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Removal of Rhodamine B (A Basic Dye) and Acid Yellow 17 (An Acidic Dye) from Aqueous Solutions by Ordered Mesoporous Carbon and Commercial Activated Carbon

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Abstract: In this work, adsorption of rhodamine B (RB) and acid yellow 17 (AY17) was investigated on ordered mesoporous carbon material obtained by soft-templating method with hydrochloric acid (ST-A). For comparison, the adsorption process on commercial activated carbon CWZ-22 was also carried out. The sorbents were characterized by nitrogen adsorption/desorption isotherms and scanning electron microscopy. Langmuir and Freundlich adsorption isotherm models were applied to simulate the equilibrium data of RB and AY17. Adsorption isotherm data could be better described by the Langmuir model than the Freundlich model. The adsorption kinetics of RB and AY17 on studied carbons could be well depicted by using pseudo-second-order kinetic modeling. The adsorption capacity increased with temperature increase in the range of 298–315 K. In the whole diffusion process, the intraparticle diffusion was involved, but not the whole rate-controlling step. The calculated thermodynamic parameters, including Gibbs free energy (Δ G), enthalpy (Δ H), and entropy (Δ S) suggested that adsorption processes of RB and AY17 on ST-A and CWZ-22 were endothermic and spontaneous.

Keywords: ordered mesoporous carbon; activated carbon; dye; adsorption; kinetic; thermodynamics

1. Introduction

Water is needed for life. Different pollutants (including dyes) from a constantly evolving industry get into water [1]. In the textile and dye industry, synthetic dyes are very often used and, unfortunately, have a harmful effect on human and animal health [2]. These colorful compounds affect the change in the color of water and, thus, have a detrimental effect on fauna and flora [3]. Many of them, even at low concentrations, have toxic and carcinogenic effects and can affect water organisms and the digestive system of humans [4]. They are extremely resistant to the effects of temperature, light, and other factors, such as chemicals, and are therefore extremely difficult to remove [5]. Many techniques [6–9] used in wastewater treatment are known, but adsorption, due to its many advantages, is most commonly used. The adsorption process is primarily simple and has many economic advantages, but it is worth considering that it catches toxic substances at very low concentrations [1,10].

Rhodamine B and acid yellow 17 are widely used in food, paper and textile dyes industry, among others. Due to the carcinogenic nature, the use of RB was prohibited. However, this has changed and although RB carries a risk to human and animal health, it is being used again, especially in the textile industry. AY17 is also used for the production of personal care, laundry, and cleaning agents [11,12].

Nowadays, the key is to exploit selective and efficient adsorbents that will adsorb dyes from the aquatic environment in the shortest possible time and with the highest efficiency [3,13].



In recent years, many studies have been carried out on the adsorption of dyes on various carbon adsorbents [14–26], on waste materials (vegetable waste, fruit waste, agricultural and industry waste, natural inorganic materials, and bioadsorbents) [27–32], and on synthetic carbon materials such as carbon nanotubes [33,34], ordered mesoporous carbons (OMCs) [35–42], and others.

OMCs, due to their unique properties, are gaining more and more interest in adsorption processes. They are characterized by high specific surface area, large pore volume, and good mechanical stability [3].

In this work, ordered mesoporous carbon material ST-A and commercial adsorbent (activated carbon CWZ-22) have been studied for the removal of RB and AY17 from aqueous solutions. The surface properties of applied adsorbents were characterized by the methods: nitrogen adsorption isotherms and scanning electron microscopy (SEM). The efficiency of the adsorption process was analyzed based on the effect of contact time, initial dye concentration, and temperature. Adsorption isotherm models (Langmuir and Freundlich), were used to analyze the experimental data. Three various kinetic models (pseudo-first-order, pseudo-second-order, and intraparticle diffusion model) for the adsorption of dyes are also presented. In addition, thermodynamic parameters were calculated to better explain the adsorption process.

