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Kinetic And Thermodynamic Studies Of The Adsorption Of Malachite Green Oxalate Dye Onto Activated Carbon From Periwinkle Shell

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***Abstract*—The studies of the kinetic and thermodynamic of the adsorption of malachite green oxalate onto Periwinkle shell was carried out. The Periwinkle shell was washed, dried and carbonized at 400°C. It was ground, sieved and activated at 800°C. 1000mg of the adsorbent was mixed with 50ml of 50mg/l of malachite green oxalate. Six samples were prepared and placed in a temperature controlled water bath. It was withdrawn at 30 minutes interval, filtered and the concentration of the filtrate was determined with a UV spectrophotometer at 618nm. The adsorption followed a second order reaction with a correlation coefficient of 0.999 and rate constant of 0.1278, 0.1132 and 0.1081g/mg.min at 30, 40 and 50°C respectively. The activation energy, E_a = -6.85KJ/mol, frequency factor, A = 0.0083(min^{-1}). The enthalpy change, ΔH° = 19.74KJ/mol, entropy change, ΔS°, = 72.21J/mol.K and the change in Gibbs free energy, ΔG°= -1.53, -3.03, -3.13, -3.37, -3.54 and -3.63KJ/mol. These results show that activated carbon from Periwinkle shell will be a good substitute to commercial activated carbon for the removal of malachite green oxalate from aqueous solution.**

Keywords—Periwinkle shell, Malachite green oxalate, kinetic and thermodynamic

Introduction

The discharge of highly coloured effluents into natural water bodies is not only aesthetically displeasing, but it also impedes light penetration, thus upsetting biological processes within a stream [4]. Colour is a visible pollutant and the presence of even very minute amount of coloring substance makes it undesirable due to its appearance. Adsorption on activated carbons has been proven to be very effective in removing dyes from aqueous solutions. However, commercial activated carbon is still considered expensive and currently the research is focused on the development of low-cost adsorbents for this purpose. Low-cost adsorbents include natural, agricultural, and industrial by-product wastes. They are attractive because of their abundant availability at low or no cost and their good performance in removing dyes from aqueous solutions. Previously, researchers had proved several low-cost materials such as palm ash, pomelo (Citrus grandis) peel, sunflower seed hull, oil palm trunk fibre, durian peel and rice straw-derived char, biomass fly ash, dried biomass of Baker's yeast, water-hyacinth for the removal of dyes from its aqueous solutions and a host of others [2].

The objectives of this work include investigation of the potential of Periwinkle shell as a low-cost adsorbent to remove malachite green oxalate from aqueous solution, to determine the kinetic and thermodynamic behavior of the process.

Theory

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.

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

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

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

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \qquad (4)$$

The plot of (t/q_t) and t of equation 4 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].

Activation energy

The rate equation which the adsorption process follows is used as the adsorption kinetic data of the studied system.

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

This equation is described as:

$$\ln K = -\frac{E_a}{RT} + \ln A \qquad (5)$$

Where K is the rate constant, E_a is the activation energy. 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[6].

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} [7].

The thermodynamic parameters of the adsorption process were determined from the experimental data obtained at various temperatures using equations 6 to 8

$$\Delta G = -RT\ln K_d \qquad (6)$$

$$K_d = \frac{qe}{Ce} \qquad (7)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (8)$$

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 $\Delta S^o$are change in Gibbs free energy, change in enthalpy and entropychange 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 [1].

Materials and Methods

Preparation of adsorbents

Samples of Periwinkle shell were picked from the environment in Elele, Rivers State, Nigeria. The Periwinkle shell was washed with tap water several times to remove the dust and other water- soluble materials. The washing process continues until the water was colorless, then dried in the open air. The dried Periwinkle shell was 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 [5].

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.50mg of the dye was weighed and dissolved in $1dm^3$ de-ionized water to prepare the standard solution.

Adsorption experiment

1000mg of the activated carbon of Periwinkle shellwas mixed with 50ml of 50mg/l Malachite green oxalate solution(6 samples) 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 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 experiment was also carried out with 6 samples, with 1000mg of the activated carbon for each sample at 40 and 50ºC. The samples were withdrawn after 30minutes respectively filtered and the concentration measured.

Theamount of Malachite green oxalate dye adsorbed onto the Periwinkle shell adsorbent at equilibrium was calculated with the following equation:

$$q_e = \frac{(C_o - C_e)V}{X} \qquad (9)$$

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.

Results

The results of the adsorption experiment are presented in the figures 1 - 3 below.

