

# Optimization, Kinetic and Thermodynamic Study of Rhodamine B Removal by Zinc Chloride-activated *Arachis hypogaea* (Groundnut Husk) biochar

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## Abstract

Adsorption of dye from industrial effluent before discharge into the environment has become a major challenge to the food, pharmaceutical, textile, photographic and cosmetic industries. This has led scientists to the search for suitable green solutions. Carbonized and zinc chloride activated *Arachis hypogaea* (groundnut husk) in a 1:1 ratio was used as an adsorbent for the removal of Rhodamine B from aqueous solution. The adsorbent was characterized by ash content, bulk density, moisture content, pH, Iodine number, surface area and functional group analyses. Key parameters such as initial pH, initial concentration of Rhodamine B dye, temperature and contact time were investigated. The equilibrium data obtained were correlated with Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. It was found that both the Freundlich and Langmuir isotherms fit well to the data. The Langmuir isotherm model best describes the uptake of Rhodamine B onto zinc chloride activated groundnut husk biochar with  $R^2 > 0.997$ . Maximum Rhodamine B. dye removal was observed at a pH of 11.0, with an adsorbent dosage of 1.0 g, a contact time of 125 min, an initial dye concentration of 20 mg/L and a temperature at 315 K. The efficiency of zinc chloride activated groundnut husk biochar for Rhodamine B removal was 99.55% for dilute solutions at 50 g/L. The Fourier Transform Infrared (FTIR) spectra recorded before and after activation showed the numbers of functional groups available for Rhodamine B. molecules to bind onto in the studied adsorbent. The kinetic data were best described by the pseudo-first-order and pseudo-second-order models, while the thermodynamic studies indicated a spontaneous and endothermic nature in the adsorption of Rhodamine B by the zinc chloride modified groundnut husk. This research clearly details an innovative approach to utilizing carbonized and zinc chloride-activated *Arachis hypogaea* (groundnut husk) as an eco-friendly adsorbent for the removal of Rhodamine B from industrial effluents.

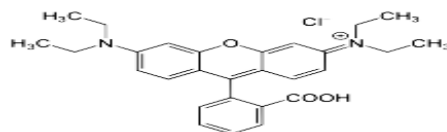
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## 1. Introduction

Dyes colour materials by altering the crystal structure of the coloured substance (Othmer, 2004; Bafana *et al.*, 2011; Ahmad and Hameed, 2010; Ahuja *et al.*, 2010). They are classified as natural, derived from plants and insects, or synthetic, chemically produced and often modified versions of natural dyes (Bafana *et al.*, 2011). Rhodamine B, a synthetic dye used in textiles, cosmetics, research, and food production industries, is toxic and persistent in the environment (Cai and Stark, 1997; Sudarshan *et al.*, 2022). Its IUPAC name is 9-(2-Carboxyphenyl)-6-(diethylamino)-N,N-diethyl-3H-xanthen-3-iminium chloride. This fluorescent dye is used in biology for staining acid-fast organisms and in biotechnology for fluorescence microscopy and other

applications (Birtalan *et al.*, 2011). Due to its possible carcinogenic effects, products that include Rhodamine B are required to display a warning label (Sudarshan *et al.*, 2022).



**Figure 1.** Chemical structure of Rhodamine B.

The textile industries in Nigeria in the past happen to be the largest employer of labour and played a very pivotal role in the economy of the nation (Owena *et al.*, 2016). Dyes are extremely valuable in paper printing, textile, food, pharmaceutical, leather, cosmetics and photographic industries (Zollinger, 1987, Carneiro *et al.*, 2007). 10-15% of dyes are lost during different production processes and find their way into the environment due to the incomplete exhaustion of dyes onto textile fibre from aqueous dyeing process which is disposed as effluent without proper treatment has become a major concern in recent years (Hassan, 2017; Ananthashankar, 2012). The textile processing industry uses huge amount of freshwater during rinsing process because it requires cleaning product lines in a sequence of storage tanks with freshwater. The conventional dyeing and rinsing steps of textile manufacturing are responsible for nearly 20% of today's industrial pollution (Kant, 2011). Before releasing the effluent into the environment, they should be degraded to a non-toxic form or must be below permissible limit of discharge. Many strategies of dyestuff removal from wastewater have been proposed to find a smart, cost effective and ecologically friendly solution such as physical, chemical and biological, or combined remedy processes, and other technologies to treat textile wastewater. Some of the processes include photocatalytic (Falah and Thekra, 2010), membrane (Bukola *et al.*, 2022), and adsorption (Olasehinde *et al.*, 2020a, Olasehinde *et al.*, 2020b) techniques have been established to control environmental pollution from textile industries. Adsorption process seems to be the favourable alternative, the cheapest, the most available and quicker to deploy techniques in the treatment process of textile wastewater (Dabrowski, 2001). Groundnut shell is a carbonaceous, fibrous solid waste which encounters disposal problem and is generally used for its fuel value for cooking in the locals (Pham *et al.*, 2019). By this, it is imperative to prepare a higher value product such as activated carbon from groundnut shell. These products have the advantage of greater percentage of non-carbon constituents in their composition compared to coal or peat and therefore offer a greater chance of retaining functional groups, especially oxygenated groups in the carbonized product (Ahmedna *et al.*, 2000).

There are two different processes for the preparation of activated carbon: Physical and Chemical activation. Physical activation involves carbonization of carbonaceous precursor followed by activation of resulting char in the presence of activating agents such as carbon dioxide or steam. Chemical activation on the other hand, involves the carbonization of precursor in the presence of chemical agents (Ahmedna *et al.*, 2000). In physical activation, elimination of large amount of internal carbon mass is necessary to obtain a well-developed porous structure, why for chemical activation process, chemical activated carbon covers a wide spectrum of applications such as drinking water treatments and wastewater treatments in the food, beverage, pharmaceutical and chemical industries (Hamdaoui and Chiha, 2007). The objective of this study was to evaluate the potential of zinc chloride activated groundnut husk biochar as adsorbent. Given that adsorption processes for purification of dye wastewaters can be carried out either discontinuously, in batch or continuous fixed-bed columns, but the performance of the adsorbent was evaluated in batch tests and the effect of various process parameters were studied which include pH, adsorbent dose, initial Rhodamine B concentration, contact time and temperature have been investigated. The data may be used for environmental engineering design for treatment of effluent from dye industries.

