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Kinetic and thermodynamic models for the removal of amino-phenol (dye) from aqueous solutions using groundnut *(Arachis hypogea)* shells as the biomass

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ABSTRACT

The sorption of amino-phenol (dye) from aqueous solution using groundnut (Arachis hypogea) shells via kinetic and thermodynamic approaches has been investigated. From the various experimental parameters analyzed, the amount of dye adsorbed increased from 0.202mg/g-0.218mg/g as the adsorbent dosage was increased from 2-6g.In a similar manner, the amount of dye adsorbed was increased from 0.l9lmg/g-0.2l0mg/g with increases in contact time from 20- 100mins. Also, when the operating temperature was increased from 30°C to 70°C,the the amount of dye adsorbed increased from 0.207mg/g-0.2l0mg/g. The adsorption capacity increased from 0.186mg/g to 1.028mg/g with an increase in concentration of dye from l0mg/g-50mg/g. While examining the bio-sorption efficiency, Langmuir and Freundlich models were used. The coefficient of determination (R^2) for both isotherms were 0.996 and 0.994 respectively. Pseudo-first order kinetics and Pseudo-second order kinetics were used to analyze the experimental data in which the rate constants k_1 and k_2 were observed to be 0.053 and 1.465 respectively. Thermodynamic parameters like free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of the system were also determined and it was found that the adsorption process was endothermic in nature, non- spontaneous and a reversible isothermal process.

Keywords: Dye adsorption, sorption kinetics and thermodynamics

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INTRODUCTION

Pollution is the burning topic of the modern world. The most dangerous type of the pollution is water pollution .Various toxic metal ions present in industrial effluents are the major sources of the pollution.[1] Industries such as plastic, cosmetics, paper, textile, food and pharmaceuticals, use chemical compounds such as Azo dyes, which are synthetic compounds characterized by the presence of one or more Azo group (-N=N-) bound to aromatic rings. The textile industry is the largest consumer of these products, which accounts for more than 50% of the worlds' dyestuff material [2]

However, the waste discharged from textile industries consist essentially of these dyes. Consequently such discharge into natural bodies of water is undesirable for several reasons. For example, it diminishes the aesthetic quality of water bodies and can also be devastating to the health of its consumers because of its persistence and non-biodegradability characteristics. Also, small concentrations of these dyes in effluent water are highly visible.

Consequently, the removal of colour from effluents containing various kinds of synthetic dyes becomes important [3].

Conventional methods such as ion-exchange, ultra-filtration, chemical precipitation etc., have been used in wastewater treatment, but the complexity and high cost of using these methods have made it necessary to employ the use of non-conventional agricultural by-products. The adsorption method whereby activated carbon is the most widely used adsorbent has been shown to be an effective method for colour removal. It has been widely recognized that dye removed by activated carbon adsorption is due to the surface action between the dye and the functional groups present in the surface of the carbon[4].Due to its high cost, carbon is now prepared from digested sewage and wastes. These materials are easily acquired, effective and cheap. They include the use of maize cob and husk [3], coconut fiber nuts, sugarcane, begasse, orange peals[5], palm fruit particles, sunflowers stalks, barley husk, wood[6], tree fern[7], etc.

Hence in this study, we investigated the use of groundnut *(Arachis hypogea)* shell biomass in the adsorption removal of Azo dyes from aqueous solutions. It is a low cost agro-industrial waste that is common both in the Northern and Southern part of Nigeria. Experimental parameters affecting the adsorption process such as effect of initial dye ion concentration, contact time, adsorbent dosage and temperature were studied. The equilibrium adsorption data were fit into the Langmuir and Freundlich Isotherms, Pseudo – first order and Pseudo – second order equations were considered for data interpretation. Thermodynamic parameters were also estimated in order to study the nature of the system.

MATERIALS AND METHODS

a. Sample Collection and Preparation of the Adsorbent

Groundnuts were bought from Abraka Market in Ethiope East Local Government Area of Delta State, Nigeria. The seeds were removed and the shells were sun-dried for some days. The dried samples were pounded and sieved using 450nm sieve. The sieved adsorbent was stored in a plastic container for analyses.

b. Preparation of Dye Solution

The dye (Amino-Phenol) used in this study was obtained from a commercial market without further purification. The dye stock solution was prepared by dissolving 10mg of dye in 1 liter of water.

