

REMOVAL OF DYES FROM TEXTILE WASTEWATER BY SORPTION ONTO LIGNO-CELLULOSIC MATERIALS♦

Daniela Suteu^{1*}, Doina Bilba¹, Carmen Zaharia¹,
Alina Popescu²

¹ "Gh. Asachi" Technical University of Iași,
Faculty of Chemical Engineering and Environmental Protection,
Department of Environmental Engineering and Management,
Blvd. D. Mangeron, 71A, Iasi - 700050, Romania

² INCDTP – București, Romania

*Corresponding author: danasuteu67@yahoo.com

Received: 07/07/2008

Accepted after revision: 11/08/2008

Abstract: Wastewater from textile industry contains various contaminants, among them dyes being considered to be highly toxic to the aquatic biota. The aim of this paper was to investigate in batch experiments the decolorization of synthetic aqueous solutions containing some cationic and anionic dyes by sorption on ligno-cellulosic solid wastes, such as softwood sawdust. Operating variables studied were: *pH*, sorbent dose and particle size, dye concentration, temperature and contact time. The sawdust-dye sorption systems were described using Freundlich and Langmuir isotherm models. The obtained results allow to estimate that the sawdust can

♦ Paper presented at the fifth edition of: "Colloque Franco-Roumain de Chimie Appliquée – COFrRoCA 2008", 25 – 29 June 2008, Bacău, Romania.

be useful in implementation of a new cheap technology for textile wastewater treatment.

Keywords: *dyes, Brilliant Red HE-3B, Methylene Blue, Rhodamine B, Crystal Violet, sorption, sawdust, textile wastewaters*

INTRODUCTION

Dyes, which represent a large and important group of synthetic chemicals, are also important water pollutants, present in the effluents of the textile, leather, paper, synthetics, cosmetics, and dye manufacturing industries. The release of these compounds into the environment is undesirable, not only for aesthetic reasons, but also because many azo dyes and their breakdown products are toxic and/or mutagenic for life forms. Some conventional technologies (precipitation, adsorptive techniques, ion exchange, coagulation, flocculation, UV/ozone treatment, electrochemical reduction, photocatalytic degradation, biological treatment) may be efficient in the removal of dyes, but their operational costs are very high [1-5]. Among these methods, adsorption is one of the most economic methods in decolorization of textile effluents because of simple design and operation, availability, non-toxicity, superior removal of pollutants. The great advantage of this method is the possibility to use like sorbents many inexpensive and readily available materials with adsorptive and ion exchange properties, such as activated charcoal produced from agricultural wastes, natural zeolites, sphagnum peat, fly ash, ligno-cellulosic materials as natural or waste materials from industry or agriculture, and active or inactive biomass resulted from industrial fermentative technology (food and pharmaceutical industry) [3, 4, 6-13]. In accordance with the tendency of replacing synthesized compounds, wastewaters treatment by sorption onto unconventional natural or biological materials ("green" or "environmental friendly") have recently become the subject of considerable interest.

The objective of this work was to determine the efficiency of removal of acid dye Brilliant Red HE-3B and of three basic dyes (Methylene Blue, Rhodamine B and Crystal Violet) from aqueous solutions, in various experimental conditions, using Romanian conifer sawdust like sorbent.

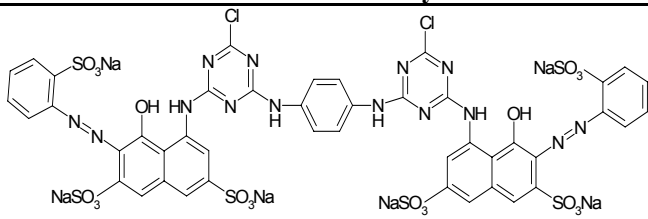
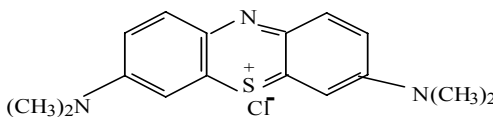
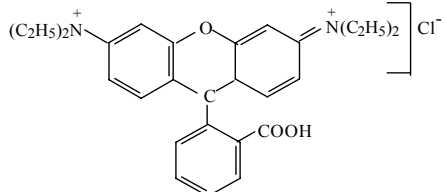
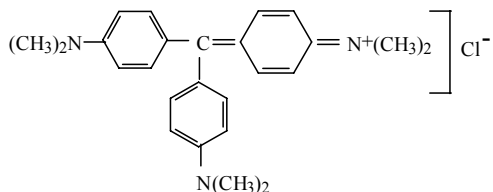
MATERIALS AND METHOD

