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Full Length Research Article

STUDIES ON THE MECHANISM OF ADSORPTION OF METHYLENE BLUE ONTO ACTIVATED CARBON USING THERMODYNAMIC TOOLS

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ABSTRACT
The mechanism of adsorption of methylene blue onto palm kernel shell based activated carbon was studied using thermodynamic approach employing batch adsorption technique. The negative value of the free energy indicates that the process is feasible and spontaneous. The mean value of the entropy of the system was 138.08±21.21 which showed an increased disorder and randomness at the solid solution interface. The results showed that the magnitude of isosteric enthalpy, ΔH obtained (32.09±6.58 kJ mol^{-1}) was clearly indicative of chemisorptions process and the free energy was negative at all temperatures and became more negative with increasing temperature. This behavior is characteristic of both endothermic and chemisorptions process.

Keywords: Adsorption, Chemisorption, Organic pollutant, Activation energy

INTRODUCTION

The study of adsorption of methylene blue from aqueous medium by activated carbon is important for the general understanding of the interaction between organic solutes and porous solids. This is because the phenomena form the basis of the several applications ascribable to wastewater treatments, purification and separation techniques.

An understanding of the mechanisms of adsorption is therefore essential for improving the efficiency of these processes. Information on adsorption mechanism can be derived from the nature of adsorption isotherm, rate constant (Abechi *et al.*, 2011) and energy parameters obtained from thermodynamic studies. Thermodynamic properties help predict the properties of carbon, reliable chemical equilibria and heat requirements for the adsorption process (Storvic and Sandler, 1977).

The thermodynamic parameters such as isosteric enthalpy, entropy, equilibrium constant and standard free energy were calculated for the adsorption of CO_2 onto dehydrated Palladium/Cobalt-based Cyanogels by Bocarsly *et al*., (2002) and used to establish the nature of the adsorption process. Thermodynamics provides a practical tool for the estimation of the chemical states of adsorbent and solution in chemical industry applications. Thermodynamic parameters, such as free energy of adsorption, ΔG^o, enthalpy of adsorption, ΔH^o, entropy of adsorption, ΔS^o were important in understanding the adsorption mechanism of fluorine onto aluminosilicate modified trepel (Zelentsov and Datsko, 2013). Several other researchers have established the mechanism of adsorption through studies of thermodynamic properties (Kavitha *et al*., 2014, Jodeh *et al.,* 2015, Soreta *et al*., 2015, Eldien *et al*.,2016, Yun-yu, 2016, Ebrahim *et al.,* 2017, Karim *et al*., 2017, Wang *et al*., 2018). Kok *et al*. (2016) studied the adsorption mechanisms of methylene blue onto microcrystalline cellulose. The values of Gibbs free energy for thermodynamics studies were found to be within the range of -20 kJ/mol and 0 kJ/mol, indicating physical adsorption. The mechanism of adsorption of phosphorous from wastewater on palm kernel shell was determined through thermodynamic properties such as change in free energy and change in entropy (Babayemi, 2016). The adsorption of phosphorus was established to be endothermic and nonspontaneous through the thermodynamic studies.

Thermodynamic parameters can improve our understanding on the inherent energetic changes involved in adsorption processes (Yu-Feng *et al*, 2014). The thermodynamic parameters are therefore invaluable tools for a holistic understanding of adsorption phenomena. This research work is aimed at investigating the mechanism of adsorption of methylene blue, a model adsorbate for adsorption of organics onto activated carbon from the thermodynamic point of view.

