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KINETIC CONSIDERATIONS OF TEXTILE DYES ADSORPTION FROM WATER ON A SORBENT FROM CELLULOSIC WASTE

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ABSTRACT. The synthesis of a new sorbent based on waste cotton cellulose and kinetics of adsorption of reactive textile dye from aqueous solution are the subject of the study in this manuscript. The sorbent is made of waste cotton fibbers collected from the textile plants for spinning yarn and weaving fabrics after being physically and chemically modified. Qualitative and quantitative characterization of the sorbent shows that carbon is dominant in the chemical composition. The sorbent used is a relatively finely divided material with heterogeneous porous particles, generally below 300 μm in size. Maximum adsorption capacity and the rate constant of the pseudo-second order generally depend on the amount of the cellulose-based sorbent, the initial dye concentration and the temperature. A new kinetic model based on the results of adsorption capacity and pseudo second order rate constant was defined. The low value of the activation energy means that the adsorption is mostly of a physical nature. Thermodynamic parameters, change of free Gibb's energy, change of enthalpy and change of entropy, as well as activation energy according to the standard equation confirm the adequacy of the new kinetic model of dye adsorption.

Keywords: *adsorption, reactive dye, pseudo-second order, cellulose-based sorbent, new kinetic model, thermodynamic parameters.*

INTRODUCTION

The textile industry is a significant exploiter of synthetic dyes used for dyeing and printing textiles in factory plants. Unfortunately, some of those dyes are carcinogenic and mutagenic because they were derived hazardous

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chemicals. In addition, the spillage of dyed liquid waste into the receiving waters affects their aesthetic nature, interferes with the transmission of sunlight and reduces photosynthetic activity, which jointly disturbs the natural balance by affecting the waters of the world and the food chain [1].

Development of new systems for treatment of synthetic dyes in wastewater, as well as the improvement of the existing ones, is closely related to the industrial and technological development. The main goal of any treatment method or procedure is to visually remove the dye first, and then to remove the dye residues until it is safe to release them into the watercourses or their reuse. It is usually the application of one or a combination of several procedures of physical, chemical and biological nature. Procedures that follow the nature and the natural way of removing pollutants are prioritized [2, 3].

Sorbents are used for wastewater treatment, which enable the control of sorption and desorption processes. Natural sorbents, such as clay, loam and ash have an insufficient, small specific particle surface of 200 $m^2 \cdot g^{-1}$ and sorbents based on granulated activated carbon and synthetic sorbents have a particle surface up to 2000 $m^2 \cdot g^{-1}$. The effect of adsorption on wastewater treatment is exceptional. Therefore, adsorption is usually applied for final fine water treatment [4-6].

The design and the scope of the adsorption system requires knowledge of the adsorption equilibrium, as well as the adsorption kinetics. Progress in understanding kinetics is limited by the theoretical complexity of the adsorption mechanism to a large extent. Many models of various complexities have been developed for predicting the sorption speed of adsorbate on a sorbent. Pseudo-first order and pseudo-second order models are the two most used empirical models in liquid adsorption studies [7].

Most of the papers are focused on the research of new materials that serve as sorbents in adsorption processes. Kinetic studies in those papers, in which the experimental data are fitted with suitable models, serve only as supplements in the assessment of the suitability of the sorbents. In an ideal case, the model should discover the speed limitation mechanism, with minimum complexity, and extrapolate the results to the operating conditions that are of interest [8, 9].

Specific research deals with the formation of a new sorbent based on waste cotton textiles and the adsorption of reactive dye kinetics in its own manner. Namely, a new kinetic model was proposed based on the analysis of parameters of importance, on mutual comparison, as well as on the assumptions about the relations that can be seen from the experimental results. Such research has not been the subject of study recently, nor have papers been presented related to a specific sorbent and a new model of kinetics.

RESULTS AND DISCUSSION

According to the applied procedure, the yield after modification of waste cotton fibbers into a cellulose-based sorbent ranged between 40-45%. Yield was calculated based on the differences in the mass of raw fiber and the final product–sorbent.

The surface morphology of the obtained cellulose-based sorbent is shown in micrograph, in Figure 1. The sorbent used is a relatively finely divided material with heterogeneous porous particles, of dispersed shape and form, generally below 300 µm in size. There are pronounced cracks, cavities and channels present in the depths of larger particles that represent the basis of the material micro porosity.

Apart from that, high porosity is characteristic for similar sorbents, and it is enabled precisely by the presence of particles of very irregular shapes, a high degree of amorphization and many voids in the structure. It is assumed that the dye molecules easily penetrate the interior of the particles through these pores and channels, where they are adsorbed on numerous internal active centres. The porous structure of the particle surface facilitates the diffusion of dye into the interior of the pores, which has been noted in other studies as well [10,11].