Materials

The experiments were carried out using Romanian sawdust obtained as waste material from the softwood processing. The sawdust was dried in air, sieved and two fractions were collected: sawdust 1 (particle size 1 – 2 mm, designed SD-1) and sawdust 2 (powdered, particle size < 0.1 mm, SD-2). The major constituents of sawdust are cellulose, hemicelluloses and lignin; the humidity was of 4%.

The selected dyes were used as commercial salts and characterized in Table 1.

Table 1. Characteristics of the selected dyes

Structure of the dye	Characteristics
	Brilliant Red HE-3B (Reactive Red 120) C.I. 25810 Anionic, bifunctional reactive dye; MW = 1463 g.mol ⁻¹ ; λ _{max} = 530 nm; Concentration of the stock solution – 500 mg.L ⁻¹
	Methylene Blue (Basic Blue 9); C.I. 52015 Cationic, phenothiazine dye MW = 319.85 g.mol ⁻¹ ; λ _{max} = 660 nm; Stock solution – 320 mg.L ⁻¹
	Rhodamine B (Basic Violet 10); C.I. 45170 xanthenic dye; MW = 479.2 g.mol ⁻¹ ; λ _{max} = 550 nm; Concentration of the stock solution – 479 mg.L ⁻¹
	Crystal Violet (Basic Violet 3); C.I. 42555 cationic triphenylmethane dye MW = 407.99 g.mol ⁻¹ ; λ _{max} = 590 nm; Concentration of the stock solution – 408 mg.L ⁻¹

Abbreviations: BRed -Brilliant Red HE-3B; MB– Methylene Blue; BR–Rhodamine B; CV-Crystal Violet

Method

Sorption experiments were performed in batch conditions, by suspending weighted samples of sawdust in 50 mL of aqueous dyes solutions of known initial concentration in 150 mL flasks placed in a thermostated bath at desired temperature. The initial solution *pH* was adjusted by adding dilute HCl or NaOH solutions and measured with a Radelkis OP-271 *pH*-Ion analyzer. After a determined time (usually 24 h), the supernatant was spectrophotometrically analyzed with an UV-VIS Digital Spectrophotometer, model S104D /WPA. The sorption capacity of the sawdust was evaluated by means of the amount of dye sorbed:

$$q = \frac{(C_0 - C) \cdot V \cdot 10^{-3}}{G} \text{ (mg of dye/g of sawdust)}$$

and by percent of dye removal:

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

where: C_0 and C are the initial and equilibrium concentration of dye (mg.L⁻¹), G is the amount of sawdust (g), V is the volume of solution (L).

RESULTS AND DISCUSSIONS

Effect of pH

The effect of initial solution pH on the sorption of studied dyes onto sawdust (SD-1) was examined and the results are presented in Figure 1.

