Isothermal, Kinetic and Thermodynamic Studies of the Adsorption of Erythrosine Dye onto Activated Carbon from Periwinkle Shell

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Abstract— *Isothermal, kinetic and thermodynamic studies of the adsorption of erythrosine dye onto activated carbon from Periwinkle shell was carried out. The Periwinkle shell were washed, dried, carbonized at 400ºC, crushed, sieved, chemically activated at 800ºC, cooled, washed and dried at 110ºC. Variable influencing factors, such as contact time, temperature and concentration were studied through single-factor experiment, while other factors are kept constant (at 30min, 30ºC and 50mg/L) in each adsorption experiment. From the adsorption isotherms, the correlation coefficient for Redlich-Peterson is closer to unity than others used in the adsorption. The adsorption kinetic followed pseudo-second order reaction, while the thermodynamic parameters, (ΔH) = 13.49KJ/mol, (ΔS) = 43.48J/mol.K and (ΔG) = 0.4, 0.06, -0.15, -0.27, -0.54, -7.30KJ/mol. These results obtained show that activated carbon from Periwinkle shell will be a good low-cost adsorbent for the removal of erythrosine from aqueous solution.*
Keywords— *Adsorption, Erythrosine, Kinetic, Periwinkle shell, Thermodynamic.*

I. INTRODUCTION

Discharge of colored wastewater from textile, paper, plastics, cosmetics and food industries in the waterways are the first detectable contaminants and in appearance create adverse conditions. Since most of the dyes are stable against light and heat and remain biologically indecomposable, it is difficult to remove them from the water. In some cases, decolorization of the industrial wastewater proved to be a major environmental issue [4].

The coloration of the water by the dyes causes inhibitory effect on photosynthesis affecting aquatic ecosystems. The role of dyes in connection with variety of skin, lung and other respiratory disorder has been reported worldwide. The discharge of highly colored effluent into natural water bodies is not only aesthetically displeasing, but it also impedes light penetration, thus upsetting biological processes within a stream. In addition, many dyes are toxic to some organisms causing direct destruction of aquatic communities. Therefore, it is required to adopt appropriate methods for treatment of such wastewater before its discharge to the environment [5].

In this study, the ability of Periwinkle shell carbon to remove erythrosine by adsorption is been studied. The adsorption capacity of the dye will also examined using the adsorption isotherm technique. The Langmuir, Freundlich and Redlich-Peterson isotherms will used to fit the equilibrium data. Pseudo-first order, pseudo-second order models, activation energy and thermodynamic equations will be used to fit the experimental data [3].

II. RESEARCH METHOD

2.1 Preparation of adsorbents

Sample of Periwinkle shells were picked from the environment in Elele, Rivers State, Nigeria. The Periwinkle shells were washed with tap several times to remove the dust and other water- soluble materials. The process continues until the washing water was colorless. They were respectively dried in the open air. The dried Periwinkle shell was carbonized in a furnace (SX-5-12) at 400˚C for 3 hours and the charred were allowed to cool to room temperature, ground and sieved (150 - 600μm). It was chemically activated by weighing 100gram of the ground carbonized charred in 300 ml of 0.1M HCl solution, thoroughly mixed and heated until it formed slurry. The slurry was transferred to a crucible and heated in a furnace (SX-5-12) at 800˚C for 3 hours and allowed to cool to room temperature and washed with de-ionized water, dried in an oven at 110˚C for 2 hours [1].

2.2 Preparation of adsorbate

The Erythrosine used is of laboratory grade (KEM LIGHT, India). The solution was prepared in de-ionized water from Ion-exchange (Indian) Ltd, Eleme, Port Harcourt, Nigeria. An accurately weighed quantity of the dye was dissolved in de-ionized water to prepare the standard solution.

Experimental solutions of the desired concentrations were obtained by successive dilutions with de-ionized water.

