilfield Water Treatment by Adsorption.

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Abstract

High quantities of wastewater are polluted from producing natural gas and oil from the aquifer, which is called polluted water. The polluted water was comprised of dissolved solids, suspended solids, emulsified oil, and organic and inorganic compounds. That should be treated it's before disposal because it causes harm to the environment. This study takes the polluted water from the southern Iraqi oilfield drilling company to adsorption by the Cane papyrus as a natural and low-cost adsorbent. The analysis was completed by using Fourier transforms infrared spectroscopy, EDX spectra and Scanning Electron Microscopic (SEM) for Cane papyrus. Investigating the effect of many parameters such as adsorbent dosage, temperature and contact time, the best results were adsorbent dosage 0.4g/100mL, the temperature at 60°C and 90 min contact time. The Langmuir, Freundlich, Temkin and Harkins-Henderson isotherm models were tested, and the results were 0.9811, 0.6675, 0.8964 and 0.9459 respectively. The Langmuir model was more suitable to describe the adsorption process than the other models, the adsorption capacity at this condition was 0.563 mg/g. The kinetics results were, 0.9643 for Pseudo-first-order, 0.8580 for Pseudo-second order is, 0.8744 for Intra particle diffusion study and 0.8807 for the Elovich model, Pseudo-first-order kinetic equation best described the kinetics of the reaction. The thermodynamics study affects temperature changes on the thermodynamic parameters such as standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°). The experimental data obtained demonstrated that Cane papyrus is a suitable adsorbent for removing oil from polluted water.

Keywords: Adsorption, Cane Papyrus, Oily water, Polluted water, Isotherm, Kinetic.

1. Introduction

The crude oil-producing operations generate a great volume of polluted water, many international companies suffer from this problem. The treatment challenge to these oily water production is very difficult because of the increased waste product and the oily water volume, it's considered the largest source of environmental pollution associated with oil production activities [1]. The nature of this water depends on the geological formation, the hydrocarbon nature polluted, methods of extraction, the reservoir lifetime drawn up from it's, and the field geographical site. This water has a variable complex organic and inorganic compounds because it's come to the external through oil or gas extraction from the hydrocarbon reservoir [2]. Generating high quantities of water polluted in the southern Iraqi drilling oilfield company, the company looking for many ways to treat it's before disposing it to the environment carries huge toxic materials, thus disposal without treatment will cause serious environmental problems[3].

There are many conventional techniques available to treat the polluted water, such as membrane process(ultrafiltration and nanofiltration membranes)[4], microfiltration and biological processes[5], coagulation[6], flocculation[7], flotation[8], air flotation[9], emulsion breaking[10], activated sludge[11], chemical precipitation[12], ion exchange[13], biochemical and biological treatment[14], advanced oxidation process [15], electrocoagulation[16], extraction[17], and adsorption[18]. There are many disadvantages to utilizing these techniques, like not being efficient at lower concentrations, needed high power consumption, slow kinetics[13], not efficiently removing the organic pollutants[19], increased initial capital and maintenance costs, increased costs of disposal sludge, low flow rate [20].

Adsorption is the best key to making bio-sorption an applicable technology, low-cost biosorbent, by using renewable, agricultural, raw materials waste, it's extra economically than traditional technologies[21]. Many adsorbent materials are used to removed and minimize the oil in polluted oily water such as hydrated cellulose[22], polyurethane foam[23], straw[24][18], cotton[25], artificial or synthetic materials based on viscose[26], sawdust[27], expanded graphite[28], thermoplastic materials[26], wood flour[29]... etc.). Other researchers utilized Auricularia polytricha as adsorbents for removed the oil from polluted water [30][31]. Also, eggshell[32], kapok fiber[33][34][35], walnut shell media[36], and modified sugarcane bagasse[37] as adsorbents media and the results showed a high ability to remove the oil from oily water.

Cane Papyrus is a natural, sustainable, eco-friendly, exotic plant and low-cost absorption to eliminate oil from oily water. It is grown in many places in the world, in Iraq, its main growth in the marshes of southern Iraq. Cane Papyrus grows naturally at high density and using for many tasks there, so it can be (a biological absorbent) is a viable technology due to its availability, sustainability, renewable and low cost.



This research aims to remove the oil from polluted water resulting from the southern Iraqi drilling oilfield company using harmful, invasive and natural growing plants as adsorbents under several conditions like Temperature, adsorbent dose, contact time and pH, finding a general equation relating these conditions to give its optimum value and studying the adsorption isotherm, kinetics and thermodynamic.

