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Textile Wastewater Treatment Using Granular Activated Carbon Adsorption in Fixed Beds

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ABSTRACT

This work involved the treatment of industrial wastewater from a nylon carpet printing plant which currently receives no treatment and is discharged to sea. As nylon is particularly difficult to dye, acid dyes are required for successful coloration and cause major problems with the plant's effluent disposal in terms of color removal. Granular activated carbon Filtrasorb 400 was used to treat a ternary solution of acid dyes and the process plant effluent containing the dyes in a fixed-bed column system. Experimental data were correlated using the bed depth service time (BDST) model to previously published work by the authors for single dye adsorption. The results were expressed in terms of the BDST adsorption capacity, in milligrams of adsorbate per gram of adsorbent, and indicated that there was a 12–25% decrease in adsorption capacity in the ternary system compared to the single component system. This reduction has been attributed to competitive adsorption occurring in the ternary component system. Dye adsorption from the process plant effluent showed an approximate 65% decrease in adsorption capacity compared to the ternary solution system. This has been attributed to interference caused by the other colorless textile effluent pollutants found in the process wastewater. A chemical oxygen demand analysis on these components indicated that the dyes accounted for only 14% of the total oxygen demand.

Key Words. Adsorption; Dyestuffs; Activated carbon; Textile process effluent; Bed depth service time model

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INTRODUCTION

In the design of industrial adsorption towers the effect of many process parameters need to be quantified. The effect of effluent flow rate, effluent concentration, and adsorbent particle size have been investigated in pilot scale adsorption towers by many researchers (1, 2). The effluents used in these systems were simulated effluents from process industries containing single component adsorbates including dyes (3), metal ions (4), and trace organic compounds (5). Little research has been published to date on the effect of multicomponent adsorption in fixed-bed systems (6) and in particular on actual process effluents containing not only the target adsorbate species but numerous other pollutants associated with industrial effluent. This work attempts to redress this shortfall by comparison of dye adsorption from single solution, ternary solution, and actual textile industry effluent by use of the bed depth service time (BDST) analysis which offers a simple approach and rapid prediction of adsorber performance.

EXPERIMENTAL

Adsorbate Specifications

Tectilon Blue 4R-01 (TB4R)

TB4R is an acid anthraquinone dye manufactured by Ciba-Giegy and is supplied as in 50% liquid solution containing 40% 6-caprolactam. TB4R is miscible in water giving a pH of 6.0–7.5, yielding a royal blue color in aqueous solution, and has the Colour Index classification C.I. Acid Blue 277:1. The chemical structure of TB4R is shown in Fig. 1.

Tectilon Red 2B (TR2B)

TR2B is an acid monoazo dye manufactured by Ciba-Giegy and is supplied in 50% liquid solution and is miscible in water with a pH of 6.0–7.0. TR2B

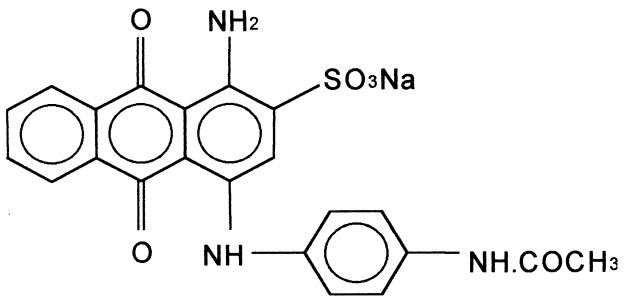

FIG. 1 Chemical structure of TB4R.

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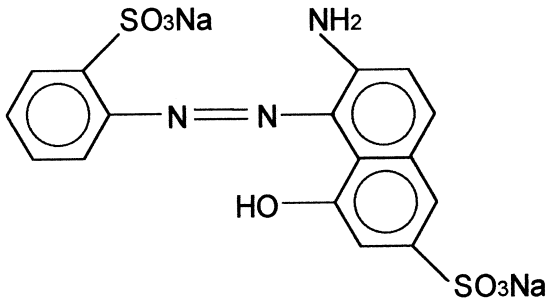

FIG. 2 Chemical structure of TR2B.

produces a dull blood red shade in aqueous solution and has the Colour Index classification C.I. Acid Red 361. The chemical structure of TR2B is shown in Fig. 2.

