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Physicochemical Interactions in Systems C.I. Direct Yellow 50—Weakly Basic Resins: Kinetic, Equilibrium, and Auxiliaries Addition Aspects

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Abstract: Intensive development of many industries, including textile, paper or plastic, which consume large amounts of water and generate huge amounts of wastewater-containing toxic dyes, contribute to pollution of the aquatic environment. Among many known methods of wastewater treatment, adsorption techniques are considered the most effective. In the present study, the weakly basic anion exchangers such as Amberlyst A21, Amberlyst A23 and Amberlyst A24 of the polystyrene, phenol-formaldehyde and polyacrylic matrices were used for C.I. Direct Yellow 50 removal from aqueous solutions. The equilibrium adsorption data were well fitted to the Langmuir adsorption isotherm. Kinetic studies were described by the pseudo-second order model. The pseudo-second order rate constants were in the range of 0.0609–0.0128 g/mg·min for Amberlyst A24, 0.0038–0.0015 g/mg·min for Amberlyst A21 and 1.1945–0.0032 g/mg·min for Amberlyst A23, and decreased with the increasing initial concentration of dye from 100–500 mg/L, respectively. There were observed auxiliaries (Na_2CO_3 , Na_2SO_4 , anionic and non-ionic surfactants) impact on the dye uptake. The polyacrylic resin Amberlyst A24 can be promising sorbent for C.I. Direct Yellow 50 removal as it is able to uptake 666.5 mg/g of the dye compared to the phenol-formaldehyde Amberlyst A23 which has a 284.3 mg/g capacity.

Keywords: Amberlyst; anion exchanger; direct dye; removal; resins; sorption; wastewaters



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1. Introduction

Water is indispensable for life. Every organism contains water and needs it to live. The land is covered with 71% of water, where the vast majority, about 97%, is in the seas and oceans and is inaccessible to human consumption, while the remaining 3% is occupied by fresh water (ice sheets, glaciers, eternal snow and ground ice as well as underground water). Of these 3%, only 0.06% is easily accessible to plants, animals and humans [1].

The rapid increase in the world numbers and extensive industrial activities have caused the demand for water to double globally every 21 years. Nearly 80 countries, representing 40% of the world's population, are struggling with water crises. The United Nations estimated that by 2025 water shortages could affect as many as 2.7 billion people [1,2]. What is more, many of these countries suffer from a lack of drinking water. About 5–10 million people die annually from diseases associated with the consumption of polluted water [1]. The demand for water grows every year. Therefore, it is necessary to search for more modern, and more economical, technologies for water/wastewater treatment. Reclamation, recycling and reuse of wastewater are necessary to meet the requirements for irrigation water, industry and domestic applications due to the growing population [1–4]. Sewages are constituted by water used for specific purposes and contain various types of industrial, agricultural and urban pollution that must be removed before water re-enters the environment. Untreated sewages cause contamination of surface and underground

water and exclude it from economic and social uses. The most hazardous environmental pollutants are included in industrial sewages and contain mostly organic and inorganic compounds, such as dyes, phenolic and aromatic compounds, as well as heavy metals [4–6]. In the textile effluents, auxiliary agents such as salts, acids, alkalis, surfactants and oxidants can also be present [7–10]. Dyes may also be found in wastewater from the paper industry, plastic and cosmetics manufacturing, food industry, paints, varnishes and stains, leather and rubber dyeing and dye manufacturing. Dyes impede light penetration into the water and inhibit photosynthesis. They are mutagenic, carcinogenic and teratogenic towards living organisms present in water, especially microorganisms and fish [11–13]. Dyes penetrate into the human body and cause dysfunction of the kidneys, liver, brain, reproductive system and central nervous system (Figure 1) [11]. In addition, they can trigger asthma and allergies [11,12]. In addition, dyes can undergo transformations during degradation under aerobic or anaerobic conditions into products with even greater toxicity than the parent dyes [13]. Therefore, removing dyes and other chemicals from wastewaters is of great importance in the field of water purification.

