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Using six different lignocellulosic biomass materials for removal of methylene blue by biosorption

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ORIGINAL RESEARCH ARTICLE

ABSTRACT

This study illustrates the feasibility of using lignocellulosic sources, such as agricultural residues (e.g. straws) and wood processing industry wastes (e.g. sawdust) to remove basic dyes such as methylene blue (MB) from water and wastewater. Specifically, wheat straw, chickpea straw, lentil straw, Norway Spruce (*Picea abies*) sawdust, algae (*Posidonia oceanica*) and cork were used as absorbents for MB. The adsorption was characterised using seven adsorption models, including the Freundlich, Langmuir, Sips, Radke-Prausnitz Modified, Radke-Prausnitz, Tóth and UNILAN. The maximum adsorption capacity according to the Langmuir isotherm model was 147.1 mg/g for algae and the lowest adsorption capacity was recorded for spruce sawdust as 33.5 mg/g. The adsorption processes followed the second-order kinetic model in comparison with first order and intra-particle diffusion kinetic models. In addition, desorption experiments was performed using pure water as desorbent. Also the adsorbents were characterized using scanning electron microscopy and Fourier transform-infrared spectroscopy

KEYWORDS

adsorbent; agricultural residues; Biomass; lignocellulosics; straw

1. INTRODUCTION

About 10,000 different dyes weighing approximately 0.7 million tons are manufactured annually for various industrial processes. An extensive amount of these dyes are discharged into the effluent during the dyeing process. Several of these dyes have been classified as toxic or even carcinogenic to aquatic organism as well as to human life (Ahmad and Rahman, 2011).

As a result, many treatment methods were developed for the removal of dyes from industrial effluents. The most popular methods are biodegradation (El-Sheekh et al., 2009), flocculation–coagulation (Canizares et al., 2006), electrochemical oxidation (Raghu et al., 2009) and adsorption (Sidiras et al., 2011). Among these methods, the adsorption has been identified as an efficient and attractive technique for the treatment of dye-bearing wastewaters (Yao et al., 2010).

Biomass and specifically lignocellulosic residues offer a low-cost and renewable source for adsorbents, which can be used as it is or modified/transformed into activated carbon. These waste materials have little or no economic value and often present a disposal problem. Therefore, there is a drive to valorize these low-cost by-products. Various low-cost adsorbents from agricultural by-products have been studied to remove dyes from aqueous solutions. These include fruit peel (Hameed and Hakini, 2008), wheat straw (Batzias et al., 2009), papaya seeds (Hameed, 2009), peanut husk (Song et al., 2011), cotton stalk (Deng et al., 2011), pistachio hull (Moussavi and Khosravi, 2011), sugar beet pulp (Makekbala et al., 2012), peach gum (Zhou et al., 2014), bamboo (Guo et al., 2014), defatted algal biomass (Sarat Chandra et al., 2015) and almond gum (Bouaziz at al., 2015).

The objective of the present work is to study the removal of Methylene blue (MB) from water using

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six low cost and widely available adsorbents. This research is also intended to understand the adsorption kinetics and adsorption isotherms, to determine the rate and mechanism of adsorption and to study the factors controlling the rate of adsorption (Batzias and Sidiras, 2004; Sidiras et al., 2011; Sidiras et al., 2013). Methylene blue is selected as a representative cationic/ basic dye, owing to its wide applications, including coloring paper, dying cottons, wools, silk, leather and coating for paper stock (Dogan et al., 2009). Batch adsorption studies are conducted to obtain the key parameters such as isotherm constants and pore diffusivity.

2. MATERIALS AND METHODS

2.1. Adsorbent

In this study, six low-cost lignocellulosic materials were used as adsorbents. These materials were spruce sawdust, wheat straw, lentil straw, chickpea straw, algae and cork. The Norway Spruce (*Picea abies*) sawdust used was obtained from a local furniture manufacturing company. The wheat, chickpea and lentil straws were obtained from Thessaly (Central Greece). The algae, *Posidonia oceanica* was acquired from seashore of Lefkada Island in Greece. The cork is a byproduct from a wine bottle industry in Naousa City (North Greece). The materials were crushed using hammer mill and were sieved to particle sizes of 0.1 - 1 mm. They were washed with distilled water for a number of times. Also these materials were dried for 10 days at room temperature to minimize humidity.