Tectilon Orange 3G (TO3G)

TO3G is an acid di-azo dye manufactured by Ciba-Giegy and is supplied in 33% liquid solution containing 2% of 2-(2-butoxyethelene)-ethanol and is miscible in water. TO3G has a neutral pH, produces a dull rusty orange shade in aqueous solution, and has the Colour Index classification C.I. Acid Orange 156. The chemical structure of TO3G is shown in Fig. 3.

The textile process effluent used in this work was taken from the discharge from a carpet printing plant in Northern Ireland and consisted of not only of a ternary solution of the three dyes but also a thickener (Guaranate), surfactants (Aphrogen, Verolan, Thiotan, Sand Acid), and finishing agents (Dyapol, Irgadypol) used in the dyeing process (see Table 1). All of these additives are not adsorbed on the nylon carpet and are therefore discharged from the plant in the aqueous effluent. The effluent contained 100 mg/L of the dyes in approximately equal concentrations; therefore, total dye concentration in the ternary solution was also taken as 100 mg/L for accurate comparison.

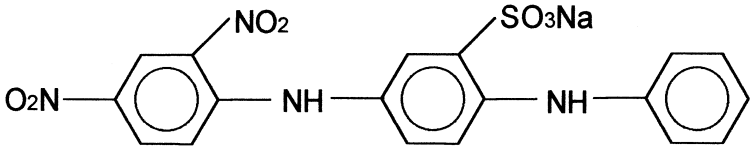

FIG. 3 Chemical structure of TO3G.

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TABLE 1
Composition and COD of Process Effluent

Component	Composition (mg/L)	COD (mg O_2/g)	COD (mg O_2/L effluent)
Tectilon Blue	33	1200	40
Tectilon Red	33	570	19
Tectilon Orange	33	603	20
Guaranate	44	1500	66
Aphrogen	67	1484	99
Dyapol	90	942	85
Irgadypol	110	1305	143
Sand Acid	67	272	18
Verolan	18	120	2
Thiotan	90	858	77

Adsorbent Specifications

The adsorbent used in this study was the granular activated carbon Filtrasorb 400. The adsorbent was washed in deionized water and sieved into 1000–1400 μm particle size range before contacting with the adsorbate solutions. The physical properties of the activated carbon are given in Table 2.

Experimental Procedure

The equipment used during these fixed-bed column studies is described by McKay and Bino (1) and Walker and Weatherley (3). It consisted of a 120-L PVC make-up tank in which aqueous dye solutions were formulated or the process effluent added. The solution was then gravity fed to a feed tank with a volume of 120 L and from which the effluent was pumped using a peristaltic pump at constant flow rate. The effluent solution was fed through a bed of GAC F400 in the up-flow mode.

TABLE 2
Physical Properties of GAC F400

Total surface area [N2 BET method ($m^2 \cdot kg^{-1}$)	$(1.05–1.20) \times 10^6$
Solid phase density ($kg \cdot m^{-3}$)	2100
Particle density (wetted in water) ($kg \cdot m^{-3}$)	1300–1400
Porosity	0.4
Iodine number	1000–1100
Methylene Blue Number	280–300

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The carbon beds were contained in Perspex columns of 25 mm (i.d.) diameter to which an end plate with an inlet nozzle was attached. The carbon bed was supported in the column by several layers of glass beads of various sizes located on a support plate, which ensured good liquid distribution. Each column had five 5 mm (i.d.) Perspex sample ports stoppered with an Suba-seal bung. This gave a standard bed height of 250 mm which resulted in beds with a carbon mass of approximately 75 g. Samples were drawn at regular time intervals from these ports using a syringe with a hypodermic needle capable of taking a sample from the center of the bed.

