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Sorption Studies of Methylene Blue Using Activated Carbon Produced from Rice Husk

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Abstract: *Activated carbon was produced from rice husk and used for the removal of methylene blue dye from aqueous solutions through batch adsorption method. The results obtained indicated that the adsorption of methylene blue did not depend significantly on particle size but on the period of contact, adsorbent dosage and initial concentration of the dye. The adsorption responded significantly to the assumptions establishing Freundlich and Langmuir isotherm. The adsorption was also spontaneous and supported the mechanism of physical adsorption.*

Key Words: *Aquatic pollution, methylene blue, remediation, adsorption, activated carbon*

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1.0 Introduction

Our environment is largely contaminated by some by anthropogenic. However, industrial activities account for the main source of environmental pollution (Venkatesharaju, 2010). Many industries such as leather, printing and textile industries use dye in various units of processing operations. In the textile industries, the main cause of pollution originates from the dyeing and finishing sections which require relatively large amount of chemicals and dyestuffs, whch are organic compounds of complex structures (Kumar, 2011). Textile industries use significant quantity of dye and are known to constitute major source of enrichment of textile waste water (Chavan, 2001). Most dyes used in textile processing are stable when exposed to detergents and sunlight, indicating that they may not be easily attack by microorganism or be biodegradable. However, due to their aromatic nature, they can undergo chemical changes that leads to genotoxic or carcinogenic effects (Crini, 2005; Odoemelam *et al*., 2018; Wang and Chu, 2011). Dye rich waste water discharge to water bodies can affects the colour of the water and constitute a major source of obstruction to light penetration and thus retard photosynthesis and the amount of dissolve oxygen in the water (Karadag *et al*., 2007). The consequence is that aquatic life will be grossly threatened (Eddy and Udoh, 2006).

Adsorption is a surface process that has been successfully applied in removing contaminants from water (Okwunodulu and Eddy, 2013). It is regarded as one of the best options that can be easily implemented within ease of raw materials accessibility, cost and sound environmental confinements (ref). Several classes of adsorbents have been successfully applied in the removal of water contaminants including plant materials, natural clay, human hair, synthetic materials, plant waste, nano materials, metal organic framework, etc (Srivastava *et al*., 2006). However, one of the most customary and sustainable adsorbents is activated carbon. Activated carbons are complex products which are difficult to classify on the basis of their behavior, surface characteristics and other fundamental criteria (Uchechukwu *et al*., 2018). However, it can be classified based on its: particle size, preparation method and industrial application which are powdered activated carbon, granular activated carbon, extruded activated carbon, bead activated carbon, impregnated carbon, polymer coated carbon etc. Activated carbon is used for

removal of color pigments, removal of odour and various catalytic functions (Uchechukwu *et al*., 2015). Several forms of activated carbon have been developed and applied for the removal of dyes from aqueous solution through adsorption process. The results obtained in all cses have shown that activated carbon has good adsorbent sites for most dyes (Malik, 2004; Mheshwari *et al*., 2017; Zhang *et al*., 2015; Zheng *et al*., 2018). Current environmental innovations on charcoal chemistry are centered on the production of activated carbon from plant materials. Therefore, the present study is aimed synthesizing activated carbon from rich husk for the adsorption removal of methylene blue dye from aqueous solution.

Rice husk is a bye product of paddy grinding processing of rice (Jintanawasan, 2011) and are known to be rich in carbon and silica (Sharma, 2011). The husk is a waste material indicating that its utilization for dye adsorption will not only presents solution for dye removal but also a major contribution to waste management through resource recovery.

2.0 Materials and Methods

Rice husk was collected from Sabo market in Chikun Local Government of Kaduna State Nigeria. The samples were thoroughly washed with distilled water to remove the yellow colour and dried in an oven maintained at 60 °C for 6 hours. The dried samples were pulverized to different particle sizes, namely, 450 and 600 µm respectively. 15g of each sample were respectively transferred into separate crucibles, impregnated with 0.2 M H_2SO_4 in a ratio 1:1 and then dried in the oven at a temperature of 80 °C for 3 hours. The dehydrated sample was carbonized at 400 °C for 20 minutes, removed, cooled and washed with distilled water to neutral pH. The washed samples were filtered and re-dried to constant weight.

