COMPARATIVE ADSORPTION OF CRUDE OIL USING COCONUT SHELL AND COCONUT SHELL ACTIVATED CARBON

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ABSTRACT

Coconut shell (CS) and Coconut Shell Activated Carbon (CSAC) as effective adsorbents for removal of crude oil were examined in this work through batch experiments. Variation in adsorption efficiencies was observed with respect to adsorbate loading, adsorbent loading, contact time, temperature, rotational speed, and pH of the mixture. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms were used to study the adsorption of the crude oil for both adsorbents, and it was observed that the mechanism of adsorption was of a multi-molecular-layer in nature. Fourier Transform infrared (FTIR) spectroscopy analyses were also carried out on the two adsorbents, before and after adsorption. The results indicated the presence of crude oil component functional groups on the two adsorbents. Optimum values of the six variable parameters for CS and CSAC adsorption were obtained using design of experiments (DOE). Optimum crude oil removal with CS was 51.32% at pH of 6.9, 49.18℃, mixed for 52.35 minutes at a speed of 347.50 rpm, using 3.76 g absorbent on a 0.06 g/L adsorbate mixture, while 91.25% removal was observed when CSAC was used at optimum pH of 6.2, 62.93℃, mixed for 70.12 minutes at a speed of 482.50 rpm, using 4.26 g absorbent on a 0.07 g/L adsorbate mixture. The enhanced effect from CS activation was justified statistically using ANOVA and Bonferroni-Holm Posthoc significance test, confirming that CS and CSAC are useful for crude oil adsorption.

KEYWORDS: *Activated carbon; adsorption; coconut shell; crude oil; adsorbate*

1.0 INTRODUCTION

Environmental pollution is posing a more serious problem, and so the need for anti-pollution devices from low cost and easily available materials (especially agricultural waste materials) for use, particularly in contaminated water treatment, is imperative. Conventional measures used for the management

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of wastewater fouled with crude oil are very expensive and advanced in technology. Hence, the need to source for cheap, economical and locally available alternatives which will suit our local needs and enhance environmental sustainability becomes necessary.

The environmental impact of crude oil exploration, production, and processing have come to be seen as a major problem in the economic development of oil producing communities in Nigeria. During exploration, transportation by pipeline, and/or storage in tanks, oil may be spilled into the environment, and the harmful effects of oil spill on the environment are many. The common methods used to remove spilled oil involve oil booms, dispersants, skimmers, in-situ burning, sorbents and so on. The major hindrances of some of these procedures are their high cost and the utterly inefficient trace-level adsorption according to Wardley-Smith (1983). Also, most of the dispersants are often flammable and cause health risks to the operators and potential damage to plants, animals and aquatic life; as well as air pollution. Adsorption process is seen to be better in the efficient removal of spilled oil in ambient conditions because of its comparative affordability, ease of operation, convenience, and relatively simple setup.

There are several reports on biosorption of crude oil and its derivatives. Annunciado, Sydenstricker and Amico (2005) performed an experimental investigation of various vegetable fibres as sorbent material for oil spill and concluded that silk floss fibre showed a very huge degree of hydrophobicity and oil capacity of 85 g oil/g sorbent. Uzoije, Onunkwo and Egwuonwu (2011) have reported adsorption of crude oil onto activated groundnut shell carbon (AGSC) and submitted that AGSC is a good mop-up and low-cost alternative medium for oil spilled surfaces. Behnood et al., (2013) investigated the adsorption of petroleum hydrocarbons from aqueous solution by sugarcane baggase and concluded that the adsorbent displayed a rapid oil-sorption characteristic with a good adsorption capacity of approximately 7 g oil/g sorbent. Olufemi, Jimoda, and Agbodike (2014) reported the potential of using corncobs a typical agro-based waste as an adsorbent for the removal of oil from contaminated water. Parametric variations were investigated and meshed corncobs with 80 micrometer particle size exhibited highest affinity for crude oil adsorption at 15 °C. Conclusively, meshed corncobs adsorbent was convincingly oleophilic or hydrophobic, suitable for crude oil adsorption. Mango shell (MS) and mango

shell activated carbon (MSAC) had been reported for the adsorption of crude oil by Olufemi and Otolorin (2017), and it was observed that the pseudo first order kinetics gave a better fit for crude oil adsorption with both MS and MSAC.

Furthermore, on the usage of agro-waste for biosorption studies, Tran, Kabiri, Sim, and Losic (2015) worked on selective adsorption of oil–water mixtures using polydimethylsiloxane (PDMS)–graphene sponges. They concluded that the prepared sponge exhibited high adsorption performance for the removal of petroleum products, organic solvents and emulsified oil–water mixtures, especially under a continuous vacuum regime, with the attainment of an adsorption capacity of 4.5 L of hexane in 30 min. Razak, Hazmi and Tahrim (2013) did a comparative adsorption studies by using low cost adsorbents of rice husk and rice husk ash on methylene blue dye removal, in which the optimal parameters were 7.5 ppm initial concentration, 0.6 g adsorbent dosage and pH value of 5.8. Furthermore, Saruchi, Kaith, Jindaland Kumar (2015) recently examined the adsorption of crude oil from an aqueous solution using a Gum tragacanthpolyacrylic acid based hydrogel. From their findings, effect of pH, contact time, acrylic acid, and glutaraldehyde concentration for the adsorption of oil from aqueous solution was determined with maximum crude oil adsorption from synthesized hydrogel obtained at 40% of acrylic acid concentration.

Some specific coconut-biosorption capabilities have been reported. Song, et al. (2013) evaluated the adsorption studies of coconut shell carbons prepared by KOH activation for removal of lead (II) ions from aqueous solutions. From their findings, kinetic studies indicated that adsorption behavior can be described by a pseudo-second-order kinetic model, with external diffusion and intra-particle diffusion available in the adsorption process. Wankasi and Dikio (2015) did a comparative study of coconut shell and palm kernel shell biomass as adsorbents for sorption of Pb (II) ions from aqueous solution, whereby a second order kinetics prevailed. Yong and Zaini (2016) also worked on the adsorption of Rhodamine B by palm kernel shell adsorbents where the adsorption operation agreed well with the Redlich-Peterson model, suggesting monolayer coverage on the heterogeneous surface. Ifelebuegu and Momoh (2015) carried out an evaluation of the adsorptive properties of coconut husk for oil spill cleanup, in which the adsorption kinetics followed a pseudo-second order kinetic model and fitted to the Freundlich adsorption isotherm model. Kelle and Eboatu

(2018) embarked upon the evaluation of coconut husk sorbent for the cleanup of petroleum contaminated environments. They confirmed that Langmuir adsorption model and pseudo second order models fitted the sorption process more precisely.

