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Removal of Methyl Red from Aqueous Solution by NaOH-Activated Cassava Peels Carbon in a Fixed-Bed Column

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Abstract: The uptake of methyl red, an azo dye from aqueous solution onto NaOH-activated cassava peels carbon in a fixed-bed column was studied in this research. The effects of inlet dye concentration, adsorbent bed height and solution flow rate were investigated. The pH of the solution was natural and temperature 28-31°C. Experimental results were applied to the Thomas and Yoon-Nelson Models. Results show that the experimental values of adsorption capacity increased with increase in concentration, decrease in adsorbent bed height and increase in flow rate. However, inlet concentration of 50 mg L^{-1} showed better performance for the parameters than 100 mg L^{-1}. Optimum adsorption capacity of 206.08 mg g^{-1} was obtained at carbon bed height of 20 cm, inlet concentration of 200 mg L^{-1} and flow rate of 13.3 mL min^{-1}. The trend in total removal with respect to inlet concentration, bed height and flow rate was inverse to that of adsorption capacity. The maximum removal of 78.62% was obtained for inlet concentration of 50 mg L^{-1}, carbon bed height of 30 cm and flow rate of 13.3 mL min^{-1}. The experimental results fitted well into the Thomas and Yoon-Nelson Models with $R^2>0.90$ generally.

Key words: Fixed bed column, adsorption capacity, methyl red, Thomas, Yoon-Nelson Models, cassava peels carbon

INTRODUCTION

Progress in industrial activities during recent years has led to the discharge of unprecedented amount of wastewater containing synthetic dyes which pollutes the rivers and consequently causes harm to human and other living organisms. A majority of the used dyes are azo reactive dyes (Haris and Sathasivam, 2009). These are bright color dyes due to the presence of one or several azo groups associated with substituted aromatic structures (Forgacs *et al*., 2004). Effluents from textile, leather, food processing, cosmetics, paper and dye manufacturing industries are some examples of the sources of discharged azo dyes (Bhatnagar and Jain, 2005). These dyes or their breakdown products are toxic to living organisms (Chung *et al*., 1981). Furthermore, dyes in wastewater are difficult to remove because they are stable to light, heat and oxidizing agents. They are not easily degradable (Leechart *et al*., 2009; Jain and Sikarwar, 2008).

Methyl red is a commonly used monoazo dye in laboratory assays, textiles and other commercial products however, it may cause eye and skin sensitization (Hayes *et al*., 2004) and pharyngeal or digestive tract irritation if inhaled or swallowed (Badr *et al*., 2008). Furthermore, methyl red is mutagenic under aerobic conditions: it undergoes biotransformation into 2-aminobenzoic acid and N-N^1-dimethyl-p-p henylene diamine (Haris and Sathasivam, 2009).

Adsorption is the concentration of a substance at the surface. The adsorption at a surface or interface is largely as a result of binding forces between atoms, molecules and ions of the adsorbate on the surface (Tahir and Rauf, 2003; Barrow, 1996; Levine, 1995). Adsorption is widely used because of its simple design, easy operations and relatively simple regeneration (Tang *et al*., 2007). Growing interest in the application of adsorption processes for the treatment of industrial wastewater as well for the recovery of organic compounds from aqueous solution has been observed. These processes are used particularly in the care where impurities did not undergo biological degradation and their concentration is very low. In general, the adsorption methods are used as the final stage in industrial wastewater treatment (Pelech *et al*., 2006).

Batch experiments are usually done to measure the effectiveness of adsorption for removing specific adsorbates as well as to determine, the maximum adsorption capacity. The continuous adsorption in fixed-bed column is often desired from industrial point of view.

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It is simple to be operated and can be scaled up from a laboratory process (Ahmad and Hameed, 2010; Chern and Chien, 2002). Adsorption in fixed-bed columns using activated carbon has been widely used in industrial processes for the removal of contaminants from aqueous textile industry effluents since it does not require the addition of chemical compounds in the separation process (Chern and Chien, 2003).

Commercially available activated carbons are expensive (Chakraborty *et al.*, 2005). This is due to the use of non-renewable and relatively expensive starting materials such as coal which is unjustified in pollution control applications (Martin *et al.*, 2003).