2.2. Adsorbate

The dye used in batch experiments was Methylene blue. The dye was provided by Merck (CI 52015) and has a chemical formula of $C_{16}H_{18}ClN_3S.xH_2O$ (x=2 - 3) with molecular weight of 319.86 10^{-3} kg/mol (anhydrous). A stock solution was prepared by dissolving 5 g of MB in 25 L distilled water. Working solutions were 1.6 - 156 mg/L. MB concentration was estimated by measuring the absorption values in each experiment using a HACH DR4000U UV-VIS spectrophotometer at λ = 664 nm. The solution pH was near to 8.0 and was not adjusted during the experiment. The pH was adjusted using small quantities of NaOH or H_2SO_4.

2.3. Adsorption isotherm studies

Isotherms were obtained from individual batch experiments. The known quantity of the adsorbent was transferred to 0.8 L bottles, where 0.5 L of adsorbate solution was added. The adsorbent weight was 0.5 g, the temperature was T = 23 °C, the initial MB concentration (C_o) ranged from 1.6 to 156 mg/L. The bottles were sealed and mechanically stirred at 600 rpm for a period of 7 days. This time period was chosen after pilot studies (the time varies from 4 hours to 14 days) to ensure that equilibrium conditions were achieved. The adsorbent was separated from MB solution after equilibrium using a 0.1 mm nylon filter. The concentration of the resulting solution was determined and balance data from each bottle represented one point on the adsorption isotherm plots. The values of solution pH were near 8. The amounts of MB adsorbed per unit mass of the adsorbent (in mg/g) at equilibrium time ($t \to \infty$) (q) and adsorption time t (q_t) were calculated as follows,

$$q = (C_0 - C_e)V/m \quad (1)$$

$$q_t = (C_0 - C)V/m \quad (2)$$

where C, C_o and C_e are the concentrations of MB in the bulk solution at time t, 0 and equilibrium (mg/L), respectively, m is the weight of the adsorbent used (in g), and V is the solution volume (L).

2.4. Adsorption kinetic studies

Adsorption rate batch experiments were conducted in a 2 L glass totally mixed reactor equipped with a twisted blade agitator type, operating at 600 rpm, for maintaining the lignocellulosic material in suspension. The reactor, containing 1 L aqueous solution of dye, was placed in a water bath to maintain constant temperature at the desired level. The adsorbent mass (m) was 1 g, the temperature was 23 °C, the initial concentration of MB was C_o = 3.1 - 156 mg/L. Every 5 min, 10 mL samples were taken from the reactor using a pipette and the adsorbent was separated from MB solution using a 0.1 mm nylon filter. Then, MB concentration was measured as described above in Section 2.2.

2.5. Analytical techniques

The scanning electron microscope (SEM) used in the present study was a JEOL JSM-6700F Field Emission Scanning Electron Microscopy. The SEM analyses were carried out by coating samples with Pt (5 nm) using a JEOL JSM-6700F Field Emission Scanning

Table 1. Estimated parameter values for the alternative isotherm models of Methylene blue adsorption on six different adsorption materials

	K_F [(mg/g)(L/mg)$^{1/n}$]	K_L (L/mg)	q_m (mg/g)	n	s	SEE
Wheat Straw						
Freundlich	4.95			2.24		3.91
Langmuir		0.058	41.8			1.97
Sips		0.073	38.1	0.838		1.94
Radke-Prausnitz modified		0.034	64.5	0.804		1.96
Radke-Prausnitz		0.025	81.6	0.872		1.94
Tóth		0.010	36.3	0.644		1.91
UNILAN		0.058	41.8		0.0001	2.08
Lentil Straw						
Freundlich	5.72			1.88		8.44
Langmuir		0.046	72.0			6.18
Sips		0.110	51.9	0.383		3.41
Radke-Prausnitz modified		0.011	276.1	0.423		6.12
Radke-Prausnitz		0.005	579.6	0.679		5.87
Tóth		0.001	53.8	0.335		5.44
UNILAN		0.046	72.0		0.00003	6.52
Chickpea Straw						
Freundlich	4.31			1.39		7.50
Langmuir		0.020	144.0			7.69
Sips		0.002	450.7	1.28		7.91
Radke-Prausnitz modified		0.191	19.1	2.55		7.73
Radke-Prausnitz		0.260	17.3	1.87		7.81
Tóth		0.152	1437.4	2.96		7.84
UNILAN		0.020	144.0		0.010	8.11
Spruce Sawdust						
Freundlich	6.40			2.78		2.87
Langmuir		0.116	33.6			0.975
Sips		0.102	34.9	1.09		0.972
Radke-Prausnitz modified		0.135	30.1	1.04		1.01
Radke-Prausnitz		0.143	29.0	1.03		1.00
Tóth		0.167	35.1	1.15		0.988
UNILAN		0.105	43.6		1.04	0.987
Algae						
Freundlich	7.70			1.53		2.78
Langmuir		0.034	147.1			2.59
Sips		0.014	224.2	1.21		2.30
Radke-Prausnitz modified		0.205	31.6	1.99		1.96
Radke-Prausnitz		0.236	31.8	1.56		2.07
Tóth		0.166	458.3	2.22		2.14
UNILAN		0.003	354.0		3.55	2.26
Cork						
Freundlich	7.98			2.54		2.47
Langmuir		0.099	47.8			3.70
Sips		0.002	157.3	2.13		2.45
Radke-Prausnitz modified		1.15	10.2	1.48		2.19
Radke-Prausnitz		1.50	11.9	1.44		2.21
Tóth		0.937	313.1	5.18		2.33
UNILAN		0.003	117.6		5.59	2.61

