# STUDIES ON THE ADSORPTION OF NAPHTHALENE AND PYRENE FROM AQUEOUS MEDIUM USING RIPE ORANGE PEELS AS ADSORBENT

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## ABSTRACT

The effectiveness of dried ground orange peels in adsorbing naphthalene and pyrene from an aqueous stream has been investigated in terms of variation in concentration, adsorbent dosage, agitation time and particle size. Experimental batch data was correlated by Freundlich and Langmuir isotherm models. The Freundlich isotherm best described the adsorption process as the adsorption data fitted well into the model. The adsorption capacity and energy of adsorption were obtained as 7.519mg/g and 0.0863mg$^{-1}$, and 3.8168mg/g and 0.0334mg$^{-1}$ for naphthalene and pyrene respectively. The adsorption from the aqueous solution was observed to be time dependent while equilibrium time was found to be 100 and 120 minutes for naphthalene and pyrene respectively. Adsorption increased with increase in adsorbent dosage and was maximum at between 5 to 7g for naphthalene and 6 to 8g for pyrene. The maximum adsorption was observed using a particle size of 2.0mm. The rate of adsorption using the first order rate expression by Lagergren for naphthalene and pyrene were 0.007 and 0.006 min$^{-1}$ respectively. These results therefore suggest that naphthalene is more selectively adsorbed than pyrene using ripe orange peel as adsorbent.

**KEY WORDS:** Naphthalene, Pyrene, Adsorption, Adsorbent, Ripe orange peels.

## 1.0 INTRODUCTION

The issues arising from oil spillages have become a subject of very serious concern for both the government and non government organization because of the potential adverse effects on the quality of the environment where the oil field, petroleum and petrochemical industries are primarily located, and ultimately, the multiplying effects on the larger society (Nwilo and Badejo, 2001, Akpofure et al., 2007). The activities of the industries are always associated with the discharge of organic compounds like polycyclic aromatic hydrocarbons arising from the process of refining crude oil or production of petrochemical products. Polycyclic aromatic hydrocarbons generally known as PAHs are highly lipophilic, being readily soluble in oil than water (Luch, 2005).

The use of adsorbent particularly activated carbon in the treatment of waste water has been a subject of many excellent reviews. However, due to the high cost of purchase of this material, the quest for other sources which are affordable and readily available have given rise to the discovery of the use of agricultural solid wastes as alternative sources of adsorbents. Recent researches shows that agricultural wastes such as banana pith, coconut husk and saw dust, biogas residual slurry, rice hulls, orange peels and bagasse (Namasivayam et al., 1994, Gaijwad, 2004, Khan et al., 2004, Okieimen et al., 2004, Amuda and Ibrahim, 2006, Hanafiah, et al., 2007) can be used as an adsorbent for the removal of dyes and heavy metals from aqueous medium.

The removal of PAHs from aqueous medium using ripe orange peels, a relatively low cost agricultural waste which is readily available in Nigeria, is advanced in this study. The study also examines the adsorptive capacity of the orange peels under the effect of varying experimental conditions using the Freundlich and Langmuir isotherms models.

## 2.0 THEORY
### Adsorption model

The Freundlich and Langmuir adsorption isotherms are two common isotherms used to describe adsorption equilibria studies. Adsorption equilibrium is a dynamic concept achieved when the rate at which molecules adsorb onto a surface is equal to the rate at which it desorbs (McCabe et al., 1993).

The Langmuir adsorption isotherm on the one hand is based on the theoretical principle that only a single adsorption layer exists on an adsorbent containing a finite number of identical sites. It assumes uniform energies of adsorption over the surface and no transmigration of adsorbate on the outer surface of the adsorbent. The linearized model equation is expressed as (Sivaraj et al. 2001):

$$\frac{C_e}{x/m} = \frac{1}{ab} + \frac{1}{a}C_e$$

where $x/m = q_e = \dfrac{C_O - C_e}{m}$

$q_e = x/m$ = mass of adsorbed solute per unit mass of adsorbent

$C_e$ = concentration of solute in solution in equilibrium

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with that on the solid

$b$ = energy of adsorption (mg$^{-1}$)

$C_o$ = initial concentration (mg/l)

$$\frac{1}{a} = Q_o = \text{adsorption capacity (mg/g)}$$

The adsorption capacity $Q_o$ and energy of adsorption b are obtained from the slope and intercept of the plot of $C_e/q_e$ against $C_e$ (Treybal, 1980 and Richardson and Harker, 2006). The Freundlich adsorption isotherm is an indicator of the extent of heterogeneity of the adsorbent surface (adsorptive sites). In this case, the surfaces of the ripe orange peels are made up of small heterogeneous adsorption patches which are homogeneous in themselves. The model equation is expressed as (Sivaraj et al. 2001):

$$q_e = k_f \, C^{1/n} \qquad\qquad 2$$

where $\quad k_f \quad$ = adsorption capacity, $\quad n$ = adsorption

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \qquad\qquad 3$$

intensity

$k_f$ and n are the Freundlich constants and represent the adsorption capacity and intensity of adsorption, respectively. The magnitude of n is an indication of suitability of the adsorption process. Values of n > 1 indicate favorable adsorption conditions. $k_f$ and $n$ are calculated from the intercept and slope of the plot of log $C_e$ against log $q_e$ (Treybal, 1980).

