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Mathematical Modeling of Fixed-Bed Columns for the Adsorption of Methylene Blue on to Fired Clay Pot

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Abstract : continues and patch adsorption study in a fixed-bed column was carried out by using fired clay pot as an adsorbent for the removal of methylene blue (MB) from aqueous solution.The effect of flow rate, influent MB concentration and bed depth on the adsorption characteristics of adsorbent was investigated at pH 7. Five kinetic models Thomas, Yoon–Nelson and Clark were applied to experimental data to predict the breakthrough curves using nonlinear regression and to determine the characteristic parameters of the column that are useful for process design, while a bed-depth service time (BDST) model was used to express the effect of bed depth on breakthrough curves and to predict the time needed for breakthrough at other conditions. The Yoon –Nelson and Clark models were found suitable for the description of whole breakthrough curve. The BDST model was successfully applied to analyze the column performance and to evaluate the model parameter. The empty bed residence time model (EBRT) has been used to correlate the fixed bed pilot plant experimental results and also it was found that the adsorbent exhaustion rate decreased with increasing EBRT. Error analysis was carried out to test the adequacy and accuracy of the model equations.

Key Words : Design Models, Adsorption, Fired clay pot.

1. Introduction

1. 1general

Due to the toxic nature of most dyes to plants and micro-organisms, colored wastewater cannot be discharged without adequate treatment [1]. To remove dyes and other colored contaminants from wastewaters; several physical, chemical, and biological methods have been developed, such as membrane separation, flocculation- coagulation, adsorption, ozonatioin, and aerobic or anaerobic treatment [2]. Among these processes, adsorption has been found to be an effective and cheap technique for removing dyes and having wide potential applications [3]. Adsorption is a complex phenomenon and involves passive separation of the adsorbate from an aqueous/ gaseous phase onto the solid phase. It occurs between two phases in transporting pollutants from one phase into another [4].

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In recent years a large number of cost effective adsorbents have been reported to possess color removal capacity. Few are phoenix tree leaf [5], Wool Fiber and Cotton Fiber [6], kaolinite [7], natural zeolite [1] and fired clay. Among the wide range of adsorbent materials that have been attempted for color uptake, selection is based on removal capacity, design simplicity, local availability of materials and chemicals and user preference.

Clay is an important constituent of all soils. High specific surface area, high porosity, chemical and mechanical stability, layered structure, and high cation exchange capacity has made clay an excellent adsorbent with the capability to adsorb positively charged species. Its sorption properties are a result of high surface area and porosity. The presence of both Bronsted and Lewis acidity in clay boosts the adsorptive capacities [8].

The use of clays as adsorbent have advantages upon many other commercially available adsorbents in terms of low-cost, an abundant availability, high specific surface area, excellent adsorption properties, non-toxic nature, and large potential for ion exchange [9].

1.2 Analysis and Modeling of Breakthrough Profile

The service times of a unit plant are correlated with the initial sorbate concentration, flow rate, and adsorption capacity of the adsorbentfor a given bed depth, to be used.Along these lines, acquiring an important and dependable loading capacity of the adsorbent turns critical in efficient process layout and operation.This requires a cautious evaluation and analysis of the trial information,to anticipate the impact of difference in operational parameters of the sorption procedure, through modeling [10].

1.2.1 Thomas Model

Assuming Langmuir kineticsof adsorption–desorption with no axial dispersion and that the rate-driving force obeys second-order reversible reaction kinetics was the base of deriving this model.To calculate the maximum solid-phase concentration of sorbate on the sorbent and the adsorption rate constant, the data obtained in fixed bed column studies are utilized.The articulation by Thomas for an adsorption column is given as follows:

$$\frac{C_t}{C_o} = \frac{1}{1+exp\,(\frac{K_{Th}q_{Th}M}{Q} - K_{Th}C_o t)} \quad (1)$$

The kinetic coefficient K_{Th} and the adsorption capacity of column q_{Th} can be resolvedfrom a plot of ln [(C_0/C_t) - 1] against t at a given flow rate [10].

