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Removal of Reactive Black 5 dye from Aqueous Media using Powdered Activated Carbon – Kinetics and Mechanisms

Odstranjevanje barvila Reactive Black 5 iz vodnih medijev z uporabo praškastega aktivnega oglja – kinetika in mehanizmi

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Abstract

The textile industry is considered one of the major environmental polluters, primarily due to the quantity and composition of wastewater. It is therefore important to examine its different treatment methods. For this purpose, the isothermal adsorption of Reactive Black 5 dye on powdered activated carbon at 25(±1) °C and 45(±1) °C was carried out to determine the effect of initial dye concentration, contact time and temperature on the adsorption process. In order to investigate the mechanism of adsorption of Reactive Black 5 dye on activated carbon, kinetic studies have also been carried out. Experimental data were analysed using a pseudo-first-order and pseudo-second-order kinetic models, as well as an intraparticle diffusion model. Standard Gibbs free energy values of the adsorption process were also calculated, while the morphological analysis of activated carbon before and after adsorption was performed using a scanning electron microscope. The efficiency of activated carbon as an adsorbent for Reactive Black 5 dye is evidenced by the fact that more than 60% of dye is adsorbed after 30 minutes regardless of initial concentration and temperature. The experimental data also showed that adsorption is kinetically controlled assuming a pseudo-second-order process, and that intraparticle diffusion is not the only process that influences the adsorption rate. Negative values of standard Gibbs free energy indicate that the adsorption reaction is spontaneous, while a higher negative value for temperature of 45 °C compared to 25 °C shows that a higher temperature is more energetically favourable for the adsorption of Reactive Black 5.

Keywords: adsorption, activated carbon, Reactive Black 5, kinetics, intraparticle diffusion

Izvleček

Tekstilna industrija velja za eno glavnih onesnaževalk okolja, predvsem zaradi količine in sestave odpadnih voda, zato je pomembno preučiti različne metode njihove obdelave. V ta namen je bila izvedena izotermična adsorpcija barvila Reactive Black 5 na praškasto aktivno oglje pri 25 °C ± 1 °C in 45 °C ± 1 °C, da bi ugotovili vpliv začetne koncentracije barvila, časa stika in temperature na postopek adsorpcije. Za preučitev mehanizma adsorpcije barvila Reactive Black 5 na aktivno oglje so bile izvedene tudi študije kinetike. Eksperimentalni podatki so bili analizirani s kinetičnimi modeli psevdoprvega in psevdodrugega reda, kot tudi z modelom difuzije delcev snovi. Za proces adsorpcije je bila določena standardna Gibbsova prosta energija. Morfološka analiza aktivnega oglja je bila izvedena z rastrskim elektronskim mikroskopom. Učinkovitost aktivnega oglja kot adsorbenta za barvilo Reactive Black 5 je razvidna iz dejstva, da se je več kot 60-odstotkov barvila adsorbiralo po 30 minutah, ne glede na začetno koncentracijo in temperaturo. Eksperimentalni podatki so pokazali tudi, da je adsorpcija

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kinetično nadzorovana, pri čemer se predpostavlja proces psevdodrugega reda in da difuzija delcev ni edini proces, ki vpliva na hitrost adsorpcije. Negativne vrednosti standardne Gibbsove proste energije nakazujejo, da je reakcija adsorpcije spontana, višja negativna vrednost pri temperaturi 45 °C v primerjavi s 25 °C pa kaže, da je višja temperatura energijsko ugodnejša za adsorpcijo barvila Reactive Black 5.

Ključne besede: adsorpcija, aktivno oglje, Reactive Black 5, kinetika, difuzija delcev

1 Introduction

At the end of the 20th century, with all of the inventions and technical aids used every day, the relationship between man and nature was disrupted, and the Earth's ecosystem broken. Due to human knowledge and creativity over the last 250 years, a modern way of life, industrial development, advancing technology and agriculture, the use of large amounts of energy and natural resources, as well as the pursuit of a better and more comfortable life have led to the emergence of environmental hazards and their consequences (i.e. acid rain, desertification, ozone depletion, climate change and other harmful phenomena). A great deal of attention worldwide has been given to environmental protection, the effect of harmful substances on human health and the entire ecosystem. Particular attention is given to industry, as it is no longer possible to continue expanding production and waste accumulation without inflicting permanent damage to nature.

