

DECONTAMINATION OF COLORED WASTEWATERS USING NATURAL SORBENTS

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The capacities of natural sorbents in removing of dyes from synthetic wastewater have been investigated. The investigated sorbents were two natural wood samples (silver fir and beech) for the removal of two disazo direct dyes derived from 4,4'-diaminobenzanilide (*PDP* and *RDC*). The effects of the support's nature, the dose of natural fibres, initial concentration, and temperature on the dye removal were investigated. The obtained results showed a better retention capacity of Beech sawdust. The quantity of dye absorbed per unit of dry natural support decreased, but the efficiency of the dye adsorption (removal percentage) increased when the weight of fibre was doubled. The uptake of the studied dyes increased with the increase in initial dye concentration and with the decrease in the size of the dye molecules. In order to explain the effect of temperature on the dyes adsorption the experiments were conducted at 298, 313, and 333 K. The adsorption decrease with an increase in temperature indicated that the process is exothermic in nature. Kinetics of adsorption obeyed second order rate equation in case of using investigated sorbents. The best isotherm model that fits the experimental data with lower error was the Sips isotherm model.

Keywords: Direct Dye; Silver fir; Beech; Adsorption; Kinetics

INTRODUCTION

Dye factories (textile, paper, plastics) across the world use great quantities of water, and chemical substances, and dumping millions of tons of dye effluent into rivers. Highly coloured industrial wastewater has been a serious environmental problem as it are aesthetically unpleasant, and can produce serious pollution problems blocking sunlight for photosynthesizing plant species in the water [1-3]. For these reasons discharge of dye pollutants has become an ecological concern.

Direct dyes, widely used for dyeing textiles and leather, have a complex aromatic structure, which makes them more stable and hardly biodegradable. The potential toxicity of direct dyes arises from the reduction of the azo group, under the action of the enzyme and intestine microflora, which can produce carcinogenic, and mutagenic aromatic amines [4-7]. Synthesis of benzidinic direct dyes was forbidden, due to the carcinogenic activity of benzidine and the most of its derivatives [8, 9]. In this way finding substitutes for this kind of compounds is an increased demand and a relevant subject. Dyes derived from 4,4'-diaminobenzanilide, are relatively new types of direct dyes, which successfully replace the benzidinic dyes.

Due to the high stability of direct dyes, the conventional treatments of wastewater: electrochemical reduction [10,11], biodegradation [12,13], and chemical oxidation [14], have a reduced efficacy [15]. Effective results are observed in the wastewater treatment, using several physical or chemical methods: coagulation [16,17], ultra-filtration [18], and adsorption [19-21]. Among them, adsorption process provides an attractive alternative for the treatment of dye-contaminated waters because of its simplicity, selectivity and efficiency [22]. In recent years, attention has focused on various natural solid supports, which are able to remove pollutants from contaminated water at low cost.

The by products from wood industries are abundant, inexpensive, requires little processing and often present a disposal problem. Therefore, and due to their physico-chemical characteristics, it could be assumed as adsorbents. Silver Fir and Beech are abundant by products of the wood industry, so are easily available at negligible price. Therefore, they could be valorised as low cost adsorbents.

The purpose of study was the removal of direct dyes from aqueous solutions using natural adsorbents. Effect of process variables as contact time, adsorbent dose, and temperature has been investigated. The kinetic rate constants and the thermodynamics characteristic parameters of adsorption have been calculated.

EXPERIMENTAL

Materials

We investigated two direct disazo dye derived from 4,4'-diaminobenzanilide *PDP*, and *RDC* with the structures presented in Fig. 1. The dyes were synthesized in our laboratory, and were characterized by UV-Vis spectroscopy, thin layer chromatography, and mass spectroscopy [23, 24].

