

Industrial Cellulignin Wastes as Adsorbent for Removal of Methylene Blue Dye from Aqueous Solutions

Daniela Suteu ^{a,*} and Teodor Malutan ^b

Cellulignin, a by-product from the wood processing industry, was studied as a new, eco-friendly adsorbent for the removal of methylene blue cationic dye from aqueous solutions, using a batch adsorption procedure. Experimental data were processed in order to study the equilibrium, thermodynamics, and kinetics of methylene blue adsorption onto cellulignin. Between the two studied isotherm models (Freundlich and Langmuir) the Langmuir model better described the equilibrium adsorption data at temperatures higher than 25 °C; the mean free energy (E) values obtained from the Dubinin-Radushkevich isotherm model show that the sorption of dye occurs via surface electrostatic interactions with the active sites of the cellulignin. The equilibrium data were used to calculate the free energy, enthalpy and entropy changes, and isosteric heat of adsorption (ΔH_x). Results confirm the feasibility and the endothermic nature of the adsorption process, suggesting that adsorption is a physico-chemical process. The isosteric heats of adsorption indicated energetic heterogeneity of adsorption sites and possible interactions between the adsorbed dye molecules. Kinetic assessment suggests that the adsorption process followed a pseudo-second order model and the rate-limiting step may be the binding of dye onto the adsorbent surface. The diffusion models show that intraparticle diffusion is not the sole rate-limiting step; the external mass transfer also influences the adsorption process in its initial period.

Keywords: Cellulignin; Equilibrium; Isosteric heat of adsorption; Kinetics; Methylene blue; Thermodynamics

*Contact information: a: "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Organic, Biochemical and Food Engineering, 71A Prof. Dr. Docent D. Mangeron Blvd, 700050 Iasi, Romania; b: "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Natural and Synthetic Polymers, 71A Prof. Dr. Docent D. Mangeron Blvd, 700050 Iasi, Romania; e-mail: thmalu@ch.tuiasi.ro; *Corresponding author: e-mail: danasuteu67@yahoo.com; fax: +40 232 271 311*

INTRODUCTION

Dyes are frequently used in different industries, such as textile, rubber, paper, plastics, leather, food, and cosmetics, and may generate large amounts of aqueous, colored effluents. It is estimated that there are currently more than 10,000 commercially available dyes with an annual production of over 0.7 million tons worldwide, of which 10 to 15% is lost in industrial effluents during manufacture and processing operations (Zaharia *et al.* 2012; Anjaneyulu *et al.* 2005). Releasing colored effluents into natural bodies of water has become a major source of water pollution, causing many significant problems. The presence of very small amounts of dye in water (< 1 ppm for some dyes) causes aesthetic deterioration and diminishes the solubility of dissolved oxygen, water transparency, and sunlight permeability, affecting aquatic life and the food chain (Zaharia

and Suteu 2012a). In addition, some dyes and/or their degradation products (*e.g.*, aromatic amines) may have toxic, carcinogenic, mutagenic, or teratogenic effects on the health of humans and aquatic organisms.

Environmental legislation has become stricter in many countries, allowing only low effluent color limits and, consequently, requiring color removal from wastewater before its discharge, making dye one of the major issues in wastewater pollution. Because many dyes are resistant to microbial attack and stable to actions of light, heat, and oxidizing agents, treatment of dye-containing wastewater is difficult. However, the treatment of wastewater contaminated with dyes is necessary in order to comply with international regulations regarding the quality of the effluent discharged into the environment.

In the case of colored wastewaters, color can be expressed by the absorbance measured in comparison with a blank with distilled water at three characteristic wavelengths: 436, 525, and 620 nm, in accordance with the Romanian standard SR ISO 7887-97 or by the Hazen color index (ISO 1973). The Hazen color index represents the conversion of absorbance measured at 456 nm to Hazen units (HU) (*i.e.*, an absorbance of 0.069 at 456 nm corresponds to 50 HU) (Zaharia and Suteu 2012b). The limits of HU units imposed by environmental legislation are < 200 in surface water and < 50 HU in sewage systems (Anjaneyulu *et al.* 2005; Zaharia 2008). In the case of industrial wastewater, an absorbance measurement at 436 nm in the supernatant (apparent color) or filtrate (real color) is compulsory.

Textile effluent characteristics vary, so that the treatments for color removal include many different physical, chemical, and biological treatment methods, such as coagulation-flocculation, adsorption on activated carbon, ozonation, membrane processes, electrochemical treatment, and aerobic or anaerobic biodegradation. The advantages and disadvantages of each technique have been extensively reviewed (Anjaneyulu *et al.* 2005; Zaharia and Suteu 2012b; Latif *et al.* 2010; Suteu *et al.* 2009; Han *et al.* 2011; Hubbe *et al.* 2012; Salleh *et al.* 2011;).

Adsorption is an efficient and economical method for removing dyes from industrial effluents. In this process, a substance (soluble dye) from the liquid phase (wastewater) is transferred to the surface of a solid, highly porous material (adsorbent), to which it binds physically or chemically (Zaharia and Suteu 2012b). The adsorption technique is preferable to other wastewater treatment techniques in terms of efficiency, low cost, simplicity, ease of operation, and inactivity towards toxic substances. Moreover, the specific advantage of this method is that the adsorbent can be chosen from a large variety of materials. The selection of an adsorbent is based on the following requirements: high selectivity and capacity of adsorption, favorable kinetic features, physico-chemical stability, mechanical strength, ease of regeneration, and availability at low cost (Zaharia and Suteu 2012b). Unconventional low cost materials are used more and more as adsorbents in dye-containing wastewater as alternatives to conventional adsorbents, such as activated carbon or synthetic polymers, in order to avoid several disadvantages related to the latter (high cost, difficulties in preparation and/or regeneration, pollution resulting from their manufacture). Low cost, abundance, high adsorption properties, and potential for ion exchange are the main characteristics of low-cost adsorbents. These adsorbents, used in batch or dynamic conditions, can be naturally occurring materials (wood, peat, coal, chitin and chitosan, biomass, clays, *etc.*), as well as industrial/agricultural wastes or byproducts (fly ash, red mud, blast furnace slag, metal hydroxide sludge, sawdust, bark, lignin, sunflower stalks, maize cob, rice husk, hazelnut

shells, olive stones, seashell, *etc.*) (Zaharia and Suteu 2012a,b; Crini 2006; Bozlu *et al.* 2012; Suteu *et al.* 2009; Ayan *et al.* 2011; ; Zhang *et al.* 2011a ; Sulak and Yatmaz, 2012).

