

Received July 23, 2019; reviewed; accepted October 4, 2019

Removal of acid, direct and reactive dyes on the polyacrylic anion exchanger

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Abstract: In the present study the polyacrylic anion exchanger Amberlite IRA 478 (IRA 478) was used for removal of textile dyes such as C.I. Acid Red 18 (AR18), C.I. Reactive Blue 21 (RB21) and C.I. Direct Yellow 142 (DY142) from aqueous solutions. Sorption of the above-mentioned dyes was carried out by the static and dynamic methods. The obtained results were analyzed by determining the adsorption isotherm parameters using the Langmuir and Freundlich models. Kinetic parameters of dyes sorption were calculated from the pseudo-first order, pseudo-second order and intraparticle diffusion models. The monolayer sorption capacities of IRA 478 determined from the Langmuir isotherm were found to be 1098.5 mg/g for AR18 ($R^2=0.994$), 46.8 mg/g for DY142 ($R^2=0.820$) and 23.5 mg/g for RB21 ($R^2=0.987$). Kinetic studies revealed that effectiveness of AR18, DY142 and RB21 uptake increases with increasing phase contact time and initial dyes concentration. The kinetics of the dyes sorption process on the anion exchanger is best described by the pseudo-second order model (PSO) due to the high values of the determination coefficients R^2 (linearity condition of the plot t/q_t vs. t). The rate constants of the pseudo-second order kinetics k_2 are reduced from 0.1001 to 0.0008 g/mg-min for AR18, from 0.0147 to 0.0112 g/mg-min for DY142 and 0.0489 to 0.0072 g/mg-min for RB21 with an increase of initial concentration of dyes. The presence of salts and surfactants had an impact on the retention of direct and reactive dyes.

Keywords: dye removal, polyacrylic anion exchanger, reactive dye, direct dye, acidic dye

1. Introduction

Effective methods used to remove dyes are chemical and physical processes, among them: oxidation and electrochemical, coagulation, membrane processes, flocculation, ion exchange and adsorption. The effectiveness of the adsorption process depends on the conditions in which the process is carried out (Koyuncu, 2012; Koyuncu and Kul, 2014). Over the past few years, the search for new and cheap sorbents has become an important and widely analysed issue by research centres. The essence of the problem is the replacement of expensive traditional sorbents with cheap ones, which are often produced from waste materials (low-cost). Some of these sorbents, formed from waste substances that no longer find any use, include rice hulls, peels, citrus fruit stones, agricultural waste, fly ash, peat, slag and many others (Rafatullah et al., 2010; Heibati et al., 2014). Examples of such sorbents together with determined sorption capacities in relation to dyes are presented in Table 1. They are characterized by quite low sorption capacity in comparison with the anion exchangers or activated carbon. Among the wide group of sorbents used for dyes removal from wastewaters anions exchangers resins are very popular. Anions exchangers were synthesized at the end of the 1940s and their intensive development results from their use for the purification and production of water for industrial and food purposes, catalysing reactions in organic synthesis, biotechnology and biochemistry, industrial purification processes, food and medicine production, and environmental protection. Anions exchangers as reactive polymers are macromolecular compounds, insoluble in water and organic solvents, constructed from a spatially cross-linked porous matrix containing reactive functional groups (Kociołek-Balawajder and Surowiec,

2006; Wołowicz, 2015). These groups have ion-exchange (anion-exchange or cation-exchange), oxidizing, reducing or complex-forming properties. They may have the ability to react with different type with organic and inorganic compounds.

Table 1. List of low-cost sorbents used to remove dyes

Sorbents	Dyes	Results	Ref.
Rice bran/rice husks	C.I. Reactive Blue 4	- sorption capacity 151.3 mg/g (T=333K) - change of pH 2-9 caused a decrease in sorption capacity - as the temperature increased, the amount of adsorbed dye increased	(Hong and Wang, 2017)
	C.I. Reactive Orange 16	- sorption capacity 60.24 mg/g - optimum pH 4-6	(Ong and Lee, 2007)
Wheat husk	C.I. Direct Blue 71	- sorption capacity 46.30 mg/g (T=293K) - the increase in temperature caused the increase in sorption capacity - change of pH 2-7 resulted in an increase in biosorption efficiency	(Bulut et al., 2007)
Orange peel	C.I. Acid Violet 17	- sorption capacity 19.88 mg/g - maximum dye removal at pH 2	(Sivaraj et al., 2001)
Garlic straw	C.I. Direct Red 12B	- sorption capacity 37.96 mg/g (T=328K) - dye sorption decreased with increasing pH, optimum pH 2	(Asfaram et al., 2014)
Papaya seeds		- sorption capacity 555.6 mg/g (T=303K) - change of pH 3-10 caused an increase in sorption capacity	(Hameed, 2009)
Oil palm biomass		- sorption capacity 277.78 mg/g (T=303K)	(Ahmad et al., 2011)
Alkaline treated timber sawdust	C.I. Basic Blue 9	- sorption capacity 1928.31 mg/g	(Ahmad et al., 2015)
Dried prickly pear cactus		- sorption capacity 189.83 mg/g	
Chitosan modification by pyromelliticdi-anhydride		- sorption capacity 935.0 mg/g	(Vakili et al., 2014)
Palm-based adsorbents		- sorption capacity 240 mg/g	(Ahmad et al., 2012)

