

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

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Abstract

Coconut fibre activated carbon was used for the adsorption of Congo red dye from aqueous solution. Variable influencing factors, such as contact time, temperature and concentration were studied through single-factor experiment, while other factors were held constant each. The adsorption isotherms studied shows that the correlation coefficient of Freundlich gives better fit for the adsorption. The adsorption kinetic followed pseudo-second order, the surface area of the activated carbon was obtained as $129.26\text{m}^2/\text{g}$, while the values of the basic thermodynamic parameters are: $(\Delta H) = 16.92\text{KJ/mol}$, $(\Delta S) = 79.08\text{J/mol. K}$ and $(\Delta G) = -6.71, -6.94, -7.26, -7.52, -7.88$ and -8.20KJ/mol . Therefore, activated carbon from coconut fibre will be an excellent low-cost adsorbent for the removal of Congo red dye from industrial wastewater.

Keywords: Coconut fibre, adsorption isotherm, kinetic, thermodynamic, Congo red

Introduction

Coloured effluents are extensively released from different industries such as textile, paper, rubber, plastic, leather, cosmetic, food, and drug industries into natural water bodies (Nsami and Mbadcam, 2013). These dyes can cause allergic dermatitis, skin irritation, cancer and mutation in living organisms. They can also cause eye burns, which may be responsible for permanent injury to the eyes of human beings and animals. On inhalation, it can cause short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion, painful micturation, and methemoglobinemia-like syndromes (Valliammai *et al*, 2015). The Nigerian textile industries, as well as other dye-using industries are currently in dire need of available and economical adsorbents to treat their effluents since the use of imported adsorbents is not cost effective.

In this research work, the ability of coconut fibre activated carbon to remove Congo red by adsorption was studied. The adsorption capacity of the activated carbon was examined using the adsorption isotherm techniques and kinetic models (pseudo-first and pseudo-second order models). The Langmuir and Freundlich isotherms was used to fit the data to determine which gives the best fit for the experimental data (Hakan *et al*, 2008).

Materials and Methods

Preparation of adsorbents

Samples of coconut fibre were gotten from Elele town in Rivers State, Nigeria. The coconut fibre was washed and dried in open air. The dried coconut fibre was carbonized in a furnace (SX-5-12) at 400°C for 3 hours and the charcoal was allowed to cool to room temperature.

100gram of the ground carbonized coconut fibre was added to a 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) set at 800°C for 3 hours, then allowed to cool to room temperature, washed with de-ionized water and dried in an oven set at 110°C for 2 hours (Gumus and Okpeku, 2015).

Preparation of adsorbate

The Congo red dye 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. 150mg of Congo red was carefully weighed and placed in 50ml pycnometer and de-ionized water of known volume was added to prepare standard solution of known volume of the solute and solvent. The solution was then transferred into 1000ml volumetric flask and make up with de-ionized water, stirred properly to obtain the 150mg/l concentration. Other dilute solutions of the desired concentration were obtained by successive dilution with de-ionized water.

Adsorption experiment

1000mg of the activated carbon was mixed with 50ml of 50mg/l concentration of Congo red solution at 30°C in six conical flasks each and placed in a temperature controlled water bath with constant stirring. The samples were withdrawn after 30, 60, 90, 120, 150 and 180 minutes respectively and filtered using Whatmann filter paper. The concentrations of the filtrate were measured with a UV spectrophotometer (2OD) at 496nm. The experiment was repeated at equilibrium condition using 1000mg of the activated carbon with 50ml of Congo red solution of the desired concentrations (25, 50, 75, 100, 125 and 150mg/l) at 30°C, in a temperature controlled water bath with constant stirring. All the samples were withdrawn after 90 minutes and were filtered with Whatmann filter paper. The concentration of the filtrate was measured with a UV spectrophotometer (2OD) at 496nm. Again, 1000mg of the activated carbon was mixed with 50ml of 50mg/l concentration of Congo red solution at 30, 35, 40, 45, 50 and 55°C and placed in a temperature controlled water bath (DK – 420) with constant shaking. The samples were withdrawn after 90 minutes respectively, filtered and the concentration measured.

