Utilization of activated carbon for the removal of basic dyes in fixed-bed microcolumn

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Abstract
Liquid-phase adsorption processes were performed using basic dyes (methylene blue (MB), basic red (BR) and basic yellow (BY)) in an activated carbon microcolumn. The effects of initial dye concentration, column diameter and particle size were investigated. The performance of the fixed-bed adsorber was evaluated through the concept of breakthrough curves. The Thomas model was employed to predict the breakthrough curves and compared with the experimental breakthrough curves Furthermore, the Empty Bed Residence Time (EBRT) has been applied to the data to determine the minimum residence time and the minimum adsorbent exhaustion rate. Column studies showed effective use of adsorbents. The results reflected the significance of the experimental parameters on the efficient removal of basic dyes from aqueous solution. The Thomas model predicts the experimental data well.
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Keywords: Adsorption; Microcolumn; Basic dyes; Activated carbon; Breakthrough curve.

1. Introduction
Adsorption is a physicochemical wastewater treatment method, which is gaining prominence in the wastewater industry because of the high quality treated effluents it produces [1]. Continuous flow or flow through adsorbers is commonly fixed-bed systems of either the packed or expanded type. The application of the fixed bed system has been shown to have several distinct advantages for water and wastewater treatment application [2]. In fact, a fixed-bed continuous flow column is an effective process for cyclic adsorption/desorption, as it makes the best use of the concentration difference driving force for adsorption. It also allows for a more efficient utilization of the adsorbent capacity and results in better quality effluent [3, 4].
Fixed bed operations are widely used in chemical processes and pollution control processes such as the separation of ions by an ion-exchange bed or the removal of toxic organic compounds by carbon adsorption beds. This method is preferred in adsorption processes mainly due to the ease of operation, inexpensive fabrication, minimal attrition of adsorbent and no carbon loss problems [5, 6]. The fixed bed continuous flow operation results in maximum utilization of the carbon's adsorptive capacity. The carbon in the column acts like a series of layers, with each layer in contact with fresh solution of constant solute concentration [3]. In the operation of a fixed-bed adsorber, the objective is to reduce the concentration in the effluent so that it does not exceed a pre-defined breakthrough value [7].

The microcolumn technique has gained favour recently due to the fact that quick initial results can be obtained using this technique and therefore, was adopted in the current column studies. Liu and Weber [8] have proposed a microcolumn technique for simultaneous determination of external and internal mass transfer resistances. Li *et al*. [2] used the microcolumn technique to generate breakthrough profiles of dissolved organic matter (DOM). According to the authors, parameters obtained by the calibration of fixed-bed adsorption models with microcolumn data could satisfactorily simulate the bed performance for large column.

The focus of this work is directed at the evaluation of the success of the physical activation process in producing highly effective activated carbons in large industrial scale and to test their applicability in adsorption processes in continuous mode. A further aim is focused on the evaluation of the effects of the experimental parameters on the performance of activated carbon microcolumns in removing basic dyes from aqueous solution. The research also investigates the potential replacement of large columns by microcolums in continuous operation mode studies as to save time and materials. Several tests were conducted using a microcolumn setup in order to assess the feasibility of using activated carbon in fixed-bed microcolumns. The concentration-history profile of the effluent and breakthrough time were measured and correlated with the experimental parameters. As a preliminary test, existing mathematical models; the Thomas model and the Empty Bed Residence Time model were applied to the experimental data.

2. Mathematical modelling

2.1 Thomas model

As reported previously, the prediction of column adsorption process requires prediction of breakthrough curves for the effluent. The maximum adsorption capacity of an adsorbent is also required in the design of the column. The Thomas model is used to fulfil the purpose. The mathematical representation for a fixed bed column with ideal breakthrough curve can be expressed as follows [4, 9]:

$$\frac{C_t}{C_o} = \frac{1}{1 + \exp\left[k_T\left(q_o m - C_o V\right)/F\right]} \tag{1}$$

and

$$Ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_T q_o m}{F} - \frac{k_T C_o}{F} V \tag{2}$$

where C_o is the initial solute concentration (mg/dm^3), C_t is the solute concentration at time, t, (mg/dm^3); F is the volumetric flow rate (dm^3/min); k_T is Thomas rate constant (dm^3/min.mg); q_o is maximum solid-phase concentration of the solute (maximum column adsorption capacity) (mg/g); V is the throughput volume (dm^3) and m is the mass of adsorbent (g).

k_T and q_o can be determined from the slope and the intercept of the linear plot of Ln ((C_o/C_t)-1) versus V, respectively.

