



Adsorption of Kerosene by locally formulated adsorbent from Clay and Sawdust

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ABSTRACT

Experimental and theoretical approach was used in the formulation of adsorbent, made from clay and sawdust for the adsorption of kerosene in water medium environment. Three formulations of clay and sawdust with the code ratio of R9:1, R17:3 and R4:1 and with control clay sample, were investigated to obtain the suitable mixing ratio that will give optimum percentage removal of kerosene in water medium. The formulated adsorbents were further studied using the Langmuir and Freundlich adsorption isotherms concept. The predicted results of the Langmuir and Freundlich adsorption isotherm was compared with experimental results for each of the clay-sawdust mixing ratio. The results obtained revealed that the adsorption of kerosene in water medium was more effective using mixture of clay and sawdust than clay alone. Thus, increasing the percentage of sawdust in the mixture increased the removal efficiency as the R4:1 formulation (i.e. 80% clay and 20% sawdust) outperformed the other mixing ratios at

any initial concentration of kerosene in water. Also, the adsorption process of kerosene in water was best described by the Langmuir isotherm than the Freundlich isotherm. Thus, with initial kerosene concentration of 81.0mg/ml in water at equilibrium, the maximum adsorption capacity obtained from the experiment, Langmuir and Freundlich isotherm were 83.989mg/g, 89.965mg/g and 81.608mg/g for control sample; 134.158mg/g, 131.563mg/g and 105.6113mg/g R9:1; 143.44mg/g, 127.717mg/g and 104.856mg/g for R17:3; and 150.14mg/g, 161.728mg/g and 123.309mg/g for R4:1. The results showed that a mixture of clay and sawdust are effective for the removal of kerosene in water, therefore, can be utilized for remediation of kerosene polluted water especially.

Key words: Adsorption, kerosene, locally formulated adsorbent, Clay, sawdust

1. INTRODUCTION

Crude oil and its fractions are often associated with lot of challenges which are detrimental to organisms in aquatic and terrestrial environments. Though, the exploitation of crude oil has contributed immensely to the economy of many nations especially, Nigeria. Nigeria and indeed, the Niger Delta region are faced with diverse of environmental challenges resulting from the exploration and exploitation of crude oil. These environmental issues include destruction of the deforestation; soil pollution, which had led to poor agricultural yield; air pollution due to gas flaring, which had impaired negatively on the air quality resulting to diverse of respiratory diseases; water pollution, which had led to death of aquatic animals and contamination of surface water and hence, groundwater as a result of runoff water from polluted land and water environments. These had seriously reduced the quality of drinking water. Of course, crude oil or its fractions is composed of several chemicals, biological and physical substances that are contaminable to the environment. These contaminants, besides their negative impacts on plants and animals, find their way into sources of drinking water or are being aided by human activities (Ukpaka *et al.*, 2016; Karkush and Abdul Kareem, 2018; Oramadike, 2018).

Also, these petroleum products gets to the different environment through tanker leakage, accident or collapse, leakage in ship carrying them, explosion or leakages from pipelines transporting them and direct discharge by humans (Al Zubaidy *et al.*, 2015). And because of their variation in types, they exhibits different properties which equally, determines the gravity of their impact on the environment (Cirne *et al.*, 2016 and Fingas, 2018). The differences in properties was as a result of their geological source, for instance, gasoline, kerosene or diesel fuels are crude fractions with less carbon and hydrogen atoms compared to heavier fractions, therefore their properties are more specific and less variable (Fingas, 2018; Rajeshwar Man Shrestha, 2018).

However, due to the challenges posed by the pollution of the environment, efforts are seriously made globally to reduce the effect of pollutants on our environment (Dharmendra and Rasma, 2015). Most technologies applied in addressing these hazards had not actually been successful; hence the continuous search for alternative means of reducing these risks. For instance, the practice of burning oil polluted sites yielded no good result as the air is re-polluted due products of combustion. On the other hand, the use of emulsifying detergents caused the oil to separate into fine particles (Olga *et al.*, 2015). Most adsorbent used for clean-up are toxic and not suitable while others are effective but economically not feasible. Recent technologies have applied the use of microorganism in the biodegradation of hydrocarbons function (Al-Sulaimani *et al.*, 2010), but this method also have its drawback as it is only suitable at certain temperatures to enable the microorganisms perform its intended function.

Surface water and groundwater have been the major sources of drinking water for man (Ukpaka, 2016), but these water are continually contaminated. The sources of water pollution are enormous, and considering the importance of water to man and its habitants, it becomes imperative that our water bodies are free of contaminants. However, methods are available for water cleanup, which include mechanical, physicochemical and biological methods.

Amongst the known methods for treatment of contaminated water, adsorption technology has proven to be reliable and effective for removal of impurities in solution. This is the use of solid substance, either from plant, animal or soil based. Adsorption has proven to be advantageous over the other methods as its design is simple with low cost investment, and it has been widely applied for treatment of industrial wastewater polluted by organic and inorganic compounds (Gupta *et al.*, 2009; Tong *et al.*, 2010). Locally source materials like clay and agricultural based materials can be utilized as low-cost adsorbents.

Adsorption of contaminants takes place on the surface of the adsorbent, whereby the pollutant is removed. When a contaminated solution comes into contact with a solid with highly porous surface structure, intermolecular forces of attraction of the liquid-solid comes into play, such that the solute molecules in the solution adhered onto the solid surface (Rashed, 2013). The adhered substance on the solid surface during adsorption processes is called adsorbate, while the solid which retained the solute is called adsorbent. Therefore, adsorption can simply be defined as the removal of solute in solution using adsorbent.

During adsorption, vacant sites exist on the surface of the adsorbent for bonding of the solute's atom in the bulk liquid. However, according to Rashed, (2013), "atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates". He stated further that the exact nature of the bonding depends on the details of the species involved. Adsorption process is generally as result of Van Der Waals forces or chemisorptions and may also occur as a result of electrostatic attraction (McCabe *et al.*, 2005 and Seader and Henley, 2006). This study is aimed at investigating the performance of different formulations made from clay and sawdust for adsorption of kerosene in contaminated water as a substitute for expensive adsorbents used for removal of kerosene and other petroleum fractions.