The textile industry is one of the major environmental polluters. It uses significant quantities of water [1], which is eliminated as wastewater after being processed. Taking into account total industrial water pollution, textile finishing is considered one of the largest water consumption and pollution processes. The quantity and composition of wastewater depend on the type of basic raw material being processed (cotton, wool, flax, silk, synthetic fibres, blends, etc.) and textile finishing process used (laundering, bleaching, dyeing, printing, etc.), i.e. the type of chemicals used during some processes and the number of consecutive processes during production. In addition, the use of certain special finishing agents often results in specific and greater pollution of wastewater. Textile industry wastewater has a wide range of pH values and temperatures, it may be coloured and mainly contains various types of pollutants, most commonly dyes, surfactants, pesticides, oils, fats, solvents, heavy metals, inorganic salts, waste fibres, etc. [2]. Special attention is given to dyes and pigments because they are

highly visible materials so that even the minimum amount released into the environment may cause the appearance of colour in open waters. Besides being aesthetically deficient, coloured water prevents the penetration of light into natural water, which negatively affects the entire natural water ecosystem, i.e. organisms depending on water quality. There are more than 100,000 commercially available dyes with over 700,000 tonnes produced annually. Wastewater stream from the textile dyeing process contains unutilised dyes (about 8–20% of the total pollution load due to incomplete dye exhaustion) and auxiliary chemicals [3]. Besides, some dyes have been proven to have allergenic, toxic and/or carcinogenic properties that make them not only dangerous or potentially harmful to the environment, but also to human health in contact with human skin [4]. The continuous monitoring of dye content in wastewaters should therefore be an integral part of the technological process of textile materials and permitted concentrations regulated by law. Dyeing and printing should be carried out by achieving the maximum effect using a minimum amount of dye, not only for ecological reasons (reduced quantity of unused textile auxiliaries in wastewater), but also for economic reasons.

Taking all of the above-mentioned facts into consideration, it is necessary to treat the wastewater by reducing the amount of harmful substances to legally limited concentrations. There are numerous methods for the treatment and disposal of textile industry wastewater: coagulation and flocculation, chemical oxidation, biological treatment, membrane separation, reverse osmosis, etc. [3, 5, 6]. Although high quality effluents can be obtained through water treatment with each of the previously mentioned processes, some of them have limitations/disadvantages, such as the use of excess chemicals, the formation of larger amounts of sludge that needs adequate care, and the incomplete removal of colour. Removal of dyes from wastewater is generally difficult. They are usually non-biodegradable, resistant to aerobic digestion,

and stable to light, heat and oxidising agents. One of the most commonly used and effective treatment methods for coloured water is adsorption, which is based on the accumulation of the substance from the solution in a solid phase. Adsorption is one of the best treatment methods due to its flexibility, simplicity of design, and sensitivity to toxic pollutants. Furthermore, adsorption generally does not result in the formation of harmful substances [3, 7–9]. Activated carbon is the most popular adsorbent used for wastewater treatment due to its adsorption efficiency and great capacity, although some other adsorbents are less expensive and easily available. It is efficient in the removal of different types of dyes, including reactive dyes [10–15].

It is known that adsorption is a time-dependent process, and it is therefore necessary to know the adsorption rate for removal of dyes from wastewater. The most important factor in the design of adsorption systems is thus prediction of the rate of adsorption for a given system. This paper aims to present adsorption efficiency of commercial activated carbon for the removal of Reactive Black 5 dye (RB5). The effect of contact time, initial dye concentration and temperature on adsorption were monitored. The pseudo-first-order and pseudo-second-order models were used to correlate the adsorption kinetic data, while intraparticle diffusion was used to evaluate the diffusion mechanism of the adsorption process. Activated carbon was also characterised before and after the adsorption of RB5 using a scanning electron microscope.

2 Materials and methods

2.1 Materials

Reactive Black 5 dye (Drimarene Black R-3B, supplied by Clariant GmbH, C.I. 20505, chemical formula: $C_{26}H_{21}N_5Na_4O_{19}S_6$, $M_r = 991.82$), was used for the adsorption experiment. The chemical structure of the dye prepared by the Accelrys Draw program is shown in Figure 1. One thousand milligrams per litre stock solution of dye was prepared by dissolving the required amount of dye in deionised water. The solutions of appropriate concentrations were prepared by diluting the stock solution with deionised water. Powdered activated carbon was purchased from the Croatian company Kemika. Adsorbent was dried in an oven at 105 °C for 24 hours and stored in a desiccator until it was used.

