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Dynamic sorption of methylene blue by cedar sawdust and crushed brick in fixed bed columns

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Abstract

The dynamic removal of methylene blue by cedar sawdust and crushed brick was studied in packed bed columns. The values of column parameters were predicted as a function of flow rate and bed height. On evaluating the breakthrough curves, the sorption isotherms of methylene blue onto cedar sawdust and crushed brick in 20 °C aqueous solution were experimentally determined in batch conditions. Both the Freundlich and the Langmuir models were found to fit the sorption isotherm data well, but the Langmuir model was better. A series of column tests using cedar sawdust and crushed brick as low-cost sorbents were performed to determine the breakthrough curves with varying bed heights and flow rates. To predict the breakthrough curves and to determine the characteristic parameters of the column useful for process design, five kinetic models; Bohart and Adams, bed depth service time (BDST), Clark, Wolborska, and Yoon and Nelson models were applied to experimental data. All models were found suitable for describing the whole or a definite part of the dynamic behavior of the column with respect to flow rate and bed height, with the exception of Bohart and Adams model. The simulation of the whole breakthrough curve was effective with the Yoon and Nelson and the Clark models, but the breakthrough was best predicted by the Wolborska model.

Keywords: Methylene blue; Dynamic sorption; Fixed bed; Modeling; Cedar sawdust; Crushed brick

1. Introduction

Industrial growth and associated sophistication have resulted in many environmental problems. Many industries use dyes to color their final product. Such extensive use of dyes often poses problems in the form of colored wastewater that require pretreatment for color prior to disposal into receiving water bodies or publicly owned treatment works. Discharge of such colored effluents imparts color to the receiving water bodies (rivers and lakes) and interferes with its intended beneficial use. Color impedes light penetration, retards photosynthetic activity, inhibits the growth of biota, and also has a tendency to chelate metal ions that produce micro-toxicity to fish and other organisms [1].

The removal of color from dye-bearing effluents is a major problem due to the difficulty in treating such wastewaters by conventional treatment methods. Furthermore, these processes are costly and cannot effectively be used to treat the wide range of dye wastewater. Among the various treatment processes, adsorption is one of the effective and attractive processes to remove dyes and also to control chemical and biochemical oxygen demands [1,2]. Several adsorbents are eligible for such a purpose. Activated carbon (powdered or granular) is the most widely used adsorbent because it has excellent adsorption efficiency for organic compounds. However, the activated carbon is considered an expensive adsorbent, which makes the wastewater treatment a prohibitive cost step. Several studies have tried to replace the activated carbon with less expensive materials. Therefore, there is a growing interest in using low-cost, easily available materials for the adsorption of dye colors. Consequently, a number of low cost, easily available materials are being studied for the removal of different dyes from aqueous solutions at different operating conditions [3–9].

Methylene blue has wider applications, which include coloring paper, temporary hair colorant, dyeing cottons, wools, coating for paper stock, etc. In this study, methylene blue is selected as a model compound in order to evaluate cedar sawdust and crushed brick capacities for its removal from aqueous solutions

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Nomenclature

A	constant in the Clark model
b	Langmuir adsorption constant ($L\,mg^{-1}$)
C	effluent methylene blue concentration ($mg\,L^{-1}$)
C_e	nonadsorbed methylene blue concentration at equilibrium ($mg\,L^{-1}$)
C_S	methylene blue concentration at the solid/liquid interface in the column ($mg\,L^{-1}$)
C_0	inlet (feed) or initial methylene blue concentration ($mg\,L^{-1}$)
D	axial diffusion coefficient ($mm^2\,h^{-1}$)
K_{BA}	kinetic constant in the Bohart and Adams model ($L\,mg^{-1}\,h^{-1}$)
K_C	mass transfer coefficient in the Clark model (h^{-1})
K_F	Freundlich adsorption constant ($mg^{1-1/n}\,L^{1/n}\,g^{-1}$)
K_{YN}	kinetic constant in the Yoon and Nelson model ($L\,h^{-1}$)
n	Freundlich adsorption constant
N_0	maximum sorption capacity ($mg\,L^{-1}$)
q	methylene blue concentration in the solid phase in the column at any time ($mg\,L^{-1}$)
q_e	equilibrium methylene blue uptake per g of sorbent ($mg\,g^{-1}$)
q_m	maximum sorption capacity in the Langmuir model ($mg\,g^{-1}$)
Q	flow rate ($mL\,h^{-1}$)
r	constant in the Clark model (h^{-1})
t	flow time (h)
t_b	time at breakthrough (h)
$t_{1/2}$	time required for 50% sorbate breakthrough (h)
U_0	superficial velocity ($mm\,h^{-1}$)
v	migration rate ($mm\,h^{-1}$)
V	volume of solution (L)
W	weight of sorbent (g)
Z	height of the bed (mm)
Z_0	thickness of mass transfer zone (mm)

Greek letter

β_a	kinetic coefficient of the external mass transfer in the Wolborska model (h^{-1})

in continuous process. Crushed brick and cedar sawdust were selected for their abundance, availability, and/or economical relevance. Cedar sawdust and crushed brick are capable of removing methylene blue and can be considered as an efficient and low-cost sorbents for dyes [10]. This study [10] has been conducted in batch mode, which is usually limited to the treatment of small quantities of wastewater. The sorption capacity parameter obtained from a batch experiment is useful in providing information about effectiveness of sorbate–sorbent system. However, the data obtained under batch conditions are generally not applicable to most treatment system (such as column operations) where contact time is not sufficiently long for the attainment of equilibrium. Hence, there is a need to perform equilibrium studies using columns. Additionally, no work has been regarded for the sorption of methylene blue by cedar sawdust and crushed brick in continuous mode using fixed bed column.

In the practical operation of full-scale adsorption processes, continuous-flow fixed bed columns are often preferred. In such systems the concentration profiles in the liquid and adsorbent phases vary in both space and time. As a result, design and optimization of fixed bed columns are difficult to carry out a priori without a quantitative modeling approach. From the perspective of process modeling, the dynamic behavior of a fixed bed column is described in terms of the effluent concentration–time profile, i.e. the breakthrough curve. The purpose of the present paper is to study and model the removal of methylene blue from aqueous solutions by sorption onto cedar sawdust and crushed brick in fixed bed columns. This research work basically deals with the design parameters of fixed bed sorption column. The effects of flow rate and bed height are explored during the column test.

