Equilibrium Isotherm, Kinetic and Thermodynamic Studies of the Adsorption of Erythrosine Dye onto Activated Carbon from Coconut Fibre

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Abstract – *Equilibrium isotherm, kinetic and thermodynamic studies of the adsorption of erythrosine dye onto activation carbon from coconut fire was carried out. The coconut fibre obtain from Elele, Rivers State Nigeria, was washed, dried, carbonized at 400ºC, crushed, sieved and activated at 800ºC, before it was washed and dried at 110ºC. Variable influencing factors, such as contact time, temperature and initial concentration were studied through single-factor experiment, while other factors are kept constant (at 30min, 30ºC and 50mg/L) in each adsorption experiment. The Freundlich isotherm fits adsorption compare to others used, the adsorption kinetic followed pseudo-second order reaction, while the thermodynamic parameters, (ΔH) = 28.73KJ/mol, (ΔG) = 94.45J/mol.K and (ΔS) = -0.10, -0.27, -0.82, -1.05, -1.77, -2.49KJ/mol. From the results obtained, activated carbon from coconut fibre, will be an excellent low-cost adsorbent for the removal of Erythrosine from industrial waste water.*

Keywords— Adsorption, Coconut fibre, Erythrosine, Kinetic, Thermodynamic.

I. INTRODUCTION

Erythrosine or Acid Red is a water soluble synthetic dye that is often used as a food colorant. Beside application in drugs and cosmetics, erythrosine is applied for dying many food stuffs including biscuits, chocolate, luncheon meat, sweets, and chewing gums [5]. When excessively consumed, it can cause sensitivity to light, affecting thyroid hormone levels and lead to hyperthyroidism in some cases [1]. The maximum allowed level of erythrosine is 200 mg/kg in some food stuffs [5]. Monitoring and eliminating erythrosine is a necessary job due to its potential toxicity and pathogenicity. The high toxicity of erythrosine was behind many environmental studies to remove this dye from water. Photochemical degradation using TiO_2 particles, biochemical degradation, and adsorption by activated carbon/natural adsorbents, were the most applicable procedures. Dyes removal by adsorption technique is often recommended due to the low running costs and no harmful by-products are generated as the case in other destructive procedures. In fact, most food dyes are often present at trace levels (usually in μg or ng levels) in water streams which may retard their direct quantification by most instruments [6].

In this study, the ability of coconut fibre carbon to remove erythrosine by adsorption is been studied. The adsorption capacity of dye will also be examined using the adsorption isotherm technique. The Langmuir, Freundlich Redlich-Peterson isotherms will used to fit the equilibrium data. Pseudo-first order, pseudo-second order models, activation energy and the thermodynamic equations will also be used to fit the experimental data [4].

II. MATERIALS AND METHODS

2.1 Preparation of adsorbents

Sample of coconut fibre was picked from the environment in Elele, Rivers State, Nigeria. The coconut fibre was washed with tap several times to remove the dust and other water- soluble materials. The process continued until the washing water was colorless. They were respectively dried in the open air. The dried coconut fibre was carbonized in a furnace (SX-5-12) at 400˚C for 3 hours and the charred coconut fibre was allowed to cool to room temperature. It was chemically activated by weighing 100gram of the ground carbonized coconut fibre 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 (MINO/75/F/DIG) at 110˚C for 2 hours [3].

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 coconut fibre was mixed with 50ml of Erythrosine solution of the desired concentrations (25, 50, 75, 100, 125 and 150mg/L) at 30°C 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 30, 40 and 50°C 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 was mixed with 50ml of 50mg/L concentration of erythrosine solution at 30, 35, 40, 45, 50 and 55°C 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 coconut fibre adsorbent at equilibrium was calculated with the following equation:

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

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.

2.4 Theory

2.4.1 Adsorption isotherms

Adsorption isotherms of Erythrosine were measured using concentration-variation method at constant temperature, time and volume [7].

2.4.2 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

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

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

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.

2.4.3 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:

$$K_f\, C_e^{1/n} \qquad (4)$$

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

$$\text{Log}\,q_e = \text{Log}\,(K_f) + \frac{1}{n}\,\text{Log}\,C_e \qquad (5)$$

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.

2.4.4 Redlich-Peterson isotherm (model)

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

$$q_e = \frac{K_R C_e}{1 + a_R\, C_R^{\beta}} \qquad (6)$$

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.