**Kinetics of adsorption**

In order to consider kinetics effects, the Lagergren pseudo first order equation (Sivaraj et al., 2001), was used to determine the adsorption rate constant which is expressed as:

$$\log_{10} \left( q_e - q \right) = \log_{10} q_e - \frac{k_{ad} t}{2.203} \qquad\qquad 4$$

where, $q_e$ and q are the amounts of either naphthalene or pyrene adsorbed (mg/g) at equilibrium and at a given time, respectively and $k_{ad}$ is the rate constant of adsorption.

## 3.0 MATERIALS AND METHODS

### 3.1 Materials

The orange peels used as adsorbent was freshly obtained from an orange fruit market located at Uselu, Benin city, Edo state, Nigeria. Naphthalene and pyrene with minimum assay of 99% purchased from Griffin and George Loughborough, England and FL laboratories respectively were obtained from the Chemical Engineering Laboratory, University of Benin, Benin City. Ethanol of boiling point 78$^{\circ}$C and 99% alcohol strength was purchased from Alconi Nigeria Limited Lagos. The instruments used include mechanical agitator (model THZ 82), analytical weighing balance (model-PM 4800) and spectrophotometer (model-T70 UV/VIS). Distilled water was used for sample preparation and dilution.

## 3.2 METHODS

### 3.2.1 Preparation of standard solution of naphthalene and pyrene

1g of Naphthalene was measured and dissolved in 1000ml of ethanol. The solution was thereafter stirred to obtain a homogenous solution.

### 3.2.2 Preparation of the adsorbent

The ripe orange peels were cut into small sizes, sun dried for four days in order to reduce the moisture content and to make them brittle for grinding and reduction to the desired particle size. The dried sample was thereafter stored in an air tight container.

### 3.2.3 Effect of varying concentration of adsorbent on adsorption of naphthalene and pyrene

50, 100, 150, 200, 250 and 300mg/l of the adsorbate (pyrene or naphthalene) was prepared from the standard solution. 2g of the adsorbent (orange peels) was measured and added into each of the six samples solution of ripe orange peels in ethanol was also prepared. The blank solution and the six sample solution were agitated in a mechanical shaker for 2 hours. Subsequently, the solutions were filtered to remove the adsorbent. The equilibrium concentration of pyrene and naphthalene from the filtrate was measured using the UV spectrophotometer.

### 3.2.4 Effect of agitation time on the adsorption of pyrene and naphthalene

50mls of the 100mg/l standard solution of naphthalene and pyrene were measured into six conical flasks. 2g of the ground ripe orange peels was measured and added to the samples. The samples were placed in the mechanical shaker for agitation. After 20mins, the first sample was removed, and it was immediately filtered to remove the adsorbent. This was continued [at intervals of 20mins] until all six samples were exhausted. The equilibrium concentration of the effluent solutions (naphthalene and pyrene) was measured using the UV spectrophotometer.

### 3.2.5 Effect of varying particle sizes on the adsorption of pyrene and naphthalene

2g of the adsorbent of varying particle sizes (0.075, 0.15, 0.30, 0.60, 1.2, 1.6 and 2.0mm) were measured and added to 50ml standard solution of naphthalene and pyrene already contained in seven different conical flasks. The conical flasks were agitated in the mechanical shaker for 2 hours. Subsequently the solutions were removed and filtered to remove the adsorbent. The equilibrium concentration of naphthalene and pyrene was determined using the spectrophotometer.

### 3.2.6 Effect of varying adsorbent dosage on the adsorption of pyrene and naphthalene

Using the same volume of the standard aqueous solution as in sections 3.2.4 and 3.2.5, varying dose of the adsorbent was measured from 1.0-10g into 10 conical flasks, and was agitated for 2 hours and later filtered. The amount of pyrene and naphthalene

removed was determined by using the UV spectrophotometer.

## 4.0 RESULTS AND DISCUSSION

The partitioning of naphthalene and pyrene between the solid (ripe orange peels) and the aqueous phases are described using the adsorption isotherms presented in Figs. 1-4. The effects of varying

experimental conditions on the adsorption of pyrene and naphthalene are shown in Figs. 5-10.