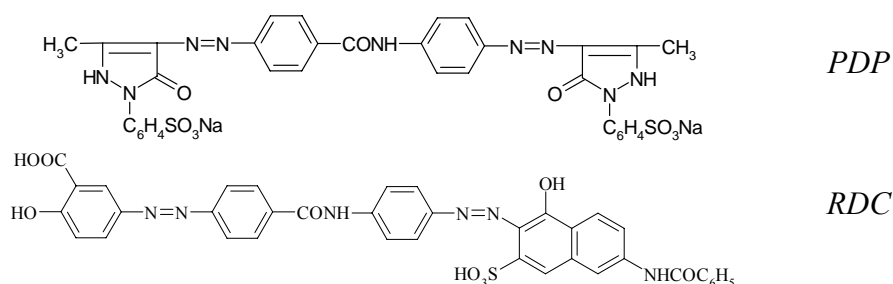


Figure 1. The investigated direct dyes structures

Two types of natural cellulose fibers - *Silver fir* and *Beech*, were tested as sorbents for the dyes removal from laboratory wastewaters. Wood samples in form of shavings were purchased from the local wood processing industry; Company Gref Forest S.R.L. These samples resulted from wood processing, and could be reused without additional cost. Wood samples were washed in distilled water under constant stirring for 2 hours to release impurities, filtered and then dried at 90°C. Distilled water was used for preparing the solutions.

Method

100 mL dye aqueous solutions (of different concentrations) were treated with two types of natural sorbents. The mixture was maintained under magnetic stirring (250 rpm), at 45°C, and pH 7 a sufficient and necessary time for reaching the equilibrium.

The influence of the nature and the quantity (0.1 g and 0.2 g) of the investigated biosorbents on dyes removal was studied. The obtained specifically adsorbent was separated by filtration, washed twice with 50 mL distilled water, and dried at 40°C.

Scanning electron microscopy (SEM) was used for the structural characterization of the studied fibres, before and after dye adsorption, using PHILIPS XL 30 CP scanning microscope, in low vacuum module. Apparatus details: accelerating voltage 300 kV, cathode LaB₆, point-to-point resolution 0.17 nm, line resolution 0.14 nm objective lens, Cs 0.6 mm objective lens, Cc 1.3 mm tilt ± 20.

The obtained data were used to calculate the adsorption capacity (q_t), relation (1), and also the dye removal percentage (η).

$$q_t = \frac{(C_0 - C_t) \cdot V}{W} \quad (1)$$

where: q_t is the quantity of dye absorbed per unit of dry biosorbent (mg/g), C_0 initial concentration of the dye solution (mg/L), C_t dye concentration at different periods of time (mg/L), V : volume of solution (L), and W amount of adsorbent (g).

The percentage of dye removal (η) was evaluated using relation (2):

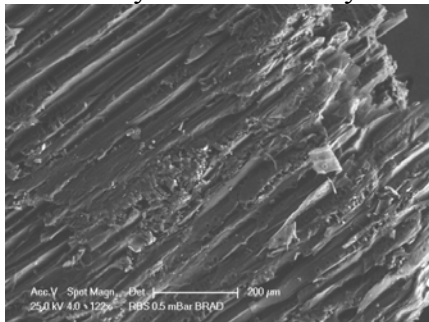
$$\eta = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C_e is the dye concentration at equilibrium (mg/L).

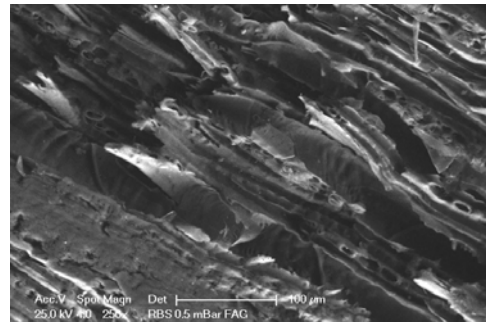
RESULTS AND DISCUSSION

Characterization of dye, copolymer and dye adsorbed on support

The morphology of the wood samples was investigated by SEM microscopy. In Figure 2 are presented the SEM images of the wood samples before (a, b), and after dyeing with investigated dyes (c, d) dye. The SEM photographs of the coloured fibres showed a uniform and persistent coloration of the samples, the texture and shape of the original wood fibers being unaffected by the adsorbed dye.



