

## Dye adsorption by calcium chloride treated beech sawdust in batch and fixed-bed systems

F.A. Batzias, D.K. Sidiras\*

*Laboratory of Simulation of Industrial Processes, Department of Industrial Management and Technology, University of Piraeus, 80 Karaoli & Dimitriou, GR 18534 Piraeus, Greece*

Received 8 April 2004; received in revised form 30 July 2004; accepted 17 August 2004  
Available online 29 September 2004

### Abstract

Batch and column kinetics of methylene blue and red basic 22 adsorption on  $\text{CaCl}_2$  treated beech sawdust was investigated, using untreated beech sawdust as control, in order to explore its potential use as a low-cost adsorbent for wastewater dye removal. The adsorption capacity, estimated according to Freundlich's model, and the adsorption capacity coefficient values, determined using the Bohart and Adams' bed depth service model indicate that  $\text{CaCl}_2$  treatment enhanced the adsorption properties of the original material.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Dyes; Adsorption; Wood; Sawdust; Pretreatment; Calcium chloride; Column studies

### 1. Introduction

Recent EU environmental policy, including measures affecting all member states, requires that zero synthetic chemical compounds should be released into the marine environment. Due to their chemical structure, dyes, present in the wastewater streams of many industrial sectors, such as dyeing, textile, tannery and the paint industry, are resistant to exposure to light, water and many chemicals and therefore difficult to decolourise once released into the aquatic environment [1]. Activated carbon is the most efficient adsorbent used widely, but its high cost limits its applicability. Research is currently focusing on the use of low-cost commercially available organic materials as viable substitutes for activated carbon; in fact, sawdust, a relatively abundant and inexpensive material, is being extensively investigated as an adsorbent for removing contaminants from water [2]. Other adsorbent materials that have been studied include wood and agricultural residues, untreated [3–11] or treated in various ways [12–18].

Among the untreated materials that have been investigated, wood shavings are commonly used as an adsorbent, especially for basic dyes, with capacities varying according to the structure of the dye and the mesh size [4]. Many agricultural residues, such as wood chips, wheat straw, corncobs, barley husk and apple pomace have been successfully used to adsorb individual dyes and dye mixtures in textile effluents [1,5–7]. Removal of methylene blue and other basic dyes has been carried out using coir pith (an unwanted by-product from coir processing industry) [8], banana/orange peels [9] and palm-fruit bunch particles [10,11].

Formaldehyde- and concentrated sulphuric acid-treated sawdust and dilute acid-hydrolysed charred sawdust were successfully used as adsorbents for a variety of dyes [2,12]. Many chemical ( $\text{NaOH}$ ,  $\text{NH}_4\text{OH}$ ,  $\text{FeCl}_3$ ) and physical treatments (steam, milling) have been used to help break down the complex lignin complex in order to improve the adsorption performance of many lignocellulosic materials (wheat straw, corncob, barley husk) [13]. Cellulose-based anionic dye adsorbents have been prepared by lignocellulosic residues (e.g. wood sawdust) treated with cross-linked polyethylenimine [14]; also, carbonised agricultural wastes such as coir pith [15], cassava peel [16], bagasse [17] and kudzu [18] have

\* Corresponding author. Tel.: +30 210 414 2360; fax: +30 210 414 2366.  
E-mail address: sidiras@unipi.gr (D.K. Sidiras).

## Nomenclature

$c$	intercept of the intra-particle diffusion equation
$C$	concentrations of methylene blue or red basic 22 in the bulk solution at time $t$ in the case of batch adsorption process; also, the effluent concentration (mg/L) in the case of the column adsorption process
$C_e$	equilibrium concentration of the adsorbate (mg/L) for $t \rightarrow \infty$
$C_i$	influent concentration (mg/L) in the case of column adsorption process
$C_0$	initial dye concentration (mg/L)
$E$	adsorption activation energy
$k$	first order rate constant for the adsorption process (in $\text{min}^{-1}$ ).
$k_p$	intra-particle diffusion rate constant in $\text{mg g}^{-1} \text{min}^{-0.5}$ .
$K$	adsorption rate coefficient ( $\text{L mg}^{-1} \text{min}^{-1}$ ) in the case of column adsorption process
$K_F$	Freundlich constant related to adsorption capacity
$K_L$	Langmuir constant related to the energy of adsorption (L/mg)
$n$	inverse of the slope of the Freundlich isotherm, is the constant related to adsorption intensity
$N$	adsorption capacity coefficient (mg/L) in the case of column adsorption process
$p$	frequency factor at the Arrhenius law ( $\text{min}^{-1}$ )
$q$	amount adsorbed per unit mass of the adsorbent (mg/g)
$q_m$	Langmuir constant related to the amount of dye adsorbed (mg/g) when the saturation is attained
$q_t$	amounts of dye adsorbed per unit mass of the adsorbent (in mg/g) at time $t$
$R_L$	dimensionless constant called 'equilibrium parameter' or 'separation factor' expressing the essential characteristics of the Langmuir isotherm
$t$	adsorption time (min)
$T$	adsorption temperature (K)
$u$	linear velocity (cm/min) in the case of column adsorption process
$x$	bed depth of the adsorption column (cm)

been successfully utilized for the removal of dyes from aqueous solutions.

