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Anion-Exchange Resins for C.I. Direct Blue 71 Removal from Aqueous Solutions and Wastewaters: Effects of Basicity and Matrix Composition and Structure

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Ⓢ Supporting Information

ABSTRACT: In this work, eight ion exchangers with different functional groups and various polymeric matrixes (Amberlite IRA 67, Lewatit MonoPlus MP 62, Lewatit MonoPlus MP 64, Amberlite IRA 458, Amberlite IRA 900, Amberlite IRA 958, Lewatit MonoPlus MP 500, and Lewatit MonoPlus M 500) were used for the removal of C.I. Direct Blue 71 textile dye from aqueous solutions and wastewaters. For comparison, the sorption parameters of the low-cost sorbent prepared from orange peel were also measured. The sorption process of the dye was investigated by the column and batch sorption methods. High values of the monolayer sorption capacity (1630.6 mg/g), working ion-exchange capacity (13 mg/mL), and total ion-exchange capacity (128 mg/mL) were obtained for the macroporous anion exchanger Amberlite IRA 958 with quaternary ammonium functionalities. The amount of C.I. Direct Blue 71 retained by Amberlite IRA 958 was found to be dependent on the initial dye concentration and the phase contact time. The solution pH and salt (NaCl and Na_2SO_4) and anionic surfactant (SDS) concentrations do not influence the anion-exchange resin performance, whereas the presence of the cationic surfactant (CTAB) decreased the dye sorption on Amberlite IRA 958 significantly. Desorption of the dye occurred with 85.4% yield using 1 M NaOH in methanol. The results obtained in the purification of raw wastewaters confirmed that Amberlite IRA 958 can be a promising adsorbent for the removal of textile dyes from wastewaters of different types.

1. INTRODUCTION

The textile industry consumes large amounts of water, and its effluents contain a wide range of contaminants. They are characterized not only by strong color but also by high pH, suspended and dissolved solids, chemical oxygen demand (COD), and biochemical oxygen demand (BOD).[1] Typical characteristics of textile wastewaters are presented in Table 1.[1-3] One of the main problems of the textile industry is dye

Table 1. Typical Composition of Textile Wastewaters[1-3]

parameter	range
color (Pt−Co)	50−2500
pH	6.2−11.5
biochemical oxygen demand (BOD) (mg/L)	80−6000
chemical oxygen demand (COD) (mg/L)	150−12000
total suspended solids (mg/L)	15−8000
total dissolved solids (mg/L)	2900−3100
surfactants (mg/L)	1−134
chloride (mg/L)	1000−1600
total Kjeldahl nitrogen (mg/L)	70−80
total chromium (mg/L)	1−5

removal from wastewaters. Several different methods have been developed for the treatment of textile effluents, and the characteristics of these techniques with their main advantages and disadvantages have been comprehensively discussed in some articles.[4-6] The most important ones that have been mentioned in the literature include biological methods (aerobic and anaerobic processes), coagulation and precipitation, irradiation, oxidation (using the Fenton's reagent, ozonation, sodium hypochlorite), adsorption (activated carbon, ion exchangers, low-cost sorbents), membrane filtration, photo-catalysis, and sonication.[6-11] Some examples of methods for the removal of the hazardous dye C.I. Direct Blue 71, which has a high worldwide consumption, from aqueous solutions and wastewaters are presented below. Biodegradation of C.I. Direct Blue 71 by *Pseudomonas* sp. under aerobic conditions was investigated as a function of pH and the presence of nutrients (nitrate and sulfate) by Oranusi and Ogugbue.[12] The highest rate of decolorization was 72.4%, and the rate decreased with increasing concentration of nitrate and sulfate. Theerachat et al.[13] compared C.I. Direct Blue 71 uptake by the whole cell and a laccase-enriched extract from *Trametes versicolor* DSM11269, 23% decolorization was observed after 3 h at 50 °C. According to Jin et al.,[14] genetically engineered microorganisms such as *Escherichia coli* JM109 in bioaugmented reactors were efficient around pH 9 and at a salinity of 1−3% during C.I. Direct Blue 71 wastewater decolorization. The C.I. Direct Blue 71 concentration decreased from 150 to 27.4 mg/L in 12 h.[14] The removal of C.I. Direct Blue 71 by laccase from the strain of *Trametes modesta* was performed effectively under acidic conditions at 50 °C. The decolorization rate of this laccase increased with increasing temperature and in the presence of

mediators such as HBT (1-hydroxybenzotriazole) and MPT (2-methoxyphenothiazine).[15]

The degradation of C.I. Direct Blue 71 contained in textile wastewaters by ozonization was remarkable under basic conditions of pH 12; after 26 min of ozone treatment, the process was completed. Tunç et al.[16] showed that the decolorization of C.I. Direct Blue 71 by the Fenton process was effective. The optimum conditions for decolorization of 2.94×10^{-5} M C.I. Direct Blue 71 were 2.5×10^{-5} M Fe^{2+} and 5.0×10^{-3} M H_2O_2 at pH 3.5 and 45 °C. The rate of decolorization was found to decrease with increasing reaction temperature.

Electrochemical oxidation of C.I. Direct Blue 71 for the treatment of simulated wastewaters was investigated by Parsa et al.[17] The most suitable conditions for the degradation and mineralization of C.I. Direct Blue 71 were found to be 5 g/L NaCl, neutral pH, and an applied voltage of 15 V. C.I. Direct Blue 71 can be highly degraded using a TiO_2 catalyst suspension and irradiation with a UV lamp in a circulating upflow photoreactor.[18] Degradation of more than 97% of the dye was achieved by applying the optimal operating parameters: 40 mg/L of catalyst, pH 6.22, and 45 °C during 120 min of irradiation. Removal of 50% of COD could also be obtained at the same time.

Among physicochemical processes, adsorption technology is considered to be one of the most effective and proven technologies, having potential applications in the treatment of both water and wastewater. Yavuz and Aydin[19] studied removal of C.I. Direct Blue 71 from aqueous solutions by commercial activated carbon (CAC), activated carbon obtained from the shell of hazelnut (HAC), raw kaolinite (KC), and montmorillonite (MC). The adsorption capacities of CAC, HAC, KC, and MC determined according to the Langmuir isotherm model for C.I. Direct Blue 71 at pH 6.4 were found to be 100, 26, 22, and 48 mg/g, respectively. The sorption properties of activated carbon (TPAC) and polymer composite (PPC) prepared from the wood of *Thevetia peruviana* for C.I. Direct Blue 71 were compared by Raffiea Baseri et al.[20] The monolayer adsorption of dye on the surface of TPAC increased from 129.9 to 188.7 mg/g and from 294.1 to 344.8 mg/g for PPC as the temperature was increased from 30 to 45 °C. A high adsorption capacity of 625 mg/g was reported for iron-based waterworks sludge by Kayranli.[21] The good sorption ability of palm ash for C.I. Direct Blue 71 was confirmed by Ahmad et al.[22] The equilibrium sorption capacity of palm ash determined according to the Langmuir equation was found to be 400 mg/g at 30 °C. The rate of adsorption followed pseudo-second-order kinetics.[22] Sunflower stalks were found to exhibit a low sorption capacity for C.I. Direct Blue 71 (26.8 mg/g) compared with chemically modified sunflower stalks (216 mg/g).[23,24] There is a lack of literature data on C.I. Direct Blue 71 dye retention on anion exchangers. Therefore, the aim of this work was to remove C.I. Direct Blue 71 from aqueous solutions and textile wastewaters by the ion-exchange method. Eight different anion exchangers were applied for this purpose. The effects of the resin basicity as well as the composition and structure of the resin matrix on the dye adsorption were estimated. The dye removal process was performed using the column and batch methods.

