

Adsorption of Anionic Textile Dye Acid Green 9 from Aqueous Solution onto Weak or Strong Base Anion Exchangers

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ABSTRACT: The aim of this work is to study the thermodynamic and kinetic studies with regard to the adsorption of Acid Green 9 (AG9) on the most efficient resin, namely, acrylic weak base anion exchange resin with ethylenediamine-functional groups (A1) selected from several anion exchange resins. The influence of the various experimental parameters such as, pH, initial dye concentration, contact time, temperature, and adsorbent dose was investigated by batch experiments. The extent of the dye adsorption increased with the decrease of the initial dye concentration and the increase of the contact time, temperature, and amount of the adsorbent. Adsorption process was quantitative and very fast at low concentrations of the dye. To investigate the mechanism of the adsorption and potential rate-controlling steps, pseudo first- and second-order, as well as intraparticle diffusion kinetic equations

have been used. The adsorption kinetic of AG9 dye from aqueous solution onto A1 could be described by the pseudo second-order reaction model. The obtained results are in agreement with the Langmuir and Freundlich models. In the optimum conditions established, an adsorption capacity of 500 mg textile dye (72% purity) g⁻¹ adsorbent (at 293 K) was reached. Desorption experiments by batch and dynamic methods were performed using a solution of 0.05 mol L⁻¹ NaOH. A series of 13 adsorption-desorption cycles were carried out by the dynamic method with a quantitative adsorption and the desorption efficiency higher than 95%. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 615–627, 2009

Key words: Acid Green 9; anion exchange resin; adsorption; desorption; kinetic study; thermodynamic study

INTRODUCTION

The presence of textile dyes in the industrial aqueous effluents causes serious pollution of the environment because most of these are organic recalcitrant compounds, toxic, and highly resistant to degradation, and this imposes their treatment.¹ Environmental standards have been established and control organisms have been created with a view to apply restrictive legislation for the level of pollutants in the effluents.²

Several methods of removal such as adsorption on various sorbents, chemical decomposition by oxidation, photodegradation, and microbiological discoloration were tested. The advantages and disadvantages of these methods are discussed and their efficacies are compared with many reviews.^{3–11}

From the literature, data emerge that despite the existence of a variety of chemical and physical treatment processes, the removal of dyes from the envi-

ronment is very difficult. Adsorption process is considered to be one of the most effective method for the removal of dyes and proven technology having applications in the wastewaters treatment. Its superiority over others techniques can be assessed in terms of initial cost, flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants, and the advantage of not leading to harmful products.^{3,12} Adsorption techniques are widely used to remove certain classes of dyes from waters, especially those that are not easily biodegradable that represent one of the problematic groups.⁵ Activated carbons (AC) are effective adsorbents because of their highly developed porosity, large surface area, variable characteristics of surface chemistry, and high degree of surface reactivity, but their widespread use is restricted because of the high cost.¹³ There is a strong trend of using nonconventional sorbents that are efficient, cheap, and widely available.^{5,6,9,14–16}

Ion exchange is an alternative method for the removal of dyes. Its main advantages are the adsorbent not being lost during the regeneration, recovery of the solvent after use, and the removal of soluble dyes. A major disadvantage is the cost. Complementary methods such as biosorption and

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biodegradation and chemical or electrochemical techniques, followed by ion exchange for recycling of textile dye wastewaters have been used.^{3,4,17}

The weak basic adsorbent MP62 (Bayer) showed the most favorable profile for reactive dyes and can be completely regenerated with alkaline methanol. Sorption onto this sorbent in fixed bed filters would be an interesting option for the removal of reactive dyes from textile wastewaters.^{18,19} Loadings of the strong basic type S6328a (Bayer) were high, but regeneration was difficult.¹⁹ Strong base anion exchange resins namely, Dowex 1-X8 and Dowex 2-X8 by Dow Chemical Company were successfully used for the immobilization of some azo dyes.^{20,21} An efficient removal of the anionic reactive dyes from water was performed on the weak anion exchange membrane DE81 (Whatman) based on cellulose with diethylaminoethyl groups.²² Semiinterpenetrating polymer networks based on polysulfone and poly (acrylic acid) were used to produce the ion-exchange ultrafiltration membranes for water treatment.²³ Evaluation of hypercrosslinked polymeric sorbents on dye (Acid Red 14) removal process showed that Purolite Macronet support MN300 containing tertiary amine groups is more efficient than nonfunctionalized MN200.^{24,25}

Also, the amphoteric hydrogels based on amino-functionalized acrylamide-maleic acid were studied as the new sorbents for the removal of Indigo Carmine from aqueous solution.²⁶

Useful information including the usage of poly (glycidyl methacrylate)-grafted sulfonamide-based polystyrene resin with tertiary amine showed the dye sorption capacity of 0.90 g dye Everzol Red RBN/g resin.²⁷

By quaternization, the organic materials are transformed into cheap weak basic anion exchangers with good sorption capacities for reactive dyes (60–420 mg g⁻¹); but no successful regeneration has been reported as well.²⁸ By crosslinking starch with epichlorohydrin in the presence of NH₄OH, a material which possess good sorption properties for acid, reactive, and disperse dyes was obtained, but is ineffective against basic dyes.^{29–32} Also, starch modified by acrylonitrile (AN) and conversion to the amidoxime form was tested for the adsorption of Basic Violet 7, Basic Blue 3, Direct Yellow 50, and Acid Red 37 from aqueous solutions.³³

Water-soluble acid and reactive dyes are the most problematic ones as they tend to pass through conventional treatment unaffected.⁹ There are preoccupations on the removal of the acid dyes by the adsorption as described in the reviews cited earlier.

In this article, some weak base anion exchange resins based on the acrylic-crosslinked copolymers functionalized with various amines and pyridine strong base anion exchange resins (both adsorbents of gel and macroporous type structures) were tested

for their adsorption capacity of textile acid dye Acid Green 9 (AG9). Experiments were carried out to establish the performances of the adsorption procedures of AG9 onto acrylic copolymers functionalized with ethylenediamine (EDA; A1), which presented the highest efficiency of this adsorbent-adsorbate pair. The effect of various experimental parameters such as, pH, initial dye concentration, contact time, temperature, and adsorbent dosage were investigated. Kinetic and thermodynamic parameters that describe the adsorption of the dye were established. Also, the desorption of the retained dye was studied under both static and dynamic conditions.

