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Assessment of Crude Oil Mopping Efficiency of Ground Chicken Feathers: Kinetic and Adsorption Isotherm Studies

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Authors' contributions

This work was carried out in collaboration between both authors. Author KHI designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors KHI and UIP managed the analyses of the study. Author UIP managed the literature searches. Both authors read and approved the final manuscript.

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Original Research Article

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ABSTRACT

Aims: To determine and compare the equilibrium adsorption capacity and adsorption process of crude oil onto ground chicken feathers and mixture of crude oil on water onto ground chicken feathers with that of a conventional synthetic sorbent mat determined under the same experimental condition as ground chicken feathers.
Study Design: The study was designed to use ground chicken feathers and a conventional synthetic sorbent mat to mop crude oil and mixture of crude oil on water so as to assess the effectiveness of ground chicken feathers as an oil spill sorbent by comparing its mopping profile with that of a standard; a conventional synthetic sorbent mat.
Place and Duration of Study: Department of Chemistry Laboratory, Federal College of Education (Technical), Asaba, Delta State, Nigeria, between September – October, 2010.
Methodology: The adsorption of crude oil onto ground chicken feathers/synthetic sorbent mat was carried out in two stages. The first stage of the study involves kinetic study of the adsorption

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process to determine the equilibrium adsorption capacity (q_e) of crude oil onto ground chicken feathers and the standard, and the equilibration time of the adsorption process. The second stage of the study involves verification of the adsorption process using adsorption isotherms of Langmuir, Freundlich, Elovich, Temkin and Dubinin-Radushkevich. To determine the mopping profile of crude oil on water onto ground chickens and synthetic sorbent, the experiment was repeat with mixture of crude oil on water. The experiment was carried out at room temperature; 28℃.

Results: The equilibrium adsorption capacity of crude oil onto ground chicken feathers/synthetic sorbent obtained from the kinetic study of the adsorption of crude oil onto ground chicken feathers/synthetic sorbent are 13.60 g/g at equilibration time of 80 minutes and 11.44 g/g at 60 minutes respectively. The linearized form C_eq_e versus C_e of Langmuir isotherm model fitted the experimental data with a coefficient of determination r^2 of 0.999 for both sorbents, indicating that the Langmuir isotherm can describe the adsorption of crude oil onto ground chicken feathers sand synthetic sorbent. The moderate (less than 10%) average percentage error value (APE %) of 4.6 and 4.8 obtained for ground chicken feathers and synthetic sorbent in the verification of the validity of the Langmuir model in describing the experimental data, confirms the validity of the Langmuir isotherm in describing the experimental data. The adsorption isotherm model shows that one molecule of crude oil is adsorbed on a layer of ground chicken feathers/synthetic and there is no interaction between the adsorbed molecules of crude oil. The intensity of adsorption of ground chickens feather and the conventional synthetic sorbent used as the standard are both 1.00 indicating that ground chicken feathers compared well with the standard in terms of affinity for crude oil and adsorption of crude oil. 14.70 g/g was obtained as the maximum equilibrium adsorption capacity q_m of the adsorption of crude oil onto ground chicken feathers, while 11.11 g/g was obtained for the adsorption of crude oil onto conventional synthetic sorbent. The result suggests that ground chicken feathers has larger surface area than the standard and is a better sorbent than the standard. The dimensionless separation factor equilibrium parameter K_R Of 0.0011 for both sorbents shows that the adsorption of crude oil onto ground chicken feathers and synthetic sorbent are favourable. About 12.00 g/g and 9.00 g/g of the adsorbed oil can be recovered from ground chicken feathers and conventional synthetic sorbent respectively. This make ground chicken feathers a better sorbent when oil recovery is required. The amount of water adsorbed together with crude oil on water was negligible, which means that both sorbents can be used to mop crude oil spill on land and on water.

Conclusion: The result of the study shows that ground chicken feather adsorbed more crude oil per unit mass than the conventional synthetic sorbent used as the standard in this study. Ground chicken feathers are an efficient natural sorbent that can be used to mop crude oil spill on land and water, and it is efficient for oil recovery.

Keywords: Equilibrium adsorption capacity; chicken feather; synthetic sorbent mat and crude oil.

1. INTRODUCTION

Crude oil is a complex mixture of hydrocarbons and other organic compounds, including some heavy metals and metallic compounds [1]. However, the percentage of hydrocarbons is higher. In its raw state, crude oil is of little use. Its value lies in what is created from it: Fuels (natural gas, petrol, kerosene, heating oil, lubricating oils, waxes, asphalt, petrochemicals) [2]. The wide application of oil has put a huge demand of it by both industrialized and developing countries [3].

Petroleum exploration and exploitation as well as transportation of crude oil from production wells to the refineries often times spill oil. The environmental effects of oil spill among many include destruction of farm crops and soil fertility, fire outbreak, massive bird kills, killing of marine plants and animals etc. [4]. Due to the adverse effects of oil spill on the environment there is need to mop up the oil as soon as it happens. There are different sorbents available for oil spill mop such as synthetic and natural sorbents. Natural sorbents include organic and inorganic sorbents [5].

Solid waste generation is increasing with population expansion, industrialization and urbanization. Current world cities generate about 1.3 billion tonnes of solid waste per year. The global impacts of solid waste are growing fast. Solid waste is a large source of methane, a green house gas (GHG). When organic waste decomposes in landfills and uncontrolled dumps, it produces methane, one of the major green house gases contributing to climate change [6]. In most developing countries, open dumping with open burning is the norm [7]. Improperly managed solid waste poses a risk to human health and the environment. In addition, it may result in safety hazards from fires or explosions. However, through proper solid waste management such as waste prevention, recycling, composting, controlled burning, or land filling, these problems can be eliminated (6). Recycling makes use of materials that otherwise would become waste by turning them into valuable resources. Recycling helps to reduce green house gas emissions, in part, by diverting waste from landfills.

Chicken feathers are poultry waste and are normally thrown out [8]. It is inexpensive, abundant and readily available in all countries that eat poultry. There are over three billion pounds of chicken feathers thrown out just in the United States [8]. In Nigeria, chicken feather are not properly disposed. They constitute an environmental menace. Feathers are processed to make animal feed, but, the use of feather is considered a low grade substitute that could cause disease in other animals. So they are thrown out as waste instead, filling landfills and incinerators [8]. In the European Union, for example, poultry feather meal has been banned since 2001 [9]. As an organic waste, chicken feather may be capable of releasing methane into the atmosphere during biodegradation, when buried in the landfill. Instead of allowing this to happen, they could be recycled into more useful products. Again, the use of agricultural products as a source of raw materials for the chemical and materials industry is growing in importance and value. Chicken feather is a renewable material whose supply is reliable and none depleting. It could serve as a source of raw materials for the chemical industry in the production of oil spill sorbents.

The assessment or performance of sorbing materials often needs to be compared [10]. In order for the comparison of two or more sorbents to be fair, it must be done under the same experimental conditions. By performance of the sorbent is usually meant its uptake (q) of a sorbate. The sorbents can be compared by their respective maximum equilibrium adsorption capacity q_m values which are calculated. A good sorbent would feature a high sorption uptake capacity qm. Also desirable is a high affinity between the sorbent and sorbate. The amount of a sorbate adsorbed onto a sorbent can be obtained using kinetics and adsorption isotherms [11]. The kinetics experiment is done as a function of time. Then by plotting amount adsorbed against time a graph is produced from which the equilibrium adsorption capacity of the sorbent, equilibration time of the adsorption process and the rate of adsorption can be obtained. Adsorption isotherm is defined as a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium, and it shows the distribution of adsorbable solute between the liquid and solid phases at various equilibrium concentrations [10,12]. The three well-known isotherms are Freundlich, Langmuir and BET adsorption isotherms [13]. Adsorption process is usually described through adsorption isotherms. Usually, to obtain experimental data to be fitted into an adsorption model, different initial concentrations of the sorbate and/ or different mass of the sorbent is used during the experiment, so as to produce other values of equilibrium adsorption capacity (qe) and equilibrium concentration (Ce) at the end of the experiment [10].

