Sustainable Oil Adsorption from Produced Water using Cane Papyrus as Natural Biosorbent.

Mohammed Jaafar Ali Alatabe
Department of Environmental Engineering, College of Engineering, Mustansiriyah University, Baghdad, Iraq.
Email: mohammedjafer@uomustansiriyah.edu.iq

Abstract

High quantities of wastewater produced from producing natural gas and oil from the aquifer, which called produced water. The produced 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 produced water from the southern Iraqi oilfield drilling company to adsorption by the Cane papyrus as natural and low-cost adsorbent. The analysis 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, solution pH, mixer speed and contact time. The Langmuir, Freundlich, Temkin and Harkins-Henderson isotherm models were tested, the results were 0.998, 0.966, 0.931 and 0.966 respectively. The Langmuir model was more suitable described the adsorption process than the other models. The kinetics results were, 0.984 for Pseudo-first-order, 0.938 for Pseudo-second order is, 0.979 for Intra particle diffusion study and 0.912 for the Elovich model, the Pseudo-first-order kinetic equation best described the kinetics of the reaction. The thermodynamics study effect temperature changes on the thermodynamic parameters such as standard free energy change ($\Delta G^o$), standard enthalpy change ($\Delta H^o$) and standard entropy change ($\Delta S^o$). The experimental data obtained demonstrated that Cane papyrus is a suitable adsorbent for removing oil from produced water.

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

1. Introduction

The crude oil-producing operations generate a great volume of produced water, many international companies suffer from this problem. The treatment challenge to these oily water production is very difficult because of increase 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 natures produced, methods of extraction, the reservoir lifetime draw 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 produced 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 produced water, such as membrane process(ultrafiltration and nanofiltration membranes)[4], gravity separation[5], skimming[6], neutralization[7], microfiltration and biological processes[8], coagulation[9][10], flocculation[11], flotation[12], air flotation[13], emulsion breaking[14], activated sludge[15], chemical precipitation[16], membrane bioreactor[17], ion exchange[18], electrochemical[19], biochemical and biological treatment[20], electrocoagulation[21], extraction[22], and adsorption[23]. There are many disadvantages in utilizing these techniques, likes not efficient at lower concentrations[24], needed high power consumption, slow kinetics[18], not efficiently removed the organic pollutants[25], increased initial capital and maintenance costs, increased costs of disposal sludge, low flow rate [26].

Adsorption has piqued people's interest in recent years since it appears to be a promising methodology for long-term successful treatments as well as a cost-efficient strategy for removing oily water. Adsorption is a crucial process in today's world, because to its adaptability and ease of use. Mass transfer from a liquid phase to the adsorbent surface is referred to as "adsorption." [27]. The benefits of using adsorption to remove or minimize oily water, particularly at low concentrations, include expanding the use of adsorption as a valuable and practical...
technique. The efficacy of adsorption techniques is primarily classified based on the nature of the contaminants that spread in solution, the contaminant’s molecular size and polarity, as well as the type of adsorbent utilized. Adsorption can also be caused by interactions between surfaces and the species being adsorbed at molecular levels [28]. Physical adsorption and chemisorption are two different types of adsorption. Physical adsorption is a reversible process that occurs when molecules of the adsorbent and adsorbate interact through intermolecular forces of attraction. Chemisorption, on the other hand, causes chemical reactions between solid and adsorbed compounds [29]. Chemisorption, also known as active adsorption, is an irreversible process. Physical adsorption is increased at temperatures near the critical temperature of a given gas, whereas chemisorption occurs at temperatures above the critical temperature. Furthermore, depending on the situation, both processes are likely to occur at the same moment or independently [30].