2. MATERIALS AND METHODS

Materials

The materials used for the experiment include: clay, sawdust, kerosene, water, calibrated plastic container (bucket), weighing balance, shovel, sack bags, 10 litres plastic container (Jerry can), spoon, oven, thermometer, sieve, measuring cylinder, beaker, calculator, stop watch, knife, retort stand, thread and detergent.

Experimental Procedures

The various steps taken to achieve the objectives of this study were stated sequentially in this section. All experiments were performed in the Chemical/Petrochemical laboratory, Rivers State University, Nkopolu-Oroworukwo, Port Harcourt, Rivers State.

Sample Collection

The clay used for the experiment was collected from Omoku in Ogba/Egbema/Ndoni Local Government Area of Rivers State. Omoku and its neighbouring communities is a major oil producing communities in Nigeria. The clay was collected through shovel in swampy area. Sawdust from black afara wood was collected from timber milling shop at Timber Market, Mile 2, Diobu, Port Harcourt. A 10 liter (10000ml) of kerosene was bought from a licensed filling station at Mile 3, Diobu, Port Harcourt. Water was collected through tap at the laboratory.

Sample Preparation

After collection of samples, they were transported to the laboratory and prepared for analysis.

Preparation of Clay Sample

The clay sample was first, cleaned according to method described in the works of Dianati, (2012) and Vijayakumar *et al.* (2012). The clay was dissolved in plastic bucket filled with clean water and manually stirred with hand for about 30 minutes, and then allowed to settle for about 24 hours. The floated debris of fibrous roots of plants and other particulate matters on the surface of the supernatant, which could have altered the properties of the clay, were gently skimmed off along with water. The dissolved clay sample which settled on the bottom of the container was recovered and dried in oven until moisture content was evaporated off.

Preparation of Sawdust

The preparation of the sawdust was adopted according to the method described in the work of Abd El-Latif, (2010). The collected sawdust was washed with distilled water to remove soluble impurities and surface adhered particles. It is then sundried for 2 days. The dried sample was transferred into sieve of 1.40mm mesh size and sieved to obtain a uniform size distribution.

Adsorption Experiment

The adsorption experiment was conducted according to method described by Retseck, (2015) for oil clean-up using solid adsorbent.

Adsorption Isotherm

A calibrated container of 3 litres (3000ml) capacity was filled with 1 litre (1000ml) of water. 50ml of kerosene was measured in a cylinder and added to the container. The mixture was allowed to settle for a few minutes. 50g of the control sample was suspended through a retort stand via the thread and gently lowered into the container to about 50% immersed. The adsorbent was left suspended in the liquid mixture for 120 minutes (2 hours), but at intervals, the adsorbent was gently moved from side to side few seconds to increase the rate of adsorption. After 120 minutes, the adsorbent was removed and the new meniscus level of water recorded. Since kerosene is not miscible with water, the kerosene remaining in the container was calmly and carefully scooped via

table spoon into a measuring cylinder in order to determine the volume and weight of kerosene left in the container after 120 minutes. Thereafter, the content of the container was evacuated and the container was then washed with detergent and cleaned. The process was repeated with 100, 150, 200 and 250ml of kerosene. Also, the same procedure was repeated for R9:1, R17:3 and R4:1 formulated adsorbents.

The concentration of kerosene in the bulk liquid at equilibrium was calculated using the following expression.

$$C_e = \frac{w_l}{V_T} \quad (5)$$

Where, C_e = Concentration of kerosene in the bulk liquid at equilibrium (mg/ml), w_l = Weight of kerosene in the bulk liquid at equilibrium (mg), V_T = Total volume of liquid mixture at equilibrium (ml)

Similarly, the adsorption capacity at equilibrium was calculated using expression in the work of Vijayakumar *et al.* (2012).

$$q_e = (C_i - C_e) \frac{V_f}{w} \quad (6)$$

Where, q_e = Adsorption capacity at equilibrium (mg/g), C_i = Initial concentration of kerosene in the bulk liquid (mg/ml), V_f = Volume of kerosene in the bulk liquid at equilibrium (ml), w = Weight of adsorbent (g)

The initial concentration was calculated using the formula:

$$C_i = \frac{w_i}{V_T} \quad (7)$$

Where, w_i = Initial weight of kerosene in the bulk liquid (mg)

Adsorption Kinetics

The adsorption kinetics was performed in the same way as the adsorption isotherm. However, the experiment was performed at only with 100ml volume of kerosene same constant 50g for all the adsorbents. In each of the formulated adsorbent, the experiment was performed for 90 minutes (1.5 hours). At every 10 minutes intervals, the adsorbent was removed and the new meniscus level of water recorded. The kerosene remaining in the container was carefully scooped into a measuring cylinder to determine the volume and weight. The process was again, repeated for the R9:1, R17:3 and R4:1 formulated adsorbents.

The concentration of kerosene in the bulk liquid at any time was calculated using the expression.

$$C_t = \frac{w_t}{V_T} \quad (8)$$

Where, C_t = Concentration of kerosene in the bulk liquid at time t (mg/ml)

Again, the adsorption capacity at any time was calculated using expression.

$$q_t = (C_i - C_t) \frac{V_f}{w} \quad (9)$$

Where, q_t = Adsorption capacity at time, t (mg/g)

Adsorption Models

To study the model that best describe the adsorption kerosene at equilibrium, experimental data were fitted to the Langmuir and Freundlich isotherm. Also, the pseudo first order and second order were applied to studied the kinetics of the formulated adsorbents

Langmuir Isotherm

The Langmuir isotherm is expressed as

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (10)$$

Re-arrangement of equation (6) gives

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (11)$$

A plot of $\frac{C_e}{q_e}$ versus C_e gives a straight line graph with slope equivalent to $\frac{1}{q_m}$ and the intercept as $\frac{1}{K_L q_m}$.