1.2.2 Bed Depth Service Time (BDST) Model

BDST is a straightforward model for predicting the relationship between bed profundity, Z, and service time, t, in terms of process concentrations and adsorption parameters. The BDST model is based on the presumption that the rate of adsorption is controlled by the surface response between adsorbate and the unused ability of the adsorbent.The values of breakthroughtime acquired for different bed heights utilized in this research were introduced into the BDST model. A linear relationship between bed depth and service time is given by Eq. (2)[5].

$$\mathbf{t} = \frac{N_o}{C_o u} Z - \frac{1}{KC_o} ln(\frac{C_o}{C_t} - 1) \quad (2)$$

The dynamicbed capacity (N_o) and the adsorption rate constant (K) can be evaluated by the linearretreating of the following straight-line relationship:

$$t = aZ + \mathbf{b} \quad (3)$$

Where slope:

$$a = \frac{N_o}{C_o u} \quad (4)$$

Intercept:

$$b = -\frac{1}{KC_o} \ln(\frac{C_o}{C_t} - 1) \quad (5)$$

If there is a change in the initial solute concentration C_O to a new value Co', the new values of a' and b' can be, respectively, obtained from the slope and the intercept according to the relations proposed by Hutchins:

$$\boldsymbol{a}' = \boldsymbol{a}\left(\frac{\boldsymbol{C_o}}{\boldsymbol{C_o'}}\right)(6)$$

$$\boldsymbol{b}' = \boldsymbol{b}\left(\frac{\boldsymbol{C_o}}{\boldsymbol{C_o'}}\right)\frac{\ln(\boldsymbol{C_o'}/\boldsymbol{C_b}-\boldsymbol{1})}{\ln(\boldsymbol{C_o}/\boldsymbol{C_b}-\boldsymbol{1})}\ (7)$$

If the linear velocityisvaried from u to u', the newslopea' can be calculated as follows:

$$\boldsymbol{a}' = \boldsymbol{a}\left(\frac{\boldsymbol{u}}{\boldsymbol{u'}}\right)(8)$$

The intercept stays unaltered, because it only depends on the entry solute concentration C_0. This isbeneficial to scale up theoperation for other flow rates withoutmoreover experimental run [10].

1.2.3 Yoon–Nelson Model

The rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent is the base on the assumption of this model.This model requires no definite information with respect to the qualities of adsorbate, the kind of adsorbent and physical properties of the adsorption bed and it is less complicated .The model is expressed as pursues:

$$\frac{\boldsymbol{C_t}}{\boldsymbol{C_O}} = \frac{\boldsymbol{1}}{\boldsymbol{1+exp\ [K_{YN}(\tau-t)]}}(9)$$

The parameters K_{YN} and τ may be determined from the plot of ln $[C_t / (C_0 - C_t)]$ versus sampling time (t) [10].

1.2.4 Clark Model

The Clark defined a new simulation of breakthrough curves. The model developed by Clark was based on the use of a mass-transfer concept in combination with the Freundlich isotherm [11]:

$$\frac{\boldsymbol{C_t}}{\boldsymbol{C_O}} = \left(\frac{\boldsymbol{1}}{\boldsymbol{1+Ae^{-rt}}}\right)^{\boldsymbol{1/(n-1)}} \qquad (10)$$

From a plot of ln $[(C_0/C_t)^{n-1} - 1]$ versus time, the values of r and A can be determined from its slope and intercept, respectively [10].

1.2.5 Empty Bed Residence Time (EBRT)

The empty bed residence time (EBRT), sometimes called the empty bed contact time (EBCT), is used to determine the optimum resin usage in a fixed-bed column. McKay and Bino[9] proposed that the capital and operating costs for a fixed-bed ion exchange (or adsorption) system were dependent on the EBRT and the resin exhaustion rate.

The EBRT is defined as the time required for the liquid to fill the volume of the resin bed and is a direct function of the liquid flow rate and volume of the resin bed. It enables system designers to determine the resin column size required.

$$\boldsymbol{EBRT} = \frac{\textbf{resin bed volume}}{\textbf{volumetric liquid flow rate}}(11)$$

The resin exhaustion is the amount of resin in the column exhausted per unit volume of liquid treated when breakthrough occurs:

$$\textbf{resin exhaustion} = \frac{\textbf{mass of resin exhausted at breakthrough}}{\textbf{volume of liquid treated at breakthrough}}$$

$$= \frac{\boldsymbol{m}\ (\boldsymbol{g})}{\boldsymbol{V}_{\textbf{at breakthrough}}(\boldsymbol{L})} \quad (12)$$

The resin exhaustion can be plotted against the EBRT values to generate an operating line representing that of an ion exchange column. When the operating conditions, such as flow rate, initial feed concentration, and resin particle sizes, are varied, different operating lines can be generated. The operating line approaches asymptotes on both axes. The minimum EBRT and the minimum resin exhaustion can be determined from the asymptotes of the operating lines [12].

