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Kinetics, isotherm and thermodynamic studies of Reactive Black 5 removal by acid acrylic resins

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ABSTRACT

The removal of Reactive Black 5 from aqueous solutions onto the strongly basic acrylic anion exchangers of type 1, namely Amberlite IRA-458 and Amberlite IRA-958 were investigated. According to the results, the equilibrium time was found to be 180 min for each Reactive Black 5-anion exchanger system. Adsorption experiments indicated that the amount of the dye adsorbed on both Amberlite IRA-458 and Amberlite IRA-958 was dependent on the initial dye concentration in the range of 50–500 mg/L. Modeling of kinetic results showed that the sorption process of the dye adsorption on both anion exchangers was best described by the pseudo second-order kinetic model in the entire investigated concentration domain. The effect of temperature on dye removal showed that the maximum capacity was obtained at 318 and 308 K for the dye adsorption on Amberlite IRA-458 and Amberlite IRA-958, respectively. The adsorption isotherm data were fitted well to the Langmuir isotherm and according to this model, Amberlite IRA-458 and Amberlite IRA-958 exhibited the highest monolayer sorption capacity of 1295.93 and 1723.964 mg/g. Various thermodynamic parameters, such as ΔG, ΔH and ΔS were evaluated and revealed that Reactive Black 5 adsorption process on both Amberlite IRA-458 and Amberlite IRA-958 was endothermic and favourable.

1. Introduction

Dyes usually have a synthetic origin and complex aromatic molecular structures which possibly come from coal-tar based hydrocarbons such as benzene, naphthalene, anthracene, toluene and xylene. They can be classified into three categories: (1) anionic: acid, direct and reactive dyes; (2) cationic: basic dyes; and (3) non-ionic: disperse dyes [1]. Reactive dyes are typically azo-based chromophores combined with different types of reactive groups, e.g., vinyl sulfone, chlorotriazine, trichloropyrimidine, difluorochloropyrimidine. Almost 45% of all textile dyes produced annually belong to the reactive class as a consequence of an intensive use of these dyes for colouring cellulose and viscose-rayon fibres. They are extensively used in many textile industries due to their favourable characteristics, such as bright colour, waterfastness, and simple application techniques. The expanded use of reactive dyes during the last decade has made an impact on conventional methods for treating textile effluents due to generally poor biodegradation of such dyes (especially those containing azo groups) in an aerobic environment and decomposition of most of them into potential carcinogenic aromatic amines under anaerobic conditions. Furthermore, reactive dyes have been identified as problematic compounds in textile wastewaters because they are water-soluble, and found in the wastewater at higher concentrations than other dye classes mainly in their spent, hydrolysed form [2–5]. It is estimated that 10–20% of reactive dyes remain in wastewater during production and nearly 50% of reactive dyes may be lost to the effluents during the dyeing process, and their removal from effluent is difficult by conventional physical/chemical as well as biological treatment [6].

Adsorption/ion exchange seems to be an alternative method for the removal of reactive dyes. Recent research [7,8] has explored applying commercial anion exchange resins to water contaminated with a broad range of reactive dyes and it has been shown that anion exchangers possess excellent adsorption capacity (200–1200 μmol/g) and demonstrate efficient regeneration property for their removal and recovery [9,10]. However, the investigations by Karcher et al. reported in [7,8] are related to the anion exchangers derived from styrene-divinylebenzene copolymers and in the current literature, there is a lack of information about anion exchangers based on the acrylic copolymers used for reactive dyes removal. However, the applicability of ion exchange resin containing acrylic matrix for removing other classes of dyes is well documented [11–14]. It is predicted, and subsequently confirmed, that an anion exchange resin based upon an acrylic matrix should demonstrate beneficial exchange equilibria and kinetics towards large organic ions compared with the styrenic structures. A direct explanation for this lies with greater hydrophilic nature of the

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aliphatic skeletal structure of the acrylic matrix, which, in turn, means a weaker van der Waals type attraction between the resin matrix and the hydrocarbon structure of an organic counter-ion [15]. Acrylic anion exchangers have also higher values of the anion exchange capacities and pollute a much lower degree than styrenic resins do when used in applications where high levels of organic compounds are present [16].

In the present study, two commercial strong acid anion exchange resins based on the acrylic copolymers with quaternary ammonium groups were applied to remove Reactive Black 5 from aqueous solutions. The system variables studied included initial dye concentration, phase contact time and temperature. The kinetic, equilibrium and thermodynamic studies were carried out to observe the effects of the above mentioned various process parameters.

Reactive Black 5 was chosen in this study because it is a dye widely used in textile industry of different commercial names such as Cavalite Black B, Celmazol Black B, Diamira Black B, Drimarene Black R/K 3B, Intracron Black VS-B, Levafix Black E-B, Primazin Black BN, Remazol Black B, Remazol Black GF, Sumifix Black B. It is a black disazo reactive vinylosulfonyl dye used for urea- and sodium bicarbonate-padded cotton utilizing stream or dry heat for fixing [17].

