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Removal of basic dyes from aqueous environment in single and binary systems by sugarcane bagasse in a fixed-bed column

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ABSTRACT

The ability of natural sugarcane bagasse in the removal of Basic Blue 3, Methylene Blue and Basic Yellow 11 in both single and binary system from aqueous solutions was studied. Important parameters such as influent concentration, flow rate and sorbent dosage were investigated. Results revealed that the breakthroughs were influent concentration, flow rate and bed height dependent. Increase in influent concentration and flow rate resulted in faster breakthrough while increase in column height yielded longer service time. The sorption data were applied to the Thomas, Belter and Chu, and bed-depth service time (BDST) model. Theoretical breakthrough curves generated using Chu model agreed closely with the experimental values for all the dye systems under studied. In the regeneration study, BB3 dye could be recovered almost quantitatively by eluting the column with 0.1 M HCl and the column could be used repeatedly for at least 3 cycles.

Keywords: Sorption; Desorption; Column Regeneration; Column study; Sugarcane bagasse; Basic dyes

1. Introduction

Synthetic dyes have been widely used in every industry to color their products. Total world colorant production is estimated to be 800,000 tons per year, however at least 10% of the used dyestuff enters the environment through wastes [1,2]. This type of pollutant is aesthetically unpleasant because it is highly visible even at low concentration [3]. Besides, dyes are generally difficult to degrade as they are relatively stable to light and oxidizing agents, and are resistant to aerobic digestion. Hence, the increasing discharge of dyes to the environment has caused great concern.

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Adsorption with activated carbon is widely used to remove dyes in many industries due to its high adsorptive capability. However, disadvantages such as prohibitively expensive and problems with regeneration of the spent carbon has prompted the growing research interest in the development of low-cost sorbents from a large variety of biological, agricultural and industrial by-products.

Various non-conventional and low cost materials have been studied for the removal of dyes from aqueous solution. These include orange peel, rice husk, sugarcane bagasse, pineapple stem, spent tea leaves and wheat straw [4–11].

The sorption data obtained from batch studies are useful in providing information about the effectiveness of the sorption process; they are, however, generally not applicable under continuous flow conditions in which the contact time is not long enough to attain equilibrium. Therefore, this current study has been undertaken under the continuous flow conditions which are more useful in large scale water treatment. The sorption performance of sugarcane bagasse in the removal of Basic Blue 3 (BB3), Methylene Blue (MB) and Basic Yellow 11 (BY11) was studied in both single and binary systems under various conditions.

2. Materials and methods

2.1. Preparation of sorbent

Sugarcane bagasse was collected and cut into small pieces. Then the bagasse was boiled for 3 h to remove the sugar residue within it. It was rinsed several time with tap water and dried overnight at 60°C. The dried bagasse was ground and sieved through a 3 mm sieve and labeled as NSB.

2.2. Preparation of dye solutions

Synthetic dye solutions of BB3, MB and BY11 were the sorbates used in this study. The cationic dye BB3 (C.I. = 378011, 25% dye content), MB (C.I. = M9140, 82% dye content) and BY11 (C.I. = B7133, 20% dye content) were used without further purification. All synthetic dyes used in this study were purchased from Sigma-Aldrich Pte. Ltd. (United States of America). The binary dye solutions were obtained through the mixing of BB3 and BY11 or MB and BY11. Standard dyes solutions of 1000 mg/l were prepared as stock solutions and subsequently diluted when necessary.

