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MODELLING AND SIMULATION OF ADSORPTION OF CRUDE OIL CONTAMINATED SOIL

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ABSTRACT
The study used adsorbent pad adsorbents (AP) and chicken feather waste (CFW) for the biosorption of hydrocarbon-contaminated soil. The materials for the adsorbents were obtained locally, processed appropriately, and made ready for the adsorption procedure. Crude oil will be adsorbed from the contaminated soil for analysis at intervals of 0 weeks, 4 weeks, 8 weeks, 12 weeks, 15 weeks, and 20 weeks. Additionally, in a beaker containing the crude oil-polluted soil, 1g, 1.5g, 2g, 3.5g, and 6g of each of the adsorbents (pulverized CFW and PA) were added in turn. Samples were gathered every week in accordance with the investigation of the adsorption process over the course of several weeks. Analysis was done on these samples. They produced Figures 4.1 to 4.4b and Tables 4.1 to 4.5. During the experiment, it was found that two effective adsorbents for the adsorption of crude oil from the soil were absorbent pad (AP) and chicken feather waste (CFW). Pollutants from the soil are strongly attracted to both adsorbents. The strength of crude oil adsorption from the soil was tested using adsorbents produced from chicken feather waste (CFW) and adsorbent pad (AP). Isotherms and kinetics models were applied to the experimental data in order to evaluate and analyze them. In comparison to other kinetics, the results of the evaluations and analysis show that second order kinetic describes the adsorption for both adsorbents in crude oil-contaminated soil, as their coefficient of determination values were highest in ranges of 0.5618-0.9935 and 0.959-0.996, respectively, for 1g-6g masses of adsorbents. To identify the adsorption isotherm model that best describes the adsorption process, the Langmuir, Freundlich, Tempkin, and Elovich isotherms were investigated. The Tempkin isotherm model was found to be the most appropriate isotherm.

Key words: Biosorption, Contaminated Soil, Chicken Feather Waste, Adsorbent Pad, Isotherms

INTRODUCTION

Nigeria has the world's tenth-largest proven crude oil resource, is the eleventh-largest petroleum producer, the eighth-largest crude oil exporter, and one of Africa's top producers of crude (Akuru & Okoro, 2019). The majority of Nigeria's oil-producing communities are struggling with a variety of detrimental environmental effects linked to leaks and unintentional spills that frequently occur during the exploration, refining, transportation, and storage of crude oil and its products due to the country's high level of oil exploration activities (Oyodele et al., 2016). In addition to carbon and hydrogen molecules, crude oil also contains nitrogen, oxygen, sulfur, and a number of metals (Yu et al., 2020). Its four primary constituents—saturated hydrocarbons, aromatic hydrocarbons, asphaltene, and colloids—pose a serious threat to human health and the environment due to their carcinogenic and mutagenic properties (Romanus et al., 2015). In addition to destroying the traditional means of subsistence in the majority of Nigeria's oil-producing regions, the crude oil spill has resulted in environmental pollution that impacts weather patterns, soil fertility, waterways, aquatic habitats, and

wildlife (Onwurah et al., 2020). Low crop production results from soil coagulation caused by crude oil, which lowers soil porosity and air content, slows down germination, and reduces soil nutrient composition (Udo & Fayemi, 2017). There are ongoing efforts to use a variety of biosorption strategies to detoxify settings contaminated by crude oil.

The process of using biological materials as absorbents is called biosorption. It offers a chance to lessen pollution and potential pollution-related issues by removing dangerous chemicals from soil, groundwater, sediment, and surface water (WHO, 2018). There are several methods for soil biosorption, including but not limited to physical and chemical biosorption, to treat soil contaminated by crude oil. Nevertheless, these methods are costly and may cause pollutants to partially decompose (Ding et al., 2020, Yu et al., 2020). Natural disasters like hurricanes, earthquakes, and volcanic eruptions can cause oil pollution, as can human intervention like terrorism, oil bunkering, tanker and oil rig accidents, to name a few. It is a common occurrence in nations that produce oil, such as Nigeria, which raises concerns about how to address the environmental problems caused by oil pollution. This is due to its numerous effects on both the terrestrial and aquatic environments. Adsorption, absorption, ion exchange, coagulation, and other techniques have been developed to remove various contaminants like used engine oil. urban storm bacteria, viruses, fungus, and water overflow from various sewage lines, among other things, but not without restrictions. Due to the high cost of commercial activated carbon (CAC), which is used as an adsorbent to remove crude oil from aqueous environments, it is necessary to create more affordable and environmentally friendly adsorbents from agricultural waste that may cause environmental problems.

According to Buehholz and Graham (2018), Zohuriam-Mehr et al. (2019), and Kim et al. (2016), the absorption mechanism occurs not just on the surfaces but mostly inside the polymer matrix with a significant polymer matrix swelling. The polymer chains are often cross-linked to create a network structure in order to stop the polymer from dissolving in the solution. As anticipated, this volume enlargement provides a much greater absorption capacity, making it appropriate for applications involving liquid storage. With the exception of certain superabsorbent hydrogels, the kinetics to achieve the saturation level are often rather sluggish (Peppas et al., 2021; Jang and Kim, 2018; Xue et al., 2020; Osada et al., 2004; Yu et al., 2017). According to Flory (Huggins, 2017; Szerling, 2005; Alberda et al., 2000; Arroyo et al., 2018; Elliot et al., 2004), the absorption capacity is typically proportional to the swelling ability of the absorbent polymer, which is controlled by a combination of the cross-linking density and the absorbate−substrate $\chi 1$-interaction parameter.