**Effect of varying concentration on the adsorption of pyrene and naphthalene**

The effect of the variation of concentration of pyrene and naphthalene in an effluent solution is described by using the Langmuir and Freundlich Isotherm model. These isotherms are graphically represented in Figs. 1-4.
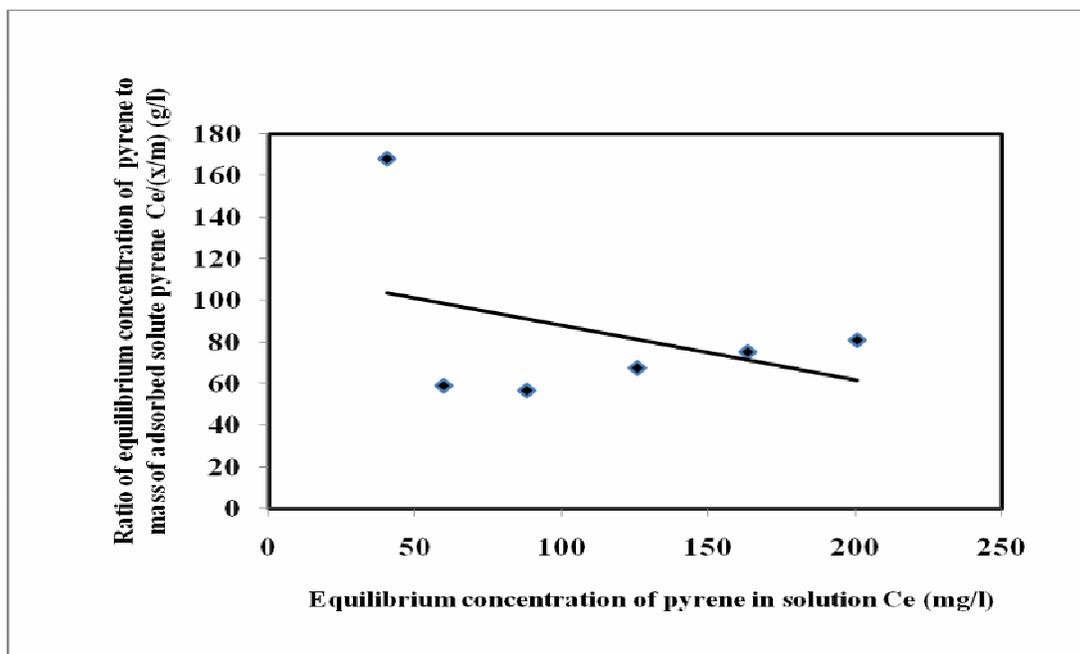


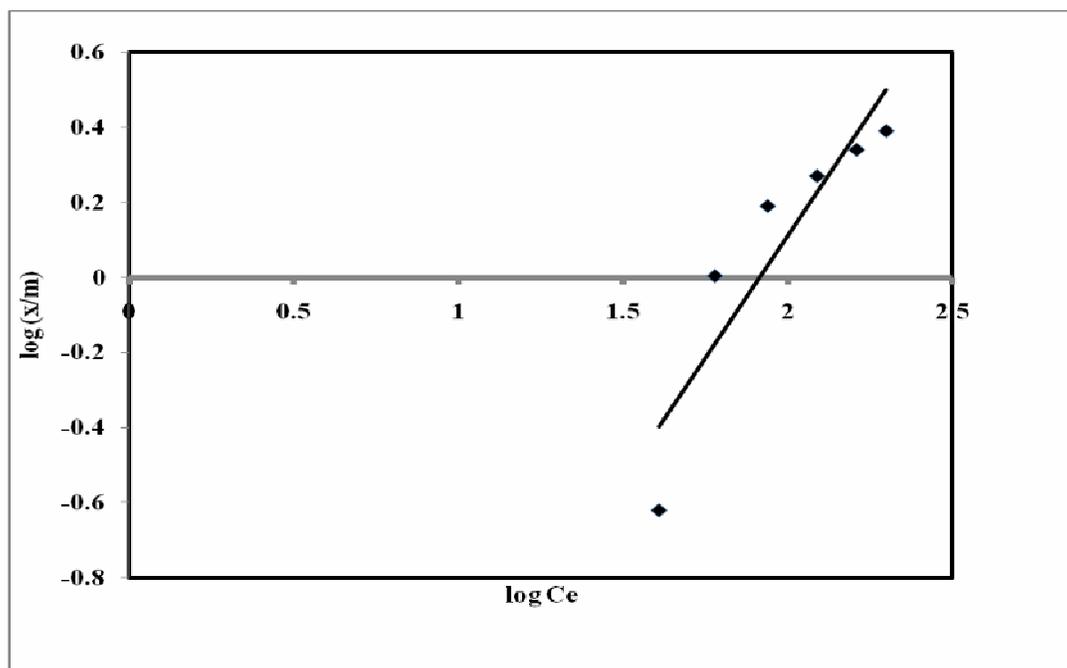**Fig 1: Langmuir plot for the variation of concentration of effluent pyrene solution.**