## 2. Materials and Methods

### 2.1 Adsorbate

All the primary chemicals used were of analytical grade. The standard stock solution of Rhodamine B with the

formula  $C_{28}H_{31}N_2O_3.Cl$  used in this study ( $1000\text{ mgL}^{-1}$ ) was prepared by dissolving the weighed required quantity of Rhodamine B in distilled water. Experimental solutions with the desired concentrations were prepared by diluting the stock solution with distilled water.

## 2.2 Adsorbent Preparation

*Arachis hypogaea* (Groundnut husk), an agricultural waste was gathered from each waste bin from the Faculty of Life Sciences, University of Benin, Benin City Edo State Nigeria. It was taken to the Chemistry Laboratory of the Department Science Laboratory Technology. Standard procedures were followed in washing, drying and grinding of the groundnut husk. The powdered groundnut husk was mixed with Zinc chloride at ratio 1:1 and carbonized at  $450\text{ }^\circ\text{C}$  for 15 min. After cooling, the excess zinc chloride present in the activated biochar was leached out by immersing in 1 M hydrochloric acid solution for 12 hours in a water bath at  $80\text{ }^\circ\text{C}$ . Thereafter the activated biochar was then washed repeatedly with deionized water to eliminate traces of Hydrochloric acid and Zinc chloride. This was verified by analyzing the wash water each time using silver nitrate. The biochar was oven dried, grind and sieved to get a particular mesh size and kept in an airtight container for further use.

## 2.3 Characterization and Adsorption Studies

The activated biochar was characterized using standard methods: moisture content was determined by drying and weighing, ash content by pyrolysis at high-temperature, pH by suspending in water and measuring with a pH meter, bulk density by mass-to-volume ratio, iodine number by iodine adsorption and titration, surface area was determined using Brunauer-Emmett Teller (BET) method through gas adsorption onto the sorbent surface, which provides insights into its surface characteristics and functional groups by Fourier-transform infrared spectroscopy (FTIR) which provide an easy way on how infrared signal that passes through organic compound is absorbed at different characteristic frequencies, which are then transformed into a unique spectrum. The adsorption experiments were carried out batch wise. A weighed amount of adsorbents and 100 ml of Rhodamine B solution was shaken using mechanical shaker at room temperature. The effect of varied contact time, concentration, pH and temperature were studied by performing equilibrium adsorption tests. The isotherms of Rhodamine B on the adsorbent were studied at concentration  $5\text{-}100\text{ mgL}^{-1}$ . The adsorption kinetics studies were carried out under optimized conditions from 25-125 min. The mixture was filtered and the concentrations of the remaining Rhodamine B in the filtrates were determined using the UV-VIS Spectrophotometer (PG instrument model T18). The concentration of Rhodamine B uptake by 1 g of the adsorbent was calculated from the following mass balance equation:

$$q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

Where  $q_e$  ( $\text{mgg}^{-1}$ ) is the amount of Rhodamine B uptake from solution,  $C_e$  ( $\text{mg L}^{-1}$ ) the Rhodamine B concentration in solution after adsorption,  $C_o$  ( $\text{mg L}^{-1}$ ) the initial Rhodamine B concentration,  $M$  the amount of adsorbent (g) and  $V$  the volume of solution (L).

Percentage removal was calculated using the formula:

$$\text{Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

## 2.4 Adsorption Isotherm

Adsorption isotherms predict the relationship between adsorbent and adsorbate (Mittal *et al.*, 2010). Isotherms explain how adsorbing materials interact with pollutants and hence, they are important in optimizing the use of adsorbents. The equilibrium of adsorption is an important physiochemical parameter that is used in evaluating adsorption process. Adsorption of Rhodamine B. by zinc chloride activated groundnut husk biochar was analyzed by modeling the adsorption behaviour with four adsorption studies and their correlation with experimental data. These models included the Dubinin-Radushkevich, Freundlich, Langmuir and Temkin isotherm.

### 2.5 Dubinin-Radushkevich isotherm model

Dubinin-Radushkevich isotherm model was applied to the equilibrium data to determine if adsorption had occurred by physical or chemical processes. The D-R isotherm model is a semi-empirical equation where adsorption follows a pore filling mechanism. The Dubinin-Radushkevich isotherm model is expressed as given in equation below (Dubinin, 1960; Olasehinde *et al.* 2018):

$$\ln q_e = \ln q_m - K_{ad}\epsilon^2 \quad (3)$$

where  $\epsilon$  is given as:

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \text{ is Polanyi potential} \quad (4)$$

where,  $q_e$  is the amount of Rhodamine B. adsorbed per unit mass in  $\text{mg g}^{-1}$ ,  $q_m$  is the maximum amount of adsorbate adsorbed per unit weight of adsorbent, and  $K_{ad}$  ( $\text{mol}^2 \text{kJ}^{-2}$ ) is the constant related to sorption energy. The mean free energy of adsorption ( $E$ ) defined as the free energy change when 1 mole of ion is transferred to the surface of the adsorbent from infinity in solution can be evaluated from the  $\epsilon$  value obtained.

$$E = 1/\sqrt{2K_{ad}} \quad (5)$$

If the magnitude of  $E$  is between 8 to 16  $\text{kJ mol}^{-1}$ , then the sorption process is supposed to proceed via chemisorption reaction, while for values of  $E < 8 \text{ kJ mol}^{-1}$ , the sorption process is physical in nature (Kundu and Gupta 2016).

### 2.6 Freundlich isotherm model

The Freundlich model can be applied for non-ideal sorption onto heterogeneous surfaces involving multilayer sorption. The Freundlich model isotherm was applied for the adsorption of Rhodamine B and is expressed as;

$$q_e = K_F C_e^{\frac{1}{n}} \quad (6)$$

The linearized form of Equation 6 is given as:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (7)$$

where  $q_e$  is the amount of Rhodamine B. adsorbed per unit mass,  $C_e$  is the Rhodamine B. concentration at equilibrium,  $K_F$  and  $n$  are Freundlich constants. The magnitude of the exponent  $n$  gives an indication of the favourability of the adsorption. It is generally stated that the value of  $n$  in the range 2-10 represent good, 11-20 moderately difficult and less than 1 is poor adsorption characteristics (Treybal, 1980). Based on the correlation coefficient values, it has been deduced that Freundlich model better fitted to the experimental data.

