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KINETICS AND THERMODYNAMICS STUDIES ON ALIZARIN RED ADSORPTION ONTO ADSORBENT DERIVED FROM ORANGE PEELS

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ABSTRACT
Simplicity and economic advantages are what make adsorption one of the most recommended methods for the treatment of water from textile effluents. In this research, activated carbon based adsorbent was prepared from orange peels by heating the peels at elevated temperature in a furnace followed by chemical activation using $ZnCl_2$ solution. Kinetics studies showed that the experimental data did not fit very well into the pseudo-first order model. However, pseudo-second order equation showed the best fitting with R^2 value of 0.999 and experimental value q_e (mg/g) of 6.612 which is very closed to that calculated as 6.757. Intra-particle diffusion and Bangham's models were used to study the diffusion mechanism and the final conclusion was made using the Boyd model. With the effective diffusion coefficient D_i, calculated to be 2.14 x 10^{-8} cm^2s^{-1}, its clear that the rate of the process was governed by film-diffusion. Moreover, in the thermodynamics studies, the value of the activation energy, Ea was calculated as 45kjmol,$^{-1}$ and which suggests that the process was chemisorption in nature. ΔH term was found to be positive which simply noted that the adsorption AR onto OP was an endothermic process. The negative values of ΔG were found that show that the adsorption is highly favorable and spontaneous across all the temperatures.

INTRODUCTION

For several years now, environment has been the major victim of human activities, including burning domestic garbage, human waste, contributing domestic sludge, discharging different types of smokes by burning fuels, and automobile exhaust (Pal *et al.*, 2017). Additionally, chemicals are being used as reactants, intermediates, or catalysts and are discharged as effluents into different water bodies. Subsequently, these are escaped into agricultural soils upon irrigation. Ultimately, these reaches human body, as human beings are a big consumer (Naik *et al.*, 2013). Such movement of chemicals from industrial areas to human body has a serious threat to quality of life. Hence, green environment has become the best option for assuring better quality of life. Among different chemicals used in different industrial processes, dyes are one of the major classes. Dyes are used for coloring different materials like leather tanning, textile, food materials, paints, and paintings. Textile industrial effluent is reported to be rich in dyes, and in this way, dyes are the major source of water pollution (Latif *et al.*, 2019)

The objective of this work was s to explore the effects kinetics and thermodynamics

Among textile effluents, synthetic dyes are a necessity in various significant industries such as the leather, paper, and textile industries for its colour-giving properties. For example, the wastewaters produced by dye manufacturing and textile finishing industries contain heavy metals, which are used as a mordant in the dyeing process (Xiaodong and Yunjin, 2019). Since dyes are recalcitrant, stable, colorant, and even possibly toxic and carcinogenic, releasing these pollutants into the environment will lead to serious consequences on the health of human beings, microbes, animals and plants. Dyes are distributed throughout every environmental matrices and great advances have been made in the elimination of these dyes from the environment (Wang *et al.*, 2018). The conventional methods for treating dye containing wastewaters are electrochemical treatment, coagulation and flocculation, chemical oxidation, liquid–liquid extraction and adsorption (Lawal and Muhammad, 2019). However, the fast and sensitive adsorption and detection of dyes in water are still attracting much attention since water remediation is a global challenge (Muhammad *et al.*, 2019).

parameters on the batch adsorption of alizarin red in aqueous solution using adsorbent derived from orange peels

