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Weak Base Anion Exchanger Amberlite FPA51 as Effective Adsorbent for Acid Blue 74 Removal from Aqueous Medium – Kinetic and Equilibrium Studies

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In this work, the macroporous anion exchange resin – Amberlite FPA51, is proposed as the effective adsorbent for the removal of Acid Blue 74 from aqueous solutions. The sorption mechanism was investigated under static conditions taking into account the phase contact time, solution pH, initial dye concentration, and temperature. The equilibrium data were fitted to the Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models. The maximum monolayer capacity Q_0 was 123.8 mg/g. The adsorption kinetics was found to follow the pseudo-second order model. The sorption energy was equal to 14.5 kJ/mol and indicated that the adsorption process of the dye may be described via a chemical anion-exchange mechanism.

Keywords acid blue; anion exchanger; dye; kinetics; removal

INTRODUCTION

Acid Blue 74 (AB74, Indigo Carmine, Saxon Blue, Acid Blue W) is one of the oldest dyes and still one of the most important used (1–4). The ancients extracted the natural Acid Blue from several species of plants as well as sea snails, but nearly all this dye produced today is synthetic. Historically, Acid Blue 74 played an important role in many countries' economies because natural blue dyes were rare. Nowadays, Acid Blue 74 is used as a textile coloring agent (blue jeans and denim) as well as a food and pharmaceutical additive. It is also applied in cosmetic industry, medicine, biology and analytical chemistry. Acid Blue 74 is considered as highly toxic as it can cause skin and eye irritations (3–5). The toxicity tests of the dye revealed long-term toxicity in mice and short term toxicity in pigs (3).

Improper treatment and disposal of dye-contaminated wastewaters from textile, dyeing, printing, and related industries have provoked serious environmental concerns all over the world. As regulations become more stringent, a complicated and multi-step treatment for dye wastewaters is required (6,7). A number of methods such as microbiological decomposition, coagulation, filtration, ozonation, and membrane process has been developed in recent years, but adsorption is generally preferred for dyes removal because of its high efficiency, easy handling, and availability of different adsorbents (6,8). Almost complete removal of impurities with negligible side effects evidences its wide application in treatment of dye bearing wastewaters. There is a strong trend of using nonconventional sorbents that are widely available (9–15). Inexpensive sorbents such as rice husk ash, bottom ash as well as de-oiled soya obtained from waste materials are characterized by large capacities towards hazardous AB74 and can be successfully used in the purification of wastewaters (2,3). Numerous studies have demonstrated the effectiveness of activated carbon, too (16–20). It is characterized by highly developed porosity and large surface area but its widespread use is restricted because of costs (21,22). Ion exchangers are considered as not effective adsorbents for dyes removal. It is commonly believed that they cannot adsorb a wide range of dyes and perform poorly in the presence of other additives in wastewaters (22,23). According to our knowledge, such view is erroneous, since according to the literature, at least one successful ion exchange treatment is known (24,25). Good sorption results for the materials presented in (24–33) indicate that cation and anion exchangers, in general, could be efficient sorbents for dyes removal.

Purification of wastewaters particularly those containing Acid Blue 74 becomes more and more important. Its aim is to avoid potential threat for the environment. Different sorbents were used in treatment of wastewaters contaminated by indigo carmine. Hydrogels based on poly (N-hydroxymethylacrylamide) (PHMA) and their functionalized derivatives were recommended for the sorption of Acid Blue 74 from aqueous solutions by Kaşgöz (6). PHMA hydrogels possessing amide, hydroxymethyl, and

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amine groups adsorbed AB74 effectively whereas PHMA of amide and hydroxymethyl groups did not. The capacities of amine functionalized hydrogels towards AB74 varied between 149.7 and 237.6 mg/g.