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 [31]. Many adsorbent materials used to removed and minimize the oil in produced oily water such as hydrated cellulose [32], peat-moss [33], hemp [34], synthetic fibers [35], polyurethane foam [36], straw [37] [23], wood shavings [38], cotton [39], artificial or synthetic materials based on viscose [40], sawdust [41], clay [42], turf [34], thermoplastic materials [40], wood flour [43]… etc.). Other researchers utilized Auricularia polytricha. Also, removed the oil from water using as adsorbents [44] [45], eggshell [46], kapok fiber [47] [48] [49], Zink Oxide Nano Particle as Catalyst [50], walnut shell media [51], modified sugarcane bagasse [52] 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 grow in many place in the world, in Iraq, it's mainly growth in the marshes southern Iraq. Figure 1 shown the growth places distribution of Cane papyrus in the marshes southern Iraq. Cane Papyrus growing naturally at high density and using for many tasks there, so it's can be (a biological absorbent) is a viable technology due to availability, sustainability, renewable and low cost.

Figure 1. The marshes southern Iraq Map.

This research aims to remove the oil from produced water resulting from the southern Iraqi drilling oilfield company using harmful, invasive and natural growing plants as adsorbent 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 began in October 2019, when the leaves of the Cane Papyrus plant had already developed and appeared to be quite fresh. The leaves were carefully removed from the plant stems and properly cleaned with tap water to remove dirt, soil particles, and debris before being sun-dried for at least 10 days. Using a hammer mill, the dry biomass was ground to a fine powder with a mesh size of (100-200) m for use in experiments, and then weighed. After grinding, the materials were dried in a 105°C oven for 24 hours. Desiccators
were used to keep samples from absorbing any more moisture. After that, dried samples were placed in a porcelain crucible with a lid and heated in a control muffle furnace at 150 °C for an hour. The samples were first rinsed in 1M hydrochloric acid solutions, followed by distilled water until the pH reached 7.0. The samples were washed and dried in a 105°C oven for 24 hours. The samples were then dried and stored in desiccators to prevent further moisture absorption. The adsorbent had a fluffy, porous, and rough microstructure with some gaps and cracks that made it appropriate for oil adsorption.

**Instruments.**

There are many equipment utilized to complete the experiments of this research such as:

1. A sensitive balance of 0.00001 accuracies (Fig. 2A).
2. Shaker with the perforated platform, Tablar 2000, Heidolph (Fig. 2B).
3. Hot plate with a magnetic stirrer and controlling thermostat (Fig. 2C).
4. Water bath, model WNB, Memmert company, (Fig. 2D).
5. UV-visible spectrophotometer, model GenesysTM 10, Thermo company, (Fig. 2E), and
6. Shimadzu XRD-6000 X-ray diffraction equipment for qualitative analysis and energy dispersion, X-ray spectroscopy (EDX-7000, Shimadzu, device for quantitative analysis), (Fig. 2F).

Also, acid-washed glassware, measuring pipette, conical flask, volumetric flask, cylinders, beakers were used.

![Image of instruments](A) (B) (C) (D) (E) (F)

**Figure 2.** The instruments utilized in experimental work.

Cane Papyrus properties clear by FTIR, SEM and EDX tests shown in Figures 2 and 3.

**2.1 Investigation for Fourier Transform Infrared Spectroscopy (FT-IR).**

The Cane Papyrus FT-IR spectra images were recorded and shown in Figure 2(A). The medium length and two peaks observed at 2,150 cm$^{-1}$ and 4000 cm$^{-1}$ are attributed to the presence of the C-H asymmetrical stretching and symmetrical stretching respectively. The peak at 850 cm$^{-1}$ was assigned to C=O stretching of the carboxylate group, 1540 cm$^{-1}$ is related to C=C stretching of the alkenes group. Chaudhary et.al, "indicate the main functional groups responsible into adsorption opration are aldehyde, alkene, carboxylic acids, nitro compound, and phosphate groups".