Mineral salts, mostly calcium chloride and in lesser extent sodium chloride, potassium chloride, zinc chloride, have been used to increase cork biomass sorption capacity [19], activate wood charcoals [20] and regenerate activated carbon [21].

The suitability of a range of materials as dye adsorbents (e.g. activated carbons from bamboo dust, coconut shell, groundnut sell, rice husk and straw) is often established using the kinetics of methylene blue adsorption during batch and continuous (column) processes [22].

In the present study, the removal of chemical grade methylene blue and commercial red basic 22 by  $\text{CaCl}_2$  treated beech sawdust was studied using untreated beech sawdust as control; the batch and column adsorption kinetics of the two dyes were used to estimate the adsorption capacity of the untreated and treated beech sawdust. The effect of the  $\text{CaCl}_2$  treatment temperature on the adsorption capacity was also investigated.

## 2. Materials and methods

### 2.1. Material development

The beech sawdust used was obtained from a local furniture manufacturing company, as a suitable source for full-scale/industrial applications. The moisture content of the material when received was 9% w/w; after screening, the fraction with particle sizes between 0.2 and 0.8 mm was isolated. The composition of the raw material was as follows (expressed in % w/w on a dry weight basis): 41.5% cellulose (80% degree of crystallinity), 27.3% hemicelluloses, 25.7% acid-insoluble lignin, 0.05% ash, and approximately 5.5% extractives and other components.

The  $\text{CaCl}_2$  treatment process was performed in a 500 mL glass batch reactor, equipped with an internal thermocouple, immersed in a heating oil bath. The  $\text{CaCl}_2$  treatment time was 1 h; 20% w/v  $\text{CaCl}_2$  solution catalysed the reaction at a liquid-to-solid ratio of 10:1. In pretreatment-1, the reaction ending temperature was 23 °C, whereas in pretreatment-2  $\text{CaCl}_2$  treatment occurred at 100 °C. The yields of the pretreated beech sawdust were really the same (95–97% w/w of the original dry material), for both pretreatment-1 and pretreatment-2.

### 2.2. Adsorption studies

Adsorption isotherms were derived from batch experiments. Following the batch procedure, accurately weighed quantities of adsorbent were transferred into 0.8 L bottles, where 0.5 L of buffered adsorbate solution were added. The bottles were sealed and mechanically tumbled for a period of 14 days. The resulting solution concentrations were determined and the equilibrium data from each bottle represented one point on the adsorption isotherm plots.

### 2.3. Kinetic studies

Adsorption rate batch experiments were conducted in a 1.5 L completely mixed glass reactor fitted with a twisted blade-type stirrer, operating at 300 rpm for keeping the lignocellulosic material in suspension. The reactor, containing

1 L aqueous dye solution, was placed into a water bath to keep temperature constant at the desired level. The effect of stirring was studied in the range of 0–600 rpm. The pH effect was studied in the range of 1.5–13 (the initial pH of the dye solutions was adjusted using dilute H<sub>2</sub>SO<sub>4</sub> or NaOH solutions, as appropriate).

#### 2.4. Column studies

Fixed-bed up-flow adsorber studies were conducted in 10 cm × 2 cm and 20 cm × 2 cm glass columns. The experimental set-up consisted of three parallel columns, fed by a multi-channel peristaltic pump at a constant flow rate, ranging from 5 to 15 mL/min. Interconnecting tubing and fittings were made of polytetrafluoroethylene (PTFE). Effluent samples were analysed to yield output concentration breakthrough curves.

#### 2.5. Analytical techniques

The degree of crystallinity of wood cellulose was measured with the X-ray diffraction method proposed by Segal et al. [23]. Following the technique proposed by Saeman et al. [24], the lignocellulosic materials were hydrolysed to glucose and reducing sugars in nearly quantitative yields; the filtrates were analysed for glucose using the Glu-cinet test and for reducing sugars using the Somogyi technique [25]. Based on these results the cellulose and hemicelluloses content of the adsorbents were estimated. Finally, the acid-insoluble lignin (Klason lignin) was determined according to the Tappi T222 om-88 method [26].

The concentration of methylene blue and red basic 22 in the solution was obtained by measuring OD at 663 and 530 nm ( $\lambda_{\max}$ ) respectively, using a HACK DR4000U UV-vis spectrophotometer.

### 3. Results

#### 3.1. Adsorption isotherms

The comparison of the adsorption capacity of the untreated and pretreated beech sawdust samples was based on the Freundlich and Langmuir isotherm models, both commonly used for investigating the sorption of a variety of dyes on e.g. sawdust [2], wood shavings [3], coir pith [8], banana/orange peels [9], palm-fruit bunch particles [10], dried kudzu [18], activated carbons [15,17,22,27–31] and lyocell fibres [25].