The Thomas solution is one of the most general and widely used methods in column performance theory. The Thomas model is based on the following assumptions; i) Langmuir kinetics of adsorption-desorption; ii) no axial dispersion which is derived with the assumption that the rate driving force obeys second-order reversible reaction kinetics; iii) a constant separation factor; iv) it is applicable to either favorable or unfavorable isotherms. The main weakness of the Thomas solution is that its derivation is based on second order reaction kinetics. Adsorption is usually not limited by chemical reaction kinetics but is often controlled by interphase mass transfer [4, 9].

2.2 The empty bed residence time model

The Empty Bed Residence Time (EBRT) is a design procedure used for the design of an adsorber. Two major design parameters, namely, the empty bed residence time (or empty bed contact time) and the adsorbent exhaustion rate (or adsorbent usage rate) can be correlated for a fixed-bed adsorption column to determine the capital and operating costs of the adsorption system [10, 11].

Negrea *et al.* [12] and Guo *et al.* [13], reported that the empty bed contact time is a critical parameter in the adsorption processes specially if the adsorption mainly depends on the contact time between the adsorbent and adsorbate.

The empty bed residence time EBRT is the time required for the liquid to fill the empty column and determines the residence time during which the solution being treated is in contact with the adsorbent:

$$EBRT\,(\text{min}) = \frac{\text{Bed volume}}{\text{Volumetric flowrate of the liquid}} \qquad (3)$$

The adsorbent exhaustion rate is the mass of adsorbent used per volume of liquid treated at breakthrough:

$$\text{Adsorbent Exhaustio rate (g/dm}^3) = \frac{\text{Mass of adsorbent used}}{\text{Volume of liquid treated at breakthrough}} \qquad (4)$$

The adsorbent exhaustion rates are plotted against the EBRT values, and a single- operating line can be constructed to correlate these two variables. Thus, to select the optimum combination of adsorbent exhaustion rate and the liquid retention time, the operating line should first be established.

Inspection of equations (3 and 4) reveals that the lower the adsorbent exhaustion rate, the larger the volume to be treated at breakthrough point, thus longer EBRT and smaller amount of adsorbent is needed per unit volume of feed treated which implies a lower operating cost; however, a larger column will have to be used. On the other hand, the higher the adsorbent exhaustion rate, the smaller the EBRT, the higher the operating cost and a smaller column is needed which will reduce the construction cost.

3. Experimental

3.1 Material
Due to the toxicity of basic dyes, their high tinctorial value and their high affinity for negatively charged adsorbent surfaces [14, 15], three basic dyes were chosen as model adsorbates in single systems. These include; methylene blue C. I. 52015 (MB), supplied by ACROS Organics, USA; basic red C. I. 22 (BR); basic yellow C. I. 21 (supplied by Dyestar, GmbH & Co., Frankfurt. All dyes were commercial samples and were used without further purification. Figure 1 depicts the chemical structures.

Two activated carbons were used in this work, PAC2 produced by the steam activation of New Zealand bituminous coal on an industrial scale and Filtrasorb 400 supplied by Chemviron Carbon, (UK). F400 is produced by the gas activation of bituminous coal. F400 was used for comparison purposes. Table 1 shows physical and chemical characteristics for the activated carbons.

