Simulation of dye adsorption by beech sawdust as affected by pH

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Abstract

The effect of pH on the batch kinetics of methylene blue adsorption on beech sawdust was simulated, in order to evaluate sawdust potential use as low cost adsorbent for wastewater dye removal. The zero point of charge pH_{pzc} of the sawdust, in order to explain the effect of pH in terms of pH_{pzc}, was measured by the mass titration and the automatic titration methods. The adsorption capacity, estimated according to Freundlich's model, indicate that increase of the pH enhances the adsorption behaviour of the examined material. The lower adsorption of methylene blue at acidic pH is due to the presence of excess H^+ ions that compete with the dye cation for adsorption sites. As the pH of the system increases, the number of positively charged sites decreases while the number of the negatively charged sites increases. The negatively charged sites favour the adsorption of dye cation due to electrostatic attraction. The increase in initial pH from 8.0 to 11.5 increases the amount of dye adsorbed.
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1. Introduction

Dyes are present in the wastewater streams of many industrial sectors, such as dyeing, textile, tannery and the paint industry; due to their chemical composition they are resistant to fading on exposure light, water and many chemicals and therefore difficult to decolourise once released into the aquatic environment. Activated carbon is the most efficient adsorbent used up to date, 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, wood sawdust and agricultural residues, relatively abundant and inexpensive materials, have been extensively investigated as adsorbents for removing contaminants from water [1–3].

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 effluent [3–6]. Among the lignocellulosic materials that have been investigated, sawdust is commonly used as adsorbent, especially for basic dyes, with capacity varying according to the structure of the dye and the mesh size [7]. Removal of methylene blue and other dyes has been carried out using coir pith [8], banana/orange peels [9] and palm-fruit bunch particles [10]. Also, many chemical/physical treated lignocellulosic materials [2,11,12] and a range of activated carbons produced from MDF (medium density fibreboard) sawdust [13], kudzu [14], coir pith [15], cassava peel [16] and bagasse [17] have been successfully utilized for the removal of dyes from aqueous solutions. The suitability of a range of materials as dye adsorbents is often established using the kinetics of methylene blue adsorption during batch processes [18,19].

In the present study, the simulation of the removal of chemical grade methylene blue by beech sawdust was studied; the batch adsorption kinetics of this dye were used to estimate the adsorption capacity of the examined material. The effect of the pH on the proposed simulation model and especially on the sawdust adsorption capacity was also investigated. The results indicate that this lignocellulosic material exhibits improved adsorption properties by increasing the pH of the methylene blue solution. Considering the abundance and low cost of the lignocellulosic material and the vast applicability of adjusting the acid water/wastewater pH to a value slightly higher than 8, render the beech sawdust as an extremely cost-effective adsorbent for basic dyes.

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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 of the representative 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 the following (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.

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 adsorbate solution were added. The bottles were sealed and mechanically tumbled for a period of 7 days. The resulting solution concentrations were determined and the equilibrium data from each bottle represented one point on the adsorption isotherm plots. The pH effect was studied in the range of 1.7–13.0. The pH values of the dye solutions were adjusted to this range using dilute H_2SO_4 or NaOH solutions, as appropriate. The initial dye solution pH-value was equal to 8.0 for $C_0 = 14.0$ mg/L methylene blue. The pH-values varied from 7.8 to 8.0 for $C_0 = 1.4$–14.0 mg/L methylene blue and they were adjusted to 8.0 using dilute NaOH solution.

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 aquatic 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 also studied in the range of 1.7–13.0 (the pH of the dye solutions were similarly adjusted using dilute H_2SO_4 or NaOH solutions).

2.4. Analytical techniques

The degree of crystallinity of wood cellulose was measured with the X-ray diffraction method proposed by Segal et al. [20]. Following the technique proposed by Saeman et al. [21], the lignocellulosic materials were hydrolysed to glucose and reducing sugars in nearly quantitative yields; the filtrates were analysed for glucose using the Glucinet test and for reducing sugars using the Somogyi technique [22]. 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.

The concentration of methylene blue in the solution was obtained by measuring OD at 664 nm (λ_{max}), using a HACH DR4000U UV–vis spectrophotometer. For pH $\geq$ 11.5 the OD was also measured at 620 and 596 nm and the reference curve was estimated as a function of time and pH, because in alkaline solutions, methylene blue is stepwise demethylated to other common dyes, namely trimethylthionine (azure B), dimethylthionine (azure A), and monomethylthionine (azure C) [23].

The zero point of charge pH_{pzc} of the sawdust was measured by the mass titration [24,25] and the automatic titration [26] methods.

3. Results

3.1. Adsorption isotherms

The comparison of the adsorption capacity of the beech sawdust samples as affected by pH was based on seven isotherm models. One of them is the Freundlich isotherm model, 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 [14], activated carbons [15,17,19,27–30] and lyocell fibres [31]. The Freundlich isotherm form 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 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 at acidic (Fig. 1) and basic conditions (Fig. 2). The Freundlich parameter values are shown in Table 1. It is worthwhile noting that the non-linear regression parameter estimated values did not differ significantly than the linear ones. Furthermore, linear regression analysis was adopted herein due to compatibility with the available data from numerous researchers. The applicability of the Freundlich equation to
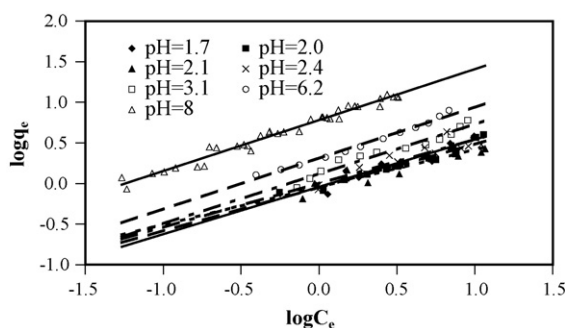

Fig. 1. Freundlich isotherms for the removal of methylene blue by adsorption on original beech sawdust as affected by pH (23 °C, pH $\leq$ 8).
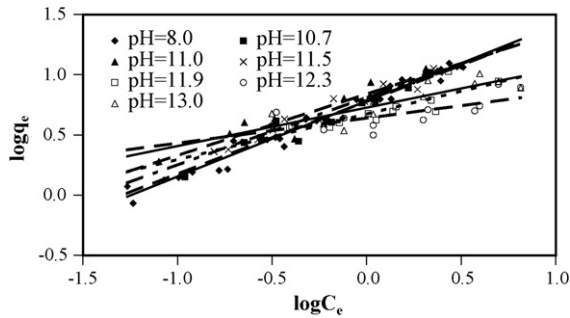
Fig. 2. Freundlich isotherms for the removal of methylene blue by adsorption on original beech sawdust as affected by pH (23 °C, pH ≥ 8).