### 2.7 Langmuir isotherm model

The Langmuir model represents one of the first theoretical treatments of non-linear sorption and suggests that uptake occurs on a homogenous surface by monolayer absorption without interaction between the adsorbed molecules. The linear form of the Langmuir adsorption isotherm is represented by the equation 8 (Langmuir, 1916).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (8)$$

The shape of this isotherm can also be expressed in terms of separation factor ( $R_L$ ), which is given as (Foo, 2010):

$$R_L = \frac{1}{1 + K_L C_0} \quad (9)$$

where,  $q_e$  is the amount of Rhodamine B. adsorbed per unit mass in  $\text{mg g}^{-1}$ ,  $C_e$  is the Rhodamine B. concentration at equilibrium in  $\text{mg L}^{-1}$ ,  $q_m$  is the maximum amount of adsorbate adsorbed per unit weight of adsorbent,  $K_L$  ( $\text{L/mg}$ ) is Langmuir constant, and  $C_0$  is the initial Rhodamine B. concentration in  $\text{mg L}^{-1}$ . The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation

factor for equilibrium parameter  $R_L$ .  $R_L$  value determines the shape of the isotherm to be unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ).

### 2.8 Temkin model

This isotherm model explicitly takes into account the adsorbent-adsorbate interactions, by ignoring the extremely low and large value of concentrations. The model assumes that the heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage due to interactions between adsorbent and adsorbate (Temkin and Pyzhev 1940; Aharoni and Ungarish 1977). As implied in the equation, its derivation is characterized by a uniform distribution of the binding energies (up to some maximum binding energy) was carried out by plotting the quantity adsorbed  $q_e$  against  $\ln C_e$  and the constant were determined from the slope and intercept. The model is given by the following equation (Temkin and Pyzhev 1940):

$$q_e = B \ln K_T + B \ln C_e \quad (10)$$

where B is Temkin constant related to the heat of adsorption measured in  $\text{kJ mol}^{-1}$ , and  $K_T$  is the empirical Temkin constant which denotes the equilibrium binding constant related to the maximum binding energy ( $\text{L mg}^{-1}$ ).

### 2.9 Adsorption Kinetics

In order to have quantitative understanding of adsorption mechanism, kinetic models can be employed.

#### 2.9.1 Pseudo-first order kinetic model

Pseudo-first order kinetic model assumes that the rate of adsorption on adsorbent is proportional to the number of available active sites on the adsorbent. The rate constant for the adsorption for this present study for determining a linearized form of pseudo-first order rate equation is as stated below (Senthilkumaar, 2005):

$$\text{Log} (q_{eq} - q_t) = \text{log} (q_{eq} - \frac{K_1 t}{2.303}) \quad (11)$$

where  $q_{eq}$  is the amount of Rhodamine B adsorbed at equilibrium ( $\text{mg g}^{-1}$ ),  $q_t$  is the amount of Rhodamine B adsorbed at time  $t$  ( $\text{mg g}^{-1}$ );  $k_1$  is the equilibrium rate constant of pseudo-first sorption ( $\text{min}^{-1}$ ). The first kinetic model is the generalized first-order kinetic equation proposed by Annadurai and Krishnan (Annadurai and Krishnan, 1996).

$$\frac{1}{q_t} = \frac{K_1}{q_e} \cdot \frac{1}{t} + \frac{1}{q_e} \quad (12)$$

#### 2.9.2 Pseudo-second-order kinetic model

The pseudo-second-order kinetic model assumes that the rate limiting step may be chemical sorption involving valence forces through the sharing or exchange of electron between the Rhodamine B. and adsorbent. According to the pseudo-second order kinetic model, the rate of adsorption reaction decreases non-linearly with time. The pseudo-second order linearized equation is expressed as in equation 13 stated below (Ahmad *et al.* 2014; Olasehinde *et al.*, 2020a):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \quad (13)$$

where,  $q_t$  is the amount of Rhodamine B adsorbed at time  $t$  ( $\text{mg g}^{-1}$ );  $k_2$  is the equilibrium rate constant for the pseudo second- order adsorption ( $\text{g/mg/min}$ ).

#### 2.9.3 Thermodynamic studies

Thermodynamics studies the relationship between heat, work, temperature and energy. Thermodynamic parameters such as Gibbs free energy change ( $\Delta G$ ), enthalpy changes ( $\Delta H$ ) and entropy change ( $\Delta S$ ) provide a

better understanding of the temperature effect on the adsorption process. The obtained experimental data from batch adsorption experimental were analyzed using the following thermodynamic equations:

$$K_c = \frac{C_s}{C_e} \tag{14}$$

where,  $C_s$  is the Rhodamine B. concentration on the adsorbent at equilibrium in  $\text{mg L}^{-1}$ ,  $C_e$  is the equilibrium concentration of the Rhodamine B. is a solution in  $\text{mg L}^{-1}$  and  $K_c$  is the thermodynamic equilibrium constant. The Gibbs free energy,  $\Delta G^0$  ( $\text{kJ mol}^{-1}$ ) for the adsorption Rhodamine B. onto the adsorbents can be calculated as follows:

$$\Delta G^0 = -RT \ln K \tag{15}$$

where T is the absolute temperature (K) and R is the universal gas constant ( $8.314 \text{ Jmol}^{-1}\text{k}^{-1}$ ). Enthalpy and entropy are obtained using Vant Hoff's equation (Deepak *et al.*, 2017; Olasehinde *et al.*, 2020b). The change in free energy is related to other thermodynamic properties as:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{16}$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{17}$$

where T is the absolute temperature (K) and R is the universal gas constant ( $8.314 \text{ Jmol}^{-1}\text{k}^{-1}$ ),  $\Delta H^0$  is the change in enthalpy and  $\Delta S^0$  is the degree of disorderliness of a reaction.  $\Delta H^0$  and  $\Delta S^0$  can be obtained from the plot of  $\ln K_c$  against  $1/T$ .

