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Equilibrium and kinetic studies on the sorption of acidic dye by macroporous anion exchanger

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ABSTRACT

Synthetic diazo dye Acid Blue 29 was removed from aqueous solution using the strongly basic anion exchanger of macroporous structure – Purolite A-520E. The influence of phase contact time (1–180 min), anion exchanger dosage (0.25–1.0 g), solution pH (1–8), initial dye concentration (100–500 mg/L) and temperature (20–50 °C) was studied by the batch method. Additionally, the obtained results were compared with those for the activated carbon Purolite AC-20G. The amounts of Acid Blue 29 adsorbed at equilibrium using the strongly basic anion exchanger were equal to 9.9, 19.9, 29.9 and 48.2 mg/g for the dye solutions of the initial concentrations 100, 200, 300 and 500 mg/L, respectively. The experimental data were analyzed by means of the Langmuir, Freundlich and Temkin models of adsorption. The maximum monolayer capacity Q_0 for sorption of the dye on the activated carbon was 30.2 mg/g. The Q_0 obtained for the strongly basic anion exchanger was ten times higher (321.5 mg/g) than that obtained for Purolite AC-20G. The kinetic data obtained at different concentrations were modelled 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.

1. Introduction

Since the environmental pollutions are increasing day-by-day, the need to reduce the impurities particularly in wastewaters of textile industry is important. The textile sewages contain not only dyes but also detergents, grease, oils, solvents and inorganic salts. Of them colour removal is of significant importance. Many studies have been conducted to evaluate the sorption of different dyes onto low-cost materials [1–5] and activated carbon [6–10]. Literature about removal of dyes using such sorbents as ion exchange resins is very scarce [11–15]. 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 materials or later incorporated during the manufacture of a synthetic ion exchanger [16,17]. The fixed ions or reactive ionic groups of ion exchangers have the ability not only to undergo ion exchange reactions, but also to store ionic species as counter ions.

Karcher et al. [11,12] analyzed the removal of Reactive Red 120, Reactive Red 198 and Reactive Black 5 from wastewaters by the weak and strong base anion exchangers of commercial names Lewatit S-6328A and Lewatit MP-62. Complete regeneration without a loss of capacity was carried out using NaOH solutions or alkaline methanol–water mixtures [11,12]. The investigations performed by Dulman et al. [13] on the applicability of the acrylic-cross-linked copolymers functionalized with various amines and pyridine (of gel and macroporous structures) for the removal of Acid Green 9 are of significant importance. The strong base anion exchangers, namely Dowex 1-X8 of benzyltrimethyl ammonium functional groups and Dowex 2-X8 of benzyldimethyl-(2-hydroxyethyl)-ammonium functional groups, were successfully used in sorption of 1,8-dihydroxy-2-(imidazol-5-ylazo)-naphthalene-3,6-disulphonic acid (IACA) and 1,8-dihydroxy-2-(pyrazol-5-ylazo)-naphthalene-3,6-disulphonic acid (PACA) from aqueous solutions [18,19]. The hyper-cross-linked polymeric sorbents, known as Macronet MN200 and MN300, were used in the recovery process of Acid Red 14 from aqueous solutions by Valderrama et al. [20]. Macronet MN300 containing tertiary amine groups was characterized by higher capacity (108 g/kg) towards Acid Red 14 than non-functionalized Macronet MN200 (65 g/kg). Kaşgöz [21] synthesized new hydrogels (poly(N-hydroxymethylacrylamide), PHMA) functionalized with amine groups for Indigo Carmine removal. The sorption capacity of functionalized hydrogels varied between 149.7 and 237.6 mg/g. As reported in [22] the weak and strong base anion exchange resins, e.g. Amberlite IRA-67, Amberlite IRA-402, Amberlite IRA-958 and Lewatit M-600, can be used in sorption of Indigo Carmine from aqueous solutions. The ion exchange capacities of Amberlite IRA-67, IRA-402, and IRA-958 and Lewatit M-600 towards Indigo Carmine were equal to 0.1 mmol/g, 0.17 mmol/g, 1.5 mmol/g and 0.21 mmol/g, respectively.

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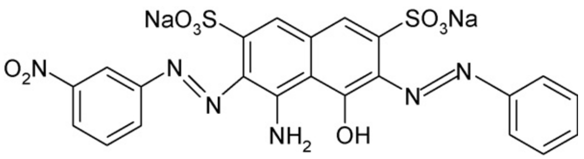


Fig. 1. Chemical structure of Acid Blue 29.