Some of the various bio-adsorbents investigated for removal of dyes from aqueous solutions are listed in Table 1.

Table 1. Brief Review of Applications of Bio-adsorbents in Removal of Dyes

Bio-adsorbent	Dye	Reference
peel of <i>Cucumis sativa</i> fruit	malachite green	Santhi and Manonmani 2011
almond shell (<i>Prunus dulcis</i>)	rhodamine 6G	Senturk <i>et al.</i> 2010
wheat shells	methylene blue	Bulut and Aidin 2006
silkworm exuvates	methylene blue	Chen <i>et al.</i> 2011
rice husk ash	methylene blue congo red	Chowdhury <i>et al.</i> 2009
rattan sawdust	malachite green	Hameed <i>et al.</i> 2008
bagasse fly ash	orange - G methyl violet	Mall <i>et al.</i> 2006
seashells waste	Brilliant Red HE-3B	Suteu <i>et al.</i> 2011a
sunflower seed shells	Orange 16	Suteu <i>et al.</i> 2011 b
sunflower seed shells corn cob	methylene blue	Suteu <i>et al.</i> 2012
rice husk	methylene blue	Vadivelan and Kumar 2005
straw	methylene blue	Zhang <i>et al.</i> 2011b
waste newspaper fiber	malachite green	Tan <i>et al.</i> 2012
sugar extracted spent rice biomass	methylene blue	Rehman <i>et al.</i> 2012

The aim of this work is to evaluate the efficiency of using cellolignin – a by-product of the wood industry – as adsorbent for the removal of methylene blue (MB) from an aqueous environment. Equilibrium, thermodynamic, and kinetic studies were performed with this purpose in mind. The obtained results give some insight with respect to utilization of cellolignin as an eco-friendly adsorbent in textile industry wastewater treatment. Thus, these results may be applied for predicting the adsorption mechanism, for characterization and optimization of the process, and for equipment and process design.

EXPERIMENTAL

Materials

Adsorbent

The adsorption experiments were carried out using cellolignin as an adsorbent. The cellolignin is a residual lignocellulosic material resulting from the production of furfural from chestnut wood. It was provided by Tanin Sevnica, Slovenia, and was used without other physical-chemical treatment. The main physical characteristics of cellolignin (from the guidelines of the manufacturer) were: solids: 93%, solubility: > 90% in aqueous alkali (1% aqueous NaOH). The chemical composition included: 47.2% cellulose, 0.6% xylan, 0.3% mannan, and 47.4% lignin. The total OH group content comes to 4.53 mmol/g, the specific surface area (S_{BET}) of the sample, calculated from adsorption isotherm data using the Brunauer–Emmett–Teller method (BET) (Brunauer *et*

al. 1938) is $63 \text{ m}^2/\text{g}$, and the particle size is $210 \mu\text{m}$. The FT-IR spectrum of cellolignin (Fig. 1) revealed the presence of numerous peaks assigned to various functional groups of cellulose and lignin structures, some of which are able to interact with molecular or ionic species (species like 3408 cm^{-1} O-H stretch in alcohols, phenols, 1714 cm^{-1} C=O stretch in non-conjugated ketones and carboxyl groups, 1610 cm^{-1} stretching vibration of C=O in conjugated ketones, 1365 cm^{-1} O-H bending, 1057 cm^{-1} stretching vibration of C-O of alcohol groups, $900\text{-}350 \text{ cm}^{-1}$ skeletal deformation of aromatic rings) in lignin (Bodirlau *et al.* 2008; Malutan *et al.* 2008).

Dye

Methylene blue (Basic Blue 9; Standard Fluka AG) is a phenothiazine cationic dye (C.I. 52015) with molecular formula $\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}$, MW = 319.85 g/mol , and a heterocyclic aromatic chemical structure. It is generally used as a model basic dye (target contaminant) in studies concerning techniques for textile wastewater decolorization (Rafatullaf *et al.* 2010), and for this reason it was chosen for this study.

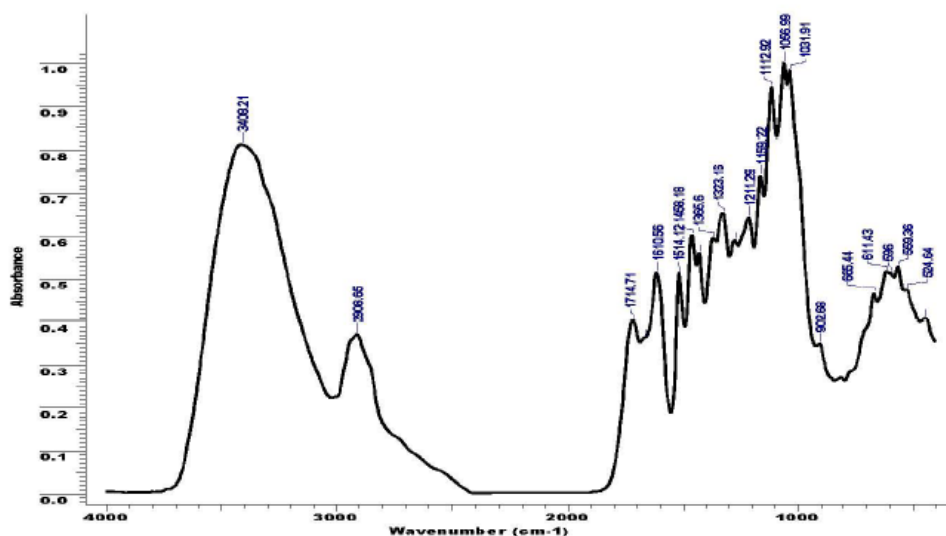


Fig. 1. FT-IR spectrum of cellolignin

Methods

Equilibrium adsorption experiments

Batch adsorption experiments were performed in 150 mL conical flasks by mixing 0.1 g of cellolignin with 25 mL aqueous methylene blue solution of a known concentration. The concentration of aqueous dye stock solution was 320 mg/L ; the working solutions with concentrations between 19 and 280 mg/L were obtained by appropriate dilutions. The flasks were placed in a thermostatic bath (Poleko SLW 53) at three constant temperatures: 5, 25, and $45 \text{ }^\circ\text{C}$. The initial pH of the aqueous dye solutions was nearly neutral (6.5-7) and was adjusted to the required value using 1N HCl and NaOH solutions. After a contact time of 24 h, the cellolignin was separated by filtration, and the dye concentration into filtrate was determined spectrophotometrically (see analytical methods).