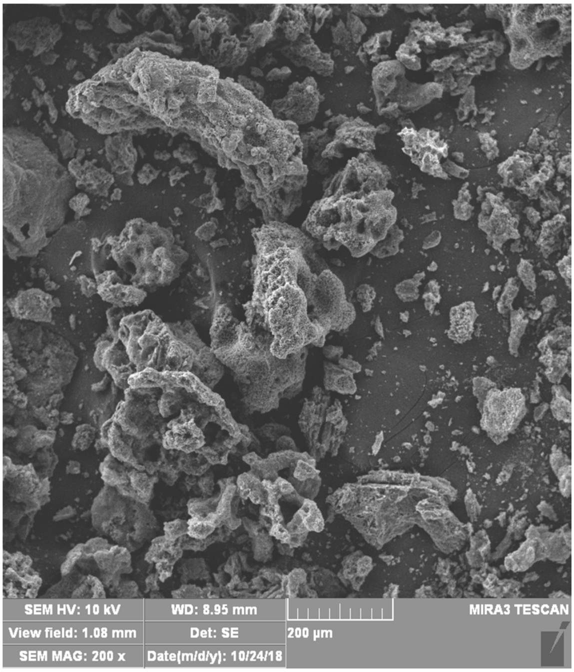

Figure 1. Micrograph of the applied cellulose-based sorbent

Table 1 shows the results of the quantitative composition of the sorbent, i.e., the percentage of one element in relation to the sum of all detected elements (EDS analysis). Based on the data, it can be concluded that carbon is dominant, while the greater presence of oxygen can be related to oxides of aluminium, silicon or aluminosilicate. However, since there is very little aluminium and silicon, it is assumed that the sorbent ability to react with oxygen from air is dominant.

Similar sorbents, active carbons exposed to air, are subject to adsorption of atmospheric oxygen, which results in an increase of the number of surface functional groups, such as phenolic, lactonic, carboxylic, etc. The presence of sulphur is interesting, which occurs, for instance, in the structure of active carbons in the elementary form, as well (usually up to 5 %) in the form of organic or inorganic compounds. Carbon complexes with sulphur, in the structure of active carbons, are very stable and they cannot be removed even at temperatures higher than 1100 °C, unless a reducing atmosphere of hydrogen is present [11,12].

Table 1. Cellulose-based quantitative sorbent composition based on EDS analysis

Spectrum	C	O	Na	Al	Si	S	Ca	Total
Mean	67.26	29.05	2.98	0.03	0.00	0.51	0.17	100.00
Std. deviation	1.44	2.02	0.47	0.04	0.00	0.27	0.10	-
Max.	69.53	31.15	3.49	0.09	0.00	0.72	0.29	-
Min.	65.84	26.04	2.41	0.00	0.00	0.22	0.07	-

Figure 2 shows the dependence of the percentage of dye removed (%Removal) and the adsorption capacity (q_t) on the initial dye concentration (C_0) during the 60-minute adsorption on a sorbent of mass 1 g. The % Removal decreases nonlinearly as the initial dye concentration increases, while the q_t increases linearly with increasing C_0.

In Table 2, comparative results of published research papers are shown for the degree of dye removal from aqueous solutions through the sorbent based on similar waste cellulosic material.

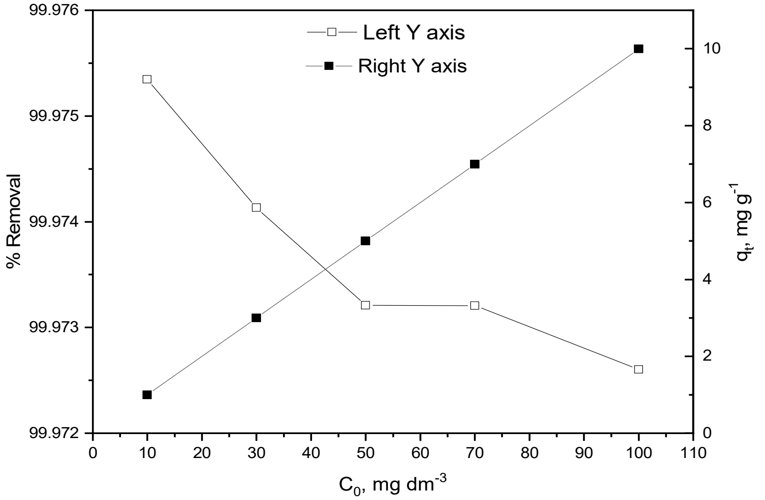

Figure 2. Influence of initial dye concentration on %Removal and q_t

Table 2. Comparative data for the degree of dye removal in different studies

Dye	Sorbent	%Removal	References
Reactive Blue 2	Based on waste cellulose	99	This research
Methylene blue	Activated carbon derived from pyrolysis of *Vetiveria zizanioides*	79	[13]
Congo red		69	
Reactive Blue 19	Agricultural waste of corn silk	84	[14]
Reactive Red 218		85	
Bezaktiv Red S-Max	Activated carbons from jujube stones	55	[15]
	Activated carbons from palm rachis	92	
Crystal violet	Elephant grass-based lignin	97	[16]