The aim of this study is to determine the efficacy of chicken feathers in the mopping of crude oil on land and water. This is done by comparing the adsorption of crude oil, and crude oil on water onto chicken feathers, determined under the same experimental condition, with that of one of the conventional synthetic sorbent used in mopping oil spill in the oil industry. The result if favourable, can project the effectiveness of chicken feathers as an oil spill sorbent mop on land and water. Thereby encouraging its use in the production of oil spill sorbent and invariably help to solve the solid waste generated by chicken feathers and reduce the emission of methane gas in the environment.

2. MATERIALS AND METHODS

2.1 Sampling Area and Sample Collection

The crude oil used in this study was obtained from Shell Petroleum Development Company, Warri, Delta state, Nigeria, while chicken feathers was obtained from Hausa market located in Asaba, Delta state, Nigeria. Conventional synthetic sorbent mat used as the standard in this study to compare the mopping efficacy of chicken feathers was obtained from Shell

Petroleum Development Company, Port Harcourt, Rivers State, Nigeria.

2.2 Sample Preparation

The chicken feathers was thoroughly washed with distilled water and detergent, rinsed several times with copious amount of water and dried under the sun for two weeks. The feathers were ground using a mechanical blender, but, the blender could not blend it into particulate form, rather into a fluffy form. The standard which was in form of a mat was cut into smaller dimension.

2.3 Analysis of Sample

The experiment of the adsorption of crude oil onto ground chicken feathers/synthetic sorbent mat was carried out in two stages. The first stage of the experiment involves kinetic study of the adsorption process to establish the exposure time necessary for the given sorbents to reach the equilibrium state (equilibration time of the adsorption process) and the equilibrium adsorption capacity (q_e) of the adsorbent. In the second stage of the study performed at the equilibration time obtained from the kinetic study, five different initial concentrations of crude oil were used in the experiment to determine the adsorption process of the adsorption of crude oil onto ground chicken feathers and synthetic sorbent mat. The experimental data; equilibrium adsorption capacity (q_e) and the concentration of crude oil at equilibrium (Ce) obtained were fitted into Langmuir, Freundlich, Elovich Temkin and Dubinin-Radushkevich adsorption models to describe the adsorption process.

2.3.1 Kinetic determination of the adsorption of crude oil onto ground chicken feathers/synthetic sorbent mat

One (1) dm^3 of crude oil was poured into a pre-weighed 2000 ml beaker and weighed. The weight of crude oil was obtained by difference in weight. The weight of the crude oil was used as the initial concentration of crude oil. Exactly five (5) grams of ground chicken feathers/synthetic sorbent was weighed and added into the crude oil in the beaker. The sorbate – sorbent system was left for a contact time. The contact time used in this study is 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 minutes intervals. At the end of each contact time, the sorbate (crude oil) was carefully (ensuring that no sorbent was decanted along with the sorbate) decanted into another pre-weighed 2000 ml beaker. The remaining content (sorbent and some sorbate) in the beaker was passed through Whatman filter paper 185 mm fitted onto a glass funnel. The glass funnel was inserted into the 2000 ml beaker containing the previous decanted sorbate. At the end of the filtration, the weight of the 2000 ml beaker containing the unadsorbed oil (decanted and filtered oil) was weighed. The weight of the unadsorbed crude oil was obtained by difference in weight. The weight of the unadsorbed oil was used as the final concentration of crude oil.

The amount of crude oil adsorbed onto a unit mass of chicken feathers/synthetic sorbent was calculated from:

$$q = \frac{C_i - C_f}{M}$$

Where q = the amount of crude oil adsorbed onto a unit mass of chicken feathers/synthetic sorbent, C_i = initial concentration of crude oil in grams (g), C_f = final concentration of crude oil in grams, M = mass of sorbent in grams (g).

or

q = [(Initial weight of crude oil – Final weight of crude oil) / M]

At the end of the experiment, graph of amount of crude oil adsorbed onto ground chicken feathers/synthetic sorbent mat (q) at different contact time used in the study was plotted. From the graph, the equilibration time of the adsorption process and the equilibrium adsorption capacity (q_e) of crude oil were determined for both sorbents.

2.3.2 Recovery of crude oil adsorbed onto ground chicken feathers/synthetic sorbent mat

Ground chicken feathers/synthetic sorbent retained on the filter paper at each contact time was weighed and the weight noted. The filter paper was folded over the sorbents and subjected to pressing using a carver hydraulic press, Model M, serial No. 12000 – 137, operated at a pressure of 25 tonnes for five minutes at 28℃. After pressing, the weight was noted and the weight of crude oil recovered was determined by weight difference.

The amount of crude oil recovered per unit mass of the sorbents was determined from the expression:

$$q = \frac{\text{Initial weight} - \text{Final weight}}{\text{Mass of sorbent}}$$

Average of three (3) determinations was made for the adsorption and recovery and the standard deviation calculated.

The experiment was conducted at room temperature 29℃.

The amount of crude oil retained per unit mass of the sorbents was obtained from the expression:

q = Quantity of oil adsorbed per unit mass of sorbent – Quantity of oil recovered per unit mass of sorbent.

2.3.3 Verification of adsorption process of crude oil onto ground chicken feathers/synthetic sorbent using adsorption isotherm

The adsorption of crude oil onto five (5) grams of chicken feather/synthetic sorbent mat, using five different initial concentrations of crude oil; 0.5 dm^3 (442 g), 0.75 dm^3 (651 g), 1.00 dm^3 (866 g), 1.25 dm^3 (1110 g) and 1.5 dm^3 (1320 g) was determined at this stage, using the same procedure and experimental condition as in 2.3.1 above. The sorbate – sorbent system was left to contact for 2 hours (120 minutes) allowing additional time for equilibrium to be achieved. Triplicate determination was conducted for each initial concentration, and the average taken.

The experimental data (q_e and C_e) obtained were fitted into Freundlich, Langmuir, Elovich, Temkin and Dubinin-Radushkevich adsorption models.

2.3.4 Determination of adsorption and recovery of crude oil on water from ground chicken feathers and synthetic sorbent mat

The experiment was repeated with crude oil on water so as to determine the behavior and mopping ability of chicken feathers and synthetic sorbent when crude oil spill on water. Four (4) dm^3 of water was poured into a pre-weighed transparent plastic bowl of 10 dm^3 capacity and weighed. The weight of the water was obtained by difference in weight and recorded. Exactly 2 dm^3 of crude oil whose initial weight had been predetermined was added into the water in the bowl. Crude oil is immiscible with water; hence it floated on the water. Five grams of ground chicken feathers/synthetic sorbent was weighed and added into the crude oil on water. The sorbent – sorbate system was left for a contact time. The contact time was same as used in the kinetic study in 2.3.1 above.

It was observed that the ground chicken feathers/synthetic sorbent remained in the crude oil (organic) layer. At the end of each contact time, the crude oil layer containing the ground chicken feathers/synthetic sorbent was carefully decanted into another pre-weighed transparent bowl. The remaining sorbate (crude oil) containing the sorbent, was carefully passed through a filter paper fitted onto a glass funnel which was placed inside the transparent bowl containing the previous decanted crude oil. Small amounts of crude oil which formed the boundary layer between water and crude oil were not separated from water during the filtration, because water will be lost. These (crude oil) was carefully removed using syringe and added to the crude oil in the transparent bowl.

The separated crude oil and water were weighed, and their weight obtained by difference. The experiment was conducted at room temperature 29℃. Two determinations were performed for each contact time and the average and standard deviation calculated. The amount of crude oil adsorbed onto a unit mass of the sorbents at each contact time was calculated, the graph plotted from which the equilibration time of the adsorption process and the equilibrium adsorption capacity (q_e) were determined for both materials.