The Freundlich isotherm is given by the following equation:

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

where  $q$  is the amount adsorbed per unit mass of the adsorbent (mg/g),  $C_e$  the equilibrium concentration of the adsorbate (mg/L) and  $K_F$ ,  $n$  are the Freundlich constants related to

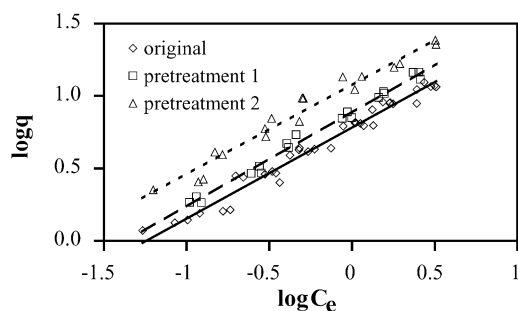


Fig. 1. Freundlich isotherms for the removal of methylene blue by adsorption on original and CaCl<sub>2</sub> treated beech sawdust.

adsorption capacity and intensity, respectively. Deriving the logarithmic form of Eq. (1):

$$\log q = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

The Freundlich constants  $K_F$  and  $n$  were estimated by linear regression analysis from the experimental adsorption data obtained at 23 °C for methylene blue (see Fig. 1) and red basic 22. The Freundlich parameter mean values are shown in Table 1; the confidence interval (given in brackets for each parameter) is not symmetrical to the relevant mean value due to the linearization of Eq. (1). However, the non-linear regression parameter estimated values did not differ significantly than the linear ones. Furthermore, linear regression analysis is preferred for the sake of simplicity and for achieving comparable results with those obtained by other researchers for other adsorbents. The  $K_F$  values estimated for the CaCl<sub>2</sub> treated samples were significantly higher than those of the untreated materials for both dyes, indicating an increased adsorption capacity of the former; among pretreatments higher values were obtained for the treated sawdust at 100 °C. The Langmuir isotherm applies to adsorption on completely homogeneous surfaces with negligible interaction between adsorbed molecules. In contrast, the Freundlich model, which is an empirical model used to describe adsorption in aqueous systems, applies to adsorption on heterogeneous surfaces with interaction between adsorbed molecules. The adequate applicability of the Freundlich equation to our data showed that the adsorbents' surface was heterogeneous.

The Langmuir isotherm equation is based on the following 'pseudo-monolayer' adsorption model.

$$\frac{1}{q} = \left( \frac{1}{q_m} \right) + \left( \frac{1}{K_L q_m} \right) \left( \frac{1}{C_e} \right) \quad (3)$$

where  $K_L$  is the Langmuir constant related to the energy of adsorption (L/mg) and  $q_m$  the amount of dye adsorbed (mg/g) when the saturation is attained. In cases where the isotherm experimental data approximates the Langmuir equation, the parameters  $K_L$  and  $q_m$  can be obtained by plotting  $1/q$  versus  $1/C_e$ . Table 2 presents the estimated parameter values for the data gathered in the present study. The adsorption capacities ( $q_m$ ) obtained for untreated beech sawdust were lower

Table 1  
The Freundlich parameters of adsorption isotherms (confidence interval 95%)

Parameter	Original beech sawdust	Beech sawdust pretreated with 20% w/v CaCl <sub>2</sub> for 1 h	
		At 23 °C	At 100 °C
<b>Methylene blue</b>			
$K_F$	6.05 (5.78–6.33)	7.76 (7.45–8.11)	11.99 (11.02–13.04)
$n$	1.59 (1.51–1.69)	1.53 (1.45–1.62)	1.61 (1.47–1.79)
Correlation coefficient ( $R$ )	0.987	0.995	0.982
SEE (mg/g)	0.565	0.548	1.30
<b>Red basic 22</b>			
$K_F$	4.77 (4.40–5.16)	5.42 (5.19–5.68)	6.22 (5.88–6.57)
$n$	1.64 (1.50–1.80)	1.49 (1.42–1.56)	1.44 (1.36–1.53)
Correlation coefficient ( $R$ )	0.978	0.998	0.994
SEE (mg/g)	1.72	0.450	1.04

than the values for the CaCl<sub>2</sub> treated samples; the superiority of the CaCl<sub>2</sub> treated at 100 °C sample over the pretreated at 23 °C was confirmed as per both dyes, with methylene blue exhibiting better results. The fitting of the Langmuir's adsorption model to the present data was also satisfactory but to a lesser degree than the Freundlich model, as shown by the corresponding standard error of estimate (SEE) values given in Table 2.

The essential characteristics of the Langmuir isotherm can be described by a dimensionless constant called 'equilibrium parameter' or 'separation factor'  $R_L$  [10,15,17,22], defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where  $C_0$  is the initial dye concentration (mg/L) and  $K_L$  the Langmuir constant (L/mg). It is generally accepted that  $R_L$  values indicate the type of isotherm, while an  $R_L$  value close to zero indicates favourable adsorption. At present, the  $R_L$  values were found to be close to zero for both dyes and dye concentrations  $C_0$  in the range of 1.4–14.0 mg/L for methylene blue and 2.1–21.0 mg/L for red basic 22 (see Table 2), for all adsorbents studied.

