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KINETIC AND EQUILIBRIUM ISOTHERM OF PESTICIDES (ATRAZINE) ADSORPTION UNTO ACTIVATED CARBON OF CALABASH (*LAGENARIA SICERARIA)*

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ABSTRACT

The adsorption of pesticides (Atrazine) from water onto activated carbon prepared from calabash was investigated. The kinetic and equilibrium study was carried out, and data obtained showed that time duration, the concentration of the solution, the dosage of activated carbon and the pH of the solution greatly influenced the adsorption process. The adsorption kinetic study of the pesticide was done using various models. The result best fits pseudo-second-order using the coefficient regression value (0.9922) and intraparticle diffusion. Equilibrium isotherm data were analysed using the Langmuir isotherm model and Freundlich isotherm model. The result of the regression value provided Freundlich isotherm as the best fit to the experimental data, indicating the presence of heterogeneous layer sorption from the regression value of 0.7294. This study suggested that the activated carbon of calabash as a low-cost material is suitable for the adsorption of pesticides from water. Hence it could be applied as a cheap and effective material in removing pesticides in water bodies or industrial waste before disposal.

KEYWORDS: ***Pesticides, activated carbon, adsorption capacity, isotherm, kinetic study, calabash.***

1. INTRODUCTION

Pesticides are any chemical agent used to kill or control undescribed insects, weeds, rodents, fungi, bacteria or organisms. Chemical pesticides are frequently applied on an agricultural farm to ensure a good harvest. Since the need for food is directly related to population growth, this has led to increased pesticide usage from the mid-1950s to tackle the anticipated food shortage. Water scarcity and insufficient energy resources are expected to occur due to projected population growth expected to hit 9.3 billion by 2050. In recent years, a few hundred organic pollutants have been reported to be potent water contaminating agents [1, 2].

The term "pesticide" is defined by the World Health Organization (WHO) as any chemical substance intended to kill pests (weeds, rodents, insects, and fungus) [3]. Due to the excessive or improper use of pesticides, the rising demand for food production worldwide has produced a significant decline in food quality and severe environmental effects [4, 5], but it has also had an adverse impact on human health. More than 20% of pesticides are estimated to reach non-target species and air, water, and soil. Surface water and groundwater—two significant drinking water sources worldwide— frequently contain traces of these pollutants [6]. The public and authorities are highly concerned about various pesticides and their derivatives in water due to the increased unfavourable health consequences caused by exposure, even at low concentrations (pg/L to ng/L). Pesticides have significantly increased agricultural yields reducing pests and plant infections and preventing insect-borne diseases that affect human health [7, 8]. For instance, since using pesticides, food grain production has increased significantly in many nations. Pesticides have been crucial to those processes, even while productivity increases are credited to various variables (such as fertilizers, better plant varieties, and improved technology). By reducing pests and plant illnesses and battling insect-borne diseases for human health, fewer pesticides have significantly increased agricultural production [7].

Atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine) is a Triazine class herbicide to prevent pre-and post-emergence broadleaf and grassy weeds in crops such sorghum, maize, sugarcane and others [9]. Atrazine remains in the soil for months (although some soils can persist for at least 4 years) and can migrate from soil to groundwater. Once in groundwater, it degrades slowly, primarily through microbial activities. Its effects in humans and animals mainly involve the endocrine system and hormonal imbalance [10]. These pesticides adversely affect aquatic life and the ecosystem, causing biodiversity loss and being carcinogenic in nature [11].

To humans, exposure effects can range from mild skin irritation to congenital disabilities, tumours, genetic changes, blood and nerve disorders, endocrine disruption, coma or death [11]. The known environmental effects have led researchers to put great effort into detecting these pesticides in our environment and the area of removal methods. Much research has reported several methods for removing organic pollutants from water. However, to the best of our knowledge, non has reported on the removal of Atrazine using activated carbon of calabash. The study tends to evaluate the efficiency of this activated carbon of calabash in the removal of Atrazine as a low-cost adsorbent through the determination of its physiochemical properties, morphological study, the study effect of time, pH, concentration and dosage on the adsorption process, as well as the kinetic and equilibrium.

2.0. MATERIALS AND METHODS

2.1. Material collection and preparations.

The sample calabash was purchased from a shop in a local market in Enugu, Enugu State, Nigeria. The calabash was thoroughly washed with water to remove dust, fungus, and other foreign materials. It was sun-dried for 16hrs (4 hrs each day) and then left to dry in the oven at 65°C. It was pulverized with a mortar and pestle and sieved through 30 standard British sieves (BSS sieve). The pesticide (Atrazine) and other chemicals used in this study were purchased from Sigma-Aldrich and were of analytical grade.

2.2. Chemical and thermal activation of the calabash.

A sieved sample of calabash (100 g) was impregnated with 20 % $ZnCl_2$ in the ratio of 1:10 for 24hrs. The slurry was dried in an oven at 80^oC before activation in a muffle furnace at 100°C for 30mins. The resulting carbons were washed with distilled water until neutral pH before oven drying at 105°C for 4hrs.

