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# Equilibrium Sorption Studies of Basic Blue-9 Dye from Aqueous Medium Using Activated Carbon Produced from Water Hyacinth (Eichornia Crassipes)

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## Abstract

*The study shows that water hyacinth could be used as novel raw material for the production of effective activated carbon for the adsorption (removal) of Basic Blue- 9 dye from aqueous solution. Optimum removal of 86% dye was obtained which decreased to 62% with an increase in concentration from 50 to 300mg/l, though sorption capacity was found to increase with an increase in concentration. Both Langmuir and Freundlich isotherms were suitable for describing the experimental data in this study with high regression coefficients ($R^2$) of 0.9852 and 0.9905 respectively. The Langmuir maximum sorption capacity ($q_m$) was found to be 421mg/g. It was further observed that the intensity of adsorption, n, was found to be 1.84 which shows that the sorption process was favourable. The equilibrium parameter, $R_L$, value of 0.138 also shows that the adsorption of Basic Blue-9 dyes onto the activated carbon was favourable. The macropore and micropore diffusion constants show that the rate limiting step is the micropore diffusion stage since the micropore diffusion constant ($K_{id2}$) value of 0 is lower than the macropore diffusion constant ($K_{id}$) value of 0.2543, thus the rate of micropore diffusion is the slower step and the rate determining step. The study also showed that the sorption process was predominantly controlled by intra-particle diffusion, though film diffusion also played a significant role.*

**Keywords:** *Equilibrium, studies, Basic Blue-9, activated carbon, water hyacinth.*

## Introduction

Removal of colour from dye bearing wastewaters is one of the major environmental problems because of the difficulty in treating such wastewaters by conventional methods due to low biodegradability of dyes and since most dyes are stable to heat and oxidizing agents. The presence of even minute amount of colouring substances make the water unsuitable for drinking or other recreational purposes due to its undesirable appearance. Today more than 9000 types of dyes have been incorporated in the colour index[1]. Dyes constitute a large and important group of industrial chemicals among the different pollutants in aquatic ecosystems for which world production was estimated at $7x10^5$ tonnes[2]. Presently, reactive dyes are widely used for dyeing cotton fabrics, but nearly 50% of reactive dyes may be lost to the effluent after dyeing of cellulose fabrics[3], and have therefore been identified as problematic compounds in textile effluents[4]. Most dyestuffs are designed to be resistant to environmental conditions like light, pH and microbial attack[5]. Hence, their presence in wastewater is unwanted or undesirable, and it is necessary to remove coloring materials from effluent before their discharge into the recipient environment.

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The adsorbent used in this study is activated carbon produced from water hyacinth (Eichornia crassipes) impregnated with hydrogen peroxide. Water hyacinth is an aquatic plant which can live and reproduce floating freely on the surface of fresh waters or can be anchored in mud[6]. It grows in mats up to two meters thick which can reduce light and oxygen, change water chemistry, affect flora and fauna and cause significant increase in water loss due to evapo-transpiration. It also causes problems for marine transportation, fishing and irrigation schemes. It is now considered a serious threat to biodiversity[7].

The objective of this study is to produce activated carbon from water hyacinth using hydrogen peroxide as the activating reagent and to investigate the equilibrium removal of Basic Blue- 9 dye from aqueous medium using the activated carbon as sorbent. Some physicochemical characteristics of the activated carbon would also be determined to know the suitability of the carbon as a sorbent.

## Experimental Methods

The fresh water weed, viz; water hyacinth (Eichornia crassipes) was collected from the Epie River in Yenagoa of Bayelsa State. The sample collected was washed thoroughly with water and then rinsed with deionised water and air-dried. The air-dried weed was then cut into small pieces and carbonized.

### *Carbonization of Water Hyacinth*

The dried plant based biomaterial was carbonized according to the method described elsewhere[8].

### *Chemical Activation of Carbon using Hydrogen peroxide*

The activation followed the method described by Toles et al.,[9].

### *Adsorbate*

Basic Blue –9 (a cationic dye) was used for the adsorption studies. Basic Blue-9 (C. I. 52015, $\lambda_{max}$ = 664nm) was manufactured by Gurr, BDH Chemicals Ltd, Poole England. The molecular formular of Basic Blue- 9 dye is $C_{16}H_{18}ClN_3S$ with a molecular weight of 319.86. A stock solution of the dye with a concentration of 1000mg per liter was prepared. This was done by weighing 1.0g (1000mg) of dye and transferred into a 1000ml volumetric flask. The dye was dissolved in the volumetric flask using de-ionized water and the solution made up to the 1000ml mark in the flask. Serial dilutions of the stock solution were made to obtain specific concentrations required for the adsorption study.

