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Comparison of the Efficiency of Amberlite IRA 478RF for Acid, Reactive, and Direct Dyes Removal from Aqueous Media and Wastewaters

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S Supporting Information

ABSTRACT: The acrylic anion exchange resin of the quaternary ammonium and tertiary amine functionalities (Amberlite IRA 478RF) was tested as the effective sorbent for the removal of anionic dyes of increasing molecular size. The sorption of Acid Orange 7 (AO7), Reactive Black 5 (RB5), and Direct Blue 71 (DB71) was investigated by the batch and column methods. Modeling of kinetic results showed that the sorption of DB71 dye was best described by the pseudo first-order Lagergren equation. The pseudo second-order kinetics was found to be closer to the experimental data in the systems containing 200 mg/L AO7 or RB5. The Langmuir monolayer capacities were found to be 1279.2, 150.5, and 41.8 mg/g for AO7, RB5, and DB71, respectively. The influence of electrolytes such as Na_2SO_4 , Na_2CO_3 , and NaCl on the anion exchanger loading was also investigated. Methanol addition to the 1 M HCl, 1 M NaOH, and 1 M KSCN solutions improved dye desorption. Purification of the acid and direct wastewaters by means of Amberlite IRA 478RF was effective; 97% and 69.5% reduction of color was obtained, respectively.

1. INTRODUCTION

Dyeing is a fundamental operation during the textile fiber processing. This operation causes the production of more or less colored wastewaters, depending on the degree of fixation of the dyes on the substrates, which varies with the nature of the substances, the desired intensity of coloration, and the application method.¹ The dye bearing effluents are considered to be a very complex and inconsistent mixture of many pollutants ranging from organic-chlorine based pesticides, alkalis, oils, detergents, salts of organic and inorganic acids, to heavy metals.^{1–3} An overview of the environmental loads is given in Figure S1 (see the Supporting Information). In the textile dyeing processes, a large volume of dye-contaminated effluent is discharged, and it was estimated that 7–20% of acid dyes, 5–20% of direct dyes, and 20–50% of reactive dyes were lost in the effluents.³ There are well documented facts that the effluents of textile industry are posing a serious hazard to aquatic living organisms. Many dyes are nonbiodegradable, hinder light penetration into water, and inhibit the photosynthesis process, increasing chemical and biological demand for oxygen.² Thus, it is necessary to reduce and eliminate these life threatening compounds from wastewater before it is discharged. The dyes removal technologies can be divided into three categories: biological, chemical, and physical. Because of high cost and disposal problems, many of these conventional methods for treating dye wastewaters have not been widely applied on a large scale in the textile industry. At present, there is no single process capable of treatment, mainly due to the complex nature of the effluents;⁴ combination of the above-mentioned techniques provides effective treatment of colored wastewaters.² According to Babu et al.,⁵ more than 100 references in the bibliographical review of textile wastewater treatment prove that combination techniques permit not only

the reduction of suspended solids, organic substances, and color but also recovery of process chemicals (Figure S2, see the Supporting Information).

Nevertheless, ion exchange is a very versatile and effective tool for the treatment of aqueous hazardous wastes.⁶ The role of ion exchange in dye effluents treatment is to reduce the magnitude of hazardous load by converting them into a form in which they can be reused, leaving behind a less toxic substance in its place or to facilitate ultimate disposal by reducing the hydraulic flow of the stream bearing the toxic substance. Another significant feature of the ion exchange process is that it has the ability to separate as well as to concentrate pollutants.⁶

Ion exchange resins known as reactive polymers are highly ionic, covalently cross-linked, insoluble polyelectrolytes supplied usually as beads.^{7–9} Ion exchange resins have been classified on the basis of the charge of the exchangeable counterion (cation exchanger or anion exchanger) and the ionic strength of the bound ion (strong exchanger or weak exchanger). Thus, there are four primary types of ion exchange resins: (a) strong cation exchange resins, containing $-\text{SO}_3^-\text{H}^+$ groups or the corresponding salts, (b) weak cation exchange resins, containing $-\text{COO}^-\text{H}^+$ groups or the corresponding salts, (c) strong anion exchange resins of quaternary ammonium groups (type I resins containing $-\text{CH}_2\text{N}(\text{CH}_3)_3^+\text{Cl}^-$ groups and type II resins containing $-\text{CH}_2\text{N}(\text{CH}_3)_2(\text{CH}_2\text{CH}_2\text{OH})^+\text{Cl}^-$ groups), (d) weak anion exchange resins of primary ($-\text{NH}_2$), secondary ($=\text{NH}$), or tertiary-

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amine ($\equiv\text{N}$) functional groups in the chloride or hydroxide form.^{8,9}

The resin beads have either a dense internal structure with no discrete pores (gel resins, also called microporous) or a porous, multichannelled structure (macroporous or macroreticular resins). They are commonly prepared from styrene and various levels of the cross-linking agent-divinylbenzene, which controls the porosity of the particles. Popular ion exchangers available on the market are those of acrylic, epoxy-amine, and phenol-formaldehyde matrixes. The common choice is between styrene-divinylbenzene and acrylic-divinylbenzene copolymer. Disregarding structural features (gel or macroporous) for the time being, the acrylic matrix is particularly tough being more elastic than the more rigid styrene based copolymer. However, the elastic resilience of acrylic matrix could be of concern where the columns of resin operate under a high net compression force.