EXPERIMENTAL PROCEDURES

a. Effect of Dye Ion concentration on Adsorption

The experiment on the effect of the dye ion concentration on adsorption was performed according to the previous works of[8].Several standard dye solutions of 10, 20, 30, 40 and 50mg/l were prepared. 50m1 of each of the solution was added to accurately weighed 2±0.0lg adsorbent in five different conical flasks and agitated for 20 minutes. At the end of the time, the suspension was filtered using Whatman No. 1 filter paper, then centrifuged. The dye in concentration was determined using U-V Spectrophotometer.

b. Effect of Contact Time on Adsorption

The experiment on the effect of contact time on the adsorption of the dye ion by the groundnut shell adsorbent was performed according to the previous works of[8].2g of the adsorbents was weighed into five different conical flasks. Concentration of l0mg/L of the dye was prepared using distilled water.50m1 of the dye solution was then measured into the five flasks. The flasks were then labeled for time intervals of 20, 40, 60, 80 and 100 minutes. The flasks were tightly covered and agitated at the appropriate time intervals. At the end of each time intervals, the suspensions were filtered using Whatman No. I filter paper and then centrifuged. The dye in concentration was determined using U – V Spectrophotometer.

c. Effect of Adsorbent Dosage on Adsorption

The experiment on the effect of adsorbent dosage on the adsorption of dye ion by the groundnut shells adsorbent was performed according to the previous works of[8]. 2, 3, 4, 5 and 6g of the adsorbent were weighed into five different conical flasks. 50ml of the dye solution was measured into the five conical flasks. The flasks were then labeled for dosage differences of 2, 3, 4, 5 and 6g. The flasks were tightly covered and agitated for 20mins and thereafter the suspensions were filtered using Whatman No. I filter paper, then centrifuged. The dye ion concentration was determined using U-V Spectrophotometer.

d. Effect of Temperature on Adsorption

The experiment on the effect of temperature on adsorption was performed according to the previous work of [9].2g of the adsorbent was weighted into five conical flasks and 50ml of the dye solution (l0mg/L) was measured into the five flasks. The flasks were labeled for temperature difference of 30, 40, 50, 60 and 70°C. The flasks were tightly covered and heated at the appropriate temperature using thermostatic water bath at 20mins each. At the end of the timing schedule, each of the flasks was brought out and agitated for about 5 minutes. Then the suspensions were filtered using Whatman No. 1 filter paper and centrifuged. The dye ion concentration was determined using U-V Spectrophotometer.

Data Evaluation

a. Calculation of the Degree of Dyes Removed in Aqueous Solution

The amount of amino phenol dyes removed by the adsorbent during the experiments were determined using a mass balance equation expressed as shown below:

$$q_e = \frac{V}{M}(C_O - C_e)$$

Where;

q_e = dye concentration on the biomass (mg/g) at equilibrium.

C_e = dye concentration in solution (mg/l)

V = Volume of initial dye solution used (m1)

M = mass of adsorbent used (g)

(b) Kinetic Treatment of Experimental Data

In order to comprehensively investigate the mechanisms of adsorption, the equations of Pseudo – first order and pseudo-second order mechanisms were applied to the experimental data.

The linear form of pseudo-first order model which has been described previously is given as:

$$\ln(q_e - q_t) = \ln q_e - Kt$$

Where

q_e = Mass of dye adsorbed at equilibrium (mg/g)

q_t = Mass of dye adsorbed at time t(mg/g)

k = equilibrium constant. The linear plot of In($q_e - q_t$) versus t confirms this model.

The linear form of pseudo-second order model as was used by [10] is given as:

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{t}{q_e}$$

Where

q_t = Amount of dye ion on the adsorbent surface (mg/g) at time t.

q_e = Amount of dye ion adsorbed at equilibrium (mg/g min) the initial adsorption rate, h_o is further defined by the equation $ho=K_2qe^2$

Where K_2 is the pseudo second order rate constant (g/mg min).

A linear plot of *t/qt* against t confirms the model.

RESULTS AND DISCUSSION

a. The Effect of Contact Time

The effect of stay time for the adsorption of the dye was studied between the intervals of 20mins and was varied from 20 to l00mins. Figure I illustrate the adsorption of dye at different time duration. As the contact time was increased, the amount of dye adsorbed was increased from 0.191mg/g to 0.2l0mg/g. Similar trend was observed for Pb^{2+} adsorption on teak leaves activated carbon[12]

From the Figure I below, it indicates that the amount of dye removed increased with increase in time, as well as percentage of dye removed in which maximum percent (83.91%) was obtained at l00mins. This may be due to the

fact that, as the dye solution adsorbent system is being agitated at longer time, more of the molecule or atoms of the dye will accumulate on the surface of the adsorbate until equilibrium is reached.