1.2.6 Error analysis

As different formulate used to calculate R^2 values would affect the accuracy more significantly during the linear regressive analysis, the nonlinear regressive analysis can be a better option in avoiding such errors. So the parameters of different kinetic models were obtained using nonlinear analysis according to least square of errors.

In order to confirm which model was better, error analysis was performed. The relative mathematical formula of *SS* is:

$$\boldsymbol{SSE} = \frac{\sum[(\boldsymbol{C_t}/\boldsymbol{C_O})_{\boldsymbol{c}} - (\boldsymbol{C_t}/\boldsymbol{C_O})_{\boldsymbol{e}}]^2}{\boldsymbol{N}} \qquad (13)$$

where $(C_t/C_0)c$ is the ratio of effluent and influent MB concentrations obtained from calculation according to dynamic models, and $(C_t/C_0)e$ is the ratio of effluent and influent MB concentrations obtained from experiment, respectively; N is the number of the experimental point. In order to confirm the best fit isotherm for the adsorption system, it is necessary to analyze the data using *SS*, combined with the values of the determined coefficient (R^2)

For Bed Depth Service Time Model the SS equation is:

$$\boldsymbol{SS} = \frac{\boldsymbol{t_c} - \boldsymbol{t_e}}{\boldsymbol{t_e}} \times \mathbf{100}\% \quad (14)$$

Where $t_c$is service time obtained from calculation according to dynamic models; t_e is service time obtained from experiment [5].

2. Experimental

2.1. Materials

Fired clay pots were purchased from the Iraqi market and then crushed down manually into grains. The grains were sieved using the American Sieve Standards in the environmental laboratory of the University of Babylon. Then, grains were thoroughly washed at several times with distilled water to remove impurities and dried by exposure to the sun light for 12hr. Particle size selection was made and particles with (1mm) in diameter were selected for MB removal by packing them in a mini column experiment in a fixed bed depth.

2.2. Methylene blue solution

Methylene Blue (MB) dye was used as an adsorbate in the present study. The choice of MB dye as an adsorbate is due to its known strong adsorption on to solids. The MB dye used was supplied by the scientific bureaus in Iraqi commercial markets.A stock solution of methylene with 30 mg/L concentration was prepared by dissolving 0.03 gm of powder in 1 L of distilled water; other required concentrations were prepared by diluting.

2.3. Methods of adsorption studies

Continuous flow adsorption experiments were conducted in a glass column made of Pyrex glass tube, the glass column of various length (Z1=10, Z2=20, Z3=30 cm) and 2.2 cm internal diameter were used while the height of reactor is 30 cm.It was equipped with a total of three equidistant ports (10 cm) (excluding inlet and outlet) of 1.5 cm diameter for collecting liquid sample along the height of reactor.The glass column and ports are fitted with glass fins that work to fix the glass wool up and down the bed and through the ports to prevent the flow of adsorbent together with the effluent. Then, the bed was rinsed with distilled water and left overnight to ensure a closely packed arrangement of particle without voids, channels, or cracks.Synthetic Methylene Blue solution of known concentration (5 , 10 , 15 , 20 and 25 mg/l) was fed through a bed of Fired clay pot in up-flow mode to avoid channeling due to gravity and to ensure a uniform distribution of the effluent thought out the column. The experiments were carried out at room temperature. A drain pump was used to control the flow rates (20, 40, 60, 80 and 100 ml/min) and maintained constant during each experiment.

3. Results

3.1. Effect of flow rate on breakthrough curve

The breakthrough curves at various flow rates are shown in Fig (1),where it very well may be seen that the breakthrough for the most part happened quicker with a higher flow rate.Breakthrough time achieving saturation was expanded altogether with a decrease in the flow rate.At a low rate of influent, MB had more opportunity to be in contact with adsorbent,which conduct in a major removal of MB molecules in column.So the flow rate is inversely proportional to removal efficiency.