The internal structure of the resin beads, i.e., whether microporous (gel-type) or macroporous, is important in the selection of an ion exchanger. Macroporous resins, with their high effective surface area, facilitate the ion exchange process. Also, they give access to the exchange sites for larger ions, can be used with almost any solvent, irrespective of whether it is a good one for the un-cross-linked polymer, and take up the solvent with little or no change in volume. They make more rigid beads, facilitating the ease of removal from the reaction system. In the case of the microporous resins, since they have no discrete pores, solute ions diffuse through the particle to interact with the exchange sites. Despite diffusion limitations on the reaction rates, these resins offer certain advantages: they are less fragile, requiring less care in handling, and react faster in functionalization and application reactions as well as possess higher loading capacities.⁹

Taking into account high capacity and selectivity of ion exchange resins for different colors, they seem to be proper materials for dyes sorption from textile effluents. Applicability of the ion exchange resins such as Lewatit S6328A,¹⁰ Amberlite XAD-4 modified by calix[4]arene,¹¹ *p*-tert-butylcalix[4]arene based silica resin,¹² Amberlite IRA 67,¹³ Amberlite IRA 458,¹³ Amberlite IRA 958,^{14,15} Lewatit MonoPlus MP 62,¹⁶ and Lewatit MonoPlus MP 500¹⁷ in removal of Reactive Black 5 (RB5) and Acid Orange 7 (AO7) from aqueous solutions and wastewaters was confirmed in some papers. There is a lack of literature data on the Direct Blue 71 dye retention on the anion exchangers. 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.^{18–20} Dragan and Dinu²⁰ studied the interactions of some azo dyes such as Ponceau SS, Crocein Scarlet MOO, Congo Red, and Direct Blue 1, differing in either the position of sulfonic groups or the number of anionic groups, with quaternized poly(dimethylaminoethyl methacrylate) and stated that the number of sulfonic groups, position of the anionic charges, and the whole structure of the dye determined the most effective dye removal by the sorbent.²⁰ Wojaczyńska and Kolarz^{18,19} investigated the sorption behavior of different dyes such as Methyl Orange, Acid Orange 10, Acid Red 44, and Direct Blue 1 on the divinylbenzene weak base anion exchangers of mono- and diethanolamine functional groups and found that the copolymer gel heterogeneity has a marked effect on the degree of sorption and its course.¹⁹ With constant anion exchange capacity, the sorption properties decreased with an increase in the gel heterogeneity.¹⁸ The dyes

with a higher sulfonic group content were found to be sorbed mainly by the formation of aggregates in the anion exchanger whereas Direct Blue 1 dye because of large size has the tendency to form aggregates in the solution rather than in the resin.¹⁹

The major interest of this study was to investigate the sorption of three dyes of increasing molecular size such as Acid Orange 7 (AO7), Reactive Black 5 (RB5), and Direct Blue 71 (DB71) from aqueous solutions containing different auxiliaries and from wastewaters using the intermediate base anion exchanger Amberlite IRA 478RF of the acrylic gel structure.

2. MATERIALS, METHODS, AND CALCULATIONS

2.1. Chemicals. Three different dyes were used: Acid Orange 7 (C.I. No. 15510), Reactive Black 5 (C.I. No. 20505), and Direct Blue 71 (C.I. No. 34140). The molecular weights of AO7, RB5, and DB71 are equal to 350.32, 991.82, and 1029.88 g/mol, respectively. Molecular structures of the above-mentioned dyes are presented in Table S1 (see the Supporting Information). The dyes were purchased from Sigma-Aldrich (Germany) and used without further purification. These dyes were selected for the studies because they are extensively used in the textile industry. AO7 is applied to fibers such as silk, wool, and nylon using neutral to acid dye baths. Direct Blue 71 is used for cotton, paper, leather, wool, silk, and nylon dyeing. Reactive dyes, e.g., RB5 are by far the best choice for dyeing of cotton and other cellulose fibers. The stock solutions of the concentrations 10 000 mg/L were prepared in distilled water, and the working solutions were obtained by appropriate dilution.

Amberlite IRA 478RF is the anion exchange resin of the quaternary ammonium and tertiary amine functional groups incorporated in the cross-linked acrylic matrix. This anion exchanger of gel structure is produced by Dow Chemical Company (USA) as transparent white beads of harmonic mean size 0.78–0.98 mm in free base and chloride form. The total exchange capacity and the moisture holding capacity are ≥ 1.15 eq/L and 57–65%, respectively. The maximum operating temperature of the anion exchanger is 35 °C. Prior to use, Amberlite IRA 478RF was contacted with 1 M NaOH and 1 M HCl to remove organic and inorganic impurities and to convert the ion exchange sites to the chloride form. Then, it was washed several times with distilled water.

Sodium chloride, sulfate, and carbonate were purchased from POCh (Poland). The other chemicals used were produced by POCh (Poland) and were of analytical grade.

2.2. Batch and Column Tests. In the batch experiments, the dyes solutions (50 mL) were shaken with the dry anion exchanger (0.5 g) in conical flasks using a thermostated laboratory shaker Elphin (Poland) at 20 °C. The experiments were conducted in the two parallel series with the reproducibility of 5%. The amount of dye adsorbed after time t , q_t (mg/g), was calculated from eq 1:

$$q_t = \frac{(C_0 - C_t)}{w} \times V \quad (1)$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of dye at the time $t = 0$ and after time t , respectively, V (L) is the volume of solution, and w (g) is the mass of dry anion exchanger.

To test the influence of shaking speed on dyes removal, preliminary experiments were carried out by varying the

shaking speed from 140 to 200 cpm. The best results were obtained for the shaking speed of 180 cpm. Therefore, 180 cpm was used in all batch experiments.