Cassava peels biomass is a waste produced in large quantity from homes and industries in Nigeria. This material is of no industrial use and contributes to land pollution (CIN, 2006; African Agriculture, 2007).

The purpose of this research was to generate NaOH-activated cassava peels carbon from this cassava waste and study its efficiency in removing methyl red from aqueous solution in a fixed-bed column. The effects of adsorbent bed height, initial adsorbate concentration and flow rate were determined.

MATERIALS AND METHODS

Adsorbate: Acid and base forms of methyl red is given in Fig. 1.

Preparation of activated carbon: The cassava peels biomass was obtained from Egbeada, an agricultural area in the Mbaitoli Local Government Area of Imo State, Nigeria. The biomass was washed to remove dirt and soil materials and then dried under the sun and later in a hot air oven. The dry biomass was carbonized at 550°C for 7 h and cooled. The char formed was crushed and sieved to obtain 10×30 mesh particles and impregnated with 22.27% w/v H_3PO_4 at a ratio of 1 part char:3 parts acid overnight. Excess acid was drained off and the impregnated carbon dried under the sun for 3 days. Activation was completed by heating at 500°C for 4 h. After cooling the activated carbon was leached with hot distilled water until the leachate was at pH 6-7. Drying of the carbon was done in a hot-air oven at 110°C until constant weight. It was cooled and packaged in an airtight plastic container.

Experimental set up: The fixed-bed column was made of pyrex glass cylinder 1.0 cm inner diameter and 43 cm height. The bottom of the column was plugged with glass wool. A known quantity of the activated carbon was packed in the column to yield the desired bed height 10, 20 and 30 cm, respectively. The adsorbent was sealed with glass wool and the column filled up with glass beads in order to provide a uniform flow of the solution through the column. Dye solution of known concentration (50, 100 and 200 mg L^{-1}) at natural pH was pumped upward with a peristaltic pump through the column at a desired flow rate (13.3, 25 and 34 mL min^{-1}). The effluent metanil yellow solution samples were collected at regular interval of 30 min the samples were analyzed with a UV-V is spectrophotometer (Shimadzu Model 752 Japan) at 400 nm. The experiments were carried out at 27-31°C without pH adjustments.

Analysis of fixed-bed column data: The time for breakthrough appearance and the shape of the breakthrough curve are paramount in determining the operation and the dynamic response of an adsorption fixed-bed column. The breakthrough curves show the loading behavior of dye to be removed from solution in a fixed-bed column and is usually expressed in terms of

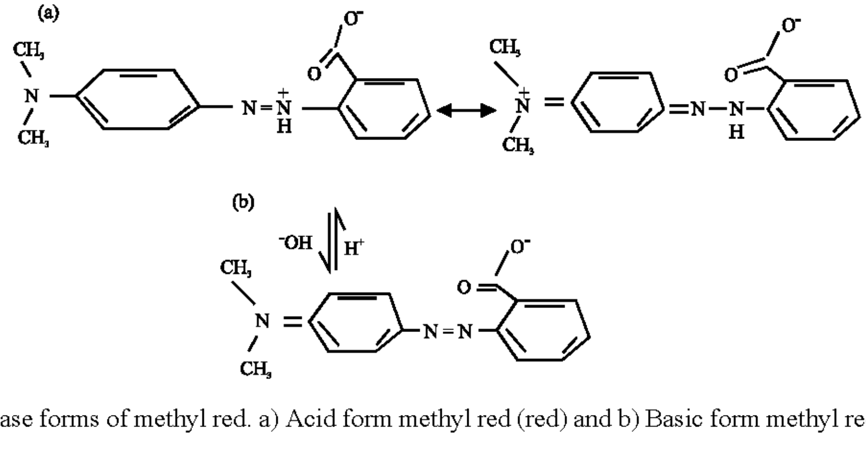

Fig. 1: Acid and base forms of methyl red. a) Acid form methyl red (red) and b) Basic form methyl red (yellow)