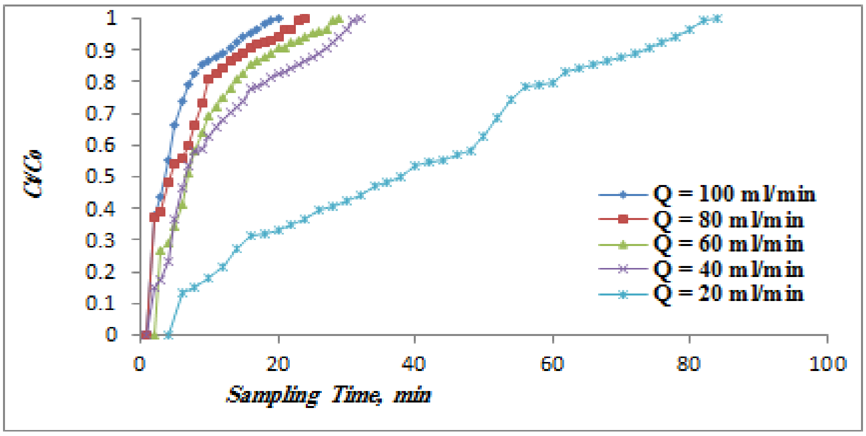

Fig.(1) Breakthrough curve: the effect of Flow rate on MB adsorption (C_0=20 mg/L, Z=30 cm, pH=7).

3.2. Effect of influent MB concentration on breakthrough curve

The effect of influent MB concentration on the shape of the breakthrough curves is shown in Fig 2.It is illustrated that both the breakthrough and exhaustion time were decreased with increasing initial MB concentration. It could be seen that the percent of MB removal was decreased with increasing initial MB concentration to 25 mg/L,because the binding sites became more quickly saturated in the column. A decrease in the MB concentration gave an extended breakthrough curve indicating that a higher volume of the solution could be treated.

3.3. Effect of different bed depths on breakthrough curve

The breakthrough curves at various bed profundities are appeared in Fig.(3)where it is seen that as the bed high (adsorbent mass) increments,MB had more opportunity to contact Commercial enacted Carbon (CAC) that resulted in higher removal efficiency of MB particles in column.So the higher bed column brought about a lowering in the profluent concentration at a similar service time.The slope of the breakthrough curve diminished with expanding bed height, which brought about a widened mass transfer zone.

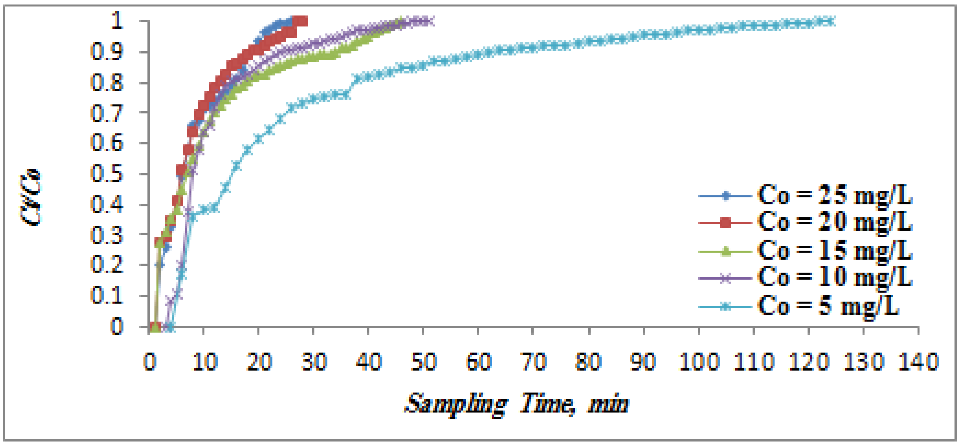

Fig.(2) Breakthrough curve: the effect of influent concentration on MB adsorption (Q=60ml/min, Z=30 cm, pH=7).

