

## **Research Article**

### **Adsorption of methylene blue dye from aqueous solution using activated carbon produced from water hyacinth in a fixed-bed column system.**

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**Abstract:** This paper investigates the ability of activated carbon produced from water hyacinth to remove methylene blue dye from aqueous solution in a packed bed down-flow column. The experiments were performed with different bed heights (3-9 cm) and using different concentrations (200-300 mg/l) in order to obtain experimental breakthrough curves. The study shows 100% reduction of dye from start of experiment up to 0.42, 5.00 and 10.42 hrs for bed heights of 3, 6 and 9 cm respectively. Zero percentage reduction and highest effluent concentration of 250 mg/l were obtained at 15.83, 27.50 and 33.33 hrs, while half of influent concentration (125 mg/l) and 50% reduction of initial dye concentration (125 mg/l) occurred at the critical time of 11.70, 17.95 and 26.25 hrs for the bed heights of 3, 6 and 9 cm respectively. The volume of dye solution treated to achieve exhaustion concentration was 1.75, 2.70 and 3.60 L for 3, 6 and 9 cm bed heights respectively. Increasing the initial dye concentration from 200 to 300 mg/l results in a decrease in the volume of dye solution treated from 950 to 300 ml at the breakthrough point. When initial dye concentration increased from 200 to 300 mg/l, bed adsorption capacity also increased from 29.11 to 32.24 mg/g.

**Keywords:** Removal, methylene blue, Water hyacinth, Activated carbon, Fixed-bed

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## **INTRODUCTION**

Industrial effluents are one of the major causes of environmental pollution. Dyes and pigment industries are generally known to generate wastewaters with characteristically high colour, high organic matter content, low Biochemical oxygen demand (BOD) and high chemical oxygen demand (COD). Presently, it has been estimated that about 10,000 different commercial dyes and pigments exist and over  $7 \times 10^5$  tones are produced annually worldwide[1]. Some of the important sources of dye pollution include textile, food processing, dyeing, cosmetics, paper and dye manufacturing. It has also been reported that many dyes and pigments have toxic, carcinogenic, mutagenic and teratogenic effects on aquatic life as well as humans[2]. It is therefore necessary to remove dyes in industrial effluents before discharging such effluents into the recipient environment.

Conventional methods used for treating dye containing wastewaters are adsorption onto sludge of wastewater treatment plant, as well as other physicochemical techniques such as coagulation, flocculation, ozonation, reverse osmosis and filtration. However, these processes are costly and cannot effectively be used to treat the wide range of dye wastewaters. Among various industries, the textile industry ranks first in the use of dyes for coloration of

fibre. Today more than 9000 types of dyes have been incorporated in the colour index[3]. Adsorption processes using activated carbon have been investigated as an efficient and effective method to remove dyes from wastewater. The most widely used adsorbent for industrial application in wastewater treatment is activated carbon. The objective of this study is to investigate the removal of methylene blue dye from aqueous medium in a fixed-bed column using activated carbon derived from water hyacinth as the sorbent. The choice of methylene blue dye as a pollution marker was informed by its widespread use in factories making textiles, battery, paper, cosmetics, food processing and shoe making, etc. It is therefore a major component of wastewater effluents from these factories and need to be removed before discharging into the environment.

## **MATERIALS AND METHODS**

The fresh water weed, 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 de-ionized 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 as described elsewhere [4].

**Chemical Activation of Carbon**

Studies have shown that chemical activation using phosphoric acid at moderate temperatures produce, in certain lignocellulosic materials, a high surface area and a high degree of microporosity [5]. The activation followed the method described elsewhere[6].