2. EXPERIMENTAL SECTION

2.1. Materials. Eight anion-exchange resins with different compositions, structures, and functional groups (Amberlite IRA 67, Lewatit MonoPlus MP 62, Lewatit MonoPlus MP 64, Amberlite IRA 458, Amberlite IRA 900, Amberlite IRA 958, Lewatit MonoPlus MP 500, and Lewatit MonoPlus M 500) were used in sorption studies (see Table S1, Supporting Information). The resins were washed with both 1 M HCl and distilled water to remove impurities and change the ionic form to the chloride form. The resins were dried at room temperature to a constant mass. For comparison, a low-cost sorbent prepared from orange peels was also used. The orange peels were first washed to remove any adhering dirt and were then dried, crushed, and sieved. They were air-dried to constant weight at room temperature. After being dried, the peels were passed through a 0.63-mm sieve.

C.I. Direct Blue 71 (Sigma-Aldrich Gmbh, Munich, Germany), with the empirical formula $C_{40}H_{27}N_7Na_4O_{13}S_4$ (Color Index Number 34140), was used without further purification (dye content 50%). It is commonly applied in the cotton textile industry as well as for paper, leather, wool, silk, and nylon dyeing. The stock solution was prepared in distilled water, and the working solutions were obtained by appropriate dilution.

The anionic surfactant sodium dodecyl sulfate (SDS) and the cationic surfactant cetyltrimethylammonium bromide (CTAB) were obtained from Sigma-Aldrich Gmbh (Munich, Germany). The other reagents used were purchased from POCh (Gliwice, Poland) as research-grade chemicals.

2.2. Column Experiments. The dynamic sorption studies were performed in glass columns (10-mm inner diameter) filled with 10 mL of the swollen anion exchanger. Feed solution of the dye with an initial concentration of 100 mg/L was passed continuously downward through the sorbent beds at a constant flow rate of 0.6 cm^3/min. The effluents were collected in fractions in which the dye concentration was determined by the UV−vis method at 587 nm. The sorption parameters such as the weight (D_w) and bed (D_b) distribution coefficients, the working (C_w) and total (C_t) ion-exchange capacities, the column efficiency (η), the time required for the mass-transfer zone (MTZ, or exchange zone) to move through its own length down the bed (t_z), the time required for the MTZ to become established and move completely out of the bed (t_e), the time needed for MTZ formation (t_f), and the parameter measuring the symmetry of the breakthrough curve (F_s) were calculated according to eqs 1−9 listed in Table S2[25−27] (see Supporting Information).

2.3. Adsorption Isotherm. The sorbent (0.5 ± 0.0005 g) was mixed with 50 mL of dye solution. Isotherm studies were performed by varying the initial dye concentration from 50 mg/L to 15 g/L at room temperature. After being shaken for 24 h, the reaction mixture was analyzed for the residual dye concentration. All experiments were duplicated, and only the mean values are reported. The applicability of equilibrium models of the adsorption process was validated by the normalized standard deviation, Δq (%), which was calculated as reported in ref 28.

The amount of dye sorbed onto the anion exchangers or orange peel sorbent, q_e (mg/g), was calculated by the following mass balance relationship

$$q_e = \frac{(C_0 - C_e)}{w}V \tag{10}$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye initially and at equilibrium, respectively; V (L) is the volume of solution; and w (g) is the mass of dry sorbent.

The effects of sodium chloride and sulfate concentrations varying from 1 to 25 g/L on the dye sorption at equilibrium on nine sorbents were studied by shaking the corresponding anion exchanger or orange peel sorbent with dye solution (100 mg/L) containing different amounts of salt at constant temperature. The sorbents were separated from the solution by decantation, and the concentration of the dye was determined by analysis of the absorbance value. The effects of two different surfactants on the dye sorption using anion exchangers and orange peel sorbent were studied by agitating them with a solution containing 100 mg of the dye and 0.1−1 g of surfactant per liter. The C.I. Direct Blue 71 concentration after sorption was measured spectrophotometrically.

The differences in the spectra of the anion exchangers before and after the sorption of C.I. Direct Blue 71 were investigated by attenuated-total-reflection (ATR) Fourier transform infrared (FT-IR) spectroscopy (Cary 630, Agilent Technologies, Palo Alto, CA).

2.4. Adsorption Kinetics. The effects of contact time on the sorption of the direct dye onto the anion exchangers and orange peel sorbent were determined by the batch technique. Samples of sorbent (0.5 ± 0.0005 g) were added with stirring (amplitude, 8; cycles per minute, 180; laboratory shaker, Elpin 358+, Katowice, Poland) to 50 mL of dye solution with an initial concentration of 100 mg/L. After phase contact times of 1, 3, 5, 10, 15, 20, 30, 60, 120, and 180 min, the solution samples were withdrawn and analyzed for residual dye concentration using the UV−vis spectrophotometric method at 587 nm (Specord M-42, Carl Zeiss, Oberkochen, Germany). The extent of sorption is expressed in terms of the fractional attainment of equilibrium

$$F = \frac{q_t}{q_e} \tag{11}$$

where q_t and q_e (mg/g) are the amounts of dye sorbed at time t and at equilibrium, respectively.

The decolorization of model wastewater (denoted as sample I) and real textile wastewaters (denoted as samples II−V) obtained from a textile company containing different dyes and auxiliaries was studied using the batch method. The compositions of the wastewaters were as follows:

- Sample I contained C.I. Direct Blue 71 (1 g/L) + C.I. Direct Red 75 (1 g/L) + C.I. Direct Red 81 (1 g/L) + C.I. Direct Black 22 (1 g/L) + NaCl (5 g/L) + Na$_2$CO$_3$ (2 g/L); wastewater pH = 10.95.
- Sample II contained C.I. Reactive Black 5 (6.25 g/L) + Na$_2$CO$_3$ + NaOH + NaCl + Perigen LDR (liquid dispersing and sequestering agent); wastewater after the ozonation step; wastewater pH = 6.64.
- Sample III contained Synozol Yellow KHL (0.694 g/L) + Synozol Red K3BS (1.347 g/L) + Synozol Blue KBR (0.069 g/L) + Na$_2$CO$_3$ + NaOH + NaCl + Perigen LDR; wastewater pH = 11.1.
- Sample IV contained Synozol Yellow HB (0.352 g/L) + Synozol Red HB (0.221 g/L) + C.I. Direct Blue 71 (0.585 g/L) + Na$_2$CO$_3$ + NaCl + Perigen LDR; wastewater pH = 11.95.
- Sample V contained Bezaktiv Turquois VG (2.309 g/L) + Bezaktiv Blau SFR (0.030 g/L) + Na$_2$CO$_3$ + NaOH + NaCl + Perigen LDR; wastewater pH = 11.38.

In this experiment, a dosage of 0.5 ± 0.0005 g of the anion exchanger was shaken with 50 mL of the model/real wastewater for 1−144 h. During these experiments, small samples were withdrawn after various phase contact times to estimate the color removal by analysis of the absorbance values at the maximum absorbance wavelength. All samples I were diluted 100 times before their absorption spectra were recorded, whereas all samples II and III were not diluted before measurements. The absorption spectrum of untreated sample IV (at 0 h) was recorded after twice repeated dilution. Samples V were diluted 10 times at phase contact times of 0 and 1 h before spectra were recorded.

2.5. Desorption. Regeneration tests for the anion-exchange resins were conducted with different elution agents (1 M HCl, 1 M NaOH, 1 M NaCl, 1 M Na$_2$SO$_4$, 1 M Na$_2$CO$_3$, and 90% methanol). The loaded resins (0.5 ± 0.0005 g) containing 10 mg/g of the dye were put into flasks in contact with 50 mL of different eluting agents. The flasks were agitated for 3 h, and the dye concentrations in the solutions were determined at the maximum absorbance wavelength. The desorption percentage (%) was calculated as

$$\text{desorption} = \frac{m_{\text{des}}}{m_{\text{ads}}} \times 100\% \tag{12}$$

where m_{des} is the mass of dye desorbed (mg) and m_{ads} is the mass of dye adsorbed (mg).

