Simulation of methylene blue adsorption by salts-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*

Abstract

Batch and column kinetics of methylene blue adsorption on calcium chloride, zinc chloride, magnesium chloride and sodium chloride treated beech sawdust were simulated, 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, the Langmuir constant K_L and the adsorption capacity coefficient values, determined using the Bohart and Adams' bed depth service model indicate that salts treatment enhanced the adsorption properties of the original material. Since sawdust is an industrial waste/byproduct and the salts used can be recovered as spent liquids from various chemical operations, this process of adsorbent upgrading/modification might be considered to take place within an 'Industrial Ecology' framework.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Simulation; Dyes; Methylene blue; Adsorption; Wood; Sawdust; Pretreatment; Column; Salts; Calcium chloride; Zinc chloride; Magnesium chloride; Sodium chloride

1. Introduction

Adsorption techniques are widely used to remove certain classes of pollutants from waters, especially those that are not easily biodegradable. Commercial activated carbon is the preferred sorbent for colour removal, but its widespread use is restricted due to high cost. Alternative non-conventional waste materials from industry and agriculture can be obtained and employed as inexpensive sorbents [1]. Wood sawdust and agricultural/industrial residues (wheat straw, corncobs, barley husk, apple pomace, coir pith, banana/orange peels, palm-fruit bunch particles, cedar sawdust, hazelnut shells, Posidonia oceanica fibre, etc.) untreated or treated (with H_2SO_4, HCl, HNO_3, NaOH, NH_4OH, $CaCl_2$, $ZnCl_2$, $MgCl_2$, NaCl, KCl, $FeCl_3$, formaldehyde, cross-linked polyethylenimine, etc.), relatively abundant and inexpensive materials, have been extensively investigated as adsorbents for removing contaminants from water [2–12]. The suitability of a range of materials as dye adsorbents is usually established using the kinetics of methylene blue adsorption during batch and continuous (column) processes [4,6,9,11,12].

In the present study, the removal of chemical grade methylene blue by salts ($CaCl_2$, $ZnCl_2$, $MgCl_2$, NaCl) treated beech sawdust was studied using untreated beech sawdust as control; the batch and column adsorption kinetics of this dye were used to estimate/compare the adsorption capacity of the untreated and treated beech sawdust. The choice of methylene blue as adsorbate facilitates comparison with other adsorption systems cited in technical literature and provides a sound platform for simulation and scale up/down with high information reliability/granularity.

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

* Corresponding author. Tel.: +30 104142360; fax: +30 104142392.
E-mail address: sidiras@unipi.gr (D.K. Sidiras).

Nomenclature

c	intercept of the intra-particle diffusion equation
C	concentrations of methylene blue 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 $t \to \infty$
C_i	influent concentration (mg/L) in the case of column adsorption process
C_0	initial dye concentration (mg/L)
E	adsorption activation energy (kJ/mol or kcal/mol)
k	first order rate constant for the adsorption process (in min^{-1})
K	adsorption rate coefficient ($\mathrm{L\,mg^{-1}\,min^{-1}}$) in the case of column adsorption process
K_F	Freundlich constant related to adsorption capacity
$K_{F,0}, K_{F,e}, k_F$	empirical parameters of Eq. (3)
K_L	Langmuir constant related to the energy of adsorption (L/mg)
$K_{L,0}, K_{L,e}, k_L$	empirical parameters of Eq. (5)
k_p	intra-particle diffusion rate constant in $\mathrm{mg\,g^{-1}\,min^{-0.5}}$
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
N_0, N_e, k_N	empirical parameters of Eq. (13)
p	frequency factor at the Arrhenius law (min^{-1})
q	amount adsorbed per unit mass of the adsorbent (mg/g)
q_m	Langmuir constant related 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)
z	driving force for adsorption, as a function of concentration, temperature and surface nature/topology

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 salt treatment process was performed in a 500-mL glass batch reactor, equipped with an internal thermocouple, immersed in a heating oil bath. The salt treatment time was 0.5–5 h (not including 40 min preheating time); 20% (w/v) salt (calcium chloride, zinc chloride, magnesium chloride or sodium chloride) solution catalyzed the reaction at a liquid-to-sawdust ratio of 10:1 (the salt solution volume was 400 mL and the material dose was 40 g). The reaction ending temperature was 100 °C (reached after 40 min preheating time). The yields of the pretreated beech sawdust were really the same (95.6 ± 1.1% (w/w) of the original dry material), for the four salts used for the pretreatment, as shown in Table 1.