MATERIALS AND METHODS

Preparation of Adsorbent from the Orange peels

The preparation of the adsorbent from orange peel was achieved by the procedure described by Lawal and Muhammad (2019). In this method, orange peels obtained from sale points were thoroughly washed to remove dirt and unwanted particles adhered to them. They were cut into small pieces making them easy to handle. These small pieces of were dried in a hot air oven (GENLAB, MINO/100/F) at a temperature of 70^{o}C for two hours. 25g of the well dried sample was then soaked into 1.0M aqueous zinc chloride solution at 1:5 ratio for chemical activation The mixture was allowed for 24 hours before heating to form paste. The paste was placed in a furnace and carbonized at 350 °C for 1 hour in the absence of oxygen (or reduced to the lowest minimum). The sample was then withdrawn from the furnace at this point and the activated carbon formed was cooled and washed with distilled water to constant pH. The sample was then dried at 100 °C in an oven and later removed to cool down at room temperature. This was thus crushed with a pestle in a very clean mortar and the resultant powder was sieved through mesh sieve. Finally the activated carbon was stockpiled in air tight packets and labeled as OP. The characterizations of the OP formed was described by Lawal and Muhammad (2019).

Batch Adsorption Studies

Comprehensive aqueous batch adsorption studies for the Alizarin Red (AR) dye onto OP were conducted and the influence of different relevant parameters was investigated. To optimize the operational conditions, adsorptions of the AR onto the surface of OP adsorbent were observed at predetermined initial conditions, whereby a fixed quantity of the OP was added to the AR solutions and the mixtures were agitated in a shaker at predetermined time intervals; the AR solution was separated from the adsorbent via centrifugation followed by filtration. The filtrate was taken and the amount of the dye adsorbed by the adsorbent was quantified using uv/visible spectrophotometer at 430nm (Zhao *et al.*, 2010).The amount of AR adsorbed at equilibrium, q_e was calculated using equation (1):

$$q_e = \left(\frac{C_0 - C_e}{W}\right) V \qquad (1)$$

Where C_0(mg g^{-1}) is the initial concentration, C_e(mgg^{-1}) is the dye concentration at equilibrium, V(L) is the volume of the solution, and W (g) is the mass of the adsorbent (Namasivayam and Yamuna, 1995).

RESULTS AND DISCUSSION

Kinetics Studies

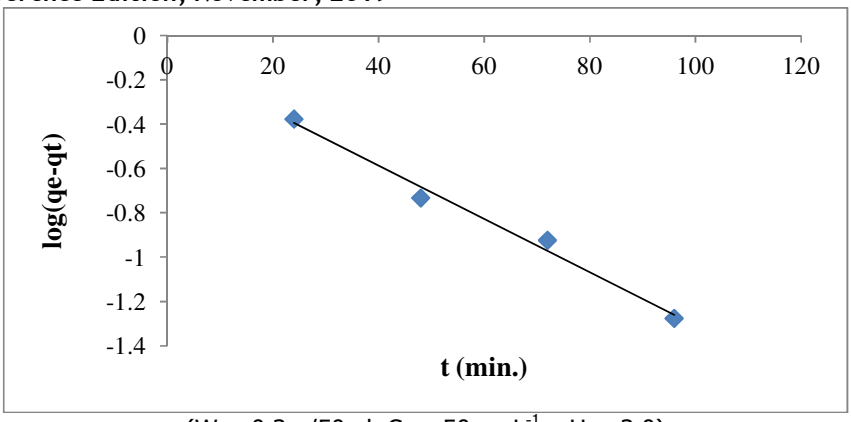
Adsorption kinetic indicates the rate of solute uptake which leads to determine residence time. It is also important to get information of the efficiency and characteristics of adsorbent (Arivoli and Thenkuzhal 2008). Some of the kinetics models were used to study the mechanism of the adsorption of AR onto the OP adsorbent and the following results were obtained:

Pseudo-First order model

Lagergren pseudo-first-order model is a common equation for the kinetic adsorption of solute from aqueous solution based on the capacity of the solid. The model can be written in the following form (Orlando *et al.*, 2002).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (2)$$

where q_e and q_t (mg/g) are the amount of targeted molecules adsorbed at equilibrium and at time t respectively and k_1 (min^{-1}) is the equilibrium rate constant for pseudo-first-order adsorption process. For the adsorption of AR dye by OP adsorbent, it is clear that that the plot of ln(qe-qt) versus t presented in figure 1 only yielded straight line graph. This shows that experimental data fit Lagergren model, which is depicted by high values of the linear regression coefficient R^2, of 0.987. Since the high R^2 value is obtained, but the intercept is not equal to log q_e, thus the process does not seem to follow pseudo-first-order kinetic model (Badruddoza *et al.*, 2010).