2. Materials and Methods

The cane Papyrus Collecting process started in October 2019, in this time the leaves of Cane Papyrus had already been grown and seemed very fresh. The leaves were carefully detached from the plant stems and washed thoroughly with tap water to remove dirt, soil particles, and debris, then to get sun-dried for at least 10 days. The dry biomass was ground to fine powder into 100 µm mesh size to use in experiments, by a hammer mill(Fitzmill Mill Hammer, L1A, R24330, China), and then weighed with a sensitive balance of 0.00001 accuracies to prepare for the experiments. After milling, the materials got dried in an oven at 105°C for 24 hr. To avoid further moisture absorption, samples were preserved in desiccators. Dried samples were then taken in a porcelain crucible and covered with a lid to be placed in a control muffle furnace at 150°C for an hour. Firstly, the samples were washed with 1M hydrochloric acid solutions and then with distilled water until the pH value reached 7. After washing, the samples were dried in an oven at 105°C for 24 h. Then the dried samples were preserved in desiccators to avoid further moisture absorption. The adsorbent showed a fluffy, highly porous, and rough microstructure, containing some voids and cracks which were suitable for the adsorption of oil. Properties clear by FTIR (UV-visible spectrophotometer, model Genesys TM 10, Thermo company), and EDX tests (X-ray diffraction device (XRD-6000, Shimadzu, device for qualitative analysis), and energy-dispersion X-ray spectroscopy (EDX-7000, Shimadzu, device for quantitative analysis).

The morphology of the sample was evaluated using an EmCraft(Korea): Table-top scanning electron microscope (SEM Cube-1000). Samples were dehydrated by putting them into critical point drying equipment or freeze-dried. The Cane Papyrus powder was fixed in an aluminum plate (specimen holder), using an electrically conductive tap and a coating of gold at 10 mbar for 90 Sec. was applied. Each sample was transferred to the microscope for observation. The procedure was applied to gain information about the arrangements of particles that correlated with the structure of samples.

2.1 Experimental Work.

Firstly coagulation\flocculation process was conducted using 30 ppm of Ferric sulfate and a flocculent dose concentration of 2.5 mg/L of polyacrylamide to treat polluted water. The oil content was reduced to 53.56 mg/L in previous work[38][15]. After that, 500 ml of polluted water was used to study the ability of Cane Papyrus to adsorb oil from polluted water. The variables investigated were pH of the solution (3,5,7 and 9), adsorbent dose (0.05,0.1,0.2 and 0.4)g/100mL and Shaker with a perforated platform, Tablar 2000, Heidolph for mixing the Cane Papyrus, temperature (30,40,50 and 60)°C with (Hot plate with a magnetic stirrer and controlling thermostat for heating and mixing the solution and water bath, model WNB, Memmert company for heating and controlling the adsorption temperature) and the contact time (15,30,60 and 90) min. The rotational speed of the mixer was (150 rpm). The oil concentration of the samples was analyzed by TD-500. The optimal design for the adsorption of oil is a very important aspect of the development of the adsorption process. Cane Papyrus properties are clear by FTIR, EDX and SEM tests shown in Figures 1 and 2(A)&(B).

2.2 Adsorption capacity.

Equation 1, utilized for calculate adsorption capacity(q)[39]:

$$q = \frac{V(C_0 - C_e)}{M} \quad (1)$$

When q "adsorption capacity" in (mg/g), C_0 "initial concentration" in (mg/L), C_e "equilibrium concentration", M "adsorbent dosage" in (g) and V "solution volume" in (L). From equation 2 can calculate the oil removal percentage:

$$(\%) \text{Oil removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

3. Results and Discussion

The properties of the Cane Papyrus were examined using FTIR, EDX and SEM.

3.1 Scanning Electron Microscopic (SEM).

Figure 1 indicated the SEM images, which was an irregular and rough surface with many creases, the white region in the SEM showed a spectrum for Si ions.

