



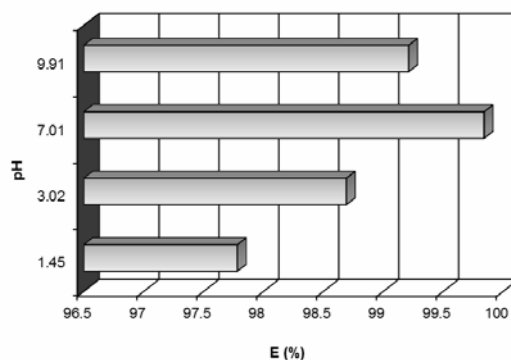
METHYLENE BLUE (MB) SYNTHETIC WASTEWATER DECOLOURIZATION USING ROUMANIAN FIR TREE SAWDUST – THERMODYNAMICS, EQUILIBRIUM AND KINETICS

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The purpose of this paper was to establish the optimum pH and temperature for the biosorption of methylene blue (MB) from aqueous solutions on Romanian fir tree sawdust (*Abies alba*), RFTS. The maximum biosorption efficiency (99.93%) of MB occurred at 303 K and pH = 7. Also, standard thermodynamic parameters, ΔG° , ΔH° and ΔS° were calculated, the results indicating that the considered biosorption process is endothermic and favourable. Equilibrium data were modelled using Langmuir and Freundlich isotherms. The experimental data fitted well with the Langmuir isotherm model, suggesting the monolayer biosorption of the MB onto RFTS. The MB biosorption kinetics was analysed using pseudo-first- and pseudo-second-order models. The results indicated that decolourization of aqueous solutions was best described by the pseudo-second-order model. The obtained results indicate that RFTS can be an economic and attractive option for dye removal from diluted industrial effluents.



INTRODUCTION

Pollution of the water sources by organic and inorganic contaminants is a major concern in many industrialized countries. The industries, for example textile, dyestuff, paper and plastics use dye for their products by consuming substantial volumes of water. Consequently, they generate a considerable amount of coloured wastewater.¹ More than 100,000 are commercially available and produced annually all over the world.² It has been estimated that 10-15% of the dye is lost in the dyeing effluent.³ The coloured effluents damage the aesthetic quality of water and reduce light penetration and photosynthesis, and some of them are toxic or mutagenic, carcinogenic and allergenic.⁴

Dyes are broadly classified as anionic, cationic and non-ionic depending on the ionic charge of the chromophore group. Cationic dyes are more toxic than anionic dyes.⁵ Hence, decolourization of the coloured-bearing effluents represents an important environmental goal. Various techniques like coagulation, adsorption, chemical oxidation, froth flotation, etc. have been used for the removal of organics as well as inorganics from wastewater.⁶ Amongst these, biosorption has been found as an attractive alternative to replace or supplement the present dye removal processes from wastewater.^{7,8} Biosorption potential of a biomaterial is based on interactions between contaminants and hydroxyl, carboxyl, phosphoryl and other charged groups localized on the cell wall structure of organisms or

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biomasses, composed of macromolecules such as heteropolysaccharides, proteins and lipids.⁹ Adsorption, complexation, chelation and ion exchange can play a role in the biosorption mechanisms.^{10,11}

In the recent years, non-conventional adsorbents, including natural materials, such as waste from agro-industrial activities, have been successfully used as alternative low-cost adsorbents for the removal of several dyes from aqueous solutions.¹²⁻¹⁵

Methylene blue (MB) is a dark-green powder or a crystalline solid cationic dye.¹⁶ MB is usually discharged in high quantities in industrial wastewater, specially textiles, paper and cosmetics industries. The complex structure of MB dye makes it very stable and difficult to degrade, leading to many environmental problems such as: preventing sunlight penetration into water, reducing photosynthetic activity and causing bad appearance of water surface.^{17,18} MB is a heterocyclic aromatic compound with chemical formula $C_{16}H_{18}N_3Cl$, FW = 319.85 g/mol. MB is widely used as a redox indicator in analytical chemistry. Solutions of this substance are blue when are in an oxidizing environment, but will turn colourless if exposed to a reducing agent.