Table 2  
The Langmuir parameters of adsorption isotherms (confidence interval 95%)

Parameter	Original beech sawdust	Beech sawdust pretreated with 20% w/v CaCl <sub>2</sub> for 1 h	
		At 23 °C	At 100 °C
<b>Methylene blue</b>			
$q_m$ (mg/g)	9.78 (7.93–12.8)	13.02 (9.89–18.7)	16.05 (10.9–30.5)
$K_L$ (L/mg)	1.60 (1.33–1.83)	1.44 (1.12–1.70)	2.13 (1.37–2.65)
Correlation coefficient ( $R$ )	0.976	0.980	0.949
SEE (mg/g)	1.62	1.85	3.08
$R_L$	0.037–0.349	0.040–0.389	0.026–0.343
<b>Red basic 22</b>			
$q_m$ (mg/g)	20.2 (16.1–27.1)	23.9 (17.7–36.6)	29.1 (20.6–49.9)
$K_L$ (L/mg)	0.34 (0.28–0.39)	0.34 (0.25–0.40)	0.30 (0.19–0.38)
Correlation coefficient ( $R$ )	0.980	0.982	0.980
SEE (mg/g)	3.45	3.72	3.08
$R_L$	0.109–0.630	0.107–0.653	0.112–0.710

### 3.2. Kinetics of adsorption

The kinetics of adsorption of methylene blue on various materials has been extensively studied using various kinetic equations [8,9,32]. The widely used Langergren equation [33] is shown below:

$$q - q_t = q e^{-kt} \quad (5)$$

where  $q$  and  $q_t$  are the amounts of dye adsorbed per unit mass of the adsorbent (in mg/g) at equilibrium time ( $t \rightarrow \infty$ ) and time  $t$ , respectively, while  $k$  is the pseudo-first order rate constant for the adsorption process (in min<sup>-1</sup>). Moreover,  $q = (C_0 - C_e)/m$  and  $q_t = (C_0 - C)/m$ , where  $C$ ,  $C_0$ ,  $C_e$  are the concentrations of methylene blue in the bulk solution at time  $t$ , 0, and  $\infty$ , respectively, while  $m$  is the weight of the adsorbent used (in g). Further modification of Eq. (5) in logarithmic form gives:

$$\ln(q - q_t) = \ln q - kt \quad (6)$$

The plots of  $\ln(q - q_t)$  versus  $t$  for all methylene blue adsorbent systems were found to be linear, indicating the first order nature of the adsorption process. The values of the first order rate constants, the correlation coefficients ( $R$ -values) and the SEE were estimated.

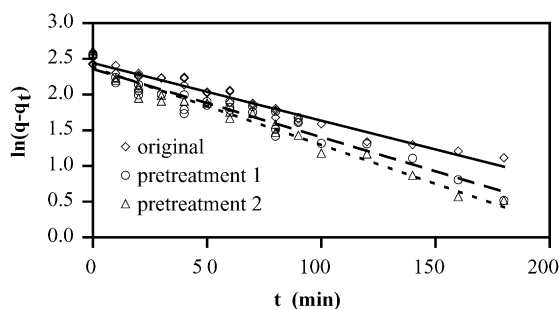


Fig. 2. The Langergren plots for the removal of methylene blue by adsorption on original and  $\text{CaCl}_2$  treated beech sawdust at adsorption temperature =  $23^\circ\text{C}$  ( $C_0 = 14.0\text{ mg/L}$ ).

All the linear correlations were found to be statistically significant, as evident by the  $R$ -values and the SEE-values, indicating the applicability of this kinetic equation to the adsorption of methylene blue. The calculated first order rate constant value ( $k$ ) of the Langergren equation for the untreated beech sawdust was found to be lower than that estimated for the  $\text{CaCl}_2$  treated at  $23^\circ\text{C}$  material, whereas the value  $k$  for the  $\text{CaCl}_2$  treated at  $100^\circ\text{C}$  material was the highest. The Langergren plots are shown in Fig. 2.

According to the Langergren model and the Arrhenius law  $k = p \exp(-E/RT)$ , the activation energy for the adsorption of methylene blue on untreated and pretreated beech sawdust was estimated by linear regression of  $\ln k$  (rate constant  $k$  in  $\text{min}^{-1}$ ) on  $1/T$  ( $T$  in K), as shown in Fig. 3. The methylene blue adsorption activation energy  $E$  (Table 3) was found equal to  $3.31\text{ kcal/mol}$  ( $13.8\text{ kJ/mol}$ ) and  $3.66\text{ kcal/mol}$  ( $15.3\text{ kJ/mol}$ ) for the  $\text{CaCl}_2$  treated at  $23$  and  $100^\circ\text{C}$  material, respectively, approximately equal to the activation energy of the original material ( $3.62\text{ kcal/mol}$  or  $15.1\text{ kJ/mol}$ ). This indicates that a physical process, i.e. the intra-particle diffusion, is the controlling step of the adsorption process.