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

The aim of this paper was, therefore, to study the applicability of the commercially available macroporous anion exchanger Purolite A-520E of $-N^+(CH_3)_3$ functional groups for the removal of Acid Blue 29 from aqueous solution. The sorption capacities of the anion exchanger for Acid Blue 29 were investigated by determining the equilibrium isotherms. Kinetic studies were carried out taking the initial dye concentration in the range 100–500 mg/L 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, pH and anion exchanger dosage on the dye adsorption were examined too. Additionally, the obtained results were compared with those for the activated carbon Purolite AC-20G.

2. Experimental

2.1. Adsorbate and adsorbent

Acid Blue 29 ($C_{22}H_{14}N_6O_9S_2Na_2$) is the synthetic diazo dye of the molecular weight 616.5 g/mol. The dye was purchased from Sigma–Aldrich (Germany). It is a water-soluble dye. The structure of Acid Blue 29 is presented in Fig. 1. The stock solution of Acid Blue 29 was prepared by dissolving the accurately weighed amount of dye in 1 L of distilled water. All working solutions were prepared by diluting the stock solution with distilled water.

In the investigations the polystyrene anion exchanger Purolite A-520E and the activated carbon Purolite AC-20G produced by Purolite International Ltd. (UK) were used. Short specification of the anion exchange resin is listed in Table 1. The resin was washed with 1 M NaOH and 1 M HCl as well as double distilled water in order to remove impurities and dried.

Purolite AC-20G is regenerable granular activated carbon, manufactured from bituminous mineral coals of 800–1300 μm particle size. Before the use the activated carbon was washed with doubly distilled water and dried.

2.2. Equilibrium studies

Equilibrium experiments were carried out by adding 0.25 g of the adsorbent and 0.025 L of Acid Blue 29 solution (100–5000 mg/L) into 0.1 L conical flasks without adjusting pH. The flasks were placed in the thermostatic shaker (Elphin 358 S, Poland) and agitated at a constant speed of 170 rpm at 20 °C for 360 min.

Table 1
Physicochemical properties of applied anion exchanger.

Name	Purolite A-520E
Type	Strong base
Matrix and structure	Macroporous polystyrene cross-linked with divinylbenzene
Functional groups	Quaternary ammonium
Physical form	Spherical beads
Ionic form as shipped	Chloride
Total capacity	≥1.0 equiv./L
Moisture holding capacity	50–56%
Mean size	0.60–0.85 mm
pH limit	0–14 (stability), 4.5–8.5 (operating)
Maximum operating temperature	100 °C
Producer	Purolite Ltd., UK

The amount of dye adsorbed at equilibrium, q_e (mg/g), was calculated from Eq. (1):

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

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

The dye concentrations were measured using a double beam UV–vis spectrophotometer Specord M42 (Carl Zeiss Jena, Germany) at the maximum absorbance wavelength (λ_{max} = 596 nm).

2.3. Kinetic studies

The effect of phase contact time (1–180 min), initial concentration of dye (100–500 mg/L), adsorbent dosage (0.25–1.0 g), solution pH (1–8) and temperature (20–50 °C) on the removal of Acid Blue 29 from aqueous solution by batch studies was investigated.

The procedure of kinetic experiments was identical to that of equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of dye were measured in a similar manner. 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. (2):

$$q_t = \frac{C_0 - C_t}{w} V \qquad (2)$$

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

The applicability of the kinetic model to describe the adsorption process was validated by normalized standard deviation, Δq (%), which was calculated as:

$$\Delta q\ (\%) = 100\sqrt{\frac{\sum[(q_{exp} - q_{cal})/q_{exp}]^2}{N-1}} \qquad (3)$$

where N is the number of data points, q_{exp} and q_{cal} (mg/g) are the experimental and calculated sorption capacities, respectively [23].

3. Results and discussion

3.1. Effect of phase contact time and initial dye concentration

The influence of phase contact time on the adsorption of Acid Blue 29 on Purolite A-520E and Purolite AC-20G was studied varying the initial dye concentration from 100 to 500 mg/L at 20 °C. The results indicate that the amount of dye adsorbed per mass unit of the strongly basic anion exchanger or activated carbon increased with time and initial Acid Blue 29 concentration.

