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ADSORPTION OF REACTIVE DYES AND THEIR MIXTURES ON ACTIVATED CARBON. KINETIC, EQUILIBRIUM AND THERMODYNAMIC EVALUATION

The adsorption of three reactive dyes (Reactive Bezactiv Yellow (RBY), Reactive Bezactiv Blue (RBB) and Reactive Bezactiv (RBR)) on a commercially available activated carbon (CAC) has been evaluated. It was shown that CAC is capable to effectively remove these dyes from a solution. The adsorption increased with higher contact time, adsorbent dose, and initial dye concentration. The data indicated that the adsorption kinetics of dyes on CAC followed a pseudo-second order model. The adsorption isotherms followed the Langmuir isotherm model. Evaluation of thermodynamic parameters revealed that the adsorption process is endothermic for all dyes and spontaneous in a single system and became spontaneous in mixture systems at high temperature, except RBY and RBB in the ternary mixture. Adsorption was higher for RBY, followed by RBB, and was lowest for RBR. The total adsorption efficiency was confirmed by chemical oxygen demand (COD) measurements.

1. INTRODUCTION

The use of synthetic dyes is widespread in various industrial sectors, including plastics, cosmetics, textiles, and paper. In terms of dye production, the most significant industrial users are textile industries, in which a variety of synthetic dyes is used that possess a chemical affinity with textile fibers for the dyeing of cloth [1]. Among various types of textile dyes, reactive dyes are most widely used for the dyeing of cotton and other cellulosic fibers. The wastewater produced after a reactive dye treatment of textiles, however, can still contain up to 20–30% of the initial amount of dye applied. On

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average, concentrations around 2 g/dm^3 are frequently encountered. These effluents are hence highly colored and cannot be recycled. Additionally, high salt concentrations are present (up to $60\text{--}100 \text{ g/dm}^3$) [2].

Traditional methods of treating dye-polluted wastewater include biological treatment, coagulation/flocculation, ozone treatment, chemical oxidation, and membrane filtration, application of ion exchange materials, photocatalytic degradation and adsorption [3]. The most common adsorbent materials used for dye pollutants are activated carbon, clays, zeolites, and a variety of different residues from agriculture, biomass, and polymeric material. Activated carbon (AC) is the most popular adsorbent and has been used with great success [4]. AC has been studied by several researchers as an adsorbent for the capture of dyes from single dye solutions [5].

In this work, the ability of a commercially available activated carbon was tested for the removal of three reactive dyes which are widely used in the dyeing of cotton and other cellulosic fibers. Apart from single dye adsorption tests, also the adsorption behavior in mixtures of two and three dyes was explored. The influence of the most relevant parameters affecting the dye adsorption was studied: adsorbent dose, contact time, initial dye concentration, temperature, dye composition, and the presence of salts (Na_2CO_3 and Na_2SO_3). The adsorption isotherms and kinetic models were developed, and a thermodynamic study was carried out to describe the mechanism involved in the adsorption process.

2. MATERIALS AND METHODS

Materials and chemicals. The adsorbent used throughout the experiments was steam activated, wood-based commercial activated carbon (CAC) with a crystallite size of 1.75 nm and a density of $1.8\text{--}2.1 \text{ g/cm}^3$ obtained from Lobachemie (India). The reactive dyes, i.e., Reactive Bezactiv Yellow (RBY), Reactive Bezactiv Red (RBR) and Reactive Bezactiv Blue (RBB) were obtained from Bezema AG (Switzerland). They are anionic reactive dyes mostly used in the industrial dyeing of cotton and cellulose fiber.

Batch adsorption tests. Before the experiments, an initial stock solution of each dye was prepared at a concentration of 1000 mg/dm^3 by dissolving a weighed quantity of dye in demineralized water. The adsorption of RBY, RBR, and RBB onto CAC in a single component solution was carried out. Also, their adsorption was evaluated in binary mixtures (a mixture of 2 dyes (ROC orange color (RBR + RBY), RGC green color (RBY + RBB) and RV: violet color (RBB + RBR)) and a ternary mixture of three dyes (RBrC brown color (RBR + RBY + RBB)). All experiments were performed in a batch system using 100 cm^3 of dye solution with an unaltered pH, which equaled 5.7 for RBY, 6.2 for RBR, and 5.7 for RBB (pH_i).

To obtain the required dye concentration, the concentrated stock solutions (containing 1000 mg/dm^3 of the respective dyes) were first diluted and then mixed to obtain the

required concentrations (between 30 and 250 mg/dm³) for the binary and ternary mixtures. For example, the ternary mixture containing 250 mg/dm³ RBR, 250 mg/dm³ RBY and 250 mg/dm³ RBB was composed by diluting 3 stock mixtures (each containing a single dye) to a concentration of 750 mg/dm³ and then mixing them in equal parts (1/3 RBR + 1/3 RBY + 1/3 RBB). The concentrations of the dyes in all mixtures used in this study are given in Table 1.

Table 1

Dye concentration in single, binary and ternary mixtures, mg/dm³

Single system	Binary system						Ternary system		
	ROC		RGC		RVC		RBrC		
	RBY	RBR	RBY	RBB	RBR	RBB	RBY	RBR	RBB
30	30	30	30	30	30	30	30	30	30
60	60	60	60	60	60	60	60	60	60
90	90	90	90	90	90	90	90	90	90
120	120	120	120	120	120	120	120	120	120
150	150	150	150	150	150	150	150	150	150
180	180	180	180	180	180	180	180	180	180
210	210	210	210	210	210	210	210	210	210
250	250	250	250	250	250	250	250	250	250

CAC was added at the start of the experiment. Throughout the adsorption experiments, the mixture was stirred using a magnetic bar stirrer. At fixed times, samples were taken from the reaction mixture to determine the dye concentration (RBY, RBR, and RBB) in the liquid. Before analysis, the samples were filtered using a nylon syringe filter with a pore size of 0.45 μm . All experiments were repeated 3 times and average values are reported.

Various adsorption test runs were carried out to evaluate the influence of the following process parameters on dye adsorption: adsorbent dose from 1 to 10 g/dm³, contact time from 10 to 120 min, temperatures 25, 35, and 45 °C, dye concentration from 30 to 250 mg/dm³; simultaneous presence of different dyes (RBY, RBR, and RBB), and added salts (Na₂CO₃ and Na₂SO₃), which are frequently encountered in dye-containing water. For the latter tests, Na₂CO₃ and Na₂SO₃ were added to the adsorption mixture at a concentration of 20 g/dm³ and 70 g/dm³, respectively.

Chemical analyses. The individual dye concentrations were measured using an UV-visible spectrometer (Jasco V-730), the concentrations of RBY, RBR, and RBB were determined by measuring the absorbance at their maximum absorption wavelengths of 412 nm, 520 nm, and 608 nm. The calculations made to determine the individual dye concentrations for the binary and ternary mixtures are explained in detail hereafter.

