Journal of Engineering and Applied Sciences 8 (9-12): 282-289, 2013
ISSN: 1816-949X

Adsorption of Metanil Yellow on Chemically-Activated Carbon in a Packed-Bed Column: Effect of Activation Reagent

[1]O.B. Isiuku, [2]M. Horsfall Jnr and [2]A.I. Spiff
[1]Department of Chemistry, Imo State University, Owerri, Nigeria
[2]Department of Pure and Industrial Chemistry, University of PortHarcourt, Nigeria

Abstract: The aim of this study was to investigate the ability of H_3PO_4 and NaOH-activated carbons derived from cassava (*Manihot esculenta*) peels to remove metanil yellow dye from aqueous solution in fixed beds. The effects of initial dye concentration, bed height and flow rate at natural pH on the breakthrough characteristics were determined. The highest experimental values for the equilibrium adsorption capacities were 19.216 and 4.118 mg g^{-1} for H_3PO_4 and NaOH-activated carbon, respectively, at initial dye concentrations 50,10 mg L^{-1} respectively, flow rate 13.3 mL min^{-1}, bed height 10 cm, natural pH and temperature of 28-31°C. Total dye removal of 12.04 and 12.90% for H_3PO_4 and NaOH-activated carbons respectively at initial dye concentrations 50 and 10 mg L^{-1}, respectively bed height 20 cm, flow rate 13.3 m L^{-1} min, temperature 28-31°C and natural pH were obtained. Experimental results were fitted into the Thomas and Yoon-Nelson Models. The maximum adsorption capacities with respect to the Thomas model (%) were 118.35 mg g^{-1} for H_3PO_4-activated carbon and 118.061 mg g^{-1} for NaOH-activated carbon. For the Yoon-Nelson Model, the maximum adsorption capacities were 1186.959 and 890.359 mg g^{-1}, respectively for the H_3PO_4 and NaOH-activated carbons.

Key words: Column adsorption, metanil yellow, activated carbon, adsorption models, Nigeria

INTRODUCTION

Synthetic dyes which include a wide range, of aromatic water-soluble dispersible organic colorants are used extensively in textile study printing, cosmetic and food industries. Effluents containing synthetic dyes not only produce visual pollution but also are hazardous to ecological systems and public health (Wang *et al*., 2008; Yesiladah *et al*., 2006). Dye waste waters discharged from textile and dyestuff industries have to be treated due to their impacts on water bodies and particularly growing public concern over their toxicity and carcinogenicity (Banat *et al*., 1996). It has been difficult to treatdye wastewater by conventional biological and physical-chemical processes because of the complex molecular structure of the dye (Fu and Viraraghavan, 2002).

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. It is simple to operate and can be scaled up from a laboratory process (Ahmad and Hameed, 2010; Chern and Chien, 2002). A continuous packed-bed adsorber does not run under equilibrium conditions and the effect of flow condition (hydrodynamics) at any cross-section in the column affects the flow behavior downstream. The flow behavior and mass transfer aspects become peculiar beyond a particular length to diameter ratio of the column (Ahmad and Hameed, 2010; Singh *et al*., 2009). In order to design and operate fixed-bed adsorption process successfully, the breakthrough curves under specified operating conditions must be predictable. The shape of this curve is influenced by the individual transport process in the column and in the adsorbent (Vasquez *et al*., 2006).

Breakthrough determines bed height and the operating life span of the bed and regeneration times (Walker and Weatherley, 1997). 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).

Activated carbon adsorption has been found to be superior for wastewater treatment compared to other physical and chemical techniques, such as flocculation, coagulation, precipitation and ozonation as they possess inherent limitations such as high cost, formation of hazardous by-products and intensive energy requirements (Padmesh *et al*., 2006).

Commercially available activated carbons are expensive (Chakraborty *et al*., 2005). This is due to the

Corresponding Author: O.B. Isiuku, Department of Chemistry, Imo State University, Owerri, Nigeria

use of non-renewable and relatively expensive starting material such as coal which is unjustified in pollution control applications (Martin *et al*., 2003). This has prompted a growing research interest in the production of activated carbon from renewable and cheaper sources which are mainly industrial and agricultural by-products (Al-Degs *et al*., 2009).