In order to determine if three Polymer Concretes (PCs) created from unsaturated polyester resin and natural sand from the Niger Delta region of Nigeria contaminated with crude oil were suitable for use as materials for local civil construction, Izionworu & Amadi (2016) examined their mechanical properties. The decreased compressive strength demonstrated the development of thermoset composite material with a weak three-dimensional network structure as a result of the impact of crude oil contamination on the binding effect of unsaturated polymers and sand in polymer concrete, which is presently being researched as a substitute for inexpensive building materials in earthquake-prone areas and the Niger Delta Region of Nigeria. The use of chicken feather waste as an adsorbent for cleaning up crude oil from contaminated water was studied by Okoya et al. (2020). The morphological features and surface texture of CFW were revealed by the scanning election microscopy results. With the exception of the beginning concentration of 20/30, which falls in the case of Commercial Activated Carbon (CAC), the adsorption efficiencies of both adsorbents will rise with initial concentration.

Ogoni et al. (2016) created models to show the diffusion limited region and the primarily reaction-controlled region for Γ_P>3 with high or big diffusion; however, the chemical reaction and diffusion beginning happened at Ψ_P=0.3. The created model shows how K3C* and N/Nmax relate to each other for different incremental steps of K2L. The observed result shows that an increase in K3C* led to an increase in N/Nmax until an optimal value of N/Nmax was reached, after which the values remained constant with an incremental value on K3C*.

In 2015, Kettle and Udeozo conducted research on the evaluation of ground chicken feathers' crude oil mopping efficiency by kinetic and adsorption isotherm studies. Crude oil, chicken feathers, a mechanical mixer, distilled water, a synthetic sorbent mat, and detergent are the ingredients. The equilibrium adsorption capacity of crude oil onto ground chicken feathers sorbent was found to be 13.60 glg at equilibrium time of 80 minutes and 11.44g/g at 60 minutes based on the kinetic investigation of crude oil adsorption onto ground feathers sorbent.

The physical and morphological structure of chicken feathers in their native, chemically, and thermally modified forms was studied by Debora et al. (2012). The supplies included argon, ovens, tube furnaces, sodium hydroxide, and chicken feathers. The techniques include mineralogical analysis and morphological structure. Although it lost its hooks, the keratin fiber (KF) NaOH structure was rougher than the KF (Keratin fiber). In their study on oil absorption and desorption by absorbent fibers, Raman et al. (2017) evaluated the oil absorbency and desorption properties of several absorbent kinds. For the procedure, different fiber fineness levels were employed. Sorption capacity (g/g) was higher in finer fibers than in coarser ones. The study's specific goals were to determine the characteristics of the adsorbents (absorbent pad & chicken feather) using a gas chromatography (GC) analyzer, analyze the adsorption of contaminants from crude oil-contaminated soil using pre-existing adsorption kinetics and isotherm models, validate the findings, and compare the adsorption performance of the two adsorbents.

Okoya et al. (2021) and Ifelebuegu & Chinonyere (2016) examined the utilization of chicken feather on the adsorption of pollutants from crude oil-polluted soil as appropriate measures to accomplish the research goal. While Nam et al. (2016) examined adsorbed pollutants from crude oil contaminated soil using petrogels, a novel class of polymer, and Asadu et al. (2021) employed mango seed shell adsorbent for the biosorption of crude oil contaminated soil, Al-Jabari (2017) studied the kinetics of adsorption of contaminants from crude oil contaminated soil in a batch vessel.

However, for the biosorption of hydrocarbon-contaminated soil, researchers have employed adsorbents such as moringa seed shell, elephant grass, and lemon grass, particularly employing the oil, leaf, and stem. However, no researcher has yet to compare the effects of cotton wool and chicken feather waste on the adsorption of crude oil from hydrocarbon-contaminated soil in any of these published studies. Therefore, the purpose of this study is to investigate the biosorption of crude oil-contaminated soil in Nigeria's Niger Delta Region using chicken feather waste and absorbent pad.

MATERIALS AND METHOD

Materials

Materials for the study are chicken feather, Absorbent pad (AP), Hydrogen perioxide, NaOH, Hexane, Oven, Peptone, Yeast, Crude oil and Soil sample.

Methods

Crude oil was collected from Shell Petroleum Development Cooperation (SPDC) in Port Harcourt and soil sample collected from the Ogoni land in Rivers State Nigeria and taken into Chemical Engineering

Laboratory, University of Benin. The soil and crude oil were mixed together thoroughly for the mixture to become contaminated soil sample.

Also, absorbent Pad (AP) was obtained from Eleme Petrochemical Company Limited, Indorama Eleme LGA, Rivers State as waste materials from the polymerization of olefins, Absorbent Pad (AP) is a synthetic polymer and adsorbent suitable for the biosorption of this contaminated soil.

The agricultural wastes is chicken feathers waste (CFW) sourced from a local market at mile 3, Port Harcourt Rivers State Nigeria, where chickens are trained and harvested for consumption.

Characterization of Chicken Feather waste (CFW) and Absorbent Pad (AP) Using Gas Chromatography (GC) Analyzer

The pulverized chicken feather waste (CFW) was characterized using Scanning Electron Microscopy (SEM) and Particle-induced X-ray Emission (PIXE) (equipment model) from Centre for Energy Research and Development (CERD). Adsorbent pad (AP) is also characterized using gas chromatography analyzer.