The data resulting from the adsorption experiments were used to evaluate the cellolignin adsorption capacity, q (mg of dye/g of cellolignin),

$$q = \frac{C_0 - C}{G} V \quad (1)$$

and the percent of dye removal, $R\%$,

$$R \% = \frac{(C_0 - C) \cdot 100}{C_0} \quad (2)$$

where C_0 and C are the initial and the residual dye concentrations (mg/L), G is the adsorbent mass (g), and V is the solution volume (L).

Kinetic adsorption experiments

The influence of contact time on the adsorption of dye by cellolignin powder was studied in batch experiments, mixing 0.1 g of cellolignin and 25 mL of MB solution (64 mg/L, pH = 6.5-7) at temperatures of 5, 25, and 45 °C for time intervals ranging from 10 min to 6 h. Finally, the adsorbent was separated by filtration and the dye content in the remaining aqueous phase was analyzed using a similar procedure to the equilibrium experiments. The extent of adsorption was expressed by the fractional attainment of equilibrium, F ,

$$F = \frac{q_t}{q} \quad (3)$$

where q_t and q (mg/g) are the dye adsorbed at time t and at equilibrium (24 h).

Analytical methods

The residual concentrations of MB in filtrate samples were determined spectrophotometrically by measuring the absorbance at the maximum dye wavelength of 660 nm with a JK-VS-721N VIS spectrophotometer and interpolating using a calibration curve (working concentration range in the Lambert-Beer region is 1.3-5.1 mg/L).

Infrared spectroscopic measurements of the cellolignin powder were recorded on a FT-IR BioRad spectrometer FTS2000 with 4 cm⁻¹ resolution for 32 scans, using KBr pellets.

Nitrogen adsorption-desorption isotherms at 77 K were obtained with a Sorptomatic Carlo – Erba Series 1800 apparatus. Surface area was calculated with BET equation (Brunauer *et al.* 1938).

Adsorption Modeling

Isotherm models

The experimental data were processed using three of the most well known adsorption isotherm models, as presented in Table 2 (Crini and Badot 2008; Foo and Hameed 2010), in order to obtain information about the adsorption capacity, the degree of affinity, and surface characteristics of the cellolignin, as well as to establish the equilibrium relationship and mechanism of MB adsorption onto the studied adsorbent.

Kinetic modeling

Generally, the dye adsorption process at the solid-liquid interface could be described by the following steps: (i) diffusion of the dye molecules from bulk solution to the adsorbent surface through the boundary layer (film diffusion), (ii) diffusion of dye ions from the surface into the pores of the solid particle (pore diffusion or intraparticle diffusion), and (iii) interaction of dye with the active sites on the surface of the adsorbent (Crini and Badot 2008).

Table 2. Equations and Parameters of the Applied Adsorption Isotherm Models

Adsorption isotherm model	Isotherm model parameters	Fundamental characteristics
<i>Freundlich</i> $q = K_F C^{1/n}$ linearized form: $\lg q = \lg K_F + \frac{1}{n} \lg C$	K_F : adsorption capacity, mg.L ^{1/n} /g.mg ^{1/n} n : measure of adsorption intensity or surface heterogeneity	Multilayer adsorption on heterogeneous surface with an exponential distribution of active sites of different energy
<i>Langmuir</i> $q = \frac{K_L C q_0}{1 + K_L C}$ linearized form: $\frac{1}{q} = \frac{1}{q_0 K_L C} + \frac{1}{q_0}$	q_0 : saturation capacity, mg/g K_L : binding (adsorption) energy, L/mg	Monolayer adsorption on homogeneous surface containing a finite number of energetically equivalent sites, without interactions between the adsorbed species
<i>Dubinin-Radushkevich</i> $\ln q = \ln q_D - \beta_D \varepsilon^2$ $\varepsilon = RT \ln \left(1 + \frac{1}{C} \right)$ $E = \frac{1}{\sqrt{-2\beta_D}}$	q_D : the maximum amount adsorbed, mg/g β_D : activity coefficient related to mean adsorption energy, mol ² /kJ ² ε : Polanyi potential E : mean free energy of adsorption, kJ/mol	A Gaussian energy distribution onto a heterogeneous surface, usually applied to distinguish the physical and chemical adsorption by the mean free energy value

The overall adsorption rate is controlled by the slowest step, but a combined effect of a few steps is also possible. Several theoretical treatments have been proposed to describe the kinetics of adsorption. These kinetic models can be grouped in two classes: adsorption reaction models and adsorption diffusion models (Siminiceanu *et al.* 2010; Hameed and El-Khiary 2008). The kinetic models chosen to model the data from this study are presented in Table 3.

Table 3. Equations and the Parameters of the Applied Kinetic Models*

Kinetic model	Kinetic model parameters	Fundamental characteristics
<p><i>Pseudo-first order</i> (Lagergreen model)</p> $\frac{dq_t}{dt} = k_1(q - q_t)$ <p>linearized form:</p> $\lg(q - q_t) = \lg q - \frac{k_1}{2.303} t$	<p>k_1: rate constant of pseudo-first order model, (1/min) q_t and q (mg/g): the amounts of dye adsorbed at time t and at equilibrium (24 h), respectively</p>	<p>Adsorption reaction model based on adsorption capacity (q)</p>
<p><i>Pseudo-second order</i> (Ho model)</p> $\frac{dq_t}{dt} = k_2(q - q_t)^2$ <p>linearized form:</p> $\frac{t}{q} = \frac{1}{k_2 q^2} + \frac{1}{q} t$	<p>k_2: rate constant of pseudo-second order model, g/mg min $k_2 q^2 = h$: initial adsorption rate, mg/g min</p>	<p>Adsorption reaction model; the driving force of the process is the fraction of available adsorption sites ($q - q_t$)</p>
<p><i>Intraparticle diffusion model</i> (Webber-Morris model)</p> $q = k_d t^{1/2} + c$	<p>k_d: rate constant for intraparticle diffusion, mg/g min^{1/2} c: intercept to the y axis</p>	<p>Diffusion-controlled kinetics; pore diffusion is the rate-limiting step if the plot q_t vs. $t^{1/2}$ is linear and passes through origin</p>
<p><i>Boyd model</i></p> $F = 1 - \frac{6}{\pi^2} \sum \frac{1}{n^2} \exp(-n^2 Bt)$ <p>Bt is calculated with Reichenberg relation</p> $Bt = \left(\sqrt{\pi} - \sqrt{\pi - \frac{\pi^2 F}{3}} \right)^2$ <p>(for F values < 0.85)</p>	<p>Linearity test of plot Bt vs. t</p>	<p>Diffusion-controlled kinetics; pore-diffusion controls the rate of mass transfer if the plot Bt-t is linear and passes through origin; a nonlinear plot or non-passing through origin indicates film diffusion as rate-limiting step</p>

*(Crini and Badot 2008)

RESULTS AND DISCUSSION

Effect of Solution pH on Dye Adsorption

The effect of the pH on the MB adsorption onto cellolignin was studied in solutions with initial dye concentration of 89.6 mg /L and cellolignin dose of 4 g/L within pH range 1 to 9 adjusted by adding HCl or NaOH solutions (Fig. 2).