2.3. Column studies

Column studies were performed using a glass column of 1.0 cm internal diameter. NSB was packed into the glass column and covered with a thin layer of sulphuric acid washed sand to prevent it from floating. Distilled water was run through the column prior to the dye solutions to achieve hydraulic equilibrium. It was then fed with dye solution and the eluants were collected at 10 ml fractions. The flow rate of the eluant was controlled by using a peristaltic pump. For the effect of flow rate on the sorption of dyes, it was studied by using the flow rate of 7, 10, and 15 ml/min. The effect of different influent concentrations of the breakthrough curve was investigated by varying the dye concentration from 5 to 20 mg/l. As for the effect of bed depth on dyes sorption, it was tested by packing the column to 12, 18 and 24 cm, corresponding to 0.50, 0.75 and 1.00 g of NSB, respectively. The concentration of dye in solution was determined using a Perkin Elmer Lambda 35 UV-vis spectrophotometer. All measurements were made at the wavelength corresponding to maximum absorption; for BB3, $\lambda_{max} = 654$ nm, MB, $\lambda_{max} = 664$ nm and for BY11, $\lambda_{max} = 412$ nm. Dilutions were made when measurements exceeded the linearity of the calibration curves.

2.3.1. Sorption-desorption study

To study the sorption-desorption process, 1 l of 10 mg/l of single dye solution was passed through a column of 11.8 cm bed depth with 2.0 g of NSB at a flow rate of 10 ml/min. After the sorption process, the BB3 loaded column was eluted with 0.1 M HCl, at a flow rate of 1 ml/min. Fifty fractions of eluants were collected at the flow rate of 1 ml/min and analyzed for their dye concentrations. The eluted column was then washed thoroughly with distilled water to remove excess acid before being used for the next sorption/desorption cycle.

3. Results and discussion

3.1. Effect of flow rate

The effect of flow rate on the breakthrough curves of single BB3 at flow rate of 7.0–15.0 ml/min and a fixed bed of 12 cm are shown in Fig. 1. With the introduction of the same influent concentration, the results showed that breakthrough occurs faster as the flow rate increased. An early breakthrough was observed at highest flow rate (15 ml/min), meanwhile the lowest flow rate (7 ml/min) exhibited a longer retention time. With lower flow rate,

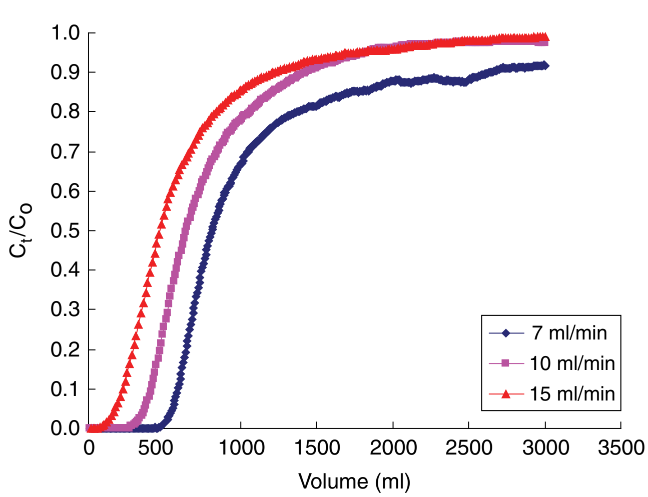

Fig. 1. Breakthrough curves of BB3 in single dye solution at different flow rates with the bed depth of 12 cm and influent concentration of 10 mg/l.

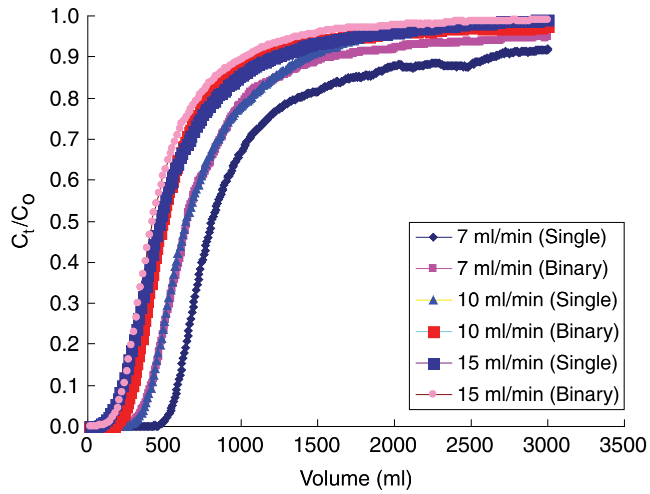

Fig. 2. Comparison of breakthrough curves of BB3 in single and binary dye solution at different flow rates with the bed depth of 12 cm and influent concentration of 10 mg/l.