Carbon particles with diameters less than 150 μm were removed by wet sieving using distilled water. This ensured that fine particles would not block the needle of the syringe when samples were being taken. One of the most common causes of poor fixed-bed column performance is that the carbon is not deaerated prior to the adsorption test (3). If deaeration is not carried out, air pockets form in the column which can lead to channeling, increase in pressure drop, and premature breakthrough due to the air pockets, thereby reducing the surface available for mass transfer between the carbon and the solution. To counteract this problem, carbon particles were wetted for 24 hours in distilled water. They were then fed into the test column (which was also filled with water) as a slurry and allowed to settle for an additional 24 hours. The effect of process variables on bed performance was investigated. These included effluent flow rate, effluent concentration, and carbon particle size. Individual dye concentrations were determined using spectrophotometric analysis.

The optical absorption coefficient, k, for each dye was obtained by plotting dye concentration versus optical density using a Perkin-Elmer spectrophotometer. To achieve maximum absorbance and therefore a more accurate plot, k was determined for each dye at its maximum absorbance wavelength which for the three days in this study are TB4R 602 nm, TR2B 503 nm, and TO3G 385 nm. The correlation coefficients for these plots were excellent with $r^2 > .998$. For muticomponent systems with three dyes, with maximum absorbances λ_1, λ_2, and λ_3, respectively, each dye concentration can be calculated by measuring the optical density of each sample at λ_1, λ_2, and λ_3 using a standard matrix technique outlined by McKay and Al-Duri (7). The optical density of the nondye components in the plant effluent were found to have negligible optical density at the wavelengths and concentrations used in this study.

BED DEPTH SERVICE TIME MODEL

The BDST model is well established for dye adsorption in fixed-bed systems (3), therefore only a brief description is included. In the operation of fixed-bed adsorbers the objective is to reduce the concentration in the effluent so that it does not exceed a predefined breakthrough value, C_b. Initially, when

the activated carbon is unsaturated, the actual effluent concentration is lower than C_b, but as the effluent is pumped through the bed the carbon becomes saturated and the effluent concentration approaches C_b, i.e., the breakpoint is reached. The original work on the bed depth service time (BDST) model was carried out by Bohart and Adams (8), who proposed a relationship between bed depth, Z, and the time taken for breakthrough to occur. The service time, t, was related to the process conditions and operating parameters:

$$\ln\left(\frac{C_0}{C_b} - 1\right) = \ln(e^{K_a N 0 Z/F} - 1) - K_a C_0 t \tag{1}$$

Hutchins (9) proposed a linear relationship between the bed depth and service time:

$$t = \frac{N_0}{C_0 F} Z - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_b} - 1\right) \tag{2}$$

The critical bed depth, Z_0, is the theoretical depth of adsorbent sufficient to prevent the adsorbate concentration from exceeding C_b at $t = 0$. By letting $t = 0$, Z_0 is obtained from Eq. (2) by solving for Z. Since the exponential term is usually much larger than unity, the unity term within parentheses on the right-hand side of Eq. (1) is often neglected:

$$Z_0 = \left(\frac{F}{K_a N_0}\right) \ln\left(\frac{C_0}{C_b} - 1\right) \tag{3}$$

Equation (2) enables the service time, t, of an adsorption bed to be determined by a specified bed depth, Z, of adsorbent. The service time and bed depth are correlated with the process parameters and initial pollutant concentration, solution flow rate, and the adsorption capacity.

EXPERIMENTAL RESULTS AND DISCUSSION

Experimental data obtained from spectrophotometry analysis of samples taken from the fixed-bed columns are illustrated as breakthrough curves of dimensionless concentration versus volume of effluent treated in Figs. 4, 5, and 6. The breakthrough data of TR2B from the ternary solution, illustrated in Fig. 4, indicates that the curves do not follow the ideal "S" shape profile found with the adsorption of small molecular weight pollutants (1), but are shallow. This is indicative of a large adsorption zone within the bed and inefficient use of the adsorbent.