2. Materials and Methods

2.1. Materials

RB ($C_{28}H_{31}ClN_2O_3$) with molar weight 479.01 g·mol⁻¹ and AY17 ($C_{16}H_{10}Cl_2N_4Na_2O_7S_2$) with molar weight 551.29 g·mol⁻¹ (Sigma-Aldrich, Darmstadt, Germany) were used as the adsorbates. The maximum wavelength of the dyes are 553 and 402 nm, respectively. The structural formulas of dyes are presented in Figure 1a,b.



Figure 1. Structural formulas of rhodamine B (RB) (a) and acid yellow 17 (AY17) (b).

Mesoporous carbon, obtained by the soft-templating method with hydrochloric acid, was prepared using a slightly modified synthesis procedure described in the work of Choma et al. [43], and used as the adsorbent. During the synthesis of the adsorbent, silver nanoparticles were not added and the Pluronic F127 triblock copolymer was used instead Lutrol F127. The remaining stages of the synthesis were analogous to [43]. For comparison, the adsorption process on commercial activated carbon CWZ-22 from GRYFSKAND (Hajnowka, Poland) was also carried out.

2.2. Characterization of Adsorbents

Low-temperature nitrogen adsorption/desorption isotherms were measured at -196 °C on an ASAP 2020 volumetric analyzer (Micromeritics Inc., Norcross, GA, USA) in the Structural Research Laboratory of Jan Kochanowski University in Kielce. Before the measurements, all samples were degassed at 200 °C for at least 2 h. Using experimental low-temperature nitrogen adsorption

isotherms for studied adsorbents, standard parameters of the porous structure were determined [44–50]. Brunauer–Emmett–Teller (BET) method was involved for investigated carbon materials specific surface area determination. S_{BET} was calculated in the range of relative pressure from 0.05 to 0.2, considering the surface occupied by a single molecule of nitrogen in an adsorptive monolayer (cross-sectional area equal 0.162 nm²) [44]. The sum of micropores volume (V_{mi}) and mesopores (V_{me}), being the total pore volume (V_t), was determined from one point of nitrogen adsorption isotherm, corresponding to the relative pressure p/p₀ equal to 0.99 [45]. The pore size distribution functions (PSDs) were calculated from the adsorption branch of isotherms using the Kruk-Jaroniec-Sayari (KJS) method [49] based on the Barrett–Joyner–Halenda (BJH) calculation procedure for cylindrical pores [50].

SEM images were taken using a scanning electron microscope manufactured by Zeiss (Germany) mod. Ultra Plus, EDS Bruker Quantax 400. It is a high-resolution low energy microscope with field emission Schottky cathode. The applied voltage of measurements was 2 kV.

The functional acidic and basic groups on the studied carbon materials were determined using Boehm's titration method [51,52]. According to Boehm's method, sodium bicarbonate can neutralize carboxyl groups; sodium carbonate can neutralize carboxyl and lactone groups; sodium hydroxide can neutralize carboxyl, lactone, and phenol groups; sodium ethoxide can neutralize carboxyl, lactone, phenolic, and carbonyl groups; and hydrochloric acid can neutralize total basic groups. The obtained carbon materials (0.2 g) were dispersed in the following solutions: sodium bicarbonate, sodium carbonate, sodium ethoxide, and hydrochloric acid. Then, each solution with carbon material was shaken for 48 h at room temperature. The sample was then filtered, and 10 mL of filtrate were titrated with 0.1 mol dm⁻¹ HCl to determine acidic groups and 0.05 mol dm⁻¹ NaOH to determine total basic groups.

2.3. Adsorption Experiments

For adsorption investigations, ST-A (with grain size from 0.2 to 0.8 mm) and commercial activated carbon were applied. Before experiments, all carbon materials were dried in the laboratory dryer at temperature 373 K to constant masses. The parameters presented in Table 1 were applied for adsorption isotherms and adsorption kinetic experiments. Concentrations of RB and AY17 were determined in solution at a maximum adsorption wavelength of 553 and 402 nm respectively, before and after adsorption, using the spectrophotometric method by spectrophotometer SP-830 Plus from Metertech. Adsorption processes were performed in a 100 mL Erlenmeyer's flask. To each flask, 0.1 g of studied carbon and 50 cm³ of RB or AY17 with defined concentration were added. Next, the flasks were placed in the incubator for specified time (Table 1). The adsorption capacities of studied carbon for RB and AY17 were calculated applying Equation (1):

$$q_e = \frac{(C_0 - C_e)}{m} \tag{1}$$

where q_e is the RB or AY17 adsorption capacity (mg g⁻¹); C_0 is the concentration of RB or AY17 in solution before adsorption (mg dm⁻³); C_e is the concentration of RB or AY17 in solution after adsorption (mg dm⁻³); V is the volume of the dye solution used for adsorption process (dm³); and m is the carbon mass (g).

