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Adsorption of Reactive Black 5 and Tatrazine Dyes onto Groundnut Shell Activated Carbon: Equilibrium, Kinetics and Thermodynamics Studies

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Abstract

The removal of hazardous dyes has become a major economic and health concern to treat wastewater. In this study, the adsorption potential of groundnut shell activated carbon (GAC) as an affordable adsorbent for the removal of anionic dyes (reactive black 5 and tatrazine) was investigated. The adsorption studies were conducted using batch experiments. The effect of initial concentration, adsorbent dosage, contact time, temperature and pH were evaluated. The optimum removal of reactive black 5 (q_e = 494.95 mg/g) and tatrazine dyes (q_e = 329.78 mg/g) was achieved at pH 2.0 The FT-IR spectroscopy of GAC revealed the presence of O-H, C-O, and C=C stretching vibrations. The SEM analysis of GAC showed several clear visible pores and irregular cavities on its surface. The kinetic study showed that pseudo-second order model best described the adsorption of dyes. The adsorption equilibrium data were fitted into Langmuir, Freundlich and Temkin isotherm models. The monolayer adsorption capacity of GAC was 82.03 mg/g and 20 mg/g for RB5 and TART respectively. The thermodynamics analysis revealed that adsorption of dyes on GAC was an endothermic process with an increase in randomness at the adsorbate-adsorbent interface. Increasing the adsorbent doses from 10 mg to 90 mg resulted into a decrease in adsorption capacity. Therefore, GAC can be cost effective adsorbent for the removal of dyes in wastewater

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Introduction

Attaining a sustainable water resources management in an integrated way is one of the major challenges faced by most countries in the world. Sustainable water management entails a standard for wastewater treatment, which is important in successfully managing wastewater and maintaining water quality (Nizam *et al*., 2021). Underground water is the main source of drinking water. The underground water is being polluted by the wastewater containing a large number of contaminants such as acids, bases, toxic organics, inorganics, heavy metals, dyes discharged by industries (Nethaji *et al*., 2013). However, water pollution from dyes has become a major environmental and health problem that poses a threat to all living organisms (Masoudian *et al*., 2019).

Approximately, 800,000 tons of synthetic dyes are produced annually and about 50% of these are azo dyes (Greluk and Hubicki 2011). Reactive black 5 and tatrazine dyes are azo dyes used in paper, textile, leather, printing, food, cosmetics, plastics and rubber. Some of these dyes are toxic, persistent and non-biodegradable. The presence of dyes in aqueous solutions can interfere with the photosynthetic functions of aquatic plants by blocking the sunlight with its aromatic compounds resulting to a reduction in dissolved oxygen (Pashaei-Fakhri *et al*., 2021; Esvandi *et al*., 2020).

Several technologies have been employed for the removal of dyes, including coagulation, chemical oxidation, membrane separation, electrochemical process, and adsorption (Sahnoun *et al*., 2018). Among these techniques, adsorption proved to be an efficient and economical process for the treatment of dye containing effluents. The efficiency of an adsorption process depends on the choice of the adsorbent. The chosen adsorbent should be easily available, cheap and should have no economic value. Activated carbon is the most widely used adsorbent for the removal of dyes from waste water, it is characterized by large surface area, re-usability and ability to remove bigger-sized compounds such as dyes (Zhang *et al*., 2012). The disadvantage of its use in wastewater treatment is that it is expensive.

This has led to the use of low cost activated carbons derived from agricultural waste materials such as fig leaves (Gebreslassie, 2020), cassava sievate biomass (Chukwuemeka-Okorie, 2021), activated carbon from wild almond shell and coir pith (Thitame and Shukla, 2016), rubber seed activated carbon (Nizem *et al*., 2021), sugar cane bagasse (Sharma and Nandi, 2013), ginger waste (Ahmad and Kumar, 2010) and banana stalk (Hameed *et al*., 2008) for the removal of dyes from waste water.