2.4 Fourier Transform Infrared (FTIR) Spectroscopic Analysis of the Conventional Synthetic Sorbent Mat

To obtain the chemical composition of the synthetic sorbent mat used in this study, as it was not disclosed by the oil company it was obtained from, the functional groups present in the sorbent were determined by FTIR spectroscopy. The FTIR analysis was carried out using SHIMADZU FTIR-8400S spectrophotometer with a NaCl cell. The sample was ground into fine powder and spread uniformly in between two NaCl based cells. The cells were fixed into the machine and an incident ray of light passed through it. The FTIR spectrophotometer was operated under the following conditions; interferometer: Michelson type with 30° incident angle, dynamic alignment, sealed desiccated, optical system: single beam optics, beam splitter: germanium-coated HBr plate, light source: high brightness ceramic, detector: temperature controlled high sensitivity detector (DLATGS detector), S/N ratio: greater than 20,000: 1 (KRS-5 window), 4cm^{-1} , 1 minute, 2200 cm^{-1}, P-P, wave number: 7,800 cm^{-1}-350 cm^{-1} , resolution: 0.85, 1, 2, 4, 8, 16 cm^{-1} , mirror speed: 3 steps; 2.8, 5, 9 mm/sec, data sampling: He-Ne laser, sample compartment: W200 mm x D230 mm X H170 mm, temperature: 15-30°, relative humidity: less than 70%.

3. RESULTS AND DISCUSSION

The result of the kinetic study of the adsorption of crude oil onto ground chicken feathers/ synthetic sorbent mat are shown on Tables 1 and 2, and Fig. 1. From Fig. 1, the time for the equilibrium adsorption of crude oil onto chicken feathers is 80 minutes, while the equilibrium adsorption capacity (q_e) is 13.60 g/g. From the same graph, the equilibration time of the adsorption of crude oil onto the synthetic sorbent mat is 60 minutes while the equilibrium adsorption capacity (q_e) is 11.44 g/g. The kinetic study shows that chicken feathers adsorbed more crude oil per unit mass than the synthetic sorbent mass.

Table 1. Amount of crude oil adsorbed onto ground chicken feathers (q), recovered from ground chicken feathers and retained by ground chicken feathers

Amount of crude oil adsorbed per unit mass (q) (g/g)	Amount of crude oil recovered per unit mass (g/g)	Amount of crude oil retained per unit mass (g/g)	Contact time (Min)
13.65±0.97	12.90±0.31	0.75	10
13.67±0.94	12.93±0.66	0.74	20
13.72±1.01	13.10±0.91	0.62	30
13.64±0.98	12.81±0.47	0.83	40
13.80±0.91	13.10±0.89	0.70	50
13.62±1.03	12.69±0.70	0.93	60
13.64±0.95	13.00±0.51	0.64	70
13.60±1.11	12.78±0.54	0.82	80
13.61±0.96	12.64±0.88	0.97	90
13.66±0.91	13.02±0.72	0.64	100

Table 2. Amount of crude oil adsorbed onto synthetic sorbent mat (q), recovered from synthetic sorbent mat and retained by synthetic sorbent mat

Amount of crude oil adsorbed per unit mass (q) (g/g)	Amount of crude oil recovered per unit mass (g/g)	Amount of crude oil retained per unit mass (g/g)	Contact time (Min)
11.48±0.50	9.88±0.69	1.60	10
11.45±0.65	9.55±0.55	1.90	20
11.46±0.61	9.61±0.98	1.85	30
11.45±0.23	9.65±0.46	1.80	40
11.45±0.11	9.60±0.33	1.85	50
11.44±0.27	9.57±0.39	1.87	60
11.46±0.78	9.66±1.04	1.80	70
11.47±0.30	9.65±0.72	1.82	80
11.45±0.42	9.58±0.94	1.87	90
11.44±0.30	9.64±0.87	1.80	100

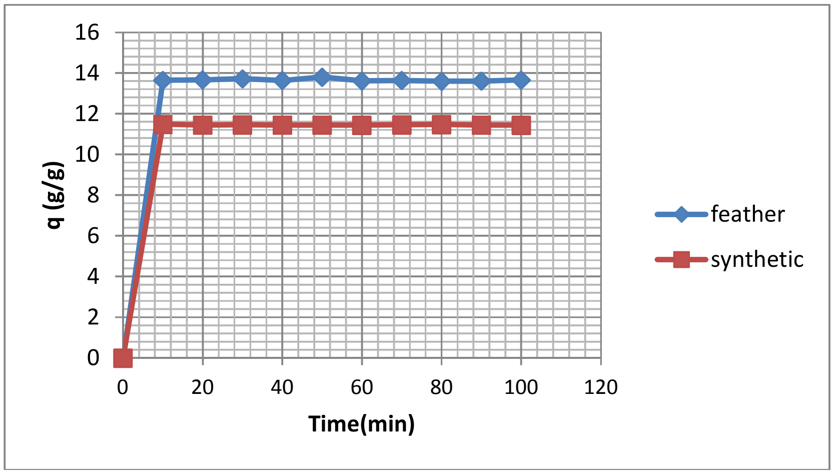

Fig. 1. Amount of crude oil adsorbed onto ground chicken feathers and synthetic sorbent mat per unit mass against time

The experimental data obtained using five different initial concentrations of crude oil to verify the adsorption process are shown on Tables 3 and 4. The adsorption isotherms applied to the experimental data to describe the adsorption process are Freundlich, Langmuir, Elovich, Temkin and Dubinin-Radushkevich adsorption models. The Freundlich equation can be written as $q_e = K_F\ C_e\ ^{l/n}$ [14]. K_F is a constant indicative of the relative adsorption capacity of the adsorbent (mg $^{l-(l/n)}$ L $^{l/n\ g-l}$ and n is a constant indicative of the intensity of the adsorption. The Freundlich expression is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases. The Freundlich isotherm can be linearized by plotting Log q_e against Log C_e or ln q_e against ln C_e. The Langmuir equation may be written as

$$q_e = \frac{q_m b C_e}{1 + bC_e}$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg /g), C_e the equilibrium concentration of the solute in the bulk solution (mg L $^{-1}$), q_m the maximum adsorption capacity (mg/g), and b is the constant related to the energy of adsorption and temperature, and affinity between the sorbent and sorbate [10,15].

The assumptions made in the derivation of the Langmuir model are that: adsorption is a reversible process, fixed number of adsorption sites, a fraction of the surface sites ϴ is occupied by adsorbed molecules, and the fraction 1 – ϴ is free, all sorption sites are uniform i.e. constant heat of adsorption, one sorbate molecule reacts with one active site, no interaction between sorbed species [10]. The Langmuir isotherm relation is of a hyperbolic form, a plot of q_e versus C_e produces a non linear graph. It can be linearized to five different forms, out of which the forms $1/q_e = 1/bq_m\ 1/c_e + 1/q_m$ (plot $1/q_e$ vs. $1/C_e$) and $C_e/q_e = 1/q_m C_e + 1/q_m b$ (plot C_e/q_e $_{vs}$ C_e) are the most frequently used by several researchers because of the minimized deviations from the fitted equation resulting in the best error distribution. Accordingly, a plot of C_e/q_e against C_e produces a linear graph with slope = $1/\ q_m$ and intercept $1/\ K_a q_m$ and a plot of $1/\ q_e$ versus $1/C_e$ gives a linear graph with slope $=1/\ K_a q_m$ and intercept $1/\ q_m$.

The equation defining the Elovich [16] model is based on a kinetic principle assuming that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption. It is expressed by the equation:

$$q_e/q_m = K_E C_E \exp\ (q_e/q_m)$$

where K_E is the Elovich equilibrium constant (L mg $^{-1}$) and q_m is the Elovich maximum adsorption capacity (mg $^{-1}$). If the adsorption obeys Elovich equation, Elovich maximum adsorption capacity and Elovich constant can be calculated from the slopes and the intercepts of the linear plot

$$\ln\ (q_e/C_e) \text{ versus } q_e.$$

The Temkin [17] isotherm equation assumes that the heat of adsorption of all molecules in the layer decreases linearly with coverage due to adsorbent-adsorbent interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. Temkin model is given by

$$q_e = \frac{RT}{b} \ln(A_T C_e)$$

$$q_e = \frac{RT}{b} \ln A_T + (RT/b)\ln C_e$$

$$B = RT/b_T$$

$$q_e = B\ln A_T + B\ln C_e$$

where

A_T = Temkin isotherm equilibrium binding constant (L/q)
b_T = Temkin isotherm constant
R = universal gas constant (8.314J/mol)
T = Temperature at 298k
B= Constant related to heat of sorption(J/mol)

From the linear plot q_e against $\ln C_e$ the constants can be determined from the slope and intercept.

