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Colour Removal from a Simulated Methyl Red Wastewater by Adsorption on Carbon in a Fixed Bed

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Abstract: The aim of this research was to evaluate H_3PO_4-activated carbon from cassava peels waste in removing methyl red from aqueous solution (simulated wastewater) by adsorption in a fixed-bed column. Effects of influent concentration, adsorbent bed height and solution flow rate were studied. Experimental results were applied to Thomas and Yoon-Nelson Models. The adsorption capacity, rate constant, correlation coefficient associated with each model were calculated and mentioned. The maximum experimental adsorption capacity of 133.63 mg g^{-1} was obtained with influent concentration of 200 mg L^{-1}, bed height 20 cm and flow rate 13.3 mL min^{-1}. Adsorption capacity, q_o, increased with increase in influent concentration, increase in bed height and decrease in flow rate. Maximum adsorption capacity related to the Thomas and Yoon-Nelson Models were 24.341 and 260.042 mg g^{-1}, respectively at influent concentration 200 mg L^{-1}, bed height 20 cm and flow rate of 13.3 mL min^{-1}. Correlation coefficients show that the results fitted well into the Thomas and Yoon-Nelson Models.

Key words: Fixed-bed column, cassava peels, activated carbon, methyl red, Thomas and Yoon-Nelson Model

INTRODUCTION

Dyes include a broad spectrum of different chemical structures, primarily based on substituted aromatic and heterocyclic groups such as aromatic amine (C_6H_5–NH–) which is a suspected carcinogen, phenyl ($C_6H_5CH_2$–) and naphthyl ($C_{10}H_7$–). A large number of dyes are azo compounds (–N=N–) which are linked by an azo bridge (Talarposhti *et al*., 2001; Kirk *et al*., 1984). Due to the complex chemical structures of synthetic organic pigments in dyes, they are resistant to breakdown and remain fast for the life time of the fabric; they will not break down on exposure to sunlight, water, soap, etc. and are difficult to treat in a wastewater. Colour in wastewater is an obvious indicator of water pollution (Anliker and Clark, 1987). The wastewater characteristics from a dye house are highly variable from day to day and even hour to hour, depending on the type of dye, the type of fabric and the concentration of the fixing agents added. Treatment of such wastewaters is therefore essential but difficult.

The discharge of dye house wastewater into the environment is aesthetically displeasing, impedes light penetration, damages the quality of the receiving streams and may be toxic to treatment processes to food organisms and to aquatic life. The degradation of molecules of dyes in the environment by micro organisms is likely to be slow (Meyer, 1981) which means that is possible for high levels of dye to persist and potentially accumulate. Furthermore, any degradation that does occur may produce smaller molecules equally unfamiliar to the environment such as amines and which may be toxic.

Methyl red (4-dimethylaminobenzene-2[l]-carboxylic acid) is a commonly used monoazo dye in laboratory assays, textiles and other commercial products: however, it may cause eye and skin sensitization and pharyngeal or digestive tract irritation if inhaled or swallowed. Methyl red is mutagenic under aerobic conditions: it undergoes biotransformation into 2-aminobenzoic acid and N-N[l]-dimethyl-p-phenylenediamine (Haris and Sathasivam, 2009).

Many organic compounds in water supplies are resistant to conventional treatments and many others are toxic or nuisances (odor, taste, color forming). Low concentration of organic contaminants are not readily removed by conventional treatment method but activated carbon has an affinity for various organics and its use for organic contaminants removal from water supplies has been widely implemented (Clark, 1987) conventional treatments of textile effluents are either ineffective, costly, complicated or have sludge disposal problems (Pazarlioglu *et al*., 2005).

Adsorption is the concentration of a substance at the surface. The adsorption at a surface or interface is largely

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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 particularity in the case 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. 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 material 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 aim of this research was to generate activated carbon from cassava peels biomass and evaluate its capacity in removing methyl red from aqueous solution in a laboratory scale fixed-bed column.