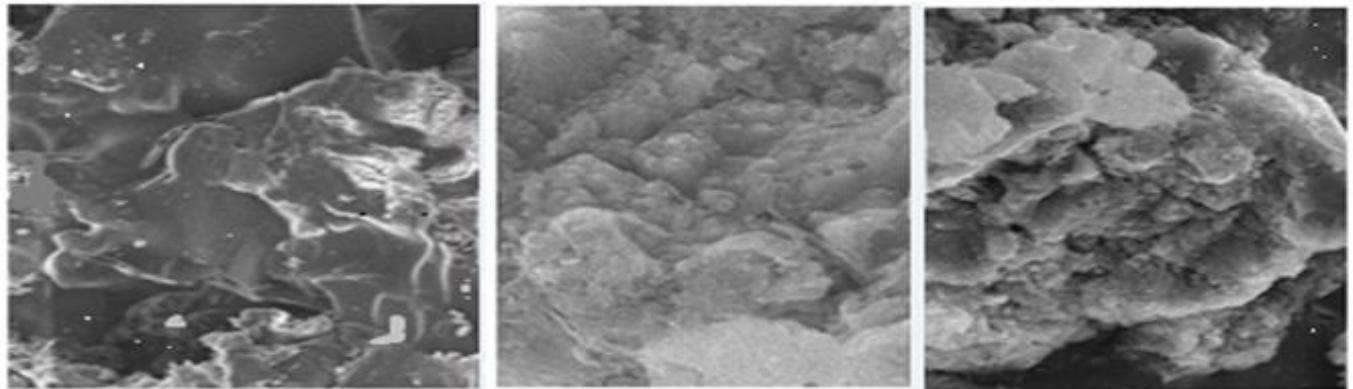
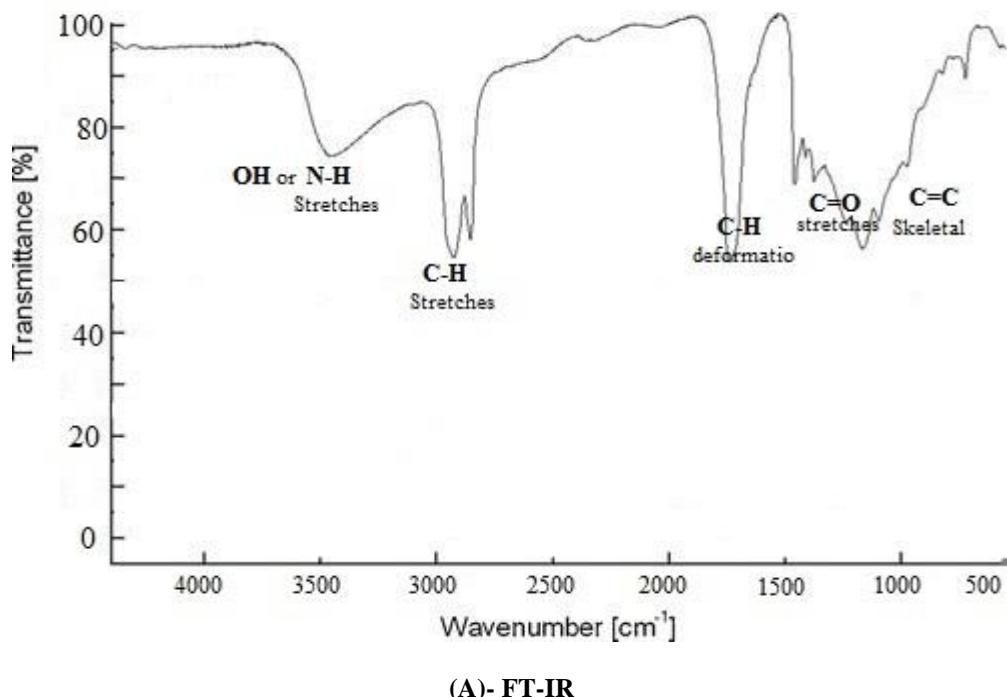


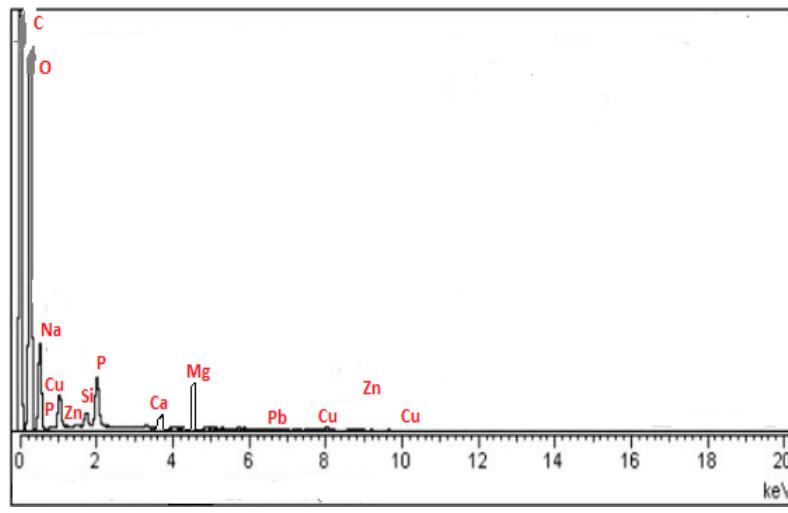
Figure1. Scanning Electron Microscopic (SEM) of Cane Papyrus.

3.2 Investigation for Fourier transform infrared spectroscopy (FT-IR) and Energy Disperse X-ray spectra (EDX) investigations.

The Cane Papyrus FT-IR spectra images were recorded and shown in Figure 2(A). The medium length and two peaks observed at 2930 cm^{-1} , and 1650cm^{-1} , are attributed to the presence of the C-H asymmetrical stretches and symmetrical deformation respectively. The two peaks at 1400 cm^{-1} and 1075 cm^{-1} were assigned to C=O stretching vibration of the carboxylate group, Due to various coupling factors and rotational isomerism, this absorption frequently occurs as a multiplet with broad bands. 1050 cm^{-1} and less which is related to C=C skeletal of the alkenes group, Consequently, it can be said that double bonds have partially deteriorated.The peak 3480 cm^{-1} is attributed to presence of O-H or N-H stretching. EDX spectra of the Cane Papyrus surface are shown in Figure 2(B). The presence of large amounts of silica could enhance the adsorption capacity of the adsorbent[EDX is a very good tool for identifying elements on the adsorbent surface]. The presence of C, O, Si and P ions on the Cane Papyrus surface were confirmed by the peaks at (0.2, 0.5, 1.7 and 2) keV, respectively.