**Fig 2: Freundlich plot for the variation of concentration effluent pyrene solution**
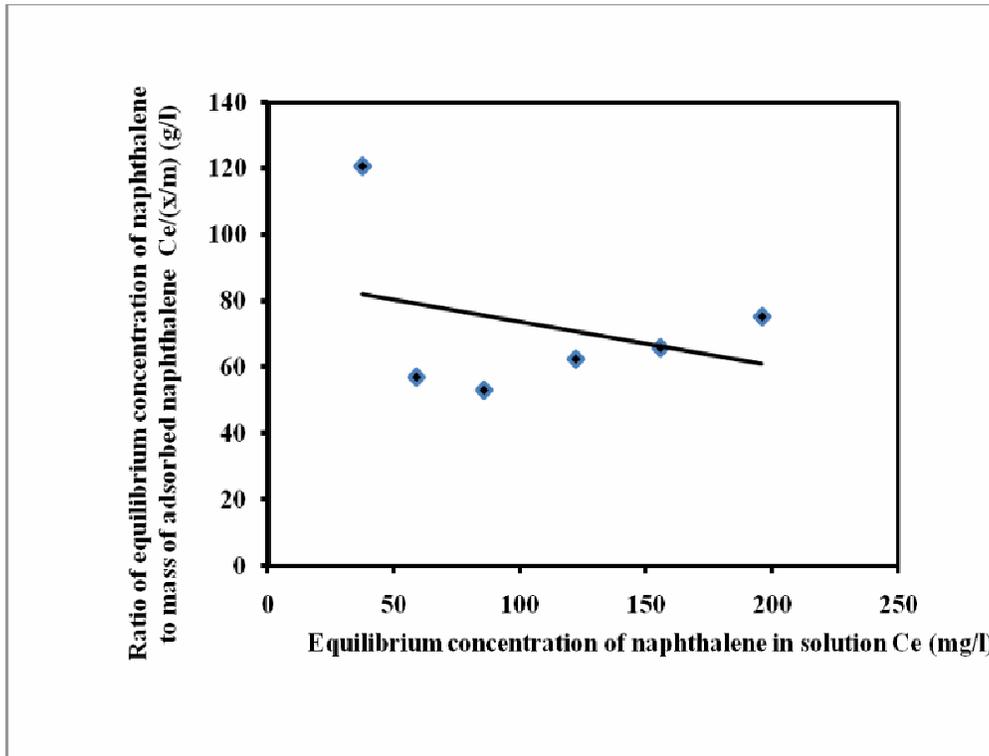
**Fig 3: Langmuir plot for the variation of concentration of effluent naphthalene solution**
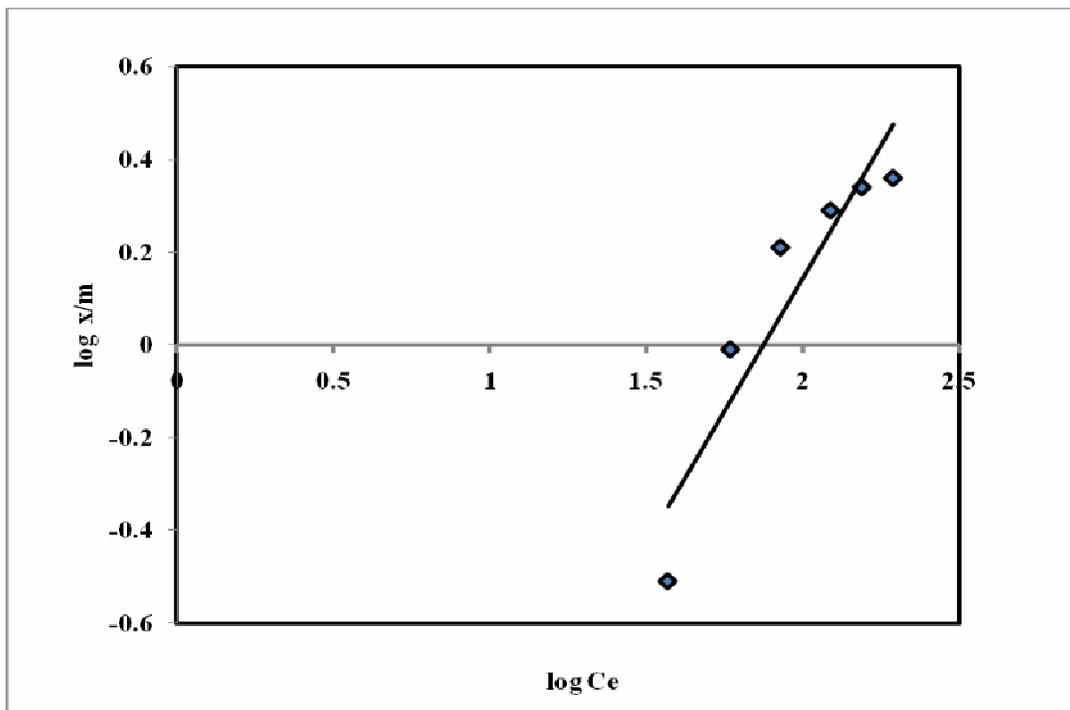


**Fig 4: Freundlich plot for the variation concentration of effluent naphthalene solution**

Figs.1-4 above show that the equilibrium concentration and the amount of pyrene or naphthalene adsorbed increases as the initial effluent concentration increases. The Langmuir and Freundlich isotherm constants are calculated from the slope and intercept of the graphs. The Freundlich isotherm plots in Figs. 2 and 4 gave a linear plot of correlation coefficient 0.864 and 0.826 for naphthalene and pyrene respectively, which imply that the experimental data fit the Freundlich model (Treybal, 1980). The adsorption capacity $Q_o$ (mg/g) and energy of adsorption b (mg$^{-1}$) for naphthalene were obtained as 7.52 and 0.09 respectively while for pyrene, they were 3.82 and 0.03 respectively. The results show that the assumption of uniform binding surface characteristics of the adsorbent is not valid. It thus implies that the adsorbent structure and coverage were non homogeneous. This observation could be attributed to the particle sizes which ranged from 0.075 to 2.0mm used for the adsorption study. This variability could be responsible for the different surface adsorption energies. The implication of these values is that naphthalene has a higher adsorption capacity and energy of adsorption than pyrene, and will therefore, be adsorbed faster than pyrene, thereby resulting in the removal of more naphthalene from solution.