AG9 is a textile dye with different commercial names such as Bezanyl Grun F-2B (Bezema Elvetia), Triacid Green 6B (Chemische Fabriek Triade, Olanda), ORCOACID Fast Green B (Organic Dyestuffs Corporation, ORCO din, USA), Acid Green E-6B (Tianjin Dongpeng Industry and Trade, China). Acidic dyes are water-soluble molecules containing one or more anionic groups (most often sulfonic acid). The studied dye is a acidic one mostly being used for the dyeing of proteic fiber. The AG9 dye has been mentioned in the literature only as part of some research involving also some other triarylmethane dyes as hydrological tracer, in regard to their sorption characteristics onto a sandy soil.^{34,35}

EXPERIMENTAL

Polymeric adsorbents

Two types of adsorbents, namely, weak and strong base anion exchange resins, were used in the adsorption experiments. Weak base anion exchange resins are based on the crosslinked acrylic copolymers, which were functionalized by polymer-analog reactions with various amines such as EDA, triethylenetetramine (TETA), and dimethylaminopropylamine (DMAPA).³⁶

The acrylic copolymers were obtained by water-suspension radical polymerization of divinylbenzene (DVB), AN, and ethylacrylate (EtA) at different amounts of the crosslinking agent (DVB) in the presence of toluene or benzene as porogenic agent and 0.5% styrene : ammonium maleate copolymer water solution as a continuous phase. The mixture of the suspended and continuous phases was stirred at 200–220 rpm for 4 h at 65°C and then for 8 h at 85°C. The beads of the obtained copolymers were filtered, washed with distilled water, air-dried at 50°C, and then Soxhlet-extracted with dichloroethane to remove residual monomers, oligomers, and porogenic agents. The content of DVB was considered to be equal with those of the monomer mixtures. The copolymers obtained were aminolysed-hydrolyzed with EDA, TETA, and DMAPA for

16 h at a copolymer: amine ratio of 1 : 3 and temperatures of 110, 180, and 125°C, respectively. The beads of the functionalized acrylic copolymers were recovered by filtration and washed with distilled water to remove excess of amines. Then, they were regenerated with 1 mol L⁻¹ NaOH solution and washed with distilled water up to the absence of the basicity in the effluent.

Strong base anion exchange resins are based on the 4-vinylpyridine (4-VP)-crosslinked copolymers, which were functionalized by nucleophilic substitution reactions with different halogenated compounds such as methyl iodide, ethyl iodide, butyl iodide, benzyl chloride, and 2-chloroacetamide.^{37,38} The starting 4-VP : DVB copolymer was obtained by the suspension copolymerization of 4-VP with DVB using 1.5 wt % benzoyl peroxide as initiator in the presence or absence of toluene, as porogenic agent. The aqueous phase consisted of 3 wt % NaCl, 0.12 wt % gelatine, and 0.5 wt % ammonium salt of poly(styrene-*co*-maleic anhydride). The organic : aqueous phase ratio was 1 : 3 v/v. The content of DVB was considered to be equal with those of the monomer mixtures. The copolymerization reaction was allowed to proceed for 10 h at 80°C and 2 h at 90°C. After copolymerization, the copolymer beads were separated by filtration, washed with warm distilled water, and then extracted with methanol in a Soxhlet apparatus to remove traces of residual monomers, linear oligomers of 4-VP, and toluene, and finally, vacuum-dried at 50°C for 48 h.

The quaternization reactions of 4-VP : DVB with methyl iodide, ethyl iodide, butyl chloride, and benzyl chloride were performed in a round-bottomed flask equipped with stirrer, reflux condenser, and thermometer. The following method was applied: the copolymer beads of 0.3- to 0.8-mm diameter size were poured into the flask, and then the methanolic solutions of 20% (v/v) concentration of the halogenated compounds were added. The ratio between halogenated compounds and nitrogen corresponds to 2 : 1. The reactions were carried out at 60°C for 48 h. After this, the compounds were isolated by filtration and washed with methanol. The subsequent treatment with NaCl meant the passing of NaCl aqueous solution of 5% concentration through the quaternized products packed out into column up to the absence of iodide ions in the effluent.

The alkylation reaction with 2-chloroacetamide was performed as follows: the copolymer beads were soaked into a solution of chloroacetamide (1.5 mol) in dimethylformamide. The mixture was continuously shaken at 60°C for 48 h. The yielded compounds were filtered out, washed with methanol and distilled water, and then dried at room temperature.

All the synthesized compounds were characterized by the following features: volume exchange

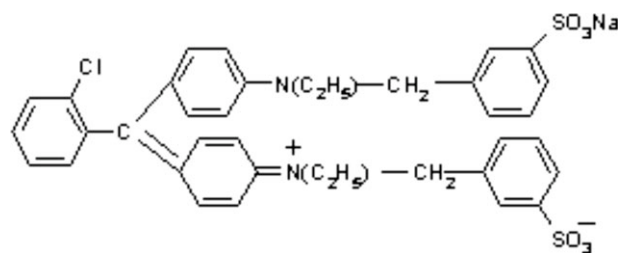


Figure 1 Chemical structure of Acid Green 9 dye.

capacity (expressed in mequiv mL⁻¹) and weight exchange capacity (expressed in mequiv g⁻¹).

The volume of weak base anion exchange capacity was determined according to the following method: a known volume of the ion exchange resin was treated with a specific volume of 1 mol L⁻¹ HCl of known concentration, and then the excess of hydrochloric acid was removed by passing the resin through the mixture solution of water : methanol, 1 : 2 (v/v). The eluent was measured by titration to the mixed indicator end point with 1 mol L⁻¹ NaOH solution.

The volume of strong base anion exchange capacity was determined by the elution of chloride ions with 5% Na₂SO₄ aqueous solution, and the chloride ions being potentiometrically determined with 0.02 mol L⁻¹ AgNO₃ aqueous solution.

The weight of weak and strong base anion exchange capacities were determined by drying known volume of the weak and strong base anion exchange resins at 110°C up to constant weight.

Dye

AG9 or Benzanyl Grun F-2B (AG9) with 72% dye content, a commercial product, was purchased from Faculty of Textiles and Leather, Iasi (Romania). The dye structure is shown in Figure 1.

As it can be seen from Figure 1, the dye is in the form of the sulfonic acid salts, which determines its solubility in water. Aqueous solutions of 1000 µg mL⁻¹ textile dye (used without a preliminary purification) were prepared using double distilled water and then subsequently diluted when necessary.

Adsorption experiments

Preliminary adsorption tests were performed to establish the preference of the synthetic adsorbents for the investigated acid dye. A fixed amount of 0.1 g adsorbents was contacted with 50 mL aqueous dye solution having a concentration of 40 µg mL⁻¹ with adjusted pH. The percentage of the dye removed was determined by measuring the absorbance of the solution at the maximum absorption wavelength of $\lambda_{\text{max}} = 643 \text{ nm}$ after 24 h contact time.

