Isothermal and Batch Adsorption Studies of Malachite Green Oxalate Dye onto Activated Carbon from Snail Shell

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Abstract—*Adsorption efficiency, kinetic and thermodynamic studies of the adsorption of Malachite green oxalate onto activated carbon from snail shell was carried out. The cleaned Snail shell was carbonized at 400ºC, crushed and sieved before it was activated with 0.1m HCl at 800ºC in a furnace. Batch adsorption experiment was carried out at variable concentration, time and temperature while other factors are kept constant. The adsorption isotherms used show that the correlation coefficient of Freundlich isotherm is closer to unity compare to that of Langmuir isotherm. The adsorption follows the Pseudo second order kinetic with adsorption capacity of 1.7544 (mg/g) and rate constant of 0.471(g/mg.min). The thermodynamic parameters: change in enthalpy, ΔH = 15.90 KJ/mol, change in entropy ΔS = 60.16J/mol. K and the change in Gibbs free energy ΔG = -1.69, -2.98, -3.64, -3.24, -3.43 and -3.51 KJ/mol at 303, 308, 313, 318, 323 and 328K respectively. These results show that activated carbon from snail shell has the potential of a good low cost adsorbent for the removal of this hazardous dye from wastewater.*
Keywords— *Adsorption, kinetic, Malachite green oxalate, snail shell, thermodynamic.*

I.   INTRODUCTION

The textile, paper, printing and dye industries consume large quantities of water at its different steps of dyeing and finishing processes. Due to the large volume of water consumption, the production of huge volume of wastewater is inevitable. Generally, the wastewater from printing and dyeing units in these plants contain residue of dyes and chemicals [5]. The presence of these dyes in wastewater is not desirable because of their toxic nature to the life and environment into which they are discharged. Therefore, the removal of such compounds from wastewater is a vital task.

Adsorption process using activated carbons is widely used to remove pollutants from wastewaters. However, commercially available activated carbon is expensive. In the last years, special emphasis on the preparation of activated carbons from several agricultural by-products has been given, due to the growing interest in low cost activated carbons from renewable, copious, especially for application concerning treatment of wastewater. Researchers have studied the production of activated carbon from palm-tree cobs, plum kernels, cassava peel, bagasse, jute fiber, rice husks, olive stones, date pits, fruit stones and nutshells [2].

In this study, the ability of snail shell carbon to remove Malachite green oxalate by adsorption is been studied. The Langmuir and Freundlich isotherms will used to fit the equilibrium data. Pseudo-first order and pseudo-second order models will be used to fit the experimental data and the thermodynamic study will also be carried out [3].

II.   THEORY

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

2.1.1 Pseudo-first order equation

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

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad (1)$$

$$\text{Log } (q_e - q_t) = \text{Log}(q_e) - \frac{K_1}{2.303} t \qquad (2)$$

The values of Log ($q_e - q_t$) were linearly correlated with time 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.

2.1.2 Pseudo-second order equation

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

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}\, t \qquad\qquad (3)$$

Where K_2 is the rate constant of the pseudo second order adsorption (g/mg.min). The plot of (t/q_t) and t of equation 3 should give a linear relationship from which q_e and K_2 can be determined [4].

2.2 Thermodynamic studies

The determination of the basic thermodynamic parameters such as enthalpy (ΔH), Gibb's free energy (ΔG) and entropy (ΔS) of the adsorption is important, as it determines 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 $\Delta H < 84$ kJ mol^{-1} and as chemical when ΔH lies between 84 and 420 kJ mol^{-1} [9].

Using equations 4 to 6

$$\Delta G = -RT\,\mathrm{In}K_d \qquad\qquad (4)$$

$$K_d = \frac{q_e}{C_e} \qquad\qquad (5)$$

$$\mathrm{In}K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad\qquad (6)$$

The thermodynamic parameters of the adsorption process were determined from the experimental data obtained at various temperatures.

Where K_d is the distribution coefficient for the adsorption, q_e is the amount of dye (mg/l) adsorbed 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 (8.314 J.K^{-1}.mol^{-1}), ΔG, ΔH, and ΔS are change in Gibbs free energy, change in enthalpy 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 [1].

2.3 Adsorption isotherm

2.3.1 Langmuir adsorption isotherm (model)

The Langmuir equation is probably the best known and most widely applied adsorption isotherm. It is represented as follows in equation 7

$$\frac{C_e}{q_e} = \frac{1}{b\, Q_o} + \frac{C_e}{Q_o} \qquad\qquad (7)$$

From which values of Q_o and b can be determined from the slope and intercept respectively of the plot of C_e/q_e versus C_e

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.

2.3.2   Freundlich adsorption isotherm (model)

The Freundlich isotherm is an empirical relationship which often gives a more satisfactory model of experimental data. It can be expressed as follows:

$$\mathrm{Log}\, q_e = \mathrm{Log}\,(K_f) + \frac{1}{n}\,\mathrm{Log}\, C_e \qquad\qquad (8)$$

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[8].