The functional groups present in the adsorbents were determined by using Model Perkin Elmer 2000 Fourier transform infrared (FTIR) spectroscopy with the KBr disc method at a pressure of 180kPa. The wavenumber was recorded in the range of 4000-400 cm-1. Crude oil adsorption-desorption isotherm was performed at 77 K using a gas sorption analyzer, model ASAP 2020V4.01 instrument, to determine the textural surface properties of the samples. The micropore volume (V_{mic}), the surface area by Brunauer-Emmett-Teller (BET), SBET, micropore surface area (S_{mic}), mesopore surface area (S_{meso}), total pore volume (V_{total}), micropore volume (V_{mic}) and average pore size diameter were computed using the isotherm. Thermal stability was evaluated by using Perkin Elmer STA 6000 Thermogravimetric analyzer (TGA) with a heating rate of 30 °C/min and under the oil flow of 20 mL/min. The X-ray diffraction (XRD) patterns were obtained with Bruker AXS D8 Advance by recording the 2θ diffraction angles from 10° to 90°. The scanning electron microscope (SEM) model Carl Zaiss Leo Supra 50VP Field Emission equipped with Oxford INCA-X energy dispersive microanalysis system (EDX) was used to examine the surface morphology and the elemental distribution.

Physicochemical Properties of Crude Oil

The physical properties of crude oils are the quantitatively measurable parameters of crude oils. They depend upon the composition of the oil, the relative abundance of the groups of hydrocarbons, and essentially depend on reservoir temperatures and pressures. Crude oil consists of liquid paraffin hydrocarbon compounds such as pentane to pentadecane ($C_5 – C_{15}$). These hydrocarbon compounds are made of various groups like the normal paraffins, iso-paraffins (branched chain paraffins), alkyl paraffins, naphthenes (or cycloparaffins), alkylbenzene and nuclear aromatics. The normal paraffins are the saturated, low molecular weight hydrocarbons. The related gaseous phases are within this group. The naphthenes (or cycloparaffins) are extensively bonded, high molecular weight hydrocarbons. All crude oils contain some notable amount of the naphthene compounds, (10% by composition). Crude oils also contain a substantial variety of heteroatomic chemical constituents, including sulphur, oxygen, carbon dioxide, nitrogen and trace metals. Nitrogen varies from 0.01 to 2% as dissolved gas in the crude oil (Levinson, 2019; Chinenyeze, 2017). Oxygen occurs in different forms in oxygen-bearing resinous substances. The GC analyzer is used to conduct an experiment to enable the determination of this properties.

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Batch Adsorption of Crude Oil using the Chicken Feather Waste (CFW) and Absorbent Pad (AP)

Adsorbents (pulverized CFW) will be added to the crude oil polluted soil in a beaker in turns. The beakers and its contents will then allow for some days. AP as an adsorbent will also be used to adsorb the oil from the contaminated soil. The time intervals for the adsorption of crude oil from the contaminated soil for analysis are 0week, 4weeks, 8weeks, 12weeks, 15weeks, and 20weeks.

Also, 1g, 1.5g, 2g, 3.5g and 6g of each of the adsorbents (pulverized CFW and PA) was added to the crude oil polluted soil in a beaker in turns. The beakers and its contents were placed on a digital orbital shaker (JINOTECH INSTRUMENTS), and shaken at 300 rpm for 20 mins. The contents of the beakers were then filtered to separate the wetted adsorbent from the filtrate. The weight of the wetted adsorbent was recorded and the weight of the filtrate (oil) as well as the separated oil from the filtrate was recorded separately. Adsorbed oil content was determined by subtracting the soil sample content and the initial adsorbent weight from the total wetted sorbent. The weight of the oil adsorbed was then recorded as gg-1 (gram of oil/gram of adsorbent).

Adsorption Kinetics Models

The model that best describe the adsorption process at equilibrium, experimental data are fitted to Langmuir, Freundlich and Tempkin isotherm models. Also, the pseudo first order and second order as well as intra-particle diffusion are used to study the kinetics of the adsorption process with chicken feather waste (CFW) and adsorbent pad (AP) adsorbents.

The pseudo-first-order kinetic models are applied in this research work to explain the relationship between the rate of the sorption sites of the adsorbents occupied and the number of the unoccupied sites.

$$ln\ ln\ (q_e - q_t) = k_1 t + ln\ ln\ q_e \quad (2.1)$$

where:

q_e is amounts of heavy metal absorbed by the adsorbent at equilibrium (mg/g)

q_t is concentration of heavy metal absorbed by the adsorbent at particular time, t (mg/g)

k_1 is Rate constant of absorption (hr^{-1}).

The Pseudo-second-order kinetics model is used to describe the adsorption of crude oil hydrocarbon contaminated soil is given according to Ho, (2004) as,

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_t^2 k_2} \quad (2.2)$$

where:

k_2 = Pseudo-second-order rate constant (g/mg.hr),

t = measured time of adsorption (hr)

The Elovich model was applied to describe surface diffusion-controlled processes and adsorption in a non-ideal state. According to Qiu et al., (2009), Elovich Kinetic model is defined as,

$$q_t = \frac{lnln\ (\varphi a)}{b} + \frac{1}{b}\ lnt \quad (2.3)$$

where, φ and a are determinant Energy (b) for chemisorption in (g/mg),

Weber & Morris, (1963) developed the intra-particle diffusion kinetics model which has been effective in many cases of adsorption of heavy metals and expressed according to Pasavant et al., (2006) as,

$$q_t = k_d\sqrt{t} \quad (2.4)$$

where:

q_t = Amount of heavy metal absorbed at time, t (mg/g),
k_d = Weber and Morris intra-particle diffusion rate constant (mg/g.hr$^{0.5}$),
t = time of adsorption (hr).