Experimental Item	Studied Carbon	RB Solution Concentration (mg dm ⁻³)	AY17 Solution Concentration (mg dm ⁻³)	Sampling Time (min)	Temperature (K)	Vibration Rate (rpm)
Adsorption isotherms	ST-A	30–730	30-310	RB: 360, 240, 180 AY: 240, 180, 120	298, 308, 315	200
	CWZ-22	30–730	30–310	RB: 420, 360, 180 AY: 360, 240, 180	298, 308, 315	200
Adsorption kinetics	ST-A	15	30	RB: 15, 30, 45, 60, 120, 180, 240, 360, 420 AY: 15, 30, 45, 60, 120, 180, 240, 360	298, 308, 315	200
	CWZ-22	15	30	RB: 15, 30, 60, 120, 180, 360, 420, 480 AY: 15, 30, 45, 60, 120, 180, 240, 360, 420	298, 308, 315	200

Table 1. The adsorption isotherms and kinetics—conditions and runs.

3. Results and Discussion

3.1. Characterization of Adsorbents

Nitrogen adsorption isotherms are shown in Figure 2a. According to IUPAC classification of adsorption isotherms [53], the experimental isotherm for studied ST-A material is type IV, which is characteristic for mesoporous solids. The H1 hysteresis loops confirm the presence of accessible mesopores. The isotherm for CWZ-22 carbon is type I. A type I isotherm indicates high adsorption in the range of low relative pressures, i.e., refers to adsorbents with highly developed microporosity (porosity, which forms pores with linear dimensions less than 2 nm). In the area of medium and high relative pressures, the isotherm for CWZ-22 carbon has a course almost parallel to the abscissae axis, which indicates that mesoporosity (pores with dimensions of 2 to 50 nm) is poorly developed [54]. The type H4 hysteresis loop for CWZ-22 carbon is associated with narrow slit pores.



Figure 2. Nitrogen adsorption isotherms (**a**) and pore size distribution functions (PSDs) (**b**) for studied carbon materials.

Pore size distribution functions (PSDs) for the adsorbents studied are shown in Figure 2b. The PSD curve for the carbon ST-A exhibit two maxima. The first, occurring for pore sizes 1.83 nm, corresponds to the width of micropores, whereas the second, for pore sizes 9.24 nm, corresponds to the width of mesopores. The PSD curve for the carbon CWZ-22 exhibit one maximum for pore sizes 1.82nm, which corresponds to the width of micropores. The values w_{mi} and w_{me} are presented in Table 2.

Carbon Materials	S _{BET} m²/g	V _t cm ³ /g	V _{me} cm ³ /g	V _{mi} cm ³ /g	w _{me} nm	w _{mi} nm	Mesoporosity %
ST-A	670	0.68	0.51	0.17	9.24	1.83	75
CWZ-22	775	0.43	0.20	0.23	-	1.82	47

Table 2. Structural parameters of the studied carbon materials.

 S_{BET} —specific surface area; V_t —single-point total pore volume calculated at $p/p_o = 0.99$; V_{me} —mesopore volume calculated by subtracting V_{mi} from V_t ; V_{mi} —volume of micropores obtained by α_s -method; w_{mi} , w_{me} —micropore/mesopore diameter at the maximum of the PSD curve obtained by the KJS method; Mesoporosity—the percentage of the volume of mesopores to the total pore volume.