The aim of this study, was to prepare and evaluate acid (H_3PO_4) and alkali (NaOH) activated carbons from cassava peels in removing metanil yellow dye from aqueous solution in fixed-bed column. Important design parameters, such as initial dye concentration, column bed height and solution flow rate were investigated using a laboratory scale fixed-bed column. The breakthrough curves were analyzed using Thomas and Yoon-Nelson Models.

MATERIALS AND METHODS

Adsorbate: The metanil yellow used in this study, a product of E. Merck was purchased at Onitsha, Nigeria and used directly. Its formula is $C_{18}H_{14}N_3NaO_3S$. The IUPAC name is 3 (4-anilinophenylzo) benzene sulphonic acid sodium salt. Other names are C.I Acid Yellow 36, Tropaeoline G and Acid Leather Yellow R (Fig. 1).

Preparation of activated carbon: The cassava peels waste 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. A part of the carbon was impregnated with 22.27% w/v H_3PO_4 at a ratio of 1 part char, 3 parts acid by mass.

The 2nd part was impregnated with 4.17% w/v sodium hydroxide solution at a ratio of 1 part char, 3 parts alkali by mass. Excess acid or alkali was 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.

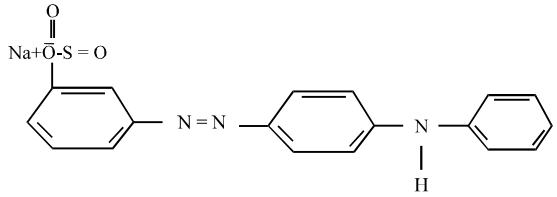

Fig. 1: Structure of metanil yellow

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 (10, 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^{-1} min). Effluent metanil yellow solution samples were collected at regular intervals of 30 min. The samples were analyzed with a uv-vis spectrophotometer (Shimadzu model 752 Japan) at 440 nm. The experiments were carried out at 28-31°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 adsorbed dye Concentration (C_{ad}), inlet dye Concentration (C_o), outlet dye Concentration (C) 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-Custodes *et al*., 2005) Effluent Volume (V_{eff}) can be calculated from Eq. 1:

$$V_{eff} = Qt_{tot} \quad (1)$$

Where:

t_{tot} = Total flow time (min)

Q = Volumetric flow rate (mL min^{-1})

The area under the breakthrough curve obtained by integrating the adsorbed concentration (C_{ad}; mg L^{-1}) 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:

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

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

$$m_{tot} = \frac{C_o Qt_{tot}}{1000} \quad (3)$$

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}) (Eq. 4):

$$\text{Totl removal (\%)} = \frac{q_{tot} \times 1000}{m_{tot}} \quad (4)$$

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:

$$q_e = \frac{q_{tot}}{x} \quad (5)$$

Unadsorbed dye concentration at equilibrium in the column (C_e; mg L^{-1}) can be defined by Eq. 6:

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

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 (Aksu and Gonen, 2004). 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 (Pelech *et al*., 2006).

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.

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 (Unuabonah *et al*., 2010; Fu and Viraraghavan, 2003) is given as follows:

$$\frac{C_t}{C_o} = \frac{1}{1+\exp[K_{TH}(q_o X - C_o V_{eff})/Q]} \quad (7)$$

Where:

C_t = The effluent dye concentration (mg L^{-1})
C_o = The inlet dye concentration (mg L^{-1})
x = The mass of the used adsorbent (g)
V_{eff} = The effluent volume (m L^{-1})
Q = The flow rate (mL min^{-1})
K_{th} = The Thomas rate constant (mL/mg/min)
q_o = The maximum dye adsorption capacity of the adsorbent (mg g^{-1})

