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Adsorption of Malachite green oxalate dye onto activated carbon from Coconut fibre

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Abstract: The study of the adsorption of Malachite green oxalate from aqueous solution was carried out with activated carbon prepared from Coconut fibre. The Coconut fibre was washed, dried, carbonized, crushed, sieved and eventually activated at 800^oC with 0.1Mol HCl. Adsorption experiment was carried out with various concentrations of the adsorbate at constant time, temperature, volume and dosage. It was repeated at varying time, while other influencing factors were kept constant. Finally, the experiment was carried at varying temperature while other variables were kept constant. The adsorption process fits the Freundlich isotherm with correlation coefficient of 0.8940. The adsorption also followed the second order kinetic with rate constant of 0.1433, 0.1568 and 0.1570(g/mg.min) at 30, 40 and 50^oC respectively. The activation energy under this condition is 3.80KJ/mol and the thermodynamic parameters: ΔH^o = 20.45KJ/mol, ΔS^o = 74.34J/mol.K and the ΔG^o = -1.49, -2.93, -3.11, -3.37, -3.48 and -3.63J/mol for the various temperatures used. These results affirm the fact that activated carbon from Coconut fibre has the efficacy of a good adsorbent.

Keywords: Adsorption, Coconut fibre, kinetic, Malachite green oxalate; thermodynamic

I. INTRODUCTION

Discharge of wastewaters from different industries, particularly from textile, paper, rubber, plastic, leather, cosmetic, food, and drug industries were dyes and pigments are used into natural streams and rivers, can cause allergic dermatitis, skin irritation, cancer and mutation in living organisms. It can also cause eye burns, which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to 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 etal, 2015).

Many treatment methods have been adopted to remove dyes from wastewater, which can be divided into physical, chemical, and biological methods. Generally, physical methods which include coagulation, reverse osmosis, photo degradation, electrochemical oxidation, ion exchange, membrane filtration and adsorption are effective for removing dyes without producing unwanted by-products. Adsorption is considered to be superior to other techniques because of its low cost, easy availability, simplicity of design, high efficiency and ease of operation, biodegradability and ability to treat dyes in more concentrated forms (Valliammai etal, 2015). The objectives of this work include investigation of the potential of Coconut fibre as a low-cost adsorbent to remove Malachite green oxalate from aqueous solution, to determine the kinetic, the parameters of some equilibrium isotherms, activation energy and some thermodynamic parameters of the process.

II. THEORY

Adsorption isotherms

Some adsorption isotherms were selected for the process:

Langmuir adsorption isotherm (model)

The model represents one of the first theoretical treatments of non-linear sorption and suggests that uptake occurs on a homogenous surface by monolayer sorption 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 expressed as follows:

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

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, which are used to suggest whether the adsorption of a material can be modeled by Langmuir isotherm (Yuh-Shan, 2009).

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:

$$\mathrm{Log}\, q_e = \mathrm{Log}\,(K_f) + \frac{1}{n}\,\mathrm{Log}\, C_e \qquad 2$$

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 the logarithm of adsorption capacity, log q_e against logarithm equilibrium concentration log C_e (Yuh-Shan, 2009).

Redlich-Peterson isotherm (model)

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

$$q_e = \frac{K_R C_e}{1 + a_R\, C_R^{\beta}} \qquad 3$$

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.

Furthermore, the R-P equation incorporate three parameters into an empirical isotherm and therefore, can be applied either in homogenous or heterogeneous systems due to its high versatility (Yuh-Shan, 2009).

Adsorption kinetics

The pseudo first order and second order kinetic models need to be tested to determine which model is in good agreement with experiment q_e (adsorption capacity) value, thus suggesting which model the adsorption system follows.

Pseudo-first order equation

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

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad 4$$

$$\mathrm{Log}\,(q_e - q_t) = \mathrm{Log}(q_e) - \frac{K_1}{2.303}\,t \qquad 5$$

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.