Structural parameters determined from adsorption isotherms are shown in Table 2. The ST-A adsorbent is characterized by a slightly lower specific surface area (S_{BET}) in comparison to CWZ-22 (670 and 775 m²/g, respectively). However, the total pore volume (V_t) for carbon ST-A is much larger: 0.68 cm³/g in comparison to carbon CWZ-22: 0.43 cm³/g. Micropore volume (V_{mi}) changes in the range from 0.17 (ST-A) to 0.23 cm³/g (CWZ-22). The synthesized carbon ST-A has a much larger volume of mesopores. The mesoporosity expressed as a percentage (Table 2) confirms that studied carbon ST-A is, in fact, mesoporous, and commercial active carbon CWZ-22 is microporous.

The SEM images confirm the properties of the studied carbons (Figure 3). The ST-A carbon presented interesting mesoporous structure with visible canals of mesopores (Figure 3a). Commercial carbon CWZ-22 is characterized by a much less developed porosity in comparison with the obtained carbon ST-A, which is observed in the image (Figure 3b).



Figure 3. SEM images of carbons: ST-A (a), CWZ-22 (b).

Table 3 lists the different functional groups available on studied adsorbents. The obtained carbon (ST-A) has more acidic properties and the commercial carbon (CWZ-22), on the contrary, has more basic properties.

Table 3. Functional groups available on studied carbons.

Adsorbents	Total Basic	Total Acidic	Phenolic	Lactone	Carboxylic	Carbonyl
	Groups	Groups	Groups	Groups	Groups	Groups
	(mmol g ⁻¹)					
ST-A CWZ-22	0.24 0.85	0.69 0.36	0.35	-	-	0.34 0.36

The ST-A carbon, due to the fact that it has acidic groups on its surface (phenolic and carbonyl), adsorbs the basic dye RB. It is the opposite of CWZ-22 because, due to the presence of more basic groups on its surface, it better adsorbs AY 17, which is an acidic dye. This is confirmed by the data in Table 4. Electrostatic interactions of the dye–adsorbent play an important role during the processes.

Carbon	Dve	Temp.		Langmuir		Freundlich			
Materials	_) -		$q_m (mg g^{-1})$	$K_L (dm^3 mg^{-1})$	R ²	n	$K_F (\mathrm{mg}^{1-1/\mathrm{n}}\ (\mathrm{dm}^3)^{1/\mathrm{n}} \mathrm{g}^{-1})$	R ²	
	RB	298	83	0.022	0.988	3.91	15.10	0.940	
		308	91	0.028	0.994	3.51	15.35	0.960	
ST-A		315	100	0.040	0.998	3.51	17.74	0.952	
51 1	AY17	298	35	0.061	0.999	3.33	7.08	0.907	
		308	40	0.134	0.998	3.64	10.12	0.782	
		315	53	0.150	0.999	3.50	13.27	0.829	
		298	58	0.024	0.998	2.74	6.93	0.923	
	RB	308	69	0.026	0.998	3.16	10.51	0.969	
CWZ-22		315	87	0.029	0.996	3.14	13.55	0.915	
		298	46	0.060	0.999	3.54	10.35	0.876	
	AY17	308	56	0.066	0.999	3.45	12.63	0.870	
		315	71	0.073	0.999	3.36	15.83	0.883	

Table 4. Langmuir and Freundlich isotherm parameters for the RB and AY17 adsorption on studied carbon.

3.2. Adsorption Experiments

3.2.1. Adsorption Isotherms

The adsorption isotherm is used to describe the distribution of the adsorbate between the aqueous and solid phase in point of adsorption process equilibrium. On the basis of the shape of the isotherm, the nature of the studied process can be determined [55].

The experimental isotherms were compared to the Langmuir and Freundlich isotherm model [56,57].

The Langmuir isotherm can be presented in the form:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}.$$
(2)

Equation (2) in linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{q_mK_L},\tag{3}$$

where C_e is the equilibrium concentration of dye aqueous solution (mg dm⁻³); q_e is the amount of dye adsorbed by elementary mass of adsorbent (mg g⁻¹); q_m is the maximum adsorption capacity (mg g⁻¹); and K_L is the adsorption equilibrium constant (dm³ g⁻¹).

In order to check the validity of the model fit to the Langmuir adsorption isotherm, the obtained graph was plotted C_e/q_e vs. C_e (Figure 4a–d). The calculated isotherm parameters are shown in Table 4.