**Effect of varying adsorbent dosage on the adsorption of pyrene and naphthalene**
In studying the effect of increasing adsorbent dosage on percentage (%) removal of the solutes, the profiles in Fig. 5 were observed.
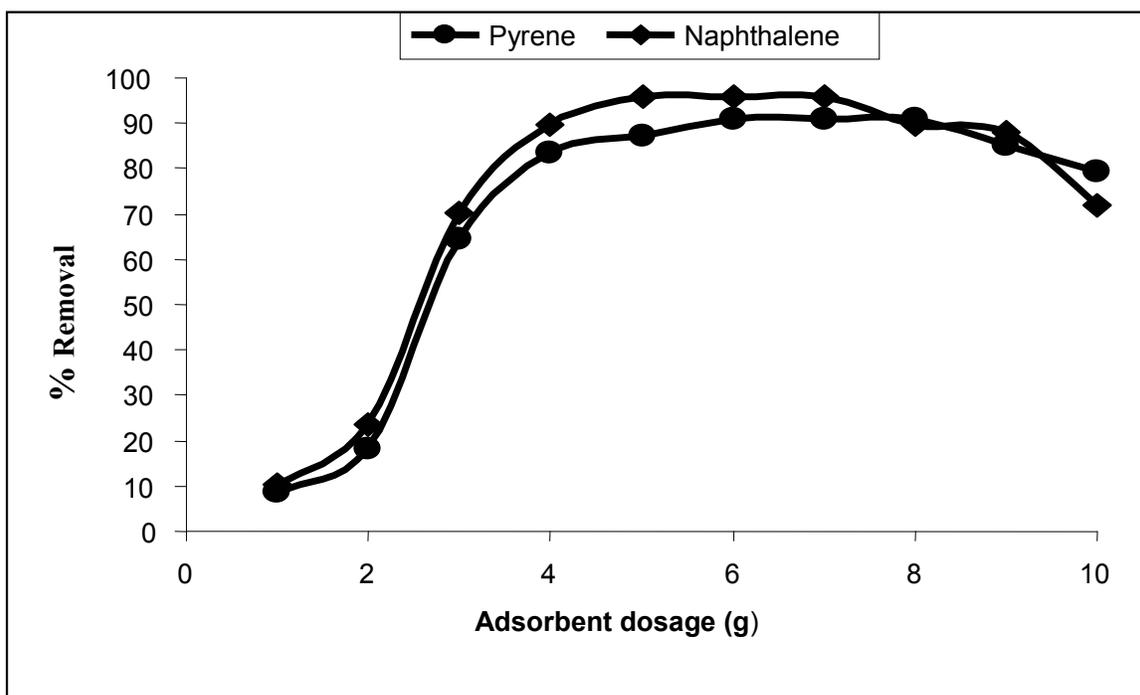


**Fig 5: Effect of adsorbent dosage on the adsorption of pyrene and naphthalene**

Increasing the dosage of the adsorbent in steps of 1g, the % removal from solution gradually increased, with an exponential increase observed when the dosage increased from 2 to 3g for both naphthalene and pyrene. Beyond this loading (3g), the increase in loading drops such that increases above 6g for pyrene and 5g for naphthalene results in no significant increase in % removal. Loadings beyond 8g for pyrene and 7g for naphthalene results in a drop in % removal. The amount of pyrene and naphthalene adsorbed increases as the adsorbent dosage increases and a point is reached beyond which the surface of the adsorbent becomes saturated (equilibrium is attained) and there is a need for regeneration or the input of fresh adsorbent.