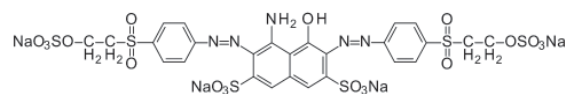


Figure 1: Chemical structure of Reactive Black 5

2.2 Batch mode adsorption studies

Adsorption studies were conducted by contacting 50 ml of dye solution of different initial concentrations ($c_0 = 300, 500$ and 700 mg/dm^3) with 0.2 g of activated carbon in glass bottles. The experiments were repeated three times under identical conditions to confirm their repeatability. Experimental points presented in figures are the average values of three the repetitions. Suspensions were shaken at different contact times (15, 30, 45, 60, 90, 120, 180, 240 and 360 minutes and 16 hours until equilibrium was reached) with an impeller speed of 250 rpm at $25(\pm 1)^\circ\text{C}$ and $45(\pm 1)^\circ\text{C}$ (Heidolph Unimax 1010 with Incubator 1000). Experiments after 360 minutes for initial concentration of $c_0 = 300 \text{ mg/dm}^3$ were not performed due to extremely low dye concentration after an adsorption time of 240 minutes. Suspensions were filtered after agitation through filter-paper blue ribbon. The residual liquid-phase dye concentration after adsorption was determined spectrophotometrically by monitoring the absorbance using a UV-Vis spectrophotometer (Lambda 20, Perkin Elmer) at a maximum absorbance wavelength ($\lambda_{\text{max}} = 598 \text{ nm}$). The calibration graph of absorbance versus concentration followed a linear Beer-Lambert relation. The amount of adsorbate adsorbed at any time t , q_t (mg/g), and the amount of adsorbate adsorbed at equilibrium, q_e (mg/g), were calculated using the following equation:

$$q = \frac{v \cdot (c_0 - c_t)}{m} \quad (1)$$

where c_0 (mg/dm^3) represents the initial dye concentration, c_t (mg/dm^3) represents the dye concentration in the liquid phase after appropriate time of adsorption and when equilibrium is reached ($t = 16$ hours), V represents the volume of the liquid phase (dm^3), and m represents the mass of the adsorbent (g). Percentage of adsorbed dye (% ads.) is calculated using the equation:

$$\% \text{ ads.} = \frac{c_s}{c_0} \times 100 \quad (2)$$

where c_s (mg dm^{-3}) represents the concentration of the adsorbed dye in a solid phase ($c_s = c_0 - c_t$).

2.3 Morphological analysis of adsorbent and dye-adsorbent samples

A field emission scanning electron microscope (Mira, Tescan) was used for visualization of the adsorbent's morphology before and after adsorption. The accelerating voltage was 10.00 kV, while scanning was performed in situ on a sample powder. Samples were pre-coated with gold/palladium in a sputter coater. Optical micrographs were recorded using a Nikon Elipse E 400 microscope.

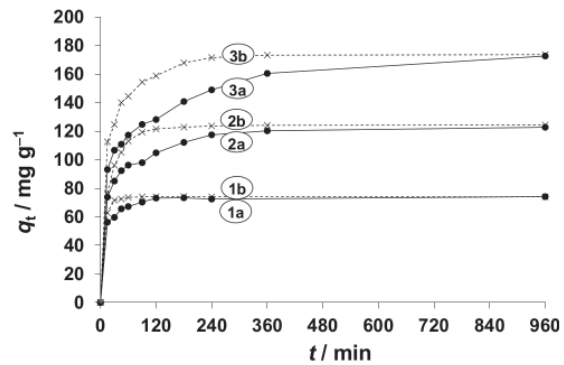


Figure 2: Effect of initial concentration and temperature on the amount of adsorbed RB5 on activated carbon after appropriate time (initial concentrations, c_0 : ① 300 mg/dm³, ② 500 mg/dm³, ③ 700 mg/dm³; temperatures: a) 25 °C, b) 45 °C)

3 Results and discussion

3.1 Effect of contact time, temperature and initial dye concentration on the adsorption process

The objective of this work was to assess the effectiveness of activated carbon for the treatment of

Table 1: Percentage of adsorbed RB5 (% ads.) and amount of adsorbed RB5 at any time t (q_t) for three initial dye concentrations (c_0) at both temperatures

T (°C)	t (min)	$c_0 = 300 \text{ mg/dm}^3$		$c_0 = 500 \text{ mg/dm}^3$		$c_0 = 700 \text{ mg/dm}^3$	
		% ads.	q_t (mg/g)	% ads.	q_t (mg/g)	% ads.	q_t (mg/g)
25	15	74.9	56.2	59.0	73.8	53.2	93.1
	30	79.5	59.6	68.0	85.0	60.9	106.6
	45	87.4	65.6	73.9	92.3	63.3	110.8
	60	89.6	67.2	76.9	96.2	67.0	117.2
	90	93.7	70.3	78.3	97.9	71.2	124.7
	120	97.5	73.1	83.9	104.8	73.2	128.1
	180	97.7	73.3	89.7	112.1	80.4	140.7
	240	96.5	72.4	93.9	117.4	85.1	148.9
	360 ^a	---	---	96.1	120.2	91.7	160.4
	960	98.8	74.1	98.2	122.7	98.6	172.6
45	15	83.8	62.8	61.2	76.5	64.2	112.5
	30	95.4	71.6	76.9	96.1	71.2	124.6
	45	96.6	72.5	84.1	105.1	80.0	140.0
	60	98.1	73.6	90.4	113.1	82.5	144.4
	90	98.7	74.0	95.4	119.3	88.2	154.3
	120	98.7	74.0	97.2	121.5	90.7	158.7
	180	99.0	74.2	98.2	122.8	95.9	167.8
	240	98.7	74.0	98.8	123.6	98.0	171.5
	360 ^{a)}	---	---	99.3	124.1	98.9	173.2
	960	98.7	74.0	99.4	124.3	99.2	173.6