Fig. 2 shows the influence of phase contact time on Acid Blue 29 uptake from aqueous solutions of different initial concentrations by Purolite A-520E and AC-20G. From the obtained results it is evident that the sorption process proceeded in two distinct phases. Within 60 min the amounts of dye adsorbed by Purolite A-520E were equal to 9.3, 19.3, 27.1 and 36.9 mg/g for the dye solutions of the initial concentrations 100, 200, 300 and 500 mg/L. After that period of time, the sorption rate was slower and the q_t values changed insignificantly with the exception of the solution of the initial concentration 500 mg/L. The amounts of Acid Blue 29 adsorbed at equilibrium using Purolite A-520E were equal to 9.9,

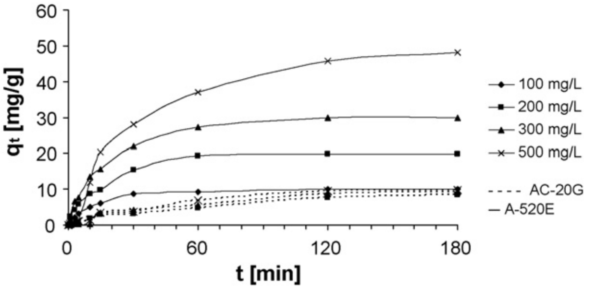


Fig. 2. Effect of phase contact time and dye initial concentration on removal of Acid Blue 29 from aqueous solutions by the strongly basic anion exchanger Purolite A-520E and activated carbon Purolite AC-20G at 20 °C.

19.9, 29.9 and 48.2 mg/g for the dye solutions of the initial concentrations 100, 200, 300 and 500 mg/L, respectively. It was found that q_t values determined for the activated carbon were very low compared with those obtained for the anion exchanger. The time of contact necessary to reach equilibrium using Purolite AC-20G was 120 min. As the initial concentration increased from 100 to 500 mg/L the adsorption capacities increased from 5.2 to 9.7 mg/g, respectively.

Similar phenomenon was observed for the sorption of Acid Green 9 on the weak and strong base anion exchange resins [13] and for Methylene Blue on activated carbon [23].

3.2. Effect of adsorbent dosage

In order to investigate the influence of adsorbent dosage on dye adsorption, experiments were carried out at initial concentration of 200 mg/L, while the amount of adsorbent added was varied. Fig. 3 shows the effect of the anion exchanger and activated carbon dose on the adsorbed amount of Acid Blue 29 at equilibrium. The values of q_t decreased from 19.9 to 4.9 mg/g and from 8.4 to 4.9 mg/g with the increase of Purolite A-520E and Purolite AC-20G dose from 0.25 to 1.0 g. It is due to the change in the concentration gradient between the dye content in solution and in the surface of the anion exchanger (or activated carbon). Very fast superficial sorption is observed on the sorbent at higher concentration ratio of dye and sorbent. The determined mass of the anion exchanger (or activated carbon) can adsorb only a certain amount of dye. A similar observation was previously reported by Vadivelan and Kumar [24], Janoš et al. [25], Lata et al. [26] as well as Yeddou and Bensmaili [27].

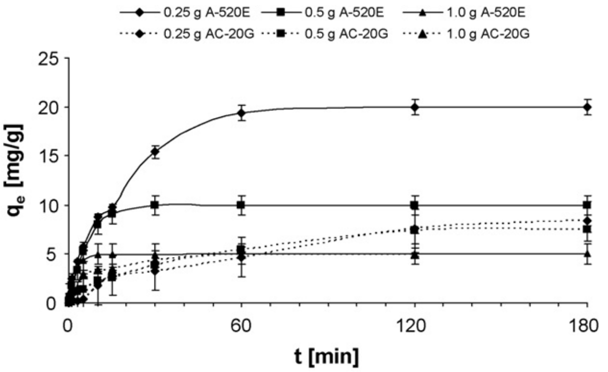


Fig. 3. Effect of Purolite A-520E and Purolite AC-20G dosage on removal of Acid Blue 29 from 200 mg/L system at 20 °C (C_0 = 200 mg/L, V = 0.05 L, $w = 0.25–1$ g, $\Delta q = \pm 5\%$).

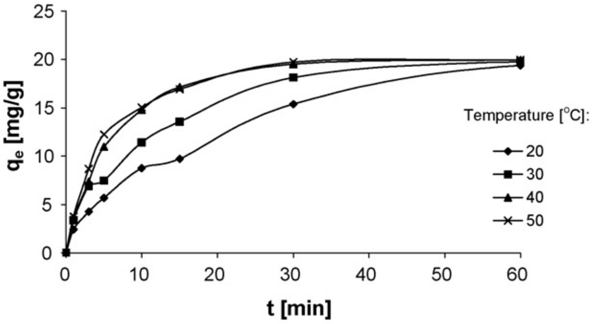


Fig. 4. Effect of temperature on removal of Acid Blue 29 from aqueous solution (C_0 = 200 mg/L) by the strongly basic anion exchanger Purolite A-520E.