2.2. Adsorption isotherm 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 adsorbate solution was added. The sorbent weight was 0.5 g, the temperature was 23 °C, the initial methylene blue concentration varied from 1.4 to 14.0 mg/L. The bottles were sealed and mechanically tumbled for a period of 7 days. This equilibrium time was chosen after experimental studies (the equilibrium time varied from 3 h to 14 days), to ensure that nearly equilibrium conditions were achieved. 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 2-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 sorbent dose was 1 g, the temperature was 23 °C, the initial methylene blue concentration varied from 1.4 mg/L to 14.0 mg/L. The effect of stirring was studied in the rage 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_2SO_4 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 bed height was 10 cm and 20 cm, respectively. 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. The initial dye concentration was 14.0 and 60.0 mg/L. Interconnective 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. [13]. Following the technique proposed by Saeman et al. [14], the lig-

Table 1
The yields of the salts-treated beech sawdust

Pretreatment time t (h)[a]	Calcium chloride	Zinc chloride	Magnesium chloride	Sodium chloride
1.17	95.5	96.2	97.0	97.0
1.67	95.0	95.5	95.8	96.1
2.67	96.4	95.5	96.7	96.0
3.67	97.3	95.2	96.4	95.1
4.67	94.6	92.9	95.0	95.0
5.67	96.1	94.0	95.4	95.8
Average	95.8 ± 2.0	95.0 ± 2.4	96.3 ± 1.6	95.8 ± 1.4

[a] Preheating time 40 min is included.

nocellulosic 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 [15]. 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 [16].

The concentration of methylene blue in the solution was obtained by measuring O.D. at 663 nm (λ_{max}), respectively, using a HACH DR4000U UV–visible spectrophotometer.

3. Results and discussion

3.1. Adsorption isotherms

The comparison of the adsorption capacity of the untreated and pretreated beech sawdust samples was based on the Freundlich [17] and Langmuir [18] isotherm models, both commonly used for investigating the sorption of a variety of dyes on various lignocellulosic materials (sawdust, wood shavings, etc.) and activated carbons.

The Freundlich [17] isotherm is given by the following equation:

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

where q is the amount adsorbed per unit mass of the adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L) and K_F, n are the Freundlich constants related to adsorption capacity and intensity, respectively. Deriving the logarithmic form of Eq. (1):

$$\log q = \log K_F + \frac{1}{n}\log C_e \tag{2}$$

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. Fig. 1 presents methylene blue adsorption isotherms by original and salts-treated sawdust (salts-treatment time = 5 h). The theoretical curves are estimated according to the Freundlich equation. The Freundlich parameter mean values are shown in Table 2. The K_F values estimated for the salt treated samples were significantly higher than those of the untreated materials, indicating an increased adsorption capacity of the former; among pretreatments higher values

were obtained for the treated sawdust with NaCl. The parameter n was not significantly affected by the treatment time t and was found to be 1.43 ± 0.22 for CaCl$_2$ treated beech sawdust, 1.40 ± 0.08 for ZnCl$_2$ treated beech sawdust, 1.39 ± 0.12 for MgCl$_2$ treated beech sawdust, and 1.50 ± 0.12 for NaCl treated beech sawdust, comparable with the parameter $n = 1.49$ for the original material (see Table 2).

The Freundlich adsorption capacity parameter K_F for the removal of methylene blue by adsorption on beech sawdust as affected by salts-treatment time (t in hours) was found to be

$$K_F = K_{F,e} - (K_{F,e} - K_{F,0})e^{-k_F t} \tag{3}$$

where $K_{F,0}$, $K_{F,e}$ and k_F are empirical parameters (see Table 3)

The Langmuir isotherm equation [18] is based on the following 'pseudo-monolayer' adsorption model.

$$\frac{1}{q} = \left(\frac{1}{q_m}\right) + \left(\frac{1}{K_L q_m}\right)\left(\frac{1}{C_e}\right) \tag{4}$$

where K_L is the Langmuir constant related to the energy of adsorption (L mg^{-1}) and q_m the amount of dye adsorbed (mg g^{-1}) 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 4 presents the estimated parameter values for the data gathered in the present study. The Langmuir constant related to the energy of adsorption K_L values obtained for untreated beech sawdust were lower than the values for the salt treated samples; the superiority of the NaCl-treated
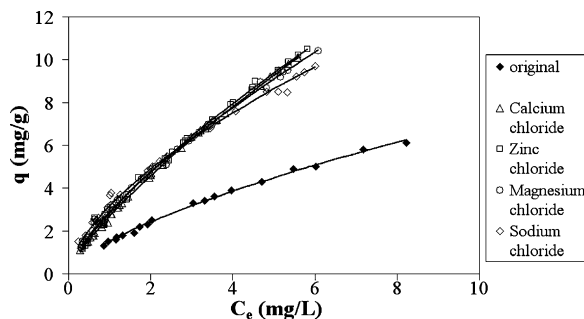

Fig. 1. The adsorption isotherms of methylene blue by original and salts-treated beech sawdust. Adsorption temperature 23 °C, salts-treatment time $t = 5$ h (preheating time 40 min is not included). The theoretical curves are estimated according to the Freundlich equation.