2.3. Physicochemical characterization of the activated carbon.

2.3.1. Determination of bulk density

The apparent or bulk density was determined using the method as described by Ekpete and Horsefall (2001) and then calculated using;

$$\boldsymbol{BD}_{(g/mol)} = {}^{\boldsymbol{W}}\!/_{\boldsymbol{V}} \qquad \text{------------------------------------}(1)$$

Where W_{mol} = weight of dry materials

V_{net} = volume of dry sample.

BD = bulk density

2.3.2. Determination of pore volume

The pore volume was determined by the method as described by Kavaz et al. [12], thus calculated using;

$$\mathbf{P} = \frac{W_1 - W_0}{D} \qquad \text{-----------------------------}(2)$$

Where P = pore volume

W_1 = final weight of the sample

W_0 = initial weight of the sample

D = density of water

2.3.3. Determination of moisture content

A portion of the sample (2g) of each adsorbent was measured into a washed glass and then placed in the oven for 24hrs at 105^0c. The samples were reweighed and recorded, then Calculated using;

$$\mathbf{MC} = \frac{W_1 - W_0}{W_0} \; X \; \frac{100}{1} \qquad \text{---------------------------}(3)$$

Where Mc = moisture content

W_1 = weight after drying

W_0 = weight before drying

2.3.4. Determination of pH

The pH of the sample was determined using the method described by Aigbe et al. with slight modification [13]. In 1.5 ml of de-ionized water, 0.5 g of the material was weighed and dissolved. To achieve sufficient sample dilution, the liquid was heated and agitated for three minutes using a digital pH meter. The pH of the solution was measured after filtering and removal.

2.3.5. The morphological study of the activated carbon

The morphological analysis was also carried out in Zaira in Nigeria at 10.00 kv for the samples of activated carbon before and after the adsorption study.

2.4. Adsorption equilibrium study

The batch adsorption experiments were carried out in 100ml Erlenmeyer flasks where 1g of the adsorbent and 50ml of the atrazine solutions of (50-300mg/l) were added, and the pH of the solution was adjusted to 6. The flasks were placed on a shaker at 120rpm at 30^0c for 40 mins. The concentration of the atrazine in the solution after equilibrium was measured using UV-Visible spectrophotometer model 752 at 460 nm. The amount of adsorption at equilibrium q_e(mg/g) is then calculated by:

$$q_e = \frac{(C_o - C_e)V}{W} \quad \text{------------------------------------}(6)$$

Where C_o = initial concentration

C_e = concentration at equilibrium

V = volume of solution in L

W = weight of dry adsorbent in g

q_e = absorption capacity

To study the effect of pH, the absorbent with weight (0.1g), temperature(30^oc), and time of 40 mins were kept constant, and the experiments were carried out by varying pH between 2-10. In the same way, the effects of time and dosage were studied by the varying time between (5-40mins) and weights of 0.1 g – 0.5 g, respectively, while leaving other variables constant.

3. RESULTS AND DISCUSSIONS

3.1. Analysis of physicochemical properties.

The results, as shown in Table 1 below, depicts the physiochemical properties of the activated carbon, which gives an insight into the adsorption efficiency of the activated carbon. From the table, it was observed that the bulk density for AC calabash (0.306 g/cm^3) is slightly higher than the values reported by the American Water Works Association (AWWA) [14], giving the lower limit of bulk density as 0.25 g/cm^3 for GAC, but compared with the value of 0.5 g/cm^3 for decolourization of sugar as reported by Khadija et al. [15] and closer to the AC of corncob from Nwadiogbu et al. [16], 0.327 g/cm^3. The pore volume of the calabash is 1.003 ml, possibly due to the pore structure and the nature of the walnut material. The observed result from this study is slightly higher than the 1.10 ml value reported by Madu and Lajide [17] for melon husk. The pH results for calabash as shown in Table 1 below. The pH for calabash (7.15) was observed to be slightly neutral. This indicates that the AC was prepared properly. The result obtained from this study was similar to the values 7.8 and 8.9 as reported by Nwadiogbu et al. respectively [17, 16]. The moisture content was 0.363, which could be due to the longer time of carbonization of the calabash and indicates that the carbon was prepared properly. The result showed much higher values for melon husk (27.61%) and doum fruits (2.2%) as reported by Mdeni et al. [3].

Table 1: physicochemical properties of the activated carbon

PROPERTIES	CALABASH SHELLS
PORE VOLUME	1.003
MOISTURE %	0.363
BULK DENSITY	0.306
pH	7.15

3.2. Effect of Time

The result obtained for the study of the effect of time, as shown in Figure 1, showed that the adsorption capacity increased from 36500 mg/g to 40835 mg/g for calabash with increased contact time from 5 mins to 50 mins. This increase in the activated carbon adsorption capacity could be due to the abundance and availability of the active site. Similar patterns were reported by Brenes et al. [18] in the study of adsorption capacities for Organochlorine pesticides using modified unsaturated polyester resin which showed increased adsorption with the increased contact time. Also, Ramesh observed that metal ions or adsorption removal increase with contact time [19].

