



Research Article

Equilibrium and kinetic studies on the adsorption of acidic dye by the gel anion exchanger

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ABSTRACT

In the present study, the gel anion exchanger Purolite A-850 of $-N^+(CH_3)_3$ functional groups was used in order to remove the acidic dye (Acid Blue 29) from aqueous solutions. Batch experiments were conducted to study the effect of phase contact time (1–180 min), initial concentration of dye (100–500 mg/L), solution pH (1–8), anion exchanger dosage (0.25–1.0 g) as well as temperature (20–40 °C). The contact time necessary to reach equilibrium was 40 min with the exception for the solution of the initial concentration 500 mg/L. The amounts of Acid Blue 29 adsorbed at equilibrium using the strongly basic anion exchanger were equal to 9.97, 19.97, 29.96 and 49.90 mg/g for the dye solutions of the initial concentrations 100, 200, 300 and 500 mg/L, respectively. The equilibrium sorption capacity slightly increased when the temperature of dye solution increased from 20 to 40 °C. The experimental data were analyzed by the Langmuir, Freundlich and Temkin models of adsorption. The adsorption isotherm data were fitted well to the Langmuir isotherm and the monolayer adsorption capacity was found to be 83.303 mg/g at 20 °C. The value of R_f was equal to 0.00054 (favourable). The kinetic data obtained at different concentrations were modeled using the pseudo-first order, pseudo-second order and intraparticle diffusion equations. The experimental data were well described by the pseudo-second order kinetic model.

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1. Introduction

Coloured wastewater is a consequence of batch process both in the dye manufacturing and dye-consuming industries. Two percent of dyes that are produced are discharged directly in aqueous effluent and 10–15% are subsequently lost during the textile colouration process [1–4]. The presence of these dyes in water, even at very low concentrations, is highly visible and undesirable. Many dyes are difficult to degrade due to their complex structure, some of them can be toxic, mutagenic and carcinogenic [5,6]. Therefore, their removal from the industrial effluents before discharging into the environment is extremely important. Although various methods such as biological treatments [7–9], membrane technology [10], coagulation [11,12] and oxidation [13] are used, adsorption has some specific benefits. Adsorption processes can treat high-flow wastewaters with good final quality and no harmful substance production [14]. Adsorption is found to be superior to other techniques in terms of initial costs, simplicity of design as well as ease of operation. The most widely used sorbents in the treatment of wastewaters containing dyes are activated carbon [14–19] and low-cost materials [20–25].

There is still very little information in literature about removal of dyes using such sorbents like ion exchangers [26–28]. The term ion exchangers today denotes insoluble polymeric or macromolecular substances with fixed ions. The reactive groups are dissociable and either present in a naturally occurring exchange material or later have been incorporated during the manufacture of a synthetic ion exchanger [29–31]. The fixed ions or reactive ionic groups of ion exchangers have the ability to undergo ion-exchange reactions, but they are also able to store ionic species as counterions.

Karcher et al. [26,27] proved that the weakly and strongly basic anion exchange resins commercially known as Lewatit S6328A and Lewatit MP-62 exhibit good sorption characteristics for reactive dyes (Reactive Red 120, Reactive Red 198, Reactive Black 5) contained in wastewaters from textile industry. Complete regeneration without loss of capacity can be carried out using NaOH solutions or alkaline methanol–water mixtures [26,27]. Macroporous anion exchange resins of $-N^+(CH_3)_3$ and $-N^+(CH_3)_2C_2H_4OH$ functional groups produced by Rohm and Haas were applied in removal of Tartrazine from aqueous solutions [28]. Taking into account high values of working ion capacities of Amberlite IRA-900 (134.5 mg/cm³) and Amberlite IRA-910 (117.7 mg/cm³) towards Tartrazine, they can find practical application in removal of this dye from wastewaters. Dragan et al. [32] synthesized a new resin based on acrylonitrile and divinylbenzene [P(AN-co-DVB)] with different functional groups for sorption of Tiron and Ponceau 4R. The sorption of these dyes

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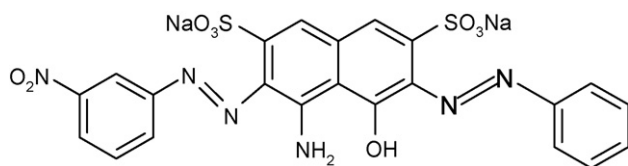


Fig. 1. Chemical structure of Acid Blue 29.

depended both on the chemical structures of functional groups of the resin and on its porosity. The investigations performed by Dulman et al. [33] on the applicability of the acrylic weak base anion exchange resin with ethylenediamine functional groups for the sorption of Acid Green 9 (AG9) are of significant importance. Under the optimum conditions the adsorption capacity of 500 mg dye (72% purity) per 1 g of adsorbent (at 20 °C) was reached. The regeneration of anion exchanger both by dynamic and batch methods could be achieved with the solution of 0.05 mol/L NaOH with the efficiency higher than 95%.