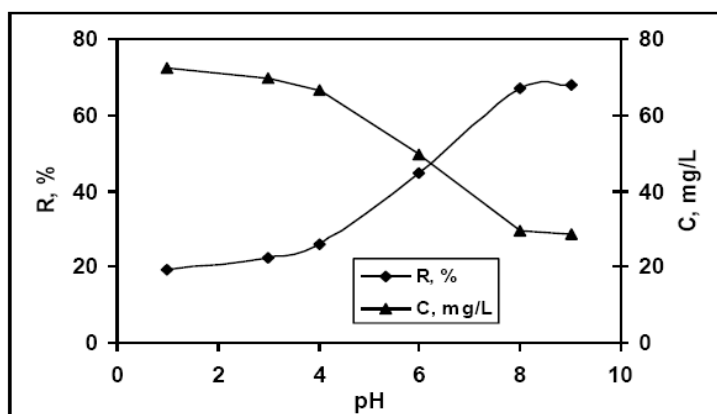


Fig. 2. Effect of pH on dye adsorption onto cellolignin $C_0 = 89.6$ mg dye/L; 4g adsorbent/L, 24h, $T = 25$ °C

Adsorption Equilibrium

Adsorption isotherms describing the distribution of MB between solid (cellulignin) and liquid phases at three temperatures are shown in Fig. 3.

In order to find the most suitable correlations for the equilibrium curves and to understand the dye behavior in the case of adsorption of MB by the cellulignin, the isotherm models presented in Table 1 were used. The specific isotherm parameters were calculated from the slope and y-intercept of the plots $\lg q$ vs. $\lg C$, $1/q$ vs. $1/C$, and ε^2 vs. $\ln q$. The results are listed in Table 4. The conformity between experimental data and the model-predicted values was estimated using the coefficient of determination for the linear regression R^2 (Table 4).

The comparison of the experimental data with the Freundlich, Langmuir, and Dubinin-Radushkevich isotherms, as shown in Fig. 3, suggests that at 5°C, the Freundlich model is more suitable for simulation of adsorption isotherms. At increased temperatures (25°C and 45°C) the Langmuir isotherm is the best one in simulation of the sorption isotherms; however, when increased adsorbent loading was used, the Freundlich model gave a better fit.

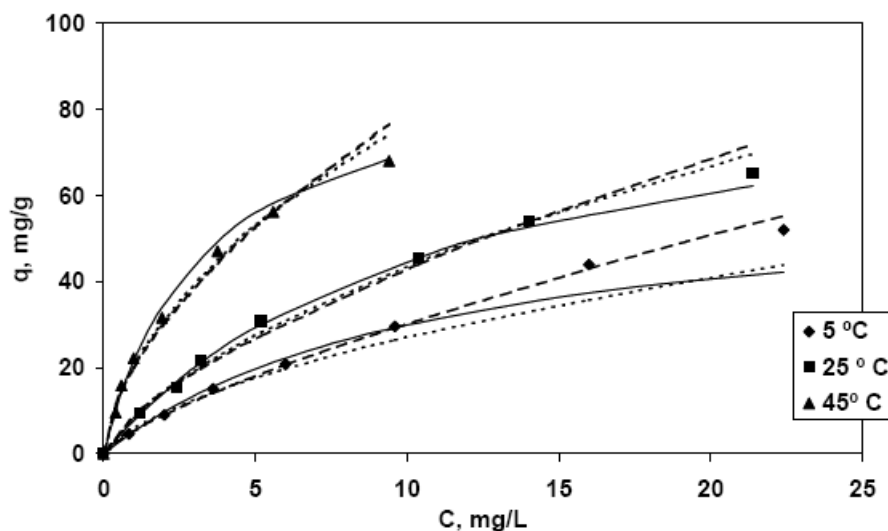


Fig. 3. Adsorption isotherms of MB on the cellulignin at three temperatures with the results fitted to the Freundlich equation (---), Langmuir equation (—) and D-R equation (.....); ♦, ▲, ■: experimental points

The coefficient of determination values ($R^2 > 0.97$) confirmed a good agreement between the experimental data and Freundlich isotherm parameters; the fractional values of the Freundlich constant $1/n$ as a measure of adsorption intensity, showed efficient adsorption.

Table 4. Characteristic Parameters of the Adsorption Isotherm Models for MB Adsorption by Cellulignin

Isotherm model	Isotherm parameter	Temperature, K		
		278	298	318
Freundlich	$1/n$	0.7485	0.6804	0.6002
	$K_F, \text{mg}\cdot\text{L}^{1/n}/\text{g}\cdot\text{mg}^{1/n}$	5.4	8.9516	19.9526
	R^2	0.9975	0.9856	0.9754
Langmuir	$q_0, \text{mg/g}$	76.336	95.238	121.951
	$K_L, \text{L/mg}$	0.07039	0.08868	0.21925
	R^2	0.9959	0.9951	0.9861
Dubinin-Radushkevich (DR)	$E, \text{kJ/mol}$	9.534	10.00	11.785
	$\beta_D, \text{mol}^2/\text{kJ}^2$	0.0055	0.005	0.0036
	$q_D, \text{mg/g}$	622.832	1217.65	1135.1
	R^2	0.9676	0.9921	0.9838

The Langmuir model also gave a good fit with the MB adsorption isotherms onto the cellulignin ($R^2 > 0.97$). The highest value of monolayer adsorption capacity, q_0 , was 121.95 mg MB/g cellulignin and was reached at 45 °C. By decreasing the temperature, the adsorption capacity of cellulignin also decreased. However, the value obtained at 25°C (95.238 mg/g) is comparable with the Langmuir capacities of other low-cost materials used for MB sorption (Rafatullah *et al.* 2010). Thus, for the maximum (monolayer) adsorption capacity of this dye onto adsorbents based on lignocellulosic wastes, the literature reports a wide range of values: 914.59 mg/g obtained in the case of teak wood bark as adsorbent, 141.92 mg/g for pumpkin seed hull, 99 and 99.01 mg/g for coconut husk and coffee husk, respectively, 38.22 mg/g in the case of hazelnut shell, 18.149 mg/g for rice husk ash, and 9.78 mg/g for raw beech sawdust (Chowdhury *et al.* 2009; Rafatullah *et al.* 2010). The values of the Langmuir isotherm parameter K_L , which defines the strength of interactions between cationic dye and adsorption sites from the cellulignin, increased with increasing temperature.