At the moment, anion exchangers are quite popular adsorbents of various types of pollutions. The role of anion exchangers in wastewater treatment is to reduce the amount of pollutants emitted to the environment by converting them into a less toxic form or finally removing them. Another important feature of the ion exchange process is that it has the ability for both separate and concentrate contaminants. Polyacrylic resins, not only microporous but also macroporous, are very popular and are characterized by better hydrophilic properties as well as higher sorption capacity compared to polystyrene or phenol-formaldehyde resins (Fig. 1). What's more, they are very flexible which enables efficient use of all ion exchange sites. They are particularly recommended for removing organic impurities of various types due to the presence of a carbonyl group and the ability to form hydrogen bonds. Resins, among others polyacrylic, were used by Shuang et al. (2015) to remove humic acid. The sorption capacities were found to be in the range of 385.5–616.6 mg/g depending on the temperature. Cabrera and Fernandez-Lahore (2006, 2007) used weakly basic anion exchangers of different structures: gel (Amberlite IRA 67) and macroporous (Amberlite IRA 96) to remove cochineal red A from aqueous solutions. Their research proved that the polyacrylic Amberlite IRA 67 has a higher sorption capacity

compared to the polystyrene Amberlite IRA 96. In addition, polyacrylic sorbents can be used to remove metal ions. Xiao et al. (2016) used four polyacrylic anion exchange resins (D730, D314, 312 and 213) with various functional groups to remove Cr(VI). Functional groups had a significant effect on exchangeability, adsorption rate, regeneration efficiency and oxidative stability for Cr(VI).

Anion exchangers are characterized by high sorption efficiency, selectivity as well as a well-developed specific surface, thanks to which they are widely used in the sorption process of various dyes as well as organic and inorganic compounds from aqueous solutions. In accordance with the above, the aim of the work was to evaluate the effectiveness of the medium-basic Amberlite IRA 478 in the sorption process of C.I. Acid Red 18, C.I. Direct Yellow 142 and C.I. Reactive Blue 21.

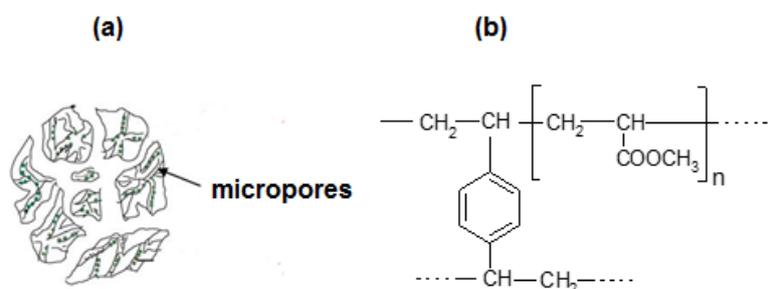


Fig. 1. Resin structure (a) and polyacrylic matrix (b)

2. Materials and methods

Amberlite IRA 478 is the polyacrylic anion exchanger whose physicochemical properties are shown in Fig. 2. The sorbent used in the study was washed with 1 M HCl and distilled water to remove impurities and change the ionic form to chloride one. It was then dried at room temperature to a constant weight. Sodium chloride, sulphate and carbonate as well as sodium hydroxide and hydrochloric acid were purchased from POCh (Poland). The anionic surfactant sodium dodecyl sulfate (SDS) and the non-ionic surfactant 4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol (Triton X-100) were purchased from Sigma-Aldrich (Germany). All chemicals were used as research chemicals.

The initial aqueous solutions of three textile dyes - C.I. Acid Red 18, C.I. Reactive Blue 21 and C.I. Direct Yellow 142 (Sigma-Aldrich, Germany), at a specified concentration, were prepared in a 1 dm³ volumetric flask into which a weighed quantity of dye was introduced, and then the flask was made up to the mark with distilled water. Physicochemical properties and structures of the used dyes are shown in Fig. 3.

2.1. Equilibrium studies

The weighted amount of dry anion exchanger (0.5 g) was put into a 100 cm³ conical flask and filled with 50 cm³ of dye solution. Conical flasks were mechanically shaken (Elphin + 358S, Poland) and at 180 cpm at room temperature for 24 hours. After this time the adsorbent was separated from the adsorbate by decanting. Concentration of dyes in solution before and after sorption was measured spectrophotometrically (Cary 60, U.S.A) at maximum wavelength, i.e. 507 nm for AR18, 663 nm for RB21 and 400 nm for DY142. The amount of adsorbed dye in equilibrium q_e (mg/g) was calculated from the formula:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where: C_0 - output concentration of dye (mg/dm³), C_e - equilibrium concentration of dye (mg/dm³), V - volume of the solution (dm³), m - mass of resin (g).

In addition, the adsorption isotherms were determined using the Langmuir (Hammed and El-Khaiary, 2008) and Freundlich models (Freundlich, 1906) (Table 2).

The attenuated total reflection (ATR) was recorded using infrared Fourier transform spectroscopy on a spectrometer Cary 630 (USA) equipped with a diamond crystal, in order to examine retention mechanism of dyes on the resin. The spectra were recorded in the range of 600–4000 cm⁻¹ with 32 scans per spectrum at a resolution of 4 cm⁻¹.