2. Materials and methods

2.1. Sorbate and sorbents

The organic sorbate chosen for these studies was methylene blue dye since its analysis by visible absorption spectroscopy is easy down to extremely low levels. Methylene blue, a basic dye, was purchased from Merck, CI Classification No. 52015. The stock solutions at the desired concentration were prepared with bidistilled water.

The sorbents (cedar sawdust and crushed brick) were obtained from local industries (Annaba, Algeria) and were used without an additional pre-treatment except of washing, grinding and a size classification by sieving. The fraction with grain sizes in the range 80–315 μm was used for laboratory experiments.

2.2. Sorption isotherms

Equilibrium studies were carried out by agitating a series of flasks containing 10 mL of dye solutions of initial methylene blue concentration 40 $mg\,L^{-1}$ with different weighed amounts of sorbent (cedar sawdust or crushed brick) with a constant agitation speed of 350 rpm. The temperature was controlled at 20 °C. Agitation was provided for 5 h, which is more than sufficient time to reach equilibrium. After equilibrium, the flasks contents were centrifuged at 3000 rpm for 15 min to separate the sorbents from the suspension. The supernatant was analyzed for sorbate concentration using a Hewlett Packard 8453 UV–vis spectrophotometer at 665 nm. Moreover, in order to ensure the quality of the data, blank sample was prepared and handled in parallel for each sorption test. In all cases, the working pH was that of the solution and was not controlled.

The amount of methylene blue uptake by the sorbents, q_e ($mg\,g^{-1}$), was obtained as follows

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e (mg L^{-1}) are the initial and final concentrations of methylene blue, respectively, V the volume of solution (L), and W is the weight of sorbent (g).

Preliminary experiments had shown that methylene blue sorption losses by centrifugation were negligible. Additionally, all the experiments were carried out in duplicate and the mean values are presented.

2.3. Sorption in continuous flow column

In fixed bed columns, the solute concentration in the effluent is free of the target solute until breakthrough of solute occurs. On that account, the behavior of cedar sawdust and crushed brick in a fixed bed column operation at constant temperature (20 °C) was studied to determine the breakthrough point that will lead to the column scale-up approach. A glass column (0.8 cm in diameter) was packed with different bed heights (8, 12, and 16 mm) of sorbents on a glass–wool support and was loaded with 40 mg L^{-1} of methylene blue solution. The working pH was that of the solution and was not controlled. Fixed-bed up-flow sorber was fed by a peristaltic pump at a constant flow rate, ranging from 23 to 120 mL h^{-1}. Interconnecting tubing and fittings are made of polytetrafluoroethylene (PTFE). Effluent samples were analyzed to yield output concentration breakthrough curves.

The breakthrough time (the time at which dye concentration in the effluent reached 3% of the initial concentration) and bed exhaustion time (the time at which dye concentration in the effluent reached influent concentration) were used to evaluate the breakthrough curves.

3. Results and discussion

3.1. Isotherms

The sorption isotherms of methylene blue onto cedar sawdust and crushed brick were determined. A detailed study on the sorption equilibrium isotherms can be found in a previous publication [10]. The equilibrium sorption data can be modeled by using different simple models such as Freundlich and Langmuir, given respectively by the equations:

$$q_e = K_F C_e^{1/n} \quad (2)$$

$$\frac{q_e}{q_m} = \frac{bC_e}{1 + bC_e} \quad (3)$$

where C_e is the liquid-phase concentration of the sorbate at equilibrium (mg L^{-1}), q_e the amount of sorbate sorbed at equilibrium (mg g^{-1}), K_F a constant indicative of the sorption capacity of the sorbent (mg$^{1-1/n}$ L$^{1/n}$ g^{-1}), n an empirical constant related to the magnitude of the sorption driving force, q_m the maximum sorption capacity (mg g^{-1}), and b is the Langmuir constant related to the energy of sorption (L mg^{-1}).

The values of Freundlich and Langmuir parameters are presented in Table 1. The correlation coefficients indicate that both Langmuir and Freundlich equations were satisfactory, but the Langmuir isotherm fits the equilibrium data better.

Table 1
Freundlich and Langmuir isotherm constants for the sorption of methylene blue by cedar sawdust and crushed brick [10]

Model	Parameters	Cedar sawdust	Crushed brick
Freundlich	K_F (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	92.78	44.93
	n	3.94	2.83
	R	0.990	0.981
Langmuir	q_m (mg g^{-1})	142.36	96.61
	b (L mg^{-1})	3.04	1.03
	R	0.995	0.999
	R_L	8.16×10^{-3}	23.7×10^{-3}

In order to predict the sorption efficiency of the sorption process, the dimensionless equilibrium parameter of Hall was determined by using the following equation [11]:

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

where C_0 is the initial concentration. Values of $R_L < 1$ represent favorable adsorption. The R_L-values for cedar sawdust and crushed brick are 8.16×10^{-3} and 23.7×10^{-3}, respectively. The obtained values show that our systems are favorable.

The magnitude of the exponent n gives an indication of the favorability of sorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics [12]. The studied materials are good sorbents for methylene blue ($n > 2$).

The applicability of both Langmuir and Freundlich isotherms to both sorbent systems implies that both monolayer adsorption and heterogeneous surface conditions exist under the used experimental conditions.

In general, the values of isotherm constants obtained in a batch system show the maximum values of these constants and are considerably higher than those obtained in a fixed bed as flow rate of solution is zero in batch system, that is, the contact time between sorbate solution and sorbent approximates infinite. These experimental data are generally used in further studies concerning the dynamic sorption of solute in column studies for the prediction of breakthrough curves. However, it is important to note that sorption isotherms and constants determined in a fixed bed should be used for evaluating the breakthrough curves and kinetic constants to model such a system mathematically.