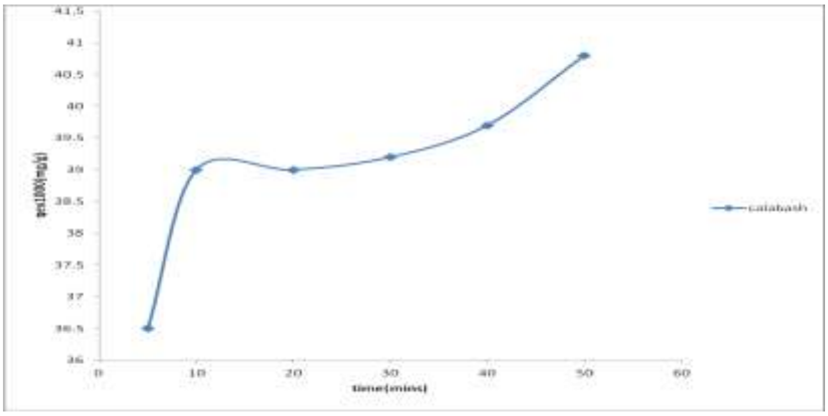

Figure 1. Graph showing the study of the effect of time.

3.3. Effect of concentration

This study was done by varying the initial concentration of Atrazine in solution from 50 mg/l – 250 mg/l at 0.1g of the absorbent. The result showed an increase in percentage removal from 66.66 to 86.00 and adsorption capacity of 16665 to 107500 as the concentration increased, as shown in Figure 2. This means it would take longer to attain equilibrium, revealing that Ac calabash would be a promising adsorbent. These findings are in line with Akash et al. result, which depicts that adsorption occurs in the entire range of concentrations [20].

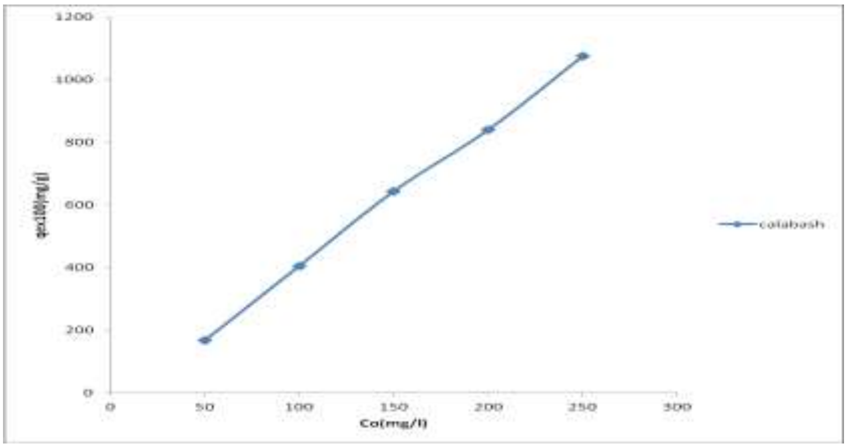

Figure 2. Graph showing the study of the effect of concentration

3.5. Effect of pH

The result for the effect of the pH on the adsorption study of Atrazine, as shown in Figure 3 below, reveals a steady increase in the percentage removal and adsorption capacity from pH 2 (61.4%, 30700 mg/g for calabash) to pH 8 (79%, 39500 mg/g for calabash) before experiencing a decrease in percentage removal and adsorption. The adsorption can be affected by the change in pH of the solution because this parameter affects the degree of ionization of the pesticides and the surface properties of the sorbents. When the pH of a solution is increased, the positive charges in the solution interface decrease and the absorbent surface appears to be negatively charged.

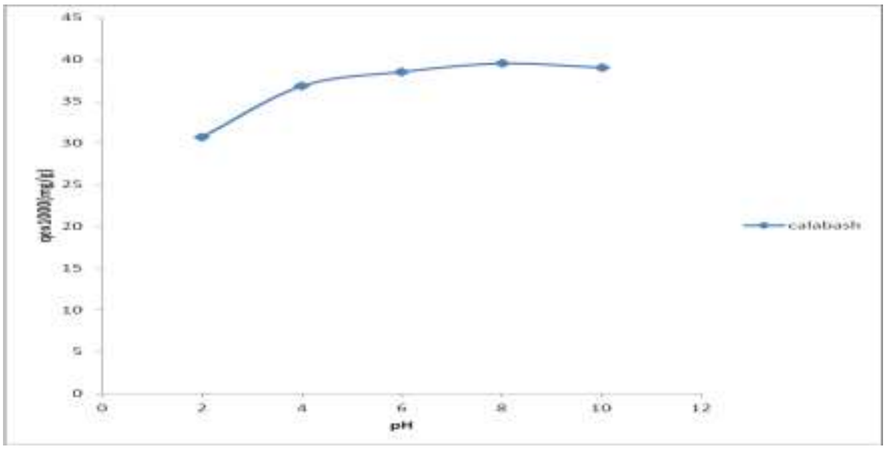

Figure 3. Graph showing the study of the effect of pH

3.6. Effect of dosage

The study result is presented in Figure 4, where it was observed that there was a steady increase in % the removal of the atrazine from solution (69% - 78%) with a steady decrease in the adsorption capacities for (34835 mg/g – 7800mg/g). The increment in % removal at high dosage is expected due to increased adsorbent surface area and availability of more adsorption sites. Similar results were reported by Dehghani et al. in the removal of 2,4 – Dichlorophenolyxacetic acid (2,4 D) herbicide in the aqueous phase using modified granular activated carbon [21].