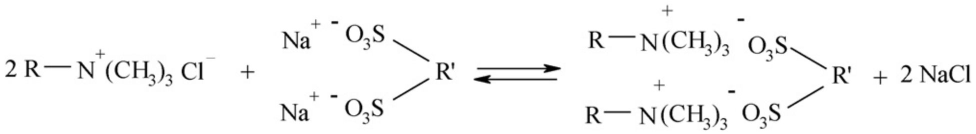
3.3. Effect of temperature

The influence of temperature on Acid Blue 29 sorption by Purolite A-520E was studied with the constant initial concentration of 200 mg/L (Fig. 4). The equilibrium sorption capacity increased when the temperature of dye solution increased from 20 to 50 °C. The same effect of temperature was observed for activated carbon.

The enhancement in adsorption with temperature may be attributed to increase in the number of active surface sites available for adsorption. This may also be 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. The fact that the sorption of the acidic dye is in favour of temperature indicates that the mobility of the dye molecules increases with the temperature rise.

3.4. Effect of solution pH

The reaction of Acid Blue 29 ($R'(SO_3)_2Na_2$) with Purolite A-520E ($R–N^+(CH_3)_3Cl^-$) can be described as ion exchange mechanism:



$$2\,R-\overset{+}{N}(CH_3)_3\,Cl^- + \begin{matrix} Na^+\;{}^-O_3S \\ Na^+\;{}^-O_3S \end{matrix} R' \rightleftarrows \begin{matrix} R-\overset{+}{N}(CH_3)_3\;{}^-O_3S \\ R-\overset{+}{N}(CH_3)_3\;{}^-O_3S \end{matrix} R' + 2\,NaCl$$

The reaction involves the interaction between anionic groups of dye and functional groups of the anion exchanger. Acid Blue 29 contains groups (–OH, $–NH_2$, $–NO_2$, –N=N–) that can participate in 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 backbone network. The physical adsorption and π–π dispersion forces can arise from the aromatic nature of the resin and the dye. Similar conclusions were reported in [28–30].

The relationship between initial pH of Acid Blue 29 solutions and the adsorption capacity using Purolite A-520E was studied in the system containing 200 mg dye/L at 20 °C. Decrease in sorption capacity with increasing pH of initial solution was observed. The q_t values decreased from 9.9 to 7.9 mg/g with increasing pH of initial solution from 1 to 8 (figure not shown).

3.5. Isotherm analysis

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm [31]. The parameters obtained from the different isotherm models provide important information on the sorption mechanism and the surface properties as well as affinities to the sorbent. It is important to establish the most appropriate correlation between experimental data and isotherm model in order to optimize the design of adsorption system.

The fitting of sorption of Acid Blue 29 on the strongly basic anion exchanger and activated carbon was investigated by three common isotherm models, namely, the Langmuir model (Eq. (4)), Freundlich model (Eqs. ((6) and (7)) as well as Temkin model (Eq. (8)). Linear regression was used to determine the best-fitting isotherm. The applicability of isotherm equations was compared by estimation of the correlation coefficients.

3.5.1. *Langmuir isotherm*

Langmuir isotherm is derived on the assumption of monolayer coverage of adsorbate over a homogenous adsorbent surface [23,32,33]. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \tag{4}$$

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

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by Eq. (5):

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

where C_0 is the highest initial concentration of adsorbate (mg/L) and b (L/mg) is the Langmuir constant.

The value of R_L indicates the shape of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [34].

3.5.2. *Freundlich isotherm*

The Freundlich isotherm is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \tag{6}$$

Eq. (6) can be linearized as Eq. (7):

$$\log\ q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \tag{7}$$

where C_e is the equilibrium concentration of the dye (mg/L); q_e is the amount of the dye sorbed per mass unit of adsorbent (mg/g); K_F (mg/g) and n are the Freundlich constants.

The values of K_F and n can be estimated from the intercept and slope of the linear plot $\log q_e$ *vs.* $\log C_e$. K_F is the adsorption capacity of the anion exchanger which can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto anion exchanger for a unit equilibrium concentration. The slope $1/n$ ranging from 0 to 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogenous as its value gets closer to zero. The value $1/n$ below 1 indicates normal isotherm while above 1 is indicative of cooperative adsorption [23].

3.5.3. *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 coverage [23,35]. The Temkin isotherm equation is given as:

$$q_e = \left(\frac{RT}{b_T}\right)\ \ln A + \left(\frac{RT}{b_T}\right) \ln C_e \tag{8}$$

Table 2
Values of isotherm parameters for removal of Acid Blue 29 from aqueous solution using the strongly basic anion exchanger Purolite A-520E and activated carbon Purolite AC-20G.

Isotherm model	Parameters	
	Purolite A-520E	Purolite AC-20G
Langmuir		
Q_0 (mg/g)	321.5	30.2
b (L/mg)	0.003	0.004
R_L	0.065	0.047
r^2	0.889	0.987
Freundlich		
K_F (mg/g)	21.4	1.8
n	4.4	2.7
r^2	0.835	0.929
Temkin–Pyzhev		
A (L/g)	0.139	0.076
b_T	76.5	607.3
r^2	0.692	0.730

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.

