Adsorption of reactive dye on activated carbon: kinetic study and influence of initial dye concentration

Adriana Gaščić, univ. bacc. ing. techn. text.
Prof. **Ana Sutlović**, Ph.D.
Prof. **Branka Vojnović**, Ph.D.
Prof. **Mario Cetina**, Ph.D.
University of Zagreb, Faculty of Textile Technology
Prilaz baruna Filipovića 28a, Zagreb, Croatia
e-mail: mario.cetina@ttf.unizg.hr

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Although many of the dyes used in dyeing process are not toxic, dyed effluents have harmful and negative aesthetic and biological effect on water systems, and therefore dyes should be removed from wastewaters. This paper deals with isothermal adsorption of Reactive Black 5 dye on commercial activated carbon. Batch adsorption study was carried out in different periods, from 30 minutes to 16 hours, when equilibrium was reached. Results show exponential lowering of dye concentration after adsorption, from 500 mg dm^{-3} to 118 mg dm^{-3} at equilibrium. In order to investigate the mechanism of adsorption kinetic studies have been performed, and pseudo-second order kinetic model better describes adsorption process of this system. The aim of this work was also to compare influence of initial dye concentration on the adsorption process; percentage of adsorbed dye at equilibrium for initial dye concen-tration c_0 = 300 mg dm^{-3} is for 18 % bigger than that of c_0 = 500 mg dm^{-3}.

Keywords: *isothermal adsorption, wastewaters, activated carbon, reactive dye, adsorption kinetics*

1. Introduction

Textile industry is one of the most environmentally intensive industries because it generates huge quantities of water with complex mixture of chemical substances as a part of unused materials during production. Effluents very often include dyes in the form of coloured wastewater. Thus, one of the largest pollutants are the textile dyeing and textile printing industries, which produce coloured effects on textile materials. Chromophore groups, such as azo, carbonyl and nitro in the dyes are responsible for colour, and they cause contamination rendering unacceptable colour to the textile wastewater. Discharge of such wastewater into environ-ment results in misbalance of ecosystem, causing various undesirable changes [1, 2].

Among the various dye classes, reactive dyes are one of the most used for cotton dyeing, and contribute significantly to colouration of textile wastewaters. The amount of the dye loss from the dyeing process to the effluent is estimated to be sometimes almost 50 % for reactive dyes, so it is necessary to remove them from wastewaters [3]. Methods for dye removal and decolouration are numerous. Biological and chemical methods have been applied for dye removal, although these techniques have a relatively low removal efficiency for reactive dyes, because the most of textile dyes were targeted synthesized to

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*Paper presented at the 2nd International Conference “The Holistic Approach to Environment”, May 28, 2021, Sisak, Croatia be non-biodegradable, stable to light, heat and oxidizing agents. All these methods have disadvantages such as incomplete removal, high reagent and energy consumption and generation of toxic sludge or other waste products that require properly disposal. Among the other decolouration methods, adsorption is proved as an efficient and cost-effective water treatment method. Adsorption also does not result in the formation of harmful substances [1, 2, 4].

The objective of this work was to investigate adsorption efficiency of commercial activated carbon for the removal of Reactive Black 5 (RB5) dye. Additional aims were to determine the rate and mechanism of adsorption for this system, and to compare equilibrium adsorption capacities and percentage of adsorbed dye for two initial dye concentrations. Finally, the standard Gibbs free energy of adsorption were calculated in order to ascertain if adsorption process is spontaneous.

2. Experimental

2.1. Materials

Reactive Black 5 dye (Everzol Black B supplied by Everlight Chemical Industrial Corp., C.I. 20505, chemical formula: $C_{26}H_{21}N_5Na_4O_{19}S_6$, M_r = 991.82) and powdered activated carbon (Kemika company, Croatia) were used for adsorption experiment. Adsorbent was dried prior to experiment in an oven at 105 °C for 24 hours, and stored in desiccator until it is used.