MATERIALS AND METHODS

Adsorbate: The methyl red used in this study, a dark red crystalline powder with molecular formula $C_{15}H_{15}N_3O_2$, molecular mass 269.30, melting point 179-182°C, a product of Merck was obtained from the Clinical Biochemistry Laboratory, Imo State University, Owerri, Nigeria and used without further purification. Other names for methyl red include 2-(4-(dimethylamino) phenylazo) benzoic acid; benzenediazonium-2-carboxylate; 4-dimethylamin obenzene-2^{l}-carboxylic acid; C.I Acid Red 2. A stock solution of the dye was prepared by dissolving 1 g of the dye in 1 dm^3 of hot distilled water and filtering through Whatman filter paper (No. 1). The stock solution was stored in the dark to prevent exposure to direct light. The molecular structure of methyl red is shown in Fig. 1. It is red in aqueous solution of pH under 4.4, yellow in pH over 6.2 and orange in between.

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 dirts 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 and 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, 20 and 25 mL min^{-1}). The effluent metanil yellow solution samples were collected at regular interval of 30 min. The samples were analyzed with a

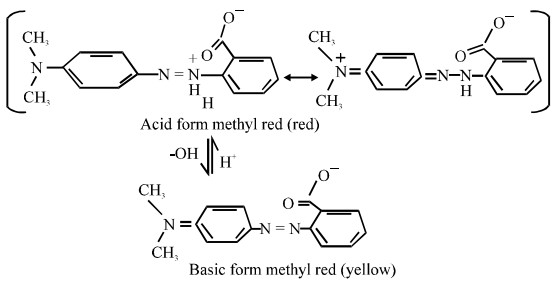

Fig. 1: Acid and base forms of methyl red

Uv-Vis 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 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:

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

where, t_{tot} and Q are the total flow time (min) and volumetric flow rate (mL/min). The area under the breakthrough curve (A) 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:

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

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:

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

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

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

Where:

C_t = The effluent dye concentration (mg/L)

C_o = The inlet dye concentration (mg/L)

x = The mass of the used 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:

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

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

$$\ln\left(\frac{C_t}{C_o}-1\right) = \frac{K_{Th} q_o x}{Q} - K_{Th} C_o t \quad (9)$$

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

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

Where:
K_{YN} = The rate (or Yoon-Nelson) constant (per min)
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 $\ln[Ct/(Co-C_t)]$ 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:

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

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 influent concentration: The effect of a variation of the influent methyl red concentration from 50-200 mg L^{-1} with adsorbent bed height 20 cm, solution flow rate 13.3 mL min^{-1}, temperature 28-31°C and natural pH is depicted by the breakthrough curves in Fig. 2. As shown in the Fig. 2, the breakthrough time for C_o 100 mg L^{-1} was 60 min and for 200 mg L^{-1}, 30 min while that for 50 mg L^{-1} was not defined. The exhaustion times for 100 and 200 mg L^{-1} was 450 min while 50 mg L^{-1} did not attain exhaustion at the maximum time of the experiment, i.e., 510 min. Table 1 shows the column parameters at influent concentrations of 50-200 mg L^{-1}.

Table 1 shows increase in adsorption capacity, q_e with increase in concentration. The order of increase in adsorption capacity was 50 mg L^{-1} (37 mg g^{-1}) <100 mg L^{-1} (116 mg g^{-1}) <200 mg L^{-1} (133.63 mg g^{-1}). Table 1 also shows decrease in total removal with increase in influent concentration except for 100 mg L^{-1} in which total removal of 68.85% was the highest. The increase in adsorption capacity with increase in influent concentration is as a result of increase in concentration difference which provides a high driving force for the adsorption process (Ahmad and Hameed, 2010).