3.2 Procedure
In order to confirm the applicability of activated carbons for dye recovery, breakthrough curves were determined for different initial dye concentrations, column diameters and particle sizes. Small scale column tests using microcolunm were conducted. Adsorption columns were constructed using columns of 10 cm length with different internal diameters (ranging from 2 to 4 mm) and the removal efficiencies of PAC2 and F400 in continuous flow system were studied. Dye solution with specific concentration was prepared and was fed to the sample tank of volume 2 dm^3. The concentration of dye solution was determined before the commencement of each experiment. Activated carbon was soaked in deionised water before it was transferred to the column. Construction of the bed in this manner prevented entrapped air from being held in the column. It is well-known in the literature that any trapped air can cause channeling during column operation and this in turn increases pressure drop and also prevents complete contact of dye solution with carbon particles. In order to prevent carbon leakage or attrition, glass wool was added above and under the activated carbon bed. Before the adsorption test commenced, the complete system was checked by circulating water for two hours. The solution was then pumped using a peristaltic pump, Watson Marlow 101 U/R, connected with Teflon tubes from the sample tank to the top of the microcolumn at the design flow rate (down flow pattern). Samples were taken from a sample point (at the bottom of the column) at specific time intervals and the concentrations of the dye in the effluent were measured using a Perkin Elmer UV/VIS spectrometer (Lambda 12 model, Germany). The experiment was terminated when the concentration of the effluent was equal to the concentration of influent.
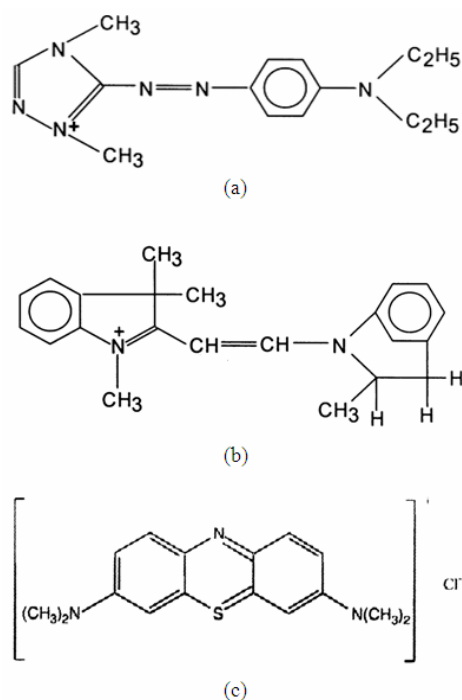
(a)

(b)

(c)

Figure 1. Chemical structure of adsorbates (a) Basic red 22; (b) Basic yellow 21and (c) Methylene blue

Table 1. Physical and chemical characteristics of activated carbons

	F400	PAC2
Total surface area (BET) ($m^2 g^{-1}$)	1216.4	857.14
Micropore surface area ($m^2 g^{-1}$)	918.70	801.83
Total pore volume ($cm^3 g^{-1}$)x10^1	8.211	4.467
Micropore volume ($cm^3 g^{-1}$)	0.456	0.389
Average pore radius (nm)	1.124	1.210
Surface acidity[a] (meq g^{-1})	0.408	0.462
Surface basicity[a] (meq g^{-1})	0.610	0.560
$pH_{solution}$ (10 wt%)	8.30	8.20
pH_{zpc}[b]	7.80	6.30

[a] Both the surface acidity and basicity of the activated carbons were determined by using titration methods as reported by Al-Degs et al. [20]
[b] Alkalimetric titration technique recommended by Al-Ghouti et al. [21] was adopted to measure surface charge density of activated carbons and to determine pH_{zpc}.

4. Results and discussion

4.1 Effect of initial dye concentration

To investigate the effect of initial dye concentration on the performance of the fixed-bed operation, a series of microcolumn experiments with different dye concentrations namely, 50, 100 and 150 ppm were conducted. Figure 2 shows the breakthrough curves for the adsorption of MB onto PAC2 at various initial dye concentrations. It can be seen from the figure that breakthrough curves display three important features: an initial lag period during which effluent MB is non-detectable, followed by a rise in concentration, and finally a period of slow increase in effluent level. It was assumed that the breakthrough dye-concentration would be 5% of the influent concentration. It is evident that by increasing initial dye concentration, the slope of the breakthrough curve increased and became much steeper, hence reducing the volume which can be treated before breakthrough occurred. A reduction of 46% in the volume treated at breakthrough point was observed as the initial dye concentration was increased from 50 to 150 ppm. This is due to the fact that by increasing the initial dye concentration, the driving force increases which enhance the rate of dye adsorption and saturates the binding sites more quickly. This is consistent with results reported by Walker and Weatherley [7] where the authors found that by increasing inlet adsorbate concentration, the slope of the breakthrough curve increased and the

volume treated before carbon regeneration reduced. This behaviour was attributed to the high concentrations which saturated the activated carbon more quickly, thereby decreasing the breakthrough time. It is also clear from Figure 2 that all the curves exhibit a characteristic "S" shape which indicates an effective use of adsorbent [16].
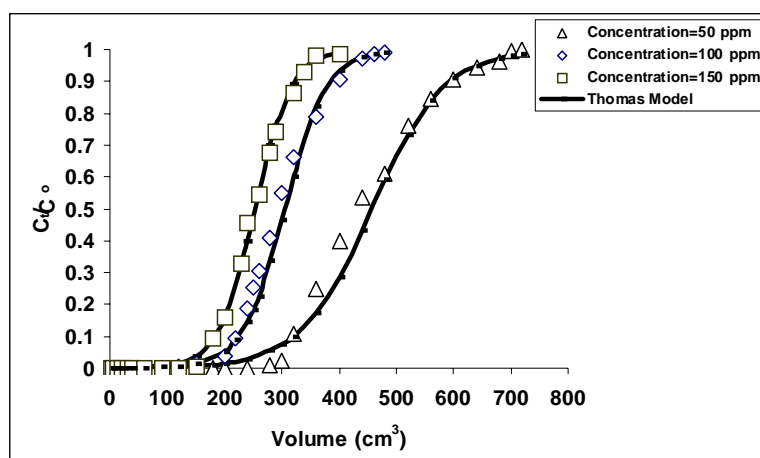