(a)



(b)

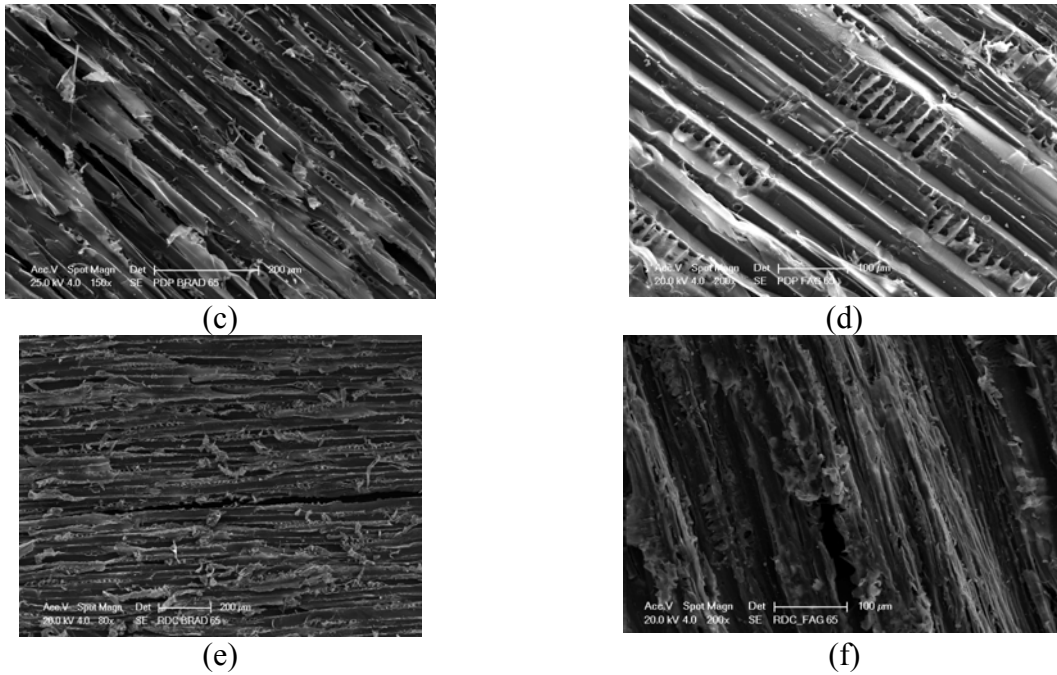


Figure 2. SEM images for: (a) Silver Fir fiber; (b) Beech fiber; (c) Fir with *PDP* dye; (d) Beech *PDP* dye; (e) Fir with *RDC* dye; (f) Beech *RDC* dye

The natural adsorbents samples before and after dye removing, were examined with the electronic microscope. Looking at the microscope, the SEM images of the dyed wood samples have a homogeneous colour. The studied samples being consist of vegetal tissues, with cellular wall impregnated with lignin, we couldn't establish an eventual selective affinity of the dye toward cellulose and lignin.

Influence of the support's nature

The adsorption capacity of the biosorbent materials is influenced by the nature of the support, the chemical structure of the support, and the number of functional groups able to interact with the dye. First in this study we investigated the adsorption capacities of two natural materials in order to determine the performance in direct dyes removal. The experiments were done using 0.1 g adsorbent, and 100 mL aqueous solutions of dye concentration $1 \cdot 10^{-5}$ M, under magnetic stirring, at 45°C , and pH 7. In Figure 3 the influence of bioadsorbent nature on the adsorption capacity is presented. The obtained results showed a better retention capacity of Beech sawdust. The dyes removal was rapid at the beginning of adsorption process, and gradually decreased as equilibrium time was approached. This may due to the saturation of the active centre, available for dye on the biosorbents surface.