### *Sorption experiments*

#### *Effect of Initial Dye Concentration*

Into various 100ml conical flasks containing 50ml dye solution with concentration of 50-300mg/l was introduced 4.0g each of activated carbon of 200µm mesh particle size. The suspensions were agitated at 150rpm on a mechanical shaker at room temperature ($30^{O}C$) and shaken for 4 hours. At the end of agitation period, the samples were centrifuged for 5 minutes and the supernatant was filtered through fiberglass filter. The dye concentration in the filtrate was determined by measuring absorbance at the wavelength of maximum absorption (664nm) using Unicam UV- visible spectrophotometer vision software $V_3$ 40. The pH of the solutions was adjusted to 7.5 by adding either HCl or NaOH solution.

#### *Effect of Contact Time*

Into various 100ml conical flasks containing 50ml dye solution of 250mg/l concentration was introduced 4.0g each of activated carbon of 200µm mesh particle size. The flasks were then labeled for time intervals of 40, 80, 120,160, 200, 240 and 280 minutes. The pH values of the suspensions were adjusted to 7.5 by adding either HCL or NaOH solution. The flasks were tightly covered with cellophane and shaken at 150rpm for the appropriate time interval. The suspension was filtered through fiber glass filters and then centrifuged for 5 minutes. The supernatants were analyzed by UV- visible spectrophotometer.

***Analysis of Experimental Data***

The equilibrium adsorption capacities ($q_e$) at different dye concentrations were determined according to the mass balance equation of the adsorbate (Eqn 1) [10].

$$q_{t=}\frac{V}{M}(C_o|C_e) \qquad (1)$$

Where Co and Ce are the initial and equilibrium concentrations of the dye (mg/l) respectively, V is the volume of the aqueous solution (L) and M is the mass (g) of activated carbon used in the adsorption.

Two adsorption isotherms, the Langmuir and the Freundlich were used to analyze the equilibrium experimental data obtained in this study. The Langmuir plot was carried out using the linearized form (Eqn 2):

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

Plot of $C_e/q_e$ against $C_e$ gives a straight line curve with slope $\frac{1}{q_m}$ and intercept $\frac{1}{q_{mK_L}}$

The linear plot of equation 2 was used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the carbon surface. The essential characteristics of a Langmuir Isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter, $R_{L,}$ and is defined (Eqn 3)[11]

$$R_L = \frac{1}{1+bC_O} \qquad (3)$$

Where b is a Langmuir constant (L/g) and Co is the initial concentration of dye (mg/l). The parameter $R_L$ indicates the shape of the isotherm and nature of the sorption process as stated below. If $R_L > 1$, the isotherm model for the sorption was unfavourable, $R_L = 1$, linear, $0< R_l < 1$, favourable, $R_L$ = O, irreversible.

The linearized Freundlich plot of equation 4 was taken, and the Freundlich constants were obtained from the slope and intercept of the straight line plot (Eqn 4):

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

If a plot of $Inq_e$ against $C_e$ of equation 3 yields a straight line, then the sorption process obeys a Freundlich adsorption Isotherm. The constants $K_F$ and $1/n$ can be obtained from the intercept and slope of the straight line.

To investigate if intra-particle diffusion was the sorption rate limiting step, Weber-Moris plot of $q_t$ versus $t^{1/2}$ was taken (Eqn 5):

$$q_t = K_{id}t^{1/2} + C \qquad (5)$$

where, $K_{1d}$ is the intra-particle diffusion rate constant (mg/g/min$^{½}$ ) and C (mg/g) is a constant that gives idea about the thickness of the boundary layer, i.e. the larger the value of C the greater is the boundary layer effect [12]. If the Weber- Morris plot of $q_t$ versus $t^{½}$ gives a straight line, then the sorption process was controlled by intra-particle diffusion only and the slope gives the rate constant, $k_{1d}$. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process.

The liquid film diffusion model was also employed in this study to investigate if the transport of the sorbate molecules from the liquid phase up to the solid phase boundary plays a major role in the adsorption as in (Eqn 6):

$$\ln(1 - F) = -K_{id}\, t \qquad (6)$$

Where F is the fractional attainment of equilibrium ($F = q_t/q_e$), $K_{1d}$ is the adsorption rate constant. A linear plot of – ln (1 - F) versus t with zero intercept would suggest that the kinetics of the sorption process is controlled by diffusion through the liquid surrounding the solid sorbent.