experimental data is evidence that the adsorbents' surface is most probably heterogeneous. The correlation coefficients (R-values) the SEE $= \sqrt{\sum (y_i - y_{i,\text{theor}})^2/(n-p)}$ (standard error of estimate) and the NSEE $= \sqrt{\sum [(y_i - y_{i,\text{theor}})/y_i]^2/(n-p)}$ (normalized standard error of estimate) were estimated. The adsorption capacity (in units of mg/g) of the adsorbent with respect to dye studied according to Freundlich model as expressed by Eq. (1) is q^*, where q^* is the value of q for $C_e = 1$ mg/L, i.e., $q^* = K_F$ but q^* is in units of mg/g and K_F is in units of $(\text{mg/g})/(\text{mg/L})^{1/n} = \text{mg}^{1-1/n}\,\text{g}^{-1}\,\text{L}^{-1/n}$.

The second one is the Langmuir isotherm equation [14,32–36] is based on the following 'pseudo-monolayer' adsorption model:

$$q = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{3}$$

or in linear form

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

where K_L is the Langmuir constant related to the energy of adsorption (L/mg) and q_m is the amount of dye adsorbed (mg/g) when the saturation is attained. In case the isotherm experimental data approximates the Langmuir equation, the parameters K_L

and q_m can be obtained by plotting $1/q$ versus $1/C_e$. It is worthwhile noting that the non-linear regression parameter estimated values did not differ significantly than the linear ones. Table 2 presents the estimated parameter values for the data obtained in the present study.

The Sips (Langmuir–Freundlich) [32,34–36] isotherm equation, also examined in this work, is based on the following adsorption model:

$$q = \frac{q_m(K_L C_e)^{1/n}}{1 + (K_L C_e)^{1/n}} \tag{5}$$

where K_L is the Langmuir constant (L/mg), q_m the amount of dye adsorbed (mg/g) when the saturation is attained, and n is the Freundlich constant. In case the isotherm experimental data approximates the Sips equation, the parameters K_L, q_m and n can be obtained by non-linear regression analysis. Table 3 presents the estimated parameter values for the experimental data obtained in the present study.

The Fritz–Schluender [32] isotherm equation is based on the following adsorption model:

$$q = \frac{K_L q_m C_e}{1 + K_L C_e^{1/n}} \tag{6}$$

where K_L is the Langmuir constant (L/mg), q_m the amount of dye adsorbed (mg/g) when the saturation is attained, and n is the Freundlich constant. Moreover, the Redlich–Peterson isotherm equation [14,33,37]:

$$q = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{7}$$

can be transformed to the Fritz–Schluender isotherm by substituting $K_R = K_L q_m$, $a_R = K_L$ and $\beta = 1/n$. In case the isotherm experimental data approximates the Fritz–Schluender equation, the parameters K_L, q_m and n can be obtained by non-linear regression analysis. Table 3 presents the estimated parameter values for the data obtained in the present study.

Table 1
The Freundlich parameters of adsorption isotherms of methylene blue adsorption on beech sawdust as affected by pH (23 °C)

pH	Linear regression analysis					Non-linear regression analysis			
	K_F	n	Correlation coefficient (R)	SEE	NSEE	K_F	n	SEE	NSEE
1.7	0.91	1.72	0.961	0.374	0.07	0.84	1.56	0.265	0.17
2.0	0.90	1.86	0.974	0.422	0.14	0.73	1.51	0.277	0.17
2.1	0.91	2.15	0.923	0.606	0.19	0.98	2.37	0.306	0.20
2.4	1.01	1.84	0.918	0.312	0.18	1.19	2.23	0.585	0.23
3.1	1.32	1.62	0.974	0.331	0.12	1.26	1.55	0.416	0.14
6.2	2.06	1.58	0.994	0.281	0.17	1.86	1.39	0.282	0.11
8.0	6.05	1.59	0.987	0.624	0.13	6.12	1.67	0.608	0.14
10.7	6.02	1.65	0.972	0.631	0.15	6.03	1.57	0.611	0.15
11.0	6.94	1.95	0.944	0.959	0.21	7.07	1.76	0.905	0.21
11.5	6.48	1.78	0.972	0.877	0.15	6.53	1.82	0.875	0.14
11.9	4.72	2.63	0.864	0.959	0.15	4.72	2.35	1.306	0.18
12.3	4.36	4.04	0.723	1.174	0.25	4.27	3.68	1.067	0.22
13.0	5.32	3.14	0.862	0.624	0.18	5.48	3.31	0.561	0.11
Total				0.678	0.16			0.650	0.16

Table 2
The Langmuir parameters of adsorption isotherms of methylene blue adsorption on beech sawdust as affected by pH (23 °C)

pH	Linear regression analysis					Non-linear regression analysis			
	K_L	q_m	Correlation coefficient (R)	SEE	NSEE	K_L	q_m	SEE	NSEE
1.7	0.46	3.13	0.895	0.616	0.24	0.11	6.77	0.324	0.22
2.0	0.59	2.72	0.919	0.695	0.22	0.08	7.87	0.356	0.27
2.1	0.42	2.94	0.917	0.318	0.19	0.33	3.32	0.299	0.19
2.4	0.25	4.59	0.970	0.540	0.16	0.30	4.31	0.532	0.18
3.1	0.22	7.15	0.981	0.547	0.14	0.13	9.40	0.513	0.18
6.2	0.55	6.42	0.970	1.135	0.18	0.10	17.66	0.426	0.21
8.0	2.21	8.26	0.952	2.042	0.24	0.54	18.37	0.648	0.19
10.7	1.01	10.20	0.969	1.833	0.27	0.49	19.01	0.790	0.22
11.0	2.45	8.16	0.912	2.246	0.30	0.78	16.93	1.094	0.29
11.5	1.54	10.95	0.971	1.242	0.17	0.88	15.01	0.937	0.17
11.9	2.28	7.13	0.818	1.687	0.20	0.76	11.06	1.394	0.23
12.3	7.42	5.22	0.654	1.531	0.26	2.26	6.70	1.368	0.29
13.0	2.65	7.92	0.739	1.563	0.26	1.29	10.13	1.245	0.24
Total				1.444	0.22			0.973	0.24