### 3.2.1. Effect of stirring speed

Agitation is an important parameter in sorption phenomena, influencing the distribution of the solute in the bulk solution and the formation of the external boundary film. The effect of stirring speed (in rpm) on the adsorption rate constant  $k$  (in  $\text{min}^{-1}$ ) of the original material was investigated. The kinetics seemed to be affected by the agitation speed for

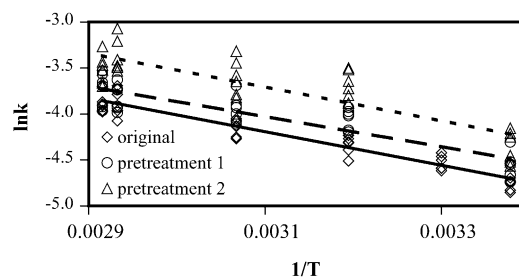


Fig. 3. The plots of  $\ln k$  (rate constant  $k$  in  $\text{min}^{-1}$ ) for the removal of methylene blue by adsorption on original and  $\text{CaCl}_2$  treated beech sawdust vs.  $1/T$  ( $T$  in K), according to the Arrhenius law.

values between 0 and 200 rpm, thus confirming that the influence of external diffusion on the sorption kinetic control plays a significant role. In contrast, the small effect of agitation in the range of 200–600 rpm showed that external mass transfer was not the rate limiting step, and implied that intra-particle diffusion resistance needed to be included in the analysis of overall sorption [8,9,32].

### 3.2.2. Effect of pH

The effect of the pH of the dye solution on the amount of dye adsorbed was studied by varying the initial pH under constant process parameters. The final concentration  $C$  of methylene blue solutions after an adsorption period of 190 min was significantly higher for pH values between 1.5 and 4 for both untreated and pretreated materials than the relevant concentration ( $C$  for  $t = 190\text{ min}$ ) for  $\text{pH} = 8$ . The lower adsorption of methylene blue at acidic pH was due to the presence of excess  $\text{H}^+$  ions that competed with the dye cation for adsorption sites. As the pH of the system increased ( $\text{pH} > 8$ ), the number of positively charged available sites decreased while the number of the negatively charged sites increased. The negatively charged sites favoured the adsorption of dye cation due to electrostatic attraction. The increase in initial pH from 8 to 13, slightly increased the amount of dye adsorbed. The final pH of the solution was found to decrease only slightly (by 0.3–0.5 pH units) after adsorption of methylene blue (in cationic form) with the release of  $\text{H}^+$  ions from the active site of the adsorbent surface. The results were in agreement with other literature reports [8,9,22,32].

Table 3  
The activation energy of methylene blue adsorption according to Langergren model

Parameter	Original beech sawdust	Beech sawdust pretreated with 20% w/v $\text{CaCl}_2$ for 1 h	
		At $23^\circ\text{C}$	At $100^\circ\text{C}$
Frequency factor ( $p$ in $\text{min}^{-1}$ )	4.27 (2.26–8.06)	3.09 (0.99–8.84)	7.45 (1.79–30.9)
Activation energy ( $E$ in $\text{kJ/mol}$ )	15.1 (13.4–16.7)	13.8 (10.7–16.6)	15.3 (11.5–19.1)
Activation energy ( $E$ in $\text{kcal/mol}$ )	3.62 (3.21–4.02)	3.31 (2.58–3.98)	3.66 (2.75–4.58)
Correlation coefficient ( $R$ )	0.953	0.876	0.841
SEE ( $\text{min}^{-1}$ )	0.00176	0.00311	0.00570

### 3.2.3. Intra-particle diffusion model

Adsorbate species are probably transported from the bulk of the solution into the solid phase through an intra-particle diffusion/transport process, which is frequently the rate-limiting step in many adsorption processes, especially in a rapidly stirred batch reactor [22]. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model [34]:

$$q_t = k_p \sqrt{t} + c \quad (7)$$

where  $q_t$  is the amount of dye adsorbed at time  $t$ ;  $c$  the intercept and  $k_p$  the intra-particle diffusion rate constant in  $\text{mg g}^{-1} \text{min}^{-0.5}$ . The  $k_p$  and  $c$  values were estimated by linear regression analysis of  $q_t$  on  $\sqrt{t}$ ; the low SEE values as well as the high  $R$ -values indicate the applicability of this model to our data. It showed that an intra-particle diffusion process took place. The estimated values of  $k_p$  were higher for  $\text{CaCl}_2$  treated beech sawdust than for the original material. The values of the intercept are related to the boundary layer thickness, i.e. the larger the intercept, the greater the boundary layer effect.

### 3.3. Column studies

Oulman proposed the use of a bed depth service model for simulating granular activated carbon (GAC) adsorption beds [35]. The model, first developed by Bohart and Adams [36], was based on surface reaction theory and is equivalent to the 'logistic curve' [37–41], an  $S$ -shaped curve given by Eq. (8), which is symmetrical around its midpoint at  $t = a/b$ ,  $C = C_i/2$ .

$$\frac{C}{C_i} = \frac{1}{1 + e^{a-bt}} \quad (8)$$

The Bohart–Adams equation is as follows:

$$\ln \left( \frac{C_i}{C} - 1 \right) = \frac{KNx}{u} - KC_i t \quad (9)$$

in which  $C$  = effluent concentration (mg/L);  $C_i$  = influent concentration (mg/L);  $K$  = adsorption rate coefficient ( $\text{L mg}^{-1} \text{min}^{-1}$ );  $N$  = adsorption capacity coefficient (mg/L);  $x$  = bed depth (cm);  $u$  = linear velocity (cm/min); and  $t$  = time (min). The above equation can be rewritten as Eq. (8) where  $a = KNx/u$  and  $b = KC_i$ .