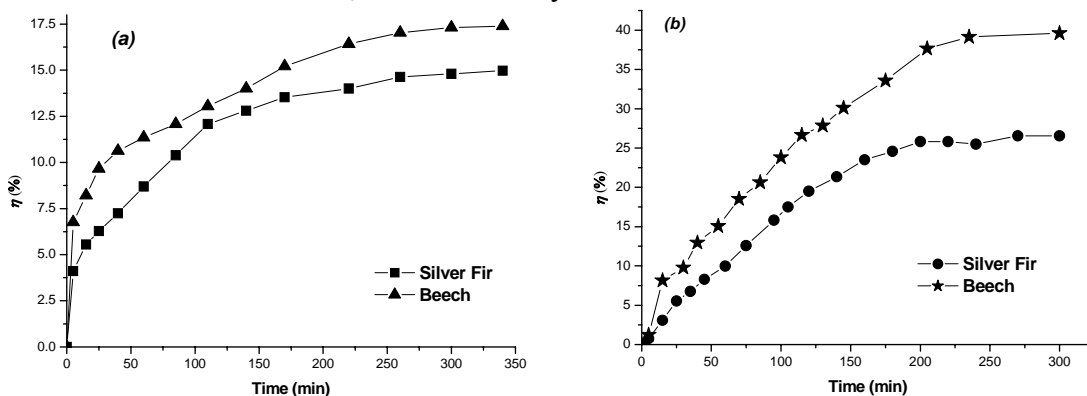


Fig. 3 Influence of the support's nature onto amount of adsorbed (a) *PDP* and (b) *RDC* dyes

Efficiency and capacity of different natural fibres in dye removal is due to the variation of chemical composition, and structural differences of the two types of investigated fibres.

Effect of natural fibre dosage.

The influence of the quantity of natural supports (0.1 and 0.2 g) towards the dye adsorption was followed at pH 7, and 45°C, in 100 ml dye solution using an apparent area of fibre ~1.0 cm². Effects of contact time on the removal process at various quantities of natural supports (*Silver Fir* and *Beech*) are presented in Figure 4.