Table 3
The (a) Sips (Langmuir–Freundlich), (b) Fritz–Schluender, (c) Radke–Prausnitz and (d) Tóth parameters of adsorption isotherms of methylene blue adsorption on beech sawdust as affected by pH (23 °C), using non-linear regression analysis

pH	Sips (Langmuir–Freundlich)					Fritz–Schluender				
	K_L	q_m	n	SEE	NSEE	K_L	q_m	n	SEE	NSEE
1.7	0.0002	194.4	1.6	0.280	0.18	1.8	1.3	2.1	0.290	0.19
2.0	0.0001	337.9	1.5	0.294	0.17	2.0	1.1	2.2	0.308	0.18
2.1	0.1871	4.1	1.3	0.310	0.20	0.7	2.1	1.2	0.312	0.20
2.4	0.4521	3.5	0.7	0.544	0.18	0.2	5.4	0.9	0.553	0.18
3.1	0.0002	292.5	1.5	0.441	0.15	2.0	1.9	2.1	0.454	0.14
6.2	0.0004	540.9	1.4	0.301	0.12	2.4	2.7	2.7	0.321	0.12
8.0	0.1141	37.2	1.4	0.596	0.13	8.7	2.6	1.8	0.602	0.13
10.7	0.0007	645.8	1.6	0.647	0.16	12.8	6.5	2.5	0.654	0.16
11.0	0.0005	555.1	1.7	0.956	0.23	15.6	7.6	2.1	0.968	0.23
11.5	0.0353	58.6	1.6	0.921	0.15	6.8	7.6	2.2	0.920	0.15
11.9	0.0006	131.1	2.2	1.378	0.19	155.6	4.8	1.0	1.377	0.19
12.3	0.00002	96.0	3.5	1.131	0.24	856.6	4.3	1.4	1.126	0.24
13.0	0.8651	11.9	1.4	1.287	0.24	1.3	10.0	1.4	1.313	0.25
Total			1.6 ± 1.4	0.818	0.17			1.8 ± 1.2	0.771	0.18

pH	Radke–Prausnitz					Tóth				
	K_L	q_m	n	SEE	NSEE	K_L	q_m	n	SEE	NSEE
1.7	258.6	0.02	2.8	0.279	0.18	0.38	97	3.7	0.295	0.19
2.0	314.8	0.02	3.0	0.292	0.18	0.33	181	4.0	0.316	0.20
2.1	0.7	1.91	1.3	0.313	0.20	0.58	5	1.7	0.311	0.20
2.4	0.5	2.93	1.2	0.572	0.19	0.76	12	2.9	0.593	0.22
3.1	197.7	0.04	2.8	0.439	0.15	0.40	277	4.3	0.460	0.15
6.2	382.2	0.03	3.5	0.298	0.12	0.29	572	3.8	0.343	0.15
8.0	7.1	2.33	2.1	0.606	0.14	0.66	154	3.5	0.600	0.13
10.7	7.9	2.09	2.2	0.694	0.17	0.57	302	3.8	0.690	0.17
11.0	12.5	2.22	1.9	1.011	0.25	0.79	132	3.6	1.007	0.25
11.5	12.9	1.90	2.0	0.919	0.15	0.84	577.29	5.69	0.92	0.15
11.9	1.1	8.70	1.1	1.454	0.24	1.11	29.71	2.86	1.40	0.21
12.3	230.6	1.53	1.3	1.179	0.25	2.36	10.67	2.52	1.26	0.26
13.0	4.2	5.00	1.2	1.332	0.24	1.70	13.69	1.92	1.30	0.24
Total			2.0 ± 1.8	0.793	0.18			3.4 ± 2.3	0.792	0.19

Table 4
The UNILAN parameters of adsorption isotherms of methylene blue adsorption on beech sawdust as affected by pH (23 °C), using non-linear regression analysis

pH	K_L	q_m	s	SEE	NSEE
1.7	0.010	16.7	3.6	0.325	0.22
2.0	0.018	14.1	2.6	0.360	0.25
2.1	0.019	8.0	4.5	0.312	0.20
2.4	0.019	10.5	4.3	0.582	0.20
3.1	0.019	20.1	3.2	0.513	0.16
6.2	0.019	36.4	2.7	0.427	0.20
8.0	0.019	55.7	4.6	0.628	0.17
10.7	0.019	57.3	4.5	1.881	0.37
11.0	0.015	55.6	5.3	1.938	0.42
11.5	0.062	37.3	4.0	0.947	0.16
11.9	0.313	15.5	2.5	1.423	0.22
12.3	0.299	11.8	4.9	1.231	0.26
13.0	0.133	19.4	4.6	1.317	0.24
Total			4.0 ± 2.0	1.011	0.24

The Radke–Prausnitz [32] isotherm equation is based on the following adsorption model:

$$q = \frac{K_L q_m C_e}{(1 + K_L C_e)^{1/n}} \qquad (8)$$

where K_L is the Langmuir constant (L/mg), q_m the amount of dye adsorbed (mg/g) when the saturation is attained, and n is the Freundlich constant. In case the isotherm experimental data approximates the Radke–Prausnitz equation, the parameters K_L, q_m and n can be obtained by non-linear regression analysis. Table 3 presents the estimated parameter values for the data of the present study.

The Tóth isotherm equation [14,32,35,37] is based on the following adsorption model:

$$q = \frac{q_m C_e}{(1/K_L + C_e^{1/n})^n} \qquad (9)$$

where K_L is the Langmuir constant (L/mg), q_m the amount of dye adsorbed (mg/g) when the saturation is attained, and n is the Freundlich constant. In case the isotherm experimental data approximates the Tóth equation, the parameters K_L, q_m and n can be obtained by non-linear regression analysis. Table 3 presents the estimated parameter values for the experimental data obtained in the present study.

The UNILAN isotherm equation [32,37] is based on the following adsorption model:

$$q = \frac{q_m}{2s} \ln \left(\frac{1 + K_L C_e e^s}{1 + K_L C_e e^{-s}} \right) \qquad (10)$$

where K_L is the Langmuir constant (L/mg), q_m the amount of dye adsorbed (mg/g) when the saturation is attained, and s is a constant. In case the isotherm experimental data approximates the UNILAN equation, the parameters K_L, q_m and s can be obtained by non-linear regression analysis. Table 4 presents the estimated parameter values for the data of the present study.