However, similar trends have been observed by some other researchers[11];[9] and[8].

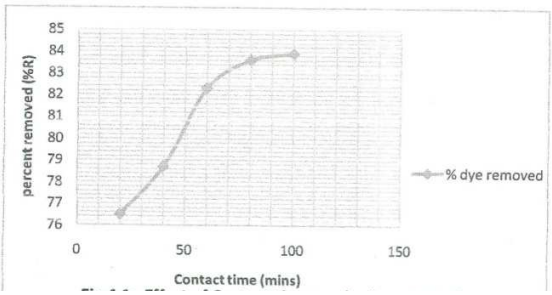

Figure I : Effect of contact time on dye removal

b. The Effect of Adsorbent Dosage

The effect of the amount of adsorbent (groundnut shell) on the adsorption of amino phenol was studied, in which the amount of adsorbent was varied from 2g to 6g. Figure II shows the effect of adsorbent dosage on the removal of the dye in which the amount of dye adsorbed increased from 0.202mg/g – 0.2l8mg as the adsorbent dosage was increased from 2-6g.

From Figure II, maximum absorption of 0.218mg/g of the dye occurred when the adsorbent dosage was 6g. More so, the maximum percentage (87.08%) of dye adsorbed at this dosage (6g) is also shown in Figure 2 below:

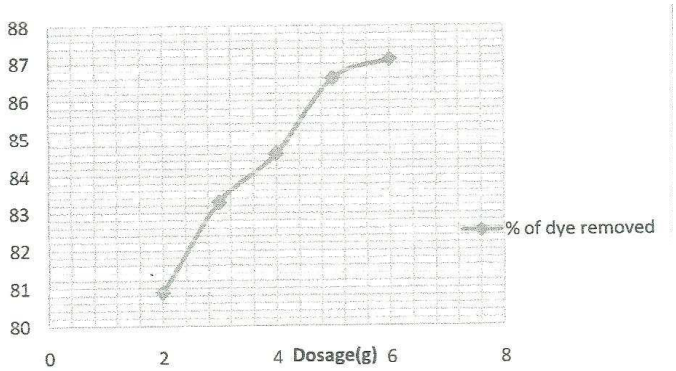

Figure II: Effect of Dosage on dye ion removal

Meanwhile, similar behaviour has been reported by other workers[13];[8] and[14].

b. The Effect of Temperature

The dependence of dye adsorption on temperature was studied within the temperature range of 30-70°C. The effect of temperature on the adsorption of dye is shown in Figure III in which the amount of dye adsorbed increased from 0.207 to 0.213mg/g with increase in temperature from 30 to 70°C.

Though the increase in the amount of dye removed as the temperature increases is not of much significance, according to[8] the higher removal due to increasing temperature may be attributed to chemical reaction taking place between the functional groups of the adsorbent and the dye. More so, at higher temperatures there would be increase in the mobility of the large dye ion thereby producing a swelling effect within the internal structure of the adsorbent. Thus, enabling the large dye molecules to penetrate further, however, the trend of increased adsorption with increased temperature has been reported by other workers[15];[11]

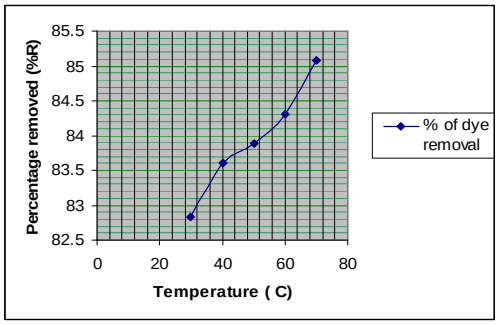

Figure III: The Effect of temperature on dye ion removal

d. Effect of Dye Ion Concentration

The experimental results as shown in Figure IV of the removal of amino phenol dye by groundnut shell from various initial dye ion concentrations are given. The adsorption capacity increased from 0.186 to 1.028mg/g with an increase in the concentration of dye from 10 to 50 mg/g, having maximum adsorption of 1.028mg/g at 50mg/g.