adsorbed dye concentration (C_{ad}), inlet dye concentration (C_o), outlet dye concentration (C_t) or normalized concentration (C_t/C_o) as a function of time or volume of effluent for a given bed height (Ahmad and Hameed, 2010; Taty-Costodes *et al*., 2005; Aksu and Gonen, 2004). Effluent volume (V_{eff}) can be calculated from Eq. 1:

$$V_{eff} = Qt_{tot} \tag{1}$$

where, t_{tot} and Q are the total flow time (min) and volumetric flow rate (mL/min). The area under the breakthrough curve obtained by integrating the adsorbed concentration (C_{ad}; mg/L) versus time (min) plot can be used to fine the total adsorbed dye quantity (maximum column capacity). Total adsorbed dye quantity (q_{tot}; mg) in the column for a given feed concentration and flow rate is calculated from Eq. 2:

$$q_{tot} = \frac{QA}{1000} = \frac{Q}{1000}\int_{t=0}^{t=t_{tot}} C_{ad}\, dt \tag{2}$$

Total amount of dye sent to column (m_{tot}) is calculated from Eq. 3:

$$m_{tot} = \frac{C_o Q t_{tot}}{1000} \tag{3}$$

Total removal (%) of dye (column performance) with respect to flow volume can also be found from the ratio of total adsorbed quantity of dye (q_{tot}) to the total amount of dye sent to the column (m_{tot}) in Eq. 4:

$$\text{Total removal (\%)} = \frac{1000 q_{tot}}{m_{tot}} \tag{4}$$

Equilibrium uptake of the sorbate (q_e) or (maximum column capacity) in the column is defined by Eq. 5 as the total amount of sorbent (x) at the end of total flow time:

$$q_e = \frac{q_{tot}}{x} \tag{5}$$

Unadsorbed dye concentration at equilibrium in the column (C_e; mg/L) can be defined by Eq. 6:

$$C_e = \frac{(m_{tot} - q_{tot})1000}{V_{eff}} \tag{6}$$

Column adsorption modeling: To design a column adsorption process, it is necessary to predict the breakthrough curve or concentration like profile and adsorption capacity of the adsorbent for the selected adsorbate under the given set of operating conditions. It is also important for determining maximum adsorption column capacity which is significant to any adsorption system.

In Equilibrium Adsorption Theory, it is assumed that the adsorption equilibrium between the solid and mobile phases is established instantly at each point of the bed. Thereby, all the mass transfer resistances are ignored. The principles that determine the equilibrium distribution of adsorbed substances in a column were given by De Vault (Pelech *et al*., 2006). The equations used for the description of this phenomenon are derived based on the following assumptions:

- Process proceeds isothermally
- Axial diffusion and radial mass transfer are negligible
- Pressure drop in a bed is insignificant

A number of mathematical models have been developed for the evaluation of efficiency and applicability of the column models for large scale operations. They include the Adam-Bohart, Wolborska, Thomas, Clark, Yoon-Nelson and the Bed Depth, Service Time (BDST) Models. However, the Thomas and Yoon-Nelson Models were used to analyze the behavior of adsorbent-adsorbate system in this investigation.

The Thomas Model: The Thomas Model is one of the most general and widely used methods in Column Performance Theory. The expression by Thomas for an adsorption column (Fu and Viraraghavan, 2003) is given as follows:

$$\frac{C_t}{C_o} = \frac{1}{1+\exp\left[K_{Th}\,(q_o x - C_o V_{eff})/Q\right]} \tag{7}$$

Where:

C_t = The effluent dye concentration (mg/L)
C_o = The inlet dye concentration (mg/L)
x = The mass of the adsorbent (g)
V_{eff} = The effluent volume (mL)
Q = The flow rate (mL/min)
K_{Th} = The Thomas rate constant (mL/mg/min)
q_o = The maximum dye adsorption capacity of the adsorbent (mg/g)

The value t (min) is:

$$t = \frac{V_{eff}}{Q} \tag{8}$$

The linear form of Thomas Model can be expressed as follows Eq. 9:

$$\text{In}\left\{\left(\frac{C_t}{C_o}\right)\text{-}1\right\} = \frac{K_{Th}\, q_o x}{Q\text{-}K_{Th} C_o t} \tag{9}$$

The Thomas rate constant (or Kinetic Coefficient) K_{Th} and the maximum dye adsorption capacity of the adsorbent q_o (mg/g) can be obtained from the plot of In $[(C_o/C_t)\text{-}1]$ versus t.