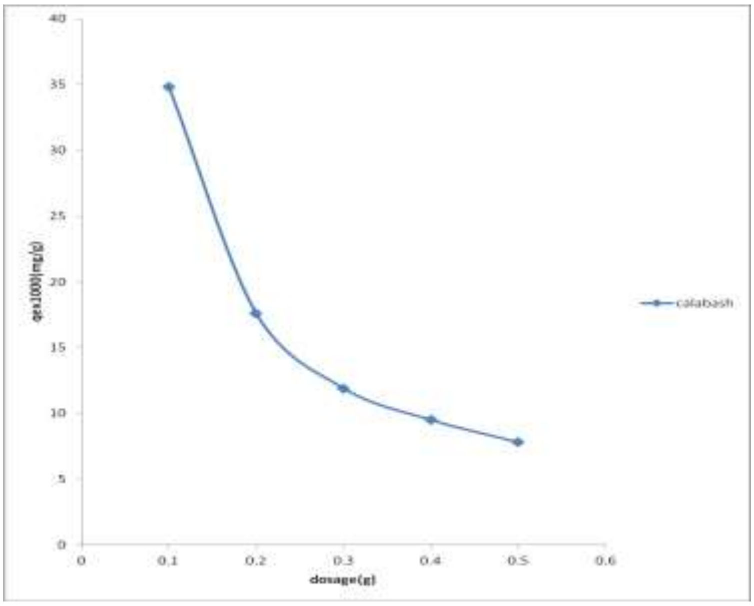

Figure 4. Graph showing the study of the effect of dosage.

3.7. Morphological studies

The Scanning Electron Microscopy (SEM) of the activated carbons before and after adsorption was carried out at 10.00 kv. The obtained image revealed the AC's morphological structure and the adhesion of atrazine pesticide to the surface of the activated carbon, as shown in Figure 5 and Figure 6 below. SEM image reveals the presence of many micropores, meso pores and large gullies as well as shattered structural formation, but after adsorption, as shown in Figure 6 unveiled, a lesser amount of gullies, more covered micro and meso pore and a more arranged structural formation which could be due to the pesticides adsorbed by the activated carbon, this could imply that AC calabash would have many pores to accommodate the pesticide during adsorption process making it an excellent adsorbent. Further analysis of the AC SEM image after adsorption showed that most of those pores and cracks had been covered up with the pesticides.

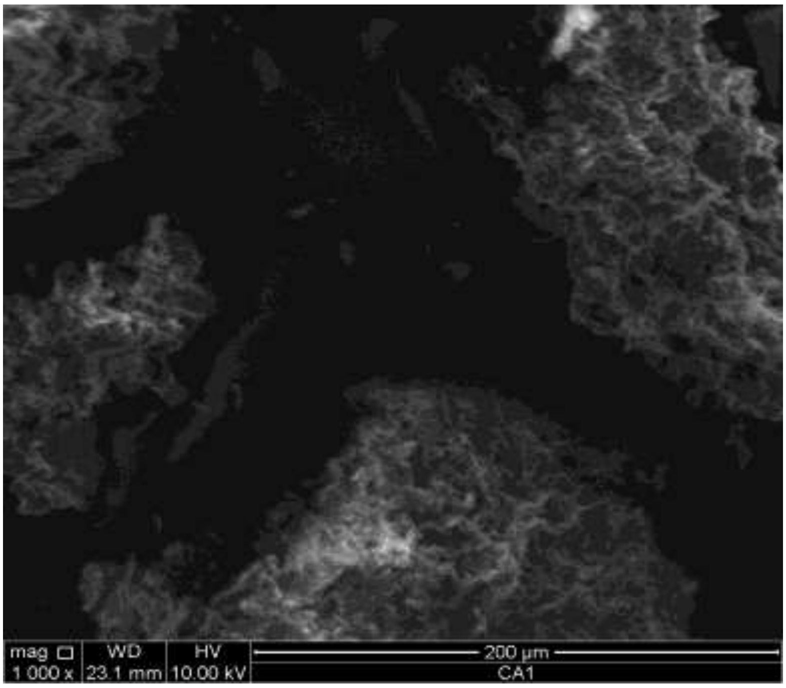

Figure 5. SEM image of the AC of calabash before the adsorption process.