TABLE I
Characteristics of the Polymeric Adsorbents

Sample code	Structural unit	% DVB ^a	Diluent/ <i>D</i> ^b	Exchange capacity	
				mequiv g ⁻¹	mequiv mL ⁻¹
A1	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{C=O} \\ \\ \text{NH---(CH}_2\text{)}_2\text{---NH}_2 \end{array}$	2	Toluene/0.3	7.22	0.53
A2	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{C=O} \\ \\ \text{NH---}[(\text{CH}_2)_2\text{---NH}]_3\text{H} \end{array}$	2	Toluene/0.3	14.66	0.91
A3	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{C=O} \\ \\ \text{NH---(CH}_2\text{)}_3\text{---N} \begin{array}{l} \swarrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array} \end{array}$	2	Toluene/0.3	6.65	0.24
A4	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{C=O} \\ \\ \text{NH---(CH}_2\text{)}_2\text{---NH}_2 \end{array}$	8	Toluene/0.3	3.90	1.03
A5	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{C=O} \\ \\ \text{NH---}[(\text{CH}_2)_2\text{---NH}]_3\text{H} \end{array}$	8	Benzine/0.25	6.78	1.52
V1	$\begin{array}{c} \\ \text{H}_2\text{C} \\ \\ \text{HC---} \langle \text{C}_6\text{H}_4 \rangle \text{---N}^+\text{---CH}_2\text{---CH}_3 \\ \\ \text{Cl}^- \end{array}$	8	–	4.90	1.90
V2	$\begin{array}{c} \\ \text{H}_2\text{C} \\ \\ \text{HC---} \langle \text{C}_6\text{H}_4 \rangle \text{---N}^+\text{---(CH}_2\text{)}_3\text{---CH}_3 \\ \\ \text{Cl}^- \end{array}$	8	–	3.94	1.81
V3	$\begin{array}{c} \\ \text{H}_2\text{C} \\ \\ \text{HC---} \langle \text{C}_6\text{H}_4 \rangle \text{---N}^+\text{---CH}_3 \\ \\ \text{Cl}^- \end{array}$	8	–	4.30	1.75
V4	$\begin{array}{c} \\ \text{H}_2\text{C} \\ \\ \text{HC---} \langle \text{C}_6\text{H}_4 \rangle \text{---N}^+\text{---(CH}_2\text{)}_3\text{---CH}_3 \\ \\ \text{Cl}^- \end{array}$	10	Toluene/0.2	3.20	1.10
V5	$\begin{array}{c} \\ \text{H}_2\text{C} \\ \\ \text{HC---} \langle \text{C}_6\text{H}_4 \rangle \text{---N}^+\text{---CH}_2\text{---C}_6\text{H}_5 \\ \\ \text{Cl}^- \end{array}$	10	Toluene/0.2	4.00	1.66
V6	$\begin{array}{c} \\ \text{H}_2\text{C} \\ \\ \text{HC---} \langle \text{C}_6\text{H}_4 \rangle \text{---N}^+\text{---CH}_2\text{---CONH}_2 \\ \\ \text{Cl}^- \end{array}$	10	Toluene/0.2	3.30	1.58

^a Crosslinking degree.

^b Dilution, *D* = volume of diluent/(volume of monomers + volume of diluent).

For the dye adsorption kinetics, 0.25 g adsorbent was added in 100 mL solution of dye with various concentrations, and then kept in the thermostatic bath and stirred at a controlled speed (mechanic stirrer S-420). Samples of 1 mL were taken at predetermined time intervals for the analysis of the dye in the solution. For the thermodynamic studies, dye solutions with different concentrations at three constant temperatures were used. Samples of the solutions were analyzed after the establishment of the equilibrium.

The absorbance values were determined using a UV-vis spectrophotometer PharmaSpec1700 (Shimadzu) with respect to the conditions of Lambert-Beer law at λ_{max} .

The influence of pH on the removal of dye was studied by varying pH from 1 to 7 with HCl and NaOH solutions.

The efficiency of the adsorbents was established by the values of the distribution coefficient K_d (mL g⁻¹) according to eq. (1) as follows:

$$K_d = \frac{\mu\text{g dye/g dry}(105^\circ\text{C}) \text{ adsorbent}}{\mu\text{g dye/mL solution}} \quad (1)$$

The specific adsorption capacity (mg g⁻¹) and percent of adsorption were also calculated.

RESULTS AND DISCUSSION

The adsorption capacity of the AG9 dye depends on the experimental conditions, type, and chemical structure of the adsorbents.

The chemical structures and the characteristics of the polymeric adsorbents are presented in Table I.

As it can be observed from Table I, all the synthesized acrylic and pyridine adsorbents are characterized by high values of the anion exchange capacity.

Effect of pH

The pH is the most important factor affecting the adsorption process allowing the selection of efficient adsorbents. Five acrylic weak base anion exchange resins and six strong base anion exchange resins based on the 4-VP : DVB copolymers were used in the adsorption experiments.

The obtained results in the adsorption of AG9 over a pH range of 1.1–7.05 on the acrylic adsorbents are depicted in Figure 2. It can be seen that the adsorption capacity is very high at a pH of 4.10 for A1 adsorbents (>90%). The weak base anion exchange resins A2 and A3 presented low adsorption capacities, but A4 and A5 are inefficient.

The investigated acrylic adsorbents are characterized by different morphological and chemical structures. Therefore, the adsorption of the dye was

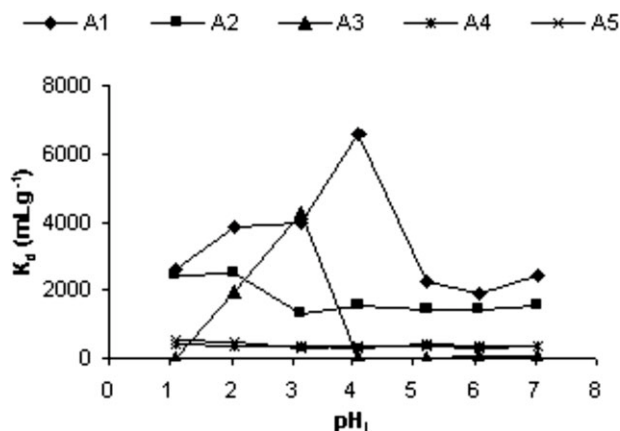
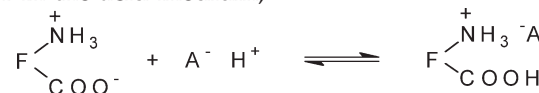


Figure 2 Effect of pH on the adsorption of AG9 on acrylic adsorbents (0.05 g adsorbent, 25 mL of the dye solution, concentration of 50 $\mu\text{g mL}^{-1}$, 9 h contact time).

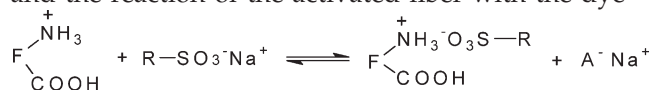
strongly influenced by the porosity and chain flexibility of the adsorbent matrix. If A1 is compared with A4 it can be confirmed that A1 has higher adsorption capacity for AG9 than A4 because of its more flexible structure due to the low crosslinking degree. This parameter allowed the easy access of the dye to the functional sites. A comparison between A2 and A5 adsorbents lead to the observation that A2 is characterized by the porosity in the swelling state, which determines high water swelling capacity. In consequence, A2 resin exhibited higher dye adsorption capacity than A5 adsorbent, which possesses the porosity in the dry state. The highest adsorption capacity of AG9 has been obtained on the A1 acrylic sample because of its flexible network and less voluminous functional groups, which allowed the complete removal of the dye.