To evaluate the kinetics of the sorption process, 50 mL solutions of 200 mg/L dyes concentration and 0.5 g of the anion exchanger samples were used. The shaking time was varied from 1 to 240 min, respectively (e.g., up to equilibrium). All the kinetic studies were carried out at the natural pHs (pH 4.98–5.83) of solutions (pH-meter; CX-742 Elmetron, Poland). The sorption kinetic parameters were calculated on the basis of the Lagergren pseudo first-order as well as Ho and McKay pseudo second-order kinetic equations:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (3)$$

where q_t and q_e (mg/g) are the amounts of the dye sorbed at time t and at equilibrium, k_1 (1/min) is the rate constant of the pseudo first-order sorption, and k_2 (g/mg min) is the pseudo second-order rate constant.^{21–23}

To investigate the phase contact time impact on the color removal from effluents, the acid, reactive, or direct wastewaters were prepared.^{24,25} The composition of the acid, reactive, or direct wastewaters is reported in Table S2 (see the Supporting Information). In this experiment, 0.5 g of the anion exchanger was shaken from 1 to 96 h with 50 mL of the model wastewater. Absorption spectra were recorded after the predetermined time interval using a spectrophotometer Specord M-42 (Carl Zeiss, Germany). The acid wastewater sample at 0 h was 5 times diluted; the other acid wastewaters after sorption were recorded without dilution. All reactive and direct wastewaters were recorded after 50-fold dilution.

Sorption isotherm studies were carried out analogously using dyes solutions of the increasing initial concentration at 20 °C for 24 h. Amount of dye retained by the anion exchanger at equilibrium q_e (mg/g) was related to the dye equilibrium concentration C_e (mg/L) using linear forms of the Langmuir and Freundlich isotherm models:²⁶

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (4)$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (5)$$

where Q_0 (mg/g) is the Langmuir monolayer sorption capacity, b (L/mg) 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 effects of salts addition on dyes uptake at equilibrium were studied by shaking the anion exchanger (0.5 g) with the 200 mg/L dyes solution containing 5–100 g/L of different salts (Na_2SO_4 , Na_2CO_3 , NaCl). The dyes concentration after the sorption was measured spectrophotometrically at the maximum absorbance wavelengths depend on the system.

Regeneration tests for the anion exchange resin were conducted with different regeneration agents (1 M HCl, 1 M NaOH, 1 M KSCN, 1 M NaCl, 1 M Na_2SO_4 , 1 M Na_2CO_3 , 90% methanol, 1 M KSCN or 1 M NaOH or 1 M HCl in 90% methanol). The loaded resin containing 20 mg/g dye was put into flasks in contact with 50 mL of different eluting agents.

The flasks were agitated for 3 h, and the dyes concentrations in the solution were determined at the maximum absorbance wavelength in order to calculate the desorption percentage (%).

The column sorption experiments were conducted using 10 mL of the swollen anion exchanger Amberlite IRA 478RF packed in glass columns (the inner diameter, 10 mm; the length, 25 cm). The feed solutions of the dyes of 200 mg/L initial concentration were passed continuously downward through the resin beads keeping the flow rate at 0.6 mL/min. The effluents were collected in fractions in which dye contents were determined by the UV-vis method at the maximum wavelengths. The sorption column parameters, i.e., the weight (K_d) and bed (K'_d) distribution coefficients as well as the working ion exchange capacity (C_w) were calculated according to eqs 6–8:²⁷

$$K_d = \frac{U - U_0 - v}{w} \quad (6)$$

$$K'_d = \frac{U - U_0 - v}{v_i} \quad (7)$$

$$C_w = \frac{V_b C_0}{v_i} \quad (8)$$

where U (mL) is the effluent volume at $C = C_0/2$, U_0 (mL) is the dead volume in the column (liquid volume in the column between the bottom edge of anion exchanger bed and the outlet), v (mL) is the void (interparticle) anion exchanger bed volume (which amounts to ca. 0.4 of the bed volume), w (g) is the dry anion exchanger mass, v_i (mL) is the volume of water swollen anion exchanger, V_b (mL) is the effluent volume to break point, and C_0 (mg/L) is the initial dyes concentration.

3. RESULTS AND DISCUSSION

3.1. Comparison of Kinetic Models. Figure 1 shows the effect of phase contact time on the amount of dye uptake by the intermediate base anion exchanger Amberlite IRA 478RF from the solutions of 200 mg/L initial concentration. It can be observed that the amount of dye uptake increased with the contact time, and at some point in time, it reaches an almost

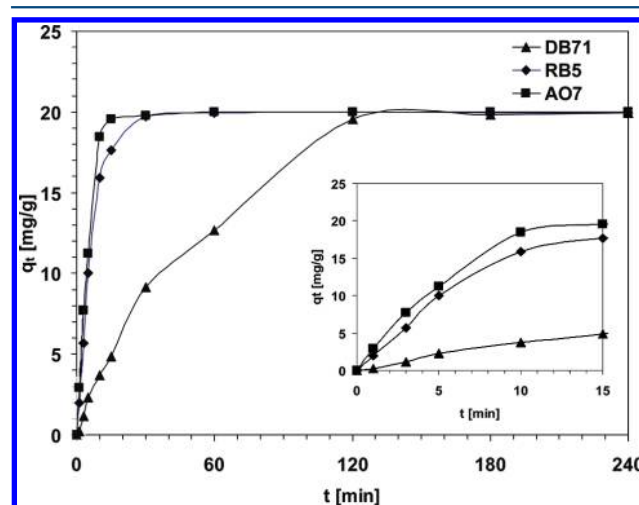


Figure 1. Kinetic curves for acid (AO7), reactive (RB5), and direct (DB71) dyes sorption on Amberlite IRA 478RF (conditions: initial dyes concentration, 200 mg/L; volume, 50 mL; sorbent mass, 0.5 g; agitation speed, 180 cpm; temperature, 20 °C).

