Oil Removal from Produced Water Using *Imperata cylindrica* as Low-Cost Adsorbent

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Abstract

Produced water is wastewater that is generated as a byproduct of the extraction of oil and natural gas from underground reservoirs. It contains emulsified oil, organic compounds, inorganic compounds, suspended solids, and dissolved solids. Untreated produced water can cause serious environmental problems. In this research, batch adsorption of produced water that came from the Iraqi Midland Oil Company using *Imperata cylinderica* as adsorbent was investigated. All the experiments were done with 100 ml of produced water in a 250 ml beaker. The factors investigated were pH of the solution (3, 5, 7 and 9), temperature (20, 40, 50 and 60°C), adsorbent dosage (0.05, 0.1, 0.2 and 0.4 g), contact time (15, 30, 60 and 90 min), and the rotational speed of the mixer (150 rpm). The Taguchi method was used to determine the operating conditions. The experimental data were analyzed using statistical optimization and the aim was to develop a general model for determining the optimum conditions that would lead to 97% oil removal, which turned out to be at 30°C, pH 9, adsorbent dose of 0.1g, and 90 min contact time. The Langmuir equation fitted the experimental data for the equilibrium isotherm of oil removal better than did other equations. A pseudo-first-order adsorption was predominant from the kinetics and thermodynamic studies.

Keywords: batch adsorption, *Imperata cylindrica*, produced water
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1. Introduction

A huge volume of produced water is generated by the Iraqi Midland Oil Company. The disposal of this water into the environment without treatment has the potential to cause serious environmental problems. The treatment process to be used in such a situation depends on nature and the quality of water needed [1]. The most often used methods for treatment of oily wastewater are skimming, gravity separation, neutralization, flotation [2], adsorption, membrane separation [3], coagulation and flocculation [4], electrochemical treatment [5], emulsion breaking [6], biochemical and biological treatment [7, 8], and activated sludge processing [9]. The low molar mass of organic

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pollutants means they cannot be removed efficiently when using coagulation and flocculation processes [10]. Ion exchange processes are too slow kinetically [11]. Membrane technologies require too much power [3]. Most techniques that have been tried to date are not efficient at lower concentrations [12].

Adsorption stands out for being effective and efficient [13]. Adsorption remains the best candidate for this important task because of its simplicity, high efficiency, and easy recovery [12]. One of the keys to making biosorption a viable technology is to have a cost-effective biosorbent. By using renewable or waste raw materials, this technology has the potential to be more economically attractive than conventional technologies [13].

Developments in the field of low-cost adsorbents have led to interest in their use in water treatment processing [14]. Sorbents may be either natural, based on plants or minerals (cotton [15], turf [16], peat-moss [17], sawdust [18], wood shavings [19], wood flour [20], hemp [21], straw [22], clay [23]), or artificial or synthetic materials based on viscose, hydrated cellulose [24], synthetic fibers, thermoplastic materials, and polyurethane foam [25].

Several researchers studied the removal of oil from oily water. Muhammad *et al*. [26] used eggshell to remove oil from oil-contaminated water. The removal rate was almost 100% at a concentration of 1.8 g eggshell/l of produced water and oil concentration as high as 194 mg/l. Wang *et al*. [27] improved the efficiency of kapok fiber for oil absorbency. Kapok fiber was treated by $NaClO_2$, HCl and NaOH. The effects of time and temperature on oil recovery were studied. The oil adsorption capacity of modified sugarcane bagasse in treating oil spills within the water was examined [28]. Oil was also removed from water using *Auricularia polytricha* as adsorbent [29]. Other researchers used eggshell as adsorbent and the process was able to remove 91.21% of the oil [30].

In this research, *Imperata cylindrica,* here considered as agricultural waste, was used. *Imperata cylindrica* has increasingly been recognized as one of the world's most problematic invasive plants [31]. Figure 1 shows the general distribution of *Imperata cylindrica* throughout the world. Its use has presented as worthy of study because biosorbants have come to be seen as a viable technology due to their low cost, renewability and availability [32].

The aims of this research is to study the removal of oil (by the use of harmful, invasive and natural growing plants as adsorbents) from produced water that results from the Iraqi Midland Oil Company, by optimizing the conditions of pH, contact time, adsorbent dose and temperature, and by finding a general equation that relates these conditions to give an optimum value for adsorption. Included are the study of the adsorption isotherms, kinetics and thermodynamics.

Figure 1. The general distribution of *Imperata cylindrica* throughout the world, depicted by areas of white [26].