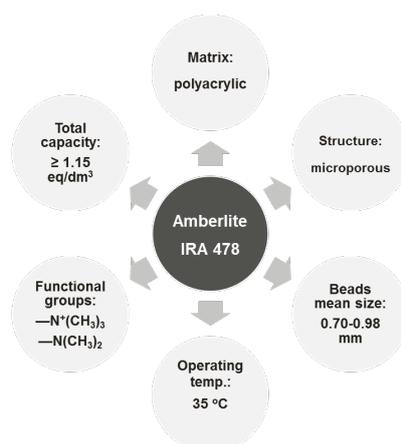


Fig. 2. Resin characteristics

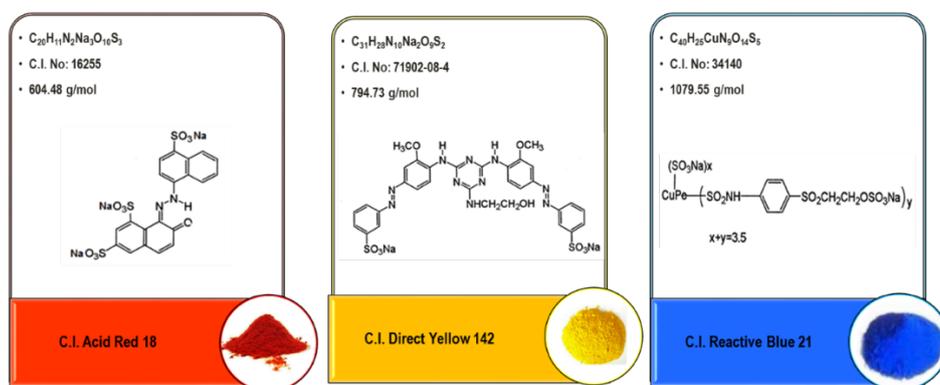


Fig. 3. Dyes characteristics

Table 2. Isotherms characteristics

Isotherms	Linear equation	Plot	Eq.	where: q_e – the amount of dyes adsorbed per unit mass of resin at the equilibrium state (mg/g), C_e – equilibrium dye concentration (mg/dm ³), Q_0 – the Langmuir constant associated with the maximum sorption capacity (mg/g), b – the Langmuir constant associated with the sorption energy (dm ³ /mg), K_F – the constant related to the sorption capacity (mg/g), n – the Freundlich constants
Langmuir	$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$	C_e/q_e vs. C_e	(2)	
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$\log q_e$ vs. $\log C_e$	(3)	

2.2. Kinetic studies

In the kinetic studies 100 cm³ conical flasks were used, in which 0.5 g (± 0.0005 g) of dry sorbent was weighed and 50 cm³ of the dye solution (initial concentrations: 100, 300 and 500 mg/dm³) was added. The flasks were placed in a mechanical shaker with constant vibration amplitude (180 cpm) (Elphin + 358S, Poland) and were stirred at room temperature for a set time. After shaking the sorbent was separated from the solution by decantation and the solution was subjected to spectrophotometric analysis (Cary 60, U.S.A.). The amount of dye adsorbed at time t – q_t (mg/g) was calculated from the equation:

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (4)$$

where: C_0 – output concentration of dye (mg/dm³), C_t – concentration of dye after sorption time t (mg/dm³), V – volume of solution (dm³), m – mass of resin (g).

In order to better understand the dynamics of the adsorption process, its mechanism and to calculate the kinetic parameters of AR18, DY142 and RB21 sorption on IRA 478, the following kinetic models were used (Table 3): pseudo-first order model based on the Lagergren equation (Lagergren, 1898), pseudo-second order model proposed by Ho and McKay (Ho and McKay, 1998) and intraparticle diffusion model by Weber-Morris (Płaziński et al., 2013).

Table 3. Kinetic models

Pseudo-first order (PFO)	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$ (5)	where: k_1 - the adsorption rate constant (1/min), t - the time (min), q_e , q_t - the amounts of dye adsorbed at equilibrium and sorption time t , respectively (mg/g), k_2 - the adsorption rate constant (g/mg·min), k_i - the intraparticle diffusion rate constant (mg/g·min ^{0.5}), C - constant illustrating the effect of the boundary layer on the sorption process
Pseudo-second order (PSO)	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ (6)	
Intraparticle diffusion (ID)	$q_t = k_i t^{1/2} + C$ (7)	

2.2.1. Effects of salts and surfactant addition

Effects of added salts (Na₂SO₄, NaCl and Na₂CO₃) and surfactants (SDS and Triton X-100) on dyes retention on IRA 478 were tested by shaking (t=15 min) the resin (0.5 g) with 50 cm³ of dye solution (500 mg/dm³) containing various concentrations of salts (5–25 g/dm³) or surfactants (0.1–0.5 g/dm³) at room temperature. The concentration of dyes after the sorption was measured spectrophotometrically at the appropriate wavelength.

2.2.1. Effect of solution pH

Effect of pH on dyes uptake by IRA 478 was investigated by shaking (t=15 min) of anion exchanger (0.5 g) with 50 cm³ of dye solution (500 mg/dm³) at room temperature and different initial pH. The solution of desired pH were prepared using 1 M HCl and 1 M NaOH. The concentration of dyes after the sorption was measured spectrophotometrically at the appropriate wavelength.

2.3. Column studies

In the dynamic method a set of ion exchange columns (Ø=1 cm) was used, in which 10 cm³ of the swollen resin was placed. A dye solution of the specified concentration (100, 300 and 500 mg/dm³) was let into the bed at the rate of 0.6 cm³/min. The concentration of dye in the effluent was determined by spectrophotometric method. Based on the breakthrough curves, the following parameters were calculated: weight distribution coefficient (D_w), bed distribution coefficient (D_b) and working exchange capacity (C_w) (Table 4).

Table 4. Column parameters

Weight distribution coefficient (D_w)	$D_w = \frac{(U - U_0 - V_v)}{m}$ (8)	where: U - volume of the effluent at $C/C_0=0.5$ cm ³ , U_0 - dead volume of the column (liquid volume in the column between the bottom edge of the ion exchange bed and the outlet of the column, under process conditions $U_0=2$ cm ³), V_v - free volume in bed (approx. 0.4 bed volume) (cm ³), m - dry resin mass in the column (g), v - resin volume in the column (cm ³), V_{bp} - column breakthrough volume (cm ³), C_0 - the influent concentration (mg/dm ³)
Bed distribution coefficient (D_b)	$D_b = \frac{(U - U_0 - V_v)}{v}$ (9)	
Working exchange capacity (C_w)	$C_w = \frac{V_{bp} C_0}{v}$ (10)	

3. Results and discussion

3.1. Isotherms

Isotherms are used to determine the balance between the solid phase adsorbate concentration and its concentration in the liquid phase. On the basis of the course of the isotherms graph, one can obtain information on the maximum adsorptive capacity of the sorbent. In these studies the Langmuir and Freundlich models were used to describe the equilibrium processes. The Langmuir model is based on the following assumptions: the solid surface is homogeneous and has a certain number of adsorption sites, one adsorbent molecule can adsorb one adsorbate molecule, adsorbate binding occurs by chemisorption, adsorbate particles form a layer of molecules interacting with the adsorbent sites while they do not interact with each other, the adsorption energy is constant when equilibrium state is established. In contrast the Freundlich's isotherm model reflects the energy heterogeneity of the adsorbent surface (Srivastava et al., 2007; Hsu et al., 2008).