3. RESULTS AND DISCUSSION

3.1. Column Experiments. In both laboratory and industrial plants, anion-exchange resins are used in columns. The water or solution to be treated flows through the resin. The quantity of resin used in laboratory experiments is around 10−150 mL. For comparison, a large industrial ion-exchange column can contain 20000 L of resin, or sometimes even more. One of the main tools used in the investigation of the efficiency of adsorption columns is breakthrough analysis. Typical breakthrough curves determined for the anion exchangers in systems containing 100 mg/L C.I. Direct Blue 71 are presented in Figure 1. Under working conditions, they were applied for determination of the weight (D_w) and bed (D_b) distribution coefficients, the working (C_w) and total (C_t) ion-exchange capacities, the column efficiency (η), the time required for the MTZ to move through its own length down the bed (t_z), the time required for the MTZ to become established and move completely out of the bed (t_e), and the time needed for MTZ
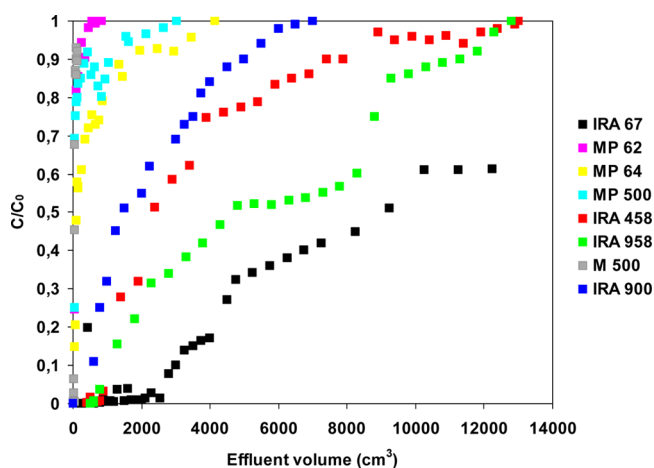
Figure 1. Breakthrough curves determined for C.I. Direct Blue 71 (C_0 = 100 mg/L) sorption on different anion exchangers.

Table 2. Breakthrough Curve Parameters Obtained for C.I. Direct Blue 71[a] Retention on Weak, Intermediate, and Strong Base Anion-Exchange Resins

anion exchanger	D_w	D_b	C_w (mg/mL)	C_t (mg/mL)	t_z (min)	t_e (min)	t_f (min)	η
Lewatit MonoPlus MP 62	20.7	6.6	0.5	8.5	1333.3	1416.7	80	0.06
Amberlite IRA 67	3905.4	924.4	28	122.5	15750	20416.7	3622.5	0.23
Lewatit MonoPlus MP 64	43.4	10.9	0.6	41.6	6833.3	6933.3	68.3	0.01
Lewatit MonoPlus M 500	17.1	4.4	0.2	1.4	200	233.3	28	0.14
Lewatit MonoPlus MP 500	19.6	4.4	0.4	30.4	5000	5066.7	50	0.01
Amberlite IRA 458	837.1	239.4	10	130	20000	21666.7	1600	0.08
Amberlite IRA 900	518.4	149.4	6	70	10666.7	11666.7	960	0.09
Amberlite IRA 958	2286.1	479.4	13	128	19166.7	21333.3	1916.7	0.1

[a]C_0 = 100 mg/L.

formation (t_f) (see also Table S1, Supporting Information). As follows from the data listed in Table 2, the weakly basic anion exchanger of the acrylic matrix Amberlite IRA 67 was found to have the highest value of the working ion-exchange capacity, equal to 28 mg/mL, but the smallest value of the parameter of symmetry of the breakthrough curve (F_s = 0.7) at the same time. The strongly basic anion exchangers of acrylic matrixes such as Amberlite IRA 958 and IRA 458 also exhibit a high efficiency of C.I. Direct Blue 71 sorption. The values of the working ion capacities were 13 and 10 mg/mL, respectively. The macroporous anion exchanger of polystyrene matrix Amberlite IRA 900 exhibited a lower working ion-exchange capacity (6 mg/L). The high values of the working ion-exchange capacities correspond to high values of the total capacities (122.5 mg/mL for IRA 67, 130 mg/mL for IRA 458, and 128 mg/mL for IRA 958). The time required for MTZ formation (3622.5 min) was the longest for Amberlite IRA 67. For Amberlite IRA 67, IRA 458, and IRA 958, the times required for the MTZ to become established and move completely out of the bed were calculated as 20416.7, 21666.7, and 21333.3 min, respectively. Taking into account the low values of the working ion-exchange capacities for the weak and intermediate base anion exchangers Lewatit MonoPlus MP 62 and MP 64 as well as for the strongly basic M 500 and MP 500, it can be stated that they cannot be applied for the removal of C.I. Direct Blue 71 from aqueous solutions and wastewaters in the column system.

3.2. Equilibrium Studies and Sorption Mechanism. Equilibrium relationships between a sorbent and a sorbate, known as sorption isotherms, describe the ratio between the quantity of sorbate retained by the sorbent and that remaining in the solution at a fixed temperature at equilibrium. The adsorption isotherm is important from both theoretical and practical points of view. The parameters obtained according to different isotherm models provide important information on the sorption mechanisms, surface properties, and affinities of the sorbent. Several isotherm equations are available for analyzing experimental sorption equilibrium data. The best known adsorption models in the linearized form for single-solute systems are the Langmuir and Freundlich models

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{13}$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{14}$$

where Q_0 (mg/g) is the Langmuir monolayer sorption capacity, b (L/g) is the Langmuir adsorption constant, k_F (mg/g) is the

Freundlich adsorption capacity, and $1/n$ is the Freundlich constant related to the surface heterogeneity.

The experimental data obtained in the present work were tested with these equations. The Langmuir constants Q_0 and b were calculated from the slope and intercept of a plot of C_e/q_e versus C_e. A plot of $\log q_e$ versus $\log C_e$ should produce a straight line with a slope of $1/n$ and an intercept of k_F. The applicability of the isotherm equations was compared by judging the correlation coefficients (R^2). The Langmuir adsorption model assumes that all adsorption sites are equivalent, that there are no interactions between adsorbed molecules and adjacent sites, and that adsorption is of the monolayer type. In comparison with the Langmuir model, the Freundlich model is valid for heterogeneous sorption on surfaces containing several types of sites.
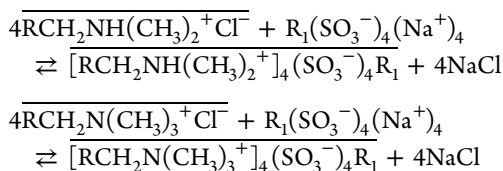
The calculated constants of these models were largely dependent on the type of the anion exchanger (Table 3). Not only the basicity of the resin but also the matrix composition and structure were found to be determining factors of sorption. The values of the monolayer sorption capacities determined from the Langmuir equation for Amberlite IRA 958, Amberlite IRA 900, Lewatit MonoPlus MP 500, Lewatit MonoPlus MP