III.   MATERIALS AND METHODS

3.1 Preparation of adsorbent

Sample of snail shells were picked from the environment in Elele, Rivers State, Nigeria. The snail 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, then dried in the open air. The dried snail shells were carbonized in a furnace (SX-5-12) at 400˚C for 3 hours, the charred were allowed to cool to room temperature and ground. 100 gram of the ground carbonized snail shells was added to 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, allowed to cool to room temperature and washed with de-ionized water, dried in an oven at 110˚C for 2 hours [7].

3.2 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 dissolved in 1000ml of de-ionized water to prepare the standard solution. Experimental solutions of the desired concentrations were obtained by successive dilutions with de-ionized water.

3.3 Adsorption experiment

1000mg of the activated carbon of snail shell was mixed with 50ml of malachite green oxalate 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 618nm. The experiment was repeated using 1000mg of the activated carbon with 50ml of 50mg/L concentration of malachite green oxalate 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 618nm. Again 1000mg of the activated carbon mixed with 50ml of 50mg/L concentration of malachite green oxalate 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 malachite green oxalate dye adsorbed onto the snail shell adsorbent at equilibrium was calculated with the following equation:

$$q_e = \frac{(C_o - C_e)V}{X} \tag{11}$$

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.

The percentage of snail shell adsorbed was calculated as:

$$\% \text{ adsorbed} = \frac{(C_o - C_e)}{C_o} \times 100 \tag{12}$$

IV. RESULTS

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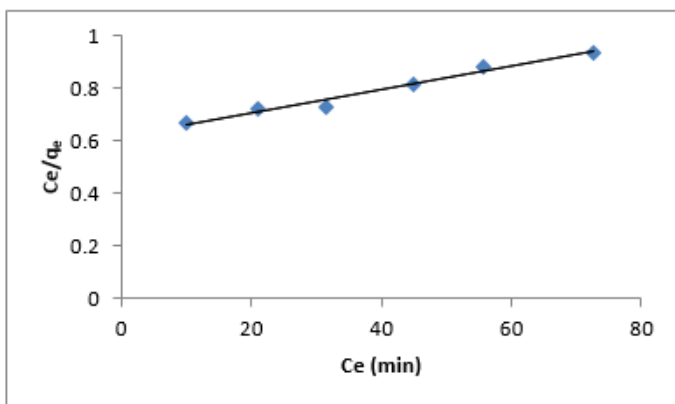

Fig.1: Langmuir model
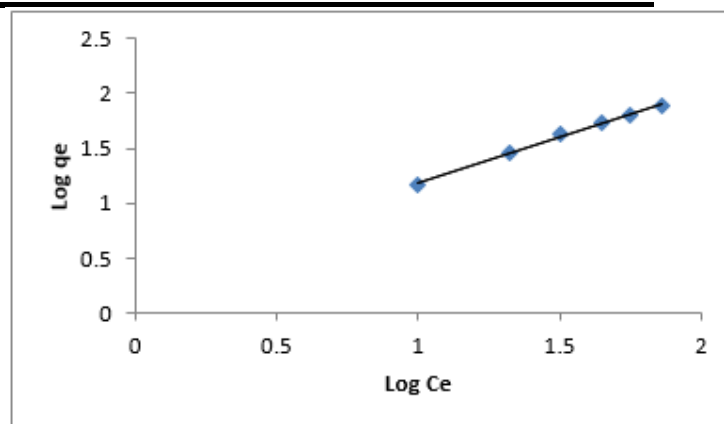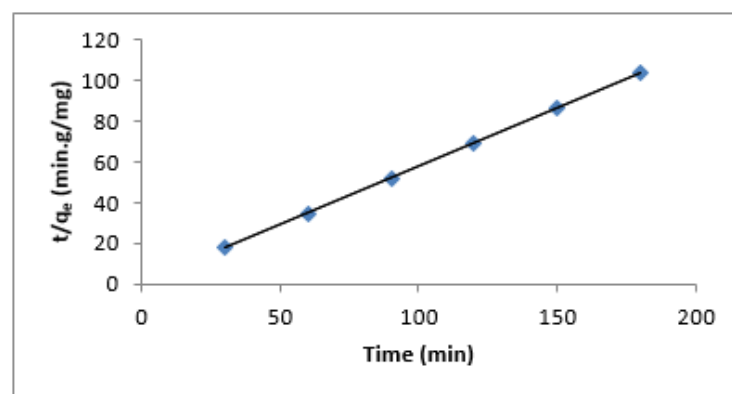