The Yoon-Nelson Model: The Yoon and Nelson (Kundu and Gupta, 2007) Model is based on the assumption that the rate of decrease in the probability of adsorbate and the probability for a single component system is expressed as:

$$\text{In}\left(\frac{C_t}{C_o - C_t}\right) = K_{YN} t - \tau K_{YN} \tag{10}$$

Where:

K_{YN} = The rate (or Yoon-Nelson) constant (min^{-1})
τ = The time required for 50% adsorbate breakthrough (min)
t = The sampling time (min)

The calculation of theoretical breakthrough curves for a single-component system requires the determination of the parameters K_{YN} and τ for the absorption from the slope and intercept, respectively of a straight-line plot of In $[C_t/(C_o\text{-}C_t)]$ versus sampling time t. The slope yields K_{YN} and the intercept-τK_{YN}. Based on the obtained value of τ, the adsorption capacity, q_{oYN} can be determined (Patel and Vashi, 2012) using Eq. 11:

$$q_{oYN} = \frac{q_{tot}}{x} = \frac{C_o Q \tau}{1000x} \tag{11}$$

so, adsorption capacity (q_{oYN}) related to Yoon-Nelson varies as inlet dye concentration (C_o), flow rate (Q), 50% breakthrough time derived from Yoon-Nelson equation (τ) and weight of adsorbent (x).

RESULTS AND DISCUSSION

Effect of inlet concentration: The effect of a variation of the inlet methyl red concentration from 50-200 mg L^{-1} with adsorbent bed height of 20 cm and solution flow rate 13.3 mL min^{-1}, temperature 28-31°C and natural pH is shown in Fig. 2. Figure 2 shows dispersed breakthrough curves for the three inlet concentrations. The cause of the dispersed breakthrough curves might be due to: slow adsorption kinetics of the dye on the adsorbent and the use of small-scale column apparatus. The order of the normalized concentration, C_t/C_o, values at the end of the adsorption, i.e., after 510 min was 50>100>200 mg L^{-1} showing 200 mg L^{-1} the best concentration. Table 1 shows increase in adsorption capacity with increase in concentration. This is due to increase in concentration gradient which provides a high driving force for the adsorption (Ahmad and Hameed, 2010). However, inlet concentration of 50 mg L^{-1} had a higher adsorption capacity than 100 mg L^{-1} and highest total removal. The reason for this observation is unknown.

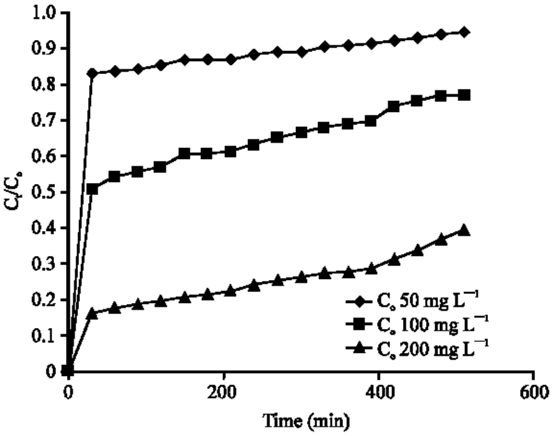

Fig. 2: Breakthrough curves for the adsorption of methyl red on NaOH-activated carbon at initial influent concentration C_o 50, 100, 200 mg L^{-1}, bed height 20 cm, flow rate 13.3 mL min^{-1} and temperature 28-31°C

Table 1: Column data parameters obtained at different methyl red initial concentrations, bed heights and flow rates for NaOH-activated carbon (T = 28-31°C)