In order to determine the efficiency of sorption of AR18, DY142 and RB21 onto IRA 478 at equilibrium state, the C_e/q_e vs. C_e and $\log(q_e)$ vs. $\log(C_e)$ plots were drawn and the specific parameters were calculated (Table 5). The adjustment of the above-mentioned adsorption models to experimental data is shown in Fig. 4.

The applicability of the isotherm equations was evaluated based on the determination coefficient R^2 . The R^2 values for the C_e/q_e vs. C_e plots were equal to 0.994, 0.820 and 0.987 for AR18, DY142, RB21 sorption on IRA 478, respectively. The monolayer sorption capacities of Amberlite IRA 478 were found to be 1098.5 mg/g for AR18, 46.8 mg/g for DY142 and 23.5 mg/g for RB21. The usefulness of the Freundlich sorption isotherm was also examined by plotting the $\log q_e$ vs. $\log C_e$. The determination coefficients of the above-mentioned graphs were successively 0.978, 0.973 and 0.938. The $1/n$ values were lower than 1 indicating that the dyes used in the study were preferably adsorbed (Table 5). Adsorption of AR18 and RB21 on Amberlite IRA 478 follows the assumptions of the Langmuir model whereas the adsorption of DY142 is better described with the Freundlich model. The highest affinity of the microporous IRA 478 is shown for AR18 dye. The mechanism of dye sorption results from the formation of ionic pairs between the positive functional groups of resin and sulfonic groups of the negative charge of dye and π - π type interactions between the aromatic ring present in the dye structure and the resin matrix. Comparing the data obtained from the conducted studies with data from the literature it can be concluded that the amount of dye removed from the wastewater depends on its type, spatial structure and mass as well as the anion exchanger used. Based on the conducted studies the dyes affinity of IRA 478 can be presented as follows: AR18 > DY124 > RB21. The highest affinity for the resin shows AR18 which is caused by its smallest size compared to the other two dyes. In the case where the dye anion is too large, there is a "sieve effect" which results from excluding of the species from the microporous resin phase. The b Langmuir constants for AR18, DY 142 and RB21 were successively 0.3733, 0.0245, 0.0183. The highest value was obtained for AR18 suggesting its strong binding with the polyacrylic anion exchanger IRA 478.

Table 5. Parameters determined from the Langmuir and Freundlich isotherms in the sorption process of AY18, DY142 and RB21 on the IRA 478 anion exchanger

Dyes	$Q_{e,exp}$ (mg/g)	Langmuir			Freundlich			
		R^2	Q_0 (mg/g)	b (dm ³ /mg)	R^2	n	$1/n$	K_F (mg/g)
AR18	1098.5	0.994	1283.3	0.3733	0.978	1.455	0.687	314.1
DY142	32.9	0.820	46.8	0.0245	0.973	1.428	0.700	0.072
RB21	23.5	0.987	25.5	0.0183	0.938	1.952	0.512	1.193

The studies conducted by Wawrzekiewicz (2012) to remove C.I. Acid Orange 7 (AO7), C.I. Reactive Black 5 (RB5) and C.I. Direct Blue 71 (DB71) using Amberlite IRA 478 confirm the fact that the affinity of the sorbent relative to the dye depends on the mass and structure of the species and on the structure of the sorbent (Wawrzekiewicz et al., 2017, 2019). Amberlite IRA 478 sorption capacities for AO7, RB5 and DY71 were 1279.2 mg/g, 150.4 mg/g and 41.8 mg/g, respectively. It is worth paying attention to

the dependence of the size and mass of dyes: AO7 < RB5 < DB71 and their effect on dye retention by the anion exchanger (Wawrzkievicz, 2012). In the case of AO7, RB5 and DB71 retention on Lewatit MonoPlus SR-7 of polystyrene matrix, the monolayer capacities were equalled to 713.4 mg/g, 957.2 mg/g and 850.2 mg/g. The affinity of Lewatit MonoPlus SR-7 dyes was in the following relationship: RB5 > DB71 > AO7. In this case the matrix of the anion exchanger itself had an effect on the dyes uptake (Wawrzkievicz et al., 2017).