Where, q_m = Langmuir constants at maximum adsorption capacity of kerosene (mg/g), K_L = Energy of adsorption (ml/mg)

To further investigate the reliability of the adsorbent in removal of kerosene in water, the Langmuir isotherm parameters was used in a dimensionless parameter called separation factor or adsorption intensity R_L , which is expressed according to Sari *et al.* (2007).

$$R_L = \frac{1}{1 + K_L C_i} \quad (12)$$

The separation factor R_L , is an important reliable indicator in adsorption process. Thus, when $0 < R_L < 1$, it indicates adsorption is favorable; when $R_L > 1$, it indicates adsorption is will not be favorable; when $R_L = 1$, it indicates adsorption is linear; and when when $R_L = 0$, it indicates adsorption is irreversible (Sari *et al.*, 2007; Toor, 2010 and Harmayani and Anwar, 2012).

Freundlich Isotherm

The Freundlich isotherm is expressed as

$$q_e = K_f C_e^{1/n} \quad (13)$$

To obtain the constants, the logarithm of both sides of equation (13) was taken to give

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (14)$$

A plot of $\log q_e$ versus $\log C_e$ gives the slope of the graph as $\frac{1}{n}$ and the intercept as $\log K_f$.

Where, K_f = Freundlich constant, n = Heterogeneity of the adsorption energy across the adsorbent surface

3. RESULTS AND DISCUSSION

The adsorption of kerosene in water by formulation of clay-sawdust mixture at varying ratios has been studied. The physicochemical properties of clay and sawdust were also determined using the X-ray diffraction instrument. The adsorption isotherm of the formulated adsorbents was investigated using the Langmuir and Freundlich isotherms, while the kinetics analysis was studies using the pseudo first and second orders.

Effect of Initial Concentration of Kerosene on Adsorption Capacity

Effect of initial kerosene concentrations in the bulk liquid on equilibrium adsorption capacity of the formulated adsorbent was studied at room temperature. The initial kerosene concentrations used are 40.5, 81.0, 121.5, 162.0 and 202.5 mg/ml.

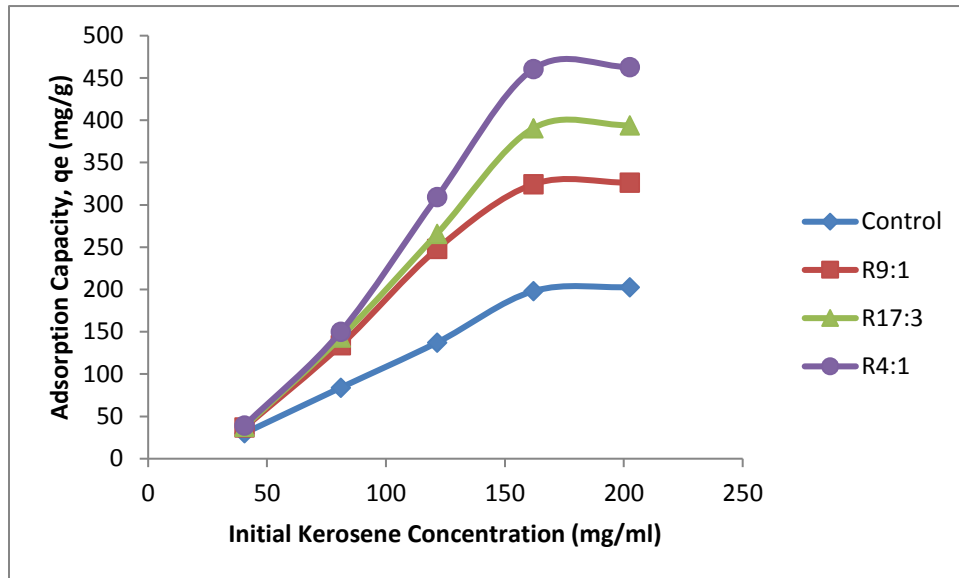


Figure 1 Effect of Initial Kerosene Concentration on Adsorption

The effect of initial concentration of kerosene in the water on the adsorption capacity of the formulated adsorbents is shown in Figure 1. Increase in adsorption capacity was observed with increase in initial concentration of the kerosene as presented in Figure 1.

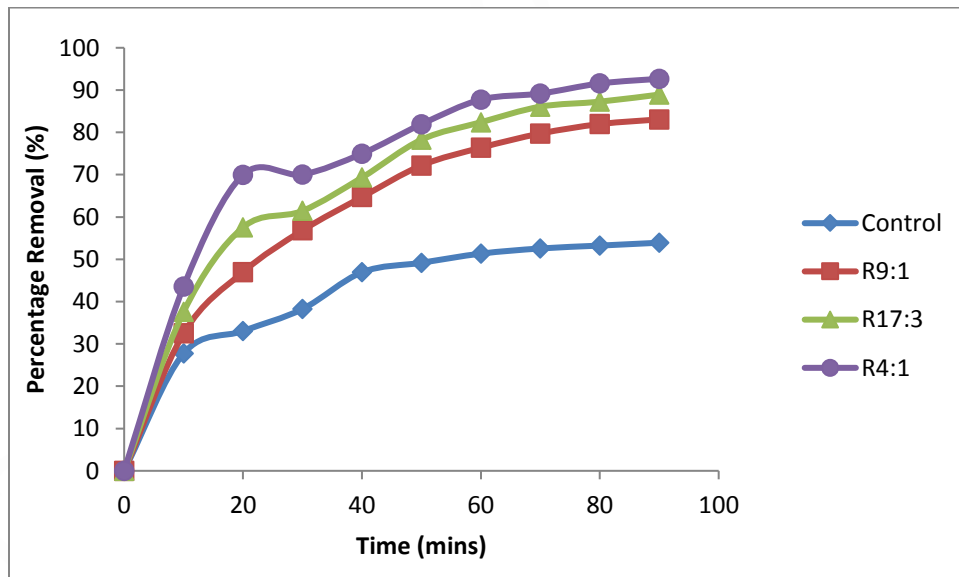


Figure 2 Efficiency of Adsorbent on Kerosene Removal

The removal efficiency of the formulated adsorbent for kerosene-water mixture was studied at initial kerosene concentration of 81mg/ml for a period of 90 minutes as shown in Figure 2.