Figure 2. Breakthrough curves for the adsorption of MB onto PAC2 at different initial dye concentrations
Temperature = 20 $^{\circ}$C, mass = 0.2 g, size = 106-180 μm, flow rate = 2 cm^3/min, column diameter = 3 mm and pH=7

The column data were fitted to the Thomas model (eqn (2)) to predict the performance of breakthrough curves at different initial dye concentration. The predicted breakthrough curves correlated quite well with the experimental breakthrough curves as illustrated in Figure 2. Thomas rate constant, k_T, and maximum solid-phase concentration of the solute, q_o, were determined from the slope and the intercept of the linear plot of Ln ((C_o/C_t)-1) versus V, respectively. Table 2 lists the values of the Thomas model constants. It is clear from the table that an increase in the initial dye concentration leads to an enhancement in the adsorption capacity, q_o, and a reduction in the rate constant, k_T. By increasing dye concentration, the concentration gradient increases and thus, increases the adsorption capacity. This is consistent with the results obtained in the equilibrium studies as the capacity is shown to increase with the increase in dye concentration. The decrease in the rate constant can be attributed to the collisions between dye molecules at high concentrations which increase the diffusional resistance. Dye agglomeration at high bulk liquid concentrations can also account for this, which would further increase the diffusional resistance [17].

It is worth mentioning that kinetics studies proved that adsorption mechanism of the adsorption of basic dyes on the PAC2 is complex, combination of pseudo second-order and intraparticle diffusion with the external mass transfer predominating in the first five minutes. The involvement of chemical reaction mechanism might explain the applicability of the Thomas model although its derivation is based on second order reaction kinetics.

4.2 Effect of particle size
An inverse relationship between adsorbent particle size and fixed-bed service time was evident as is recognised in Figure 3. By increasing the particle size from 106-180 to 250-500 (μm), 55% reduction in the amount of the volume treated at breakthrough point is evident. Breakthrough occurred after 45.5 (min) at particle size 250-500 (μm) while breakpoint appeared after 102 (min) at particle size 106-180 (μm). A more efficient concentration profile and a more efficient performance were obtained in the case of smaller particle sizes. All the curves show the classic "S" shape profile. The enhancement of the column performance with the reduction in particle size might be attributed to the higher overall rate of diffusion due to the higher available interfacial surface area and shorter intraparticle diffusion paths [7, 18]. Column results obtained are consistent with the previous isotherm and kinetic results and it was evident that the equilibrium capacity and adsorption rate were increased with the decrease in the adsorbent particle size. Ouvrard *et al.* [19] investigated the effect of the adsorbent particle size on the adsorption process of arsenate using a manganese oxide bed. The results showed that the particle size had strong influence on the breakthrough curve: the lower the particle size, the later was the onset of breakthrough and the greater the adsorption capacity.

Table 2.Values of the Thomas model constants for the adsorption of MB onto PAC2 at different experimental parameters

Concentration (ppm)	k_T*10^4 (dm³/min.mg)	q_o (mg/g)	r^2
50	6.440	114.00	0.9947
100	5.504	152.00	0.9906
150	4.153	190.00	0.9870
Size (μm)			
106-180	5.504	152.00	0.9906
180-250	5.562	130.00	0.9774
250-500	5.826	102.00	0.9882
Diameter (mm)			
2.00	7.377	116.00	0.9874
3.00	5.504	152.00	0.9906
4.00	4.423	203.00	0.9879