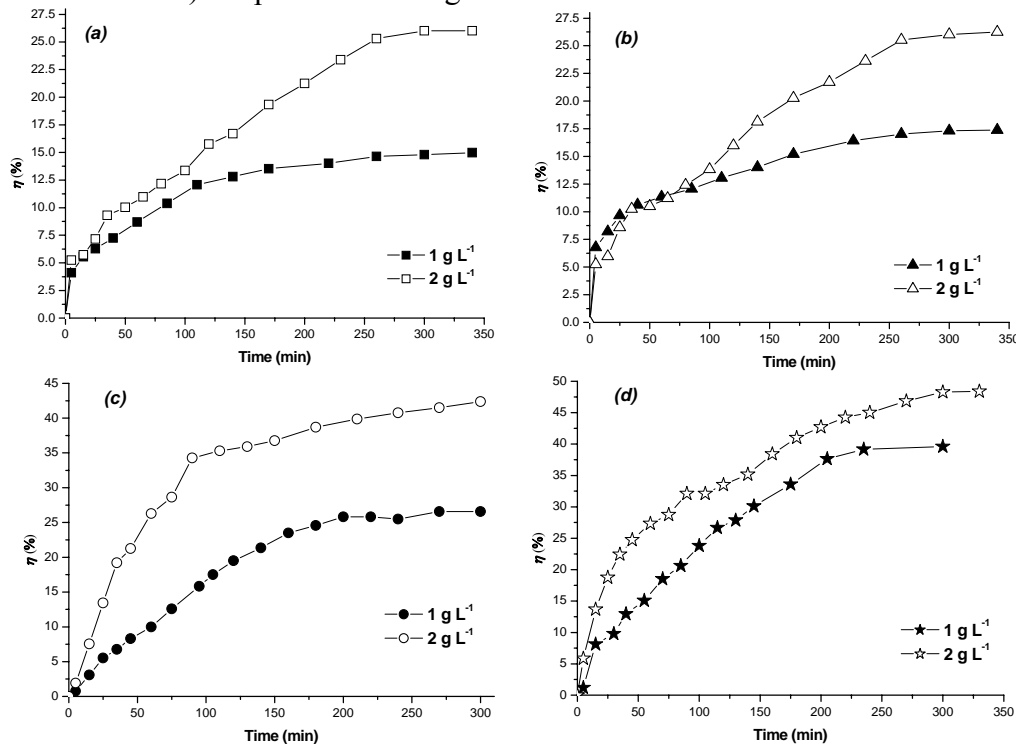
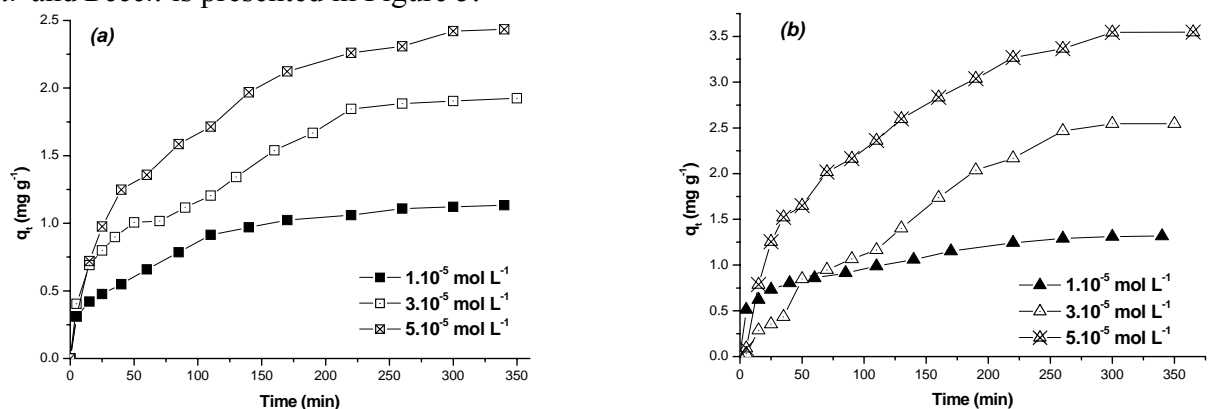


Fig. 4 Effect of fiber dosage. Amount of *PDP* dye adsorbed on: (a) *Silver Fir*, (b) *beech*; and *RDC* dye adsorbed on: (c) *Silver Fir*, (d) *beech*.

The quantity of dye absorbed per unit of dry natural support decreased, but the efficiency of the dye adsorption increased when the weight of fibre was doubled. This is due to the higher amount of dye per unit weight of fibre.

Influence of initial concentration.

The effect of initial dye concentration and contact time on the adsorption capacity of *Silver Fir* and *Beech* is presented in Figure 5.