Table 1. Comparison of Kinetic Parameters for the Acid, Reactive, and Direct Dyes Sorption on Amberlite IRA 478RF^a

dye	q_{exp} [mg/g]	parameters			
		PFO		PSO	
Acid Orange 7	20.0	q_e [mg/g]	26.8	q_e [mg/g]	20.4
		k_1 [1/min]	0.274	k_2 [g/mg min]	0.017
		R^2	0.968	R^2	0.999
Reactive Black 5	20.0	q_e [mg/g]	21.2	q_e [mg/g]	20.7
		k_1 [1/min]	0.151	k_2 [g/mg min]	0.010
		R^2	0.991	R^2	0.998
Direct Blue 71	20.0	q_e [mg/g]	19.8	q_e [mg/g]	29.9
		k_1 [1/min]	0.019	k_2 [g/mg min]	0.0004
		R^2	0.981	R^2	0.905

^aConditions: initial dyes concentration, 200 mg/L; volume, 50 mL; sorbent mass, 0.5 g; agitation speed, 180 cpm; temperature, 20 °C.

constant value where the amount of dye being removed from the aqueous solution onto the anion exchanger is in a state of dynamic equilibrium with the amount of dye desorbed from the anion exchanger. The saturation of the functional groups of Amberlite IRA 478RF was reached after 40 min of phase contact time for AO7 and RB5. The amount of DB71 adsorbed at equilibrium was equal to 20 mg/g after 180 min of phase contact time. This can be explained not only by the dyes molecule structure, i.e., number and position of chromophores and auxochromes, but also by their size. Acid Orange 7 and Reactive Black 5 have a smaller molar weight than Direct Blue 71.

In the present investigation, the Lagergren pseudo first-order equation (PFO) as well as the Ho and McKay pseudo second-order equation (PSO) were applied to analyze the kinetic data for the sorption of Acid Orange 7, Reactive Black 5, and Direct Blue 71 from the aqueous solutions of the initial concentration of 200 mg/L on the anion exchanger. The PFO and PSO parameters were calculated from the slopes and intercepts of the plots $\log(q_e - q_t)$ vs t and t/q_t vs t , respectively, and are given in Table 1. Analyzing the values listed in Table 1, it can be stated that the pseudo second-order kinetics was found to be closer to the experimental data in the whole sorption period in the systems of 200 mg/L AO7 and 200 mg/L RB5. The calculated equilibrium capacities from the PSO equation were higher than from the PFO kinetic equation for these dyes. For AO7 and RB5, they were found to be 20.4 and 20.7 mg/g, respectively, and were in good agreement with the experimental values. The determination coefficients values (R^2) for the acid and reactive dyes sorption on the anion exchanger were equal to 0.999 and 0.998, respectively, and confirmed the applicability of the Ho and McKay equation. These results are in agreement with the observation of Zhu and Ma²⁸ concerning AO7 removal from wastewaters on bentonite and of Sarkar et al.²⁹ for AO7 sorption on the surfactants modified palygorskite. Similar observations were made for RB5 retention on the magnetic chitosan resin³⁰ and on glutaraldehyde cross-linked chitosan³¹ as well as on the acid treated biomass of brown seaweed *Laminaria* sp.³²

It was observed that, for the DB71 dye, the pseudo first-order expression better predicts the sorption kinetics than the pseudo second-order one. The closeness of the pseudo first-order equilibrium capacity to the experimentally determined equilibrium capacity indicates the usage of the pseudo first-order model to describe the kinetics of Direct Blue 71 uptake by Amberlite IRA 478RF. Several authors have also shown the

applicability of the PFO kinetics in describing the sorption of dyes onto anion exchangers^{18,19} and different adsorbents.^{33–40} Numerous applications of the Lagergren equation in sorption of dyes and inorganic ions have also been reported in the paper by Ho and McKay.²³

3.2. Color Removal of Acid, Reactive, and Direct Wastewaters by the Adsorption on Amberlite IRA 478RF. Figure 2 presents the absorbance spectra of the acid, reactive, and direct wastewaters containing AO7, RB5, and DB71 before and after purification using the intermediate base anion exchanger Amberlite IRA 478RF as well as the photo images of collected samples after different phase contact times. The anion exchanger proves to be capable of color removal for the acid wastewater; after 72 h, 98% color reduction was observed. Amberlite IRA 478RF was ineffective in purification of the reactive wastewater; the absorbance value at the maximum wavelength decreased from 0.9032 at 0 h to 0.8716 at 96 h, and further increase in the phase contact time did not improve the color reduction. The direct wastewater treatment using the intermediate base anion exchanger occurred with 69.5% yield after 96 h.

The above data concerning the removal of color attained for the wastewaters of different compositions (Table S1, see the Supporting Information) suggest that Amberlite IRA 478RF can be a promising sorbent for real acid textile effluents treatment.

3.3. Sorption Isotherm Studies. The analysis of the equilibrium data based on mathematical equations is carried out in order to compare different ion exchangers and sorbents used in different treatment modes of water purification. The Langmuir and Freundlich isotherms are the most commonly used to describe the sorption characteristics of the sorbent to this end. A basic assumption of the Langmuir theory is that sorption takes place in specific sites within the adsorbent. It is assumed that once a dye molecule occupies a site, no further adsorption can take place on that site. Theoretically, a saturation value is reached beyond which no further sorption can proceed. The Freundlich model is applied for the nonideal sorption on the heterogeneous surface as well as for the multilayer sorption.

In the present paper, the sorption parameters of AO7, RB5, and DB71 on Amberlite IRA 478RF (Table 2) are satisfactorily described by the Langmuir model. The values of the R^2 are regarded as a measure of the good fit of the experimental data to the isotherm model. These values for AO7, RB5, and DB71 dye are equal to 0.999, 0.999, and 0.974, respectively, and