A groundnut shell is a carbonaceous, fibrous solid waste which is suitable for the production of activated carbon. It contains numerous bioactive and functional components which are useful for livestock feeds. But most of the deserted groundnut shells are burnt or buried resulting in environmental pollution. However, there is need for technological development in order to attain zero waste production and utilize this waste product in food, feed, paper, wastewater treatment and bioenergy industries (Adhikari *et al*., 2019). The aim of this research was to investigate the effectiveness of groundnut shell activated carbon (GAC) for the removal of reactive black 5 and tatrazine dyes from wastewater.

Preparation of Activated Carbon

The groundnut shell collected from Oja Oba Market Ilorin, Kwara State was washed thoroughly with deionized water to remove dirt and dried at room temperature. The activation process was done by impregnating 100 g of the groundnut shell with 0.1 M of H_3PO_4 in the ratio 1:1 for 24 h and heated in a pyrolyzer at 400 ^oC for 40 min. The carbonized precursor was washed with deionized water to pH of 7 and ovendried at 100 ^oC.

Characterization of the Adsorbent

The surface morphology of groundnut shell activated carbon (GAC) was determined using Scanning Electron Microscope (SEM). The Energy Dispersive X-ray Spectroscopy (EDS) was used to determine the elemental composition of the adsorbent and Fourier Transform Infrared Spectroscopy (FT-IR) was used to identify the characteristic functional groups present on its surface.

The pH of point of zero charge (pH_{pzc}) of the adsorbent (GAC) used for the adsorption studies was determined using pH drift method (Abdus-Salam, 2005). The pH of 20 ml of 0.1 M of KCl solution was adjusted by using 0.1 M HCl and 0.1 M NaOH to pH of 2, 3, 4, 5,6,7,8,9,10, 11 and 12. A 0.02 g of the adsorbent was added to the solutions in the reaction bottles and agitated on a mechanical shaker for 24 h in order to stabilize the pH. The final pH was recorded and a graph of pH difference (pHinitial – pHfinal) versus the initial pH was used to determine the $pH_{pzc.}$

Adsorption Experiment

The stock solutions of RB5 and TART dyes were prepared by serial dilution and the adsorption of dyes on GAC was conducted in batches. The influence of various physicochemical parameters such as initial dye concentration (10-650 mg/l), adsorbent dosage (0.01-0.09 g), contact time (10-120 min), temperature (303-318 K) and pH (2-10) on the adsorption process was investigated. In each of the experiments, a predetermined amount of GAC was contacted with 25 ml of the adsorbate solution of known concentration. The pH of the solutions was adjusted to the desired values with an aqueous solution of 0.1 M HNO_3 or 0.1 M NaOH. The solutions were agitated using a mechanical shaker at a constant agitation speed of 150 r.p.m for a given period of time. After the equilibrium was attained, the samples were brought out and the supernatant solution was filtered. The filtrates were analyzed using UV-Visible spectrophotometer at λ_{max} of 594 nm for RB5 and 427 nm for TART. The percentage dye removal and the adsorption capacity of the adsorbent were calculated using equations 1 and 2.

$$\% \text{ Adsorption} = \frac{(C_i - c_f)}{c_i} \times 100 \qquad (1)$$

$$q_e = (C_i - c_f)\,\frac{V}{M} \qquad (2)$$

Isotherms, Kinetics and Thermodynamics Study

The equilibrium data obtained from the adsorption of RB5 and TART dyes onto GAC was fitted into the linear form of Langmuir, Freundlich and Temkin Isotherm models. The pseudo-first order, pseudo-second order and intra-particle diffusion models were used to analyze the kinetic data of the anionic dyes. The thermodynamic parameters for the adsorption process such as standard free energy change (ΔG^o), standard enthalpy change (ΔH^o), and standard entropy change (ΔS^o).

Results and Discussion

The pH of point of zero charge (pH_{pzc}) is the pH value at which a solid immersed in an electrolyte solution exhibit zero net electronic charge on the surface (Adebayo *et al*., 2015). The pH_{pzc} of GAC was found to be 8.2. The FT-IR spectrum of GAC was taken in the range of 4000 to 500 cm^{-1} to confirm the presence of the functional groups responsible for the adsorption process. As seen in Fig.1 an absorption peak at 3419.49 cm^{-1} corresponds to hydroxyl (O-H) stretching vibrations. The peak at 1591.85 cm^{-1} was attributed to C=C stretching vibrations of the alkene group and 1217.51 cm^{-1} was due to C–O stretching of alcohols, phenols, esters or ethers (Ajala &Ali, 2020). The band at 817.97 cm^{-1} was due to C-H bending vibrations in GAC.