(A)- FT-IR



(B)- EDX

Figure 2. Fourier transforms infrared spectroscopy and EDX spectra of Cane Papyrus. The research's major aim is to detect the best parameters for the operation of oil adsorption maximize.

3.3 pH Effect on oil removal Study.

pH has no significant effect on the adsorption process because the polluted water has already been neutralized by coagulation and flocculation. Thus the adsorption capacity depends on changes in the other parameters to reach for optimum conditions to get high-efficiency oil removal from polluted water.

Contact Time Effect Study.

For achieving equilibrium, the contact time relationship, and oil removal was managed between them over the batch process as shown in Figure 3. When increased contact time, increased oil removal. At the beginning of (15-60) min, the adsorption capacity was very fast because of an increase in adsorbent surface area voids when the time at 90 min the adsorption capacity is very rapid on the surface take place. After that, the adsorption reaction decreases because of fills most of the adsorbent surface area voids[40][41].

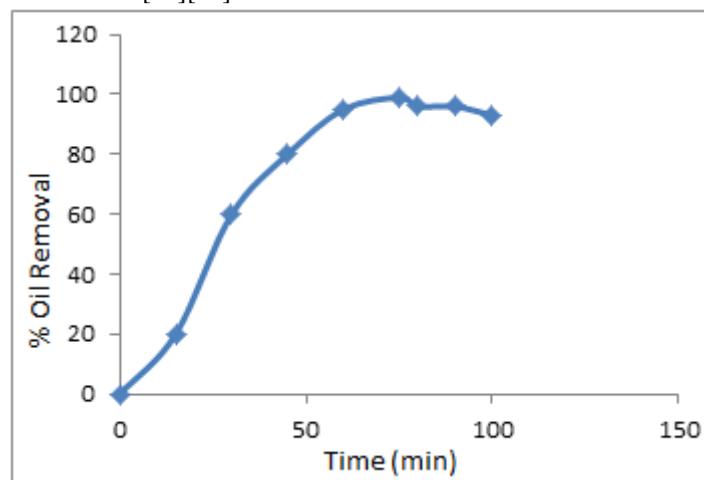


Figure 3. Contact time effect to %oil removal onto Cane Papyrus at $T= 60^{\circ}\text{C}$, Adsorbent dose= 0.4g/100mL.

3.4 Adsorbent dose Effect Study.

Figure 4 shows, the change in oil removal with changing in adsorbent dose in specific conditions, also can see, increased the oil removal when increases adsorption dosage, at an adsorbent dosage of 0.4g /100mL attained the maximum value (100%). When sorbent dosage increase, the adsorption capacity increases because the unsaturated oil binding sites increase which means an increase in the oil removal percentage[40][41].

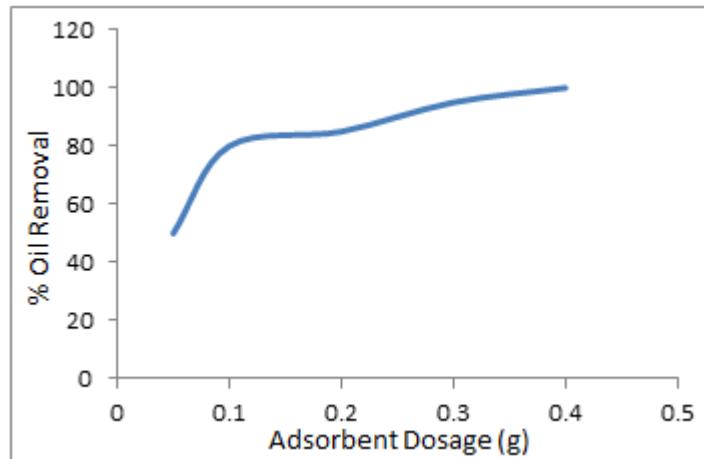


Figure 4. Adsorbent dose-effect to %oil removal at T=60°C and t=90 min.

3.5 Temperature Effect Study.

Figure 5, shows the temperature effect of oil removal, it's known oil is sticky and hydrophobic. The temperature affects the solubility of liquids. Increasing the temperature will increase the solubility, hence it improves the mass transfer processing, and the removal of oil(adsorption capacity)would increase[40][41][42].

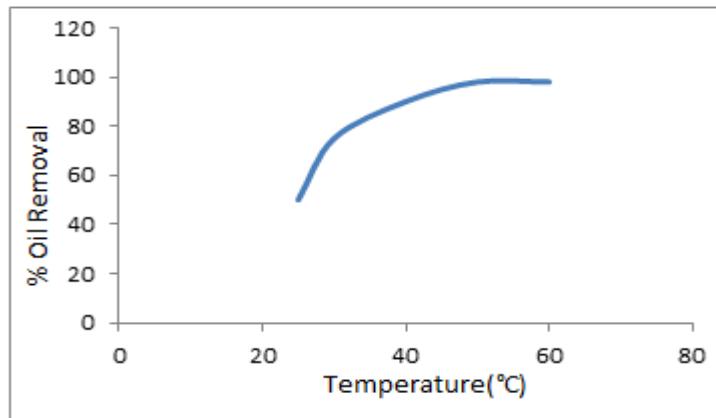


Figure 5. Temperature effect to %oil removal at t= 90min and adsorbent dose= 0.4g/100mL.