3.2. Kinetics of adsorption

The kinetics of adsorption of methylene blue on various materials has been extensively studied using various kinetic equations. The best prevailing equation is the Lagergren–Eldridge pseudo-first order kinetic model [8,9,38-40]:

$$\frac{dq}{dt} = k(q - q_t) \Rightarrow \int_{q_0}^{q_t} \frac{dq_t}{q - q_t} = k \int_0^t dt \qquad (11)$$

From Eq. (3):

$$q - q_t = (q - q_0)e^{-kt} \quad \text{or} \quad q_t = q - (q - q_0)e^{-kt} \qquad (12)$$

Assuming $q_0 = 0$ for $t = 0$:

$$q - q_t = q e^{-kt} \quad \text{or} \quad q_t = q - q e^{-kt} \quad \text{or} \quad q_t = q(1 - e^{-kt}) \qquad (13)$$

where q and q_t are the amounts of dye adsorbed per unit mass of the adsorbent (in mg/g) at equilibrium time (∞) and time t, respectively, while k is the 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 (in mg/L) at time t, 0, and ∞, respectively, while V is the volume of the solution (in L) and m is the weight of the adsorbent used (in g). Further modification of Eq. (3) in logarithmic form gives:

$$\ln(q - q_t) = \ln q - kt \quad \text{or} \quad \ln \left[\frac{q - q_t}{q} \right] = -kt \qquad (14)$$

Assuming a N-order kinetic model:

$$\frac{dq}{dt} = k(q - q_t)^N \qquad (15)$$

From the differential Eq. (15) for $N \neq 0$ we obtain:

$$\frac{(q - q_t)^{1-N}}{1 - N} - \frac{q^{1-N}}{1 - N} = -kt \quad \text{or}$$

$$(q - q_t)^{1-N} = q^{1-N} + (N - 1)kt \qquad (16)$$

or

$$q_t = q - [q^{1-N} + (N - 1)kt]^{1/(1-N)} \qquad (17)$$

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) the SEE and the NSEE were estimated (Table 5). All the linear correlations were found to be statistically significant, as evident by the R-values, indicating the applicability of this kinetic equation to the adsorption of methylene blue. The Lagergren plots are shown in Fig. 3 (acidic conditions) and Fig. 4 (basic conditions). It is worthwhile noting that the non-linear regression parameter estimated values did not differ significantly than the linear ones (Table 5). The SEE values of the pseudo-first order kinetic model were not significantly higher comparing to those of (a) the N-order pseudo-kinetic model (N-value was found equal to 1.0 for pH < 8, 1.5 for pH 8 and 1.7 ± 0.3 for pH > 8,

Table 5
The Lagergren–Eldridge pseudo-first order kinetic model's kinetic parameters of methylene blue adsorption on beech sawdust as affected by pH (23 °C, $C_0 = 14$ mg/L)

pH	q (mg/g)	Linear regression analysis				Non-linear regression analysis		
		k (min^{-1})	Correlation coefficient (R)	SEE (mg/g)	NSEE	k (min^{-1})	SEE (mg/g)	NSEE
1.7	3.6	0.0033	−0.923	0.262	0.31	0.0035	0.259	0.30
2.0	3.2	0.0028	−0.933	0.168	0.25	0.0029	0.164	0.24
2.1	2.8	0.0039	−0.919	0.230	0.29	0.0042	0.226	0.28
2.4	3.6	0.0031	−0.925	0.237	0.29	0.0033	0.231	0.27
3.1	5.1	0.0039	−0.979	0.212	0.18	0.0041	0.201	0.17
6.2	7.0	0.0046	−0.974	0.374	0.21	0.0049	0.354	0.19
8.0	11.3	0.0081	−0.989	0.427	0.09	0.0086	0.380	0.07
10.7	11.2	0.0085	−0.993	0.653	0.14	0.0092	0.595	0.11
11.0	11.4	0.0078	−0.987	0.553	0.15	0.0082	0.524	0.15
11.5	11.3	0.0079	−0.980	1.566	0.26	0.0110	1.092	0.19
11.9	10.9	0.0146	−0.976	1.230	0.16	0.0111	1.039	0.13
12.3	9.6	0.0155	−0.962	0.602	0.09	0.0089	0.590	0.09
13.0	8.9	0.0035	−0.910	0.738	0.24	0.0041	0.639	0.23
Total				0.689	0.22		0.566	0.20
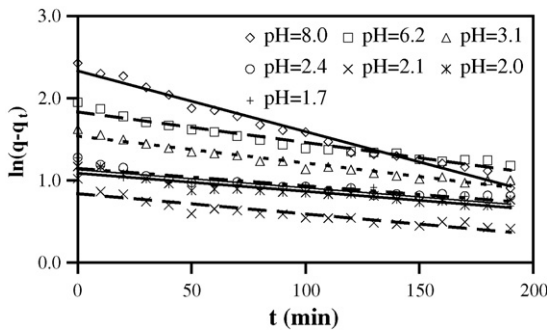
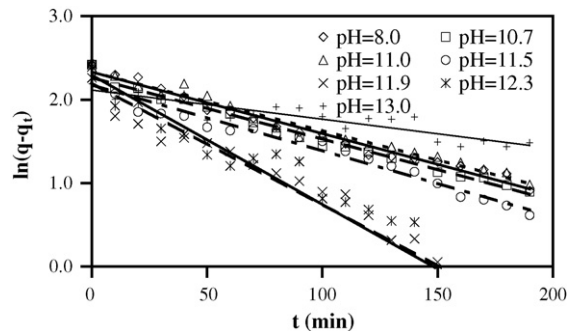Fig. 3. Effect of pH on Freundlich's adsorption capacity K_F vs. pH at 23 °C.

Fig. 4. The Lagergren curves of methylene blue adsorption on beech sawdust as affected by pH (23 °C, pH ≤ 8).

correspondingly, see Table 6) and (b) the pseudo-second order kinetic model [41,42] for $N = 2$, presented in Table 6. The NSEE values of the pseudo-first order kinetic model were lower comparing to those of (a) the N-order pseudo-kinetic model and (b) the pseudo-second order kinetic model.