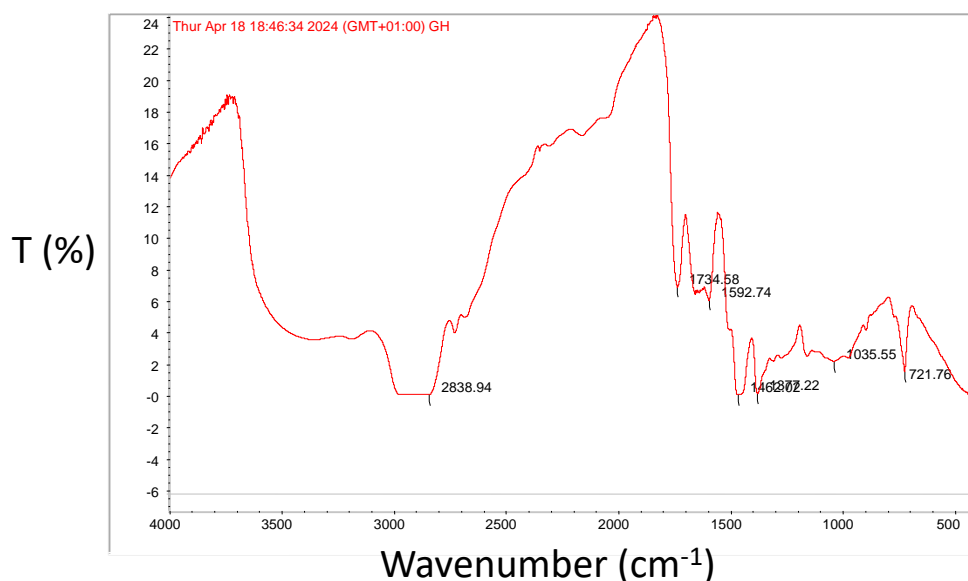
### 3. Results and Discussion

#### 3.1 Adsorption Kinetics

**Table 1** results show the zinc chloride activated groundnut husk biochar has moisture content 3.36%, ash content was found to be 7.30 %. The ash content is an indication of the quality of modified carbon. Bulk density was found to be 0.72, the pH value was 6.70, which falls within the acceptable pH ranges of between 6 to 8. The iodine number determination was found to be 103.24  $\text{mgg}^{-1}$ . For the surface area, it was  $1.00 \times 10^{-3}$  which indicates that there was better evolution and development of pore in the modified groundnut husk as compared to some previous work (Bala *et al.*, 2020; Agho and Archibong, 2023). The zinc chloride activated groundnut husk biochar generated more interspaces between carbon layers leading to more micro porosity. The increase in porosity with zinc chloride activation suggests that the porosity created by this reactant is due to the spaces left by zinc chloride after the corresponding washing. Zinc chloride activation causes electrolytic action termed as “swelling” in the molecular structure of groundnut husk biochar, which leads to the breaking of lateral bonds in the material molecules resulting in increased inter- and intra- voids. Zinc chloride promotes the development of porous structure of the activated groundnut husk biochar because of the formation of small elementary crystallites (subha and Namasivayam, 2009).

**Table 1.** Characterization of Modified *Arachis hypogaea* (Groundnut Husk) from Triplicate Analyses

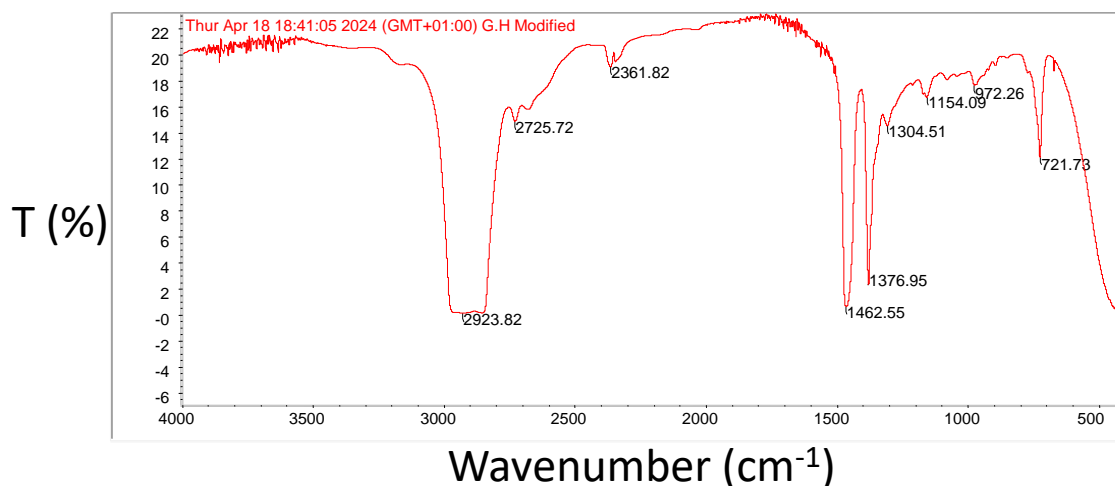
Parameters	Unit	Modified groundnut husk
Ash Content	%	7.30±0.06
Bulk Density	$\text{g/cm}^3$	0.72±0.01
Moisture	%	3.36±0.07
pH		6.70±0.13
Iodine	$\text{g/100g}$	103.24±0.26
Surface area	$\text{m}^2/\text{g}$	100.00 ±0.00
Pore volume	$\text{cc/g}$	0.1400 ±0.00
Pore size	nm	2.153 ±0.00



**Figure 2.** FT-IR spectra of Carbonized groundnut husk

**Table 2.** FT-IR spectra interpretation of carbonized groundnut husk

Frequency	Appearance	Bonds	Compounds
2838.94	Broad and weak absorption band	C-H stretch, O-CH <sub>3</sub>	Methoxy, methylether
1734.58	Medium absorption band	Ring	Six-member ring lactone
1592.74	Medium to strong absorption band	(C=C-C) stretch	Aromatic ring
1462.02	sharp and strong absorption band	(C=C-C) stretch	Aromatic ring
1377.22	Sharp and strong absorption band		Organic sulphates, Aliphatic nitro compounds
1035.55	weak to medium absorption band	C-O stretch	C-O-C, Cyclohexane ring vibration, Alkyl substituted ether
721.76	Strong and sharp absorption band	(CH <sub>2</sub> ) <sub>n</sub> rocking	Methylene, Alkenes

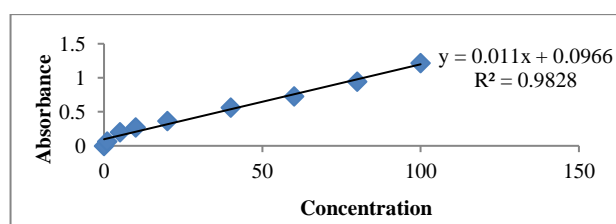


**Figure 3.** FT-IR spectra of Zinc chloride modified Carbonized groundnut husk

**Table 3.** FT-IR spectra interpretation of Zinc chloride modified carbonized groundnut husk

Frequency	Appearance	Bonds	Compounds
2923.82	Strong and broad absorption band	C-H stretch	Methylene
1462.55	sharp and strong absorption band	C-H bend	Methylene, Alkenes
1376.95	Sharp and strong absorption band	C-H bend	Methyl, Alkanes
1304.51	Medium absorption band	C-H plane bend, in plane bend, CN stretch	Vinylidene, Alkenes, primary or secondary O-H, Aromatic primary amine CN
1154.09	medium to strong absorption band	C-N stretch	Tertiary amine, CN
972.26	medium to strong absorption band	C-H out of plane bend	Vinyl, C-H
721.73	Sharp and strong absorption band	(CH <sub>2</sub> ) <sub>n</sub> rocking	Methylene, Alkenes