The goal of this study was to realize the MB biosorption onto waste fir tree sawdust from Romanian wood industry and to offer an effective and economical alternative to more expensive adsorption processes (commercial active carbon and resins). Therefore, pH and temperature influences over the biosorption process were investigated in batch conditions. Thermodynamics, isotherm and kinetic models of the considered biosorption process were discussed in details.

RESULTS AND DISCUSSION

The obtained experimental data were processed using biosorption process efficiency and biosorption capacity. Biosorption process efficiency, expressed as percentage removal, was calculated with equation (1)

$$E, (\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

and biosorption capacity was calculated using equation (2)

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (2)$$

where: C_0 is MB initial concentration (mg/L), C_e is MB equilibrium concentration in solution (mg/L), V is solution volume (L) and m is biosorbent quantity (g).^{19,20}

Biosorbent characterization

Abies alba fir is a common tree from some forest areas in Transylvania (Roumania). These trees are the main source in the local wood industry and their sawdust could be a good candidate as a green and economic alternative for dyes removal from wastewater.^{20,21} Roumanian fir tree sawdust, RFTS, was evaluated without any chemical pre-treatment.

Representative samples of RFTS were investigated using gravimetric method (humidity and apparent density) and wet chemical analyses.²¹ The studied biomass consist mainly of dry matter (96.93%) and has an apparent density of 1.09 g/cm³. Main chemical composition is crude fibre, cellulose (55.09%), hemicelluloses and lignin (33.3%).^{20,21} The presence of lignin in the sawdust structure is likely to confer to this material biosorptive properties. The bulk chemical analyses performed on sawdust samples indicate the presence of C (25.457%), H (3.668%), O (70.871%), N (0.004%). The amount of S was considered negligible.^{21,22}

Effect of pH

The pH is one of the most important controlling parameter in the biosorption process of dyes from wastewater. Hydrogen ions affect cationic dye removal because they have a great affinity for many complexing and ion-exchange sites.²³ The pH values affect the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate during the adsorption process.²⁴ In our study, four different pH values were considered, ranging between 1.45 and 9.91, in order to establish pH influence on the biosorption capacity of RFTS, Fig. 1.

As the biosorbent surface is positively charged at low pH, the electrostatic attraction between RFTS and MB molecule leads to a decrease of the biosorption capacity. As the initial pH increases, the biosorbent surface becomes less positive and therefore electrostatic attraction between the MB molecule and RFTS surface (COO^- and HO^- groups) is likely to be increased. The optimum pH that provides maximum MB removal (almost

100%) was an initial pH=7. For pH values higher than 7, a small decrease (0.63%) in dye percentage removal, was observed that could be attributed to the solubilisation of organic groups present on the biosorbent surface.¹² Similar behaviour has been frequently reported through different studies where the authors investigated dye biosorption by various biomaterials.^{12,15,25}

Decolourization of wastewater containing cationic dyes, in generally, can be explained by ion-ion interactions established between the cationic dye, MB in this case, and the anionic groups within the substrate (COO^-), which can be cellulosic or hemicellulosic one, from vegetal cell wall of the sawdust.²⁶ Cellulose does not require extreme alkalinity (pH=7-10) to generate cellulosate ions, which are many times more reactive than cellulose itself.²⁷ Furthermore, the presence of carboxylic groups from the hemicellulose structure may have enhance the affinity of wood sawdust to cationic dyes molecules that are electron deficient (positively polarized) and thus, the adsorption process can be explained by electrostatic attractions between two counter-ions.^{28,29}

Effect of temperature

MB biosorption onto RFTS was conducted using four different temperatures. It was observed that an increase in temperature led to an increase in the biosorption efficiency, suggesting that the

decolourization process is endothermic. Higher temperatures conduct to a decrease in biosorption efficiency, due to the fact that after 313 K desorption process begin. Similar results were reported in literature for the biosorption of MB onto different vegetal fibres wastes.^{15,16,18,26}

For each experiment, performed at a certain temperature, values of biosorption capacity (q_e) and MB concentration in solution at equilibrium (C_e) were determined. The equilibrium constant K_d , of the biosorption process, calculated as q_e/C_e , can be used to estimate the thermodynamic parameters, equation (3), due to its dependence on temperature.³⁰

In order to describe the thermodynamic behaviour of the biosorption of MB onto RFTS biomass, standard thermodynamic parameters, including the changes in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following equations:³¹

$$\Delta G^\circ = -RT \ln K_d \quad (3)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

where, R is the universal gas constant (8.314×10^{-3} kJ/K-mol), T is absolute temperature (K), and K_d is the distribution coefficient (L/g) calculated as q_e/C_e , where q_e is biosorption capacity (mg/g) and C_e is MB concentration in solution at equilibrium.