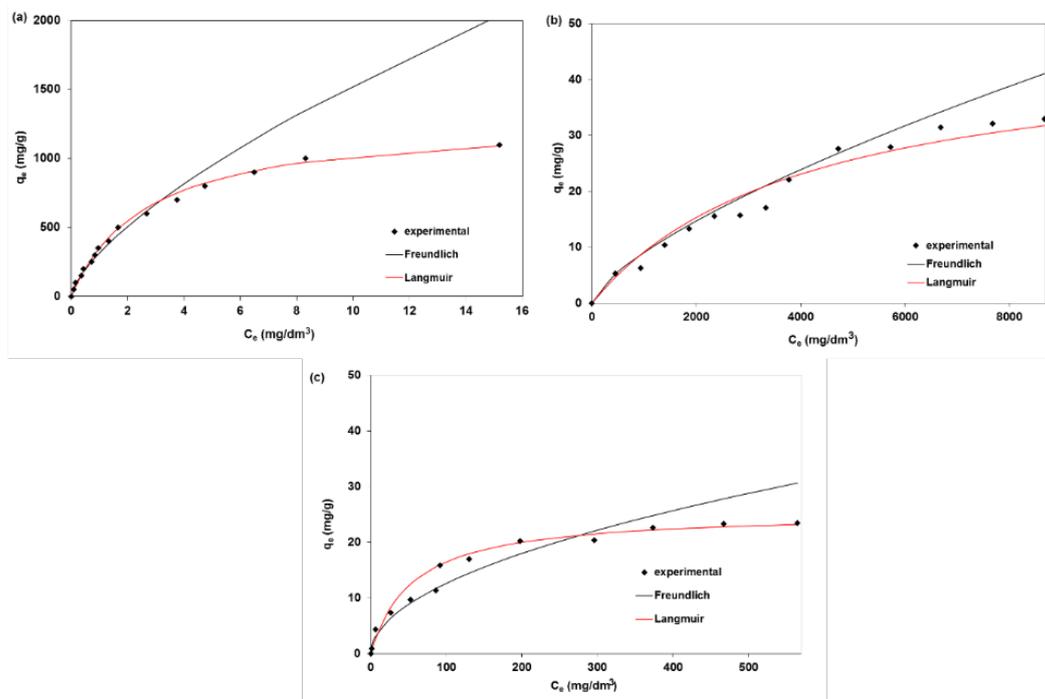


Fig. 4. Fitting of experimental sorption data of AR18 (a), DY142 (b) and RB21 (c) on IRA 478 anion exchanger to Langmuir and Freundlich models

For a more accurate analysis of the dyes retention and to determine the sorption mechanism of the AR18, DY142 and RB21 dyes on the IRA 478 anion exchanger, ATR-FT-IR spectra were recorded before and after sorption. Changes in the intensity of individual bands were observed after dyes retention as shown in Fig. 5. At 3470 cm^{-1} the bands characteristic for -OH stretching vibrations were observed as a result of water presence in the anion exchanger phase. The bands at 3028 cm^{-1} and 2940 cm^{-1} were visible and can be attributed to vibrations of C-H (ν_{as} C-H) and -CH₂ (ν_{as} -CH₂) groups in the aromatic rings of the matrix. The peak at about 1730 cm^{-1} corresponding to the stretching of C=O groups was observed. The water presence was also proved at 1635 cm^{-1} (δ O-H). The ring C-C stretching and scissoring vibrations of the methylene groups (δ_{as} -CH₂) were assigned at 1457 , 1422 and 1394 cm^{-1} . In the analyzed spectra of IRA 478 after the dyes sorption new symmetric and asymmetric vibration of the sulfonic -SO₃⁻ and -S=O groups appear at 1085 , 1145 and 1013 cm^{-1} , respectively. It may indicate that the dyes retention mechanism occurs as a result of the formation of an ionic pair between the functional groups of the resin and the sulfonic groups of the dye.

3.2. Kinetic

The adsorption phenomenon at the solution/solid interface plays a key role in many industrial processes. In particular it can be used to purify aqueous solutions from harmful components such as heavy metal ions, dyes, detergents or phenolic compounds. The search for new effective adsorbents of high capacity, good mechanical properties and other desirable traits resulted in a large number of experimental works describing the synthesis of such materials and their adsorption properties. Each average experiment is based on an adsorption equilibrium state to determine the optimal process conditions leading to the removal of as much as possible of the adsorbate from the aqueous solution. At the same time kinetic studies are carried out. Influence of phase contact time on AR18, DY142 and RB21

sorption on IRA 478 was examined changing the initial dyes concentration in the range of 100-500 mg/dm³. Figure 6 shows the effect of phase contact time and the initial concentration on the amount of dye adsorbed by IRA 478.

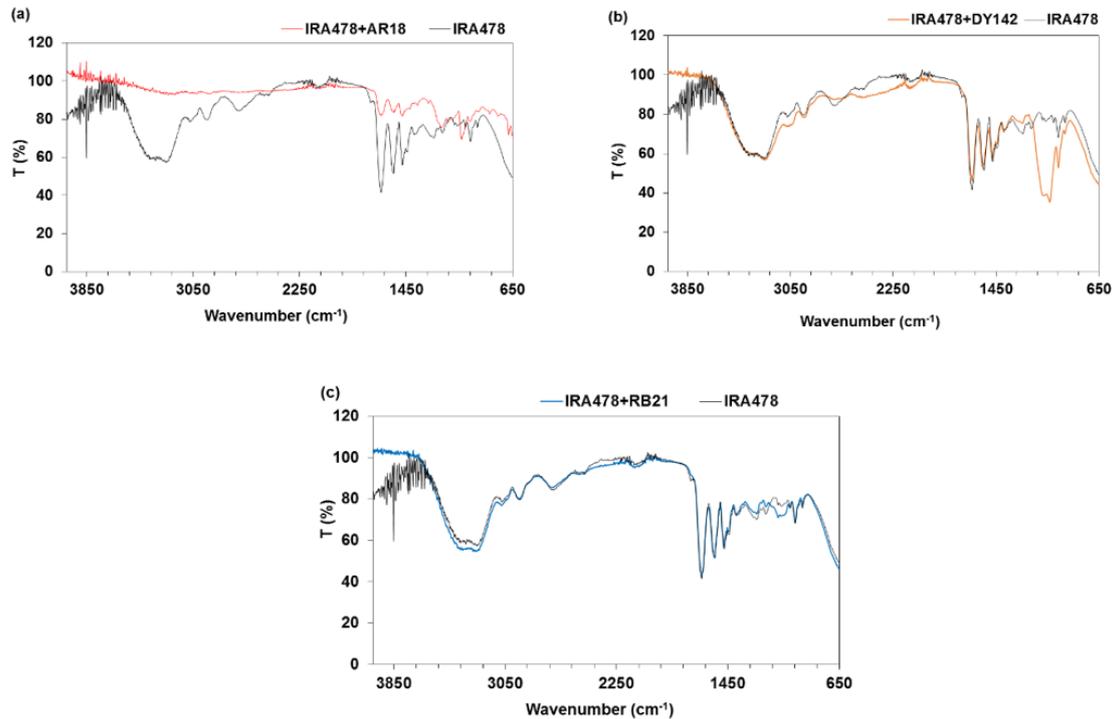


Fig. 5. ATR-FT-IR spectra of Amberlite IRA 478 before and after sorption of AR18 (a), DY142 (b) and RB21 (c)