(W = 0.3 g/50ml, C_0 = 50 mgL^{-1}, pH = 3.0)

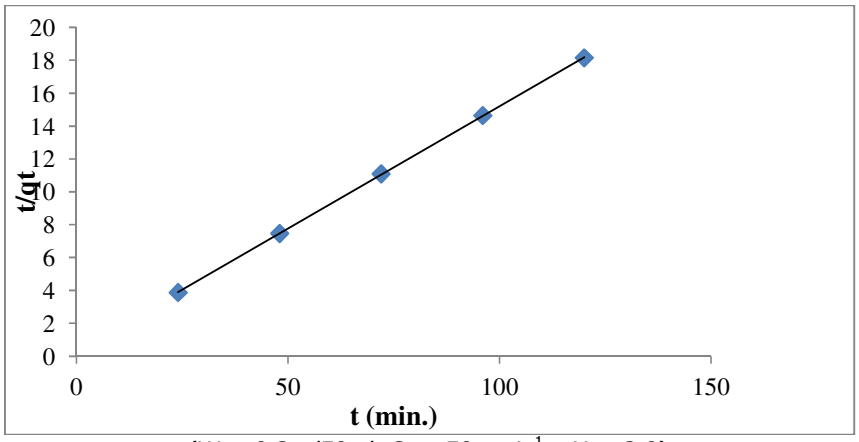
Fig.1: Plot of Pseudo-first Order model for adsorption of AR on OP

Pseudo-second Order model

The slope and intercept of the linear plot of t/q_t as a function of t using an integrated pseudo-second order model as shown by equation 3 yielded the values of qe and k_2.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3)$$

The qe value (6.757 mgg^{-1}) obtained from the second-order kinetic equation for the process was close to the experimental q_e value (6.612 mgg^{-1}), and the linear regression coefficient, R^2 value obtained for pseudo-second-order kinetics was 0.999. This result indicates that adsorption of AR by OP adsorbent follows pseudo-second-order kinetics which implies that the adsorption was better described by the pseudo-second order kinetic, indicating that the adsorption mechanisms of dyes depended on the adsorbates and adsorbents as reported by Oyelude *et al.*,(2017).



(W = 0.3 g/50ml, C_0 = 50 mgL^{-1}, pH = 3.0)

Fig. 2: Plot of Pseudo-second Order model for adsorption of AR on OP

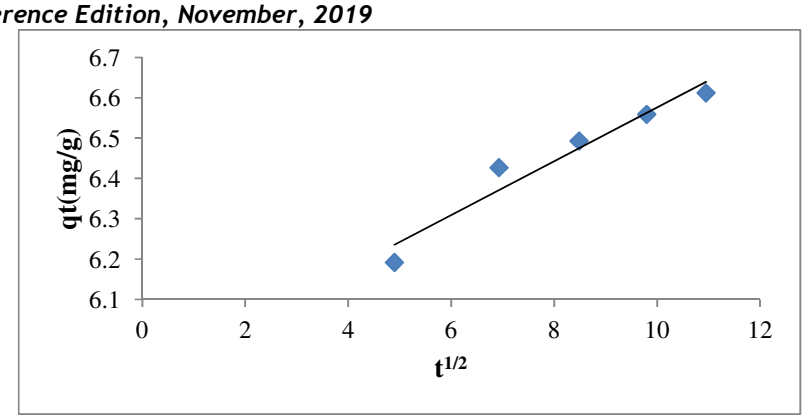
Intra-particle diffusion model

In order to gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, Weber's intraparticle diffusion model can be tested against the kinetic experimental results (Weber and Morris 1963). The initial rate of the intraparticle diffusion is expressed as:

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

Where; k_p is the intra-particle diffusion rate constant (mg g^{-1} $min^{-1/2}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{\frac{1}{2}}$. C is a constant that expresses the thickness of the boundary layer (Weber and Morris, 1963).