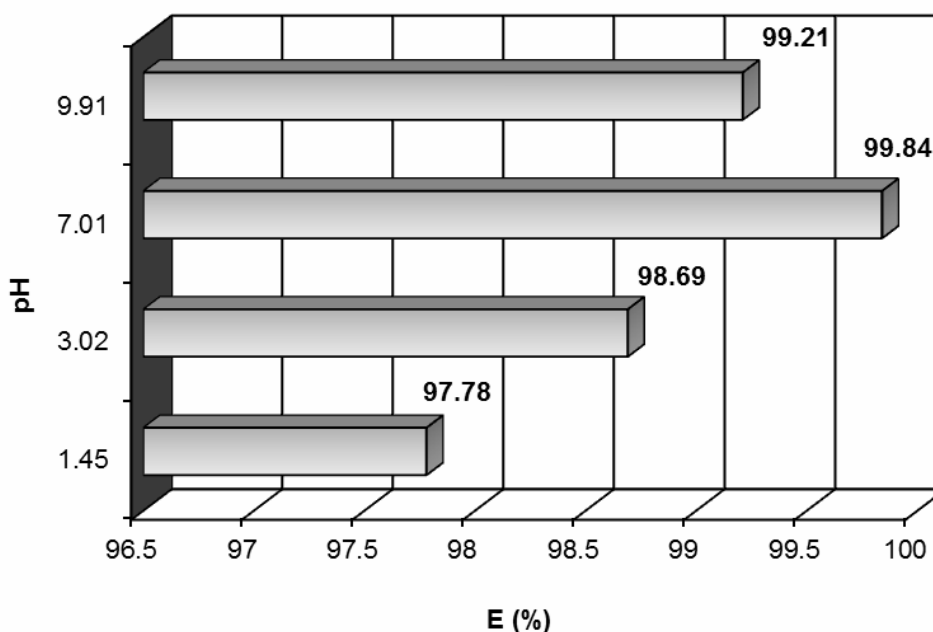


Fig. 1 – The effect of initial pH on percentage removal values for MB biosorption onto RFTS ($C_i = 100$ mg MB/L, 3g biomass, $0.4 < d < 0.6$ mm, 296 K, 200 rpm).

The ΔH° and ΔS° parameters were estimated from the following equation:

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (5)$$

from the slope and intercept of the $\ln K_d$ versus $1/T$ plot.^{32,33}

The plot of $\ln(K_d)$ as a function of $1/T$ (Fig. 2) yields a straight line ($R^2=0.947$) from which ΔH° and ΔS° were calculated, Table 1. The values of ΔG° for MB biosorption onto RTFS were found to be negative for the experimental range of temperatures (Table 1) corresponding to a favourable process. Furthermore, the decrease in the values of ΔG° with the rise in temperature indicates that the biosorption is more favoured at higher temperatures. The positive value of ΔH° (Table 1) confirms the endothermic nature of the overall biosorption process. This means that as the

temperature increases, more energy is available to enhance the biosorption. Our results are in good agreement with literature data.^{34,35} Moreover, the positive value of ΔS° (Table 1) points out the increased randomness at the solid/liquid interface during the biosorption of MB onto RFTS.³⁶

Adsorption isotherms

The adsorption isotherms are very important to design the reaction systems. They describe how adsorbate (*eg.* dyes) interact with the adsorbent surface and therefore are critical in optimizing the use of the adsorbent material.²⁶ In the present study, two parameters isotherm models, Langmuir and Freundlich were used to describe the equilibrium of MB biosorption onto RFTS. This two isotherm models are widely used to describe the biosorption of a solute from a liquid solution.