2.2. Batch mode adsorption studies

Adsorption studies were carried on by contacting 50 cm^3 of dye solution of initial concentration c_0 = 500 mg dm^{-3} with 0.1 g of activated carbon in glass bottles. All experiments were repeated in triplicate, and data in Tab.1 and experimental points presented in figures are the average values. Suspensions were shaken at different contact times (30, 60, 120, 180 and 240 minutes) and until equilibrium is reached (16 hours) with impeller speed of 250 rpm at 45±1 °C (Heidolph Unimax 1010 with Incubator 1000). Suspensions were than filtered through filter-paper blue ribbon, and residual liquid-phase dye concentration was determined spectrophotometrically by monitoring the absorbance using UV–Vis spectrophotometer (Lambda 20, Perkin Elmer) at maximum absorbance wavelength of $\lambda_{\max}$ = 598 nm. The calibration graph of absorbance versus concentration obeyed a linear Beer-Lambert relation.

Amount of adsorbate adsorbed at any time t, q_t (mg g^{-1}), and amount of adsorbate adsorbed at equilibrium, q_e (mg g^{-1}), were calculated by using following equation:

$$q = \frac{V \cdot (c_0 - c_t)}{m} \qquad (1)$$

where c_0 is the initial dye concentration (mg dm^{-3}), c_t is dye concentration in the liquid phase after appropriate time of adsorption (mg dm^{-3}), V is the volume of liquid phase (dm^3), and m is mass of the adsorbent (g).

Percentage of adsorbed dye (% *ads.*) is calculated by equation:

$$\%\,ads. = \frac{c_s}{c_0} \cdot 100 \qquad (2)$$

where c_s (mg dm^{-3}) is concentration of adsorbed dye on solid phase ($c_s = c_0 - c_t$).

3. Results and Discussion

3.1. Effect of contact time on adsorption process

A series of experiments at different times were carried out in order to evaluate the adsorption behaviour of activated carbon in the adsorption process of RB5 dye. Average values of dye concentration in liquid and solid phase, percentage of adsorbed dye and amount of adsorbate adsorbed (all at different adsorption times) are given in Tab.1.

Tab.1 Average values of dye concentration in liquid phase after adsorption (c_t), concentration of adsorbed dye on solid phase (c_s), percentage of adsorbed dye (% *ads.*) and amount of adsorbate adsorbed (q_t) at different adsorption times (t)

t / min	**c_s / mg dm^{-3}**	**c_s / mg dm^{-3}**	**% *ads.***	**q_t / mg g^{-1}**
30	332,9	167,1	33,4	83,6
60	298,7	201,3	40,3	100,7
120	235,9	264,1	52,8	132,1
180	225,0	275,0	55,0	137,5
240	213,7	286,3	57,3	143,2
960	118,3	381,7	76,3	190,9

Data in Tab.1 show that dye concentration in solution after adsorption (c_t) exponentially decreases (see also Fig.1), while consequently, concentration in the solid phase (c_s) increases. After one hour, dye concentration decreased from 500 mg dm^{-3} to 298.7 mg dm^{-3} (*ca*. 40 % of dye was adsorbed). Slightly more than 52 % of dye was adsorbed after two hours, while *cca*. 76 % of dye was adsorbed at equilibrium. Thus, adsorption process is initially faster (Fig. 1), while later it slows down; percentage of adsorbed dye difference between two and three hours, as well as between three and four hours is only *ca*. 2 %. On the other side, amount of adsorbate adsorbed (q_t) raises continuously and equilibrium adsorption capacity, ie. amount of adsorbate adsorbed at equilibrium (q_e) for this adsorption system is *ca*. 191 mg g^{-1} (Tab.1).

The second aim of this paper was to determine influence of initial dye concentration on the adsorption process. For that reason, adsorption of initial concentration of c_0 = 500 mg dm^{-3} was compared to that of c_0 = 300 mg dm^{-3} [5]. These two initial dye concentrations were chosen in purpose, because they are typical dye concentrations in dye-house wastewaters after black hues process of dying. Increase of initial dye conc. from c_0 = 300 mg dm^{-3} [5] to c_0 = 500 mg dm^{-3}, using the same experimental conditions (time, type and mass of adsorbent, impeller speed and temperature), resulted in considerable decreased dye adsorption, and consequently increased amount of adsorbate adsorbed at different times (Fig.2). From Fig.2 is obvious that adsorption capacities are bigger for initial dye concentration of c_0 = 500 mg dm^{-3}.