**Adsorbate**

Methylene blue dye (a cationic dye) was used for the adsorption studies. Methylene blue dye (C. I. 52015, λmax = 664 nm) was manufactured by Gurr, BDH Chemicals Ltd, Poole England. The molecular formula of methylene blue dye C<sub>16</sub>H<sub>18</sub>CIN<sub>3</sub>S with a molecular weight of 319.86. A stock solution of the dye with a concentration of 1000 mg per liter was prepared. This was done by weighing 1.0g (1000 mg) of dye and transferred into a 1000 ml volumetric flask. The dye was dissolved in the volumetric flask using de-ionized water and the solution made up to the 1000 ml mark in the flask. Serial dilutions of the stock solution were made to obtain specific concentrations required for the adsorption study.

**Column studies**

The sample of activated carbon was sieved using a laboratory sieve of size range 150-300 μm and used for the different sorption studies. Preliminary studies carried out on the carbon sample showed that this size range provides a suitable distribution of flow and adsorption rates. A glass column (30 x 1.4 cm) was packed with the activated carbon on a glass wool support. The fixed bed column of activated carbon was prepared by a dry packing technique[7]. The bed was flushed several times with de-ionized water to ensure a close packing of the activated carbon particles to avoid cracks, channels or void during the transit of the wastewater through the column. The bed was allowed to drain completely before the loading of the activated carbon bed with the sorbate.

The waste water was stored in a 2 liter capacity reservoir at the bottom of which was provided with a tap to control its flow rate into the column packed with activated carbon. The influents (i.e. waste water) were allowed to transit through the bed by gravity flow. Samples of the effluent were collected periodically at fixed volume (100 ml) and the time of each collection

noted, the samples were analyzed for the remaining dye concentration using a spectrophotometer. This experiment was carried out using flow rate of 2 ml/min at different bed heights and concentrations in order to determine the effect of each parameter on the column performance.

**Data Analyses**

The breakthrough curves show the loading behaviour of dye to be removed from solution in a fixed-bed column and are usually expressed in terms of adsorbed dye concentration (C<sub>ad</sub>) as given in Eq. (1):

$$C_{ad} = C_0 - C_t \text{ ----- (1)}$$

Where C<sub>0</sub> is inlet dye concentration (mg/l), C<sub>t</sub> is outlet dye concentration at time, t.

Total adsorbed dye quantity (q<sub>total</sub>: mg) in the column for a given feed concentration and flow rate (F) is calculated from Eq. (2):

$$q_{total} = F/A = F/100 = \int_{t=0}^{t_{total}} C_{ad} dt \text{ -----(2)}$$

Where A is the area under the breakthrough curve and is obtained by the integration given in Eq. (2),[8].

Total amount of dye sent to column (M<sub>total</sub>) is calculated from Eq. (3):

$$M_{total} = C_0 F t_{total} / 1000 \text{ ----- (3)}$$

Total removal of dye was calculated using Eq. (4)

$$\text{Total removal (\%)} = q_{total} / M_{total} \times 100 \text{ -----(4)}$$

Equilibrium dye uptake (q<sub>eq</sub>) or maximum capacity of the column is defined as the total amount of dye sorbed (q<sub>total</sub>) per gram of sorbent (x) at the end of total flow time and was obtained from Eq. (5).

$$q_{eq} = q_{total} / x \text{ -----(5)}$$

**RESULTS AND DISCUSSION**

Characterization of carbon: The data for proximate analyses, physical properties of the activated carbon are presented in table 1.

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

Property	Activated carbon
Moisture	19.80 ± 0.01
Porosity	0.893 ± 0.015
Iodine number	152.39 ± 0.10
Ash content	27.60 ± 0.92
Volatile matter	37.36 ± 0.15
Density	0.256 ± 0.052
pH	6.92 ± 0.10
Surface area (m <sup>2</sup> /g)	106.01 ± 9.00