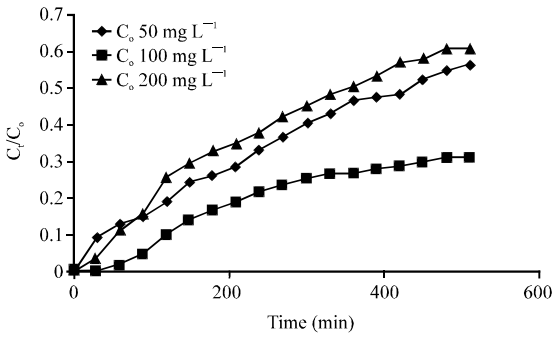

Fig. 2: Breakthrough curves for the adsorption of methyl red on H_3PO_4-activated carbon at bed height 20 cm, flow rate 13.3 mL min^{-1} temperature 28-31°C and influent concentration C_o 50, 100 and 200 mg L^{-1}

Table 1: Column data parameters obtained at different methyl red initial 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})	Total 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

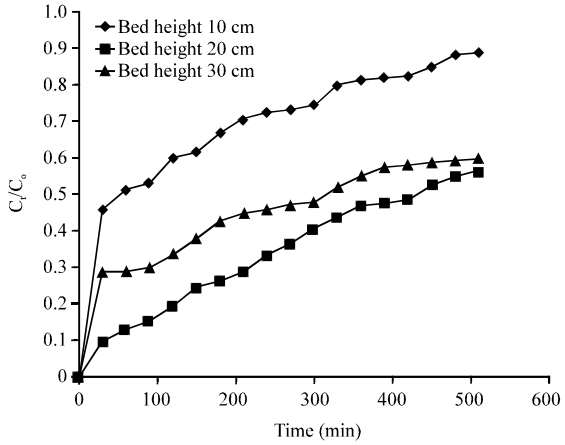

Fig. 3: Breakthrough curves for the adsorption of methyl red on the H_3PO_4-activated carbon at bed height 10, 20 and 30 cm, influent concentration C_o 50 mg L^{-1}, flow rate 13.3 mL min^{-1} and temperature 28-31°C

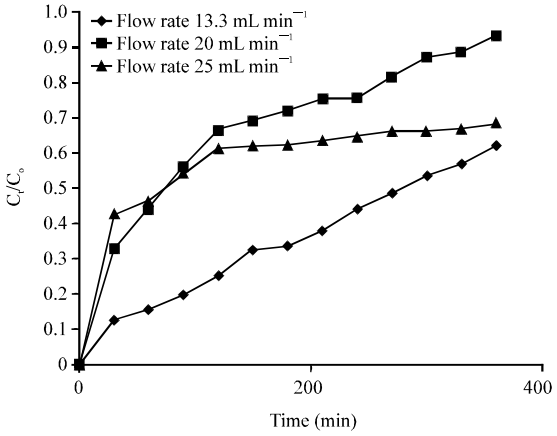

Fig. 4: Breakthrough curves for the adsorption of methyl red on H_3PO_4-activated carbon at flow rates 13.3, 20, 25 mL min^{-1}, influent concentration C_o 50 mg L^{-1}, bed height 20 cm and temperature 28-31°C

Table 2: Thomas Model parameters for the column adsorption of metanil yellow on H_3PO_4-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	5.70	0.562	0.8707
10	10	13.3	9.80	1.231	0.7646
10	20	13.3	5.70	0.562	0.8707
10	30	13.3	4.50	0.660	0.8551
10	10	13.3	7.40	0.317	0.8949
10	20	25.0	4.40	2.285	0.8591
50	20	13.3	0.50	14.286	0.6638
50	10	13.3	0.10	118.350	0.8078
50	20	13.3	0.50	14.286	0.6638
50	30	13.3	0.42	69.577	0.6493
100	20	13.3	0.44	34.832	0.6454