**2.2 Scanning Electron Microscopic (SEM) and Energy Disperse X-ray spectra (EDX) investigations.**

The SEM images and EDX spectra of the Cane Papyrus surface are shown in Figures 4 and 3(B). It's clear from the Figure the irregular and rough surface with many creases. The white region in the SEM spectrum indicated Si. The presence of large amounts of silica could enhance the adsorption capacity of adsorbent[ref EDX is a very good tool for identifying elements on the adsorbent surface. The presence of C, O, and Si, ions on the Cane Papyruzsurface were confirmed by the peaks at 0.2, 0.5, and 1.7 keV, respectively.
Figure 3. Fourier transforms infrared spectroscopy and EDX spectra of Cane Papyrus.

Figure 4. Scanning Electron Microscopic (SEM) of Cane Papyrus.

2.3 Produced water

The samples collected from the southern Iraqi drilling oilfield company, the analysis of these samples from the source, its content at this results in Table 1.

Table 1. Oily water produced analyzes and specifications.

| compound              | Concentration(mg/l) |
|-----------------------|---------------------|
| TDS                   | 189420              |
| TSS                   | 35.7                |
| Chloride              | 111534              |
| Calcium               | 8530                |
| Sulphate              | 5194                |
| Magnesium             | 3825                |
| Bicarbonate           | 686.8               |
| Oil and grease        | 625                 |
| Manganese             | 25                  |
| Zinc                  | 2.5                 |
| Chromumme             | <0.5                |
| Iron                  | <0.5                |
| Nickel                | <0.5                |
| Carbonate             | Nil                 |
2.4 **Experimental procedure**

Firstly coagulation/flocculation process was conducted using 70mg/l of KlarAid CDP1326 and 2.5 mg/l of Zetag 8140 to treated produced water. The oil content reduced to 54.6 mg/l in previous work [10]. After that, 100 ml of produced water was used to study the ability of Cane Papyrus to adsorb oil from produced 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, temperature (30,40,50 and 60) °C 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.

2.5 **Adsorption capacity.**

Equation 1, utilized for calculate adsorption capacity(q)[53]:

\[
q = \frac{V(C_0 - C_e)}{M} \tag{1}
\]

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:

\[
(\%) \text{ Oil removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}
\]

3. **Results and Discussion**

The research major aim is to detect the best parameters of the operation to oil adsorption maximize.

3.1 **Contact Time Effect Study.**

For achieving an equilibrium, the contacts time relationship, and oil removal was managing between them over the batch process as shown in Figure 5. When increased contact time, increased oil removal. At the beginning of (5-40) min, the adsorption was very fast because of an increase in adsorbent surface area voids when time at 60 min the adsorption be very rapid on the surface take place. After that, the adsorption reaction decreases because of fill most of the adsorbent surface area voids[54].

![Figure 5](image)

**Figure 5.** Contact time effect to %oil removal onto Cane Papyrus at T= 60°C, Adsorbent dose= 0.5 g/100 ml.

3.2 **Adsorbent dose Effect Study.**

Figure 6 show, the changing in oil removal with changing in adsorbent dose in specific conditions, also can see, increased the oil removal when increases adsorption dosage, at adsorbent dosage of 0.753 g/100 ml attained the maximum value (100%). When sorbent dosage increase, the adsorption process decreased because of the unsaturated oils binding sites increases [46].
3.3 Temperature Effect Study.

Figure 8, show the temperature effect into oil removal, it's know oil is sticky and hydrophobic. The temperature affects the solubility of liquids. Increasing the temperature will increase the solubility, hence its improves the mass transfer processing, the removal of oil would increase[55].

3.4 Adsorption isotherms models

Pollutants distribution among the liquid and solid phases call for the adsorption isotherm [56]. In this research, studying four models of isotherm toward get finest model appropriate with oil removal by Cane Papyrus:

3.4.1 The Langmuir model

The Langmuir isotherm assumes monolayer adsorption. Equation 1 was used to describe this type of isotherm[57][58],

$$q_e = \frac{K_l C_e}{1 + a_l C_e}$$  \hspace{1cm} (3)

when "K_l" in (dm$^3$/g) & "a_l" in (dm$^3$/mg) are Langmuir constants.