The obtained results concerning the removal of Acid Blue 29 from aqueous solution by means of Purolite A-520E and Purolite AC-20G are presented in Table 2. Fig. 5 shows the equilibrium adsorption isotherm of Acid Blue 29 and fitting of the models to experimental data on the strongly basic anion exchanger Purolite A-520E and activated carbon AC-20G. It exhibits a steep increase at low concentrations for Purolite A-520E, indicating high affinity towards the solute. Adsorbed amount of Acid Blue 29 by activated carbon increased slightly, showing almost horizontal plateaus at high concentrations. It was found that Acid Blue 29 sorption on Purolite A-520E and AC-20G was well described by Langmuir isotherm. The correlation coefficients r^2 for plots of C_e/q_e *vs.* C_e were equal to 0.889 and 0.987 for Purolite A-520E and AC-20G, respectively. The maximum monolayer capacity Q_0 for sorption of the

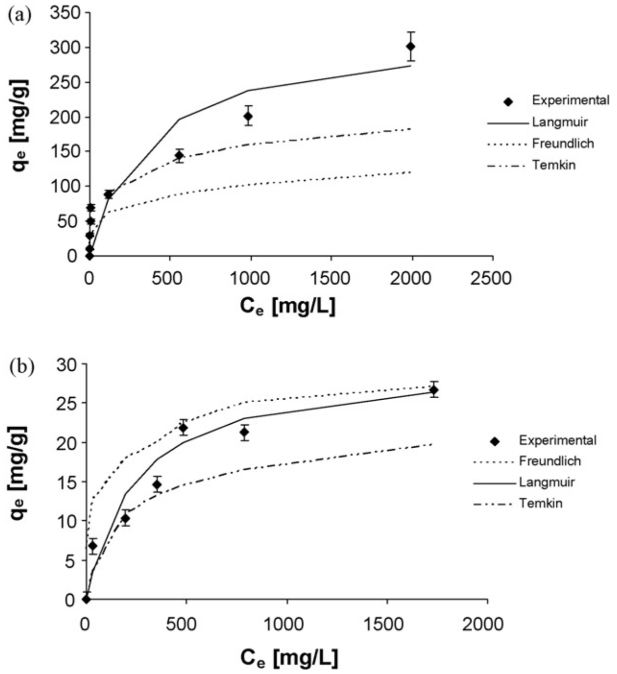


Fig. 5. Comparison of experimental adsorption isotherms of Acid Blue 29 with isotherm models for adsorption on Purolite A-520E (a) and Purolite AC-20G (b) at 20 °C ($\Delta q = \pm 5\%$).

dye on the activated carbon was 30.2 mg/g. The Q_0 obtained for the strongly basic anion exchanger was ten times higher (321.5 mg/g) than that obtained for Purolite AC-20G. The values of R_L were in the range of 0 and 1, and confirmed that the acidic dye sorption was favourable (Table 2).

The applicability of Freundlich sorption isotherm was studied by plotting $\log q_e$ *vs.* $\log C_e$. The correlation coefficients (0.835 for Purolite A-520E and 0.929 for Purolite AC-20G) showed that the Freundlich model was comparable to the Langmuir model. The $1/n$ values were lower than 1, indicating that Acid Blue 29 was favourably adsorbed (Table 2).

The adsorption data were analyzed according to the linear form of Temkin's equation (8). Examination of the data shows that the Temkin isotherm fitted worse to Acid Blue 29 adsorption data on Purolite A-520E and AC-20G (Table 2). The heat of adsorption was found to be 76.5 and 607.3 J/mol for the anion exchanger and activated carbon, respectively. The correlation coefficients obtained from Temkin model were lower than those obtained for Freundlich and Langmuir equations.

3.6. *Kinetic studies*

Three common kinetic models, namely, the Lagergren pseudo-first order model (Eq. (9)), Ho pseudo-second order model (Eq. (10)) as well as Weber and Morris intraparticle diffusion model (Eq. (11)) [21–23,31–35] were fitted to the experimental data of Acid Blue 29 sorption on Purolites:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (10)$$

$$q_t = k_i t^{0.5} \quad (11)$$

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

The conformity between the experimental data and the model predicted values was expressed by the correlation coefficients. From the slopes and intercepts of plots $\log(q_e - q_t)$ *vs.* t obtained at the initial concentrations of 100, 200, 300 and 500 mg/L at 20 °C, the first order rate constant k_1 and calculated equilibrium adsorption capacities $q_{e,cal}$ were determined. Fig. 6 shows the $\log(q_e - q_t)$ *vs.* t plots for Acid Blue 29 sorption on Purolite A-520E. A comparison of the results with the correlation coefficients is shown in Table 3. The correlation coefficients r_1^2 determined for Acid Blue 29 sorption using the Lagergren model obtained at all studied initial concentrations were relatively high, ranging from 0.908 to 0.997 and from 0.697 to 0.977 for the anion exchanger and activated carbon, respectively. The higher k_1 values were obtained for Purolite A-520E than for Purolite AC-20G. 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 onto the strongly basic anion exchanger and activated carbon did not follow the first order kinetics.