3.6 Adsorption isotherms models

Pollutants distribution among the liquid and solid phases call for the adsorption isotherm. In this research, studying four models of isotherm to get the finest model appropriate for oil removal (adsorption capacity)by Cane Papyrus:

- The Langmuir model [39].

$$q_e = \frac{K_L C_e}{1+a_L C_e} \quad (3)$$

where K_L (dm³/g) and a_L (dm³/mg) represent Langmuir constants.

- The Freundlich model. [40]

$$q_e = a_f C e^{b_f} \quad (4)$$

a_f (mg/g) indicates the multilayer adsorption capacity and b_f an empirical parameter related to the the intensity of adsorption.

- Temkin isotherm model [41].

$$q_e = \frac{RT}{b} \ln ACe \quad (5)$$

Here ($\frac{RT}{b}$)= B (J/mol), which is Temkin constant, A (L/g) is the equilibrium binding constant, R is the universal gas constant and $T(K)$ is the absolute solution temperature

- Harkins-Henderson Model [41].

$$q_e = \frac{K_{H-H}^{1/n}}{c_e^{1/n}} \quad (6)$$

n and K_{H-H} are isotherm constants.

From the above isotherm models the results were obtained, The linearized form of Langmuir, Freundlich, Temkin, and Harkins-Henderson isotherm models, using equations(3), (4), (5 and (6) respectively, were analyzed using Microsoft Excel Software to find the isotherm constants. These constants are presented in Table 1, it is visible that (R2) "regression correlation coefficient" for the equation of the Langmuir model ($R^2 = 0.9811$) is more linear compared with the other model's equations, the inclusion of the data of adsorption isotherm were fully proportioned with the Langmuir isotherm. The experimental curve and isotherm model curves are shown in Figure 6. The adsorption capacity at this condition and Langmuir model was 0.563 mg/g.

Table 1. The isotherm model constants for oily polluted water.

Isotherms	Parameters	Values
Langmuir	a_L	0.1504
	K_L	0.0143
	R^2	0.9811
Freundlich	b_f	0.0724
	a_f	2.5310
	R^2	0.6675
Temkin	B	0.0406
	A	0.1524
	R^2	0.8964
Harkins-Henderson	n	0.0600
	K_{H-H}	0.3000
	R^2	0.9459

The experimental data fit the Langmuir isotherm very well-meaning the process is a single-layer and the maximum oil molecules adsorption onto the surface of Cane Papyrus. The Langmuir isotherm assumes "active sites available in a finite number over the adsorbent surface and there is no interaction among the molecules of adsorbed "[40].

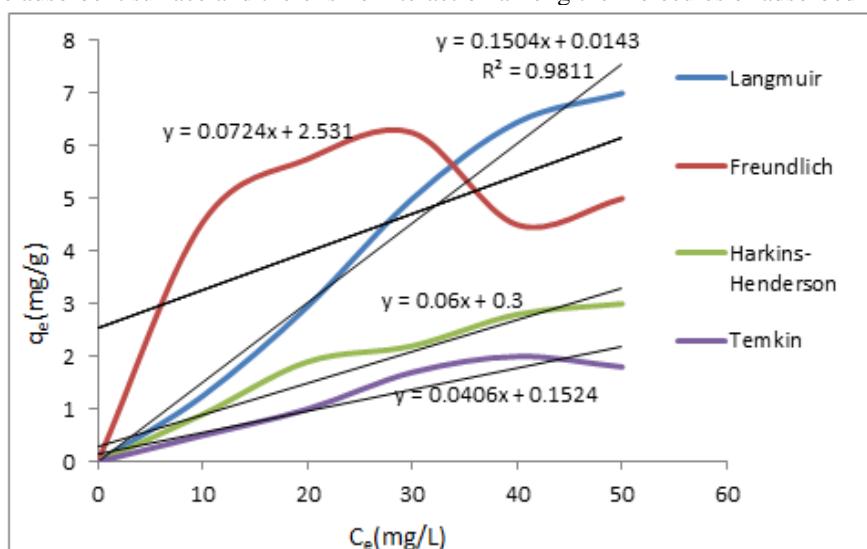


Figure 6. Isotherm adsorption of Oily water adsorption onto Cane Papyrus.

3.7 Adsorption Kinetics Study

Adsorption kinetics studying shows the adsorbed rate and adsorbate rate onto adsorbent, so it's required for finding the best-operating environments [42]. Many kinetic models analyze the adsorption kinetics data.