The value t (min) is:

$$t = \frac{V_{eff}}{Q} \quad (8)$$

The linearized form of Thomas model can be expressed as follows Eq. 9:

$$\ln\left[\left(\frac{C_t}{C_o}\right) - 1\right] = \frac{K_{TH} q_o X}{Q} - K_{TH} C_o t \quad (9)$$

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 $[(C_t/C_o)-1]$ 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:

$$\ln\frac{C_t}{C_o - C_t} = K_{YN} t - t K_{YN} \quad (10)$$

Where:

K_{YN} = The rate (Yoon-Nelson) constant (min^{-1})
T = 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 $[Ct/(Co-C_t)]$ versus sampling time t. The slope yields K_{YN} and the intercept-τ K_{YN}. Based on the obtained value of τ, the adsorption capacity, q_{OYN} can be determined (Patel and Vashi, 2012) using Eq. 11:

$$q_{OYN} = \frac{q_{tot}}{x} = \frac{C_o Ct}{1000x} \quad (11)$$

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 initial dye concentration: The effect of a variation of the initial metanil yellow concentration from 10-200 mg L^{-1} with adsorbent height 20 cm, solution flow rate 13.3 mL min^{-1}, natural pH and temperature 28-31°C are shown in Fig. 2 and 3. Within a time interval of 180 min the effluent dye concentration had reached 92.4, 94.3, 99.7 and 100% of the inlet concentrations of 10, 50, 100 and 200 mg L^{-1}, respectively for H_3PO_4-activated carbon. For NaOH-activated carbon within 30 min of adsorption, the effluent dye concentration had reached 91.9, 97.2, 97.5 and 100% of the initial dye concentration of 10, 50, 100 and 200 mg L^{-1}, respectively. The breakthrough curves do not depict defined breakthrough times. This might arise from the length to diameter ratio of the column (Pelech *et al*., 2006). For initial dye concentration 200 mg L^{-1} there were no adsorptions. This might be due to the fact that exhaustion times had been reached before the first sampling time of 30 min. The effluent concentrations reported earlier show that within 30 min of adsorption, the carbon beds had reached saturation (Unuabonah *et al*., 2010) in both cases. Table 1 shows highest experimental adsorption capacities (%) of 19.216 and 4.118 mg g^{-1}, respectively for H_3PO_4 and NaOH-activated carbons, respectively. Total removal of 12.04 and 12.90% were obtained for H_3PO_4 and NaOH-activated carbons, respectively. The earlier values researchers obtained at initial dye concentrations of 50 and 10 mg L^{-1} bed height 10 cm and flow rate 13.3 mL min^{-1}, respectively for H_3PO_4 and NaOH-activated carbons. Results show appreciable metanil yellow removal by both H_3PO_4 and NaOH-activated carbons. Both adsorbents remove the dye almost equally, hence the agent of activation has almost no effect.

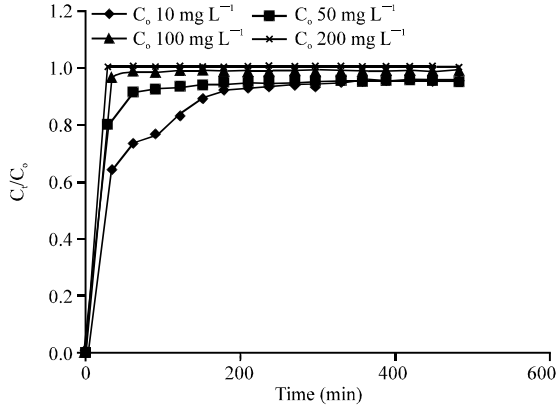

Fig. 2: Breakthrough curves for the adsorption of metanil yellow on H_3PO_4-activated carbon