3.2. Dynamic sorption

Accumulation of dyes in fixed bed column is largely dependent on the quantity of sorbent inside the column. On the other hand, flow rate is one of the important characteristics in evaluating sorbents for continuous-treatment of dye-laden effluents on an industrial scale. The sorption breakthrough curves obtained by varying the bed height from 8 to 16 mm for different flow rates (23, 52 and 120 mL h^{-1}) and 40 mg L^{-1} initial methylene blue concentration for cedar sawdust and crushed brick are given in Figs. 1 and 2. The breakthrough curves were obtained by plotting the variation of solute concentration in the aqueous solution (normalized with the initial concentration of the dye in

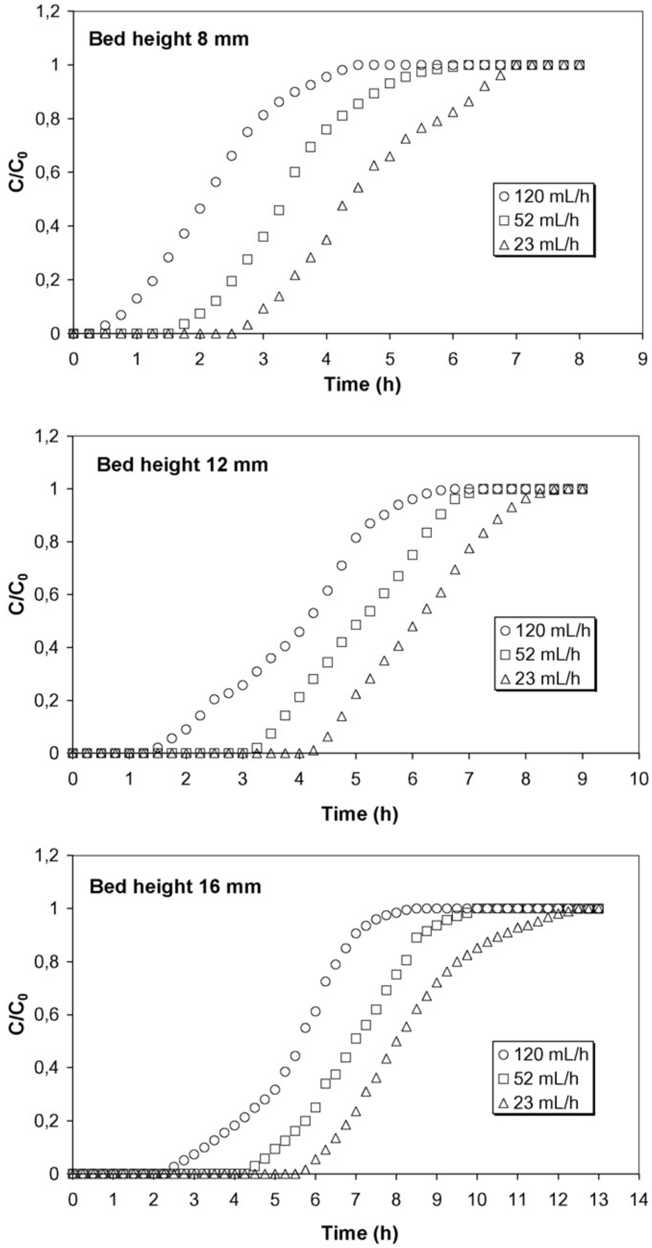

Fig. 1. Breakthrough curves for the sorption of methylene blue by cedar sawdust at different bed heights and flow rates.

the solution) with time. The most efficient sorption performance will be obtained when the shape of the breakthrough curve is as sharp as possible. Figs. 1 and 2 show that for short times methylene blue in the feed is taken up completely by the column. After a while dye breakthrough occurs and the effluent concentration increases with time. The breakthrough times were measured when the methylene blue concentration (C) reached $0.03C_0$ (initial concentration). The saturation point is reached when the effluent concentration becomes equal to the feed concentration.

The variation of breakthrough and saturation times for both sorbents with respect to operating variables, influent flow rate and bed height, is shown in Figs. 3 and 4. Both breakthrough and exhaustion times increase with the increase in the height of the bed, as more binding sites are available for sorption. The mass of the sorbent forming the homogenous fixed bed is proportional to the bed height and as a result the number of sorption sites increases with the increase in bed height leading to a larger sorption capacity of the reactor. As expected, for a given bed height, the breakthrough and saturation times are strongly influenced by the flow rate. Figs. 3 and 4 show that by reducing the flow rate, the breakthrough and exhaustion times increased for a given bed height. This means that the volume of methylene blue solution that can be treated is effectively increased. This flow rate dependence can be accounted for by the fact that for lower value of flow rate, the contact time is longer and hence the interaction between the dye and the sorbent is also greater. This leads to higher rate of dye sorption. On the other hand, for higher flow rate, the contact time is shorter and the dye sorption is also lower due to lesser interaction.

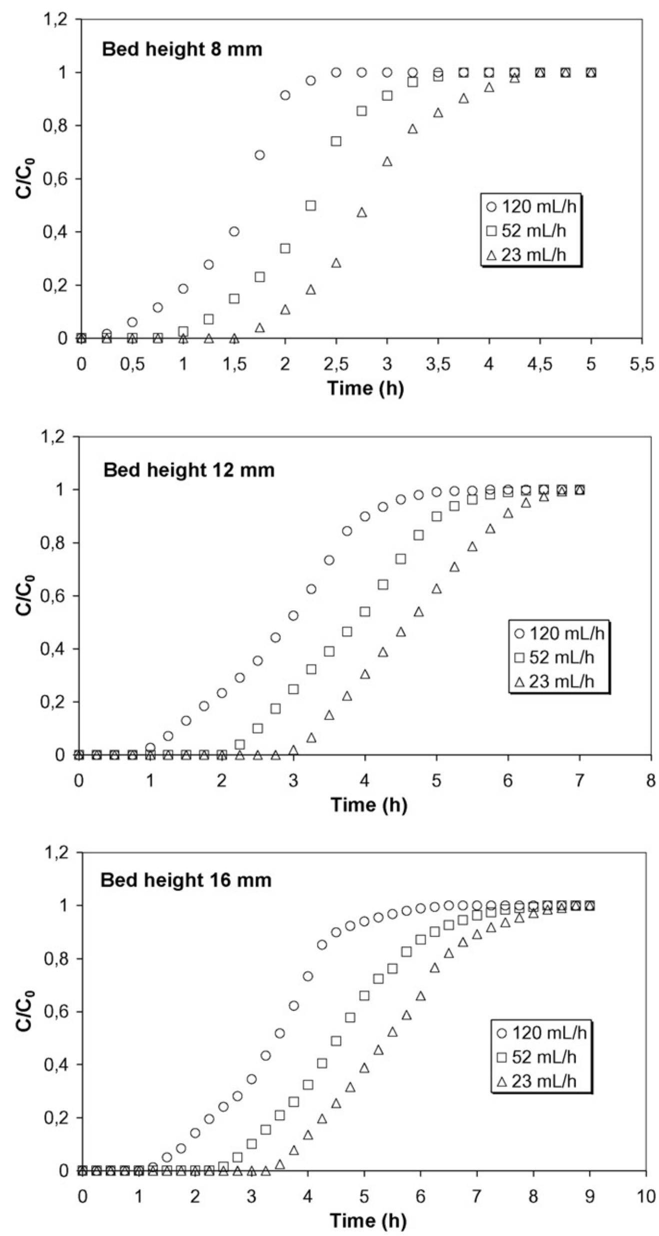

Fig. 2. Breakthrough curves for the sorption of methylene blue by crushed brick at different bed heights and flow rates.