One of the limitations of the 'simple logistic function' is that it requires symmetry. However, many breakthrough curves are not perfectly symmetrical owing to the nature of the adsorption system under study. Clark [38] has developed an alternative to the 'simple logistic function', called the 'generalized logistic function', that incorporates the parameter  $n$  of the Freundlich adsorption isotherm:

$$C = \left[ \frac{C_i^{n-1}}{(1 + A e^{-rt})} \right]^{1/n-1} \quad (10)$$

where  $n$  = inverse of the slope of the Freundlich isotherm;  $A = e^a = e^{KNx/u}$ ;  $r = b = KC_i$ .

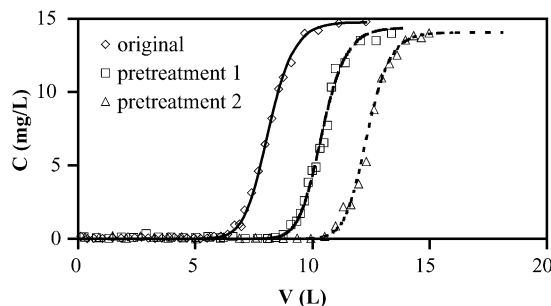


Fig. 4. Breakthrough curves for fixed bed of original and  $\text{CaCl}_2$  treated beech sawdust (methylene blue solution flow rate 10 mL/min and bed height 10 cm).

Eq. (10) was applied to the effluent data from the column adsorber, using linear regression (Fig. 4). Transforming Eq. (10):

$$\left( \frac{C_i}{C} \right)^{n-1} - 1 = A e^{-rt} \quad (11)$$

Linearizing Eq. (11):

$$\ln \left[ \left( \frac{C_i}{C} \right)^{n-1} - 1 \right] = \ln A - rt \quad (12)$$

The values of  $A$  and  $r$  can be thus estimated from the column effluent data assuming  $C_i$  = column influent and  $C$  = the column effluent at time  $t$ . As can be observed in Fig. 4, the theoretical estimations sufficiently simulate the experimental data. In addition, the adsorption rate coefficient ( $K$ ) and the adsorption capacity coefficient ( $N$ ), shown in Table 4, were estimated from the  $A$  and  $r$ -values. The adsorption capacity coefficient values were found higher for the  $\text{CaCl}_2$  treated materials than the original one.

## 4. Discussion

Untreated and  $\text{CaCl}_2$  treated beech sawdust were both found to strongly adsorb methylene blue and red basic 22. The  $K_F$  values and the adsorption capacities ( $q_m$ ), estimated using the Freundlich and the Langmuir models respectively, showed that the adsorption properties of the beech sawdust were enhanced with  $\text{CaCl}_2$  treatment. The temperature of pretreatment was also found to affect adsorption, as noted by the difference in the values of  $K_F$  for the  $\text{CaCl}_2$  treated at 23 and 100 °C material. The superiority of the treated over the untreated material was further verified by the  $R_L$  values referring to the same dye concentrations. Moreover, applying a bed depth service model for the simulation of sawdust adsorption beds, the adsorption capacity coefficient ( $N$ ) values were found higher for the  $\text{CaCl}_2$  treated beech sawdust than those for the original one.

The content of hemicelluloses, cellulose and lignin of the original beech sawdust remained practically unchanged by the  $\text{CaCl}_2$  treatment. The efficient swelling of the hemicellu-

Table 4  
Estimated parameter values for methylene blue and red basic 22 adsorption according to the Bohart–Adams bed depth service model

Parameter	Original beech sawdust	Beech sawdust pretreated with 20% w/v CaCl <sub>2</sub> for 1 h	
		At 23 °C	At 100 °C
<b>Methylene blue</b>			
Adsorption rate coefficient ( $K$ in $\text{mg}^{-1} \text{L min}^{-1}$ )	$0.00082 \pm 0.00008$	$0.00086 \pm 0.00027$	$0.00089 \pm 0.00028$
Adsorption capacity coefficient ( $N$ in $\text{mg/L}$ )	$3950 \pm 210$	$4269 \pm 324$	$5067 \pm 242$
SEE ( $\text{mg/L}$ )	0.167	0.420	0.395
<b>Red basic 22</b>			
Adsorption rate coefficient ( $K$ in $\text{mg}^{-1} \text{L min}^{-1}$ )	$0.00038 \pm 0.00010$	$0.00060 \pm 0.00008$	$0.00039 \pm 0.00010$
Adsorption capacity coefficient ( $N$ in $\text{mg/L}$ )	$5873 \pm 1130$	$6138 \pm 611$	$7641 \pm 672$
SEE ( $\text{mg/L}$ )	0.675	0.758	0.833

loses and cellulose results in ‘opening’ of the structure of the lignocellulosic matrix [1], which possibly accounts for the advanced adsorption properties of the CaCl<sub>2</sub> treated materials over the untreated ones. Furthermore, the CaCl<sub>2</sub> treatment of the material leads to the activation of the internal surface of beech sawdust particles, thus increasing the number of active sites available for dye binding [19,20,21].