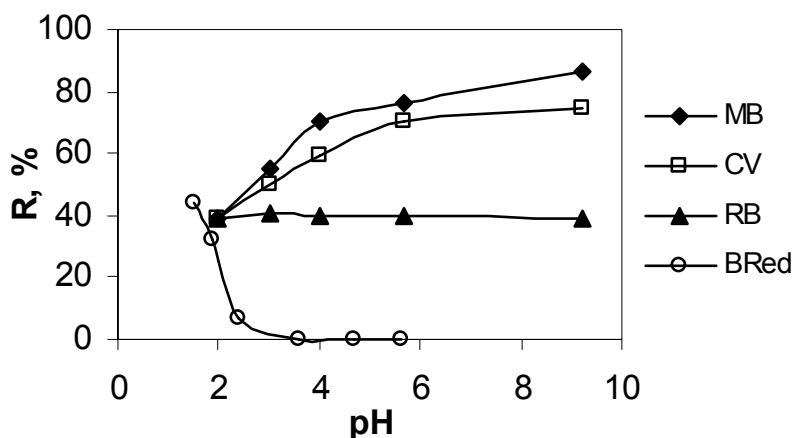


Figure 1. Effect of initial pH of solution on the sorption of dyes:
BRed -100 mg.L⁻¹; SD-1 dose-8 g.L⁻¹; MB -32 mg.L⁻¹; RB - 47.93 mg.L⁻¹;
CV- 40.8 mg.L⁻¹; SD-1 dose - 4 g.L⁻¹;
 $t = 24\text{ h}$, $T = 20^{\circ}\text{C}$

It is evident that the anionic dye is retained only from acidic media ($pH \leq 2$) and cationic dyes are better sorbed from slightly acid-neutral solutions. In order to explain the effect of solution pH on the removal of dyes, the zero point of charge pH (pH_{PZC}) of the sawdust was measurement by method proposed by Nouri and Haghseresht [14]; the value of pH_{PZC} was 4.6. Thus, at values of $pH < pH_{PZC}$ the sorbent surface is positively charged (protonation of polyhydroxy polyphenolic groups) and capable to electrostatic bind anionic dye Brilliant Red HE-3B. At $pH > pH_{PZC}$ values, the sorbent surface is negatively charged (dissociation of carboxylic groups) and is available to bind cationic dyes Methylene Blue, Rhodamine B and Crystal Violet. However, the removal of Rhodamine B is not affected by the variation of solution pH .

Effect of sawdust dose

To investigate the effect of sawdust dose on the removal capacity of dyes from aqueous solutions in determined concentrations and at the favorable pH , sorption experiments were carried out with different sawdust amounts; the results are presented in Figure 2.

It can be see that the percent of dyes removal increases with the increasing of the sawdust doses, due to the higher number of available sorption sites. In case of dyes MB and CV a dose of 6 g.L⁻¹ sawdust is adequate for advanced decolorization of solutions ($R \approx 80\%$), but for Rhodamine B and for more voluminous molecules of reactive dye BRed the sawdust dose which assures a suitable removal percent is higher than 10 g.L⁻¹.

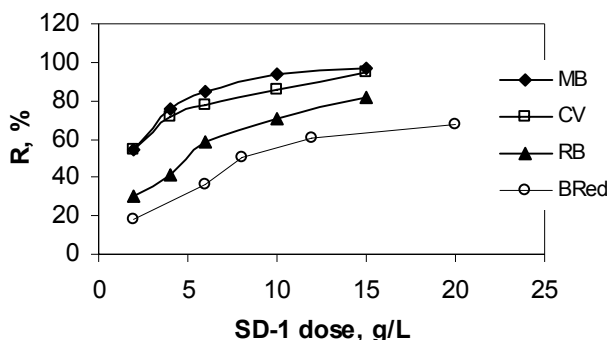


Figure 2. Effect of sawdust dose on the dyes sorption:

BRed - $C_0 = 100 \text{ mg.L}^{-1}$, $\text{pH} = 1.5$;
 MB - $C_0 = 32 \text{ mg.L}^{-1}$, RB - $C_0 = 47.93 \text{ mg.L}^{-1}$, CV - $C_0 = 40.8 \text{ mg.L}^{-1}$, $\text{pH} = 5.7$;
 $t = 24 \text{ h}$, $T = 20^\circ\text{C}$

Effect of initial dye concentration and of sawdust particle size

The sorption capacity of softwood sawdust for selected dyes was determined at the favorable pH in solutions with different initial dye concentrations and different particle size of the sorbent.