Table 2
The Freundlich parameters of methylene blue adsorption isotherms on original and salt treated beech sawdust

Pretreatment time t (h)[a]	Beech sawdust pretreated with 20% (w/v)			
	Calcium chloride	Zinc chloride	Magnesium chloride	Sodium chloride
Freundlich adsorption capacity constant K_F				
0			1.53	
1.17	2.77	2.69	2.71	2.88
1.67	2.63	2.83	2.74	3.00
2.67	3.25	2.82	3.09	3.12
3.67	2.94	2.76	2.69	3.24
4.67	3.28	2.98	2.96	3.12
5.67	2.70	2.85	2.91	3.18
Freundlich adsorption intensity constant n				
0			1.49	
1.17	1.36	1.42	1.40	1.48
1.67	1.34	1.36	1.32	1.51
2.67	1.57	1.39	1.50	1.46
3.67	1.50	1.45	1.36	1.51
4.67	1.50	1.41	1.38	1.43
5.67	1.30	1.35	1.41	1.61
Average	1.43 ± 0.22	1.40 ± 0.08	1.39 ± 0.12	1.50 ± 0.12
Correlation coefficient (R)				
0			0.9231	
1.17	0.9950	0.9387	0.9654	0.9781
1.67	0.9706	0.9581	0.9423	0.9466
2.67	0.9584	0.9205	0.9472	0.9371
3.67	0.9641	0.9384	0.9445	0.9643
4.67	0.9905	0.9655	0.9705	0.9589
5.67	0.9827	0.9575	0.9616	0.9736
SEE (mg/g)				
0			0.41	
1.17	0.35	0.40	0.38	0.37
1.67	0.37	0.38	0.39	0.39
2.67	0.38	0.41	0.39	0.40
3.67	0.38	0.40	0.39	0.38
4.67	0.36	0.38	0.37	0.38
5.67	0.36	0.38	0.38	0.37

[a] Preheating time 40 min is included.

sample over the pretreated with the other salts was presently confirmed. 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' values (SEE-values) given in Table 4. SEE = $\sqrt{\sum (y_i - y_{i,\text{theor}})^2/(n - p)}$, where: y_i is the experimental value of the depended variable, $y_{i,\text{theor}}$ is the theoretical/estimated value of the depended variable, n is the number of the exper-

Table 3
The simulation parameters of the Freundlich adsorption capacity constant K_F values (non-linear regression analysis)

Simulation parameters	Calcium chloride	Zinc chloride	Magnesium chloride	Sodium chloride
$K_{F,0}$			1.53	
$K_{F,e}$	3.02	2.86	2.91	3.18
k_F	1.29	1.81	1.59	1.43
SEE	0.28	0.08	0.15	0.05

imental measurements and p is the number of parameters ($n−p$ is the number of the degrees of freedom). The Langmuir constant related to the amount of dye adsorbed q_m (mg g^{-1}) when the saturation is attained, was not significantly affected by the treatment time t and was found to be 12.2 ± 1.8 for CaCl$_2$ treated beech sawdust, 13.2 ± 2.0 for ZnCl$_2$ treated beech sawdust, 15.6 ± 2.4 for MgCl$_2$ treated beech sawdust, and 9.7 ± 0.6 for NaCl treated beech sawdust, comparable with the parameter $n = 13.6$ for the original material (see Table 4).

The Langmuir constant related to the energy of adsorption K_L (L mg^{-1}) for the removal of methylene blue by adsorption on beech sawdust as affected by salts treatment time (t in hours) was found to be

$$K_L = K_{L,e} - (K_{L,e} - K_{L,0})\, e^{-k_L t} \tag{5}$$

where $K_{L,0}$, $K_{L,e}$ and k_L are empirical parameters (see Table 5)

The essential characteristics of the Langmuir isotherm [18] can be described by a dimensionless constant called 'equilibrium parameter' or 'separation factor' R_L, defined by the following

Table 4
The Langmuir parameters of methylene blue adsorption isotherms on original and salt treated beech sawdust