The adsorption process of the acid dyes on the weak base sorbents is similar to dyeing. The acid dyes are sodium salts of the organic sulfonic acids with general formula of R-SO₃Na and represent specific dyes for the protean and polyamide fibers.³⁹

The reaction between acid dyes and fiber is a chemical process with an ionic linkage of salt type carried out in two steps, namely, activation of the fiber in the acid medium,

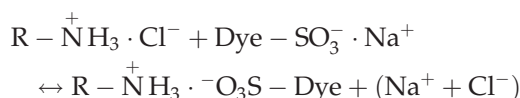


and the reaction of the activated fiber with the dye



The chemical reaction involves the interaction between anionic groups that belong to the dye and the protonated amine groups from activated fibers. The weak base anion exchange resins with amine

groups in the acid medium undergo the protonation of the nitrogen atoms, which favored the maximum adsorption at $\text{pH} = 4.10$ of the acid AG9 dye by ion-exchange process according to the following general equilibrium:



The chemical structure shows that the dye has a positively charged nitrogen atom and two sulfonic groups. UV spectroscopy was used to investigate the chemical stability of the AG9 dye in the pH range of 1–7. The absorption spectra for the solution concentration of dye of $48.38 \mu\text{g mL}^{-1}$ at initial pH (pH_i) and final pH (pH_f) showed the chemical stability of the dye in the studied range of pH.

In the case of A1 adsorbent, the decrease in the adsorption capacity of AG9 at $\text{pH} < 4.10$ may be attributed to the decrease in its dissociation, which leads to a lower concentration of the anionic dye species available to interact with the active sites of the resin. An excess of H_3O^+ corresponding to a low pH resulted in the strong competition of the anions, brought about by the acid used for varying of pH, and the adsorption capacity significantly decreased. In addition, the dye is a commercial compound with the purity of 72%. The other components could take part at the competitive equilibria, which means a significant effect on the adsorption depending on the pH. The adsorption of the dye decreases at the pH higher than 4.10, which could be attributed to the deprotonation of amino group.

Acid Orange 10 (AO10) has a similar behavior like AB9 having the maximum of adsorption at pH 3. The observed differences of the adsorption maxima between the two acid dyes, AO-10 and AO-12, onto the monoamine-modified silica particles could be attributed to (i) the differences in the dissociation of Dye- SO_3H group in the two dyes and (ii) the differences in the spatial structure of the two dyes. Effect of the structural properties of acid dyes on their adsorption behavior from aqueous solutions by amine-modified silica has also been clarified.⁴⁰

The adsorption of acid dye Acid Blue 9, which differ by a sulfonic group instead of chlorine one to AG9 on a highly mesoporous activated carbon fiber (Y-ACF) obtained from pitch-containing yttrium acetylacetonate, was investigated in terms of size of the dye molecules and pore size and surface charge of the AC fiber. The results were compared with that on a microporous AC fiber (A-20). The high amounts of sterically small size of acid dyes and basic dyes were adsorbed on both Y-ACF and A-20. The results obtained in the adsorption of the same dye on meso-

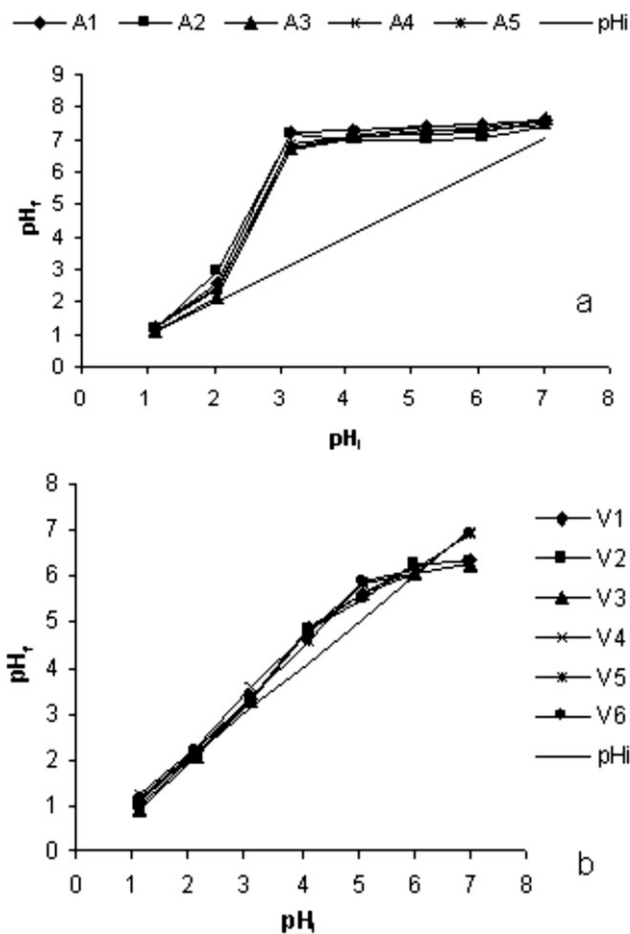


Figure 3 Modification of the pH after adsorption of Acid Green 9 dye on the acrylic (a) and pyridinic (b) adsorbents (pH_i , initial pH; pH_f , pH final; after which the equilibrium was reached).

porous or microporous AC fiber showed that sterically small size of the same dye lead to the high amounts retained on both supports.⁴¹

Removal of Acid Blue 9 from aqueous solution by sorption is highly dependent on the pH of the solution, which affects the surface properties of the sorbent and dye structure. In the pH range of 2.0–3.0, the dye removal remained constant, and a maximum value of 41 mg g^{-1} is attained.⁴²

After adsorption of dye on the acrylic adsorbents, the pH of the solution strongly increased for an initial pH of 3, followed by a slight and constant increase [Fig. 3(a)].

The pyridine strong base anion exchange resins based on the 4-VP : DVB copolymers have maximum adsorption capacity in the acid range of pH 1.1–3.0 [Fig. 4]. From this figure, it can be seen that the adsorption capacity values are lower than that obtained for the weak base anion exchange resins.

Pyridine exchange resins have different adsorption capacity values for AG9 dye depending on the chemical and morphological structure. Therefore, the

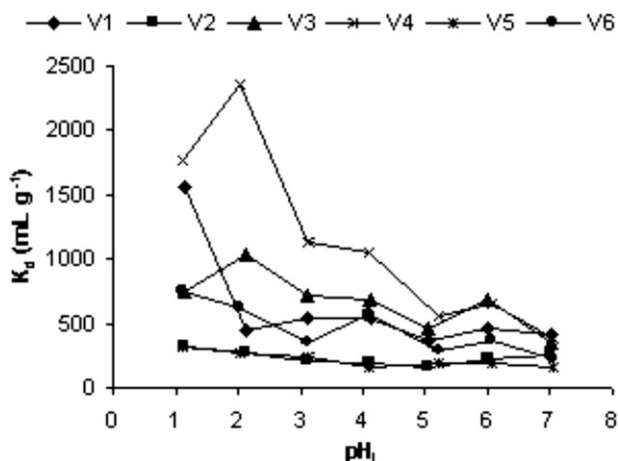
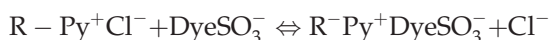


Figure 4 Effect of pH on the adsorption of AG9 on the pyridine ion exchange resins (0.05 g adsorbent, 25 mL of the dye solution, concentration of 50 μg mL⁻¹, 9 h contact time).

highest adsorption values were obtained with the highest hydrophilic structures, namely, pyridine resins with butyl (V4), ethyl (V1), and methyl (V3) functional groups attached to the matrix. In this case, the adsorption of AG9 dye was also carried out by an ion-exchange mechanism according to the equation:



For this reason, the retained dye on the pyridine adsorbents did not strongly influence the pH of the solution after adsorption [Fig. 3(b)]. This behavior could be explained by the reduced access of the dye to the ionic exchange sites of the resins because of its voluminous size.