The adsorption amount of Congo red dye onto the coconut fibre adsorbent at equilibrium was calculated with the following equation:

$$q_{eq} = \frac{(C_0 - C_{eq})V}{X} \quad 1$$

Where C_0 (mg/l) and C_{eq} (mg/l) are the initial and equilibrium concentration of the dyes, V (l) is the volume of solution, X (g) is the weight of adsorbent in one container.

Theory

Surface area of activated carbon

The surface area of the activated carbon from periwinkle shell is expected to influence dye adsorption, as a greater surface area provide a greater number of adsorption sites where dye adsorption should occur.

Surface area (S_T) values were calculated from the experimental adsorption isotherm over a relative pressure range of 0.1 to 0.3 (Hill, 1997), using the standard BET (Brunauer, Emmett and Teller) method (Brunauer *et al.*, 1938). The BET equation is given as:

$$\frac{P}{V(P^0 - P)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \left(\frac{P}{P^0} \right) \quad 2$$

$$\frac{x}{V(1-x)} = \frac{1}{V_m C} + \left(\frac{C-1}{V_m C} \right) x \quad 3$$

Where $x = p/p_0$

$$V_m = \frac{1}{\text{Slope} + \text{Intercept}} \quad 4$$

Where, V is the volume of the solute adsorbed (cm^3/g), V_m is the volume of monolayer capacity (cm^3/g), and the term C , is the BET constant, it is related to the energy of adsorption in the first adsorbed layer and its value is an indication of the magnitude of the adsorbent-adsorbate interactions (Song *et al*, 2014; Hill, 1993).

Adsorption isotherms

Adsorption isotherm expresses the relationship between the amount of adsorbate adsorbed by the adsorbent in solution at equilibrium and temperature conditions (Iryani *et al*, 2017). The adsorption of Congo red was measured using concentration-variation method at constant temperature, time and volume (Yahaya *et al*, 2012).

Langmuir adsorption isotherm (model)

This 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 (Ikhazuangbe *et al*, 2017). The rate change of concentration due to adsorption should be equal to the rate of change of concentration due to desorption. As a result, the Langmuir isotherm is as expressed in equation 5

$$\frac{C_e}{q_e} = \frac{1}{b Q_o} + \frac{C_e}{Q_o} \quad 5$$

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 mixture (Zhang *et al*, 2011).

Freundlich adsorption isotherm (model)

The Freundlich model is an empirical relationship which normally gives a more satisfactory model of experimental data. The Freundlich model can be applied to heterogeneous surface involving multilayer adsorption (Nsami and Mbedcam, 2013). It can be expressed as follows:

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

Where C_e is the concentration at equilibrium, q_e the adsorption capacity at equilibrium, K_f and n are Freundlich constants which take into consideration all the 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 (Zhang *et al*, 2011).

Adsorption kinetics

The pseudo first order and second order kinetic models were tested at different temperatures in this study to determine which model is in good agreement with experimental q_e (adsorption capacity) value, thus suggesting which model the sorption system follows.

Pseudo-first order equation

The Lagergren model describes adsorption process in a solid-liquid system based on the capacity of solids. It assumes a first order adsorption kinetics and can be represented by the equation (Iryani *et al*, 2017).

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

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

The values of $\text{Log } (q_e - q_t)$ were linearly correlated with t . The plot of $\text{Log } (q_e - q_t)$ 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.

Pseudo-second order equation

The second order pseudo-kinetic equation shows how the adsorption rate depends on the adsorption capacity of the adsorbent rather than the adsorbate concentration (Iryani *et al*, 2017). The pseudo-second-order adsorption kinetic rates equation is expressed as

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

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad 10$$

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 (Zhang *et al*, 2011).