A comparison of breakthrough data of the three dyes in the ternary system is made in Fig. 5. The shape of the breakthrough curves for the three dyes is roughly the same, with a shallow gradient experienced at higher dimensionless concentrations. It can be seen that TB4R shows breakthrough before TR2B, followed by TO3G. These breakthrough data correlate with equilibrium adsorption

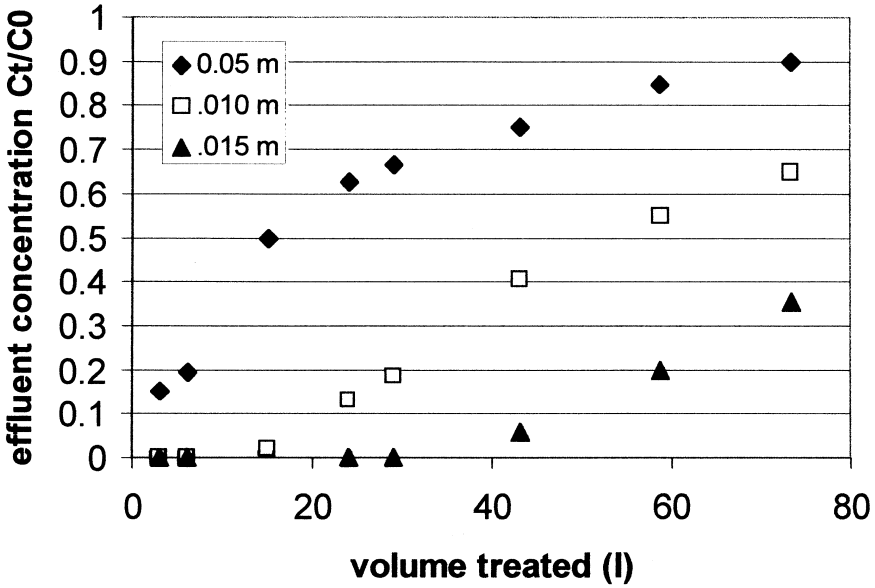

FIG. 4 Breakthrough data for TR2B in ternary solution with variation in bed height (flow rate = 0.01 L/min, dye concentration = 3 × 33 mg/L, particle size = 1000–1400 μm).