The batch adsorption experiments were carried out as reported elsewhere. Effect of initial concentration, period of contact and adsorbent dosage was investigated. Initial concentration tests were conducted using 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/L solutions of the dye respectively while effect of contact time was established for 5, 10, 20, 30, 60 and 90 minutes respectively. The batch adsorption process was also implemented for 0.1, 0.2, 0.3, 0.4, 0.5 and 0.8 g of the adsorbent in order to established the effect of adsorbent dosage. In each adsorption experiment, the variable to be investigated while other variables were kept at constant value. The equilibrium amount of dye adsorbed was calculated using equation 1(ref)

$$q_e = \frac{C_0 - C_e}{m} \times \frac{V}{1} \qquad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of the dye in the solution, m is the mass of the adsorbent while V is the volume of the solution.

3.0 Results and Discussion

Fig. 1 shows a plot for the variation of equilibrium amount of methylene blue dye adsorbed with time. The plot reveals that the amount of dye adsorbed first increases with time and then become constant after an optimum time. The observed trend can be explained in terms of the gradual occupation of available activated sites as diffusion progresses with time until a limit is approached where further diffusion does not lead to corresponding adsorption of the dye due to completely filling of active adsorption sites. Similar trend has been observed by others (Eddy, 2009). Therefore, the optimum time for the attainment of maximum adsorption capacity was 60 minutes. The observed trend was similar for both particle sizes hence the attainment of equilibrium as a function of time is independent of the particle size.

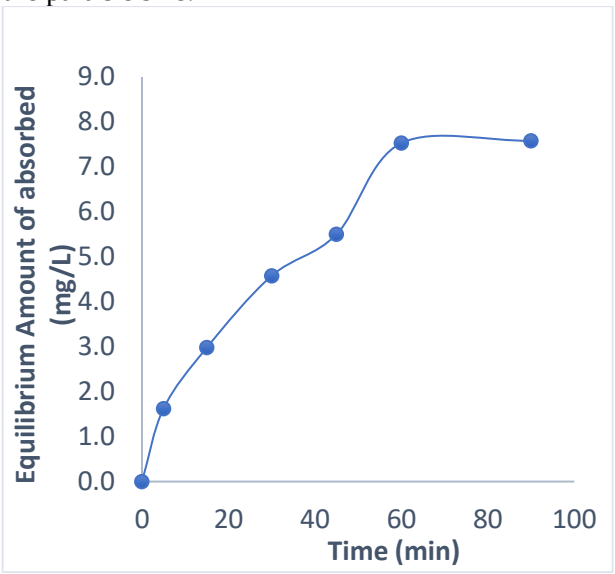

Fig. 1: Variation of equilibrium amount of dye adsorbed by activated carbon with time (Particle size = 450 µm)

The percentage of dye removed for a fixed period of time and constant temperature was also found to vary proportionally with adsorbent dosage at first

instant and then becomes steady after adsorbent dosage of 0.5 g g as shown in Fig. 2. The observed trend also reveals that there is a critical adsorbent dosage, above which further increase may not yield a corresponding increase in dye removal efficiency. Maximum efficiency was > 90%.

Therefore, the performance of the synthesized rice husk activated carbon for the adsorption of methylene blue from aqueous solution does not depends on the mass of the adsorbent alone but on several other factors, which must be taken into account if optimum removal efficiency must be realized. Diffusion of the adsorbate can be one of the major factors that can limit the adsorption process (Eddy *et al*., 2004; Ekop and Eddy, 2010). If diffusion does not favours further migration of the dye molecules to the surface of the adsorbent, adsorption process would be retarded (Ekuma *et al*., 2017).

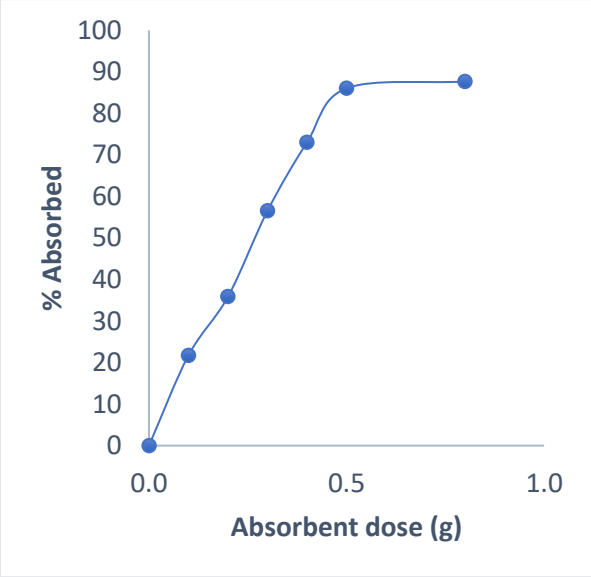

Fig. 2: Variation of percentage dye removal with adsorbent dosage

Adsorption isotherm is a useful approach for understanding the adsorption characteristics of methylene dye unto the activated husk. Tests carried out to select best fitted adsorption isotherm revealed the suitability of Langmuir and Freundlich adsorption models with good degree of linearity.