The adsorption kinetic data obtained were used to plot q_t vs. $t^{1/2}$ which is the intra-particle diffusion equation, the value of intra-particle diffusion constant, k_p, was obtained from the slope of the straight-line portions of the plot as shown in figure 3.



(W = 0.3 g/50ml, C_0 = 50 mgL^{-1}, pH = 3.0)

Fig.3: Plot of Intra-particle diffusion model for adsorption of AR on OP

The value of the regression coefficient, R^2 for the intra-particle diffusion model was found to be 0.942 and this show that there is good agreement between the intra-particle diffusion equation and the experimental data; this furthermore indicates that particle diffusion is involved in the adsorption of AR dye by the OP adsorbent even though the straight line in the plot did not pass through the origin which further implies that the intra-particle diffusion is not the rate-determining step as reported by Arami *et al.,* (2008). The intercept gives an idea of the thickness of the boundary layer i.e. the larger the intercept, the greater the boundary layer effect (Tan and Hameed, 2010). It can be seen that the value of the intra-particle diffusion constant was found to be 5.909 and this is an evident that the boundary layer has significant effect about the diffusion mechanism of AR uptake onto the OP adsorbent. In the figure 3, the deviation of the plot from the origin might be due to the difference in the mass transfer rate in the initial and final stages of adsorption process (Mohanty *et al.*, 2005).

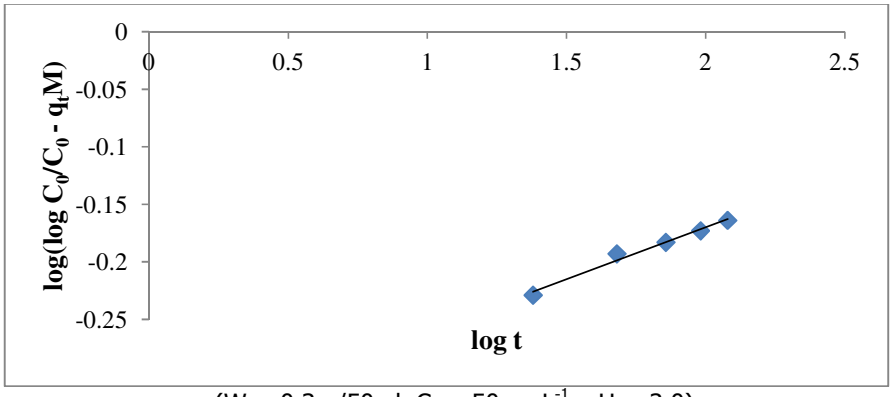
Bangham's model

Kinetics data were further used to know about the slow step occurring in the present adsorption system using Bangham's equation (Sumanjit *et al.*, 2016)

$$\log\log\left(\frac{C_0}{C_0-q_tM}\right) = \log\left(\frac{K_0M}{2.303V}\right) + \alpha\log t \qquad (5)$$

Where C_o, is the initial concentration of dye in solution (mg/L). V is the volume of the solution (ml), M is the weight of adsorbent per liter of solution (g/L). qt (mg/g)is amount of dye adsorbed at time t. α(<1) and K_o are constants (Bhatnagar., 2005).