Electron Microscopy. The magnifications were 750X, 7,500X and 20,000X.

Fourier transform infrared (FTIR) spectra were obtained using MAGNA-IR 750 Spectrometer, Serrie II, Nicolet. The sampling technique used was diffuse reflectance. The powder samples were scanned for wavenumber 650 - 4000 cm^{-1}.

3. RESULTS AND DISCUSSION

The study of MB adsorption using six different lignocellulosic materials was performed through batch mode of operation. In batch studies, the performance of adsorbents was evaluated through kinetic and isotherm data.

3.1. Adsorption isotherms

The isotherm results are presented in Figure 1. The comparison of the adsorption capacity of the seven different adsorption materials was based on the Freundlich (Freundlich, 1906), Langmuir (Langmuir, 1916) Sips (Sips, 1948), Radke-Prausnitz modified (Chern and Wu, 2001), Radke-Prausnitz (Radke and Prausnitz, 1972; Chern and Wu, 2001), Tóth (Tóth, 2000) and UNILAN (Chern and Wu, 2001), isotherm models. The first two models are widely used for investigating the adsorption of various dyes onto different lignocellulosic materials and activated carbons. The Freundlich (Freundlich, 1906) isotherm is given by the following equation:

$$q = K_F \cdot (C_e)^{\frac{1}{n}} \quad (3)$$

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), K_F [(mg/g)(L/mg)$^{1/n}$] and n are the Freundlich constants related to adsorption capacity and intensity, respectively. Deriving the logarithmic form of Eqn. (3):

$$\log q = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

The K_F and n values were estimated by non-linear regression analysis (NLRA) from the experimental adsorption data obtained at 23 °C for MB. From the technological point of view, parameter K_F is the most important parameter representing the adsorption capacity of the materials for low MB concentration C_e = 1 mg/L.

The Freundlich parameter values are shown in Table 1. The cork has the highest value of K_F equal to 7.98, followed by algae (7.70) and spruce sawdust (6.40). Comparing the straw materials, the lentil straw recorded higher K_F value than wheat straw and chick-pea straw (Table 1). The n values were similar for all materials.