2. Materials and methods

2.1. Materials

2.1.1. Dye

The textile dye, Reactive Black 5 (abbreviation: RB5, C.I. number: 20,505, molecular formula: $C_{26}H_{21}N_5Na_4O_{19}S_6$, molecular weight: 991.82 g/mol) was purchased from Sigma–Aldrich (Germany) and used without further purification (dye purity: 55%). RB5 [4-amino-5-hydroxy-3,6-bis((4-((2-(sulfooxy)ethyl)sulfonyl) phenyl)azo)-2,7-naphthalenedisulfonic acid tetrasodium salt] is dissociated anionic sulfonate in aqueous solution with the molecular structure presented in Fig. 1. The dye is highly soluble, of >50 g/L. Its molecule has a size of 3.15 nm × 1.23 nm × 0.92 nm [18].

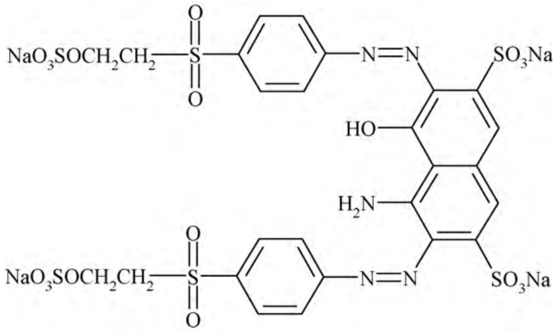

Fig. 1. Chemical structure of Reactive Black 5.

2.1.2. Resins

The commercial synthetic, strongly basic anion exchange resins with the acrylic skeleton: Amberlite IRA-458 of gel type structure and Amberlite IRA-958 of macroporous structure were obtained from Rohm & Haas (France). The physico-chemical properties and specifications of ion exchange resins are presented in Table 1 [19].

Both Amberlite IRA-458 and Amberlite IRA-958 were chosen in the study on the dye removal because they are referred as the anion exchange resins being particularly useful as an organic scavenger for effective adsorption of the naturally occurring organic molecules present in many water supplies.

The resins were washed with distilled water to remove impurities and dried.

2.2. Methods

2.2.1. Sorption kinetics

For the kinetic studies, 20 mL Reactive Black 5 solution at a respective initial dye concentration varying from 50 to 500 mg/L was introduced into a 100 mL joint-stopper conical flask containing 0.2 g of the dried anion exchanger. The flask was capped and agitated at a constant temperature of 298 K in the thermostatic shaker (Elphin +358S, Poland) at 180 rpm for 1–240 min. After that time, the resin was filtered off and the concentration of the residual dye was determined spectrophotometrically at 598 nm using an UV/vis spectrophotometer (Specord M 42, Carl Zeiss Jena, Germany). The amount of solute adsorbed at time t, q_t was calculated as:

$$q_t = \frac{(c_0 - c_t)}{w} \times V \qquad (1)$$

where c_0 and c_t (mg/L) are the liquid-phase concentrations of solutes at the initial and given time t, respectively, V (L) is the volume of solution and w (g) is the mass of dry resin.

2.2.2. Sorption kinetic models

The pseudo-first-order Lagergren equation based on solid capacity is given as:

$$\frac{dq_e}{dt} = k_1(q_e - q_1) \qquad (2)$$

Table 1
Physico-chemical properties of the anion exchangers.

Characteristics	Amberlite IRA-458	Amberlite IRA-958
Physical characteristics		
Physical form	Transparent white beads	White opaque beads
Shipping weight	720 g/dm3	
Uniformity coefficient	≤1.90	≤1.80
Particle size range	0.300 mm: 2% max1.800 mm: 20% max	0.355 mm: 1% max1.180 mm: 5% max
BET surface area	2.03 m^2/g	2.03 m^2/g
Average pore diameter	3.6 nm	6.46 nm
Temperature limitations	35 °C	80 °C
Effective size	0.600–0.900 mm	0.630–0.850 mm
Chemical characteristics		
Matrix	Crosslinked acrylic structure	
Structure	Gel	Macroporous
Functional groups	Quaternary ammonium	
Ionic form	Chloride	
pH limitations	None	
Total exchange capacity	≥1.25 eq/dm^3	≥0.8 eq/dm^3
Moisture retention	57–64%	66–72%

Integrating Eq. (3) and applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, this equation may be rearranged for linearised data plotting as shown by Eq. (3):

$$\log(q_e - q_1) = \log q_1 - \frac{k_1 t}{2.303} \tag{3}$$

where q_e and q_1 are the amounts of dye adsorbed at equilibrium (mg/g) and at time t, respectively, and k_1 is the rate constant of pseudo-first-order sorption (1/min).

A straight line of $\log(q_e - q_1)$ vs. t suggests the applicability of this kinetic model and the values of $\log q_1$ and k_1 can be determined by the intercept and the slope of this linear plot respectively [2,4,20–25].

The pseudo second-order Ho equation based on the sorption capacity of the solid phase and the assumption that the sorption process involves chemisorption mechanism is expressed as:

$$\frac{dq_{\mathrm{e}}}{dt} = k_2(q_{\mathrm{e}} - q_2)^2 \tag{4}$$

After taking the boundary conditions into account, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the integrated form of Eq. (5) can be rearranged to obtain Eq. (5):

$$\frac{t}{q_2} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where q_2 is the amount of dye adsorbed at equilibrium (mg/g), k_2 is the equilibrium rate constant of pseudo second-order sorption (g/mg min).

