

# Study of a Trisazo Direct Dye Adsorption on Wood Fibre Using a Comparison of Different Adsorption Isotherms

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*The purpose of this work was investigation of the dyeing mechanism of cellulose natural fibre with azo direct dyes. Two types of cellulose natural fibre - silver fir, beech - were investigated as potential adsorbents for a trisazo direct dye. The effect of dye concentration, temperature, and the adsorbent, on the adsorption was studied. Different adsorption isotherms models are used: Langmuir, Freundlich, Sips, Redlich-Peterson and Dubinin-Raduskevich. Statistical data analysis indicates that the better fitted model with the experimental data was the model described by Sips isotherm. The adsorption capacity values obtained for Sips isotherm were used for the calculation of the main dyeing thermodynamics parameters (affinity, enthalpy and entropy of dyeing).*

*Keywords: trisazo dye, dye adsorption, adsorption isotherms, thermodynamic parameter*

Dyeing and printing technology is one of the oldest occupations of the human being. Dyeing (tinctorial process) is a complex process [1, 2]; although it was extensively studied, it was not satisfactorily explained yet, different interpretation of this process being proposed. A tinctorial process implies several steps: dye diffusion from solution to external surface area, adsorption on the external surface of the fibre, diffusion into the fibre interior, and adsorption on the internally surface of the fibre [3]. The last step is the most important, dyeing process being conditioned by the nature and the size of dye-fiber established forces, meaning dye-fiber affinity. Some authors sustain that adsorption is a monomolecular process [4], while others demonstrated that it is a diffuse process, in multiple layers [5-7].

The vegetal origin textile fibers represent one of the most important group of materials with similar behavior in tinctorial process and great practical applications. Wood is a heterogeneous, hygroscopic, cellular and anisotropic material; it presents important mechanically, acoustically and isolating properties as well as esthetically qualities. Furthermore wood is a regenerative, biodegradable material, which implies low cost energy consumption for processing. It is composed of cells, and the cell walls are composed of microfibrils of cellulose (40 – 50%) and hemicellulose (15 – 25%) impregnated with lignin (15 – 30%). For all this reasons, wood presents an increasing interest, whereas the recent decade concern regarded the environment quality [8]. Silver fir is moderately soft and white, is a homoxil wood which contain only wooden vessels (parenchyma). Beech wood structure (hardwood) is more complex, consist of wooden vessels with different thickening types (spiral, reticulate, dotted), and wooden tissue elements (fibre, parenchyma) [9-11].

Direct or substantive dyes are water-soluble compounds, which have an affinity for cellulose fiber, and are taken up directly without any pre-treatment. Direct dyes derived by 4,4'-diaminobenzanilide are one of the newest class of direct dyes; they replace successfully benzidine dyes.

The purpose of the work was the experimental and theoretical study of the adsorption of a direct trisazo dye on two types of wood fibre. We investigated the adsorption of a direct dye derived from 4,4'-diaminobenzanilide, that fulfil all the structural characteristics of direct dyes: linear, oblong shape of molecule, coplanarity of molecule, the presence in molecule of soluble groups, and groups capable to establish hydrogen bonds with cellulose fibre.

## Experimental part

### Materials and method

Direct triazo dye VD with the molecular formula  $C_{36}H_{25}N_9O_{13}S_2$  (molecular weight 855) was chosen as adsorbate. VD dye was purified by several recrystallizations from distilled water and characterized by thin layer chromatography, electronic spectra and mass spectroscopy [12]. We investigated two types of wood fibre - silver fir and beech wood, as potential adsorbents for VD dye. The samples of wood as shavings, obtained from Gref Forest SRL, were first washed to remove any adhering dirt, kept in water for 24 h, and then were dried at room temperature. The samples weight was in every case 0.050 g. Scanning electron microscopy (SEM) was used for the structural characterization of the studied fibres using INSPECT-S scanning microscope, at 10 nm and 3 kV resolutions, in low- vacuum module.