These results suggest that anion exchangers in general could be effective sorbents for dyes removal.

The aim of this paper was, therefore, to apply the commercially available gel anion exchanger of $-N^+(\text{CH}_3)_3$ functional groups for removal of Acid Blue 29. The sorption capacities of the anion exchanger for Acid Blue 29 were investigated by determining the equilibrium isotherms. In addition, kinetic studies were carried out taking the initial dye concentration into account. The experimental data were analyzed using the pseudo-first and second order kinetic models as well as the intraparticle diffusion equation. The effects of phase contact time, temperature and anion exchanger dosage on the dye adsorption were examined, too.

2. Experimental

2.1. Materials

Acid Blue 29 (Sigma–Aldrich, Germany) is a synthetic diazo dye. The molecular structure of Acid Blue 29 ($\text{C}_{22}\text{H}_{14}\text{N}_6\text{O}_9\text{S}_2\text{Na}_2$; molecular weight 616.5 g/mol) is shown in Fig. 1. Acid Blue 29 is a water-soluble dye widely used in textile industry to colour fibres. It can be applicable to all kinds of natural fibres like wool, cotton and silk as well as to the synthetics like polyesters, acrylic and rayon. But it is not substantive to cellulosic fibres. It is also used in paints, inks, plastics, and leather.

Solutions containing Acid Blue 29 were prepared by dissolving the accurately weighed amount of dye in 1 L of distilled water.

The properties of the applied anion exchange resin are presented in Table 1.

2.2. Adsorption studies

The batch sorption experiments were carried out in 0.1 L conical flasks where 0.25 g of the dry anion-exchanger and 0.025 L of Acid Blue 29 solution (100–2000 mg/L) were added without adjusting pH. The flasks were agitated in the thermostated shaker (Elphin 358 S, Poland) at a constant speed of 170 rpm and temperature 20 °C for 360 min to achieve equilibrium. The dye concentration after equilibrium adsorption was measured using the UV–VIS spectrophotometer (Specord M42; Carl Zeiss Jena, Germany) at the maximum absorbance wavelength. The amount of dye adsorbed at equilibrium, q_e (mg/g), was calculated from Eq. (1):

$$q_e = \frac{C_0 - C_e}{w} \times V \quad (1)$$

where C_0 and C_e are the concentrations of the dye at the beginning and in the equilibrium, respectively (mg/L); V is the volume of the solution (L); w is the mass of the dry anion-exchanger (g).

All collected values in this paper are the average of three independent experiments.

2.2.1. Langmuir isotherm

The Langmuir isotherm is derived on the assumption of monolayer coverage of adsorbate over a homogenous adsorbent surface [34–36]. The linear form of the Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad (2)$$

where C_e is the equilibrium concentration of the dye (mg/L); q_e is the amount of dye adsorbed per unit mass of the anion exchanger at equilibrium (mg/g); Q_0 (mg/g) and b (L/mg) are the Langmuir constants related to adsorption capacity and the rate of adsorption, respectively.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L [37].

2.2.2. Freundlich isotherm

The Freundlich isotherm is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (3)$$

Table 1
Anion exchanger characteristic.

Name	Purolite A-850
Type	Strong base
Matrix and structure	
Physical form	Translucent beads
Ionic form as shipped	Chloride
Total capacity	≥ 1.25 eq/dm ³
Moisture holding capacity	57–62%
Harmonic mean size	+1.2 mm < 5%, –0.3 mm < 1%
Maximum operating temperature	40 °C
Producer	Purolite Ltd., UK

Eq. (3) can be linearized as Eq. (4):

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (4)$$

where C_e is the equilibrium concentration of the dye (mg/L); q_e is the amount of dye adsorbed per unit mass of the anion exchanger (mg/g); K_F (mg/g) and n are the Freundlich constants [34,35].