Table 3

Kinetic parameters for Acid Blue 29 sorption on the strongly basic anion exchanger and activated carbon at 20 °C for different initial concentrations of dye.

Parameters	Initial concentration (mg/L)			
	100	200	300	500
Purolite A-520E				
$q_{e,exp}$ (mg/g)	9.9	19.9	29.9	48.2
Pseudo-first order				
$q_{1,cal}$ (mg/g)	9.6	17.7	24.3	49.7
k_1 (1/min)	0.067	0.039	0.090	0.030
r_1^2	0.997	0.965	0.990	0.908
Δq (%)	2.7	4.2	3.9	3.0
Pseudo-second order				
$q_{2,cal}$ (mg/g)	10.7	21.6	30.8	62.6
k_2 (g/mg min)	0.009	0.004	0.008	0.0004
r_2^2	0.998	0.997	0.999	0.983
Δq (%)	1.0	1.1	0.8	5.4
Purolite AC-20G				
$q_{e,exp}$ (mg/g)	5.2	8.4	9.3	9.7
Pseudo-first order				
$q_{1,cal}$ (mg/g)	9.9	20.4	30.7	50.2
k_1 (1/min)	0.006	0.011	0.008	0.0004
r_1^2	0.860	0.977	0.697	0.902
Δq (%)	10.2	8.0	9.5	10.2
Pseudo-second order				
$q_{2,cal}$ (mg/g)	8.9	9.9	11.1	13.7
k_2 (g/mg min)	0.001	0.001	0.0001	0.0001
r_2^2	0.994	0.963	0.917	0.798
Δq (%)	3.2	2.3	5.7	6.1

Using Eq. (10), t/q_t was plotted against t ranging the initial dye 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 plots of t/q_t *vs.* t, as presented in Fig. 7, show a good agreement between the experimental $q_{e,exp}$ and the calculated $q_{e,cal}$ values for the strongly basic anion exchanger. It was found that the $q_{e,cal}$ values determined for Acid Blue 29 increased from 10.7 to 62.6 mg/g and from 8.9 to 13.7 mg/g with increase in initial concentration from 100 to 500 mg/L for the anion exchanger and activated carbon, respectively (Table 3). The correlation coefficients r_2^2 were very high, ranging from 0.983 to 0.999 for the anion exchanger. As Table 3 shows, the correlation coefficients for Purolite AC-20G varied from 0.798 to 0.994. At 500 mg/L initial concentration the pseudo-second order model provided higher values of calculated sorption capacities than expected: 62.6 mg/g (for

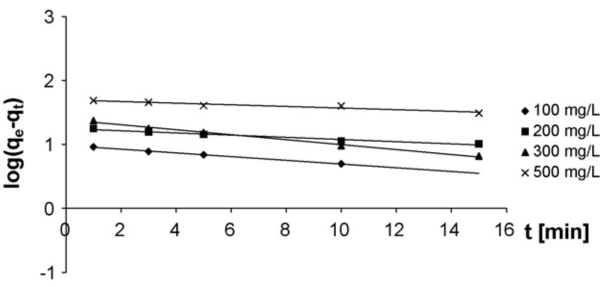


Fig. 6. Pseudo-first order kinetics for adsorption of Acid Blue 29 on Purolite A-520E at different initial concentrations of dye at 20 °C.

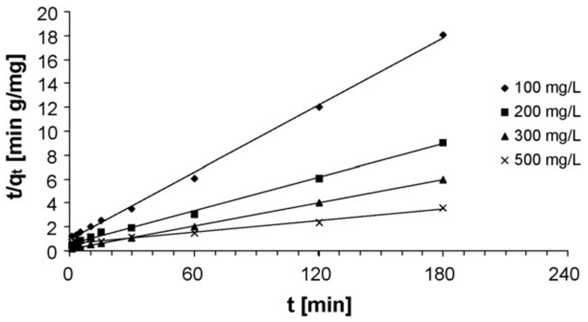


Fig. 7. The fitting of pseudo-second order model for Acid Blue 29 sorption on Purolite A-520E at different initial concentrations of dye at 20 °C.

A-520E) and 13.7 mg/g (for AC-20G). No distinct relationship can be established between the values of k_2 and initial dye concentration.