The Freundlich isotherm can be presented in the form:

$$q_e = K_F C_e^{1/n}. (4)$$

Equation (4) in linear form:

$$logq_e = logK_F + \frac{1}{n}logC_e,$$
(5)

where K_F is the Freundlich isotherm constant (mg^{1-1/n} (dm³)^{1/n} g⁻¹), describing relative intensity; and 1/n is adsorption ability.

In order to check the validity of the model fit to the Freundlich adsorption isotherm obtained, a graph of $logq_e$ vs. $logC_e$ was plotted (data not shown). The correlation coefficients and isotherm constants were calculated and presented in Table 4.



Figure 4. Langmuir isotherm plots for adsorption of RB on ST-A (**a**) and CWZ-22 (**c**), and adsorption of AY17 on ST-A (**b**) and CWZ-22 (**d**).

The experimental adsorption isotherms of investigated dyes on ordered mesoporous carbon and commercial carbon CWZ-22, at temperature 298, 308, and 315 K are presented in Figure 5.

Analyzing data presented in Table 4, it can be observed that adsorption of dyes (RB and AY17) on studied carbons (ST-A and CWZ-22) proceeded in compliance with Langmuir isotherm model ($\mathbb{R}^2 \ge 0.988$). The adsorption capacity (q_m) of the AY17 on carbon ST-A at 298, 308, and 315 K is 35, 40, and 53 mg/g, respectively. On the other hand, the adsorption values of AY17 on the CWZ-22 commercial carbon compared are, successively, 46, 56, and 71 mg/g. When comparing the obtained results, it can be concluded that the adsorption capacity of commercial carbon is higher than the synthesized carbon ST-A at all temperatures. In the case of RB, the situation is the opposite. Higher adsorption values were obtained for this dye on synthesized carbon ST-A. The values from the lowest to the highest temperature were, respectively, 83, 91, and 100 mg/g. Adsorption of RB on commercial carbon reached significantly lower values of 58, 69, and 87 mg/g.

Table 5 compares the maximum adsorption capacities of the studied carbons with different carbon adsorbents reported [1-5,11,58-65] for the removal of RB and AY17. The maximum adsorption capacity (q_m) of RB and AY on the analyzed materials was moderate compared to other described adsorbents. The OMC materials obtained in works [3,65] have much better adsorption properties relative to RB than the adsorbent ST-A obtained in this work. This may be the result of a different synthesis method caused by the introduction of tetraethyl orthosilicate (TEOS) into the reaction system at the synthesis stage. The removal of silica with HF or NaOH results in materials with significantly higher specific surface area, more developed pore volume and, thus, better adsorption properties obtained in case of RB.



Figure 5. Adsorption isotherms of RB on ST-A (a) and CWZ-22 (c), and AY17 on ST-A (b) and CWZ-22 (d).

Adsorbent	<i>q_m</i> (mg/g) RB	<i>q_m</i> (mg/g) AY17	Reference
ST-A	83-100	35–53	This study
CWZ-22	58-87	46-71	This study
PK-AC ¹	413.9		[1]
EAC ²	281-389		[2]
Co/OMC ³	879		[3]
Activated SDC ⁴		183	[4]
Activated RHC ⁵		86.9	[4]
C-AC ⁶	32–40		[5]
Graphene	201.20		[11]
Activated carbon	85-250		[58]
Activated carbon	102-114.68		[59]
AC-MnO ₂ -NC ⁷	76.92		[60]
PLAC ⁸	500-560		[61]
APTC ⁹	307.2		[62]
RPAC ¹⁰		49-220	[63]
PAN/AC ¹¹		217 20	[64]
OMC	1028	217.39	[65]

Table 5. Comparison of the q_m of RB and AY17 on different absorbents.

¹ PK-AC – phosphorus acid modified activated carbon obtained from rice husk,² EAC – Elaeagnus activated carbon, ³ Co/OMC – ordered mesoporous carbon with cobalt, ⁴ SDC - sawdust carbon, ⁵ RHC – rice husk carbon,⁶ C-AC – activated carbons obtained from lignocellulosic waste,⁷ AC–MnO₂–NC – activated carbon with MnO₂ - nanocomposite, ⁸ PLAC - P.orientale Linn activated carbon, ⁹ APTC - activated pyrolytic tire char, ¹⁰ RPAC - rambutan peel activated carbon, ¹¹ PAN/AC - polyacrylonitrile/activated carbon.