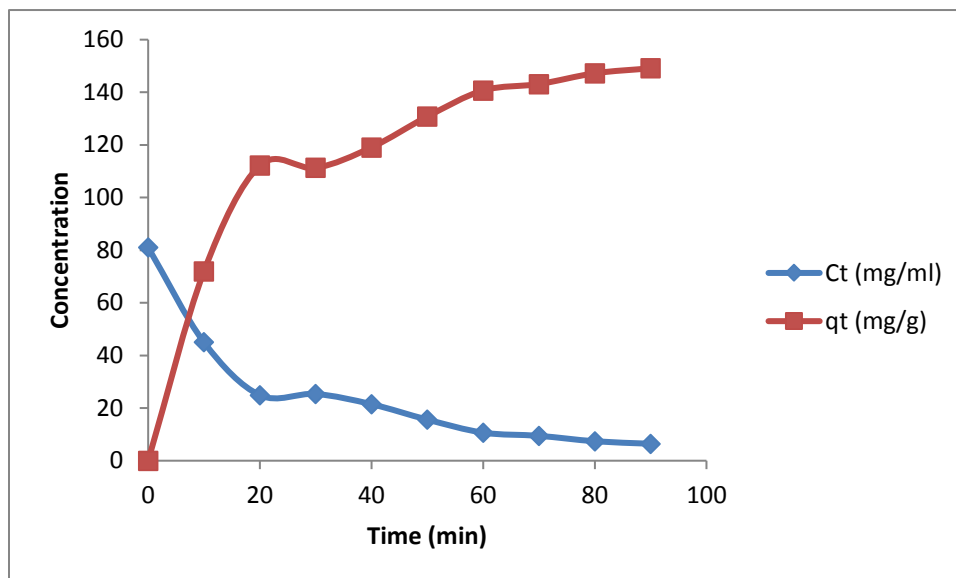


Figure 3 Change in Concentration with Time at R4:1 Mix

To study the progress of the adsorption in the solid and liquid phases, the profiles of adsorption capacity and concentration of kerosene over time for adsorbent R4:1 mix is shown in Figure 3.

Evaluation of Adsorption Isotherm Constant Parameters

To investigate the adsorption isotherm of the formulated clay-sawdust adsorbents, the constants in the Langmuir and Freundlich models were determined by fitting the experimental data. Figures 4 to 7 show the plot for determination of Langmuir parameters for the formulated adsorbents, while Figures 8 to 11 shows the plot for Freundlich parameters determination. The equations of the curve and the square roots of the best fit for Figures 4 to 11 is well shown in their as presented in this research work.