SEM and EDS are important analytical tools for elucidating the characteristics of an adsorbent. The SEM micrographs of GAC (Fig.2) revealed several clear visible pores and irregular cavities which was due to the release of volatiles within the microstructure as a result of activation (Ajala & Ali, 2020). The Numerous cracks and small pits on the external surface of GAC indicate a good interaction of the activating agent with the precursor during carbonization resulting into a product with large surface area and porous structure (Abdul-Khalil *et al*., 2013). EDS results revealed that groundnut shell activated carbon (GAC) consists mainly of carbon.

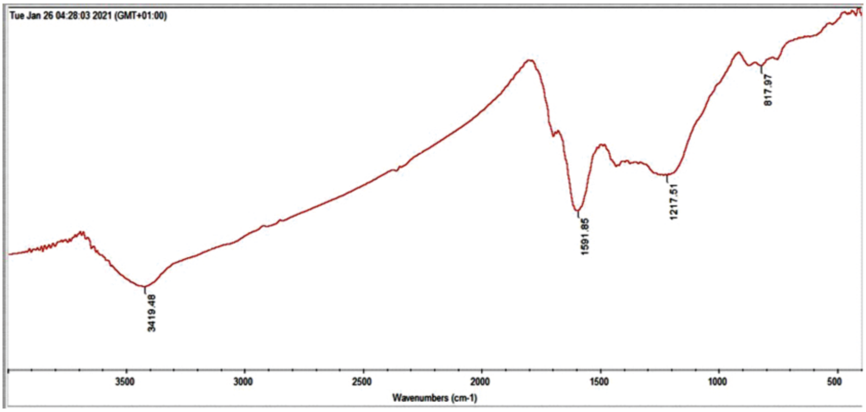

Figure 1: FT-IR Spectrum of GAC

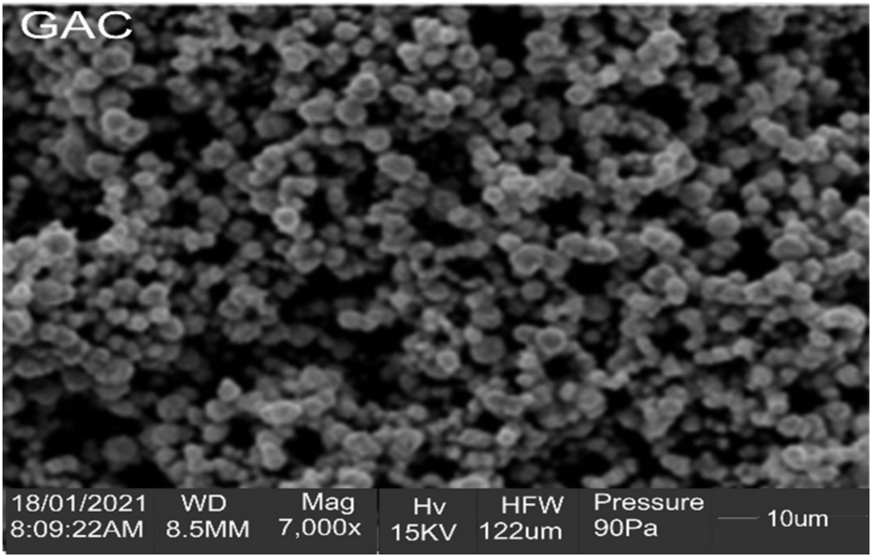

Figure 2: SEM Micrograph of GAC

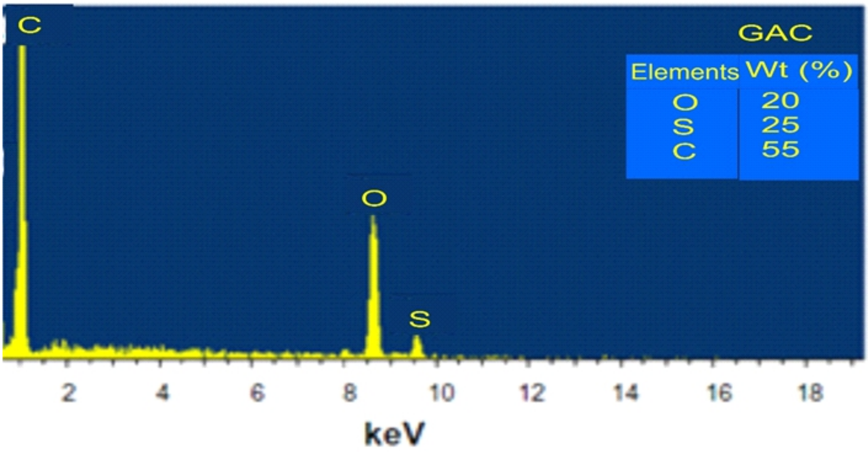

Figure 3: EDS Spectrum of GAC

Adsorption Studies

Effect of Initial Dye Concentration

The influence of the initial dye concentration depends on the immediate interaction between the dye concentration and the available binding sites on an adsorbent surface (Gautam *et al*., 2014). In order to determine the effect of initial dye concentration on the extent of adsorption of reactive black 5 (RB5) and tartrazine (TART) onto ground shell activated carbon (GAC), initial concentrations of RB5 and TART were varied from 100 to 650 mg/L. It is apparent that the amount of RB5 