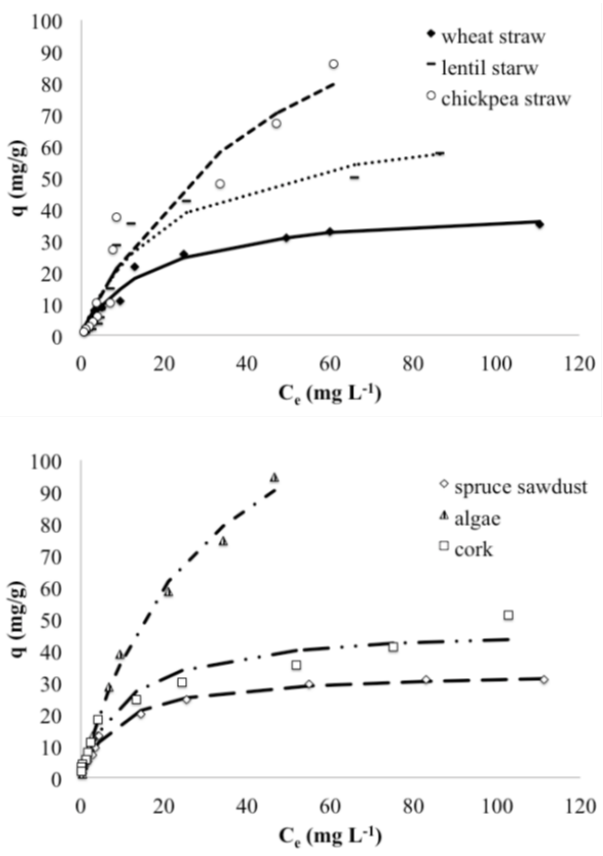

Figure 1. The Langmuir isotherm curves of MB adsorption onto wheat, lentil and chickpea straws (top figure) and spruce sawdust, algae, cork (bottom figure) as affected by MB initial concentration. Adsorption process: temperature 23 °C, MB initial concentration=1.6-156 mg/L, m/V=1 g/L

The standard error of estimates (SEE)-values was calculated by the following equation:

$$SEE = \sqrt{\sum_{i=1}^{n'} (y_i - y_{i,theor})^2 \,/\, (n' - p')} \quad (5)$$

where: y_i is the experimental value of the depended variable, $y_{i,theor}$ is the theoretical (estimated) value of the depended variable, n' is the number of the experimental measurements and p' is the number of parameters, i.e., (n' – p') is the number of the degrees of free-

dom. The fitting of the Freundlich adsorption model to the experimental data was very satisfactory (Table 1) giving low SEE-values.

The Langmuir isotherm equation (Langmuir, 1916) is based on the following 'pseudo-monolayer' adsorption model.

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

or

$$\frac{1}{q} = \left(\frac{1}{q_m}\right) + \left(\frac{1}{K_L \cdot q_m}\right) \cdot \left(\frac{1}{C_e}\right) \tag{7}$$

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 saturation is attained. In cases where the isotherm experimental data approximates the Langmuir equation, the parameters K_L and q_m can be estimated either by plotting 1/q versus $1/C_e$ or by NLRA. From the technical point of view, parameter q_m is the most important parameter representing the maximum adsorption capacity of the materials.

The characteristics of the Langmuir isotherm can be described by a dimensionless constant called 'equilibrium parameter' or 'separation factor' R_L:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \tag{8}$$

where C_o is the initial MB concentration (mg/L).

Moreover, Figure 1 shows Langmuir isotherm curves and Table 1 presents the NLRA parameter value estimates for the data obtained in the present study. The values of q_m obtained for algae were higher than the values for the other five materials. The q_m values recorded were 147.1, 144.0, 72.0, 47.8, 41.8 and 33.5 mg/g for algae, chickpea straw, lentil straw, cork, wheat straw and spurce sawdust, respectively.

The fitting of the Langmuir's adsorption model to the present data was also very satisfactory as shown by the corresponding SEE-values given in Table 1.

For this work, the R_L values were found between 0 and 1 for all MB concentrations and adsorbents studied. This fact indicates a favorable adsorption, while $R_L > 1$ represents an unfavorable adsorption and $R_L = 1$ represents the linear adsorption. Moreover, the adsorption operation is irreversible if $R_L = 0$ (Gupta and Babu, 2009).

The Sips (Langmuir – Freundlich) (Sips, 1948) isotherm model, also examined in the present work, can be expressed as:

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

where K_L and q_m are the Langmuir constants and n is the Freundlich constant. The Sips model parameter values obtained for the experimental data are presented in Table 1. The description of the Sips adsorption model to the present data was satisfactory for MB adsorption, better than the other isotherm models, as indicated by the corresponding SEE-values (Table 1).

The Radke–Prausnitz (Radke, 1972; Chern and Wu, 2001) isotherm equation can be expressed as,

$$q = \frac{K_L \cdot q_m \cdot C_e}{1 + K_L \cdot C_e^{1/n}} \tag{10}$$

The Modified Radke – Prausnitz (Chern and Wu, 2001) isotherm equation can be presented as,

$$q = \frac{K_L \cdot q_m \cdot C_e}{(1 + K_L \cdot C_e)^{1/n}} \tag{11}$$

The modified Radke – Prausnitz and the Radke–Prausnitz parameters values are shown in Table 1. The lentil straw has the highest value of q_m according the Radke–Prausnitz model.

The Tóth (Tóth, 2000) isotherm equation can be written as,

$$q = \frac{q_m \cdot C_e}{\left(1/K_L + C_e^{\,n}\right)^{1/n}} \tag{12}$$

The Tóth parameters values are shown in Table 1. The chickpea straw has the highest value of q_m according to the Tóth isotherm model.