The FTIR spectrum data of the modified groundnut husk from **Figure 3** and **Table 3** show a strong absorption band at 2924 cm<sup>-1</sup> which indicates stretching vibrations of C-H bonds in comparison with the carbonized groundnut husk at 2838.94 cm<sup>-1</sup> which shows a broad and weak band which characterizes asymmetric and symmetric stretching of C-H group. This is characteristic of methylene (CH<sub>2</sub>) groups, which are abundant in organic compounds like cellulose and lignin found in plant materials such as groundnut husks. Cellulose is polysaccharide materials that consist of glucose units linked together. It forms the structural framework of plant cell walls and provides mechanical strength. These molecules are composed of repeating units of glucose linked by β-1, 4-glycosidic bonds and contribute to the presence of numerous methylene groups (CH<sub>2</sub>) in the polymer chain. Lignin is a complex aromatic polymer that provides rigidity and impermeability to plant cell walls. It contains a variety of C-H bonds in its aromatic rings and aliphatic side chains, contributing to the overall spectrum of C-H stretching vibrations in plant materials. A band between 1463 and 1377 cm<sup>-1</sup>, which is present in both carbonized-modified and carbonized groundnut husk. The band in the carbonized-modified is sharper and stronger compared to the band in the carbonized groundnut husk which in the both adsorbent they are assigned to the bending of C-H ring of the alkanes and alkenes. A band near 1305 cm<sup>-1</sup>, related to the bending of primary or secondary O-H, aromatic ring and primary amine CN which appears in the carbonized-modified groundnut husk while for the carbonized the band near 1036 is a weak to medium absorption band which relates to C-O stretch band which indicates a cyclohexane ring vibration or alkyl substituted ether; a band near 1154 cm<sup>-1</sup> in the carbonized-modified groundnut husk is assigned to the stretching of the tertiary amine CN. Their presence reaffirms the organic nature of the modified groundnut husk, suggesting that the material retains its natural composition after modification. The nitrogen-containing groups present in the carbonized-modified groundnut husk are known to enhance the adsorption capacity of materials which contributes to the modified groundnut husk's ability to remove Rhodamine B. or other organic pollutants from aqueous solutions. The presence of amino groups on the surface of modified groundnut shell-based carbon can also be attributed to its leguminous plant origin as evident from high content of N and S in elemental analysis (Agho and Archibong, 2023).



**Figure 4.** Calibration plot for Rhodamine B. concentration.



**Table 4.** Standard calibration curve for Rhodamine B.

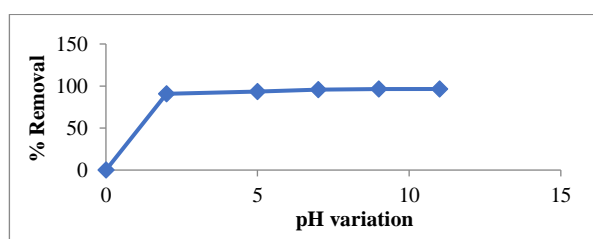
Concentration (mg/l)	Absorbance
0	0.000
1	0.065
5	0.202
10	0.271
20	0.365
40	0.562
60	0.725
80	0.942
100	1.218

**Table 5.** Parameters for plotting Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Adsorption Isotherms of Rhodamine B. unto Zinc chloride activated groundnut husk biochar

S/N	C <sub>0</sub> (mg/l)	C <sub>e</sub> (mg/l)	1/C <sub>e</sub>	Log C <sub>e</sub>	Ln C <sub>e</sub>	q <sub>e</sub> (mg/g)	1/q <sub>e</sub>	Log q <sub>e</sub>	Ln q <sub>e</sub>	C <sub>e</sub> /q <sub>e</sub> (g/l)	ε <sup>2</sup>
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	20	3.03	0.33	0.48	1.11	8.49	0.12	0.93	2.14	0.36	5.22x10 <sup>5</sup>
3	40	7.07	0.14	0.85	1.96	16.47	0.06	1.22	2.80	0.43	1.12x10 <sup>5</sup>
4	60	11.23	0.09	1.05	2.42	24.39	0.04	1.39	3.19	0.46	4.64x10 <sup>4</sup>
5	80	17.59	0.06	1.25	2.87	31.21	0.03	1.49	3.44	0.56	1.94x10 <sup>4</sup>
6	100	29.28	0.03	1.47	3.38	35.36	0.03	1.55	3.57	0.83	7.00x10 <sup>3</sup>

**Effect of pH**

The effect of pH on the adsorption of Rhodamine B. was carried out over the pH range of 2 to 11, while all other parameters were kept constant. Adsorption was found to increase gradually with increasing pH. This occurrence could be described by increasing total net negative charges of surface adsorbent which raises electrostatic forces in the adsorption process (Zamil *et al.*, 2008). However, with increasing pH, total number of negative groups available for the binding of Rhodamine B. increased and therefore competition between proton and analytes become less pronounced; results showed that the zinc chloride activated groundnut husk biochar possessed optimum sorption capacity for Rhodamine B. at pH 11 (Zamil *et al.*, 2008).



**Figure 5.** Effect of pH on Rhodamine B. removal

**Effect of adsorbent dosage**

It is clear from the experimental results that increasing dosage, decreases amount of contaminant adsorbed per unit mass. The understandings that the available adsorption sites and surface area increase, explains the increasing adsorbent dose and thus increase in the amount of contaminant adsorbed from the solution. Though percent adsorption increases with increase in adsorbent dose, but amount adsorbed per unit mass decreases. This statement is supported from the results that the trend in % adsorption shows very sharp increase from

84.85 to 97.2% at the dose increment from 0.2 g – 1.0 g 100 ml<sup>-1</sup> but on further increasing the dose, the maximum % adsorption i.e. 97% is attained at the dose of 1.0 g 100 ml<sup>-1</sup> (Rafatullah *et al.*, 2010).