and TART adsorbed per unit mass of GAC increased with increase in initial dye concentration (Fig.4). However, maximum removal was observed at 650 mg/L for RB5 while for TART it was achieved at 500 mg/L with 65.77 mg/g and 20.33 mg/g respectively as the maximum quantity adsorbed. The rapid increase in the rate of adsorption could be attributed to the increase in the driving force of the concentration gradient, as the initial dye concentration increases (Chiou and Li, 2002). Similar trend was reported by Abdus-Salam and Buhari (2014) in which as the adsorbate concentration increases the rate of dye removal also increases. The optimum concentration obtained in both cases was kept constant for further studies on the effect of various parameters such adsorbent dose, time, pH and temperature on adsorption.

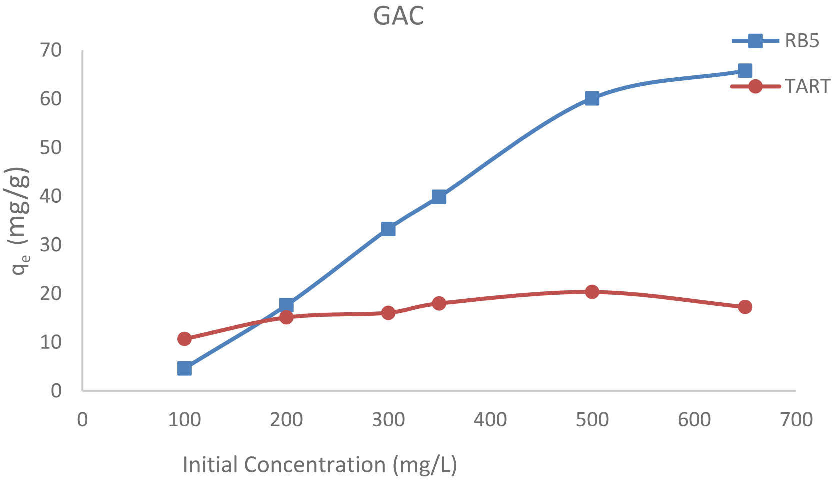

Figure 4: Effect of initial concentration on Adsorption of RB5 and TART onto GAC

Effect of Adsorbent Dosage

The effect of adsorbent dose of GAC on adsorption of RB5 and TART was carried out by variation of adsorbent dosage in the range of 0.01 to 0.09 g while the initial dye concentration, pH, contact time and other operating conditions were kept constant as shown in Fig. 5. It can be observed that by increasing the adsorbent dosage, GAC showed a gradual decrease in RB5 and TART removal from 385.45 mg/g to 41.67 mg/g and 119.1 mg/g to 9.37 mg/g respectively.