Kinetic studies using the Langergren equation provided values of  $k$  for the CaCl<sub>2</sub> treated material higher than the estimated for the original material under the same conditions. Moreover, the methylene blue adsorption activation energy for the pretreated samples was found to be approximately 14–15 kJ/mol, at the same range with the activation energy of the original material (15.1 kJ/mol). The fact that the activation energies are low, strongly suggested that a physical stage was the controlling step of the adsorption process.

The removal of methylene blue by adsorption on various materials was found to be rapid at the initial period of contact time and then to become slow and stagnate with the increase in contact time. The possible mechanism for the removal of the cationic dye by adsorption was assumed to involve the following four steps [22]:

- migration of dye from bulk of the solution to the surface of the adsorbent;
- diffusion of dye through the boundary layer to the surface of the adsorbent;
- adsorption of dye at an active site on the surface of the adsorbent;
- intra-particle diffusion of dye into the interior pores of the adsorbent particle.

The boundary layer resistance was affected by the rate of adsorption and the contact time. An increase in contact time will reduce the resistance and thereby increase the mobility of dye during adsorption. Since the uptake of the dye at the active sites of adsorbent is a rapid process, the rate of adsorption is mainly governed by either a liquid phase mass transfer rate or an intra-particle mass transfer rate [9,11,22,30]. In the present study it was found that the intra-particle diffusion model was sufficiently applicable indicating the intra-particle mass transfer rate as the rate-determining step. Evidently, this was an approximation, as in adsorption the steps or stages

were not strictly in series over the whole surface under consideration (a spatial distribution of rates seems to be a more realistic approach).

## 5. Conclusions

The results presented herein showed that the CaCl<sub>2</sub> treatment of the beech sawdust enhances its adsorption properties considerably. The Freundlich adsorption capacity  $K_F$  (batch studies) for methylene blue increased by 28% for pretreatment at 23 °C and 98% for pretreatment at 100 °C. The  $K_F$  value for red basic 22 increased by 14 and 30% for pretreatment at 23 and 100 °C, respectively. The adsorption capacity coefficient  $N$  according to the Bohart–Adams bed depth service model (column studies) for methylene blue increased by 8% for pretreatment at 23 °C and 28% for pretreatment at 100 °C. The  $N$  value for red basic 22 increased by 5 and 30% for the same pretreatments, respectively. Thus, this low cost adsorbent could be made widely available for use as an alternative to commercial activated carbons for the removal of basic dyes from water/wastewater effluents.

## References

- [1] T. Robinson, B. Chandran, P. Nigam, The effect of pretreatments of three waste residues, wheat straw, corncobs and barley husks on dye adsorption, *Biores. Technol.* 85 (2002) 119.
- [2] A. Shukla, Y.-H. Zhang, P. Dubey, J.L. Margrave, The role of sawdust in the removal of unwanted materials from water, *J. Hazard. Mater.* B95 (2002) 137.
- [3] V.J.P. Poots, G. McKay, J.J. Healy, Removal of basic dye from effluent using wood as an adsorbent, *J. Water Poll. Contr. Fed.* 50 (5) (1978) 926.
- [4] S.I. Abo-Elela, M.A. el-Dib, Color removal via adsorption on wood shaving, *Sci. Tot. Environ.* 66 (1987) 269.
- [5] P. Nigam, G. Armour, I.M. Banat, D. Singh, R. Marchant, Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues, *Biores. Technol.* 72 (2000) 219.
- [6] T. Robinson, B. Chandran, G.-S. Naidu, P. Nigam, Studies on the removal of dyes from a synthetic textile effluent using barley husk in static-bath and in a continuous flow, packed-bed, reactor, *Biores. Technol.* 85 (2002) 43.