3.2.2. Adsorption Kinetics

The solute uptake rate can be described by adsorption kinetics, which are very important for designing suitable technologies of adsorption [66].

Pseudo-first-order kinetic model [67], pseudo-second-order kinetic model [68], and intraparticle diffusion model [69] were investigated for the adsorption of RB and AY17 on studied carbon materials (ST-A and CWZ-22).

The pseudo-first-order equation is expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

where k_1 is the pseudo-first-order rate constants (min⁻¹); t is time of contact between the adsorbent and adsorbate (min); q_e is the adsorption value after the equilibrium stabilization (mg g⁻¹); and q_t is the adsorption value in given time t (mg g⁻¹).

Equation (6) in linear form:

$$\ln\left(q_{e-}q_{t}\right) = lnq_{e} - k_{1}t\tag{7}$$

The rate constants, k_1 , were calculated from the linear plots of $\ln(q_e - q_t)$ versus t (data not shown), data are presented in Table 5.

The pseudo-second-order equation is given as follows:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2. \tag{8}$$

Equation (8) can be transformed into linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e},$$
(9)

where k_2 is the pseudo-second-order rate constants (g mg⁻¹·min⁻¹).

The rate constants, k_2 , were calculated from the linear plots of t/q_t versus t (Figure 6a–d), and the data are shown in Table 6.



Figure 6. Pseudo-second-order kinetic model for RB adsorption onto ST-A (**a**) and CWZ-22 (**c**), and for AY17 adsorption onto ST-A (**b**) and CWZ-22 (**d**).

Carbon	Dve	Temp.	q_e (exp)	Pseudo-F	Pseudo-First-Order		Pseudo-Second-Order		
Materials	j -	ľ	$(mg g^{-1})$	k_1	R ²	q_e (cal) (mg g ⁻¹)	<i>k</i> ₂	R ²	
		298	7.5	0.0010	0.960	7.9	0.004	0.993	
	RB	308	8.2	0.0013	0.907	8.2	0.02	0.999	
ST-A		315	8.6	0.0016	0.881	8.6	0.02	0.999	
0111 -	AY17	298	17.8	0.05	0.854	17.9	0.0012	0.993	
		308	20.8	0.02	0.918	21.2	0.0013	0.978	
		315	22.1	0.02	0.947	25.1	0.0017	0.983	
		298	6.8	0.006	0.874	7.0	0.0025	0.992	
	RB	308	7.0	0.01	0.947	7.0	0.0083	0.997	
CWZ-22 _		315	7.9	0.01	0.930	7.3	0.0092	0.998	
		298	19.8	0.008	0.978	20.6	0.001	0.992	
	AY17	308	21.1	0.01	0.979	21.8	0.0012	0.996	
		315	22.9	0.013	0.935	23.5	0.0018	0.998	

Table 6. Kinetic parameters of RB and AY17 adsorption on the carbon studied.

The adsorption results (Table 6) confirmed that the adsorption kinetics for RB and AY17 on studied carbon materials can be described by pseudo-second-order kinetic equation.

To investigate the adsorption mechanism of studied compounds on used adsorbents, the Weber–Morris diffusion model was applied. The diffusion model is expressed by the following form:

$$q_t = k_{id} t^{1/2} + c, (10)$$

where k_{id} is the intraparticle diffusion rate constant (mg g⁻¹ min^{-1/2}) and *c* is the intercept which represents the thickness of the boundary layer (mg g⁻¹).