The Dubinin-Radushkevich isotherm estimates the characteristics porosity of the sorbent and apparent energy of adsorption [18]. The model is represented as:

$$q_e = q_D \exp(-B_D[RT \ln(1+1/C_e)]^2$$

Where, B_D is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the adsorbent from infinite distance in the solution and q_D is the Dubinin-Radushkevich isotherm constant related to the degree of sorbate sorption by the sorbent surface.

The linear form of equation is given as:

$$\ln q_e = \ln q_D - 2B_D RT\ln(1+1/Ce)$$

The plot of $\ln q_e$ against RT ln $(1+C_e)$ yields straight line. The values of q_D and B_D can be calculated from the intercept and slope.

Tables 3 and 4 shows the experimental data obtained for the adsorption of crude oil onto chicken feathers and synthetic sorbent, while Table 5 shows the values used to plot the adsorption models. Figs. 2 to 14 shows that the linearized form C_e/q_e versus C_e of the Langmuir adsorption isotherm produced the best fitted isotherm for the adsorption of crude oil onto ground chicken feathers and the synthetic sorbent. This shows that the adsorption obeys the Langmuir model. This implies that the interaction of both sorbents with crude oil is monolayer adsorption, that is, one sorbate molecule is adsorbed on a layer of adsorbent. There is no interaction between adsorbed molecules.

Table 3. Experimental Data obtained for the adsorption of crude oil onto ground chicken feathers

Initial concentration(C_O) in volume (dm^3)	Initial concentration(C_O) in gram (g)	Equilibrium concentration (C_e) (g)	Equilibrium adsorption capacity (q_e) (g/g)
0.50	442.00	370.00	14.40
0.75	651.00	581.90	13.82
1.00	866.00	796.50	13.90
1.25	1110.00	1039.35	14.13
1.50	1320.00	1249.95	14.01

Table 4. Experimental Data obtained for the adsorption of crude oil onto synthetic sorbent mat

Initial concentration(C_O) in volume (dm^3)	Initial concentration(C_O) in gram (g)	Equilibrium concentration (C_e) g	Equilibrium adsorption capacity (q_e) g/g
0.50	442.00	382.50	11.90
0.75	651.00	593.00	11.60
1.00	866.00	808.60	11.48
1.25	1110.00	1049.60	12.08
1.50	1320.00	1262.35	11.53

Table 5. Data for plotting Langmuir and Freundlich adsorption isotherms

	C_e (g)	q_e (g/g)	$1/q_e$	$1/C_e$	Ce/qe	Log q_e	Log C_e	ln q_e	ln C_e	RT ln (1+1/C_e
Chicken feathers	370.00	14.40	0.069	0.0027	25.69	1.15	2.56	2.66	5.91	6.44
	581.90	13.82	0.072	0.0017	42.10	1.14	2.76	2.62	6.36	3.96
	796.50	13.90	0.072	0.0012	57.30	1.14	2.90	2.63	6.68	2.72
	1039.35	14.13	0.070	0.0009	73.55	1.15	3.01	2.64	6.94	1.98
	1249.95	14.01	0.071	0.0008	89.21	1.14	3.09	2.64	7.13	1.73
Synthetic sorbent mat	382.50	11.90	0.084	0.0026	32.14	1.07	2.58	2.47	5.94	6.19
	593.00	11.60	0.086	0.0016	51.12	1.06	2.77	2.45	6.38	3.71
	808.60	11.48	0.087	0.0012	70.43	1.06	2.90	2.44	6.69	2.72
	1049.60	12.08	0.082	0.00095	86.88	1.08	3.02	2.49	6.95	1.98
	1262.35	11.53	0.086	0.00079	109.48	1.06	3.10	2.44	7.14	1.48

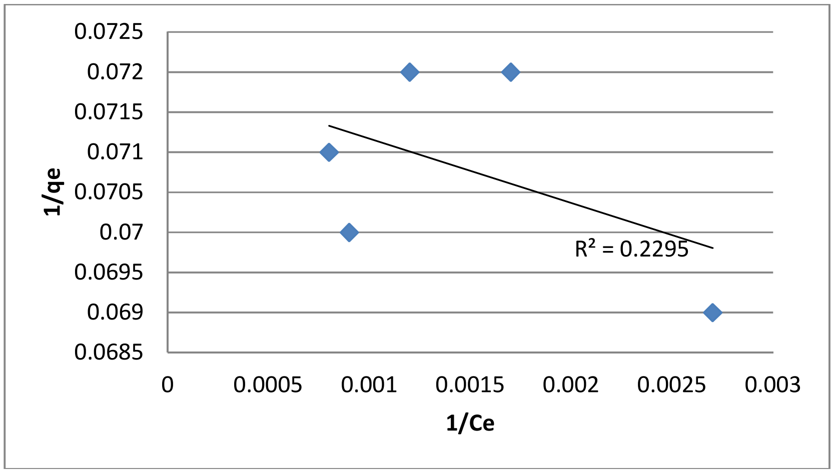

Fig. 2. Langmuir isotherm 1/qe versus 1/Ce of the adsorption of crude oil onto chicken feathers

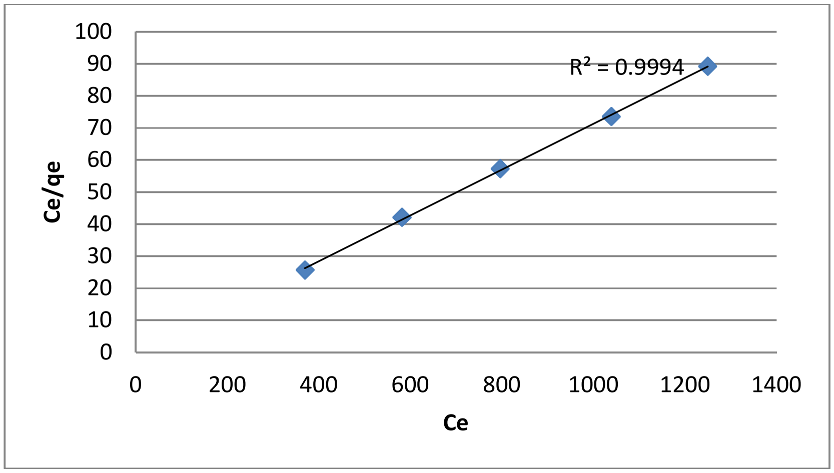

Fig. 3. Langmuir isotherm C_e/q_e versus C_e of the adsorption of crude oil onto chicken feathers

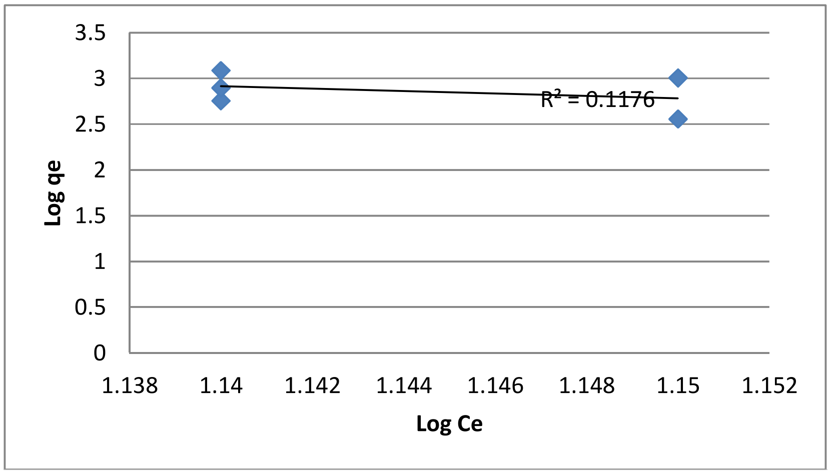

Fig. 4. Freundlich isotherm Log qe versus Log Ce of the adsorption of crude oil onto chicken feathers