The UNILAN (Chern and Wu, 2001) isotherm equation is

$$q = \frac{q_m}{2s} \ln\left(\frac{1 + K_L.C_e \cdot e^{s}}{1 + K_L \cdot C_e \cdot e^{-s}}\right) \tag{13}$$

where s is UNILAN isotherm model constant. The UNILAN parameters values are shown in Table 1. The values of q_m obtained for algae were higher than the values of other adsorbents.

The parameters of all the presented isotherm models were estimated by NLRA. Among the isotherm models examined, the Sips model provided better description of experimental data (Table 1).

3.2. Kinetics of adsorption

The kinetics of MB adsorption onto various adsorbents were described using different kinetic equations. The widely used Lagergren equation (Lagergren, 1898) is shown below:

$$q - q_t = q \cdot e^{-k_1 t} \tag{14}$$

where q and q_t are the amounts of MB adsorbed per unit mass of the adsorbent (mg/g) at equilibrium time ($t \to \infty$) and adsorption time t, respectively; k_1 is the pseudo-first order rate constant for the adsorption process (1/min). Further modification of Eqn. (14) in logarithmic form gives:

$$\ln(q - q_t) = \ln q - k_1 \cdot t \tag{15}$$

Table 2 presents the values of k_1 (1/min), q_e (mg/g) and SEE for all lignocellulose materials at six different initial MB concentrations. The range of initial MB concentration was from 3.1 to 156 mg/L. For example, for C_0=14 mg/L the NLRA estimates of the first order rate constants k_1 were 0.0190-0.1579 1/min (0.019 1/min for algae and 0.158 1/min for cork), and the SEE-values were 0.251 - 0.996 (0.251 for wheat straw and 0.996 for chickpea straw).

The commonly used second-order kinetic model (Ho et al., 2000) is as follows:

$$q_t = q - \left[q^{-1} + k_2 t\right]^{-1} \tag{16}$$

(or)

$$q_t = q - \frac{1}{\frac{1}{q} + k_2 t} \tag{17}$$

where k_2 is second-order kinetics rate constant (g/mg min). The prediction of the second order kinetics is presented in Figure 2 for all adsorbents. The NLRA-estimated values of the second order rate constants k_2 were 0.002 - 0.040 g/mg min (0.002 g/mg min for algae and 0.040 g/mg min for cork) and the SEE-values were 0.122 - 0.295 for C_0 = 14 mg/L (Table 3).

Table 2. Parameters of Lagergren kinetic models of Methylene blue adsorption on six different adsorption materials

C_0 (mg/L)	Wheat straw	Lentil straw	Chickpea straw	Spruce sawdust	Algae	Cork
Adsorption rate constant k_1 (1/min)						
156	0.034	0.046	0.014	0.033	0.026	0.054
78	0.001	0.004	0.020	0.100	0.008	0.027
31	0.027	0.034	0.056	0.057	0.010	0.054
14	0.033	0.054	0.056	0.055	0.019	0.158
7.8	0.031	0.083	0.114	0.054	0.037	0.514
3.1	0.064	0.066	0.115	0.064	0.040	0.409
q (mg/g)						
156	21.7	28.8	45.3	42.8	40.6	27.4
78	192.7	64.1	35.5	19.3	40.9	25.2
31	7.23	10.3	14.3	13.5	26.6	16.1
14	4.53	3.23	5.44	6.57	4.88	5.88
7.8	1.50	2.80	3.45	4.55	3.29	5.58
3.1	2.53	1.50	1.66	2.52	1.77	2.50
Standard Error of Estimation *SEE*						
156	1.36	2.69	1.323	2.40	3.70	1.21
78	0.855	0.896	0.732	0.842	0.969	1.09
31	0.251	0.574	0.996	0.891	0.761	0.811
14	0.290	0.263	0.311	0.318	0.144	0.474
7.8	0.069	0.154	0.234	0.231	0.236	0.063
3.1	0.173	0.078	0.089	0.136	0.098	0.035

Table 3. Parameters of second-order kinetic model of Methylene blue adsorption on six different adsorption materials