The relationship shown in Figure 7a–d allows us to identify the adsorption mechanism. The multilinear plot (solid line on the plot) indicates that in the adsorption process, several steps take part, not just intraparticle diffusion. First, the steep section corresponds to adsorption on the external surface of the adsorbent grain or an immediate adsorption. The second linear part of plot corresponds to a gradual phase, mild adsorption, where intraparticle diffusion is a controlling step of the whole adsorption. The third step corresponds to the stabilization of the adsorption process. If adsorption would only occur due to intraparticle diffusion, then the dependency q_t vs. $t^{1/2}$ would be rectilinear in the whole range; in addition, the curve would pass through the origin of the graph [3,13,62]. The data (Figure 7a–d) indicate that intraparticle diffusion is involved in the adsorption process, but it is not a stage controlling the speed of the entire process.





Figure 7. Intraparticle diffusion model for RB adsorption onto ST-A (**a**) and CWZ-22 (**c**), and for AY17 adsorption onto ST-A (**b**) and CWZ-22 (**d**).



The effect of contact time (plots of q_t versus t) was presented in Figure 8a–d.

Figure 8. Effect of contact time on adsorption of RB on ST-A (**a**) and CWZ-22 (**c**), and adsorption of AY17 on ST-A (**b**) and CWZ-22 (**d**) at 298, 308, and 315 K.

Analyzing the results, it was observed that the adsorption rate increases with increasing temperature for all studied cases (Figure 8a–d).

3.2.3. Thermodynamic Parameters

The standard free energy change (Δ G), enthalpy change (Δ H), and entropy change (Δ S) were calculated applying the following Equations (11)–(13), to investigate the dye adsorptions (RB and AY17) on ST-A and CWZ-22, thermodynamically [2,3].

$$\Delta G = -RTlnK_L,\tag{11}$$

$$\Delta G = \Delta H - T \Delta S,\tag{12}$$

$$lnK_L = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R},\tag{13}$$

where *R* is the universal gas constant (8.314 J/mol K), T is the absolute temperature in Kelvin, and K_L is the equilibrium constant obtained from Langmuir equation.

The ΔH and ΔS values were found from the slope and intercept of *ln* K_L versus 1/T plots (Figure 9). Table 7 lists the thermodynamic parameters values obtained at different temperatures for RB and AY17 adsorption on ST-A and CWZ 22.



Figure 9. The van't Hoff plots of lnK_L vs. 1/T for ST-A (RB, AY17) and CWZ-22 (RB, AY17).

Carbon Materials	Dye	Temp. (K)	ΔG (kJ/mol)	Δ <i>H</i> (kJ/mol)	ΔS (J/mol K)	R ²
ST-A	RB	298 308 315	-22.99 -24.33 -25.86	26.27	165.03	0.931
31-A	AY17	298 308 315	-25.82 -28.70 -29.65	42.84	230.88	0.917
CW7-22	RB	298 308 315	-23.19 -24.12 -24.99	7.94	104.36	0.903
Cwz-22	AY17	298 308 315	-25.77 -26.89 -27.75	8.89	116.26	0.987

Table 7. Thermodynamic parameters for RB and AY17 adsorption on ST-A and CWZ-22.

Analyzing the determined thermodynamic parameters (Table 7) and negative ΔG values, it can be stated that the adsorption process of studied dyes is spontaneous in nature. The ΔH values (less than 40 kJ/mol) are positive, indicating that the adsorption process is endothermic. The positive values

of ΔS show that an increase occurs in the randomness in the system at the solid/solution interface during the adsorption process.

4. Conclusions

Ordered mesoporous carbon and commercial activated carbon were applied in adsorption studies of rhodamine B and acid yellow 17. The adsorption results confirmed that the adsorption kinetics for RB and AY17 on studied carbon materials can be described by pseudo-second-order kinetic equation. The adsorption process of RB and AY17 on investigated carbon adsorbents proceeds in compliance with the Langmuir adsorption model. The commercial carbon had a higher adsorption capacity of AY17 than the synthesized carbon ST-A at all temperatures. In the case of RB, the situation is the opposite. Higher adsorption values were obtained for this dye on ST-A synthesized carbon. The negative value of ΔG and the positive value of ΔH indicate the spontaneous and endothermic nature of adsorption, respectively. The positive value of ΔS demonstrates that the randomness increased during the adsorption process. These results exhibited that ST-A and CWZ-22 carbon materials were effective adsorbents for dye removal from aqueous solutions.

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