The aim of this work is to examine the adsorptive capacity of agro-waste coconut shell and coconut shell activated carbon as a relatively cheap and effective means in cleaning up of crude oil. The objectives are to examine adsorption on the CS and CSAC, varying the values of different parameters like adsorbate loading, adsorbent loading, mixing/contact time, temperature, rotational speed, and pH of mixture for proper understanding and future equipment design. This will further involve the determination of the optimum parameters for adsorption of crude oil on both CS and CSAC useful for optimum adsorption conditions. The kinetics of adsorption as well as fitting with the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms will further be investigated, while statistical evaluation and relevance of process parameters will also be verified to avail researchers and industrialist appropriate design and operational principles.

2.0   MATERIALS AND METHODS

The experiments carried out were similar to the procedures given by Bernard, Jimoh and Odigure (2013) as well as Olufemi, Jimoda, and Agbodike (2014). An oil spill simulation of known initial concentration (C_o) was made by pouring 25 g of crude oil into 1000 ml of water in a beaker. A 200ml sample of the simulated oil spill was measured into a 500 ml beaker.

For each batch run, the quantity of crude oil adsorbed per unit weight of adsorbent, denoted as q_e (mg/g), was determined in Equation (1) as follows:

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

Adsorption isotherms defined as mathematical models portray the dispersal of species between two phases when an adsorption process builds up to an equilibrium state. The experimental data obtained in this study were fitted to the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The numerical values of $1/q_e$ were plotted against $1/C_e$, from which linear plots are

expected each time, according to the Langmuir equation. The Freundlich (ln q_e vs ln C_e), Temkin (q_e vs ln C_e), and the Dubinin-Radushkevich (ln q_e vs ε^2) isotherm plots were also done to make comparisons.

The Langmuir isotherm is expressed in Equation (2) as:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{K_L Q_0} \tag{2}$$

where K_L and Q_0 are Langmuir constants related to energy of adsorption and adsorption capacity, respectively.

The Freundlich isotherm is given in Equation (3) as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

with K_F and n as the adsorption constants.

The Temkin isotherm is expressed in Equation (4) as:

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \tag{4}$$

where

$$B = \frac{RT}{b_T} \tag{5}$$

R is the gas constant (8.314 J/mol K), T is the absolute temperature (K), b_T is the Temkin constant (J/mol), B is a constant related to heat of adsorption, and A_T is the Temkin isotherm equilibrium binding constant (L/mg).

The Dubinin–Radushkevich isotherm is is given in Equation (6) as:

$$\ln q_e = \ln q_s - (K_{ad} \varepsilon^2) \tag{6}$$

where,

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{7}$$

In Equations (6 and 7), ε is a Dubinin–Radushkevich parameter, q_s is the theoretical isotherm saturation capacity (mg/g), K_{ad} is a Dubinin–Radushkevich isotherm constant (mol²/kJ²).

2.1   Apparatus and Reagents

The following materials and apparatus were used for the experimental work: England Meshing Machine (Magimix Cuisine System 5000), mesh sieve (B.S. 410/43), Canada Fisher Scientific Company Orbital Shaker (HY-2, NYC), Germany made Merck -10 to 250oC Mercury in glass thermometer, England Pyrex beakers (50-500 mL), England Pyrex conical flasks (50-500 mL), England Pyrex measuring cylinders (50-1,000 mL), Germany Weighing Balance (AL Mettler Toledo GmbH) and boat, Germany Merck KGaA Whatman (Model1001-125) 125 mm diameter filter paper, England Gallenkamp Vacuum Oven Ovl 570-0300 8465f 01, coconut shells obtained from Badagry, Lagos, Nigeria, coconut shell activated carbon, United Kingdom Cole Parmer Porcelain Mortar and Pestle, United Kingdom Jenway Model 6405 Ultraviolet (UV) spectrophotometer, Bonny Export Blend crude oil sample from the Niger Delta of Nigeria, deionized water, 85% w/w ortho-phosphoric acid and United States Perkin Elmer Fourier Transform Infrared (FTIR) Spectrophotometer.

2.2   Preparation of Adsorbents

The coconut shell collected was washed, dried in the sun for one week and cracked using hammer. The shell was then removed and dried under the sun for another two weeks. The shell was oven dried at 105°C after which they were crushed using laboratory mortar and pestle. The particles were then sieved with 80 μm sieve size. For activation purpose, the sieved samples were impregnated in H_3PO_4 at an impregnation ratio of 1:1 by measuring 100 g of sample in 100 ml of acid. The impregnated sample was left at room temperature (28 - 33°C) for 24 hours. After impregnation, the excess solution was filtered off. The resulting sample was carbonized in a heated furnace at temperatures of 400°C for 30 minutes. The activated carbon was rinsed with deionized water and dried at 105°C for 1 hour in the furnace. Finally, the activated carbon produced was kept in a tightly closed polyethylene plastic bottle.

2.3   Characterization of the Adsorbents

The functional groups present in the coconut shell and CSAC samples were investigated using Fourier Transform Infrared (FTIR) spectroscopic analysis. The spectra were measured from 4000 to 400 cm^{-1} wave number. Typical average porosity, moisture content, specific gravity and bulk density were determined by adopting the methods described in Olufemi and Ogboneyenetan (2018).

2.4   Adsorption with Different Adsorbate Doses

Batch adsorption experiments were performed with different adsorbate doses, where by 2.0 g of meshed adsorbent was shaken with 2, 4, 6, 8, and 10 g of crude oil samples per 200 ml of neutral water (pH of 7.0) mixed in a 500 ml beaker to give varying oil concentrations at about 200 rpm for 60 minutes at 25°C. Afterwards, the wetted adsorbent was removed from the beaker, by passing the mixture through a filter paper, and the filtrate was measured using the UV absorbance machine. The spectroscopic absorbance values were then taken correctly and the corresponding equilibrium concentration (C_e, mg/L) values were recorded.

2.5   Adsorption with Different Adsorbent Loadings

Simulated oil-water samples with an initial concentration C_O of 0.025 g/L made from deionized water with a pH of 7.0 was added to masses of 1.0, 2.0, 3.0, 4.0 and 5.0 g of adsorbent respectively in beakers at 25°C. The contents of the beakers were then stirred at 200 rpm and 25°C for an hour each. The equilibrium mass of crude oil in water for each measured sample was then determined using a UV spectrophotometer at a wavelength of 380 nm. The mass M of the adsorbent, volume V of a simulated oil spill, and the corresponding equilibrium concentration (C_e, mg/L) values were determined.