The total adsorption efficiency was determined by measuring COD using sealed test tubes according to the standard method [6]. The COD of RBY, RBR, and RBB was

tested for both before and 40 min after adsorption for RBY, RBR, RBB, and their mixtures 120 min after adsorption for RBR and its mixtures.

The obtained removal data were expressed in terms of COD reduction and quantified using R (%), as calculated from:

$$R = \frac{[\text{COD}]_0 - [\text{COD}]_f}{[\text{COD}]_0} \times 100\%$$

where the subscripts 0, f refer to the COD before and after adsorption.

Data treatment. The concentrations of RBY, RBR, and RBB in a single system were directly determined by measuring the absorbances at maximum absorption wavelengths (λ_{max} for RBY 412 nm, for RBR 520 nm, and for RBB 608 nm). Typical spectra are shown in Fig. 1.

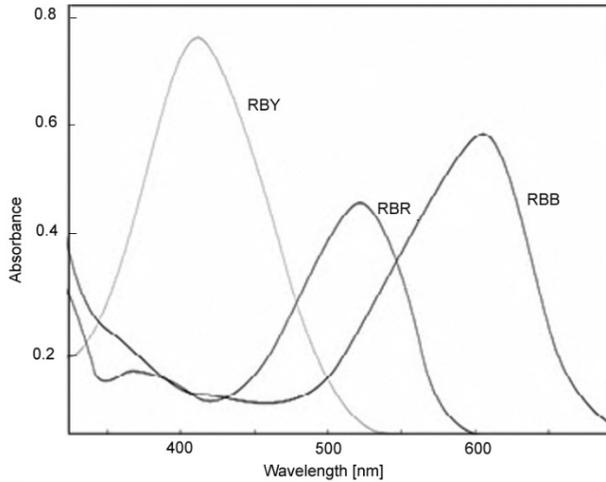


Fig. 1. UV-Vis absorption spectra of RBY, RBR and RBB

The concentrations of binary and ternary mixtures were determined using a matrix method developed by Hamdaoui et al. [7], which allows one to calculate the concentration of individual dyes in a mixture containing multiple components. First, linear calibration curves for the individual dyes were developed (all with $R^2 > 0.99$, Fig. 2).

For a mixture of three dyes, the absorbance A_s of the sample at the wavelengths (λ_y , λ_R and λ_B) are given by:

$$A_s(\lambda_y) = A_y(\lambda_y) + A_R(\lambda_y) + A_B(\lambda_y)$$

$$A_s(\lambda_R) = A_y(\lambda_R) + A_R(\lambda_R) + A_B(\lambda_R) \quad (1)$$

$$A_s(\lambda_B) = A_y(\lambda_B) + A_R(\lambda_B) + A_B(\lambda_B)$$

where $A_s(\lambda_y)$, $A_s(\lambda_R)$, $A_s(\lambda_B)$ are absorbances of the sample, $A_y(\lambda_y)$, $A_y(\lambda_R)$, $A_y(\lambda_B)$ absorbances of RBY dye, $A_R(\lambda_y)$, $A_R(\lambda_R)$, $A_R(\lambda_B)$ absorbances of the RBR dye, $A_B(\lambda_y)$, $A_B(\lambda_R)$, $A_B(\lambda_B)$ absorbances values of the RBB at λ_y , λ_R and λ_B , respectively.

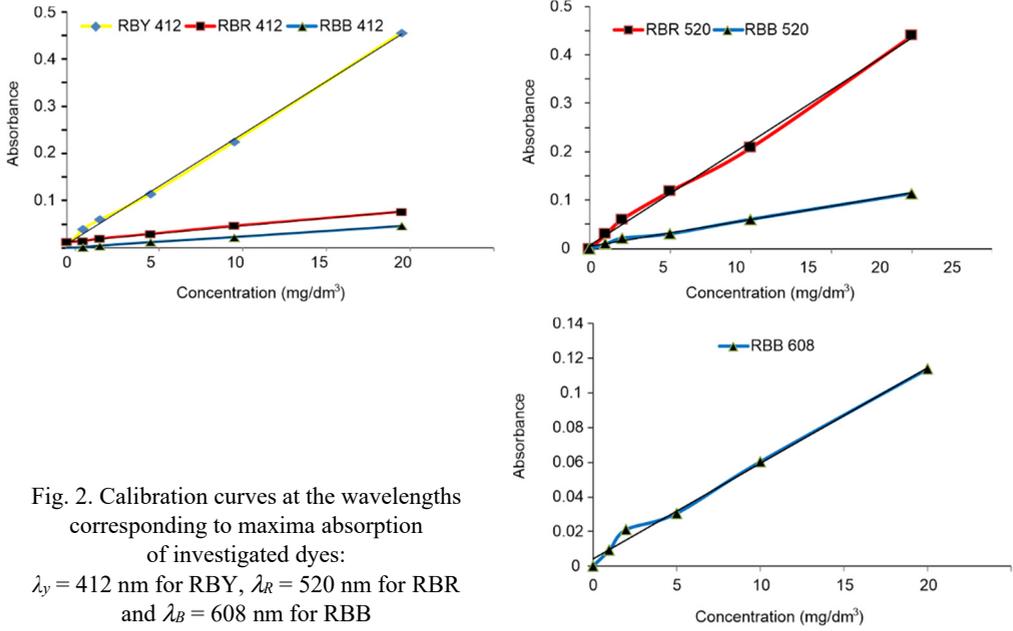


Fig. 2. Calibration curves at the wavelengths corresponding to maxima absorption of investigated dyes:
 $\lambda_y = 412$ nm for RBY, $\lambda_R = 520$ nm for RBR
 and $\lambda_B = 608$ nm for RBB

For each component i in the sample, the Beer–Lambert law (eq. (1)) at λ_j can be written as

$$A_i(\lambda_j) = K_i(\lambda_j)C_i \quad (2)$$

Substituting into eq. (1) we arrive at:

$$A_s(\lambda_y) = k_y(\lambda_y)C_y + k_R(\lambda_y)C_R + k_B(\lambda_y)C_B$$

$$A_s(\lambda_R) = k_y(\lambda_R)C_y + k_R(\lambda_R)C_R + k_B(\lambda_R)C_B \quad (3)$$

$$A_s(\lambda_B) = k_y(\lambda_B)C_y + k_R(\lambda_B)C_R + k_B(\lambda_B)C_B$$

This set of equations can be written in the following matrix notation:

$$\begin{bmatrix} A_s(\lambda_y) & k_y(\lambda_y) & k_R(\lambda_y) & k_B(\lambda_y) \\ A_s(\lambda_R) & k_y(\lambda_R) & k_R(\lambda_R) & k_B(\lambda_R) \\ A_s(\lambda_B) & k_y(\lambda_B) & k_R(\lambda_B) & k_B(\lambda_B) \end{bmatrix} = \begin{bmatrix} C_y \\ C_R \\ C_B \end{bmatrix} \quad (4)$$