Fig.2: Freundlich model

Fig. 3: Pseudo second order reaction
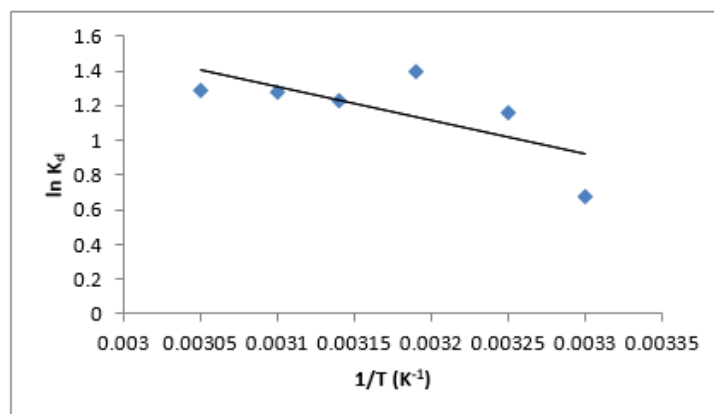
Fig. 4: Vant's Hoff model

Table.1: Adsorption efficiency

Variable time		Variable temperature		Variable concentration	
Time (min)	% Adsorption	Temp °C	% Adsorption	Conc. (mg/L)	% Adsorption
30	64.73	30	64.73	25	81.09
60	75.82	35	76.55	50	79.27
90	76.13	40	76.91	75	73.33
120	76.36	45	78.18	100	72.45
150	76.36	50	78.91	125	71.71
180	76.36	55	79.09	150	70.91

Table.2: Adsorption isotherm constants for coconut fibre activated carbon

Langmuir			Freundlich		
$Q_o(\frac{g}{mg})$	$b(\frac{mg}{l})$	R^2	$K_f(\frac{mg}{g})$	$n(\frac{l}{g})$	R^2
250	0.0065	0.978	2.3067	1.206	0.995

Table.3: Thermodynamic parameters for erythrosine adsorption by activated carbon

Temperature (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol.K)
303	-1.69	15.90	60.16
308	-2.98		
313	-3.64		
318	-3.24		
323	-3.43		
328	-3.51		

V.   DISCUSSION

The efficiency of the adsorption presented in table 1, shows that adsorption increases as time increases until 120min when the active sites were filled, then the adsorption efficiency becomes constant. The table also shows that adsorption increases with increase temperature, but after 35°C, increasing the temperature will no longer be economical. As the concentration of the adsorbate is increased, the efficiency of adsorption decreases, though highest at 25mg/l, but it is more economical with 50mg/l.

The values of the adsorption models presented in table 2 shows that the correlation coefficient of Freundlich isotherm is closer to 1 than that of Langmuir, indicating that it a heterogeneous adsorption process.

The kinetic of adsorption of Malachite green oxalate onto snail shell was studied using pseudo first-order and second-order equations for the examined system. The pseudo second-order kinetic model provided the best correlation for the experimental data.

From the thermodynamic point of view, the positive value of ΔH indicates that the adsorption of Malachite green oxalate on snail shell is endothermic and a physical process. The positive value of ΔS shows the existence of structural changes at the solid–liquid interface and ΔS favors ion exchange and stability of adsorption.

Table.4: Adsorption capacities of some adsorbents for MG oxalate removal

Adsorbent	T°C	Adsorption capacity(mg/g)	Reference
Rattan sawdust	30	22.4	Hameed and El-Khaiary (2008)
Prawn-Carbon	30	1.5249	Santhi (2009)
Prawn-Raw	30	5.6635	Santhi (2009)
Activated charcoal		0.180	Iqba and Ashiq (2007)
Sugar cane dust		4.88	Khattri and Singh (1999)
Bentonite		178.6	Bulut etal (2008)
Nickel ferrite		4.67	Manohar (2015)
Wood apple shell	25	34.56	Ashish etal. (2014)
Carbon prepared from Borassus bark	30	20.70	Arivoli et al. (2009)
Carbon prepared from Arundo donax root	30	8.69	Zhang et al. (2008)
Periwinkle shell	30	1.96	Ikhazuangbe etal, (2017)
Coconut fibre	30	1.88	Ikhazuangbe etal, (2017)
Snail shell	30	1.75	Present

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

Adsorbent	ΔH°	ΔS°	Reference
Thevetia peruviana	61.127	227.0	Baseri et al, (2012)
Pandanus leaves	60.762	231.4	Hema and Arivoli (2008)
Bentonite	13.21	62.85	Bulut et al, (2008)
Wood apple shell	1.581	6.375	Ashish et al, (2014)
Coconut fibre	20.45	74.34	Ikhazuangbe etal, (2017)
Periwinkle shell	19.74	72.21	Ikhazuangbe etal, (2017)
Snail shell	15.90	60.16	Present

VI.   CONCLUSION

From the adsorption efficiency, kinetic and thermodynamic studies of the adsorption of Malachite green oxalate onto activated carbon from snail shell studied, the results obtained from the analysis show that snail shell has good potential as low cost adsorbent for the removal of this hazardous dye from wastewater.

VII.   ACKNOWLEDGEMENTS

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