Table 3. Sorbent Capacities Determined from the Langmuir and Freundlich Isotherm Models

sorbent	Langmuir isotherm model			Freundlich isotherm model		
	Q_0 (mg/g)	b	R^2	k_F (mg/g)	n	R^2
Amberlite IRA 67	90.9	0.005	0.909	1.02	1.57	0.998
Lewatit MonoPlus MP 62	470.6	0.0003	0.874	1.47	0.86	0.931
Lewatit MonoPlus MP 64	420.4	0.021	0.997	24.2	2.35	0.510
Lewatit MonoPlus M 500	2.02	0.165	0.692	0.14	1.06	0.509
Lewatit MonoPlus MP 500	523.6	0.0023	0.959	2.65	1.39	0.874
Amberlite IRA 458	48.4	0.034	0.982	5.6	2.84	0.650
Amberlite IRA 958	1630.6	0.0001	0.987	0.65	1.26	0.965
Amberlite IRA 900	778.2	0.0001	0.828	0.21	1.18	0.901
orange peel sorbent	73.4	0.006	0.694	1.42	0.88	0.945

64, Amberlite IRA 458, and Lewatit MonoPlus M 500 were found to be 1630.6 mg/g ($R^2 = 0.987$), 778.2 mg/g ($R^2 = 0.828$), 523.6 mg/g ($R^2 = 0.959$), 420.4 mg/g ($R^2 = 0.997$), 48.4 mg/g ($R^2 = 0.982$), and 2.02 mg/g ($R^2 = 0.692$), respectively. The influence of isotherm shape on whether adsorption is favorable or unfavorable was considered using the dimensionless constant separation factor R_L.[29] It was observed that values of R_L in the range of 0−1 confirm the favorable uptake of the dye by Amberlite IRA 958 ($R_L = 0.3922$), Lewatit MonoPlus MP 500 ($R_L = 0.0460$), Lewatit MonoPlus MP 64 ($R_L = 0.0047$), Amberlite IRA 458 ($R_L = 0.3846$), and Lewatit MonoPlus M 500 ($R_L = 0.1315$).

However, a comparison of the R^2 values indicates that the experimental data for C.I. Direct Blue 71 adsorption onto Amberlite IRA 67, Amberlite IRA 900, Lewatit MonoPlus MP 62, and orange peel sorbent were more appropriate for the Freundlich isotherm model. According to the results presented in Table 3, the k_F values determined for Amberlite IRA 67, Lewatit MonoPlus MP 62, Amberlite IRA 900, and orange peel sorbent were found to be in the range of 0.21−1.47 mg/g. The parameter n from the Freundlich equation is a measure of the adsorption deviation from linearity. Its value indicates the degree of nonlinearity between the solution concentration and the adsorption as follows: If the value of n is equal to unity, the adsorption is linear; if the value is less than unity, the adsorption process is chemical; and if the value is greater than unity, adsorption is a favorable physical process.[30] The values of n were calculated as 1.57 for Amberlite IRA 67, 1.18 for Amberlite IRA 900, 0.86 for Lewatit MonoPlus MP 62, and 0.88 for the orange peel sorbent. These results are in agreement with the aggregation tendency of the C.I. Direct Blue 71 dye, especially at high concentrations, and with the possibility of dye uptake through many types of interactions. Similar observations were reported for C.I. Basic Blue 9 sorption onto Purolite C 145 and C 107E resins by Suteu et al.[29] Under the experimental conditions, sorption of C.I. Direct Blue 71 dye occurred between the sulfonic groups of dye $\left[R_1(SO_3^-)_4(Na^+)_4\right]$ and the functional groups of the weakly $\overline{(RCH_2NH(CH_3)_2{}^+Cl^-)}$ or strongly $\overline{(RCH_2N(CH_3)_3{}^+Cl^-)}$ basic anion exchangers in chloride form

$$4\overline{RCH_2NH(CH_3)_2{}^+Cl^-} + R_1(SO_3^-)_4(Na^+)_4$$
$$\rightleftarrows \overline{[RCH_2NH(CH_3)_2{}^+]_4}(SO_3^-)_4R_1 + 4NaCl$$

$$4\overline{RCH_2N(CH_3)_3{}^+Cl^-} + R_1(SO_3^-)_4(Na^+)_4$$
$$\rightleftarrows \overline{[RCH_2N(CH_3)_3{}^+]_4}(SO_3^-)_4R_1 + 4NaCl$$

The exchangeable chloride anions compensating the positive electric charge of the tertiary amine or quaternary ammonium groups of the anion exchanger were replaced by the dye anions $\left[R_1(SO_3^-)_4\right]$. The formation of ion pairs between these groups was observed. The ATR FT-IR spectra of loaded anion exchangers confirmed the presence of such interactions. The absorption peaks at 1170−1047 and 1019 nm are attributed to the presence of —SO$_3^-$ and —S==O groups, respectively (Figure 2). Although ion exchange is the significant mechanism in C.I. Direct Blue 71 sorption by anion exchangers, some extent of physical adsorption can also occur. For example, hydrophobic interactions including π−π interactions between the aromatic rings of the dye and the matrix of the anion exchanger ("like attracts like") can play a role in adsorption of the dye.[31] In the case of polyacrylic resins such as Amberlite
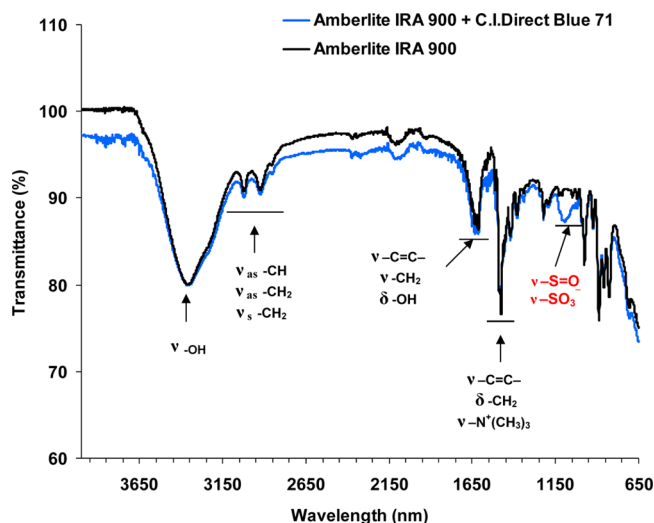

Figure 2. ATR FT-IR spectra of the polystyrene anion exchanger before and after loading of C.I. Direct Blue 71.