If pseudo second-order kinetics is applicable, the plot of t/q against t of Eq. (5) should give a linear relationship, from which q_{e} and k_2 can be determined from the slope and intercept of the plot and there is no need to know any parameters beforehand [2,23,26,27].

The applicability of the Lagergren and Ho models was checked by attempting to obtain a linear fit of the experimental data by the appropriate equations. The corresponding parameters of different kinetic models were determined by linear regression. The conformity between the experimental data and the values obtained from the two equations mentioned above was expressed by the correlation coefficients, r^2. A relatively high r^2 value indicates that the equation successfully describes the kinetics of Reactive Black 5 adsorption.

2.2.3. Sorption isotherms

For adsorption isotherms studies, 0.2 g of the dried anion exchanger was equilibrated separately with 20 mL solutions containing different Reactive Black 5 concentrations (50–24,000 mg/L) in a 100 mL joint-stopper conical flask. The contents were shaken thoroughly at the temperatures of 298, 308 and 318 K using a thermostatic shaker (Elphin +358S, Poland) rotating at 180 rpm. The solutions were then filtered and the equilibrium concentrations of Reactive Black 5 concentrations were determined using the UV/vis spectrophotometer (Specord M 42, Carl Zeiss Jena, Germany). The amount of solute adsorbed at equilibrium, q_t was calculated as:

$$q_e = \frac{(c_0 - c_e)}{w} \times V \tag{6}$$

where c_0 and c_e (mg/L) are the liquid-phase concentrations of solutes at the initial and equilibrium time t, respectively, V (L) is the volume of solution and w (g) is the mass of dry resin.

2.2.4. Sorption isotherm models

The Langmuir sorption isotherm is most widely used for the sorption of a pollutant from liquid solutions. The model is based on several basic assumptions: (i) sorption takes place on specific homogeneous sites within the adsorbent; (ii) a dye molecule occupies a site; (iii) the adsorbent has a finite capacity for the adsorbate (at equilibrium, a saturation point is reached and further adsorption can proceed); (iv) all sites are identical and energetically equivalent (adsorbents are structurally homogeneous). The linear form of the Langmuir equation is represented as follows:

$$\frac{c_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \tag{7}$$

where q_0 is the maximum capacity of adsorbate to form a complete monolayer on the surface (mg/g), b is the Langmuir constant related to the heat of adsorption (L/mg).

By plotting c_e/q_e versus c_e, it is possible to obtain the value of q_0 from the slope which is $1/q_0$ and b from the intercept which is $1/q_0 b$.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called an equilibrium parameter, R_{L}, which perfectly determines the favourability and shape of the isotherm of the adsorption process by applying Eq. (8):

$$R_{\mathrm{L}} = \frac{1}{(1 + bc_0)} \tag{8}$$

The R_{L} values indicate the type of isotherm to be either irreversible ($R_{\mathrm{L}} = 0$), favourable ($0 < R_{\mathrm{L}} < 1$), linear ($R_{\mathrm{L}} = 1$), or unfavourable ($R_{\mathrm{L}} > 1$) [10,28].

The Freundlich isotherm is the earliest known relationship describing the adsorption equation. The model applies to adsorption on heterogeneous surfaces with the interaction between the adsorbed molecules and the application of the Freundlich equation suggests that the adsorption energy exponentially decreases on completion of the adsorption centres of an adsorbent. This model also predicts that the dye concentration on the material will increase as long as there is an increase of the dye concentration in the solution (this is not restricted to the monolayer in the adsorbent). This isotherm is an empirical equation employed to describe the heterogeneous system and is expressed by the following linearized Eq. (9):

$$\log q_e = \log K_{\mathrm{F}} + \frac{1}{n} \log c_e \tag{9}$$

where K_{F} (mg/g) is the Freundlich constant related to the adsorption capacity of the adsorbent and $1/n$ is another constant related to the surface heterogeneity. On this basis, the latter constant can be classified as irreversible ($1/n = 0$), favourable ($0 < 1/n < 1$) and unfavourable ($1/n > 1$).

The plot of $\log q_e$ versus $\log c_e$ should give a straight line with a slope of $1/n$ and the intercept of $\log K_{\mathrm{F}}$ [29–32].

2.2.5. Thermodynamic parameters

The Gibbs free energy change of the adsorption process can be calculated by using the following Eq. (10):

$$\Delta G = -RT \ln K_d \tag{10}$$

where T (K) is the solution temperature, R is the gas constant (8.314 J/mol K) and K_d is the distribution coefficient for the adsorption.