Figure 3 shows the examination results of reactive dye sorption kinetics on a cellulose-based sorbent for different amounts of sorbent and initial adsorbate concentrations in accordance with the pseudo-second order model. This model includes all phases of adsorption, such as the external diffusion, adsorption and internal diffusion in particles, since a pseudo model is in question. Since the reaction takes place in the adsorbed layer on the surface of the sorbent, the reaction rate depends on the concentration of the reactants in the layer on the sorbent surface.

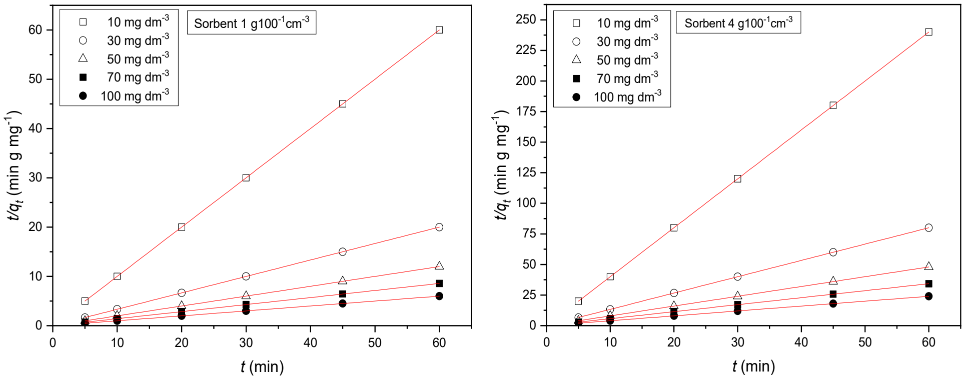

Figure 3. Reactive dye adsorption kinetics (pseudo-second order) at 20 °C for minimum and maximum amount of sorbent

Table 3 shows the results of kinetic parameters of the reactive dye adsorption for the smallest and largest amount of cellulose-based sorbent. The applicability or validity of the pseudo-second order kinetic model was valorized by the coefficient of determination. Since this parameter has a maximum value (R^2=1), it can be concluded that full functionality is achieved when the model can be fully used to describe the process of the reactive dye adsorption on a cellulose-based sorbent. In addition, the differences between the parameters $q_{e,cal}$ and $q_{e,exp}$ are minimal for this model, or practically insignificant. Similar results were obtained for the medium amounts of sorbent and for treatments at 40 and 60 °C.

Furthermore, according to the data from Table 3, the rate constant of the pseudo-second order depends on the initial dye concentration in the solution and the amount of sorbent.

Table 3. Kinetic parameters for reactive dye adsorption on cellulose-based sorbent

Sorbent amount g	Initial dye concentration mg·dm^{-3}	$q_{e,exp}$ mg·g^{-1}	Pseudo-second order, 20 °C		
			k_2 g·mg-1·min^{-1}	$q_{e,cal}$ mg·g^{-1}	R^2
1	10	0.9997	248.88	0.9998	1
	30	2.9992	82.35	2.9993	1
	50	4.9987	49.81	4.9987	1
	70	6.9981	34.92	6.9984	1
	100	9.9973	24.61	9.9980	1
4	10	0.2499	920.68	0.2500	1
	30	0.7499	310.89	0.7499	1
	50	1.2498	204.55	1.2498	1
	70	1.7496	153.36	1.7497	1
	100	2.4995	107.43	2.4996	1

Similar research confirms the above, namely the use of cheap and ecological bio-sorbents from agricultural cellulosic waste (lignocellulosic waste, activated carbons, textile sludge) has shown to be efficient for the adsorption of reactive dye from water. The kinetic pseudo-second order model stands out as the basic model in describing the sorption rate of the reactive textile dye [10,15, 17].

There is an interesting relationship between the adsorption capacity, that is the rate constant of the pseudo-second order from the amount of cellulose-based sorbent, initial dye concentration and temperature.

The analysis of the results of experimental studies of the dye adsorption kinetics of cellulose-based sorbent showed that the maximum adsorption capacity q_e and the rate constant of the pseudo-second order k_2 generally depend on the amount of the cellulose-based sorbent, the initial dye concentration and the temperature. Figure 4 illustrates the dependence of the adsorption capacity from the initial concentration at various sorbent amounts of the cellulose-based sorbent at a constant temperature (20 °C) with fitted straight lines. Identical dependence was detected at other temperatures (40 and 60 °C), so these relations are not shown in the graph.