## Results

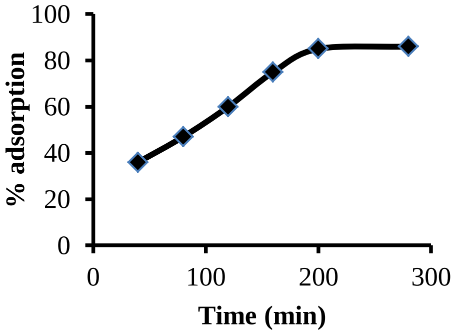
Table 1 shows the proximate analyses of the physical properties of the activated carbon.

**Table 1:** *Physicochemical characteristics of activated carbon from water hyacinth*

| Property | Activated Carbon |
|---|---|
| Moisture | 23.70±0.15 |
| Porosity | 0.913±0.006 |
| Iodine number | 152.20±0.17 |
| Ash Content (%) | 22.40±0.10 |
| Volatile Matter (%) | 37.47±0.15 |
| Density (g/cm$^3$) | 0.199±0.053 |
| pH | 8.01±0.01 |
| Surface area (m$^2$/g) | 106.12±1.20 |

The experimental adsorption rate curve for Basic Blue-9 dye by the activated carbon is shown in figure 1. Figure 1 indicates that the percent removal of dye increase with time and attains equilibrium in 3 hr and 20 min for initial dye concentration of 250mg/l. No significant change in dye removal was observed after about 3 hr 20min.

The effect of initial concentration on the percentage removal of Basic Blue-9 dye was studied and shown in fig. 2. As shown in fig 2, the percentage removal of dye decreases with an increase in dye concentration. The adsorption efficiency decreased from 86 to 62% when the initial dye concentration changes from 50 to 300 mg/l. Fig. 3 shows the effect of initial dye concentration on the sorption capacity of the activated carbon sample. The figure shows that sorption capacity increases with a corresponding increase in dye concentration. The suitability of the experimental data for Basic Blue -9 dye adsorption to Langmuir and Freundlich isotherms are shown in figures 4 and 5 respectively. Based on the regression coefficients ($R^2$), the adsorption data fitted well to both the Langmuir ($R^2 = 0.985$) and Freundlich ($R^2 = 0.99$) isotherms respectively. However, the fit to Freundlich adsorption model ($R^2 = 0.99$) was greater than that of Langmuir ($R^2 = 0.985$). The Langmuir and Freundlich constants calculated from the slopes and intercepts and regression coefficients of the plot of figures 4 and 5 are presented in table 1. The Langmuir dimensionless separation factor or equilibrium parameter, $R_{L,\text{ was found to be } 0.138.}$ In order to obtain the rate determining step in the sorption process, intra-particle diffusion model was used to analyze the results obtained from this study. According to the intra-particle diffusion model, if a plot of the amount of



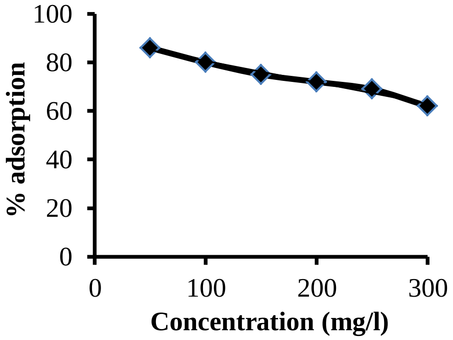
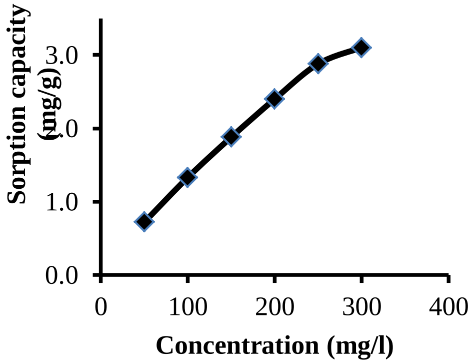


***Fig.1(left):*** *Effect of contact time on the percentage removal of Basic Blue-9 dye from solution by the activated carbon sample.* ***Fig. 2 (right):*** *Effect of initial dye concentration on the percentage removal of Basic Blue-9 dye from solution by the activated carbon sample.*