Initial concn. (mg L^{-1})	Carbon bed height (cm)	Flow rate (mL min^{-1})	q_{tot} (mg)	q_e (mg g^{-1})	Total removal (%)
50	10	13.3	180.77	90.380	53.30
50	20	13.3	209.26	52.310	61.70
50	30	13.3	180.16	30.030	78.62
50*	20	13.3	98.92	24.730	41.32
50*	20	20.0	133.49	33.370	37.08
50*	20	25.0	128.07	32.018	28.46
100	20	13.3	155.53	38.880	22.93
200	20	13.3	824.00	206.080	60.74

*Adsorption ran for 360 min while other 570 min

Effect of carbon bed height: The effect of carbon bed height on the adsorption of methyl red on NaOH-activated cassava peels carbon at inlet dye concentration of 50 mg L^{-1}, bed heights 10, 20 and 30 cm and flow rate 13.3 mL min^{-1}, natural pH and temperature of 28-31°C is shown in Fig. 3. Figure 3 shows deformed breakthrough curves for the three bed heights. The 50% breakthrough could not be achieved in 510 min. However, bed height of 20 cm showed the lowest C_t/C_o value. The results show that much more time was needed for exhaustion of the adsorbent for the three bed heights. Table 1 shows increase in adsorption capacity with

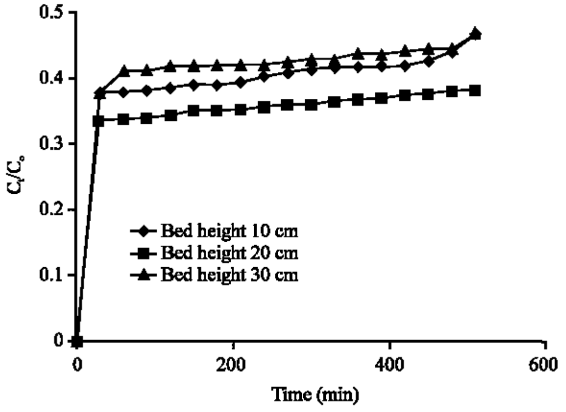

Fig. 3: Breakthrough curves for the adsorption of methyl red on NaOH-activated carbon at bed height 10, 20 and 30 cm, influent concentration C_0 50 mg L^{-1}, flow rate 13.3 mL min^{-1} and temperature 28-31°C

decrease in bed height but increase in total removal with increase in bed height. The cause of the trend is not known.

Effect of flow rate: The effect of flow rates of 13.3, 20 and 25 mL min^{-1} at inlet dye concentration of 50 mg L^{-1}, bed height 20 cm, natural pH and temperature 28-31°C is depicted in Fig. 4. Figure 4 shows flow rates of 13.3 and 20 mL min^{-1} producing C_t/C_0 value which are almost equal at the maximum time of 360 min of adsorption which is lower than for 25 mL min^{-1}. Table 1 shows the adsorption capacity values for flow rates of 20 and 25 mL min^{-1}. Table 1 also shows that total removal increased with decrease in flow rate. The trend of results obtained is a reverse of the research of Patel and Vashi (2012). The reason for the reverse trend is not known.

Application of the Thomas Model: Experimental results obtained were fitted into the Thomas Model in order to determine the Thomas parameters. Table 2 shows that maximum adsorption capacity, q_o, increased with increase in inlet concentration (except for 100 mg L^{-1}), increase in flow rate and decrease in bed height of the adsorbent. The highest value of maximum adsorption capacity related to the Thomas Model was 49.476 mg g^{-1} at inlet concentration of 200 mg L^{-1}, carbon bed height 20 cm and flow rate 13.3 mL min^{-1}. Generally, the correlation coefficients $R^2 \geq 0.9$ were obtained showing that the experimental results fitted well into the Thomas Model.