The state of equilibrium of the sorption process in the AR18 - IRA 478 system is fixed after 20 minutes in a solution with a dye concentration of 100 mg/dm³, after 30 minutes in a solution with a dye concentration of 300 mg/dm³ and after 60 minutes in the case of a solution with a dye concentration of 500 mg/dm³. This means that the higher concentration of dye, the longer the equilibrium is established. In the case of sorption process of DY142 and RB21 on IRA 478 the time required to reach equilibrium is longer and increases with the increase of the initial dye concentration up to reaching the plateau.

Knowledge of adsorption kinetics enables such control over the whole process, so that its effectiveness is as large as possible. In the case of kinetic processes modelling such equation as PFO, PSO and ID are usually used. The modelling process itself is about matching the measured data with several different equations and choosing the one that best correlates the data. These models are based on defining the amount of substance adsorbed by the unit of adsorbent mass per unit time (q_t) as shown in Fig. 6. Based on the calculated kinetic parameters (Table 6) it can be concluded that the best fit of experimental data was obtained using PSO model. This is evidenced not only by the high values of the R^2 , but also the values of q_e which are similar to those obtained experimentally $q_{e,exp}$. The rate constant of the pseudo-second order kinetics k_2 are reduced from 0.1001 to 0.0008 g/mg·min for AR18, from 0.0147 to 0.0112 g/mg·min for DY142 and 0.0489 to 0.0072 g/mg·min for RB21 with an increase in the concentration of dyes from 100 mg/dm³ to 500 mg/dm³. Based on this information it is suggested that the process of the dyes uptake by IRA 478 is a chemical reaction (chemisorption). A similar phenomenon was observed during the C.I. Acid Green 9 sorption on weak and strong base anion exchange resins (Dulman et al., 2009).

Lagergren's equation did not apply to the description of the sorption kinetics of AR18, DY142 and RB21 on IRA 478. This is due not only to the non-linear dependence of $\log(q_e - q_t)$ vs. t (deviation from the linearity near the equilibrium) as well as a small values of $q_{e,exp}$ and R^2 calculated from this equation.

Due to the porosity of the used anion exchanger the Weber -Morris model can also find application in the description of kinetic data. The experimental points did not go through the origin of the graph q_t

vs. $t^{0.5}$ and the values of the R^2 are in the range of 0.804–0.983. Therefore, the intraparticle diffusion is not the rate limiting step.

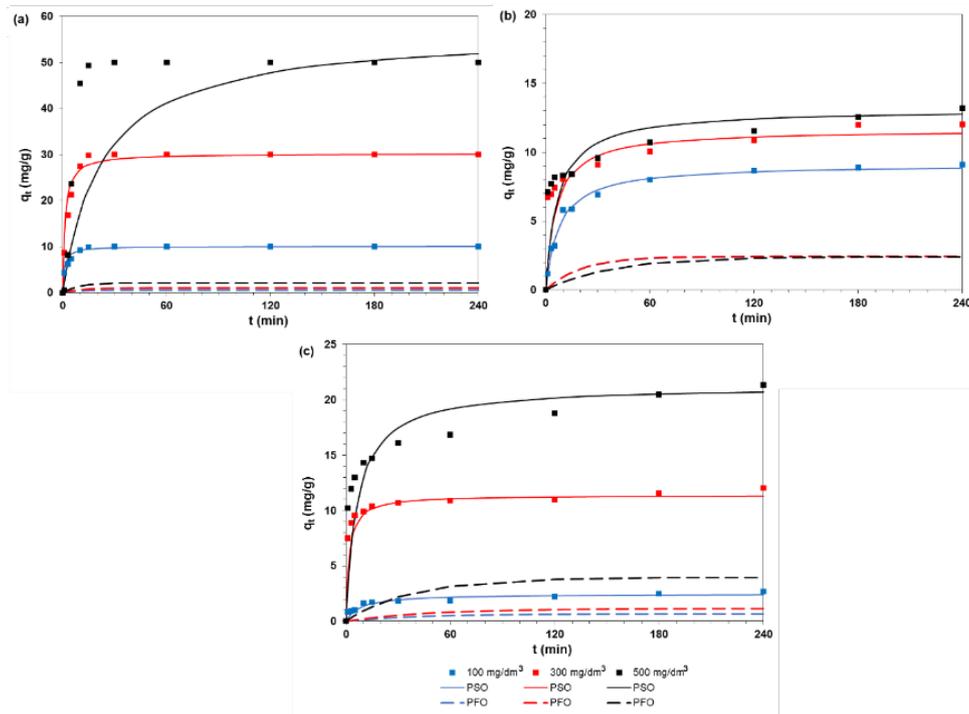


Fig. 6. Influence of phase contact time and initial concentration of AR18 (a), DY142 (b) and RB21 (c) on the amount of dye adsorbed by IRA 478

Table 6. Parameters determined from PFO, PSO and ID equations related to the dyes sorption process on IRA 478 anion exchanger