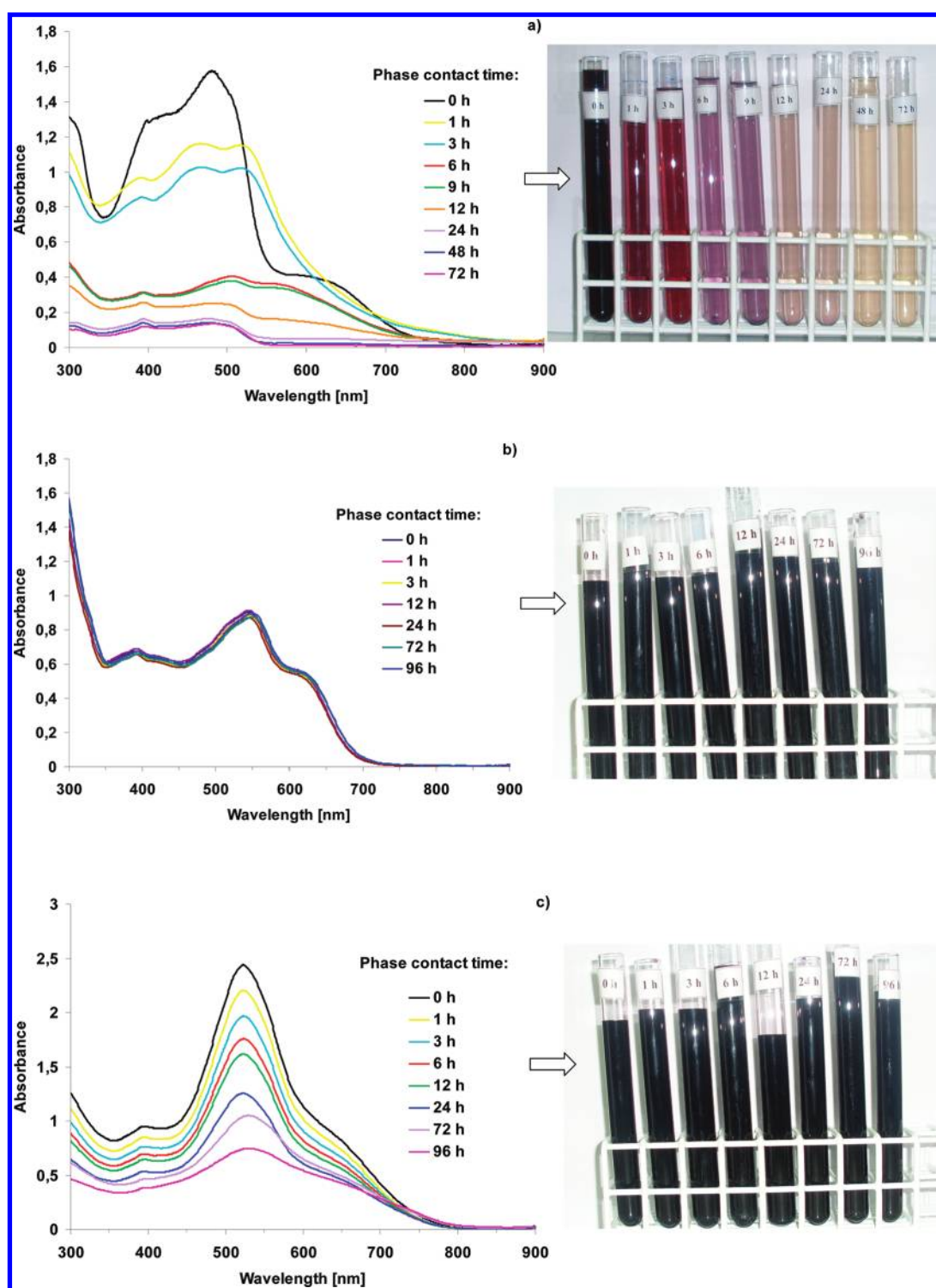


Figure 2. Absorbance spectra of acid (a), reactive (b), and direct (c) wastewaters purified by means of Amberlite IRA 478RF and photo images of these samples (conditions: for wastewaters composition, see Table S2 (the Supporting Information); volume, 50 mL; sorbent mass, 0.5 g; agitation speed, 180 cpm; temperature, 20 °C; phase contact time, 1–96 h).

strongly support the fact that the dye-anion exchanger adsorption closely follows the Langmuir model of adsorption. The Langmuir maximum sorption capacities of Amberlite IRA 478RF were 1279.2 mg/g for AO7, 150.4 mg/g for RB5, and 41.8 mg/g for DB71. On the basis of these values, the affinity series of the dyes of increasing molecules size toward the intermediate base anion exchanger can be presented as follows: Acid Orange 7 > Reactive Black 5 > Direct Blue 71. The affinity

of such species for a gel acrylic resin is influenced not only by ion and its size (ionic mass) but also by resin structure. It is believed that the larger organic anion the greater seems to be the affinity for an anion exchange resin due to van der Waals type intermolecular forces between the hydrocarbon structures of the organic ion and resin ("like attracts like"). In the case of large dye anions, the above argument seems to be valid, because

Table 2. Values of Isotherm Parameters for the Acid, Reactive, and Direct Dyes Sorption on the Intermediate Base Anion Exchanger Amberlite IRA 478RF^a

dye	isotherm parameters			
	Langmuir		Freundlich	
Acid Orange 7	Q_0 [mg/g]	1279.2	K_F [mg/g]	213.0
	b [L/mg]	0.166	$1/n$	0.339
	R^2	0.999	R^2	0.642
Reactive Black 5	Q_0 [mg/g]	150.4	K_F [mg/g]	93.0
	b [L/mg]	0.057	$1/n$	0.062
	R^2	0.999	R^2	0.906
Direct Blue 71	Q_0 [mg/g]	41.8	K_F [mg/g]	4.67
	b [L/mg]	0.0047	$1/n$	0.279
	R^2	0.974	R^2	0.969

^aConditions: phase contact time, 24 h; volume, 50 mL; sorbent mass, 0.5 g; agitation speed, 180 rpm; temperature, 20 °C.

if the dye anion is too large it is excluded from the resin structure ("sieve effect").