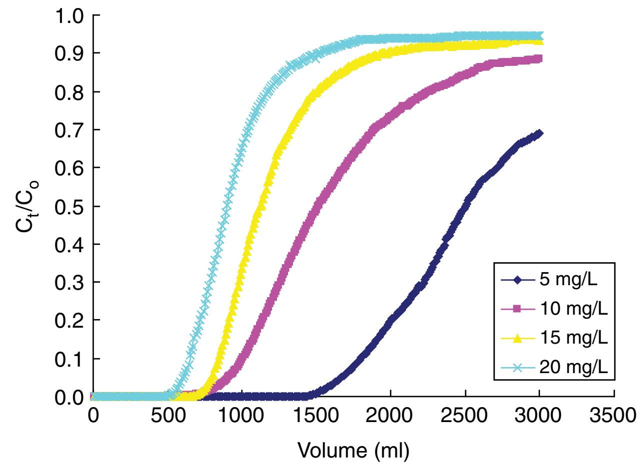

Fig. 3. Breakthrough curves of MB in single dye solution at different influent concentrations and at a flow rate of 10 ml/min with bed height of 24 cm.

the contact time between the sorbent and sorbate will be longer, thus more sorbate can be retained within this interaction period [12–14]. In addition, the breakthrough time needed to achieve saturation decreased at higher flow rate. This phenomenon might be attributed to the lower diffusion effects with the increasing flow rate. Therefore, lower flow rates were desirable for effective dye removal in column mode. Similar trend was observed for the other single dye systems.

Fig. 2 shows the comparison of breakthrough curves between the single and binary BB3 dye solution. A faster breakthrough was observed in all the binary dye systems and this phenomenon can be explained by the competition of two different dyes for the available binding sites. Similar trend was observed in all the binary dye systems within the scope of this study.

3.2. *Effect of influent concentration*

Fig. 3 shows the effect of influent concentration for the sorption of single MB onto NSB at various concentrations. Overall, the breakthrough time increased with decreasing of dye concentration for all studied systems. The breakthrough curve shifted to left and steeper breakthrough curve was obtained as the dye concentration increased.

The driving force for sorption is actually the concentration difference between the solute on the sorbent and the solute in the solution [15]. Therefore, with the introduction of lower influent concentration, this will cause a delay in breakthrough curve due to the reduced transport of dye at lower concentration gradient. With increasing influent concentration, the dye loading rate will be higher, leading to a greater driving force for mass transfer which in turn results a decrease in the sorption zone length [16]. This shows that both saturation rate and breakthrough time are concentration gradient dependent process. Similar observation was observed for all the studied single dye solutions.

A comparison of breakthrough curves between single and binary dye solutions (Figs. 4–6) all exhibited the same trend, which is a faster breakthrough time in all the binary dye solutions. This phenomenon indicates the competition for available sorption sites by two different kinds of dyes.

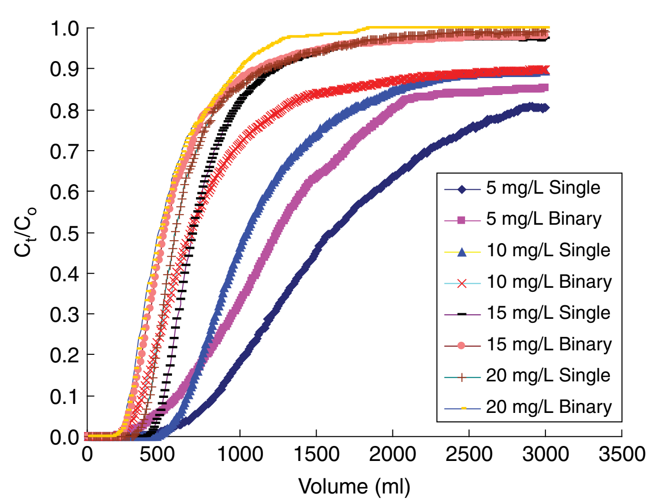

Fig. 4. Comparison of breakthrough curves of BB3 in single and binary dye solution at different influent concentrations and at a flow rate of 10 ml/min with bed height of 24 cm.