**Effect of agitation time on the adsorption of pyrene and naphthalene**
In studying the effect of agitation time on the adsorption of pyrene and naphthalene, the following trends shown in Fig. 6 were observed.
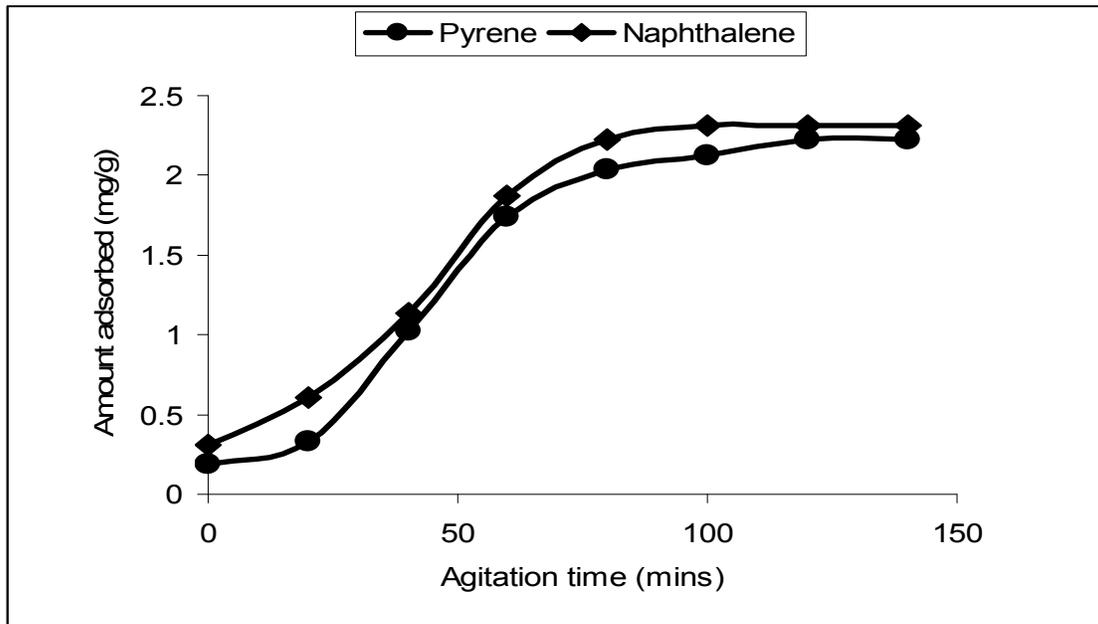
**Fig 6: Effect of agitation time on the adsorption of pyrene and naphthalene**
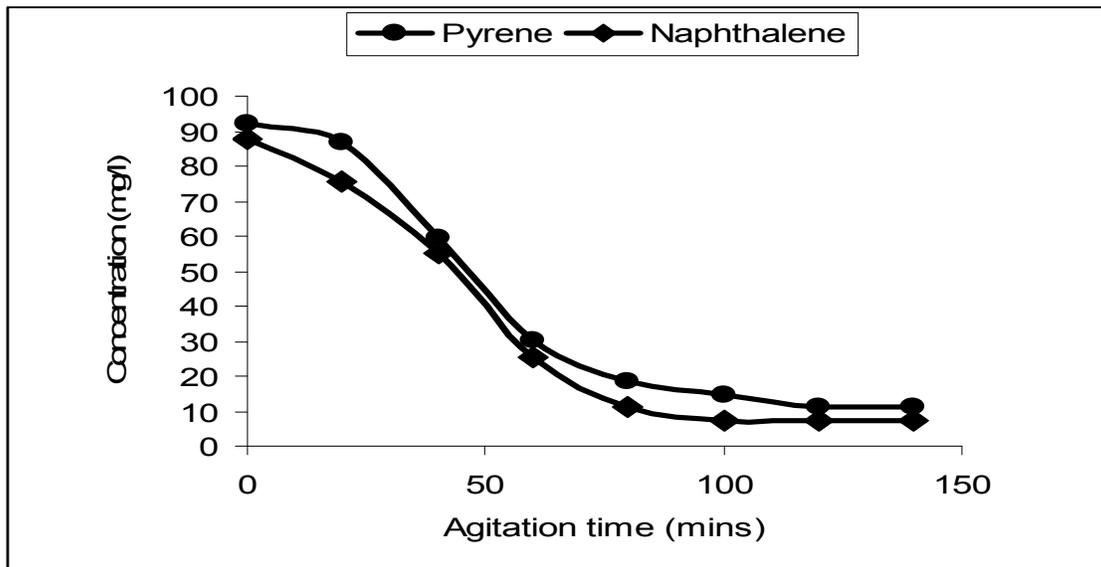


**Fig 7: Adsorption kinetics for the adsorption of pyrene and naphthalene**

The amount of pyrene and naphthalene adsorbed increased as the agitation time increases and an equilibrium time was reached beyond which the extent of amount of removal becomes negligible and in the long run becomes constant.

The batch adsorption kinetic data for naphthalene and pyrene are presented using Fig. 7. The removal of pyrene and naphthalene was rapid at the initial stages of agitation and gradually decreases with lapse of time until saturation. Equilibrium adsorption time for naphthalene was 100mins while for pyrene it was 120mins. The adsorption profile was characterized by a biphasic curve and the curve was observed to be single, smooth and continuous indicating monolayer coverage of pyrene and naphthalene on the outer surface of the adsorbent. Naphthalene has a lower equilibrium time than pyrene due to its low molecular weight and higher solubility. The resultant effect is an adsorption process.