2.5 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.

2.5.1 Pseudo-first order equation

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

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad (7)$$

$$\text{Log } (q_e - q_t) = \text{Log}(q_e) - \frac{K_1}{2.303} t \qquad (8)$$

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.

2.5.2 Pseudo-second order equation

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

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad (9)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (10)$$

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.

2.6 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.

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2} \qquad (11)$$

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

$$\ln K = -\frac{E_a}{RT} + \ln A \qquad (12)$$

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.

2.7 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 it allows to estimate if the process is favorable or not from thermodynamic point of view, 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 ΔH° lies between 84 and 420 kJ mol^{-1} [8].

The thermodynamic parameters of the adsorption process were determined from the experimental data obtained at various temperatures using equations 13 to 15

$$\Delta G = -RT\text{In}K_d \qquad (13)$$

$$K_d = \frac{qe}{Ce} \qquad (14)$$

$$\text{In}K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (15)$$

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, ΔG^o, ΔH^o, and ΔS^o are Gibbs free energy change, enthalpy change and entropy change, respectively. The values of enthalpy change (ΔH^o) and entropy change (ΔS^o) are obtained from the slope and intercept of $\text{ln}K_d$ versus 1/T plots [2].

III. RESULTS AND DISCUSSION

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

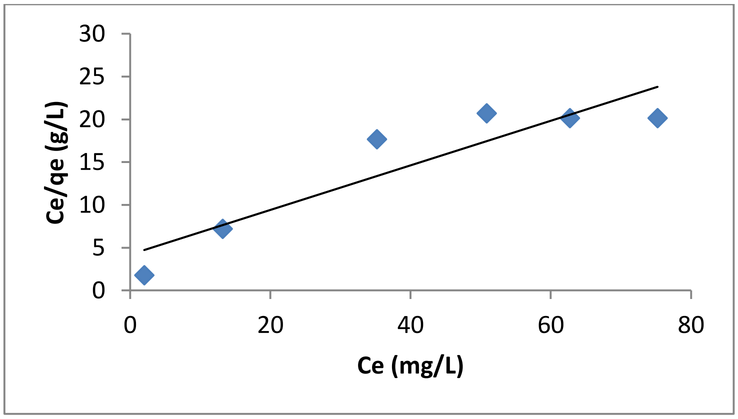

Fig.1: Langmuir model of Erythrosine

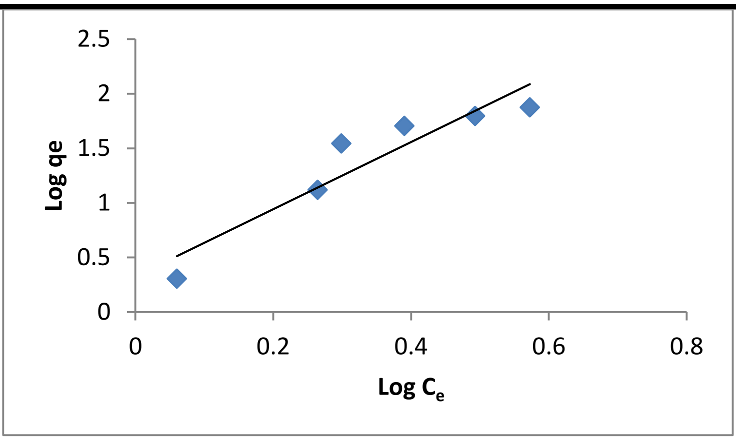

Fig.2: Freundlich model of erythrosine

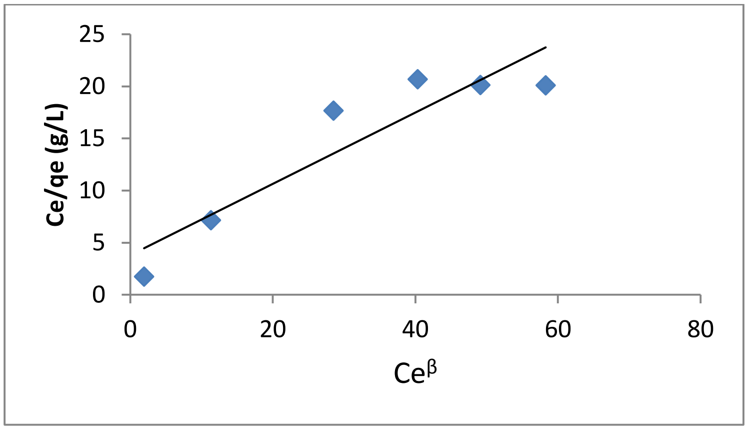

Fig. 3: Redlich-Peterson model for erythrosine

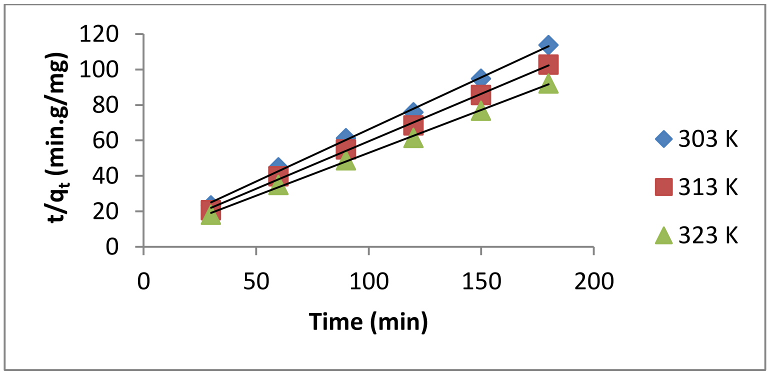

Fig. 4: Pseudo-second order reaction

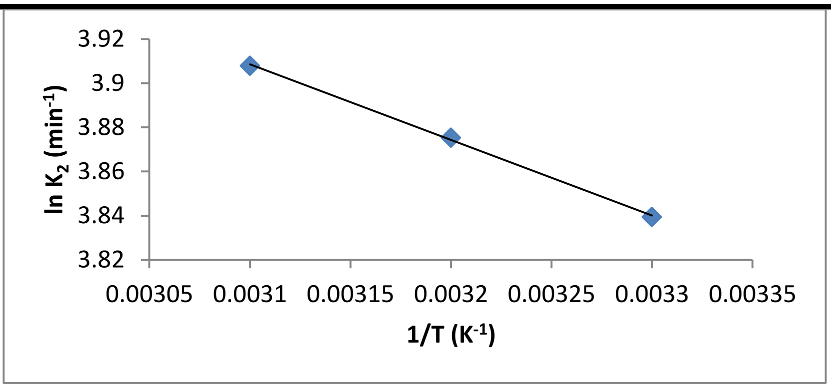

Fig. 5: Temperature dependency of reaction rate

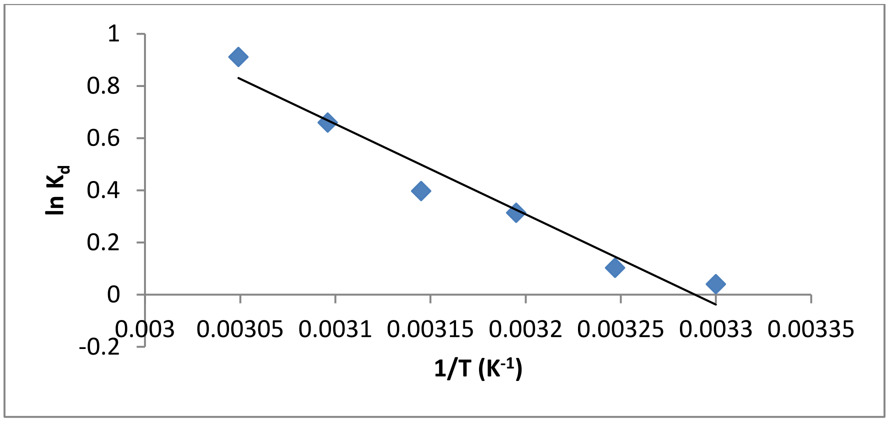

Fig. 6: Effect of temperature on erythrosine adsorption

3.1 Adsorption isotherm

The Freundlich isotherm plotted in Fig. 2 has correlation coefficient value higher than both Langmuir and Redlich-Peterson values while Redlich-Peterson is higher than Langmuir. Therefore, the Freundlich equation represents a better fit of the experiment. The parameters are presented in Table 1.