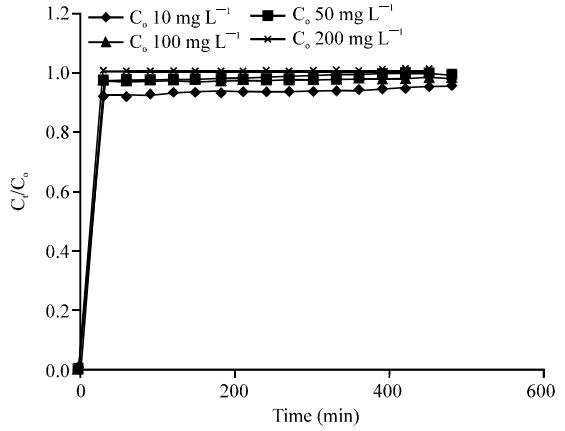

Fig. 3: Breakthrough curves for the adsorption of metanil yellow on NaOH-activated carbon

Effect of carbon bed height: The effect of carbon bed height on the adsorption of metanil yellow on H_3PO_4 and NaOH-activated cassava peels carbon at bed heights of 10, 20 and 30 cm, initial dye concentrations 10 and 50 mg L^{-1}, flow rate 13.3 mL min^{-1}, natural pH and 28-31°C temperature are depicted in Fig. 4 and 5, respectively. Figure 4 shows carbon bed height of 20 cm having the highest exhaustion time of 180 min for H_3PO_4-activated carbon at initial dye concentration 10 mg L^{-1}. Figure 5 shows 30 cm bed height having the highest exhaustion time of 180 min for H_3PO_4-activated carbon. Figure 6 and 7 show that the highest exhaustion time for initial dye concentration 10 mg L^{-1} was 30 min for the three bed heights 10, 20 and 30 cm but for 50 mg L^{-1} initial concentration, bed height 30 cm showed the highest

Table 1: Column data parameters for H_3PO_4-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})	Removal (%)
50	10	13.3	38.12	19.06	10.36
50	20	13.3	148.00	37.00	43.64
50	30	13.3	136.47	22.75	40.24
50*	20	13.3	90.00	22.67	37.59
50*	20	20.0	127.51	31.88	35.42
50*	20	25.0	142.83	35.71	31.74
100	20	13.3	467.00	116.00	68.85
200	20	13.3	534.00	133.63	39.36

*Adsorption was for 360 min

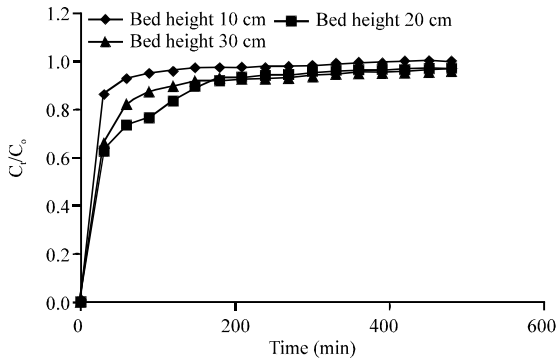

Fig. 4: Breakthrough curves for the adsorption of metanil yellow on H_3PO_4-activated carbon

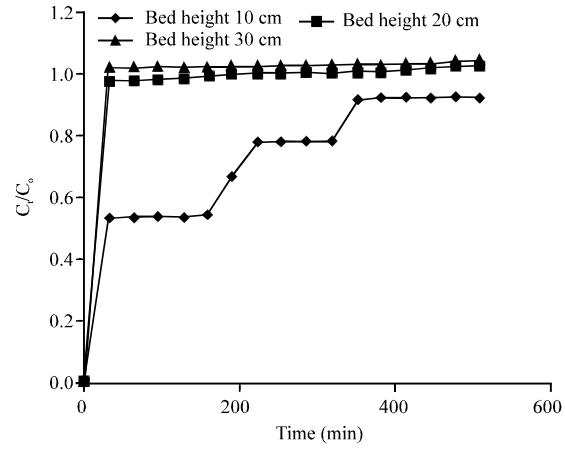

Fig. 5: Breakthrough curves for the adsorption of metanil yellow on NaOH-activated carbon at influent concentration C_o 10 mg L^{-1}