Pseudo-second order equation

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

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad 6$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}\,t \qquad 7$$

The plot of (t/q_t) against t of equation 7 should give a linear relationship from which q_e and K_2 can be determined from the slope and intercept of the plot, respectively (Adie etal, 2012).

Activation energy

The rate equation which the adsorption process follows is used as the adsorption kinetic data of the studied system. From the Van't Hoff equation, for isobaric and isochoric conditions, Arrhenius developed another equation called Arrhenius equation which characterizes the dependence of the rate constant K of a chemical reaction on the temperature.

We can write

$$\frac{d\ln k_1}{dT} - \frac{d\ln k_2}{dT} = \frac{E_1}{RT^2} - \frac{E_2}{RT^2} = \frac{\Delta H}{RT^2} \qquad 8$$

It can be considered with an accuracy that

$$\frac{d\ln k_1}{dT} = \frac{E_1}{RT^2} + C \qquad 9$$

$$\frac{d\ln k_2}{dT} = \frac{E_2}{RT^2} + C \qquad 10$$

Where C which is a constant has been proven to be zero, hence

$$\frac{dlnK}{dT} = \frac{E}{RT^2} \qquad 11$$

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

$$\ln \frac{k_{T2}}{k_{T1}} = \frac{E\,(T_2 - T_1)}{R\,T_1 T_2} \qquad 12$$

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

K_{T1} = rate constant of chemical reaction at T_1, R is the universal gas constant (8.314 $J.K^{-1}.mol^{-1}$) and T is the absolute temperature (Dara, 2009).

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} (Zhang et al, 2011).

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

$$\Delta G = -RTInK_d \qquad 13$$

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

$$InK_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad 15$$

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 in Kelvin, R is gas constant, ΔG^o, ΔH^o, and ΔS^o are change in Gibbs free energy, change in enthalpy and entropy change respectively. The values of enthalpy change (ΔH^o) and entropy change (ΔS^o) are obtained from the slope and intercept of lnK_d versus 1/T plots (Bulut et al, 2008).

III. MATERIALS AND METHODS

Preparation of adsorbents

Samples of Coconut fibre were picked from the environment in Elele, Rivers State, Nigeria. The Coconut fibre were washed with tap water several times to remove the dust and other water- soluble materials; then dried in the open air. The dried Coconut fibre were carbonized at 400˚C for 3 hours, ground, sieved (200 - 600μm) and chemically activated by weighing 100gram 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, washed with de-ionized water and dried in an oven at 110˚C for 2 hours (Gumus and Okpeku, 2015).

Preparation of adsorbate

The Malachite green oxalate 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 the dye was weighed and dissolved in $1dm^3$ de-ionized water to prepare the standard solution. Dilute solutions of the desired concentrations were obtained by successive dilutions with de-ionized water

Adsorption experiment

1000mg of the activated carbon of Coconut fibre was mixed with 50ml of 50mg/l Malachite green oxalate solution (6 samples) at 30^oC 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 618nm. Also, 1000mg of the activated carbon was mixed with 50ml of 25, 50, 75, 100, 125 and 150mg/l of the adsorbate at 30^oC. The samples were withdrawn after 30 minutes and filtered; the concentration of the filtrate was measured with the UV. Again 1000mg of the activated carbon was mixed with 50ml of 50mg/L concentration of malachite green oxalate solution at 35, 40, 45, 50 and 55^oC 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 experiment was also carried out with 6 samples, each containing 1000mg of the activated carbon at 40 and 50^oC. The samples were withdrawn after 30minute intervals respectively, filtered and the concentration measured.

The amount of malachite green oxalate dye adsorbed onto the Coconut fibre adsorbent at equilibrium was calculated with the following equation:

$$q_e = \frac{(C_o - C_e)V}{X} \tag*{16}$$

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.