**Effect of particle size on the adsorption of naphthalene and pyrene**

In studying the effect of particle size on the adsorption of pyrene and naphthalene, the trends in Fig. 8 were observed.
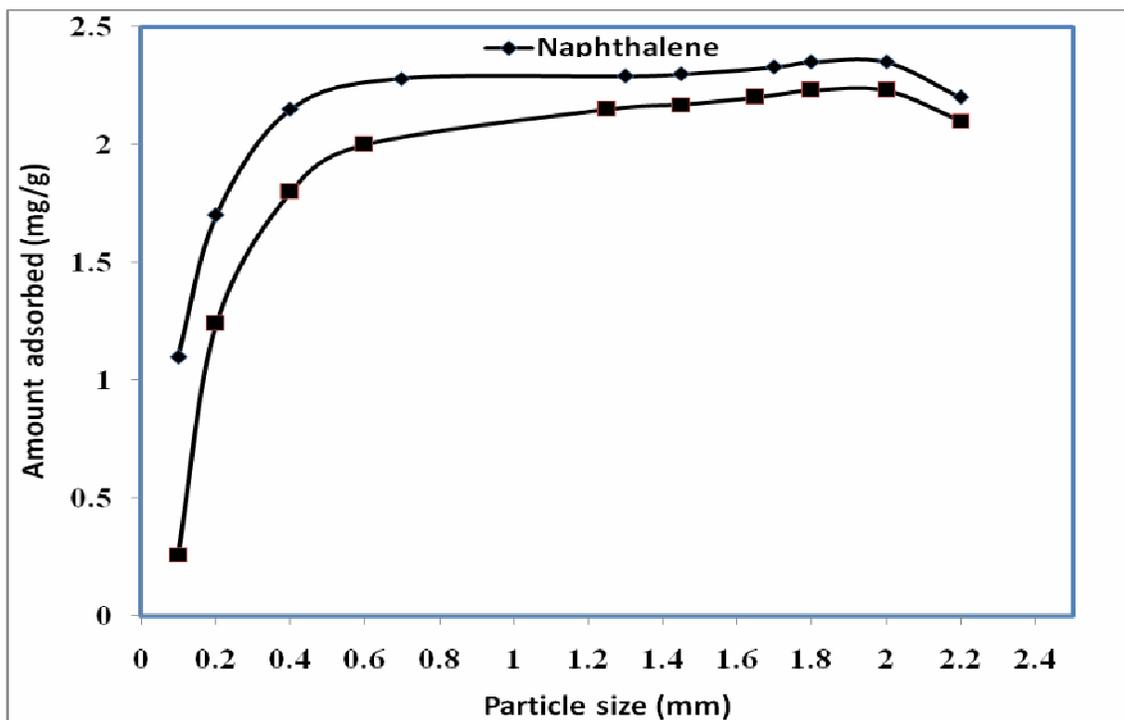
**Fig 8: Effect of varying particle size on the adsorption of pyrene and naphthalene**

The results show that the adsorption of pyrene and naphthalene from an aqueous stream is dependent on the particle size used. Increasing the particle size, increases the amount of pyrene and naphthalene adsorbed. Maximum adsorption was attained at particle size of 1.8mm to 2.0mm and a drop in the amount of contaminant solute was observed in particle size of 2.0mm for both naphthalene and pyrene. Furthermore, at all particle sizes used, the removal of naphthalene was faster than that of pyrene. This is affirmed using the experimental results on the adsorption capacity and energy of adsorption.

**Adsorption rate constant**

The adsorption rate curve for naphthalene and pyrene are shown in the Figs. 9 and 10. The straight line of the Lagergren plot confirms the applicability of the first order rate expression. The experimental batch data was well fitted into the equation as indicated by the high correlation values obtained.
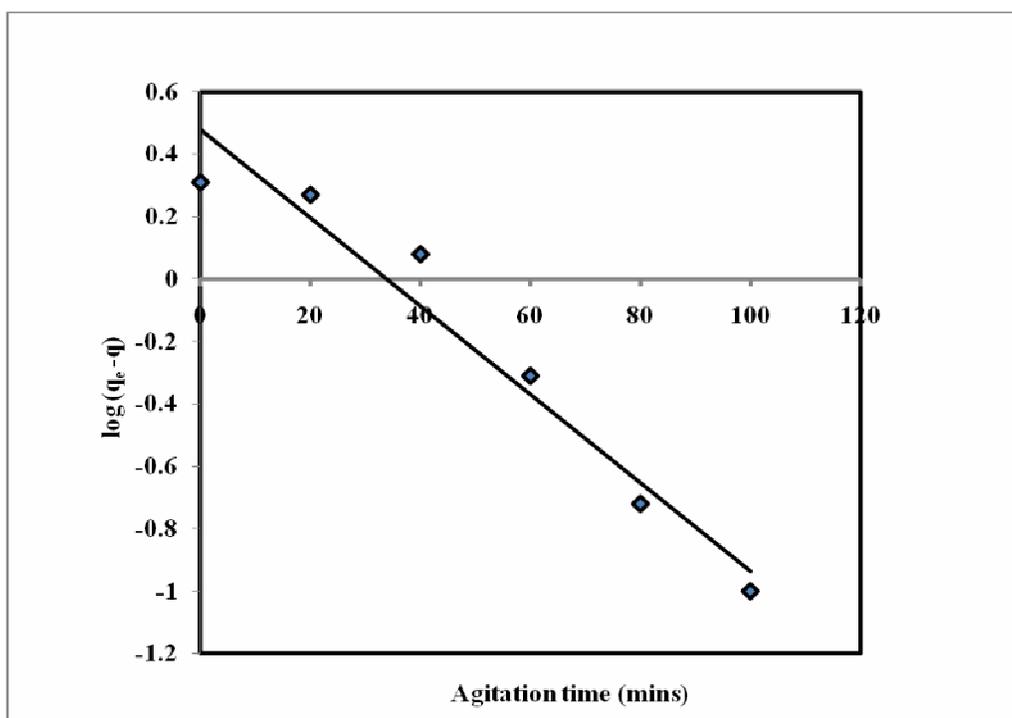