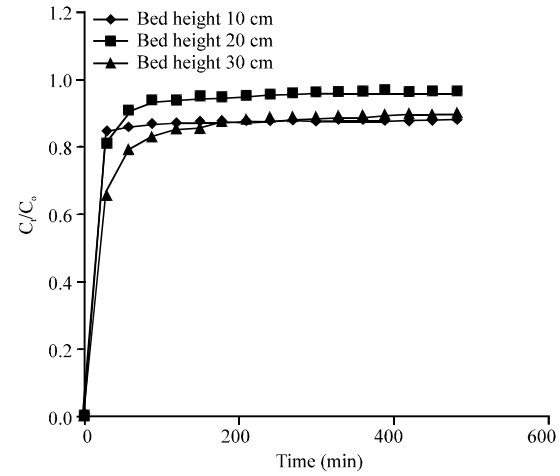

Fig. 6: Breakthrough curves for the adsorption of metanil yellow on H_3PO_4-activated carbon at influent concentration C_o 50 mg L^{-1}

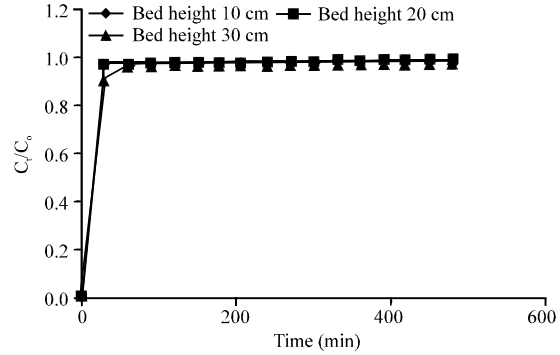

Fig. 7: Breakthrough curves for the adsorption of metanil yellow on NaOH-activated carbon at influent concentration C_o 50 mg L^{-1}

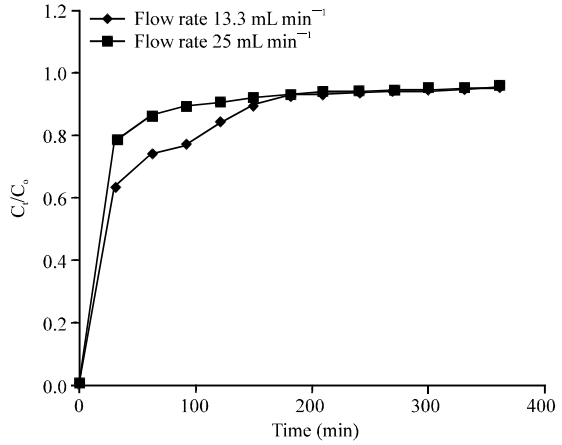

Fig. 8: Breakthrough curves for the adsorption of metanil yellow on H_3PO_4-activated carbon at initial influent concentration C_o 10 mg L^{-1}

exhaustion time of 60 min. Figure 6 and 7 are for NaOH-activated carbons. The results obtained generally show decrease in adsorption capacity with increase in bed height.

Effect of flow rate: The column adsorption was carried out at flow rates of 13.3 and 25 mL min^{-1} for H_3PO_4-activated carbon and 13.3, 25 and 34 mL min^{-1} for NaOH-activated carbon. Figure 8 depicts the effect of flow rate on adsorption of metanil yellow on H_3PO_4-activated carbon. Figure 8 shows that at flow rate of 13.3 mL min^{-1}, the exhaustion time was 180 min but for 25 mL min^{-1} the exhaustion time was 90 min. The adsorption capacities of 0.575 and 1.058 mg g^{-1} for 13.3 and 24 mL min^{-1}, respectively. Figure 9 shows the effect of flow rate on the adsorption of metanil yellow on NaOH-activated carbon. Figure 9 shows 30 min as the exhaustion time for the flow

rates 13.3, 25 and 34 mL min^{-1}. The adsorption capacities were 0.634, 0.113 and 0.428 mg g^{-1} for the flow rates, respectively. The values of the adsorption capacities in Fig. 9 show increase in adsorption with decrease in flow rate. This is due to the fact that the higher the flow rate, the shorter the residence time for contact between the adsorbate and adsorbent and hence equilibrium not attained (Kundu and Gupta, 2007). The results in Fig. 8 show a reversal. The reason for this is unknown.