Adsorption Isotherm Models

The Langmuir Isotherm model is expressed (Balouch et al., 2013) as,

$$\frac{C_e}{C_{ads}} = \frac{1}{Q_b} + \frac{C_e}{Q} \quad (2.5)$$

where:
C_{ads} = the amount of heavy metal and other ions absorbed at equilibrium,
B = sorption constant (mg/l) at a given temperature, related to the energy of sorption,
Q = maximum sorption capacity (mg/g).

Linearizing the model of the Freundlich Isotherm (Dada et al., 2012; Huston & Yang, 2017) give,

$$ln\ ln\ q_e = \frac{1}{n} ln\ ln\ c_e + ln\ ln\ k_f \quad (2.6)$$

where:
k_f = Freundlich Isotherm constant, n is adsorption intensity,
q_e = equilibrium concentration of adsorbate (mg/l),
C_e = the amount of heavy metal and other ions absorbed at equilibrium.

The Tempkin Isotherm Model is expressed as,

$$q_e = B\ ln\ ln\ A_T + B\ ln\ ln\ c_e \quad (2.7)$$

where,
B = $\frac{R_T}{b_T}$; A_T is Temkin Isotherm equilibrium binding constant (l/g)
b_T = Tempkin Isotherm constant,
R_T = universal gas constant (8.314 J/mol K),
T = Temperature at 298K
B = Constant related to the heat of sorption (J/mol).

A_T and b_T are determined from the intercept and slope, respectively of the plot of q_e versus $ln\ ln\ c_e$.

The Dubinin-Radushkevich isotherm model is expressed as,

$$ln\ ln\ q_e = ln\ ln\ q_s - \beta\varepsilon^2 \quad (2.8)$$

where:
q_e = the number of ions adsorbed at equilibrium (mg/g),
β = Dubinin-Radushkevich isotherm constant (mol^2/KJ^2),
ε = Polanyi potential

Description of Isotherm models Used for Biosorption of Crude Oil Contaminated Soil

The equilibrium adsorption isotherm may offer valuable information on the affinities and surface characteristics of the adsorbent as well as the interactions between the adsorbate and the adsorbent (Foo & Hameed, 2010). To correlate experimental equilibrium results, three distinct pure-species isotherm models—the Freundlich, Langmuir, and Temkin isotherm equations—were employed.

RESULTS AND DISCUSSION

The experiment carried out for the adsorption of crude oil as hydrocarbon using chicken feather waste and absorbent pad adsorbents, gave experimental data. Various results are displayed below in tables and figures which were equally discussed.

Table 1: Results obtained from first order Kinetic Parameters Values for the Adsorption of Crude Oil from Contaminated Soil using Adsorbents

Chicken Feather Waste (CFW)			Absorbent Pad (AP)	
Mass(g)	K_1	R^2	K_1	R^2
1	0.0754	0.1302	0.1382	0.0794
1.5	0.1663	0.159	0.01	0.0012
2	-0.2194	0.4642	-0.0202	0.004
3.5	0.0754	0.0321	0.00095	0.0004
6	0.012	0.0006	0.0061	0.0002

Table 1 shows the results obtained from 1st order kinetics parameter calculations for chicken feather waste and absorbent pad show that the kinetic constants for the different volumes of adsorbents utilized are low due to the low R^2 values for adsorption of hydrocarbon from contaminated soil.

Table 2: Results obtained from second order Kinetic Parameters Values for the Adsorption of Crude Oil from Contaminated Soil using Adsorbents

Chicken Feather Waste (CFW)				Absorbent Pad (AP)		
Mass(g)	K_2	R^2	q_e	K_2	q_e	R^2
1	1.761	0.5618	0.431	9.643	0.202	0.959
1.5	3.592	0.7895	0.4080	15.974	0.139	0.976
2	13.280	0.9951	0.233	28.329	0.112	0.988
3.5	21.097	0.968	0.086	38.610	0.240	0.998
6	28.490	0.9935	0.202	48.544	0.137	0.996

Table 2 shows the results from the 2nd order kinetics parameter values (adsorption rate constant and equilibrium concentration, qe). Table 4 shows that for chicken feather waste and absorbent pad show that they are higher due to high values of R^2 for the adsorption of crude oil from contaminated soil. Though both adsorbents follow 2nd order kinetic adsorption process, the 2nd order kinetics parameters for absorbent pad have higher R^2 values and the data are best fitted for hydrocarbon (crude oil) adsorption compared to the adsorption done by CFW adsorbent.

Table 3: Results obtained from Elovich Kinetics Parameter Values for the Adsorption of Crude Oil from Contaminated Soil using Adsorbents

Chicken Feather Waste (CFW)				Absorbent Pad (AP)		
Mass(g)	Φ	A	R^2	Φ	A	R^2
1	2.863	0.075	0.0949	-3.426	-4438.43	0.0816
1.5	2.351	5.188	0.0991	-11.494	-341175.689	0.0051
2	0.349	1936.627	0.5059	-7.996	-9.415×10^{10}	0.0063
3.5	0.310	777767.55	0.247	-4.771	-9.485×10^{15}	0.0579
6	0.217	248590215.7	0.2627	-2.904	-2.60×10^{20}	0.0478

Table 3 shows the results of Elovich kinetics parameters for CFW and AP adsorbents show poor adsorption of crude oil from contaminated soil because of very low R^2 values and hence poorly fitted

for the adsorption of hydrocarbon (crude oil). This implies that the adsorption process does not follow this type of kinetic, compared to 2nd order kinetics.