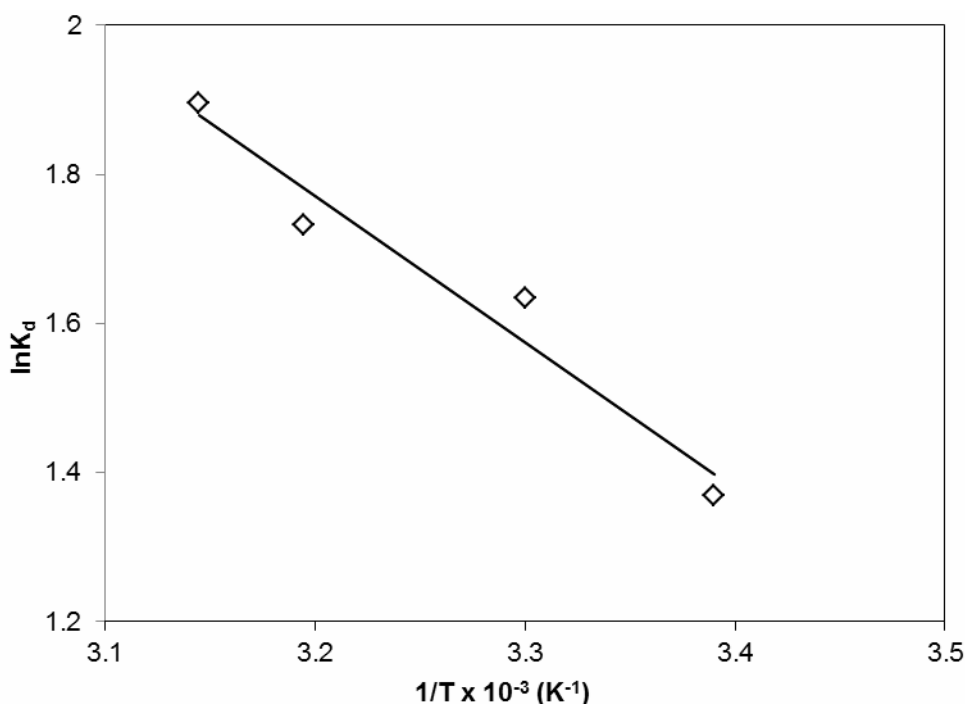


Fig. 2 – Plot of $\ln K_d$ versus $1/T$ for MB biosorption onto RFTS ($C_i = 100 \text{ mg/L}$, 3 g biomass , $0.4 < d < 0.6 \text{ mm}$, $\text{pH}=7$, 200 rpm).

Table 1

Thermodynamic parameters for MB biosorption onto RFTS at various temperatures ($C_i = 50\text{--}200 \text{ mg/L}$, 3 g biomass , $0.4 < d < 0.6 \text{ mm}$, $\text{pH}=7$, 200 rpm)

Biomass	ΔS° (kJ/mol·K)	ΔH° (kJ/mol)	ΔG° (kJ/mol)			
			296 K	303 K	313 K	318K
RFTS	0.066	16.362	-3.376	-3.912	-4.581	-4.915

Freundlich isotherm model assumes a heterogeneous adsorbent surface and active sites with different energy and that the molecules adsorbed can react with each other.³⁷ Freundlich isotherm model in linear form is expressed by equation (6), where, K_f ($\text{mg}^{(1-1/n)} \text{L}^{1/n}/\text{g}$) and n are the Freundlich equilibrium constants, which can be determined from the plot of $\log q_e$ versus $\log C_e$.³⁸

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

The Langmuir isotherm is based upon an assumption of monolayer adsorption onto the surface of the adsorbent containing a finite number of adsorption sites of uniform energies of adsorption³⁹ and it can be written in linear form as follows:⁴⁰

$$\frac{1}{q_e} = \frac{1}{q_m b} \cdot \frac{1}{C_e} + \frac{1}{q_m} \quad (7)$$

where, q_e and C_e are the solute concentration in liquid and solid phases at equilibrium, (mg/g) and (mg/L), respectively, q_m is the quantity of adsorbate required to form monolayer on unit mass of adsorbent (mg/g) and b is the adsorption

equilibrium constant that is related to the apparent energy of adsorption, (L/mg).

Isotherm parameters q_m and b can be obtained from $1/q_e$ versus $1/C_e$ plot.