Application of the Thomas Model: Experimental results were fitted into the Thomas Model for adsorption on H_3PO_4 and NaOH-activated cassava peels carbon, to generate the Thomas Model parameters, depicted in Table 2 and 3. Table 2 show that the maximum adsorption capacities for both H_3PO_4 and NaOH-activated cassava peels carbon decreased with increase in bed height, increase in initial dye concentration and decrease in flow rate. The highest values of 118.35 and 118.061 mg g^{-1} for maximum adsorption capacity were obtained for H_3PO_4 and NaOH-activated carbons respectively at initial dye concentration of 50 mg L^{-1}, bed height 10 cm and flow rate 13.3 mL min^{-1}. The R^2 values ranged from 0.6454-0.8949 for H_3PO_4-activated carbon and 0.6081-0.9576 for NaOH-activated carbon. Results show the Thomas model fitted more to the NaOH-activated carbon adsorption than the H_3PO_4-activated carbon.

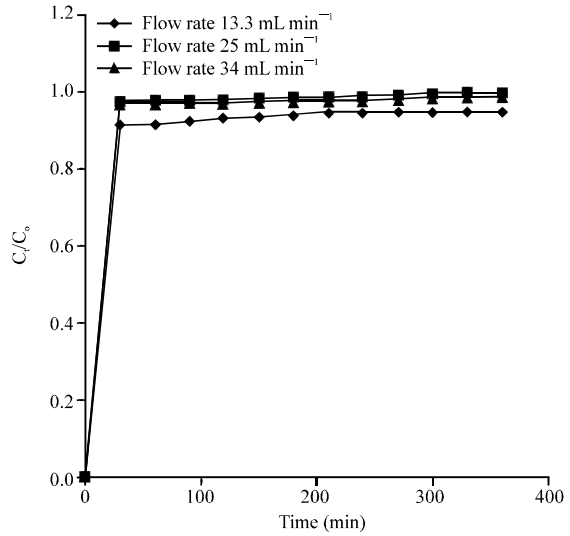

Fig. 9: Breakthrough curves for the adsorption of metanil yellow on NaOH-activated carbon at initial influent concentration C_o 10 mg L^{-1}

Application of the Yoon-Nelson Model: Experimental data with respect to flow rate, initial dye concentration and bed height were fitted into the Yoon-Nelson Model. A linear regression analysis was used on each set of data to determine the Yoon-Nelson parameters as shown in Table 4-6. The values of the Yoon-Nelson rate constant decreased with increase in inlet concentration, bed height and flow rate; maximum adsorption capacity increased with increase in flow rate, decrease in bed height and increase in inlet concentration for H_3PO_4-activated carbon.

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

Initial concn. (mg L^{-1})	Carbon bed height (cm)	Flowrate (mL min^{-1})	K_{Th} (mL min^{-1} mg)	q_o (mg g^{-1})	R^2
50	20	13.3	0.5.0	9.510	0.9735
50	10	13.3	0.12	29.720	0.9001
50	20	13.3	0.10	23.142	0.9898
50	30	13.3	0.10	9.290	0.8318
50	20	13.3	0.12	3.589	0.9729
50	20	20.0	0.32	0.723	0.9125
50	20	25.0	0.22	15.088	0.9490
100	20	13.3	0.24	0.310	0.9803
200	20	13.3	0.12	49.476	0.9727

Table 3: Yoon-Nelson Model parameters for column adsorption on H_3PO_4-activated cassava peels carbon

Initial concn. (mg L^{-1})	Carbon bed height (cm)	Flow rate (mL min^{-1})	K_{YN} (L min^{-1})	τ (min)	q_o	R^2
50	20	13.3	0.0050	413.280	68.708	0.9557
50	10	13.3	0.0044	42.136	14.010	0.9845
50	20	13.3	0.0050	412.120	68.515	0.9541
50	30	13.3	0.0030	325.830	36.113	0.9587
50	20	13.3	0.0072	279.790	46.515	0.9862
50	20	20.0	0.0040	179.350	44.838	0.9708
50	20	25.0	0.0028	45.679	14.275	0.8048
100	20	13.3	0.0052	572.270	190.280	0.7090
200	20	13.3	0.0054	391.040	260.042	0.7395