2. Materials and Methods

2.1 *Imperata cylindrica*

Imperata cylindrica, as an agriculture waste, was collected from roadsides and abandoned farmland around Baghdad, Iraq. Its properties were determined by FTIR, SEM, and EDX tests, the results of which appear in Figures 2 to 4 in the next section. It was washed and milled into 150-210 µm mesh size to use in experiments.

2.2 Experimental procedure

A coagulation/flocculation process was conducted using 70 mg/l of KlarAid CDP 1326 and 2.5 mg/l of Zetag 8140 to treat produced water. The oil content was reduced to 54.6 mg/l as reported in previous work [33]. After that, 100 ml of the produced water was used as a sample to study the ability of *Imperata cylinderica* to adsorb oil. The parameters investigated were pH of the solution (3, 5, 7 and 9), temperature (30, 40, 50 and 60 °C), adsorbent dose (0.05, 0.1, 0.2 and 0.4 g) and 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, as described in previous work [34].

2.3 Instruments

The equipment and instrumentation utilized to complete the experiments of this research included the following:

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

2.4 Adsorption isotherms models

The distribution of the contaminant between the solid and liquid is the Adsorption isotherm [35, 36].

2.4.1 The Langmuir model

The Langmuir isotherm assumes monolayer adsorption. Equation 1 was used to describe this type of isotherm [37-39]:

$$q_e = \frac{K_l C_e}{1+a_l C_e} \tag{1}$$

where K_l (l/g) and a_l (l/mg) represent Langmuir constants.

2.4.2 The Freundlich model

In this type of isotherm, the adsorption sites are distributed exponentially [38], and the isotherm is represented by equation 2 [40, 41]:

$$q_e = a_f C_e^{b_f} \quad (2)$$

where q_e is the oil adsorbed (mg/g), a_f (mg/g) is the capacity of multilayer adsorption, and b_f an empirical number that indicates the intensity of adsorption.

2.4.3 Temkin isotherm model

This model was obtained with consideration of adsorption interaction and adsorption substances [42], and in this model the heat of adsorption decreases linearly with coverage. Equation 3 describes this relation:

$$q_e = \frac{RT}{b}\ln AC_e \quad (3)$$

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

2.4.4 Harkins-Henderson model

This model assumes a multilayer adsorption [43]. Equation 4 describes the Harkins-Henderson isotherm:

$$q_e = \frac{K_{H-H}^{1/n}}{c_e^{1/n}} \quad (4)$$

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

2.5 Adsorption kinetics

The study of the adsorption kinetics shows the adsorbed rate of adsorbate on the adsorbent. It is therefore required for finding the best-operating conditions for the batch process [44]. There are many kinetic models that analyze adsorption kinetics data.

2.5.1 Pseudo-first-order kinetic model

This model was proposed by Lagergren [45]. The linearized form is shown in equation (5).

$$\text{Log}(qe-qt)= \text{log}qe–k1t/2.303 \quad (5)$$

In this equation, qe (mg/g) and qt (mg/g) are the adsorption capacities at equilibrium and at time t, respectively, where k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) [46].

2.5.2 Pseudo-second-order kinetic model

The pseudo-second-order kinetic model can be represented as follows [47]:

$$\frac{dq_t}{dt}= k_s(q_e-q_t)^2 \quad (6)$$

where k_s is the rate constant of adsorption, g/(mg.min).

2.5.3 Intra particle diffusion study

In the intraparticle diffusion model, adsorption occurs on the surface of the adsorbent initially, then the sorbate diffuses into the interior pores of the adsorbent. The following relationship describes this process:

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

where k_{id} and C are the intra-particle diffusion rate constants.

2.5.4 Elovich model

Heterogeneous chemisorption is assumed in the Elovich model. It is widely used in liquid-solid adsorption [47]. Equation 8 describes this type:

$$q_t = 1/\beta \ln(\alpha \beta) + 1/\beta \ln t \qquad (8)$$

where α is the initial bio-sorption rate (mg/g.min) and β is related to the extent of surface coverage and the activation energy for chemisorption (g/mg).

2.6 Adsorption capacity

Equation 9 was used to calculate the adsorption capacity (q) [32]:

$$Q = \frac{V(C_0 - C_e)}{M} \qquad (9)$$

where Q is the capacity of adsorption (mg/g), C_o is the initial concentration (mg/l), C_e is the equilibrium concentration, M is the dosage of adsorbent (g), and V is the volume of solution (l). The percentage of the oil removal is calculated using equation 10:

$$(\%)\ \text{Oil removal} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (10)$$

3. Results and Discussion

3.1 Produced water

The specification of the sample supplied by the Midland Oil Company was TDS= 157,790 mg/l and TSS = 21.6 mg/l. The other substances' concentrations in produced water are shown in Table 1.