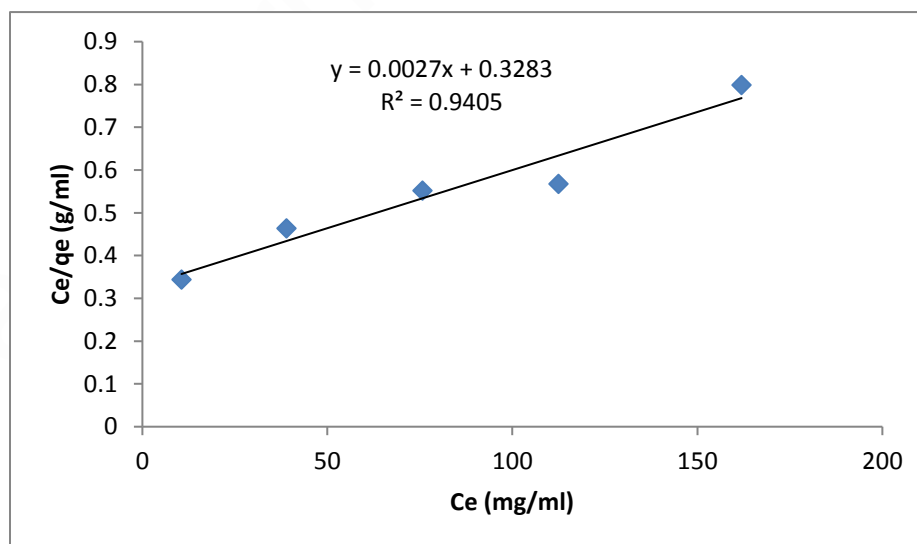


Figure 4 Langmuir Isotherm for Control

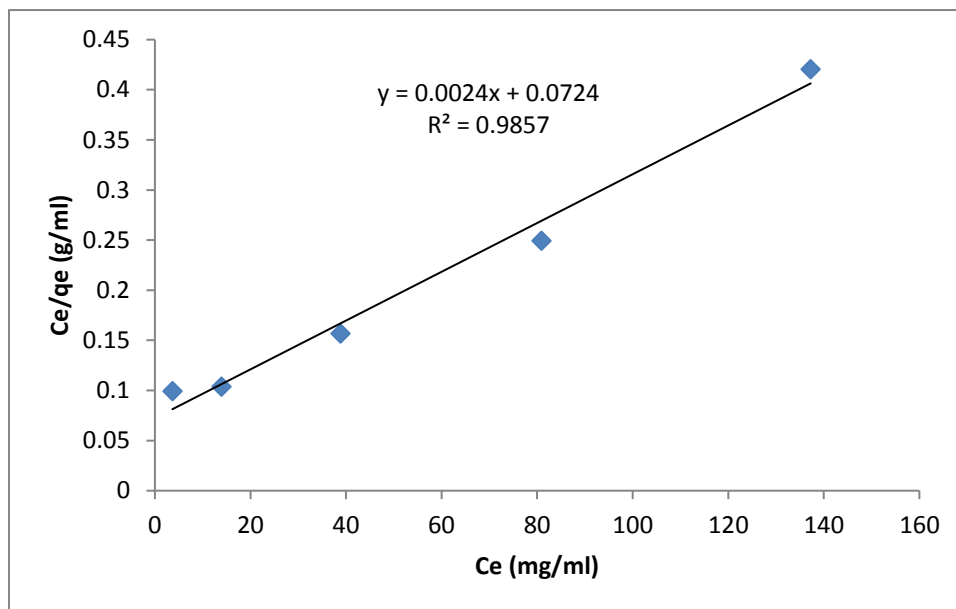


Figure 5 Langmuir Isotherm for R9:1 Mix

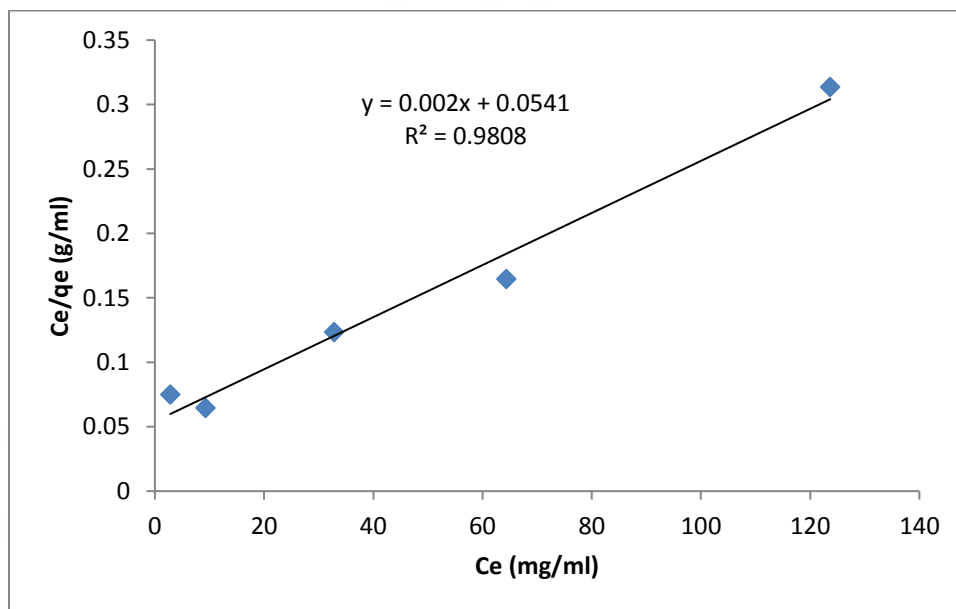


Figure 6 Langmuir Isotherm for R17:3 Mix

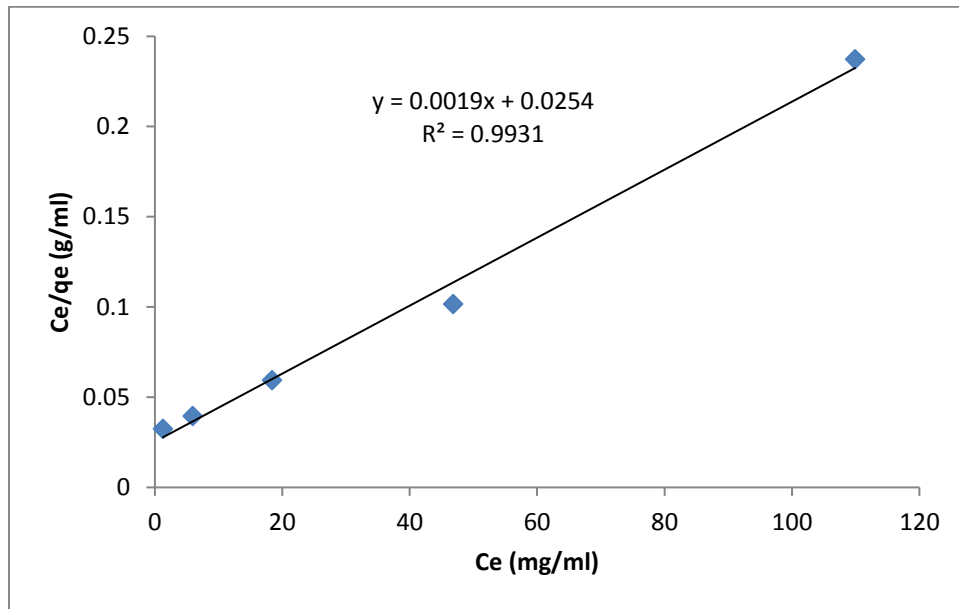


Figure 7 Langmuir Isotherm for R4:1 Mix

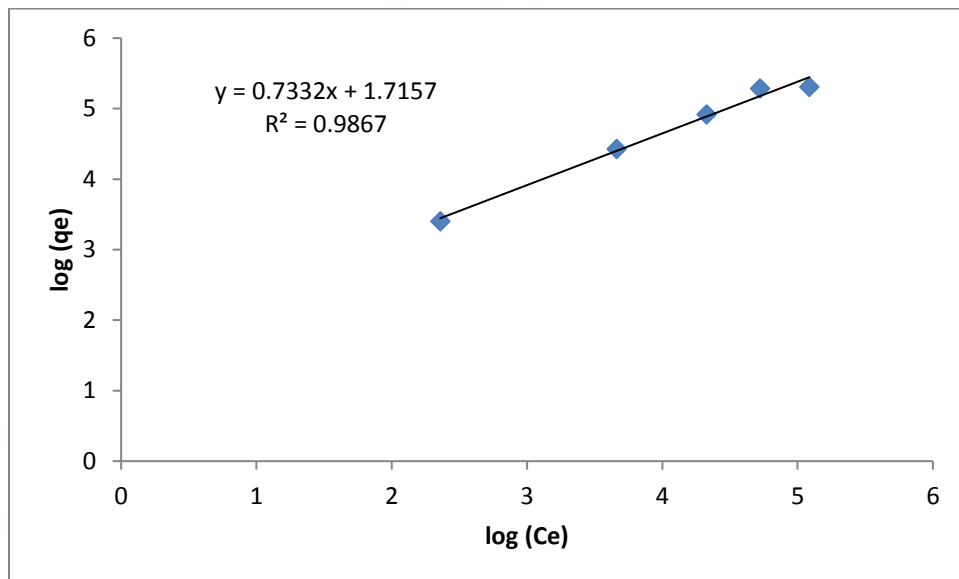


Figure 8 Freundlich Isotherm for Control

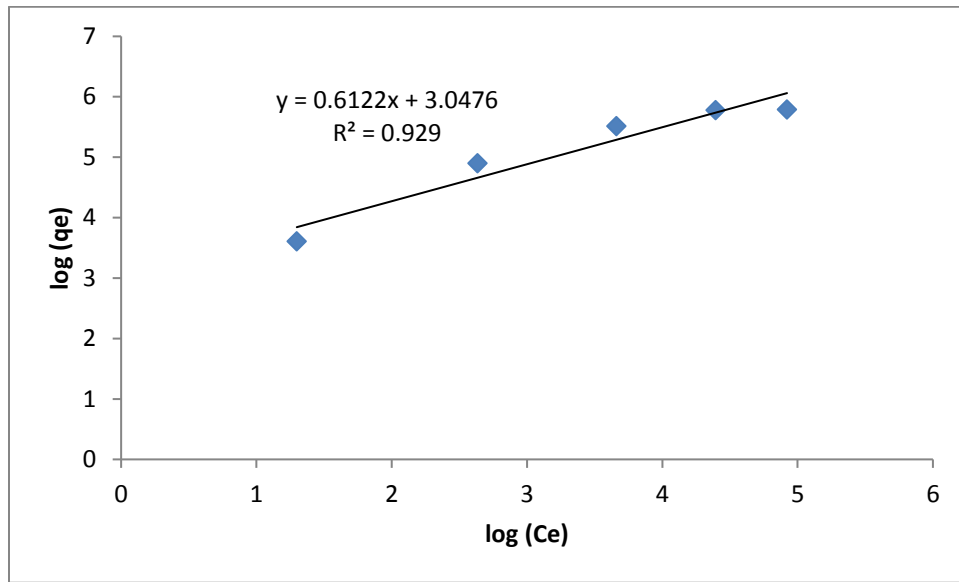