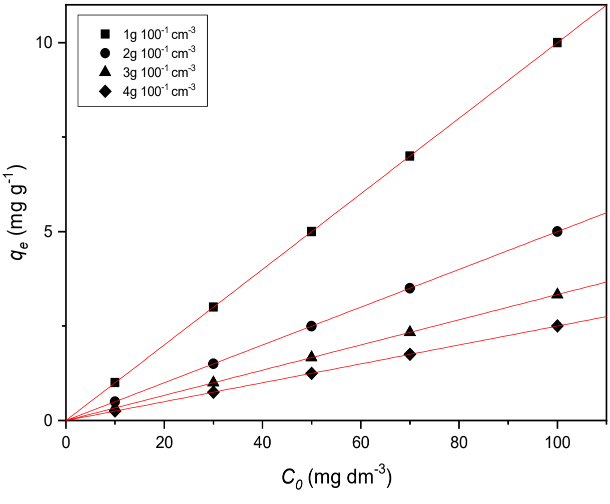

Figure 4. Dependence of the adsorption capacity on initial dye concentrations for different amounts of sorbent at 20 °C

According to the results shown in Figure 4, the maximum adsorption capacity increases linearly along with increasing the initial dye concentration, and the slope of the fitted lines decreases along with increasing the sorbent amount. The values of the slope of the fitted lines at different sorbent amounts at temperatures 20, 40 and 60 °C were calculated by the linear regression method and they are presented in Table 4. The data from this table indicate that the adsorption capacity does not depend on the temperature. The influence of temperature on adsorption is interesting. Namely, as the temperature increases, the speed of the chemical reaction increases, so if the process of suppression is hemi-sorption, then the sorption capacity will be higher at a higher temperature (equilibrium could occur). But if the process is physical adsorption, then higher temperatures could have negative adsorption results. Also, it should be considered that the temperature can chemically change the sorbent and its adsorption sites, as well as the adsorption activity. Better adsorption at higher temperatures may also indicate the endothermic nature of this process.

Table 4. The influence of sorbent amount and temperature on slope values fitted straight lines

Sorbent amount g·100-1·cm^{-3}	**Slope, dm^3·g^{-1}**		
	20 °C	**40 °C**	**60 °C**
1	0.09997	0.09997	0.09998
2	0.04999	0.04999	0.04999
3	0.03333	0.03333	0.03333
4	0.02499	0.02500	0.02500

Figure 5 shows a graph of the dependence of the slope or the proportionality constant on the sorbent amount, *w*. As in graph from Figure 5, the fitted straight lines completely coincide for various temperatures, while the slope value of these fitted lines decreases with the increase of the sorbent amount.

The following dependence between the maximum capacity of adsorption and the initial concentration exists:

$$q_e = Slope \cdot C_0 \tag{1}$$

The proportionality constant or slope from the equation (1), depends on the sorbent mass, *w*:

$$Slope = f(w) \tag{2}$$

Since the logarithmic scale of the abscissa and ordinates is shown in the graph of Figure 5, then:

$$Slope = k \cdot w^m \tag{3}$$

$$\log(Slope) = \log(k) + m \cdot \log(w) \tag{4}$$

where: *K* – is the proportionality constant (from the graph in Figure 5).

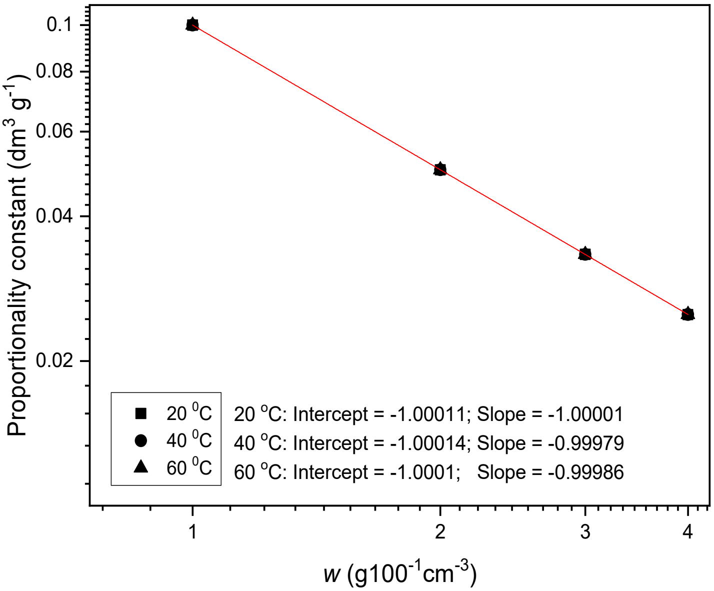

Figure 5. Dependence of the proportionality constant (slope) of fitted straight lines on the sorbent amount for all temperatures