^{a)} Due to extremely low dye concentration after the adsorption time of 4 hours, an adsorption experiment after 6 hours for initial concentration of $c_0 = 300 \text{ mg/dm}^3$ was not performed

dye-rich textile wastewater with special focus on the reduction of colour pollutants. The initial concentration of RB5 varied from 300 to 700 mg/dm³, which is a possible range of dye concentration in textile industry wastewater after the process of dyeing. The dependence of the amount of adsorbate adsorbed after appropriate time (q_t) versus time (t) is presented in Figure 2, while data are given in Table 1.

It is evident from Figure 2 that a higher initial concentration of the dye increases the adsorption capacity and that the amount of adsorbed RB5 is higher at higher temperature for all concentrations. As equilibrium for the initial concentration $c_0 = 300$ mg/dm³ was reached very quickly, the amount of adsorbate adsorbed was monitored from 15 minutes to 4 hours, while for the other two initial concentrations were monitored from 15 minutes to 6 hours. The plots can be approximately divided into three regions. The first region includes a very fast initial adsorption, probably governed by a rapid external diffusion process, which mainly includes adsorption of dye on the surface of activated carbon. After this step follows the second region, with a milder and gradual increase of adsorbed dye, and the third region where a state of equilibrium was almost reached.

The sorption capacity at equilibrium at both temperatures increased from ca. 74 to ca. 173–174 mg/g with an increase of the initial dye concentration from 300 to 700 mg/dm³ (Table 1). Initially, differences in adsorbed RB5 between two temperatures for the same initial dye concentration were more significant, while after a longer period of adsorption, quantities of adsorbed RB5 became very similar. Also, as expected, less time was needed to obtain high dye adsorption percentage values for lower concentra-

tions of dye (Figure 3). Thus, approximately 90% of RB5 was adsorbed at 25 °C for initial concentrations of $c_0 = 300, 500$ and 700 mg/dm³ after 1, 3 and 6 hours, respectively (Table 1). At 45 °C, these times are significantly shorter, and they were between 15 and 30 minutes for $c_0 = 300$ mg/dm³, 1 hour for $c_0 = 500$ mg/dm³ and 2 hours for $c_0 = 700$ mg/dm³. The efficiency of activated carbon for the adsorption of RB5 is also evidenced by the fact that more than 60% of dye is adsorbed after 30 minutes, regardless of initial concentration and temperature.

3.2 Kinetics of adsorption

Kinetic studies were performed in order to investigate the mechanism of adsorption and potential rate controlling steps. Kinetic study is important to an adsorption process because it depicts the uptake rate of the adsorbate and controls the residual time of the whole adsorption process for a given system. The experimental data were analysed using three kinetic models: pseudo-first-order and pseudo-second-order kinetic models, and an intraparticle diffusion model. The pseudo-first-order and pseudo-second-order models are used most frequently for determining of kinetic parameters.

Pseudo-first-order kinetic model

Lagergren [16] proposed a rate equation for the sorption of solute from a liquid solution based on solid capacity. The kinetic model of this the most widely used rate equation is expressed using the following equation:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{3}$$

where k_1 represents the rate constant of the pseudo-first-order (min⁻¹).