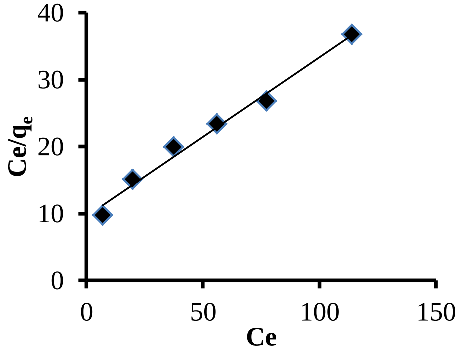
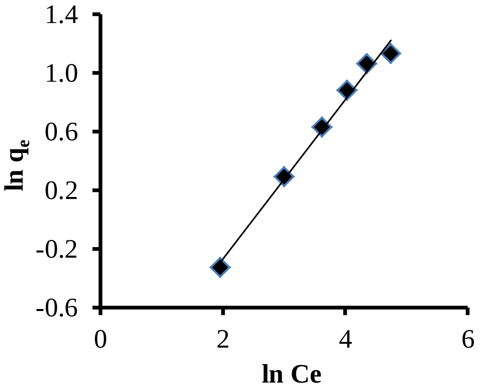


***Fig. 3 (left):*** *Effect of initial dye concentration on the sorption capacity of the activated carbon sample.* ***Fig. 4 (right):*** *Langmuir plot for the sorption of various concentrations of Basic Blue-9 dye from solution by the activated carbon sample.*



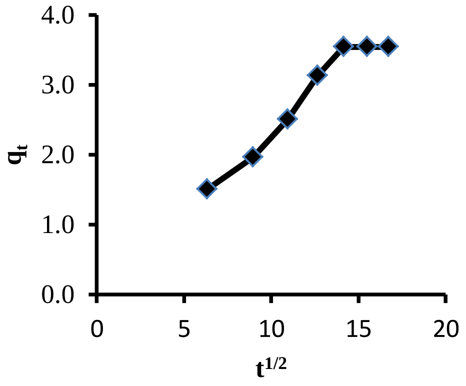


***Fig.5 (left):*** *Freundlich plot for the sorption of various concentrations of Basic Blue-9 dye from solution by the activated carbon sample.* ***Fig. 6(right):*** *Plot of intra-particle diffusion kinetics of Basic Blue-9 dye onto the activated carbon sample.*

sorbate adsorbed per unit weight of sorbent, ($q_t$), versus square root of contact time, $t^{1/2}$ gives a straight line, then the sorption process is controlled by intra-particle diffusion/pore diffusion only. However, if the data exhibit multi-linear plots as predicted by Weber and Morris, then two or more steps influence the sorption process[12]. It is assumed that the external resistance to mass transfer surrounding the particles is significant only in the early stages of adsorption. This is represented by first sharper portion. The second linear portion is the gradual adsorption stage with intra-particle diffusion dominating. The intra-particle diffusion model plot in this study is presented in figure 6 in which the data points are linked by two lines. This shows that two or more steps control the sorption process. In order to test for the possibility of diffusion of dye molecules, from the bulk liquid phase to the surface of the activated carbon, playing a significant role in the determination of the rate of adsorption, -In(I-F) was plotted against t, in accordance with the liquid film diffusion model. A linear plot of – In (1-F) versus t, with zero intercept would suggest that the kinetics of the sorption process was controlled by diffusion through the liquid film surrounding the activated carbon. The liquid film diffusion model plot was presented in figure 7. The liquid film diffusion parameters as obtained from the slope and intercept of the plot in figure 7 is shown in table 2.

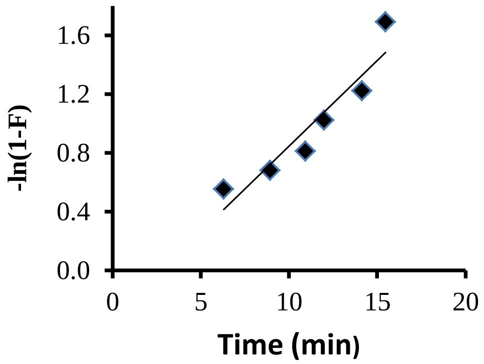


***Fig. 7:*** *Plot of liquid film diffusion kinetics of Basic Blue-9 dye onto the activated carbon sample.*

**Table 2:** *Langmuir and Freundlich constants and regression coefficients for the sorption of Basic Blue-9 dye onto the activated carbon sample.*

| Langmuir Constants | | | | Freundlich Constants | | |
|---|---|---|---|---|---|---|
| Sorption capacity $q_m$(mg/g) | Adsorption/desorption energy $K_L$(L/g) | Regression Coefficient $R^2$ | Equilibrium Parameter $R_L$ | Intensity of Adsorption n | Adsorption Capacity $K_F$ | Regression Coefficient $R_F^2$ |
| 421 | 0.025 | 0.9851 | 0.138 | 1.84 | 0.26 | 0.9905 |