On the other side, as expected, values of percentage of adsorbed dye are bigger for initial dye concentration of c_0 = 300 mg dm^{-3} [5]. Thus, percentage of adsorbed dye at equilibrium for initial dye concentration of c_0 = 300 mg dm^{-3} is for 18 % bigger than that of 500 mg dm^{-3}. This is because all active sites of adsorbent are occupied more rapidly for lower initial dye concentration. There can be distinguished few stages during the dye adsorption (Fig.2). Adsorption rate is initially higher and corresponds to instantaneous adsorption, probably due to an electrostatic attraction between dye and the external surface of adsorbent. The amount of adsorbed substance on the adsorbent and diffusion of dye from solution to adsorbent and into its pores decreases with time, and represents gradual adsorption stage where diffusion rates decreases with increasing the contact time. After that stage follows equilibrium stage when dye molecules occupy all active sites of the adsorbent [6].

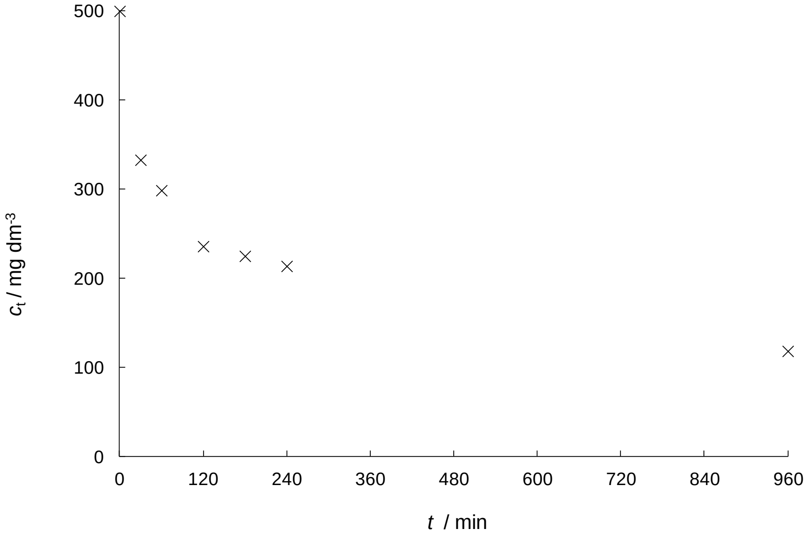

Fig.1 Effect of contact time on the RB5 dye concentration in the liquid phase after adsorption

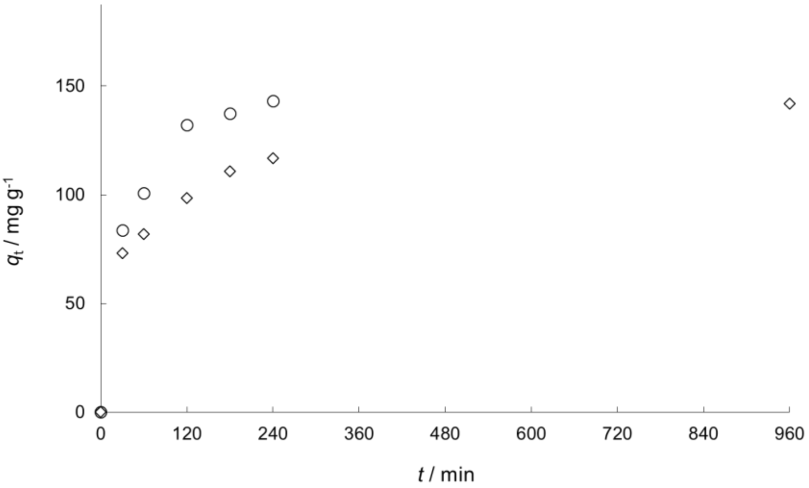

Fig.2 Effect of contact time on RB5 dye adsorption capacity of initial concentrations: ○ – c_0 = 500 mg dm^{-3} and ◇ – c_0 = 300 mg dm^{-3} [5]

3.2. Kinetics of adsorption

In order to investigate the mechanism of adsorption kinetic studies have been performed. Kinetic study is important for an adsorption process because it depicts the uptake rate of adsorbate, and controls the residual time of the whole adsorption process for a given system. The experimental data for initial dye concentration c_0 = 500 mg dm^{-3} were analysed by a pseudo-first order and pseudo-second order kinetic models.