The Thomas model shows a good correlation with the experimental data obtained at different particle sizes as can be seen in Figure 3. The calculated values of the Thomas model constants, Thomas rate constant, k_T, and maximum solid-phase concentration of the solute, q_o, are listed in Table 2. A decrease in the adsorption capacity, q_o, from 152-102 (mg/g) and an increase in Thomas rate constant, k_T, from 5.504 to 5.826 $*10^{-4}$ (dm³/min.mg), were observed with the increase in particle size from 106-180 to 250-500 (μm).
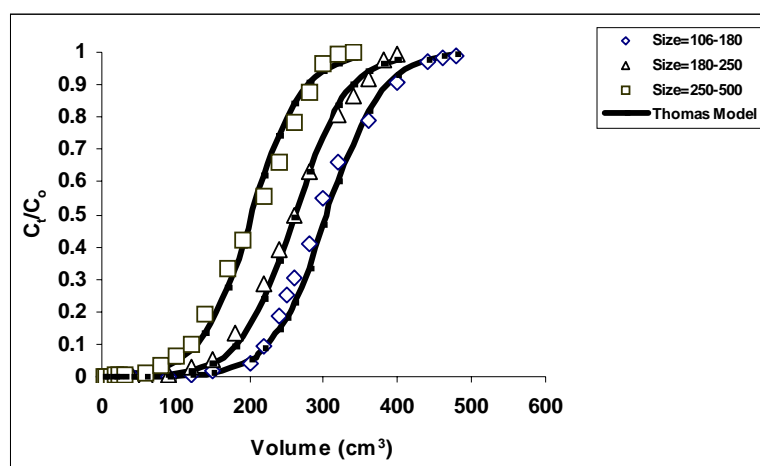

Figure 3. Breakthrough curves for the adsorption of MB onto PAC2 at different particle sizes Temperature = 20 °C, mass= 0.2 g, concentration =100 ppm, column diameter = 3mm, flow rate = 2 cm³/min and pH=7. Size in μm

4.3 Effect of column diameter
A series of column adsorption tests were carried out using three different column diameters, namely 2, 3 and 4 (mm) to investigate the effect of the variation in column diameters on the adsorption process of MB onto PAC2. The results were also correlated with the Thomas model. New sets of breakthrough curves are shown in Figure 4 as a dimensionless concentration versus the throughput volume of liquid treated at different column diameters. Table 2 summarised the calculated values of the Thomas model constants. It can be seen from Figure 4 that increasing the column diameter from 2 to 4 (mm), enhanced the column performance and increased the volume treated at breakthrough point from 145 to 269 (cm³) and delayed the time for the breakpoint to occur from 72 to135 (min). The results in Table 2 attested to this trend as it is evident from the increase in the bed capacity (116-203 mg/g) with the increase in column diameters. The Thomas model correlates the experimental data quite well as it can be seen in Figure 4. The enhancement in the column performance with the increase in the column diameter can be attributed to the increase in contact time between dye molecules and the activated carbon bed, hence, an enhanced diffusional process. Kinetics studies proved that diffusional processes have important effect on

the adsorption process of MB onto PAC2, therefore, the longer the contact time, the more effective will be the performance of activated carbon bed.
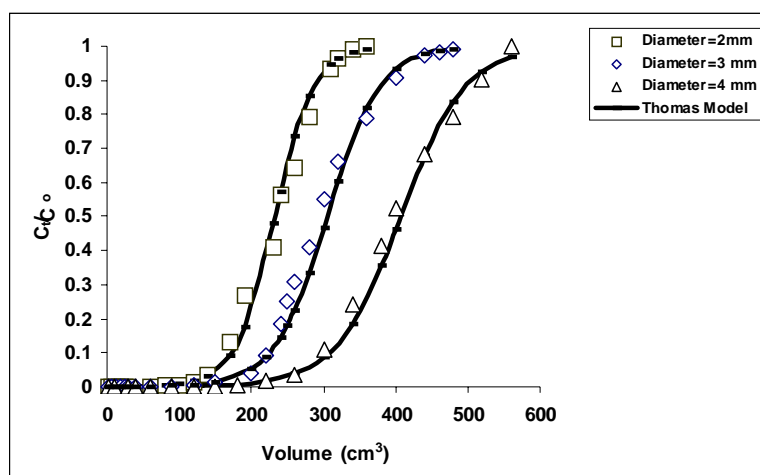

Figure 4. Breakthrough curves for the adsorption of MB onto PAC2 at different column diameters. Temperature = 20 ^{o}C, mass= 0.2 g, concentration =100 ppm, flow rate = 2 cm^3/min, size = 106-180 μm and pH=7