However, the actual percent removal of the dye was found to increase with increase in initial dye concentration (Figure IV). This may be due to the fact that as the dye concentration is increasing, more dye is available for adsorption on the adsorbent. This is due to the effect of concentration gradient which is the main driving force for the adsorption process[9]. Similar trends have been observed by other workers[11].

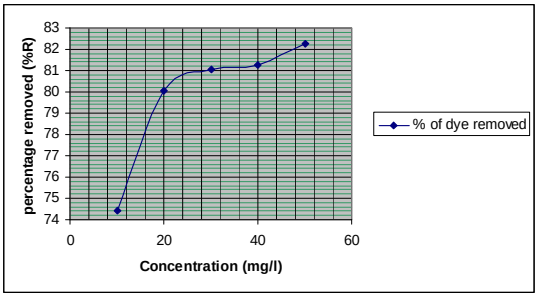

Figure IV: Effect of concentration on dye ion removal

e. Langmuir Isotherm

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surfaces. The plots of specific adsorption (c_e/q_e) against the equilibrium concentrations (c_e) are shown in Figure V and the linear isotherm parameters, q_m, K_L and the coefficient of determinations are presented in Table I

$$S_f = \frac{1}{1 + K_L C_o}$$

Where;

K_L = Langmuir isotherm constant

C_o = Initial dye ion concentration of 10mg/l.

The S_f parameter indicates the shape of the isotherm as follows:

$S_f > 1$ unfavorable isotherm

$S_f = I$ linear isotherm

$S_f = 0$ irreversible isotherm

$0 < S_f < 1$ favorable isotherm

The separation parameter had been used by [16],to study the adsorption ofpb2+ and Ni2+ ions on maize cob biomass.

The separation parameter for the dye is less than unity indicating that the groundnut shell biomass is an excellent adsorbent for amino phenol ions. The Langmuir isotherm parameters are shown in Table I below:

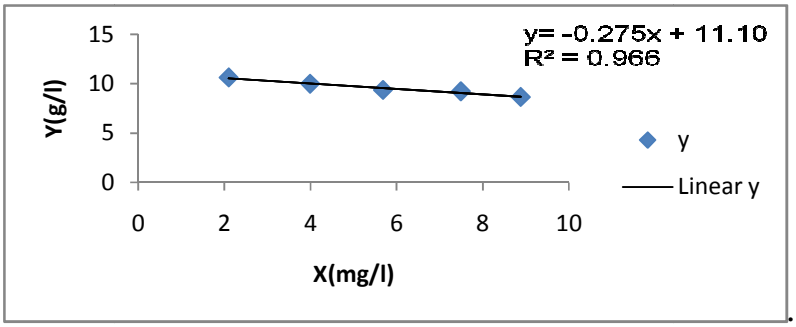

Figure V: The Langmuir isotherm plot

Where; $Y=C_e/q_e$ and $X=C_e$

TABLE I: LINEAR LANGMUIR ISOTHERM PARAMETERS

Dye ion	q_m(mg/g)	K_L(L/g)	R^2	S_f
Amino phenol	-3.636	-40.36	0.996	-0.0025

f. Freundlich Isotherm

The Freundlich model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface. The 1inear Freundlich isotherm for the adsorption of the dye ion into groundnut shell waste biomass are presented in Figure VI. Examination of the plot reveals that the Freundlich isotherm is also an appropriate model for the adsorption process under consideration. Table II shows the linear coefficient of determination (R^2).

Based on the value of R^2, the linear form of the Langmuir isotherm(R^2=0.996) appears to produce a more reasonable model for the adsorption of amino phenol dye than the Freundlich's model(R^2=0.994).