3.2.1. Pseudo-first order kinetic model

Pseudo-first kinetic model, proposed by Lagergren [7], is expressed by following equation:

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

where k_1 is the rate constant of pseudo-first order (min^{-1}). Integrating this equation for the boundary conditions t = 0 to $t = t$ and q_t = 0 to $q_t = q_t$ gives:

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

The kinetic constant k_1 can be determined by plotting $\ln(q_e - q_t)$ against time (t). If the first-order equation is applicable, the plot should give a linear relationship, and allows the calculation of 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 value of the correlation coefficient (R^2) of the line equation is 90.9 %, while the calculated kinetic constant k_1 is 0.0039 min^{-1}. However, despite the relatively high value of R^2, this kinetic model is not suitable for the description of this adsorption system. Calculated value of amount of adsorbate adsorbed at equilibrium from the line equation ($q_{e,calc}$) amounts 111.0 mg dm^{-3}, what is not consistent with the experimentally obtained value, Tab.1 ($q_{e,exp}$ = 190.9 mg dm^{-3}).

3.2.2. Pseudo-second order kinetic model

Ho and McKay [8, 9] developed a pseudo-second order kinetic model given by following equation:

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

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

Integrating this equation for the same boundary conditions as for the first-order gives equation, which in the linear form is presented as:

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

If the pseudo-second order equation is applicable, the plot of t / q_t against time (t) should give a linear relationship, and allows the calculation of amount of adsorbate adsorbed at equilibrium ($q_{e,calc}$) from the slope and afterwards rate constant of pseudo-second order (k_2) from the intercept.

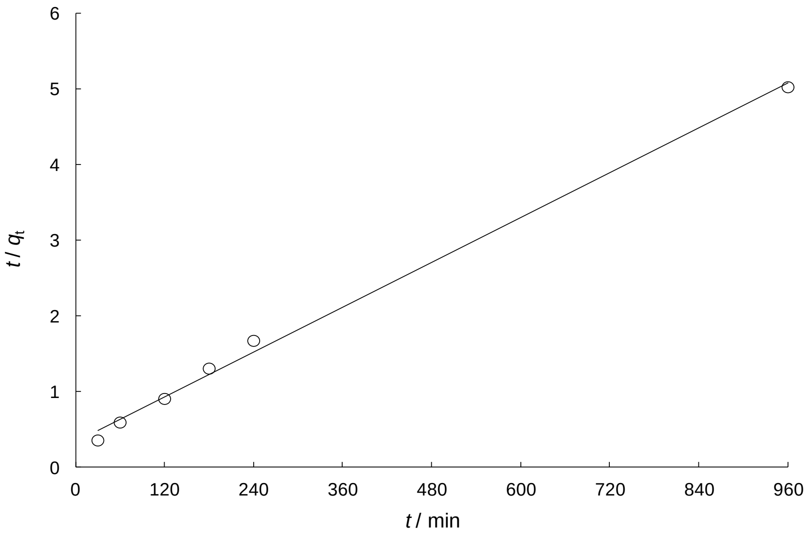

Fig.3 Graphical representation of linear form of pseudo-second order kinetic model for adsorption of RB5 dye on activated carbon