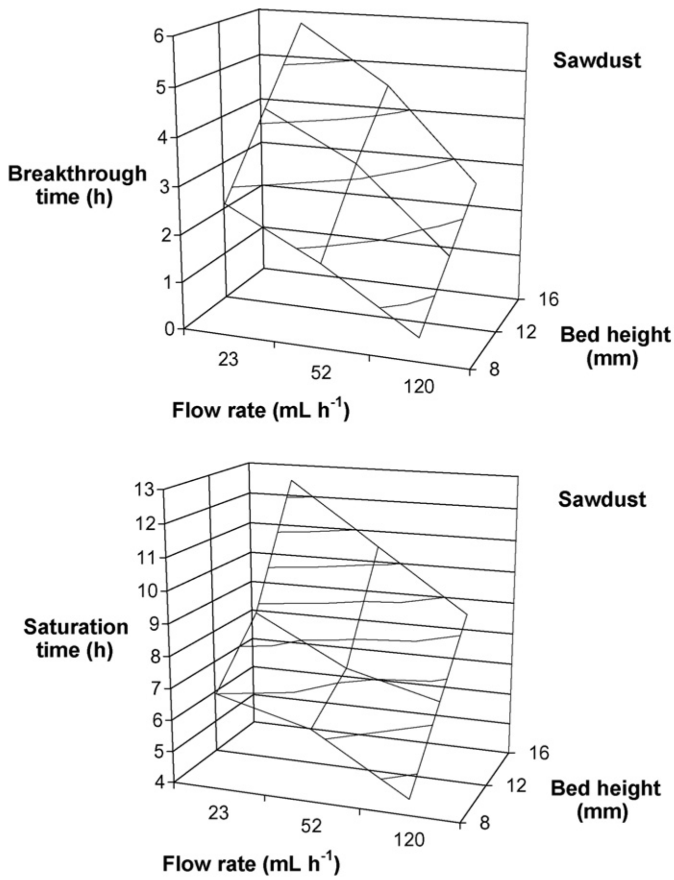

Fig. 3. Variation of breakthrough and saturation times with bed height and flow rate for methylene blue sorption by cedar sawdust.

The comparative study of the effect of the operating conditions on cedar sawdust and crushed brick fixation performance of the sorbents columns showed that both the breakthrough and saturation times depended on $1/U_0$ ($1/Q$) and Z parameters; $U_0 = Q/S$ is the superficial velocity (mm h^{-1}), which is the average rate of the liquid flow when the column is empty, S is the column section (mm^2), Q the flow rate (mL h^{-1}), and Z is the bed height (mm).

Figs. 1–4 show that both breakthrough and saturation times obtained for crushed brick are lower than those determined for cedar sawdust, whatever the operating conditions are. For all the studied bed heights and flow rates, it seems that cedar sawdust presents better sorbent properties than crushed brick. This confirms the results obtained in batch conditions [10].

3.3. Modeling of dynamic sorption

Successful design of a column sorption process required prediction of the concentration–time profile or breakthrough curve for the effluent. Various mathematical models can be used to describe fixed bed sorption. The dynamic behavior of the column was predicted with the Bohart and Adams, bed depth service time (BDST), Clark, Wolborska, and Yoon and Nelson models. The breakthrough curves showed the superposition of experimental results (points) and the theoretical calculated points (lines). Linear correlation coefficients (R) showed the fit between experimental data and linearized forms of Bohart and Adams, Clark, Wolborska, and Yoon and Nelson equations while the average percentage errors (APE) calculated according to Eq. (5) indicated the fit between the experimental and predicted values of C/C_0 used for plotting breakthrough curves:

$$\mathrm{APE}\,(\%) = \frac{\sum_{i=1}^{N} \left| \frac{(C/C_0)_{\mathrm{experimental}} - (C/C_0)_{\mathrm{predicted}}}{(C/C_0)_{\mathrm{experimental}}} \right|}{N} \times 100 \quad (5)$$

where N is the number of experimental data.

3.3.1. Application of the Bohart and Adams model

Bohart and Adams [13] established the fundamental equations describing the relationship between C/C_0 and t for the adsorption of chlorine on charcoal in fixed bed column. Although the original work by Bohart and Adams was done for the gas–charcoal adsorption system, its overall approach can be applied successfully in quantitative description of other systems. This model assumes that the adsorption rate is proportional to both the residual capacity of the activated carbon and the concentration of the sorbing species. The mass transfer rates obey the following equations:

$$\frac{\partial q}{\partial t} = -K_{\mathrm{BA}} q C \quad (6)$$

$$\frac{\partial C}{\partial Z} = -\frac{K_{\mathrm{BA}}}{U_0} q C \quad (7)$$

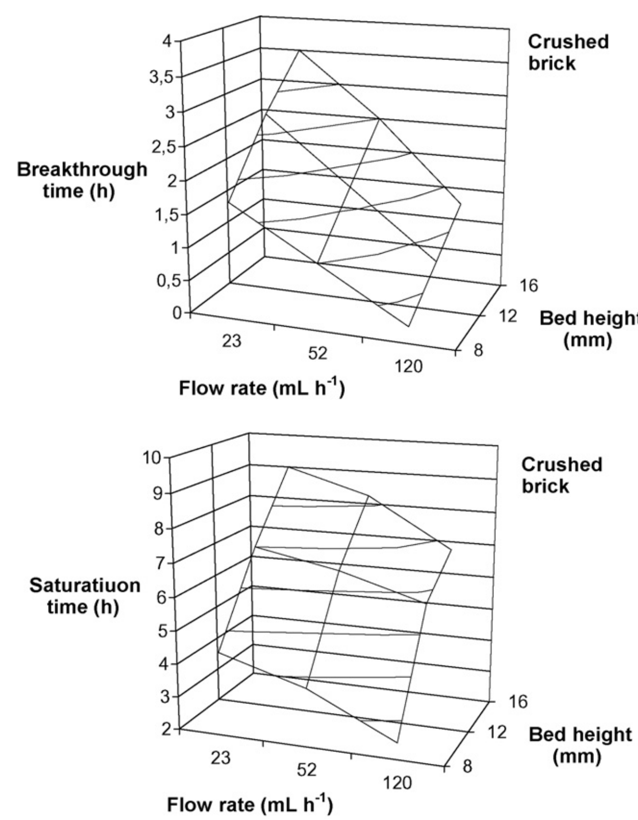

Fig. 4. Variation of breakthrough and saturation times with bed height and flow rate for methylene blue sorption by crushed brick.

where K_{BA} is the rate constant ($L\,mg^{-1}\,h^{-1}$). Some assumptions were made for the solution of these differential equation systems:

- the concentration field is considered to be low;
- for $t \to \infty$, $q \to N_0$, where N_0 is the sorption capacity ($mg\,L^{-1}$).