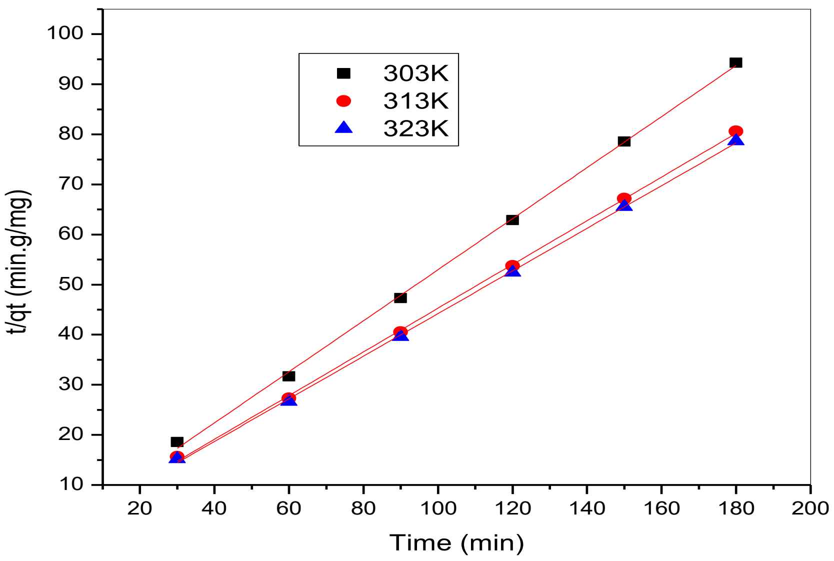

Fig.1 Pseudo second order reaction

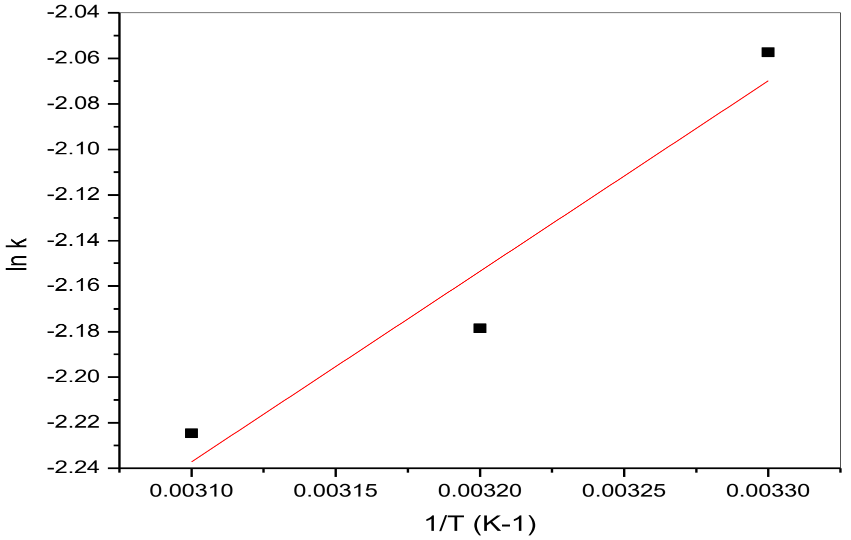

Fig.2 Temperature dependence of reaction rate

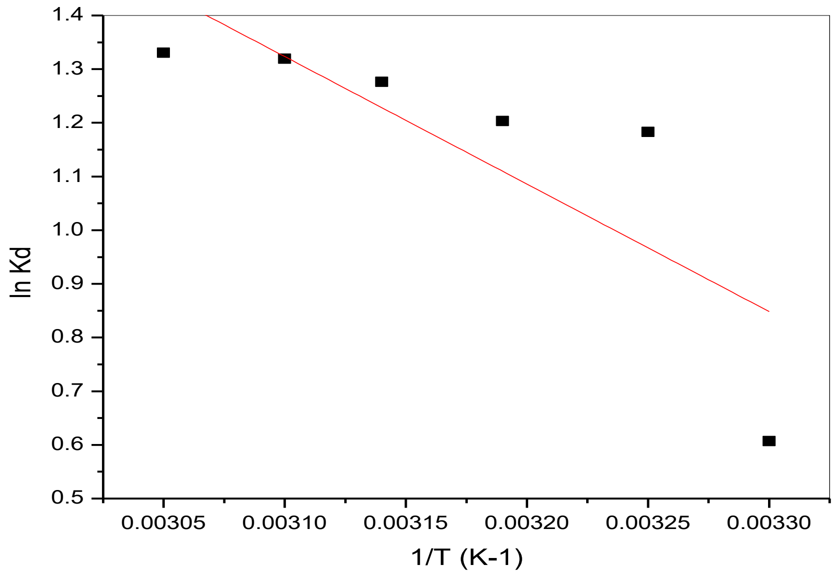

Fig.3Effect of temperature on the adsorption

Table 1: Kinetic and energy parameters

2nd order kinetic	
30ºC	
K_2(g/mg.min)	0.1278
q_e (mg/g)	1.9646
R^2	0.999
40ºC	
K_2(g/mg.min)	0.1132
q_e (mg/g)	2.2936
R^2	0.999
50ºC	
K_2(g/mg.min)	0.1081
q_e (mg/g)	2.3529
R^2	0.999
Activation energy	
E(KJ/mol)	-6.85
A(min^{-1})	0.0083

Table2: Thermodynamic parameters for erythrosine adsorption by activated carbon

Temperature (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol.K)
303	-1.53	19.74	72.21
308	-3.03		
313	-3.13		
318	-3.37		
323	-3.54		
328	-3.63		

Discussion of results

The pseudo second-order kinetic model provided the best correlation of the experimental data, with correlation coefficient of 0.999 at 30, 40 and 50^{o}C (fig. 1) and adsorption capacity of 1.9646, 2.2936 and 2.3529 respectively.

The activation energy was obtained from the rate constants of the pseudo second order kinetic model at 30, 40 and 50^{o}C (fig. 2) and was found to be -6.85KJ/mol.

Equations 6 – 8 were used to obtain the thermodynamic data and are presented in table 2. The value of ΔHindicates that the adsorption of Malachite green oxalate on Periwinkle shellactivated 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 and separation work requirement of the adsorption process.

Conclusion

From the kinetic and thermodynamic studies of adsorption of Malachite green oxalate onto activated carbon from Periwinkle shell carried out, the results obtained show that Periwinkle shell has potentials of a good low cost adsorbent, for the removal of this hazardous dye from wastewater.

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