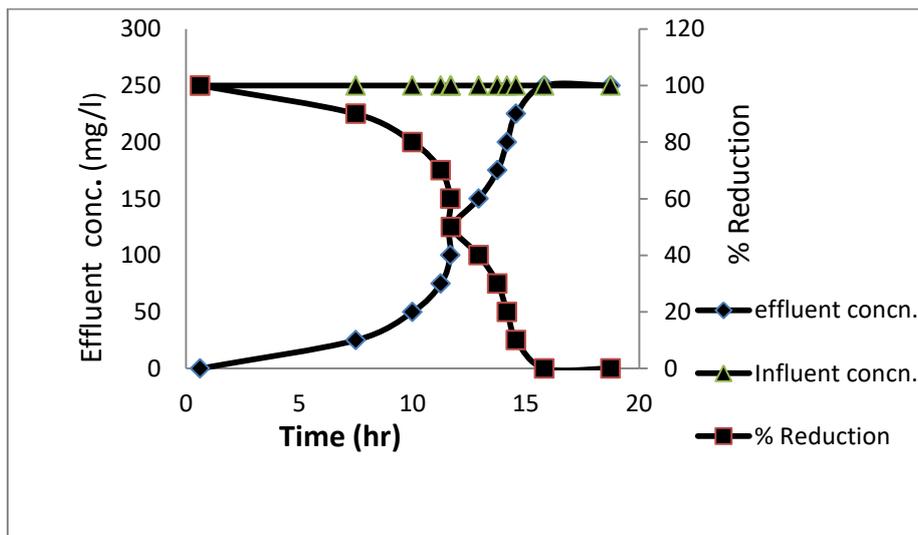
The results in table 1 show a low amount of moisture, ash and volatile matter, indicating that the particle density is relatively small and that the carbon should be excellent for use in batch sorption systems. The porosity, iodine number, surface area and pH are comparable to other materials used for column and batch analyses [9-11].

**Effect of Bed Height on Packed Bed Column**

The sorption performance of the activated carbon was tested at various bed heights (3, 6 and 9 cm) at 2 ml/min

flow rate and 250 mg/l initial methylene blue dye concentration. To produce different bed heights of 3, 6 and 9 cm respectively in the column, 2.10, 3.45 and 5.73 g of activated carbon was added to the glass column.

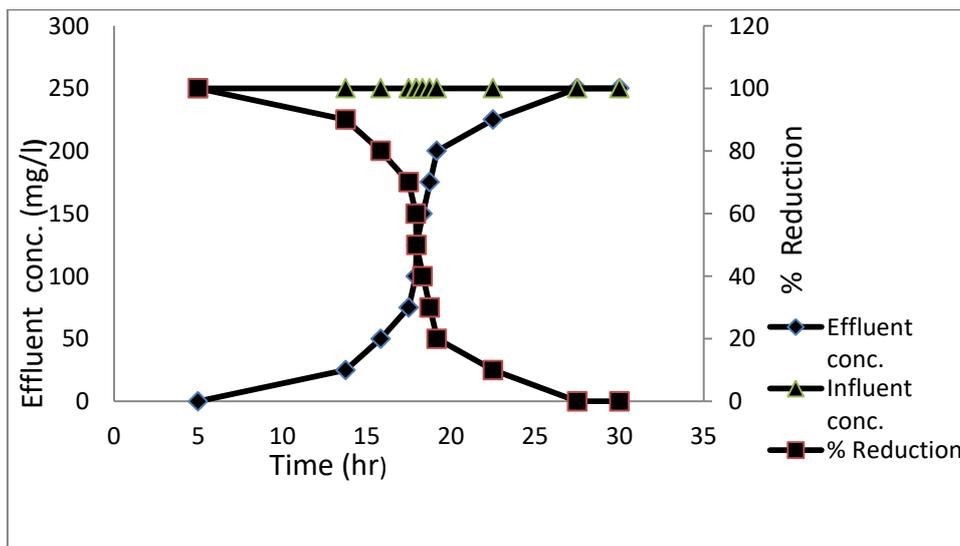
Figure 1 shows the changes in the influent and effluent concentrations of the fixed bed column reactor and percentage dye reduction for the feed concentration of 250 mg/l at the bed height of 3 cm.