Using this notation, the absorbance A_s of the mixture sample of (RBY, RBR, RBB) dyes used in this study can be written as

$$\begin{bmatrix} A_s(\lambda_Y) & k_Y(\lambda_Y) & k_R(\lambda_Y) & k_B(\lambda_Y) \\ A_s(\lambda_R) & 0 & k_R(\lambda_R) & k_B(\lambda_R) \\ A_s(\lambda_B) & 0 & 0 & k_B(\lambda_B) \end{bmatrix} = \begin{bmatrix} C_Y \\ C_R \\ C_B \end{bmatrix} \quad (5)$$

By using equation 5, the matrix of concentrations can be determined (when $(C_i)_{t=0} \neq 0$) by the following equation:

$$[C] = [K]^{-1}[A] \text{ if } (C_i)_{t=0} \neq 0, \quad (C_i)_{t=\infty} = 0 \text{ if } (C_i)_{t=0} = 0 \quad (6)$$

A solution can be found by inverting the matrix of the Beer–Lambert coefficients $[K]$, as shown below:

$$\mathbf{K}^{-1} = \begin{pmatrix} \frac{1}{k_Y(\lambda_Y)} & -\frac{k_R(\lambda_R)}{k_R(\lambda_R)k_Y(\lambda_Y)} & \frac{k_R(\lambda_Y)k_B(\lambda_R) - k_B(\lambda_Y)k_R(\lambda_R)}{k_Y(\lambda_Y)k_R(\lambda_R)k_B(\lambda_B)} \\ 0 & \frac{1}{k_R(\lambda_R)} & -\frac{k_B(\lambda_R)}{k_B(\lambda_B)k_R(\lambda_R)} \\ 0 & 0 & \frac{1}{k_B(\lambda_B)} \end{pmatrix}$$

Using equation (6), the concentration matrix identifying each dye concentration in the mixtures' solution can be determined. In this case, the invert of the matrix $[K]^{-1}$ of the mixture sample of RBY, RBR, and RBB dyes can be written as

$$\mathbf{K}^{-1} = \begin{pmatrix} 45.4545 & -6.4935 & -3.3977 \\ 0 & 47.619 & -13.8427 \\ 0 & 0 & 58.1395 \end{pmatrix}$$

The mass of dye adsorbed per unit mass of CAC at any time t was calculated by determining the dye concentrations in the liquid phase at the start of the experiment and at time t

$$q_t = \frac{C_0 - C_t}{m} V \quad (7)$$

where q_t , mg/g, is the mass of dye adsorbed per unit mass of CAC at time t , C_0 , mg/dm³, the initial dye concentration in the liquid phase, C_t , mg/dm³, the dye concentration in the liquid phase at time t , V , dm³, the volume of the aqueous solution, and m , g, the mass of CAC.

At equilibrium time, the mass of dye adsorbed per unit mass of CAC was calculated similarly

$$q_e = \frac{C_0 - C_e}{m} V \quad (8)$$

with q_e , mg/g, the mass of dye adsorbed per unit mass of CAC at equilibrium and C_e the dye concentration in the liquid phase at equilibrium.

The dye removal R was further calculated by determining the dye concentrations in the liquid phase at the start of the experiment, at time t , and at equilibrium

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (9)$$

Kinetic modeling. The adsorption kinetics was evaluated by applying pseudo-first order and pseudo-second order kinetic models [5]. The pseudo-first order model, developed by Lagergren and Svenska, is the most widely used for describing adsorption kinetics

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (10)$$

where K_1 is the pseudo-first order rate constant, 1/min, q_e , mg/g, is the adsorption capacity at equilibrium, and q_t , mg/g, is the adsorbed amount of dye after time t , min [8].

The pseudo-second order model assumes that the adsorption rate is proportional to the number of vacant sites

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

where K_2 is the pseudo-second order rate constant, g/(mg·min).

Adsorption isotherms. The results from the adsorption tests were used to determine the adsorption isotherms. Both Langmuir and Freundlich equations were fitted.

The Langmuir isotherm [9] is presented by

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (12)$$

where q_{\max} , mg/g, is the maximum adsorption capacity and K_L , dm³/mg, the Langmuir constant. Both constants need to be determined by fitting the model equation to the experimental results.

The essential characteristics of the Langmuir isotherm can be expressed by dimensionless equilibrium parameter R_L

$$R_L = \frac{1}{1 + K_L C_0} \quad (13)$$

Depending on the value of R_L , the adsorption process is considered to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($R_L < 1$) or irreversible ($R_L = 0$) [5].

The Freundlich isotherm is introduced as an empirical model by

$$q_e = K_F C_e^{1/n} \quad (14)$$

With K_F , mg/g, and n temperature-dependent model parameters, corresponding to the adsorption capacity and the adsorption intensity, respectively. Their values are most frequently determined by linearizing the Freundlich isotherm equation

$$\ln q_e = \log K_F + \frac{1}{n} \log C_e \quad (15)$$

Thermodynamic evaluation. The thermodynamic properties of the reactive dye adsorption process were determined using the van't Hoff equation

$$\ln K_e = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (16)$$

with K_e , dm³/mg, being the thermodynamic equilibrium constant equal to the product of q_{\max} and K_L obtained from the Langmuir isotherm [10]; ΔH° , J/mol, and ΔS° , J/(mol·K), are the standard enthalpy and standard entropy of the adsorption and R is the universal gas constant. The values of ΔH° and ΔS° were calculated from the slope and intercept of the linear plot of $\log K_e$ vs. $1/T$.

The free Gibbs energy ΔG° , J/mol, was further calculated via the Gibbs energy equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (17)$$

Alternatively, ΔG° can be calculated from K_e [10]

$$\Delta G^\circ = -RT \ln K_e \quad (18)$$

3. RESULTS AND DISCUSSION

3.1. EFFECT OF ADSORBENT DOSE

The influence of the CAC dose on the adsorption process was evaluated by varying the amount of CAC added to the dye solution between 1 and 10 g/dm³. In all test runs, the other operational parameters were kept constant at an initial dye concentration (C_0) of 250 mg/dm³, unaltered pH, which was 5.7 for RBY, 6.2 for RBR, and 5.7 for RBB (pH_i), and temperature (T) of 25 °C. The adsorption was assumed to have reached equilibrium when no further change in C_t in the function of time was observed.