Table 4: Results obtained from Intra-particular Diffusion Kinetics Parameters Values for the Adsorption of Crude Oil from Contaminated Soil using Adsorbents

Chicken Feather Waste (CFW)			Absorbent Pad (AP)	
Mass(g)	K_d	R^2	K_d	R^2
1	0.2937	0.2207	1.5226	0.365
1.5	0.5345	0.2296	2.6816	0.4348
2	2.6846	0.6515	4.82	0.4409
3.5	3.5276	0.4324	6.6562	0.4368
6	4.8551	0.4282	8.3008	0.4331

Table 4 shows the results of Intra-particular diffusion kinetic parameter values for the different volumes of adsorbents (CFW and AP) show that they are very low R^2 values for the adsorption of hydrocarbon (crude oil) contaminated soil. These results agree with the works of Ogoni *et al*., (2016) and Izionworu & Amadi, (2016). The works of these authors stated that the crude oil contaminated soil had shown very low R^2 values for adsorption. Also, about $12.00g/g$ and $9.0g/g$ of the absorbed oil can be recovered from ground chicken feathers are better sorbent when oil recovery is required was the results they obtained. The kinetics of crude oil follows a second order kinetics for crude oil contaminated soil for best adsorption process.

Table 5: Results obtained from Adsorption Isotherm Parameters Values for the Adsorption of Crude Oil from Contaminated Soil using Adsorbents

		Chicken Feather Waste	Absorbent Pad
1.	Longmuir	Hydrocarbon	Crude
	Qm	-1.771	-16.502
	K_L	-0.0877	-0.2235
	R^2	0.838	0.892
2.	Freundlich		
	N	0.2187	0.461
	K_f	0.00042	3.184
	R^2	0.6997	0.864
3.	Tempkin		
	B (l/g)	42.848	53.876
	A_T	0.155	0.663
	b_T	58.793	46.758
	R^2	0.557	0.884

Table 5 shows the results of adsorption isotherm models were investigated on Langmuir with R^2 value of 0.838 and R^2 value of 0.842 for the adsorption process respectively using CFW and absorbent pad as absorbents. Also, the Freundlich isotherm gave R^2 values of 0.6997 and 0.864 for hydrocarbon adsorption from contaminated using respectively CFW and absorbent pad as adsorbents. Furthermore, the Tempkin isotherm gave as R^2 values of 0.557 and 0.884 for the adsorption process of hydrocarbon oil from contaminated soil using CFW and absorbent pad adsorbents. These results agree with the

works of Ogoni et al., (2016), Izionworu et al., (2021) and Izionworu and Amadi, (2016). The works of these authors stated that the R^2 values of crude oil sorption is highest for Freundlich isotherm as compared to other isotherms used. The isotherm of Freundlich is best for crude oil contaminated soil when Chicken Feather Waste and pad adsorbent are used than that of either Tempkin or Langmuir during adsorption process.

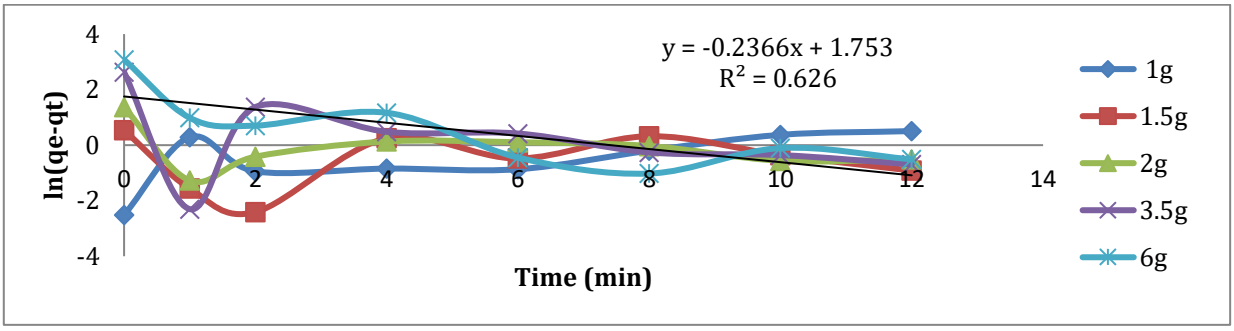


Figure 3: Profiles of Ln (qe-qt) versus Time from the different Chicken Feather Adsorbent Volumes on Adsorption of Crude Oil from Contaminated Soil

Figure 3 depicts the 1st order kinetics parameter values obtained from different volumes of chicken feather waste (CFW) with time. Among the different masses of adsorbent used, 6g of the adsorbent is reliable and fitted well for the adsorption of crude oil from contaminated soil with good kinetic constants, compared with other masses of 1g to 3.5g which have very poor adsorptive properties of the hydrocarbon.