3.7.1 Pseudo-first-order kinetic model

This model was planned via Lagergren[43]. Equation (7) shows the linearized form.

$$\log(qe - qt) = \log qe - \frac{k_1 t}{2.303} \quad (7)$$

" q_e " & " q_t " are adsorption capacity at equilibrium and at time t respectively in (mg/g), " k_I " rate constant of pseudo-first-order adsorption in (min^{-1}) [20].

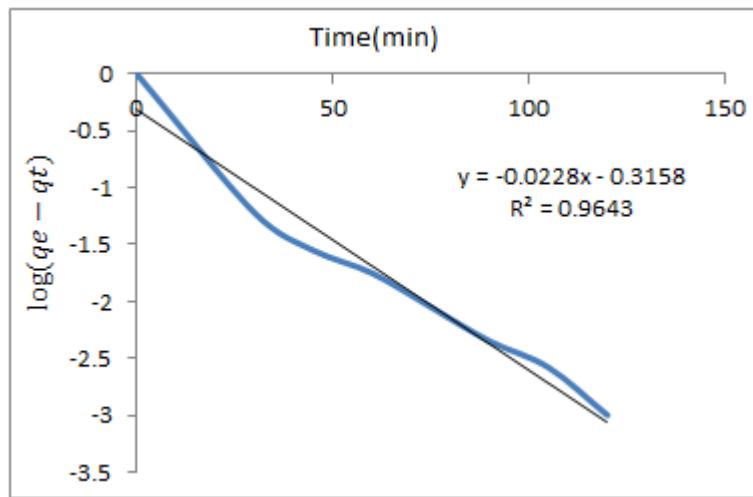


Figure 7. Oily water adsorption by Cane Papyrus, Pseudo-first-order adsorption kinetics.

3.7.2 Pseudo-second-order kinetic model

This model of kinetic appeared in the following equation [44]:

$$\frac{dq_t}{dt} = ks(qe - qt)^2 \quad (8)$$

When " k_s " adsorption rate constant in g/(mg.min).

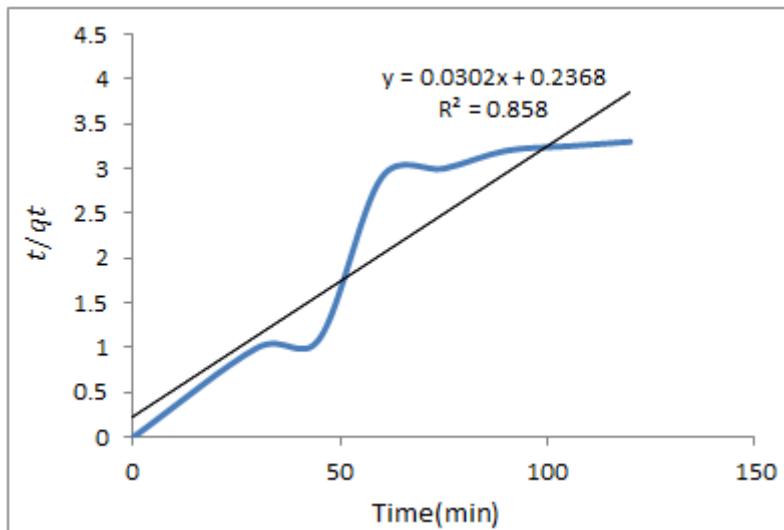


Figure 8. Oily water absorption by Cane Papyrus, Pseudo-second-order adsorption kinetics.

3.7.3 Intra particle diffusion study

In the intraparticle diffusion, the adsorption occurs on the absorbent surface initially, then the sorbate will spread into the adsorbent substance's interior pores. The following relationship describes this process[45]:

$$qt = k_{id}t^{\frac{1}{2}} + C \quad (9)$$

When " k_{id} " & "C" are rate constant of intra-particle diffusion.

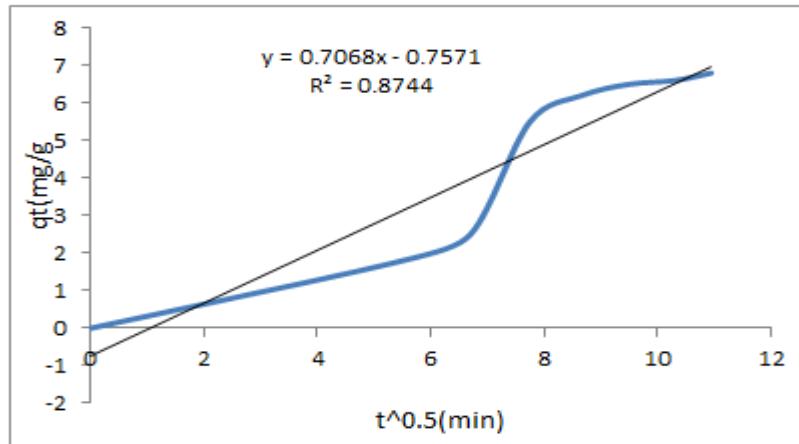


Figure 9. Intra particle adsorption kinetics of oily water onto Cane Papyrus.