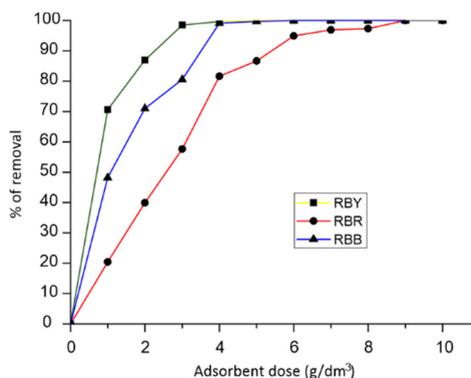


Fig. 3. Effect of adsorbent dose on the adsorption of RBY, RBR, and RBB; $C_0 = 0.250$ g/dm³, $T = 25$ °C

As shown in Fig. 3, full dye removal could be reached for all dyes tested for the adsorbent doses at least 3, 4, and 9 g/dm³ for RBY, RBB, and RBR, respectively. It appears that RBY adsorbs most readily to the CAC, followed by RBB and RBR. The initial increase in percentage removal with increasing CAC dosage can be attributed to the availability of a larger surface area and hence more adsorption sites [4].

3.2. EFFECT OF CONTACT TIME

To determine the time dependence of the adsorption of RBY, RBR, and RBB, time was varied between 10 and 120 min. In all test runs, the other operational parameters were kept constant at an initial dye concentration (C_0) of 250 mg/dm³, a CAC dosage of 5 g/dm³, unaltered pH, which was 5.7 for RBY, 6.2 for RBR, and 5.7 for RBB (pH_i), and temperature (T) of 25 °C. Apart from the single dyes, also the binary mixtures (ROC, RGC, RVC) and the ternary mixture (RBrC) were examined. The results of the adsorption experiments for the single dye systems are presented in Fig. 4.

For the single dye adsorption tests, q_e (50 mg/g) is already obtained after 10 min for RBY and RBB. The adsorption of RBR was much slower – even after 120 min, only a q_t of 45.2 mg/g was obtained. No appreciable increase in adsorption rates was observed beyond this time. These tests confirm earlier observations that the affinity of RBR for activated

carbon is probably low and it needs other process parameters such as temperature, dosing of bases and salt to be increased.

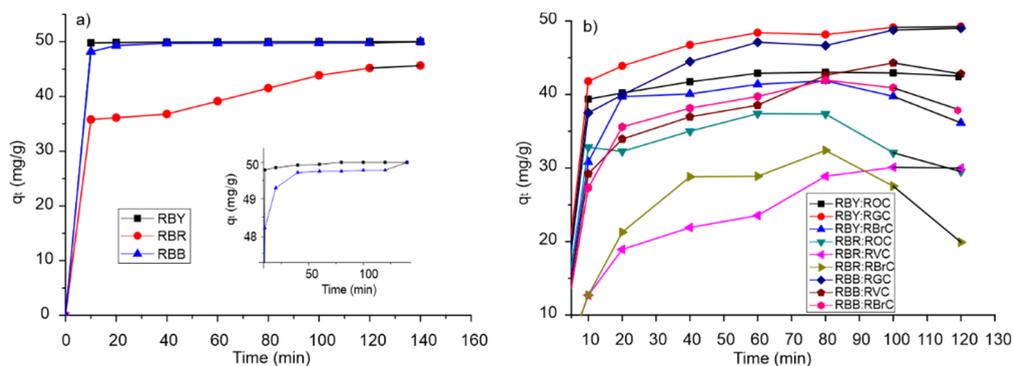


Fig. 4. Effect of time on the adsorption of RBY, RBR, RBB; adsorbent dose = 5 g/dm³, $C = 0.250$ g/dm³, $T = 25$ °C: a) single dyes, b) mixed system

For binary systems, similar observations were made. The adsorption of RBY and RBB occurred fast and became much slower or constant after 40 min. High q_e values were obtained for both dyes, whereas for both combinations, the adsorption of RBR was significantly lower. For RGC, both of RBY and RBB, the q_e was over 49 mg/g after 120 min, which is not significantly different from the single system q_e values. For ROC, the maximum q_t values were limited to 42 and 37 mg/g for RBY and RBR, respectively. For RVC, the q_t values were 44.3 and 30.1 mg/g for RBB and RBR, respectively. They were lower than for the RGC system, which indicates competitive adsorption between RBB/RBY and RBR. In the ternary system (RBrC), these results were confirmed, with q_t values of 41.9, 41.9 and 32.4 mg/g for RBB, RBY and RBR, respectively. In such cases competition occurs between various dyes, leading to lower adsorption capacities for the individual dyes. Furthermore, a significant decrease in q_t was observed for RBR in the ROC, RVC and RBrC mixtures after 100 min. This result can be explained by the presence of the other dyes in the solution (RBB and RBY), for which CAC has a higher adsorption affinity, leading to a competition for the adsorption sites, resulting in desorption of RBR.

3.3. EFFECT OF TEMPERATURE

The effect of the temperature on q_e was studied at 25, 35, and 45 °C. The other operational parameters were kept constant (cf. Section 3.2). The adsorption time was 40 min for RBY and RBB and 120 min for RBR. The results are shown in Fig. 5.

For single system adsorption tests, no effect of the temperature on the adsorption of RBB and RBY was observed (Fig. 5a) and q_e of 50 mg/g was obtained. For RBR (Fig. 5b),

a clear adsorption increase was observed with increasing temperature (q_e of 43 at 25°C, and 50 mg/g at 35 and 45 °C). For the binary systems, the temperature dependence of the adsorption capacity occurred for all dyes, while it was not observed for the ternary system. First, it seems that at a higher temperature, adsorption will be faster. As was seen from the previous experiments (Section 3.2), the adsorption equilibrium was attained at 40 min for the single systems (RBY and RBB). For the other systems, a primary reason for the increase in q_t will be the increase in the adsorption rate.

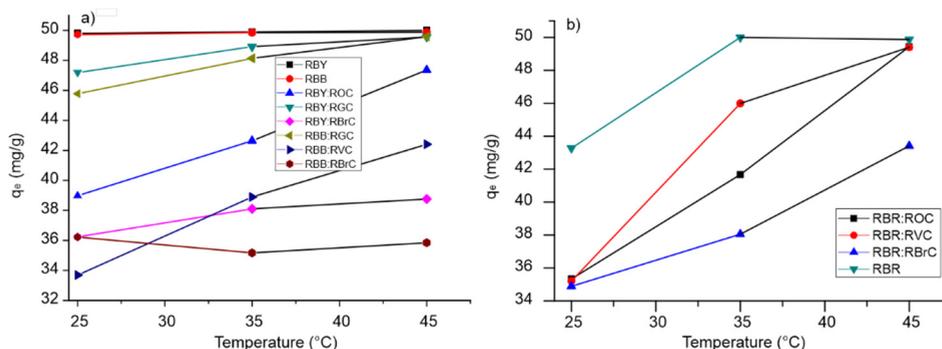


Fig. 5. Effect of temperature on the adsorption of: a) RBY-RBB, b) RBR; adsorbent dose = 5 g/dm³, $C_0 = 0.250$ g/dm³, $t = 40$ min for a) and 120 min for b)

At higher temperatures, the mobility of dye molecules increases, which ensures better contact between dye molecules and the active sites on the surface of CAC [11]. However, the influence of temperature on the adsorption of binary systems plays only a marginal role and the meaning of other factors should be considered.