Pretreatment time t (h)[a]	Beech sawdust pretreated with 20% (w/v)			
	Calcium chloride	Zinc chloride	Magnesium chloride	Sodium chloride
Langmuir constant related to the energy of adsorption K_L (L mg^{-1})				
0			0.151	
1.17	0.243	0.260	0.216	0.506
1.67	0.360	0.289	0.184	0.485
2.67	0.455	0.270	0.259	0.517
3.67	0.376	0.339	0.240	0.608
4.67	0.444	0.269	0.219	0.611
5.67	0.398	0.292	0.288	0.613
Langmuir constant related to the amount of dye adsorbed q_m (mg g^{-1})				
0			13.6	
1.17	12.6	13.4	15.0	10.2
1.67	11.5	13.0	17.7	9.9
2.67	11.5	14.2	15.0	9.6
3.67	13.7	12.6	15.3	9.7
4.67	11.4	14.3	16.4	9.5
5.67	12.3	11.7	14.2	9.2
Average	12.2 ± 1.8	13.2 ± 2.0	15.6 ± 2.4	9.7 ± 0.6
Correlation coefficient (R)				
0			0.9769	
1.17	0.9948	0.9327	0.9580	0.9475
1.67	0.9450	0.9074	0.9264	0.8885
2.67	0.9427	0.9698	0.9029	0.8230
3.67	0.9484	0.9285	0.9442	0.9440
4.67	0.9799	0.9496	0.9528	0.9539
5.67	0.9420	0.9501	0.9691	0.9330
SEE (mg/g)				
0			0.84	
1.17	0.81	0.92	0.87	0.89
1.67	0.90	0.97	0.93	1.01
2.67	0.90	0.85	0.98	1.18
3.67	0.89	0.93	0.90	0.90
4.67	0.83	0.89	0.88	0.88
5.67	0.90	0.89	0.85	0.92
R_L (original material)			0.322–0.826	
R_L (pretreated materials)	0.136–0.746	0.174–0.733	0.199–0.795	0.104–0.596

[a] Preheating time 40 min is included.

equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{6}$$

where C_0 is the initial dye concentration (mg/L) and K_L is the Langmuir constant (L/mg). At the present work, the R_L values were found to be close to zero for all dye concentrations C_0 in

Table 5
The simulation parameters of the Langmuir constant K_L values (in L mg^{-1}) related to the energy of adsorption (non-linear regression analysis)

Simulation parameters	Calcium chloride	Zinc chloride	Magnesium chloride	Sodium chloride
$K_{L,0}$			0.151	
$K_{L,e}$	0.434	0.295	0.275	0.603
k_L	0.663	1.326	0.398	0.980
SEE	0.053	0.029	0.031	0.040

the range of 1.4–14.0 mg/L for methylene blue (see Table 4), for all adsorbents (salts-treated and untreated sawdust) studied.

3.2. Kinetics of adsorption

The kinetics of adsorption of methylene blue on various materials has been extensively studied using various kinetic equations. The widely used Lagergren equation [19] is shown below:

$$q - q_t = q e^{-kt} \tag{7}$$

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^{-1}). Moreover, $q = (C_0 - C_e)V/m$ and $q_t = (C_0 - C)V/m$, where C, C_0, C_e are the concentrations of methylene blue in the bulk solution at time t, 0, and ∞, respec-

tively, while m is the weight of the adsorbent used (in g), and V is the solution volume (in mL). Further modification of Eq. (7) in logarithmic form gives:

$$\ln(q - q_t) = \ln q - kt \tag{8}$$

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. Fig. 2 presents methylene blue adsorption kinetics by original and salts-treated beech sawdust (salts-treatment time = 5 h). The theoretical curves are estimated according to the Lagergren equation. The values of the first order rate constants, the correlation coefficients (R-values) and the SEE were estimated (see Table 6).

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
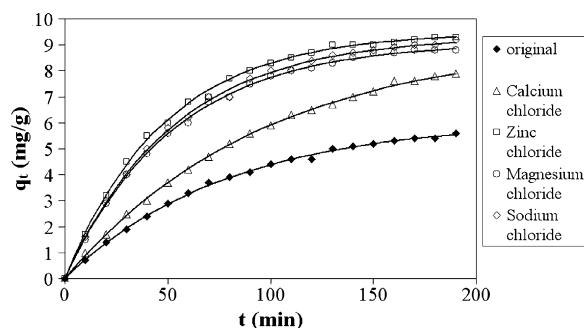

Fig. 2. The adsorption kinetics of methylene blue by original and salts-treated beech sawdust. Initial methylene blue concentration $C_0 = 14.0$ mg/L, adsorption temperature 23 °C, salts-treatment time $t = 5$ h (preheating time 40 min is not included). The theoretical curves are estimated according to the Lagergren equation.