The decrease in adsorption capacity with increase in adsorbent dosage could be as a result of saturation of adsorbent sites during the adsorption process (Yu *et al*., 2003). It can also be due to aggregation of active adsorption sites as the adsorbent dosage increases resulting to a decrease in surface area of the adsorbent which led to a reduction in dye removal.

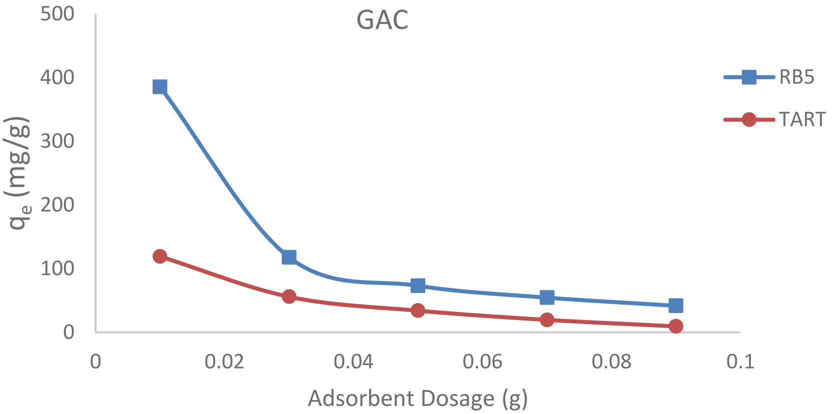

Figure 5: Effect of adsorbent dosage on adsorption of RB5 and TART onto GAC

Effect of Contact Time

Contact Time is important for adsorption studies because it predicts the rate at which a pollutant is removed from aqueous solutions and provides a means by which valuable data are evaluated to determine the mechanism of the adsorption process. The effect of contact time on removal of RB5 and TART onto GAC is shown in Fig. 6, it is obvious that the adsorption process had a biphasic kinetic, the initial fast phase and a second slow phase. At the initial phase, the rate of dye removal was rapid due to availability of many vacant active sites and after the initial fast adsorption was achieved the remaining vacant surface sites were difficult to access due to repulsive forces between the solute molecules on the solid and bulk phases. Similar observation was reported in literature (Mohan *et al*., 2006). Thus, maximum uptake of RB5 was observed within 45 min of the experiment with adsorption capacity of 376.35 mg/g while that of TART was seen at 60 min with adsorption capacity of 107.53 mg/g.

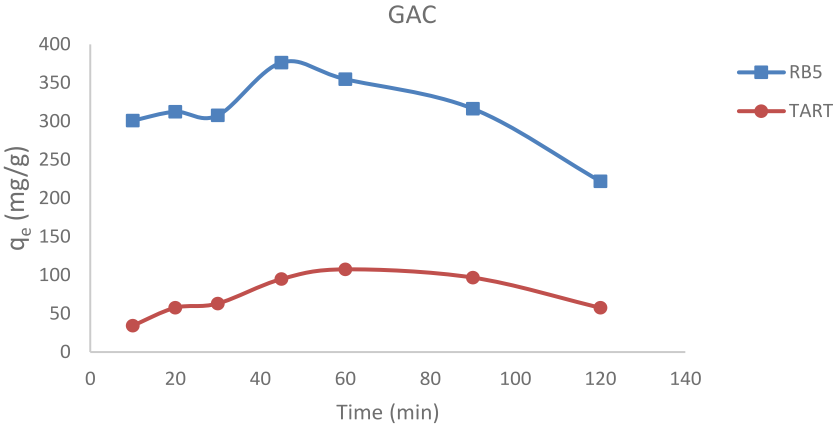

Figure 4: Effect of contact time for adsorption of RB5 and TART onto GAC

Effect of Temperature

The effect of temperature on the adsorption capacity of GAC is represented by the plot of quantity adsorbed versus temperature for RB5 and TART (Fig.5). There was an increase in the quantity adsorbed with increase in temperature for removal of the pair of dyes onto GAC, indicating the endothermic nature of the adsorption process. The increase in adsorption capacity with initial increase in temperature was due to the increase in kinetic energy of adsorbent molecules which also increases the interaction between adsorbate and adsorbent. Hence, the collision frequency between adsorbent and adsorbate increases which enhances adsorption onto the active site of the adsorbent (Tamirat *et al*., 2014).