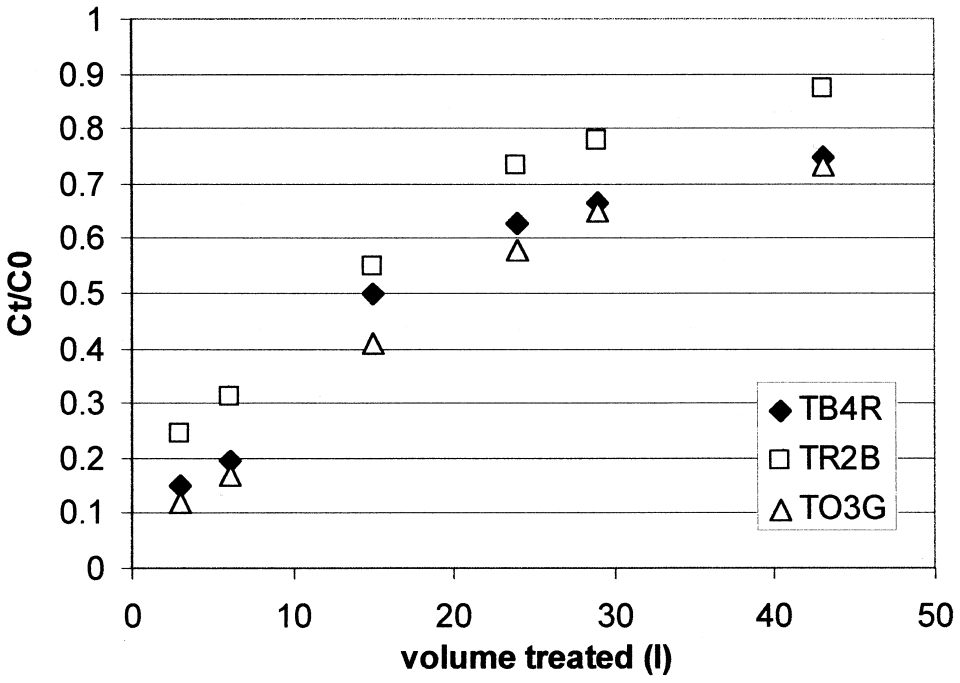

FIG. 5 Breakthrough data for dyes in ternary solution (bed height = 0.05 m, flow rate = 0.01 L/min, dye concentration = 3 × 33 mg/L, particle size = 1000–1400 μm).

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capacities of 537, 535, and 852 ($mg \cdot g^{-1}$) for TB4R, TR2B, and TO3G, respectively (3), in that a dye possessing a high adsorption capacity will show a long breakthrough time and relatively efficient use of carbon in column systems.

The breakthrough data plotted in Fig. 6 show the effect on breakthrough of actual process effluent compared to the simulated ternary solution effluent for dye adsorption. The results indicate that the additional impurities found in the process effluent impair the adsorption of the TR2B dye. The dye breakthrough curve for the process effluent breaks through much more quickly than that of the ternary dye solution. Furthermore, the gradient of the process effluent breakthrough curve is steeper, with high dimensionless concentrations reached at low effluent volumes treated. Similar results were observed for the adsorption of TB4R and TO3G from the process effluent.

BDST analysis was applied to the data from the breakthrough curves with examples of this analysis illustrated in Figs. 7 and 8. The breakthrough was set at a dimensionless concentration of 0.2, with the breakthrough data producing a directly proportional relationship between bed service time (to breakthrough) and bed height. Figure 7 illustrates a BDST plot comparison for the three dyes in the ternary solution with the slope of the plot indicative of bed performance, i.e., the steeper gradient for the linearization of the TO3G data results from a higher throughput for breakthrough at a given bed height. A similar BDST analysis was applied to dye adsorption from the process effluent, and a comparison with dye adsorption from ternary solution is illustrated in Fig. 8 for

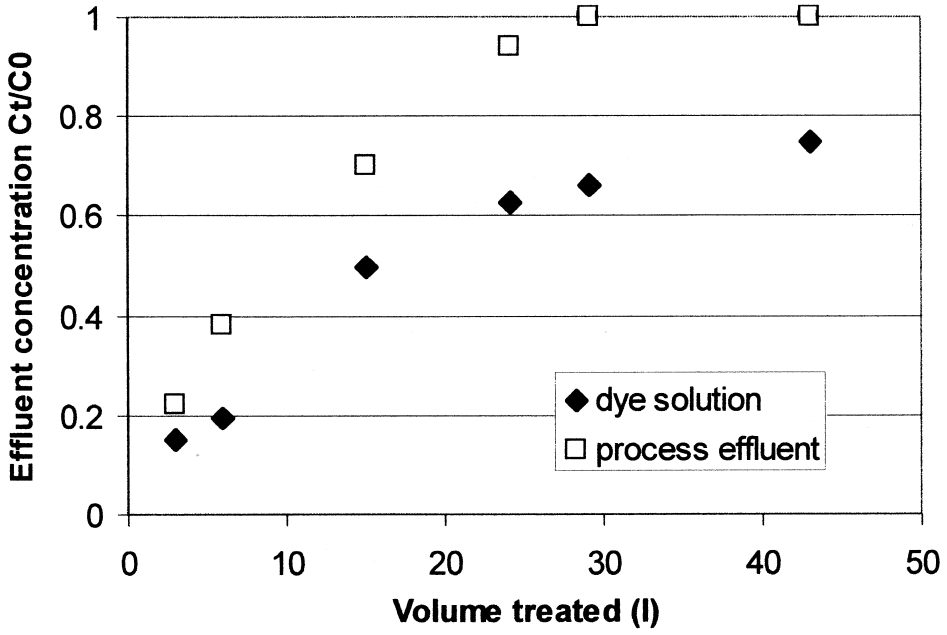

FIG. 6 Breakthrough data for TR2B in dye solution and in process effluent (bed height = 0.05 m, flow rate = 0.01 L/min, dye concentration = 3 × 33 mg/L, particle size = 1000–1400 μm).