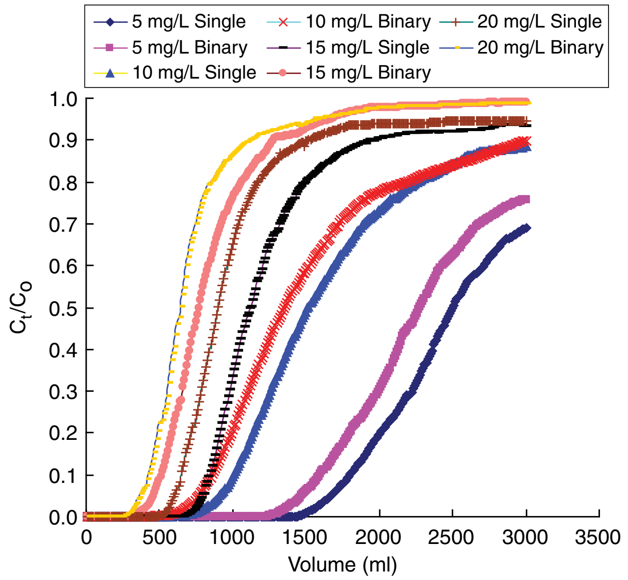

Fig. 5. Comparison of breakthrough curves of MB in single and binary dye solution at different influent concentrations and at a flow rate of 10 ml/min with bed height of 24 cm.

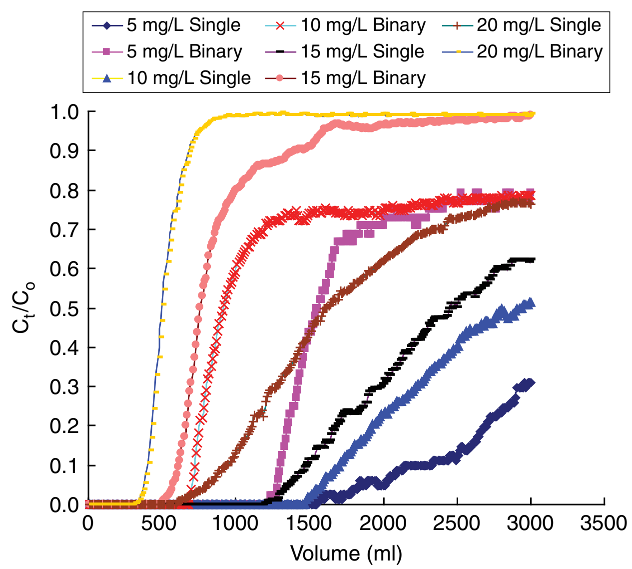

Fig. 6. Comparison of breakthrough curves of BY 11 in single and binary BB3-BY11 dye solution at different influent concentrations and at a flow rate of 10 ml/min with bed height of 24 cm.

3.3. Effect of bed height

The breakthrough curves of BB3 in Fig. 7 show that the higher the bed height, the longer the service time before breakthrough occurred. This result can be due to the increase in the availability of the sorption sites as well as the contact time of dye cations with the sorbent. The increment in the axial dispersion of the dye over the column with increasing bed height would be beneficial for dye removal in column mode [17]. Similar observation was reported in the removal of Acid Blue 92 and Basic Red 29 using non-conventional sorbent [12].