2.6   Adsorption with Different Times of Contact

An initial concentration 0.025 g/L oil sample made from neutral pH water was added to 2.0 g of adsorbent in a 500 ml beaker. The mixture was stirred at 200 rpm and 25°C for specified periods of 15, 30, 45, 60, and 75 minutes. The equilibrium mass of crude oil in water for each measured sample was then determined using a UV spectrophotometer at a wavelength of 380 nm. The mass M of the adsorbent, volume V of a simulated oil spill, and the corresponding equilibrium concentration (C_e, mg/L) values were noted.

2.7   Adsorption with Different Temperature Settings

Experiments were carried out at 25, 35, 45, 55 and 60°C with 2.0 g of meshed adsorbent shaken with 0.025 g/L oil sample in a beaker. The mixture was stirred at 200 rpm for each batch for 60 minutes. Adequate equilibrium adsorption at the various temperatures was achieved. The equilibrium mass of crude oil in water

for each measured sample was then determined using a UV spectrophotometer at a wavelength of 380 nm. The mass M of the adsorbent, volume V of a simulated oil spill, and the corresponding equilibrium concentration (C_e, mg/L) values were determined.

2.8   Adsorption with Different Rotational Speeds

The adsorption operation in terms of rotational speed were studied experimentally by adding 0.025 g/L oil sample from neutral pH water to 2.0 g of adsorbent in a beaker, and the contents stirred at 25°C for 60 minutes, with different speeds of 100, 200, 300, 400, and 500 rpm. The equilibrium mass of crude oil in water for each measured sample was then determined using a UV spectrophotometer at a wavelength of 380 nm. The mass M of the adsorbent, volume V of a simulated oil spill, and the corresponding equilibrium concentration (C_e, mg/L) values were also recorded.

2.9   Adsorption with Difference in pH of Solution

Batch adsorptions were carried out with different solutions of selected pH values of 5.0, 6.0, 7.0, 8.0 and 9.0, using 0.1 M HCl and 0.1 M NaOH. Hence, 2.0 g of meshed adsorbent was shaken with 0.025 g/L oil sample at 25°C and at 200 rpm speed for 1 hour per batch. The equilibrium mass of crude oil in water for each measured sample was then determined using a UV spectrophotometer at a wavelength of 380 nm. The mass M of the adsorbent, volume V of a simulated oil spill, and the corresponding equilibrium concentration (C_e, mg/L) values were determined.

3.0   RESULTS AND DISCUSSION

3.1   Physical Properties of Adsorbents

The physical properties of the adsorbents are given in Table 1. As can be deduced from the values, CSAC has higher moisture content and porosity than CS. This showed the availability of higher pore spaces due to activation. However, the CSAC has a lower bulk density and specific gravity than CS. This also confirmed the effect of activation in which the weight per unit volume had been reduced.

Table 1. Typical Average Physical Properties of Adsorbents

Properties	Coconut Shell	Coconut Shell Activated Carbon
Moisture content (%)	1.10	1.70
Bulk density (g/ml)	0.60	0.41
Specific gravity	1.30	0.40
Porosity	0.77	0.93

3.2   Calibration of Absorbance

A calibration relationship was established in order to translate absorbance values into concentration equivalents using the methods of Aslam and Choudhary (2017).

3.3   Coconut Shell (CS) and Coconut Shell Activated Carbon (CSAC) Adsorption Data with Isotherms

Parametric variations of variables with equilibrium concentrations are given in Tables 2 and 3 for CS and CSAC adsorption respectively.

3.3.1   *Effect of Adsorbate Concentration*

The results of the adsorption of adsorbate (crude oil) with varied masses as given in Tables 2 and 3 revealed that the adsorption of crude oil reduced with higher adsorbate doses for adsorbents, coconut shell and CSAC, respectively. As the amount of crude oil increased from 0.01 g/L to 0.05 g/L with a constant weight of 2.0 g of adsorbent, the amount of crude oil adsorbed reduced. This is because of the relatively constant area of adsorption sites that is available for the increasing amount of adsorbate. As more of the adsorbate gets adsorbed, the smaller the remaining area for adsorption of more adsorbate molecules, and therefore, the percentage removal of the adsorbate reduces with an increased initial mass of adsorbate.

With respect to individual adsorbents, it is seen that given the same concentration of the adsorbate, the activated carbon of the shell is able to withdraw a significantly larger amount of adsorbate when compared with the unprocessed coconut shell. Nevertheless, the shell itself carried out adsorption to a respectable degree, but its activated carbon does so to a higher level.

Table 2. Crude Oil Adsorption by Coconut Shell with varying Parameters

Adsorption by Coconut Shell with varying Adsorbate Concentration at 25 °C and 200 rpm					
Adsorbate Concentration (g/L)	0.01	0.02	0.03	0.04	0.05
C_e (mg/L)	0.27	4.50	10.57	18.57	29.68
Adsorption of 0.025 g/L Oil by Coconut Shell with varying Mass of Adsorbent at 25 °C and 200 rpm					
Adsorbent Mass (g)	1.0	2.0	3.0	4.0	5.0
C_e (mg/L)	13.65	7.80	5.36	3.23	1.26
Adsorption of 0.025 g/L Crude Oil by Coconut Shell with varying Time of Mixing at 25 °C and 200 rpm					
Mixing time (min.)	15	30	45	60	75
C_e (mg/L)	16.93	13.95	7.85	7.80	6.35
Adsorption of 0.025 g/L Crude Oil by Coconut Shell with varying Temperature at 200 rpm					
Temperature (°C)	15	25	35	45	55
C_e (mg/L)	6.44	7.78	11.82	13.24	15.49
Adsorption of 0.025 g/L Crude Oil by Coconut Shell with varying Mixing Speed at 25°C					
Mixing speed (rpm)	100	200	300	400	500
C_e (mg/L)	12.33	7.80	6.56	5.74	5.41
Adsorption of 0.025 g/L Crude Oil by Coconut Shell with varying pH Values at 25°C and 200 rpm					
pH	5.0	6.0	7.0	8.0	9.0
C_e (mg/L)	11.98	10.13	7.67	10.96	13.42

3.3.2   *Effect of Adsorbent Mass*

In Tables 2 and 3, the result of adsorption of crude oil onto different adsorbent masses, for either adsorbent, showed that the adsorption of said adsorbate increased with higher adsorbent doses. As the adsorbent dose increased from 1.0 to 5.0 g the amount of crude oil adsorbed increased. This is because more adsorption sites are available for the same concentration of the adsorbate. The increased in initial adsorbent mass, which having more adsorption sites at higher adsorbent doses, caused an increase in percentage removal of the crude oil adsorbate.