The experimental study implied the assessment of the system variable values ( $t$ ,  $T$ ,  $C_0$ ), maintaining constant the other parameters (the weight of samples, electrolyte concentration, the dyeing bath volume), and determination of the final dye concentration in solution ( $C_s$ ), and in fibre ( $C_f$ ). Initial dyeing bath concentrations were from 0.008 g/L to 2.4 g/L. Electrolyte (sodium chloride) concentrations in the dyeing bath were in every case 4 g/L. The dyeings were performed at three different temperatures; 25, 45 and 65°C, in round flasks (100 mL), equipped with stirrer, and a thermometer.

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### Experimental evaluation of the time necessary for reaching equilibrium

The necessary time for reaching equilibrium, for each dyeing temperature, was evaluated in a series of preliminary experiments. This way, several identical dyeings were done, at different periods of time, varying from 1 to 12 h. The dyed samples were removed from the dyeing bath and rinsed in cold water to remove the surface adsorbed dye. The dye from the samples was extracted with several portions of 25% aqueous pyridine at about 80°C. The concentrations of the dye in the final solution, and in fiber were determined by means of UV-vis spectrophotometer (CECIL CE 7200) in the wavelength range 200 to 800 nm. When along with increasing the dyeing time, no change in the system was observed, the equilibrium was achieved. From this experiments we determined the equilibrium time; results are presented in table 1.

This equilibrium time was used as contact time in the isotherm experiments. The subsequent dyeing experiments were based on the results obtained in these preliminary experiments.

### Equilibrium experiments

In the sorption experiments adsorbents were added to dye solutions with different concentrations, varying between  $10^{-6}$  and  $10^{-3}$  M into glass flasks, and placed on a shaker at different temperatures, for a period of time determined in the preliminary experiments as being necessary and sufficient for reaching the equilibrium. The next steps were similar with those described in the preliminary experiments. The dye concentrations in the dyeing bath as well as for the

extracted dye from the substrate were established spectrophotometrically.

### Results and discussions

In this study we investigate adsorption of a triazo direct dye, derived from 4,4'-diaminobenzanilide: salicylic acid  $\leftarrow$  4,4'-diaminobenzanilide  $\rightarrow$  1-amino-8-hydroxi-3,6-naftalindisulfonic acid  $\rightarrow$  *p*-nitroaniline (VD), with the chemical structure shown in figure 1.

#### Analysis of the dyed samples

The investigated samples were analysed by SEM microscopy. In figure 2 are presented the SEM images of the studied fibres before (2.a., 2.b.), and after dyeing with VD dye. The SEM photographs of the coloured fibres (2.c, 2.d.) show a uniform coloration of the samples.

The coloured samples were examined with the electronic microscope. Looking at the microscope the dyed wood samples have a homogeneous colour. The studied samples consisting of vegetal tissues, with cellular wall impregnated with lignin, we couldn't establish an eventual selective affinity of the dye toward cellulose and lignin.

#### Adsorption isotherm

The study of dye distribution, at equilibrium, in solution and in the substrate is very important for the understanding of the mechanism of dyeing [13]. It is possible to express the results of experimental sorption measurements - dye concentration in fibre  $C_f$  (mol/kg) respectively in solution  $C_s$  (mol/L), in the form of equilibrium sorption isotherms. In figure 3 are presented the experimental results obtained for the VD dye adsorption on silver fir (3.a.), and on beech wood (3.b.), at three different temperatures 25, 45, and 65°C.

Table 1  
EQUILIBRIUM TIME AT 25, 45 AND 65°C FOR INVESTIGATED SYSTEMS

Dye_Fibre	Time (min)		
	T = 25°C	T = 45°C	T = 65°C
VD_Silver fir	285	230	175
VD_Beech wood	260	215	165