IRA 958, IRA 458, and IRA 67, this statment is relevant, and these interactions play a more extensive role than those for the polystyrene-based materials. The high affinity of the dye for the anion exchangers can also result from the formation of H-bonds, which can occur between nitrogen of the quaternary ammonium groups of the strongly basic anion-exchange resin and nitrogen of the —NH$_2$ group of the dye as well as oxygen of the carbonyl group of the resin and the —NH$_2$ group of the dye. Also, the oxygen atom of the carbonyl group of the anion exchanger and the oxygen atom of the hydroxyl group or nitrogen atom of the azo group of the dye through the water molecules could interact.[32] Possible interactions between the anions of C.I. Direct Blue 71 and the strongly basic anion exchangers of polystyrene and polyacrylic matrixes are shown in Figures 3 and 4, respectively. The studies on the sorption of dyes and organic compounds on the ion exchangers reported so far showed that the size of the sorbate molecules has a considerable effect on the degree of sorption. Organic dye molecules differing in either the position of sulfonic groups or the number of anionic groups as well as position of the anionic charges and the whole structure of the dye can interact in different ways with ion exchangers. Of significant importance in the removal of dye anions by an anion exchanger is the type of resin structure. When the exchange of high-molecular-weight species such as dyes is concerned, the macroporous property becomes important in providing an easier diffusion path for the uptake of such species compared with the gel structure. Amberlite IRA 958 as the anion exchanger with a macroporous structure contains significant porosity in comparison with gel Amberlite IRA 458 or IRA 67. Therefore, the sorption capacity of Amberlite IRA 958 (1630.6 mg/g) is more than 33 times larger than that of Amberlite IRA 458 (48.4 mg/g) with the same functional groups. In the case of the strongly basic anion exchanger Lewatit MonoPlus M 500 with a polystyrene matrix and gel structure, the affinity for the dye is essentially evident and expressed in a very low capacity (2.02 mg/g). Additionally, the flat structure of C.I. Direct Blue 71 can inhibit interactions of the sorbate−sorbent type. If the dye anion is too large, it is excluded from the resin structure ("sieve effect"); in addition, because of its large size, C.I. Direct Blue 71 dye has a tendency to form aggregates in the solution rather than in the resin.[33]
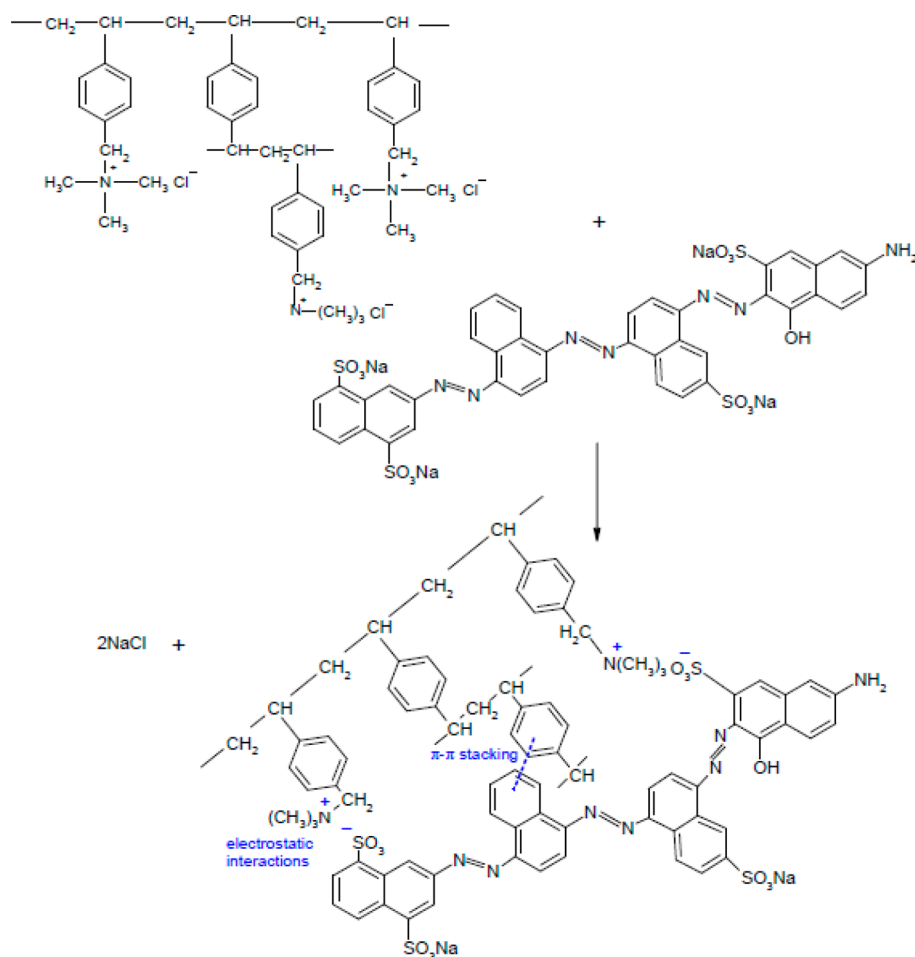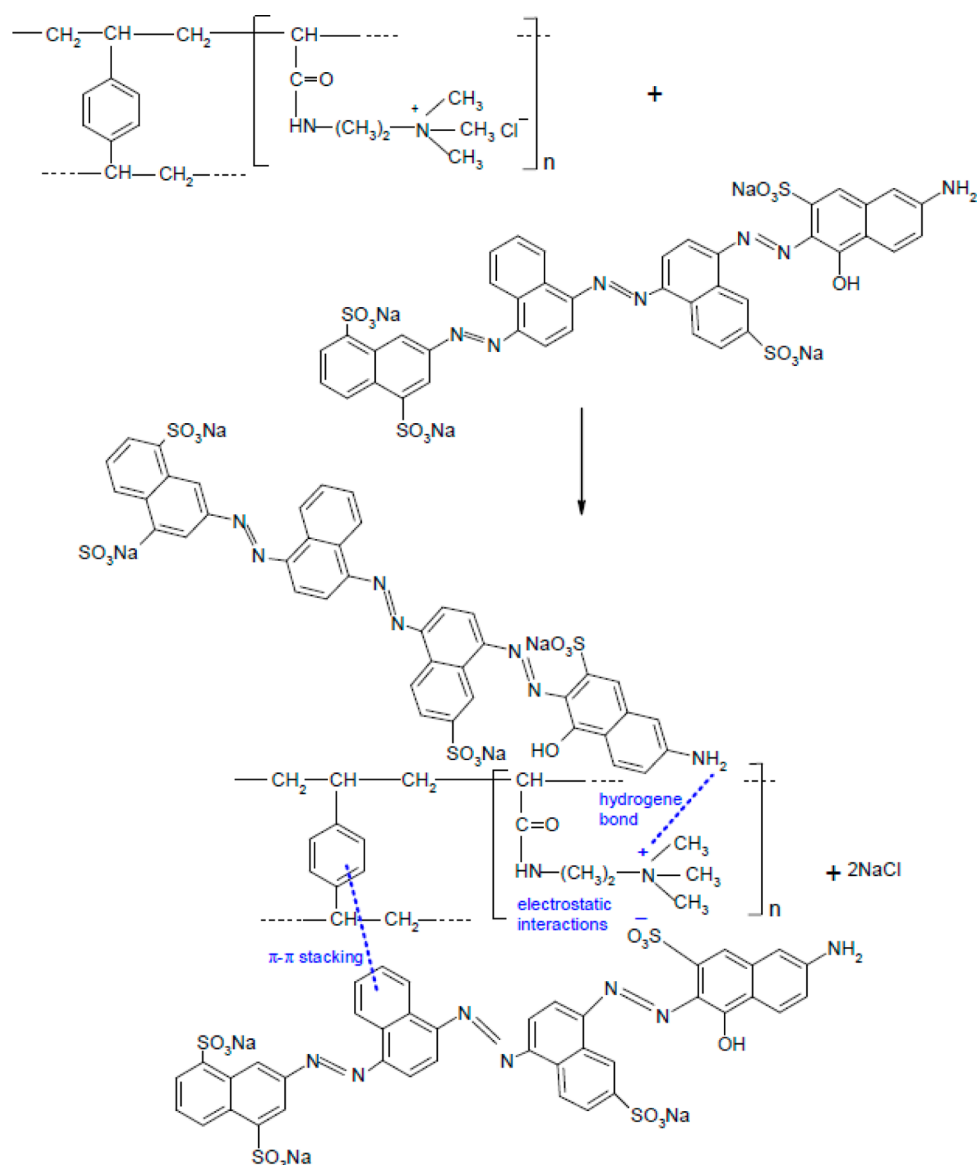
Figure 3. Possible interactions between the anions of C.I. Direct Blue 71 and strongly basic polystyrene anion exchangers.