The value of the mean free energy per molecule of adsorbate, E , calculated using the Dubinin-Radushkevich equation (Table 4), increased from 9.534 kJ/mol at lower temperatures (5°C), up to 11.785 kJ/mol at a temperature of 45°C. Values around 10 are quite small, but even so they are in the domain characteristic for an ion exchange mechanism, *i.e.*, 8 to 16 kJ/mol (Foo and Hameed 2010). This suggests that MB binding onto cellulignin may be due to relatively weak van der Waals forces, hydrogen bonding, dipole-dipole interactions, and strong electrostatic interactions between the negatively charged surface of the cellulignin (as a result of dissociation of lignin phenolic hydroxyl and carboxyl groups) and the cationic dye.

Thermodynamic Parameters

The thermodynamic parameters of the adsorption process, such as free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0), give information about spontaneity, heat change, and the degree of freedom of the adsorbed species. They are also very important for predicting the adsorption mechanism, for characterization and optimization of the process, as well as for equipment and process design.

Based on the values of free energy change and enthalpy change, two types of adsorption processes have been detected. Generally, the change in free energy from -20 to 0 kJ/mol and the enthalpy up to 4.2 kJ/mol are characteristic of physical adsorption (due to relatively weak van der Waals attraction forces), whereas the change in free

energy between -80 and -400 kJ/mol and enthalpy more than 21 kJ/mol indicate chemical adsorption (due to stronger interactions involving ionic or covalent bonding sorbate-sorbent) (Senturk *et al.* 2010; Weng *et al.* 2008; Chen *et al.* 2011; Khormaei *et al.* 2007).

The thermodynamic parameters of the studied adsorption systems were determined using the values of the Langmuir constant, K_L (expressed in L/mol), and conventional equations for ΔG^0 , ΔH^0 , and ΔS^0 (Crini and Badot 2008):

$$\Delta G^0 = -RT \ln K_L \quad (4)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

where ΔG^0 is free energy (kJ/mol), ΔH^0 is enthalpy (kJ/mol), ΔS^0 is entropy change (J/mol K), R is the gas ideal constant (8.314 J/mol K), and T is the absolute temperature (K).

The values of ΔG^0 were obtained from Equation 3. ΔH^0 and ΔS^0 were determined from the slope and intercept of the plot of free energy change *versus* temperature (Fig. 4) and are listed in Table 5.

Table 5. Thermodynamic Parameters of the Adsorption of MB Dye onto Cellolignin

T , K	ΔG^0 , kJ/mol	ΔH^0 , kJ/mol	ΔS^0 , J/mol K
278	- 23.163	21.196	158.5
298	- 25.402		
318	- 29.501		

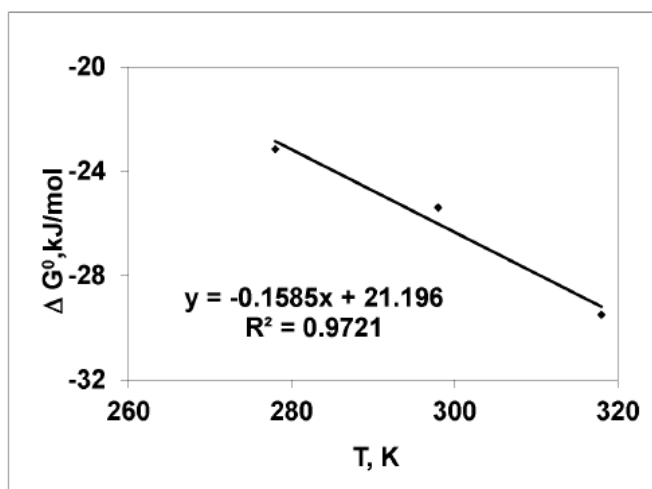


Fig. 4. Plot of free energy change *versus* temperature

The negative values of ΔG^0 indicate the feasibility and spontaneity of MB adsorption by cellolignin. A decrease in the negative value of ΔG^0 concomitant with an increase of temperature shows that the adsorption process is more favorable at higher temperatures, probably as a result of the increased mobility of dye species in solution.

The positive value of enthalpy change shows that the adsorption process is endothermic. The positive values of ΔS^0 indicate the affinity of the cellolignin towards

the adsorbed dye and a high (increased) randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent. These changes could be ascribed to the displacement of water molecules sorbed on the solid surface (which is released into the bulk solution) with dehydrated dye cations.

As seen from Table 5, the values of thermodynamic parameters obtained in this study suggest that the adsorption of MB by cellolignin is a combined physico-chemical process. Various interactions such as π - π dispersive interactions between aromatic rings of the lignin and conjugated structure ($-\text{N}=\text{C}-\text{C}=\text{C}-$) of the MB, hydrogen bonding interactions ($-\text{OH}$ of the cellolignin as the hydrogen donor and nitrogen atoms from MB as the hydrogen acceptor), as well as electrostatic interactions (ion exchange) between cationic dye and weak acid sites of the adsorbent (different carboxylic and phenolic groups of the lignin with various dissociation constants) are assumed to have occurred.

The effects of heat during the adsorption process are better described by the isosteric heat of sorption (ΔH_X), defined as the energy difference between the state of the system before and after adsorption of a differential amount of adsorbate on the adsorbent surface. To calculate the isosteric heat of adsorption, the Clausius-Clapeyron equation was used (Chowdhury *et al.* 2011),

$$\frac{d(\ln C)}{dT} = -\frac{\Delta H_X}{RT^2} \quad \text{or} \quad \frac{d(\ln C)}{d(1/T)} = -\frac{\Delta H_X}{R} \quad (6)$$

where C is the equilibrium concentration of adsorbate in the solution (mg/L) at a constant amount of surface load, R is the ideal gas constant, and T is the temperature (K).

The slope of the plot of $\ln C$ vs. $1/T$ gives $\Delta H_X/R$. The magnitude of ΔH_X provides information about whether physical adsorption (ΔH_X below 80 kJ/mol) or chemical ion exchange adsorption (ΔH_X ranges between 80 and 400 kJ/mol) has taken place. Additionally, ΔH_X values can be used to assess the adsorbent surface heterogeneity (Saha and Chowdhury 2011). The isosteres for the adsorption of MB on cellolignin (from the adsorption data at different temperatures and at a constant amount of retained dye) are given in Fig. 5.