Poly(DMAEMA-AMPS-HEMA) terpolymer/montmorillonite nanocomposite hydrogels, prepared by the in situ polymerization technique using 2-(N,N-dimethylamino)-ethyl methacrylate (DMAEMA), 2-acrylamido-2-methyl-propane sulfonic acid (AMPS), 2-hydroxyethyl methacrylate (HEMA) monomers in the clay suspension media were investigated as a new adsorbent for the removal of AB74 from aqueous medium (34). The adsorption capacities determined from the Langmuir isotherm model decreased from 168.07 to 74.13 mg/g with the increasing montmorillonite content (34).

Not only Acid Blue 74 but also Basic Blue 9, Tetraethyl Rhodamine, and Xylidine Ponceau 2 R can be effectively adsorbed on N-vinyl-2-pyrrolidone/acrylonitrile hydrogels as proved by Şahiner et al. (35).

The studies of applicability of sewage sludge based activated carbons were of significant importance in the sorption of Acid Blue 74 and Crystal Violet from mixed binary solutions (36). The experiments performed by Prado et al. (37) were focused on the sorption of AB74 by chitin and chitosan from aqueous media. The maximum capacities were $1.24 \pm 0.16 \times 10^{-5}$ and $1.54 \pm 0.03 \times 10^{-4}$ mol/g for chitin and chitosan, respectively. The interaction processes were accompanied by an increase of entropy value for chitosan and a decrease for chitin. Thus, the AB74/chitosan interaction showed favorable enthalpic and entropic processes, reflecting thermodynamic stability of the formed complex, whereas the dye/chitin interaction showed an exothermic enthalpic value and a largely unfavorable entropic effect. Cestari et al. (38) improved the chemical and mechanical features of chitosan by glutaraldehyde cross-linking. The results obtained in this study showed that the changes affected the adsorption levels of AB74.

Silica gel modified with humic acids ($SiHA_{PS}$ and $SiHA_{FL}$) exhibited high affinity for indigo carmine (39). The capability of these materials of removing AB74 was determined by the values of max number of moles adsorbed ($6.82 \pm 0.12 \times 10^{-4}$ and $2.15 \pm 0.17 \times 10^{-4}$ mol/g for $SiHA_{PS}$ and $SiHA_{FL}$, respectively).

In our previous work (5) we confirmed that AB74 can be removed from aqueous solution using the weakly (Amberlite IRA67) and strongly (Amberlite IRA402, Amberlite IRA958, Lewatit M600) basic anion exchangers. The quantitative purification was performed by the strongly basic polyacrylic anion exchanger of macroporous structure, namely Amberlite IRA958. Taking into account the values of the sorption capacity of Amberlite IRA67 (possesses gel structure) for AB74 (0.1 mmol/g), it cannot be applied in the removal of this dye. As reported in (33), the macroporous anion exchangers derived from styrene–divinylobenzene copolymers seem to occupy a special position among the anion exchangers used in the field of dyes removal because of excellent physical strength and resistance to the degradation by oxidation, hydrolysis or elevated temperatures. These advantages make the styrene–divinylobenzene resins promising material for dyes removal. Not only Karcher et al. (26,27) but also Dragan et al. (29) suggested that the sorption mechanism was correlated to the structure of the polymer. Hence, it is considered worthwhile developing a procedure for AB74 removal using a weakly basic anion exchanger of macroporous structure.

This study is an attempt to explore the possibility of the macroporous polystyrene anion exchanger Amberlite FPA51 usage for the removal of Acid Blue 74 from aqueous solution by the batch method.

EXPERIMENTAL

Characteristics of Dye and Anion Exchange Resin

Acid Blue 74 is a synthetic dye of the chemical name indigo-5,5′-disulfonic acid disodium salt (Fig. 1). It is a dark blue powder, soluble in water, decomposes at the melting point 360°C. The dye was purchased from Sigma-Aldrich (Germany), dye purity ~85%. The stock solution of the dye, without further purification, 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. The dye concentration was measured using a double beam UV-VIS spectrophotometer Specord M42 (Carl Zeiss Jena, Germany) at the maximum absorbance wavelengths.