The traditional way to realize parameter estimation is linearization and linear regression of the isotherm models. In this case, linearity of the plots expressed by linear regression coefficient, R^2 , can give some information about the fitting between the experimental data and the isotherm model, the closest to linearity could be considered as describing better the adsorption equilibrium in a certain system.^{25,41}

The linear plot of the Langmuir isotherm for MB biosorption onto RFTS is presented in Fig. 3.

Adsorption equilibrium constants and linear regression coefficients obtained from Langmuir and Freundlich isotherm models are presented in Table 2. The monolayer saturation capacity of MB was calculated to be $9.718 \text{ mg}/\text{g}$, while Langmuir constant, which is related to the adsorption energy, was determined to be $0.524 \text{ L}/\text{mg}$. Freundlich isotherm constants were also calculated (Table 2). The obtained R^2 , Table 2, values suggested that the experimental results fitted best on Langmuir isotherm model.

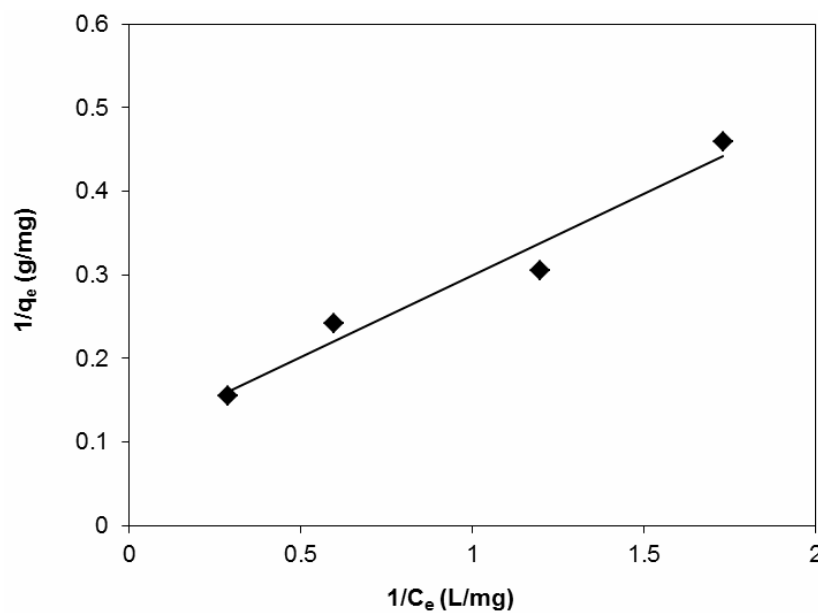


Fig. 3 – Langmuir plot for MB biosorption onto RFTS ($C_i = 50\text{-}200 \text{ mg}/\text{L}$, 3 g biomass, $0.4 < d < 0.6$, 296 K , $\text{pH}=7$, 200 rpm).

Table 2

Langmuir and Freundlich coefficients for MB biosorption onto RFTS ($C_i = 50\text{-}200 \text{ mg}/\text{L}$, 3 g biomass, $0.4 < d < 0.6$, 296 K , $\text{pH}=7$, 200 rpm)

Langmuir isotherm			Freundlich isotherm		
b (L/mg)	q_m (mg/g)	R^2	n	K_f ($\text{mg}^{(1-1/n)} \text{L}^{1/n}/\text{g}$)	R^2
0.524	9.718	0.961	1.446	2.690	0.733