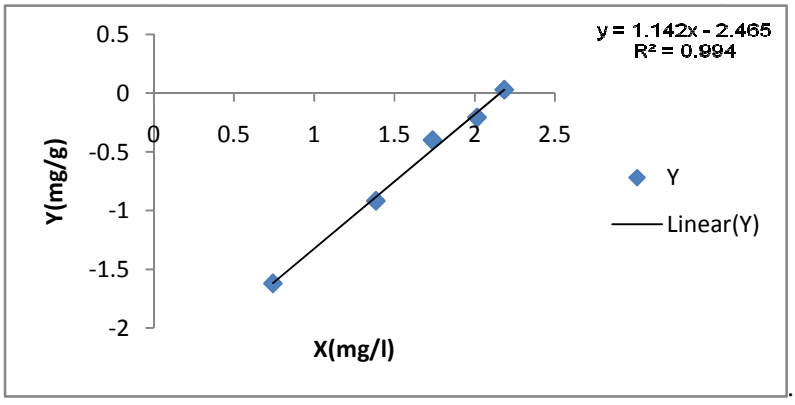

Figure VI: Freundlich isotherm plot

Where;$Y=\ln q_e$ and $X=\ln C_e$

TABLE II: FREUNDLICH ISOTHERM MODEL

Dye ion	q_m(mg/g)	K_L(L/g)	R^2	S_f
Amino phenol	0.876	-0.463	0.994	-0.075

g. Adsorption Kinetics

The kinetics of adsorption is probably the most important factor in predicting the rate at which adsorption takes place for a given system.

A plot of In(q_e-q_t) against t as shown in Figure VII gave the pseudo-first order kinetics. From the plot, it is observed that the relationship between dye ion diffusivity, ln(q_e-q_t) and time is linear which confirms the model's ability to describe the data. In Table III, the value of coefficient of determination R^2 is shown and the value indicates that Pseudo-first order model provide a good description for the adsorption of amine- phenol on the groundnut shell biomass.

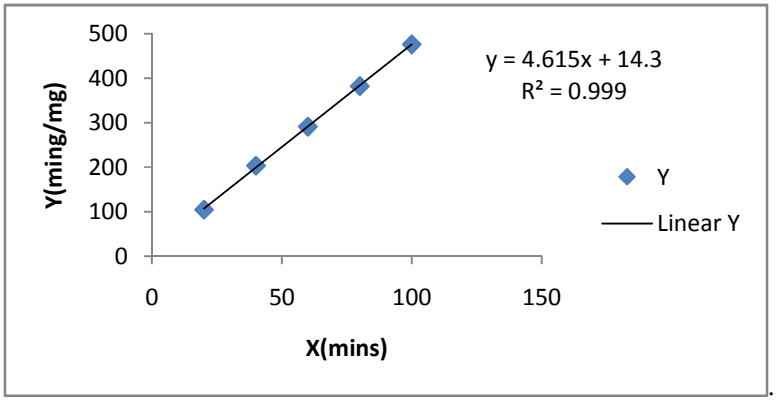

Figure VII: Pseudo-first order plot

Where; Y=ln(q_e-q_t) and X=t

TABLE III: PSEUDO-FIRST ORDER KINETIC PARAMETER

Dye ion	K_1	q_e(mg/g)	R^2
Amino phenol	0.876	-0.463	0.994

However confirming the linearity of the Pseudo-First Order Model, the same observation has been reported by[15] for the absorption of basic dye on strongly chelating polymer.

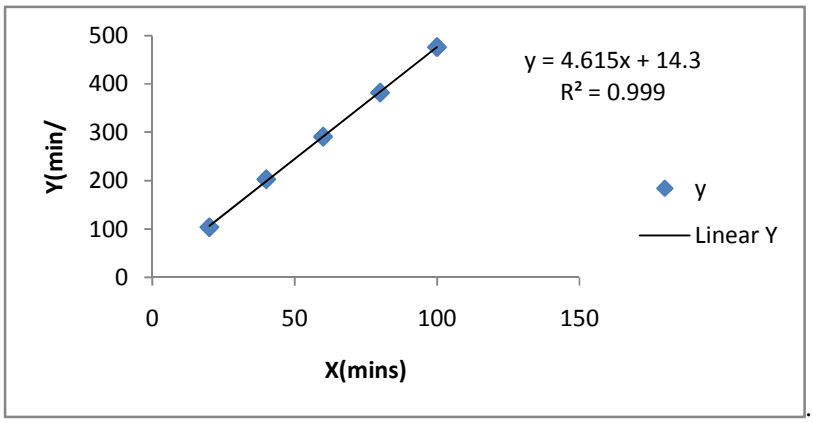

Figure VIII: Pseudo-second order plot

Where; Y=t/q_t and X=t

TABLE IV: VALUES OF PSEUDO-SECOND ORDER KINETIC VALUES

Dye ion	h_o(mg/g/min)	K_2(mg/g/min)	q_e(mg/g)	R^2
Amino phenol	0.069	1.465	0.217	0.999

Pseudo-Second Order Model

A plot t/q_t against t as shown in Figure VIII gave the Pseudo-Second Order Kinetics. From the plot, it is observed that the relationship between t/q_t and t is linear which confirms the model. Also, the initial sorption rate h_0, the equilibrium adsorption capacity q_e, the Pseudo-Second Order rate constant K_2 and the coefficient of determination R^2 are presented in Table IV below. Based on the value of R^2,the pseudo-second order model provide a better description for the adsorption process better than the pseudo-first order model. This observation has been reported by[17] for the adsorption of basic blue using clay-based activated carbon adsorbent.