**Fig 9: Lagergren first order rate constant plot for the adsorption of pyrene using ripe orange peels**

From the figures, the rate constant for the adsorption of pyrene from the Lagergren first order equation was 6.1 x

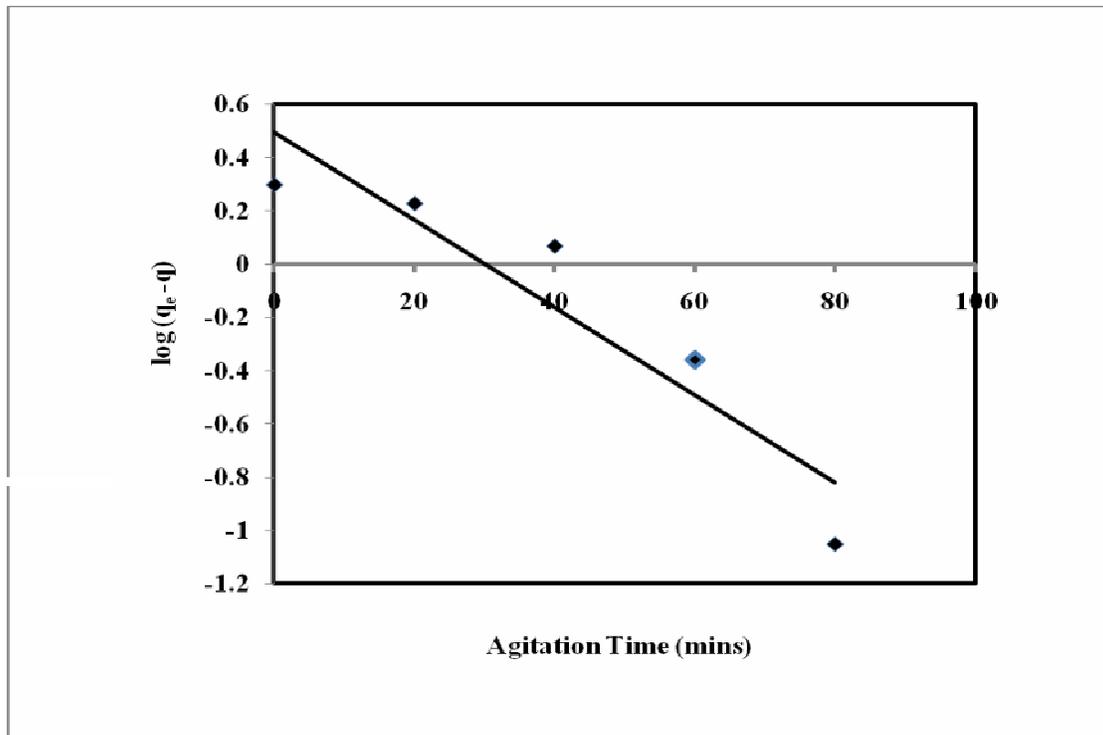$10^{-3}$min$^{-1}$ while that of naphthalene was 7.0 x $10^{-3}$ min$^{-1}$.



**Fig 10: Lagergren first order rate constant plot for the adsorption of naphthalene using ripe orange peels**

This result once again affirms the selective removal of naphthalene from an aqueous solution of the mixture.

**CONCLUSIONS**

From the results obtained it can be concluded that ripe orange peels which is regarded as waste materials can be used as adsorbent for the removal of polycyclic aromatic hydrocarbons like naphthalene and pyrene. The results obtained from the study shows that the equilibrium at the external surface of the adsorbent obeyed Freundlich isotherm model in confirmation to the fact that Freundlich isotherm best explain the adsorption process from solutions.
Increase in the adsorbent dosage also increased the amount of pyrene and naphthalene adsorbed. The removal of naphthalene is more rapid than that of pyrene. This is due to the fact that lower molecular weight compounds adsorb faster than the higher ones. Also, naphthalene has a higher solubility than pyrene. Increase in particle size increases the amount of naphthalene or pyrene removed. The equilibrium adsorption time occurred at 100 minutes for naphthalene and 120mins for pyrene at an initial concentration of 100mg/l.
Naphthalene has a higher adsorption capacity and energy of adsorption with an experimental adsorption rate constant of 7.0 x $10^{-3}$ min$^{-1}$ and 6.1 x $10^{-3}$min$^{-1}$ for pyrene.

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