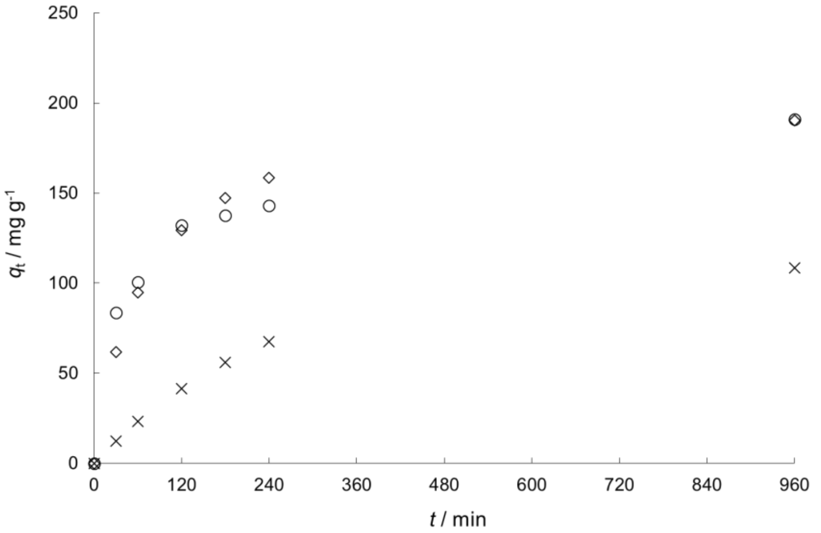

Fig.4 Fitting of pseudo-first and pseudo-second order kinetic models with experimental data for RB5 dye adsorption on activated carbon:
○ – experimental data, × – pseudo-first order, ◇ – pseudo-second order

Graphical representation of linear form of this model (Fig.3) gives a very high value of the correlation coefficient of 99.7 %. Amount of adsorbate adsorbed at equilibrium ($q_{e,calc}$) calculated from the line equation amounts 204.1 mg dm^{-3}, what is approximately equal to the experimentally obtained value of 190.9 mg dm^{-3} (Tab.1). The kinetic constant k_2 calculated from the line equation is 7.07·10^{-5} g mg^{-1} min^{-1}.

Fig.4 shows good agreement of the data with the pseudo-second order equation, compared to pseudo-first order equation. The experimental points are shown together with the theoretically generated ones for both kinetic models, and they well fit to pseudo-second order kinetic model. The pseudo-second order model accounts chemical adsorption as the rate-limiting process [10].

As time approaches zero, according to pseudo-second order model, the initial adsorption rate h (mg g^{-1} min^{-1}) can be calculated using following equation [9, 11]:

$$h = k_2 \cdot q_{e,calc}^2 \qquad (7).$$

Calculated initial adsorption rate value amounts 2.94 mg g^{-1} min^{-1}. As expected, calculated h value for initial dye concentration of c_0 = 300 mg dm^{-3} [5] is much higher, ie. it is *cca*. 5 times higher than that of c_0 = 500 mg dm^{-3} (h = 15.36 mg g^{-1} min^{-1}).

3.3. Thermodynamics

Standard Gibbs free energy value (ΔG^0, kJ mol^{-1}) of adsorption process can be calculated from the equation:

$$\Delta G^0 = -R \cdot T \cdot \ln (K_c) \quad (8),$$

where R is the universal gas constant, T is temperature (T = 318.15 K) and K_c is equilibrium constant. Equilibrium constant K_c could be calculated from ratio of concentration of dye adsorbed on solid phase at equilibrium (c_s) and concentration of dye at equilibrium in the liquid phase (c_e) [12]:

$$K_c = \frac{c_s}{c_e} \quad (9).$$

The negative value of ΔG^0 indicates that the adsorption process is spontaneous, ie. reflects the feasibility of the process. Calculated ΔG^0 value for this adsorption system is −3.1 kJ mol^{-1}, showing that the adsorption of RB5 dye on activated carbon was a spontaneous process in nature whereby no energy input from outside of the system was required.

4. Conclusions

In this paper isothermal adsorption of Reactive Black B dye of initial concentration c_0 = 500 mg dm^{-3} on powdered activated carbon was presented. The results showed that dye concentration in solution exponentially decreases with adsorption time. Approximately 76 % of dye is adsorbed at equilibrium, while equilibrium adsorption capacity is *ca*. 191 mg g^{-1}. At equilibrium, dye of initial concentration c_0 = 500 mg dm^{-3} is adsorbed for *ca*. 18 % less than that of initial concentration c_0 = 300 mg dm^{-3}. Adsorption of RB5 dye on commercial activated carbon is kinetically controlled assuming a pseudo-second order rather than a pseudo-first order process. Finally, calculated standard Gibbs free energy of adsorption value confirmed that the adsorption of Reactive Black 5 dye on activated carbon was a spontaneous process.

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