3.2.1. Influence of Salts and Surfactant Addition on C.I. Direct Blue 71 Removal. In the textile industry, high concentrations of various inorganic salts such as NaCl, Na_2SO_4, Na_2CO_3, and KCl are frequently used to improve the dyeing rate. Because of the high negative charge of direct dyes in the water bath, they are repelled by the surface of the fibers with a negative electrokinetic zeta potential. The addition of the electrolyte causes a decrease in the negative zeta potential, thus facilitating the access of dye anions to the fiber surface. Therefore, huge amounts of inorganic salts are discharged to the effluents. For this reason, mainly the effect of two inorganic salts, NaCl and Na_2SO_4, on dye removal by anion exchangers and orange peel sorbent from systems containing 100 mg/L dye in the presence of 1−25 g/L NaCl or Na_2SO_4 was investigated. It was observed that, for the strongly basic anion exchanger Amberlite IRA 958, which had the highest sorption capacity for C.I. Direct Blue 71 dye among the applied sorbents, the presence of NaCl and Na_2SO_4 in the whole examined concentration range of 1−25 g/L did not influence the adsorption capacity (9.98 mg/g). The dye sorption was quantitative. The same results were obtained for the strongly basic anion exchanger Amberlite IRA 458. The above-mentioned anion exchangers have the same matrix composition (cross-linked acrylic polymer) but different structures (gel or macroporous). Amberlite IRA 67 with tertiary amine functionalities exhibited an insignificant drop of the sorption capacity with increasing amount of electrolytes. It can be concluded that, in the case of polyacrylic anion-exchange

resins with different basicities, no significant influence of the matrix structure was observed. The presence of NaH_2PO_4, Na_2HPO_4, and Na_2SO_4 on C.I. Acid Orange 7 (AO7) retention by Amberlite IRA 958 was studied by Greluk and Hubicki[32] in systems containing 200 mg/L AO7 and 0.1−2.0 g/L salts. Removal of AO7 dye was not affected by these salts.

The effect of the presence of NaCl and Na_2SO_4 on C.I. Direct Blue 71 removal using Lewatit MonoPlus M 500 was rather negligible, as increases in the amount of dye adsorbed at equilibrium from 2.2 to 3.0 mg/g and from 2.2 to 2.8 mg/g were observed for 1 and 25 g/L salt concentration, respectively. The gel structure of Lewatit MonoPlus M 500 hindered diffusion of C.I. Direct Blue 71 anions to the pores and interactions with internal functional groups of the anion exchanger. A similar dependence was found for the orange peel sorbent, as the addition of 25 g/L NaCl or Na_2SO_4 enhanced the sorption yield by about 30% compared with the system without these auxiliaries. A marked increase in adsorption capacities was observed during dye uptake by the polystyrene anion exchangers of macroporous structure Amberlite IRA 900 and Lewatit MonoPlus MP 500, MP 64, and MP 62 in a system containing 1−25 g/L NaCl or Na_2SO_4 and 100 mg/L C.I. Direct Blue 71 (Figure 5a). Amberlite IRA 900 exhibited a sorption capacity for C.I. Direct Blue 71 about 30% higher in the presence of the electrolytes than in the system without salts. At the equilibrium time, the sorption capacity of Lewatit MonoPlus MP500 increased from 1.89 to 9.98 mg/g and from 1.89 to 9.95 mg/g with increasing amounts

Figure 4. Mechanism of interactions between the anions of C.I. Direct Blue 71 and strongly basic polyacrylic anion exchangers.

of NaCl and Na$_2$SO$_4$, respectively, in the range of 1−25 g/L. Sorption enhancements were observed for Lewatit MonoPlus MP 64 from 1.9 to 9.97 mg/g and from 1.9 to 9.95 mg/g with increasing concentrations of NaCl and Na$_2$SO$_4$, respectively. The dye uptake by the weakly basic anion exchanger Lewatit MonoPlus MP 62 also increased in the presence of the salts, with the values of q_e increasing from 5.86 to 9.9 mg/g with increasing concentration of both electrolytes. Direct dyes, being salts of sulfonic acids, are strong electrolytes and dissociate in aqueous batch solution into the colored anions and sodium cations. Having a flat molecular structure and a high molar weight (usually 600−1000 g/mol), they reveal a tendency to form associated ions (colloidal electrolytes) as follows

$$B^{z-}(Na^+)_z \rightleftarrows B^{z-} + zNa^+$$

$$nB^{z-} \rightleftarrows (B^{z-})_n$$
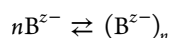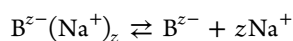
where B^{z-} is the dye anion, z is the number of sulfonic groups, and n is the degree of association.

With increasing salt concentration in the system, the associated molecules of dyes disintegrated, causing the same

increase in dye sorption. Yang[34] observed that C.I. Acid Blue 40 and C.I. Acid Green 20 sorption on wool fibers first decreased with increasing salt (Na$_2$SO$_4$ and NaH$_2$PO$_4$) concentration and then increased with increasing electrolyte concentration. To explain this behavior, a modified Donnan model was proposed. This modification was based on the understanding that salt anions are either kosmotropes (water-structure makers) or chaotropes (water-structure breakers). They affect the free energy of the dye bath through their influence on water structure. The change in dye sorption with salt concentration was the combined effect of salt on both ionic and physical interactions. When the salt concentration was low, its effect on ionic interactions predominated over its effect on physical interactions. When the salt concentration was high, the influence of the salt on the physical interactions between the dye and the fibers increased.[34]

Surfactants are widely used as wetting, penetrating, dispersing, and leveling agents in dyeing processes. The main role of surfactants is to increase the solubility of dyes in water, to improve the dye uptake and dye fastness. Therefore, dye wastewaters contain not only dyes, but also other auxiliaries

a)

b)
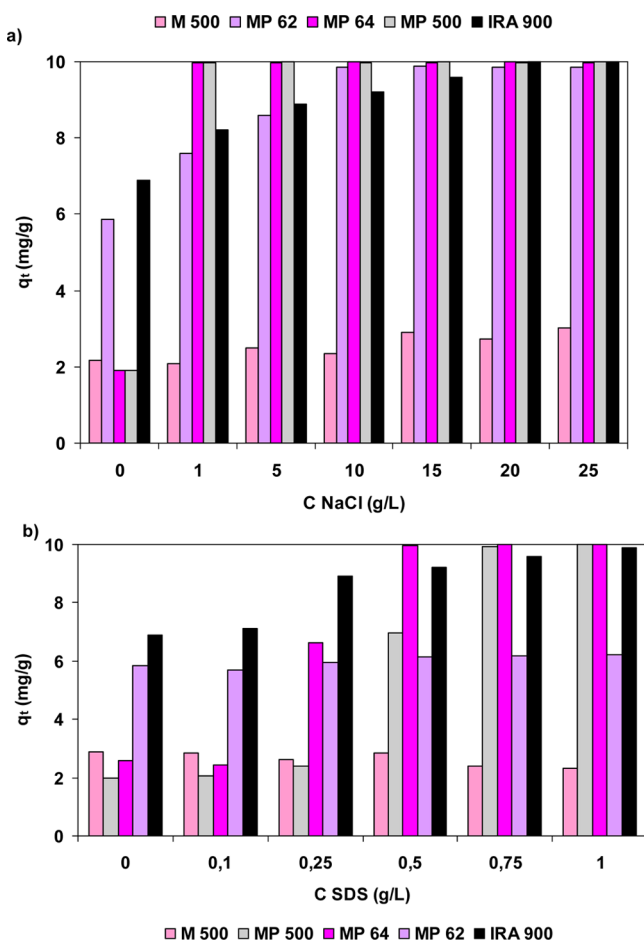
Figure 5. Effect of (a) sodium chloride and (b) anionic surfactant SDS addition on the C.I. Direct Blue 71 uptake by anion exchangers in the following systems: 100 mg/L C.I. Direct Blue 71—1—25 g/L NaCl and 100 mg/L C.I. Direct Blue 71—0.1—1 g/L SDS.

such as salts and surfactants. The effects of the addition of such surfactants as sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) on the dye removal by the sorbents used were studied for systems containing 100 mg/L dye in the presence of 0.1—1 g/L SDS or CTAB.