Table 6
The first order rate constant k (min^{-1}) of Methylene Blue adsorption according to Lagergren model

Pretreatment time t (h)[a]	For C_0 (in mg/L)						Average
	14.0	10.0	7.1	4.1	2.9	1.4	
Original beech sawdust							
0	0.0127	0.0137	0.0149	0.0168	0.0182	0.0199	0.0160 ± 0.0054
CaCl$_2$-treated beech sawdust							
1.17	0.0090	0.0118	0.0166	0.0185	0.0167	0.0140	0.0144 ± 0.0070
1.67	0.0135	0.0152	0.0202	0.0155	0.0200	0.0170	0.0169 ± 0.0054
2.67	0.0100	0.0140	0.0160	0.0166	0.0177	0.0198	0.0157 ± 0.0068
3.67	0.0122	0.0136	0.0144	0.0229	0.0216	0.0126	0.0162 ± 0.0096
4.67	0.0141	0.0157	0.0210	0.0160	0.0206	0.0174	0.0172 ± 0.0058
5.67	0.0103	0.0145	0.0166	0.0169	0.0182	0.0202	0.0161 ± 0.0070
Average	0.0115 ± 0.0040	0.0141 ± 0.0026	0.0174 ± 0.0050	0.0177 ± 0.0054	0.0191 ± 0.0038	0.0168 ± 0.0062	0.0161 ± 0.0068
ZnCl$_2$-treated beech sawdust							
1.17	0.0187	0.0203	0.0218	0.0228	0.0238	0.0232	0.0218 ± 0.0038
1.67	0.0196	0.0202	0.0216	0.0226	0.0234	0.0232	0.02182 ± 0.0032
2.67	0.0211	0.0200	0.0214	0.0229	0.0248	0.0236	0.0223 ± 0.0036
3.67	0.0204	0.0210	0.0223	0.0232	0.0243	0.0238	0.0225 ± 0.0030
4.67	0.0211	0.0226	0.0236	0.0244	0.0240	0.0243	0.0233 ± 0.0026
5.67	0.0207	0.0214	0.0232	0.0232	0.0233	0.0226	0.0224 ± 0.0022
Average	0.0203 ± 0.0018	0.0209 ± 0.0020	0.0223 ± 0.0018	0.0232 ± 0.0014	0.0239 ± 0.0012	0.0234 ± 0.0012	0.0223 ± 0.0030
MgCl$_2$-treated beech sawdust							
1.17	0.0127	0.0137	0.0149	0.0168	0.0182	0.0199	0.0202 ± 0.0040
1.67	0.0174	0.0179	0.0210	0.0218	0.0215	0.0217	0.0219 ± 0.0068
2.67	0.0194	0.0200	0.0177	0.0234	0.0266	0.0240	0.0210 ± 0.0034
3.67	0.0189	0.0191	0.0208	0.0225	0.0222	0.0227	0.0220 ± 0.0034
4.67	0.0198	0.0202	0.0219	0.0226	0.0237	0.0239	0.0218 ± 0.0036
5.67	0.0190	0.0201	0.0224	0.0232	0.0234	0.0226	0.0213 ± 0.0024
Average	0.0190 ± 0.0018	0.0196 ± 0.0018	0.0209 ± 0.0034	0.0226 ± 0.0012	0.0233 ± 0.0036	0.0228 ± 0.0020	0.0214 ± 0.0040
NaCl-treated beech sawdust							
1.17	0.0127	0.0137	0.0149	0.0168	0.0182	0.0199	0.0209 ± 0.0040
1.67	0.0184	0.0188	0.0207	0.0218	0.0223	0.0233	0.0197 ± 0.0032
2.67	0.0176	0.0186	0.0192	0.0210	0.0220	0.0199	0.0202 ± 0.0042
3.67	0.0178	0.0182	0.0198	0.0205	0.0220	0.0232	0.0206 ± 0.0020
4.67	0.0197	0.0196	0.0201	0.0211	0.0217	0.0217	0.0215 ± 0.0042
5.67	0.0189	0.0195	0.0207	0.0226	0.0233	0.0238	0.0208 ± 0.0036
Average	0.0187 ± 0.0018	0.0189 ± 0.0012	0.0202 ± 0.0012	0.0215 ± 0.0016	0.0225 ± 0.0016	0.0220 ± 0.0032	0.0206 ± 0.0036

[a] Preheating time 40 min is included.

(k) of the Lagergren equation for the untreated beech sawdust was found to be lower than that estimated for all the salt-treated materials.

The adsorption rate $dq_t/dt = q \cdot k$, for $C_0 = 14.0$ mg/L and $t = 0$, was found to be 50.8–103.7% higher for the salt treated sawdust compared to the original one, i.e. 50.8% higher for CaCl$_2$, 103.7% higher for ZnCl$_2$, 99.6% higher for MaCl$_2$ and 92.8% higher for NaCl treated sawdust.