Amberlite FPA51 (Rohm and Haas, France) is the macroreticular, weakly basic anion exchange resin containing tertiary amine functionalities (at least 85%) on the crosslinked polystyrene matrix. The total capacity, harmonic mean size, and moisture holding capacity are equal to 1.3 eq/L, 0.49–0.69 mm, and 54–60%, respectively. The maximum operating temperature is 100°C. Amberlite FPA51 is advisable for the purification of wastewater streams containing large organic molecules in the food processing industries (40).

The resin was washed with 1 M NaOH and 1 M HCl as well as doubly distilled water in order to remove the

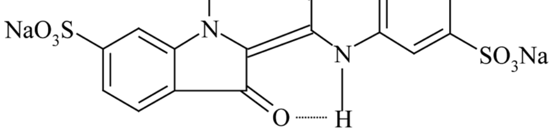

FIG. 1. Structure of Acid Blue 74.

impurities. The dried resin was used for further experimental studies.

Equilibrium and Kinetic Studies

Equilibrium experiments were carried out by means of the batch method. 0.25 g of the anion-exchanger and 0.025 L of dye solution (100–1500 mg/L) were placed in 0.1 L conical flasks without adjusting the pH. The flasks were shaken in the thermostatic shaker (Elphin 358 S, Poland) with a constant speed of 170 rpm at 20°C for 1–360 min.

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

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

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

Kinetic experiments were identical to those of the equilibrium tests. The aqueous samples were taken at the preset time intervals and the concentrations of dye were similarly measured. All the kinetic studies were carried out at the natural pHs (pH 4.7) of solutions (pH-meter; CX-742 Elmetron, Poland) ranging the initial dye concentration (100, 200, 300, and 500 mg/L). The amounts of dye adsorbed at time t, q_t (mg/g) were calculated by analogy from Eq. (1). The kinetic data obtained at different concentrations were modelled using the pseudo-first order, pseudo-second order, and intraparticle diffusion equations.

The influence of solution pH (1–8) and temperature (20–60°C) on the amount of dye adsorbed by Amberlite FPA51 was determined, too.

All collected values in this paper are the average of three independent experiments, the normalized standard deviation was in the range of 1.69 to 3.21%.

RESULTS AND DISCUSSION

Effect of Contact Time and Initial Dye Concentration

The adsorbate concentration and contact time between the adsorbent and adsorbate play a significant role in the process of dyes removal from wastewaters by adsorption.

The influence of phase contact time on AB74 adsorption on Amberlite FPA51 was studied ranging the initial dye concentrations from 100 to 500 mg/L at 20°C and is presented in Fig. 2. The amount of AB74 adsorbed per unit mass of the anion exchanger increased with the increasing initial dye concentration. It is also noted that the rate of dye removal is faster at lower concentration and decreases with the increasing concentration. This follows from the fact that a large number of surface sites is available for adsorption at the beginning and after the laps of time, the remaining sites are difficult to be occupied because of repulsion between the dye molecules of the solid and the bulk phases (41). A similar phenomenon was observed for the sorption of Acid Blue 74 (5) and Acid Green 9 (30) on the weak and strong base anion exchange resins.

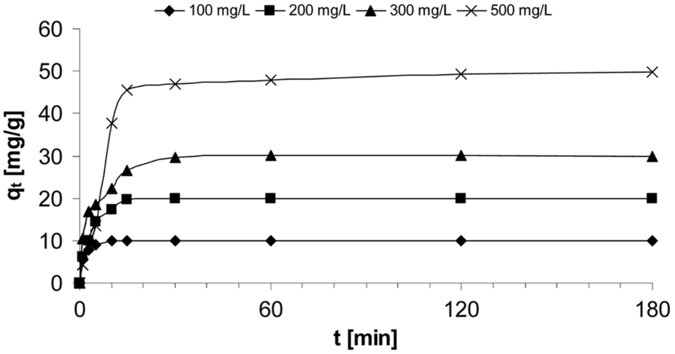

FIG. 2. Influence of contact time and initial concentration on removal of AB74 from aqueous solutions by Amberlite FPA51 at 20°C.