3.4. EFFECT OF INITIAL DYE CONCENTRATION ON ADSORPTION

The effect of the dye concentration on adsorption was studied for various initial concentrations as shown in Table 1. In all test runs, other operational parameters were kept constant similarly as those presented in Section 3.2. The dependences of the initial dye concentration on the adsorption capacity are shown in Fig. 6.

The adsorption capacity of CAC towards all dyes increases when the dye concentration increases. For the single systems, the increase in RBR adsorption is not so clear as for RBR and RBY. The same trend is also visible for the binary systems. RBY and RBB follow the same trend, whereas the adsorption capacity for RBR increases more slowly upon increasing initial concentration. The effect of initial dye concentration will be treated in more detail in the following part of the paper.

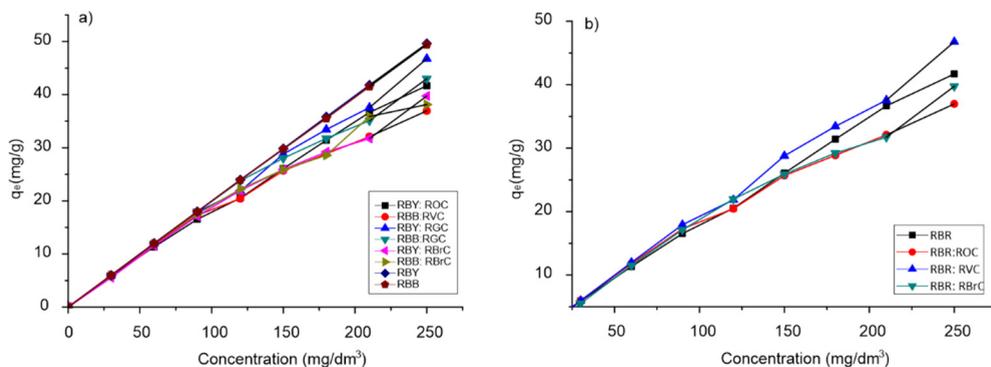


Fig. 6. Effect of temperature on the adsorption of: a) RBY-RBB, b) RBR; adsorbent dose = 5 g/dm^3 , $T = 25 \text{ }^\circ\text{C}$, $C_0 = 0.250 \text{ g/dm}^3$, $t = 40 \text{ min}$ for a) and 120 min for b)

3.5. EFFECT OF THE COMPOSITION OF DYE MIXTURES ON ADSORPTION

The effect of the composition of dye mixtures on the adsorption of RBY, RBR, and RBB onto CAC in the mixed systems (ROC, RGC, RVC, and RBrC) was also investigated. For the conditions of the experiments, cf. Section 3.2.

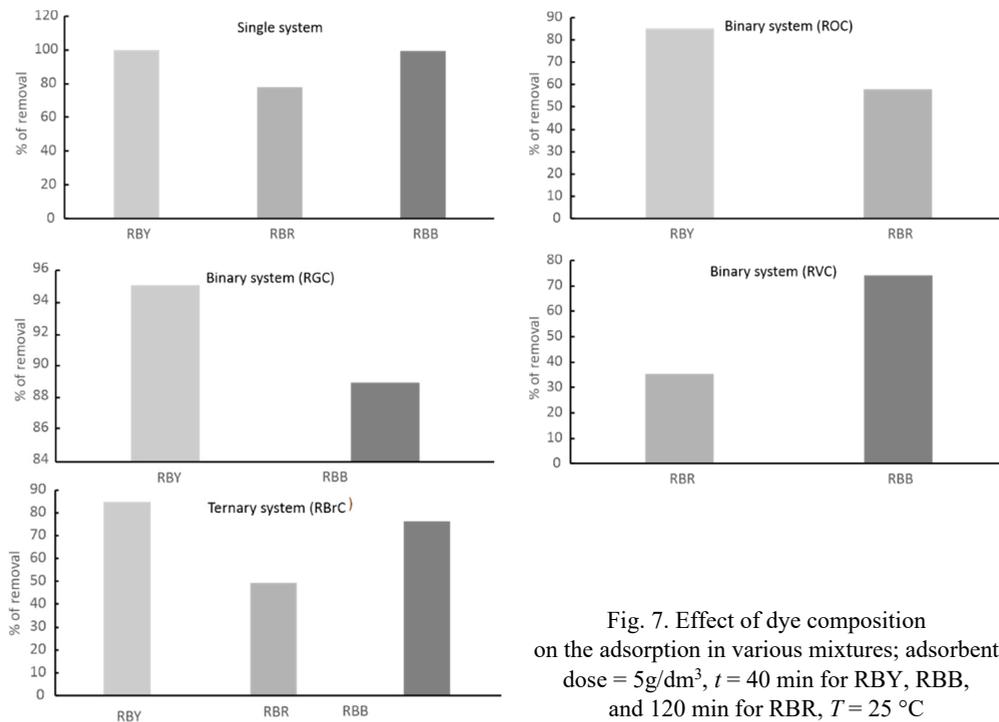


Fig. 7. Effect of dye composition on the adsorption in various mixtures; adsorbent dose = 5 g/dm^3 , $t = 40 \text{ min}$ for RBY, RBB, and 120 min for RBR, $T = 25 \text{ }^\circ\text{C}$

The results show that in the case of single system, RBY ($R = 100\%$) and RBB (R equal to 99.7%) are better adsorbed than RBR ($R = 78\%$), however in binary mixtures, the removal of RBY was 95% in the case of RGC (50% RBY + 50% RBB), whereas in the ROC mixture (50% RBY + 50% RBR) the percentage decreased to 85% ; in the case of mixing RBR with RBY (ROC), and with RBB (RVC: 50% RBR + 50% RBB) the percentage removal decreased from 57.7% to 35% . For RBB, R was 89% in the case of (RGC) and 74% in (RVC) mixture (Fig. 7). For the ternary mixture RBrC (33% RBY + 33% RBR + 33% RBB), the removal percentage of RBY was 81% , RBB 76% and RBR 50% .

The removal rate of RBY was the highest, followed by RBB and RBR. These differences are due to the competition between RBY, RBR and RBB to occupy the reaction sites on the CAC surface [11], and for a different adsorption capacity for different dyes. These results again confirm that CAC is characterized by better adsorption capacity towards RBY and RBB than for RBR.