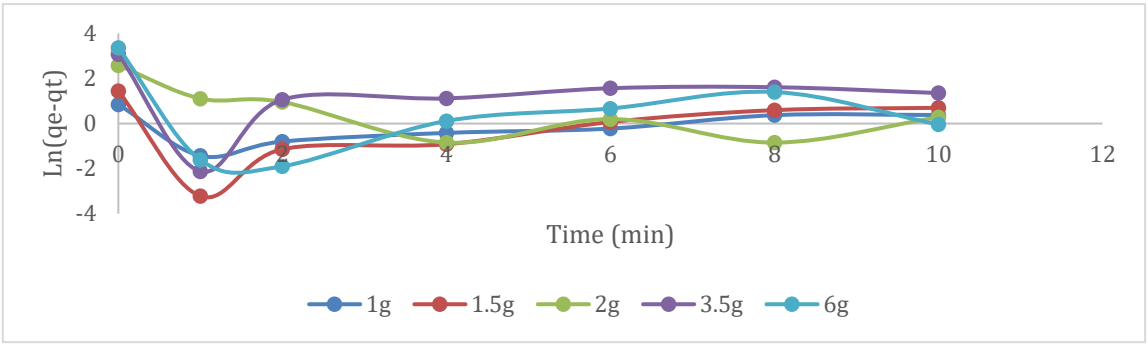


Figure 4: Profiles of Ln (qe-qt) versus Time from the different Absorbent Pad Adsorbent Volumes on Adsorption of Crude Oil from Contaminated Soil

Figure 4 depicts the 1st order kinetic parameter values obtained from the use of absorbent pad as adsorbent in the adsorption of hydrocarbon contaminated soil. As shown in Figure 4.1b, the adsorption process with the adsorbent pad (AP) was very poor since the R^2 values are very small, not up to 1% out of 100% which is 0.00204 (i.e R^2 = 0.00204). This implies that the 1st order kinetics cannot be apply here for the adsorption of crude oil from contaminated soil using AP compared to CFW adsorbent.

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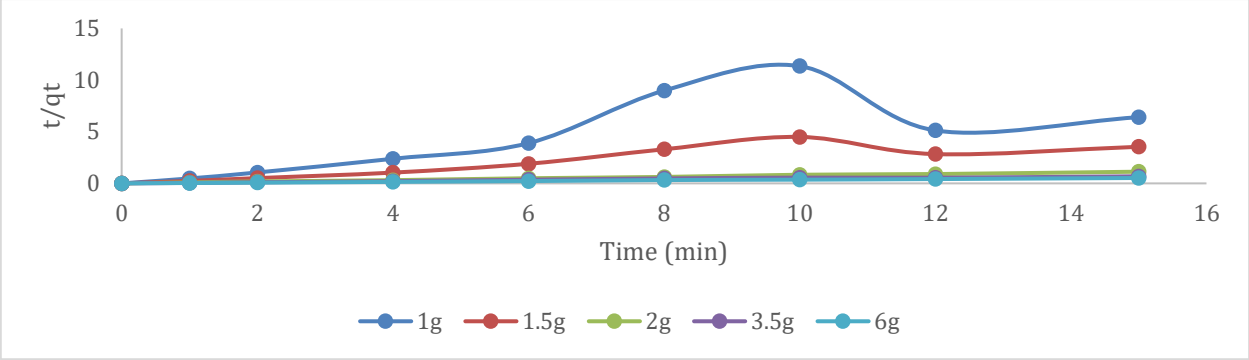


Figure 5: Profiles of t/qt versus Time for the different Volume of Chicken Feather Waste Adsorbents on Adsorption of Crude Oil from Contaminated Soil

Figure 5 depicts the adsorption of crude oil from contaminated soil using chicken feather waste (CFW) follow the 2nd order kinetic process as the R^2 values ranges from 0.56, 0.790, 0.995, 0.968, and 0.994 for the different masses of adsorbent of 1g, 1.5g, 2g, 3.5g, and 6g. This shows that the data obtained experimentally are reliable, acceptable and fitted well for the adsorption process. Among the volumes used, 25ml of the adsorbent best described the adsorption process using CFW as adsorbent. This is shown in Figure 5 and it can be observed that 2nd order kinetic is the best for the adsorption process.

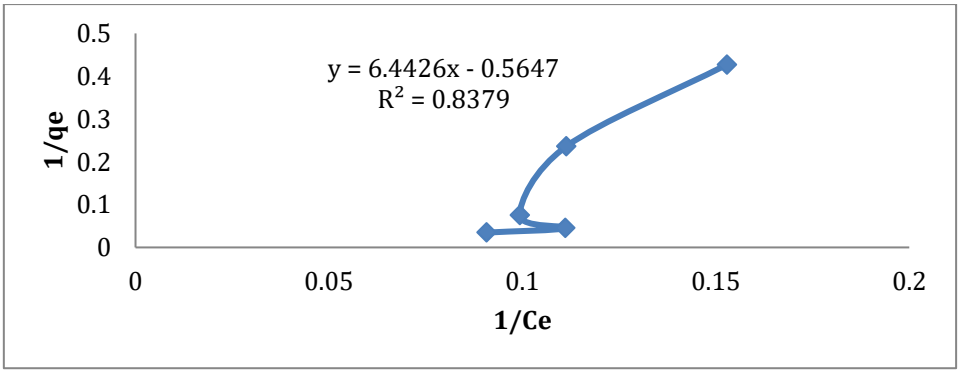


Figure 6: Graph of 1/qe versus 1/Ce of Chicken Feather Waste Adsorbent on Adsorption of Crude Oil from Contaminated Soil

Figure 6 depicts the Langmuir isotherm was used to study the adsorption of hydrocarbon from polluted soil and was found out that R^2 value was 0.838, meaning that the reliability, acceptability and the way the data fitted into the straight line curve was good. This indicate that Langmuir isotherm can be used to describe the adsorption process using CFW adsorbent.