The anionic surfactant affected the dye sorption in two ways. The sorption of C.I. Direct Blue 71 was slightly reduced with increasing amount of SDS in the system for the weakly and strongly basic anion exchangers such as Amberlite IRA 67, Lewatit MonoPlus M 500, Amberlite IRA 958, and Amberlite IRA 458, as well as the orange peel sorbent. Both C.I. Direct Blue 71 and SDS are negatively charged, and the interactions between the anionic SDS and the dye anion must be repulsive, independent of the surfactant concentration. Competition between these species for adsorption sites causes a reduction of the dye uptake. For the polystyrene anion exchangers of macroporous structure, namely, Lewatit MonoPlus MP 62, MP64, and MP 500 and Amberlite IRA 900, a diverse trend was noticed (Figure 5b). Increasing the concentration of SDS in the range of 0.1—1 g/L resulted in an enhancement of dye anion sorption. The surfactant can be adsorbed on the active sites or on the hydrophobic parts of the matrix of the anion exchangers in the form of relatively poorly ordered surface aggregates and can interact with the aromatic rings or anionic groups of the dye. Janoš and Šmídová[35] explained in detail the sorption mechanisms between basic dyes and the organomineral

sorbent—iron humate in the presence of different surfactants taking into account not only the charge of dyes and surfactants in the aqueous phase but also the surfactant concentration in the system. Three different cases of interactions were broadly discussed.[35]

Increasing the CTAB concentration from 0.1 to 1 g/L in the system initially containing 100 mg/L dye resulted in a dramatic decrease in the sorption of C.I. Direct Blue 71 on the anion exchangers and orange peel sorbent. For example, the amount of dye retained by Amberlite IRA 958 at equilibrium dropped from 9.98 to 0.31 mg/g with increasing concentration of CTAB. This was attributed to attractive interactions between the ionized form of the dye and the cationic surfactant that caused the formation of highly ordered aggregates (micelles) that solubilize the dye molecules.

The obtained results suggest that the strongly basic anion-exchange resin Amberlite IRA 958 with a polyacrylic matrix can exhibit good sorption characteristics not only for synthetic dye solution but also for textile wastewaters with concentrations of salts and surfactants.

3.3. Sorption Kinetic Studies. In the present discussion, the kinetic behaviors of the ion exchangers and orange peel sorbent toward C.I. Direct Blue 71 were examined in systems with an initial dye concentration equal to 100 mg/L. As can be seen in Figure 6, the time required for the maximum removal of the dye in these systems was found to be 12 h for the polyacrylic anion exchangers and 4 h for the polystyrene anion exchangers and the orange peel sorbent. Applicability series of the used sorbents based on the amount of dye retained at equilibrium can be presented as follows: Amberlite IRA 958 (9.93 mg/g) ≈ Amberlite IRA 458 (9.92 mg/g) ≈ Amberlite IRA 67 (9.9 mg/g) > Amberlite IRA 900 (6.9 mg/g) > Lewatit MonoPlus MP 62 (5.86 mg/g) > orange peel sorbent (6.2 mg/g) > Lewatit MonoPlus M 500 (2.15 mg/g) ≈ Lewatit MonoPlus MP 64 (1.9 mg/g) ≈ Lewatit MonoPlus MP 500 (1.89 mg/g). The sorption half times ($t_{1/2}$) required to reach 50% of equilibrium were found to be 11 min for the orange peel sorbent, 19 min for Amberlite IRA 900, 21 min for Amberlite IRA 958, 66 min for Lewatit MonoPlus MP 62, 67 min for Amberlite IRA 458, 68 min for Amberlite IRA 67, 163 min for Lewatit MonoPlus M 500, 186 min for Lewatit MonoPlus MP 64, and 205 min for Lewatit MonoPlus MP 500. The anion-exchange resins based on an acrylic matrix demonstrate favorable kinetics toward large organic ions such as dye anions compared with the styrene structures. A simplified explanation for this behavior lies with the more hydrophilic nature of the aliphatic skeletal structure of the acrylic matrix, which, in turn, indicates weak van der Waals-type attractions between the resin matrix and the hydrocarbon structure of the organic counterion.[36]

To characterize the actual rate-controlling step involved in the dye sorption process, that is, whether the rate of removal of the dye took place through the particle diffusion or film diffusion mechanism, the sorption data were analyzed by plotting $\log(1 - F)$ versus time.[36-39] The plot is based on the assumption that adsorption follows Fick's law. As can be seen from Figure 6b, deviations from linearity were observed for the anion exchangers and the orange peel sorbent, which supports the fact that the adsorption of C.I. Direct Blue 71 on the applied sorbents does not proceed by film diffusion.

3.3.1. Wastewater Treatment. The adsorption of C.I. Direct Blue 71 on the strongly basic anion exchanger Amberlite IRA 958 (as well as the other anion exchangers used) was pH-
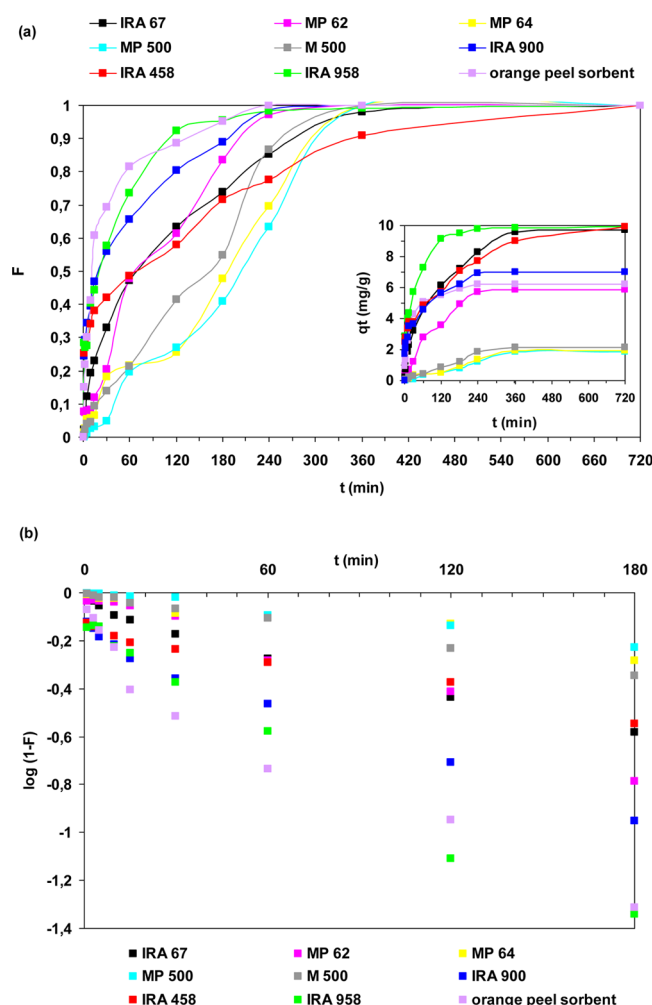
Figure 6. Effect of phase contact time on (a) the fractional uptake of adsorbate F and (b) $\log(1 - F)$ in the system C.I Direct Blue 71 (100 mg/L)−anion exchanger/orange peel sorbent.

independent, and pH had practically no influence on the amount of dye adsorbed on the resin (data not given). Similar observations have been reported for the sorption of C.I. Reactive Black 5, C.I. Reactive Red 2, and C.I. Acid Orange 7 on weakly and strongly basic anion exchangers such as Amberlyst A 21, Amberlites IRA 958, IRA 458, IRA 900, and IRA 910.[40,41] Therefore, purification of wastewaters with different compositions and pH values was investigated. The UV−vis spectra of the wastewaters (model and real), both untreated and treated with the resin, were recorded after different phase contact times, as shown in Figure 7. The absorption spectra of the model wastewaters (samples I) were recorded after repeated dilution (100 times), and the absorbance values of these wastewaters did not decrease significantly even after 144 h of phase contact time. The photographs of these samples included in Figure 7a confirm a negligible color reduction. A decolorization efficiency exceeding 87% after only 1 h of contact time was observed for the wastewaters denoted as samples II (Figure 7b). For samples III of wastewaters (Figure 7c), a visible change in color was observed during 12 h of phase contact time, and the absorbance value at the maximum wavelength decreased from 2.439 (before purification) to 0.1901 (after 12 h). A yield of decolorization equal to 88.3% was found after 3 h of adsorption

for samples IV of wastewaters, and increasing the phase contact time to 144 h did not increase the adsorption efficiency significantly (Figure 7d). Upon analyzing the absorption spectra of untreated and purified wastewaters designated as samples V, one can see a significant color reduction after 12 h of phase contact time (Figure 7e).