Figure 9 Freundlich Isotherm for R9:1 Mix

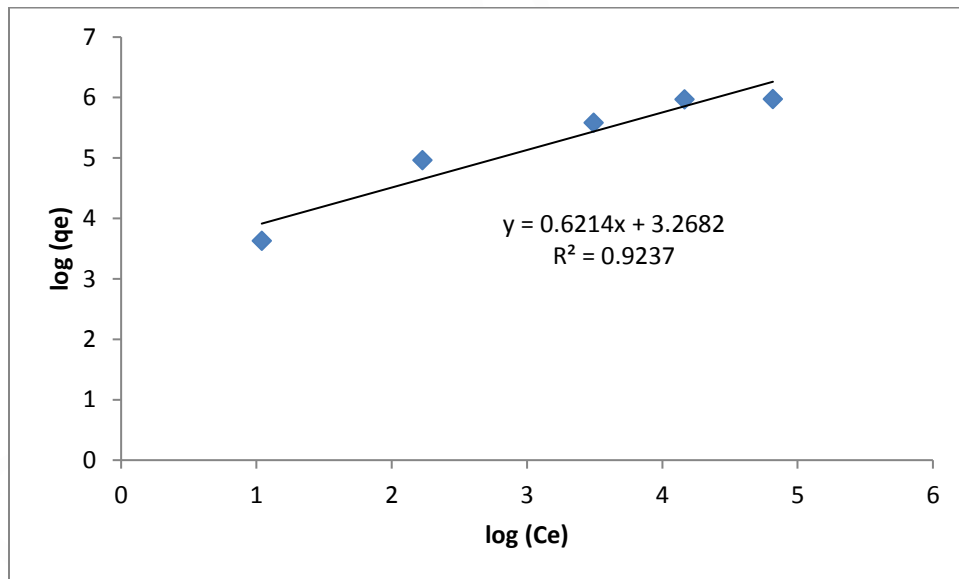


Figure 10 Freundlich Isotherm for R17:3 Mix

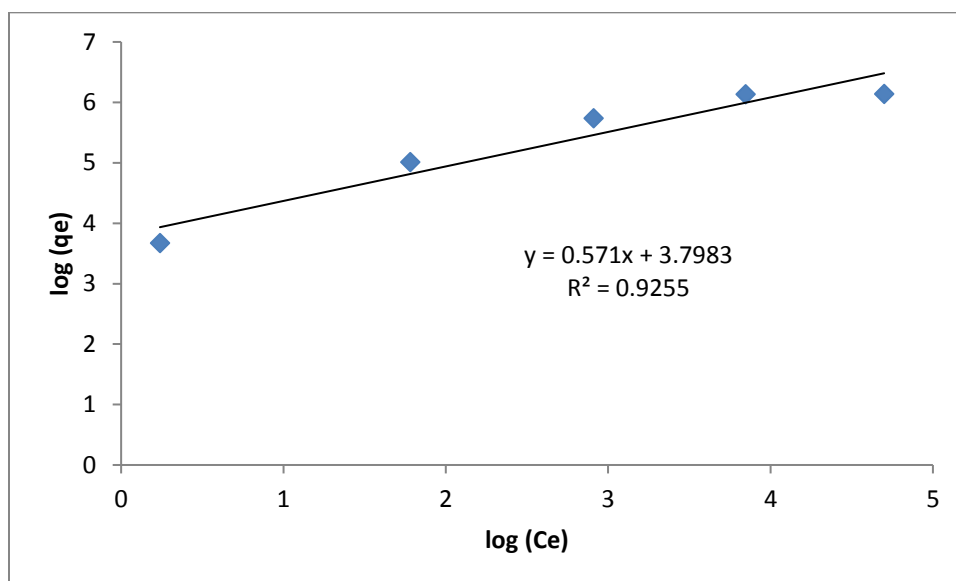


Figure 11 Freundlich Isotherm for R4:1 Mix

Comparison of Clay-Sawdust Adsorption Isotherms

The results obtained from the Langmuir and Freundlich isotherm models were compared with the experimental results to determine which isotherm model best describe the adsorption of kerosene in water using the formulated adsorbents.