4.4 Adsorption of basic dyes onto F400 and PAC2

Figure 5 shows the breakthrough curve for the adsorption of MB onto F400 at particle size = 250-500 (μm). It can be seen from the figure that breakthrough curves exhibit a characteristic "S" shape with breakthrough volume = 123 (cm^3) corresponding to breakpoint time = 62 (min). Comparing the performance of F400 with that of PAC2 at the same experimental conditions, it is recognised that F400 is more efficient for the removal of MB from aqueous solution using a fixed-bed adsorber. A longer delay in the occurrence of breakpoint in the case of F400 (62 min) was observed than that of PAC2 (45.5 min). Thus, more MB solution can be treated using F400. This trend is consistent with the findings of the equilibrium and kinetics studies where F400 shows a higher adsorptive capacity and a higher adsorption rate than PAC2 at the same experimental conditions. This can be attributed to the physical characteristics of F400 as the studies of nitrogen adsorption demonstrated that F400 has better physical characteristics (surface area and pore structure) than that of PAC2. Figure 5 illustrates the good fit of the Thomas model to the experimental data.

A comparison for the efficiency of removing BR dye from aqueous solution using F400 and PAC2 showed that breakthrough point occurs at time = 49 min (equivalent to throughput volume = 97 cm^3) in the case of PAC2 whereas the breakpoint occurs at time = 25.5 min (equivalent to throughput volume = 41 cm^3) in the case of F400. This is in good agreement with the earlier findings of equilibrium studies as higher BR uptake was achieved in the case of PAC2 than that in the case of F400. Regarding the BY dye, F400 showed better performance than PAC2 for the removal of BY dye. This is evident from a comparison of the time required to reach breakthrough point, time = 46 min (corresponding to volume = 92 cm^3) in the case of F400 and time = 33 min (corresponding to volume = 67 cm^3) in the case of PAC2. Both breakthrough curves of BY adsorption showed the characteristic "S" shape with good use of the Thomas model to predict the breakthrough curves.

Table 3 summarised the results of Thomas model constants for the adsorption of MB, BR and BY onto PAC2 and F400. It is clear from the table that maximum solid-phase concentration of the solute, q$_o$, increased in the order of MB<BR<BY for both adsorbents, PAC2 and F400, and this is correlated well with the results of equilibrium studies in which both adsorbents show adsorption preference in the order of MB<BR<BY. It should be remembered in a comparison of the performance of certain adsorbents according to the equilibrium, kinetic and column studies, that there are some instances in which the results of each study do not match the results of other studies. This can be attributed to the different experimental conditions applied in each study. For example, the adsorption capacities obtained in the column studies are much lower than those observed in the equilibrium studies. This can be ascribed to the fact that equilibrium time for batch equilibrium studies is much longer than that in the case of dynamic kinetic and dynamic column studies, so there is enough time for intra-particle diffusion

processes to participate in the adsorption process. The kinetic studies emphasized the significant role of the diffusion processes in the adsorption of the basic dyes under investigation.

The consistency in the behaviour of adsorbents toward basic dyes between the equilibrium and column studies accentuates the effectiveness of using the microcolumn technique as a rapid method to predict the performance of the adsorbent in the adsorption processes.
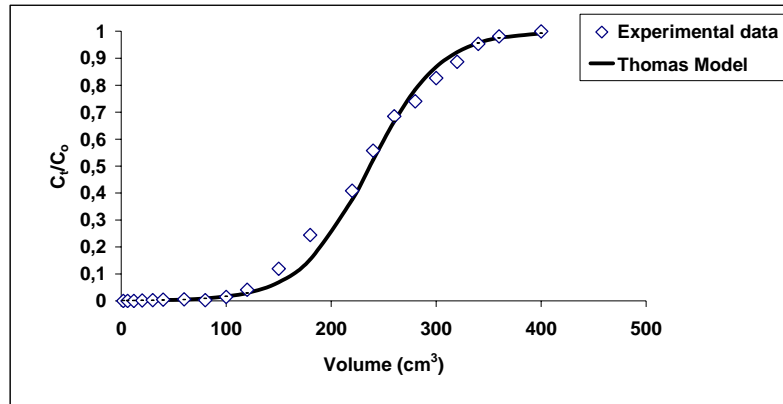

Figure 5. Breakthrough curves for the adsorption of MB onto F400. Temperature = 20°C, mass= 0.2 g, concentration =100 ppm, flow rate = 2 cm^3/min, column diameter = 3 mm, size = 250-500 μm and pH=7

Table 3.Values of Thomas model constants for the adsorption of MB, BR and BY onto PAC2 and F400