**Figure-1: Dye Reduction at a bed height of 3cm for the activated carbon packed column**

The graph shows 100% reduction of dye and zero effluent concentration from start of experiment up to 0.42 hrs. Zero percentage reduction and highest effluent concentration of 250 mg/l were obtained at 15.83 hours. Half of influent concentration (125 mg/l) and 50% reduction of initial dye concentration (125 mg/l) occurred at the critical time of 11.70 hours.

Figure 2 shows the changes in the influent and effluent concentration of the fixed bed column reactor and percentage dye reduction for the feed concentration of 250 mg/l at the bed height of 6 cm.



**Figure-2: Dye Reduction at a bed height of 6cm for the activated carbon packed column**

The graph shows 100% reduction of dye and zero effluent concentration from start of experiment up to 5.00 hours. Zero percentage reduction and highest effluent concentration of 250 mg/l were obtained at 27.50 hours. Half of influent concentration (125 mg/l) and 50% reduction of initial dye concentration (125 mg/l) occurred at the critical time of 17.95 hours.

Figure 3 shows the changes in the influent and effluent concentration of the fixed bed column reactor and percentage dye reduction for the feed concentration of 250 mg/l at the bed height of 9 cm.

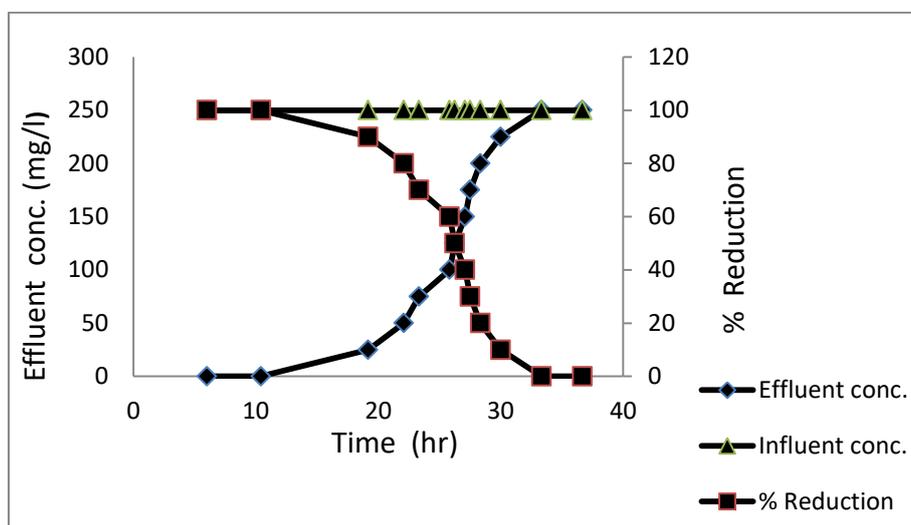


Figure-3: Dye Reduction at a bed height of 9cm for the activated carbon packed column

The graph shows 100% reduction of dye and zero effluent concentration from start of experiment up to 10.42 hours. Zero percentage reduction and highest effluent concentration of 250 mg/l were obtained at 33.33 hours. Half of influent concentration (125 mg/l) and 50% reduction of initial dye concentration (125 mg/l) occurred at the critical time of 26.25 hours.

and time taken for maximum effluent concentration (250 mg/l) and zero percentage reduction of dye to occur increased with bed height. Although, the time varied with bed height for the activated carbon sample studied, the critical concentration and maximum effluent concentration were found to be independent of time. This study shows that longer bed heights required longer time for the dye solution to transit through them.

It was observed generally from figures 1 to 3 that, as bed height increases the time taken to achieve 100% reduction and zero effluent concentration also increased. The figures also reveal that, the critical time

Figure 4 shows the breakthrough curves of methylene blue dye sorption at different bed heights for the activated carbon.