Furthermore, numerous slope and segment values for all temperatures obtained by the linear regression method are entered in the graph of Figure 5. It can be noticed that these numerous values overlap to a large extent. After rounding the digits, without major errors, it can be said that the segment and the slope have the same numerical value, -1 each (the segment has a numerical value -1, the slope has a numerical value of -1), for all temperatures:

$$\log(Slope) = -1 - 1 \cdot log(w) \tag{5}$$

$$\log(Slope) = -1 + log\left(\frac{1}{w}\right) \tag{6}$$

$$Slope = 0.1 \cdot \frac{1}{w} \tag{7}$$

After the transformation of equation (1) the following is obtained:

$$q_e = \frac{0.1}{w} \cdot C_0 \quad \text{i.e.} \quad q_e = 0.1 \cdot \frac{C_0}{w} \tag{8}$$

The graph in Figure 6 illustrates the dependence of the pseudo-second order rate constant from the initial concentration at different amounts of cellulose-based sorbent at 20 °C; identical dependence was observed at other temperatures (40 and 60 °C). The value of the pseudo-second order rate constant decreases when increasing the initial dye concentration and the decrease of the sorbent amount when increasing the temperature.

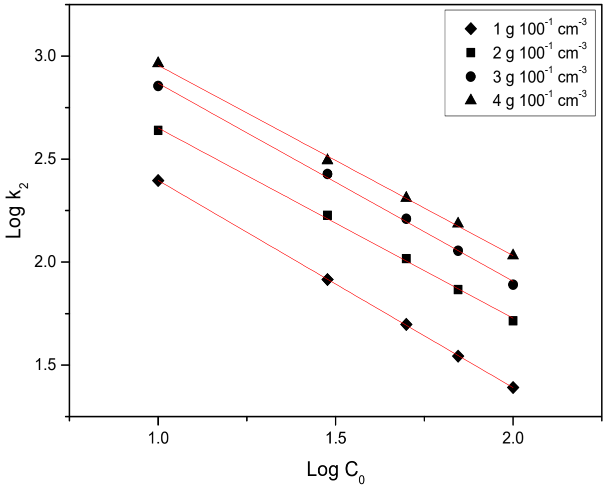

Figure 6. Dependence of the pseudo-second order constant rate on the initial dye concentration at a constant temperature (20 °C)

Based on the previous results and the presented dependencies, it is assumed that there is a complex dependence of the following form between the rate constant of the pseudo-second order and the amount of the cellulose-based sorbent, the initial dye concentration and the temperature:

$$k_2 = A_1 \cdot w^m \cdot C_0^n exp\left(-\frac{E_a}{R \cdot T}\right) \tag{9}$$

Equation (9) is first transformed into a linear form:

$$\ln(k_2) = \ln(A_1) + m \cdot \ln(w) + n \cdot ln(C_0) - \frac{E_a}{R} \cdot \frac{1}{T} \tag{10}$$

The multiple linear regression method (Table 5) was used to calculate the parameter values of the equation (10) *m*, *n* and E_a. Analysis of variance (ANOVA) showed that all factors and the model itself were statistically significant, with the probability of 95% (Table 5 and 6). Furthermore, the coefficient of determination and the adjusted coefficient of determination have the same values, close to 1 (0.997).

Based on the results of multiple linear regression, the following mathematical dependence was determined between the rate constant of the pseudo-second order and the amount of the cellulose-based sorbent, the initial dye concentration and the temperature:

$$\ln(k_2) = 8.32756 + 1.02005 \cdot \ln(w) - 0.95763 \cdot ln(C_0) - 196.73 \cdot \frac{1}{T} \quad (11)$$

that is:

$$k_2 = 4136.3 \cdot w^{1.02} \cdot C_0^{-0.96} exp\left(-\frac{196.73}{T}\right) \quad (12)$$

Therefore, the pseudo-second order rate constant is directly proportional to the amount of cellulose-based sorbent and inversely proportional to the initial dye concentration, whereas the effect of temperature is in accordance with *Arrhenius'* exponential law.

The value of activation energy (E_a) can easily be calculated from the equation (12). For the observed system it is 1.63 kJ·mol^{-1}. A low value of Ea means that the adsorption of dye on the sorbent is mostly of a physical nature. On the other hand, lower E_a may indicate the fact that the increase in the reaction rate is achieved according to: facilitated electron transfer, moving to a more favorable position in the system, larger cellulose-based sorbent–dye molecule, better mutual orientation, etc. [11].