The isosteric heat of adsorption (35.21 kJ/mol, 29.455 kJ/mol, 28.303 kJ/mol, and 28.209 kJ/mol for $q = 10$ mg MB/g, 20 mg/g, 30 mg/g, and 40 mg/g, respectively) was calculated using data from Fig. 5. The calculations confirmed that the adsorption process is endothermic in nature and follows a physical adsorption mechanism.

The ΔH_X variation with cellolignin surface loading can be attributed to the possibility of lateral interactions between the adsorbed molecules (Saha and Chowdhury 2011). At lower q values, cellolignin-dye interactions take place with high heats of adsorption; with increasing surface coverage, dye-dye interactions occur with lower adsorption heat values. This behavior may be the result of the association of MB to form dimers or larger aggregates in a solution and in the adsorbed state, especially at an increased dye concentration (Abd El-Latif *et al.* 2010; Qi *et al.* 2011).

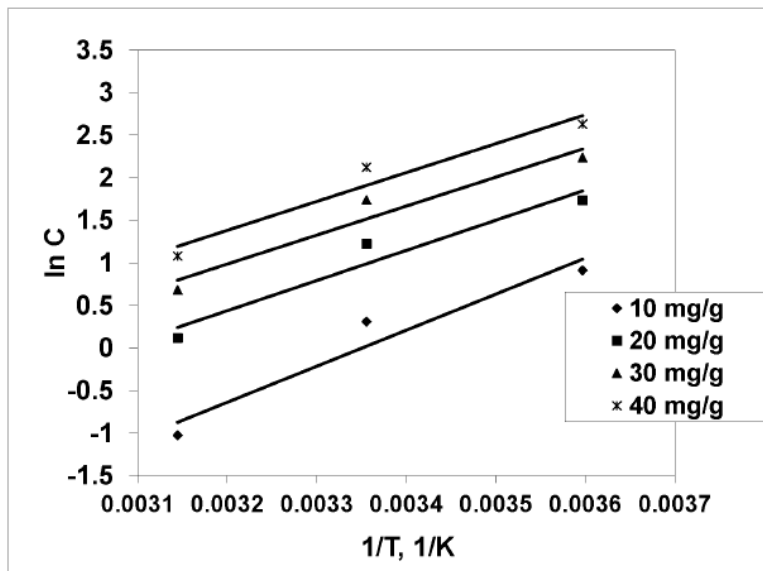


Fig. 5. Plots of $\ln C$ versus $1/T$ for the adsorption of methylene blue on cellulignin at constant surface coverage

Kinetic Study

The adsorption kinetic study is important in predicting the mechanisms (chemical reaction or mass-transport process) that control the rate of the pollutant removal and retention time of adsorbed species at the solid-liquid interface (Bulut and Aidin 2006). That information is important in the design of appropriate sorption treatment plants.

The effect of contact time of the phases on removal of MB by cellulignin from solutions of initial concentration equal to 64 mg MB/L at three different temperatures (5 °C, 25 °C, and 45 °C) is presented in Fig. 6.

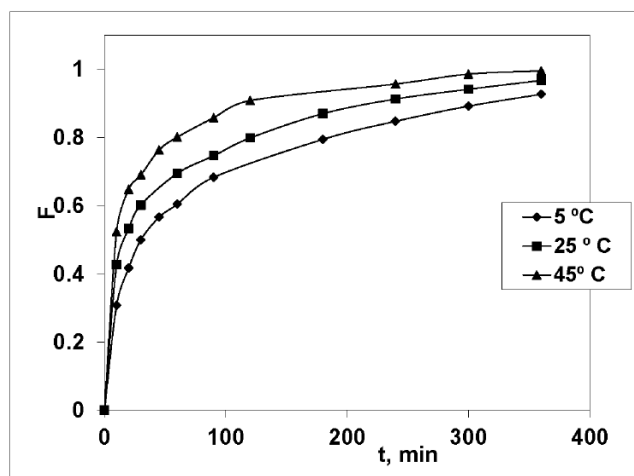


Fig. 6. Effect of contact time on the methylene blue sorption onto cellulignin

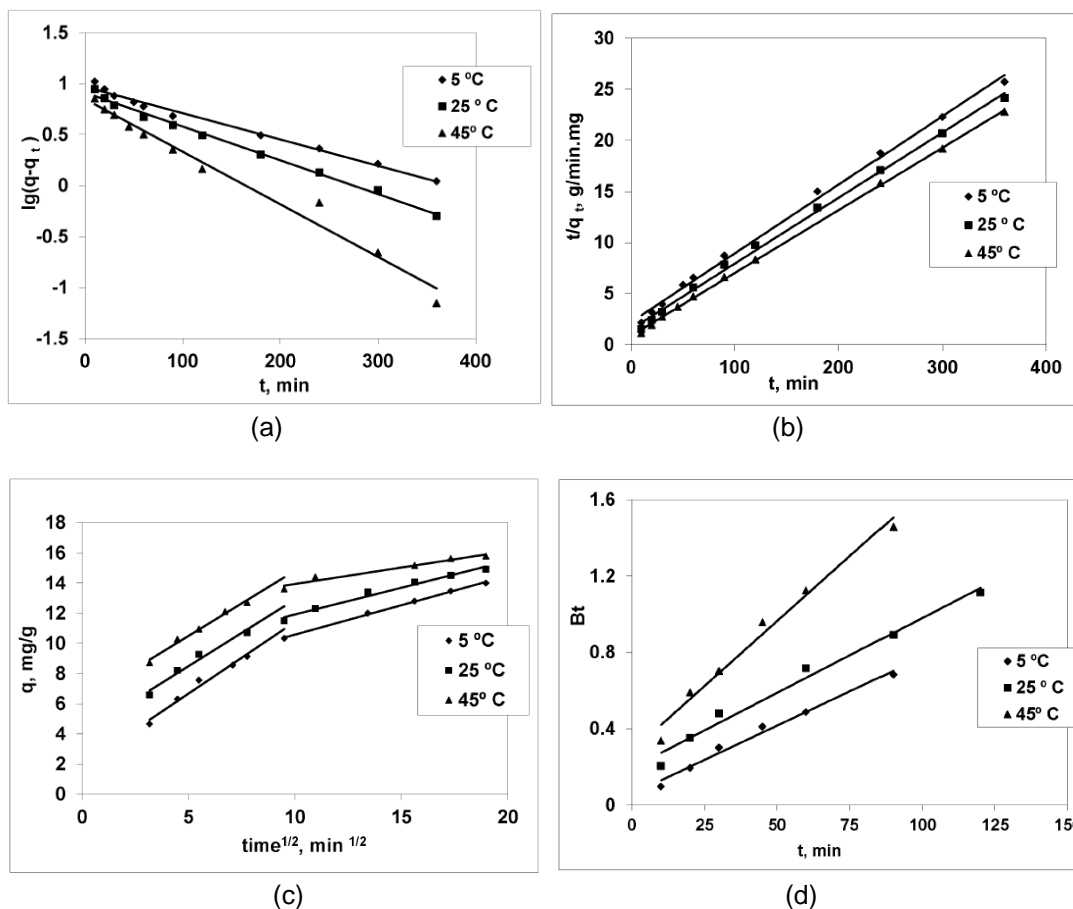


Fig. 7. The applicability of the pseudo-first order (a), pseudo-second order (b), intraparticle diffusion (c), and Boyd-Reichenberg (d) kinetic models in MB adsorption by cellulignin