C_0 (mg/L)	Wheat straw	Lentil straw	Chickpea straw	Spruce sawdust	Algae	Cork
k_2 (g/mg min)						
156	0.0012	0.0016	0.00013	0.0006	0.0004	0.0019
78	0.00002	0.00004	0.00028	0.007	0.00008	0.0007
31	0.0021	0.0026	0.0043	0.004	0.0002	0.0033
14	0.0056	0.018	0.011	0.008	0.002	0.040
7.8	0.0137	0.036	0.047	0.012	0.010	0.407
3.1	0.0235	0.047	0.092	0.028	0.018	0.523
q (mg/g)						
156	27.8	34.5	70.6	55.3	53.6	32.8
78	99.2	90.8	52.2	21.4	64.2	34.0
31	10.1	13.2	16.8	15.9	39.3	19.2
14	5.82	3.81	6.43	7.82	7.10	6.36
7.8	2.01	3.18	3.79	5.43	4.11	5.64
3.1	3.03	1.75	1.84	2.94	2.23	2.55
Standard Error of Estimation *SEE*						
156	1.11	2.08	1.37	2.04	3.37	0.787
78	1.31	0.902	0.740	0.424	0.999	0.898
31	0.268	0.441	0.668	0.568	0.768	0.440
14	0.244	0.191	0.185	0.158	0.122	0.295
7.8	0.059	0.075	0.133	0.134	0.185	0.044
3.1	0.192	0.052	0.055	0.072	0.073	0.022

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. The possibility of intraparticle diffusion can be verified by the applicability of the intra-particle diffusion model (Weber and Morris, 1963) as

presented below:

$$q_t = c + k_p \cdot \sqrt{t} \quad (18)$$

where q_t is the amount of MB adsorbed at time t, c is a constant (mg/g) and k_p is the intra-particle diffusion rate constant (mg/g min).

The intra-particle diffusion model parameter values are given in Table 4 as estimated by NLRA. The results indicated the involvement of intra-particle diffusion process. For C_o = 14 mg/L, the intra-particle diffusion model rate constants k_p were 0.317 - 0.652 mg/g min (0.317 for lentil straw and 0.652 for spruce sawdust) and the SEE-values were 0.120 - 0.709 (0.120 for algae and 0.709 for cork).

From the results, it was found that second-order kinetic model described the experimental MB kinetics data of six lignocellulosic materials well as the SEE-values were found to be lower than those of the first-order kinetic model and intra-particle model.

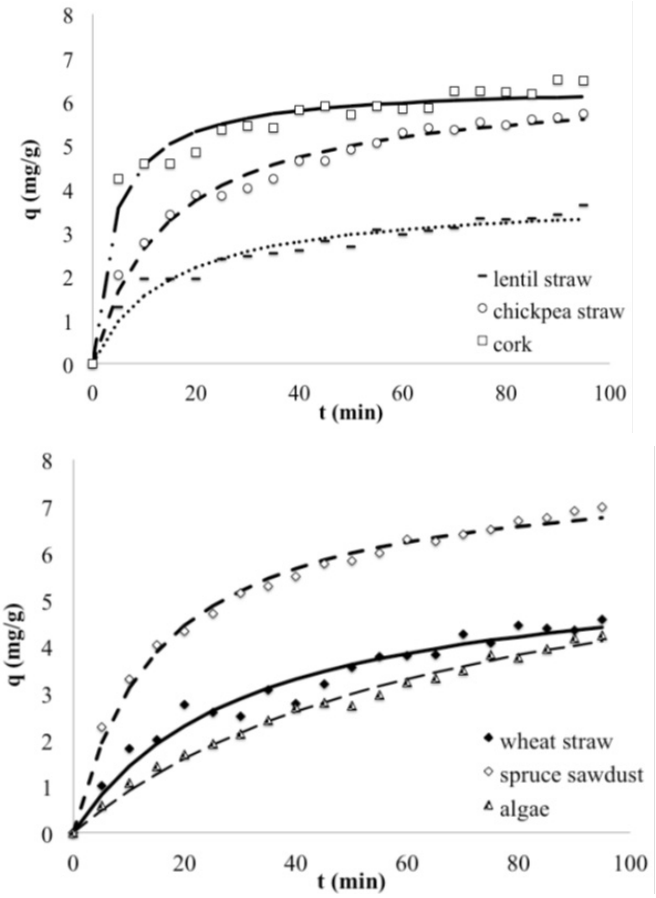

Figure 2. The second order kinetics of MB adsorption on lentil straw, chickpea straw, cork (top image) and spruce sawdust, algae, wheat straw (bottom image). Adsorption process: temperature 23 °C, MB initial concentration=14 mg/L, m/V=1 g/L.