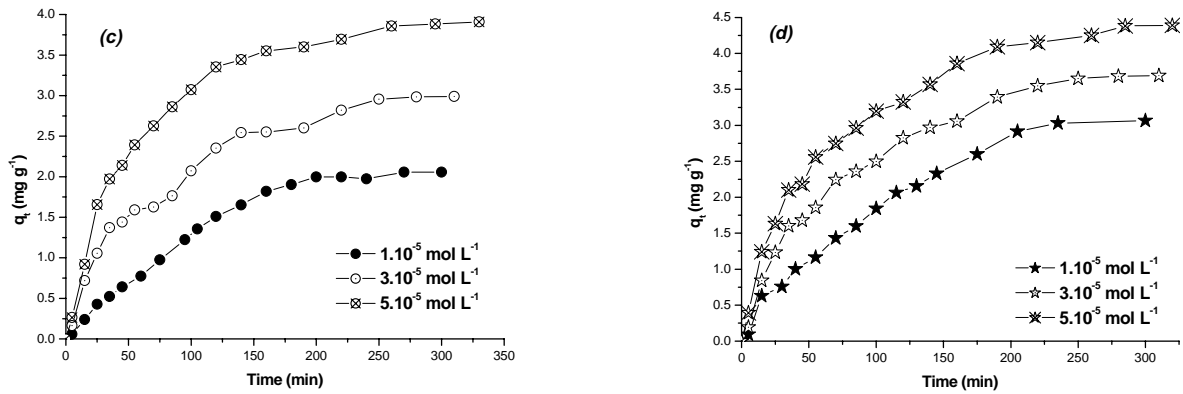


Figure 5 Adsorption of *PDP* (a), and *RDC* (b) at different initial concentrations.

The adsorption is rapid in the initial stages and after reaching the equilibrium time, it remained nearly constant, due to the saturation of the available active centre for dye on the adsorbent surface. The necessary time for reaching the equilibrium increased with increasing the dye concentration, and with increasing the molar mass of investigated dyes $PDP < RDC$. This is due to the fact that adsorption could occur both at the surface and in the pores of the sorbent, and the diffusion of adsorbates into the internal adsorption sites is stimulated by the increasing of the initial dye concentration. The uptake of the studied dyes increased with the increase in initial dye concentration while the percentage removal decreased.

Influence of temperature on the adsorption process

In order to explain the effect of temperature on the dyes adsorption the experiments were conducted at 298, 313, and 333 K. Figure 6 illustrates the effect of temperature on adsorption for different dye-adsorbent systems.

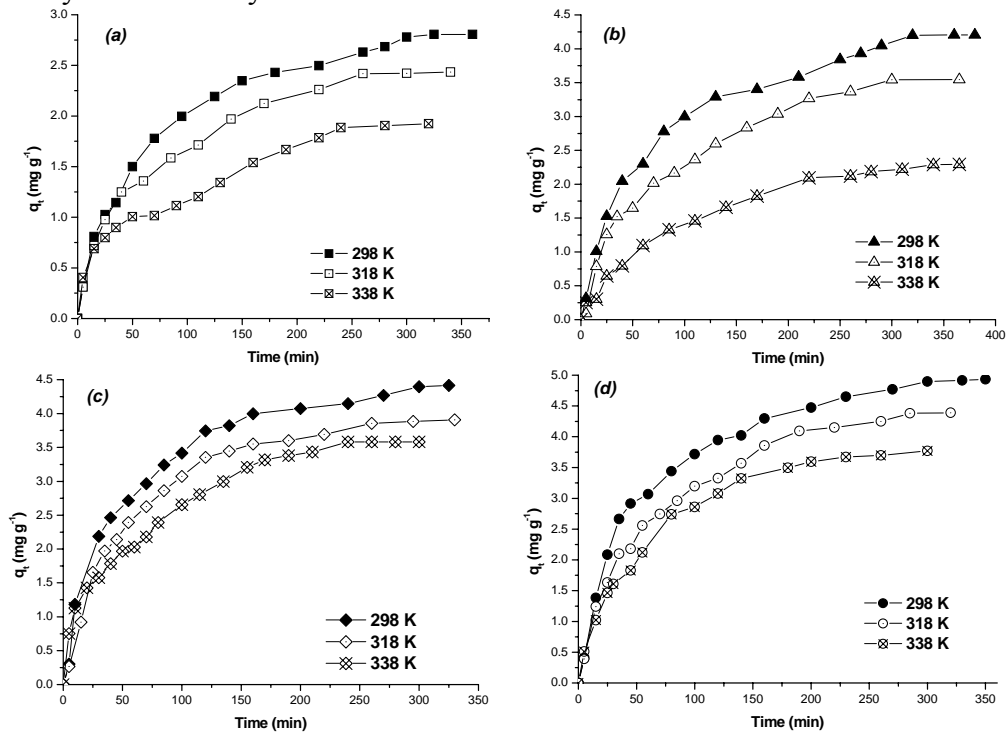


Fig. 7 Effect of temperature on uptake of *PDP* on: (a) Fir fibre; (b) Beech fibre, and of *RDC* on: (c) Fir fibre; (d) Beech fibre,

It is shown that the adsorption of investigated direct dyes decreases as the solution temperature increases. This can be explained by the exothermic spontaneity of the adsorption

process and by the weakening of bonds between dye molecules and active sites of adsorbents at high temperatures.