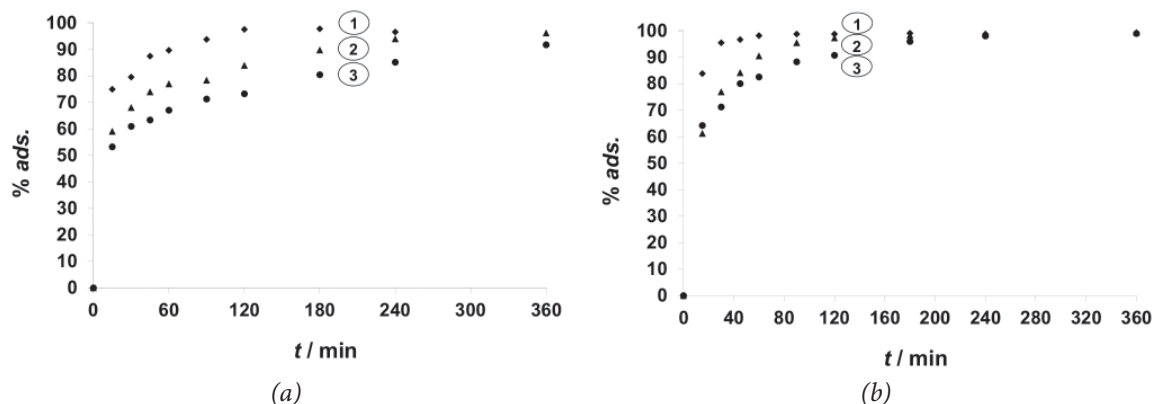


Figure 3: Effect of initial concentration on percentage of adsorbed RB5 (% ads.) at temperatures of (a) 25 °C and (b) 45 °C (initial concentrations, c_0 : ① 300 mg/dm³, ② 500 mg/dm³, ③ 700 mg/dm³)

Integrating this equation for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ results in:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \quad (4).$$

The kinetic constant k_1 can be determined by plotting $\ln(q_e - q_t)$ against time (t), and if the first-order equation is applicable, the plot should give a linear relationship, and facilitates the calculation of the rate constant of pseudo-first-order (k_1) from the slope and amount of adsorbate adsorbed at equilibrium ($q_{e,calc}$) from the intercept. The values of the constants of the pseudo-first-order model for adsorption of RB5 onto activated carbon are given in Table 2.

The values of the correlation coefficient (R^2) obtained from the linear plot (Eq. 4) are relatively high (from 94.6% to 99.8%), the exception being the initial concentration of $c_0 = 300 \text{ mg/dm}^3$ at 25°C (71.1%). However, for all concentrations and at both temperatures, there is considerable disagreement between the

experimental and calculated values of the amount of adsorbed RB5 at equilibrium ($q_{e,exp}$ and $q_{e,calc}$). This suggests that this sorption system is not a first-order reaction and that a pseudo-second-order model might provide a better correlation of the data.

Pseudo-second-order kinetic model

Ho and McKay [17, 18] developed a second-order equation based on adsorption capacity. This kinetic model is illustrated by the following equation:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (5),$$

where k_2 represents the rate constant of the pseudo-second-order ($\text{g mg}^{-1} \text{min}^{-1}$).

Integrating the equation (5) for the same boundary conditions used for the first-order results in the equation presented below in the linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \quad (6).$$

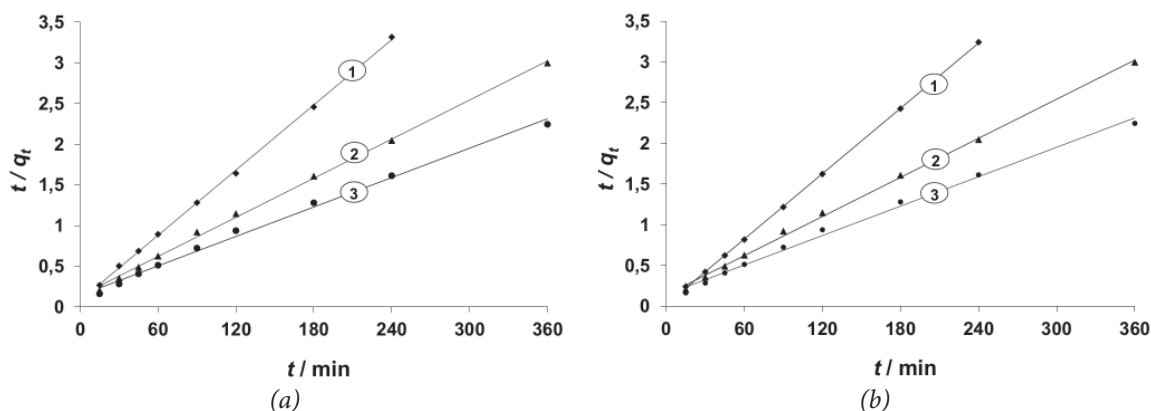


Figure 4: Pseudo-second-order kinetic model for three initial concentrations of RB5 at temperatures of (a) 25°C and (b) 45°C (initial concentrations, c_0 : ① 300 mg/dm^3 , ② 500 mg/dm^3 , ③ 700 mg/dm^3)