When the differential equation systems solved, the following equation was obtained with parameters K_{BA} and N_0:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{K_{BA} N_0 Z}{U_0} - K_{BA} C_0 t \qquad (8)$$

where C is the effluent concentration ($mg\,L^{-1}$), C_0 the influent concentration ($mg\,L^{-1}$), K_{BA} the sorption rate coefficient ($L\,mg^{-1}\,h^{-1}$), N_0 the sorption capacity ($mg\,L^{-1}$), Z the bed height (mm), U_0 the linear velocity ($mm\,h^{-1}$) and t is the time (h).

The model constants K_{BA} and N_0 can be determined from a plot of $\ln[(C/C_0) - 1]$ against t at given flow rate and bed height. The model gave a good fit of the experimental data at all flow rates and all bed heights examined with high correlation coefficients lower than −0.974. The parameters of Bohart and Adams model for both sorbents are tabulated in Table 2. It seems that sorption capacity of the low cost sorbents increases with increasing the flow rate. For all flow rates and bed heights used in this work, the sorption capacity of cedar sawdust is higher than that of crushed brick.

The simulated breakthrough curves are given in Figs. 5 and 6. These figures show the superposition of experimental results (points) and theoretical calculated points (lines). It appears that neither the breakthrough nor the whole breakthrough curves are well predicted by the Bohart and Adams model for both sorbents.

Table 2
Bohart and Adams model parameters for methylene blue sorption by cedar sawdust and crushed brick at different bed heights and flow rates

Z (mm)	Q ($mL\,h^{-1}$)	K_{BA} ($\times 10^3\,L\,mg^{-1}\,h^{-1}$)	N_0 ($mg\,L^{-1}$)	$-R$
Cedar sawdust				
	23	34.14	10516	0.983
8	52	44.13	17566	0.996
	120	44.01	25791	0.994
	23	45.01	9265	0.974
12	52	42.71	17395	0.976
	120	36.85	30292	0.980
	23	26.59	9520	0.984
16	52	32.52	17889	0.995
	120	33.33	31218	0.983
Crushed brick				
	23	66.41	6478	0.996
8	52	75.45	11193	0.998
	120	87.23	16877	0.985
	23	48.56	7061	0.984
12	52	48.85	12960	0.991
	120	47.89	21850	0.993
	23	35.91	6236	0.993
16	52	36.64	11998	0.993
	120	42.00	19839	0.994

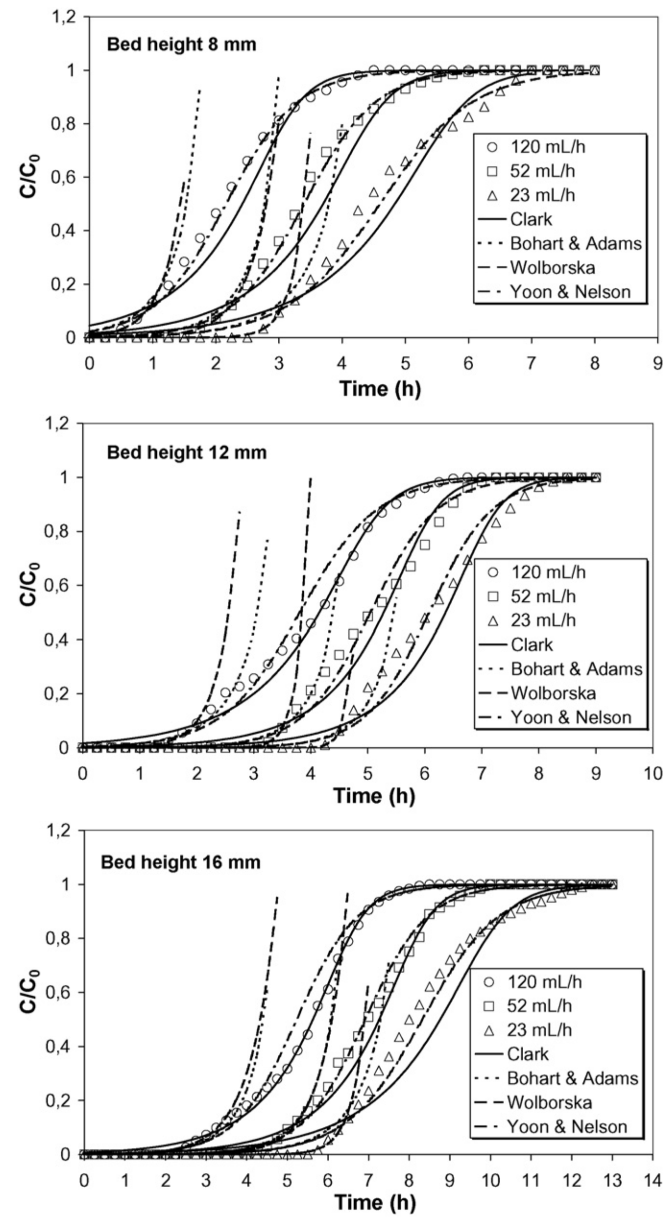

Fig. 5. Comparison of the experimental and predicted breakthrough curves obtained at different flow rates and bed heights according to the studied models for methylene blue sorption by cedar sawdust.