**Table 3:** *Intra-particle and Liquid film diffusion constants and Regression coefficients ( $R^2$ ) for Basic Blue-9 dye sorption by the activated carbon sample.*

| Intra-particle Diffusion | | | | | | Liquid Film Diffusion | | |
|---|---|---|---|---|---|---|---|---|
| $Kid_1$ | Intercept | $R_1^2$ | $Kid_2$ | Intercept | $R_2^2$ | $K_{fd}$ | Intercept | $R_f^2$ |
| 0.2543 | -0.1981 | 0.972 | 0 | 3.54 | NA | 0.0129 | -0.1311 | 0.9292 |

## Discussion

The analyses (table 1) shows a low amount of moisture, ash and volatile matter, indicating that the particle density is relatively small and that the carbon should be an excellent material for use in batch sorption systems. The porosity, iodine number, surface area and pH are comparable to other materials used for column and batch analyses [13, 14, 15].

Figure 1 shows that the percent removal of dye was constant after the equilibrium time, probably due to surface saturation. The figure further shows that the uptake of dye molecules was fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. This may be due to the fact that a large number of vacant surface sites were available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the dye molecules on the adsorbent and bulk phases. Figure 1 also shows that at the end of equilibration time, the activated carbon sample was able to remove 85% dye from solution. Fig 2 shows that the percentage removal of dye decreases with an increase in dye concentration. This is because, at lower concentration, the carbon is able to remove large amounts of dye from solution. However, as the initial concentration of dye increases, the binding sites gradually become occupied, which reduces the overall percentage of dye removed. These removal characteristics indicate that surface saturation is dependent on the initial dye concentration and that the active sites take up the available dye more quickly at low concentrations. Figure 3 shows that the amount of dye removed (sorption capacity) by the activated carbon sample increased with increasing dye concentration. At higher concentrations, surface saturation occurs, leading to an increase in the actual amount of dye removed. Although the Basic Blue -9 dye adsorption data showed a significant fit to both Langmuir and Freundlich isotherms, the Freundlich model proved to be more suitable as compared to the Langmuir model based on their regression coefficient ($R^2$) values. From the data in table 2, the sorption capacity ($q_m$) which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage, shows that the activated carbon has a high sorption capacity (421mg/g). Table 2 further reveals that the apparent energy of sorption ($K_L$) was low, which suggests that the energy of sorption of the activated carbon sample for Basic Blue-9 dye was favourable. The value of the dimensionless separation factor, $R_{L\ (0.138)}$ in table 2 indicates that the adsorption data on to the activated carbon was also favorable. Similar result was obtained [16] for the adsorption of Bismark Brown dye on activated carbons. From table 2, it was further observed that the intensity of adsorption, n, was found to be 1.84. A favourable adsorption corresponds to a value of $1<n<10$. Therefore the adsorption process as obtained from the Freundlich isotherm model was favourable.

The graph presented in figure 6 shows that the data points can be related by two straight lines. The first straight line portion depicts macropore diffusion and the second represents micropore diffusion [12]. Extrapolation of the linear portions of the plot back to the y-axis gives the intercept, which provide a measure of the boundary layer thickness. The deviation of straight line from the origin (fig. 6) may be due to difference in rate of mass transfer in the initial and final stages of adsorption. Further, such deviation of straight line from the origin indicates that the pore diffusion is not the sole rate-controlling step. The macropore and micropore diffusion rate parameters ($K_{id1}$ and $K_{id2}$) and regression coefficients, $R^{2,}$ are given in table 3. A comparison of the $K_{id}$ values for both the macropore and micropore diffusion constants (table 3) shows that the rate limiting step is the micropore diffusion stage. This is because the micropore diffusion constant ($K_{id2}$) value of 0 is lower than the macropore diffusion constant ($Kid_1$) value of 0.2543 which is a pointer to the fact that the rate of micropore diffusion is the slower step and the rate determining step. The boundary layer effect, as obtained from the intercepts of the plot in figure 6 as shown in table 3 was also of greater effect at the micropore diffusion stage (3.54 ) than at the macropore diffusion stage (-0.1981 ). Table 3 further reveals that, though the intercept value (-0.1311) in figure 7 was not zero, it was close to the origin indicating the significance of the liquid film diffusion in rate determination of the sorption process. The regression coefficient value was quite high (0.9292), thus showing the relevance of film diffusion as a rate determining factor in the sorption process.

## Conclusion

From the result of this study it can be concluded that water hyacinth could be used as novel raw material for the production of effective activated carbon for the adsorption (removal) of Basic Blue- 9 dye from aqueous solution. Optimum removal of 86% dye was obtained which decreased to 62% with an increase in concentration from 50 to 300mg/l, though sorption capacity was found to increase with an increase in concentration.

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