2.2.3. Temkin–Pyzhev isotherm

Heat of adsorption and the adsorbent-adsorbate interactions were studied by Temkin and Pyzhev. They suggested that due to these interactions the heat of adsorption of all molecules in the layer decreased linearly with the coverage [34]. The Temkin isotherm equation is given as:

$$q_e = \left(\frac{RT}{b_T}\right) \ln A + \left(\frac{RT}{b_T}\right) C_e \quad (5)$$

where b_T is the Temkin constant related to heat of sorption (J/mol), A is the Temkin isotherm constant (L/g), R is the gas constant (8.31 J/mol K) and T (K) is the temperature.

2.3. Kinetic batch studies

To examine the effect of phase contact time (1–180 min), initial concentration of dye (100–500 mg/L), anion exchanger dosage (0.25–1.0 g), pH (1–8) and temperature (20–40 °C) on the removal of Acid Blue 29 from aqueous solutions batch studies were conducted.

Kinetic experiments were identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of dye were similarly measured. All the kinetic studies were carried out at the natural pHs (pH 4.93) of solutions (pH-meter; CX-742 Elmetron, Poland).

The amount of dye adsorbed at time t , q_t (mg/g) was calculated from Eq. (7):

$$q_t = \frac{C_0 - C_t}{w} \times V \quad (6)$$

where C_0 and C_t are the concentrations of the dye in the solution at the beginning and after time t , respectively (mg/L); V is the volume of the solution (L); w is the mass of the dry anion-exchanger (g).

The fitting of sorption of Acid Blue 29 on the strongly basic anion exchanger was investigated by three common kinetic models, namely, the Lagergren pseudo-first order model (Eq. (7)), Ho pseudo-second order model (Eq. (8)) as well as Weber and Morris intraparticle diffusion model (Eq. (9)) [37–47]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

$$q_t = k_i t^{0.5} \quad (9)$$

where q_e and q_t are the amounts (mg/g) of dye adsorbed at equilibrium and at time t (min) respectively; and k_1 is the constant rate of pseudo-first order adsorption (min^{-1}); k_2 is the constant rate of the pseudo-second order adsorption (g/mg min); k_i is the intraparticle diffusion rate ($\text{mg/g min}^{0.5}$).

2.4. ATR-FTIR analysis

The differences in the spectra of anion exchanger before and after sorption of Acid Blue 29 were investigated by using the FTIR technique (spectrometer type Alpha with ATR attachment, Bruker Optics, Germany). The spectra were recorded from 4000 to 400 cm^{-1} .

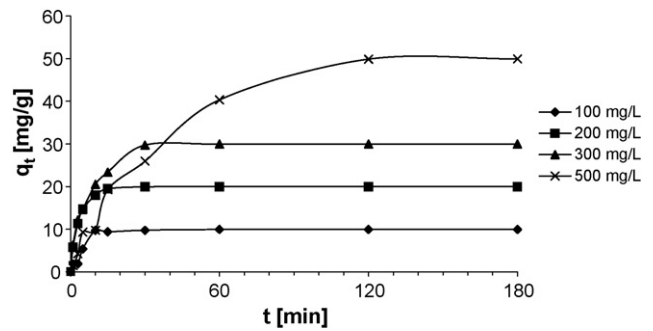


Fig. 2. Effect of phase contact time and dye initial concentration on removal of Acid Blue 29 from aqueous solutions by the strongly basic anion exchanger Purolite A-850 at 20 °C.

3. Results and discussion

3.1. Effects of initial dye concentration and phase contact time

The influence of phase contact time on Acid Blue 29 adsorption on Purolite A-850 was carried out ranging the initial dye concentration from 100 to 500 mg/L at 20 °C. The amount of the adsorbed dye onto the strongly basic anion exchanger increased with time. Fig. 2 shows the influence of phase contact time on Acid Blue 29 uptake from aqueous solutions of different initial concentrations by Purolite A-850. The contact time necessary to reach equilibrium was 40 min with the exception for the solution of the initial concentration 500 mg/L. A similar result was reported for the adsorption of Acid Green 9 by the acrylic anion exchange resin with ethylenediamine functional groups [33]. The initial dye concentration had little influence on the time of contact necessary to reach equilibrium. The amounts of Acid Blue 29 adsorbed at equilibrium using Purolite A-850 were equal to 9.97, 19.97, 29.96 and 49.90 mg/g for the dye solutions of the initial concentrations 100, 200, 300 and 500 mg/L, respectively.