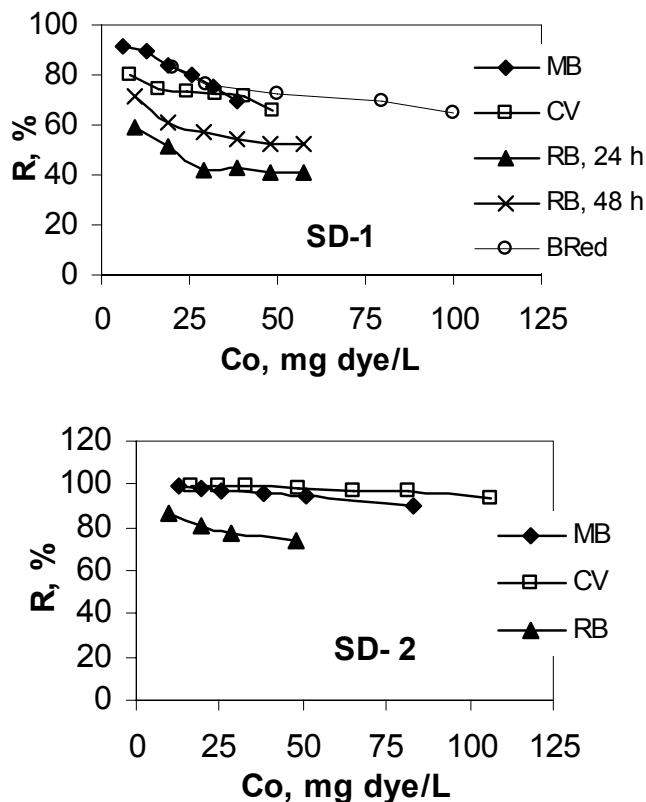


Figure 3. Effect of dye concentration on the sorption onto sawdust:

BRed - $\text{pH} = 1.5$, sawdust dose 20 g.L^{-1} ; MB, RB, CV - $\text{pH} = 5.7$,
 sawdust dose 4 g.L^{-1} ; $t = 24 \text{ h}$, $T = 20^\circ\text{C}$.

The results presented in Figure 3 shows that the percent of dye removal (R , %) onto sawdust particles with higher size (SD-1) is maximum in dilute solutions and decrease with an increase in initial dye concentration up to 50 mg.L⁻¹. The removal of Rhodamine B is smallest, but increase with time increasing. At the same time, removal of Methylene Blue and Crystal Violet is almost quantitative onto powdered sawdust (SD-2) even in solutions with initial concentration of dye of 100 mg.L⁻¹, and also, the Rhodamine B removal is better; with decreased sawdust particle size, sorption of all dyes increases.

Effect of temperature

The dye sorption onto softwood sawdust is temperature dependent. As seen in Table 2, the amount of dye sorbed on the sawdust SD-1 increases with increasing of solution temperature. After 4 h, at temperature of 40 °C, the removal percents of all dyes are greater as those at 20 °C and 24 h. These behaviors suggest that the sorption process is of endothermic nature and the fact that the high temperatures favor the dye molecule diffusion at the sorption sites of the sawdust.

Table 2. *The influence of temperature on the sorption of the selected dyes onto sawdust DS-1*

Type and concentration of dye		Conditions		Dye removal, R [%]		
Type	Concentration C_0 [mg.L ⁻¹]	pH	Dose [g SD-1/L]	$T = 3\text{ }^{\circ}\text{C}$ (24 h)	$T = 20\text{ }^{\circ}\text{C}$ (24 h)	$T = 40\text{ }^{\circ}\text{C}$ (4 h)
MB	19.2	5.7	4	47.33	83.44	86.36
	32.0			42.73	75.64	83.86
CV	24.5	5.7	4	58.17	73.53	89.45
	40.8			50.12	71.7	85.64
RB	28.7	5.7	4	30.16	44.7	58.17
	47.9			22.59	42.4	56.25
BRed	80.0	1.5	20	41.75	65.74	95.02
	100			21.50	64.68	91.74