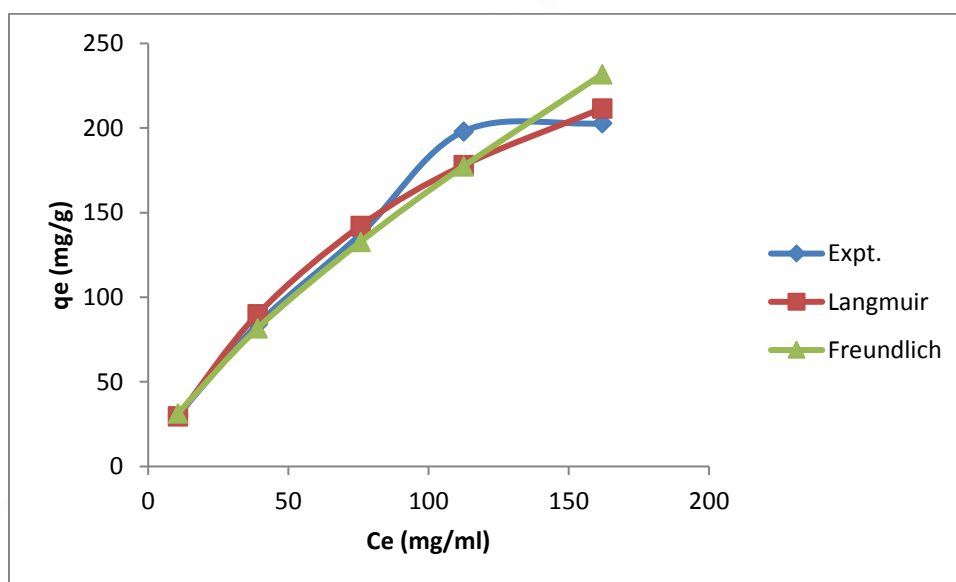


Figure 12 Comparison of Adsorption Isotherms for Control

Figure 12 shows adsorption capacity obtained from the experiment and those predicted by the Langmuir and Freundlich isotherm model against the concentration of kerosene in the bulk liquid at equilibrium for the control sample. The result obtained shows a good match revealing the reliability of the approach used in this investigation.

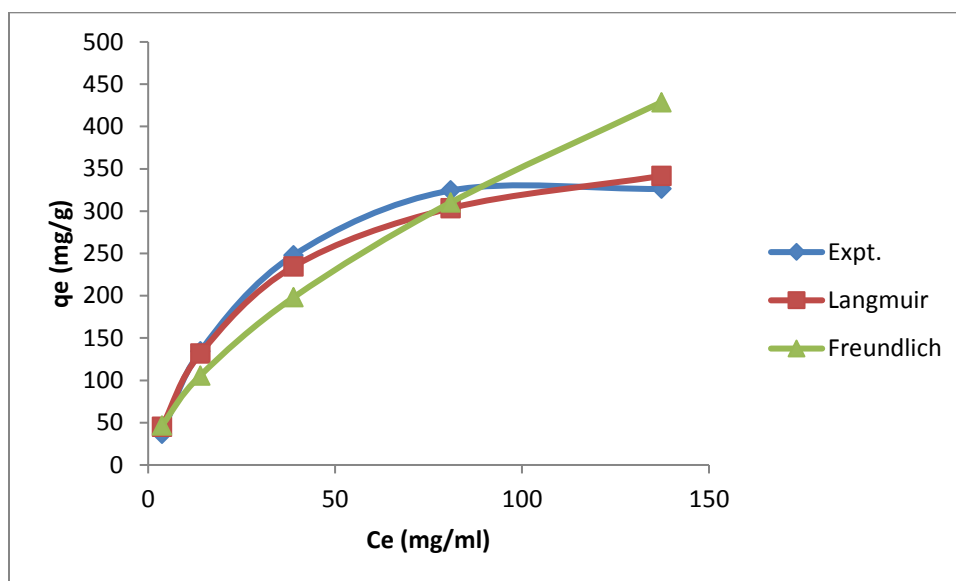


Figure 13 Comparison of Adsorption Isotherms for R9:1 Mix

The adsorption capacity obtained from the experiment as well as the predicted Langmuir and Freundlich isotherm model, as function of the kerosene concentration in the bulk liquid at equilibrium for the R9:1 mix are shown in Figure 13.

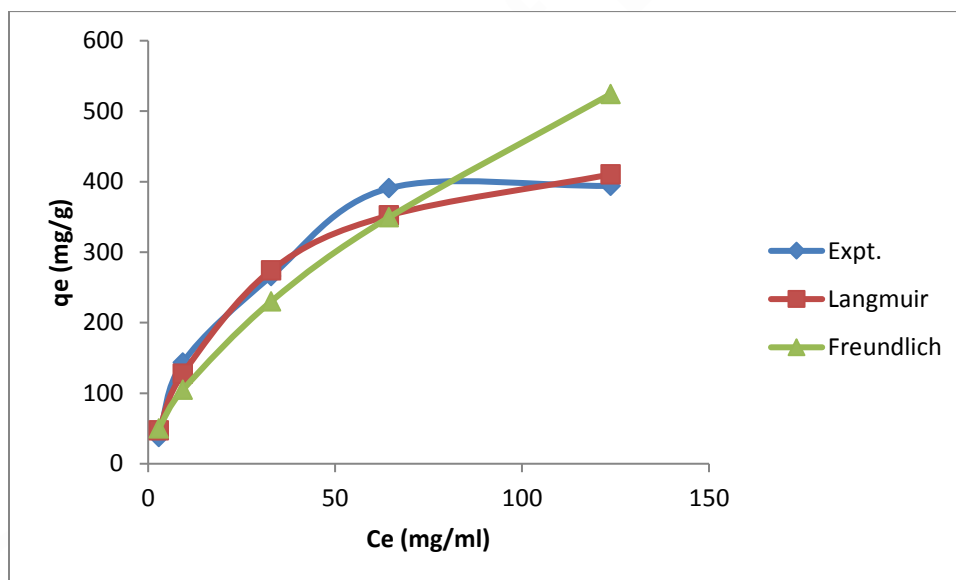


Figure 14 Comparison of Adsorption Isotherms for R17:3 Mix

Figure 14 shows the comparison of adsorption capacity obtained from the experiment as well as the predicted Langmuir and Freundlich isotherm models at equilibrium for the R17:3 mix. Again, the adsorption capacity predicted by the Langmuir isotherm model fits the experiment data better than the Freundlich isotherm model as seen in the profiles and the correlation coefficient. Thus, the correlation coefficient, R^2 for Langmuir isotherm and Freundlich isotherm obtained for the R17:3 mix are 0.9808 and 0.9237 respectively.