For the adsorption of AR dye by the OP adsorbent, $\log\log\left(\frac{C_0}{C_0-q_tM}\right)$ was plotted against $\log t$. The Bangham's constants α and K_0 were determined from the slope and intercept of the plot respectively. The inear plot shows tha tthe diffusion of adsorbate into the pores of adsorbents is not the only rate controlling step (Sumanjit *et al.*, 2016)



(W = 0.3 g/50ml, C_0 = 50 mgL^{-1}, pH = 3.0)

Fig.4: Plot of Bangham's model for adsorption of AR on OP

The Boyd kinetics model

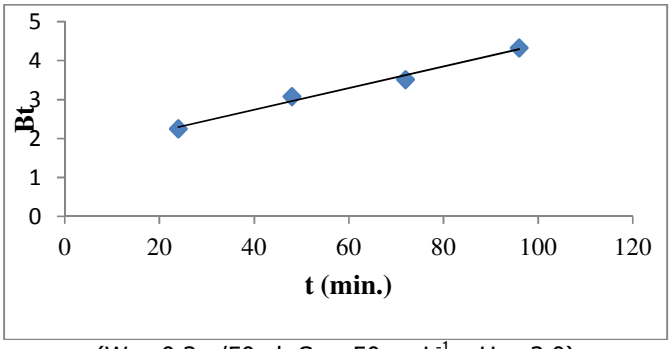
To suggest the slow step involved in the adsorption process, the kinetics data were also treated using the Boyd kinetics model (Michelson *et al.*, 1975).

The fractional attainment of equilibrium parameter, F, at any time, t was found to be greater than 0.85(i.e. F > 0.85) throughout this research, and therefore the approximate values of Bt were obtained by the transformation of equation (6) to give the Reichenberg equation (7) applicable when the F values are greater than 0.85 (Karthikeyan *et al.*,2010)..

$$F = 1 - \frac{6}{n^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp^{(-n^2 B_t)} \quad (6)$$

$$B_t = -0.4977 - \ln(1 - F) \quad (\text{For } F > 0.85) \quad (7)$$

After calculating the values of Bt at different time intervals for AR dye adsorption by the OP adsorbent, Bt against time, t (min) were then plotted as shown in figure 5.



(W = 0.3 g/50ml, C_0 = 50 mgL^{-1}, pH = 3.0)

Fig. 5: Plot of Boyd model for adsorption of AR on OP

As can be seen from figure 5, the relationship between Bt and t yielded a linear plot but the straight line does not pass through the origin, this indicates that in the initial step of the process, the slowest step could be film diffusion. Also the value of the effective diffusion coefficient D_i calculated was found to be 2.14 x $10^{-8}cm^2s^{-1}$ and this further confirmed that film diffusion was the rate determining step (since the value of D_i calculated is in the range of 10^{-6} to 10^{-8}) (Karthikeyan *et al.*,2010).

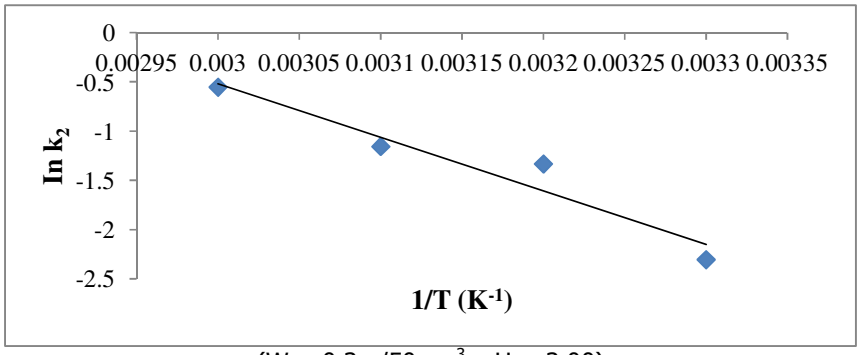
Table 1: Adsorption Kinetics parameters for AR adsorption on OP

Kinetic Model	Parameters	Value
Pseudo-first order	$q_{e/exp}(mgg^{-1})$	6.612
	$q_{e/cal.}(mgg^{-1})$	0.785
	$k_1(min.^{-1})$	3.60 x 10^{-3}
	R^2	0.987
Pseudo-second order	$q_{e/exp}(mgg^{-1})$	6.612
	$q_{e/cal.}(mgg^{-1})$	6.757
	k_2 $(min.^{-1})$	6.70 x 10^{-2}
	h (mg/gmin.)	3.039
	R^2	0.999
Intra-particle diffusion	kp (mg/g $min^{0.5}$.)	6.6 x 10^{-2}
	C	5.909
	R^2	0.942
Boyd model	B (Slope)	0.027
	D_i (cm^2 sec^{-1})	2.14 x 10^{-8}
	R^2	0.986