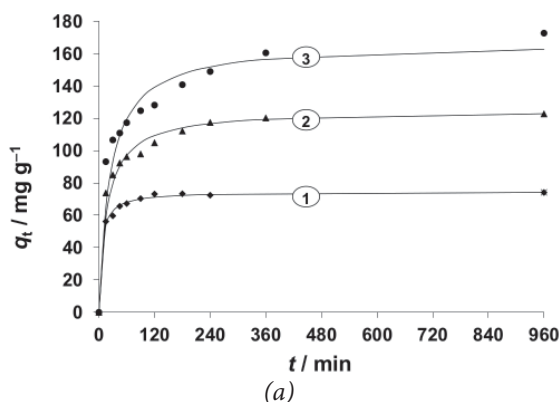
Table 2: Kinetic parameters for the effect of initial dye concentration on adsorption at temperatures of 25°C and 45°C

T ($^\circ\text{C}$)	c_0 (mg/dm^3)	$q_{e,exp}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model			
			$q_{e,calc}$ (mg/g)	R^2	k_1 (min^{-1})	$q_{e,calc}$ (mg/g)	R^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	h ($\text{mg g}^{-1} \text{min}^{-1}$)
25	300	74.1	14.3	0.7108	0.0129	74.6	0.9995	0.002295	12.77
	500	122.7	48.6	0.9888	0.0085	125.0	0.9983	0.000463	7.23
	700	172.6	79.4	0.9948	0.0052	166.7	0.9944	0.000252	7.00
45	300	74.0	26.1	0.9656	0.0674	74.6	0.9999	0.009075	50.51
	500	124.3	32.5	0.9463	0.0154	128.2	0.9998	0.000935	15.36
	700	173.6	72.9	0.9975	0.0145	178.6	0.9997	0.000437	13.95

If the pseudo-second-order equation is applicable, the plot of t/q_t against time t should give a linear relationship and facilitates the calculation of the amount of adsorbate adsorbed at equilibrium ($q_{e,calc}$) from the slope, and then the rate constant of the pseudo-second-order (k_2) from the intercept. The values are given in Table 2, while linear plots are presented in Figure 4.

Based on this model, calculated q_e values ($q_{e,calc}$) and experimental equilibrium values ($q_{e,exp}$) demonstrate a much better correlation (Table 2). Moreover, the values of correlation coefficients are very close to 1 (higher than 99.4%) for all initial dye concentrations and at both temperatures. Figure 5 shows the good correlation of the data with the pseudo-second-order equation. The experimental points are shown together with the theoretically generated lines, and they fit nicely for all concentrations and at both temperatures, although slightly better for the temperature of 45 °C. The adsorption of RB5 dye on commercial activated carbon is thus kinetically controlled assuming a pseudo-second-order rather than a pseudo-first-order process. The pseudo-second-order model assumes chemical sorption or chemisorption as the rate-limiting process. Maximum k_2 values were obtained for the smallest initial dye concentration ($c_0 = 300 \text{ mg/dm}^3$), while values for temperature of 45 °C are approximately 2–4 times higher than those for 25 °C. Also, as time approaches zero, according to the pseudo-second-order model, the initial adsorption rate h ($\text{mg g}^{-1} \text{ min}^{-1}$) can be calculated using the following equation [18, 19]:

$$h = k_2 \cdot q_{e,calc}^2 \tag{7}$$



The obtained h values are also presented in Table 2. As for k_2 , values of the initial adsorption rate increase with a decrease of initial dye concentration, and increase with an increase in temperature.

Intraparticle diffusion model

We used an intraparticle diffusion model to evaluate the diffusion mechanism for adsorption of RB5 on activated carbon. Most adsorption reactions are carried out using a multistep mechanism and involve several steps:

- (i) external mass transfer of the adsorbate from the solution to the adsorbent surface;
- (ii) adsorption at a site on the adsorbent surface; and
- (iii) intraparticle diffusion of the adsorbate in the pores of the adsorbent and adsorption on the site.

Step (ii) is often assumed to be very fast, and thus cannot be treated as a rate limiting step. Generally, the rate of adsorption is limited by external mass transfer for a system with poor mixing, low adsorbate concentration, its high affinity to the adsorbent and the small adsorbent particles. The adsorption of large molecules, for which longer contact time is needed to reach equilibrium, is always considered to be diffusion controlled by external film resistance and/or internal diffusion mass transport or intraparticle diffusion [20]. Theoretical treatments of intraparticle diffusion yield complex mathematical relationships that differ in form as functions of the geometry of the adsorbent particle. The intraparticle diffusion model is based on the following equation [19, 20]:

$$q_t = k_i \cdot t^{0.5} \tag{8}$$

where k_i represents the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{ min}^{-0.5}$).