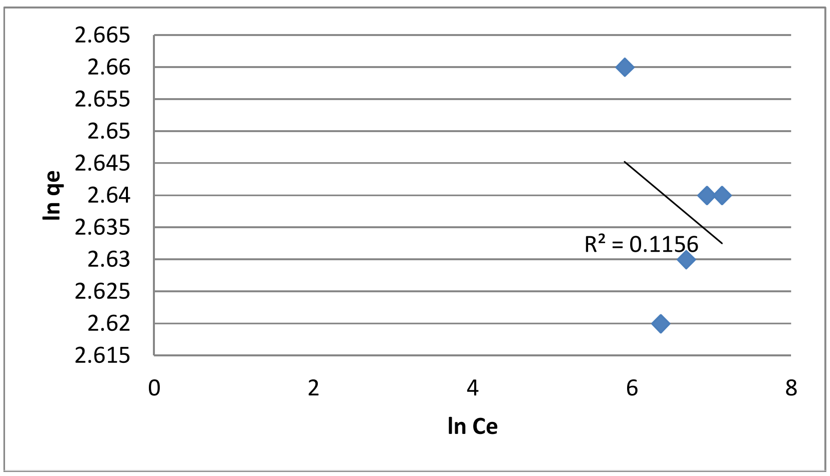

Fig. 5. Freundlich isotherm ln qe versus ln Ce of the adsorption of crude oil onto chicken feathers

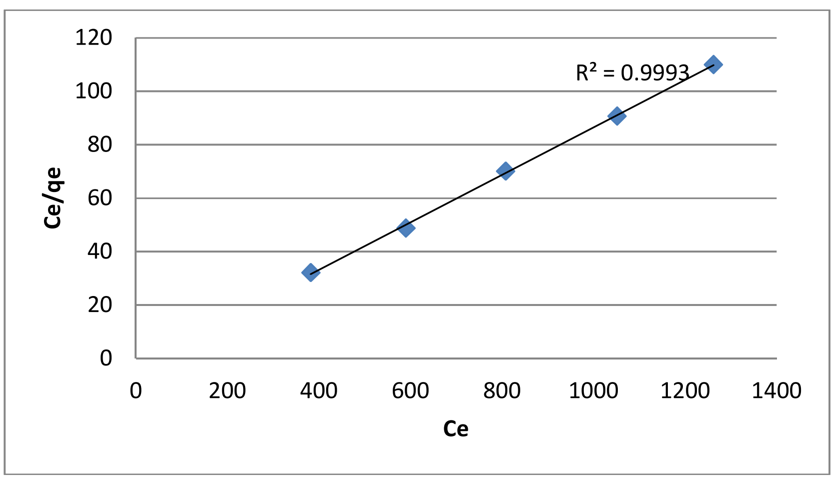

Fig. 6. Langmuir isotherm Ce/qe versus Ce of the adsorption of crude oil onto synthetic sorbent mat

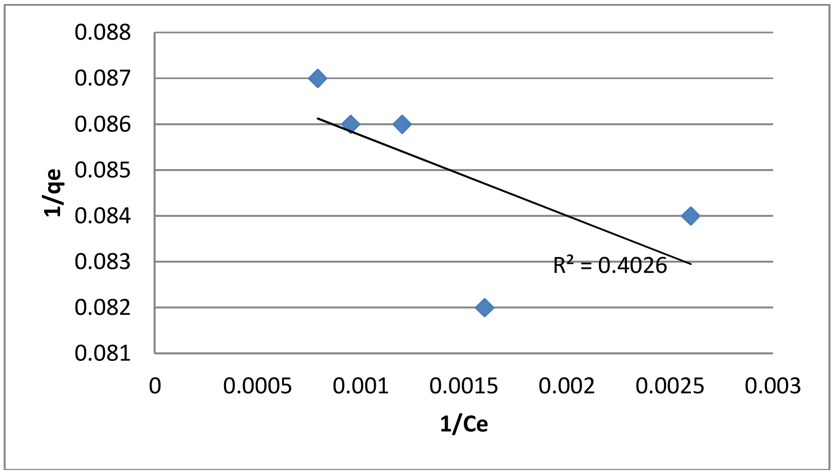

Fig. 7. Langmuir isotherm 1/qe versus 1/Ce of the adsorption of crude oil on synthetic sorbent mat

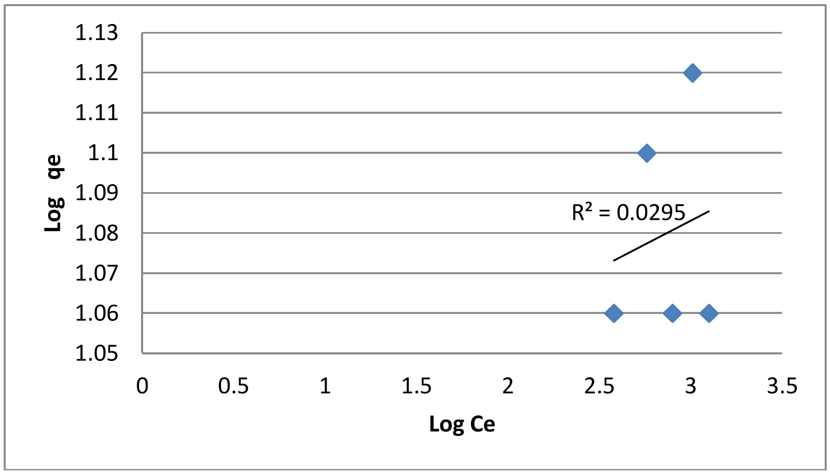

Fig. 8. Freundlich isotherm Log qe versus Log Ce of the adsorption of crude oil onto synthetic sorbent

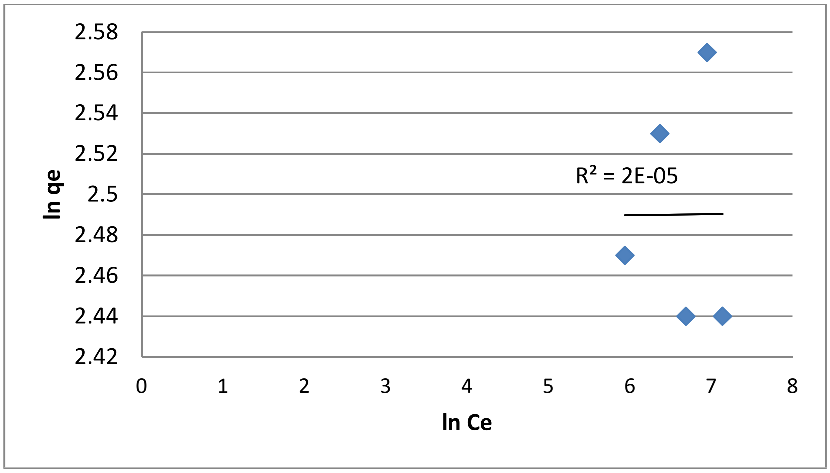

Fig. 9. Freundlich isotherm ln qe versus ln Ce of adsorption of crude oil onto synthetic sorbent

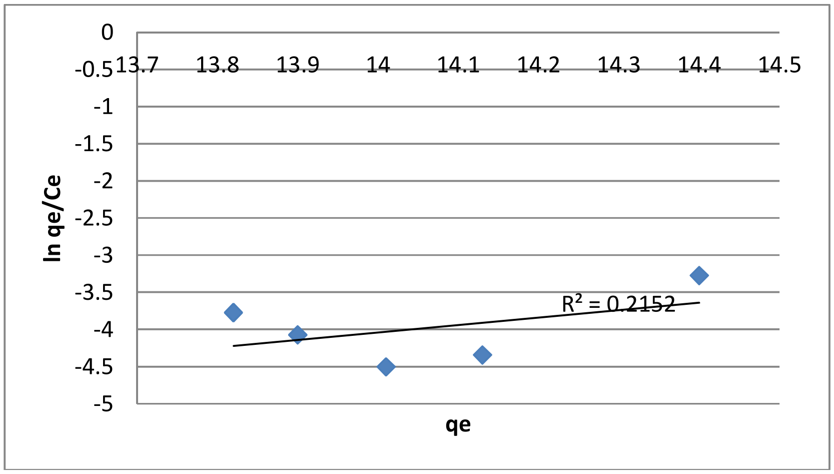

Fig. 10. Elovich isotherm lnqe/Ce versus qe of adsorption of crude oil onto ground chicken feathers