The amounts of AB74 adsorbed at equilibrium were equal to 10.0, 20.0, 30.0, and 49.9 mg/g for the dye solutions of the initial concentrations 100, 200, 300, and 500 mg/L, respectively. The saturation of active sites was reached after 30 min of phase contact time.

Effect of Temperature

The influence of temperature on Acid Blue 74 sorption onto the weakly basic anion exchanger was studied with the constant initial concentration of 200 mg/L and is shown in Fig. 3. The sorption capacity increased when the temperature of dye solution increased from 20 to 60°C during the first 20 min of phase contact time. The fact that the sorption of the acidic dye is in favor of temperature indicates that the mobility of dye molecules increases with the temperature rise.

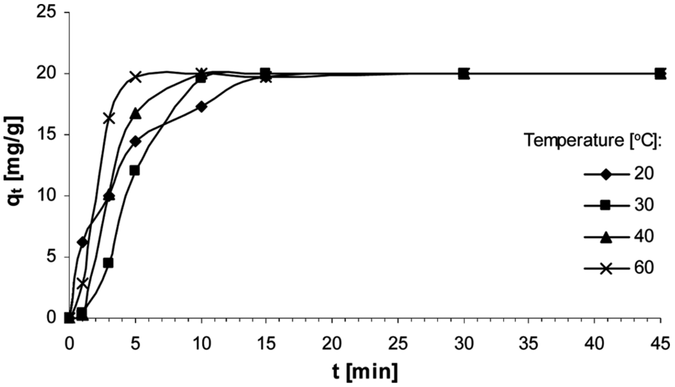

FIG. 3. Influence of temperature on AB74 ($C_0 = 200$ mg/L) uptake by Amberlite FPA51.

Effect of Solution pH

The relation between the initial pH of AB74 solutions and the adsorption capacity using the weakly basic anion exchanger was studied in the system containing 200 mg of dye per 1 L at 20°C. Decrease in sorption capacity with the increasing initial solution pH was observed. The q_t values decreased from 19.9 to 15.3 mg/g with the increasing initial solution pH from 1 to 8 at the phase contact time 45 min (Fig. 4) due to the fact that the capacity of the weak base anion exchange resin is a function of pH (it decreased with the increase of pH, their functional groups are protonated significantly only at high acid concentration). In aqueous solution, Acid Blue 74 ($R'(SO_3)_2Na_2$) is dissolved and strongly acidic sulphonate groups of the dye were dissociated and converted to anionic dye ions:

$$R'(SO_3)_2Na_2 \xrightarrow{H_2O} R'(SO_3)_2^{2-} + 2Na^+$$

Then the adsorption process proceeded due to the interaction between the anionic dye and the functional groups of the anion exchanger. Acid Blue 74 forms a stable ion pair in the anion exchanger phase. The occurrence of double bond serves to enhance the interaction between the dye and the anion exchanger macromolecule. 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 (42–44).

Isotherm Analysis

In this study the equilibrium isotherms are described in terms of the Langmuir, Freundlich, and Dubinin-Radushkevich equations. The values of the correlation coefficients indicated isotherm equations' applicability. Linear regression was used to determine the best-fitting isotherm.