2.3 Adsorption experiment

1000mg of the activated carbon of Periwinkle shell was mixed with 50ml of Congo red solution of the desired concentrations (25, 50, 75, 100, 125 and 150mg/L) at 30ºC in a temperature controlled water bath with constant shaking. The samples were withdrawn after 30 minutes and dye solutions were separated from the adsorbent using Whatmann filter paper. The concentration of the filtrate was measured with a UV spectrophotometer (2OD) at 524nm. The experiment was repeated using 1000mg of the activated carbon with 50ml of 50mg/L concentration of erythrosine solution at 30ºC in a temperature controlled water bath with constant shaking. The samples were withdrawn after 30, 60, 90, 120, 150 and 180minutes respectively and filtered using Whatmann filter paper. The concentration of the filtrate was measured with a UV spectrophotometer (2OD) at 524nm. Again 1000mg of the activated carbon mixed with 50ml of 50mg/L concentration of erythrosine solution at 30, 35, 40, 45, 50 and 55ºC in a temperature controlled water bath (DK – 420) with constant shaking was also carried out. The samples were withdrawn after 30minutes respectively filtered and the concentration measured.

The adsorption amount of erythrosine dye adsorbed onto the Periwinkle shell adsorbent at equilibrium was calculated with the following equation:

$$q_e = \frac{(C_o - C_e)V}{X} \qquad\qquad 1$$

Where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of the dye, V (L) is the volume of solution, X (g) is the weight of adsorbent in one container.

III. THEORY

3.1 Adsorption isotherms

Adsorption isotherms of erythrosine were measured using concentration-variation method at constant temperature, time and volume [3].

3.1.1 Adsorption Isotherm Langmuir adsorption isotherm (model)

The model represents one of the first theoretical treatments of non-linear adsorption and suggests that uptake occurs on a homogenous surface by monolayer adsorption without interaction between adsorbed molecules. The rate change of concentration due to adsorption should be equal to the rate of concentration due to desorption. As a result, the Langmuir isotherm is as expressed in equation 3

$$q_e = \frac{a\,b\,C_e}{1 + a\,C_e} \qquad\qquad 2$$

$$\frac{Ce}{qe} = \frac{1}{b\,Qo} + \frac{Ce}{Q_o} \qquad\qquad 3$$

Where Q_o and b are Langmuir constants q_e, is amount of solute removed or adsorbed at equilibrium. C_e, is equilibrium concentration of mixtures. Thus Q_o, b and the squared of the regression coefficient (R^2), are adsorption parameters estimated by Langmuir model. It has been well documented that the essential characteristic of the Langmuir isotherm may be expressed in terms of the dimensionless parameter (R_L) has been defined as isotherm shape that predicts if an adsorption system is favorable or unfavorable. R_L is considered as a reliable indicator of the adsorption process. R_L also indicates the assumption characteristics:

$R_L > 1$ (is unfavorable)

$R_L = 1$ (linear adsorption)

$0 < R_L < 1$ (is favorable)

$$R_L = \frac{1}{1 + b\,C_o} \,[3] \qquad\qquad 4$$

3.1.2 Freundlich adsorption isotherm (model)

The Freundlich isotherm is an empirical relationship which often gives a more satisfactory model of experimental data. The Freundlich model can be applied onto heterogeneous surface involving multilayer adsorption. It can be expressed as follows:

$$K_f C_e^{1/n} \qquad\qquad 5$$

However, the linearized Freundlich adsorption isotherm can be expressed in the form;

$$Log\,q_e = Log\,(K_f) + \frac{1}{n} Log\,C_e \qquad\qquad 6$$

Where C_e and q_e are equilibrium concentration and adsorption capacity at equilibrium stage, while K_f and n are Freundlich constants which incorporates all factors affecting the adsorption process (adsorption capacity and intensity). Values of K_f and n can be obtained from the intercept and slope of a plot of adsorption capacity, q_e against equilibrium concentration C_e. Both parameters K_f and n affect the adsorption isotherm. The larger the K_f and n values, the higher the adsorption capacity. Furthermore, the magnitude of the exponent n gives an indication of the favorability of the adsorption process [3].