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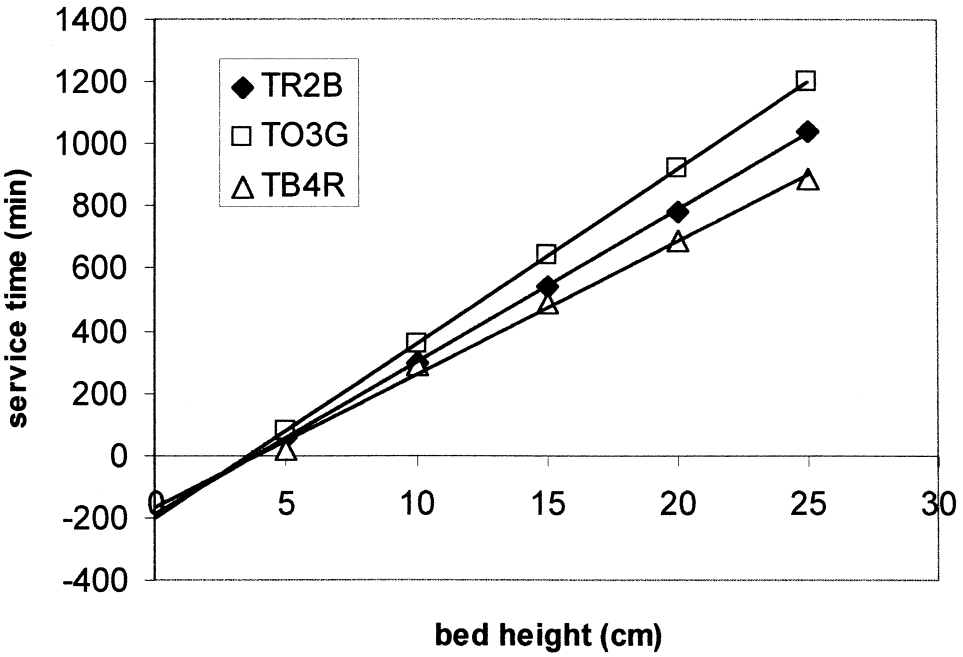

FIG. 7 BDST plot for dyes in ternary solution (flow rate = 0.01 L/min, dye concentration = 3 × 33 mg/L, particle size = 1000–1400 μm, breakthrough = 20%).