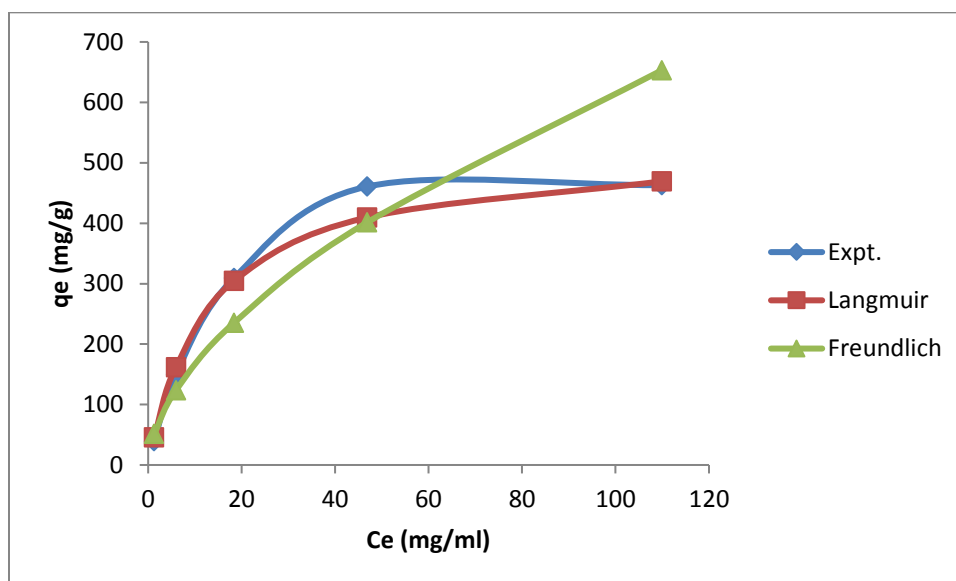


Figure 15 Comparison of Adsorption Isotherms for R4:1 Mix

Figure 15 shows the comparison of adsorption capacity obtained from the experiment as well as the predicted Langmuir and Freundlich isotherm models at equilibrium for the R4:1 mix. Again, like the R9:1 and R17:3 mixes, the adsorption capacity predicted by the Langmuir isotherm model agrees with the experiment data than the Freundlich isotherm model as indicated by the correlation coefficient. The correlation coefficient, R^2 for Langmuir isotherm and Freundlich isotherm obtained for the R4:1 mix is 0.9931 and 0.9255 respectively. The performance of clay as adsorbent has shown to be more effective if mixed with sawdust.

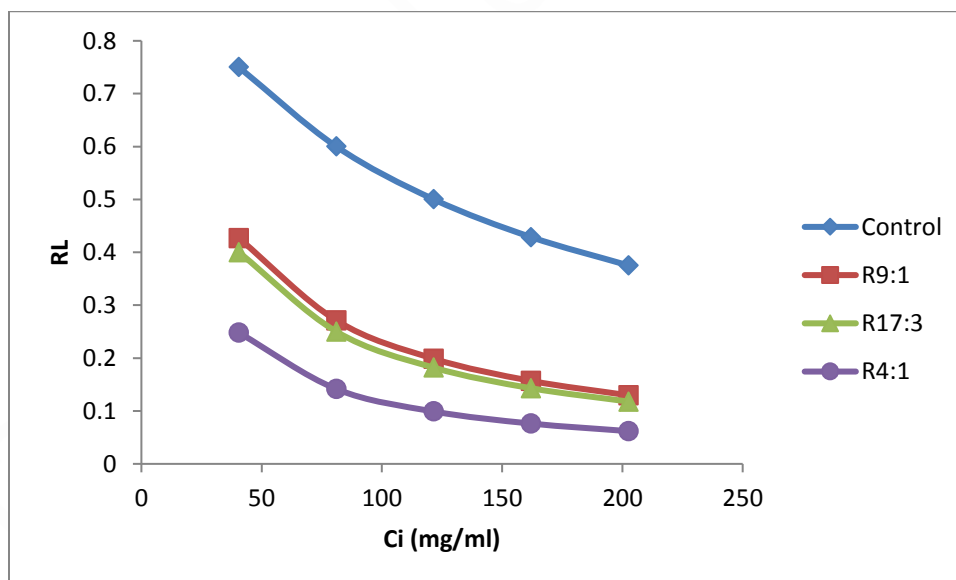


Figure 16 Separation Factor at Different Adsorption Isotherms for R4:1 Mix

The favourability of the formulated adsorbents to adsorb kerosene in water was investigated as shown in Figure 4.16. Thus, in all the initial concentration of kerosene used, the separation factor, R_L values were greater than zero but less than unity ($0 < R_L < 1$) as presented in Figure 16. This shows that the formulated adsorbents, including the control are favourable for adsorption of kerosene in water.

4. CONCLUSION

Investigations on the adsorption of kerosene in water by different mixtures of clay and sawdust have been performed. Also, the adsorption of kerosene by the formulated adsorbents has been studied using the well-known Langmuir and Freundlich adsorption isotherms. Further, the adsorption process was equally studied using the pseudo first and second order adsorption kinetics. The physicochemical properties of the Omoku clay and sawdust were analyzed prior to the investigation.

At each mixing proportion, comparison was made between the experiment, Langmuir and Freundlich adsorption isotherms. Likewise, the experimental results were compared with the pseudo first and second order adsorption kinetics at every mixing ratio. The results obtained showed that the adsorption of kerosene in water was more effective using mixture of clay and sawdust than clay alone. However, a mixture of 80% clay and 20% sawdust outperformed the other mixing ratios at any initial concentration of kerosene in water.

Also, the adsorption process of kerosene in water can be effectively studied using the Langmuir isotherm than the Freundlich isotherm, while the kinetics suitable for the description of the rate of kerosene adsorption in water is the pseudo second order. Again, the values obtained from the analysis of the separation factor, R_L shows further that adsorption process of kerosene in water using the formulated adsorbent, is favourable and therefore, suitable for remedial process.

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