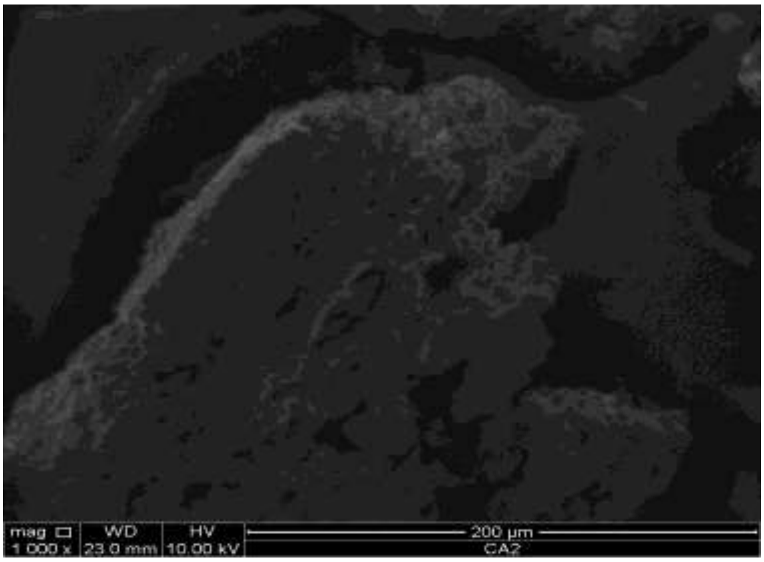

Figure 6. SEM image of AC of calabash after adsorption process.

3.8. Adsorption kinetic study

The kinetic study of adsorption was done using four standard models, which would help analyze the rate and mechanism of atrazine absorption. They are; the Langergen pseudo-first-order model, Pseudo second order model, Intraparticle diffusion model and Liquid film diffusion model. Pseudo first order, also called Langergen first order rate, has an equation expressed as; Dawodu and Akpomie [22].

$$In\,(q_e - q_t) = Inq_e - K_1 t \quad \text{-------------------------(7).}$$

Where q_t (mg/g) is the amount of atrazine adsorbed at time t (mins) and q_e is the amount of atrazine adsorbed at equilibrium. The graph of In($q_e - q_t$) was plotted against time t (mins), and the slope and intercept were obtained as a function of this graph to generate the rate constant q_e and other values, as shown in Table 2 below.

The pseudo-second-order model can be expressed as; Mackay (1998)

$$T/q_t = \frac{1}{K_2 q_e^2} + t/q_e \quad \text{------------------------------------ (8)}$$

Where k_2 (g/mg s^{-1}) is the rate constant of this pseudo-second-order, q_e and k_2 values were calculated from the slope and intercept of a linear plot of t/q_t against time t (mins) and the values generated are listed in Table 2 below.

Analyzing the values generated, it was observed that the adsorption study agrees with the pseudo-second-order model as the q_e calculated for AC calabash (50000 mg/g) are closer to the q_e experimental for AC calabash (40835 mg/g) when compared with those obtained as q_e calculated for AC calabash (3535.5 mg/g) from the pseudo-first-order model. The coefficient of regression (R^2) obtained from the pseudo-second-order model is 0.9922, compared to the R2 values for the pseudo-first-order, which is 0.7026. Therefore, we can analytically conclude that the data obtained best fits pseudo-second order and the observed high rate constants of each sorption process appear to be controlled by the chemisorption process [23, 2]. Similar results were reported by Fontecha-Ca'mara et al. [24] for the kinetic of diuron and amitrole adsorption from aqueous solutions onto activated carbon and Igwe et al. [25, 26] in the kinetic and equilibrium isotherms of pesticides adsorption onto Boiler Fly Ash. Most studies on the sorption process are said to take place by a multi-step mechanism consisting of; Diffusion across the liquid film surrounding the solid particles, Diffusion within the particles itself assuming a pore diffusion mechanism (intraparticle diffusion) and Physical or chemical adsorption at a sorption site [25]. The Intraparticle diffusion model can be expressed as [27, 28].

$$q_t = K_d . t^{1/2} + C \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Where k_d($mg/gs^{1/2}$) is the rate constant and the slope obtained from a plot of q_t against $t^{1/2}$ and C is the intercept which indicates the presence of the boundary layer effect. Intraparticle diffusion is the rate-determining step when the plot is linear and passes through the Origin (Dawodu et al.; 2014) and when the intercept is more significant, it shows that the surface sorption, which contributes more to the rate-determining step, is greater [16, 29]. Results obtained from the plot of q_t against $t^{1/2}$ are shown in Table 2 below, which indicates the R^2 valve of 0.7863 for AC calabash with a non-zero intercept of 35.783. This suggests that the R^2 value is close to 1, and AC calabash had a high regression value indicating the intraparticle diffusion mechanism. In addition, the presence of a non-zero intercept suggests a boundary layer effect confirming further the occurrence of surface sorption, meaning that other rate-limiting steps were involved. It should be noted that deviation from the origin indicates differences in mass transfer between the initial and final stages of the sorption process [30, 31].

Another important mechanism involved in the movement of the adsorbate from the liquid phase to the solid phase is the liquid film diffusion which its equation can be expressed as; (Tatfarel and Rubio; 2009).

$$\ln(1 - F) = -K_{fd} . t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Where F is the fractional attainment of equilibrium obtained by this, q_t/q_e and K_{fd} ($meq^{-1}s^{1/2}$) is the rate constant derived from a plot of In (1-F) against t. The values obtained as shown in Table 2 below indicate a very close range of R^2 values between those obtained from intraparticle diffusion and liquid film diffusion, implying that both surface sorption and penetration into the material's pore occurred almost the same rate, but more penetration into the material.