3.1.3 Redlich-Peterson isotherm (model)

The Redlich-Peterson (R-P) isotherm model can be represented as

$$q_e = \frac{K_R C_e}{1 + a_R C_R^{\beta}} \qquad\qquad 7$$

Where K_R is the R-P isotherm constant (1/mg), a_R is also a constant $(\frac{1}{mg})^{\frac{1}{\beta}}$ and β is the exponent which lies between 0 and 1.

3.2 Adsorption kinetics

The pseudo first order and second order kinetic models need to be tested at different concentrations in this study to determine which model is in good agreement with

experiment q_e (adsorption capacity) value, thus suggesting which model the adsorption system follows.

3.2.1 Pseudo-first order equation

The Largergren model assumes a first order adsorption kinetics and can be represented by the equation.

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad 8$$

$$\text{Log}(q_e - q_t) = \text{Log}(q_e) - \frac{K_1}{2.303}t \qquad 9$$

The values of Log $(q_e - q_t)$ were linearly correlated with t. The plot of Log $(q_e - q_t)$ versus t should give a linear relationship from which K_1 and q_e can be determined from the slope and intercept of the plot, respectively.

3.2.2 Pseudo-second order equation

The pseudo-second-order adsorption kinetic rates equation is expressed as

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad 10$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \qquad 11$$

The plot of (t/q_t) and t of equation 10 should give a linear relationship from which q_e and K_2 can be determined from the slope and intercept of the plot, respectively.

3.2.3 Kinetic parameters of activation

From the Van't Hoff equation, for isobaric and isochoric conditions, Arrhenius developed another equation called the rate constant K of a chemical reaction on the temperature.

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2} \qquad 12$$

For the adsorption process, upon integration and evaluation, the logarithm of the rate constant (K) could be represented as a straight line function of 1/T

$$\ln K = -\frac{E_a}{RT} + \ln A \qquad 13$$

Where k is the rate constant, A is a frequency factor, R is the universal gas constant (8.314 $J.K^{-1}.mol^{-1}$) and T is the absolute temperature. The value of E_a is calculated from the slope of plotting lnk versus 1/T, and A (min^{-1}) is determined from the intercept.

Equation 11 can also integrated within the limits T_1 to T_2 to give

$$\ln\frac{k_{T2}}{k_{T1}} = \frac{E(T_2 - T_1)}{R\,T_1 T_2} \qquad 14$$

Where K_{T2} = rate constant of chemical reaction at T_2

K_{T1} = rate constant of chemical reaction at T_1[9].

3.3 Thermodynamic studies

The determination of the basic thermodynamic parameters: enthalpy of adsorption (ΔH), Gibb's free energy of adsorption (ΔG) and entropy of adsorption (ΔS), is important as these determines if the process is favorable or not from thermodynamic point of view, also to assess the spontaneity of the system and to ascertain the exothermic or endothermic nature of the process. An adsorption process is generally considered as physical if $\Delta H\circ < 84$ kJ mol^{-1} and as chemical when $\Delta H\circ$ lies between 84 and 420 kJ mol^{-1} [11].

The thermodynamic parameters of the adsorption process were determined from the experimental data obtained at various temperatures using equations 15 to 17

$$\Delta G = -RT\ln K_d \qquad 15$$

$$K_d = \frac{qe}{Ce} \qquad 16$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad 17$$

where K_d is the distribution coefficient for the adsorption, q_e is the amount of dye (mg) adsorbed on the adsorbent per L of solution at equilibrium, C_e is the equilibrium concentration (mg/L) of the dye in solution, T is the absolute temperature, R is gas constant, $\Delta G^o, \Delta H^o$, and ΔS^o are Gibbs free energy change, enthalpy change and entropychange, respectively. The values of enthalpy change (ΔH^o) and entropy change (ΔS^o) are obtained from the slope and intercept of $\ln K_d$ versus 1/T plots [1].