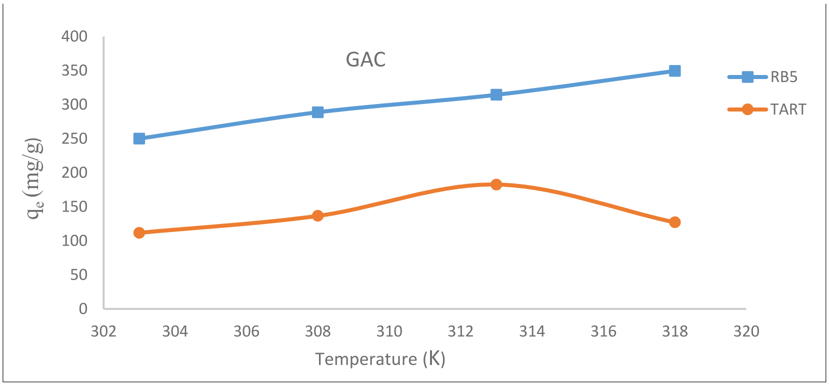

Figure 5: Effect of Temperature on Adsorption of Dyes onto GAC

Effect of pH

The pH of the solution is an important factor that controls the surface charge of the adsorbent and the degree of ionization or polarity of the adsorbate in the solution (Sakkayawong *et al*., 2005). The effect of pH on the adsorption capacities of GAC was conducted by varying the pH from 2 to 10. It can be observed in Fig.6 that the maximum adsorption of both anionic dyes was achieved at pH 2 and then decreased with a rise in pH from 3 to 10 for RB5. This was due to dissociation of RB5 in aqueous solution (Wawrzkiewicz and Hubicki, 2009). In acidic solutions, the adsorbent surface is positively charged, which favours the adsorption of anionic dyes as a result of increased electrostatic interactions between the positively charged adsorbent's surface and negatively charged SO_3^- group of RB5. In Alkaline medium, competition exists between anionic dyes and excess OH^- in solution which resulted into a decrease in adsorption capacity of GAC.

However, TART showed a rise in adsorption capacity after pH 8 for its adsorption onto GAC in which a subsequent increase in pH resulted into an increase in adsorption capacity. This may be due to the presence of partially charged groups in the tartrazine structure, such as COO^-, SO^-_3, and OH^-. The double bond enhances the interaction between TART and adsorbents (Habila *et al*., 2014). It has been reported by several researchers who studied the relationship between pH and the adsorptive removal of anionic dyes by various adsorbents that the adsorption reached its peak at low pH values (Alhujaily *et al*., 2020; Un and Ates 2019; Munagapati *et al*., 2018).

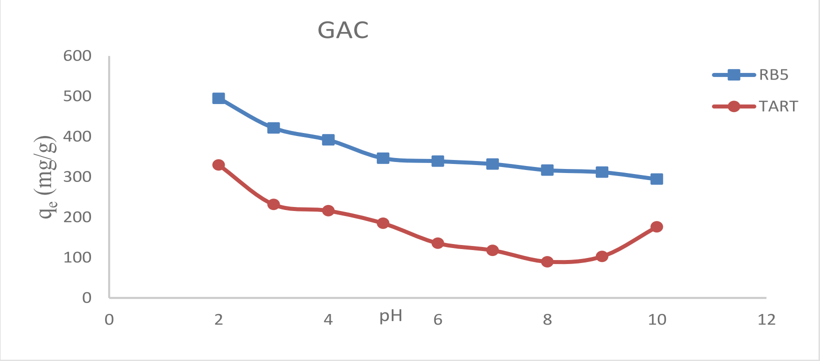

Figure 6: Effect of pH on Adsorption of RB5 and TART Dyes on GAC

Adsorption Isotherm

The adsorption isotherm provides essential information needed to understand the interactions between adsorbates and adsorbents (Mahmoud *et al*., 2016). The linearized form of Langmuir, Freundlich and Temkin isotherm equations are presented in equations 3-5 **(**Gebreslassie, 2020)**:**