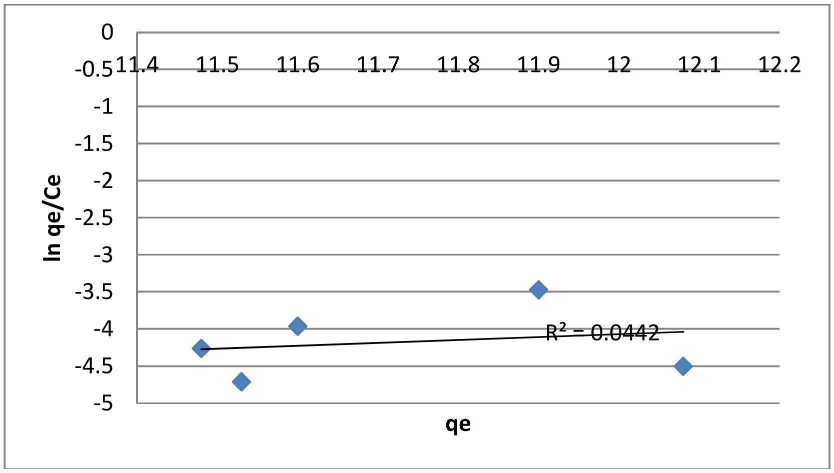

Fig. 11. Elovich isotherm lnqe/Ce versus qe of adsorption of crude oil onto synthetic sorbent

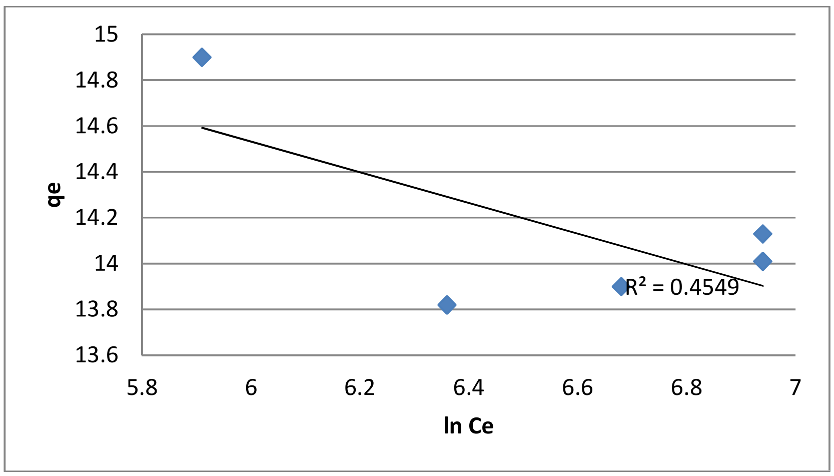

Fig. 12. Temkin isotherm qe versus lnCe of adsorption of crude oil onto ground chicken feathers

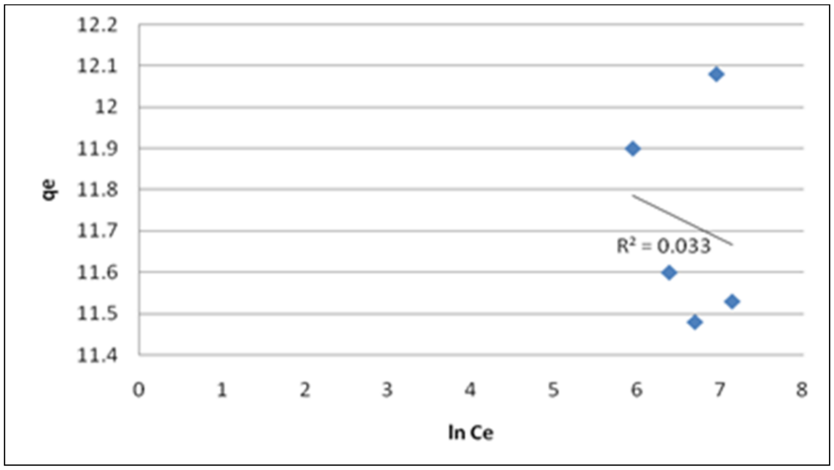

Fig. 13. Temkin isotherm qe versus lnCe of adsorption of crude oil onto synthetic sorbent mat

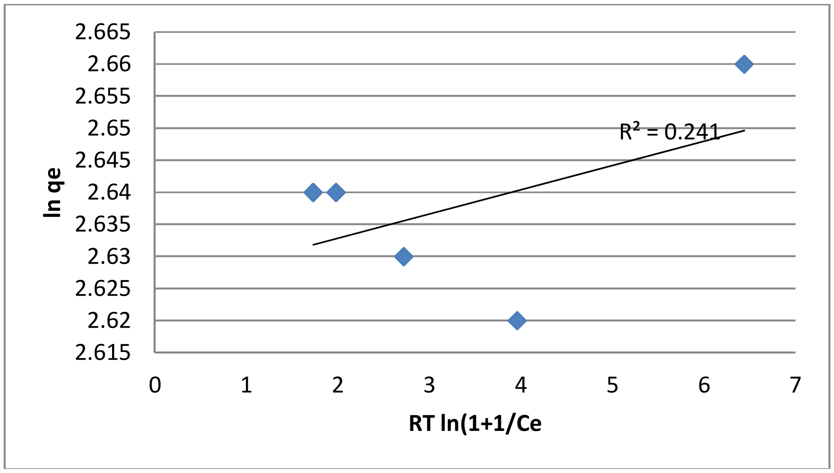

Fig. 14. Dubinin Radushkevich isotherm lnqe versus RT ln(1+1/Ce) of adsorption of crude oil onto chicken feathers

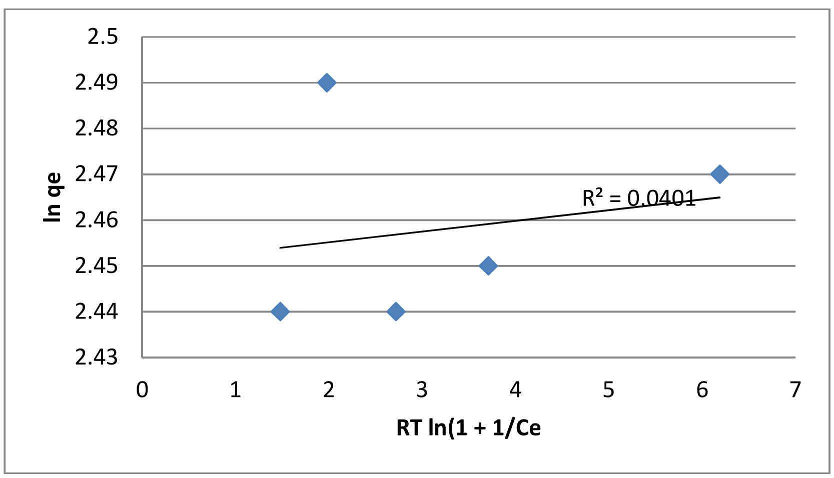

Fig. 15. Dubinin Radushkevich isotherm ln qe versus RT ln(1 + 1/Ce). of adsorption of crude oil onto synthetic sorbent mat

Sorbents can be compared by their respective maximum adsorption capacity q_m and b values obtained from the Langmuir equation [10]. The maximum adsorption capacity q_m is obtained from the isotherm model while q_e is the equilibrium adsorption capacity obtained from experiment [19]. q_m can be interpreted as the total number of binding sites that are available for sorption, and q_e as the number of binding sites that are in fact occupied by the sorbate at the concentration C_e [10]. The constant b and q_m are obtained from the slope and interception of the plot and are presented in Table 6. The b values for both chicken feathers and synthetic sorbent are 1.00. This implies that both sorbents have same affinity for crude oil. The q_m value of 14.70 g/g for chicken feathers is higher than that of synthetic sorbent, 11.11 g/g. This indicates that ground chicken feathers has more total number of binding sites than the synthetic sorbent, which implies that, ground chicken feathers has a larger surface area and higher crude oil uptake/removal than the synthetic sorbent. The q_m shows that ground chicken feathers is a better sorbent than the conventional synthetic sorbent mat. The value of the maximum adsorption capacity is higher than the experimental equilibrium adsorption capacity for ground chicken feathers, while it is lower than the experimental value for synthetic sorbent. It implies that the linearized form Ce/qe versus Ce of the Langmuir isotherm provided a better fit to the experimental data for ground chicken feathers than synthetic sorbent.