The Langmuir adsorption model is established by assumptions that can be summarized according to equation 2 (Essien and Eddy, 2014),

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (2)$$

where C_e is the equilibrium concentration of adsorbate (mg/l), q_e is the amount of adsorbate adsorbed per unit mass of the adsorbent (mg/g), b is the Langmuir adsorption constant which is related to affinity between the adsorbate and the adsorbent while q_m is the theoretical monolayer saturation capacity. From the Langmuir equation, a plot of $\frac{C_e}{q_e}$ versus C_e should be linear if the Langmuir assumptions are valid. The essential feature of the Langmuir adsorption model is the separation factor, defined as $R_L = \frac{1}{(1+q_m C_0)}$. If $0 \leq R_L \leq 1$, the adsorption is favourable. When $R_L = 0$ the adsorption is irreversible, when $R_L = 1$, a linear adsorption is favoured and $R_L > 1$ indicates unfavourable adsorption (Odoemelam *et al*., 2018). Fig. 3 shows the Langmuir plot for the adsorption of methylene blue dye on the surface of activated carbon. 9.0135

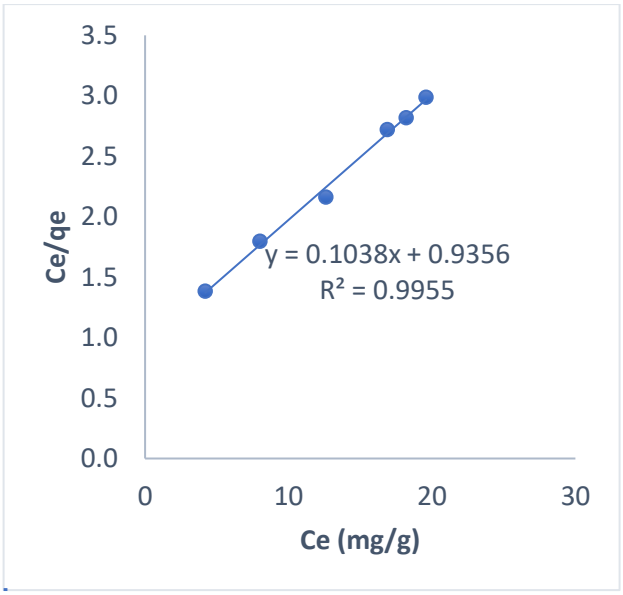

Fig. 3: The Langmuir isotherm for the adsorption of methylene blue dye on the surface of activated carbon

The observed fitness of the adsorption mechanism to the Langmuir isotherm (R^2 = 0.9955) with slope value less than unity suggest the existent of multimolecular layer of adsorption (Odoemelam and Eddy, 2008). Maximum adsorption capacity obtained fr= om the Langmuir plot (9.63 mg/g) is close to the experimental adsorption capacity. The Langmuir adsorption constant, b was obtained as 0.1109 and from the Gibb Helmholtz equation

expressed in equation 4, the free energy of adsorption can be estimated (Eddy *et al*., 2010),

$\Delta G^0_{ads} = -2.303RTlog(b)$ (3)

The calculated standard free energy change (-5540.91 J/mol) is very low and points towards the mechanism of physical adsorption. Also, calculated value of the separation factor (R_L) was less than unity, which indicated that the adsorption is favourable.

The Freundlich equation implies that the energy of adsorption on a homogeneous surface is independent of surface coverage.

The Freundlich adsorption model can be expressed according to equation 4

$lnq_e = lnK_F + \frac{1}{n} lnC_e$ (4)

where K_F is the Freundlich adsorption constant

(related to the free energy of adsorption according to equation 3), 'n' is adsorption intensity which indicates the relative distribution of the energy and the heterogeneity of the adsorbate sites.