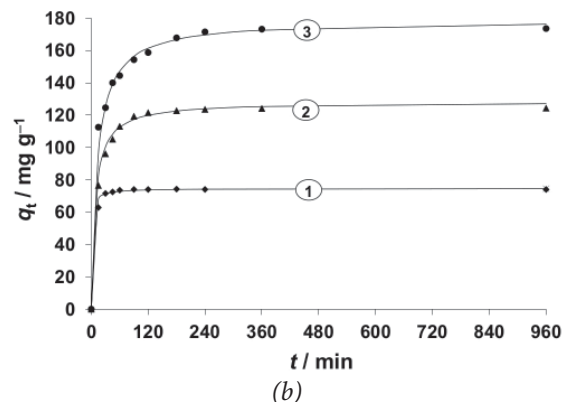


Figure 5: Fitting of pseudo-second-order kinetic model with experimental data at temperatures of (a) 25 °C and (b) 45 °C (initial concentrations, c_0 : ① 300 mg/dm^3 , ② 500 mg/dm^3 , ③ 700 mg/dm^3)

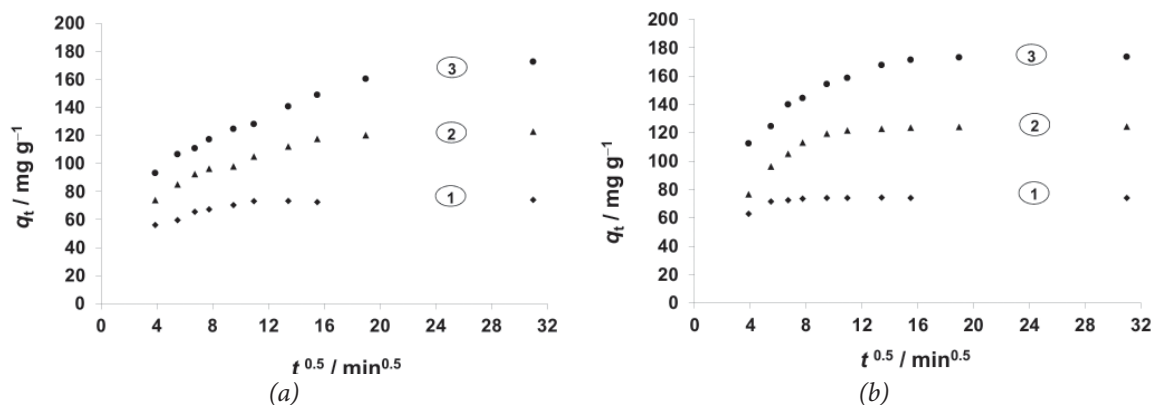


Figure 6: Root time plots for the adsorption of RB5 for three initial dye concentrations (c_0 : ① 300 mg/dm³, ② 500 mg/dm³, ③ 700 mg/dm³) at temperatures of (a) 25 °C and (b) 45 °C

If the intraparticle diffusion is a rate limiting step of adsorption, *i.e.* intraparticle diffusion controls the rate of adsorption, then plot q_t versus $t^{0.5}$ should be linear and pass through the origin. If the plot of q_t versus $t^{0.5}$ exhibit multi-linearity, this indicates that two or more rate controlling steps occur in the adsorption processes [20–22]. Figure 6 shows the root time plots for the adsorption of RB5 onto activated carbon at temperatures of 25 and 45 °C.

It is evident from the above figure that the plots are not linear, *i.e.* that they exhibit multi-linearity with several sections. It can thus be concluded that intraparticle diffusion is not the only process that influences the adsorption rate and that multiple steps took place during the adsorption process. Few stages can be distinguished during the dye adsorption. The adsorption rate is initially higher and corresponds to instantaneous adsorption, probably due to an electrostatic attraction between the dye and the external surface of the adsorbent. The amount of adsorbed substance on the adsorbent and diffusion decreases over time, and represents a gradual

adsorption stage where diffusion rates decreased by increasing the contact time. This process usually includes the intraparticle diffusion of the molecules through the pores of the adsorbent. That stage is followed by the equilibrium stage when dye molecules occupy all active sites of the adsorbent [19]. Diffusion in the pores of the adsorbent is usually determined by the fact that there are several different pore sizes in the adsorbent, and that controlling regions correspond to the dye diffusion to the activated carbon pores of different dimensions. Since the dye molecules diffuse into the inner structure of the adsorbents, the pores for diffusion become smaller and thus the free path of the molecules in the pore decreases.