The distribution coefficient indicates the adsorbent capability of retaining the solute and also the extent of its movement in a solution phase. It is expressed as:

$$K_d = \frac{c_a}{c_e} \tag{11}$$

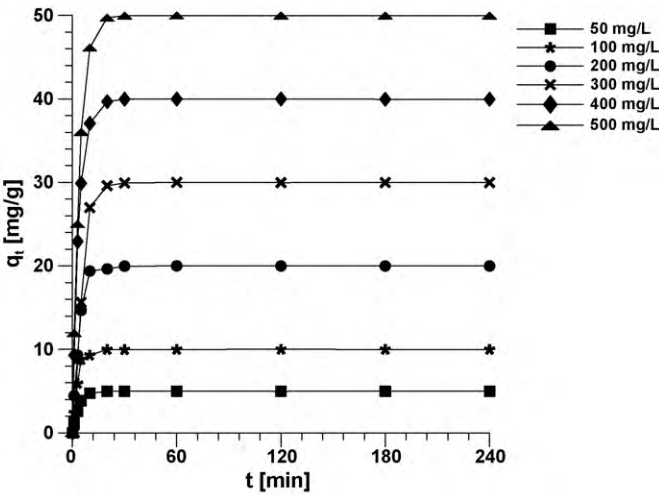

Fig. 2. Influence of the initial Reactive Black 5 concentration on the sorption of the dye on gel Amberlite IRA-458 (conditions: volume: 20 mL, resin mass: 200 mg, temperature: 298 K, agitation rate: 180 rpm).

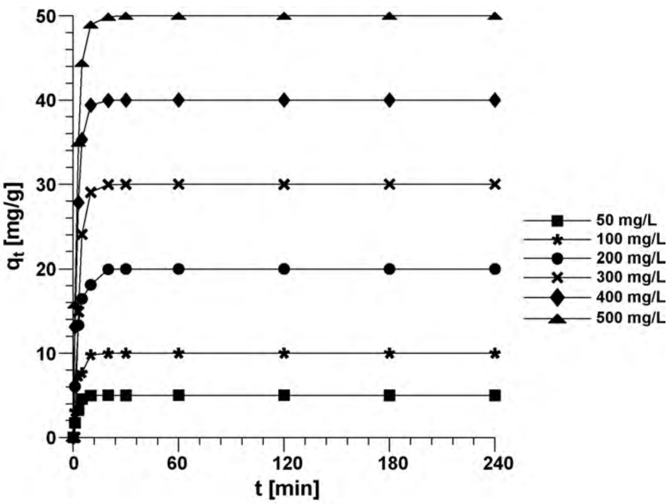

Fig. 3. Influence of the initial Reactive Black 5 concentration on the sorption of the dye on macroporous Amberlite IRA-958 (conditions: volume: 20 mL, resin mass: 200 mg, temperature: 298 K, agitation rate: 180 rpm).

where c_a (mg) is the amount of dye adsorbed on the adsorbent at equilibrium.

The standard enthalpy and entropy change values of adsorption can be calculated from the van't Hoff equation given as below:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{12}$$

As can be seen from Eq. (12), if the equilibrium constants for an adsorption reaction at different temperatures are known, the values of standard enthalpy and entropy changes for adsorption can be estimated from the slope and intercept of the linear van't Hoff plots of $\ln K_d$ vs. $1/T$ [28,30].

3. Results and discussion

3.1. Kinetic studies

3.1.1. Effect of the initial dye concentration

The adsorption data for uptake of Reactive Black 5 on Amberlite IRA-458 and Amberlite IRA-958 vs. contact time at different initial dye concentrations for the fixed anion exchanger dose of 10 g/L are presented in Figs. 2 and 3.

The concentration of the dye in solution can strongly affect the sorption kinetics. When the initial dye concentration increases from 50 to 500 mg/L, the adsorbed amount of Reactive Black 5 increases from 5.00 to 49.98 mg/L for Amberlite IRA-458 and from 4.99 to 49.99 mg/L for Amberlite IRA-958. It is due to the increase in the driving force with an increase in the initial dye concentrations. At high initial Reactive Black 5 concentrations, the driving force favours adsorption because the gradient between the dye solution and the center of the anion exchanger particle enhances the dye diffusion through the film surrounding the particle.

The concentration of the dye in the solution can also affect strongly the mechanism controlling the overall kinetic coefficient. It is evident that Reactive Black 5 concentration hardly influences the time required to reach equilibrium and it is found that the time of 20 min of contact time is sufficient to achieve complete uptake of dye in the whole examined dye concentration range. Using chitosan, Gibbs et al. [17] observed that, in the concentration range 50–100 mg/L, Reactive Black 5 concentration hardly influenced the time required to reach equilibrium. Robinson et al. [33] also observed a limited effect of the dye concentration on sorption kinetics of Reactive Black 5 using agricultural waste residues, corncob and barley husk, in the dye concentration range 50–200 mg/L. However, Reactive Black 5 adsorption on a high lime fly ash was found to be significantly influenced by the initial dye concentration [20].

The concentration of the dye solution drastically decreases to zero within the first minutes of contact because the used amount of both Amberlite IRA-458 and Amberlite IRA-958 is in excess. Because of a large ratio between the anion exchange sites (large anion exchanger dosages) and the solute amounts in solution, there is a sufficient number of ion exchange sites at the surfaces of both anion exchange resins for complete reduction of the residual concentration. Thus, the contribution of intraparticle diffusion to kinetic control cannot be correctly estimated, and a false conclusion on the nature of limiting kinetic steps can be drawn [17]. However, it seems that the intraparticle diffusion may not be active in the control of sorption kinetics in the examined dye concentration range because the external surface areas of anion exchangers are probably high enough to adsorb the total amount of Reactive Black 5 at the initial dye concentration below 500 mg/L.