3.7.4 Elovich model

The heterogeneous chemisorption was assumed in the Elovich model. It's widely used in liquid-solid adsorption. Equation 10 described this type[45]:

$$qt = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t \quad (10)$$

When "α" initial bio-sorption rate in (mg/g.min) & "β" surface coverage connected to the extent and the chemisorption activation energy in (g/mg).

The batch process instantaneous adsorption was investigated using four different models. These kinetic models included the "pseudo-first-order", "pseudo-second-order", "intra-particle diffusion", and "Elovich" models. The experimental results were employed to derive kinetic parameters using these models[40].

The contacts for these models were obtained using Microsoft Excel Software. Table 2 shows the results of this analysis and Figures 7 to 10 represent the adsorption capacity with the fitted model. Figure 7 represents the relation of log (qe-qt) and time for the "pseudo-first-order" model, Figure 8 represents the relation of (time/qt) and time for the "pseudo-second-order" model, Figure 9 represents the relation of qt and (time)^{0.5} for the "intra-particle diffusion" model, and Figure 10 represents the relation of qt and ln(time) for "Elovich" model[40].

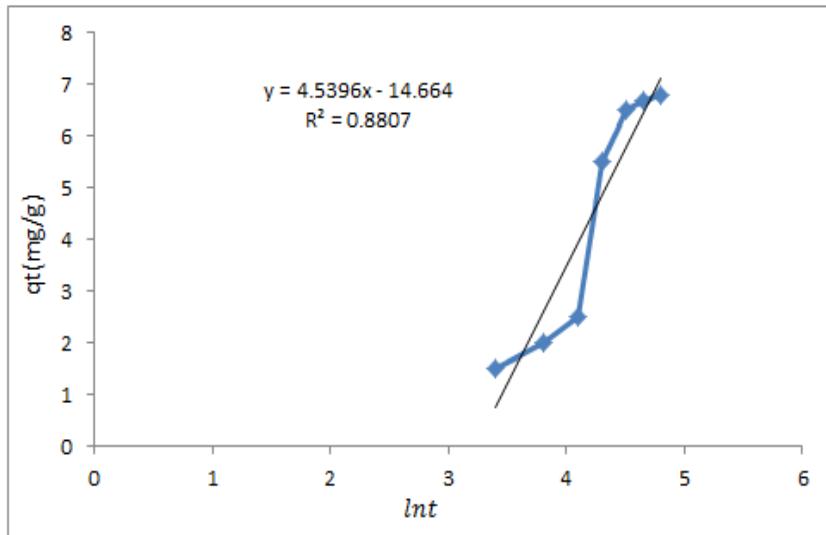


Figure 10. Elovich model for adsorption kinetics of oily water onto Cane Papyrus.

By comparing the correlation coefficient (R²) values of each curve for all four models listed in table 2, it seems that the kinetics of the oil content adsorption onto Cane Papyrus was found to be fitted through a "pseudo-first-order" model more than further models, that shows Lagergren kinetic model applicability for defining the oily water adsorption process by the Cane Papyrus[40].

Table 2. Kinetic constants models for the adsorption of oily water onto Cane Papyrus.

Model	Parameters	Values
"Pseudo-first order" Equ. (5)	q_e	0.0228
	K_I	0.3158
	R^2	0.9643
"Pseudo-Second Order" Equ. (6)	q_e	0.0302
	K_s	0.2368
	R^2	0.8580
"Intra-Particle Diffusion" Equ. (7)	K_{id}	0.7068
	C	0.7571
	R^2	0.8744
"Elovich" Equ. (8)	α	4.5396
	β	14.664
	R^2	0.8807

3.8 Adsorption Thermodynamic Results

Oily water adsorption effect on the temperature was deliberate at a ranging temperature between 20°C toward 60 °C. "The Gibbs energy change" (ΔG°) specifies an adsorption process spontaneity degree, and advanced undesirable value reproduces extra dynamically promising adsorption[45]. Parameters of thermodynamics like "standard free energy change" (ΔG°), "standard enthalpy change" (ΔH°) and "standard entropy change" (ΔS°) are calculated utilizing the these equations [46]:

$$\Delta G^\circ = -RT \ln K_c \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

when "R" universal gas constant equal to (8.314 J/mol. K), "T" temperature in (K) and "Kc" thermodynamic constant of equilibrium (without units).

