INTRODUCTION

Oil is the world most important source of energy. Extraction of oil and gas is accompanied by the release of vast amounts of water, known as produced water, as a by-product. The proportion of water created in oil varies based on a variety of conditions, but in mature or ancient fields, it can exceed 98 percent of the material taken from oil wells. Due to the volume of oily water and waste products increasing, treating problems of this oily water production is quite difficult. It is regarded as the primary cause of environmental pollution caused by oil extraction operations. Geological formation, extraction methods, natures created, hydrocarbon reservoir lifespan drawn up from it, and field location all have an impact on the nature of this water. Because it was brought to the surface through the extraction of oil or gas from a hydrocarbon reservoir, this water contains a variety of complex organic and inorganic chemicals (Galvão 2017).

Many traditional techniques available to treat the produced water, like flotation (da Silva et al. 2015), air flotation (Panneer Selvam 2018; Al-Shamrani, James, and Xiao 2002), skimming (Hobson 1996), gravity separation (Pintor et al. 2016), neutralization (Elmi et al. 2021), biological microfiltration processes (Ghimire and Wang 2018), membrane bioreactor (Capodici et al. 2017), membrane process (ultrafiltration and nanofiltration membranes) (Elhady et al. 2020), extraction (Vegas Mendoza et al. 2019), coagulation (Zhao et al. 2021; Jabbar and M.J. Alatabe 2021), flocculation (Jabbar and M.J. Alatabe 2021; Jabbar and M.J.A. Alatabe 2021), electrocoagulation (Hassan, AlJaber, and AL-Khateeb 2022), ion exchange (Charles et al. 2016), emulsion breaking (You et al. 2018), activated sludge (Alexandre et al. 2016), chemical precipitation (Altash and
Büyükşengör (2008), electrochemical (Druskovic et al. 2021), biochemical and biological treatment (Acharya et al. 2020), and adsorption (Hamid et al. 2016). These approaches have various drawbacks, including low flow rates, delayed kinetics, high power requirements, ineffective removal of organic pollutants, increased upfront capital and maintenance expenses, and inefficient removal of organic pollutants at lower concentrations (Jaafar and Alatabe, 2019).

Adsorption is the greatest way to make bioseparation a practical technology that is more cost-effective than conventional methods by employing waste from sustainable agricultural sources of raw materials (Rajakovic et al. 2007). Numerous adsorbent substances, including hydrated cellulose, were utilized to extract and reduce the oil in the resulting oily water (El Achaby et al. 2018), peat-moss (Pandey and Alam 2019), hemp (Devi and Khanam 2019), polyurethane foam (Nikkhah et al. 2015), straw (Ibrahim, Wang, and Ang 2010), sawdust (Fugaeva, Malyshkina, and Glushchenko 2021), cotton (Ge et al. 2014), turf (Pasila 2004), wood flour (Aranguren, González, and Mosiewicki 2012). Other researchers used Auricularia polytricha to adsorbents to extract the oil from polluted water (Yang et al. 2014; Pintor et al. 2016), eggshell (Muhammad et al. 2012), kapok fiber (Rengasamy et al. 2011; Wang et al. 2012; Wang et al. 2013), walnut shell media (Srinivasan and Viraraghavan 2008), modified sugarcane bagasse (Behnood et al. 2016) to obtain a strong ability to extract the oil from oily water, as adsorbers media. Sedge cane is a low-cost, exotic, natural, and eco-friendly plant that can be used to absorb oil from oily water. It is cultivated all over the world. Due to availability, sustainability, renewable resources, and low cost, sedge cane (a biological absorbent) is a viable technology. Sedge cane grows naturally at high density and is used for various tasks there.

By employing natural plants (Sedge cane) as adsorbent under a variety of conditions, including temperature, adsorbent dose, and contact time. Manuscript intends to recover the oil and treated generated water while also examining the isotherm, kinetics, and thermodynamics of adsorption.

MATERIALS AND METHODS

Collection process of the sedge cane, when the sedge cane’s leaves had already sprouted and appeared to be in excellent condition. The leaves were carefully separated from the plant stems, properly washed with tap water to remove dirt, soil, and debris, and then allowed to dry in the sun for at least a week. The desiccated biomass was powdered into a fine mist using (100–200) 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. Following grinding, the materials were dried for 24 hours at 105 °C in an oven. The dried samples were then kept in desiccators to stop them from absorbing any more moisture. The adsorbent had a microstructure that was fluffy, extremely porous, rough, and contained some gaps and cracks that were ideal for adsorbing oil. SEM tests (X-ray diffraction device (XRD-6000, Shimadzu, equipment for qualitative analysis) and FTIR (UV-visible spectrophotometer, model Genesys TM 10, Thermo firm) demonstrate the sedge cane’s qualities.