While both adsorbents eventually reach a high percentage removal, CSAC reaches a higher efficiency at a comparatively lower mass than CS. While coconut shell, for example, has a 94% removal at 5.0 g, CSAC has this approximate value at 2.0 g, which goes to say that 2.5 times the amount of CSAC would be required for this high percentage removal if coconut shell adsorbent were to be used. The

economies of scale would have to be evaluated when making a choice between the two adsorbents, depending on the necessary clean-up circumstances.

3.3.3   *Effect of Mixing Time*

The result of the adsorption of crude oil at different time intervals of mixing/ contact showed that the adsorption of crude oil onto the adsorbents, and consequently the oil removal, increased with time. At 25°C, as the time increased from 15 to 75 minutes, the adsorption capacity and removal of crude oil from water increased. The result showed that the rate of adsorption and oil removal was very high initially, especially between 15 and 45 min; subsequently, a slow-down of the adsorption rate, or say quasi-stationary states, were seen from 60 to 75 minutes. Comparing the two adsorbents, it is apparent that both substances similarly reach a plateau, but CSAC is at a higher efficiency, around 94.2%, at 45 minutes of mixing, while coconut shell is at a removal efficiency of 68.6%. They are both of good efficiencies at this point.

Table 3. Crude Oil Adsorption by CSAC with varying Parameters

Adsorption by CSAC with varying Adsorbate Concentration at 25 °C and 200 rpm					
Adsorbate Concentration (g/L)	0.01	0.02	0.03	0.04	0.05
C_e (mg/L)	0.05	0.79	1.85	3.25	5.20
Adsorption of 0.025 g/L Oil by CSAC with varying Mass of Adsorbent at 25 °C and 200 rpm					
Adsorbent Mass (g)	1.0	2.0	3.0	4.0	5.0
C_e (mg/L)	2.39	1.37	0.94	0.57	0.22
Adsorption of 0.025 g/L Crude Oil by CSAC with varying Time of Mixing at 25 °C and 200 rpm					
Mixing time (min.)	15	30	45	60	75
C_e (mg/L)	3.44	2.78	1.44	1.43	1.11
Adsorption of 0.025 g/L Crude Oil by CSAC with varying Temperature at 200 rpm					
Temperature (°C)	15	25	35	45	55
C_e (mg/L)	1.14	1.43	2.32	2.64	3.13
Adsorption of 0.025 g/L Crude Oil by CSAC with varying Mixing Speed at 25 °C					
Mixing speed (rpm)	100	200	300	400	500
C_e (mg/L)	2.90	1.42	1.02	0.75	0.64
Adsorption of 0.025 g/L Crude Oil by CSAC with varying pH Values at 25 °C and 200 rpm					
pH	5.0	6.0	7.0	8.0	9.0
C_e (mg/L)	1.91	1.65	1.37	1.95	2.52

3.3.4   *Effect of Temperature*

As depicted in Tables 2 and 3, the result of batch adsorption experiments carried out in different temperatures of adsorbent showed that adsorption capacity was higher at lower temperatures. Adsorption was most pronounced at 15°C for the temperature range of 15 – 55°C considered. The results further showed that the percentage removal of the crude oil decreased with increase in temperature, indicating the dependence of adsorption on temperature. It is seen here that with decreasing temperature, adsorption increases. Below 15°C, if not at this temperature itself, there will likely be a peak performance point, because when the temperatures get even lower, a point will be reached where the energy for adsorption will decrease with decreasing temperature. This peak/optimum temperature point varies, depending on the values of the other parameters which affect adsorption. At every temperature, it is clear that CSAC outperforms coconut shell, but coconut shell gets close enough at 15°C with a 74.24% removal, compared with 95.44% for CSAC. The performance gap between the two adsorbents widens as temperatures deviate from this point, and makes CSAC even more preferable down the line.

3.3.5   *Effect of Mixing Speed*

The result of the adsorption of crude at different mixing speeds in Tables 2 and 3 showed that the adsorption of crude oil onto the adsorbents and the oil removal increased with speed. Lin and Liu (2000) reported that the mass transfer rate increases with the increase in stirring speed, and that the increase in stirring speed resulted in a reduction in surface film resistance, thereby allowing residual oil to reach the particle surface more easily. Surface film resistance slowed down the rate of adsorption. The rate of oil adsorption increased with an increase in mixing speed. For a temperature of 25°C, as the mixing speed increased from 100 to 500 rpm, the adsorption capacity and removal of crude oil from water increased. The result showed that the rate of adsorption and oil removal steadily increased with speed and the most notable adsorption occurred at around 500 rpm. It is clear that with increasing speed, the propensity for crude oil molecules to meet a vacant adsorption site becomes higher.

3.3.6   Effect of Solution pH

The result of batch adsorption experiments carried out for different values of pH of solution as depicted in Tables 2 and 3 showed that the adsorption of crude oil on either adsorbent is dependent on pH. It is known that positive ions in aqueous solution tend toward adsorption upon carbonated adsorbents, and with pH varied using 0.1 M NaOH for a higher pH and 0.1 M HCl for a lower pH, the presence of either Na^+ or H^+ ions compete with the crude oil molecules for adsorption sites. The higher or lower the pH, the higher the concentration of the respective ion, and thus the lower the uptake of crude oil molecules by the adsorbent. At around pH 7.0, the maximum adsorption was observed. The Na^+ and H^+ ions have different competitive powers for adsorption sites, so the pattern is not a mirror image about the vertical line through the maximum. And of course, the CSAC is more effective at all pH values.