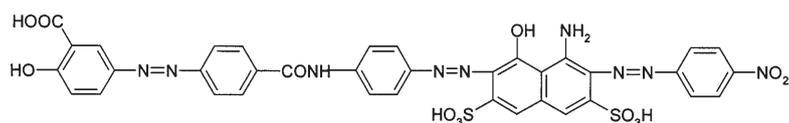


Fig. 1. Molecular structure of the direct green dye VD

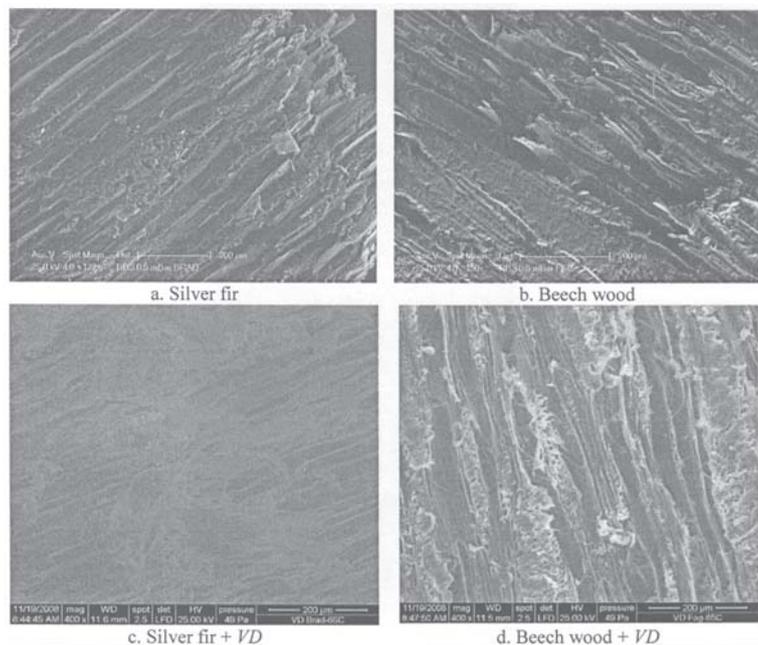


Fig. 2. SEM images of the natural fibre - silver fir, and beech wood, before (a, b), and after dyeing (c, d) with direct dye VD

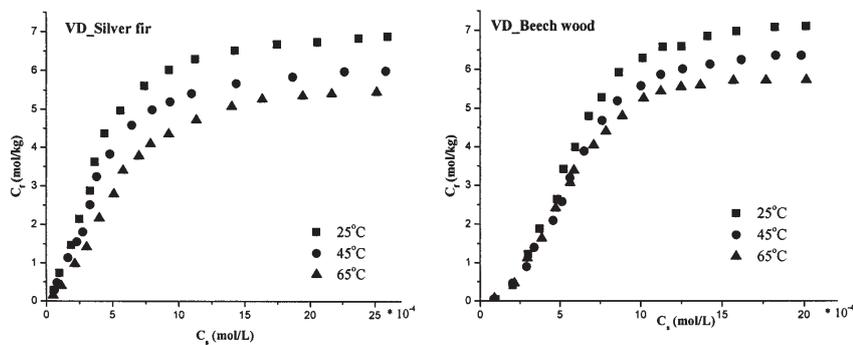


Fig. 3. Experimental adsorption isotherms of VD dye on silver fir (a), and beech wood (b)

The experimental data were fitted to the theoretical adsorption isotherms. In this study, we investigated five types of isotherms, namely Langmuir, Freundlich, Sips, Redlich-Peterson, and Dubinin-Raduskevich (tabel 2.).

Table 2

THEORETICAL ADSORPTION ISOTHERM MODELS INVESTIGATED

Isotherm	Equation
Langmuir	$C_f = \frac{S_f \cdot K_L \cdot C_S}{1 + K_L \cdot C_S}$
Freundlich	$C_f = K_F C_S^{1/n}$
Sips	$C_f = \frac{S_f \cdot (K_S \cdot C_S)^{1/n}}{1 + (K_S \cdot C_S)^{1/n}}$
Redlich-Peterson	$C_f = \frac{K_{RP} C_S}{1 + a_{RP} C_S^g}$
Dubinin-Raduskevich	$C_f = S_f \cdot e^{-B \cdot \varepsilon^2}$ $\varepsilon = RT \ln\left(1 + \frac{1}{C_S}\right)$

The comparison between experimental data and fit adsorption isotherm curves is presented in figure 4.

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. The

principal statistical criteria were the standard deviation (SE) and the squared multiple regression coefficient ( $R^2$ ). The SE and  $R^2$  values computed by non-linear curve fitting for the five types of isotherms are presented in table 3 for all adsorbents.