According to these considerations based on the *K_d* values for the adsorption of AG9 dye on the tested adsorbents, the adsorption results on A1 weak base anion exchange resin will be presented only in the following sections.

The effect of contact time and initial dye concentration

The kinetic study of the adsorption of AG9 dye on the A1 sorbent was performed to investigate the effect of the initial dye concentration on the adsorption rate in the range of 52–400 μg mL⁻¹ concentration. The subsequent estimation of the kinetic parameters (order and rate constant) allowed some insight into the adsorption mechanism. From the analysis of the curves in Figure 5, it is obvious that the specific adsorption as well as the time needed to reach the equilibrium increases with the increasing dye concentration. The process is very fast, as for low concentration, the dye is quantitatively removed in 15 min, whereas for a solution of 400 μg mL⁻¹ concentration more than 93% was removed in 60 min.

Adsorption dynamics

The rate constant for the adsorption of AG9 on the A1 adsorbent was obtained using the equations of pseudo first-order system (Lagergren) and pseudo second-order system (Ho). The intraparticle diffusion was also considered. A detailed approach of these models for acid and basic dyes is given in many articles.^{42–44}

Pseudo first-order model

The linear form of Lagergren equation is as follows:

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303} t \tag{2}$$

where *q_e* is the amount of dye adsorbed at equilibrium (mg g⁻¹); *q_t* is amount of dye adsorbed at time *t* (mg g⁻¹); *k₁* is equilibrium rate constant of pseudo first-order sorption (min⁻¹).

The constant *k₁* was calculated from the slopes of the linear plots obtained by graphical representation of lg(*q_e* - *q_t*) against *t*, and the results are presented in Table II. Maximum *k₁* values were obtained for low concentrations of dye. There is a great disagreement between experimental and calculated values of concentration at equilibrium because of the inadequacy of the pseudo first-order model for the adsorption of AG9 on the A1 acrylic adsorbent.

Pseudo second-order model

The linear form of the equation that describes the adsorption kinetics corresponding to the pseudo second-order model³⁶ is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

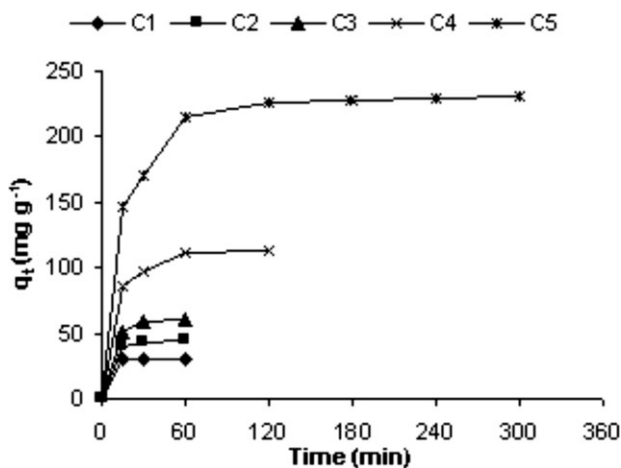


Figure 5 Effect of contact time and dye concentration on the adsorption of AG 9 dye on A1 adsorbent (C1 = 52 μg mL⁻¹; C2 = 78 μg mL⁻¹; C3 = 104 μg mL⁻¹; C4 = 200 μg mL⁻¹; C5 = 400 μg mL⁻¹; 0.2 g adsorbent; volume of the dye solution = 100 mL; pH_i = 4.1).

TABLE II
Kinetic Parameters of the Adsorption in the Case of the Effect of the Initial Dye Concentration

C_0 (mg L ⁻¹)	First order					Second order			Intraparticle diffusion	
	q_e experimental (mg g ⁻¹)	q_e calculated (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	q_e calculated (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	h (mg g ⁻¹ min ⁻¹)	R^2	k_i (mg g ⁻¹ min ^{-1/2})	R^2
104	60.37	38.027	0.0979	1	63.69	0.005391	19.64637	0.9997	2.1745	0.8482
200	113.81	82.129	0.0608	0.9807	120.48	0.001538	19.92032	0.9994	4.0041	0.8472
400	230.72	74.092	0.0184	0.9235	238.10	0.000492	26.,17801	0.9995	1.5528	0.8126

where k_2 is the rate constant of pseudo second order reaction (g mg⁻¹ min⁻¹).

The linear plot of t/q_t versus t (Fig. 6) allows the calculation of k_2 and q_e values and the correlation coefficient R^2 . Also, as time approaches zero, according to the pseudo second-order model, the initial adsorption rate h (mg g⁻¹ min⁻¹) is calculated (Table II).

$$h = k_2 q_e^2 \quad (4)$$

Experimental data follow the linear relationship of pseudo second-order adsorption model reasonably well (Fig. 6). By comparison of the experimental ($q_{e,experimental}$) and calculated ($q_{e,calculated}$) equilibrium concentrations, a good agreement has been observed. The regression coefficients for the linear plots were higher than 0.999. The initial adsorption rate h increases with the increase of dye concentration.

Intraparticle diffusion

The intraparticle diffusion model is based on the following equation for the rate constant:

$$q_t = k_i t^{1/2} \quad (5)$$

where k_i is the intraparticle diffusion rate constant (mg g⁻¹ min^{-1/2}).

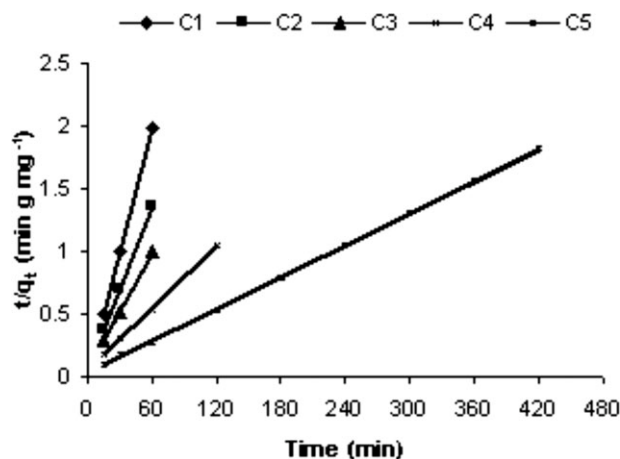


Figure 6 H_0 plots for the sorption of Acid Green 9 dye onto A1 (C1 = 52 µg mL⁻¹; C2 = 78 µg mL⁻¹; C3 = 104 µg mL⁻¹; C4 = 200 µg mL⁻¹; C5 = 400 µg mL⁻¹; 0.2 g adsorbent; volume = 100 mL; pH_i = 4.1).