Table 5. Results of applying the multiple linear regression method for calculating the parameters of mathematical expression of new kinetic model

Parameter	Value	Error	t- Value	Prob>|t|
Y- Intercept	8.32756	0.13645	61.02974	<0.0001
w	1.02005	0.01326	76.90882	<0.0001
C_0	-0.9576	0.00862	-111.06828	<0.0001
$1/T$	-196.73	41.2291	-4.77173	<0.0001
R-Square(COD)	Adj. R-Square	Root-MSE(SD)	-	-
0.997	0.997	0.05349	-	-

Table 6. ANOVA for the observed system cellulose-based sorbent–reactive dye

Item	Degrees of Freedom	Sum of Squares	Mean Square	F Statistic	Prob>F
Model	3	52.28	17.43	6091.3	<0.0001
Error	56	0.16	0.00286	-	-
Total	59	52.44	-	-	-

To check the previous modelling and analysis, thermodynamic parameters (changes in free energy, enthalpy and entropy) and activation energy (for maximum initial dye concentration, 100 mg·dm^{-3} and sorbent amount of 1 g) were calculated according to standard calculation formulas (equation 15).

Graph ln(k_2/T) versus 1/T gives a straight line with slope -$\Delta H/R$ and intercept $ln\left(\frac{k_b}{h}\right)+\frac{\Delta S}{R}$ from which enthalpy and entropy changes were calculated, shown in Figure 7. Coefficient of determination is was 0.997, which is excellent functionality for accepting results.

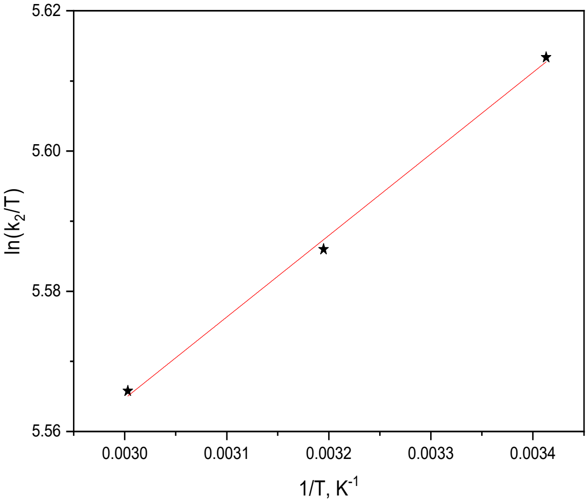

Figure 7. Dependence graph ln(k_2/T) of 1/T for calculating thermodynamic parameters

After the calculation (equation 15, 16), the following data were obtained: ΔS is -0.15 кJ·K^{-1}·mol^{-1}, ΔH = -0.97 kJ·mol^{-1}, while the change in free energy, ΔG, has values of 30.1, 32.2 and 34.4 kJ·mol^{-1}, for 20, 40 and 60 °C, respectively.

As entropy is a state that can be viewed as a measure of the "bound" energy of a closed material system, negative changes in entropy change correspond to a decrease in the degree of freedom of adsorbed dyes, i.e., indicate that the disordered system on the particle-solution interface is reduced during the adsorption of dye on the sorbent [18].

Negative and relatively small values for enthalpy change indicate the exothermic nature of the adsorption interactions of applied dye and sorbent and a stable energy process. Variations in values for individual adsorption conditions should be explained by the fact that the bonds between bulky adsorbate molecules and the sorbent surface are broken, since the adsorbed dye molecules are not firmly bound to the sorbent surface.

The small value of the required amount of heat (-0.97 $kJ\cdot mol^{-1}$) characterizes mainly the phenomenon of physisorption. The enthalpy of physical sorption ranges up to 20 $kJ\cdot mol^{-1}$ while the change in enthalpy of chemisorption ranges from 40 to 400 $kJ\cdot mol^{-1}$ and mainly depends on the nature of the sorbent. Chemisorption is slower than physisorption and is irreversible. Physical sorption is usually a reversible and fast process (does not require activation energy), which takes place at low temperatures [19].

The change in free *Gibb's* energy increases continuously with increasing temperature and has a positive value, which means that the adsorption of dye to the sorbent is unspontaneous but feasible. The results are explained by the fact that the entropy of adsorption plays a leading role in this case, namely the driving force of the adsorption process is more dominant than the force of chemical bonding [20].

From the graphical relation, $\ln(k_2) : 1/T$, the value of factor A (47.92 $g\cdot mg^{-1}\cdot min^{-1}$) and activation energy (E_a = 1.62 $kJ\cdot mol^{-1}$) were calculated, shown in Figure 8. Determination coefficient for this dependence is 0.996, so the results, statistically, are absolutely accepted.