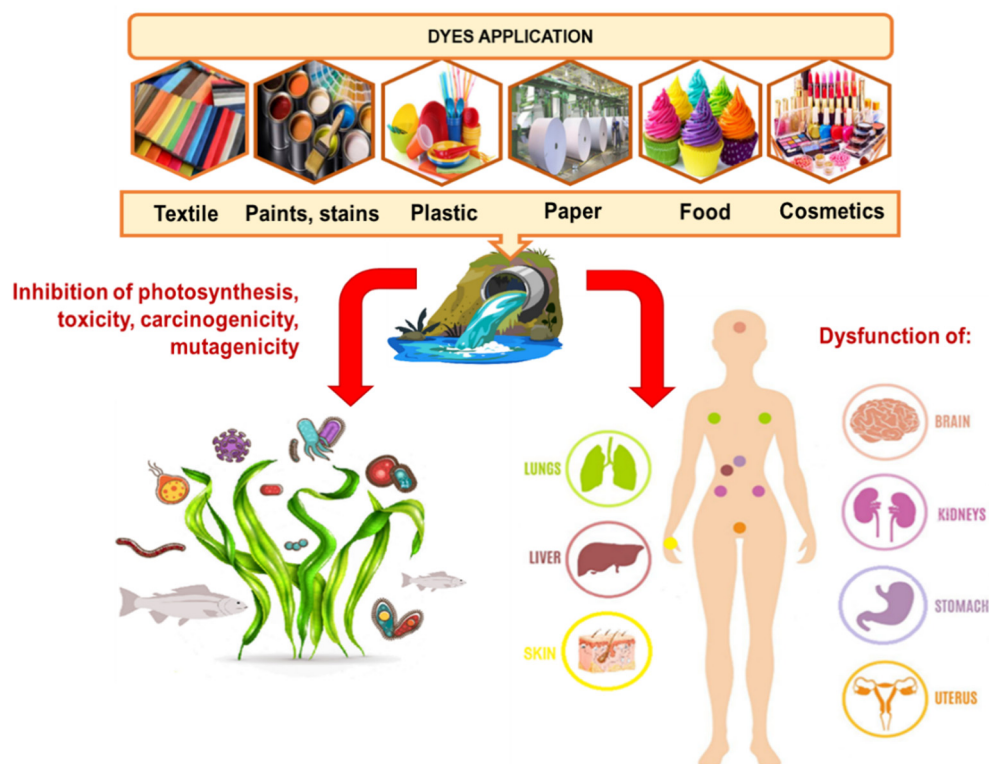


Figure 1. Application of dyes and their impact on living organisms and human body [11–13].

The basic treatment methods of textile wastewaters can be divided into four groups: mechanical, biological, chemical and/or physical methods (e.g., oxidation, flocculation, flotation, adsorption and combination of the previously mentioned ones) [14–19]. One of the most effective methods with a great potential for removal of dyes from wastewaters are adsorption techniques [20–22]. The effectiveness of the adsorption process depends mainly on the selection of the appropriate adsorbent and the conditions under which the process is run. The most commonly used sorbent is activated carbon due to the large specific surface area, developed porous structure, possibility of modification and reactivity [23–30]. Its disadvantage is the relatively high price, which limits its use to some extent. One of the sorbents used in the purification processes are those produced from waste materials (low-cost adsorbents). Some of these materials are formed from waste substances that no longer have any use, e.g., peels, citrus stones, agricultural waste, fly ash, peat, slag and many others [31–43]. They are mainly characterized by their availability and cheap production cost, while their disadvantage is the relatively low sorption capacity compared

with activated carbons or polymeric resins [34–40]. Ion exchange resins are now of major interest due to properties such as large sorption capacity, good chemical resistance and high mechanical strength, making them able to stand up to high temperatures, significant osmotic shock, and exposure to oxidizing agents, as well as high efficiency and no loss of sorbent in the regeneration process. Disadvantages of ion exchangers applications are possibility of bed fouling by substances occurring in water (such as organic matter or Fe^{3+} ions) and high initial capital cost of installation [39,44,45]. The prices of ion exchange resins vary depending on the manufacturer, type, quality and bead size. The average cost of 1 ft^3 for weak/strong acid resins is from \$40 to \$200 while for weak/strong base resins it is \$130 to \$200 [44–46]. These costs are compensated by high sorption capacity and the possibility of regeneration and reuse without a significant loss of capacity in the subsequent cycles of operation. Owing to the introduction of macroporous ion exchangers with a sponge-like structure into the industry, it was possible to improve the kinetic sorption parameters of these resins [47]. The use of a given ion exchanger depends on the type of its functional groups which are responsible for ion exchange and determine the optimum efficiency of a given resin at various pH levels. In a large group of ion exchangers, anion exchangers with different basicity of functional groups found the largest practical application in the sorption process of acid, direct and reactive dyes [48–51]. Other important parameters affecting the efficiency of dye retention are matrix composition (polyacrylic, polystyrene, phenol formaldehyde) and porosity.

The purpose of the paper was to assess the efficiency of C.I. Direct Yellow 50 uptake from aqueous solutions by the weakly basic anion exchangers differing in matrix composition. C.I. Direct Yellow 50 is commonly used to dye cellulosic fabric, paper, leather etc. In addition, direct dyes are superior to others in terms of cost, better lightfastness, ease of application or shorter dye cycle. There is no complete information in the literature so far on the use of weakly basic anion exchange resins with different matrix compositions for DY50 removal. Kinetic and equilibrium parameters of the sorption process were determined and the influence of such factors as time, concentration or pH on the efficiency of dye adsorption from solutions containing additional salts and surfactants was evaluated. Anion exchange resins regeneration was investigated, too.