Table.1: Adsorption Isotherm constants for coconut fibre activated carbon

Langmuir			Freundlich			Redlich-Peterson		
$Q_o(\frac{mg}{g})$	$b(\frac{L}{mg})$	R^2	$K_f(\frac{mg}{g})$	$1/n(\frac{g}{L})$	R^2	$K_R(\frac{L}{mg})$	$a_R(\frac{L}{mg})$	R^2
3.8462	0.0619	0.8420	0.8872	0.2860	0.8800	0.2638	0.0902	0.855

Table.2: Thermodynamic parameters for the adsorption

Temp(K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol.K)
303	-0.10	28.73	94.45
308	-027		
313	-0.82		
318	-1.05		
323	-1.77		
328	-2.49		

3.2 Adsorption kinetic

The plot of t/q_t versus t gives a straight line for the erythrosine adsorption as shown in Fig. 5, while the plots of Log (q_e - q_t) versus t does not show good result for the entire adsorption period, confirming the applicability of the pseudo second-order equation. Fig. 5 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 equation 12. The parameters are presented in Table 2.

3.3 Thermodynamic studies

The plot of $\ln K_d$ versus 1/T is shown in Fig 6. The values of ΔH and ΔS of erythrosine adsorption were calculated by fitting the experimental data to equation 15. The values of ΔG were obtained by using equation 13. The standard enthalpy change (ΔH) for the adsorption is positive, indicating that the process is endothermic in nature. The parameters are presented in Table 3.

Table.3: Kinetic and Activation energy parameters

2nd order	
30ºC	
K_2(g/mg.min)	0.0465
q_e (mg/g)	1.7036
R^2	0.997
40ºC	
K_2(g/mg.min)	0.0482
q_e (mg/g)	1.8692
R^2	0.998
50ºC	
K_2(g/mg.min)	0.0498
q_e (mg/g)	2.0704
R^2	0.997
Energy parameter	
E(KJ/mol)	2.85
C (min^{-1})	1.60

IV. CONCLUSION

Erythrosine adsorption onto coconut fibre activated carbon investigated in this research work; show that the pseudo-second order kinetic model provided the best correlation of the experimental data. The temperature variation values were used to evaluate the values of ΔH, ΔS and ΔG. The positive value of ΔH indicates that the adsorption of Erythrosine onto coconut fibre is an endothermic and the value falls in the range of physical adsorption process. The positive value of ΔS shows the existence of some structural changes at the solid–liquid interface. The results and parameters obtained, shows that coconut fibre will be an excellent low-cost adsorbent for the removal of Erythrosine dye from industrial wastewater.

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REFERENCES

[1] R. Bernstein, H.F. Haugen, and H. Frey, Thyroid function during erythrosine ingestion in doses encountered in therapy with conventional antibiotics, *Scand. J. Clin. Lab. Invest*. Vol. 35, pp. 49–52, 1975.

[2] B. Emrah, O. Mahmut, and I.S. Ayahan, Adsorption of malachite green onto kinetic studies and process design. *Microporous and Mesoporous material*, Vol. 115, pp.234 – 246, 2008

[3] R.H. Gumus and I. Okpeku, Production of Activated Carbon and Characterization from Snail Shell Waste (*Helix Pomatia*), *Advances in Chemical Engineering and Science*, Vol. 5, pp.51 – 61, 2015.

[4] D. Hakan, D. Ilkanur and K. Belgin, Adsorption of Textile Dye onto Activated Carbon Prepared from Industrial Waste by $ZnCl_2$ Activation, *J. int. Environmental application and Science,* Vol. 3, pp.381 – 389, 2008.

[5] A. Mittal, J. Mittal, L. Kurup and A.K. Singh, Process development for the removal and recovery of hazardous dye erythrosine from wastewater by waste materials—bottom ash and de-oiled soya as

adsorbents, *J. Hazard. Mater*, Vol. 138, pp. 95–105, 2006.

[6] J. Riu, I. Schönsee, D. Barceló and C. Ràfols, Determination of sulphonated azo dyes in water and wastewater, *TrAC Trends Anal. Chem*., Vol, 16, pp. 405–419, 1997.

[7] S.A. Yahya, A. Rajab and S.A. Samer, Analyzing adsorption data of erythrosine dye using principal component analysis, *Chemical Engineering Journal*, Vol. 34, pp.123– 126, 2012.

[8] Z. Zhang, Z., Moghaddam, L., O'Hara, I.M.O. and Doherty, W.O.S. Congo red adsorption by ball-milled sugarcane bagasse. *Chem. Eng. J*, Vol. 178, pp.122–128, 2011.