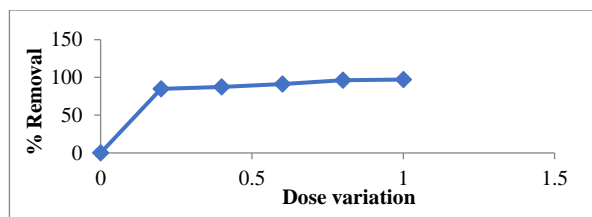


Figure 6. Effect of adsorbent dosage on Rhodamine B. removal

### Effect of Contact time

From results obtained in the experimental setup, it was observed that adsorption increased from 97.2 % to 99.3% with increased contact time from 25 to 125 min. Maximum Rhodamine B. removal was achieved within 100 min after which Rhodamine B. concentration in the test solution became constant. It may be explained from our findings that the adsorbent initially has large number of vacant sites for trapping the dye molecules, which then slows down as the sites are getting filled up due to exhaustion of remaining surface sites and repulsion force between solute molecules and bulk phase (Saravane *et al.*, 2002).

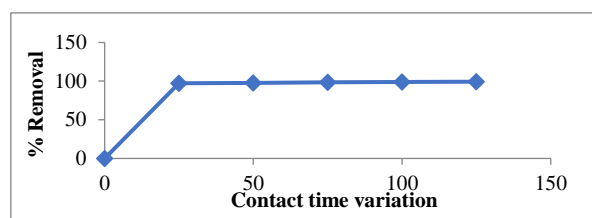


Figure 7. Effect of contact time on Rhodamine B. removal.

### Effect of initial Rhodamine B. concentration

It was observed from the adsorption experiment that there was decrease in the in the removal of Rhodamine B. from 84.82% to 70.72% with increased dye concentration from 20 – 100 mgL<sup>-1</sup>. At higher concentration, more of the Rhodamine B. is left unabsorbed due to saturation of adsorption sites. As the ratio of sorptive surface to dye molecules decreased with increasing dye concentration and so dye molecules removal was reduced. At low initial concentration of the dye, more binding sites are available. So as the concentration of the dye increases, the number of molecules competing for available binding sites in the biomass increased (Gupta *et al.*, 2012).

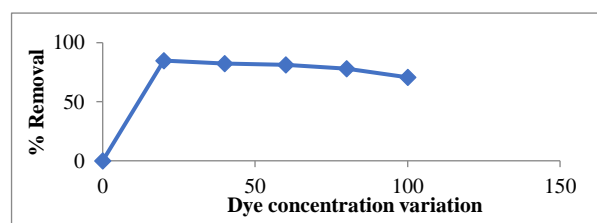
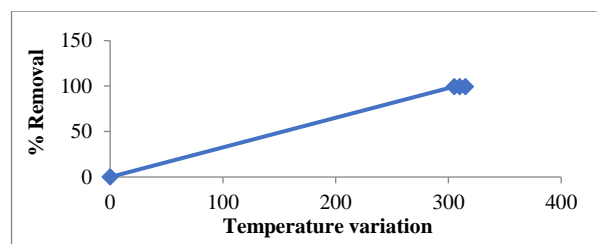


Figure 8. Effect of initial Rhodamine B. concentration on its removal

### Effect of temperature

Figure 9 shows the effect of temperature on the adsorption of Rhodamine B. from 305 -315 K. From the results it is evident that there is gradual increase in the removal percentage from 99.40% to 99.55%. The above results also showed that the adsorption was endothermic in nature. Since adsorbent is porous in nature and possibilities of diffusion of adsorbate cannot be ruled out therefore, increase in sorption with the rise of temperature may be diffusion controlled which is endothermic process, i.e. the rise of temperature favours the adsorbate transport within the pores of adsorbent (El-Shafey, 2005; Bansal *et al.*, 2009).



**Figure 9.** Effect of temperature on Rhodamine B. removal

### Adsorption isotherm

Adsorption isotherms explain how adsorbent materials interact with pollutants and hence, they are important in optimizing the use of bio-sorbents. Determination of equilibrium parameters provides important information for the design of adsorption system dye removal from solutions (Witek-Krowiak *et al.* 2011), it is therefore necessary to establish the most appropriate correlation for the equilibrium curve. The model isotherms employed in this study include Dubinin-Radushkevich (D-R), Freundlich, Langmuir and Temkin adsorption isotherms.

The Dubinin-Radushkevich isotherm model was expressed in Equation 3. The plots of  $\ln q_e$  against  $\epsilon^2$  were presented in **Figure 10** for the adsorption of Rhodamine B. onto zinc chloride activated groundnut husk biochar. The D-R constant related to sorption energy,  $K_{ad}$ , measured in  $\text{mol}^2 \text{KJ}^{-2}$  and the amount of sorbate adsorbed by sorbent,  $q_{\max}$ , in  $\text{mol g}^{-1}$  was obtained from the slope and intercept of the plots respectively and presented in **Table 6**. The mean free energy of adsorption ( $E$ ) was also calculated from  $\epsilon$  value using Equation. 5 and the value was presented in **Table 6**. According to the table, the value of the adsorption energy for the zinc chloride activated groundnut husk biochar is less than  $8 \text{ kJ mol}^{-1}$ , thereby it can be concluded that the adsorption processes were dominated by physical forces. Noteworthy, the value of  $R^2$  is higher than those obtained with other adsorption isotherms, indicating that adsorption of Rhodamine B. onto the adsorbent does fit the Dubinin-Radushkevich Isotherm model.

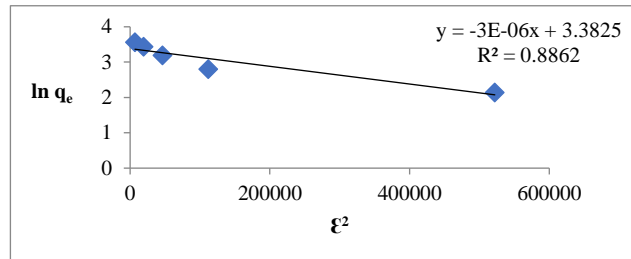
The linearized form of Freundlich isotherm model was expressed in Equation 6. The plots of  $\log q_e$  against  $\log C_e$  for the adsorption of Rhodamine B. onto zinc chloride activated groundnut husk biochar is presented in **Figure 11**. **Table 6** presents  $K_f$  and  $n$  values obtained from the intercepts and slopes of  $\log q_e$  versus  $\log C_e$ . The slope,  $(1/n)$ , ranging from 0 to 1 is a measure of intensity of adsorption or surface heterogeneity. The surface becomes more heterogeneous as the value  $1/n$  approaches zero, while a value of  $1/n$  below 1 indicates a normal Langmuir isotherm while a value of  $1/n$  above 1 is indicative of cooperative adsorption (Olasehinde *et al.*, 2018). From the data presented it does indicate that the data fits in for the Freundlich isotherm model. It is also important to note from **Table 6** that the value of  $n$  is greater than 1 for zinc chloride activated groundnut husk biochar. The value of  $n$  greater than unity indicated a favourable adsorption taking place, while the value of  $1/n$  tending towards zero revealed the heterogeneity of the surface.