3.2. Effect of temperature and solution pH

The temperature dependence on Acid Blue 29 sorption onto the strongly basic anion exchanger of gel structure was studied with the constant initial concentration (200 mg/L) of dye. Fig. 3 illustrates the effect of temperature on the sorption of Acid Blue 29 by Purolite A-850. The equilibrium sorption capacity slightly increased when the temperature of dye solution increased from 20 to 40 °C. The fact that the sorption of dye is in favour of temperature indicates that the mobility of the dye molecules increases with the temperature rise. The enhancement in adsorption with the temperature

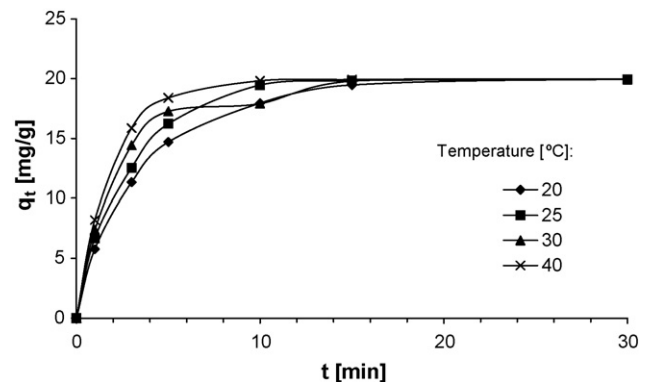


Fig. 3. Effect of temperature on removal of Acid Blue 29 from 200 mg/L system by the strongly basic anion exchanger Purolite A-850 at 20 °C.

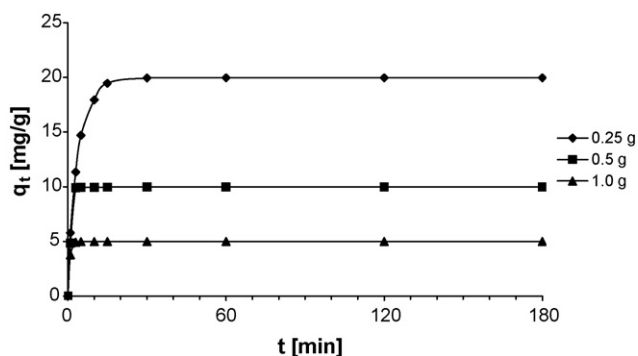
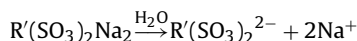


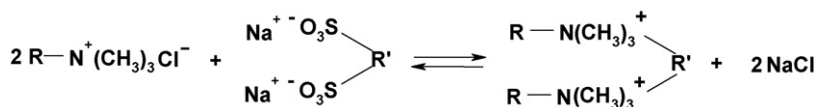
Fig. 4. Effect of anion exchanger dosage on removal of Acid Blue 29 from 200 mg/L system by the strongly basic anion exchanger Purolite A-850 at 20 °C.

may be attributed to the increase in the number of active surface sites available for adsorption, increase in the porosity and in the total pore volume of the adsorbent. This may be also a result of the decrease in the thickness of the boundary layer surrounding the sorbent with the temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases.

In aqueous solution, Acid Blue 29 ($R'(SO_3)_2Na_2$) is dissolved and the strongly acidic sulphonate groups of the dye were dissociated and converted to anionic dye ions:



The adsorption process then proceeded due to the interaction between the anionic dye and the functional groups of the anion exchanger in the chloride form ($R-N^+(CH_3)_3Cl^-$):



As follows from the above, Acid Blue 29 forms a stable ion pair in the anion exchanger phase, but the surface interactions with the aromatic ring must be also taken into account. Acid Blue 29 contains the groups ($-OH$, $-NH_2$, $-NO_2$, $-N=N-$) that can participate in covalent, coulombic, hydrogen bonding or weak van der Waals forces. The occurrence of double bond serves to enhance the interaction between the dye and the anion exchanger macromolecule. The physical adsorption and $\pi-\pi$ dispersion forces can arise from the aromatic nature of the resin and the dye. Similar conclusions were reported in [48–51].

The relationship between the initial pH of Acid Blue 29 solutions and the adsorption capacity using Purolite A-850 was studied in the system containing 200 mg of dye per 1 L at 20 °C. Negligible decrease in the sorption capacity with the increasing initial solution pH was observed. The q_t values decreased from 9.97 to 7.93 mg/g with the increasing initial solution pH from 1 to 8 (figure not shown).