The values of fractional attainment of equilibrium increased with both contact time and temperature. The dye adsorption was fast, especially during the first hour (about 50% of the MB was adsorbed within the first 15 min). Afterward, the rate of adsorption gradually decreased. The retention time required for maximum dye removal decreased from 6 h to 2 h with increasing temperature (from 5 °C to 45 °C). After that, only a minor change was observed, which led to the assumption that the system reached the equilibrium point.

The experimental kinetic data for MB adsorption by cellulignin were processed using the kinetic models shown in Table 3. The kinetic parameters related to each model, calculated from the intercepts and slopes of the corresponding linear plots (Fig. 7), are presented in Table 6. The fitting of each model to the experimental data was estimated using the linear regression correlation coefficient, R^2 .

Table 6. Kinetic Parameters of Methylene Blue Adsorption by Cellolignin

Kinetic model	Kinetic parameters	Temperature, K			
		278	298	318	
<i>Pseudo-first order</i> (Lagergreen model)	$q_{\text{experimental}}$, mg/g	15.10	15.40	15.85	
	k_1 , 1/min	0.00599	0.0076	0.0120	
	$q_{\text{calculated}}$, mg/g	9.281	8.134	7.042	
	R^2	0.9872	0.9935	0.9784	
<i>Pseudo-second order</i> (Ho model)	k_2 , g/mg min	0.00204	0.00272	0.00428	
	h , mg/g min	0.4512	0.6596	1.1348	
	$q_{\text{calculated}}$ mg/g	14.881	15.576	16.281	
	R^2	0.9965	0.9972	0.9940	
<i>Intraparticle diffusion model</i> (Webber-Morris model)	I	k_{d1} , mg/g min ^{0.5}	0.9514	0.8832	0.8633
		c (intercept)	1.922	4.084	6.186
		R^2	0.9766	0.9680	0.9855
	II	k_{d2} , mg/g min ^{0.5}	0.3896	0.3542	0.2180
		c	6.689	8.379	11.760
		R^2	0.9977	0.9779	0.9584
<i>Boyd model</i>	B (slope)	0.0094	0.0089	0.0169	
	intercept	0.8517	1.0741	1.1433	
	D_i , cm ² /s	1.682x10 ⁻⁶	9.952x10 ⁻⁸	1.889x10 ⁻⁷	
	R^2	0.9602	0.9671	0.9729	

As can be seen from Table 6, the values for the coefficient of determination ($R^2 > 0.97$) indicate that the pseudo-first order kinetic model verifies the experimental data for all temperatures. The rate constants of pseudo-first order adsorption, k_1 , increase with an increase in temperature. However, values of experimental q and calculated q from the Lagergreen model differ appreciably. This shows that MB adsorption by cellolignin cannot be best described by a pseudo-first order model.

The coefficient of determination for the pseudo-second order kinetics was greater than 0.99 and good agreement between experimental and calculated q values indicate the applicability of a pseudo-second order model in predicting the kinetics of MB adsorption by cellolignin for the entire adsorption period. Thus, the rate-limiting step of the process may be the binding of MB dye at the active sites of the adsorbent surface. Similar behavior has been observed in the retention of MB by other adsorbents such as shells (Bulut and Aidin 2006) and rice husk (Vadivelan and Kumar 2005). The calculated values of maximum adsorption capacity, q , as well as of rate constants of pseudo-second order, k_2 , increase as the temperature increases, confirming the endothermic nature of the adsorption process. h values also reflect the initial adsorption rate increase with an increase of temperature.

Usually, the adsorption rate is governed by either liquid phase mass transport or intra-particle mass transport. In order to get information about the diffusion mechanism, the kinetic results were analyzed by the intra-particle diffusion model. If the Weber-Morris plot (q versus $t^{1/2}$) is linear, then intra-particle diffusion occurs. Moreover, if the line passes through the origin, intra-particle diffusion is the sole rate-limiting step. The multi-linearity of the plots indicates that two or more steps influence the adsorption process (Qi *et al.* 2001; Han *et al.* 2009).

Graphical representation of the MB amount adsorbed by cellolignin *versus* $t^{1/2}$ (Fig. 7c) exhibited two line segments for each temperature. The first part is usually

attributed to external mass transfer (film diffusion) (Walker *et al.* 2003), while the second linear part indicates intraparticle diffusion into the porous structure of the adsorbent (Srivastava *et al.* 2006). The y-intercept of the two linear portions (c value) is a measure of the thickness of the boundary layer; the larger the value of c , the greater is the boundary effect. The data from Table 6 suggest the involvement of intraparticle diffusion in the adsorption of MB by cellolignin (pore diffusion), but that it is not the sole rate-limiting step of adsorption. The intraparticle rate constants (k_{d2}) decrease with an increase of temperature, whereas the boundary effects increase with an increase of temperature.

The two phases in the intraparticle diffusion plot suggest that the adsorption process proceeds by surface diffusion and intraparticle diffusion. In order to establish the rate-limiting step, the kinetic data were analyzed using the kinetic model of Boyd (Table 3), based on the assumption that particle diffusion is not the sole rate-controlling process. Using the Reichenberg equation applicable at F values less than 0.85, the Bt values were calculated at different time intervals for MB adsorption by cellolignin. If the plot of Bt versus time is linear and passes through the origin, the adsorption is governed by an intraparticle diffusion mechanism. If the plot is nonlinear or the straight lines deviate from the origin, the adsorption is controlled by external transport (film diffusion) or by chemical reaction (Hameed and El-Khaiary 2008). As can be seen from Fig. 7d, the relation between Bt and t is linear at all temperatures, but the straight line does not pass through the origin (see Fig. 7d and intercept value from Table 6), showing that in the initial period of the process, the slowest step in adsorption of MB by cellolignin may be either film diffusion or chemical reaction (binding of MB to active surface sites).