3.3.7   Adsorption Isotherms

Figures 1and 2 show the isotherms for crude oil adsorption by CS and CSAC respectively, with varying pH values for which the best correlation coefficient (R^2) was obtained in Figure (2c) amongst all the parameters and adsorbent type used. For both adsorbents, the Temkin followed by the Freundlich models were generally found to be better-suited for characterizing the adsorption process, while the Dubinin-Radushkevich isotherm fell behind the pack, based on the correlation coefficients (R^2 values). All the isotherm constants were computed from the slopes and intercepts of the plotted lines of best fit for varying parameters. A favourable adsorption tends to have Freundlich constant n between 1 and 10, while larger values of n implies stronger interaction between adsorbent and adsorbate (Febrianto et al., 2009), as seen for some of the CSAC adsorptions. The values for the isotherm constants for adsorption were given in Tables 4 and 5.
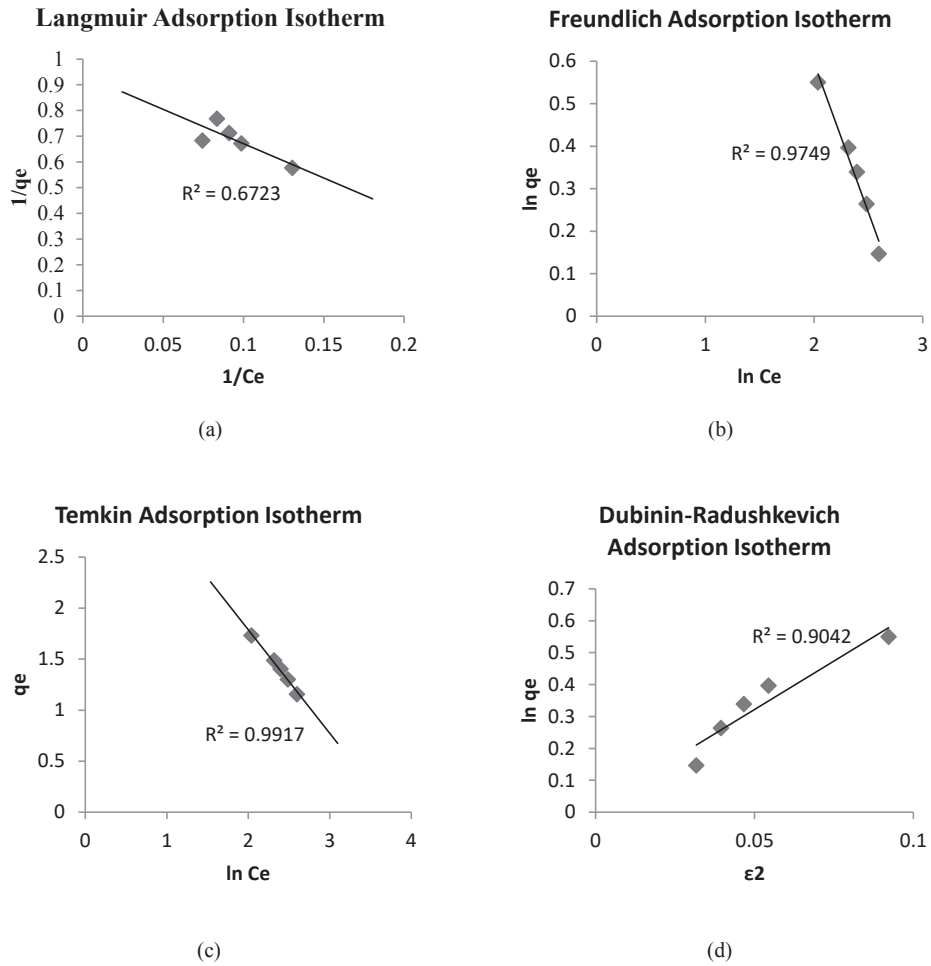
Figure 1. Adsorption Isotherm for Crude Oil Adsorption by Coconut Shell with varying pH Values at 25°C and 200 rpm (a) Langmuir, (b) Freundlich (c) Temkin (d)Dubinin-Radushkevich
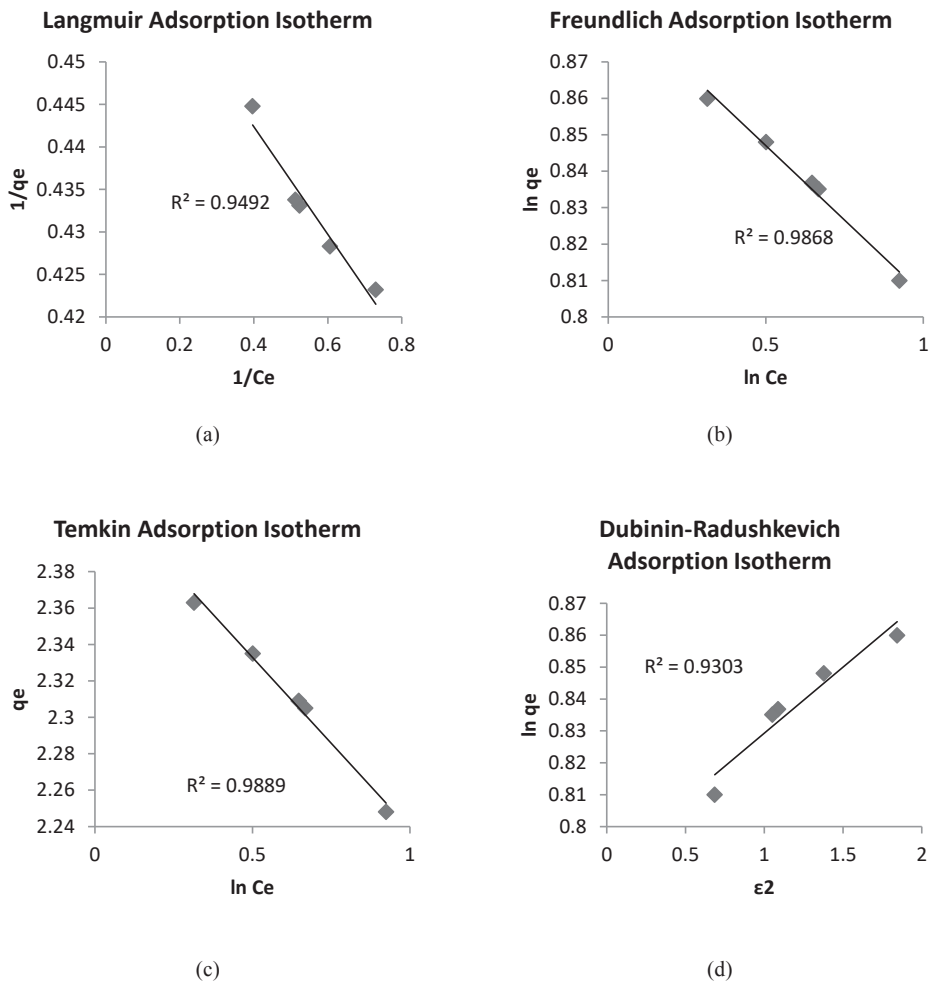
Langmuir Adsorption Isotherm

Freundlich Adsorption Isotherm

(a)

(b)

Temkin Adsorption Isotherm

Dubinin-Radushkevich Adsorption Isotherm

(c)

(d)

Figure 2. Adsorption Isotherm for Crude Oil Adsorption by CSAC with varying pH Values at 25°C and 200 rpm (a) Langmuir, (b) Freundlich (c)Temkin (d) Dubinin-Radushkevich

The Temkin and Freundlich isotherm models fitted the equilibrium data reasonably well as shown from the correlation coefficient R^2 values, suggesting a multilayer adsorption of crude oil on either adsorbent. The Temkin and Freundlich isotherm models are much more significant than those of the Langmuir and Dubinin-Radushkevich. This is similar to the findings of Sidik et al. (2012), when modified oil palm leaves adsorbent, with enhanced hydrophobicity, for crude oil removal was utilised, while the isotherms studied revealed that the experimental data agreed more with the Freundlich isotherm

model. The suggestion of the Freundlich model and the Temkin model that the heat of adsorption in the layer would decrease linearly with coverage due to interactions apparently holds here, as the Temkin model slightly outperforms the Freundlich isotherm model as observed. In comparison, of the two adsorbents involved, it was seen that the activated carbon of coconut shell is more effective in every place tested, but the coconut shell, nevertheless, is a great adsorbent for the removal of crude oil when provided in sufficient amount. From the value of the initial concentration of crude oil, CSAC adsorption capacity was better than CS for the same amount of crude oil.