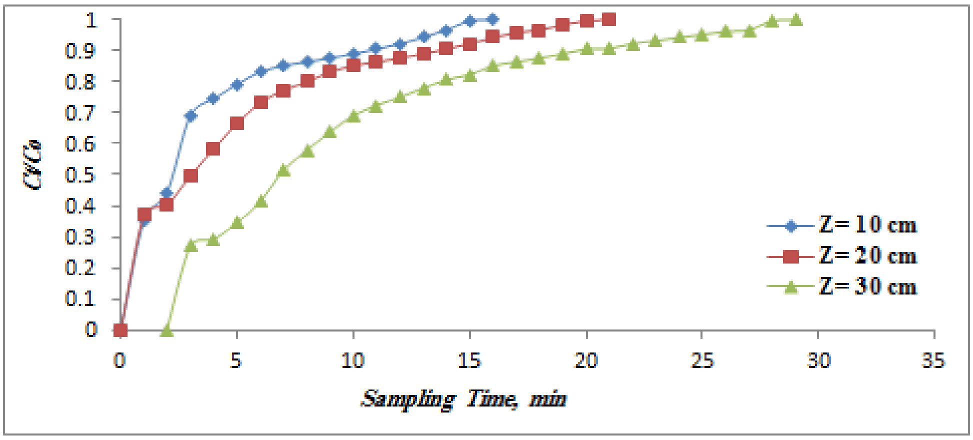

Fig.(3) Breakthrough curve: the effect of different bed Depths on MB adsorption (Q=60ml/min, C_0=20 mg/L, pH=7).

4. Discussion

All the models cited except Empty Bed Resistance Time (EBRT) were applied to investigate the breakthrough behavior of MB sorption onto Fired Clay Pot in contaminated synthetic aqueous solution.The characteristic parameters of the models acquired by direct regression were utilized to foresee the theoretical MB effluent MB concentrations.

4.1 Thomas model

The linear regression of the Thomas model with the experimental MB sorption data also shows good correlations in most of the cases. (Table1) as shown, the parameter K_{Th} of the model were found to (in most runs) decrease with higher bed depths , when the influent concentration increased, the value of qe increased, The reason was that the driving force for adsorption is the concentration difference between thedye on the adsorbent and the dye in the solution [5]. Thus the high driving force due to the higher MB concentration resulted in better column performance. Also q_{Th} increase with higher bed depth,for flow rates increasing, the value of q_{Th} decreased. The results and values of SSE are also listed in Table 1where values of R^2 range from 0.9857 to 0.7534. So the correlation of Ct/C0 and t according to Eq. (1) is significant.

Table 1: Characteristic Parameters Predicted by Thomas Model.

Initial MB Concentration (mg/L)	Bed Depth (cm)	Flow Rate (mL/min)	Thomas Model			
			K_{Th} (L/mg/min)	q_{Th} (mg/g)	SSE (%)	R^2
5	20	60	0.01006	0.01349	6.0183	0.8777
10	20	60	0.02907	0.07554	3.0787	0.8719
15	20	60	0.008193	0.05870	0.7379	0.8967
20	20	60	0.01069	0.08887	1.3563	0.9769
25	20	60	0.008132	0.11880	1.8248	0.9627
20	20	20	0.003445	0.1145	1.4403	0.9683
20	20	40	0.00997	0.0960	3.2187	0.9857
20	20	60	0.01069	0.08887	1.3563	0.9769
20	20	80	0.01188	0.04293	0.2658	0.9757
20	20	100	0.013255	0.02501	0.5310	0.9561
20	10	20	0.00556	0.1010	1.0909	0.9752
20	30	20	0.00286	0.1987	11.227	0.9798

Table 2: Characteristic Parameters Predicted by Yoon–Nelson Model.

Initial MB Concentration (mg/L)	Bed Depth (cm)	Flow Rate (mL/min)	Yoon–Nelson Model				
			K_{YN} (min^{-1})	τ_{exp} (min)	τ_{cal} (min)	SSE (%)	R^2
5	30	60	0.0558	14	10.3046	0.9109	0.828
10	30	60	0.156	6	3.91153	0.9099	0.8764
15	30	60	0.123	6	3.11056	0.2265	0.9361
20	30	60	0.2226	6	3.63117	0.0835	0.9734
25	30	60	0.2266	5	3.91835	0.1072	0.9566
20	30	20	0.0607	16	9.92586	0.0606	0.9683
20	30	40	0.2136	8	5.90215	0.0295	0.9734
20	30	60	0.2226	6	3.63117	0.0835	0.9734
20	30	80	0.2504	4	1.5475	0.0539	0.9694
20	30	100	0.3184	3	1.4795	0.1568	0.9249
20	10	60	0.2504	3	1.0523	0.3665	0.9151
20	20	60	0.1739	8	5.92754	0.1446	0.9754