Table 4: Yoon-Nelson Model parameters for column adsorption 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})	τ min)	q_o (mg g^{-1})	R^2
50	20	13.3	0.0025	572.2000	95.128	0.9723
50	10	13.3	0.0006	893.3300	297.032	0.9016
50	20	13.3	0.0004	1724.7500	286.740	0.9912
50	30	13.3	0.0005	839.6000	93.056	0.8357

Table 4: Continue

Initial concn. (mg L^{-1})	Carbon bed height (cm)	Flow rate (mL min^{-1})	K_{YN} (L min^{-1})	τ (min)	q_o (mg g^{-1})	R^2
50	20	13.3	0.0006	213.5000	35.494	0.9765
50	20	20.0	0.0015	25.3330	6.333	0.9531
50	20	25.0	0.0013	396.5400	123.919	0.9630
100	20	13.3	0.0024	3.4583	1.150	0.9864
200	20	13.3	0.0023	737.3900	490.364	0.9776

Table 5: Column data parameters obtained at different initial dye concentrations, bed heights and flow rates for H_3PO_4-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})	Removal (%)
10	20	13.3	2.107	0.527	3.30
10	10	13.3	0.128	0.064	0.20
10	30	13.3	2.170	0.362	3.40
10	20	25.0	4.230	1.058	4.70
50	10	13.3	38.432	19.216	12.04
50	20	13.3	13.280	3.320	4.16
50	30	13.3	33.388	5.565	10.46
100	20	13.3	1.596	0.399	0.25

Table 6: Column data parameters obtained at different initial dye 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})	Removal (%)
10	10	13.3	8.235	4.118	12.90
10	20	13.3	2.107	0.527	3.30
10	30	13.3	1.277	0.213	2.00
10	20	25.0	0.450	0.113	0.50
10	20	34.0	1.714	0.428	1.40
50	10	13.3	4.980	2.490	1.56
50	20	13.3	2.930	0.730	0.92
50	30	13.3	3.770	0.628	1.18
100	20	13.3	11.300	2.820	1.77

The highest maximum adsorption capacity of 118.96 and R^2 range of 0.6001-0.9417 were also obtained for H_3PO_4-activated carbon. For NaOH-activated carbon, the highest maximum adsorption capacity was 890.359 mg g^{-1} and R^2 values range generally from 0.8414-0.9669.

CONCLUSION

Column adsorption of metanil yellow on H_3PO_4 and NaOH-activated cassava peels carbons were carried out. The breakthrough curves based on effects of initial metanil yellow concentration, bed height and flow rate at natural pH and 28-31°C were plotted. The results showed undefined breakthrough points. The highest experimental adsorption capacity values were 19.216 and 4.118 mg g^{-1}; total removal of 12.04 and 12.90% for H_3PO_4 and NaOH-activated carbons, respectively under various conditions. Thomas and Yoon-Nelson Models were the two models that could be used to analyze the experimental results.

ACKNOWLEDGEMENTS

This research is completed, as part of PhD thesis in the Department of Pure and Industrial Chemistry, University of Port Harcourt. Researchers acknowledge the contributions of the department. Researchers express deep gratitude to the Staff of Chemistry Laboratory, Imo State University for assistance and for immense support to carry out the research work.

REFERENCES

Ahmad, A.A. and B.H. Hameed, 2010. Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste. J. Hazard. Mater., 175: 298-303.

Aksu, Z. and F. Gonen, 2004. Biosorption of phenol by immobilized activated sludge in a continuous packed bed: Prediction of breakthrough curves. Process Biochem., 39: 599-613.

Al-Degs, Y.S., M.A.M. Khraisheh, S.J. Allen and M.N. Ahmad, 2009. Adsorption characteristics of reactive dyes in columns of activated carbon. J. Hazard. Mater., 165: 944-949.