Effect of contact time

The sorption data for uptake of selected dyes onto sawdust as a function of contacting time are presented in Figure 4. The experimental data showed that the removal of dyes is fast in initial stages of contact period and then, amounts of dye sorbed increases slowly near the equilibrium. In case of SD-1 sorbent, after 5 hours were removed 94.85 % from amount of MB corresponding at 24 h, 90.62% for CV, 75.13% for RB, and 81.83% for BRed. The decrease of sawdust size particle determines a shorter time to equilibration; for powdered sawdust, the time was of one hour. These observations suggest that the dyes sorption kinetic is largely affected by the particle size of sawdust.

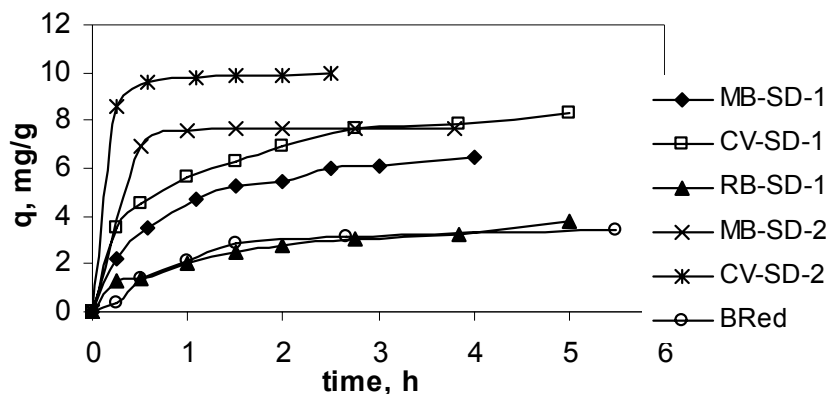


Figure 4. Effect of contact time on uptake of studied dyes onto sawdust:
Bred - $C_0 = 100 \text{ mg.L}^{-1}$, $\text{pH} = 1.5$, sawdust dose - 20 g.L^{-1} ; *MB* - $C_0 = 32 \text{ mg.L}^{-1}$,
RB - $C_0 = 32.82 \text{ mg.L}^{-1}$, *CV* - $C_0 = 40.8 \text{ mg.L}^{-1}$, $\text{pH} = 5.7$, sawdust dose - 4 g.L^{-1} ;
 $T = 20^\circ\text{C}$

Sorption isotherms

The relationship between the amount of sorbate at constant temperature and its concentration in the equilibrium solution is named the sorption isotherm. In Figure 5 are showed the sorption isotherms of the studied dyes on the sawdust of different particle size at 20°C . The shape of isotherms for MB and CV corresponds to the L2 type (Langmuir), but in case of RB and BRed the isotherms are almost linear. The amount of dyes sorbed at different particle sizes showed that the capacity of dyes sorption at equilibrium increased with the decrease in particle size. The higher sorption with smaller sawdust particle may be attributed to larger surface area of powdered sorbent, indicating that the sorption occurs through a surface mechanism.

Two models [15] were used to describe isotherms data, Freundlich and Langmuir, expressed by following linearized equations:

$$\text{Freundlich isotherm: } \log q = \log K_F + \frac{1}{n} \log C \quad (1)$$

$$\text{Langmuir isotherm: } \frac{1}{q} = \frac{1}{q_0} + \frac{1}{K_L \cdot q_0} \cdot \frac{1}{C} \quad (2)$$

where: K_F is a parameter related to the adsorption capacity and n is a measure of sorption intensity; a favorable sorption corresponds to a value of $1 < n < 10$. For $n = 1$, $K_F = K$ (linear isotherm). The Langmuir constant, K_L , is related to energy of the sorption and q_0 is the maximum value of sorption capacity (corresponding to complete monolayer coverage). The Freundlich constant K_F and n , and Langmuir constant q_0 and K_L can be calculated by plotting $\log q$ vs. $\log C$ and $1/q$ vs. $1/C$, respectively.