4.2 Yoon–Nelson model

The values of K_{YN} and τ are listed in Table 2. As seen in the table, the rate constant K_{YN} increased with both increasing flow rate and MB influent concentration and decreased with an increase in bed depths.While the 50% breakthrough time τ decreased with both increasing flow rate and MB influent and increased with an increase in bed depths.

4.3Clark model

In a batch experiment, it was found that the Freundlich model was approximately valid for the adsorption of dye .onFired Clay Pot the Freundlich constant 1/*n* (0.6129). As seen in Table 3 as both flow rate and influent dye concentration increased, the values of *r* increased.

Table3: Characteristic Parameters Predicted by Clark Model.

Initial MB Concentration (mg/L)	Bed Depth (cm)	Flow Rate (mL/min)	Clark Model			
			A	r (min^{-1})	ESS (%)	R^2
5	20	60	0.525345	0.043	0.3068	0.9408
10	20	60	2.14642	0.1189	0.6046	0.9644
15	20	60	0.84274	0.1119	0.3707	0.9266
20	20	60	0.95056	0.2029	0.121	0.9807
25	20	60	1.189103	0.2132	0.103	0.9519
20	20	20	0.86641	0.0544	0.0519	0.9822
20	20	40	1.52821	0.1898	0.023	0.9871
20	20	60	0.95056	0.2029	0.121	0.9807
20	20	80	0.71605	0.2294	0.061	0.9774
20	20	100	0.86209	0.2797	0.122	0.9584
20	10	60	0.669181	0.2376	0.3641	0.925
20	30	60	1.338567	0.1629	0.113	0.9828

Table 4: Characteristic Parameters Predicted by BDST Model for fired clay pot (C_o= 20 mg/L, Q = 60 ml/min).

Ct/Co	b (min)	a (min/cm)	K_a (L/mg/min)	N_o (mg/L)	R^2
0.1	-0.3556	0.085	0.3089460	26.846344	0.9999
0.9	2.6667	0.7	0.0411993	221.08754	0.9932

4.4 Bed Depth Service Time (BDST) Model

The adsorption capacity (N_o) and rate constant (Ka) can be obtained through the BDST model. From the lines of *t–Z* at values of C_t/C_o 0.1, 0.9 the related constants of BDST according to the slopes and intercepts of lines are listed in Table 4, respectively. From Table 4, as the value of C_t/C_o increased, the adsorption capacity of the bed per unit bed volume, N_o, increased. From the values of R^2, the validity of the BDST model for the present system is demonstrated. The BDST model constants can be helpful to scale-up the process for other flow rates and concentration without further experimental runs.

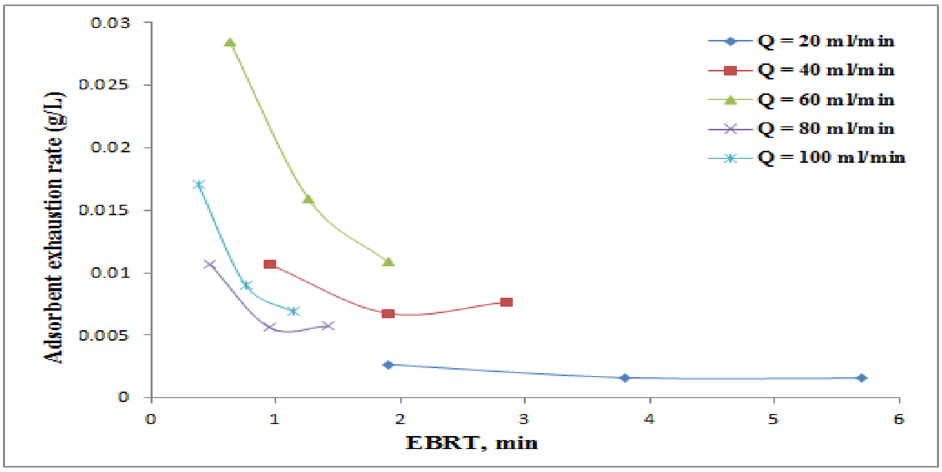

Fig4: Adsorbent exhaustion rate versus empty bed residence time for MB Adsorption by fired clay pot.