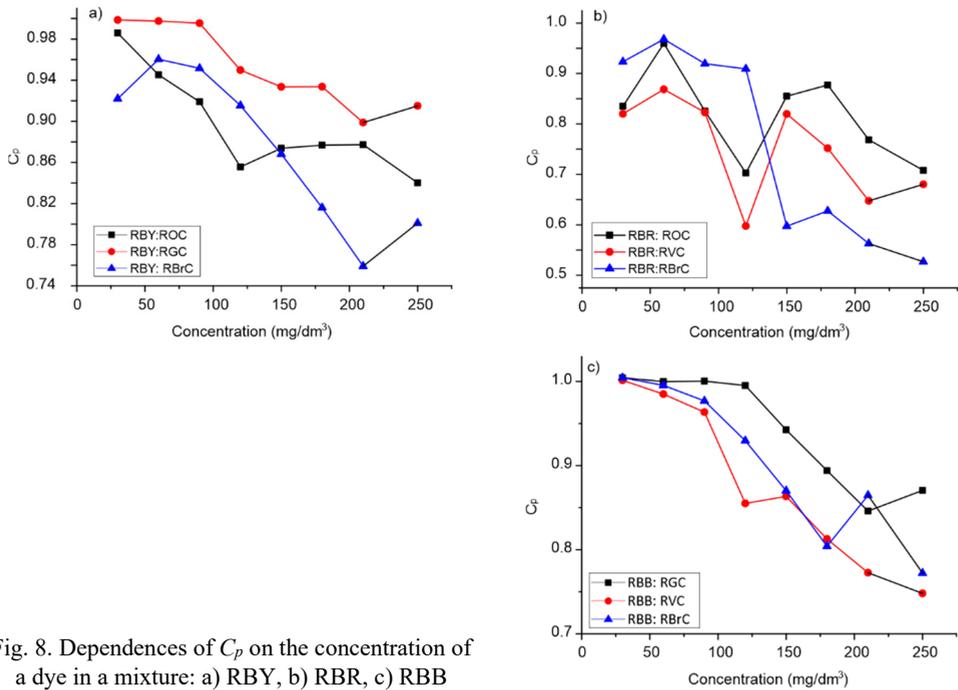


Fig. 8. Dependences of C_p on the concentration of a dye in a mixture: a) RBY, b) RBR, c) RBB

The influence of interaction between the dye in a mixture system was verified by a parameter C_p defined as

$$C_p = \frac{q_{em}}{q_{es}} \quad (19)$$

where q_{em} is the mass of dye adsorbed per unit mass of CAC at equilibrium in dye mixtures, q_{es} the mass of dye adsorbed per unit mass of CAC at equilibrium in a single system.

If $C_p < 1$, the presence of other dyes harmed the adsorption; if $C_p = 1$, no influence was observed; and if $C_p > 1$, the presence of other dyes had a positive effect on adsorption [7, 11]. The C_p values of all sample mixtures are reported in Fig. 8.

For RBY and RBB in binary and ternary mixtures, C_p was close to 1 (0.92–1.00) at concentrations between 30–90 mg/dm³, indicating that only a small influence took place at these low concentrations. At higher concentrations (120–250 mg/dm³) C_p decreased below 0.9. For RBR, C_p was lower than 0.82 already in a low concentration range (30–90 mg/dm³) and even decreased further below 0.7 in the concentration range between 120 and 250 mg/dm³. Following these results, it can be concluded that dye affinity to CAC was the highest for RBY followed by RBB and was the lowest for RBR.

The results showed that the adsorption capacity for a single dye decreased in the presence of other dyes. The reduced capacities can be due to the following factors: (i) interaction between the dyes in solution, (ii) change of the adsorbent surface charge due to adsorption and (iii) competitive adsorption between the dyes for active sites on the adsorbent surface, resulting in displacement effects to replace the other dyes from the adsorption sites [7].

3.6. EFFECT OF SALTS

To evaluate the presence of some frequently encountered salts (i.e., Na₂CO₄ and Na₂SO₃), the adsorption capacity of the dyes was evaluated in the absence (As) and presence (PS) of these salts. The results are presented in Table 2.

Table 2

Effect of the addition of 20 g/dm³ Na₂CO₄ and 70 g/dm³ Na₂SO₃ on the dye adsorption

		q_e [mg/g]	
		As	PS
Single system	RBY	50.00	50
	RBR	36.79	45.6
	RBB	50.00	50
Binary system	RBY: ROC	41.68	50
	RBR: ROC	26.51	33
	RBY: RGC	46.75	50
	RBB: RGC	43.00	50
	RBR: RVC	16.91	21.5
	RBB: RVC	36.96	46.1
Ternary system	RBY: RBrC	39.74	49.4
	RBR: RBrC	22.80	28.4
	RBB: RBrC	38.15	47.2

It was observed that the addition of salts increased adsorption in all dyes RBY, RBR, and RBB in single, binary and ternary systems. For example, q_e for RBR increased from 36.8 to 45.6, from 26.51 to 33, from 16.91 to 21.5, and from 22.8 to 28.4 mg/g for the single system, ROC, RVC and RBrC, respectively.

The beneficial effect of Na_2SO_3 on dye adsorption was earlier described by Al-Degs et al. [12], who attributed it to the aggregation of dye molecules, induced by the action of salt ions (i.e., salt ions force dye molecules to aggregate, increasing the extent of sorption on the carbon surface).

3.7. KINETIC STUDY

Pseudo-first- and pseudo-second order models were applied to model the kinetic behaviour of the adsorption of the dyes on CAC. An overview of the obtained results is provided in Table 3.

Table 3

Modeling of kinetics

System	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
	$q_{e \text{ theor}}$ [mg/g]	K_1 [1/min]	R^2	$q_{e \text{ theor}}$ [mg/g]	K_2 [g/mg·min]	R^2
RBY	0.3	0.03	0.98	50.0	0.400	1.00
RBY: ROC	3.1	0.02	0.51	43.5	0.023	1.00
RBY: RGC	12.8	0.04	0.90	52.6	0.007	1.00
RBY: RBrC	2.8	0.00	0.01	38.5	-0.015	0.99
RBR	14.9	0.02	0.91	47.6	0.003	0.99
RBR: ROC	3.7	0.03	0.57	31.3	-0.007	0.98
RBR: RVC	28.8	0.05	0.46	29.4	0.003	1.00
RBR: RBrC	6.5	0.00	0.01	20.8	-0.007	0.94
RBB	0.41	0.01	0.16	50.0	0.080	1.00
RBB: RGC	14.12	0.03	0.78	52.6	0.007	1.00
RBB: RVC	19.05	0.03	0.95	47.6	0.003	1.00
RBB: RBrC	11.59	0.02	0.91	41.7	0.009	0.99

The values of the correlation coefficients R^2 in Table 3 indicate that the pseudo-second order kinetic model much better describes the adsorption of RBY, RBR, and RBB in single, binary, and ternary mixtures onto CAC: all R^2 were higher than 0.93, indicating the applicability of this kinetic model. Besides, the theoretical ($q_{e \text{ theor}}$) values calculated based on the pseudo-second order model are very close to the experimental values (q_e) for all mixtures presented previously in Fig. 4.