According to the numerical value, E_a is very small, so it can be said that the adsorption reaction is very fast, which is confirmed by the very fast and high adsorption of the dye. It is known that if the calculated activation energy is less than 40 $kJ\cdot mol^{-1}$, the reaction rate is fast; if greater than 120 $kJ\cdot mol^{-1}$, the reaction rate is quite slow [20].

The value of activation energy gives an idea of the type of adsorption, which is mostly physical or chemical. It is known that the activation energy corresponds to the physical sorption mechanism in the range up to 40 $kJ\cdot mol^{-1}$, while the range from 40 to 800 $kJ\cdot mol^{-1}$ suggests the chemisorption mechanism [21].

If we compare the values of activation energy from the new kinetics model (E_a = 1.63 $kJ\cdot mol^{-1}$, according to equation 12) and the calculated activation energy (E_a = 1.62 $kJ\cdot mol^{-1}$, according to equation 17), absolute concordance of values is observed, which confirms the adequacy and applicability of the new model for adsorption rate.

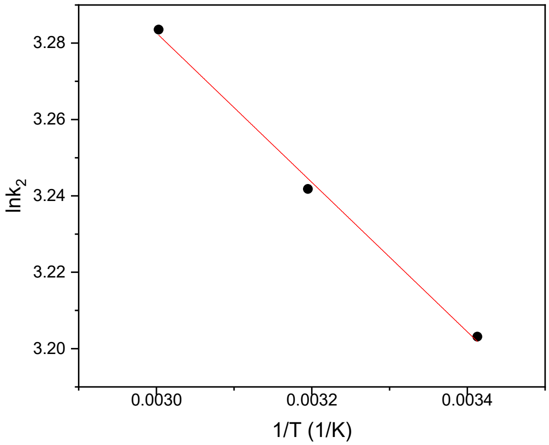

Figure 8. Dependence graph ln(k_2) : 1/T to calculate activation energy

CONCLUSION

In the research presented in this manuscript, the two most significant goals were achieved. A cheap sorbent was obtained from waste cotton textiles and a new mathematical model was formed that describes the adsorption kinetics in this case.

Furthermore, the applied unconventional and cheap sorbent from natural waste indicates high values of adsorption capacity, as well as high affinity for the reactive dye. The kinetics of adsorption of reactive dye followed the pseudo-second order model. Also, the new model of adsorption kinetics has been established, the pseudo-second order constant rate is almost directly proportional to the amount of the cellulose-based sorbent, inversely proportional to the initial concentration of the reactive dye, whereas the temperature effect is in accordance with the *Arrhenius'* exponential law.

Thermodynamic parameters, changes in free energy, enthalpy and entropy clarify and confirm the validity of the new kinetic model. The change in free energy has a positive value, which reflects the spontaneity but feasibility of the adsorption process. Negative and small value for enthalpy change reveals the exothermic nature of adsorption interactions and a stable energy process with the existence of physisorption. Negative values of entropy change indicate a decrease in the disordered system at the interface during dye adsorption on the sorbent. Very close values between the activation energy from the kinetic model and the calculated activation energy confirm the adequacy and applicability of the new kinetic model for the specific case of adsorption.

EXPERIMENTAL SECTION

The sorbent was obtained by chemical and physical modifications of cotton waste from textile plants, spinning mills and weaving mills (Jumko, Serbia). After the collection, the textile waste (short cotton fibers) was washed with Felosan NKB (CHT, Germany) in warm distilled water (60 °C). After drying, chemical modification was performed by impregnating textile waste with phosphoric acid solution (85%, Tehnohemija, Serbia); the size of the bath was 1:5, and it was kept in a desiccator for 48 h at room temperature with occasional manual stirring. After squeezing, physical modification followed, the samples were placed in stainless steel containers and annealed at 600 °C for 2 hours in the presence of air. After cooling, it was rinsed with distilled water and neutralized with a solution of baking soda until a neutral reaction. Finally, drying (100 °C) to dryness and manual grinding was performed. The sorbent based on cellulose in powder form obtained was used for research.

The adsorption test was performed in glass reactive vessels in which the cellulose-based sorbent was suspended in a reactive dye solution (adsorbate). The reaction vessels were placed on a circular motion shaker (the speed of the shaker rotation was 130 rpm) at temperatures of 20, 40 and 60 °C and they were kept for a certain period. The sorbent amount was constant, 1, 2, 3 and 4 g, whereas the amount of the solution constantly of 0.1 dm^3, contained a reactive dye of the following concentration: 10, 30, 50, 70 and 100 $mg \cdot dm^{-3}$. The processing period, with continuous stirring, was 5, 10, 20, 30, 45 and 60 min. The pH of the aqueous dye solution was adjusted at 2-3. The time of 60 min was taken as the equilibrium time because afterwards (a check went up to 120 min) there was no significant change in the amount of the adsorbed dye on the sorbent.