3.3.2. Application of the bed depth service time (BDST) model

The values of breakthrough time obtained for the various bed heights and flow rates used in this study were introduced into the bed depth service time (BDST) relation developed by Hutchins [14] and currently used

$$t_b = \frac{N_0}{C_0 U_0}(Z - Z_0) \qquad (9)$$

where t_b is the breakthrough time (h), N_0 the sorption capacity ($mg\,L^{-1}$), C_0 the initial concentration ($mg\,L^{-1}$), U_0 the superfi-

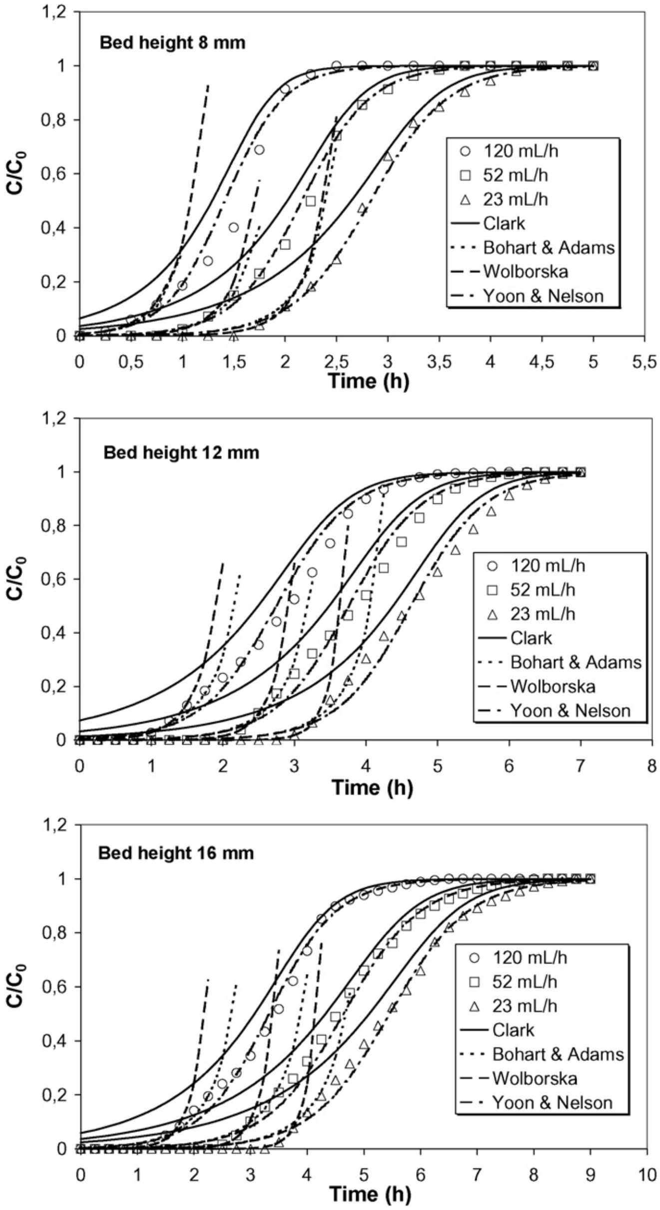

Fig. 6. Comparison of the experimental and predicted breakthrough curves obtained at different flow rates and bed heights according to the studied models for methylene blue sorption by crushed brick.

cial fluid velocity (mm h^{-1}), Z the height of the fixed bed (mm), and Z_0 is the length of the dynamic bed mass transfer zone (mm), which is equivalent to the adsorption front where sorbent material is partly saturate. This latter parameter corresponds to the critical bed depth, defined as the theoretical minimum depth of the sorbent sufficient to prevent an untimely release of pollutant in the effluent solution. According to Eq. (9), the breakthrough time depends on $1/C_0$, $1/U_0$, and Z parameters, as shown by previous experimental results.

The plot of breakthrough time against bed height at various flow rates is linear ($R \geq 0.997$) indicating the validity of BDST model for the present systems. The sorption capacity of the bed per unit bed volume, N_0, was calculated from the slope of BDST plot, assuming initial concentration, C_0, and linear velocity, U_0, as constant during the column operation. The thickness of mass transfer zone, Z_0, was calculated from the intercept of BDST plot.

Table 3
BDST model parameters for the sorption of methylene blue by cedar sawdust and crushed brick at various flow rates

	Q (mL h^{-1})	Z_0 (mm)	N_0 (mg L^{-1})	R
Cedar sawdust	23	0.67	6864	1
	52	2.79	14227	0.999
	120	6.00	23873	1
Crushed brick	23	0.19	4005	0.997
	52	2.67	7759	1
	120	6.00	11937	1

Parameters of the BDST relation for both sorbents are shown in Table 3. The sorption capacity and sorption zone values are strongly dependent on the flow rate within the range 23–120 mL h^{-1}. One might assume that the sorption process is significantly influenced by the external mass transfer of the solute through the hydrodynamic boundary layer. Results summarized in Table 3 show that the sorption capacity and the thickness of mass transfer zone increase with increasing the flow rate for both sorbents. The thickness of mass transfer zone increases with the flow rate showing the widening of the sorption zone and appearance of a faster breakthrough. However, it can be supposed that minimum bed length would be very short at the lowest flow rate. Under these experimental conditions, results suggest that the sorbents columns performance is characterized by a low critical bed length which increases with the column flow rate. The sorption capacity of cedar sawdust is higher than that of crushed brick for all flow rates and bed heights used in this study.

3.3.3. Application of the Clark model

The model developed by Clark [15] was based on the use of a mass-transfer concept in combination with the Freundlich isotherm:

$$\left(\frac{C_0}{C}\right)^{n-1} - 1 = A\,\mathrm{e}^{-rt} \tag{10}$$

where n is the Freundlich parameter and A and r are the Clark constants:

$$A = \exp\left(\frac{K_C N_0 Z}{U}\right) \tag{11}$$

and

$$r = K_C C_0 \tag{12}$$

linearizing Eq. (10):

$$\ln\left[\left(\frac{C_0}{C}\right)^{n-1} - 1\right] = \ln A - rt \tag{13}$$

Eq. (13) was applied to the effluent data from the fixed bed sorber, using linear regression. From a plot of $\ln[(C_0/C)^{n-1} - 1]$ versus time, the values of r (h^{-1}) and A can be thus determined

Table 4
Clark model parameters for methylene blue sorption by cedar sawdust and crushed brick at different bed heights and flow rates

Z (mm)	Q (mL h^{-1})	ln A	r (h^{-1})	$-R$	APE (%)
Cedar sawdust					
8	23	13.501	2.40	0.942	14.76
	52	12.179	2.78	0.969	11.50
	120	9.1337	2.99	0.962	7.50
12	23	20.798	2.97	0.934	14.62
	52	17.577	2.97	0.949	10.24
	120	12.066	2.45	0.975	6.32
16	23	17.15	1.74	0.931	13.70
	52	17.872	2.20	0.979	5.51
	120	14.448	2.23	0.992	2.84
Crushed brick					
8	23	10.832	3.38	0.987	24.87
	52	9.7583	3.89	0.993	25.89
	120	8.0622	4.78	0.991	14.53
12	23	12.667	2.46	0.974	17.44
	52	10.086	2.35	0.991	23.23
	120	7.6814	2.32	0.993	24.98
16	23	10.909	1.77	0.980	26.14
	52	9.7171	1.81	0.977	16.85
	120	8.3412	2.10	0.983	16.54

from its slope and intercept, respectively. The parameters of the Clark equation and the correlation coefficients (R) for all flow rates and bed heights are given in Table 4. The correlation coefficients for the linear regression are high showing good agreement of Clark model with the experimental data. For a given bed height, the parameter A decreases with increasing the flow rate.