IV.   RESULTS

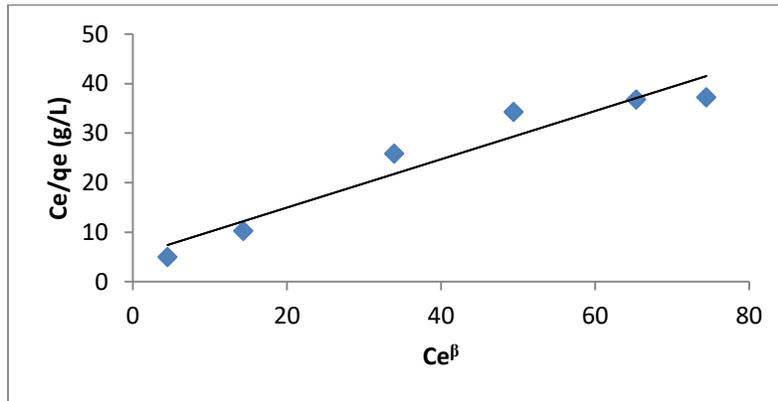The results of the adsorption experiment are presented graphically in the figures below.
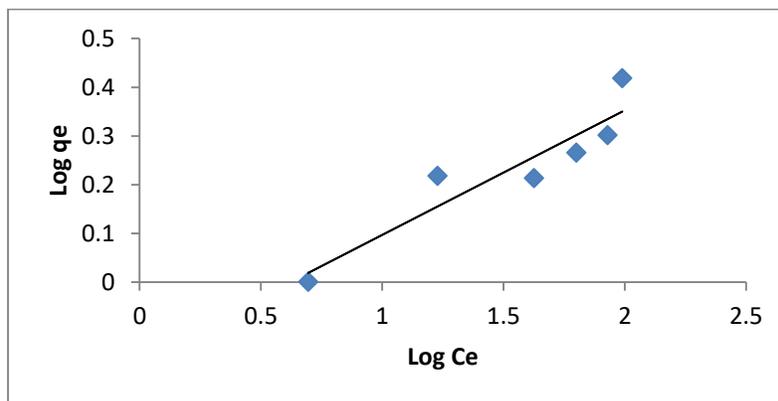

Fig. 1: Redlich-Peterson model for erythrosine
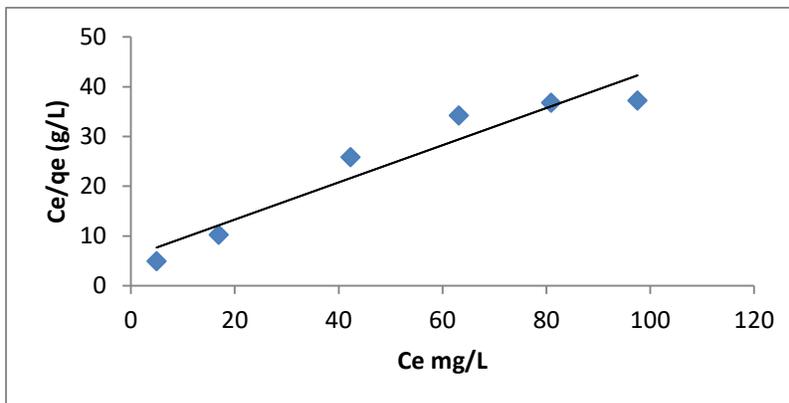