Table 4. Various Adsorption Isotherms for Langmuir, Freundlich, Temkin and Dubinin-Raduskevich Constants for Coconut Shell with Varied Parameters

Adsorption with Coconut Shell

Varied Parameter	Langmuir Constants			Freundlich Constants		
	K_L	Q_0	R^2	K_F	n	R^2
Adsorbate Concentration	3.6795	1.9440	0.9359	1.2274	1.8241	0.9695
Adsorbent Mass	0.7212	1.8811	0.7495	0.7858	1.7005	0.9109
Mixing Time	0.2227	0.6652	0.8699	9.4310	1.1686	0.9671
Temperature	0.2290	0.6770	0.7220	7.5188	1.3714	0.9625
Mixing Speed	0.3660	1.0300	0.9034	4.9515	1.8720	0.9758
pH	0.3513	1.0660	0.6723	7.4068	1.4223	0.9749

Varied Parameter	Temkin Constants			Dubinin-Radushkevich Constants		
	B	A_T	R^2	K_{ad}	q_s	R^2
Adsorbate Concentration	0.2505	168.37	0.9522	0.0461	1.9115	0.5362
Adsorbent Mass	0.5440	3.1501	0.8491	0.2964	1.6509	0.5362
Mixing Time	1.0850	37.149	0.9905	7.2814	0.8155	0.8687
Temperature	1.0413	40.447	0.9830	6.6007	0.8952	0.8817
Mixing Speed	0.8359	58.221	0.9895	2.9982	1.2128	0.8727
pH	1.0149	43.007	0.9917	6.0773	1.0180	0.9042

Table 5. Various Adsorption Isotherms for Langmuir, Freundlich, Temkin and Dubinin-Raduskevich Constants for Coconut Shell Activated Carbon with Varied Parameters

Adsorption with Coconut Shell Activated Carbon						
Varied Parameter	Langmuir Constants			Freundlich Constants		
	K_L	Q_0	R^2	K_F	N	R^2
Adsorbate Concentration	9.2688	3.1182	0.9029	2.4189	3.1299	0.9714
Adsorbent Mass	2.0744	2.9412	0.7666	2.0633	1.6168	0.8736
Mixing Time	6.4677	2.0838	0.9348	2.4271	10.950	0.9849
Temperature	7.3060	2.1155	0.9374	2.4223	11.848	0.9828
Mixing Speed	14.254	2.1993	0.8156	2.3855	15.480	0.9542
pH	7.3886	2.1381	0.9492	2.4300	12.2249	0.9868

Varied Parameter	Temkin Constants			Dubinin-Radushkevich Constants		
	B	A_T	R^2	K_{ad}	q_s	R^2
Adsorbate Concentration	0.6981	51.212	0.8644	0.0210	3.1922	0.7681
Adsorbent Mass	1.3483	5.9168	0.7315	0.0657	2.7245	0.5896
Mixing Time	0.2075	1.18×10^5	0.9872	0.0479	2.1466	0.9103
Temperature	0.1935	2.70×10^5	0.9857	0.0474	2.1563	0.9280
Mixing Speed	0.1500	8.12×10^6	0.9586	0.0177	2.2414	0.7777
pH	0.1886	388.31	0.9889	0.0414	2.1988	0.9303

3.4 Fourier Transform Infra-Red (FTIR) Spectroscopy Analysis

As typically presented in Figures 3 to 6, each adsorbent was analysed with the FTIR spectroscopy, before and after adsorption to verify the presence of adsorbed species (crude oil) on each adsorbent. Comparing the before and after images for one adsorbent at a time reveals the differences in percentage transmittance of infrared light by the adsorbent in question. The wave number in certain regions of reduced transmittance is checked in correlation tables for specific chemical bonds and functional groups which may be characteristic of some compounds found in crude oil (Socrates, 2004). The points of low transmittance indicated the presence of adsorbed matter preventing the transmittance of the wave. At certain points, characteristic bonds are found present, as indicated in the plots where C – X represents halide bonds such as C – Cl and C – Br. Comparing the images of the two adsorbents after adsorption, the coconut shell's C – H adsorption at about 3000 cm^{-1} reduced transmittance to about 75%, while CSAC reduced it to about 40%, suggesting more adsorbate adherence for CSAC. Such comparative differences may be seen at other points as well.
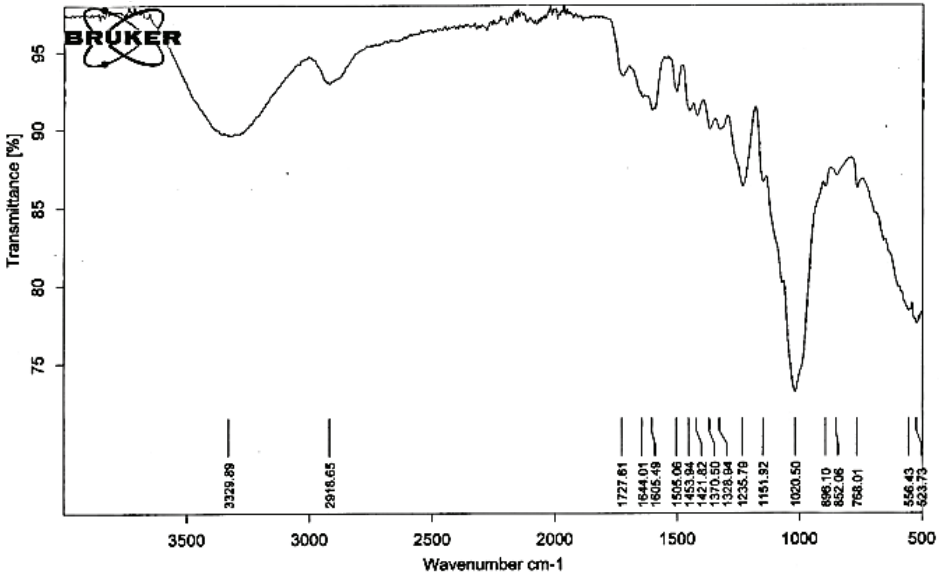
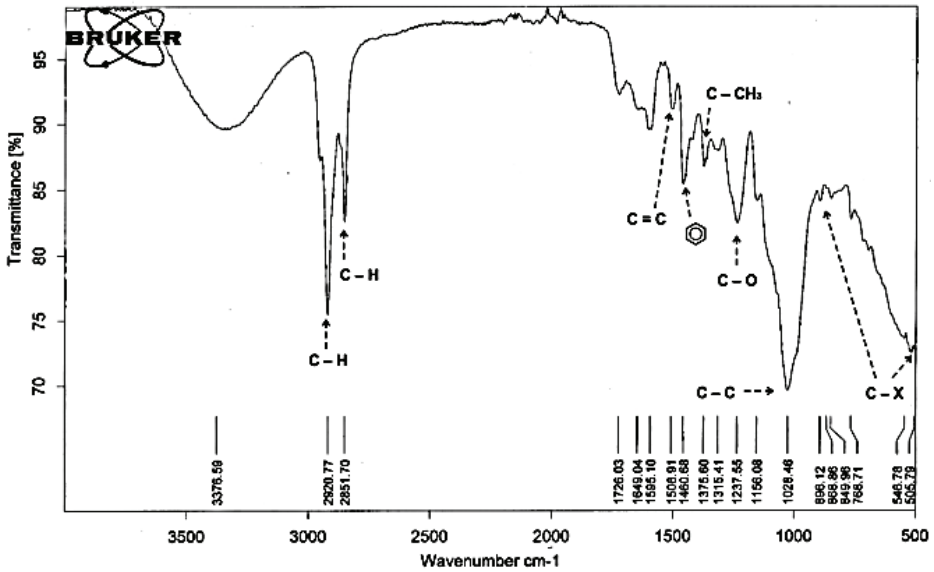Figure 3. FTIR Analysis Plot of Coconut Shell before Crude Oil Adsorption