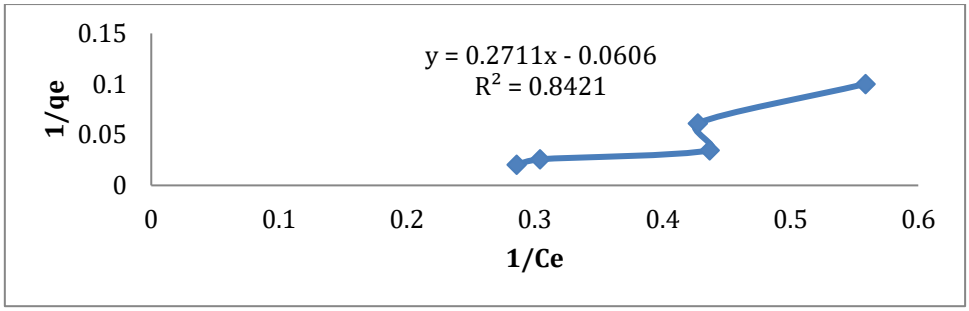


Figure 7: Graph of 1/qe versus 1/Ce of Absorbent Pad Adsorbent on Adsorption of Crude Oil from Contaminated Soil

Figure 7 depicts the Langmuir isotherm was used to study the adsorption of hydrocarbon from polluted soil and was found out that R^2 value was 0.842, meaning that the reliability, acceptability and the way the data fitted into the straight-line curve was good. This indicate that Langmuir isotherm can be used to describe the adsorption process using AP adsorbent. Compared to Figure 6, the adsorbent AP is better in terms of performance than the CFW adsorbent on to the Langmuir isotherm.

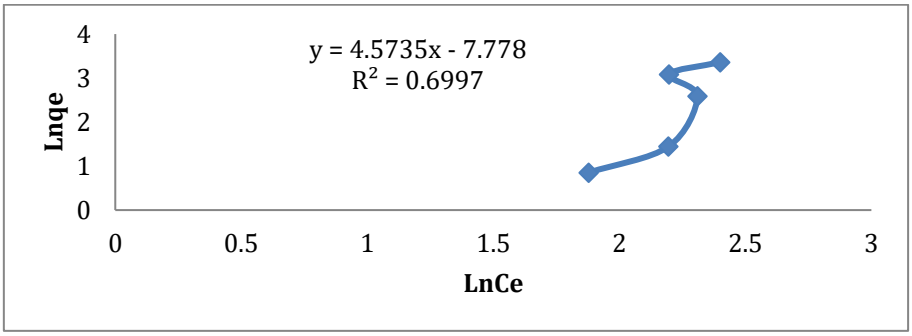


Figure 8: Freundlich plot of ln (qe) versus ln (Ce) of Chicken Feather Waste Adsorbent on Adsorption of Crude Oil from Contaminated Soil

Figure 8 depicts the investigation of this profile is to see if the Freundlich isotherm can be used to describe the adsorption of crude from contaminated soil using CFW as adsorbent. The R^2 value of 0.6997 proved true as the isotherm can be used to describe the process. So, it can be concluded that the Langmuir isotherm is better and suitable for the adsorption process than Freundlich isotherm.

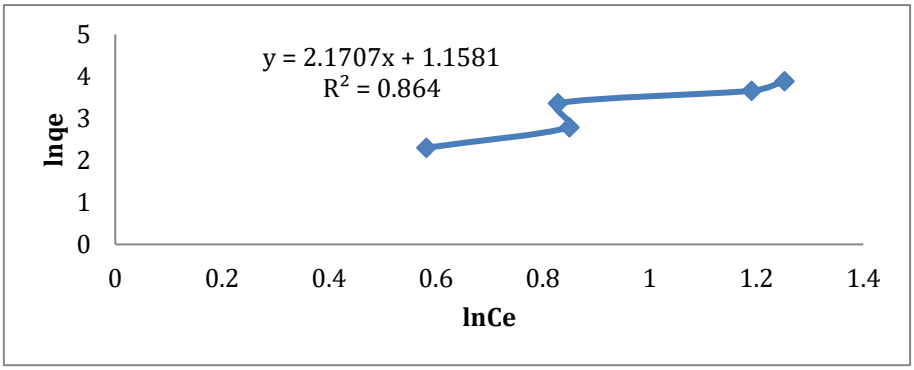


Figure 9: Freundlich plot of ln (qe) versus ln (Ce) of Absorbent Pad Adsorbent on Adsorption of Crude Oil from Contaminated Soil

Figure 9 depicts the investigation of this profile is to see if the Freundlich isotherm can be used to describe the adsorption of crude from contaminated soil using AP as adsorbent. The R^2 value of 0.864 proved true as the isotherm can be used to describe the process. However, when generally compared, Freundlich isotherm is more preferable and with a 2^{nd} order kinetics for the adsorption process and must use AP as adsorbent because of high value of coefficient of determination.