Table 4. Parameters of intra-particle kinetic model of Methylene blue adsorption on six different adsorption materials

C_o (mg/L)	Wheat straw	Lentil straw	Chickpea straw	Spruce sawdust	Algae	Cork
k_p (mg/g min$^{0.5}$)						
156	2.19	2.87	3.95	4.33	3.98	2.73
78	2.35	2.37	3.43	1.64	2.60	2.50
31	0.767	1.05	1.39	1.32	1.78	1.60
14	0.461	0.317	0.535	0.652	0.457	0.470
7.8	0.157	0.256	0.291	0.454	0.329	0.292
3.1	0.259	0.145	0.140	0.243	0.185	0.139
c (mg/g)						
156	1.27	3.83	-5.24	1.83	-0.058	4.23
78	-5.62	-3.29	-2.53	6.44	-4.75	-0.016
31	-0.394	0.512	2.65	2.40	-2.79	2.57
14	0.181	0.558	0.949	1.07	-0.305	2.35
7.8	0.003	0.764	1.205	0.717	0.265	3.41
3.1	0.401	0.306	0.576	0.525	0.113	1.46
Standard Error of Estimation *SEE*						
156	0.718	1.60	2.04	1.64	2.76	1.88
78	2.11	1.66	1.17	2.20	1.66	0.458
31	0.396	0.299	0.868	0.852	1.12	0.976
14	0.202	0.198	0.344	0.398	0.120	0.709
7.8	0.067	0.259	0.376	0.286	0.103	1.01
3.1	0.332	0.133	0.194	0.188	0.091	0.434

Table 5. FTIR of (a) spruce and (b) wheat straw

Frequency (cm^{-1})		Assignment
Spruce sawdust	Wheat straw	
3026	3415	–OH stretching of phenol group
2348	2859	–CH_2 stretching of aliphatic compound
	2121	–NH stretching
1691	1733	C=O stretching of aldehyde group
	1652	C=C stretching of phenol group
1552	1507	C=C of aromatic ring
1483	1434	–CH_2 bending
1439		–OH bending
1388	1372	C-O-H bending
1301		C–O stretching of phenolic group
1153		C–O stretching of six-member cyclic ether group

3.3. Desorption studies

Desorption experiments were performed using pure water as desorbent to replace the remained MB solution after the end of each kinetic batch experiment. Desorption was found low, equal to 9 - 21%.

3.4. Microstructure

The SEM micrographs of spruce sawdust and wheat straw, that have high adsorption ability and high availability for industrial applications, are given in Figure 3 for three different magnifications. In Figures 3a and (b) with a magnification of 750X, we observe that the

spruce sawdust and wheat straw particles have fibrous structure. The surface texture of these particles was also relatively rough as seen in Figure 3e for spruce sawdust and Figure 3f for wheat straw with a magnification of 20,000X.

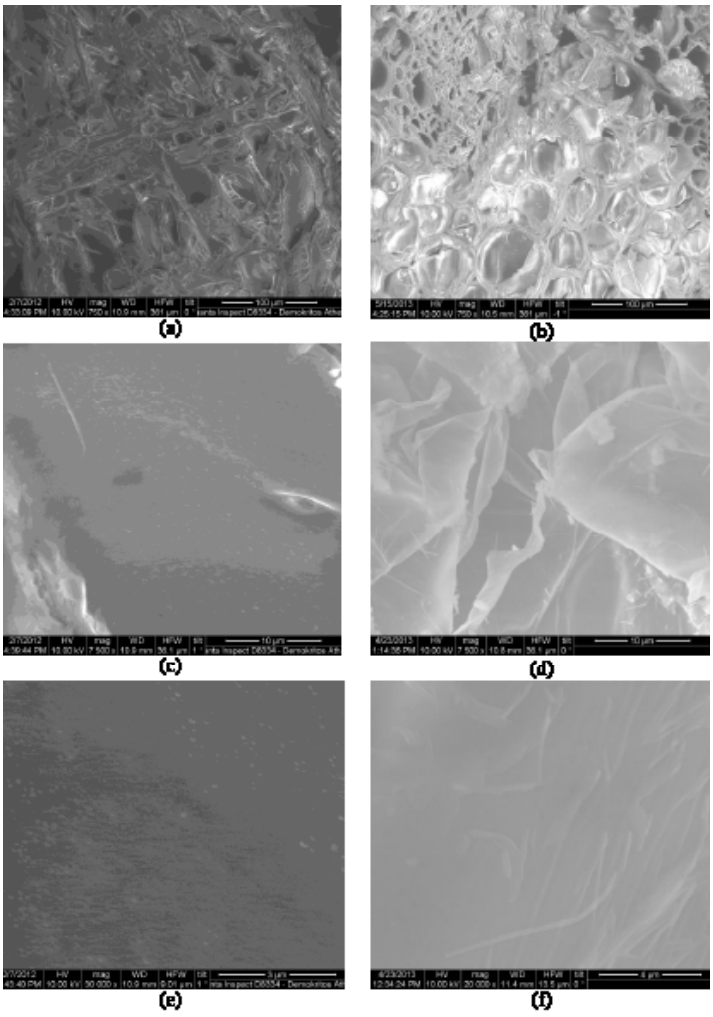

Figure 3. SEM micrographs for spruce sawdust (a, c, e) and wheat straw (b, d, f).