The second Langmuir constant b reflects the affinity of sorbent for the sorbate. The highest value of b equal to 0.166 was determined for the AO7 dye and implied strong bonding of the dye to this anion exchanger. For the RB5 and DB71 dyes, the b values were found to be 0.057 and 0.0047, respectively. To determine if the adsorption process is favorable or unfavorable for the Langmuir type sorption process, the dimensionless constant R_L was calculated.¹² The value of $R_L > 1$ indicates unfavorable, $R_L = 1$ indicates linear, $0 < R_L < 1$ is favorable, or $R_L = 0$ is irreversible sorption. The R_L values for the AO7, RB5, and DB71 dyes on Amberlite IRA 478RF were found to be 0.0004, 0.003, and 0.01, respectively.

A wide range of low cost sorbents used for purification of the textile effluents containing AO7 and RB5 was investigated, e.g., deoiled soya, brown coal fly ash, spruce wood shavings, activated carbons, and high lime fly ash.^{41–43} These materials are prepared from the substances requiring storage or utilization; however, they are characterized by low capacity toward these dyes compared with the anion exchangers. Depending on temperature from 1211 to 1368 mg of AO7 per 1 g of the strongly basic anion exchanger, Amberlite IRA 458 of polyacrylic matrix can be retained.¹³ Macroporous anion exchanger of the quaternary ammonium functionalities Lewatit MonoPlus MP 500 was used in treatment of wastewater contaminated with AO7 dye; the increase of the Langmuir adsorption capacity from 979.0 to 1004.4 mg/g with the temperature rise from 25 to 45 °C was observed.¹⁷ Eren and Acar⁴⁴ applied high lime fly ash for RB5 removal from aqueous solutions and determined the equilibrium capacity as 7.2 mg/g. Al-Degs et al.^{45–47} investigated the activated carbon Filtrasorb 400 for RB5 removal by the batch and column methods; the monolayer adsorption capacity for RB5 was equal to 278 mg/g. The Q_0 values cited in the paper by Kamboh et al.^{11,12} for the *p*-tert-butyl-calix[4]arene and *p*-tert-butyl-calix[8]arene based silica resins demonstrates that these materials have better sorption properties for RB5 than the Amberlite IRA 478RF resin.

To study the applicability of the Freundlich isotherm for the dyes adsorption onto Amberlite IRA 478RF, the linear plots $\log q_e$ versus $\log C_e$ were drawn. The values of K_F , $1/n$, and R^2 are shown in Table 2. The determination coefficients (0.642 for

AO7, 0.906 for RB5, and 0.969 for DB71) showed that the Freundlich model fitted worse to the experimental data than the Langmuir one. The $1/n$ values were lower than 1, indicating that the dyes were favorably adsorbed (Table 2).

3.3.1. Effect of Salts Concentration. The textile effluents contain many chemical substances arising from desizing, dyeing, printing, and finishing processes. The quality of textile wastewaters is variable with time and depends on the kind of process that generates them.¹⁴ According to Hessel et al.,³ a large percentage of pollution generated by textile industry activities in Europe can be attributed to such substances as salts (200 000–250 000 tons/year). Acid dyes color in the bath of pH 4.5–5 acidified with acetic acid. In the case of acid badly equalizing dyes, i.e., providing nonuniform dyeing, the electrolyte (usually Na_2SO_4) in the amount of 10–20% in relation to the fiber is added. The condition of reactive dye reaction with the fiber is the alkaline medium causing formation of the anions $\text{cel}-\text{O}^-$ from cellulose (where cel is the cellulose) as well as transforming dyes of the RB5 type into the compounds with the active vinyl group. Additionally, their substantivity increases by the addition of the electrolyte in the Na_2SO_4 form into the bath. Direct dyes of flat structure and large molecular mass tend to form associated ions (colloidal electrolytes). Alkalizing of bath promotes decomposition of associated molecules; therefore, Na_2CO_3 is often added to the dyeing bath. Because of large negative charge of direct dyes anions (2–4 sulfone groups) in the aqueous phase they are repelled by the surface of fibers of the negative electrokinetic potential ζ . Not only heating the bath but also the addition of the electrolytes such as Na_2SO_4 or NaCl causes decreases in the negative potential ζ , thus facilitating the dye anion access to the fiber surface. Therefore, it is useful to investigate the effect of various salt concentrations on the dyes adsorption behavior on the adsorbent. The competition of NaCl , Na_2CO_3 , and Na_2SO_4 salts on AO7, RB5, and DB71 adsorption on Amberlite IRA 478RF was studied for the initial dyes concentration of 200 mg/L (Figure 3). The results indicate that the presence of Na_2CO_3 and Na_2SO_4 in the whole examined concentration of 5–50 g/L does not play a meaningful role in the AO7 dye adsorption. It is also evident that CO_3^{2-} and SO_4^{2-} ions slightly compete with the SO_3^- group of the AO7 dye for ion exchange sites. The decrease in the dye amount adsorbed at the equilibrium was observed from 20 to 19.1 mg/g and from 20 to 18.6 mg/g with the increasing amounts of Na_2CO_3 and Na_2SO_4 , respectively. The addition of these salts in the amounts of 75 and 100 g/L to the AO7 solution of 200 mg/L initial concentration caused dye precipitation. The amount of AO7 dye sorbed at equilibrium in the presence of sodium chloride dropped from 20 to 15.4 mg/g with the NaCl increase in the system. Negligible effects of NaCl and CaCl_2 on AO7 uptake by oxihumolite and ash fly were observed by Janoš et al.^{43,48} Greluk and Hubicki^{13,14} observed that the large amounts of electrolytes such as Na_2SO_4 , Na_2HPO_4 , and NaH_2PO_4 do not obstruct AO7 removal by the weakly basic gel anion exchanger of the tertiary amine functional groups (Amberlite IRA 67) as well as by the strongly basic anion exchanger of the quaternary ammonium functionalities (Amberlite IRA 958).