3.2 Fourier transforms infrared spectroscopy (FT-IR) investigation

The FT-IR spectra images of *Imperata cylinderica* were recorded and shown in Figure 2. The medium-length two peaks observed at 2,916 cm^{-1} and 2,849 cm^{-1} are attributed to the presence of C-H asymmetrical stretching and symmetrical stretching, respectively. The peak at 1,731.91 cm^{-1} was assigned to C=O stretching of the carboxylate group, and the peak at 1,462 cm^{-1} is related to C=C stretching of the alkene group. Chowdhury *et al.* [41] indicated that the main functional groups responsible for the adsorption process are the alkene, aldehyde, carboxylic acid, nitro compound, and phosphate groups [48].

Table 1. Analyses of produced water

Compounds	Concentration (mg/l)
Calcium	7,840
Magnesium	2,352
Chloride	107,192
Sulphate	3,763
Bicarbonate	263.5
Carbonate	n.d.
Oil and grease	550
Iron	<0.02
Manganese	3
Chrome	<0.2
Zinc	1.1
Nickel	<0.2

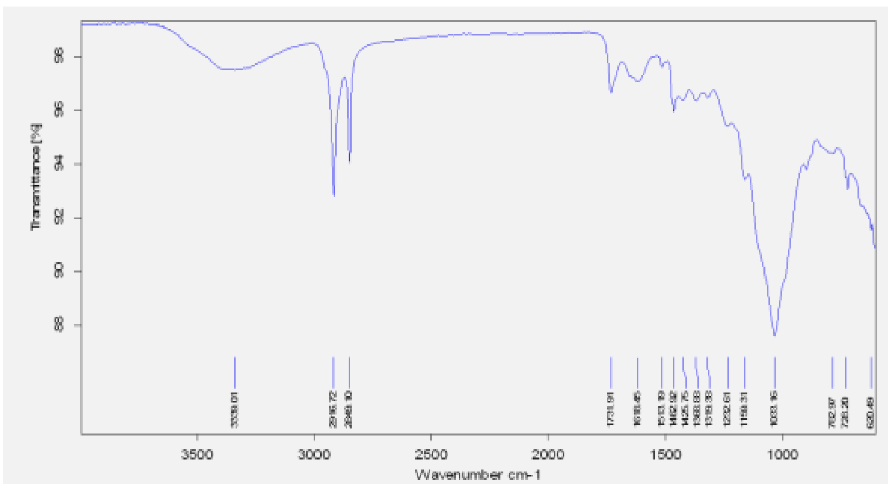

Figure 2. Fourier transforms infrared spectroscopy of *Imperata cylindrica*

3.3 Scanning Electron Microscopic (SEM) and Energy Disperse X-ray spectra (EDX) investigations

The SEM images and EDX spectra of *Imperata cylinderica* surface are shown in Figures 3 and 4. It is clear from the images that the surface was irregular and rough, and had many creases. The white region in the SEM spectrum indicated the presence of large amounts of silica (Si) can possibly enhance the adsorption capacity of adsorbent. Furthermore, EDX is a very good tool for identifying elements on the adsorbent surface. The presence of C, O, and Si ions on *Imperata cylinderica* surface was confirmed by the peaks at 0.2, 0.5, and 1.7 keV, respectively.