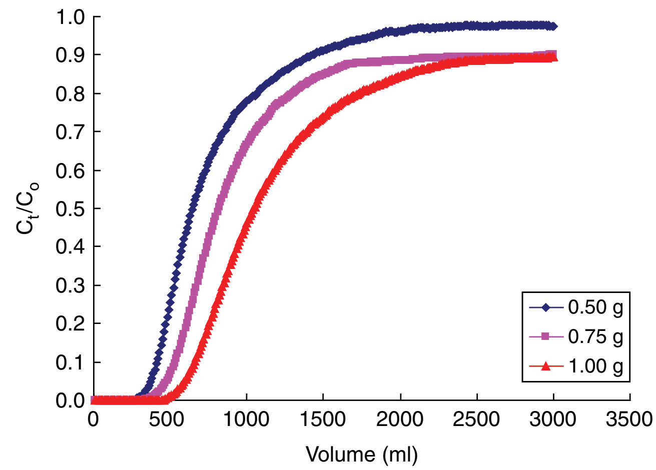

Fig. 7. Breakthrough curves of BB3 in single dye solution at different bed depths at flow rate of 10 ml/min and influent concentration of 10 mg/l.

3.4. Thomas model

Thomas model was used to calculate the sorption rate constant and the solid phase concentration of the dye on the sorbent from the continuous mode studies. Thomas model is one of the most widely used kinetic models to evaluate column performance. The Thomas model equation can be expressed as:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left[\left(k_{\mathrm{Th}} / \upsilon\right) \times \left(q_0 x - C_0 V_{\mathrm{eff}}\right)\right]} \quad (1)$$

where, C_t is effluent concentration at t (mg/l); C_0 is influent dye concentration (mg/l); k_{Th} is Thomas rate constant (ml/min mg); q_0 is equilibrium dye uptake per g of sorbent (mg/g); x is amount of sorbent (g); V_{eff} is effluent volume (ml); υ is flow rate (ml/min).

Table 1 shows the Thomas model constants for all the studied dyes. For single BB3, the bed capacity, q_0 and the Thomas rate constant, k_{Th}, increased as the influent concentration increased. The increasing k_{Th} indicated that overall system kinetics was dominated by external mass transfer [18]. The increase in q_0 indicated that the driving force for biosorption was the difference between the dye on the sorbent and the dye in solution [19]. Therefore, higher influent concentration causes higher driving force gave better column performance. As the flow rate increased, the k_{Th} increased while the q_0 decreased. Meanwhile, as the bed height increased, both q_0 and k_{Th}

Table 1
Calculated constants of Thomas model at different conditions using non-linear regression analysis for single BB3

C_0 (mg/l)	υ (ml/min)	Z (cm)	k_{Th} (ml/min mg)	q_0 (mg/g)	R^2
10	10	24	2.868	1.167	0.967
20	10	24	3.538	1.246	0.987
10	7	12	2.680	2.656	0.959
10	10	12	4.912	1.433	0.983
10	15	12	7.449	0.705	0.981
10	10	18	3.938	1.206	0.972

decreased. Thus, lower flow rate and higher influent concentration would increase the sorption of BB3 on NSB column. Similar observation was obtained for Single MB, Binary BB3 and Binary MB. The k_{Th} and q_0 for Single BY11 does not show any trend. This might be due to the shape of the breakthrough which does not exhibit a complete S-curve within the studied time frame.

The breakthrough capacity of MB calculated based on column mode was 24.08 mg/g, which was lower as compared to the batch sorption capacity, 28.25 mg/g [20]. This decrease is usually observed and generally attributed to relatively less contact time between the sorbent and sorbate surface in column study [21]. Table 2 shows the comparative uptake of MB by various low cost sorbents. It was observed that the MB sorption capacity of NSB was comparable with other low cost sorbents.

3.5. The Belter and Chu models

The two parameter fixed bed sorption model and two subsequent modifications by Chu (Eq. 3) were used to fit the data obtained from the fixed bed systems [28].