The Langmuir adsorption isotherm linearized form was given in Equation 8. Plots of  $1/C_e$  against  $1/q_e$  for the adsorption of Rhodamine B. onto zinc chloride activated groundnut husk biochar in **Figure 12** shows the values of  $q_{\max}$  and  $K_L$  ( $\text{L mg}^{-1}$ ) as Langmuir parameters, obtained from the slope and intercept of the plot of  $1/C_e$  against  $1/q_e$  respectively and correlation coefficient ( $R^2$ ) are presented in **Table 6**. As shown in the table, the correlation coefficient ( $R^2$ ) is greater than 0.996 indicating strong relationship between the adsorption data. To establish whether the adsorption process is favourable or not, a dimensionless constant known as a separation factor ( $R_L$ ) is evaluated as defined in Equation 9. The value  $1 > R_L > 0$ , indicates that the adsorption process is favourable.

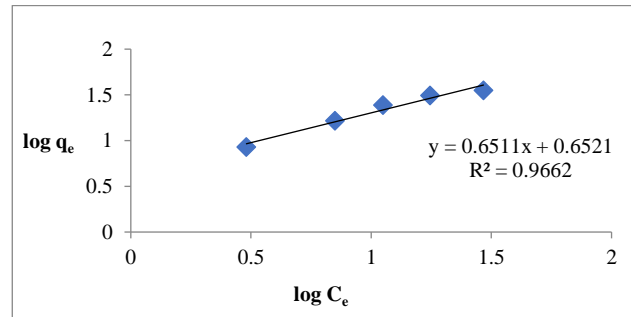
The Temkin isotherm model was stated in Equation 10. Plots of  $q_e$  versus  $\ln C_e$  are presented in **Figure 13** for zinc chloride activated groundnut husk biochar enabling the determination of the isotherm constants  $A_T$  and  $B$  from the intercept and slope of the curve. The process was endothermic as indicated by the positive energy values (Inam *et al.*, 2017). It was also observed from **Table 6** that the value of  $b_T$  is higher than  $8 \text{ kJ mol}^{-1}$ , indicating that the interaction between the adsorbent and adsorbate is strong, thus, the adsorption mechanism put into play here that of a strong physical interaction (Chogomu *et al.*, 2013).

**Table 6.** Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherm constants for the adsorption of Rhodamine B. unto zinc chloride activated groundnut husk biochar.

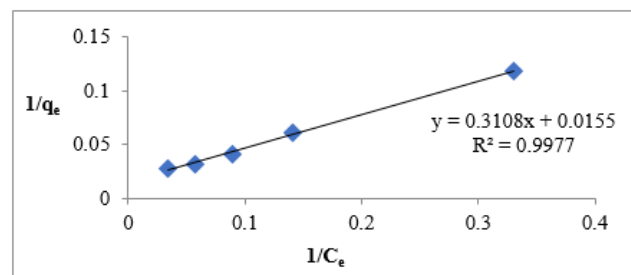
Adsorbate	Langmuir isotherm				Freundlich isotherm			
	$Q_0(\text{mg/g})$	$K_L(\text{L/mg})$	$R_L$	$R^2$	$1/n$	$N$	$K_f(\text{mg/g})$	$R^2$
Rhodamine B. dye	66.67	0.048	0.187	0.997	0.651	1.536	0.186	0.966
	Temkin isotherm				Dubinin-Radushkevich isotherm			
	$A_T(\text{L/mg})$	$b_T$	$B$	$R^2$	$q_s(\text{mg/g})$	$K_{ad}(\text{mol}^2/\text{kJ}^2)$	$E(\text{kJ/mol})$	$R^2$
	4.653	201.17	12.44	0.985	13.010	$3 \times 10^{-6}$	0.577	0.886



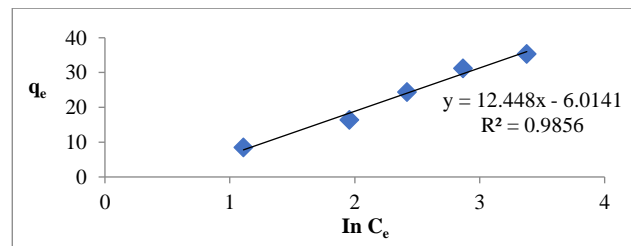
**Figure 10.** Dubinin-Radushkevich (D-R) Isotherm for zinc chloride activated groundnut husk biochar



**Figure 11.** Freundlich adsorption isotherm for zinc chloride activated groundnut husk biochar



**Figure 12.** Langmuir adsorption isotherm for zinc chloride activated groundnut husk biochar

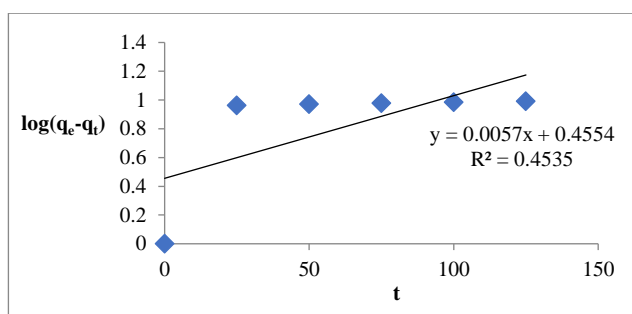


**Figure 13.** The Temkin adsorption isotherm for zinc chloride activated groundnut husk biochar

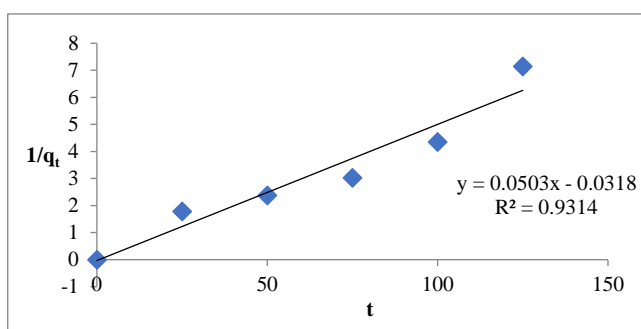
**Table 7.** The Kinetic Parameters for Rhodamine B. dye adsorption onto Zinc chloride Activated groundnut husk biochar