Effect of bed height: The effect of carbon bed height on the adsorption of methyl red on H_3PO_4-activated cassava peels carbon at bed heights 10, 20 and 30 cm, influent concentration 50 mg L^{-1}, volumetric flow rate 13.3 mL min^{-1}, natural pH and temperature 28-31°C is shown in Fig. 3. From the Fig. 3, 50% breakthrough could be achieved at about 30, 420 and 300 min for 10, 20 and 30 cm bed heights, respectively. Table 2 portrays 20 cm bed height having the highest adsorption capacity and total removal of 37 mg g^{-1} and 43.64%, respectively. Apart from 20 cm bed height, adsorption capacity and total removal increased with increase in bed height. This is due to the increase in surface area of the adsorbent which provided more binding sites for the adsorption (Patel and Vashi, 2012). The breakthrough curves are dispersed. This might be due to slow adsorption kinetics of methyl red on the adsorbent (Al-Degs *et al*., 2009).

Effect of flow rate: The impact of flow rate of 13.3, 20 and 25 mL min^{-1} at influent dye concentration 50 mg L^{-1}, bed height 20 cm, natural pH and temperature of 28-31°C is shown in Fig. 4. The periods of time for the adsorption to approximately reach 50% breakthrough, i.e., C_t/C_o = 0.5 are 270, 150 and 60 min for flow rates of 13.3, 20 and 25 mL min^{-1}, respectively. The adsorption was for 360 min for each experiment. The breakthrough curves of the lower flow rate of 13.3 mL min^{-1} tended to be more gradual, meaning that the column was difficult to be completely exhausted. From Table 1, it could be seen that increasing the flow rate resulted in a decrease in the dye removal efficiency, i.e., total removal increased with decrease in flow rate. This is attributed to the fact that low contact time between the adsorbate and adsorbent reduces the adsorption efficiency in the carbon bed. In addition, at higher flow rates, the movement of adsorption zone along the bed is faster reducing the time for adsorption of the dye on the carbon bed (Patel and Vashi, 2012).

Application of the Thomas Model: The experimental results were simulated using the Thomas Model in order to obtain the Thomas parameters which are depicted in Table 2. The Table 2 revealed that the adsorption capacity, q_o, increased with increase in influent concentration increase in bed height and decrease in flow rate, except for influent concentration of 50 mg L^{-1}, flow rate 13.3 mL min^{-1} and bed height of 20 cm when the adsorption capacity was higher than for bed height of

Table 3: Yoon-Nelson Model parameters for the column adsorption of metanil yellow 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})	T (min)	q_o (mg g^{-1})	R^2
10	20	13.3	0.0057	169.230	5.627	0.8703
10	10	13.3	0.0087	217.410	14.458	0.9417
10	20	13.3	0.0057	169.250	5.628	0.8702
10	30	13.3	0.0044	311.910	6.914	0.8473
10	20	13.3	0.0074	95.365	3.171	0.8948
10	20	25.0	0.0044	365.590	22.849	0.8593
50	20	13.3	0.0025	859.920	142.962	0.6660
50	10	13.3	0.0005	3569.800	1186.959	0.7852
50	20	13.3	0.0024	901.330	149.846	0.6784
50	30	13.3	0.0021	628.240	69.630	0.6460
100	20	13.3	0.0038	1210.320	402.598	0.6001

30 cm. The maximum adsorption capacity related to the Thomas Model was found to be 24.341 mg g^{-1} at flow rate 13.3 mL min^{-1}, influent concentration of 200 mg L^{-1} and bed height 20 cm. All results fitted well into Thomas Model with high correlation coefficient (<0.95) except for 100 and 200 mg L^{-1} where the correlation coefficients were <0.9.