The Langmuir theory assumes a homogeneous type of adsorption indicating that once a dye molecule occupies a site, no further adsorption can take place at that site (45,46). The linear form of the Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \tag{2}$$

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

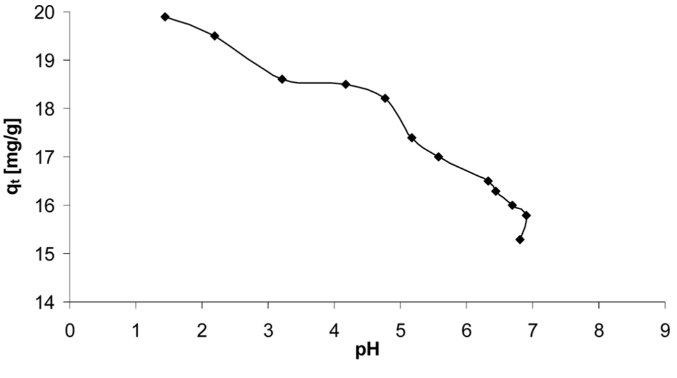

FIG. 4. Influence of solution pH on AB74 ($C_0 = 200$ mg/L) uptake by Amberlite FPA51.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L. 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 ($R_L = 0$) (47).

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces and the adsorption capacity is related to the concentration of AB74 dye at equilibrium. The linear form of the Freundlich equation (45,46) is expressed as:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \tag{3}$$

where C_e is the equilibrium concentration of the dye (mg/L); q_e is the amount of dye adsorbed per unit mass 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 versus 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 the 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 heterogeneous as its value gets closer to zero. The value $1/n$ below 1 indicates a normal isotherm whereas that above 1 is indicative of cooperative adsorption (45).

The Dubinin-Radushkevich model is often used to estimate the characteristic porosity and free energy of adsorption (46). The linear form of the Dubinin-Radushkevich equation is given as:

$$\ln q_e = \ln X_m - k_{DR}\varepsilon^2 \tag{4}$$

where k_{DR} (mol^2/kJ^2) relates to the free energy of sorption, X_m is the Dubinin-Radushkevich isotherm constant related to the degree of sorption (mg/g). The parameter ε is the Polanyi potential and is expressed as:

$$\varepsilon = RT \ln \frac{C_0}{C_e} \tag{5}$$

TABLE 1
Comparison of the coefficients isotherm parameters for Acid Blue 74 adsorption on Amberlite FPA51

Isotherm model	Parameters
Langmuir	
Q_0 [mg/g]	123.8
b [L/mg]	2.04
R_L	0.00033
r^2	0.999
Freundlich	
K_F [mg/g]	74.7
n	0.97
r^2	0.843
Dubinin-Radushkievich	
X_m [mg/g]	123.5
k_{DR}	0.00237
E [kJ/mol]	14.5
r^2	0.945

The mean free energy E (kJ/mol) of adsorption can be computed from the following relation:

$$E = (-2k_{DR})^{-1/2} \tag{6}$$

The Langmuir, Freundlich, and Dubinin-Radushkevich parameters are summarized in Table 1. These data were calculated from the plots C_e/q_e *vs.* C_e, log q_e *vs.* log C_e, and ln q_e *vs.* ε^2. Figure 5 shows the equilibrium adsorption isotherm of AB74 and fitting of the models to the experimental data. A steep increase at low concentrations is observed, indicating high affinity for the solute. The adsorbed amount of the dye increased slightly, showing almost horizontal plateaus at high concentrations.

The analysis of r^2 values showed that the Langmuir and Dubinin-Radushkevich equations have more precise correlation coefficients than the Freundlich one for modelling of AB74 adsorption on the weakly basic anion exchanger.

The r^2 value for the plot of C_e/q_e *vs.* C_e was equal to 0.999. The maximum monolayer capacity Q_0 was 123.8 mg/g. The value of R_L was found to be 0.00033, i.e., in the range of 0 and 1 and confirmed that the acidic dye sorption was favorable. Applicability of the Langmuir isotherm model indicates the homogeneous nature of the anion exchanger surface and formation of the monolayer coverage of dye molecule at the outer surface of the anion exchanger.