- [7] T. Robinson, B. Chandran, P. Nigam, Removal of dyes from a synthetic textile effluent by biosorption on apple pomace and wheat straw, *Water Res.* 36 (2002) 2824.
- [8] C. Namasivayam, M.D. Kumar, R.A. Begum, 'Waste' coir pith – a potential biomass for the treatment of dyeing wastewaters, *Biom. Bioenerg.* 21 (2001) 477.
- [9] G. Annadurai, R.-S. Juang, D.-J. Lee, Use of cellulose based wastes for adsorption of dyes from aqueous solutions, *J. Hazard. Mater.* B92 (2002) 263.
- [10] M.M. Nassar, Y.H. Magdy, Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles, *Chem. Eng. J.* 66 (1997) 223.
- [11] M.M. Nassar, Intra-particle diffusion of basic red and basic yellow dyes on palm fruit bunch, *Water Sci. Technol.* 40 (7) (1999) 133.
- [12] V.K. Garg, R. Gupta, A.-B. Yadav, R. Kumar, Dye removal from aqueous solutions by adsorption on treated sawdust, *Biores. Technol.* 89 (2003) 121.
- [13] L. Chun, C. Hongzhang, L. Zuohu, Adsorption of Cr(VI) by Fe-modified steam exploded wheat straw, *Proc. Biochem.* 39 (5) (2004) 541.
- [14] N.A. Ibrahim, A. Hashem, M.H. Abou-Shosha, Amination of wood sawdust for removing anionic dyes from aqueous solutions, *Polym. Plast. Technol. Eng.* 36 (6) (1997) 963.
- [15] C. Namasivayam, R. Radhika, S. Suba, Uptake of dyes by a promising locally available agricultural solid waste: coir pith, *Waste Manag.* 21 (2001) 381.
- [16] Rajeshwarisivaraj, S. Sivakumar, P. Senthikumar, V. Subburam, Carbon from cassava peel, an agricultural waste, as an adsorbent in the removal of dyes and metal ions from aqueous solution, *Biores. Technol.* 80 (2001) 233.
- [17] W.T. Tsai, C.Y. Chang, M.C. Lin, S.F. Chien, H.F. Sun, M.F. Hsieh, Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by  $ZnCl_2$  activation, *Chemosphere* 45 (2001) 51.
- [18] S.J. Allen, Q. Gan, R. Matthews, P.A. Johnson, Comparison of optimised isotherm models for basic dye adsorption by kudzu, *Biores. Technol.* 88 (2003) 143.
- [19] A. Chubar, J.R. Carvalho, M.J.N. Correia, Heavy metals biosorption on cork biomass: effect of the pretreatment, *Colloids Surf. A: Physicochem. Eng. Aspects* 238 (2004) 51.
- [20] G.A. El-Shobaky, A.M. Youssef, Chemical activation of charcoals, *Surf. Technol.* 7 (3) (1978) 209.
- [21] M.N.A. Jawaid, T.W. Weber, Effect of mineral salts on adsorption and regeneration of activated carbon, *Carbon* 17 (2) (1979) 97.
- [22] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons – a comparative study, *Dyes Pigments* 51 (2001) 25.
- [23] L. Segal, J.J. Greely, A.E. Martin, C.M. Conrad, An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer, *Textile Res. J.* 29 (1959) 786.
- [24] J.F. Saeman, J.F. Bubl, E.E. Harris, Quantitative saccharification of wood and cellulose, *Ind. Eng. Chem. Anal. Ed.* 17 (1945) 35.
- [25] M. Somogyi, Notes on sugar determination, *J. Biol. Chem.* 195 (1952) 19.
- [26] Tappi Standards, Atlanta, Tappi Tests Methods, 1997.
- [27] G. McKay, B.A. Duri, Simplified model for the equilibrium adsorption of dyes from mixtures using activated carbon, *Chem. Eng. Proc.* 22 (3) (1987) 145.
- [28] V. Meshko, L. Markovska, M. Mincheva, A.E. Rondrigues, Adsorption of basic dyes on granular activated carbon and natural zeolite, *Water Res.* 35 (14) (2001) 3357.
- [29] G.M. Walker, L.R. Weatherley, Adsorption of dyes from aqueous solution – the effect of adsorbent pore size distribution and dye aggregation, *Chem. Eng. J.* 83 (2001) 201.
- [30] S.V. Mohan, N.C. Rao, J. Karthikeyan, Adsorption removal of direct azo dye from aqueous phase onto coal based sorbents: a kinetic and mechanistic study, *J. Hazard. Mater.* B90 (2002) 189.
- [31] F. Carrillo, M.J. Lis, J. Valdeperas, Sorption isotherms and behaviour of direct dyes on lyocel fibres, *Dyes Pigments* 53 (2002) 129.
- [32] F.A. Batzias, D.K. Sidiras, Wastewater treatment with gold recovery through adsorption by activated carbon. Water pollution IV: modelling, measuring prediction, in: C.A. Brebbia (Ed.), *Series: Progress in Water Resources*, vol. 3, WIT Press, Southampton, 2001, p. 533.
- [33] H.C. Trivedi, V.M. Patel, R.D. Patel, Adsorption of cellulose triacetate on calcium silicate, *Eur. Polym. J.* 9 (1973) 525.
- [34] G. Crank, *The Mathematics of Diffusion*, Clarendon Press, London, New York, 1993.
- [35] C.S. Oulman, Logistic curve as a model for carbon bed design, *J. Am. Water Works Assoc.* 72 (1) (1980) 50.
- [36] G.S. Bohart, E.Q. Adams, Adsorption in columns, *J. Chem. Soc.* (1920) 42.
- [37] R.A. Hutchins, New method simplifies design of activated-carbon systems, *Chem. Eng.* 80 (19) (1973) 133.
- [38] R.M. Clark, Modeling TOC removal by GAC: the general logistic function, *J. Am. Water Works Assoc.* 79 (1) (1987) 33.
- [39] G.M. Walker, L.R. Weatherley, COD removal from textile industry effluent: pilot plant studies, *Chem. Eng. J.* 84 (2001) 125.
- [40] K.S. Low, C.K. Lee, A.Y. Ng, Column study on the sorption of Cr(IV) using quaternized rice hull, *Biores. Technol.* 68 (1999) 205.
- [41] B.M. Van Vliet, W.J. Weber, Comparative performance of synthetic adsorbents and activated carbon for specific compound removal from wastewaters, *J. Water Poll. Contr. Fed.* 53 (11) (1981) 1585.