Table 2: Values obtained in the application of various kinetic models.

KINETIC MODEL	CALABASH SHELL
q_e exp (mg/g)	40835
Pseudo first order	
q_e calcu (mg/g)	3535.5
K_1 (s^{-1})	0.0282
R^2	0.7026
Pseudo 2nd order	
q_e calc (mg/g)	50000
K_2 (s^{-1})	1.333333e-5
R^2	0.9922
Intraparticle diffusion	
Kd (meq $g^{-1}s^{1/2}$)	0.6777
R^2	0.7863
C	35.783
Liquid film diffusion	
Ked (meq g^{-1} $s^{1/2}$)	0.0282
R^2	0.701

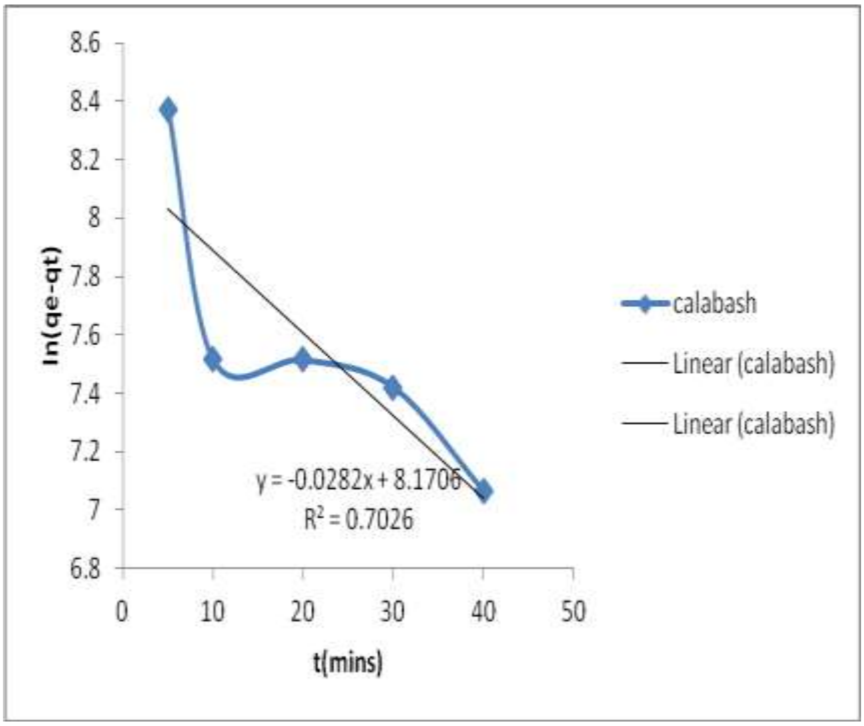

Figure 7. Graph showing pseudo-first order.

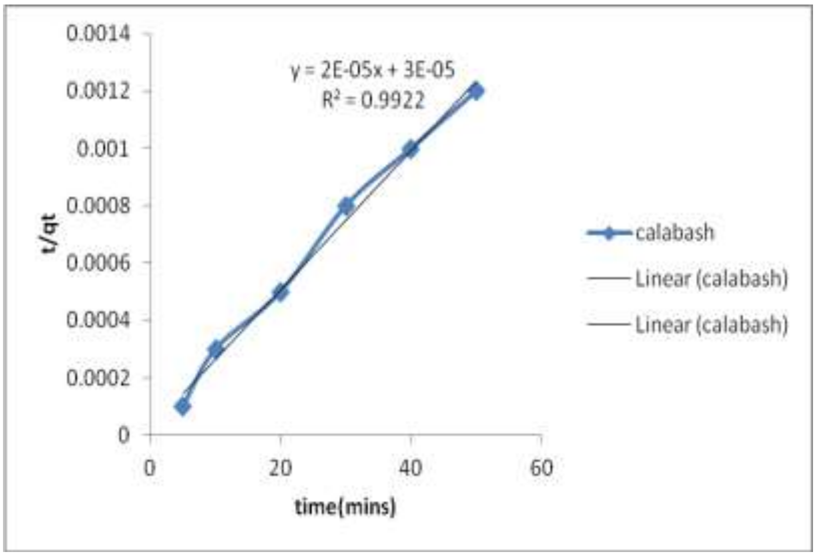

Figure. 8. linear plot of t/q_t against T(mins) showing pseudo 2nd order.