As can be seen, the best isotherm model that fits the experimental data with lower error was the Sips isotherm model. This means that the adsorption process of VD dye on studied adsorbents is going on after a combined model Freundlich and Langmuir: diffused adsorption on low dye concentration, and monomolecular adsorption with a saturation value - on high dye concentrations. Adsorption capacity decrease in order Beech wood > Silver fir, it means that the number of the adsorption active centers decrease in the same order.

#### Effect of temperature

Temperature plays an effective role in the adsorption of the dyes on natural fibres. The temperature range used in this study varied from 25 to 65°C. The maximum adsorption capacities of the silver fir and beech wood for VD dye adsorption from aqueous solution decrease with increasing the temperature (table 4); it means that increasing the temperature determine the decrease of the number of accessible pore.

Results obtained for Sips model were used for the calculation of the thermodynamic properties: standard free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ).

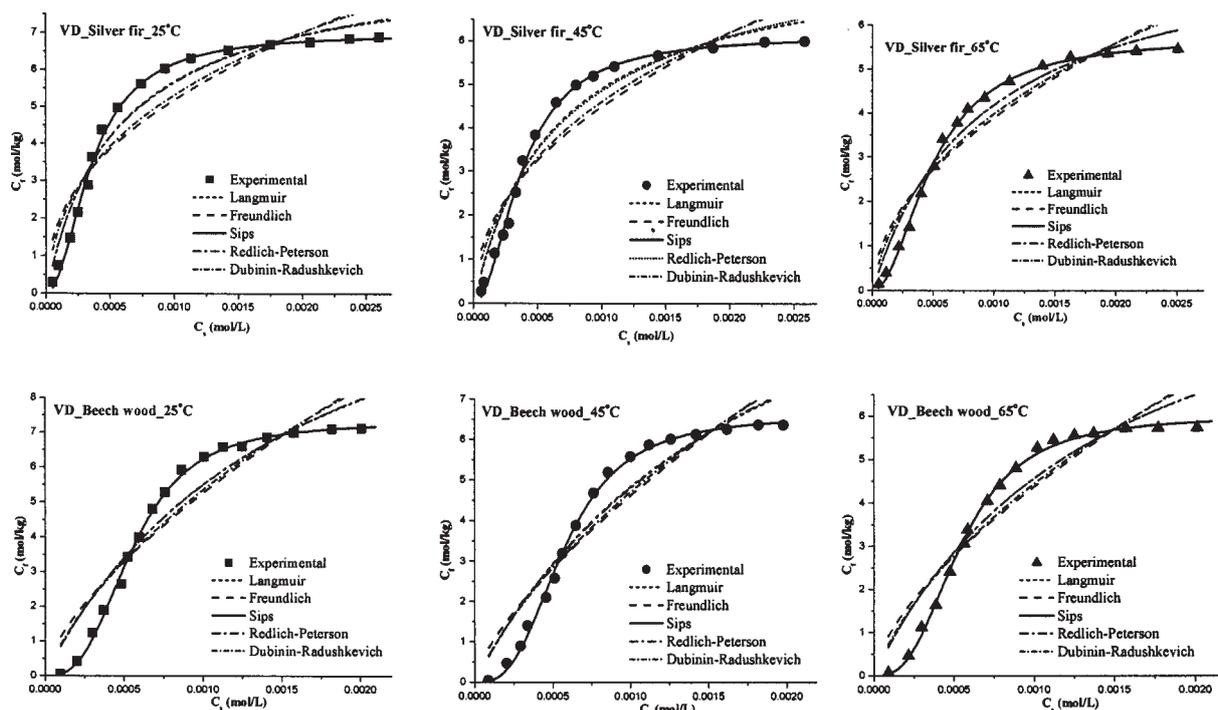


Fig. 4. Correlations between experimental data and different types of adsorption isotherms for VD dye adsorption on silver fir and beech wood, at 25, 45 and 65°C