2. Materials and Methods

2.1. Adsorbents and Adsorbate

There were three weakly basic anion exchange resins of different matrices used: polystyrene Amberlyst A21 (abbr. A21), polyacrylic Amberlyst A24 (abbr. A24) and phenol-formaldehyde Amberlyst A23 (abbr. A23) (Figure 1). The resins were purchased from Sigma-Aldrich (Taufkirchen, Germany). Prior to the adsorption test, the resins were washed with 1 M HCl and distilled water to remove impurities and to change the ionic form to the chloride form. Resins were dried at room temperature to constant weight. The stock solution of the textile dye C.I. Direct Yellow 50 (abbr. DY50) (Boruta-Zachem, Zgierz, Poland) was prepared using distilled water (Figure 2).

2.2. Other Chemicals

Sodium sulphate and carbonate, hydrochloric acid and sodium hydroxide were purchased from Avantor Performance Materials (Gliwice, Poland). The anionic surfactant sodium dodecyl sulfate (SDS) and nonionic surfactant Triton X-100 (TX-100) were purchased from Sigma-Aldrich (Germany).

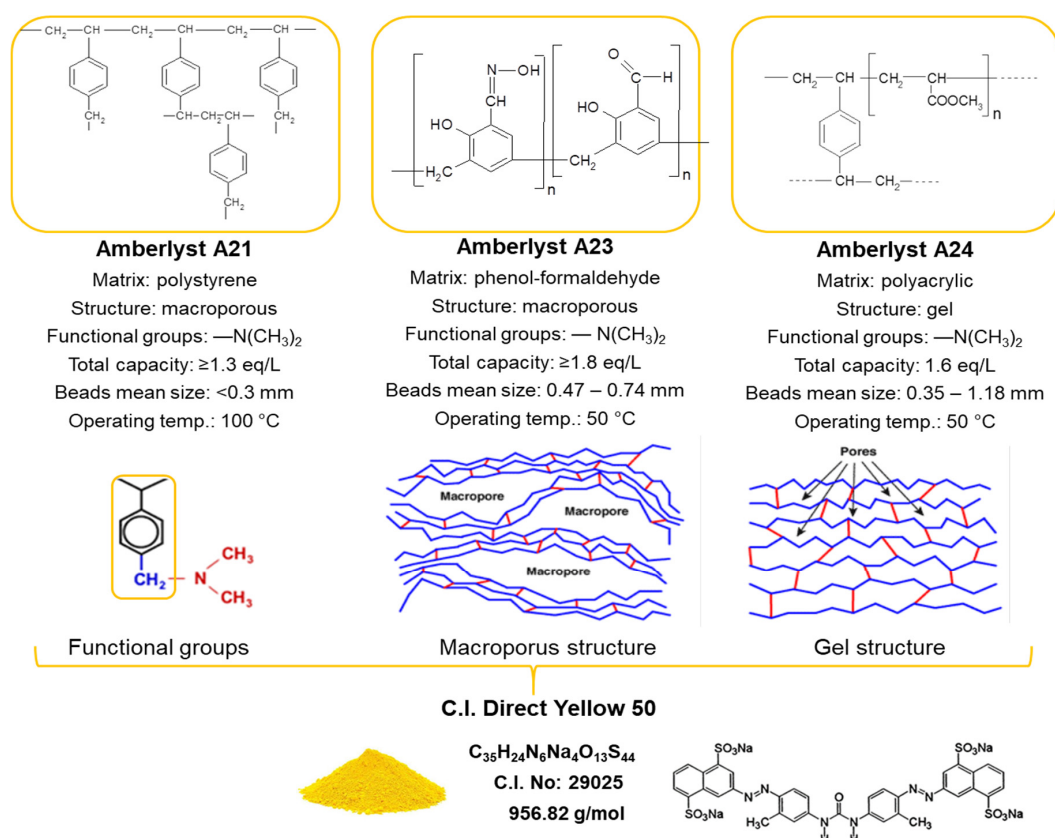


Figure 2. Physicochemical properties of the anion exchangers [52,53] and dye.

2.3. Batch Adsorption Method

In the batch method, conical flasks of the 100 mL volume closed with a silicone stopper were used. Then, 50 mL of dye solution of the initial concentrations 100–500 mg/L (kinetic studies) or 500–9000 mg/L (equilibrium studies) and 0.5 g of the anion exchanger were added. The flasks were placed in an Elphin+ 358S mechanical shaker (Elphin, Poland) with a vibration amplitude of 8 units and rotary of 180 cycles/min at 25°C and mixed from 1 to 240 min (kinetic studies) or 24 h (equilibrium studies). The effects of Na_2CO_3 and Na_2SO_4 , as well as SDS and TX-100 additions on DY50 sorption process on A21, A23 and A24 were studied using the conditions listed in Table 1. After shaking, the resin was separated from the solution, and the concentration of DY50 was measured spectrophotometrically (UV-Vis spectrophotometer Cary 60, Agilent, Santa Clara, CA, USA) at the maximum absorbance wavelength (394–403 nm depending on the auxiliaries, Table 1).