Arrhenius equation and activation energy

From the Van't Hoff equation $\frac{d(\ln k)}{dT} = \frac{\Delta H}{RT^2}$

For isobaric and isochoric conditions,

$k = \frac{k_2}{k_1}$ = chemical equilibrium constant, k_1 and k_2 are rate constants of forward and reverse reactions, H = Heat of reaction, R = Universal gas constant T = Absolute temperature

Substituting $\frac{k_2}{k_1}$ for k we get

$$\frac{d \ln \frac{k_2}{k_1}}{dT} = \frac{d \ln k_1 - d \ln k_2}{dT} = \frac{\Delta H}{RT^2} \quad 11$$

Writing the heat of a chemical reaction as the difference of the two quantities,

$$\Delta H = E_1 - E_2 \quad 12$$

We can write

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_2}{dT} = \frac{E_1}{RT^2} - \frac{E_2}{RT^2} = \frac{\Delta H}{RT^2} \quad 13$$

$$\frac{d \ln K}{dT} = \frac{E}{RT^2} \quad 14$$

Equation (14) can also be integrated within the limits T_1 to T_2 to give

$$\ln \frac{k_{T_2}}{k_{T_1}} = \frac{E(T_2 - T_1)}{R T_1 T_2} \quad 15$$

Where k_{T_2} = rate constant of chemical reaction at T_2 , k_{T_1} = rate constant of chemical reaction at T_1 (Dara, 2009).

Thermodynamic studies

The determination of the basic thermodynamic parameters such as change in enthalpy of adsorption (ΔH), change in Gibbs free energy of adsorption (ΔG) and change in entropy of adsorption (ΔS), is important as it allows to estimate if the process is favorable or not from thermodynamic point of view, also to assess the spontaneity of the system and to ascertain whether the adsorption is exothermic or endothermic in nature. An adsorption process is generally considered as physical if $\Delta H^\circ < 84 \text{ kJ mol}^{-1}$ and as chemical when ΔH° lies between 84 and 420 kJ mol^{-1} (Zhang *et al*, 2011).

These thermodynamic parameters were determined from the experimental data obtained at various temperatures using equations 16 to 18

$$\Delta G = -RT \ln K_d \quad 16$$

$$K_d = \frac{q_e}{C_e} \quad 17$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad 18$$

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° , ΔH° , and

ΔS° are Gibbs free energy change, enthalpy change and entropy change, respectively. The values of enthalpy change (ΔH°) and entropy change (ΔS°) are obtained from the slope and intercept of $\ln K_d$ versus $1/T$ plots (Emrah *et al.*, 2008).

Results and Discussions

Adsorption isotherm

The Freundlich isotherm plotted in Figure 2 has correlation coefficient value higher than Langmuir isotherm value. Therefore, the Freundlich equation represents a better fit for the experiment.