3.1.2. Adsorption kinetics modeling studies

In order to analyze the adsorption kinetics for Reactive Black 5 on Amberlite IRA-458 and Amberlite IRA-958, the pseudo first-order and the pseudo second-order equations were adopted to stimulate the data. These models basically include all steps of adsorption such as external film diffusion, internal particle diffusion, and adsorption, so they are pseudo-models [29,34,35]. The estimated pseudo first-order and pseudo second-order kinetic parameters in all concentrations tested as well as the values of correlation coefficients are shown in Table 2.

The pseudo first-order equation does not fit well for the whole range of contact time and is applicable only over the initial stages of the process equal to about 30 min in the case of Reactive Black 5 adsorption on both Amberlite IRA-458 and Amberlite IRA-958. Thus, the Lagergren expression cannot be applied for the entire process of dye adsorption. Similarly, previous studies by some researchers showed that the pseudo first-order kinetics was proved to be successful where the sorption process was found to be rapid and showed a poor-fit in the later stages. Kumar et al. [36] showed that the pseudo first-order kinetics was found to be successful only for the first 25 min where the solute uptake process was found to be rapid for methylene blue/fly ash system. A similar observation was also reported by Ho and McKay [37] for the sorption of basic dyes onto peat particles [38]. Furthermore, the pseudo first-order

Table 2
Linear estimates of the pseudo-first order and pseudo second-order parameters for the adsorption of Reactive Black 5 by gel Amberlite IRA-458 and macroporous Amberlite IRA-958 at different dye concentrations (conditions: the volume: 20 mL, resin mass: 200 mg, temperature: 298 K, agitation rate: 180 rpm).

c_0	$q_{e,exp} \pm S^a$	Pseudo-first-order kinetic			Pseudo second-order kinetic		
		k_1	$q_{1,cal}$	${r_1}^2$	k_2	$q_{2,cal}$	${r_2}^2$
Amberlite IRA-458							
50	5.00 ± 0.00	0.041	0.46	0.403	0.145	5.04	0.999
100	9.99 ± 0.01	0.207	5.21	0.847	0.088	10.06	0.999
200	19.99 ± 0.01	0.221	15.59	0.951	0.032	20.17	0.999
300	29.99 ± 0.01	0.208	27.95	0.993	0.019	30.30	0.999
400	39.96 ± 0.04	0.244	35.83	0.999	0.018	40.28	0.999
500	49.98 ± 0.03	0.280	57.26	0.998	0.013	50.43	0.999
Amberlite IRA-958							
50	4.99 ± 0.01	0.572	7.35	0.990	0.314	5.01	0.999
100	9.99 ± 0.01	0.315	8.03	0.977	0.118	10.04	0.999
200	19.99 ± 0.01	0.286	18.17	0.989	0.050	20.11	0.999
300	30.00 ± 0.00	0.124	5.43	0.694	0.037	30.18	0.999
400	39.98 ± 0.03	0.287	21.43	0.970	0.036	40.15	0.999
500	49.99 ± 0.01	0.303	33.16	0.979	0.028	50.20	0.999

c_0 [mg/L]; $q_{,exp}$, $q_{1,cal.}$, $q_{2,cal.}$ (mg/g); k_1 (1/min); k_2 (g/(mg min)); ε (%).
[a] Standard deviation.

kinetic equation does not describe the sorption kinetics of both dye-anion exchanger systems adequately because the experimental q_e values do not agree very well with those calculated. A time lag, probably resulting from the presence of the boundary layer or external resistance affecting the beginning of adsorption process, is the cause of these discrepancies. For this reason, the adsorption of Reactive Black 5 on both Amberlite IRA-458 and Amberlite IRA-958 cannot be considered as that following the pseudo first-order mechanism despite relatively high values of fitting correlation coefficients. However, it is worth noticing that for some adsorption data, the values of correlation coefficients are relatively low, ranging from 0.403 to 0.951, when the dye adsorption from the solution of 50–200 mg/L occurs on Amberlite IRA-458. Also in the case of the dye adsorption on Amberlite IRA-958, some deviations of correlation values are observed for the solution containing 300 mg/L of Reactive Black 5 (Table 2). It also confirms the fact that the pseudo first-order equation is unable to fit the kinetic Reactive Black 5 adsorption data on both examined anion exchangers.

Therefore, the most commonly used pseudo second-order model was applied to the presented sorption systems and as follows from Table 2 this kinetic expression provides a better fit to the experimental kinetic data than that of the pseudo first-order in both examined cases.

Firstly, it is seen that the Ho's model fits the experimental results with much higher correlation (=0.999) values than the Lagergren's model. The plots of t/q_t vs. t for the removal of Reactive Black 5 on Amberlite IRA-458 and Amberlite IRA-958, respectively give straight lines for all the initial dye concentrations studied with extremely high correlation coefficients.