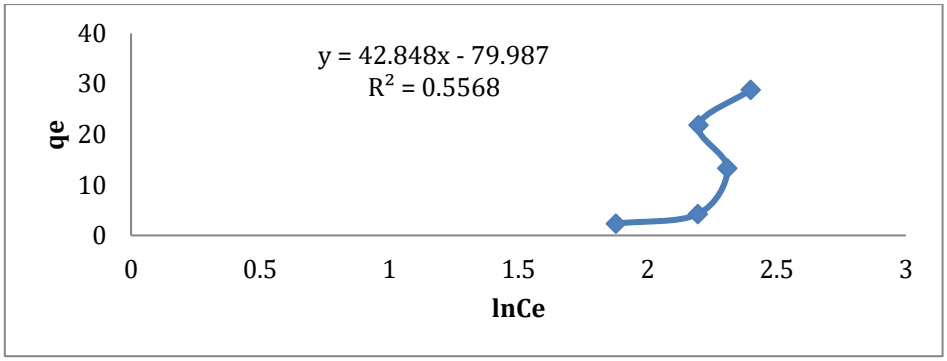


Figure 10: Tempkin plot of qe versus ln (Ce) of Chicken Feather Waste Adsorbent on Adsorption of Crude Oil from Contaminated Soil

Figure 10 depicts the Tempkin isotherm model was used to described the adsorption process with CFW adsorbent and the results shown indicates that the process can be describe by the isotherm model. Though the data obtained from the Tempkin isotherm is a good one, first order process, reliable and acceptable, but compared to the other isotherms, the adsorption of crude oil from contaminated soil cannot be described well by this type of isotherm. Hence rejected.

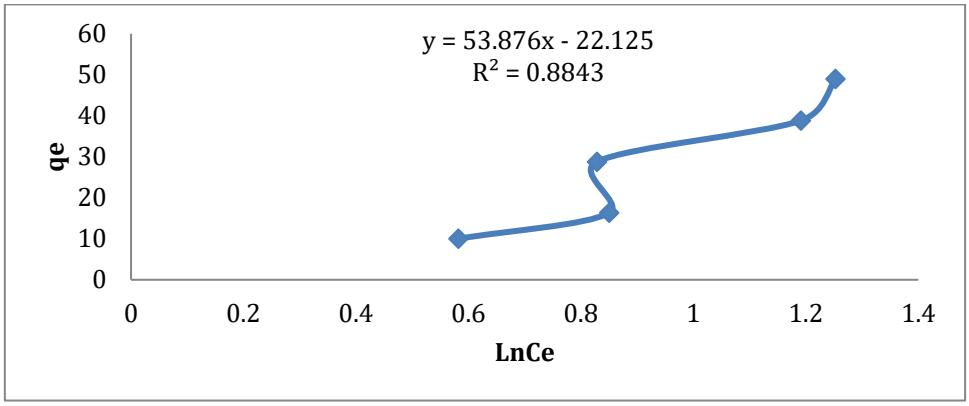


Figure 11: Tempkin plot of qe versus ln (Ce) of Absorbent Pad Adsorbent on Adsorption of Crude Oil from Contaminated Soil

Figure 11 depicts the Tempkin isotherm model was also used to describe the adsorption of hydrocarbon from polluted soil with AP and the result as shown indicated that the adsorption process is best described by Tempkin. The reason is because the coefficient of determination is 0.884. In all, hydrocarbon adsorption from polluted soil is suitable with AP as adsorbent compared to CFW and all the isotherms can be used to describe the process but Tempkin isotherm is the best isotherm.

CONCLUSION

From the results of the study, biosorption of hydrocarbon contaminated soil was carried out using two adsorbents, the chicken feathers waste and the absorbent pad. The adsorbents materials were sourced locally and prepared accordingly for the adsorption process. Meanwhile, the soil was contaminated with crude oil to serve as hydrocarbon polluted soil. The adsorbents used and the soil were all characterized and analyzed using Gas Chromatography (GC) Analyzer to determine the physicochemical properties of the soil and adsorbents before the experimentation.

The study was able to clearly identify which of the adsorbent best suitable for the adsorption process. Adsorbent pad (AP) adsorbent was best for hydrocarbon uptake compared to chicken feather waste (CFW) due to highest R^2 values shown in Tables 3 to 7 and both follow 2nd order kinetics.

Tempkin and Freundlich isotherms described the adsorption process of crude oil in contaminated soil better than Langmuir isotherm. Tempkin best explained the process compared to Freundlich using adsorbent pad (AP) as adsorbent with R^2 value respectively 0.884.

The 2nd order kinetic and isotherms can be used to describe the adsorption process of crude oil contaminated soil, as evidence from the results obtained from Figure 3 to Figure 11 and Table 3 to Table 7.

Nomenclature

q_e	Amounts of heavy metal absorbed by the adsorbent at equilibrium (mg/g)
q_t	Concentration of heavy metal absorbed by the adsorbent at particular time, t (mg/g)
k_1	Rate constant of absorption (hr^{-1}).
k_2	Pseudo-second-order rate constant (g/mg.hr),
t	Measured time of adsorption (hr)
a	Adsorption constant,
φ	Initial rate of adsorption (mg/g hr)
C_{ads}	The amount of heavy metal and other ions absorbed at equilibrium,
B	Sorption constant (mg/l) at a given temperature, related to the energy of sorption,
Q	Maximum sorption capacity (mg/g).
C_e	Equilibrium constant (mg/l),
Q_m	Maximum monolayer coverage capacity (mg/g),
K_L	Langmuir Isotherm constant (l/mg).
k_f	Freundlich Isotherm constant,
n	Adsorption intensity,
q_e	Equilibrium concentration of adsorbate (mg/l),
C_e	The amount of heavy metal and other ions absorbed at equilibrium.
A_T	Temkin Isotherm equilibrium binding constant (l/g)
b_T	Tempkin Isotherm constant,
R_T	Universal gas constant (8.314 J/mol K),
T	Temperature at 298K
B	Constant related to the heat of sorption (J/mol).
q_e	The number of ions adsorbed at equilibrium (mg/g)
β	Dubinin-Radushkevich isotherm constant (mol^2/KJ^2),
ε	Polanyi potential
AP	Absorbent pad
CFW	Chicken feather waste

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