Sorbent	Temp	Langmuir		Freundlich		Sips		Redlich-Peterson		Dubinin-Radushkevich	
		R <sup>2</sup>	SE	R <sup>2</sup>	SE	R <sup>2</sup>	SE	R <sup>2</sup>	SE	R <sup>2</sup>	SE
Silver Fir	25°C	0.959	0.236	0.872	0.755	<b>0.997</b>	<b>1.906</b>	0.957	0.253	0.903	0.573
	45°C	0.958	0.196	0.872	0.594	<b>0.996</b>	<b>1.894</b>	0.951	0.228	0.904	0.448
	65°C	0.964	0.135	0.903	0.367	<b>0.998</b>	<b>7.E-3</b>	0.964	0.136	0.928	0.271
Beech wood	25°C	0.919	0.531	0.874	0.829	<b>0.998</b>	<b>1.E-2</b>	0.918	0.542	0.897	0.678
	45°C	0.922	0.432	0.884	0.644	<b>0.998</b>	<b>1.E-2</b>	0.919	0.454	0.905	0.528
	65°C	0.922	0.329	0.873	0.537	<b>0.998</b>	<b>7.E-2</b>	0.921	0.334	0.896	0.437

**Table 3**  
GOODNESS OF FIT OF THE INVESTIGATED ISOTHERMS TO THE ADSORPTION EXPERIMENTAL DATA. VALUES CORRESPONDING TO BEST FIT ISOTHERMS ARE SHOWN IN BOLD

Dye	Sorbent	Temp. (K)	S <sub>r</sub> (mol/kg)	n	K <sub>s</sub> (L/mol)
VD	Silver fir	298	6.993 ± 8.9E-2	0.504 ± 2.5E-2	2755.58 ± 65.9
		318	6.134 ± 1.1E-3	0.507 ± 2.7E-2	2608.21 ± 76.9
		338	5.731 ± 7.5E-2	0.503 ± 1.9E-2	1977.8 ± 40.9
	Beech wood	298	7.317 ± 8.4E-2	0.342 ± 1.3E-2	1847.8 ± 24.8
		318	6.605 ± 8.7E-2	0.342 ± 1.5E-2	1815.84 ± 24.9
		338	6.011 ± 6.6E-2	0.357 ± 1.3E-2	1749.01 ± 27.6

**Tabel 4**  
SIPS ISOTHERM PARAMETERS FOR VD DYE ADSORPTION ON SILVER FIR AND BEECH WOOD, AT 25°, 45° AND 65°C

Dye	Sorbent	Temp. (K)	ΔG <sup>0</sup> (kJ/mol)	ΔH <sup>0</sup> (kJ/mol)	ΔS <sup>0</sup> (J/mol·K)
VD	Silver fir	298.15	-19.63	-7.068	42.5
		318.15	-20.79		
		338.15	-21.33		
	Beech wood	298.15	-18.64	-16.31	117
		318.15	-19.84		
		338.15	-20.98		

**Tabel 5**  
THERMODYNAMIC PARAMETERS FOR DYEING SILVER FIR AND BEECH WOOD WITH VD DYE

The change in ΔG<sup>0</sup> were calculated using equation (1)

$$\Delta G^0 = -RT \cdot \ln K_s \quad (1)$$

where  $K_s$  is Sips equilibrium constant,  $R$  is the gas constant, and  $T$  is temperature in Kelvin degrees [15].

The enthalpy (ΔH<sup>0</sup>) and entropy (ΔS<sup>0</sup>) were obtained from the slope and intercept of van't Hoff plots of ΔG<sup>0</sup> versus  $T$  [16]

$$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0 \quad (2)$$

The values are presented in table 5.

The negative values of ΔG<sup>0</sup> for all investigated systems indicate that the adsorption process is spontaneous. The negative values of ΔH<sup>0</sup> suggest exothermic adsorption of the VD dye on investigated wood fibre. From the ΔS<sup>0</sup> values can be appreciated that for VD dye + Silver fir system, the molecule orientation to bonding is more rigid (lower values of entropy).

## Conclusions

In this paper we investigated thermodynamic aspects regarding the mechanism of dyeing wood fibre with a direct dye - VD. The effect of dye concentration, temperature and the adsorbent on the adsorption was examined.

Five types of isotherms were investigated, namely Langmuir, Freundlich, Sips, Redlich-Peterson, and Dubinin-Radushkevich. The isotherm equation which best describes the adsorption of VD dye was determined according to the R<sup>2</sup> values. The Sips model was the best fit isotherm in all sorption systems. The thermodynamics parameters indicate a spontaneous and exothermic process for all studied systems.

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