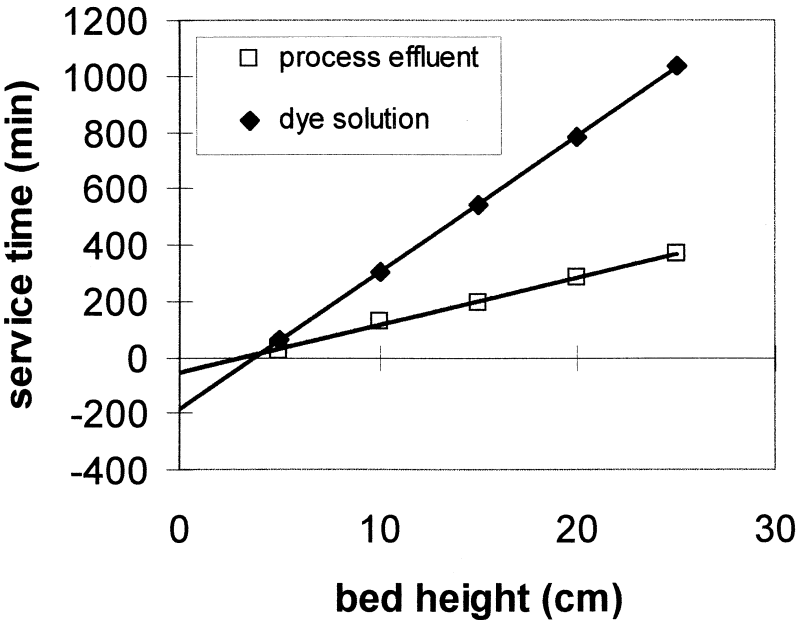

FIG. 8 BDST plot for TR2B in dye solution and in process effluent (flow rate = 0.01 L/min, dye concentration = 3 × 33 mg/L, particle size = 1000–1400 μm, breakthrough = 20%).

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TABLE 3
BDST Constants for Dyes in Ternary Mixture (flow rate = 0.01 L/min, dye concentration = 3 × 33 mg/L, particle size = 1000–1400 μm, breakthrough = 20%)

Dye	N_0 (mg·g^{-1})	K_a (L·mg^{-1}·min^{-1})	Z_0 (cm)	r^2
TB4R	25.4	2.07×10^{-5}	4.33	0.992
TR2B	25.9	2.33×10^{-5}	3.75	0.999
TO3G	30.3	2.10×10^{-5}	3.57	0.999

TR2B. This indicates a marked decrease in dye adsorption with the process effluent system compared to the ternary solution. Best fit lines through the data in the BDST plots were used to calculate the BDST adsorption capacity (N_0), the BDST adsorption rate (K_a), and the critical bed height (Z_0).

The BDST constants are correlated in Tables 3–6. Table 3 shows the constants for dye adsorption from the ternary dye solution system with the adsorption capacity (N_0), approximately 25–26 mg/g for TB4R and TR2B but significantly higher (approximately 30 mg/g) for TO3G. These results show good correlation with the equilibrium adsorption capacities described earlier. The adsorption rate constant, K_a, was similar for all three dyes in the ternary system at approximately 2.0–2.3 × 10^5 L·mg^{-1}·min^{-1}. The critical bed height, Z_0, increased from TO3G to TR2B to TB4R, which correlated from the observed results from the breakthrough curves. The linearization of the BDST data resulted in a correlation coefficient, r^2, of at least .992 in the ternary dye system, indicating excellent fit to the BDST model.

BDST constants for the adsorption of dyes from the process effluent are given in Table 4. A significant decrease in the adsorption capacity, N_0, was noted, reducing to approximately one-third the ternary solution capacity for each of the dyes. TO3G adsorption from the process effluent was again found to be better than for the other two dyes, although its relative advantage was di-

TABLE 4
BDST Constants for Dyes in Process Effluent (flow rate = 0.01 L/min, dye concentration = 3 × 33 mg/L, particle size = 1000–1400 μm, breakthrough = 20%)

Dye	N_0 (mg·g^{-1})	K_a (L·mg^{-1}·min^{-1})	Z_0 (cm)	r^2
TB4R	9.20	6.00×10^{-5}	4.12	0.989
TR2B	9.20	7.41×10^{-5}	3.33	0.972
TO3G	10.3	6.63×10^{-5}	3.33	0.989

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minished. Results for the adsorption rate constant, K_a, were approximately three times higher for each dye in the process effluent adsorption than for the ternary solution adsorption. It was also noted that the correlation coefficient, r^2, was lower in dye adsorption from process effluent than from ternary solution.

The high adsorption rate constants found in adsorption from the process effluent is a direct result of the higher value of the ordinate intercept in the BDST plot, see Fig. 8. From this plot it can be seen that, at relatively constant critical bed height, systems showing increased fixed-bed adsorption will have a lower intercept and thus a lower adsorption rate constant, i.e., $K_a \propto 1/-C$. The term "adsorption rate constant" is therefore misleading and has no physical meaning; it was difficult to correlate in this work.