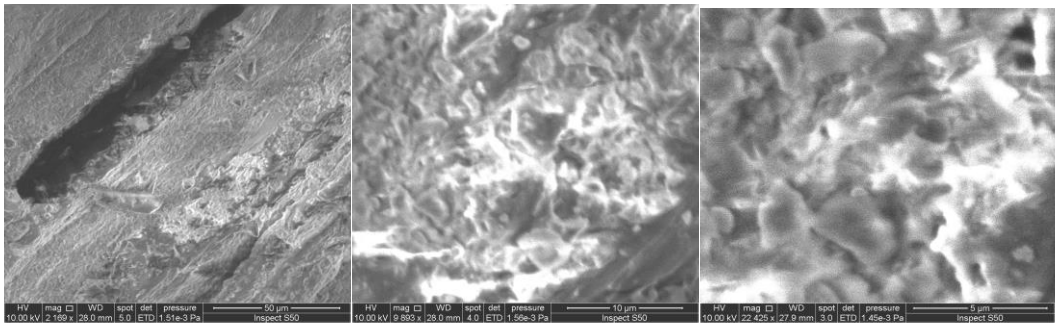

Figure 3. Scanning Electron Microscopic (SEM) of *Imperata cylinderica*

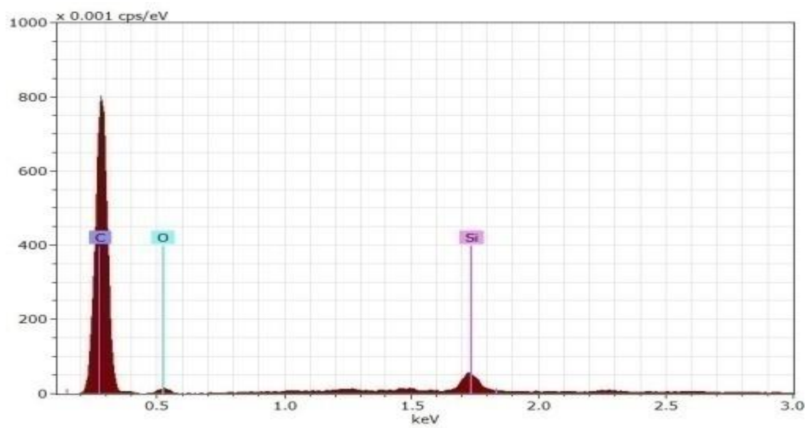

Figure 4. EDX spectra of *Imperata cylinderica*

3.4 Modeling

The main objective of this study was to find the optimal conditions for the adsorption process. The Taguchi method was used to determine the best operating conditions, as shown in Table 2. Statistical optimization was used to analyze experimental data and to develop the general model equation 11:

$$y = (68.96738-(1.02744*x_3) + (0.0136*x_2*x_3) + (1.34999*x_3*x_4)-(2.328*x_2*x_4)) \quad (11)$$

where: X_2 = Temperature , X_3 = Time , and X_4 = adsorbent dose.

3.4.1 Effects of variables

The effects of different conditions on oil adsorption by *Imperata cylinderica* using the combined variables are shown in Table 2. Sixteen experiments were conducted using the Taguchi method to design the batch adsorption experiments, then various models were used to study the isotherm and the kinetics.

The pH(X_1) has no significant effect on the adsorption process due to previous treatment using coagulation and flocculation which neutralized the produced water. Figure 5 proves that the data was distributed close to linearly (R^2 = 0.972), showing a good relationship between the observed and predicted oil concentrations.

Table 2. Experimental design for batch process

No.	pH	Temperatue (°C)	Time (min)	Adsorbent dosage (g)	Oil concentration (ppm)
1	3	30	15	0.05	32.0
2	3	40	30	0.10	13.4
3	3	50	60	0.20	6.8
4	3	60	90	0.40	8.3
5	5	30	30	0.20	22.4
6	5	40	15	0.40	15.8
7	5	50	90	0.05	2.60
8	5	60	60	0.10	5.80
9	7	30	60	0.40	32.0
10	7	40	90	0.20	12.0
11	7	50	15	0.10	19.2
12	7	60	30	0.05	14.3
13	9	30	90	0.1	1.5
14	9	40	60	0.05	9.9
15	9	50	30	0.40	14.8
16	9	60	15	0.20	8.2