Agitation is a classic 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 seems to

Table 6
The Lagergren–Eldridge N-order and seconnd order kinetic model's kinetic parameters of methylene blue adsorption on beech sawdust as affected by pH (23 °C, $C_0 = 14$ mg/L, non-linear regression analysis)

pH	q (mg/g)	N-order kinetic model				Second order kinetic model		
		k (min^{-1})	N-order	SEE (mg/g)	NSEE	k (min^{-1})	SEE (mg/g)	NSEE
1.7	3.6	0.0035	1.0	0.259	0.30	0.00006	0.287	0.33
2.0	3.2	0.0029	1.0	0.164	0.24	0.00005	0.187	0.28
2.1	2.8	0.0042	1.0	0.226	0.28	0.00006	0.268	0.33
2.4	3.6	0.0033	1.0	0.231	0.27	0.00007	0.259	0.30
3.1	5.1	0.0041	1.0	0.201	0.17	0.00015	0.231	0.19
6.2	7.0	0.0049	1.0	0.354	0.19	0.00029	0.341	0.18
8.0	11.3	0.0032	1.5	0.210	0.09	0.00124	0.328	0.13
10.7	11.2	0.0020	1.8	0.366	0.12	0.00140	0.367	0.11
11.0	11.4	0.0029	1.5	0.434	0.16	0.00116	0.481	0.17
11.5	11.3	0.0024	1.9	0.717	0.16	0.00185	0.662	0.14
11.9	10.9	0.0049	1.9	0.69	0.12	0.00384	0.657	0.11
12.3	9.6	0.0048	1.7	0.623	0.13	0.00310	0.689	0.15
13.0	8.9	0.0014	1.6	0.628	0.29	0.00061	0.599	0.29
Total				0.439	0.21		0.448	0.22
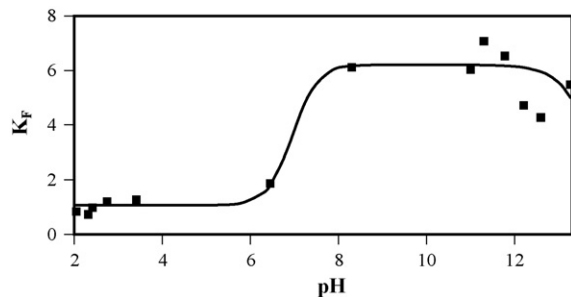
Fig. 5. The Lagergren curves of methylene blue adsorption on beech sawdust as affected by pH (23 °C, pH ≥ 8).

Fig. 6. Effect of pH on Lagergren kinetic parameter k (min^{-1}) of methylene blue adsorption on beech sawdust vs. pH at 23 °C.

be affected by the agitation speed for values between 0 and 200 rpm, thus confirming that the influence of external diffusion in the sorption kinetic control plays a significant role. On the contrary, the slight effect of agitation for the range 200–600 rpm indicates that external mass transfer is not the rate limiting step, and implies that intraparticle diffusion resistance needs to be included in the analysis of overall sorption [8,9,38–40].

3.3. Simulation of the effect of pH on adsorption process

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. In the present work, the following equation was developed to simulate the effect of pH on the Freundlich parameter K_F of adsorption isotherms of methylene blue adsorption on beech sawdust:

$$K_F = \frac{\gamma_1}{1 + e^{\alpha_1 - \beta_1 pH}} - \delta_1 \times 10^{-(14-pH)} + \varepsilon_1 \tag{18}$$

where $\alpha_1, \beta_1, \gamma_1, \delta_1, \varepsilon_1$ are empirical parameters. The parameter δ_1 was set equal to zero for the range of pH 1.7–8.0 (the pH of the dye solutions were adjusted using dilute H_2SO_4 solution) and estimated from the experimental data for the range of pH 8.0–13.0 (the pH of the dye solutions were adjusted using dilute NaOH solution). The parameter-values are shown in Table 7. The Eq. (18) simulation results are presented in Fig. 5. This empirical equation has been developed for giving
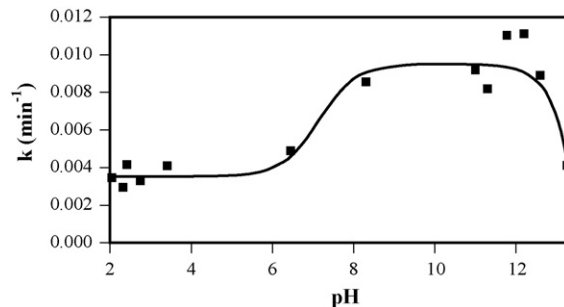
explicitly the dependence of the Freundlich parameter K_F on pH values, thus completing the Freundlich equation, according to the widely accepted methodology of 'parameter identification' which requires 'nested' models rather that expressions including all variables within the same equation; its worthwhile noting that the inner (empirical) model fits very satisfactorily the data provided by the outer (Freundlich) model, enhancing the predictability of the latter. Similarly, the parameter n can be simulated by an expression of the same form:

$$n = \frac{\gamma_2}{1 + e^{\alpha_2 - \beta_2 pH}} - \delta_2 \times 10^{-(14-pH)} + \varepsilon_2$$

or for $\delta_2 = 0$, $n = \frac{\gamma_2}{1 + e^{\alpha_2 - \beta_2 pH}} + \varepsilon_2 \tag{19}$

Also, the pseudo-first order Lagergren kinetic parameter k (in min^{-1}) of methylene blue adsorption on beech sawdust as a function of pH was simulated by the following equation, developed for the needs of the present work:

$$k = \frac{\gamma_3}{1 + e^{\alpha_1 - \beta_3 pH}} - \delta_3 \times 10^{-(14-pH)} + \varepsilon_3 \tag{20}$$

where $\alpha_3, \beta_3, \gamma_3, \delta_3, \varepsilon_3$ are empirical parameters. The parameter δ_3 was set equal to 0 for the range of pH 1.7–8.0 and estimated from the experimental data for the range of pH 8.0–13.0. The parameter-values are shown in Table 7. The Eq. (20) simulation results are presented in Fig. 6.