The coefficient of determination r^2 between the experimental data and isotherms was determined using solver add-in with Microsoft's spreadsheet, Microsoft Excel [20,21]. The results are presented in Table 6. The r^2 value shows good correlation between experimental data and the linearized form Ce/qe versus Ce of the Langmuir isotherm. This indicates that there is strong positive evidence that the adsorption process follows the Langmuir isotherm. In order to check the validity of the Langmuir model, it is interesting and essential to recalculate the adsorbed amounts using the equilibrium concentration values and Langmuir parameter $q_{m.}$ to obtain the average percentage errors (APE) according to the equation:

$$APE\ (\%) = \frac{\Sigma^{N}_{i=1}(q_e)_{,exp} - (q_e)_{,cal} / (q_e)}{N} \times 100$$

The moderately low value of APE obtained for ground chicken feathers and synthetic sorbent (Table 6) shows that the Langmuir model can describe the equilibrium data.

The favourable nature of adsorption can be expressed in terms of dimensionless separation factor equilibrium parameter of Hall et al. [22] which is defined by the following relationship, $K_R = 1/1 + K_aC_o$, where K_R is a dimensionless separation factor, C_o is initial concentration (mg L^{-1}) and K_a is Langmuir constant (L mg^{-1}). The values of K_R indicates the type of isotherm to be irreversible (K_R = 0), favourable (0<K_R <), linear (K_R = 1) or unfavourable (K_R >). The dimensionless separation factors calculated for ground chicken feather and synthetic sorbent are 0.0011. K_R values were less than 1 and greater than zero indicating favourable adsorption.

The quality of sorbent material is judged not only according to how much sorbate it can attract, but also on how much sorbate it can retain [10]. Tables 1 and 2 shows the amount of crude oil recovered and retained by ground chicken feathers and synthetic sorbent, the result shows that the synthetic sorbent mat retains more of the adsorbed crude oil than ground chicken feathers. In the light of this, ground chicken feathers with a higher crude oil uptake are better than the synthetic sorbent mat, however, in terms of retainability, the synthetic sorbent mat is better. Tables 1 and 2 and Fig. 1 shows that, substantial amount of the adsorbed/absorbed crude oil; about 12.00 g and 9.00 g was recovered from both chicken feathers and the synthetic sorbent respectively, but more of crude oil was recovered from chicken feathers. Since much crude oil was recovered from both sorbents, it means that the sorbate are attracted and held to the sorbent surfaces, including internal fibre walls by physical bonds that becomes easily broken on pressing. This also suggest that the adsorption of crude oil on the surface is greater than its absorption in the void of chicken feathers than in the void of synthetic sorbent mat, because, the adsorbed sorbates on the surfaces are easily desorbed than the sorbates absorbed within the voids. This phenomenon explains why more crude oil was retained by the synthetic sorbent mat than chicken feathers.

Fig. 17 shows the ftir spectrum of the synthetic sorbent mat. The prominent peaks are 829.42 cm^{-1} (s) c-h of alkene, 983.73 cm^{-1} (s) c-h of alkene, 1159.26 cm^{-1}, (s) c-c of alkane, 1369.50 cm^{-1} (s) c-h of alkane , 1453.41 cm-1(s) c-h of alkane, 2925.15 cm^{-1}(s) c-h of alkane. This suggest that the synthetic sorbent mat is a polyhydrocarbon.

Table 6A. Parameters of Langmuir isotherm for the adsorption of crude oil onto ground chicken feathers and synthetic sorbent mat

Isotherm	Ground chicken feathers	Synthetic sorbent mat
Langmuir (C_e /q_e versus C_e)		
b (L g^{-1})	1.00	1.00
q_m (g g^{-1})	14.70	11.11
r^2	0.999	0.999
APE (%)	4.60	4.80
K_R	0.0011	0.0011

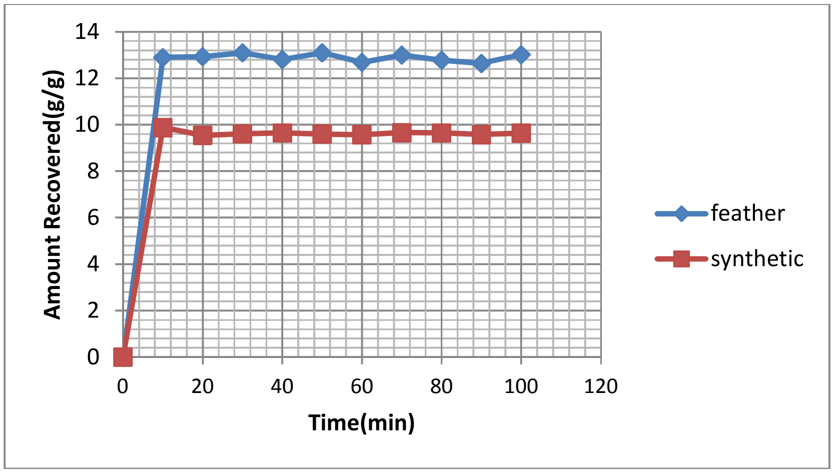

Fig. 16. Amount of crude oil recovered from ground chicken feathers and synthetic sorbent mat per unit mass against time

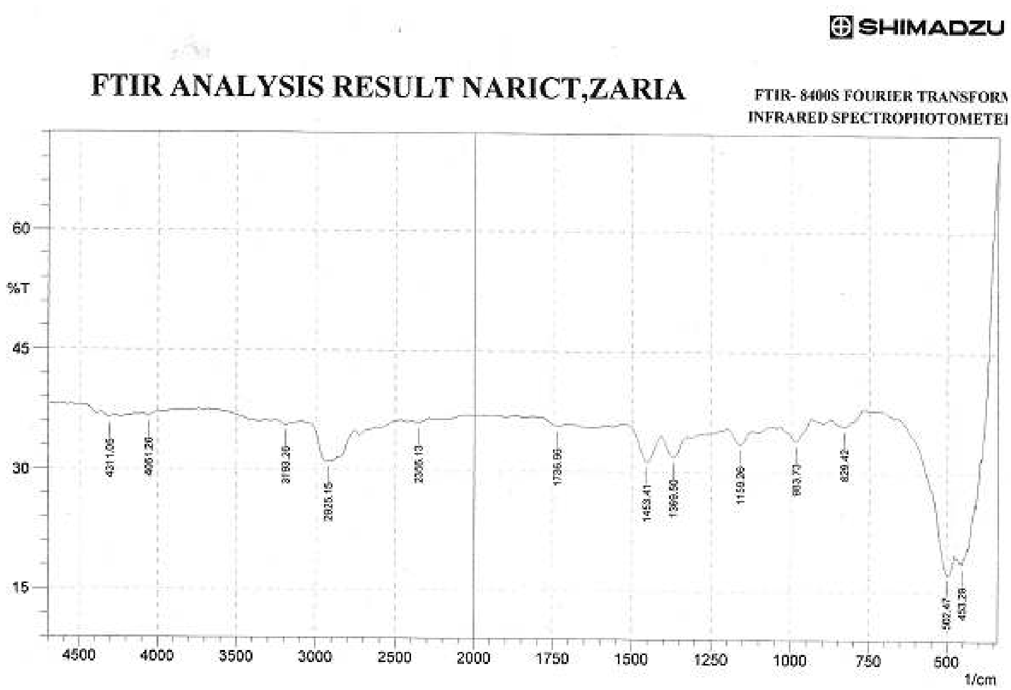

Fig. 17. FTIR spectrum of synthetic sorbent mat

Chicken feathers and all feathers are mainly composed of 91% protein (keratin) [23]. Keratins are long chains of amino acids. Based on the side chain of an amino acid, it can be classified as hydrophobic, polar or charged. The side chains of the hydrophobic amino acids are nonpolar; mainly hydrocarbon. The polar amino acids side chains are hydrocarbons containing atom(s) that can form hydrogen bond. The side chain of the charged amino acids contains hydrocarbons carrying negative or positive charges. Sorption results from a variety of different types of attractive forces between the sorbate and sorbent [24,25]. Organic sorbates chemically bond to the sorbent, if the sorbate and sorbent have mutually reactive moieties. Also, the extent of intermolecular attraction depends on molecular chain length and on surface area.