The BDST adsorption capacity, N_0, however, provides a convenient way of describing adsorber performance, with high performance and efficient use of adsorbent characterized by high BDST adsorption capacities. In this study the usual units of N_0 kilograms of adsorbate per cubic meter of adsorbent have been recalculated using the bulk density of the adsorbent to provide an adsorption capacity in terms of milligrams of adsorbate per milligram of adsorbent. Using this analysis, comparisons can then be made with equilibrium capacities for each system and thus provides a useful characterization of fixed-bed adsorber performance.

Results of such an analysis are provided in Table 5 as percentage of equilibrium capacity (Langmuir monolayer capacity) for single component, ternary component, and process effluent adsorption. Results for the single component adsorption were exprapolated from data from Walker and Weatherley (3) for identical adsorbate flow rates and concentrations and adsorbent particle size, see Table 6. Due to kinetic effects, notably intraparticle diffusion, the solid phase concentration in the column is less than the equilibrium capacities. However, a comparison of the results indicates that the highest level of adsorption, at 20% breakthrough, was achieved in the single component systems with a 12–25% decrease in adsorption capacity in the ternary so-

TABLE 5
Percentage of Equilibrium Capacity for Dyes in Single Component, Ternary Component, and Process Effluent (flow rate = 0.01 L/min, dye concentration = 3 × 33 mg/L, particle size = 1000–1400 μm, breakthrough = 20%)

Dye	Single component	Ternary component	Process effluent
TB4R	5.3%	4.7%	1.7%
TR2B	5.7%	4.8%	1.7%
TO3G	4.5%	3.6%	1.2%

TABLE 6
BDST Capacity, N_0 for Single Component Dyes: Extrapolated from Walker and Weatherley (3) (flow rate = 0.01 L/min, concentration = 33 mg/L, particle size = 1000–1400 μm, breakthrough = 20%)

Dye	Langmuir capacity ($mg \cdot g^{-1}$)	N_0 ($mg \cdot g^{-1}$)
TB4R	537	28.4
TR2B	535	30.3
TO3G	852	38.7

lution system. This reduction is not uncommon is multisolute adsorption systems and can be attributed to competitive sorption within the carbon micropore structure (7).

The comparison between the ternary solution and process effluent adsorption capacity for the dyes shows a highly significant reduction in capacity of 64–67% with the process effluent. This deterioration is due to the high loading of the process effluent with colorless adsorbable agents used in the dyeing industry; thus, a significantly higher degree of competitive adsorption was found in this case. A chemical oxygen demand analysis on the process effluent indicated an oxygen demand of 569 mg O_2/L of which the dyes accounted for 79 mg O_2/L (approximately 14%), see Table 1.

CONCLUSIONS

The BDST adsorption capacity, expressed in this work in terms of milligrams of adsorbate per gram of adsorbent, is a readily usable tool for comparison of fixed-bed adsorption systems. Furthermore, it can easily be compared to the equilibrium adsorption capacity to establish the efficiency of fixed-bed adsorption. A comparison of the single and ternary component data indicates that a degree of competitive adsorption takes place in the ternary component system with the overall adsorption capacity reduced by approximately 20%. Comparison of dye adsorption from the ternary solution to that of the process effluent showed the effect of other textile effluent pollutants on dye uptake. This reduction in adsorption capacity was found to 65% and resulted in a very short bed operating life with the process plant effluent. The thickeners, surfactants, and finishing agents found in the effluent contribute significantly (86%) to the higher COD found in the process effluent compared to the ternary dye solution. From this we can conclude that these colorless pollutants not only adversely affect the adsorption of the colored component in the effluent, but are a significant effluent disposal problem in their own right.

NOMENCLATURE

C_0 initial dye concentration ($kg \cdot m^{-3}$)
C_b breakthrough dye concentration ($kg \cdot m^{-3}$)
C_x abcissal intercept in BDST plot (min)
F linear flow rate ($m \cdot s^{-1}$)
K_a BDST adsorption rate constant ($m^3 \cdot kg^{-1} \cdot s^{-1}$)
N_0 BDST adsorption capacity ($kg \cdot m^{-3}$)
Z bed height (m)
Z_0 critical bed height (m)

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