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{K_{L}\, q_m} + \frac{1}{q_m} C_e \qquad (3)$$

$$\text{Freundlich: Log } q_e = Log\ K_f + (\frac{1}{n}) \text{ Log } C_e \qquad (4)$$

$$\text{Temkin: } q_e = \text{B In A} + \text{B In } C_e \qquad (5)$$

where q_m is the monolayer adsorption capacity (mg g−1), q_e the adsorption capacity at equilibrium (mg g−1), C_e the equilibrium solution concentration (mg L^{-1}), K_L (L mg−1) is the Langmuir isotherm constant and K_f is the Freundlich constant, and 'n' is the adsorption intensity, A is the equilibrium binding constant (Lg^{-1}) corresponding to the maximum binding energy and constant B is related to the heat of adsorption.

The linear correlation coeffcients values (R^2) obtained from the isotherm models were used to determine the suitability of each isotherm models. The isotherm parameters and constants obtained from the adsorption studies are presented in Table 1. The experimental data for the adsorption of RB5 and TART dyes fitted into the Langmuir, Freundlich and Temkin isotherm models. However, adsorption of TART fitted better into Langmuir than Freundlich and Temkin isotherm models, indicating good monolayer coverage of the dye molecules on the adsorbent. Also, the values of R_L which lies between 0 and 1 indicate a favourable adsorption of dyes on GAC. Meanwhile, the adsorption of RB5 was better described by the Freundlich isotherm than Langmuir and Temkin models. This suggests the heterogeneous nature of the surface of GAC and possibility of multimolecular layer formation on the surface of the adsorbent (Chukwuemeka-Okorie, 2021). From Table 1, the value of 1/n for RB5 was 1.323, indicating a cooperative adsorption while that of TART was 0.2701 suggesting a normal adsorption (Dada *et al*., 2010). The value of 'n' also indicate the favourability of the adsorption process, A value less than 1 indicates that sorption intensity is favourable over the entire range of concentrations, while a value greater than 1 favours adsorption at higher concentration (Abdus-Salam and Adekola, 2018). It could be concluded from the values obtained that the adsorption was favorable at higher concentrations of TART while that of RB5 over the entire range of concentrations studied.

Table 1: Table 1: Isotherm Parameters for the Adsorption of RB5 and TART Dyes onto GAC

Isotherm Model	Parameters	RB5	TART
Langmuir	q_m (mg/g)	84.03	20
	K_L (L/mg)	0.001	0.019
	R_L	0.377	0.069
	R^2	0.528	0.9678
Freundlich	K_F (L/mg)	0.023	3.526
	n	0.756	3.702
	1/n	1.323	0.2701
	R^2	0.9827	0.8217
Temkin	B (j/mol)	1.323	0.2701
	b_o	1872.27	9172.795
	A (L/mg)	0.058	106.197
	R^2	0.9827	0.8217

Adsorption Kinetics

In order to determine the mechanism and the rate controlling step involved in the adsorption of RB5 and TART onto GAC, the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetics models were used to check the fittings of the equilibrium data. The linearized form of these models are presented in equations 6-8:

$$\text{Pseudo-first-order: In } (q_e - q_t) = \text{In } q_e - K_1 t \qquad (6)$$

$$\text{Pseudo-second-order: } \frac{t}{q_t} = \frac{1}{K_{2} q_e^2} + \frac{1}{q_e} t \qquad (7)$$

$$\text{Intra-particle Diffusion: } q_t = K_{diff} t^{1/2} + C \qquad (8)$$

q_e is the amount of adsorbate at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed onto the adsorbent at any time t (mg/g), k_i (min^{-1}) and k_2 (g/mg/min) are the rate constant for the pseudo-first-order adsorption and pseudo second order equation,

K_{diff}(mg g–1 min–$^{1/2}$) is the rate constant for intraparticle diffusion and 'C' explains the thickness of the boundary layer.