If the rate-limiting step is the intraparticle diffusion, the graphical representation of the adsorbed dye (mg g⁻¹) depending on the square root of the contact time ($t^{1/2}$) should present a linear part that passes through the origin.⁴⁴ For the initial dye concentrations of 52–78 µg mL⁻¹, the adsorption is very fast and the intraparticle diffusion is involved. During the increase of the concentration, it is obvious that the adsorption is a multistage process. The experimental curves present linear domains for each concentration but they do not pass through the origin, so the intraparticle diffusion is not the only rate-controlling step (Fig. 7).

The values of the rate constants for the intraparticle diffusion (k_i) are presented in Table II being calculated from the slopes of the linear portions of the curve $q = f(t^{1/2})$.

The shapes of the obtained curves are similar with those discussed in the literature⁴⁴ for the adsorption of some basic dyes on different sorbents or for the sorption of PACA onto the anion exchange resins, which distinguished into three stages for the adsorption of dyes.²⁰ The first stage is an instantaneous adsorption, corresponding to more than 80% adsorption and is probably due to a strong electrostatic attraction between dye and the external surface of adsorbent. The second stage is a gradual adsorption

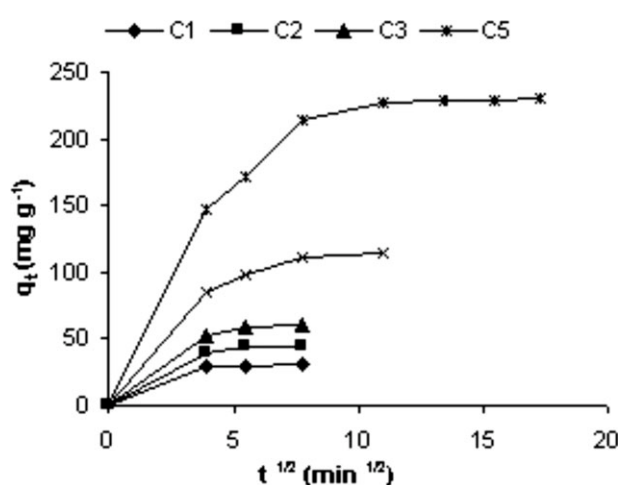


Figure 7 Amount of dye adsorbed (mg dye g⁻¹ adsorbent) versus $t^{1/2}$ for the intraparticle diffusion of Acid Green 9 dye on A1 resin.

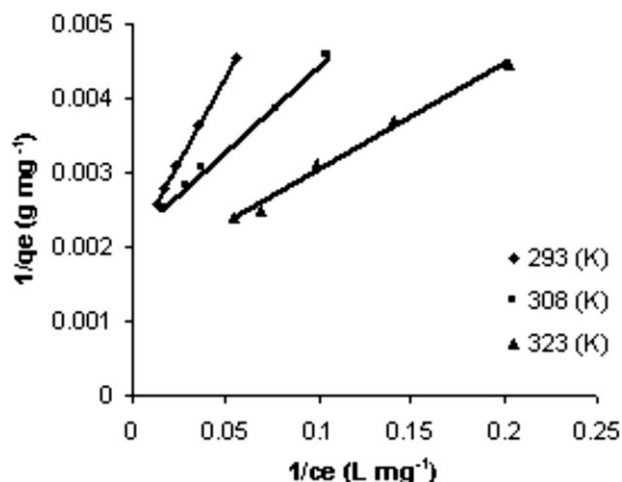


Figure 8 Langmuir plots for the sorption of dye Acid Green 9 onto A1 resin.

stage, which can be attributed to the intraparticle diffusion of dye molecules through the pores of adsorbent. The k_i values were calculated based on the data corresponding to this stage. The final stage corresponds to the equilibrium adsorption when dye molecules occupy all active sites of the adsorbent.

Langmuir isotherm

The equilibrium data obtained for various concentrations of dyes (400–750 $\mu\text{g mL}^{-1}$) have been analyzed on the basis of the Langmuir isotherm, which is expressed as follows:⁴⁴

$$q_e = \frac{q_m b c_e}{1 + b c_e} \tag{6}$$

where c_e is the equilibrium concentration of the dye in solution (mg L^{-1}); q_e is the amount of the adsorbed dye at equilibrium (mg g^{-1}); q_m is the maximum amount of the dye adsorbed (mg g^{-1}) corresponding to the monolayer coverage; b is the constant related to energy of adsorption (L mg^{-1}).

One of the linear forms of eq. (6) is as follows:

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

The values of b and q_m were calculated from the ratio of intercept/slope and $1/\text{intercept}$, respectively, of the straight-line plots of $1/q_e$ versus $1/c_e$.

The adsorption equilibrium constant K_L (L g^{-1}) is dependent on b and q_m and could be calculated based on the following relation:

$$K_L = q_m b \tag{8}$$

The essential characteristics of Langmuir isotherms may be expressed by a dimensionless constant, i.e., parameter of equilibrium or separation factor, as follows:

$$R_L = \frac{1}{1 + b c_0} \tag{9}$$

where c_0 is the initial concentration of dye (mg L^{-1}).

Values of R_L between 0 and 1 show a favorable adsorption.

The data for the adsorption of AG9 on the A1 adsorbent are presented in Figure 8, and the constants obtained by the regression analysis confirm well with Langmuir equation (Table III) as shown by the values of R^2 varying from 0.9997 to 0.9896. This good agreement is the indication for the homogeneity of the adsorbent surface.

The Langmuir analysis for the adsorption of AG9 on A1 at the three temperatures shows a monolayer capacity of 500 mg g^{-1} (at 293 K) and 625 mg g^{-1} (at 323 K). The maximum adsorption capacity increases with the increase of the temperature, which indicated that the active sites on the adsorbent’s surface are thermally activated.

The maximum sorption capacity parameter q_m derived from the Langmuir model allows to estimate the efficiency of an adsorbent. In comparison to some of the high maximum adsorption capacities reported for different adsorbents functionalized with amines or AC for acid dyes (Table IV) indicated that A1 is an effective adsorbent for dye AG9 removal.