Plotting C/C_0 against t according to these equations gives the breakthrough curves predicted by the Clark model (Figs. 5 and 6). It is clear from figures and average percentage errors shown in Table 4 that the experimental results fit the model very well at C/C_0 ratios above 0.07 for cedar sawdust and above 0.6 for crushed brick, however when the C/C_0 ratio decreased below these levels, deviation occurred and is much more pronounced for crushed brick than for cedar sawdust. Similarly, Aksu and Gönen [16] reported that adsorption breakthrough could be well described by the Clark model at the ratios of C/C_0 higher than 0.08. On the other hand, the adsorption performance of the silica gel columns could be well described by the Clark model at the ratios of concentration of effluent to influent (C/C_0) up to 0.3 for uranium(VI) and 0.5 for lead(II) [17]. Thus, the Clark model appeared to be approximately valid for methylene blue sorption on cedar sawdust column. For cedar sawdust, good fits are observed at higher flow rate (120 mL min^{-1}) and the obtained values of average percentage error are 7.5, 6.32 and 2.84% for bed heights of 8, 12 and 16, respectively. At the lowest flow rates (23 and 52 mL min^{-1}), the predicted curve slightly deviated from the experimental data. Additionally, it seems that the average percentage errors decrease with the increase of both flow rate and bed height.

3.3.4. Application of the Wolborska model

Wolborska [18] has proposed a model based on the general equations of mass transfer for diffusion mechanisms in the range of the low-concentration breakthrough curve. The mass transfer in the fixed bed sorption was described by the following equations:

$$\frac{\partial C}{\partial t} + U_0\left(\frac{\partial C}{\partial Z}\right) + \left(\frac{\partial q}{\partial t}\right) = D\left(\frac{\partial^2 C}{\partial Z^2}\right) \quad (14)$$

$$\frac{\partial q}{\partial t} = -v\left(\frac{\partial q}{\partial Z}\right) = \beta_a(C - C_S) \quad (15)$$

where C_S is the solute concentration at the solid/liquid interface (mg L^{-1}), D the axial diffusion coefficient (mm^2 h^{-1}), v the migration rate (mm h^{-1}), and β_a is the kinetic coefficient of the external mass transfer (h^{-1}). With some assumptions previously described by Wolborska [18]: $C_S \ll C$, $v \ll U_0$ and axial diffusion negligible $D \to 0$ as $t \to 0$, the solution can be approximated to

$$\ln\frac{C}{C_0} = \frac{\beta_a C_0}{N_0}t - \frac{\beta_a Z}{U_0} \quad (16)$$

with

$$\beta_a = \frac{U_0^2}{2D}\left(\sqrt{1 + \frac{4\beta_0 D}{U_0^2}} - 1\right) \quad (17)$$

where β_0 is the external mass transfer coefficient with a negligible axial dispersion coefficient D.

Wolbraska observed that in short beds or at high flow rates of solution through the bed, the axial diffusion was negligible and $\beta_a = \beta_0$. The migration velocity of the steady-state front satisfies the relation, known as Wicke's law:

$$v = \frac{U_0 C_0}{N_0 + C_0} \quad (18)$$

The plot of ln (C/C_0) versus t would give information on this model.

The Wolborska sorption model was applied to experimental data for the description of the initial part of the breakthrough curve. This approach was focused on the estimation of characteristic parameters, such as maximum sorption capacity (N_0) and kinetic coefficient of the external mass transfer (β_a). After applying Eq. (16) to the experimental data for varying flow rates and bed heights, a linear relationship between ln (C/C_0) and t was obtained for ln (C/C_0) < −2, for all breakthrough curves ($R \geq 0.961$). Respective values of N_0 and β_a were calculated from the ln (C/C_0) versus t plots at all flow rates and bed heights studied are presented in Table 5 together with the correlation coefficients. The values of kinetic constant are influenced by flow rate and bed height. This showed that the overall system kinetics is dominated by external mass transfer in the initial part of sorption in the column. β_a is also an effective coefficient which reflects the effect of both mass transfer in liquid phase and axial dispersion. Wolborska observed that in short beds or at high flow rates of solution through the bed, the axial diffusion is negligible and $\beta_a = \beta_0$, the external mass transfer coefficient. Increasing flow rate from 23 to 120 mL h^{-1} increased the

Table 5
Wolborska model parameters for methylene blue sorption by cedar sawdust and crushed brick at different bed heights and flow rates

Z (mm)	Q (mL h^{-1})	β_a (h^{-1})	N_0 (mg L^{-1})	v (mm h^{-1})	R	APE (%)
Cedar sawdust						
8	120	853.71	8156	2.23	1	0.02
	52	989.39	15952	2.59	0.993	5.66
	23	1474.05	20105	4.74	0.997	4.40
12	120	1303.28	7468	2.44	1	0.01
	52	1803.49	13785	2.99	1	0.02
	23	1620.34	22268	4.28	0.980	11.05
16	120	565.33	8191	2.22	0.961	21.00
	52	706.31	16833	2.45	0.976	11.75
	23	1090.56	28551	3.34	0.978	10.92
Crushed brick						
8	120	585.46	5840	3.11	1	0.02
	52	1016.93	9743	4.23	1	0.00
	23	1494.91	15159	6.28	0.981	14.57
12	120	720.90	5789	3.14	1	0.00
	52	1014.37	10773	3.83	1	0.04
	23	1328.61	16990	5.61	0.991	8.10
16	120	561.07	4931	3.68	1	0.06
	52	880.17	9263	4.45	0.989	10.78
	23	1323.38	14185	6.71	0.969	17.91

β_a value since increased turbulence reduces the film boundary layer surrounding the sorbent particle. Also, maximum sorption capacity (N_0) increased with increasing flow rate. For both sorbents, the migration velocity increases with increasing the flow rate.

Predicted and experimental breakthrough curves with respect to flow rate and bed height are shown in Figs. 5 and 6. It is clear from Figs. 5 and 6 and average percentage errors (7.20% for cedar sawdust and 5.72% for crushed brick) in Table 2 that there is a good agreement between the experimental and predicted values, suggesting that the Wolbraska model is valid for the relative concentration region up to 0.135 whereas large discrepancies are found between the experimental and predicted curves above this level for the methylene blue sorption by cedar sawdust and crushed brick in fixed bed column. Similarly, Tran and Roddick [17] suggested that Wolbraska model is valid for the relative concentration region up to 0.5, for the adsorption of metal ions on silica gels.