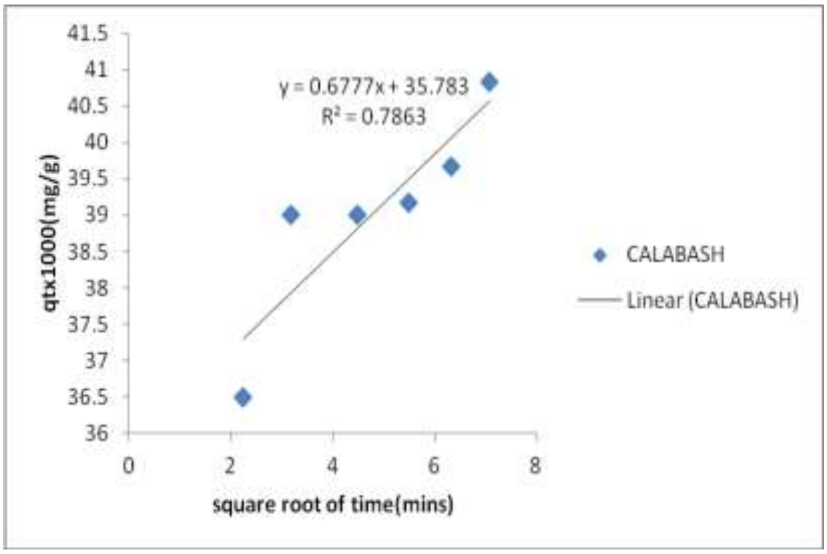

Figure 9. A linear plot showing the intraparticle diffusion model.

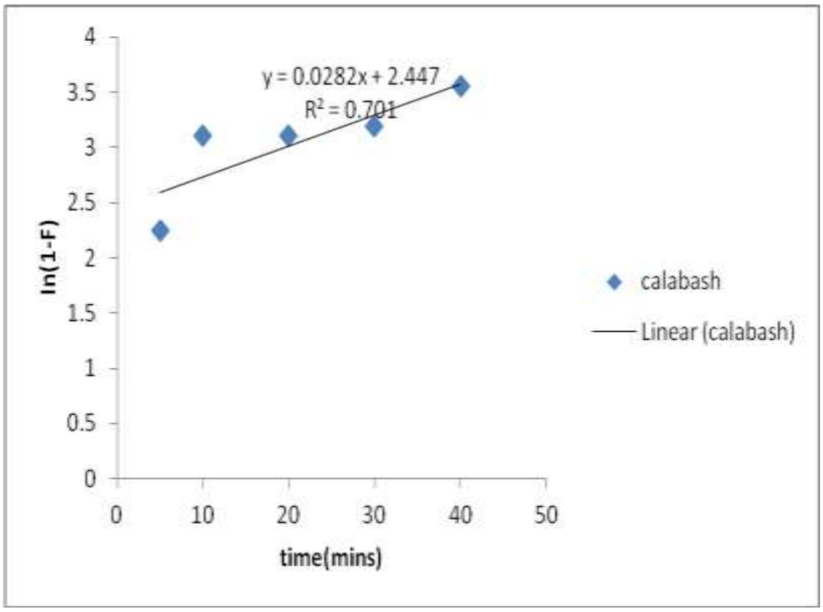

Figure 10. A linear plot showing the liquid film diffusion model.

3.9. Equilibrium isotherm study

The Langmuir and Freundlich equilibrium models were studied extensively to understand the relationship between the amount of adsorbate removed from the liquid phase and the unit mass of the adsorbent at constant temperature and varying dosage. The equilibrium parameters obtained can provide helpful information on the adsorption mechanism, surface properties and affinity of the adsorbent [16]. The Langmuir isotherm model was used to describe the adsorption phenomena and is based on the assumption that adsorption occurs uniformly on the active sites of absorbent. Also, once an adsorbate occupies an area, no further adsorption can occur at that site [16]. This model can be expressed as follows;

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (11)$$

Where q_o (mg/g) is the equilibrium monolayer adsorption capacity of the adsorbent b is the Langmuir adsorption constant (L/mg) related to the energy of adsorption, which quantitatively shows the affinity between the adsorbate and adsorbent. A graph of C_e/q_o is plotted against C_e to obtain $1/q_o$ as the slope and $1/q_ob$ as the intercept. From table 3 below, the coefficient of the regression (R^2) was 0.692 for AC calabash indicating great derivation from 1, which implies that it is not a good fit for monolayer adsorption isotherm. The separation factor R_L in this model is expressed as;

$$R_l = \frac{1}{1+bC_0} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (12)$$

Where C_o is the initial concentration of atrazine in mg/l, this R_L gives information regarding the nature of the adsorption process, i.e. when $R_l = 0$, adsorption can be considered irreversible when 0‹ R_L ‹ 1, adsorption is considered favourable, but when $R_L = 0$ or R_L ›1 adsorption is considered unfavourable [20]. In this study, the Langmuir R_L value is 0.00029 for AC calabash. The R_L value is greater than zero and less than 1, implying that the adsorption process is favourable. Freundlich model was studied to determine non-ideal sorption on the heterogeneous surface, and it can be expressed as [22];

$$\ln q_e = \ln K_f + \left(1/n\right) \ln C_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

K_f (mg/g) $(\mathrm{mg/L})^{1/n}$ and 1/n are the Freundlich adsorption capacity and intensity of the adsorbents, respectively. Table 3 below shows the values for the constants and R^2 generated from a linear plot of Inq_e as a function of InC_e where both slope and intercept were also obtained. The regression R^2 was 0.7294 for AC calabash, which is higher than the R^2 value obtained using the Langmuir isotherm model. This result indicates that the Freundlich isotherm model is a better fit in describing the sorption efficiency and further indicates heterogeneity of the adsorption process.