Furthermore, the values of q_e obtained from the Ho's equation are very close the experimental results, whereas the q_e values predicted from the pseudo first-kinetic equation are underestimated as it was mentioned above. Thus, the pseudo second-order kinetic expression can be used to predict successfully the amount of the dye adsorbed at equilibrium using the kinetic experimental data. In addition, on the contrary to the Lagergren's expression, the pseudo second-order model predicts Reactive Black 5 adsorption behaviour on both anion exchangers over the whole range of adsorption period.

These results suggested that the pseudo second-order adsorption mechanism is predominant and that the overall rate of the dye adsorption process appeared to be controlled by the chemisorption process [13,29,31,34,39,40]. Although Reactive Black 5 is an organic compound, it can be ionized in solution to form negative ions. As Amberlite IRA-458 and Amberlite IRA-958 are anion exchangers possessing numerous quaternary ammonium groups, a chemical reaction through electrostatic interaction may occur between the functional groups of the anion exchanger in the chloride form (R–N$^+$(CH$_3$)Cl$^-$) and the anions of dye molecules. However, this may indicate a major drawback to the application of such a process to the removal of the dye from wastewaters, as chemical sorption is seldom reversible, which eliminates the possibility of sorbent regeneration and reuse. This further implies that a destructive method will need to be employed to free the adsorbed dye. Both of these issues would negatively impact on the low-cost aspect usually associated with sorption processes [13,39,40].

As follows from Table 2, the pseudo second-order rate constants are affected by the initial dye concentration for both anion exchange resins and they decrease irrelevantly with the increasing initial dye concentration. Furthermore, the higher values of the pseudo second-order rate constants for Reactive Black 5 adsorption on Amberlite IRA-958 than on Amberlite IRA-458 show that the dye is more rapidly adsorbed by the macroporous than by gel anion exchange resin [22].

Kinetic adsorption of Reactive Black 5 by numerous materials was studied using Eqs. (2)–(5). The adsorption rate constants, the predicted equilibrium uptake values and the corresponding correlation coefficients for some Reactive Black 5 adsorption studies are reported in [2,4,20,41,42]. As can be seen, the present research on the adsorption of this dye on Amberlite IRA-458 and Amberlite IRA-958 is one of many cases in which the pseudo second-order model is better than the pseudo first-order one. So far the properties of the adsorption system affecting that one model is a better representation than another one, have not been known. However, it is generally accepted that for the most adsorption period, the rate is controlled by various diffusion regimes, and therefore, the Ho's expression is considered to be better than empirical equations do not reflect the actual chemical and physical phenomena taking place [43].

3.2. *Equilibrium studies*

3.2.1. *Effect of temperature*

The effect of temperature on the adsorption isotherm of Reactive Black 5 on the anion exchangers was studied at three different temperatures, 298, 308 and 318 K, with a contact time of 180 min. The results obtained for the dye adsorption on Amberlite IRA-458 and

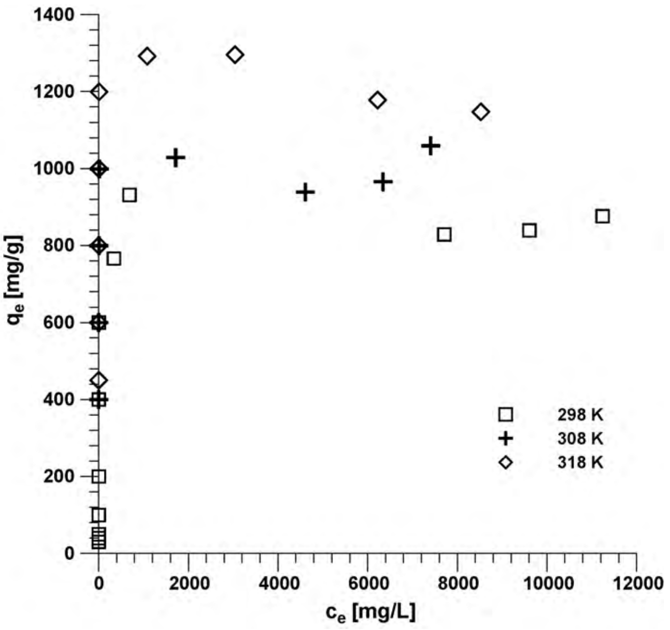

Fig. 4. Comparison of the experimental adsorption isotherms of Reactive Black 5 obtained at different temperatures for gel Amberlite IRA-458 (conditions: the phase contact time: 180 min, volume: 20 mL, resin mass: 200 mg, agitation rate: 180 rpm).

Amberlite IRA-958 are given in Figs. 4 and 5, respectively. As can be seen for Amberlite IRA-458 the equilibrium dye uptake increases with the increase of temperature in the whole examined temperature range. In the case of the dye adsorption on Amberlite IRA-958, it is observed that there is a particularly notable increase in Reactive Black uptake when the temperature is raised from 298 to 308 K. Further increase in temperature has a negative effect on the adsorption process and the dye uptake diminishes insignificantly. The difference in the values of the total adsorption capacity of Amberlite IRA-958 for Reactive Black 5 for temperatures 308 and 318 K is about 168 mg/g.