Adsorption Kinetics

The kinetics of adsorption is described by the first-order Lagergren model and pseudo second-order. The first-order rate expression of Lagergren (3) was used for determined the rate constants of first order adsorption k_1 , for the dyes removal by investigated adsorbents:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

where q_e and q_t are the amount of dye adsorbed on sorbent at equilibrium and any time t , respectively (mg/g). The plot of $\log(q_e - q_t)$ versus t will give a straight line, and the value of k_1 (min^{-1}) can be obtained from the slope of the graph.

The second-order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where: k_2 is the pseudo-second-order equilibrium rate constant (g/mg min). A plot of t/q_t as a function of t is linear, and the value of k_2 is determined from the slope and intercept.

The correlation coefficients (R^2) were used to determine the best fitting kinetic model. The computed results obtained from the first and second order kinetic models are presented in Table 1.

Table 1 Pseudo-first order and second order adsorption rate constant, and comparison of experimental and calculated q_e values for adsorption.

Dye	Sorbent	temp.* (K)	q_e (exp) (mg/g)	First order kinetic model		Second order kinetic model	
				q_e (calc) (mg/g)	$k_1 \cdot 10^3$ (min^{-1})	q_e (calc) (mg/g)	$k_2 \cdot 10^3$ (g/mg min)
PDP	Silver	298	2.81	2.63	11.95	3.00	5.61
		313	2.43	2.83	16.39	2.81	6.64
		333	1.92	2.51	13.84	2.1	7.82
	Beech	298	4.21	4.9	13.31	4.62	3.18
		313	3.55	5.06	16.86	4.25	3.23
		333	2.29	3.81	14.83	2.92	3.48
RDC	Silver	298	4.42	4.02	14.12	4.48	6.4
		313	3.91	4.45	15.52	3.83	7.15
		333	3.58	4.16	14.09	3.31	8.03
	Beech	298	4.93	5.64	14.74	5.01	3.59
		313	4.39	5.22	16.37	4.22	4.26
		333	3.77	4.46	15.01	3.64	4.51

As seen in Table 1, for the studied dyes adsorption on investigated adsorbents the best fit were obtained with the second order kinetic model, meaning that the adsorption process obeys the second order kinetic model. As the temperature was increased, an increase in the pseudo-second order rate constant k_2 was observed, indicating that the necessary time for reaching the equilibrium is reduced with increasing temperature.

Equilibrium isotherms

Dyeing is a complex process, although it was extensively studied, it was not satisfactory explained yet. The adsorption isotherms describe the way in which dyes interact with sorbents. The experimental data were fitted to the theoretical adsorption isotherms Freundlich, Langmuir, Sips and Redlich Peterson.

The analysis of the experimental data and determination of the parameters which describes the theoretical models were performed by the ORIGIN version 6.1. Program, principal statistical criteria were the standard deviation (SE) and the squared multiple regression coefficient (R^2). The best isotherm model that fits the experimental data with lower error was the Sips isotherm model (Table 2).