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.

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. The values of intraparticle diffusion rate constants k_{id} calculated for the dye from the slope of the plots q_t *vs.* $t^{0.5}$ increased from 0.317 to 2 mg/g min$^{0.5}$ and from 0.198 to 0.399 mg/g min$^{0.5}$ with the increase in the initial concentrations from 100 to 500 mg/L for Purolite A-520E and Purolite AC-20G, respectively. The values of r^2 were lower (from 0.014 to 0.304) compared to those obtained from the pseudo-second order kinetic model.

4. Conclusions

In this study, the potential of the strongly basic anion exchange resin (Purolite A-520E) and activated carbon (Purolite AC-20G) for the treatment of Acid Blue 29 solutions was evaluated. Some of the important findings include:

- Purolite A-520E showed high sorption capacities towards Acid Blue 29, ranging from 9.9 to 48.2 mg/g when the initial concentration of dye changed from 100 to 500 mg/L. It was found that q_t values determined for the activated carbon were very low compared with those obtained for the anion exchanger.
- The values of q_t decreased from 19.9 to 4.9 mg/g and from 8.3 to 4.9 mg/g with increase of Purolite A-520E and Purolite AC-20G dose from 0.25 to 1.0 g.
- The equilibrium sorption capacity of the anion exchanger increased when the temperature of dye solution increased from 20 to 50 °C. The same effect of temperature was observed for the activated carbon.
- The Langmuir isotherm described the sorption of Acid Blue 29 on both sorbents with high correlation coefficients.
- The adsorption kinetics was found to follow pseudo-second order rather than pseudo-first order model.
- This study highlighted that the anion exchanger of macroporous structure, namely Purolite A-520E, can find practical application in decolouration of industrial effluents containing Acid Blue 29.

References

[1] N. Dizge, C. Aydiner, E. Demirbas, M. Kobya, S. Kara, Adsorption of reactive dyes from aqueous solutions by fly ash: kinetic and equilibrium studies, J. Hazard. Mater. 150 (2008) 737–746.

[2] T. Robinson, B. Chandran, P. Nigam, Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw, Water Res. 36 (2002) 2824–2830.

[3] B.H. Hameed, M.I. El-Khaiary, Removal of basic dye from aqueous medium using a novel agricultural waste material: pumpkin seed hull, J. Hazard. Mater. 155 (2008) 601–609.

[4] R. Gong, Y. Sun, J. Chen, H. Liu, C. Yang, Effect of chemical modification on dye adsorption capacity of peanut hull, Dyes Pigments 67 (2005) 175–181.

[5] S. Wang, Y. Boyjoo, A. Chouebi, Z.H. Zhu, Removal of dyes from aqueous solution using fly ash and red mud, Water Res. 39 (2005) 129–138.

[6] B.H. Hameed, I.A.W. Tan, A.L. Ahmad, Optimization of basic dye removal by oil palm fibre-based activated carbon using response surface methodology, J. Hazard. Mater. 158 (2008) 324–332.

[7] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies, Desalination 225 (2008) 13–28.

[8] B.H. Hameed, A.T.M. Din, A.L. Ahmad, Adsorption of Methylene Blue onto bamboo-based activated carbon: kinetics and equilibrium studies, J Hazard. Mater. 141 (2007) 819–825.

[9] B.H. Hameed, A.L. Ahmad, K.N.A. Latiff, Adsorption of basic dye (Methylene Blue) onto activated carbon prepared from rattan sawdust, Dyes Pigments 75 (2007) 143–149.

[10] B.H. Hameed, F.B.M. Daud, Adsorption studies of basic dye on activated carbon derived from agricultural waste: *Hevea brasiliensis* seed coat, Chem. Eng. J. 139 (2008) 48–55.

[11] S. Karcher, A. Kornmüller, M. Jekel, Screening of commercial sorbents for the removal of reactive dyes, Dyes Pigments 51 (2001) 111–125.

[12] S. Karcher, A. Kornmüller, M. Jekel, Anion exchange resins for the removal of reactive dyes from textile wastewaters, Water Res. 36 (2002) 4717–4724.

[13] V. Dulman, C. Simion, A. Bârsănescu, I. Bunia, V. Neagu, Adsorption of anionic textile dye Acid Green 9 from aqueous solution onto weak or strong base anion exchangers, J. Appl. Polym. Sci. 113 (2009) 615–627.

[14] S. Dragan, M. Cristea, A. Airinei, I. Poinescu, C. Luca, Sorption of aromatic compounds on macroporous anion exchangers based on polyacrylamide: relation between structure and sorption behavior, J. Appl. Polym. Sci. 55 (1995) 421–430.