Reactive Black 5 retention by Amberlite IRA 478RF was not affected in the presence of Na_2CO_3 and Na_2SO_4 in the range of 25–100 g/L. The presence of NaCl in the solution in the range of 25–100 g/L caused a significant decrease in the amount of RB5 retained by the anion exchanger; q_e values were found to

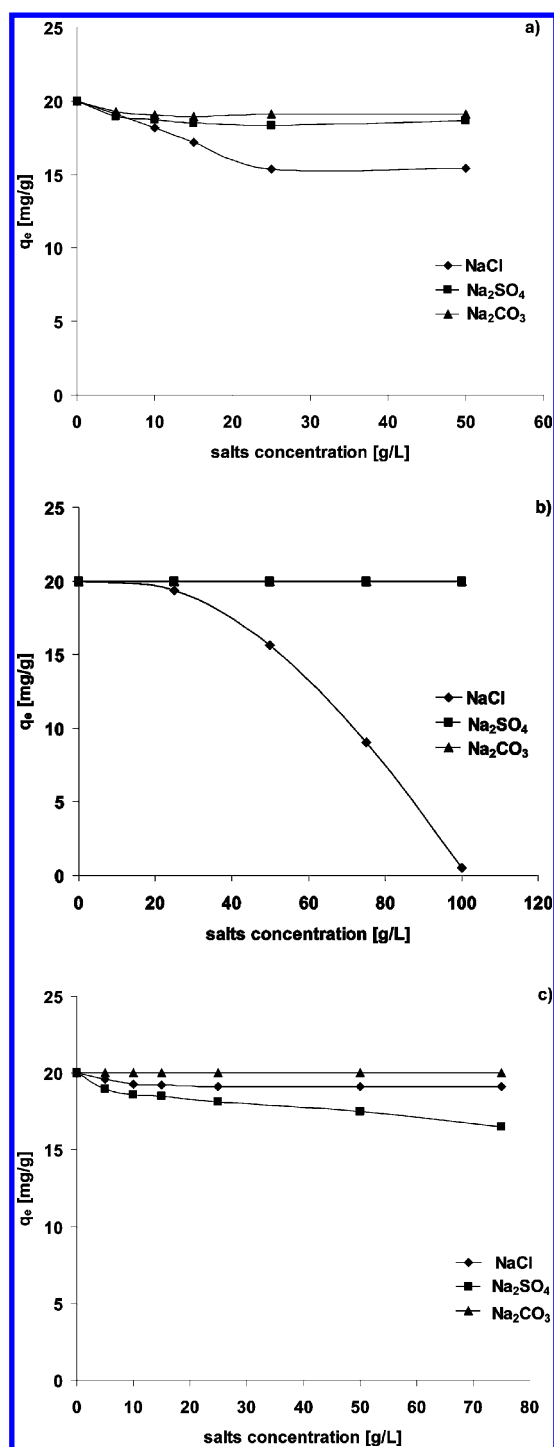


Figure 3. Effect of salts addition on AO7 (a), RB5 (b), and DB71 (c) dyes sorption by Amberlite IRA 478RF (conditions: initial dyes concentration, 200 mg/L; volume, 50 mL; sorbent mass, 0.5 g; agitation speed, 180 rpm; temperature, 20 °C).

be from 20 to 0.5 mg/g. The affinity of large organic anions for the resin is influenced not only by the ion charge but also by the structure of the ion and its size. Kamboh et al. observed that retention of RB5 on the resin obtained through immobilization of *p*-tert-butylcalix[8]arene onto silica increased with the increase of NaCl up to 11.7 g/L; further increase of NaCl to the value of 35 g/L does not influence the sorption.¹² It was reported previously¹⁶ that, in the case of RB5 adsorption on the polyacrylic Amberlite IRA 67, the effect of salt addition was

meaningful. The retention of RB5 by Amberlite IRA 67 drops when the system contains 5 and 10 g/L of Na_2CO_3 , and then, a small increase of q_e values was observed with the increasing amount of carbonate up to 20 g/L. Increasing amount of Na_2SO_4 in the system, the increase of RB5 uptake from 50.9 to 60 mg/g was found. The sorption enhancement is well documented for certain classes of chemicals, especially for low-polarity organic compounds, where the salting out effect reduces solubility of substances in the aqueous phase and promotes their sorption onto the hydrophobic part of sorbent.¹⁶ Karcher et al.^{10,49} observed that RB5 sorption on the weakly basic anion exchanger MP 62 and the strongly basic anion exchanger Lewatit S 6328A, both of macroporous structure, was not influenced by the presence of electrolytes. It leads to the conclusion that not only the type of functional groups of the resin but also matrix structure and composition play an important role in the dyes solution treatment.

Direct Blue 71 sorption on Amberlite IRA 478RF was not influenced by the presence of NaCl and Na_2CO_3 . Na_2SO_4 effect on the DB71 removal was rather negligible. Similar observations were made for the Direct Red 75 retention by the weakly and strongly basic anion exchangers of gel structure and polyacrylic matrix in aqueous solutions and wastewaters.⁵⁰ It is a very important feature for potential application of the anion exchanger for real wastewaters treatment.

4. DESORPTION STUDIES

One of the important characteristics of an adsorbent is its ability to be regenerated. Desorption studies help to evaluate the nature of the adsorption process. In this paper, desorption experiments were performed in one cycle using different regenerating agents: 1 M KSCN, 1 M NaCl, 1 M Na_2SO_4 , 1 M Na_2CO_3 , 1 M NaOH, and 1 M HCl. The aqueous salt solutions such as 1 M KSCN, 1 M NaCl, 1 M Na_2CO_3 , and 1 M Na_2SO_4 were ineffective for the dyes removal from the resin phase; desorption percent does not exceed 10%. Considering that the dyes retention by Amberlite IRA 478RF may be not only by ion exchanging (in the aqueous solution, the dyes under discussion are first dissolved and the sulfonate groups of the dyes are dissociated and converted to dye anions) as presented schematically (below) but also by the hydrophobic interaction or hydrogen bonding, methanol was chosen for breaking these nonspecific interactions. Regeneration of Amberlite IRA 478RF by 10–90% methanol solutions was completely unaffected confirming that strong electrostatic attraction between the dyes and the anion exchange matrix is a predominant mechanism of adsorption.