The B values (slope of the straight line obtained from time versus Bt graph) can be used to calculate the effective diffusion coefficient from Equation 7,

$$B = \frac{\pi^2 \cdot D_i}{r^2} \quad (7)$$

where r is the radius of the adsorbent particle assuming spherical shape (cm), and D_i is the effective diffusion coefficient (cm²/s).

Knowing that the cellolignin particles used had of the average size range 210 μm, the film diffusion coefficients for the three temperatures were calculated and listed in Table 6.

The obtained values of the effective film diffusion coefficient provide an indication that film diffusion could be the rate-determining step (D_i , in the range 10⁻⁶ to 10⁻⁸ cm²/sec.) (Karthikeyan *et al.* 2010).

Evaluation of activation energy

The activation energy in adsorption processes is defined as the energy necessary for the adsorbate species to interact with the adsorption sites on the surface of the solid phase. This parameter determines how dependent the adsorption rate is on temperature. The activation energy for the adsorption of MB onto cellolignin can be evaluated using the Arrhenius equation (Eq. 8) (Chowdhury *et al.* 2011; Ozkaya 2005).

$$k_2 = k_0 \exp\left(-\frac{E_a}{RT}\right), \text{ or in linear form: } \ln k_2 = \ln k_0 - \frac{E_a}{RT} \quad (8)$$

where k_2 is the adsorption rate constant of the pseudo-second order adsorption model, $\text{g}/\text{mg}\cdot\text{min}$, k_0 is the temperature independent factor, E_a is the activation energy of adsorption (kJ/mol), R is the gas constant ($8.314 \text{ J}/\text{mol K}$), and T is the temperature in K.

The values of activation energy and k_0 factor determined from the slope and intercept of the Arrhenius plot (Fig. 8) are $13.56 \text{ kJ}/\text{mol}$ and 1.436 , respectively. The value of activation energy also provides information on the physical and chemical nature of the adsorption process. It was suggested that the activation energy for the physisorption process ranges from 5 to $40 \text{ kJ}/\text{mol}$, while chemisorption involves a high activation energy (40 to $800 \text{ kJ}/\text{mol}$) (Wu 2007). Additionally, Lazaridis and Asouhidou suggested that low activation energy values (< 25 to $30 \text{ kJ}/\text{mol}$) indicate diffusion-controlled processes (Lazaridis and Asouhidou 2003).

The positive E_a value confirms the endothermic nature of MB adsorption onto cellolignin, which is characteristic of a physical process controlled by diffusion. This is in agreement with other results of this study, and also with the results of Han *et al.* (2009).

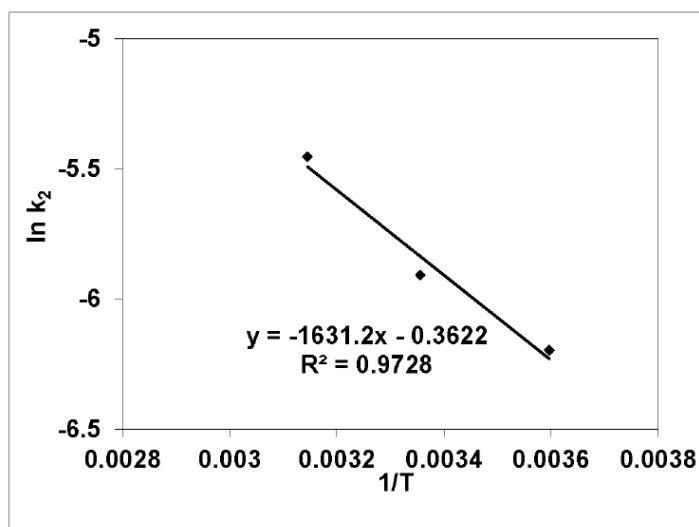


Fig. 8. The Arrhenius plot for the adsorption of MB onto cellolignin

Capitalization of the Adsorbent Loaded with Dye

The possibilities of valorization of the adsorbent loaded with dye must be evaluated in order to ensure the disposal of these materials in environmentally safe conditions. For this purpose, according to the goal and the actual situation, the following options may be considered: (i) burning after drying; (ii) capitalization; (iii) use for composite materials; (iv) composting processes of biodegradable wastes; (v) regeneration by treatment with acid or organic solvent solutions and reuse in other cycles of dye adsorption – desorption; (vi) continued use as a new adsorbent material for heavy metal ion or dye removal from aqueous media or for adsorbent for variants of affinity chromatography; (vii) evaluating a possible bacteriostatic effect of the dyed material to make it suitable for a microbial treatment processes of wastewater.

CONCLUSIONS

1. In order to discover the adsorption mechanism of the cationic dye methylene blue from an aqueous environment with a pH of 6.5 to 7 onto cellulignin, studies on equilibrium, thermodynamic, and kinetics were carried out in batch systems.
2. The equilibrium adsorption data analyzed by Freundlich, Langmuir, and Dubinin-Radushkevich isotherm models confirmed that both Freundlich and Langmuir isotherms describe the equilibrium adsorption data well. The monolayer adsorption capacity of 95.2 mg/g reached at 25 °C is in accordance with previously reported data on adsorption capacity of different low cost adsorbents. The values of the mean free energy (E) obtained from the Dubinin-Radushkevich model suggest that weak van der Waals forces (dipole-dipole interactions, hydrogen bonding) and electrostatic interactions contribute to the adsorption of the methylene blue by cellulignin.
3. The values of thermodynamic parameters confirm the feasibility and the endothermic behavior of the adsorption process and suggest that the adsorption is a physico-chemical process.
4. The values of isosteric heat of adsorption (ΔH_X), assessed using the Clausius-Clapeyron equation, slightly decrease with an increase of the adsorbent surface loading, suggesting the energetic heterogeneity of adsorption sites toward dye retention and the presence of interactions between the adsorbed dye molecules. The ΔH_X values also correspond to the physical adsorption mechanism and confirm the endothermic nature of the process.
5. Kinetic data at three temperatures were analyzed using different kinetic models (pseudo-first order, pseudo-second order, intra-particle diffusion model, and Boyd-Reichenberg model). The results showed that MB adsorption by cellulignin follows pseudo-second order kinetics and that mass transport (surface diffusion and pore diffusion) influences the overall rate of the adsorption process.
6. The positive value of E_a calculated using the Arrhenius equation confirms the endothermic nature of MB adsorption onto cellulignin. This behavior is characteristic of a physical process controlled by diffusion.
7. Taking into account the results of this study, one may conclude that cellulignin can be considered a promising, eco-friendly adsorbent, with low-cost production for the removal of dyes from an aqueous environment.

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