Although the Wolbraska model provides a simple and comprehensive approach to running and evaluating sorption-column tests, its validity was limited to the range of the used conditions.

3.3.5. Application of the Yoon and Nelson model

Yoon and Nelson [19] have developed a relatively simple model addressing the adsorption and breakthrough of adsorbate vapors or gases with respect to activated charcoal. This model was based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule was proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. The Yoon and Nelson model not only is less complicated than other models, but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent, and the physical properties of adsorption bed.

The Yoon and Nelson equation regarding to a single component system was expressed as

$$\ln\frac{C}{C_0 - C} = K_{YN}t - t_{1/2}K_{YN} \qquad (19)$$

where K_{YN} is the rate constant (h^{-1}), $t_{1/2}$ the time required for 50% sorbate breakthrough (h) and t is the time (h). The calculation of theoretical breakthrough curves for a single-component system requires the determination of the parameters K_{YN} and $t_{1/2}$ for the sorbate of interest. These values may be determined from available experimental data. The approach involves a plot of $\ln [C/(C_0 - C)]$ versus time according to Eq. (19). If the theoretical model accurately characterizes the experimental data, this plot will result in a straight line with slope of K_{YN} and intercept $t_{1/2}K_{YN}$.

The model developed by Yoon and Nelson was applied to investigate the breakthrough behavior of methylene blue onto cedar sawdust and crushed brick. The values of K_{YN} (the rate constant) and $t_{1/2}$ (the time required for 50% sorbate breakthrough) were determined from $\ln [C/(C_0 - C)]$ against t plots at different flow rates varied between 23 and 120 mL min^{-1} and at different bed heights varied between 8 and 16 mm. These values were used to calculate the breakthrough curve. The values of K_{YN} and $t_{1/2}$ are also listed in Table 6. From Table 6, the rate constant K_{YN} increased and the 50% breakthrough time $t_{1/2}$ decreased with increasing both flow rate and bed height. The data in Table 6 also indicated that $t_{1/2}$ values are in agreement with experimental results.

Table 6
Yoon and Nelson model parameters for methylene blue sorption by cedar sawdust and crushed brick at different bed heights and flow rates

Z (mm)	Q (mL h^{-1})	K_{YN} (h^{-1})	$t_{1/2}$ (h)	R	$t_{1/2}$ (experimental) (h)	APE (%)
Cedar sawdust						
8	23	1.37	4.60	0.983	4.34	6.67
	52	1.77	3.40	0.996	3.32	3.12
	120	1.76	2.16	0.994	2.09	3.18
12	23	1.80	6.07	0.974	6.07	12.51
	52	1.71	5.05	0.976	5.07	8.92
	120	1.47	3.81	0.980	4.14	9.23
16	23	1.06	8.32	0.984	8.00	7.01
	52	1.30	6.92	0.995	6.97	4.26
	120	1.33	5.23	0.983	5.63	8.21
Crushed brick						
8	23	2.66	2.83	0.996	2.78	5.51
	52	3.02	2.16	0.998	2.25	4.60
	120	3.49	1.41	0.985	1.59	6.94
12	23	1.94	4.63	0.984	4.62	10.65
	52	1.95	3.76	0.991	3.87	8.32
	120	1.92	2.75	0.993	2.92	8.02
16	23	1.44	5.45	0.993	5.41	5.51
	52	1.46	4.64	0.993	4.53	5.89
	120	1.68	3.32	0.994	3.45	4.99

The theoretical curves are compared with the corresponding experimental data in Figs. 5 and 6 and the obtained average percentage error values are regrouped in Table 6. The experimental breakthrough curves are very close to those predicted by the Yoon and Nelson model in the C/C_0 region above 0.07. Likewise, for the biosorption of phenol by immobilized activated sludge in continuous packed bed, Aksu and Gönen [15] have indicated that the breakthrough curves were very close to those predicted by the Yoon and Nelson model in the C/C_0 region from 0.08 up to 0.99. Thus, from the experimental results and data regression, the model proposed by Yoon and Nelson provided a good correlation of the effects of bed height and flow rate.

3.3.6. Comparison of models

The comparison of experimental and theoretical breakthrough curves for the sorption of methylene blue by cedar sawdust and crushed brick for different bed heights and flow rates according to the studied models is shown in Figs. 5 and 6. Five kinetic models were used to predict the breakthrough curves and to determine the characteristic parameters of the column useful for process design. All models were found suitable for describing the whole or a definite part of the dynamic behavior of the column with respect to flow rate and bed height, with the exception of Bohart and Adams model. The simulation of the whole breakthrough curve is effective with the Yoon and Nelson and the Clark models, but the breakthrough is best predicted by the Wolborska model. Studying the adsorption of methylene blue and basic red 22 by calcium chloride treated beech sawdust in fixed-bed system, Batzias and Sidiras [20] have indicated that the Clark model can simulate the experimental data.

4. Conclusions

The aim of the present work was to study and model the dynamic removal of methylene blue from aqueous solutions by sorption onto cedar sawdust and crushed brick in packed bed columns. The breakthrough curves have been determined at various flow rates and bed heights at 20 °C. The obtained results showed that both breakthrough and exhaustion times increase with the increase in the height of the bed, as more binding sites are available for sorption. For a given bed height, the lower the flow rate is, the higher are the breakthrough and exhaustion times. This flow rate dependence can be accounted for by the fact that for lower value of flow rate, the contact time is longer and hence the interaction between the dye and the sorbent is also greater.

The distribution of methylene blue molecules between the liquid phase and the solid phase was described by the Langmuir and the Freundlich models. The characteristic sorption parameters for each isotherm were determined. It was seen that the sorption equilibrium data can be fitted by the both models, but they were very well described by the Langmuir model.

Several models were applied to experimental data obtained from dynamic studies performed on fixed columns to predict the breakthrough curves and to determine the column kinetic parameters. These models gave good approximations of experimental behavior, with the exception of that of Bohart and Adams. For all flow rates and bed heights, the initial segment of the breakthrough curve was defined by the Wolborska model, while the whole breakthrough curve was well predicted by the Clark and the Yoon and Nelson models.

This work revealed that cedar sawdust and crushed brick can be successfully employed as a sorbent for dye removal from waste waters.

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