3.4.2 The Freundlich model

In this type of isotherm, the adsorption sites are distributed exponentially[59], and it is given by equation 2:

$$q_e = a_f C_e^{b_f}$$  \hspace{1cm} (4)

When "q_e" adsorbed metal ions in (mg/g), "a_f" capacity of multilayer adsorption in (mg/g) and "b_f" adsorption intensity (an empirical number).

3.4.3 Temkin isotherm model

It is obtained with consideration of adsorption interaction and adsorption substances[59] in this model the change between the adsorption heat and the coverage is decreases linearly [60]. Equation 3 describes this relation:

$$q_e = \frac{R T}{B} \ln AC_e$$  \hspace{1cm} (5)

where (\frac{R T}{B}) = "B" Temkin constant in (J/mol), "R" universal gas constant, "A" equilibrium binding constant in (1/g) and "T" absolute solution temperature in (°K).
3.4.4 Harkins-Henderson Model

This model assumes multilayer adsorption[60][61]. Equation 6 describes the Harkins-Henderson isotherm:

\[ q_e = \frac{K_{H-H}^{1/n} c^n}{c + K_{H-H}^{1/n}} \]  

(6)

\( n \) and \( K_{H-H} \) are isotherm constants.

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 presented in Table 2, it is visible that \((R^2)\) "regression correlation coefficient" for equation of Langmuir model \((R^2 = 0.998)\) is more linearity comparing with the other models equations, inclusion the data of adsorption isotherm were fully proportion with the Langmuir isotherm. Experimental curve and isotherm model curves shows in Figure 8.

Table 2. The isotherm model constants for oily water produced.

| Isotherms              | Parameters | Values |
|------------------------|------------|--------|
| Langmuir               | \( q_L \)  | 0.1404 |
|                        | \( K_L \)  | 1.17   |
|                        | \( R^2 \)  | 0.998  |
| Freundlich             | \( b_f \)  | 0.77   |
|                        | \( a_f \)  | 1.89   |
|                        | \( R^2 \)  | 0.966  |
| Temkin                 | \( A \)    | 34.47  |
|                        | \( R^2 \)  | 0.931  |
| Harkins-Henderson      | \( K_{H-H} \) | 2.29  |
|                        | \( R^2 \)  | 0.966  |

The experimental data fit the Langmuir isotherm very well-meaning the process is a single-layer and the maximum oil molecules adsorption onto 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". The same finding was observed by Sarkheil et al[52].
吸附动态研究

3.5.1 假一阶动力学模型

该模型由Lagergren[63]提出。方程（7）显示了线性化形式。

$$\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303}$$

$q_e$ 和$q_t$ 分别是吸附等量吸附容量和吸附容量在时间t时，单位是（mg/g），$k_1$是假一阶吸附速率常数，单位是（min$^{-1}$）[26]。

3.5.2 假二阶动力学模型

该模型由方程（8）表示。

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

当“$k_2$”是吸附速率常数，单位是g/(mg.min)。
3.5.3 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 interior pores. The following relationship describes this process:

\[ q_t = k_{id} t^{1/2} + C \]  

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

3.5.4 Elovich model

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

\[ q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta} \ln t \]  

When \( \alpha \) initial bio-sorption rate in \((\text{mg/g.min})\) & \( \beta \) surface coverage connected to the extent and the chemisorption activation energy in \((\text{g/mg})\).

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 for derive kinetic parameters using these models.
Figure 12. Elovich model for adsorption kinetics of oily water onto Cane Papyrus.