Carbon	MB		BR		BY	
	k_T*10^4 (dm^3/min.mg)	q_o (mg/g)	k_T*10^4 (dm^3/min.mg)	q_o (mg/g)	k_T*10^4 (dm^3/min.mg)	q_o (mg/g)
PAC2	5.826	101.59	4.129	122.69	1.776	132.39
F400	5.980	108.10	3.196	110.52	1.599	185.02

4.5 Effect of empty bed contact time (EBCT)

Figure 6 depicts the operating line for the adsorption of MB onto PAC2 as a plot of the adsorbent exhaustion rate against EBRT at various adsorbent bed heights. It can be seen from the Figure 6 that the adsorbent exhaustion rate decreased with increasing EBRT.

Table 4 shows the data of variable bed depth at a fixed flow rate (2 ml/min) in a fixed-bed column (3mm) for the removal of MB onto PAC2. The data in Table 4 shows that EBRT, Vb and Tb increased with increasing bed depth. It is clear that when the EBRT increases with a fixed flow rate, the bed volume will have to be larger, thus allowing more solution to be treated but resulting in a lower adsorbent exhaustion rate.
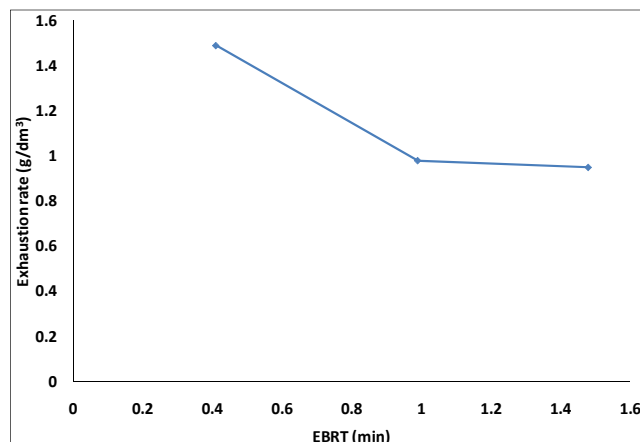

Figure 6. Operating time depicting the influence of bed height for the adsorption of MB onto PAC2 Temperature = 20°C, concentration =100 ppm, flow rate = 2 cm^3/min, column diameter = 3 mm, size = 106-180 μm and pH=7

Table 4. Data of variable bed depth at a fixed flow rate in a fixed-bed column for the removal of MB onto PAC2

Bed Depth (Z) (cm)	Bed Volume (V) (cm³)	Mass Of Adsorbent (M) (g)	EBRT (min)	V_b (dm³)	T_b (h)	Adsorbent Exhaustion Rate (g/dm³)
2.90	0.820	0.1	0.41	0.069	0.57	1.49
7.00	1.980	0.2	0.99	0.204	1.70	0.98
10.5	2.968	0.25	1.48	0.262	2.18	0.95

5. Conclusion

Several microcolumn tests were conducted to study the performance of PAC2 and F400 for the removal of basic dyes; MB, BR and BY from aqueous solution under different experimental conditions. It can be concluded that physical activation process was successful in producing activated carbon (PAC2) with good physical characteristics as indicated by the effective performance in column adsorption processes. The data from microcolumns confirm the observations of researchers using larger scale columns and this indicates the feasibility of the replacement of large columns by microcolumns in preliminary tests before implementing full scale column operation. This can save time, materials and effort which are advantageous from an economic point of view. Another advantage is that all the difficulties encountered in running large columns (channeling and high pressure drop) can be overcome by using the smaller microcolumn. Decreasing initial dye concentration, and adsorbent particle size and increasing column diameter enhanced the column performance and resulted in an increase in the time needed to saturate the adsorbent bed and a consequent increase in the volume throughput. This indicates the significant role of the experimental conditions on the adsorption processes in columns and on the resulting shape of the breakthrough curve. Comparing the performance of F400 with that of PAC2 at the same experimental conditions, F400 is more effective for the removal of MB and BY from aqueous solution using fixed-bed adsorber. This behaviour suggests that the physical characteristics (surface area and pore structure) are more highly involved in the adsorption processes of MB and BY onto F400 and PAC2. On the contrary, higher BR uptake was achieved in the case of PAC2 than that in the case of F400 which would indicate that surface chemistry might be involved in the adsorption process. The Empty Bed Residence Time (EBRT) model which optimizes the empty bed residence time and the sorbent utilization rate was successfully applied.