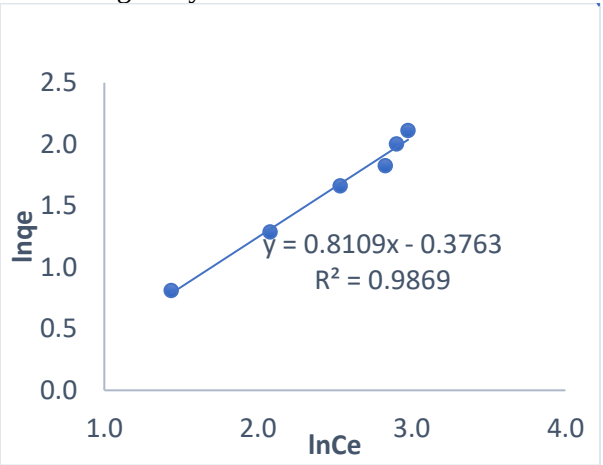

Fig. 4: Freundlich isotherm for the adsorption of methylene blue dye on activated carbon

Calculated free energy change from the Freundlich constant was -947.95 J/mol, which also points toward a physical adsorption mechanism. Value of 1/n was 0.8109, which gives n = 1.233 (i.e n>1) hence the adsorption is favourable.

Pseudo first order and pseudo second order kinetics models can be expressed according to following successive equations respectively (Odoemelam *et al*., 2018)

$ln(q_e - q_t) = lnq_e - k_1 t$ (5)

$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ (6)

Figs. 5 and 6 show pseudo first and second orders plots respectively. Excellent fitness was obtained for both pseudo first and second order plots (R^2 >0.9) but pseudo second order witness a slight difference. The pseudo-order rate constant was 0.1151 while the theoretical equilibrium amount of dye adsorbed was 1.016 which is far less than the maximum adsorption capacity. However, for the pseudo second order kinetic, the theoretical equilibrium amount of dye adsorbed was 0.9904, which is relatively close to that of the pseudo first order but far from the experimental value. On the other hand, the pseudo second order rate constant (3.5722) was larger than that of the pseudo first order

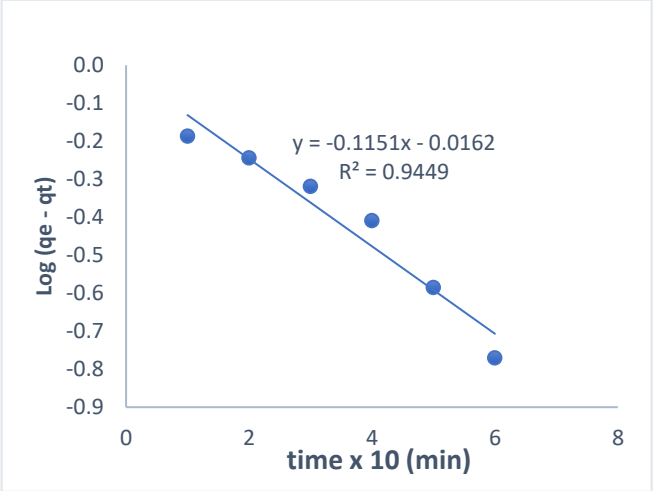

Fig. 5: Pseudo first order kinetic plot for adsorption of methylene blue on activated carbon

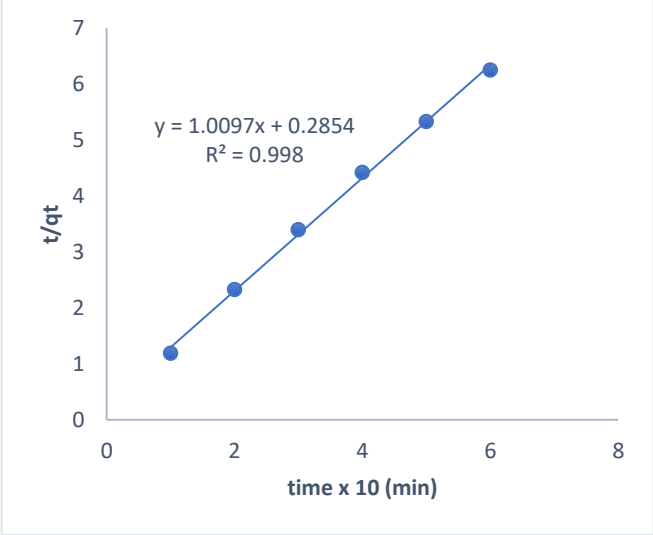

Fig. 6: Pseudo second order plot for adsorption of methylene dye on activated carbon

4.0 Conclusion

Removal of methylene blue dye from aqueous solutions by adsorption with activated carbon from

rice husk has been shown to be experimentally feasible and the dynamics of the process depends on adsorbent dose, period of contact and other variables. The percentage of colour removed increases with increasing adsorbent dosage, and with increase in the period of contact. The optimum contact time for equilibrium to be achieved is established at 60 minutes while the optimum adsorbent dose is 0.5g/10ml. The equilibrium data fitted best to the Langmuir isotherm with high correlation coefficient of R^2= 0.9955 and the adsorption is consistent with a pseudo second order with spontaneous and endothermic nature.

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