3.3. Effects of anion exchanger dosage

The adsorption of Acid Blue 29 on Purolite A-850 was studied by changing the quantity of anion exchanger (varying from 0.25 g to 1.0 g/0.025 L) in the test solution while maintaining the initial concentration (200 mg/L) and temperature (20 °C) constant as presented in Fig. 4. The amount of dye adsorbed increased from 4.99 to 19.97 mg/g as the anion exchanger dosage decreased from 1.0 to 0.25 g/0.025 L at equilibrium (180 min). Maximum dye removal was achieved within 10–20 min after which Acid Blue 29 concentration was almost constant.

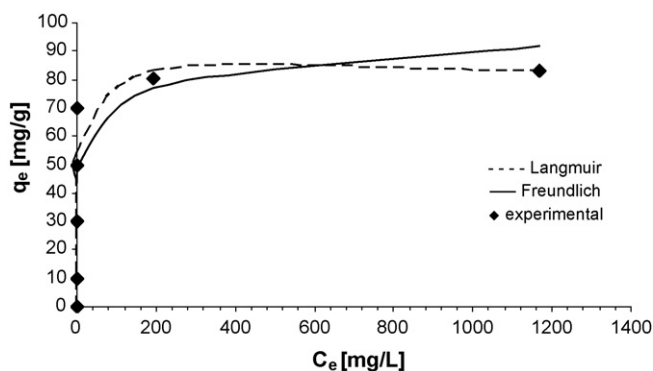


Fig. 5. Fitting of Langmuir and Freundlich isotherm models to the adsorption equilibrium results of Acid Blue 29 sorption on Purolite A-850 at 20 °C.

3.4. Sorption equilibrium

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the equilibrium state is reached. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for the design purpose [34,35]. Fig. 5 shows the equilibrium adsorption isotherm of Acid Blue 29 on the strongly basic gel anion exchanger Purolite A-850 as well as the fitting of adsorption isotherm models to experimental data. It exhibits steep increase at low concentrations, indicating high affinity for a solute. At high concentrations of Acid Blue 29, the adsorbed amounts increase slightly, showing horizontal plateaus.

Adsorption isotherm studies were carried out using the three models: the Langmuir, Freundlich and Temkin. The applicability of the isotherm equation was judged by correlation coefficients, r^2 values. The calculated constants, according to the Langmuir, Freundlich and Temkin equations, are compared in Table 2.

A straight line with the slope $1/Q_0$ was obtained from the plot C_e/q_e vs. C_e for Acid Blue 29 sorption on the gel anion exchanger (figure not shown). The correlation coefficient r^2 was equal to 0.999. It indicates that the adsorption data of Acid Blue 29 on Purolite A-850 was well fitted to the Langmuir isotherm. The Langmuir constant b was equal to 0.921. The monolayer maximum adsorption capacity was 83.303 mg/g. The value of R_L was found to be 0.00054 (favourable).

Table 2
Comparison of the coefficients isotherm parameters for Acid Blue 29 adsorption on Purolite A-850.

Isotherm model	Parameters
Langmuir	
Q_0 [mg/g]	83.303
b [L/mg]	0.921
r^2	0.999
Freundlich	
K_F [mg/g]	46.349
n	10.365
r^2	0.611
Temkin–Pyzhev	
A [L/g]	8027.594
b_T	452.343
r^2	0.710

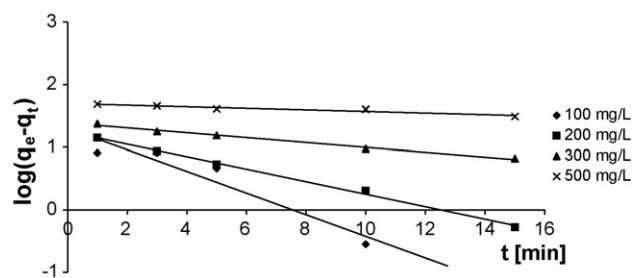


Fig. 6. Pseudo-first order kinetics for adsorption of Acid Blue 29 on Purolite A-850 for different initial dye concentrations at 20 °C.

For the Freundlich isotherm, the plot of $\log q_e$ vs. $\log C_e$ gives a straight line with the n value of 10.365. It indicated that adsorption of Acid Blue 29 on Purolite A-850 was favourable. The value of r^2 was equal to 0.611.