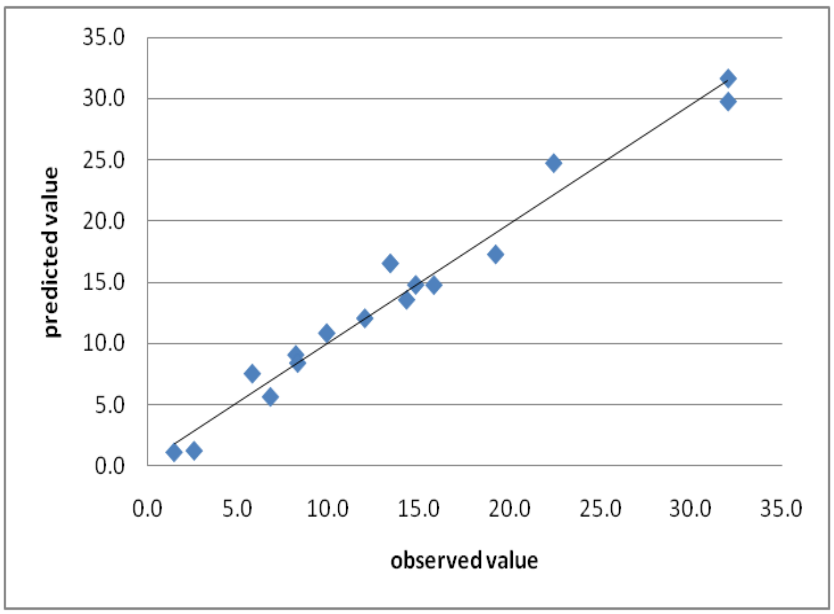

Figure 5. Observed and predicted oil concentration

Table 3 shows that the F-value is 56.65872 and the probability value (p) is 0.00016, indicating the significance of the model.

Table 3. ANOVA test results

P-value	F-value	Mean Squares	DF	Sum of Squares	Effect
Regression	4204.430	11.0000	382.2209	56.65872	0.00016
Residual	33.730	5.0000	6.7460		
Total	4238.160	16.0000			

3.4.2 Effect of contact time on oil removal

The relationship between contact time and oil removal by *Imperata cylindrica* was tested through batch experiments to achieve equilibrium as shown in Figure 6. Oil removal increased with contact time. The rapid adsorption in the first 5 to 30 min can be attributed to the high availability of vacant surface sites during the initial stages. After around 45 min, the adsorption rate started to decline as there were less available adsorption sites [49].

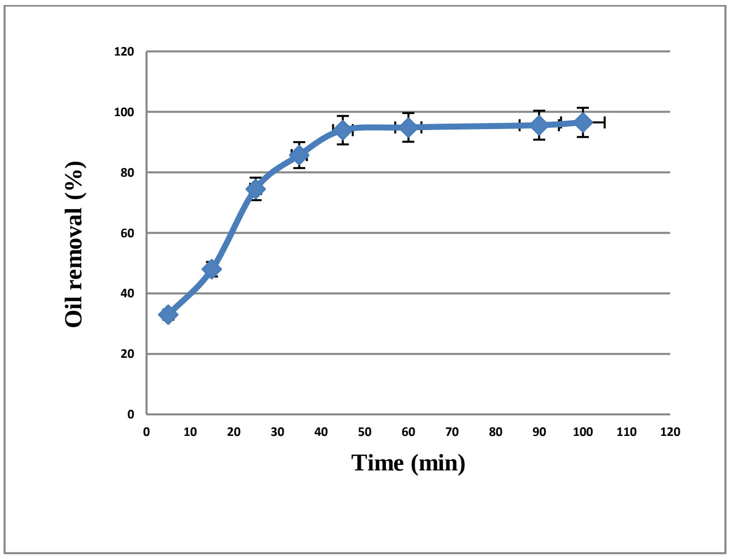

Figure 6. The effect of contact time on percent oil removal by *Imperata cylinderica* at T = 60°C, Adsorbent dose = 0.5 g/100 ml

3.5 Finding the optimal conditions by Taguchi experimental design

3.5.1 Effect of adsorbent dose on oil removal

The effect of adsorbent dosage at specific conditions on the percentage removal of oil is shown in Figure 7. It can be seen that the removal of oil increased with increasing adsorbent dosage and attained a maximum value of 100% at an adsorbent dosage of 0.753 g/100 ml. The adsorption process increased with an increase in sorbent dosage due to the increase of unsaturated oil binding sites [26].

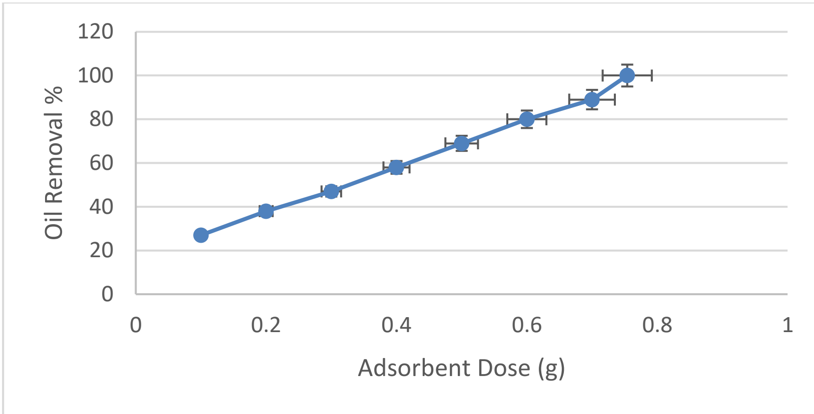

Figure 7. The effect of adsorbent dose on percent oil removal at T = 60°C and t = 45min

3.5.2 Effect of temperature on oil removal

The effect of temperature on oil removal is shown in Figure 8. It is known that oil is sticky and hydrophobic. 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 should increase [50, 51].