Dyes	C_0 (mg/dm ³)	$q_{e,exp}$ (mg/g)	PFO			PSO			ID	
			q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg·min)	R^2	k_i (mg/g·min ^{0.5})	R^2
AR18	100	10.0	1.24	0.0533	0.650	10.1	0.1001	0.999	1.2889	0.829
	300	30.0	2.40	0.0398	0.612	30.2	0.0252	0.999	4.7051	0.804
	500	50.0	4.89	0.0472	0.596	56.8	0.0008	0.868	12.2469	0.818
DY142	100	9.2	5.5	0.0211	0.912	9.1	0.0147	0.999	1.2843	0.895
	300	12.05	5.7	0.0209	0.906	11.6	0.0142	0.993	0.5558	0.983
	500	13.20	5.6	0.0115	0.984	13.1	0.0112	0.996	0.4911	0.938
RB21	100	2.7	1.5	0.0104	0.802	2.5	0.0489	0.992	0.2564	0.852
	300	12.1	2.7	0.0091	0.785	11.4	0.0481	0.999	0.6553	0.827
	500	21.5	9.11	0.01164	0.9635	21.3	0.0072	0.995	1.2601	0.936

3.2. Effects of salts and surfactant addition

Textile wastewater generated during technological processes carried out in tanneries, textiles or paper production includes not only dyes but also auxiliary agents, e.g. salts, acids, bases, surfactants, oxidants or reducers. These substances end up in sewage in the amount in which they are introduced into a colored bath and what is more they do not wear out in the process of fibers dyeing as opposed to dyes. Depending on the type and nature of the fibers as well as the intensity of the colour the amount of dyes and the concentration of auxiliaries are different. The dyeing process with acid dyes takes place in medium of pH 4.5–5 acidified with acetic acid. If the staining is unevenly, addition of salts such as Na_2SO_4 in amount of 10–20% is recommended. The presence of carbonates and bicarbonates increases the pH of the dyeing bath in case of reactive and direct dyes. Addition of auxiliaries, such as surfactants

is also very important. Water which is the main component of the bath is characterized by high surface tension therefore the addition of surfactants causes that its drops well wet the surface of the solid and thus the fibers facilitating contact of substances dissolved with this surface. In connection with the above, it is worth investigating the effect of various salts and surfactants addition on the adsorption of dyes on the anion exchange resin (Kowalska, 2009; Maciejewska-Nowak, 2006).

The influence of auxiliaries on the sorption efficiency of AR18, DY142 and RB21 on IRA 478 anion exchanger was carried out with the static method in the system containing 0.5 g resin - 50 cm³ dye solution of the concentration 500 mg/dm³. The dye solutions additionally contained from 0.1 g/dm³ to 0.5 g/dm³ of surfactants (SDS, Triton X-100) and from 5 g/dm³ to 25 g/dm³ of salt (Na₂SO₄, NaCl, Na₂CO₃). The amount of dye adsorbed by the anion exchanger was measured after 15 min of phase contact time. In the conducted studies a decrease in the values of q_t was observed with the increasing concentration of NaCl and Na₂SO₄ in the system containing RB21 and DY142. Similar observations have been made by Wawrzekiewicz (2012) who remove RB5 dye using IRA 478. The drop is the result of competitive sorption of salts anions as compared with dyes anions. In AR18 - Na₂SO₄/NaCl and DY142 - Na₂CO₃ systems the increase in salts concentration did not cause the change of q_t values (Fig. 7).

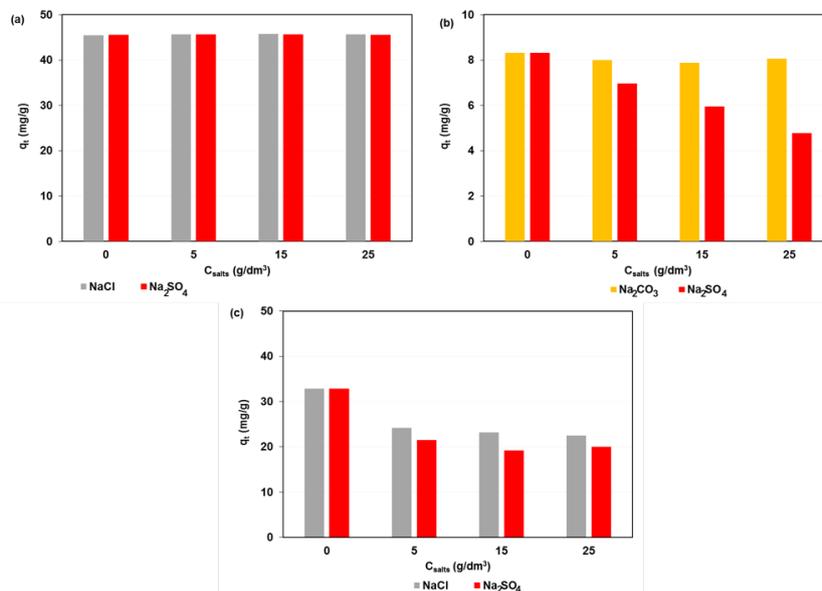


Fig. 7. The effect of salts concentration on the amount of AR18 (a), DY142 (b) and RB21 (c) adsorbed by IRA 478 anion exchanger

Unimportant effects of electrolytes, i.e. Na₂SO₄, Na₂HPO₄ and NaH₂PO₄ were observed by Greluk and Hubicki (2011) during sorption of AO7 on the weakly basic anion exchanger of polyacrylic matrix Ambrelite IRA 67 and strongly basic anion exchanger of polyacrylic matrix Ambrelite IRA 958. The presence of SDS and Triton X-100 (Fig. 8) in the system containing 500 mg/dm³ dye had no effect on AR18 sorption. However, in a system containing RB21 an increase in the concentration of SDS and Triton X-100 caused a decrease in q_t . In the case of DY142 the presence of Triton X-100 did not affect the values of q_t and an increase in SDS concentration caused a slight decrease in q_t . The reduction of sorption capacity with the increase in the concentration of surfactants in the system may be caused by the competitive sorption of surfactants with the anionic form of direct and reactive dyes.