MATERIALS AND METHODS

The preparation of the activated carbon was as described by Abechi *et al*., (2013). The palm kernel shells were collected from open market in samara, Zaria-Nigeria. The shells were washed, dried and crushed using a locally made grinder. This was sieved to 1.18mm and carbonized at 400°C for 1 hour. The carbonized material (20 grams) was mixed with 200 cm^3 KOH solution at impregnation ratio of 1:1(KOH pellet: Char). Impregnation was carried out at 80 °C on a hot plate equipped with a stirrer for 2 hours. The sample was filtered using a vacuum pump and dried overnight at 120 °C. The dried sample was then activated at a temperature of 800 °C, for 45 minutes in a furnace. The activated carbon burning was quenched with water and then washed with distilled water to remove residual chemical. It was then transferred to a beaker containing a 250 cm^3 solution of 0.1 M HCl, stirred for one hour to remove the alkali and alkaline earth metals and then washed with hot distilled water until the pH of the washing solution was 7.0. The prepared activated carbon was dried at 120 °C for 24 hours, cooled and stored for further studies. Laboratory grade methylene blue was used without further purification for the preparation of synthetic aqueous solution in the initial concentration ranging from 10 to 60 ppm. The concentration of methylene blue (MB) in the aqueous solution was determined at λ_{max} of 660 nm, using a UV-visible spectrophotometer (Helios γ).

Batch Adsorption of Methylene Blue.
25 cm^3 of methylene blue solution of known initial concentration and a 0.2 g of activated carbon were contacted in a 150 cm^3 Erlenmeyer flasks with air tight stopper. This mixture was agitated in a temperature-controlled water bath shaker, at a constant shaking speed. Equilibrium studies were carried out at temperature of 303, 313, 323, and 333K in order to study the influence of temperature on the adsorption process. The initial concentration was kept at 20 ppm and a pH 7.0. The mixture was removed from the agitation tray, filtered using a vacuum pump and absorbance readings of the methylene blue filtrate was taken using UV-Visible spectrophotometer (Helios γ)

RESULTS AND DISCUSSION
The thermodynamic functions can be obtained from the van't Hoff equation, which relates the equilibrium constant of the adsorption process to the absolute temperature (Anirudhan and Krishnan, 2003). The integrated form of vant' Hoff equation is expressed as:

$$InK = -\frac{\Delta H^o}{RT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The enthalpy change, ΔH, and entropy change, ΔS where computed from the slope and intercept of the van't Hoff plot of ln K versus 1/T (Figure 1). The thermodynamic functions have been calculated to be able to give qualitatively correct interpretation of adsorption characteristics.

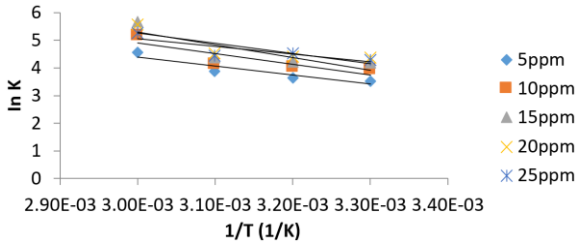

Figure 1: Vant-Hoff plot for adsorption of MB [initial conc = 5-25ppm, temp 30 - 60].

The value of the equilibrium constant K, at the different temperature were used to evaluate the free energy of the process by using Equation (3).

$$\Delta G = -RTInK \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$and \qquad \Delta S = \frac{\Delta H - \Delta G}{T} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$\Delta S^0 = \left(\frac{\Delta H^o - \Delta G^0}{T}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The Gibbs free energy ΔG, and equilibrium constant are shown in Table 1. The free energy, ΔG is negative at all temperatures and become more negative with increasing temperature, implying that the amount adsorbed at equilibrium increased with increasing temperature. The negative sign indicates that the process is feasible and spontaneous (Rounak *et al*., 2011). The mean value of the free energy was obtained as (-14.49±1.14). It is clear from Table 1 that the equilibrium constant generally increased with increase in adsorption temperature, implying a strengthening of adsorbate – adsorbent interaction at higher temperature. The equilibrium constant is temperature dependent and the amount by which its value change is related to the standard change in enthalpy of the system.