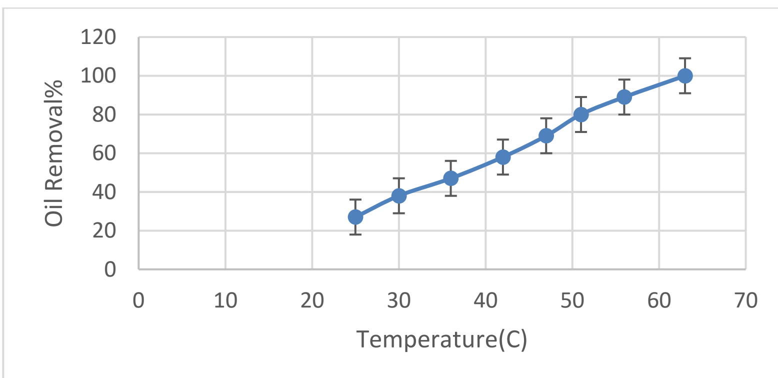

Figure 8. The effect of temperature on percent oil removal at t = 45min and adsorbent dose = 0.753 g/100ml

3.6 Adsorption isotherm results

The linearized forms of the Langmuir, Freundlich,Temkin and Harkins-Henderson isotherm models, as shown in equations (1), (2), (3) and (4), respectively, were analyzed using Microsoft Excel Software to find the isotherm constants. These constants are presented in Table 4, and it can be seen that the regression correlation coefficient (R^2) of the Langmuir equation (R^2 = 0.998) is more linear when compared with that of other equations, implying that the adsorption isotherm data are well fitted by the Langmuir isotherm. Figure 9 shows the experimental curve and isotherm model curves.

Table 4. The constants of isotherm models

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	B	0.931
	A	34.47
	R^2	0.931
Harkins-Henderson	n	1.2987
	K_{H-H}	2.29
	R^2	0.966

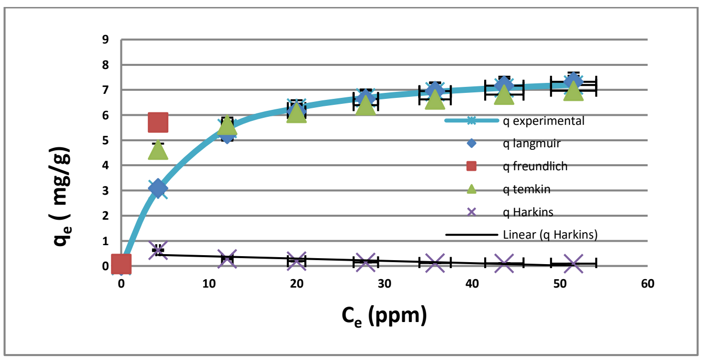

Figure 9. Adsorption isotherm of oil content adsorbed onto *Imperata cylinderica*

The experimental data fit the Langmuir isotherm very well, which means that the process is a single-layer one and the maximum adsorption of oil molecules is only on the surface of *Imperata cylinderica* [42]. The Langmuir isotherm assumes a finite number of active sites available over the surface of the adsorbent and there is no interaction among adsorbed molecules. The same finding was observed by Sarkheil *et al.* [28].

3.7 Adsorption kinetics results

The instantaneous adsorption of the batch process 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 the kinetic parameters using these models. The contacts for these models were obtained using Microsoft Excel Software. Table 5 shows the results of these analyses and Figures 10 to 13 represent the adsorption capacity with the fitted model. Figure 10 represents the relation of log (q_e-q_t) and time for a pseudo-first-order model. Figure 11 represents the relation of (time/q_t) and time for a pseudo-second-order model, Figure 12 represents the relation of q_t and (time) 0.5 for an intra-particle diffusion model, and Figure 13 represents the relation of q_t and ln (time) for the Elovich model.