It is worthwhile noting that we can relate k with partial rate constants, as follows: let z be the driving force for adsorption, as a function of concentration, temperature and surface nature/topology; under the assumption that the adsorption rate is proportional to this force, which, in turn, decreases steadily when the adsorbed amount q_t increases, we have the simple relations: $dq_t/dt = k_1 z$, $-dz = k_2 dq_t$. A combination of these equations gives $-dz/dt = -(dq_t/dt)(dz/dq_t) = k_1 k_2 z$ or $-dz/z = k_1 k_2 dt$, which is easily integrated to give $\ln(z/z_0) = -k_1 k_2 t$, or $z = z_0 e^{-k_1 k_2 t}$, where z_0 is the value of z at $t = 0$. By substituting the last expression for z into the first of the above equations, we obtain $dq_t/dt = k_1 z_0 e^{-k_1 k_2 t}$ or $q_t = (z_0/k_2)(1 - e^{-k_1 k_2 t})$, which is identical with Eq. (7) for $k_1 k_2 = k$ and $z_0/k_2 = q$.

According to the Lagergren model and the Arrhenius law $k = p \cdot \exp(-E/RT)$, 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 min^{-1}) on $1/T$ (T in K). The methylene blue adsorption activation energy E was found equal to 3.3–3.7 kcal/mol (14–15 kJ/mol) for the salt-treated materials, approximately equal to the activation energy of the original material (3.62 kcal/mol or 15.1 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 min^{-1}) of the original material was investigated. The kinetics seemed to be affected by the agitation speed for 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 intraparticle diffusion resistance needed to be included in the analysis of overall sorption [11].

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 pre-treated materials than the relevant concentration (C for $t = 190$ min) for pH = 8. The lower adsorption of methylene blue at acidic pH was due to the presence of excess H$^+$ ions that competed with the dye cation for adsorption sites. As the pH of the system increased (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 H$^+$ ions from the active site of the adsorbent surface. The results were in agreement with other literature reports [11,20].

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. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model [21]:

$$q_t = k_p \sqrt{t} + c \tag{9}$$

where q_t is the amount of dye adsorbed at time t; c is the intercept and k_p is the intra-particle diffusion rate constant in mg g^{-1} 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 salt-treated beech sawdust than for the original material.

3.3. Column studies

The 'bed depth service model' developed by Bohart and Adams [22] is as follows

$$\ln\left(\frac{C_i}{C} - 1\right) = \frac{KNx}{u} - KC_i t \tag{10}$$

in which C = effluent concentration (mg/L); C_i = influent concentration (mg/L); K = adsorption rate coefficient (L mg^{-1} min^{-1}); N = adsorption capacity coefficient (mg/L); x = bed depth (cm); u = linear velocity (cm/min); and t = time (min).

Clark [23] has developed an alternative to the 'simple logistic function', called the 'generalized logistic function' that incorporates the parameter n of the Freundlich adsorption isotherm:

$$C = \left[\frac{C_i^{n-1}}{(1 + Ae^{-rt})}\right]^{1/n-1} \tag{11}$$

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

Eq. (11) was applied to the effluent data from the column adsorber, using linear regression. Transforming and linearizing Eq. (11):

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

Table 7
Estimated parameter values for Methylene Blue adsorption according to the Bohart–Adams bed depth service model ($C_0 = 14$ mg/L)

Pretreatment time t (h)[a]	Beech sawdust pretreated with 20% (w/v)			
	Calcium chloride	Zinc chloride	Magnesium chloride	Sodium chloride
Adsorption rate coefficient (K in mg^{-1} L min^{-1})				
0		0.00056		
1.17	0.00079	0.00071	0.00063	0.00074
1.67	0.00083	0.00071	0.00059	0.00075
2.67	0.00091	0.00079	0.00066	0.00083
3.67	0.00080	0.00067	0.00053	0.00071
4.67	0.00079	0.00073	0.00067	0.00075
5.67	0.00074	0.00067	0.00060	0.00069
Average	0.00081 ± 0.00012	0.00071 ± 0.00008	0.00061 ± 0.00010	0.00074 ± 0.00010
Adsorption capacity coefficient (N in mg/L)				
0		2694		
1.17	3124	3436	3300	3368
1.67	3278	3752	3431	3592
2.67	3558	3763	3408	3586
3.67	3556	4139	4175	4157
4.67	3739	4057	3966	4011
5.67	3900	4462	4217	4339
Correlation coefficient (R)				
0		0.9811		
1.17	0.9926	0.9915	0.9903	0.9918
1.67	0.9343	0.9274	0.9205	0.9297
2.67	0.9535	0.9753	0.9970	0.9680
3.67	0.9815	0.9810	0.9804	0.9811
4.67	0.9732	0.9320	0.8908	0.9457
5.67	0.9912	0.9161	0.8410	0.9411
SEE (mg/g)				
0		0.177		
1.17	0.173	0.173	0.173	0.173
1.67	0.195	0.198	0.201	0.197
2.67	0.187	0.179	0.171	0.181
3.67	0.176	0.177	0.177	0.177
4.67	0.179	0.196	0.214	0.190
5.67	0.173	0.203	0.240	0.192

[a] Preheating time 40 min is included.