Table 3: Values obtained in the application of various isotherm models.

ISOTHERM MODELS	CALABASH SHELL
LANGMUIR	
q_o	5000
B	34
R_L	0.00029
R^2	0.692
FREUNDLICH	
K_f	9.0821
1/n	3.585
R^2	0.7294

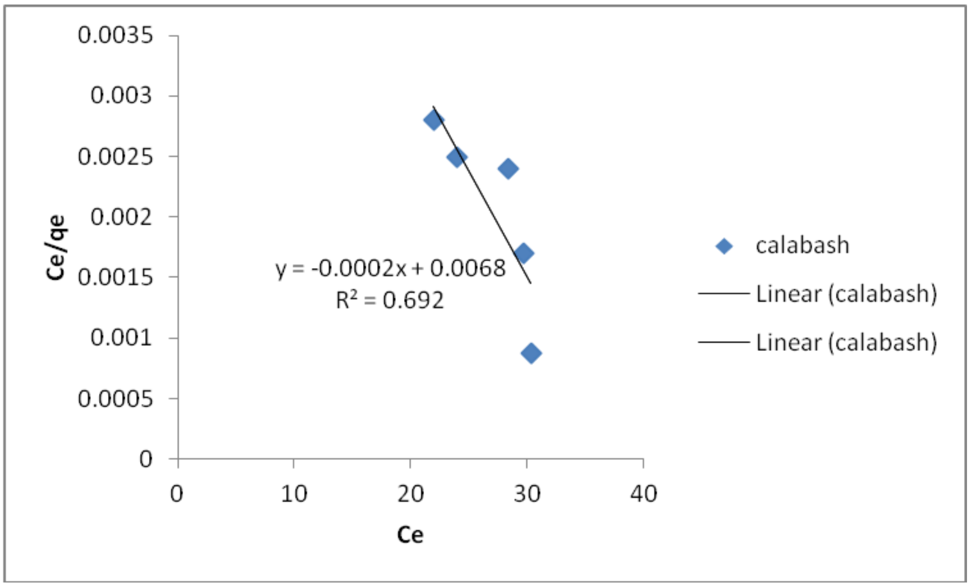

Figure 11: A linear plot showing the Langmuir model on AC calabash.

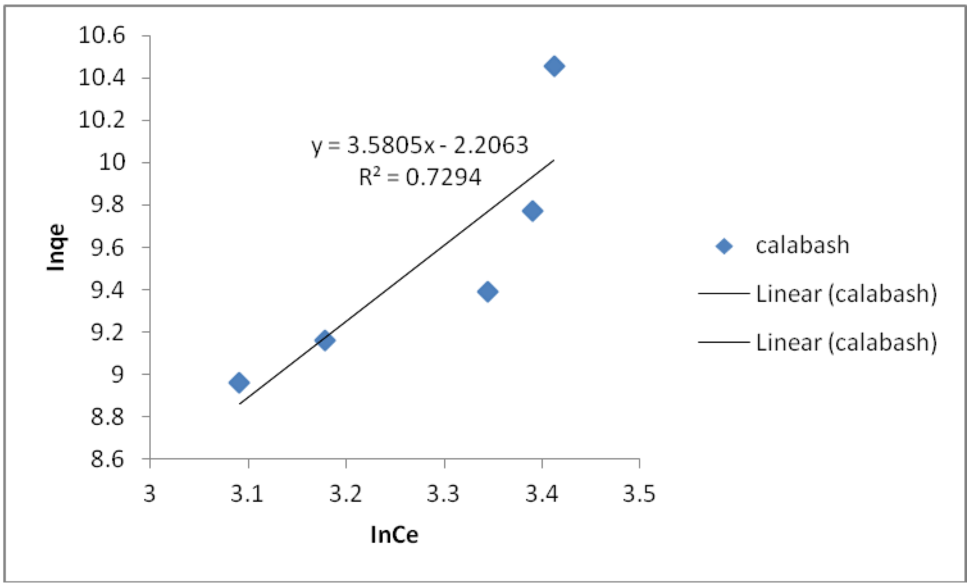

Figure 12: A linear plot showing the Freundlich model on AC calabash.

4. CONCLUSION

This study evaluated the efficiency of low-cost prepared activated carbon from calabash for adsorption of pesticides (Atrazine) through the proper evaluation of its physicochemical properties, the influence of operational conditions such as; pH of the solution, dosage of AC, the concentration of solution and timing of the process. The adsorption kinetic study result shows that the model follows pseudo-second-order and indicates intraparticle diffusion. The Langmuir and Freundlich isotherm model was studied to determine the equilibrium of the adsorption process. The results obtained best fit the Freundlich isotherm model, depicting heterogeneity of the adsorption process. Hence, using this activated carbon for adsorption of pesticides is feasible, cheap and eco-friendly. It should therefore be developed for use in the removal of pesticide pollution.

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