Table 5. Kinetic models constants for the adsorption of oil onto *Imperata cylinderica*

Model	Parameters	Values
Pseudo-first order equation (5)	q_e K_1 R^2	142.2 0.0207 0.984
Pseudo-second order equation (6)	q_e K_s R^2	0.543 1.826 0.938
Intra-particle diffusion equation (7)	K_{id} C R^2	0.967 0.474 0.979
Elovich equation (8)	α β R^2	2.895 0.515 0.912

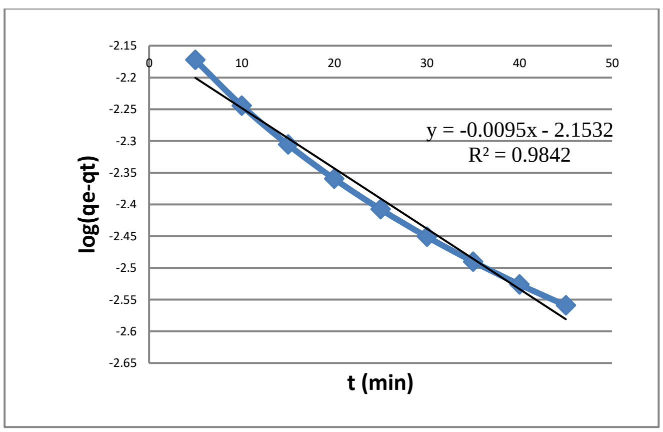

Figure 10. Pseudo-first-order adsorption kinetics of produced water onto *Imperata cylinderica*

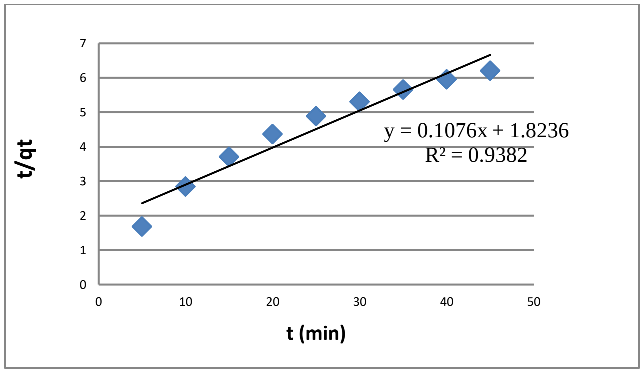

Figure 11. Pseudo-second-order adsorption kinetics of produced water onto *Imperata cylinderica*

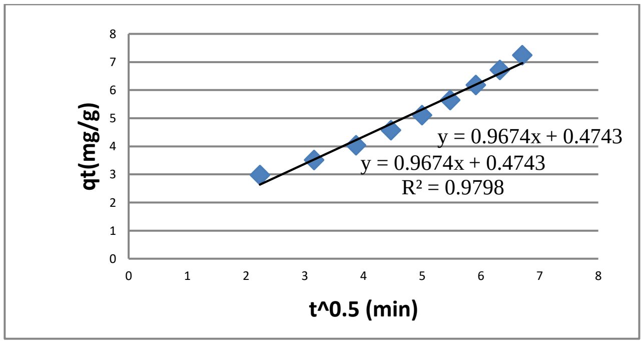

Figure 12. Intra-particle adsorption kinetics of produced water onto *Imperata cylinderica*

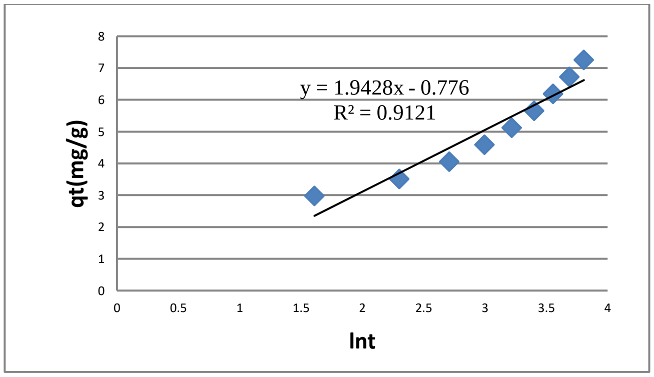

Figure 13. Elovich model for adsorption kinetics of produced water onto *Imperata cylinderica*

By comparing the correlation coefficient (R^2) values of each curve for all five models listed in Table 5, it seems that the kinetics of the oil content adsorption onto *Imperata cylinderica* was a better fit with a pseudo-first-order model than it was with other models. This indicates the applicability of the Lagergren kinetic model to describe the adsorption process of oil onto *Imperata cylindrical*. Moreover, this result is in agreement with Alam *et al*. [32].