Banat, I.M., P. Nigam, D. Singh and R. Marchant, 1996. Microbial decolorization of textile-dye-containing effluents: A review. Bioresour. Technol., 58: 217-227.

Chakraborty, S., S. De, S. DasGupta and J.K. Basu, 2005. Adsorption study for the removal of a basic dye: Experimental and modeling. Chemosphere, 58: 1079-1086.

Chern, J.M. and Y.W. Chien, 2002. Adsorption of nitrophenol onto activated carbon: isotherms and breakthrough curves. Water Res., 36: 647-655.

Chern, J.M. and Y.W. Chien, 2003. Competitive adsorption of benzoic acid and p-nitrophenol onto activated carbon: Isotherm and breakthrough curves. Water Res., 37: 2347-2356.

Fu, Y. and T. Viraraghavan, 2002. Dye Biosorption sites in *Aspergillus niger*. Biores. Technol., 82: 139-145.

Fu, Y. and T. Viraraghavan, 2003. Column studies for biosorption of dyes from aqueous solutions on immobilized *Aspergillus niger* fungal biomass. Water SA, 29: 465-472.

Kundu, S. and A.K. Gupta, 2007. As(III) removal from aqueous medium in fixed bed using iron oxide-coated cement (IOCC): Experimental and modeling studies. Chem. Eng. J., 129: 123-131.

Martin, M.J., A. Artolo, M.D. Balayer and M. Rigola, 2003. Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions. Chem. Eng. J., 94: 231-239.

Padmesh, T.V.N., K. Vijayaraghavan, G. Sekaran and M. Velan, 2006. Biosorption of Acid Blue 15 using fresh water macroalga Azolla filiculoides: Batch and column studies. Dyes Pigments, 71: 77-82.

Patel, H. and R.T. Vashi, 2012. Fixed-bed column adsorption of Acid yellow 17 dye onto tamarind seed powder. Can. J. Chem. Eng., 90: 180-185.

Pelech, R., F. Milchert and M. Bartkowink, 2006. Fixed-bed adsorption of chlorinated hydrocarbons from multicomponent aqueous solution onto activated carbon: Equilibrium column model. J. Colloid Int. Sci., 296: 458-464.

Singh, S., C.V. Srivastava and I.D. Mall, 2009. Fixed-bed study for adsorptive removal of furfural by activated carbon. Collo. Surf. A: Phys. Eng. Asp., 332: 50-56.

Taty-Custodes, V.C., H. Fauduet, C. Port and Y.S. Ho, 2005. Removal of lead (II) ions from synthetiv and real effluents using immobilized Pinus sylvestris saw dust: Adsorption on a fixed-bed column. J. Hazard. Mater. B, 123: 135-144.

Unuabonah, E.I., B.I. Olu-Owolabi, E.I., Fasuyi and K.O. Adebowale, 2010. Modeling of fixed-bed column studies for the adsorption of cadmium onto novel polymer-clay composite adsorbent. J. Hazar. Mater., 179: 415-423.

Vasquez, G., R. Alonso, S. Freire, J. Gonzalez-Alvarez and G. Antorrena, 2006. Uptake of phenol from aqueous solutions by adsorption in a *Pinus pinaster* bark packed bed. J. Hazard. Mater., B133: 61-17.

Walker, G.M. and I.R. Weatherley, 1997. Adsorption of acid dyes onto granular activated carbon in a fixed bed. Water Res., 31: 2093-2101.

Wang, B.E., Y.Y. Hu, L. Xie and K. Peng, 2008. Biosorption behavior of azo dye by inactive CMC immobilized *Aspergillus fumigates* beads. Bioresour. Technol., 99: 794-800.

Yesiladah, S.K., G. Pekin, H. Bermek, I. Arslan-Alaton, D. Orhon and C. Termerler, 2006. Bioremediation of textile azo dyes by Trichophyton rubrum LSK-27. World J. Microbiol. Biotechnol., 22: 1027-1031.