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. The theoretical estimations sufficiently simulate the experimental data. In addition, the adsorption rate coefficient (K) and the adsorption capacity coefficient (N), shown in Table 7, were estimated from the A and r-values. The adsorption capacity coefficient values were found higher for the CaCl$_2$ treated materials than the original one.

The adsorption capacity coefficient (N in mg/L) in the case of column adsorption process for the removal of methylene blue by adsorption on beech sawdust as affected by salt-treatment time (t in hours) was found to be:

$$N = N_e - (N_e - N_0)e^{-k_N t} \qquad (13)$$

where N_0, N_e and k_N are empirical parameters (see Table 8).

The adsorption rate coefficient (K) was not significantly affected by the treatment time t and was found to be 0.00073 ± 0.00018 mg^{-1} L min^{-1} (see Table 7).

It is worthwhile noting that that the content of hemicelluloses, cellulose and lignin of the original beech sawdust remained prac-

tically unchanged by the salt-treatment. The efficient swelling of the hemicelluloses and cellulose results in 'opening' of the structure of the lignocellulosic matrix, which possibly accounts for the advanced adsorption properties of the salt-treated materials over the untreated ones. Furthermore, the salt-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 [3].

The findings of the present work agree with the physicochemical mechanism of adsorption kinetics found in literature. The removal of methylene blue by adsorption on various materials was found to be rapid at the initial contact-time period 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 is assumed to involve the following four steps: (i) migration of dye from bulk of the solution to the surface of the adsorbent, (ii) diffusion of dye through the boundary layer to the surface of the adsorbent, (iii) adsorption of dye at an active site on the surface of the adsorbent, and (iv) intra-particle diffusion of dye into the interior pores of the adsorbent particle. The rate of

Table 8
The simulation parameters of the adsorption rate coefficient (K in $mg^{-1}\,L\,min^{-1}$) according to the Bohart–Adams bed depth service model (non-linear regression analysis)

Simulation parameters	Calcium chloride	Zinc chloride	Magnesium chloride	Sodium chloride
$C_0 = 14$ mg/L				
N_0			2694	
N_e	4072	4439	4616	4493
k_N	0.32	0.45	0.27	0.36
SEE	65	156	206	164
$C_0 = 60$ mg/L				
N_0			3771	
N_e	6763	5928	5609	6145
k_N	0.46	1.12	1.76	0.84
SEE	371	190	94	403

adsorption is affected by the boundary layer resistance, which, in its turn, is related with 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 [7].

The cell walls of sawdust mainly consist of cellulose and lignin, and many hydroxyl groups, such as tannins or other phenolic compounds. All those components are active ion exchange compounds. Adsorption studies, in particular kinetics and isotherms, provide information on the mechanism of sorption. These mechanisms are, in general, complicated because they implicate the presence of different interactions. In addition, a wide range of chemical structures, pH, salt concentrations and the presence of ligands often add to the complication. Some of the reported interactions include: ion-exchange, complexation, coordination/chelation, electrostatic interactions, acid–base interactions, hydrogen bonding, hydrophobic interactions, physical adsorption, and precipitation [1,2].

The salts used for modifying/upgrading sawdust as an adsorbent can be recovered from various waste fluxes, in which case a mixture of chlorides is obtained. Although sufficient experimental evidence has been reported in the present study to support the view that these salts exhibit a similar beneficial effect, further research, at least at laboratory scale, is recommended in the case of multi-constituent mixtures, especially if non-examined substances co-exist even in low concentrations.

4. Conclusions

The results presented herein showed that salt-treatment of the beech sawdust enhances its adsorption properties considerably. The Freundlich adsorption capacity K_F (batch studies) for methylene blue increased up to 98% by calcium chloride-treatment, 87% by zinc chloride-treatment, 90% magnesium chloride-treatment and 108% by sodium chloride-treatment. The Langmuir constant related to the energy of adsorption K_L increased up to 188% by calcium chloride-treatment, 96% by zinc chloride-treatment, 82% by magnesium chloride-treatment and 300% by sodium chloride-treatment. The adsorption rate dq_t/dt (for $C_0 = 14.0$ mg/L, adsorption time $t = 0$), was found to be 50.8% higher for the $CaCl_2$ treated sawdust, 103.7% higher for the $ZnCl_2$ treated sawdust, 99.6% higher for the $MaCl_2$ treated sawdust and 92.8% higher for the NaCl treated sawdust compared to the original one. The adsorption capacity coefficient N according to the Bohart–Adams bed depth service model (column studies) for influent concentration $C_i = 14$ mg/L of methylene blue increased up to 51% by calcium chloride-treatment, 65% by zinc chloride-treatment, 71% magnesium chloride-treatment and 67% by sodium chloride-treatment; for $C_i = 60$ mg/L increased by up to 79% by calcium chloride-treatment, 57% by zinc chloride-treatment, 49% magnesium chloride-treatment and 63% by sodium chloride-treatment. 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.