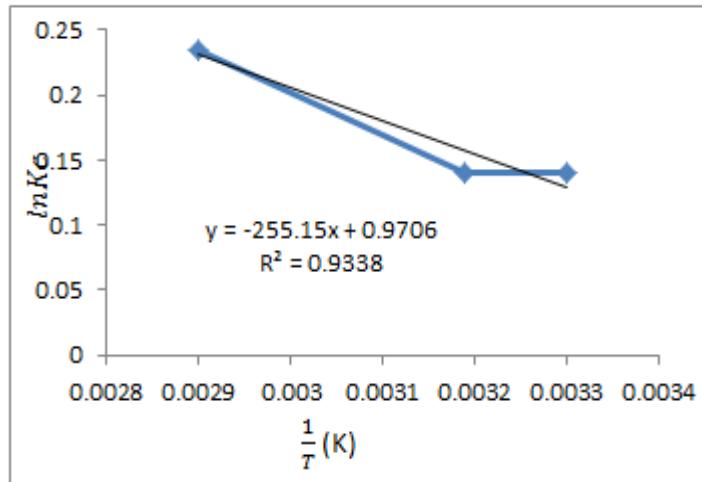


Figure11. Thermodynamic Parameters for oily water adsorption onto Cane Papyrus.

The adsorption "enthalpy change" (ΔH°) and "entropy change" (ΔS°) can be are getting from this relation:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

From Equation (13), (ΔH°) and (ΔS°) limits are intended from the slope and intercept of a plot of $\ln K_c$ versus $\frac{1}{T}$, respectively (Figure 11).

The positive value of ΔH° shown the endothermic adsorption process(0.673 KJ/mol.). A little but positive value of ΔS° (0.0198 KJ/mol.K) in the temperature range(20–60)°C suggested increased randomness at the solid-solution interface due to some water molecules being removed through oil adsorption. "Free energy change" ΔG° values were adverse checking that oil adsorption is impulsive and thermodynamically promising then ΔG° converted more adverse when the temperature indicated a high driving force and hence resulting in higher adsorption capacity at higher temperatures Table 3 [47].

Table 3. Thermodynamic Parameters for oily water adsorption onto Cane Papyrus.

Temperature (K)	ΔG° (kJ/mol)	R^2	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)
293	- 5.14	0.9338	0.673	0.0198
303	- 5.33			
333	- 5.92			

4. Conclusions

The Cane papyrus is used as a natural and low-cost adsorbent in this study to adsorb polluted water from a southern Iraqi oilfield drilling company. Fourier transforms infrared spectroscopy, EDX spectra, and scanning electron microscopy was used to examine Cane papyrus (SEM). After testing the effect of several parameters such as adsorbent dose, temperature, and contact time, pH has no significant effect on the adsorption process because the polluted water has already been neutralized by coagulation and flocculation. The best results were obtained utilizing an adsorbent dosage of 0.4g/100mL, a temperature of 60°C, and a contact length of 90 minutes. Langmuir, Freundlich, Temkin, and Harkins-Henderson isotherm models were investigated, and the results were 0.9811, 0.6675, 0.8964, and 0.9459, respectively. The Langmuir model best described the adsorption process when compared to the other models, the adsorption capacity at this condition was 0.563 mg/g. With 0.9643 for Pseudo-first-order, 0.8580 for Pseudo-second order, 0.8744 for Intra particle diffusion research, and 0.8807 for the Elovich model, the kinetics of the process was best represented by the pseudo-first-order kinetic equation. The impact of temperature variations on thermodynamic parameters such as standard free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) is studied in thermodynamics. Cane papyrus was found to be a good adsorbent for extracting oil from polluted water the studies.

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CONFLICT OF INTEREST

The author declares that there is no conflict of interest regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy have been completely observed by the authors.

Nomenclature

<u>Symbol</u>	<u>Definition</u>	<u>Unit</u>
<i>A</i>	Temkin isotherm parameter	L/g
<i>a_l</i>	Langmuir isotherm parameter	dm ³ /mg
<i>a_f</i>	Freundlich isotherm parameter	mg/g
<i>B</i>	Temkin isotherm parameter	J/mol
<i>b_f</i>	Freundlich isotherm parameter	
<i>C</i>	Constant, defined by intra-particle diffusion kinetic	mg/g
<i>C_e</i>	Concentration at equilibrium	mg/L
<i>C_o</i>	Initial concentration	mg/L
<i>K_I</i>	Pseudo-first order rate constant	1/min
<i>K_{H-H}</i>	Harkins-Henderson isotherm parameter	(mg/g)(mg/L) ^{1/n}
<i>K_{id}</i>	Constant defined by intra-particle diffusion kinetic	mg/g.min ^{0.5}
<i>K_L</i>	Langmuir isotherm parameter	dm ³ /g
<i>K_s</i>	Pseudo-second order rate constant	1/min
<i>M</i>	Mass of adsorbent	g
<i>n</i>	Harkins-Henderson isotherm parameter	mg/g
<i>q</i>	Adsorption capacity	mg/g
<i>q_e</i>	Adsorption capacity at equilibrium	mg/g
<i>q_t</i>	Adsorption capacity at time t	mg/g
<i>R</i>	Universal gas constant	8.314 J/mol.K
<i>R²</i>	Correlation coefficient	-
<i>t</i>	Time	Min

V	Volume of solution	L
α	Constant defined by Elovich kinetic	mg/g. min
β	Constant defined by Elovich kinetic	g/mg

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