Freundlich isotherm

The adsorption data for AG9 was also analyzed by the Freundlich model. The logarithmic form of Freundlich model is given by eq. (10):

$$\lg q_e = \lg K_F + \frac{1}{n} \lg C_e \tag{10}$$

where C_e is the equilibrium concentration of the adsorbate (mg L^{-1}); q_e is the amount adsorbed at equilibrium (mg g^{-1}); K_F and n are Freundlich constants

TABLE III
Analysis of Langmuir and Freundlich Isotherms

T (K)	q_m (mg g^{-1})	b (L mg^{-1})	K_L (L g^{-1})	R^2	R_L	n	K_F (L g^{-1})	R^2
293	500.00	0.0435	21.74	0.9997	0.0543–0.0297	2.56	73.046	0.9889
308	556.16	0.0775	43.10	0.9966	0.0312–0.0169	2.29	97.723	0.9794
323	625.00	0.1119	69.93	0.9896	0.0218–0.0118	2.03	103.109	0.9893

TABLE IV
Comparison of Adsorption Capacities of Some Adsorbents for Acid Dyes

Dye	Sorbent	pH	q_m (mg g ⁻¹)	Reference
Acid Red 14	Purolite Macronet nonfunctionalized MN200	2	64.52	24
	Purolite Macronet functionalized MN300-tertiary amine groups	2	107.52	
	Activated carbon	-	20.90	
Indigo carmine	Aminofunctionalized acrylamide-maleic acid hydrogels	3.0	377.1	25
Acid Orange 12	Amine-modified silica	1.0	14.29	40
Acid Orange 10		3.0	36.28	
Acid Blue 9	Mg-Al-layered double hydroxides of variable metal composition	-	7.6×10^{-2} mmol g ⁻¹	45
Acid Blue 9	Activated clay/carbon system	3.0	64.07	43
Acid Red 97	Activated carbon	-	52.08	16,46
Acid Orange 61			169.49	
Acid Brown 425			222.22	
Acid Red 114	Activated carbon	4.0	101.1	27
Acid Green 9	A1	4.10	500 (72% dye)	In this study

related to the adsorption capacity and adsorption intensity, respectively.

Table III shows the increase of the K_F values with the increase of the temperature, which is in agreement with the results obtained using Langmuir model. The values of n in the range of 2.03–2.56 represent the good adsorption characteristics.⁴⁶

Effect of the adsorbent dose

The increase of adsorbent amount, for a constant concentration of AG9 dye, leads to an increase of the adsorption degree and a decrease of the amount of dye in solution (Fig. 9). The efficiency of this ion exchangers is remarkable, as more than 99% of the dye is adsorbed, under these conditions, on a small amount of sorbent (0.05 g). The saturation occurred at 0.05 g adsorbent at which point further increase in adsorbent dosage had less effect on the adsorption. Such results should be useful for establishing

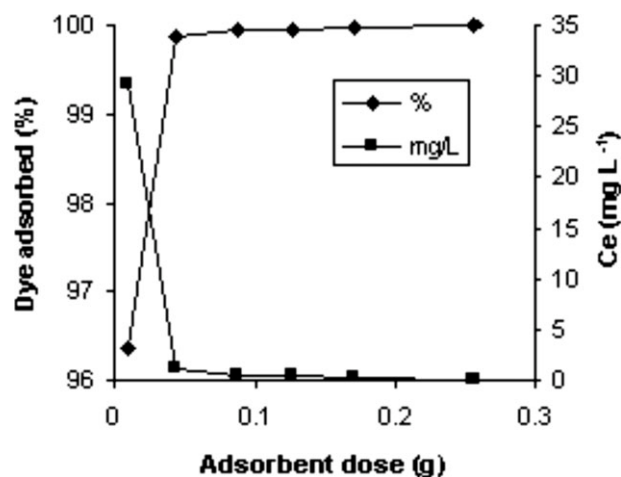


Figure 9 Effect of the adsorbent dose on the adsorption of AG9 on A1 resin (0.01–0.3 g adsorbent; volume = 25 mL; $C_0 = 800 \mu\text{g mL}^{-1}$; pH = 4.1; time = 24 h).

the optimum amount of A1 required in the removal of AG9 dye.

Thermodynamic study

Thermodynamic parameters, i.e., free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) for the adsorption systems at three temperatures (293, 308, 323 K) were calculated using the thermodynamic equations and are given in Table V.

$$\Delta G^0 = -RT \ln b \quad (11)$$

$$b = A \cdot \exp(-\Delta H/RT) \quad (12)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (13)$$

The Langmuir constant b was used to determine the enthalpy of adsorption ΔH based on Clausius-Clapeyron equation (13). The linear dependence $-\ln K_L$ versus $1/T$ is represented in Figure 10, where

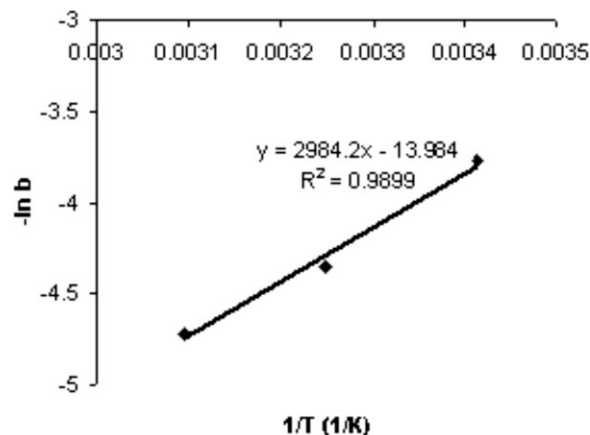


Figure 10 Plot of $\ln b$ versus temperature.

TABLE V
Thermodynamic Parameters for the Adsorption of AG9 on A1 Adsorbent

Temperature (K)	K_L (L g ⁻¹)	ΔG^0 (kJ mol ⁻¹)	$T\Delta S^0$ (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)
293	21.74	-9.19	34.05	24.17	116.21
308	43.10	-11.13	35.79		
323	69.93	-12.66	37.53		

the slope is $\Delta H/R$. The value of 24.17 kJ mol⁻¹ for ΔH was obtained. The positive value of enthalpy shows that adsorption of dye is an endothermic process. The positive value of entropy (ΔS^0) 24.17 kJ mol⁻¹ reflects the increased randomness at the solid-solution interface. The values of $|\Delta H^0|$ are lower than $|T \Delta S^0|$ at all temperatures (Table V), and this indicates that adsorption process is dominated by entropic rather than enthalpic changes.⁴⁰

Negative sign of Gibbs free energy (ΔG^0) indicated that the adsorption process was spontaneous and more pronounced when the temperature increased. These results are in agreement with those obtained from Langmuir and Freundlich parameters.

For comparison, the values of thermodynamic parameters of adsorption Acid Orange 10 onto amine-modified silica were obtained as follows: (ΔG^0) -13.78 kJ mol⁻¹ and -15.95 kJ mol⁻¹, in the temperature range from 298 to 313 K; $\Delta H^0 = 28.96$ kJ mol⁻¹; $\Delta S^0 = 142.21$ J mol⁻¹ K⁻¹.⁴⁰

The sorption of Acid Blue 9 performed in the temperature range of 293–313 K with activated clay/carbon system shows that the equilibrium sorption capacity of dye slightly decreased with increasing temperature from 41.0 to 40.1 mg g⁻¹.⁴²

Desorption of dye

To find the optimum conditions, i.e., eluent type, concentration, and contact time, for establishing the

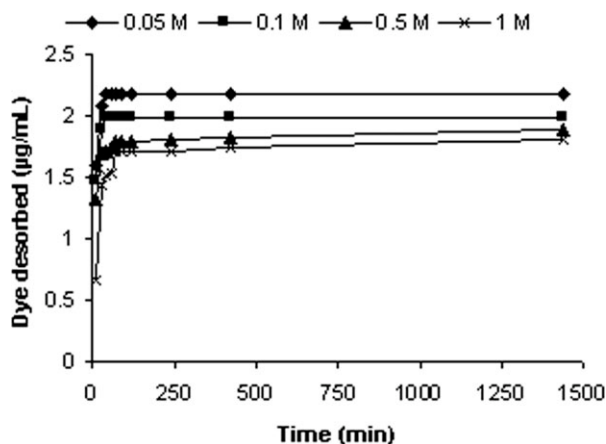


Figure 11 Desorption of AG9 with NaOH of different concentrations versus time (0.05 g A1 loaded with AG9 94 mg g⁻¹; 50 mL NaOH 0.05–1.0 mol L⁻¹; samples of 1 mL collected at various times).

optimum parameters for desorption of the dye, experimental studies by batch methods were performed. Then, the obtained results were applied under the dynamic conditions. The column with A1 sorbent loaded with 94 mg dye g⁻¹ adsorbent was used.