Procedure

First, treated produced water was flocculated using 30 ppm of ferric sulfate as the coagulant and 2.5 mg/L of polyacrylamide as the flocculant dosage. In earlier studies, the oil content decreased to 53.56 mg/L. (Alkhazraj and Alatabe 2021; Jabbar and M.J.A. Alatabe 2021). The capacity of Sedge cane to absorb oil from produced water was then investigated using 100 mL of produced water. Adsorbent dose 0.5, 1, 2, 3, 4 and 5 g, temperature 30, 40, 50 and 60 °C, used Water bath, model WNB, Memmert Company. The variables under investigation were contact duration (15, 30, 60, 90, and 120 min) and rotational speed of the mixer (250 rpm) with a hot plate with a magnetic stirrer. The TD-500 examined the materials’ oil concentration. The development of the adsorption method must consider the best design for the adsorption of oil. Additionally, beakers, cylinders, measuring pipettes, conical flasks, volumetric flasks, and acid-washed containers were employed.

Adsorption capacity

The percentage removal of Oil from water was estimated by using Equation (1):

\[
\text{Oil removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}
\]
To calculate the adsorption capacity (q) utilized Equation (2):

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

where: q is expressed as mg/g,

$C_0$ is the initial concentration,

$C_e$ is the equilibrium concentration,

M is the adsorbent dosage,

V is the solution volume (L),

(Hadi, Al-Zobai, and Alatabe 2020).

**RESULTS AND DISCUSSION**

**Investigation for Fourier transform infrared spectroscopy**

Figure 1 shows the Fourier transform infrared (FTIR) spectrum of sedge cane. In this spectra, an absorption line at 3400 cm$^{-1}$ corresponds to the axial vibration of the hydroxyl groups (O-H) in cellulose. The oscillation of CH$_2$ and CH$_3$ molecules in organic structures is shown by the band at 2850 cm$^{-1}$. Due to its limited amplitude, this band in the sedge cane May not make significant contact with the polymer matrix during the production of a composite. The link between organic molecules is represented by the band at 2360 cm$^{-1}$. The C=O aromatic groups are represented by the band at 1650 cm$^{-1}$, while the C-O and C-C bonds are represented by the band at 1250 cm$^{-1}$. Deformation of the corresponding covalent bonds C-O and C-C are responsible for the bands at 1020 and 460 cm$^{-1}$, respectively.

**Scanning electron microscopic investigation**

Scanning electron microscopic (SEM) observations of the sedge cane’s surface properties are shown in Figure 2. A relatively rough sedge cane surface, like that in Figure 2c, is usually regarded as a benefit for composite materials because it might encourage mechanical interlocking at the sedge cane-matrix interface, which might help the canes and matrix stick together. Higher magnification images, on the other hand, showed...
inhomogeneity, as shown by the difference between the rougher and smoother areas of Figure 2B. Inset of Figure 2B may show micro-cracks (arrows), which could be caused by SEM electron beam strength degradation.

The primary goal of the research is to identify the ideal operational parameters that will enhance oil adsorption.

**Effects of contact time**

In order to attain equilibrium throughout the batch process, the contacts’ time connection and oil removal between them were regulated, as shown in Figure 3. Oil removal increased with longer contact times. Due to a rise in adsorbent surface area voids, adsorption occurred very quickly on the surface between the first (15–45) and last (60–90) minutes of the experiment. Following that, the adsorption reaction maintains a steady rate and then starts to slow down as the majority of the adsorbent surface area gaps are filled.

**Effects of adsorbent dose**

Figure 4 illustrates how oil removal changes as adsorbent dose varies under particular circumstances. It also demonstrates how oil removal increases as adsorbent dosage rises, reaching its maximum level at 5 g/L (95%). Due to the Sedge cane reaching its optimal dosage, the adsorption process maintains a steady rate as the sorbent dosage increases.

**Effects of temperature**

Figure 5 shows how temperature affects oil removal; as is well knowledge, oil is hydrophobic and sticky. The temperature affects how soluble a liquid is. The solubility will rise from 25 °C to 40 °C as the temperature rises, and since the reaction will remain constant with higher temperatures, the solution will have a high solubility.