3.8 Adsorption thermodynamic results

The effect of temperature on oil adsorption was studied at temperatures ranging from 20 to 60°C. The Gibbs energy change (ΔG°) indicates the degree of the spontaneity of an adsorption process, and a higher negative value reflects more energetically favorable adsorption [52, 53]. Thermodynamic parameters such as standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated using the following relations [24]:

$$\Delta G^\circ = -RTlinKc \quad (12)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

where R is the universal gas constant (8.314 J/mol. K), T is the temperature (°K) and Kc is the thermodynamic equilibrium constant without units. The enthalpy change (ΔH°) and entropy change (ΔS°) of adsorption are obtained from the following equation

$$linKc = (\Delta S^\circ)/R - (\Delta H^\circ)/RT \quad (14)$$

According to Equation (9), (ΔH°) and (ΔS°) parameters can be calculated from the slope and intercept of a plot of linKc versus 1/T, respectively (Figure 14).

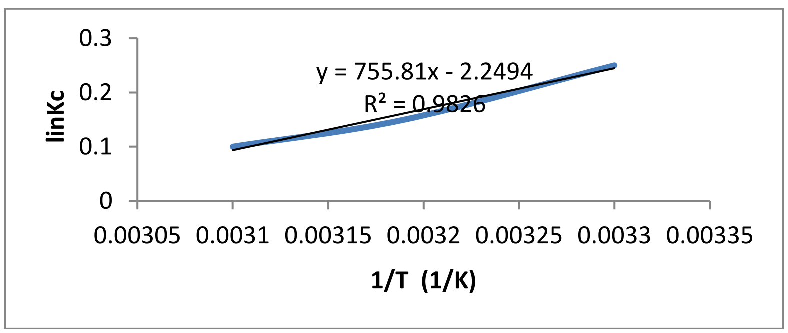

Figure 14. Thermodynamic parameters for oil adsorption onto *Imperata cylinderica*

These thermodynamic parameters can offer insight into the type and mechanism of an adsorption process. Values of free energy change ΔG° are negative confirming that oil adsorption is spontaneous and thermodynamically favorable since ΔG° became more negative (-0.27,-0.39 and-0.63 KJ/mol) with an increase in temperature at 20, 30 and 60°C, respectively, indicating a high driving force and hence resulting in higher adsorption capacity at higher temperatures. The positive value of ΔH° indicated the endothermic adsorption process (0.756 KJ/mol.). A small but positive value of ΔS° (0.0225 KJ/mol.K) in the temperature range 20-60°C suggested increased randomness at the solid-solution interface because some water molecules were dislodged during adsorption of oil [54, 55].

4. Conclusions

This study found that the *Imperata cylinderica* tested, which is one of the numerous kinds of agriculture waste, was very effective in removing oil from produced water through adsorption at low and high initial concentrations and at different temperatures. *Imperata cylinderica* was studied using X-ray diffraction and energy dispersion X-ray spectroscopy techniques, and by other techniques as well. The results showed that *Imperata cylinderica* is effective as an oil adsorbent from produced water due to the availability of effective functional groups, and the presence and nature of these groups was confirmed by FTIR. Very high oil removal efficiencies of the order of 97% were reached at temperature 30°C, pH 9, adsorbent dose 0.1 g, and 90 min contact time. The main objective of this study was to find the optimal conditions for the adsorption of oil.The Taguchi method was used to determine the best operating conditions. The method was used to design the batch adsorption experiments, and then to study the isotherm, and the kinetics. Next, statistical optimization was used to analyze experimental data and develop the general model. The adsorption isotherm was studied, and the linearized forms of the Langmuir, Freundlich, Temkin, and Harkins-Henderson isotherm models were analyzed using Microsoft Excel Software in order to find the relevant isotherm constants. The regression correlation coefficient (R^2) of the Langmuir equation (R^2 =0.998) was more linear when compared with that of other models, implying that the adsorption isotherm data fitted the Langmuir isotherm well. The instantaneous adsorption of the batch process was investigated using four different models: the pseudo-first-order, pseudo-second-order, intra-particle diffusion, and Elovich models. The experimental results were employed to derive the kinetic parameters using these models, and the kinetics of oil adsorption onto *Imperata cylinderica* was found to be best fitted with a pseudo-first-order model. Thermodynamic parameters such as standard free energy change ($\Delta G°$), standard enthalpy change ($\Delta H°$) and standard entropy change ($\Delta S°$) were studied at a temperature ranging from 20 to 60 °C. Finally, we recommend that the oil adsorbed by *Imperata cylindrica* from the produced water should be burned in oil-fired power stations as a heating source.

5. Acknowledgements

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