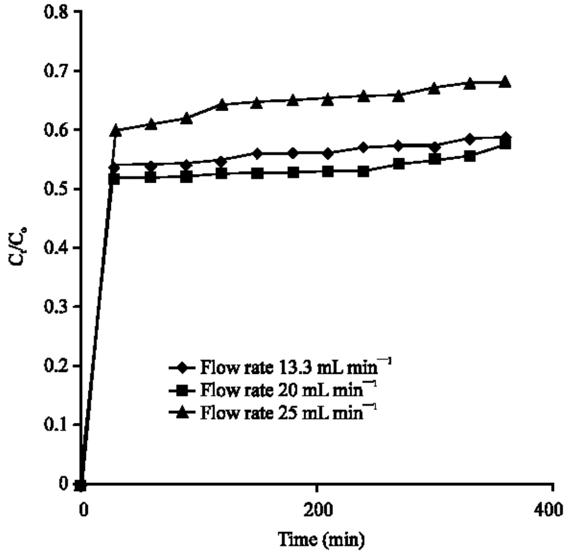

Fig. 4: Breakthrough curves for the adsorption of methyl red on NaOH-activated carbon at flow rate 13.3, 20, 25 mL min^{-1}, influent concentration C_0 50 mg L^{-1}, bed height 20 cm and temperature 28-31°C

Table 2: Thomas Model parameters for the column adsorption of methyl yellow on NaOH-activated cassava peels carbon

Initial concn. (mg L^{-1})	Carbon bed height (cm)	Flow rate (mL min^{-1})	K_{th} (mL/min mg)	q_o (mg g^{-1})	R^2
10	20	13.3	1.90	4.070	0.9450
10	10	13.3	5.40	0.452	0.9142
10	20	13.3	1.90	4.061	0.9484
10	30	13.3	1.60	4.187	0.8824
10	20	13.3	1.80	4.285	0.9418
10	20	25.0	5.30	3.673	0.9295
10	20	34.0	3.00	9.230	0.9173
50	20	13.3	0.54	20.000	0.9297
50	10	13.3	0.28	34.189	0.9576
50	20	13.3	0.52	20.895	0.9366
50	30	13.3	0.50	14.485	0.6081
100	20	13.3	0.10	118.061	0.8019

Table 3: Yoon-Nelson Model parameters for the column adsorption of metanil yellow on NaOH-activated cassava peels carbon

Initial concn. (mg L^{-1})	Carbon bed height (cm)	Flow rate (mL min^{-1})	K_{YN} (L min^{-1})	T (min)	q_o (mg g^{-1})	R^2
10	20	13.3	0.0019	1222.47	40.647	0.9374
10	10	13.3	0.0054	67.76	4.506	0.9150
10	20	13.3	0.0019	1221.95	40.630	0.9473
10	30	13.3	0.0015	2025.67	44.902	0.8939
10	20	13.3	0.0018	1290.11	42.896	0.9263
10	20	25.0	0.0048	674.00	42.125	0.9071
10	20	34.0	0.0025	1318.40	112.064	0.9197
50	20	13.3	0.0026	1259.50	209.392	0.9329
50	10	13.3	0.0014	2531.79	841.820	0.9669
50	20	13.3	0.0026	1259.69	209.423	0.9346
50	30	13.3	0.0025	1302.84	144.398	0.6127
100	20	13.3	0.0013	2677.77	890.359	0.8414

Application of the Yoon-Nelson Model: Yoon-Nelson parameters were obtained by fitting the experimental results into the Yoon-Nelson Model. Table 3 shows that the maximum adsorption capacity related to the Yoon-Nelson Model, q_o, increased with increase in inlet adsorbate concentration, decrease in adsorbent bed height and increase in flow rate except for inlet concentrations of 50 and 100 mg L^{-1} at bed height of 20 cm and flow rate 13.3 mL min^{-1}. However, the highest maximum adsorption capacity value of 490.364 mg g^{-1} related to the Yoon-Nelson was obtained at inlet dye concentration of 200 mg L^{-1}, bed height 20 cm and flow rate 13.3 mL min^{-1}. The experimental results fitted well into the Yoon-Nelson Model with correlation coefficient R^2 generally above 0.9.

CONCLUSION

The removal of methyl red from wastewater by NaOH-activated cassava peels carbon in a fixed-bed column was investigated at inlet concentrations of 50,100 and 200 mg L^{-1}, carbon bed height 30 cm and flow rate 13.3 mL min^{-1}. The experimental results fitted well into the Thomas and Yoon-Nelson Models with correlation coefficients generally above 0.9. The results also show the carbon good for methyl red removal.

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