**Adsorption isotherms models**

The adsorption isotherm is required due to the dispersion of pollutants between the liquid and solid phases [44]. In this study, four isotherm models were examined in an effort to find the best one that would work with sedge cane oil removal:

**The Langmuir model**

Assuming monolayer adsorption, the Langmuir isotherm. This kind of isotherm was described by Equation 1. (Langmuir 1918; Langmuir 1917).

\[
q_e = \frac{K_l C_e}{1 + a_l C_e}
\]

where: \(K_l\) in (mL/g) & \(a_l\) in (mL/mg) are Langmuir constants.

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**Figure 3.** Contact time effect to oil removal% onto the sedge cane at \(T = 40^\circ\text{C}\), adsorbent dose = 5 g/L

**Figure 4.** Adsorbent dose-effect to oil removal% at \(T = 40^\circ\text{C}\) and \(t = 60\) min

**Figure 5.** Temperature influence on oil removal percentage at 60 minutes and 5 g/L of adsorbent
The nonlinear adsorption process is modeled using the Freundlich equation [47]. One of the most popular isotherms for absorption is this one. The following equations yield the Freundlich model’s linear and nonlinear forms:

\[ q_e = K_f C_e^n \]  
\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]

where: \( q_e \) adsorbed metal ions in (mg/g); \( K_f (L^{1/n} \cdot mg^{1-1/n} \cdot g^{-1}) \) and \( n \) are constants, the Freundlich model will reduce to the linear model when \( n = 1 \).

Toth isotherm model

This model was created to expand the Langmuir model’s applications in diverse systems (Eq. (6) [48]). It is presumptive that the majority of adsorption locations have lower adsorption energies than the mean energy (Ho 2002).

\[ q_e = \frac{K_t C_e}{(at + C_e^z)^2} \]  

where: \( K_t (mg/g) \) stands for the constant, at (mgz/Lz) for the Toth constant, and \( z \) is a term that denotes how heterogeneous the adsorption systems are. \( z \) is not affected by temperature, whereas the number of at rises as the temperature rises (Barst et al. 2012). Toth model changes to Langmuir isotherm at \( z = 1 \). More heterogeneity in the adsorption system is indicated by a larger departure of \( z \) from 1.

Sips isotherm model

Another composite model that combines the Langmuir and Freundlich models is the Sips model [49]. The 3-parameter isotherm model for monolayer adsorption with the greatest applicability is the Sips model. Both uniform and heterogeneous systems can be described by the Sips model [50]. Equation presents the non-linear Sips isotherm model.

\[ q_e = \frac{q_{ms} K_s C_e^{n_s}}{1 + K_s C_e^{n_s}} \]

where: \( K_s (L^n \cdot mg^{-n}) \) and \( n_s \) are the Sips constants and \( q_{ms} (mgg^{-1}) \) is the maximum quantity that can be adsorbed.

When \( n_s = 1 \), the Sips model transforms into the Langmuir model, and at low \( C_0 \), it transforms into the Freundlich model. At low \( C_0 \), the Sips model does not, however, satisfy the Henry’s rule.

### Table 1. Constants created for oily water are modeled by the isotherm

<table>
<thead>
<tr>
<th>Isotherms models</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( a_L )</td>
<td>0.0962</td>
</tr>
<tr>
<td></td>
<td>( K_L )</td>
<td>1.4290</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
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</tr>
<tr>
<td>Freundlich</td>
<td>( n )</td>
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</tr>
<tr>
<td></td>
<td>( K_F )</td>
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</tr>
<tr>
<td></td>
<td>( R^2 )</td>
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<tr>
<td>Toth</td>
<td>( a_T )</td>
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<tr>
<td></td>
<td>( K_T )</td>
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<tr>
<td></td>
<td>( R^2 )</td>
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<tr>
<td>Sips</td>
<td>( n_s )</td>
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<tr>
<td></td>
<td>( K_s )</td>
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</tr>
<tr>
<td></td>
<td>( R^2 )</td>
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</tr>
</tbody>
</table>

![Figure 6. Oil adsorption onto sedge cane use isotherme model adsorption](image)

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To get the isotherm constants, the linearized forms of the Langmuir, Freundlich, Toth, and Sips isotherm models were analyzed using Equations (3), (5), (6), and (7), respectively. With the help of the constants in Table 1, it is clear that the equation for the Langmuir model \((R^2 = 0.9967)\) has greater linearity than the equations for other models. The results for the adsorption isotherm were also perfectly proportional to the Langmuir isotherm. Figure 6 displays experimental data and isotherm model curves.

The experimental results, which closely matched the Langmuir isotherm, pointed to a single-layer process with maximum oil molecule adsorption onto the surface of Sedge cane. The Langmuir isotherm assumes that the adsorbent surface has a limited number of active sites and that the molecules being adsorbed are not in contact with one another.