The pseudo-second order Lagergren kinetic parameter k (in min^{-1}) of methylene blue adsorption on beech sawdust as a

Table 7
The experimentally estimated parameters of Eqs. (18) and (19) expressing Freundlich parameters, K_F and n, of adsorption isotherms and of Eqs. (20)–(22) expressing the Lagergren kinetic parameters, k (in min^{-1}) and N, of methylene blue adsorbed on beech sawdust as a function of pH

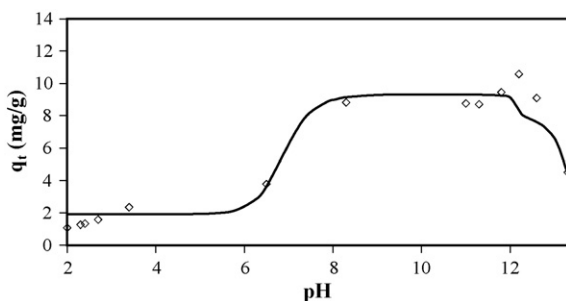| Parameters | Freundlich isotherms | | | Lagergren–Eldridge kinetics | | | | | |
|---|---|---|---|---|---|---|---|---|
| | K_F | | n | k (min^{-1}), first order | | k (min^{-1}), second order | | N-order |
| | pH ≤ 8 | pH > 8 | | pH ≤ 8 | pH > 8 | pH ≤ 8 | pH > 8 | |
| i | 1 | | 2 | 3 | | 4 | | 5 |
| α_i | 23.3 | | 197 | 14.9 | | 15.0 | | 30.6 |
| β_i | 3.50 | | 16.6 | 2.18 | | 2.01 | | 3.94 |
| γ_i | 5.14 | | 1.39 | 0.00598 | | 0.00154 | | 0.723 |
| δ_i | 0 | 13.1 | 0 | 0 | 0.0558 | 0 | 0.0105 | 0 |
| ε_i | 1.07 | | 1.78 | 0.00353 | | 0.0000910 | | 1.00 |
| SEE | 0.874 | | 0.193 | 0.00115 | | 0.000250 | | 0.119 |
| NSEE | 0.27 | | 0.10 | 0.15 | | 0.54 | | 0.07 |

Fig. 7. The plots of the adsorbed dye (q_t in mg/g) for the removal of methylene blue by adsorption on beech sawdust vs. initial pH of the dye solution at 23 °C, $C_0 = 14$ mg/L and adsorption time $t = 190$ min.

function of pH was simulated by the following equation:

$$k = \frac{\gamma_4}{1 + e^{\alpha_4 - \beta_4 pH}} - \delta_4 \times 10^{-(14-pH)} + \varepsilon_4 \qquad (21)$$

where $\alpha_4, \beta_4, \gamma_4, \delta_4, \varepsilon_4$ are empirical parameters. The parameter δ_4 was set equal to 0 for the range of pH 1.7–8.0 and estimated from the experimental data for the range of pH 8.0–13.0. The parameter-values are shown in Table 7.

Moreover, the order N of Lagergren kinetics of methylene blue adsorption on beech sawdust as a function of pH was simulated by the below equation, also developed in the present work:

$$N = \frac{\gamma_5}{1 + e^{\alpha_5 - \beta_5 pH}} - \delta_5 \times 10^{-(14-pH)} + \varepsilon_5 \quad \text{or for } \delta_5 = 0,$$

$$N = \frac{\gamma_5}{1 + e^{\alpha_5 - \beta_5 pH}} + \varepsilon_5 \qquad (22)$$

Beech sawdust was found to strongly adsorb methylene blue. The K_F values estimated using the Freundlich model, indicates that the adsorption capacity of methylene blue on beech sawdust is significantly affected by the pH. These values for pH ≥ 8 were found higher than the estimated for pH < 8 under the same experimental conditions. Especially, the values for the range of pH 11.5–13.0 were found lower than for pH 8.0–11.0 (Table 1), which was the optimum range.

Kinetic studies using the Lagergren equation provided values of k for pH ≥ 8 higher than the estimated for pH < 8 under the same conditions. There was insignificant effect of the pH on these values for the range of pH 8.0–12.3, but the k-value was decreased for pH 13.0 (Table 5).

The experimental results and the adsorption curves, estimated according to the presented simulation model, indicate that increase of the pH (but not over the 11.5 value) enhances the adsorption behavior of the examined material. An example for adsorption time $t = 190$ min is given in Fig. 7.

4. Discussion

The Freundlich equation was found to have the higher applicability (best fit) to the experimental data obtained in this work. The applicability of the Langmuir's adsorption model to the same data was at a lower level as indicated by the higher SEE and NSEE and lower R-values comparing to the Freundlich's model. The physical significance of the higher applicability of the Fre-

undlich isotherm model as compared to Langmuir's model can be explained by the basic assumption of multilayer adsorption for the Freundlich's model compared to the assumption of monolayer adsorption valid for the second model. The applicability of the Sips (Langmuir–Freundlich) adsorption model to the same data was at lower level as indicated by the same statistical values. Moreover, the high and random scattering of the estimated values of the parameters K_L and q_m versus pH decreases the convenience of this model for further simulation of the effect of the pH on the adsorption process. Last but not least, the fact that $n = 1.6 \pm 1.4$ leads to the conclusion that even the simple two parameter Langmuir model could be preferred instead of the more complicated three parameter Sips model. This last model can be obtained from the Sips model by the assumption that $n = 1$. However, the points can be mentioned referring to the Fritz–Schluender model, where $n = 1.8 \pm 1.2$, the Radke–Prausnitz model, where $n = 2.0 \pm 1.8$, and the Tóth model where $n = 3.4 \pm 2.3$. Moreover, the high and random scattering of some estimated values of the parameters versus pH also decreases the convenience of these three models for further simulation of the effect of the pH on the adsorption process. In the case of the UNILAN isotherm equation, the applicability to the same data was also at a lower level as indicated by the higher SEE and NSEE comparing to the Freundlich's model.

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 [19]: (a) migration of dye from bulk of the solution to the surface of the adsorbent, (b) diffusion of dye through the boundary layer to the surface of the adsorbent, (c) adsorption of dye at an active site on the surface of the adsorbent, and (d) intra-particle diffusion of dye into the interior pores of the adsorbent particle. The boundary layer resistance is 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 [9,19,30].

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. Lignin, the third major component of the wood cell wall, is a polymer material. Lignin molecule is built up from the phenylpropane nucleus, i.e. an aromatic ring with a three-carbon side chain. Vanillin and syringaldehyde are the two of other basic structural units of lignin molecule. The lignin content of hardwoods is usually in the range of 18–25%, whereas that of softwoods varies between 25% and 35%. For the beech sawdust used in the present work, lignin content was found 25.7%. Tannins are complex polyhydric phenols, which are soluble in water and have the property of precipitating protein (e.g. gelatin) from solution. They occur chiefly in hardwoods, and are also

present in many barks, including softwoods barks, as well as in the leaves and fruits of some trees. Natural tannins are classified as either hydrolysable or condensed tannins. The hydrolysable tannins are esters of sugar (usually glucose) with one or more polyphenolic acids, commonly gallic, digallic, or ellagic acid. The basic unit of condensed tannins is, in many cases, catechin [2].