The kinetic parameters obtained from the slope and intercepts of the plots of these models are depicted in Table 2. The applicability and reliability of a particular kinetic model for an adsorption process is determined by a high correlation coefficient (R^2) and a close agreement between the calculated and experimental q_e values ($q_{e,\ exp}$ and q_e, calc.) (Liudmyla and Marianna, 2019). However, the high correlation coefficients ($R^2 > 0.97$), closeness of values of calculated and experimental equilibrium adsorption capacity of GAC for anionic dyes removal indicate the best fittings of experimental data to pseudo-second-order model. This shows that chemical adsorption is the rate determining step (Gholizadeh *et al*., 2013). The Intraparticle diffusion model assumes that the dye molecules diffuse inward into the porous adsorbent (Chukwuemeka-Okorie, 2021). The low R^2 values obtained from the intraparticle diffusion model indicate that other mechanisms were involved in the adsorption process. The value of 'C' which reflects the thickness of the boundary layer was higher for RB5, this shows that the removal of RB5 was mainly due to surface adsorption.

Table 2: Kinetic Parameters for Adsorption RB5 and TART Dyes onto GAC

Kinetic Model	Parameters	RB5-GAC	TART-GAC
	$q_{e,}$ exp (mg/g)	376.348	107.525
Pseudo-first-order	K_1 (min^{-1})	-8.3×10^{-3}	8.8×10^{-3}
	q_e cal (mg/g)	22.847	31.365
	R^2	0.036	0.0542
Pseudo-second-order	K_2 (g/mg/min)	1.21×10^{-3}	107.525
	q_e cal (mg/g)	277.78	69.444
	R^2	0.9798	0.8298
Intraparticle Diffusion	K_{id} (mg/gmin$^{1/2}$)	-6.1774	4.8154
	C	355.26	40.123
	R^2	0.1226	0.2457

Adsorption Thermodynamics

The thermodynamic studies make it easy to comprehend the feasibility of the adsorption process and provide useful information about fundamental thermodynamics parameters of adsorption such as standard free energy change (ΔG^o), standard enthalpy change (ΔH^o), and standard entropy change (ΔS^o). These parameters are calculated based on equations 9 and 10

$$\Delta G^o = -RT \ln K \qquad (9)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H^o}{RT} \qquad (10)$$

The thermodynamic parameters obtained from this study are presented in Table 3. From this table, it is obvious that the adsorption of both anionic dyes were endothermic, because the value of ΔH^o was positive. Similar results of an endothermic adsorption were reported for the adsorption of dyes on activated carbon from core pith and almond shell (Thitame and Shukla, 2016) and activated carbon from Juglans regia shells (Nethaji *et al*., 2013). The negative value of ΔS^o for adsorption of RB5 onto GAC indicates an enthalpy driven adsorption process and also shows that no significant change occurs in the internal structure of the adsorbent during the adsorption process (Anirudhan and Radhakrishnan, 2008) while that of TART was positive, implying an increase in randomness of the dye molecules on the surface of GAC than in the solution of TART. The value of ΔG^o determines the rate of the reaction, a decrease in ΔG^o results to an increase in the rate of the adsorption process (Rida *et al*., 2013). It can be observed from Table 3 that ΔG^o decreases with increase in temperature, confirming an increase in the rate of removal of dyes with the temperature. The positive values of ΔG^0 for the adsorption of dyes on GAC suggest that the adsorption processes are not spontaneous and require some energy from an external source to enhance the removal of dyes (Saha & Chowdhury, 2011).

Table 3: Thermodynamics Parameters

Conclusion

Adsorbate	ΔH (kj/mol)	ΔS (j/mol/k)	ΔG (kj/mol)			
			303 K	308 K	313 K	318 K
RB5	0.17	-8.221	4.29	3.92	3.72	3.99
TART	12.52	0.02	5.85	5.37	4.59	5.76

This study has successfully shown the effectiveness of Groundnut Shell Activated Carbon (GAC) for the removal of reactive black 5 and tatrazine dyes from aqueous solutions. Various factors affecting adsorption, including initial concentration, adsorbent dosage, contact time, temperature and pH were optimized to evaluate the adsorption process. The equilibrium data fitted into the Langmuir, Freundlich and Temkin isotherm models. The pseudo-second-order kinetic model best described the adsorption of dyes on GAC with correlation coefficient value (R^2) close to unity suggesting that chemisorption may be the rate limiting step. These results suggest that GAC is a suitable adsorbent for the treatment of wastewater containing dyes.

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