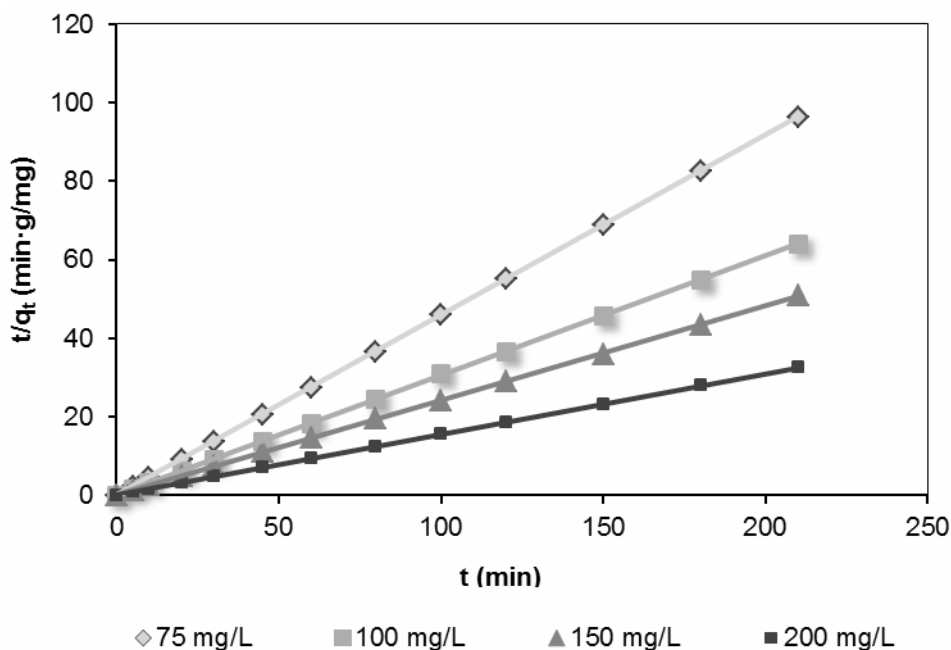


Fig. 4 – Plots of the pseudo-second-order kinetic model for MB biosorption onto RFTS ($C_i = 50\text{-}200$ mg MB/L, 3g biomass, $0.4 < d < 0.6$ mm, 296 K, pH=7, 200 rpm).

Biosorption Kinetics

Pseudo-first-order (Lagergren)⁴² and pseudo-second-order (Ho)⁴³ models were used to study the biosorption kinetics of MB onto RFTS. Linear regression was used to determine the best fitting kinetic model (linear regression coefficient, R^2). The linear form of the two models is expressed by equations (6) and (7), respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where: q_e and q_t are the amounts of MB dye biosorbed (mg/g) at equilibrium and time t , respectively and k_1 and k_2 are the pseudo-first-order and pseudo-second-order rate constants in (1/min), (g/mg·min), respectively.

Above mentioned kinetic models were used to test experimental data and to determine the kinetic constants from the slope and intercept values of the linear plots, $\ln(q_e - q_t)$ versus t , and t/q_t versus t (Fig. 4).

In case of pseudo-first-order, R^2 values between 0.636 and 0.781 were obtained, while q_e values showed great differences by comparison to experimental data, which led to the conclusion that MB biosorption onto RFTS cannot be described by this model. When pseudo-second-order kinetic model was applied for the considered biosorption process, values of 1 for R^2 were obtained for all considered concentrations, Table 3. In addition, the calculated q_e values are very close to the experimental ones (Table 3). Therefore it was concluded that MB biosorption on RFTS obeyed the pseudo-second-order kinetic model.

Table 3

Pseudo-second-order rate constants, calculated and experimental q_e values for MB biosorption onto RFTS ($C_i = 50\text{-}200$ mg MB/L, 3g biomass, $0.4 < d < 0.6$ mm, 296 K, pH=7, 200 rpm)

C (mg/L)	$q_e(\text{exp})$ (mg/g)	k_2 (g/mg·min)	$q_e(\text{calc})$ (mg/g)	R^2
75	2.182	1.716	2.181	1
100	3.286	0.881	3.287	1
150	4.162	0.501	4.152	1
200	6.453	0.185	6.472	1

EXPERIMENTAL

Biomass

The fir tree (*Abies alba*) sawdust, RFTS, was obtained from a local sawmill in Huedin, Cluj County, Romania. Prior to its utilization the considered biomass was washed several times with distilled water in order to eliminate surface impurities and dried at 105°C for 24 h. Finally, the dried biomass was ground and sieved ($0.4 < d < 0.6$ mm). The sieved RFTS was then stored in an airtight box before its utilization. No further chemical treatments were considered at this stage. Representative RFTS samples were investigated, using gravimetric method (humidity and apparent density)²⁰⁻²² and elemental analysis using a Thermo Finnigan Flash EA 1112 Series equipment.

Preparation of MB solutions

Dye stock solution (1000 mg/L) was obtained by dissolving the necessary quantity of solid substance, MB (analytical purity reagent) in distilled water. From this solution, solutions with known concentration in 50-200 mg/L range were further prepared.