Adsorption studies, in particular kinetics and isotherms, provide information on the mechanism of sorption: how is the pollutant bound within the sorbent. This knowledge is essential for understanding the sorption process. Due to the complexity of materials used and their specific characteristics (such as the presence of complexing chemical groups, small surface area, poor porosity), the sorption mechanism of polysaccharide-based materials is different from those of other conventional adsorbents. 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, precipitation. An examination of the data in the literature indicates that it is quite possible that at least some of these mechanisms are to varying degrees acting simultaneously depending on the chemical composition of the sorbent, the nature of the pollutant and the solution environment [43,44]. The existence of physiochemical actions in parallel does not permit the deduction of a rate equation based on the classical slowest-step concept, valid exclusively when a unique chain of such actions takes place in series.

The effect of pH on adsorption by sawdust can be explained on the basis of the point of zero charge pH_{pzc}, at which the adsorbent is neutral, while beyond this the material becomes either positively or negatively charged. In the present work, the pH_{pzc} of the beech sawdust measured by the mass titration [24,25] and the automatic titration method [26], was found to be 5.2 ± 0.2 and 5.6 ± 0.4, respectively. The sorption capacity of basic dye is much higher than that of acid dye because of this ionic character of sawdust (and also of the ionic charges on the dyes). Above the zero point of charge, the negative charge density on the surface of the adsorbent favors the sorption of basic (cationic) dyes like methylene blue (see Figs. 5–7). Shukla et al. [2], reported some similar pH_{zpc} values for various sawdust materials: polyacrylamide-grafted sawdust = 5.9, dyestuff-treated sawdust = 5.9, sawdust activated carbon = 6.4, polysulfide treated sawdust = 4.3, rubber wood sawdust carbon = 5.8.

In the present work, the adsorbed methylene blue on beech sawdust after an adsorption period of 190 min was significantly lower for pH 1.7–6.2. The lower adsorption of methylene blue at acidic pH can be attributed to the presence of excess H^+ ions that compete with the dye cation for adsorption sites. As the pH of the system increases, the number of positively charged sites decreases while the number of the negatively charged sites increases. The negatively charged sites favor the adsorption of dye cation due to electrostatic attraction. The increase in initial pH from 8.0 to 11.5 slightly increases the amount of dye adsorbed. This amount decreases for pH 12.3–13.0 because, in alkaline solutions, methylene blue is stepwise demethylated, to other common dyes. Moreover, 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 are in general agreement with other literature data. The concentration of methylene blue in the solution was obtained by measuring OD at 664 nm (λ_{max}) for pH 1.7–11.0 and the absorbance versus λ_{max} patterns remained practically unchanged for 7 days, proving that there was no significant chemical reaction involving methylene blue. For pH $\geq$ 11.5 the OD was also measured at 620 and 596 nm and the reference curve was estimated as a function of time and pH, because in high alkaline solutions, the absorbance versus λ_{max} patterns changed during the 7 days. According to the literature, methylene blue reacted with NaOH and stepwise demethylated to other common dyes, namely trimethylthionine (azure B), dimethylthionine (azure A), and monomethylthionine (azure C) [23]. The authors reasonably assume that this chemical transformation of methylene blue to azure A–C, explains the relatively lower adsorption capacity at these pH-values range.

In the case of heavy metal adsorption on sawdust, taking into account the components and complexing properties of the sawdust, the properties of heavy metals and the adsorption behavior, such as the effect of pH of the aqueous media, scientists have speculated that ion exchange and hydrogen bounding may be the principal mechanism for the removal of heavy metals. It has long been recognized that heavy metal cations are readily form complexes with O-, N-, S-, or P-containing functional groups in polymer materials. Although a detailed characterization of the nature of the binding sites on different sawdust materials was not conducted, from the nature of heavy metal ions and sawdust materials it can be speculated that ion exchange or hydrogen bounding may be the principal mechanism for the removal of heavy metal ions [2]. Yu et al. [45] studied the effect of pH in the case of copper sorption on sawdust for pH 2.0–10. They reported that the removal of Cu^{2+} by sawdust adsorption increases with increasing pH, from a minimum at pH 2.0 to a maximum at a pH $\approx$ 7.0. After that, the percent adsorption decreases slightly in pH range of 8.0–10.0. The greatest increase in the sorption rate of Cu^{2+} on sawdust was observed for pH 2–8. Ion exchange may be the principal mechanism for the removal of copper. From the nature of the sawdust major components (lignin, tannins or other phenolic compounds) that are efficient in capturing heavy metal ions, it can be speculated that they are the active ion exchange compounds and that active sites are the phenolic groups of those compounds. Based on the structure of these phenolic compounds, a possible mechanism of ion exchange could be considered as a divalent heavy metal ion (M^{2+}) attaches itself to two adjacent hydroxyl groups and two oxyl groups which could donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ions into solution. Assuming pK of the phenolic group in sawdust being same as that of the free phenol, the phenolate ion population would be extremely small at pH less than 3 or 4. The adsorption may fall rapidly as the pH falls.

Namasivayam et al. [8] studied the effect of pH on the percent removal of the methylene blue by 'waste' coir pith. The percent removal for methylene blue increased with increase in pH. Lower adsorption of methylene blue, at highly acidic pH is probably due to the presence of excess H$^+$ ions competing with the dye cation for the adsorption sites. Desorption studies in water at different pH values also aim to evaluate the adsorption mechanism. Percent desorption curves for all the dyes studied shown that the trend in desorption with pH is just opposite to that in adsorption, indicating that ion-exchange is probably one of the modes of the adsorption processes. The maximum desorption was low for methylene blue at pH 3. Hence, the major mode of adsorption seems to be chemisorption [8]. For methylene blue adsorption by banana and orange peel, the amount of adsorption increases when the pH is increased. The adsorption capability reaches maximum at pH 6–7, but decreases when pH is increased further. In the case of orange peel, the amount of dye adsorbed reaches a plateau at pH > 7. Solution pH would affect both aqueous chemistry and surface binding-sites of the adsorbents. It was assumed that at lower pH, H$^+$ may compete with dye ions for the adsorption sites of both peel wastes, thereby inhibiting the adsorption of dyes [9]. Vadivelan and Kumar [46] reported similar results and adsorption mechanism for methylene blue removal using rice husk. The dye uptake was found to increase with increasing pH from 3 to 8.