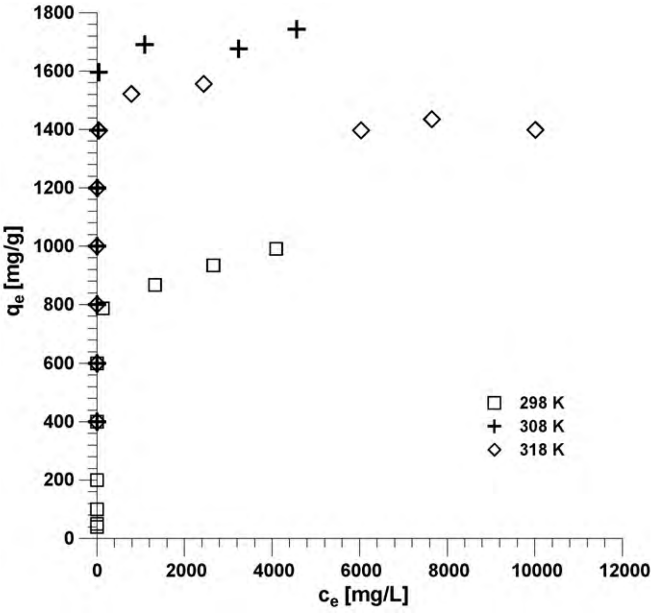

Fig. 5. Comparison of the experimental adsorption isotherms of Reactive Black 5 obtained at different temperatures for macroporous Amberlite IRA-958 (conditions: the phase contact time: 180 min, volume: 20 mL, resin mass: 200 mg, agitation rate: 180 rpm).

3.2.2. *Adsorption isotherm modeling studies*

In order to optimize the design of an adsorption system to remove dye from solutions, it is important to establish the most appropriate correlation for the equilibrium curve. Therefore, the two well-known and widely applied isotherm equations, namely the Langmuir and Freundlich models, were applied to determine the experimental data. Different equation parameters and the underlying thermodynamic presuppositions of these models often provide insight into both adsorption mechanism and surface properties of the adsorbent [31,44].

Figs. 4 and 5 show the experimental isotherm data of Reactive Black 5 on Amberlite IRA-458 and Amberlite IRA-958, respectively at three different temperatures. In the dye concentration range examined, the resulting isotherms are positive, regular, concave to the concentration axis, indicating a complete monolayer saturation of the dye covering the surfaces of both resins (or maximum adsorption) at all examined temperatures. The adsorption isotherms are also characterized by a very favourable shape: the initial slope of the curve is steep, indicating great affinity of the material for the dye molecules.

The Langmuir and Freundlich isotherm constants at different temperatures for the Reactive Black 5 adsorption on Amberlite IRA-458 and Amberlite IRA-958 are determined.

The linearized forms of the Langmuir isotherm model for Reactive Black 5 adsorption on Amberlite IRA-458 and Amberlite IRA-958 are found to be linear over the whole concentration range studied and the correlation coefficients are extremely large ($\geq$0.995). These high correlation coefficient values strongly support the fact that the dye-anion exchanger adsorption closely follows the Langmuir model of adsorption in both examined cases.

The parameters of this model were largely dependent on the type of the anion exchanger and temperature. On the basis of the Langmuir analysis, the q_0 values of Reactive Black 5 adsorption on Amberlite IRA-458 were 854.32, 1007.36, 1295.93 mg/g at 298, 308, 318 K, respectively. Also the Langmiur analysis for the adsorption of the dye on Amberlite IRA-958 at three temperatures shows the monolayer capacity of 972.56 mg/g (at 298 K), 1723.64 mg/g (at 308 K) and 1555.97 mg/g (at 318 K). As can be seen, the values of q_0 were found to be a bit larger for the Reactive Black 5-macroporous Amberlite IRA-958 system in comparison with the maximum uptake of the dye by gel Amberlite IRA-458 in the whole range of the examined temperature. The main reason is that if the exchange of large, high molecular weight species like dye molecules is concerned, the macroporous property becomes important in providing an easier diffusion path for the uptake and subsequent release of such species. Amberlite IRA-958 as the anion exchanger with the macroporous structure possesses significant porosity in comparison with gel Amberlite IRA-458 with porosity no larger than about 4 nm. Thus, accepting that the release of large fouling organic anions of Reactive Black 5 from gel Amberlite IRA-458 is impeded in part through entanglement within the structure, such release is facilitated by the resin possessing genuine porosity like Amberlite IRA-958 [11]. However, both Amberlite IRA-458 and Amberlite IRA-958 have relatively large adsorption capacities in comparison with some data obtained from literature [4,20,42,45–50]. This suggests that both examined resins exhibit very large adsorption capacities and can be suitable for Reactive Black 5 removal from aqueous solutions [50].

The second Langmuir constant b is related to the free energy adsorption and indicates the affinity of adsorbents for the dye binding. Its value is reciprocal of the dye concentration at which half of the saturation of the adsorbent is attained, thus large value of b indicates desirable steep beginning of the isotherm which reflects large affinity of the adsorbents for the adsorbate resulting in a stable adsorption product. The higher values of b obtained for the Amberlite IRA-958-dye system at temperatures of 298 and 308 K

Table 3
Thermodynamic parameters for the adsorption of Reactive Black 5 on gel Amberlite IRA-458 and macroporous Amberlite IRA-958 at different dye concentrations (conditions: the phase contact time: 180 min, volume: 20 mL, resin mass: 200 mg, agitation rate: 180 rpm).