For the desorption of the dye under bath conditions, different eluents, i.e., NaOH, Na₂CO₃, Na₃PO₄, and NaH₂PO₄ were tested. In Figure 11, the desorption of AG9 with NaOH solution is depicted. It is evident that this eluent ensures a total desorption of the dye after 45 min for a concentration of 0.05 mol L⁻¹ NaOH.

Under dynamic conditions, for the first adsorption-desorption cycle, 0.1 g resin was placed in a glass column of 1.1 cm × 8 cm. Dye solution (200 mL) of 50 µg mL concentration was repeatedly passed until total adsorption of the dye was achieved. The retained dye was eluted by NaOH solution of 0.05 mol L⁻¹ concentration up to a complete desorption. The resin was regenerated with NaOH 1N solution and washed with distilled water up to the neutral pH of the effluent. The regenerated resin have been used in 13 successive adsorption-desorption cycles, and the results are presented in Figure 12 and Table VI.

The data presented in Table VI confirmed that the A1 adsorbent could be used for the retention of AG9 dye at least for 13 adsorption-desorption cycles when the adsorption is quantitative and desorption is higher than 95%. As it can be seen, the maximum

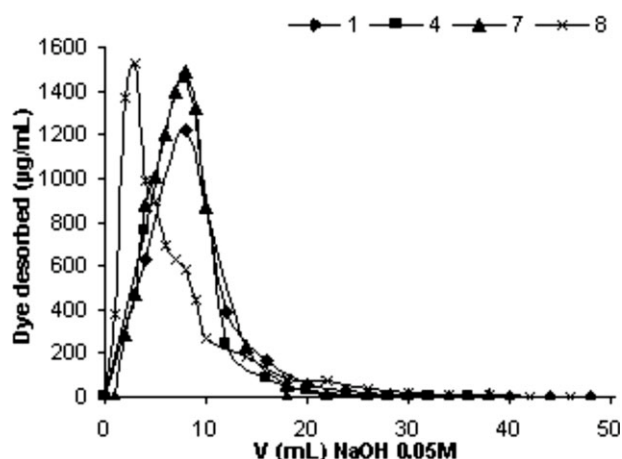


Figure 12 The curves of elution of AG9 dye with NaOH 0.05 mol L⁻¹.

TABLE VI
The Characteristics for the Adsorption-Desorption Cycles

Cycle	1	2	3	4	5	6	7	8	9	10	11	12	13
Total desorption (%)	99.9	100	99.48	99.21	98.71	99.34	95.03	95.44	97.87	97.65	97.71	97.85	97.90
Desorption (%) at the maximum peak	80.2	–		82.26	–	–	67.31	32.76	–	–	–	–	–
mL eluent at the maximum peak	8	–		8	–	–	7	3	–	–	–	–	–

in the desorption curves is reached, for the first and the fourth cycles, at an elution volume of 8 mL where $\sim 80\%$ from total adsorbed quantity is desorbed (Fig. 12). For selected elution curves, a volume of ~ 25 mL NaOH of 0.05 mol L^{-1} ensures quantitative dye desorption, corresponding to a concentration factor of 8.

In the literature it is mentioned that while the desorption value gives an idea about the quantity of physical bonding in the sorption process, the regeneration values give an idea about the degree of ion exchange taking place on the sorbent materials.⁴⁷ For some basic dyes retained onto nonconventional sorbents considerable regeneration values are obtained implying that ion exchange is involved.

Because both desorption and regeneration values for AG9 dye are high, we suggest the presence of the weak bonds between the dye and the surface of copolymer.

The fact that the weak base anion exchanger could be regenerated both by dynamic and batch methods with a solution of 0.05 mol L^{-1} NaOH allows to devise a method to concentrate the dye on the sorbent and to recover it with low volumes of eluent. From the shape of the curves, an evident peak can be seen for every elution curve. After many uses of the adsorbent, a decrease of 5% of the total desorption was obtained (Table VI).

Many sorbents that display acceptable sorption capacities (typically around $20\text{--}400 \text{ mg g}^{-1}$) for reactive dyes can be used only once and have to be disposed afterward, but commercial weak basic resins with adsorbed dyes may be completely regenerated using alkaline methanol.¹⁸ The regeneration of weak base anion exchangers loaded with dye for reuse is an important feature for using it in the industrial applications. Desorption of the loaded acid dyes onto amine-modified silica was carried out at pH 10 and found to be 10.4 and 91.6% for AO-12 and AO-10, respectively.⁴¹ The Macronet resin-functionalized MN300 regenerated only 80% with hydroalcoholic solutions after adsorption of Acid Red 14 in the dynamic experiments. This behavior was related to the sorption mechanism of polymer, which indicates the dye sorption onto Macronet MN300 as a complex process.²³

CONCLUSIONS

The ability of some weak and strong base anion exchange resins in the adsorption of the acid dye (Acid Green 9) was investigated. The adsorption capacity depends on the chemical structure of the dye, chemical and physical characteristics of the polymeric material, and the experimental conditions.

Under the established optimum conditions, the adsorption capacity of 500 mg textile dye (72% purity) g^{-1} adsorbent (at 293 K) was reached for the acrylic crosslinked copolymer functionalized with ethylenediamine (A1). The adsorption kinetic of AG9 dye from aqueous solution onto A1 could be described by the pseudo second-order reaction model.

The dependence of the adsorption on the amount of AG9 and on the temperature was investigated. The adsorption capacity was found to increase with the increasing adsorbent mass and temperature at the same dye concentration.

The values of thermodynamic parameters, i.e., free Gibbs energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) for the adsorption systems at three temperatures (293, 308, 323 K) showed that the adsorption process was spontaneous and more pronounced when the temperature increased.

The regeneration of the weak base anion exchanger both by dynamic and batch methods with a solution of 0.05 mol L^{-1} NaOH represents a possible method for the recovery of dye with low volumes of eluent. The column containing polymeric adsorbent could be reused, and this represents an important feature for using it to recirculate the wastewaters from the textile dyeing using the acid dyes.

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