The constants A and b_T , listed in Table 2, according to the Temkin equation were calculated from the plot of q_e vs. $\ln C_e$. The correlation coefficient was equal to 0.710.

It can be concluded that the Langmuir isotherm provided the best model of the sorption system taking r^2 value into account.

3.5. Sorption kinetics

In order to analyze the sorption of Acid Blue 29 on the strongly basic anion exchanger Purolite A-850, the pseudo-first order, pseudo-second order as well as Weber and Morris intraparticle diffusion kinetic models were applied to the data.

Values of k_1 and $q_{e,cal}$ for the pseudo-first order kinetic model were obtained from the slopes and intercepts of plots $\log(q_e - q_t)$ vs. t . Fig. 6 shows the $\log(q_e - q_t)$ vs. t plot for Acid Blue 29 in sorption experiments at different initial dye concentrations. A comparison of the results with the correlation coefficients is shown in Table 3. The correlation coefficients using the Lagergren model obtained at all studied initial concentrations were relatively high. However, the experimental $q_{e,exp}$ values did not agree with the calculated $q_{e,cal}$ data. This suggests that the adsorption of Acid Blue 29 on Purolite A-850 did not follow the first-order kinetics.

Using Eq. (8), t/q_t was plotted against t ranging the initial dyes concentrations in order to calculate the second order rate constant k_2 and equilibrium adsorption capacity $q_{e,cal}$ from the slope and intercept, respectively. The linear plot of t/q_t vs. t , as presented in Fig. 7, shows a good agreement between the experimental $q_{e,exp}$ and the calculated $q_{e,cal}$ values (Table 3). It was found that the $q_{e,cal}$ values determined for Acid Blue 29 increased from 10.288 to 62.564 mg/g with the increase in the initial concentration from 100 to 500 mg/L.

It was noticed that the rate constants k_2 decreased with the increase in the initial dye concentration. The correlation coefficients r^2 were very high, ranging from 0.983 to 0.999.

This suggest that the studied sorption systems followed the pseudo-second order kinetic model, based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons

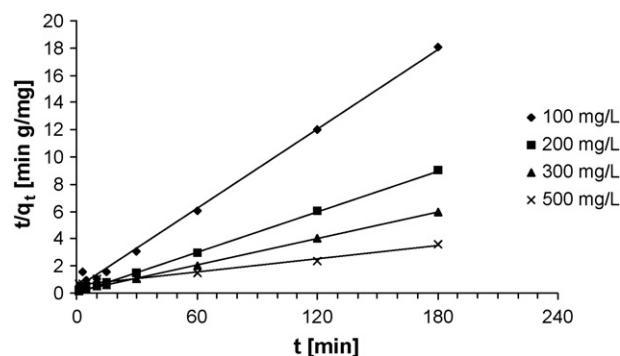


Fig. 7. Fitting of pseudo-second order model for Acid Blue 29 sorption on Purolite A-850 for different initial concentrations of dye at 20 °C.

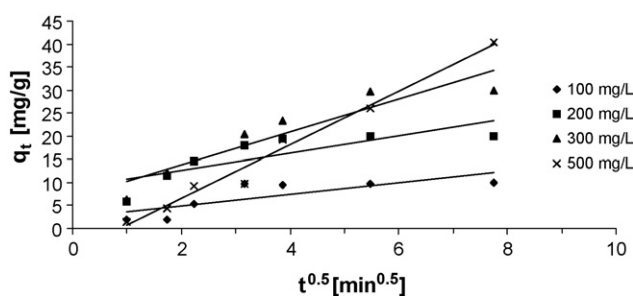


Fig. 8. Intraparticle diffusion model for adsorption of Acid Blue 29 on Purolite A-850 at 20 °C.

between sorbent and sorbate [34,37]. Dulman et al. [33], Radulescu et al. [48,49] as well as Tanaka et al. [50] confirmed the applicability of the pseudo-second order model for sorption of sulphonated dyes on anion exchange resins.

The intraparticle diffusion model controls the sorption when the graph of q_t against $t^{0.5}$ is a straight line passing through the origin [41–47,51]. The values of intraparticle diffusion rates k_i calculated for Acid Blue 29 from the slope of the plots q_t vs. $t^{0.5}$ (Fig. 8) increased from 0.065 to 1.821 mg/g min^{0.5} (Table 3) with the increase in the initial concentrations. The values of r_i^2 were lower compared to those obtained from the pseudo-second order kinetic model.