Table 2 Adsorption isotherms constants for the investigated dyes adsorption

Dye	Sorbent	Temp.	R^2				
			Freundlich	Langmuir	Sips	Redlich-Peterson	Dubinin-Radushkevich
PDP	Beech	298	0,8559	0,9223	0,9969	0,9178	0,8805
		313	0,8806	0,9411	0,9987	0,9372	0,9029
		333	0,9182	0,9593	0,9869	0,9522	0,9345
	Silver Fir	298	0,9147	0,9818	0,9982	0,9799	0,9362
		313	0,8997	0,9726	0,9973	0,9714	0,9242
		333	0,9279	0,9803	0,9973	0,9800	0,9466
RDC	Beech	298	0,9245	0,9462	0,9964	0,9462	0,9407
		313	0,9247	0,9476	0,9959	0,9476	0,9409
		333	0,9227	0,9576	0,9922	0,9576	0,9402
	Silver Fir	298	0,8715	0,9143	0,9980	0,9143	0,8931
		313	0,8966	0,9358	0,99831	0,9358	0,9162
		333	0,9014	0,9301	0,9971	0,9288	0,9184

This means that the adsorption process of investigated dyes is going on after a combined model Freundlich and Langmuir: diffused adsorption on low dye concentration, and a monomolecular adsorption with a saturation value - at high adsorbate concentrations. From the Sips sorption isotherm curves the maximum adsorption capacity of investigated adsorbents was determined (Table 3).

Table 3. Sips equation parameters

Dye	Sorbent	Temp. (K)	S_f (mol/kg)	n	K_s (L/mol)
PDP	Silver Fir	298	$3,886 \pm 0,093$	$0,345 \pm 0,029$	$4501,0 \pm 145,9$
		313	$2,850 \pm 0,136$	$0,466 \pm 0,069$	$4137,0 \pm 321,6$
		333	$2,090 \pm 0,179$	$0,674 \pm 0,207$	$3835,3 \pm 525,3$
	Beech	298	$4,576 \pm 0,095$	$0,628 \pm 0,044$	$5028,2 \pm 227,0$
		313	$3,291 \pm 0,099$	$0,572 \pm 0,057$	$4242,2 \pm 269,7$
		333	$2,366 \pm 0,114$	$0,530 \pm 0,077$	$3651,7 \pm 349,0$
RDC	Silver Fir	298	$9,576 \pm 0,197$	$0,390 \pm 0,019$	$1181,5 \pm 29,2$
		313	$7,037 \pm 0,208$	$0,408 \pm 0,030$	$1263,2 \pm 46,9$
		333	$5,172 \pm 0,244$	$0,424 \pm 0,050$	$1340,0 \pm 77,2$
	Beech	298	$11,310 \pm 0,132$	$0,334 \pm 0,013$	$2340,1 \pm 32,3$
		313	$9,084 \pm 0,188$	$0,348 \pm 0,021$	$2188,2 \pm 50,5$
		333	$7,296 \pm 0,264$	$0,361 \pm 0,034$	$2062,4 \pm 77,2$

The obtained values allow the following conclusions: adsorption capacity decreases in the order beech > silver fir, so we can say that the number of adsorption active centers decreases in the same order. As expected (adsorption is generally exothermic) the equilibrium constant (K_s) decreases with increasing temperature, which can be explained because at higher

temperature, increases the stored energy in different types of motion allowed, and weaken the physical binding forces of adsorbed molecules.

Conclusions

Adsorption of direct dyes from colored solutions on two natural sorbents was carried out at different working conditions. The best efficiency for removal of *PDP* and *RDC* dye was 48.38%, using *Beech* fibre. Increases of the amount of investigated fibres produced an increased in efficiency, and a decreased of the necessary time for reaching the equilibrium. Also, for the investigated natural fibres the adsorption capacity decreased with increasing the temperature. In case of using investigated sorbents, kinetics of adsorption follows the second-order kinetic model. The experimental data were well correlated by the Sips adsorption model, and the maximum theoretical adsorption capacities were determined

Although the yields of dye removal using natural supports are not significantly: 26.25 % for *beech* fibre, and 48.38 % for *fir* fibre, the lower prices of these supports (wastes from wood industries), and the ratio price/performance allow us to propose the investigated shavings as potential sorbents for removal of direct dyes from wastewaters.

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