The synthetic sorbent mat and crude oil are composed mainly of hydrocarbons, in order words they have mutual reactive moieties, attracting each other by Van der Waal forces, London forces and other dispersion forces. This explains why the much crude oil adsorption/absorption by the synthetic sorbent. The amino acid content of feather is highly hydrophobic; containing side chains that are mainly hydrocarbon [26]. This hydrocarbon side chains accounts for the intermolecular bonds formed between chicken feathers and crude oil, leading to the sorption of the crude oil on chicken feathers. Also, the β conformation of feather makes it have large surface area, a look under a microscope shows that there are lot of empty space in quill, shaft, rami and barbules of feather [27]. The large surface area makes it possible for the trapping, entanglement and occlusion of crude oil within the feather void. Basically chicken feathers and the synthetic sorbent have similar features, enabling them to sorb much crude oil.

Another quality attributed to an ideal sorbent is that it should be oleophilic (oil attracting) and hydrophobic (water repelling) [5]. Tables 6 and 7 shows that the amount of crude oil on water adsorbed, recovered and retained by ground chicken feathers and synthetic sorbent mat compares closely with that obtained with the experiment involving crude oil only. The equilibrium adsorption capacity of crude oil on water for ground chicken feathers and synthetic sorbent are 13.10 g/g at 90 minutes equilibration time and 10.86 g/g at 80 minutes respectively. During the experiment, the difference in volume between the initial volume of water added to transparent bowl, and final volume of water after experiment are 0.06 dm^3 and 0.04 dm^3 for synthetic sorbent and ground chicken feathers respectively. This suggests the amount of water sorbed by both sorbents is negligible. This is not surprising because the amino acid content of feather is hydrophobic [23,26]. The synthetic sorbent mat been a polyhydrocarbon is also hydrophobic. Therefore both sorbents can be conveniently used in mopping crude oil on water.

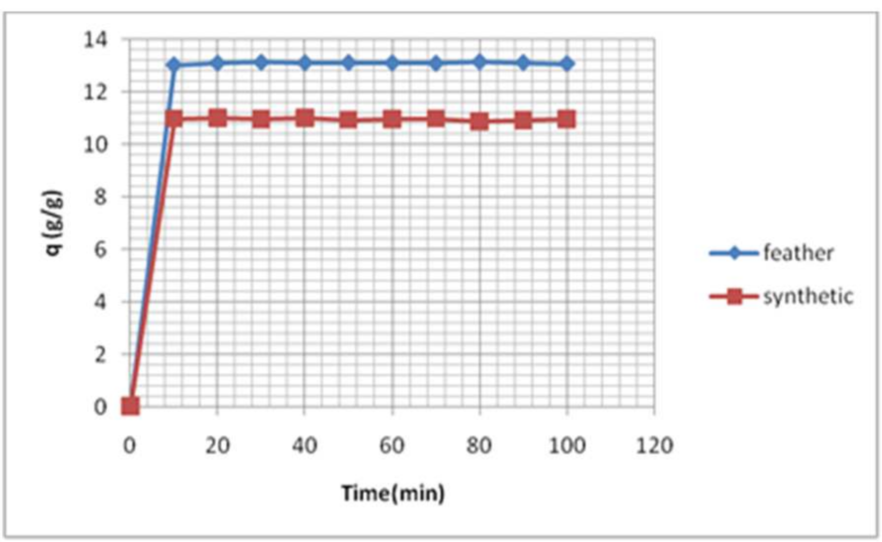

Fig. 18. Amount of crude oil on water adsorbed onto unit mass of ground chicken feathers and synthetic sorbent mat against time

Table 6B. Amount of crude oil on water adsorbed onto ground chicken feathers (q), recovered from chicken feather and retained by chicken feather

Amount of crude oil adsorbed (q) (g/g)	Amount of crude oil recovered (g/g)	Amount of crude oil retained (g/g)	Contact time (Min)
13.01±0.98	12.28±0.62	0.73	10
13.08±0.13	12.16±1.06	0.92	20
13.11±0.57	12.13±0.86	0.98	30
13.09±0.42	12.07±0.11	1.02	40
13.10±0.73	12.34±0.02	0.76	50
13.09±0.94	12.31±0.34	0.78	60
13.07±1.14	12.16±1.04	0.91	70
13.13±0.23	12.24±0.32	0.89	80
13.10±0.21	12.23±0.22	0.87	90
13.06±1.43	12.27±2.32.	0.79	100

Table 7. Amount of crude oil on water adsorbed onto synthetic sorbent mat (q), recovered from synthetic sorbent mat and retained by synthetic sorbent mat

Amount of crude oil adsorbed (q) (g/g)	Amount of crude oil recovered (g/g)	Amount of crude oil retained (g/g)	Contact time (Min)
10.98±0.13	9.18±0.21	1.80	10
11.01±0.45	9.20±0.31	1.81	20
10.96±0.51	9.13±0.32	1.83	30
11.00±0.45	9.20±0.64	1.80	40
10.94±0.42	9.07±0.72	1.87	50
10.96±0.37	9.10±0.01	1.86	60
10.97±0.75	9.07±0.33	1.90	70
10.86±0.60	9.04±0.41	1.82	80
10.90±0.43	9.04±0.10	1.86	90
10.95±0.21	9.07±1.43	1.88	100

4. CONCLUSION

The equilibrium adsorption capacity of crude oil onto chicken feathers and the synthetic sorbent used as the standard in this study, and the time for the equilibrium adsorption of crude oil onto both sorbents are 13.60 g\g at 80 minutes and 11.44 g\g at 60 minutes respectively. Ground chicken feathers adsorbed more crude oil than the synthetic sorbent.

The adsorption process of crude oil onto chicken feathers can be described by the linearized version of the Langmuir isotherm; C_e/q_e versus C_e. The values of the coefficient of determination r^2 and average percentage error obtained for ground chicken feathers and synthetic sorbent show good correlation between experimental data and Langmuir isotherm and that Langmuir isotherm can describe experimental data. However, the maximum adsorption capacity (q_m) of 14.90 g/g and 11.11 g\g obtained from the adsorption isotherm, for both ground chicken feathers and synthetic sorbent respectively, indicates that the Langmuir isotherm may not be the best fitted isotherm for the adsorption of crude oil onto synthetic sorbent, but affirms that it can be used to describe the adsorption process of crude oil onto ground chicken feathers and ground chicken feathers is a better sorbent than conventional synthetic sorbent. The interaction of ground chicken feathers with crude oil is monolayer adsorption; one molecule of crude oil is adsorbed on a layer of ground chicken feathers, there is no interaction between the adsorbed molecules of crude oil, and crude oil is held to ground chicken feathers by physical bond.

The intensity of adsorption/affinity of ground chicken feathers and synthetic sorbent are the same 1.00. This shows that ground chicken feathers compares well with standard in terms of rate of removal/ adsorption of crude oil. However, ground chicken feathers are able to adsorb more oil than the standard because of larger surface area than the standard.

The dimensionless separation factor equilibrium parameter K_R shows that the adsorption of crude oil onto ground chicken feathers and synthetic sorbent is favourable.

The amount of water adsorbed together with crude oil on water is negligible which means that both sorbents; ground chicken feathers and standard can be used in mopping of crude oil spill on water.

The result of the study shows that ground chicken feathers is an efficient sorbent for the mopping of crude oil spill both on land and water and substantial amount of adsorbed oil can be recovered from ground chicken feathers. However, particles from chicken feathers in an occupational setting can cause various lung symtoms such as fibrosis, so, ground chicken feathers should be handled carefully by wearing mask.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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