Application of the Yoon-Nelson Model: Parameters obtained by simulating the experimental results with the Yoon-Nelson Model are shown in Table 3. Table 3 shows that the adsorption capacity increased with increase in influent concentration, increase in bed height and decrease in flow rate. The highest adsorption capacity of 260.042 mg g^{-1} was obtained with influent concentration of 200 mg L^{-1} bed height 20 cm and flow rate 13.3 mL min^{-1}. The experimental results fitted well to the Yoon-Nelson Model with correlation coefficient R^2>0.95 except for 100 and 200 mg L^{-1}, bed height 20 cm and flow rate 13.3 mL min^{-1} when the R^2>0.7.

CONCLUSION

In this research, the fixed-bed column adsorption of methyl red onto cassava peels carbon activated with H_3PO_4 was studied. The breakthrough curves (C_t/C_o vs. time) were plotted. The experimental results were fitted into the Thomas and Yoon-Nelson Models. The highest experimental adsorption capacity of 133.63 mg g^{-1} was obtained with influent concentration of 200 mg L^{-1}, bed height 20 cm and flow rate 13.3 mL min^{-1} while the highest total removal of 68.85% was obtained with 100 mg L^{-1} influent concentration 20 cm bed height and 13.3 mL min^{-1} flow rate. The maximum adsorption capacity related to the Thomas Model was 24.341 and for Yoon-Nelson Model, 260.042 mg g^{-1}. The correlation coefficient values show the results fitted well to the Thomas and Yoon-Nelson Models but more to the Yoon-Nelson Model.

REFERENCES

African Agriculture, 2007. Nigeria adopts polices to encourage cassava industry. Africa News Network, March 12, 2007.

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.

Anliker, R. and E.A. Clark, 1982. International regulation of chemicals-implications for organic colorants. J. Soc. Dyers Colourists, 98: 42-55.

Barrow, G.M., 1996. Physical Chemistry. 6th Edn., McGraw-Hill, North America, Pages: 344.

CIN, 2006. Presidential research and communications unit-feature. Cassava Initiatives in Nigeria, February 22, 2006.

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.

Clark, R.M., 1987. Evaluating the cost and performance of field-scale granular activated carbon systems. Environ. Sci. Technol., 21: 573-580.

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.

Haris, M.R.H.M. and K. Sathasivam, 2009. The removal of methyl red from aqueous solutions using banana pseudostem fibers. Am. J. Applied Sci., 6: 1690-1700.

Kirk, R.E., D.F. Othmer, M. Grayson and D. Eckroth, 1984. Encyclopedia of Chemical Technology. 6th Edn., Wiley, New York.

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.

Levine, I.N., 1995. Physical Chemistry. 4th Edn., McGraw-Hill, North America.

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.

Meyer, U., 1981. Biodegradation of Synthetic Organic Colorants. In: Microbial Degradation of Xenobiotics and Recalcitrant Compounds, Leisinger, T., R. Hutte, A.M. Cook and J. Nuesch (Eds.). Academic Press, London, UK., pp: 371-385.

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.

Pazarlioglu, N.K., R.O. Urek and F. Ergun, 2005. Biodecolourization of direct blue 15 by immobilized *Phanerochaete chrysosporium*. Process. Biochem., 40: 1923-1924.

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.

Tahir, S.S. and N. Rauf, 2003. Thermodynamic studies of Ni(II) adsorption onto bentonite from aqueous solution. J. Chem. Thermodynamics, 35: 2003-2009.

Talarposhti, A.M., T. Donnelly and G.K. Anderson, 2001. Colour removal from a simulated dye wastewater using a two-phase anaerobic packed bed reactor. Water Res., 35: 425-432.

Tang, D., Z. Zheng, K. Lin, J. Luan and J. Zhang, 2007. Adsorption of p-nitrophenol from aqueous solutions onto activated carbon fiber. J. Hazard Mater., 143: 49-56.

Taty-Costodes, V.C., H. Fauduet, C. Porte and Y.S. Ho, 2005. Removal of lead(II) ions from synthetic and real effluents using immobilized *Pinus sylvestris* sawdust: Adsorption on a fixed-bed column. J. Hazard. Mater., 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.