3.8. ADSORPTION ISOTHERMS AND THERMODYNAMIC EVALUATION

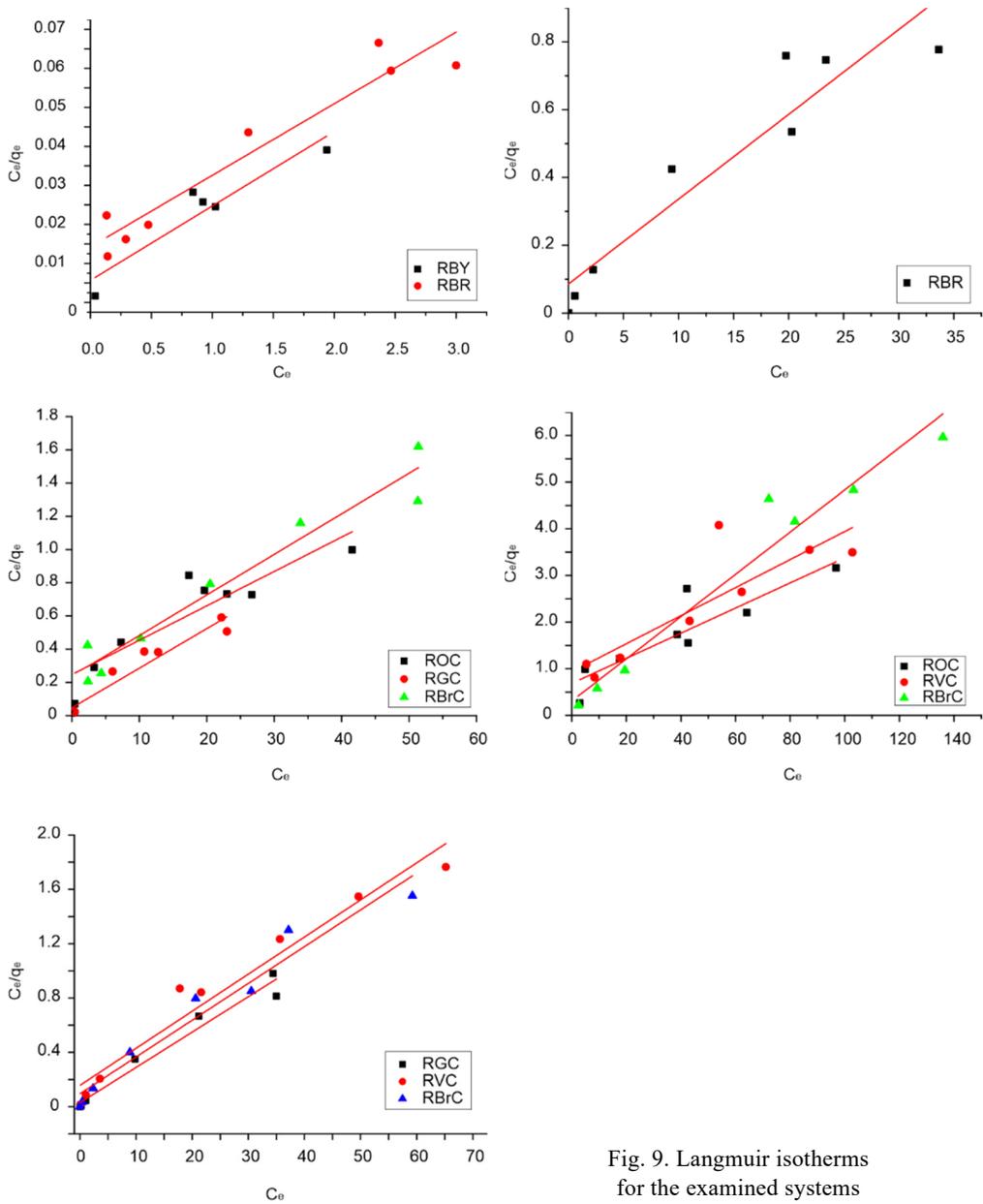


Fig. 9. Langmuir isotherms for the examined systems

Adsorption isotherms plotted for dyes in various solutions are shown in Fig. 9 and the calculated constants are presented in Table 4 for the Langmuir isotherm model. Figure 10 and Table 5 represent the Freundlich isotherm model.

Table 4

Langmuir isotherm parameters

System	q_{max} [mg/g]	K_L [dm ³ /mg]	R^2	R_L	System	q_{max} [mg/g]	K_L [dm ³ /mg]	R^2	R_L
RBV	52.4	175.4	0.89	<1	RVC: RBR	33.22	1.07	0.7419	<1
ROC: RBY	50.0	4.1	0.82	<1	RBrC: RBR	22.08	3.26	0.9615	<1
RGC: RBY	42.0	21.1	0.93	<1	RBB	54.4	70.4	0.93	<1
RBrC: RBY	41.0	4.2	0.95	<1	RGC: RBB	38.5	34.6	0.97	<1
RBR	40.00	11,64	0.8889	<1	RVC: RBB	36.6	6.4	0.96	<1
ROC: RBR	37.17	1.46	0.8037	<1	RBrC: RBB	36.9	10.6	0.96	<1