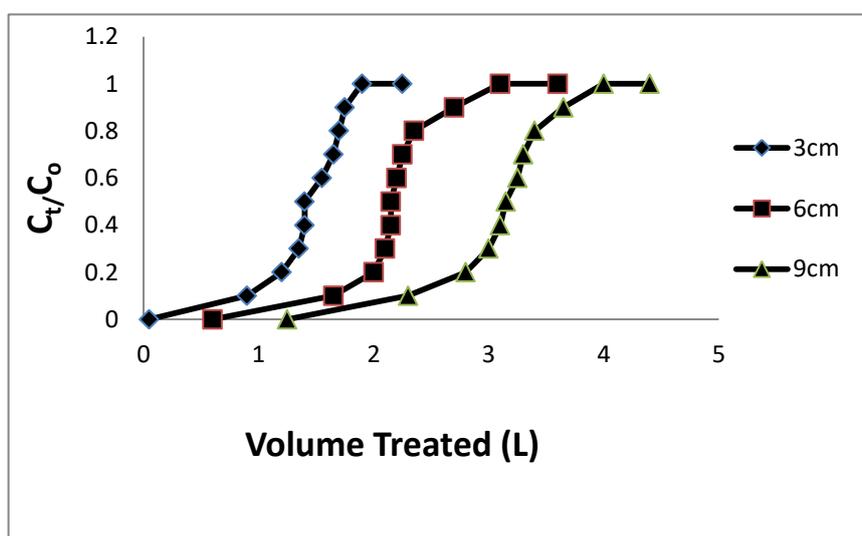


Figure-4: Effect of Bed Heights on packed Bed Column conditions; C<sub>0</sub> =250mg/l, flow rate =2ml/min, pH =7.5

The breakthrough curves of figure 4 exhibited the characteristic s-shape for most dynamic sorption studies in water and wastewater treatment, though with varying degree of steepness and position of breakthrough.

The breakthrough curves of figure 4 show that there was complete removal of colour (100%) of dye from solution before the breakthrough concentration (25 mg/l) was obtained in the effluent. This was so because the dye in solution was continuously removed by each layer of adsorbent (activated carbon) when the solution was passed through the bed. This means that removal of solute from solution was complete over the initial stages of operation and at this stage, the activated carbon was unsaturated and the actual effluent concentration was lower than the breakthrough concentration in which the volumes treated were 0.90, 1.65 and 2.30 L for 3, 6, and 9 cm bed heights respectively. As the dye solution was continuously pumped through bed, the carbon becomes saturated and the effluent concentration approached breakthrough concentration (10% of inlet concentration).

After the breakthrough point, the effluent concentration continued to rise rapidly until the exhaustion point was reached. The volume of dye solution treated to achieve exhaustion concentration was 1.75, 2.70 and 3.60 L for 3, 6 and 9 cm bed height respectively.

Beyond the point of exhaustion, the adsorbent becomes fully saturated and the dye from solution was no longer removed by the carbon in the bed. Thus, the effluent concentration was now equal to the influent concentration where  $C_t/C_0$  equals 1.0.

Breakthrough time for the various bed heights of 3, 6 and 9cm for an initial concentration of 250 mg/l were; 1.60, 4.17 and 6.50 hours respectively.

#### Effect of Initial Dye Concentration on Packed Bed

The effect of various initial dye concentrations (200, 250 and 300 mg/l) on packed-bed was also tested to examine the continuous sorption performance of the activated carbon sample. The breakthrough curves obtained by changing inlet dye concentration from 200 to 300 mg/l at 6 cm bed depth and 2 ml/min flow rate is shown in figure 5. Figure 5 is a plot of the dimensionless liquid phase concentration,  $C_t/C_0$  versus volume of liquid dye treated. It was evident from the curves that, by increasing the initial dye concentration, the slope of the breakthrough curve increased and became steeper, thus reducing the volume of dye solution treated before the breakthrough. Increasing the initial dye concentration from 200 to 300 mg/l results in a decrease in the volume of dye solution treated from 950 to 300 ml at the breakthrough point.