References

[1]   McKay, G. and Bino, M.J. Fixed Bed Adsorption for the Removal of Pollutants from Water. Environmental Pollution 1990, 66, 33-53.
[2]   Li, F., Yuasa, A., Ebie, K., and Azuma, Y. Microcolumn Test and Model Analysis of Activated Carbon Adsorption of Dissolved Organic Matter after Pre-coagulation: Effect of pH and Pore Size Distribution. J. Colloid and Interface Sci. 2003, 262, 331-341.
[3]   Faust, S.D. and Aly, O.M. Chemistry of Water Treatment. 2nd edn., Ann Arbor Press, INC. Michigan, 1998.
[4]   Aksu, Z. and Gönen F. Biosorption of Phenol by Immobilized Activated Sludge in a Continuous Packed Bed: Prediction of Breakthrough Curves, Process Biochemistry 2004, 39, 599-613.
[5]   Thomas, W.J. and Crittenden, B. Adsorption Technology and Design,. 1st edn., Butterworth-Heinemann, Oxford, 1998.
[6]   Chern, J.M. and Huang, S.N. Study of Non-Linear Wave Propagation Theory. 1. Dye Adsorption by Activated Carbon, Ind. Eng. Chem. Res. 1998, 37, 253-257.
[7]   Walker, G. and Weatherley, L. Adsorption of Acid Dyes on to Granular Activated Carbon in Fixed Beds, Wat. Res. 1997, 31(8), 2093-2101.
[8]   Liu, K.T. and Weber, W.J. Characterization of Mass Transfer Parameters for Adsorber Modeling and Design, J. WPCF 1981, 53(10), 1541-1550.
[9]   Mathialagan, T. and Viraraghavan, T. Adsorption of Cadmium from Aqueous Solution by Perlite, J. Hazardous Materials B 2002, 94, 291-303.
[10]   Perrich, J.R. Activated carbon adsorption for wastewater treatment. Boca Raton: CRC Press, 1981.
[11]   McKay, G. and Bino, M.J. Simplified optimization procedure for fixed bed adsorption systems. Water, Air, Soil Pollution 1990, 51, 33-41.

[12] Negrea, L., Lupa, M. And Negrea, P. Experimental and Modelling Studies on As(III) Removal from Aqueous Medium on Fixed Bed Column. Chemical Bulletin of "Politehnica" University of Timisoara, ROMANIA Series of Chemistry and Environmental Engineering 2011, 56(70), 2.

[13] Guo, H., Stüben, D., Berner, Z. A. and Kramar, U. Adsorption of arsenic species from water using activated siderite-hematite column filters. Journal of Hazardous Materials 2007, 151, 628-635.

[14] McKay, G. Adsorption of Dyestuffs from Aqueous Solutions with Activated Carbon I: Equilibrium and Batch Contact-Time Studies. J. Chem. Technol. Biotechnol. 1982, 32, 759-772.

[15] Murray, M. Adsorption and Desorption of Basic Dyes in the Aqueous Phase. PhD Thesis, Queen's University Belfast, 1995.

[16] Walker, G. and Weatherley, L. COD Removal from Textile Industry Effluent: Pilot Plant Studies. Chem. Eng. J. 2001, 84, 125-131.

[17] Walker, G. and Weatherley, L. Kinetics of Acid Dye Adsorption of GAC. Wat. Res. 1999, 33(8), 1895-1899.

[18] McKay, G. Blaire, H.S. and Gardner, J. The Adsorption of Dyes onto Chitin in Fixed Bed Columns and Batch Adsorbers. J. Applied Polymer Sci 1984, 29, 1499-1514.

[19] Ouvrard, S. Simonnot, M.O., de Donato, P. and Sardin, M. Diffusion-Controlled Adsorption of Arsenate on a Natural Manganese Oxide. Ind. Eng. Chem. Res. 2002, 41, 6194-6199.

[20] Al-Degs, Y.S., Khraisheh, M.A., Allen, S. and Ahmad, M.N. Effect of Carbon Surface Chemistry on the Removal of Reactive Dyes from Textile Effluents. Wat. Res. 2000, 34(3), 927-935.

[21] Al-Ghouti, M.A., Khraisheh, M.A., Allen, S. and Ahmad, M.N. The Removal of Dyes from Textile Wastewater: A Study of the Physical Characteristics and Adsorption Mechanisms of Diatomaceous Earth. J. Environmental Management 2033, 69, 229-238.

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