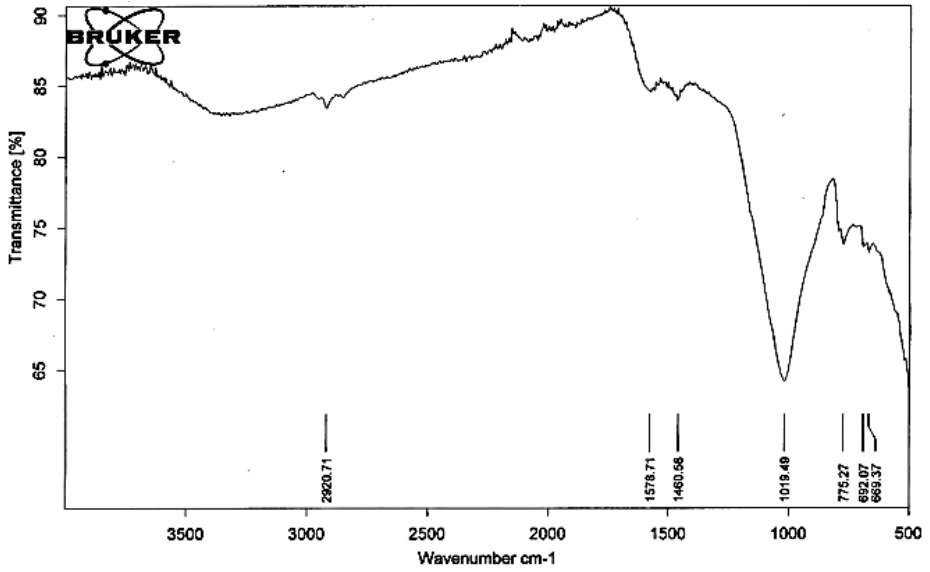Figure 4: FTIR Analysis Plot of Coconut Shell after Crude Oil Adsorption

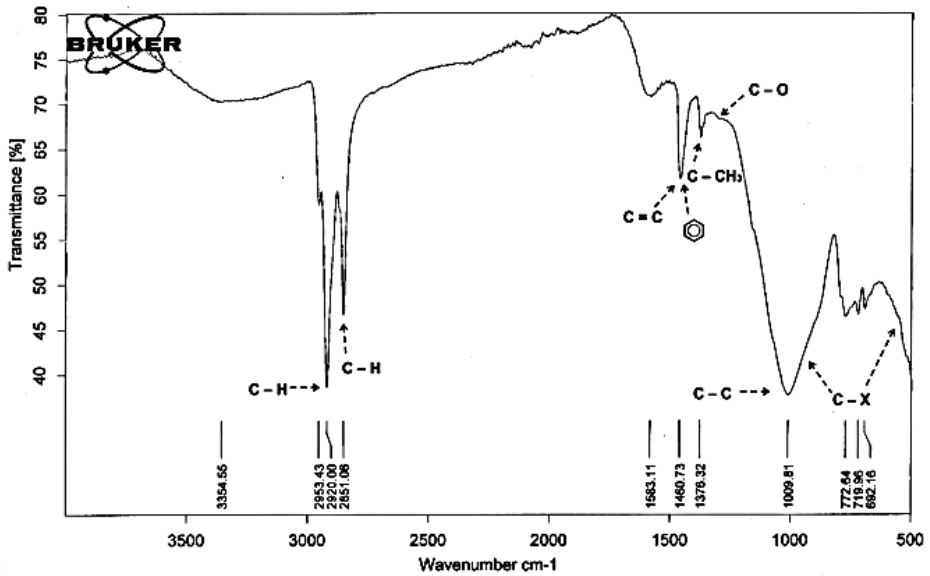Figure 5. FTIR Analysis Plot of CSAC before Crude Oil Adsorption

Figure 6. FTIR Analysis Plot of CSAC after Crude Oil Adsorption

3.5   Optimum Parameter Values

In order to obtain optimum values from the range of parameter values used in these experiments, statistical analysis and optimization of the results were carried out using Design of Experiments (DOE) with the Minitab® software. Central composite design and response surface regression helped generate the optimum parameter values for adsorption over the parameters involved for the two adsorbents as given in Table 6. The software was able to generate a "full quadratic" regression formula to describe the adsorption response for each of the adsorbents, and then six partial differentials of the equation were carried out with respect to each of the six variable parameters, labelled A, B, C, D, E, and F accordingly, with highest to lowest values ranging from 1 to -1. With each partial differential equation set equal to zero, hence, giving six unknowns in six equations and these equations were solved simultaneously in order to obtain the optimum parameters.