IV. RESULTS

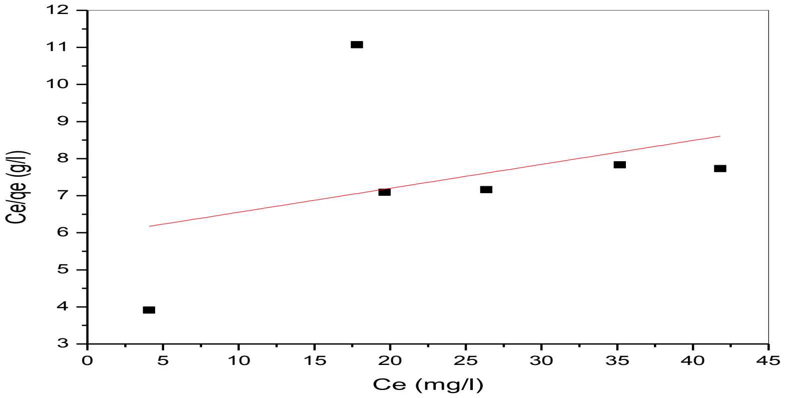

Fig. 1 Langmuir model for Malachite green oxalate

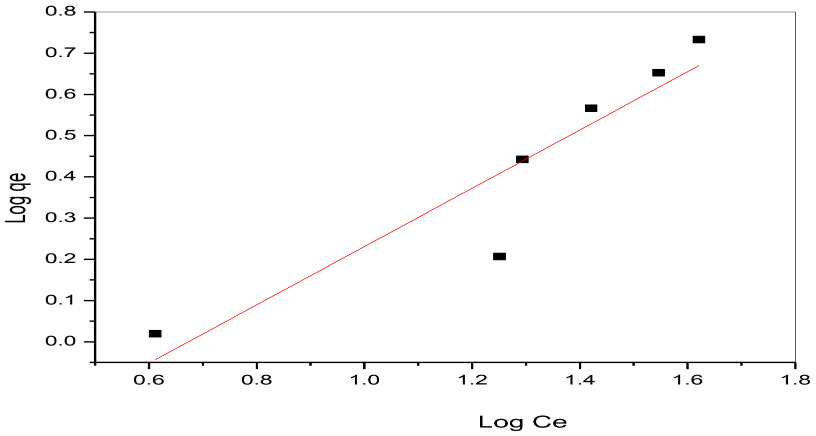

Fig. 2 Freundlich model for Malachite green oxalate

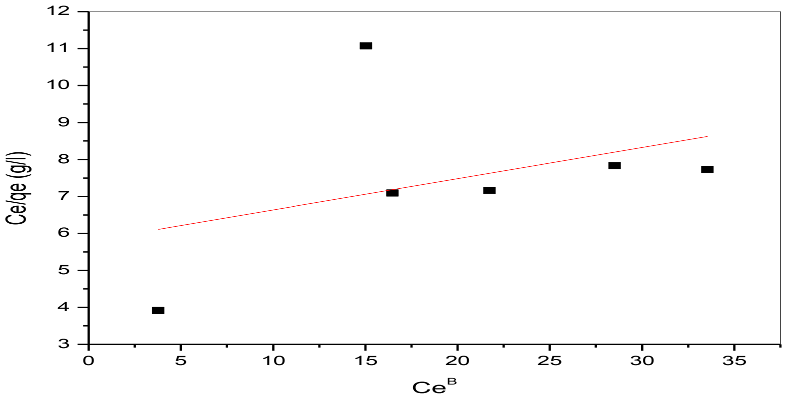

Fig.3 Redlich-Peterson model for Malachite green oxalate

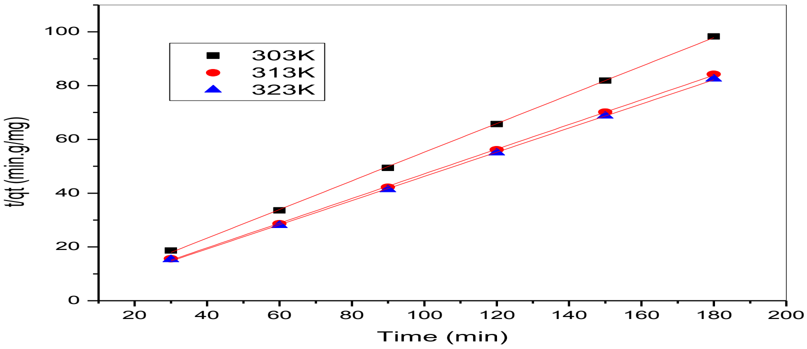

Fig. 4: Pseudo second order reaction

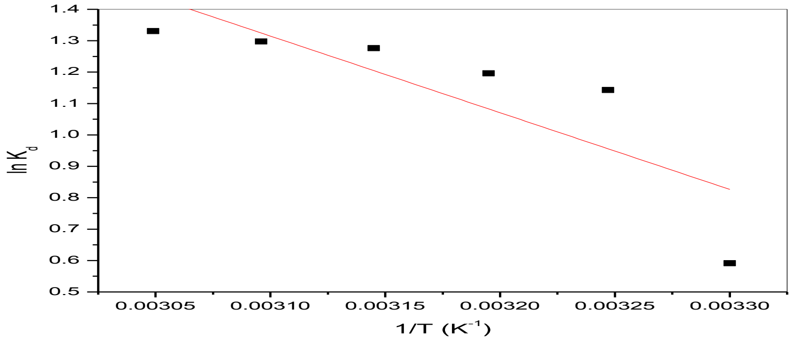

Fig. 5: Effect of temperature on malachite green oxalate

Table I: 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
15.6250	0.0108	0.1440	1.412E-16	27.6600	0.8940	0.1727	0.0145	0.1530

Table II: Energy parameters for erythrosine adsorption by activated carbon

Temperature (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol.K)
303	-1.49	20.45	74.34
308	-2.93		
313	-3.11		
318	-3.37		
323	-3.48		
328	-3.63		

Table III: Kinetic and energy parameters

2nd order kinetic	
30°C	
K_2(g/mg.min)	0.1433
q_e (mg/g)	1.8796
R^2	0.999
40°C	
K_2(g/mg.min)	0.1568
q_e (mg/g)	2.2272
R^2	0.999
50°C	
K_2(g/mg.min)	0.1570
q_e (mg/g)	2.2248
R^2	0.999
Activation energy	
E(KJ/mol)	3.80
C (min^{-1})	0.66

V. DISCUSSION OF RESULTS

Freundlich isotherm gives a better fit for the adsorption process with correlation coefficient of 0.8940, compare to the Langmuir and Redlich-Peterson which were 0.1440 and 0.1530 respectively. The adsorption process deviate appreciably from the pseudo-first order kinetic model but followed the pseudo second-order kinetic model with correlation coefficient of 0.999 at 30, 40 and 50^oC. This is represented in fig. 4 with adsorption capacity of 1.8796, 2.2272and 2.2248 respectively. The rate constants of the pseudo second order kinetic model at 30, 40 and 50^oC, were used to evaluate the activation energy by fitting them into equation 12. This was found to be 3.80KJ/mol. With equations 13 – 15, the thermodynamic parameters were obtained from fig. 6. The value of ΔH indicates that the adsorption of Malachite green oxalate on Coconut fibre activated carbon is endothermic and a physical adsorption process. The positive value of ΔS shows the existence of some structural changes at the solid–liquid interface, while the values of ΔG show the spontaneity of the process and the separation work requirement of the adsorption process.

VI. CONCLUSION

The adsorption isotherm, kinetic and thermodynamic studies of the removal of malachite green oxalate with Coconut fibre activated carbon carried out, reveals that Coconut fibre has the potentials (when converted to activated carbon) to adsorb malachite green oxalate from wastewater. As a low cost agro-based material that is readily available, this activated carbon can serve as a good substitute for commercial activated carbon.

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