Thermodynamic Parameters

The values of thermodynamic parameters like free energy (ΔG^0) enthalpy (ΔH^0) and entropy (ΔS^0) of the adsorption process were calculated from the Langmuir constant K using the following equations.

$\Delta G = -RT\,Ink$

$$Ink = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

$\Delta G = \Delta H - \Delta S$

The value of ΔH° and ΔS° were calculated from the slope and intercept of the linear variation of lnk with the reciprocal of temperature (I/T) and are given in Table V and Figure IX.

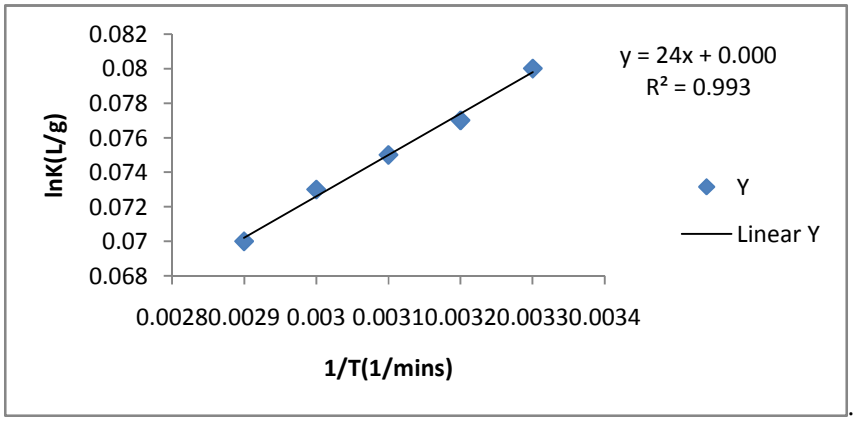

Figure IX : Thermodynamic plot

TABLE V: THERMODYNAMIC PARAMETERS OF THE ADSORPTION PROCESS

Temperature (^{0}C)	ΔH^0 (KJmole)	ΔG^0 (KJmole)	ΔS^0 (JKmole)
30	119.539	119.539	0.00
40	119.539	119.539	0.00
50	119.539	119.539	0.00
60	119.539	119.539	0.00
70	119.539	119.539	0.00

From Table V above, the values of ΔG^0 at different temperatures are positive, which shows that the adsorption process is not spontaneous. The values of enthalpy are also positive, which reveals the endothermic nature of the process according to[11] for the removal of basic dye, methylene blue by using bioadsorbents ulva lactura and sargassum. The values of entropy are zero which reveals a reversible isothermal process.

CONCLUSION

The kinetics and thermodynamics of the sorption of the azo dye (Amino- Phenol) by groundnut *(Arachis hypogaea)* shell have been studied. It was found out that the experimental parameters studied all followed the same trend. As contact time, temperature, adsorbent dosage and initial dye ion concentration increased, the amount of dye adsorbed

and the percentage removal of dyes increased. The equilibrium data fit both the Langmuir and Freundlich isotherms but the Langmuir model was found to be a better descriptor of adsorption process. The kinetic assessment of the data showed that the pseudo-second order gave a better kinetic description of the adsorption process. The thermodynamic parameters also showed that the adsorption process was endothermic but not spontaneous.

However, the data obtained showed that groundnut *(Arachis hypogaea)* shells biomass was effective as adsorbent for removing dyes from wastewater can be used in place of a conventional method. This is justified by the fact, groundnut shell waste is cheap, readily available and can also readily adsorb dyes from waste water.

The values of ΔG° at different temperatures are positive, which indicates that the adsorption process is not spontaneous. The positive values of the enthalpy, reveal that the adsorption process was endothermic in nature which is in accordance with the work of [11] for the removal of basic dye, methylene blue by using bioadsorbents ulva lactura and sargassum. The zero values of the entropy show a reversible isothermal process.

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