Wang et al. [47] studied the adsorption of methylene blue on three activated carbons for pH 3, 5 and 10. Their adsorption capacities were greatly decreased for pH 3. This was consistent with the pH$_{pzc}$. The adsorption capacities at solution pH 10 were significantly improved compared with that at lower pH values. Apparently, the adsorption of methylene blue prefers a higher solution pH values. Because of the varying amounts and nature of surface oxygen, carbon materials should be regarded as a special case of amphoteric solids. Both negative and positively charged surface sites exist in aqueous solution, depending on the solution pH. When solution pH > carbon pH$_{pzc}$, the surface of carbon is negatively charged and can attract cations from the solution; when solution pH < pH$_{pzc}$, the surface of carbon is positively charged and attractive to anions. Apparently, the higher the solution pH value, the more the negative charges on the carbon surface, the more attractive to cations the carbon surface. This is why a higher pH value is good for adsorbing methylene blue. Considering the area of the methylene blue molecule to be 1.62 nm^2, the surface of carbon occupied by this adsorbate was calculated. At the lower pH of solution, the methylene blue coverage on carbon is lower than the surface area, indicating that the methylene blue is adsorbed on the macropores and mesopores and on a certain fraction of micropores and the adsorption could be just a single layer adsorption. But, in all of the samples at solution pH 10, this surface coverage was greater than the surface area, indicating that a multilayer adsorption occurred. Kannan and Sundaram [19] carried out a comparative study on kinetics and mechanism of removal of methylene blue by adsorption on various activated carbons with similar adsorption results for pH 1.5–11.

In the case of methylene blue adsorption on cedar sawdust, Hamdaoui [48] reported that the dye adsorption was minimum at pH 2. The dye adsorption was affected for pH 2–5. At higher pH 9.5–11 the dye adsorption decreased. Optimum pH value for dye adsorption was observed at pH 7. Low pH was unfavorable for methylene blue adsorption by cedar sawdust. As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favor the adsorption of positively charged dye cations due to electrostatic repulsion. Also, lower adsorption of methylene blue at acidic pH is due to the presence of excess H$^+$ ions competing with dye cations for the adsorption sites. This, however, did not explain the slight decrease of dye adsorption at higher pH values. There might be another mode of adsorption (ion exchange or chelatation for example). It is also important to point out that cedar sawdust might be subject to hydrolysis, which creates positively charged sites. This may be one of the reasons for the adsorption decrease at high pH values.

According to Garg et al. [18] who studied the effect of pH on methylene blue adsorption on GAC (granular activated carbon) and Indian Rosewood sawdust (a timber industry waste), the dye adsorption efficiency was not affected by pH except minor variations in the pH 2–10. Initial pH of dye solution was increased after the equilibrium time. The pH increase was lesser at pH 2–4. It may be due to hydrolysis of the adsorbent in water, which creates positively charged sites.

It is apparent that by increasing the adsorbent dose the adsorption efficiency increases but adsorption density, the amount adsorbed per unit mass, decreases. It is readily understood that the number of available adsorption sites increases by increasing the adsorption dose and it, therefore, results in the increase of removal efficiency. The decrease in adsorption density with increase in the adsorbent dose is mainly due to unsaturation of adsorption sites through the adsorption reaction. Another reason may be due to the particle interaction, such as aggregation, resulted from high adsorbent dose. Such aggregation would lead to decrease in total surface area of the adsorbent and increase in diffusional path length. Particle interaction may also contribute to the desorption of some of the adsorbate which is only loosely and reversibly bound to the sawdust surface [2].

Sulfuric acid, added to decrease pH, might be partly neutralized by the ash in the sawdust. Sulfuric acid pre-treatment can improve the adsorption capacity of sawdust (hydrolysis of hemicelluloses and partial hydrolysis of cellulose), but not in the mild conditions (room temperature 23 °C) used in the present work; treatment in elevated temperatures (e.g. 100 °C) implies significant improvement of sorption properties, as we have shown recently [49].

The ionic strength is also an influencing factor. In the case of removal of copper from aqueous solutions by adsorption using sawdust, Larous et al. [50] found that was influence of the ionic strength on the capacity of adsorption. It has been tested by the addition of sodium chloride to the copper solution. The increase in ionic strength between 0.001 and 0.1 has significantly decreased the percentage of adsorption. This may be due to the following two reasons: (a) the electrostatic attraction seems to be a significant mechanism, as indicated by the results where at high ionic strength, the increased amount of NaCl can help to render the surface of the sawdust not easily

accessible to Cu^{2+} ions and hence decreasing the adsorption rate. In fact, according to the surface chemistry theory developed by Guoy and Chapman, when solid adsorbent is in contact with sorbate species in solution, they are bound to be surrounded by an electrical diffused double layer, the thickness of which is significantly expanded by the presence of electrolyte. Such expansion inhibits the adsorbent particles and Cu^{2+} from approaching, and (b) the relative competition between sodium ions and copper species for the active sites of sawdust, can also be an explaining factor.

5. Conclusions

The results presented herein on the adsorption capacity, estimated according to Freundlich's model, of methylene blue adsorption on beech sawdust as low cost adsorbent for wastewater dye removal, indicate that increase of the pH enhances the adsorption behaviour of this material. Above point of the zero charge (pH_{pzc} 5.2), the negative charge density on the surface of the adsorbent favors the sorption of basic (cationic) dyes like methylene blue. The significantly lower adsorption of methylene blue at acidic pH can be attributed to the presence of excess H^+ ions that compete with the dye cation for adsorption sites. As the pH of the system increases, the number of positively charged sites decreases while the number of the negatively charged sites increases. The negatively charged sites favor the adsorption of dye cation due to electrostatic attraction. The increase in initial pH from 8.0 to 11.5 increases the amount of dye adsorbed. This amount decreases for higher pH values, due to methylene blue stepwise demethylation. The examined low cost adsorbent was found to be a suitable alternative of the commercial activated carbons for the removal of basic dyes from non-acidic water/wastewater effluents.

Acknowledgment

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