Freundlich and Langmuir constants for the sorption of studied anionic and cationic dyes sorption onto sawdust (SD-1 and SD-2), calculated from intercepts and slopes of corresponding plots are presented in Table 3, together with the correlation coefficients (R^2) as a goodness of fit criterion.

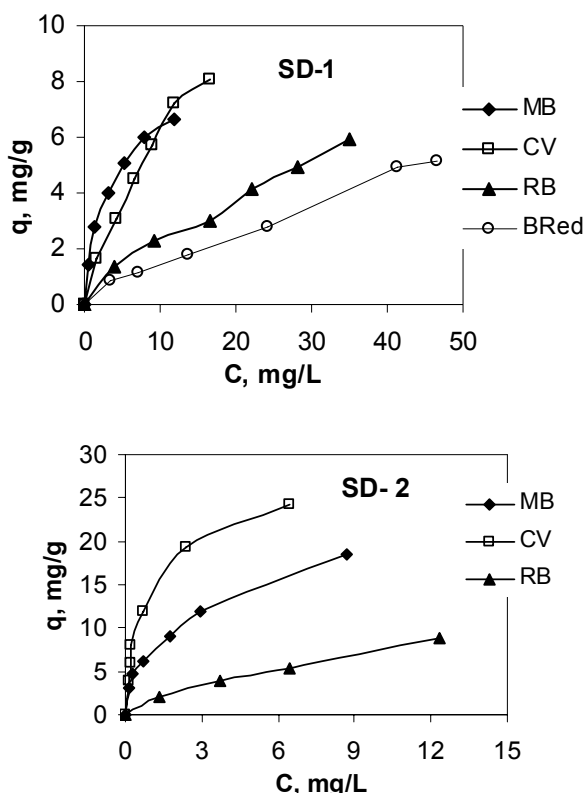


Figure 5. The sorption isotherms of the studied dyes onto sawdust: BRed – pH = 1.5, sawdust dose - 20 g.L⁻¹; MB, RB, CV – pH = 5.7, sawdust dose - 4 g.L⁻¹; $t = 24$ h, $T = 20$ °C

Table 3. The isotherms constants for the sorption of dyes onto sawdust

Sorbent	Dye	Freundlich isotherm			Langmuir isotherm		
		K_F (mg/g)(L/mg) ^{1/n}	n	R^2	q_0 [mg.g ⁻¹]	K_L [L.mg ⁻¹]	R^2
SD-1	BRed	0.293	1.360	0.9816	11.610	0.0146	0.9906
	MB	2.236	1.994	0.9551	7.215	0.4794	0.9967
	CV	1.151	1.391	0.9931	12.594	0.0899	0.9902
	RB	1.950	1.482	0.9843	7.309	0.0560	0.9716
SD-2	MB	7.256	2.290	0.9928	14.025	1.6816	0.9811
	CV	12.33	2.720	0.9677	20.877	2.4070	0.9846
	RB	1.656	1.527	0.9973	10.764	0.1725	0.9841

The values of correlation coefficients shows that the sorption of acid dye BRed follows the Langmuir isotherm, indicating the formation of monolayer coverage of dye molecules at the external surface of the sawdust. The data concerning sorption of cationic dyes MB, CV and RB are better represented by the Freundlich model, indicating a heterogeneous adsorption surface, with sorption sites of different energies and availability. The Freundlich constant n is higher than 1, reflecting the favorable sorption. On the other hand, the high values of Langmuir constant K_L confirm the

chemical nature of the dyes sorption, especially for MB and CV. The maximum sorption capacity of dyes increases with decrease of particle size of sawdust.