Table 1. Thermodynamic parameters

Temperature (K)	Equilibrium Constant, K_{eq}	ΔG^o (kJ mol^{-1})
303	60.63±15.92	-10.24±0.75
313	67.09±18.75	-10.81±0.82
323	70.05±15.95	-11.46±0.62
333	218.93±68.67	-14.49±1.14

The mean value of the entropy, ΔS of the system was 138.08±21.21 (Table 2). The high positive value of the entropy shows the increased disorder and randomness at the solid solution interface of methylene blue and the activated carbon. This is in agreement with the work of Oyekunle *et al*., 2014. The adsorbed water molecules, which have been displaced by the adsorbate specie, gain more translational entropy, thus allowing the prevalence of randomness in the system.

The magnitude of isosteric enthalpy ΔH obtained (32.09±6.58 kJ mol^{-1}), clearly, is indicative of chemisorptions process. Physisorption is characterized by enthalpy value in the range of 5-20 kJ mol^{-1} while that of chemisorptions is greater and in the region of that of chemical bonding (Vasu, 2008). The activation energy (Ea) and sticking probability (S*) were estimated from the experimental data using the modified Arrhenius type equation related to surface coverage (Θ) as employed by Najim and Yassin (2009).

Θ = [1-Ce/Ci] ……..(4)

where, Ce is the equilibrium concentration, Ci is the initial concentration of the adsorbate and Θ is the surface coverage. The sticking probability is a function of the adsorbate/adsorbent system under investigation and is given as:
$S^*=(1-\Theta)\, e^{-Ea/RT}$ ……..(5)
$\ln S^* = \ln (1-\Theta) - Ea/RT$……..(6)
$\ln (1-\Theta) = \ln S^* + Ea/RT$……..(7)

The value of E_a and S* were calculated from the slope and intercept of the plot of ln (1-Θ) versus the reciprocal of the temperature (1/T), respectively, as shown in Figure 2. The values of E_a and S* are as given in Table 2. The positive values of E_a indicates endothermic nature of the adsorption process and agrees with earlier conclusion drawn, based on the value of the enthalpy of the reaction.The values of activation energy (E_a) were found to range between 24.03 and 38.58 kJ/mol with a mean of 29.11±5.41kJ/mol. This lies in the range for energy of chemisorption and confirms the earlier conclusion based on the value of ΔH. Chemisorptions generally possess high activation energy, the reason for the high adsorption energy associated with the process.

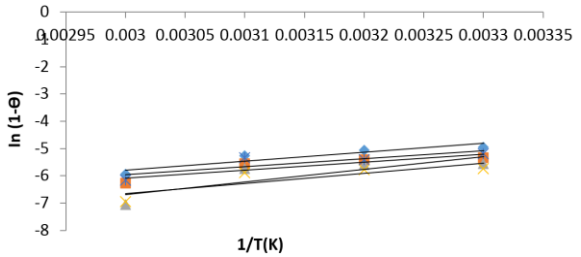

Figure 2: Plot of ln(1-Θ) versus reciprocal of temperature for the adsorption of MB onto activated carbon.

Table 2: Values of activation energy and sticking probability at various initial concentrations

Initial conc	Ea, kJ mol^{-1}	S*	R^2	ΔH^o (kJ mol^{-1})	ΔS^o (J mol^{-1})
5	27.19	1.7 x 10-7	0.85	32.09±6.58	138.08±21.21
10	24.44	3.4 x 10-7	0.78		
15	38.58	1.0 x 10-9	0.70		
20	31.34	1.5 x 10-8	0.69		
25	24.03	4.5 x 10-7	0.70		

The sticking probability (S*) values were far less than unity (Table 2), which indicates that the probability of the methylene blue ions to stick to surface of the activated carbon is very high. The S* value ranged between 1.0 x 10^{-9} to 1.7 x 10^{-7}. S* value in the range 0<S*<1 is for preferable process and it is dependent on temperature of the system. Similar result has been reported in literature (Najim and Yassin, 2009).

Conclusion

The adsorption process is characterized by high activation energy. This coupled with the magnitude of the enthalpy of adsorption, **s**howed clearly that the mechanism of the adsorption process is chemisorption.

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