Biosorption experiments

The biosorption process was conducted in batch conditions, under magnetic stirring at 200 rpm, through the contact of a certain amount of RFTS biomass with a volume of 100 mL MB aqueous solution of various concentrations. The biosorption process was realized until equilibrium was reached (240 min established from preliminary experiments).²² MB concentration in solution was determined using a Jenway 6305 UV-VIS spectrophotometer, at $\lambda_{\max} = 665$ nm, after a preliminary centrifugation (5 min at 10,000 rpm) and appropriate dilution. Water samples were collected at established time intervals.

The effect of the initial solution pH on the equilibrium adsorption of MB was analysed in 1.45 to 9.91 pH range. The initial pH was adjusted using 0.1 M HCl and 0.1 M NaOH solutions. The experiments were carried out using 100 mL solution of 100 mg/L, which was contacted with 3 g fir tree sawdust, at 296 K, under magnetic stirring at 200 rpm. pH was measured using a Consort 832 pH meter.

In order to determine the effect of temperature on the MB biosorption onto RFTS, four different temperatures were considered, 296, 303, 313 and 318 K. The experiments were realized with an initial dye concentration of 100 mg/L at pH=7, and 3 g sawdust/100 mL solution.

All the experiments were repeated three times, the values presented were calculated using averaged concentration values.

CONCLUSIONS

The decolourization of synthetic aqueous solutions containing MB dye using RFTS has been investigated under different experimental conditions (pH and temperature), in batch mode, under magnetic stirring. The maximum biosorption efficiency (99.93 %) was obtained at pH = 7 and 303 K, when 100 mg/L solution, 3 g of biomass and 240 minutes contact time were used. MB removal process followed pseudo-second-order

kinetic model while equilibrium adsorption data were best fitted on Langmuir isotherm model. The positive value of ΔH° , 16.362 kJ/mol, for the biosorption process, confirms the endothermic nature, while the negative values of ΔG° suggest that the process is favourable under the studied conditions.

In conclusion, the study confirms that the Romanian fir tree *Abies alba* sawdust, a waste of local wood industry, abundant, low-cost and green biosorbent could be successfully used as a potential biosorbent for decolourization of synthetic solutions containing methylene blue dye and, probably, in the future, a material for treating industrial wastewater.

REFERENCES

1. S. Rangabhashiyam, N. Anu and N. Selvaraju, *J. Environ. Chem. Eng.*, **2013**, *4*, 629-641.
2. V.K. Garg, R. Kumar and R. Gupta, *Dyes Pigments*, **2004**, *62*, 1-10.
3. A.N. Fernandez, C.A. Almeida, N.A. Debacher and M.M. Souza Sierra, *J. Mol. Struct.*, **2010**, *982*, 62-65.
4. E. Thiyagarajan, P. Saravanan, S. Shiyamala, P. Saranya, N. Nagendra, N. Gandhi and S. Renganathan, *J. Saudi Chem. Soc.*, **2013**, *in press*, <http://dx.doi.org/10.1016/j.jeccc.2013.07.014>.
5. O.J. Hao, H. Kim and P.C. Chiang, *Environ. Sci. Technol.*, **2000**, *30*, 449-505.
6. H. Cherifi, B. Fatiha and H. Salah, *Appl. Surf. Sci.*, **2013**, *282*, 52-59.
7. M.A. Khalaf, *Bioresour. Technol.*, **2008**, *99*, 6631-6634.
8. R. Abdallah and S. Taha, *Chem. Eng. J.*, **2012**, *195-196*, 69-76.
9. S.T. Akar, D. Yilmazer, S. Celik, Y. Yetimoglu Balk and T. Akar, *Chem. Eng. J.*, **2013**, *229*, 257-266.
10. M. Solis, A. Solis, H.I. Pérez, N. Manjarrez and M. Flores, *Process Biochem.*, **2012**, *47*, 1723-1748.
11. B. Volensky, "New biosorbers for non-waste technology", CRC Press Inc., Boca Raton, Florida, 1990, p. 3-25.
12. F.A. Pavan, E.C. Lima, E.C. Dias and A.C. Mazzocato, *J. Hazard. Mater.*, **2008**, *150*, 703-712.
13. G. Annadurai, R. Juang and D. Lee, *J. Hazard. Mater.*, **2002**, *92*, 263-274.
14. M. Hajjaji, A. Alami and A. El Bouadili, *J. Hazard. Mater.*, **2006**, *135*, 188-192.
15. V.K. Garg, M. Amita, R. Kumar and R. Gupta, *Dyes Pigments*, **2004**, *63*, 243-250.
16. R. Han, W. Zou, W. Yu, S. Cheng, Y. Wang and J. Shi, *J. Hazard. Mater.*, **2006**, *141*, 156-163.
17. O. Dursun, D. Gulbeyi and O. Ahmet, *J. Hazard. Mater.*, **2007**, *144*, 171-178.
18. H.W. Chih, T.L. Yao and W.T. Tai, *J. Hazard. Mater.*, **2009**, *170*, 419-425.
19. B. Yasemin and T. Zeki, *J. Environ. Sci. Eng.*, **2007**, *19*, 160-166.
20. C. Indolean, S. Burcă, A. Măicăneanu, M. Stanca and D. Rădulescu, *Studia UBB Chem.*, **2013**, *LVIII* 2, 23-43.