The obtained results indicate that Amberlite IRA 958 can be a promising adsorbent for the removal of textile dyes from wastewaters of different types.

3.4. Desorption Studies. A very important characteristic of an adsorbent is its regeneration ability. Desorption studies also help evaluate the nature of the adsorption process. In this work, desorption studies were performed in one cycle using different regenerating agents: 1 M NaCl, 1 M Na$_2$SO$_4$, 1 M Na$_2$CO$_3$, 1 M NaOH, and 1 M HCl. Aqueous solutions such as 1 M HCl, 1 M NaCl, 1 M Na$_2$CO$_3$, and 1 M Na$_2$SO$_4$ were ineffective for C.I. Direct Blue 71 removal from the resin phase, as the desorption percent did not exceed 5%. A desorption yield equal to 80.2% was found for 1 M NaOH. Considering the fact that dye retention by Amberlite IRA 958 cannot be only by ion exchange, methanol was chosen to break these nonspecific interactions. A methanol solution of 90% concentration was ineffective in the regeneration of Amberlite IRA 958. Mixtures of 90% methanol with 1 M NaOH improved the dye desorption to 85.4%. It was confirmed previously that regeneration of weak, intermediate, and strong base anion exchangers loaded with acid, reactive, and direct dyes is problematic and requires the use of aggressive regenerants.[42−44]

4. CONCLUSIONS

The sorption of C.I. Direct Blue 71 on weak (Amberlite IRA 67, Lewatit MonoPlus MP 62), intermediate (Lewatit MonoPlus MP 64), and strong (Amberlite IRA 458, Amberlite IRA 900, Amberlite IRA 958, Lewatit MonoPlus MP 500, Lewatit MonoPlus M 500) base anion exchangers with polyacrylic and polystyrene skeletons, as well as on the low-cost sorbent prepared from orange peel for comparison, was investigated from aqueous solutions and wastewaters. It seems that the macroporous anion exchanger Amberlite IRA 958 of quaternary ammonium functionality combines the advantageous properties of positively charged functional groups and large pores, resulting in a very high adsorption capacity for C.I. Direct Blue 71. The experimental data indicate that the amount of dye adsorbed on the anion-exchange resin is dependent on the initial dye concentration and the phase contact time. The solution pH and the concentrations of salts (NaCl and Na$_2$SO$_4$) and anionic surfactant (SDS) do not influence the anion-exchange resin performance, whereas the presence of the cationic surfactant (CTAB) decreased the dye adsorption on Amberlite IRA 958 significantly. The reversibility of adsorption depends on whether the predominant mechanism is a strong bond such as ionic bonding or weak binding forces such as van der Waals interactions or H-bonding and occurred with 85.4% yield using 1 M NaOH in methanol. The adsorption behavior of polyacrylic Amberlite IRA 958 demonstrates that it can be a promising adsorbent for textile wastewater treatment. The results obtained in the purification of raw wastewaters confirm this statement.
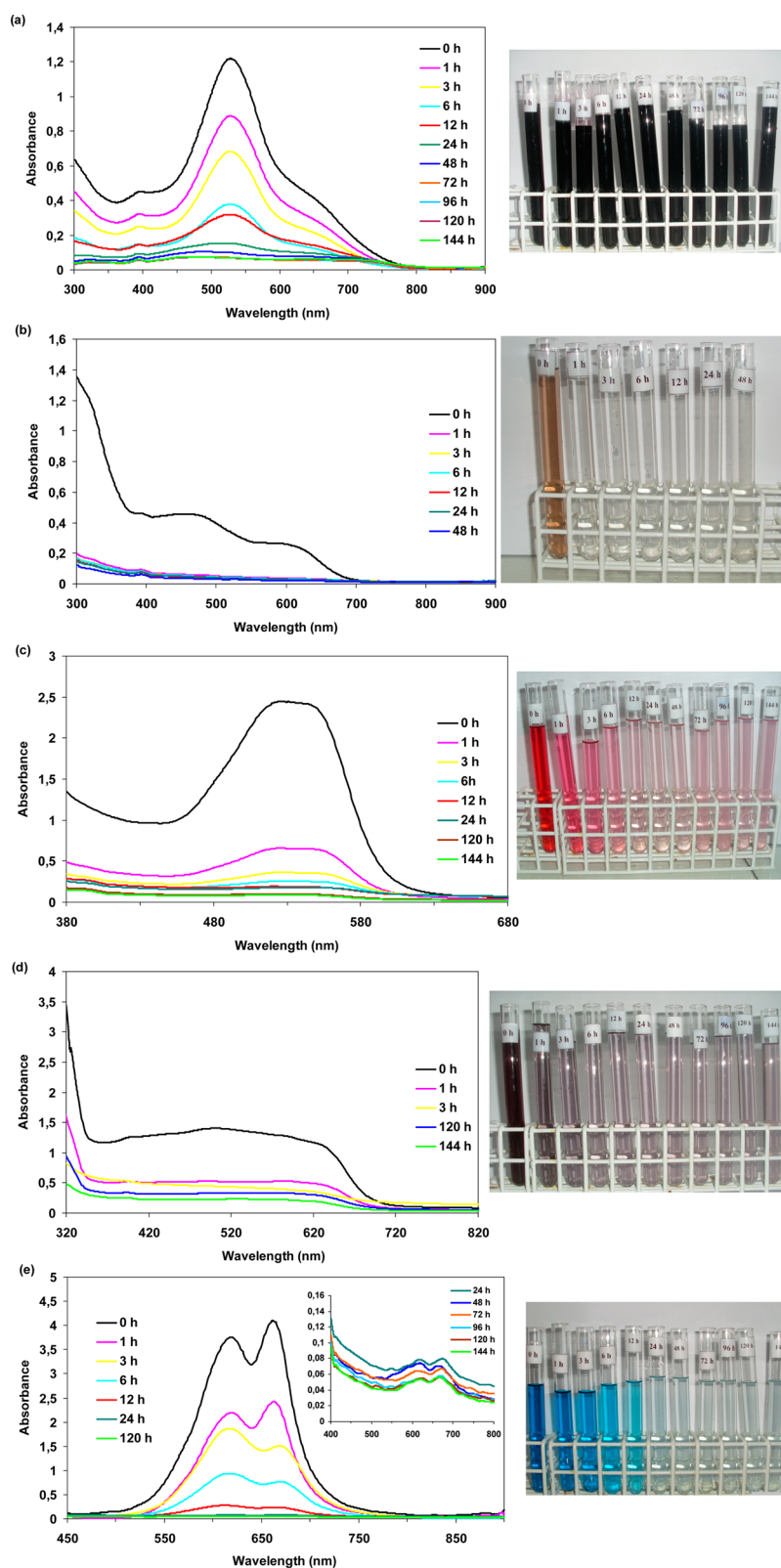
Figure 7. Absorbance spectra of untreated and purified wastewaters of different compositions (see section 2.4) using Amberlite IRA 958: (a) sample I, (b) sample II, (c) sample III, (d) sample IV, (e) sample V.

■ ASSOCIATED CONTENT

S Supporting Information

Anion-exchanger properties (Table S1) and column experiment formulas (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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