Table 2
Comparative uptake of MB by various sorbents

Sorbents	Sorption capacity, q_0 (mg/g)	Reference
Neem leaf powder	8.76	[22]
Banana peel	20.80	[23]
Orange peel	18.60	[23]
Lemon peel	29.00	[24]
Cereal chaff	20.30	[6]
Yellow passion fruit waste	44.70	[25]
Marine seaweed (*Caulerpa racemosa*)	5.23	[26]
Pospalum notatum	31.00	[24]
Dead *Streptomyces rimosus*	34.30	[27]
Natural Sugarcane Bagasse	24.08	Present study

The Belter and Chu models were based on following equations Belter model:

$$\frac{C_t}{C_0} = \frac{1}{2}\left(1 + \mathrm{erf}\left[\frac{t - t_{0.5}}{\sqrt{2}\sigma t_{0.5}}\right]\right) \tag{2}$$

Chu model:

$$\frac{C_t}{C_0} = \frac{1}{2}\left(1 + \mathrm{erf}\left[\frac{(t - t_{0.5})(\exp(\pm\sigma(t / t_{0.5})))}{\sqrt{2}\sigma t_{0.5}}\right]\right) \tag{3}$$

where, C_t is effluent concentration (mg/l); C_0 is influent concentration (mg/l); t is time (min); i is standard deviation; erf(x) is effort function of x.

By evaluating $t_{0.5}$ and σ from the experimental column, correlation may be defined, therefore allows the prediction of these two parameters resulting theoretical breakthrough curve data at untested conditions [29]. Belter model was capable of modeling only symmetric curves employing two parameters, σ and $t_{0.5,}$ empirically correlated with the process factors. Meanwhile, in Chu model (with + and – sign), this enables the modeling of both symmetric and non-symmetric curves with no additional parameters. The advantage of equation proposed by Chu is that they can fit breakthrough curves obtained from the systems, where either mass transfer limitation or flow non-idealities exist [30].

The theoretical breakthrough curves generated by both models for single BB3 were compared with the experimental breakthrough curves (Fig. 8). The result indicates a better applicability of Chu model with negative sign in exponential term than the other theoretical breakthrough

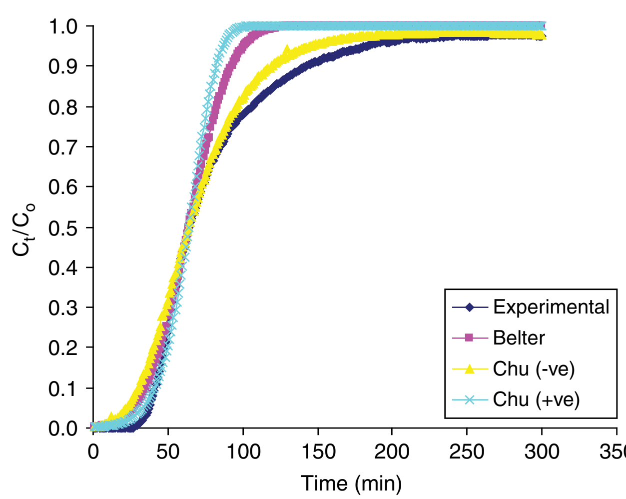

Fig. 8. Theoretical (Belter, Chu (-ve) and Chu (+ve) model) and experimental breakthrough curves of BB3 in single dye solution at a flow rate of 10 ml/min and influent concentration of 10 mg/l.

curves. Similar observation was observed in single MB, single BY11 and the both binary dye systems. Therefore, Chu model can be use as the basis for simplified scale-up design calculation for all the studied dye systems.