21. B. Nagy, A. Măicăneanu, C. Indolean, S. Burcă, L. Silaghi-Dumitrescu and C. Majdik, *Acta Chim. Slov.*, **2013**, *60*, 263-273.
22. S. Burcă, M. Stanca, C. Indolean and A. Măicăneanu, *Acta Tech. Napocensis*, **2012**, *1*, 21-27.
23. F.N. Acar and Z. Eren, *J. Hazard. Mater.*, **2006**, *B137*, 909-914.
24. M.S. Rahman and M.R. Islam, *Chem. Eng. J.*, **2009**, *149*, 273-280.
25. B.H. Hameeda and M.I. El-Khaiary, *J. Hazard. Mater.*, **2008**, *154*, 639-648.
26. S.J. Allen, G. McKay and J.F. Porter, *J. Colloid. Interface Sci.*, **2004**, *280*, 322-333.
27. J.R. Aspland, "International Conference. American Association of Textile Chemists and Colorists (AATCC)", Montreal, 1997, p. 111-114.
28. Y. Al-Degs, M.A.M. Khraisheh, S.J. Allen and M.M. Ahmad, *Water Res.*, **2000**, *34*, 927-935.
29. L. Laasri, M. K. Elamrani and O. Cherkaoui, *Env. Sci. Pollut. Res.*, **2007**, *14*, 237-240.
30. R. Baccar, P. Blanquez, J. Bouzid, M. Feki and M. Sarra, *Chem. Eng. J.*, **2010**, *165*, 457-464.
31. A. Ahmad, M. Rafutullah, O. Sulaiman, M.H. Ibrahim, Y. Chii and B.M. Siddique, *Desalination*, **2009**, *247*, 636-646.
32. L. Semerjian, *J. Hazard. Mater.*, **2010**, *173*, 236-242.
33. Y. Bulut and Z. Tez, *J. Environ. Sci.*, **2007**, *19*, 160-166.
34. G.O. El-Sayed, *Desalination*, **2011**, *272*, 225-232.
35. O. Gerçel, H.F. Gerçel, A. Savas, C. Kopalal and U.B. Ogutverenc, *J. Hazard. Mater.*, **2008**, *160*, 668-674.
36. M. Ertaş, B. Acemioglu, H.M. Alma and M. Usta, *J. Hazard. Mater.*, **2010**, *183*, 421-427.
37. H.M.F. Freundlich, *Zeitschrift fur Physicalische Chemie*, **1906**, *57A*, 385-470.
38. K.V. Kumar, V. Ramamurthi and S. Sivanesan, *Dyes Pigments*, **2006**, *69*, 102-107.
39. I. Langmuir, *J. Am. Chem. Soc.*, **1918**, *40*, 1361-1403.
40. M. Ghoul, M. Bacquet and M. Morcellet, *Water Res.*, **2003**, *37*, 729-734.
41. V. Dulman and S.M. Cucu-Man, *J. Hazard. Mater.*, **2009**, *162*, 1457-1464.
42. S. Lagergren, "Kunglig Svenska Vetenskapsakademiens", Handlingar, 1898, Band 24, p. 1-39.
43. Y.S. Ho and G. McKay, *Water Res.*, **2000**, *34*, 735-742.