The FTIR data can be used to identify the active groups on the surface of adsorbent that facilitate the adsorption process. According to the FTIR graph shown in Figure 4 for spruce sawdust, the most important peaks were identified as –OH stretching of phenol group, $-CH_2$ stretching of aliphatic compound, C=O stretching of aldehyde group, C=C of aromatic ring, $-CH_2$ bending, –OH bending, C-O-H bending, C–O stretching of phenolic group and C–O stretching of six-member cyclic ether group (Table 5). Moreover, according to the FTIR in Figure 4 for wheat straw, the most important peaks were identified as –OH stretching of phenol group, $-CH_2$ stretching of aliphatic compound, –NH stretching, C=O stretching of aldehyde group, C=C stretching of phenol group, C=C of aromatic ring, $-CH_2$ and C-O-H bending (Table 5).

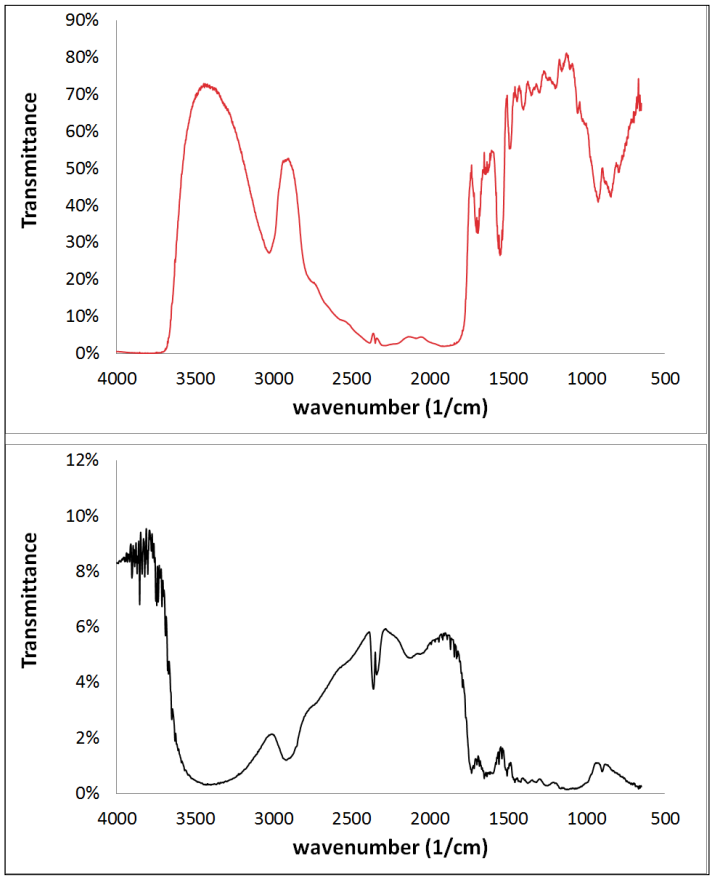

Figure 4. FTIR spectra of spruce (top image) and wheat straw (bottom image).

4. CONCLUSIONS

The present work examined wide range of non-conventional low-cost lignocellulosic biomass adsorbents for the removal of MB from wastewater. The results indicated that the experimental isotherm curves were well described by the Sips isotherm model. The chickpea straw recorded highest adsorption capacity of 450.6 mg/g according to the Sips isotherm model. The adsorption kinetic data were found to follow the pseudo-second-order kinetic model. Nevertheless, the intra-particle diffusion model was also well applicable and the maximum adsorption rate constant of 0.652 mg/g $min^{0.5}$ was recorded for spruce sawdust. In conclusion, we proved that inexpensive, locally available and effective materials can be used for the removal of MB from aqueous solution instead of expensive commercial activated carbon. The present work recommend the use of chickpea straw for high adsorption capacity and the spruce sawdust for fast

adsorption process depending on the technological application priorities.

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