Temperature (K)	K_d	ΔG [kJ/mol]	ΔH [kJ/mol]	ΔS [J/mol K]
Amberlite IRA-458				
298	0.78	0.62	34.99	115.76
308	1.43	−0.92		
318	1.89	−1.68		
Amberlite IRA-958				
298	2.42	−2.19	58.04	202.11
308	5.18	−4.21		
318	10.56	−6.23		

imply the strongest bonding of dye to this anion exchanger. Further increase of temperature to 318 K causes that affinity of Reactive Black 5 for Amberlite IRA 458 drastically increases and there is observed much stronger binding of the dye to this anion exchanger at this temperature than to Amberlite IRA-958. As the values of the isotherm constant b significantly increase with the temperature, it can be assumed that the binding force is strengthened at higher temperatures.

The values of constant R_L for both investigated resins towards the adsorption of Reactive Black 5 lie between 0 and 1 in the whole concentration range at all examined temperatures (not shown). It confirms the favourable uptake of the dye process and indicates the suitability of both resins for Reactive Black 5 adsorption. Furthermore, larger R_L values at lower dye concentrations and higher temperatures show that adsorption is more favourable at lower dye concentrations and a higher temperature.

The Freundlich isotherm model is found not to describe satisfactorily the adsorption isotherms of Reactive Black 5 over the whole concentration and temperature ranges studied in both anion exchanger systems with the correlation coefficients lower than 0.694 in all cases. This shows that the Freundlich expression exhibits poor fit to the adsorption data of the dye and suggests that this model yields much worse fit than the Langmuir one. Similar observations were reported for the adsorption of Reactive Black 5 on magnetic chitosan [51] or biomass fly ash [45]. However, in many cases the Freundlich model is more adequate to represent the Reactive Black 5 isotherm for the system studied than the Langmuir expression. It is suitable especially for fitting the data from the largely heterogeneous adsorbent system [4,20,42,46,50].

3.3. Thermodynamic studies

Table 3 summarizes the values of the obtained thermodynamic parameters.

The positive Gibbs free energy value for the dye adsorption process on Amberlite IRA-458 at 298 K indicates the presence of an energy barrier in this process [52]. The increase of temperature results in the decreasing values of this thermodynamic parameter below zero indicating the feasibility of the process and the spontaneous nature of the adsorption at temperatures of 308 and 318 K. In the case of Reactive Black 5 adsorption onto Amberlite IRA-958, the values of Gibbs free energy of the process at all temperatures are negative. The ΔG values are found to decrease as the temperature increases in both dye-anion exchanger systems suggesting that higher temperatures make the adsorption easier. The positive values of enthalpy change for both adsorption processes indicating the endothermic nature of the adsorption favourable at higher temperature and possible strong bonding between the dye and each anion exchanger. The relatively high values of enthalpy change are compatible with the formation of strong chemical bonds between the dye molecules and the functional groups on the resin surface, and the adsorption processes are likely to be chemisorption. As the ΔH value for the dye adsorption on Amberlite IRA-958 is larger than that obtained for the Reactive Black 5 adsorption on Amberlite IRA-458, it can be supposed that the interactions between the dye and Amberlite IRA-958 are stronger. The positive values of entropy change indicate good affinity of the anion exchangers for Reactive Black 5 molecules and show increase in the degree of freedom for the adsorbed species [11,14,26,30,31,42,53].

4. Conclusions

Removal of Reactive Black 5 from aqueous solution was studied using the strongly basic anion exchangers with the acrylic skeleton, namely Amberlite IRA-458 and Ambelrite IRA-958. These anion exchangers turned out to be very efficient at adsorption of the dye. Reactive Black 5 is bound to Amberlite IRA-458 and Amberlite IRA-958 through electrostatic attraction between the anionic groups of the dye and the quaternary ammonium groups of anion exchangers. The extent of the dye removal increased with the increasing the initial concentration of the dye. Furthermore, the adsorbed amounts of Reactive Black 5 increase with an increase in contact time and reach the maximum at an equilibrium with 180 min. The kinetics of adsorption process is determined to follow the pseudo second-order rate equation indicating the chemisorption as the rate-limiting step. The equilibrium data are the best fitted with the Langmuir isotherm model confirming the monolayer adsorption of Reactive Black 5 on both anion exchangers, with the maximum monolayer adsorption capacities of 1295.93 mg/g at 318 K and 1723.64 mg/g at 308 K for Amberlite IRA-458 and Amberlite IRA-958, respectively. The negative value of ΔG confirms the spontaneous nature of the adsorption process. Only the positive value of ΔG obtained for the dye adsorption on Amberlite IRA-458 at a temperature of 298 K, indicating the presence of an energy barrier is the exception to this rule. The positive value of ΔS shows that the randomness at the solid-solution interface is enhanced during adsorption. The positive value of ΔH indicates that the adsorption process is endothermic.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.06.043.

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