Table 6. Optimum Parameter Values Determined from DOE Statistical Analyses

Parameters	High Point (1)	Middle Point (0)	Low Point (-1)	Optimum CS Parameters	Optimum CSAC Parameters
Adsorbate Dose (g/L)	0.0500	0.0300	0.0100	0.0569	0.0743
Adsorbent Mass (g)	5.0000	3.0000	1.0000	3.7628	4.2636
Time of Mixing(min)	75.00	45.00	15.00	52.35	70.12
Temperature (°C)	55.00	35.00	15.00	49.18	52.93
Mixing Speed (rpm)	500.0	300.0	100.0	347.5	482.5
pH	9.0	7.0	5.0	6.9	6.2

Where one parameter was varied, optimum adsorption occurred when the process takes place at the optimum parameter values of all the other parameters. Also, it appeared that the optimum parameters for CSAC adsorption required more resources, compared with the coconut shell parameters. The coconut shell optimum adsorption was found to be at 51.32% removal, while the CSAC optimum adsorption was at 91.25%.

Table 7. Analysis of Variance (ANOVA) and Bonferroni-Holm Posthoc Significance Test for Crude Oil Adsorption by Coconut Shell with varying Parameters

Group 1	Group 2	Analysis of Variance (ANOVA) Test						Bonferroni-Holm Posthoc Significance test		
		S_{SB}	S_{SW}	D_{FB}	D_{FW}	F	P	P_C	P	Significant
C_A	C_e	402.4634	549.0585	1	8	5.864051	0.041747	0.05	0.041747	Yes
M	C_e	26.569	101.9746	1	8	2.084362	0.186808	0.05	0.186808	No
t	C_e	2962.529	2334.754	1	8	10.15107	0.012879	0.05	0.012879	Yes
T	C_e	1445.525	1057.002	1	8	10.94057	0.010736	0.05	0.010736	Yes
r	C_e	213791.2	100031.7	1	8	17.09787	0.003276	0.05	0.003276	Yes
pH	C_e	36.71056	28.52308	1	8	10.29638	0.012447	0.05	0.012447	Yes

The ANOVA and Bonferroni-Holm Posthoc significance test for crude oil adsorption by coconut shell with varying parameters is given in Table 7. The statistical computation presented were carried out with the aid of Daniel's XL Toolbox Version 6.70 © 2008 - 2013 software. There existed a statistically wide variation between the individually investigated parameters and the equilibrium concentration groups at the 95% confidence interval, as the F (1, 8) and P values are mostly within expected ranges. Fisher's F is a ratio of the variance between groups to the variance within groups and P is a probability factor that must be less than 0.05 in the ANOVA analysis. The degree of freedom between the groups was 1, while the degree of freedom within the groups was 8. The F and P values implied a strong dependence of C_e on the various parameters investigated (C_A, t, T, r and pH) except mass of adsorbent M. The Bonferroni-Holm Posthoc parametric significance test for various parameters investigated showed a strong dependence or significance to each other except for the relationship between C_e and M with a P value of 0.186808, which was greater than 0.05 in the 95% confidence interval. The significance of this may be that the mass of adsorbent used to contact the adsorbate was too much than the relevant quantity needed. Therefore, it seems not to constitute a limiting factor in the adsorption process.

Table 8. Analysis of Variance (ANOVA) and Bonferroni-Holm Posthoc Significance Test for Crude Oil Adsorption by Coconut Shell Activated Carbon (CSAC) with varying Parameters

Group 1	Group 2	Analysis of Variance (ANOVA) Test						Bonferroni-Holm Posthoc Significance test		
		S_{SB}	S_{SW}	D_{FB}	D_{FW}	F	P	P_C	P	Significant
C_A	C_e	12.07801	16.83268	1	8	5.740267	0.043455	0.05	0.043455	Yes
M	C_e	9.04401	12.81788	1	8	5.644621	0.044836	0.05	0.044836	Yes
t	C_e	4613.904	2254.105	1	8	16.37512	0.003702	0.05	0.003702	Yes
T	C_e	2700.764	1002.766	1	8	21.5465	0.001662	0.05	0.001662	Yes
r	C_e	222985.5	100003.4	1	8	17.83824	0.002902	0.05	0.002902	Yes
pH	C_e	65.536	10.7284	1	8	48.86917	0.000114	0.05	0.000114	Yes

The ANOVA and Bonferroni-Holm Posthoc significance test for crude oil adsorption by coconut shell activated carbon with varying parameters is given in Table 8. The parameters investigated showed the actual values of the sum of squares within the groups and the sum of squares between the groups. There existed a statistically wide variation between the individually investigated parameters and the equilibrium concentration groups at the 95% confidence interval, as the F (1, 8) and P values are mostly within expected ranges. Fisher's F is still the ratio of the variance between groups to the variance within groups and P is a probability factor that must be less than 0.05 in the ANOVA analysis. The degree of freedom between the groups was also 1, while the degree of freedom within the groups was still 8. The F and P values implied a strong dependence of C_e on the various parameters investigated (C_A, M, t, T, r and pH). The Bonferroni-Holm Posthoc parametric significance test for various parameters investigated, showed a strong dependence or significance on each other in the 95% confidence interval.

Comparatively, the enhanced effect brought about by activation was justified statistically as all the parametric variations with CSAC was significant, compared to one insignificant case observed when coconut shell was used despite the fact that the same mass of adsorbent was used to contact the adsorbate under similar conditions.

4.0   CONCLUSION

The ability of the coconut shell, as well as its activated carbon, as a natural adsorbent to remove crude oil from effluent water as investigated in this work demonstrated that crude oil removal by adsorption onto either material (CS or CSAC) was feasible. In comparing the two adsorbents involved, it was seen that the activated carbon of coconut shell was more effective for all tested parameters. The coconut shell, nevertheless, is a great adsorbent for the removal of crude oil when sufficiently provided. The use of CSAC will require a smaller amount, compared with coconut shell, and as such, would be more economical, especially for large operations, but it may not be economical to use CSAC for smaller tasks due to the cost of activating carbon, where a handful or two of the ground shell may suffice for the operation.

Relatively lower environmental temperatures favour the adsorption process more for either of the adsorbents, just as the more neutral the pH of the solution, the better the adsorption. Also, the longer the mixing, and the higher the rate of mixing, the more effective the clean-up process will result. Adsorption efficiencies observed with respect to adsorbate loading, adsorbent loading, contact time, temperature, rotational speed, and pH of mixture revealed a promising crude oil clean-up adsorbent with CS and CSAC. Furthermore, the enhanced effect brought about by activation was justified statistically using ANOVA and Bonferroni-Holm Posthoc significance test.

It is recommended that the use of these natural and inexpensive materials be encouraged as an effective solution to the problem of industrial and small-workshop crude oil spills, where the selection of whichever of the two adsorbents should be based on the economies of scale of the undertaking.

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