3.6. The bed-depth/service time analysis (BDST) model

The BDST model was based on physically measuring the capacity of the bed at different breakthrough values, and it works well and provides useful modeling equation for the changes of system parameters [16]. The modified form of equation which states that bed height and service time of a column carries a linear relationship and is expressed as below [31]:

$$t = \frac{N_0}{C_0 F} Z - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_t} - 1\right) \quad (4)$$

where, C_t is effluent concentration of solute in the liquid phase (mg/l); C_0 is initial concentration of solute in the liquid phase (mg/l); F is influent linear velocity (cm/min); N_0 is sorption capacity (mg/g); K_a is rate constant in BDST model (l/mg min); t is time (min); Z is bed depth of column (cm).

At 50% breakthrough $(C_0/C_t) = 2$, and $t = t_{0.5}$, the equation is reduced to:

$$t_{0.5} = \frac{N_0 Z}{C_0 F} \quad (5)$$

A linear plot of $t_{0.5}$ against bed depth (Z) passing through the origin can be obtained using the equation, provided that the sorption data follow the model. This is not the case in the present study although a linear relationship was obtained (Fig. 9). Similar deviation from the BDST model was reported in the sorption of Basic Blue 3 and Congo Red by ethylenediamine modified rice hull [13,32]. The nonconformity of the BDST model may due to the presence of more than one-limiting step in the sorption process [33].

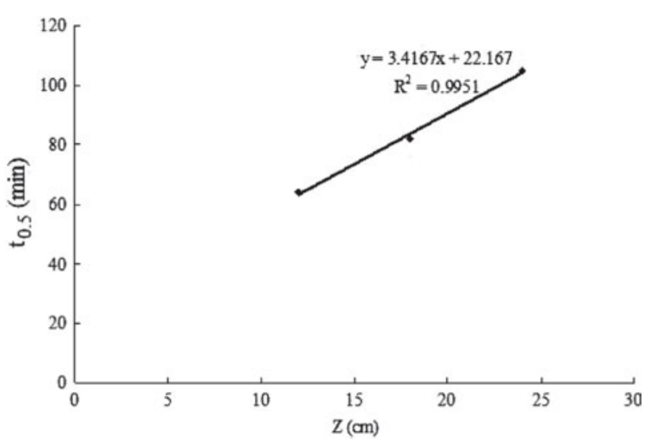

Fig. 9. BDST plots of BB3 in single dye solution at a flow rate of 10 ml/min and influent concentration of 10 mg/l.

The slope constant for a different flow rate can be calculated by equation below [34]:

$$a' = a\,\frac{F}{F'} = a\,\frac{\upsilon}{\upsilon'} \quad (6)$$

where a and F are the old slope and influent linear velocity, respectively and a' and F' are the new slope and influent linear velocity, respectively. Since the column used in this study had the same diameter, therefore the ratio of original (F) and the new influent linear velocity (F') are equal to the ration of original flow rate (υ) and the new flow rate (υ')

For other influent concentrations, the equation is given by a new slope and a new intercept:

$$a' = a\left(\frac{C_0}{C'_0}\right) \quad (7)$$

$$b' = b\left(\frac{C_0}{C'_0}\right)\left(\frac{\mathrm{In}(C'_0 - 1)}{\mathrm{In}(C_0 - 1)}\right) \quad (8)$$

where b' and b are the new and old intercept, respectively and C'_0 and C_0 are the new and old influent concentration, respectively. The prediction of sorbent performance at lower flow rate of 5 ml/min and influent concentration of 5 mg/l were shown at Table 3 and 4, respectively. The experimental and calculated data showed good agreement for all the studied systems. Therefore, the model and the constants evaluated can be used to scale up the process for other flow rate and influent concentration without further experimental run.

3.7. Column regeneration studies

The continuous usage of a sorbent material is a crucial factor determining its application potential. Regeneration of the sorbent was often done by using eluting agent. The eluting agent used must not cause damages on the capacity of the sorbent to ensure that the sorbent can be reuse several times. In addition, the regeneration process should also ensure that the eluted solution does not pose any disposal problem [35].