[15] M. Wawrzkiewicz, Z. Hubicki, Kinetic studies of dyes sorption from aqueous solutions onto the strongly basic anion-exchanger Lewatit MonoPlus M-600, Chem. Eng. J. 150 (2009) 509–515.

[16] V. Neagu, I. Bunia, Acrylic weak base anion exchangers and their chemical stability in aggressive media, Polym. Degrad. Stab. 83 (2004) 133–138.

[17] F. Helfferich, Ion Exchange, McGraw-Hill, New York, 1962.

[18] V. Vasić, J. Savić, V. Pavelkić, S. Milonjić, Kinetics of 1,8-dihydroxy-2-(pyrazol-5-ylazo)-naphthalene-3,6-disulphonic acid immobilization on anion exchangers, Colloids Surf. A: Physicochem. Eng. Aspects 215 (2003) 277–284.

[19] J. Savić, V. Vasić, Thermodynamics and kinetics of 1,8-dihydroxy-2-(imidazol-5-ylazo)-naphthalene-3,6-disulphonic acid immobilization on Dowex resin, Colloids Surf. A: Physicochem. Eng. Aspects 278 (2006) 197–203.

[20] C. Valderrama, J.L. Cortina, A. Farran, X. Gamisans, F.X. de las Heras, Evaluation of hyper-cross-linked polymeric sorbents (Macronet MN200 and MN300) on dye (Acid Red 14) removal process, React. Funct. Polym. 68 (2008) 679–691.

[21] H. Kaşgöz, New sorbent hydrogels for removal of acidic dyes and metal ions from aqueous solutions, Polym. Bull. 56 (2006) 517–528.

[22] M. Wawrzkiewicz, Z. Hubicki, Use of weakly and strongly basic anion-exchange resins for the removal of Indigo Carmine from aqueous solutions, Przem. Chem. 87 (2008) 711–714.

[23] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies, J. Hazard. Mater. 154 (2008) 337–346.

[24] V. Vadivelan, K.V. Kumar, Equilibrium, kinetics, mechanism and process design for the sorption of Methylene Blue onto rice husk, J. Colloid Interface Sci. 286 (2005) 90–100.

[25] P. Janoš, P. Michálek, L. Turek, Sorption of ionic dyes onto untreated low-rank coal—oxihumolite: a kinetic study, Dyes Pigments 74 (2007) 363–370.

[26] H. Lata, V.K. Garg, R.K. Gupta, Adsorptive removal of basic dye by chemically activated Parthenium biomass: equilibrium and kinetic modeling, Desalination 219 (2008) 250–261.

[27] N. Yeddou, A. Bensmaili, Kinetic models for the sorption of dye from aqueous solution by clay-wood sawdust mixture, Desalination 185 (2005) 499–508.

[28] E. Radulescu, V. Nedeff, C. Stanciu, G. Cantemir, Studies regarding the sorption of nitroso-R-salt on Purolite A 600-PL resin (part I), MOCM 13 (2007) 235–240 (Ed. by Romanian Technical Science Academy).

[29] E. Radulescu, G. Cantemir, O. Mitoseriu, C. Stanciu, Kinetics of nitroso-R-salt sorption on Amberlite IRA 402 resin, Ann. “DUNARES DE JOS” Univ. Galati, Fascicle IX Metall. Mater. Sci. 2 (2005).

[30] H. Tanaka, T. Nakagawa, Y. Okabayashi, H. Aoyama, T. Tanaka, K. Itho, M. Chikuma, Y. Saito, H. Sakurai, M. Nakayama, Development of functional resins by modification of ion-exchange resins and their application to analytical chemistry, Pure Appl. Chem. 59 (1987) 573–578.

[31] A.E. Nemr, O. Abdelwahab, A. El-Sikaily, A. Khaled, Removal of direct blue-86 from aqueous solution by new activated carbon developed from orange peel, J. Hazard. Mater. 161 (2009) 102–110.

[32] B.H. Hameed, Spent tea leaves: a new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions, J. Hazard. Mater. 161 (2009) 753–759.

[33] B.H. Hameed, M.I. El-Khaiary, Equilibrium, kinetics and mechanism of Malachite Green adsorption on activated carbon prepared from bamboo by K_2CO_3 activation and subsequent gasification with CO_2, J. Hazard. Mater. 157 (2008) 344–351.

[34] S.D. Khattri, M.K. Singh, Removal of Malachite Green from dye wastewater using neem sawdust by adsorption, J. Hazard. Mater. 167 (2009) 1089–1094.

[35] N. Dizge, B. Keskinler, H. Barlas, Sorption of Ni(II) ions from aqueous solution by Lewatit cation-exchange resin, J. Hazard. Mater. 167 (2009) 915–926.