Fig 2: Freundlich model of erythrosine
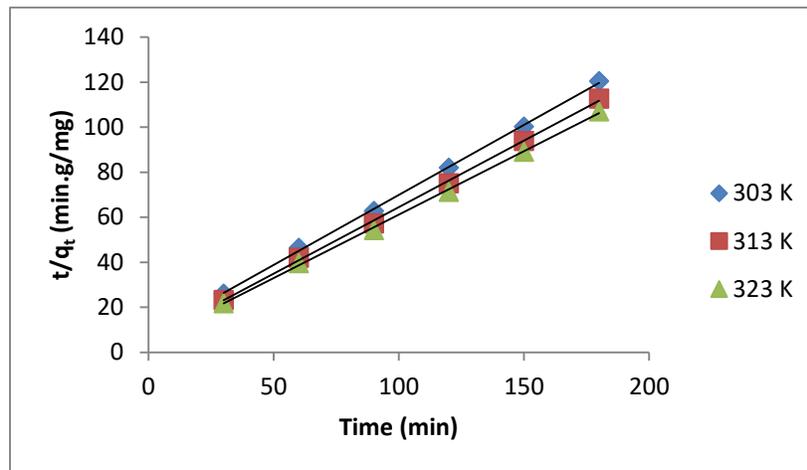

Fig. 3: Langmuir model of Erythrosine
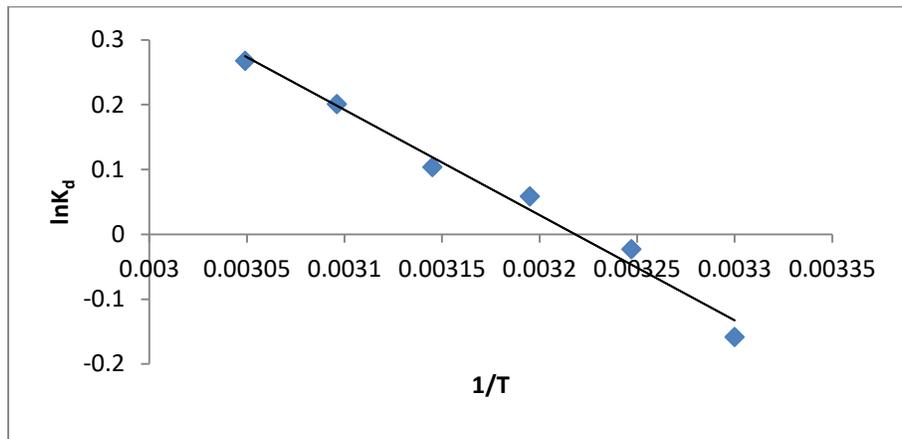
Fig. 4: Pseudo-second order reaction

Fig. 5: Effect of temperature on the adsorption distribution coefficient

Table.1: Adsorption isotherm constants of the dyes for periwinkle shell activated carbon

Langmuir			Freundlich			Redlich-Peterson			
$Q_o(\frac{mg}{g})$	$b(\frac{L}{mg})$	R^2	$K_f(\frac{mg}{g})$	$1/n(\frac{g}{L})$		$K_R(\frac{L}{mg})$	$a_R(\frac{L}{mg})$	β	R^2
2.5381	0.0720	0.9160	0.6934	0.2560	0.8590	0.2150	0.1127	0.940	0.9240

Table.2: Kinetic and activation energy parameters

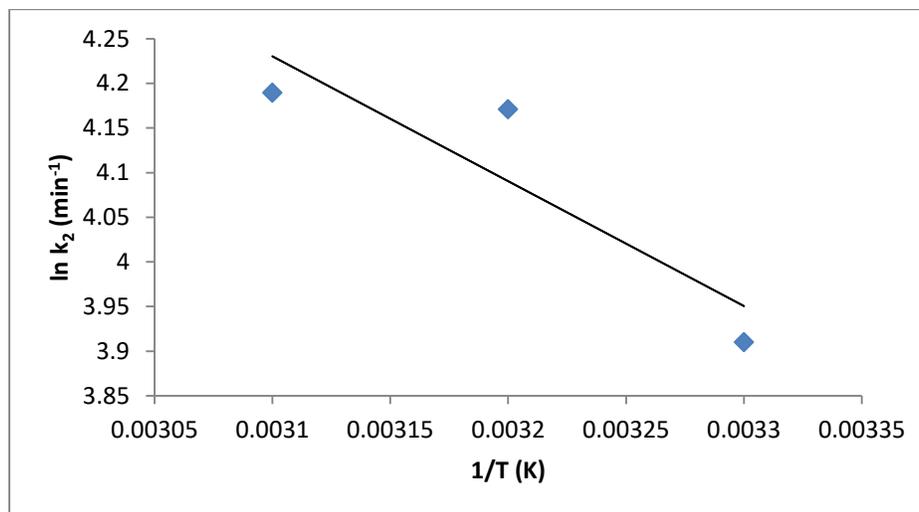|	2nd order
30ºC	
K_2(g/mg.min)	0.0499
q_e (mg/g)	1.6103
R^2	0.9993
40ºC	
K_2(g/mg.min)	0.0648
q_e (mg/g)	1.6949
R^2	0.999
50ºC	
K_2(g/mg.min)	0.0660
q_e (mg/g)	1.7762
R^2	0.999
Energy parameter	
E(KJ/mol)	11.62
C (min^{-1})	2.15