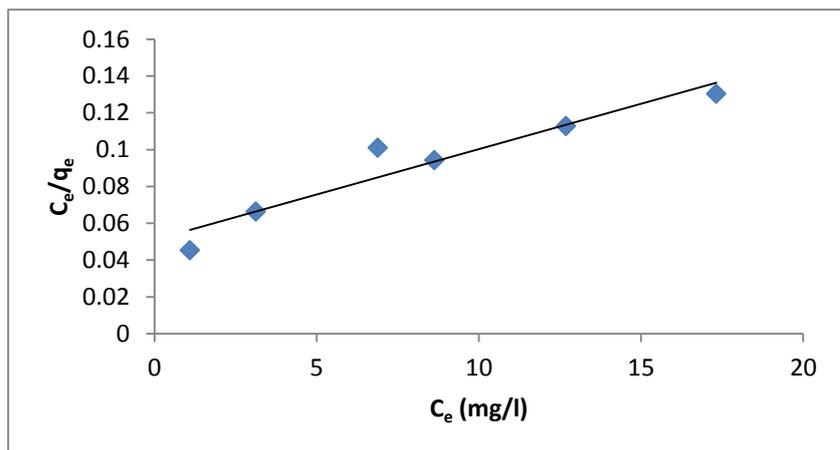


Figure 1: Langmuir Isotherm

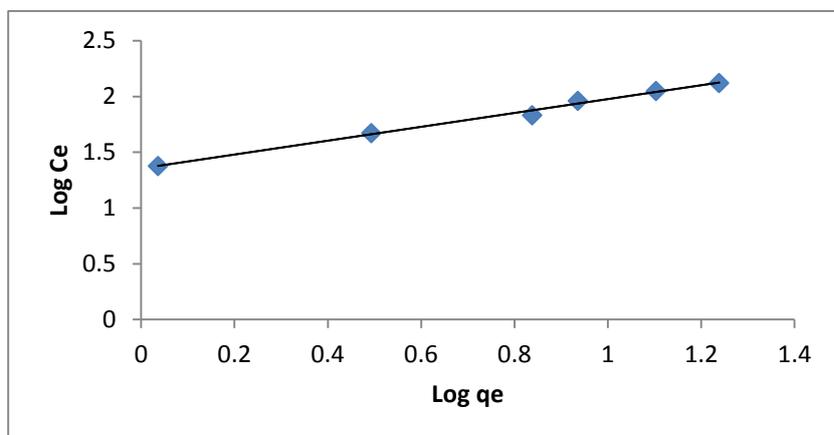


Figure 2: Freundlich Isotherm

Table 1: Adsorption Isotherm constants

Langmuir			Freundlich		
Q_o (mg/l)	b (l/mg)	R^2	K_f (mg/l)	n (L/g)	R^2
250	0.08	0.914	22.594	1.6103	0.993

Adsorption kinetic

The first order kinetic model prediction deviated considerably with the experimentally obtained data. It was therefore decided to test the experimental data using second order kinetic model. Figure 3 shows the curve-fitting of the pseudo-second order equation, confirming the applicability of the pseudo second-order equation. The activation energy (Figure 4) was also obtained using the second order rate constant at 303, 310 and 323K respectively.