Kinetic model	Parameters	Solution concentration (mg/l) at 19.86
Pseudo first order	$K_1$ ( $\text{min}^{-1}$ )	-0.0131
	$q_e$ (mg/g)	0.14
	$R^2$	0.4535
Pseudo second order	$K_2$ ( $\text{g.mg}^{-1}.\text{min}^{-1}$ )	0.080
	$q_e$ (mg/g)	19.81
	$R^2$	0.9314

A comparison of the various kinetic plots based on their linear regression coefficient ( $R^2$ ) values and having compared experimental and predicted value. **Table 7** indicates that the adsorption process follows the second order rate expression. The adsorption of Rhodamine B. on zinc chloride activated groundnut husk biochar can best be described using the pseudo-second order model.  $R^2$  value of the second order kinetic equation is obtained as 0.9314. The regression coefficient is high. Therefore, the kinetic of adsorption is explained by the second order, because the regression coefficient for first order is 0.4535 while the regression coefficient of second order is greater, 0.9314. On the other hand, when the  $q_e$  values obtained from the equilibrium are compared, the second order kinetic equation predicts closer result than the first order, the  $q_e$  value estimated by the experimentally obtained  $q_e = 19.881$  mg/g (Kilic *et al.*, 2017). It is therefore assuming that the rate limiting step in the adsorption process maybe chemical adsorption, in order word, chemisorption.



**Figure 14.** Pseudo-first order kinetic model of the adsorption of Rhodamine B. onto zinc chloride activated groundnut husk biochar



**Figure 15.** Pseudo-second order kinetic model of the adsorption of Rhodamine B. onto zinc chloride activated groundnut husk biochar

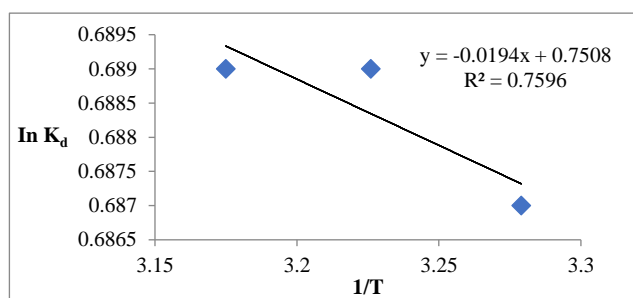
### Thermodynamic Studies

The values of the thermodynamic parameters such as change in free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) were determined using Equations 14, 15, 16 and 17, presented in **Table 8**. The plot of  $\ln K_d$  as a function of  $1/T$  yields shown in **Figure 16** is a straight line from which enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) can be calculated

from the slope and intercept, respectively. As shown in **Table 8**, negative values were observed for  $\Delta G^0$  at all working temperatures. The negative values of  $\Delta G^0$  for the Rhodamine B. adsorption onto zinc chloride activated groundnut husk biochar exhibits that the adsorption processes were spontaneous and feasible. The positive values of  $\Delta H^0$  confirmed that the adsorption of Rhodamine B. onto zinc chloride activated groundnut husk biochar is endothermic. Negative value of  $\Delta S^0$  observed for zinc chloride activated groundnut husk biochar reveals that the degree of disorderliness decreased at the zinc chloride activated groundnut husk biochar-Rhodamine B. dye interface than in the bulk solution during the adsorption of Rhodamine B. onto zinc chloride activated groundnut husk biochar predicting high energy of attraction between the adsorbent and Rhodamine B. molecules. Also, the values of adsorption energy at all temperatures are lower than  $8 \text{ kJ mol}^{-1}$ , therefore it can be concluded that the adsorption processes were dominated by physical forces.

**Table 8.** Results of Thermodynamic Studies

Temperature (°C)	1/T(K <sup>-1</sup> X 10 <sup>-3</sup> )	K <sub>d</sub>	lnK <sub>d</sub>	$\Delta G^0$	$\Delta S^0$	$\Delta H^0$
305	3.279	1.988	0.687	-1.742		
310	3.226	1.991	0.689	-1.776	-6.236	0.158
315	3.175	1.991	0.689	-1.804		



**Figure 16.** Plot of ln K against 1/T

#### 4. Conclusion

This study showed that zinc chloride-activated groundnut husk biochar is an effective and low-cost adsorbent for the removal of Rhodamine B from aqueous solutions. The findings indicate that the adsorption efficiency is influenced by key process parameters, including pH, adsorbent dose, contact time, initial dye concentration, and temperature. Optimal Rhodamine B removal was achieved at pH of 11.0, with a 1.0 g adsorbent dose, a contact time of 125 min, an initial dye concentration of 20 mg/L, and a temperature of 315 K. The equilibrium adsorption data align well with both the Freundlich and Langmuir isotherm models, indicating that the adsorption sites on the biochar are heterogeneous, but can also exhibit a maximum adsorption capacity characteristic of monolayer adsorption. In addition, analysis using the Dubinin-Raduskevich and Temkin models confirms that the adsorption of Rhodamine B is predominantly physical in nature, likely involving interactions between the dye molecules and the biochar surface. The kinetic studies reveal that the adsorption process adheres to the pseudo-second-order rate equation, suggesting that the rate-limiting step may involve chemisorption, where the dye molecules form stronger chemical bonds with the adsorbent. This indicates a potential mechanism involving the formation of covalent bonds or complexation between functional groups on the biochar and the dye as shown below:



Thermodynamic analysis indicates that the adsorption process is endothermic, suggesting that higher temperatures facilitate the removal of Rhodamine B, potentially due to increased kinetic energy that enhances the interaction between the dye and the adsorbent. The results confirm that groundnut husk biochar is a viable and sustainable option for treating textile effluent before its discharge into water bodies or for reuse in irrigation. This approach not only provides an environmentally friendly solution for wastewater treatment but also promotes the utilization of agricultural waste, contributing to a circular economy.

### Authors' Contributions

Conceptualization and design: A.T.I.; Supervision and resources: A.T.I., A.U.D; Methodology and data curation: A.T.I.; Investigation, data collection, analysis and interpretation: A.T.I., A.U.D; Writing -original draft: A.T.I., A.U.D; Writing -editing and review: A.T.I., A.U.D. Authors read and approved the submitted version.

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**Competing Interests:** None

**Availability of data and materials:** Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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