The contacts for these models were obtained using Microsoft Excel Software. Table 3 shows the results of these analysis and Figures 9 to 12 represent the adsorption capacity with the fitted model. Figure 9 represents the relation of log (qe-qt) and time for "pseudo-first-order" model, Figure 10 represents the relation of (time/qt) and time for "pseudo-second-order" model, Figure 11 represents the relation of qt and (time) 0.5 for the "intra-particle diffusion" model, and Figure 12 represents the relation of qt and ln (time) for "Elovich" model.

By comparing the correlation coefficient (R2) values of each curve for all five models listed in table 5, 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 define the oily water adsorption process by the Cane Papyrus.

Table 3. Kinetic constants models for adsorption oily water onto Cane Papyrus.

| Model                  | Parameters | Values |
|------------------------|------------|--------|
| "Pseudo-first order"   | qe         | 142.2  |
| Equ. (5)               | K1         | 0.0207 |
|                        | R²         | 0.984  |
| "Pseudo-Second Order"  | qe         | 0.543  |
| Equ. (6)               | K₄         | 1.826  |
|                        | R²         | 0.938  |
| "Intra-Particle Diffusion" | Kₐd    | 0.967  |
| Equ. (7)               | C          | 0.474  |
|                        | R²         | 0.979  |
| "Elovich"             | α          | 2.895  |
| Equ. (8)               | β          | 0.515  |
|                        | R²         | 0.912  |

3.6 Adsorption Thermodynamic Results

Oily water adsorption effect onto the temperature was deliberate at ranging of temperature between 20 toward 60 °C. "The Gibbs energy change" (ΔG°) specifies an adsorption process spontaneity degree, and advanced undesirable value reproduces extra dynamically promising adsorption [66][67][68]. Parameters of thermodynamic like "standard free energy change" (ΔG°), "standard enthalpy change" (ΔH°) and "standard entropy change" (ΔS°) are calculate utilize the these equations [67]:
\[ \Delta G^\circ = -RT \ln K_c \]  \hspace{1cm} (11)

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]  \hspace{1cm} (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). The adsorption "enthalpy change" (\( \Delta H^\circ \)) and "entropy change" (\( \Delta S^\circ \)) can be are getting from this relation:

\[ \ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \]  \hspace{1cm} (13)

From Equation (9), (\( \Delta H^\circ \)) and (\( \Delta S^\circ \)) limits are intended from the slope and intercept of a plot of \( \ln K_c \) versus \( 1/T \), respectively (Figure 14).

Figure 13. Thermodynamic Parameters for oily water adsorption onto Cane Papyrus.

Parameters of thermodynamic proposal vision in category and an adsorption process mechanism. "Free energy change" \( \Delta G^\circ \) Values were adverse checking that oil adsorption is impulsive and thermodynamically promising then \( \Delta G^\circ \) converted more adverse when temperature upsurge to (-0.27,-0.39 and-0.63)KJ/mol. at (20,30 and60)°C respectively, indicating a high driving force and hence resulting in higher adsorption capacity at higher temperatures. The positive value of \( \Delta H^\circ \) shown the endothermic adsorption process(0.756 KJ/mol.). A little but positive value of \( \Delta S^\circ \) (0.0225 KJ/mol.K) in the temperature range20–60 °C suggested increased randomness at the solid-solution interface due to some water molecules were removed through oil adsorption [69].

4. Conclusions

The study showed that the Cane Papyrus was effective in adsorption oil from Produced water due to the availability of effective functional gropes as shown in FTIR. 97% oil removal at temperature 30°C, PH 9, adsorbent dose 0.1g and 90min contact time The Langmuir equation fits the experimental data for equilibrium isotherm of oil removal more than other equations. The pseudo-first-order adsorption is predominant for kinetics and thermodynamics studies. Finally, as the Cane Papyrus adsorbed some polluted oil from the produced water, we recommended using it in oil-fired power stations as heating sources.

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CONFLICT OF INTEREST

The author states that the publishing of this article is free of conflicts of interest. Furthermore, the author have carefully considered ethical problems such as plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publishing and/or submission, and redundancy.

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