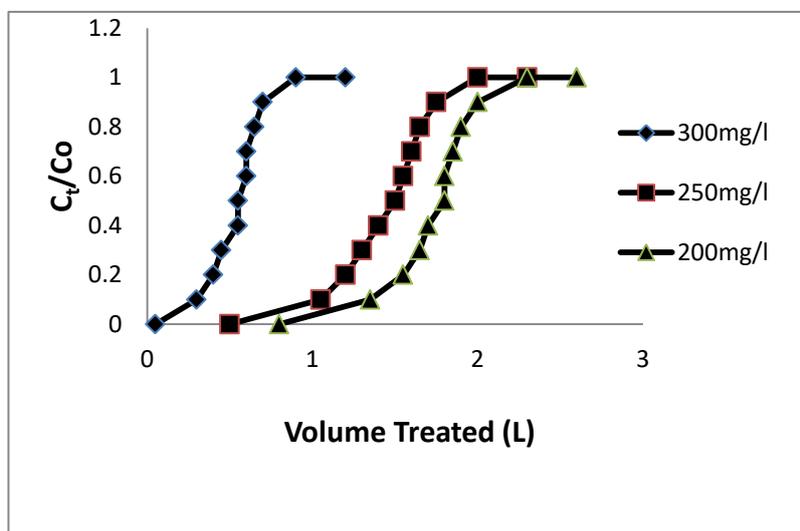


Figure-5: Effect of concentration on packed Bed Column conditions; Bed height =6cm, flow rate =2ml/min, pH =7.5

Since a constant mass of adsorbent can only adsorb a certain amount of dye, increasing the initial dye concentration led to a decrease in the breakthrough time. This may be due to the fact that, by increasing the initial dye concentration, the driving force increases which enhance the rate of dye diffusion within the adsorbent particles and saturates the binding sites more quickly.

Similar trends were observed[12-14]. The driving force for sorption is the concentration difference between the solute on the sorbent and the solute in the solution. A high concentration difference provides a high driving force, which favours sorption[15].

The effect of changes in initial concentration of dye solution into the fixed bed column was used to

evaluate the total adsorbed quantity of dye ( $q_{total}$ ), equilibrium dye uptake ( $q_{eq}$ ) and total removal

percentage on the sorption of methylene blue dye on the activated carbon sample and is presented in table 2.

**Table-2: Effect of initial dye concentration on the total adsorbed quantity of dye ( $q_{total}$ ), equilibrium dye uptake ( $q_{eq}$ ) and total removal percentage, on the sorption of methylene blue dye by the activated carbon sample.**

Initial dye Conc. (mg/l)	Flow rate (ml/min)	$q_{total}$ (mg)	$q_e$ (mg/g)	Percent dye removal (%)
200	2	100.44	29.11	58.5
250	2	105.03	30.44	68.0
300	2	11.24	32.24	73.3

It was evident from table 2 that when the initial dye concentration was increased from 200 to 300 mg/l, the corresponding bed adsorption capacity appears to increase from 29.11 to 32.24 mg/g. The table further shows that for the activated carbon sample, the total uptake capacities ( $q_{total}$ ) and the total removal percentages, all increased with an increase in the initial dye concentration from 200 to 300 mg/l.

### CONCLUSION

It was observed from this study that, as bed height increases the time taken to achieve 100% reduction and zero effluent concentration also increased. The figures also revealed that, the critical time and time taken for maximum effluent (250mg/l) and zero percentage reduction of dye to occur increased with bed height. Although, the time varied with bed height, the critical concentration, maximum effluent concentration and zero percentage reduction of dye remained the same. This trend illustrates the fact that longer bed heights required longer time for the dye solution to transit through them. The breakthrough curves exhibited the characteristic s-shape for most dynamic sorption studies in water and wastewater treatment, though with varying degree of steepness and position of breakthrough.

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