As presented in Figure 4, the mixtures of 90% methanol with 1 M KSCN, 1 M HCl, or 1 M NaOH improved the dye desorption performance in most cases. The highest desorption for AO7 dye was found to be 97%, 85%, and 60% using 1 M KSCN in 90% methanol, 1 M HCl in 90% methanol, and 1 M NaOH in 90% methanol, respectively. The lowest desorption ranging from 9% to 17% was obtained for RB5 dye. Desorption of DB71 from Amberlite IRA 478RF in the amount of ~45%

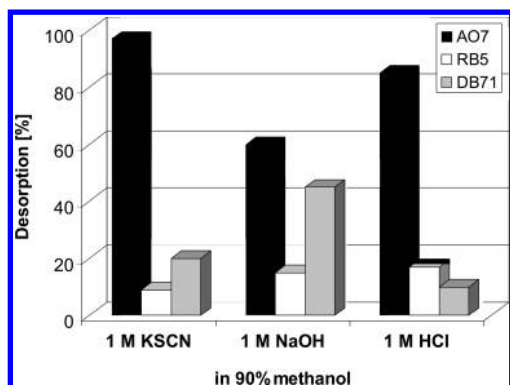


Figure 4. Desorption of AO7, RB5, and DB71 from Amberlite IRA 478RF by the batch method (conditions: dyes concentration in the resin phase, 20 mg/g; eluate volume, 50 mL; sorbent mass, 0.5 g; agitation speed, 180 rpm; time, 3 h; temperature, 20 °C).

using 1 M NaOH in 90% methanol solution shows that this eluent is effective for this process. Greluk and Hubicki,¹⁴ Karcher et al.,^{10,49} Wawrzekiewicz^{16,50} and Liu et al.⁵¹ confirmed previously that regeneration of weakly and strongly basic anion exchangers loaded with the acid, reactive, and direct dyes was problematic and required usage of aggressive regenerants.

5. COLUMN STUDIES

It should be kept in mind that the presented models of the sorption isotherms have very little theoretical justification and are based on ideal characteristics such as homogeneous sorbent surface, electroneutrality, complete reversible sorption, and accessibility of the whole surface for sorption. Therefore, the sorption process of acid, reactive, and direct dyes was also investigated by the dynamic method. In Figure 5, the

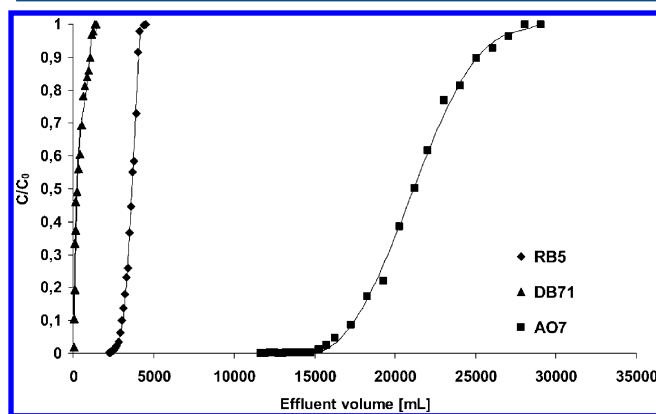


Figure 5. Breakthrough curves determined for AO7, RB5, or DB71 on Amberlite IRA 478RF (conditions: initial dyes concentration, 200 mg/L; volume of swollen resin, 10 mL; speed, 0.6 cm³/min; temperature, 20 °C).

breakthrough curves of AO7, RB5, and DB71 on the intermediate base anion exchanger Amberlite IRA 478RF are presented. The comparison of the weight (D_w) and bed (D_b) distribution coefficients as well as the working (C_w) ion exchange capacities is presented in Table 3.

6. CONCLUSIONS

An adsorption process of AO7, RB5, and DB71 was performed from aqueous solutions and wastewaters using the intermediate

Table 3. Breakthrough Curve Parameters for the Acid, Reactive, and Direct Dyes Sorption on Amberlite IRA 478RF^a

dye	D_w	D_b	C_w [g/L]
Acid Orange 7	7925.9	2119.4	228
Reactive Black 5	1359.0	363.4	42
Direct Blue 71	72.6	19.4	0.4

^aConditions: initial dyes concentration, 200 mg/L; volume of swollen resin, 10 mL; speed, 0.6 cm³/min; temperature, 20 °C.

base anion exchanger. The studies on the sorption of these dyes on the ion exchanger showed that the size of the sorbate molecules has a considerable effect on the degree of sorption. The affinity series of the dyes of increasing molecular size for the intermediate base anion exchanger can be presented as follows: Acid Orange 7 > Reactive Black 5 > Direct Blue 71. It seems that the gel anion exchanger of polyacrylic matrix Amberlite IRA 478RF can be a promising sorbent for the AO7 dye removal from the aqueous solution because of high values of the Langmuir monolayer capacity (1279.2 mg/g) and the working ion exchange capacity (228 g/L). The results indicate that the presence of Na₂CO₃, Na₂SO₄, and NaCl does not play a meaningful role in the AO7 dye adsorption. Regeneration of Amberlite IRA 478RF loaded with AO7 of 97%, 85%, and 60% yields was obtained using 1 M KSCN in 90% methanol, 1 M HCl in 90% methanol, and 1 M NaOH in 90% methanol, respectively. Very good purification of the acid wastewater containing AO7 dye confirmed that Amberlite IRA 478RF is a suitable sorbent for its removal.

■ ASSOCIATED CONTENT

Supporting Information

Figures S1 and S2 as well as Tables S1 and 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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