**Adsorption Kinetic Models Studies**

Adsorption kinetics research reveals the rate at which substances are adsorbed and adsorbate onto an adsorbent, hence it is necessary for determining the optimal operating conditions. The data on adsorption kinetics are examined by many kinetic models.

**Pseudo-First-Order (PFO) model**

The PFO model was firstly proposed by Lagergren (1898). The differential form of the PFO model is described by Eq. (8) (Lagergren 1898):

\[
\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{8}
\]

where: \(q_e\) & \(q_t\) are adsorption capacity at equilibrium and at time \(t\) respectively in (mg/g); \(k_1\) rate constant of PFO model in (min\(^{-1}\)) (Jaafar and Alatabe 2019).

**Pseudo-Second-Order (PSO) model**

The adsorption of lead onto grass was the first application of the PSO model (Eq. (9)). The PSO model was subsequently extensively used to explain the adsorption processes. In the majority of published articles, the adsorption experimental data and adsorption rate constants were predicted using the PSO model (Ho and McKay 1999):

\[
\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \tag{9}
\]

where: \(k_s\) PSO model rate constant in g/(mg.min).

**Elovich model**

The Elovich model’s fundamental presumptions were that:

1) the activation energy increased with adsorption duration and,
2) the adsorbent surface was heterogeneous.

An observational model without clear physical implications, the Elovich model. Although it is extensively used in liquid-solid adsorption, it is frequently used to model the chemisorption of gas onto solids. Eq. 10 provided a description of the Elovich model (10) (Elovich and Larinov 1962):

\[
q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \tag{10}
\]

where: the initial bio-sorption rate in (mg/g.min) is \(\alpha\) and the surface coverage \(\beta\) are linked to the extent and the activation energy of chemisorption in (g/mg).

Using four distinct models, the batch process instantaneous adsorption was studied. The "PFO", "PSO", and "Elovich" models were among these kinetic models. The models were developed utilizing the experimental results to generate the kinetic parameters.

| Table 2. Kinetic constants models for adsorption oily water onto Sedge cane |
|-----------------------------|-----------------|---------|
| Kinetics models             | Parameters      | Values  |
| PFO Equ. (7)                | \(q_0\)         | 137.40  |
|                             | \(K_1\)         | 0.0270  |
|                             | \(R^2\)         | 0.9382  |
| PSO Equ. (8)                | \(q_0\)         | 0.4380  |
|                             | \(K_2\)         | 1.3640  |
|                             | \(R^2\)         | 0.8147  |
| Elovich Equ. (10)           | \(\alpha\)      | 2.4220  |
|                             | \(\beta\)       | 0.4370  |
|                             | \(R^2\)         | 0.7880  |

![Figure 7. PFO kinetic model for adsorption oily water adsorption by Sedge cane](image-url)
change (H°), and standard entropy change (S°) are among the thermodynamic parameters that can be calculated using these equations (Alatabe 2018):

$$\Delta G^\circ = -RT \ln K_c$$  (11)
$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$  (12)

When the universal gas constant (“R”) equals (8.314 J/mol·K), T is the temperature in K, and Kc is the thermodynamic equilibrium constant (without units). The following relation can be used to calculate the adsorption enthalpy change (H°) and entropy change (S°):

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

Limits of (H°) and (S°) are intended from Equation (13), respectively, based on the slope and intercept of a plot of lnKc vs 1/T (Figure 10).

Thermodynamic proposed parameters and a mechanism for the adsorption process. Free energy change values were negative to see if oil adsorption was impulsive and thermodynamically viable; however, when the temperature increased to (-0.217, -0.335, -0.489, and -0.599) KJ/mol, the G° readings dropped even further. At higher temperatures, specifically (30, 40, 50, and 60 °C), there is a strong driving force and correspondingly greater adsorption capacity. The positive value of H° (0.694 KJ/mol) served as evidence for the endothermic adsorption process. Because some water molecules were removed by oil adsorption in the temperature range of 20 to 60 °C, a tiny but positive value of S° (0.0208 KJ/mol·K) showed increased randomness at the solid-solution interface.

**CONCLUSIONS**

According to the study, sedge cane was successful at adsorbing oil from generated water.
because it was available functional groups, which were shown by FTIR to be effective. The equilibrium isotherm of oil removal is best described by the Langmuir equation (95 percent oil removal at temperature 40 °C, adsorbent dosage 5 gm/L, and 60 min contact time) than other equations. For kinetics and thermodynamics research, the PFO model adsorption predominates. Finally, we advised employing sedge cane to recover oil from produced water in the oil drilling and production company since it absorbed the oil from the water with great efficiency.

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