3.3. Effect of solution pH

The ion exchange process depends to a large extent on the acidity or alkalinity of the solution. The pH value of the dye solution determines its ionic form (the degree of dissociation of functional groups) and thus the nature of the interaction between the dye and the anion exchanger. The AR18, DY142 and RB21 dyes selected for testing come in ionized form over the entire pH range of 2–12. The pH of the solution is a very important parameter controlling sorption processes. Amberlite IRA 478 as a medium-basic anion exchanger combines the high operating capacity normally related to the weakly basic anion

exchange resins with quaternary ammonium, type 1, strong base functionalities. It was found that the initial pH of the AR18 solution did not affect its sorption on IRA 478. In the case of DY142 and RB21, an increase in initial pH (1.95–9.80) resulted in an increase in q_t (7.53–10.9) and a decrease in q_t (4.04–0.26), respectively (Fig. 9). These results also confirm that the dye retention mechanism in the anion exchanger phase is complex and includes different types of interactions.

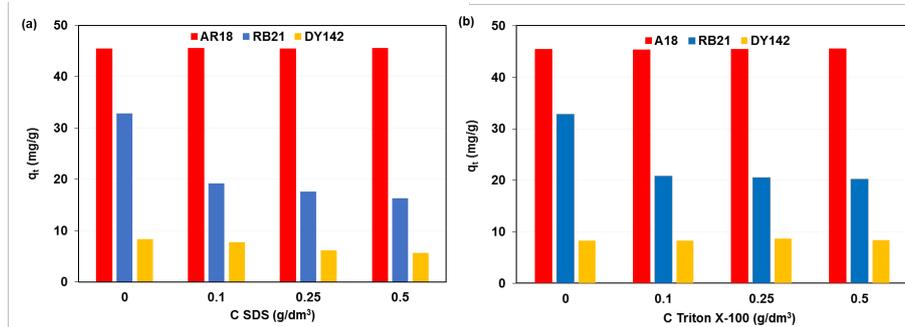


Fig. 8. Effect of anionic SDS (a) and non-ionic Triton X-100 (b) surfactants addition on dyes uptake by IRA 478 anion exchanger

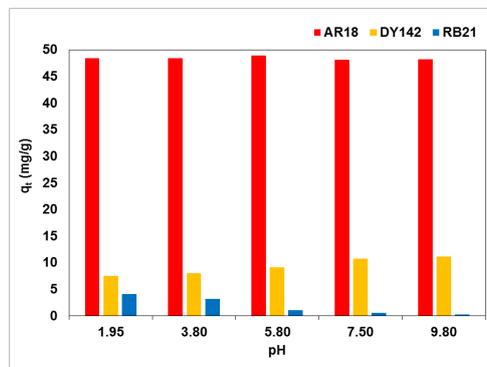


Fig. 9. Influence of initial solution pH on dye ($C_0=500$ mg/dm³) uptake by IRA 478 anion exchanger

3.4. Column studies

Numerous technological processes of ion exchange are carried out by the dynamic method in a column system. The results of such tests give a broader view on the classification of the ion exchanger under study in a relevant technological process. For this reason, it was reasonable to determine the breakthrough curves (C/C_0 vs. V effluent) in the AR18 - IRA 478 system (Fig. 10) and the working ion exchange capacity (C_w). Due to the fact that the course of these curves was symmetrical (resembling the "S" shape), it enabled the calculation of the weight (D_w) and bed (D_b) distribution coefficients (Table 7). The highest values of distribution coefficients and working ion exchange capacity were found in 100 mg/dm³ AR18 - IRA 478 system.

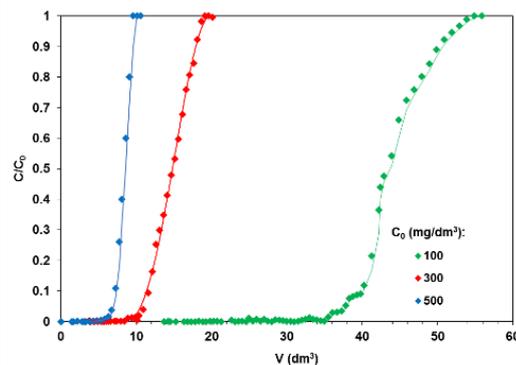


Fig. 10. Breakthrough curves in AR18 - IRA 478 system

Table 7. Comparison of weight (D_w) and bed (D_b) distribution coefficients and working ion exchange capacities in the AR18 - IRA 478 system

Dye	C_0 (mg/dm ³)	D_w	D_b	C_w (mg/cm ³)
AR18	100	14727.7	4359.4	324.8
	300	4896.6	1449.4	198.6
	500	2842.6	841.4	214.5

4. Conclusions

The process of sorption of AR18, DY142 and RB21 dyes from aqueous solutions was carried out using the polyacrylic anion exchanger Ambrelite IRA 478 of tertiary amine and quaternary ammonium functionalities. The tests were carried out using static and dynamic methods taking into account the initial concentration of dyes, phases contact time and the presence of auxiliaries such as salts (NaCl, Na₂SO₄, Na₂CO₃) and surfactants (SDS, Triton X-100). Effectiveness of AR18, DY142 and RB21 retention increases with increasing phases contact time and initial dye concentrations until the plateau is reached. The kinetics of the dyes sorption process is best described by the pseudo-second order model. The determined sorption capacities of IRA 478 using batch technique were: 1098.5 mg/g for AR18, 46.8 mg/g for DY142 and 23.5 mg/g for RB21. The presence of salts and surfactants had a pronounced effect on the retention of the direct and reactive dyes whereas in the case of the acid dye it had no significant effect. On the basis of the conducted research it can be concluded that the type of dye (structure and spatial structure, amount and type of chromophore and auxochromes) have a quite significant effect on sorption efficiency as well as matrix type and structure.

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