3.6. FTIR measurement

The infrared spectra of Purolite A-850 before and after the adsorption process were recorded in the range 4000–400 cm⁻¹ (Fig. 9). The bands around 3470 cm⁻¹ for strong bands of the –OH stretching vibrations were observed. At about 3028 cm⁻¹ (ν_{as} C–H) and 2940 cm⁻¹ (ν_{as} –CH₂) bands, related to the stretching vibrations of the ring C–H bonds and –CH₂ groups of the matrix of anion exchanger were observed. At 1635 cm⁻¹ (δ (O–H)) the presence of water in the anion exchanger phase was found. The ring carbon–carbon stretching and the scissoring vibrations of the methylene groups (δ_{as} –CH₂) appeared at 1457 and 1422 cm⁻¹ as well as at 1394 cm⁻¹. After the sorption of Acid Blue 29 the intensity of some bands changed. It was found that in the spectra of

Table 3
Kinetic parameters for Acid Blue 29 sorption on the strongly basic anion exchanger Purolite A-850.

C_0 [mg/L]	$q_{e,exp}$ [mg/g]	Pseudo-first order			Pseudo-second order			Intraparticle diffusion	
		$q_{1,cal}$ [mg/g]	k_1 [min ⁻¹]	r_1^2	$q_{2,cal}$ [mg/g]	k_2 [g/mg min]	r_2^2	k_i [mg/g min ^{0.5}]	r_i^2
100	9.97	20.129	0.398	0.911	10.288	0.033	0.996	0.065	0.007
200	19.97	17.698	0.229	0.996	20.184	0.024	0.999	0.122	0.007
300	29.96	24.332	0.089	0.990	30.837	0.008	0.999	0.252	0.014
500	49.90	49.734	0.029	0.909	62.564	0.0004	0.983	1.821	0.232

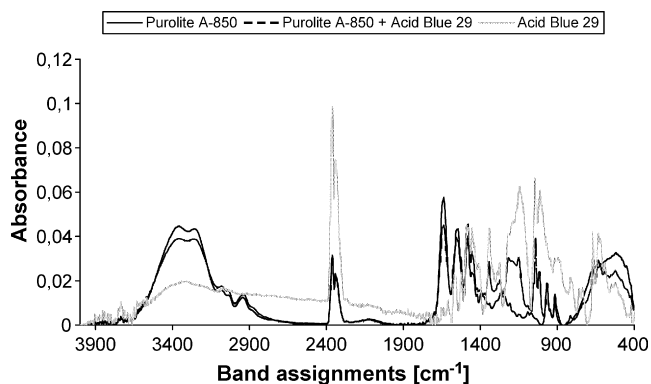


Fig. 9. FTIR spectra of Purolite A-850 before and after sorption of Acid Blue 29.

the loaded anion exchanger symmetric and asymmetric vibrations of $-\text{SO}_3^-$ groups appeared at 1085 and 1146 cm^{-1} , respectively. At 1013 cm^{-1} asymmetric vibration of $-\text{S}=\text{O}$ group was observed, too. It seems that these groups participate in dye binding.

4. Conclusions

- The initial dye concentration had little influence on the contact time necessary to reach equilibrium. The amounts of Acid Blue 29 adsorbed at equilibrium using the strongly basic anion exchanger ranged from 9.97 to 49.90 mg/g for the dye solutions of the initial concentrations 100–500 mg/L, respectively.
- The equilibrium sorption capacity slightly increased when the temperature of dye solution increased from 20 to 40 °C.
- The amount of dye adsorbed increased from 4.99 to 19.97 mg/g as the anion exchanger dosage decreased from 1.0 to 0.25 g/0.025 L at equilibrium (180 min).
- Monolayer maximum adsorption capacity according to the Langmuir equation was equal to 83.303 mg/g. The values of r^2 and R_L were found to be 0.999 and 0.00054, respectively.
- The studied sorption systems followed the pseudo-second order kinetic model, based on the assumption that the rate-limiting step may be chemical sorption.
- It was found that in the spectra of the loaded anion exchanger symmetric and asymmetric vibrations of $-\text{SO}_3^-$ and $-\text{S}=\text{O}$ groups appeared. It seems that these groups participate in dye binding.

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