In order to evaluate the feasibility of using NSB for multiple sorption cycles, sorption and desorption processes were carried out. The result shows that a complete recovery of BB3 can be obtained using HCl (Fig. 10). All the studied dye systems exhibited the same trend, which is sharp increase in the initial stage followed by gradual decrease. The introduction of acid into BB3 loaded

Table 3
Predicted breakthrough time based on the BDST constants for a new flow rate (C_0 = 10 mg/l)

Systems	*a* (min/cm)	*b* (min)	υ	υ′	*a*′	*Z* (cm)	t_c (min)	t_e (min)
Single BB3	3.417	22.167	10	5	6.833	12	104.17	106
Single MB	4.083	50.833	10	5	8.167	12	148.83	151
Single BY11	12.583	–4.500	10	5	25.166	12	297.49	300
Binary BB3	1.583	32.167	10	5	3.167	12	70.17	71
Binary BY11 of BB3-BY11	4.417	–15.167	10	5	8.833	12	90.83	93
Binary MB	4.667	23.333	10	5	9.333	12	135.33	137
Binary BY11 of MB-BY11	4.083	–7.1667	10	5	8.167	12	90.83	89

Table 4
Predicted breakthrough time based on the BDST constants for a new influent concentration (υ = 10 ml/min)

Systems	*a* (min/cm)	*b* (min)	C_0	C'_0	*a*′	*b*′	*Z* (cm)	t_c (min)	t_e (min)
Single BB3	3.417	22.167	10	5	6.833	27.972	12	109.97	108
Single MB	4.083	50.833	10	5	8.167	64.144	12	162.14	165
Single BY11	12.583	–4.500	10	5	25.166	–5.678	12	296.31	300
Binary BB3	1.583	32.167	10	5	3.167	40.590	12	78.59	81
Binary BY11 of BB3-BY11	4.417	–15.167	10	5	8.833	–19.139	12	86.86	90
Binary MB	4.667	23.333	10	5	9.333	29.443	12	141.44	140
Binary BY11 of MB-BY11	4.083	–7.1667	10	5	8.167	–9.043	12	88.96	90

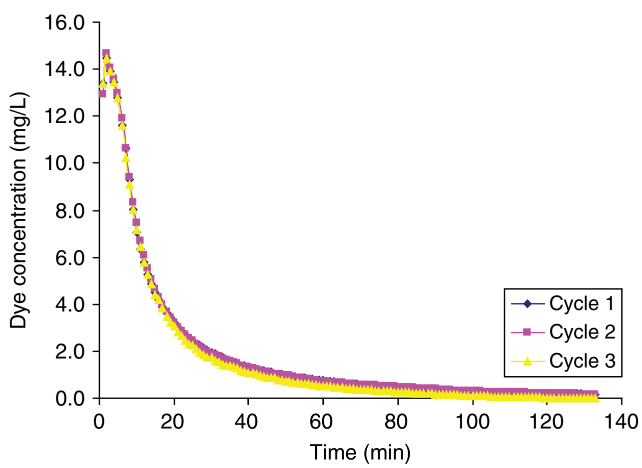

Fig. 10. Elution curves of BB3 in single dye solution using 0.1 M HCl during 3 regeneration cycles.

column protonates the functional groups that are responsible for the binding of BB3 thereby displacing BB3. A minor decrease in breakthrough time was observed during the regeneration cycles and similar observation was observed for all the studied dye systems. This might due to the gradual deterioration of NSB because of repeating usage.

4. Conclusion

The results of this study showed that NSB was capable to remove BB3, MB and BY11 in both single and binary dye systems. The breakthrough curves for all the studied dye exhibited a typical 'S' shape of fixed-bed sorption system. Increasing the bed depth and decreasing the flow rate increased the service time of the column. The experimental data agreed well with the predicted values in BDST modeling. The Thomas, Belter and Chu, and BDST models adequately described the sorption of the studied dyes onto NSB by column mode. NSB is found to be an efficient sorbent for the removal and recovery of basic dyes from aqueous solutions.

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