Measurement of the solution adsorption was performed on a UV-VIS spectrophotometer (Cary 100 Conc UV-VIS, Varian) at 620 nm (maximum wavelength of the spectrum of the solution used).

SEM measurements were performed on a TESCAN MIRA3 microscope, using a secondary electron detector, and EDS detector was used for measuring characteristic X-rays of the main elements.

The chemical structure of the reactive dye used, Reactive Blue 2 ($C_{29}H_{17}ClN_7Na_3O_{11}S_3$, M=840.11 $g \cdot mol^{-1}$) is shown in Figure 9.

It is well-known that reactive dyes are dyed substances having groups capable of rewarding covalent connections between carbon ions or dye molecules and oxygen, nitrogen or sulphur atoms from hydroxyl, amino or methanethiol groups of the corresponding substrate–textile fibers [13].

According to the structure from Figure 9, it can be noticed that it is an anthraquinone dye (anthraquinone or anthracene derivate) by a self-chlorotriazine ring via which this dye binds to a fiber (cellulose), via a chlorine atom.

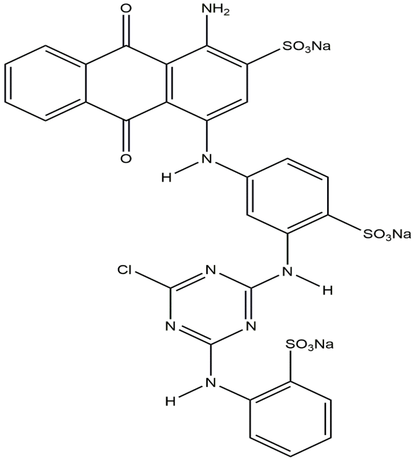

Figure 9. Structure of the applied reactive dye Reactive Blue 2

The adsorption capacity or amount of the adsorbed dye (adsorbate) per unit mass of sorbent in time t (q_t) or equilibrium balance (q_e) is determined [22] by the following expressions:

$$q_{t,e} = \frac{(C_o - C_{t,e}) \cdot V}{w} \qquad (13)$$

where: C_0 – is the initial adsorbate concentration ($mg \cdot dm^{-3}$), $C_{t,e}$ – equilibrium concentration of the adsorbate after time t and in equilibrium, respectively ($mg \cdot dm^{-3}$), w – sorbent mass (g) and V – volume of adsorption solution (dm^3).

Pseudo-second order model [14] describes the adsorption kinetics as follows:

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot (t) \qquad (14)$$

where: k_2 – is the constant rate of the second order adsorption ($g \cdot mg^{-1} \cdot min^{-1}$), q_e,q_t – the capacity of adsorption in equilibrium and after time t, respectively ($mg \cdot g^{-1}$).

The graph t/q_t towards t provides a straight line for all applied dye concentrations, whereby the applicability of the pseudo-second order equation is confirmed. The values k_2 and the equilibrium capacity of adsorption q_e were calculated from the segment and the slope of the dependence graph curve t/q_t to t, respectively.

Thermodynamic parameters for adsorption systems were calculated using the following equations [23]:

$$ln\left(\frac{k_2}{T}\right) = ln\left(\frac{k_b}{h}\right) + \frac{\Delta S}{R} - \frac{\Delta H}{R \cdot T} \tag{15}$$

$$\Delta G = \Delta H - T \cdot \Delta S \tag{16}$$

where: k_2 - second order adsorption rate constant ($g \cdot mg^{-1} \cdot min^{-1}$); T - temperature (K); k_b - *Boltzmann* constant ($1.38065 \cdot 10^{-23}$ $J \cdot K^{-1}$); h - *Planck* constant ($6.626 \cdot 10^{-34}$ $J \cdot s$); ΔS - entropy change ($J \cdot K^{-1} \cdot mol^{-1}$); R - universal gas constant (8.314 $J \cdot K^{-1} \cdot mol^{-1}$); ΔH - enthalpy change ($J \cdot mol^{-1}$); ΔG - change of free *Gibb's* energy ($J \cdot mol^{-1}$).

Activation energy is calculated according to the formula [20]:

$$\ln k_2 = \ln A - \frac{E_a}{R \cdot T} \tag{17}$$

where: E_a activation energy ($J \cdot mol^{-1}$); k_2 - second order adsorption rate constant ($g \cdot mg^{-1} \cdot min^{-1}$); A - frequency factor or frequency sorption factor ($g \cdot mg^{-1} \cdot min^{-1}$).

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