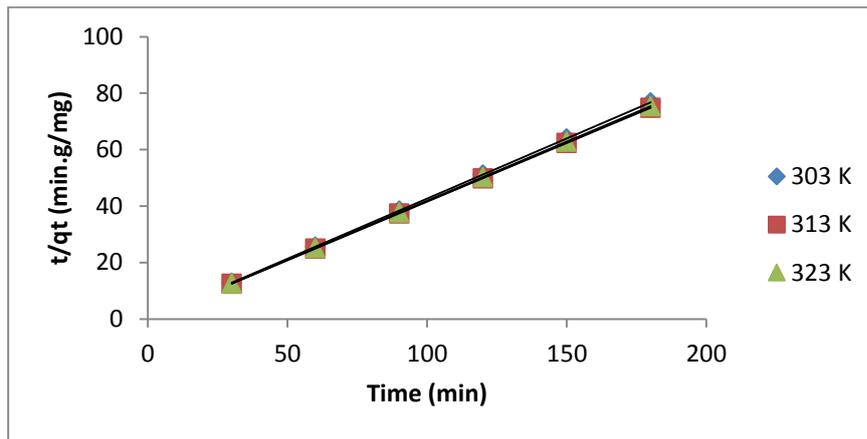


Figure 3: Pseudo-second order reaction

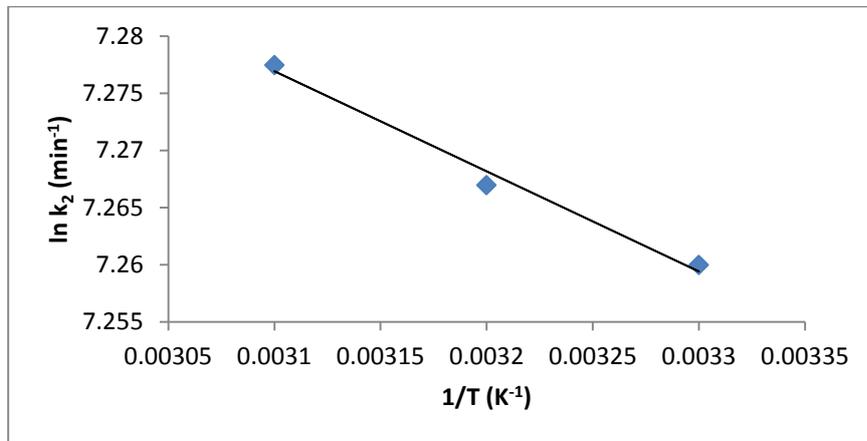


Figure 4: Temperature dependency of reaction rate

Thermodynamic studies

The plot of $\ln K_d$ versus $1/T$ is shown in Fig 5. The values of ΔH and ΔS of Congo red dye adsorption were calculated by fitting the experimental data to Eq. (18) as shown in Figure 5. The values of ΔG were obtained by using Equation 16. The standard enthalpy change (ΔH°) for the adsorption of Congo red on coconut fibre is positive indicating that the adsorption is endothermic in nature. The parameters are shown in Table 3.

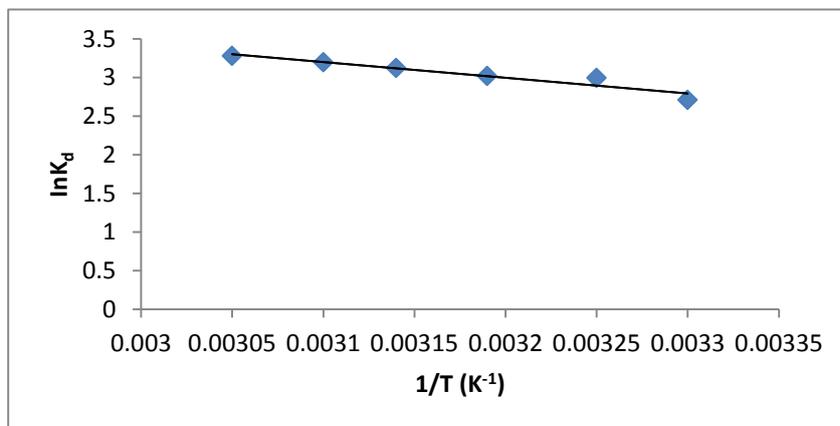


Figure 5: Effect of temperature on Congo red adsorption

Table2: Kinetic and Activation energy parameters

K ₂ (g/mg.m in)	q _e (mg/g)	R ²	K ₂ (g/mg.m in)	q _e (mg/g)	R ²	K ₂ (g/mg.m in)	q _e (mg/g)	R ²	E (KJ/m ol)	C (min ⁻¹)
30°C			40°C			50°C				
1.4223	2.3529	0.999	1.4322	2.3529	0.999	1.4473	2.4096	0.999	0.7275	2.0213

Table 3: Thermodynamic parameters

Temp(K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol.K)
303	-6.83	16.92	79.08
303	-7.68		
313	-7.87		
318	-8.27		
23	-8.60		
328	-8.95		

Conclusion

The adsorption of Congo red onto coconut fibre activated carbon was investigated in this work. The surface area of the activated carbon was obtained using the BET model. Pseudo-second order kinetic model provided the best fit for the experimental data. The thermodynamic parameters such as ΔH, ΔS and ΔG were obtained. The positive value of ΔH indicates that the adsorption is physical and endothermic. The positive value of ΔS shows the existence of some structural changes at the solid–liquid interface. This studies shows that coconut fibre will be good adsorbent for the removal of Congo red dye from industrial effluents.

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