This possibility is further enhanced by taking into account that the salts used for pre-treatment can be derived from byproducts or remaining raw materials/reagents, which are usually wasted, causing environmental damage. Therefore, the combination of residual biomass and wasted/byproduct salts results in a useful special byproduct, i.e. an upgraded/modified adsorbent, which is in accordance with the modern concept of Industrial Ecology, defined as 'the creation of a quasi closed productive agro-industrial system, analogous to a natural ecosystem (metaphor of metabolism in vivo), where waste from one anthropogenic activity can be used as input for another'. As a consequent, the investment required for the production of such materials/energy saving adsorbents can be significantly subsidised.

References

[1] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, Bioresour. Technol. 97 (9) (2006) 1061–1085.
[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) 137–152.

[3] T. Robinson, B. Chandran, P. Nigam, The effect of pretreatments of three waste residues, wheat straw, corncobs and barley husks on dye adsorption, Bioresour. Technol. 85 (2002) 119–124.

[4] O. Hamdaoui, Dynamic sorption of methylene blue by cedar sawdust and crushed brick in fixed bed columns, J. Hazard. Mater. 138 (2) (2006) 293–303.

[5] F. Ferrero, Dye removal by low cost adsorbents: Hazelnut shells in comparison with wood sawdust, J. Hazard. Mater. 142 (1–2) (2007) 144–152.

[6] M.Ch. Ncibi, B. Mahjoub, M. Seffen, Kinetic and equilibrium studies of methylene blue biosorption by *Posidonia oceanica* (L.) fibre, J. Hazard. Mater. 139 (2) (2007) 280–285.

[7] V.K. Garg, R. Gupta, A.-B. Yadav, R. Kumar, Dye removal from aqueous solutions by adsorption on treated sawdust, Bioresour. Technol. 89 (2003) 121–124.

[8] U. Kumar, M. Bandyopadhyay, Fixed bed column study for Cd(II) removal from wastewater using treated rice husk, J. Hazard. Mater. 129 (1–3) (2006) 253–259.

[9] Y. Bulut, H. Aydin, A kinetics and thermodymamics study of methylene blue adsorption on wheat shells, Desalination 194 (2006) 259–267.

[10] M. Šćiban, M. Klašnja, Biljana Škrbić, Modified softwood sawdust as adsorbent of heavy metal ions from water, J. Hazard. Mater. 136 (2) (2006) 266–271.

[11] F.A. Batzias, D.K. Sidiras, Dye adsorption by prehydrolysed beech sawdust in batch and fixed-bed systems, Bioresour. Technol. 98 (6) (2007) 1208–1217.

[12] F.A. Batzias, D.K. Sidiras, Dye adsorption by calcium chloride treated beech sawdust in batch and fixed-bed systems, J. Hazard. Mater. 114 (1–3) (2004) 167–174.

[13] 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) 786–795.

[14] J.F. Saeman, J.F. Bubl, E.E. Harris, Quantitative saccharification of wood and cellulose, Ind. Eng. Chem. Anal. Ed. 17 (1945) 35–37.

[15] M. Somogyi, Notes on sugar determination, J. Biol. Chem. 195 (1952) 19–23.

[16] Tappi Standards. Atlanta, Tappi Tests Methods, 1997.

[17] H.M.F. Freundlich, Über die adsorption in lösungen, Zeitschrift für Physikalische Chemie 57 (1906) 385–471.

[18] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[19] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe., Kungliga Svenska Vetenskapsakademiens, Handlingar 24 (1898) 1–39.

[20] F.A. Batzias, D.K. Sidiras, Simulation of dye adsorption by beech sawdust as affected by pH, J. Hazard. Mater. 141 (3) (2007) 668–679.

[21] G. Crank, The Mathematics of Diffusion, Clarendon Press, London, New York, 1993.

[22] G. Bohart, E.N. Adams, Some aspects of the behavior of charcoal with respect to chlorine, J. Am. Chem. Soc. 42 (1920) 523–544.

[23] R.M. Clark, Modeling TOC removal by GAC: the general logistic function, J. Am. Wat. Works Assoc. 79 (1) (1987) 33–131.