CONCLUSIONS

The removal of some dyes (anionic Brilliant Red HE-3B and cationic Methylene Blue Rhodamine B and Crystal Violet) from aqueous solutions was investigated using as sorbent softwood sawdust. The sorption of dyes onto sawdust is dependent on the initial solution *pH*, dose and particle size of sawdust, dye concentration and temperature. The best *pH* values were 1 – 2 for anionic dye and 5 – 9 for cationic dyes sorption. The percent of dyes sorption is highest in diluted solutions (10 – 20 mg.L⁻¹), increases with sawdust dose, temperature and contacting time increasing, and increases with particle size sorbent decreasing. The sorption data can be adequately modeled by the Langmuir and/or Freundlich adsorption isotherms. Although the sorption capacity of the sawdust is not very large, experimental results provide promising perspective for the utilization of sawdust as bio-sorbent in reducing pollution of textile effluents.

Acknowledgments

We are pleased to acknowledge the financial support from Romanian Ministry of Education and Research, National Authority for Scientific Research (ANCS) through the *Research Grant PN II – 31-053*.

REFERENCES

1. Mahbubul Hassan, M., Hawkyard, C. J.: Decolourisation of aqueous dyes by sequential oxidation treatment with ozone and Fenton's reagent, *Journal of Chemical Technology and Biotechnology*, **2002**, 834-841 (on line), DOI: 10.1002/jctb.641;
2. Cooper, P.: *Color in dyehouse effluent*, Ed. Society of Dyers and Colourist, Courtlands Textiles, Nottingham, **1995**;
3. Suteu, D., Bilba, D., Dan, F.: Synthesis and characterization of polyamide powders for sorption of reactive dyes from aqueous solutions, *Journal of Applied Polymer Science*, **2007**, **103**, 1833-1843;
4. Suteu, D., Bilba, D.: Equilibrium and kinetic study of reactive dye Brilliant Red HE-3B adsorption by activated charcoal, *Acta Chimica Slovenica*, **2005**, **52**, 73-79;
5. Vandevivere, P.C., Bianchi, R., Verstraete, W.: Treatment and reuse of wastewater from textile wet-processing industry: review of emerging technologies, *Journal of Chemical Technology and Biotechnology*, **1998**, **72**, 289-302;
6. Suteu, D., Bilba, D., Zaharia, C.: Kinetics of Blue M-EB dye sorption on ion exchange resins, *Hungarian Journal of Chemistry*, **2002**, **30**, 7-11;

7. Dong-Jin, Ju, Im-Gyu Byn, Vhang-Han, Lee, Gab-Hwan, An, Tae-Joo, Park: Biosorption characteristics of reactive dye onto dried activated sludge, *Water Practice & Technology*, **2006**, 1(3), DOI:10.2166/WPT. 2006066;
8. Kumar, K.V., Ramamurthi, V., Sivanesan, S.: A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water, *Journal Colloid Interface Science*; **2005**, 284 (1), 14-21;
9. Allen, S.J., Koumanova, B.: Decolourisation of water/wastewater using adsorption (review), *Journal of the University of Chemical Technology and Metallurgy*, **2005**, 40 (3), 175-192;
10. Babu, R.B., Parade, A.K., Raghu, S., Kumar T.P.: Cotton Textile Processing: Waste Generation and Effluent treatment, *Journal of Cotton Sci.*, **2007**, 11, 141-153;
11. Crini, G.: Non-conventional low-cost adsorbent for dye removal: a review, *Bioresource Technology*, **2006**, 97, 1061-1085;
12. Laasri, L., Elamrani Khalid, K., Cherkaoui, O.: Removal of two cationic dyes from a textile effluents by filtration-adsorption on wood sawdust, *Environmental Science and Pollution Research*, **2007**, 4, 237-240;
13. Batzias, F.A., Sidiras, D.K. : Simulation of methylene blue adsorption by salts-treated beech sawdust in batch and fixed-bed systems, *J. Hazard. Mater.*, **2007**, 149(1), 8-17;
14. Nouri, S., Haghseresht, F.: Adsorption of *p*-nitrophenol on untreated and treated activated carbon, *Adsorption*, **2004**, 10, 79-86;
15. Uddin, M.T., Islam, M.S., Abedin, M.Z.: Adsorption of phenol from aqueous solution by water hyacinth ash, *ARPJ Journal of Engineering and Applied Sciences*, **2007**, 2(2), 11-17.