4.5 Empty Bed Residence Time (EBRT) model

Fig. 4 as a plot of the adsorbent exhaustion rate against EBRT at various adsorbent bed heights such as 10, 20, and 30 cm for fired clay pot. It could be seen from Fig.4 that adsorbent exhaustion rate decreased with increasing EBRT. As shown in Table 5 the data of variable bed depth (10, 20, and 30 cm) at a different flow rate (20, 40, 60, 80 and 100 ml/min) in a column reactor for the removal of MB. The data in Table 5 showed that EBRT, Vb and Tb increased with increasing bed depth. It was clear that when the EBRT increase with a flow rate, the bed volume would have to be longer, thus allowing more solution to be treated but resulting in a lower adsorbent exhaustion rate.

Table 5: Data of variable bed depth at a fixed flow rate in a fixed-bed column for the removal of 20 mg/L of MB by fired clay pot.

flow rate (ml/min)	Bed depth (cm)	Bed volume(cm^3)	Weight of adsorbent (mg)	EBRT (min)	Vb (L)	Tb (min)	Adsorbent exhaustion rate (g/L)
20	10	37.994	22.455	1.8997	0.02	1	1.12275
	20	75.988	46.801	3.7994	0.08	4	0.58501
	30	113.982	71.396	5.6991	0.2	10	0.35698
40	10	37.994	22.455	0.9498	0.02	0.5	1.12275
	20	75.988	46.801	1.8997	0.08	2	0.585012
	30	113.982	71.396	2.8495	0.16	4	0.446225
60	10	37.994	22.455	0.6332	0.03	0.5	0.7485
	20	75.988	46.801	1.266	0.08	1.3333	0.585012
	30	113.982	71.396	1.8997	0.12	2	0.594966
80	10	37.994	22.455	0.47492	0.013	0.1625	1.7273076 92
	20	75.988	46.801	0.94985	0.08	1	0.5850125
	30	113.982	71.396	1.42477	0.16	2	0.446225
100	10	37.994	22.455	0.37994	0.0133	0.133	1.688345
	20	75.988	46.801	0.75988	0.06	0.6	0.780016
	30	113.982	71.396	1.13982	0.09	0.9	0.793288

4.6 Comparison of the Applied Models

Among the Thomas, Yoon–Nelson and Clark models, the value of error (ESS) for Clark was lowest for a given experimental condition, while it was the largest for Thomas. Thus, it was concluded that the Clark model was better in describing the process of MB adsorption in fired clay pot column. In a comparison of values of *SS* and the predicted curves and experimental data, both the Yoon-Nelson and Clark models can be used to describe the behavior of the adsorption process, but the Thomas model did not give better results. Regarding the BDST model, it is only used to predict the initial region of breakthrough curve (Ct /$C0$ less than 0.15).

5. Conclusions

On the basis of the experimental results of this investigation, the following conclusions can be drawn:

- The adsorption of MB was dependent on the flow rate, influent MB concentration and bed depth.
- The initial region of breakthrough curve was described by the BDST model well at all experimental conditions studied while the transient stage or working stage of the breakthrough curve was described well by the Yoon-Nelson and Clark models.
- The BDST model adequately described the adsorption of MB onto Fired clay pot in column mode.

6. Symbols

A — Clark constants
C_o — Influent MB concentration, mg/ L
Ct — Effluent MB concentration, mg /L
u— Linear velocity, cm/ min
Ka — Rate constant in BDST model , L/mg/min
K_{Th} — Rate constant of Thomas model, ml/min/mg
M — is the amount of adsorbent in the column (g)
K_{YN} — Rate constant of Yoon–Nelson model, min-1
n — Freundlich parameter
N_o — Adsorption capacity from BDST model, mg /L
Q — Volumetric flow rate, ml /min
r — Clark model constants
t — Effluent time, min
Z — Bed depth of column, cm
τ — Time required for 50% adsorbate breakthrough from Yoon–Nelson Model, min.
τ_{exp}— Time required for 50% adsorbate breakthrough from experiments, min.

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