3.3 Thermodynamics

Standard Gibbs free energy (ΔG^0 , kJ/mol) values of the adsorption process can be calculated using the equation:

$$\Delta G^0 = -RT \ln (K_c) \quad (9)$$

Table 3: Standard Gibbs free energy changes (ΔG^0 , kJ/mol) for the adsorption of Reactive Black 5 on activated carbon

c_0 (mg/dm ³)	T (K)	c_e (mg/dm ³)	K_c	ΔG^0 (kJ/mol)
300	298	3.7	80.1	-10.86
	318	4.0	74.0	-11.38
500	298	9.2	53.3	-9.86
	318	2.8	177.6	-13.70
700	298	9.6	71.9	-10.60
	318	5.8	119.7	-12.66

where R represents the universal gas constant and T represents temperature. K_c represents the equilibrium constant calculated from the concentration of the dye adsorbed on the solid at equilibrium ($c_s / \text{mg}/\text{dm}^3$) and the concentration of the dye when equilibrium is reached in the liquid phase ($c_e / \text{mg}/\text{dm}^3$) [23]:

$$K_c = \frac{c_s}{c_e} \quad (10).$$

The negative values of ΔG^0 indicate that the adsorption reaction is spontaneous. Thus, ΔG^0 values given in Table 3 reflect the feasibility of the process, and that the adsorption of RB5 onto activated carbon was a spontaneous process in nature, in which no energy input from outside of the system was required. The higher negative value reflects a more energetically favourable adsorption. It can thus be concluded that adsorption at 45 °C is energetically more favourable than at 25 °C.

3.4 Morphological analysis of the adsorbent and dye-adsorbent samples

In order to perform a morphological analysis of activated carbon before and after adsorption, photographs were taken using scanning electron microscopy (SEM). It is evident from recorded photographs of activated carbon that the particles differ morphologically and have different pore sizes, as assumed by the results of the intraparticle diffusion model (Figure 7).

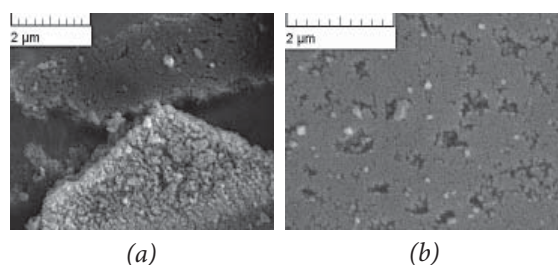


Figure 7: SEM images of activated carbon surface enlarged (a) 15000 x and (b) 20000 x

Figure 8 shows the appearance of activated carbon after the adsorption of RB 5 (adsorption time of 4 hours at a temperature 45 °C) for initial dye concentrations of $c_0 = 300 \text{ mg}/\text{dm}^3$ (Figure 8a) and $c_0 = 700 \text{ mg}/\text{dm}^3$ (Figure 8b). It is evident from the images that dye is adsorbed on the surface of activated carbon. For the initial concentration $c_0 = 300 \text{ mg}/\text{dm}^3$, some parts of the surface are almost completely straight, while the other parts are uneven. The activated carbon surface

for the initial dye concentration of $c_0 = 700 \text{ mg}/\text{dm}^3$ is flatter on most parts, an indication that activated carbon is almost completely covered with dye molecules. From this it can be assumed that, for a higher initial concentration, a certain amount of dye is further adsorbed on activated carbon.

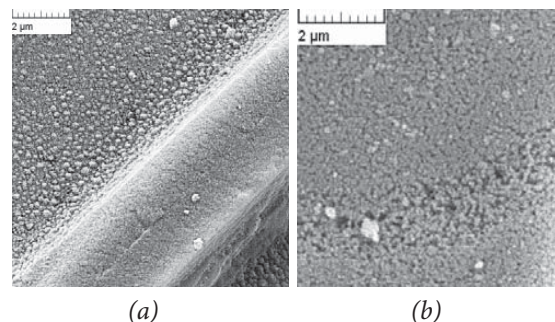


Figure 8: SEM images of activated carbon after the adsorption of dye enlarged 15000 x for initial dye concentrations of (a) $c_0 = 300 \text{ mg}/\text{dm}^3$, and (b) $c_0 = 700 \text{ mg}/\text{dm}^3$

4 Conclusion

According to the results achieved, the adsorption of Reactive Black 5 onto activated carbon was very fast. This study also confirmed that activated carbon is a very efficient adsorbent and that adsorption at higher temperature is greater. For all initial concentrations, approximately 90% of RB5 was adsorbed at 25 °C after 1 to 6 hours. On the other hand, these times are significantly shorter at a temperature of 45 °C, with the maximum value of 2 hours for the initial concentration of $c_0 = 700 \text{ mg}/\text{dm}^3$. Furthermore, the adsorption of RB5 dye on commercial activated carbon was kinetically controlled assuming a pseudo-second-order rather than a pseudo-first-order process. This study also revealed that intraparticle diffusion was not the only process that influenced the adsorption rate and that multiple steps took place during the adsorption process. Finally, the negative values of ΔG^0 indicate that the adsorption reaction was spontaneous in nature and that adsorption at 45 °C was energetically more favourable than at 25 °C. The adsorption of Reactive Black 5 dye on activated carbon was also confirmed by scanning electron microscopy.

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