The Dubinin-Radushkevich model yielded good fit with the r^2 value of 0.945. The monomolecular adsorption capacity and porosity factor (k_{DR}) are equal to 123.5 mg/g and 0.00237 mol^2/kJ^2, respectively. The mean free energy of adsorption gives information about the adsorption mechanism as a chemical ion-exchange. If the value of E is between 8 and 16 kJ/mol, then the adsorption process proceeds according to the chemical ion-exchange and if $E < 8$ kJ/mol the adsorption process is of physical nature (46). The sorption energy E determined from the Dubinin-Radushkevich equation was 14.5 kJ/mol and revealed the nature of the ion exchange mechanism in this system.

Applicability of the Freundlich sorption isotherm was studied by plotting log q_e *vs.* log C_e. As follows from the correlation coefficient value ($r^2 = 0.843$) the Freundlich

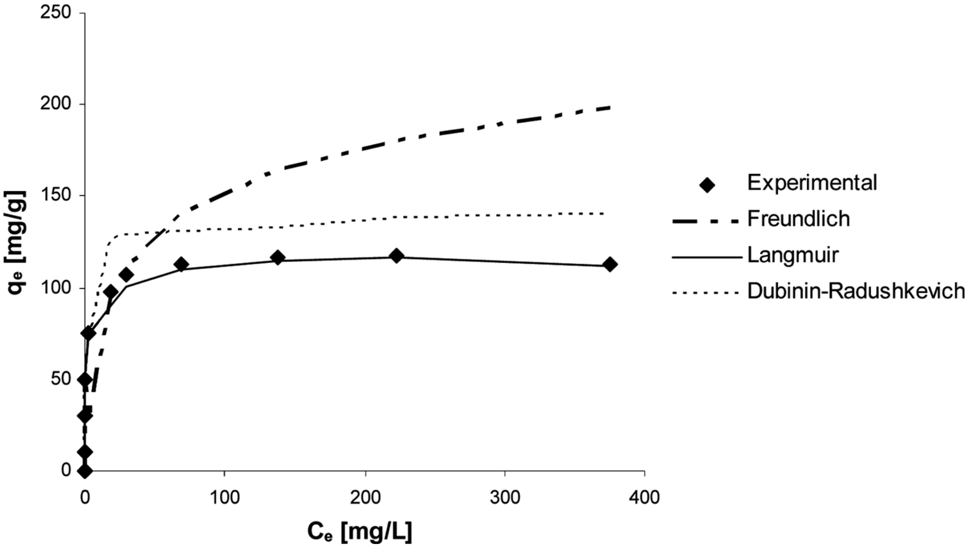

FIG. 5. Fitting of the Langmuir, Dubinin-Radushkevich and Freundlich isotherm models to the experimental data of AB74 adsorption on Amberlite FPA51 at 20°C.

model cannot be applied. The 1/n values were lower than 1, indicating that AB74 was favourably adsorbed.

Kinetic Studies

Kinetic parameters, which are helpful in the prediction of the adsorption rate, are a source of important information for designing and modelling the adsorption processes. Thus, the kinetics of AB74 adsorption on the weakly basic anion exchanger was analyzed using the pseudo-first order, pseudo-second order, and intraparticle diffusion kinetic models. Conformity between the experimental data and the predicted model was expressed by the correlation coefficients. The comparison of the obtained results is presented in Table 2.

The Langergren pseudo-first order rate expression is generally described using the following equation:

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

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 (1/min).