Fig.6: Temperature dependency of reaction rate

Table.3: Thermodynamic parameters

Temp(K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol.K)
303	0.40	13.49	43.48
308	0.06		
313	-0.15		
318	-0.27		
323	-0.54		
328	-7.30		

V. DISCUSSION

5.1 Adsorption isotherm

The constants of these isotherms were calculated from figs 1, 2 and 3 using equations 3, 6 and 7. These results show that correlation coefficient of Redlich-Peterson isotherm is highest, signifying it represents a better fit of the experiment. The parameters are presented in Table 1.

5.2 Kinetic studies

The plots of t/q_t versus t at 303, 313 and 323K all give straight line for the adsorption. The correlation coefficients for plots of t/q_t against t for the second-order equation are observed tobe close to 1. Fig.6 shows the dependency of the rate constant on temperature at 303, 313 and 323K, while values of the activation energy and frequency factor were obtained from the plot using eq (13). The parameters are presented in Table 2.

Table.4: Adsorption capacities of some adsorbents for Erythrosine removal

Adsorbent	Adsorption capacity (mg/g)	TºC	Reference
Pitch pine sawdust	20.8		Hameed *et al* (2008)
Wheat shells	16.56		Hameed *et al* (2008)
Coffee husks	90.09		As in Valliammai *et al* (*2015*)
Coir pith carbon	5.87		As in Valliammai *et al* (*2015*)
Peanut hull	68.03		As in Valliammai *et al* (*2015*)
Banana Peel	20.8		As in Valliammai *et al* (*2015*)
Orange peel	27.78		As in Valliammai *et al* (*2015*)
Bamboo dust carbon	7.20		As in Valliammai *et al* (*2015*)
Groundnut shell carbon	7.50		As in Valliammai *et al* (*2015*)
Rice husk carbon	37.57		As in Valliammai *et al* (*2015*)
Coconut shell carbon	8.16		As in Valliammai *et al* (*2015*)
Coconut fibre	1.7036	30	Ikhazuangbe *et al*, (2017)
Periwinkle shell	1.6103	30	Present

4.3 Thermodynamic studies

The plot of ln K_d versus 1/T is shown in Fig 5. The values of ΔHº and ΔSº of erythrosine dye adsorption was calculated using Eq. 17. The values of ΔGº were obtained by using Eq. 15. The thermodynamic parameters for the adsorption of Erythrosine dye is presented in Table 3.

Table.5: Enthalpy and Entropy change of some adsorbent for the dyes

Adsorbent	ΔHº	ΔSº	Reference
Bael tree bark	25.125	171.83	Valliammai *et al*, (2015)
Activated carbon	31.6	145.5	Yahya, (2012)
Coconut fibre	28.73	94.45	Ikhazuangbe *et al*, (2017)
Periwinkle shell	13.49	43.48	Present

VI. CONCLUSION

The adsorption of erythrosine dye from aqueous solution onto Periwinkle shell was examined. The adsorption follows Redlich-Peterson isotherm, pseudo-second order kinetic, while the thermodynamic parameters show that the adsorption is physical and spontaneous. Considering the adsorption capacity and other parameters obtained, activated carbon from Periwinkle shell has good potential for the removal of erythrosine dye from wastewater.

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