Thermodynamic Studies

Temperature is a significant parameter affecting adsorption capacity of adsorbents and transport/kinetic process of the dye adsorption. Thermodynamic of the adsorption process was determined via thermodynamic parameters, such as the activation energy (Ea), changes in the standard free energy (ΔG), the enthalpy (ΔH) and entropy (ΔS) associated with the adsorption process. From the Arrhenius equation (7), when $\ln k_2$ was plotted against 1/T, a straight line with slope Ea/R was obtained as shown in figure 6

$$\ln k_2 = \ln A - \frac{Ea}{RT} \quad (8)$$



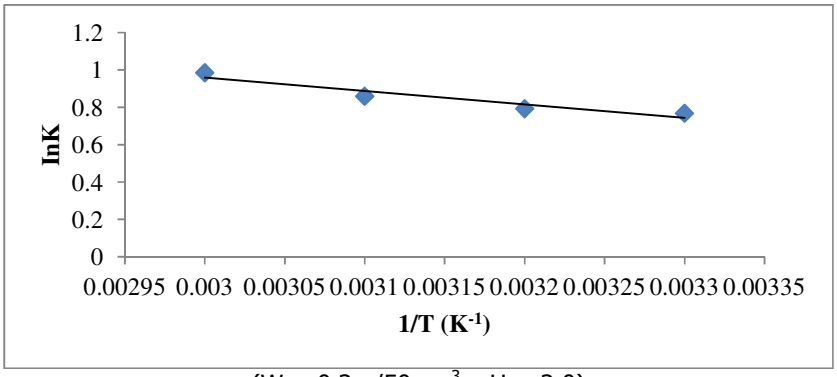
(W = 0.3 g/50 cm^3, pH = 3.00)

Fig. 6: Arrhenius plot for AR adsorption on OP

The positive value for ΔH obtained from the plot of InK against 1/T (figure 7) using the Vant Hoff equation (9) shows the endothermic nature of the adsorption which governs the possibility of physical adsorption since physical adsorption as temperature of the system increases, the extent of dye adsorption increases (increased in the values of K in table 2) (Adepoju & Ibrahim, 2018).

$$\mathrm{InK} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

The negative and positive values of ΔG and ΔS show that the adsorption is highly favorable and spontaneous under those conditions (Arivoli *et al.*, 2007).



(W = 0.3 g/50 cm^3, pH = 3.0)

Fig.7: Vant Hoff plot for AR adsorption on OP

Table 2: Adsorption Thermodynamics parameters for AR adsorption on OP

PARAMETER		**TEMPERATURE(K)**			
		313	323	333	303
ΔG (kJmol)		-1.93	- 2.10	- 2.31	- 2.73
K		2.155	2.211	2.363	2.678
Ea	45.16kJmol^{-1}				
ΔH	+ 5.96kJmol^{-1}				
ΔS	+ 25.85J$mol^{-1}K^{-1}$				

CONCLUSION

Orande peels were used as a cheap raw material in preparing adsorbents for the removal of Alizarin Red. The OP adsorbents show a promising performance during the adsorption process. The investigation of the adsorption kinetics revealed that it was best described by the pseudo-second order model whereas the effective diffusion coefficient D_i calculated confirmed that film diffusion was the rate determining step. Study of thermodynamics parameters suggested that the adsorption of alizarin red on orange peels based adsorbent was a spontaneous and temperature dependent (endothermic) process while the values of ΔH indicates that the adsorption process is physical adsorption. In conclusion, the adsorbent has been proven to be an excellent candidate fro the removal of alizarin red in aqueous solution.

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