In order to confirm the model applicability, the plot of $\log(q_e - q_t)$ against t should be a straight line. In the real first-order process, experimental $\log(q_e)$ should be equal to the intercept of the straight line (47). From the slopes and intercepts of plot $\log(q_e - q_t)$ *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 the calculated equilibrium adsorption capacities $q_{e,cal}$ were determined. The values of k_1 decreased from 0.421 to 0.116 1/min with the increasing initial concentration in the range 100–500 mg/L. The calculated equilibrium adsorption capacities $q_{e,cal}$ were found to be 12.3, 22.8, 20.9, and 66.7 mg/g. The correlation coefficients, determined for AB74 sorption using the Lagergren model, obtained at all studied initial concentrations were relatively high, ranging from 0.939 to 0.974. Despite this, the Langergren pseudo-first order rate expression cannot be used for describing the AB74 kinetic sorption on Amberlite FPA51. Better results were obtained using the pseudo-second order equations.

The pseudo-second order kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

where q_e and q_t are the amounts (mg/g) of dye adsorbed at equilibrium and at time t (min) respectively; and k_2 is the constant rate of the pseudo-second order adsorption (g/mg min).

After taking into account the boundary conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the integrated form of Eq. (8) can be rearranged to obtain Eq. (9):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{9}$$

The values of k_2 and q_e can be determined from the slope and intercept of the plot t/q_t vs. t. The k_2 decreased from 0.255 to 0.002 g/mg min with the increase of initial concentration from 100 to 500 mg/L, respectively. The best correlation of the experimental capacities $q_{2,exp}$ with the calculated $q_{2,cal}$ was observed and confirmed by the values of $r^2 = 0.999$. This suggests 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.

Weber and Morris in 1963 (47) made the assumption that sorption is proportional to the square root of contact time:

$$q_t = k_i t^{0.5} \tag{10}$$

where k_i is the intraparticle diffusion rate (mg/g min$^{0.5}$).

The intraparticle diffusion model controls sorption when the graph of q_t against $t^{0.5}$ is a straight line passing through the origin (47). Table 2 presents the intraparticle diffusion kinetics of AB74 at various initial concentrations at 20°C. The values of intraparticle diffusion rate constants k_{id} calculated for the dye from the slope of the plot q_t vs. $t^{0.5}$ decreased from 0.212 to 0.044 mg/g min$^{0.5}$ with the

TABLE 2
Kinetic parameters according to the pseudo-first order, pseudo-second order and intraparticle diffusion equations for Acid Blue 74 sorption on Amberlite FPA51 at 20°C

		Pseudo-first order			Pseudo-second order			Intraparticle diffusion	
C_0 [mg/L]	$q_{e,exp.}$ [mg/g]	$q_{1,cal.}$ [mg/g]	k_1 [1/min]	r^2	$q_{2,cal.}$ [mg/g]	k_2 [g/mg min]	r^2	k_i [mg/g min$^{0.5}$]	r_i^2
100	10.0	12.3	0.421	0.973	10.1	0.255	0.999	0.212	0.115
200	20.0	22.8	0.276	0.934	20.3	0.031	0.999	0.089	0.004
300	30.0	20.9	0.173	0.969	30.5	0.015	0.999	0.060	0.259
500	49.9	66.7	0.116	0.974	53.0	0.002	0.995	0.044	0.044

increase in the initial concentration from 100 to 500 mg/L. The values of r^2 were lower compared to those obtained from the pseudo-second order kinetic model.

CONCLUSIONS

This study shows that the weakly basic anion exchange resin (Amberlite FPA51) is an effective adsorbent for the removal of Acid Blue 74 from aqueous solutions. The saturation of active sites was reached after 30 min of phase contact time. The equilibrium sorption capacity slightly increased when the temperature of dye solution increased from 20 to 60°C. The q_t values decreased with the increasing initial solution pH from 1 to 8. It was found that AB74 sorption on Amberlite FPA51 was very well described by the Langmuir isotherm. The sorption energy E determined from the Dubinin-Radushkevich equation was 14.5 kJ/mol and revealed the nature of the ion exchange mechanism in this system. Adsorption kinetics was found to follow the pseudo-second rate expression. The weak base anion exchanger of macroporous structure – Amberlite FPA51 can find practical application in the purification of wastewaters containing Acid Blue 74.

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