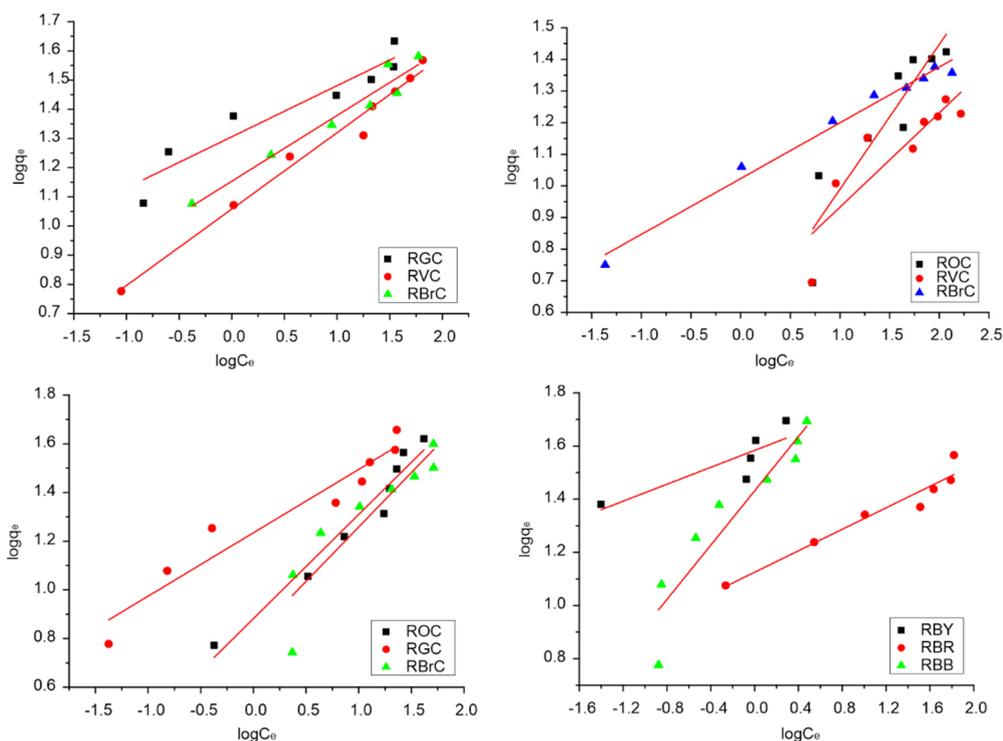


Fig. 10. Freundlich isotherms for the examined systems

The correlation coefficients (R^2) for the Langmuir model are consistently higher than for the Freundlich model. Therefore, the dye removal isotherm using CAC follows the Langmuir model which means that the adsorption of dyes takes place at specific homogeneous sites and via a one layer adsorption onto the CAC surface [13]. The K_L values for the

single and multi-mixture dyes of RBY and RBB were higher than for RBR indicating that RBR is adsorbed in the lowest amount. The R_L values for all examined dyes were between 0 and 1, indicating that the adsorption process is favorable. This confirms that the Langmuir isotherm adsorption was favorable for all dye adsorption onto CAC [10].

Table 5

Freundlich isotherm parameters

	n	K_F (mg/g)	$1/n$	R^2
RBY	6.29	38.28	0.16	0.73
RBY: ROC	1.61	4.25	0.62	0.96
RBY: RGC	3.85	17.14	0.26	0.93
RBY: RBRC	2.24	6.47	0.45	0.83
RBR	2.65	13.34	0.38	0.81
RBR: ROC	2.37	3.40	0.42	0.72
RBR: RVC	2.05	10.54	0.49	0.83
RBR: RBrC	4.38	10.91	0.23	0.6622
RBB	1.96	26.98	0.51	0.88
RBB: RGC	5.71	20.18	0.18	0.90
RBB: RVC	3.36	4.31	0.30	0.98
RBB: RBrC	3.92	14.22	0.26	0.95

The calculated thermodynamic functions are given in Table 6. In the single, binary and ternary systems, the $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$ at various temperatures. The positive values of ΔH° mean that the adsorption process is endothermic, while positive ΔS° reflect the affinity of all dyes to CAC during adsorption.

Table 6

Thermodynamic functions

	ΔH° [J/mol]	ΔS° [J/(mol·K)]	ΔG° [J/mol]		
			298	308	318
RBY	34.10	0.15	-9.88	-11.40	
RBY: ROC	61.52	0.21	0.86	-0.38	-3.37
RBY: RGC	72.09	0.26	-3.00	-5.61	-8.20
RBY: RBRC	10.32	0.03	1.59	1.14	0.98
RBR	162.8	0.56	-0.62	-18.25	-11.32
RBR: ROC	139.8	0.46	1.81	0.00	-7.52
RBR: RVC	139.5	0.46	1.84	-2.13	-7.41
RBR: RBrC	41.13	0.13	1.92	1.16	-0.73
RBB	32.48	0.14	-8.86	-10.63	-11.70
RBB: RGC	38.99	0.13	-3.61	-4.20	-8.37
RBB: RVC	37.95	0.12	2.19	0.91	-0.29
RBB: RBrC	3.98	0.01	1.85	1.74	1.70

In the single systems RBY, RBR, and RBB, and in the binary mixture RGC, the ΔG° values are negative indicating that the adsorption process is spontaneous; at elevated temperatures ΔG° becomes positive, showing that higher temperatures favor the spontaneity and feasibility of the removal process energetically [13]. In the binary system (ROC and RVC) and the ternary mixture in the case RBR, the ΔG° is positive at low temperature and becomes negative with increasing temperature, indicating that at high temperatures the adsorption process becomes spontaneous. ΔG° is positive for RBY and RBB in the ternary system (RBrC) indicating that the adsorption process is non-spontaneous and with increasing of the temperature ΔG° decreased slightly. It seems that at elevated temperatures, the mobility of dye molecules in the solution increases which further improves their adsorption on the CAC surface[14].

3.9. ADSORPTION EFFICIENCY. COD STUDIES

The reduction of COD in dye solution after adsorption treatment with respect to the values before adsorption was 99.83% for RBY, 99.17% for RBB, and only 35.21% for RBR, in a single system during 40 min of treatment (Table 7). In binary and ternary mixture and after 40 min of adsorption, the maximum reduction of COD was obtained in the case of RGC (91.5%) and only 76%, 58.44% and 72%, for ROC, RVC and RBrC, respectively. However, at equilibrium, COD removal increased to 90.11, 80.21, 74.22 and 73.1% for RBR, ROC, RVC and RBrC, respectively. These results demonstrate the effectiveness of the CAC in removing reactive dyes and reduce the COD in single, binary and ternary systems.

Table 7

Reduction of COD removal [%]

Time	RBY	RBR	RBB	ROC	RGC	RVC	RBrC
After 40 min	99.83	35.21	99.17	76	91.5	58.44	72
At equilibrium	–	90.11	–	80.21	95.55	74.22	73.1

4. CONCLUSIONS

It was shown that commercially available activated carbon is capable to effectively remove reactive dyes such as Reactive Bezactiv Yellow (RBY), Reactive Bezactiv Blue (RBB) and Reactive Bezactiv (RBR) from solutions in single, binary and ternary mixtures. The adsorption of each of the reactive dyes in the mixtures differed from each other. The adsorption increased with an increasing contact time, adsorbent dose, temperature, and initial dye concentration. The data indicated that the adsorption kinetics of dyes on CAC follow a pseudo-second order model. The adsorption isotherms followed the Langmuir isotherm. Evaluation of thermodynamic parameters revealed that the adsorption process is endothermic for all dyes and spontaneous just in single and

binary systems, and not spontaneous for the ternary system. Adsorption was higher for RBY, followed by RBB, and was lowest for RBR. The adsorption of RBR became higher with increasing temperature in the presence of salt.

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