Table 1. Adsorption process conditions in the systems containing salts and surfactants.

Conditions	System	
	$\text{Na}_2\text{SO}_4/\text{Na}_2\text{CO}_3$	SDS/TX-100
Salts/surfactants concentration (g/L)	5, 15, 25	0.1, 0.25, 0.5
Dye concentration (mg/L)	500	500
Time (min)	15	15
Volume (mL)	50	50
Anion exchanger mass (g)	0.5	0.5
Temp. ($^\circ\text{C}$)	25	25
Vibration amplitude, rotary (cycle/min)	8, 180	8, 180
Maximum absorbance wavelength (nm)	399/403	394/397

The effect of initial pH of the solution on the adsorption effectiveness of DY50 on the weakly basic resins A21, A23 and A24 was investigated by shaking 0.5 g of the resin with 50 mL of a solution of different initial pH containing 500 mg/L of dye. The pH was adjusted with 1 M NaOH and 1 M HCl. After the sorption process ($t = 15$ min), the DY50 concentration was measured spectrophotometrically.

The batch adsorption/desorption experiments were done three times, and the average values are given in the figures and tables. Maximum error was found to be $\pm 3\%$.

2.4. Kinetic Experiments

The amount of dye adsorbed at time t (q_t) ($t = 1$ –240 min) was calculated from the Equation (1):

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

where C_0 —initial DY50 concentration (mg/L), C_t —DY50 concentration after sorption time t (mg/L), V —volume (L), m —anion exchanger mass (g).

For the description of experimental data three popular models were applied based on which the kinetic parameters were calculated.

2.4.1. Pseudo First-Order Model (PFO)

The Langergren (1898 [53]) model of the first order is determined by the following Equation (2):

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

where k_1 —pseudo-first order rate constant (1/min), t —time (min), q_e , q_t —amounts of DY50 adsorbed at equilibrium and after time t (mg/g).

From the slopes and intercepts of the plots $\log (q_e - q_t)$ vs. t , k_1 and q_e were calculated.

2.4.2. Pseudo Second-Order Model (PSO)

This model proposed by Ho and McKay [54,55] in 1998 is represented by the following Equation (3):

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

where k_2 —pseudo-second order rate constant (g/mg·min), t —time (min), q_e , q_t —amounts of DY50 adsorbed at equilibrium and after time t (mg/g).

If the kinetics of the sorption process are described by the PSO model, the t/q_t vs. t graph is linear and q_e and k_2 can be determined from the slope and intercept.

2.4.3. Weber and Morris Intraparticle Diffusion Model (ID)

Due to the porosity of the anion exchange resins the intraparticle diffusion model proposed by Weber and Morris [56] was considered in order to describe if the diffusion mechanism can be the controlling step of the reaction. The Equation (4) assumes the proportionality of sorption to the square root from the time of adsorbent-solution phase contact:

$$q_t = k_i t^{0.5} + c \quad (4)$$

where q_t —amount of DY50 adsorbed at time t (mg/g), k_i —intraparticle diffusion rate constant (mg/g·min^{0.5}), c —constant illustrating the effect of the boundary layer on the sorption process, t —time (min).

2.5. Equilibrium Experiments

Adsorption isotherms are used to determine the balance between the concentration of adsorbate in the solid phase and its concentration in the liquid phase. Based on the course of the isotherm, information about the maximum adsorption capacity of the sorbent can be obtained. The most commonly used models are Langmuir and Freundlich ones.

2.5.1. Langmuir Model

The Langmuir isotherm equation describes chemical adsorption. The adsorbed substance forms a monomolecular film on the surface of the solid phase. The Langmuir adsorption isotherm is the basic and most widespread adsorption equation that can be considered as the initial equation for a number of more detailed studies [57,58]. The linear form of the Langmuir isotherm is given below (5):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (5)$$

where C_e —equilibrium DY50 concentration (mg/L), Q_0 —monolayer capacity (mg/g), b —Langmuir constant (L/mg), q_e —amount of DY50 adsorbed at equilibrium (mg/g).

The values of the Langmuir parameters were obtained from the plots C_e/q_e vs C_e .

A characteristic feature of the Langmuir isotherm is the dimensionless separation factor R_L which can be calculated as follows (6):

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

where C_0 —initial DY50 concentration (mg/L), b —Langmuir constant (L/mg).

In addition, the value of the dimensionless R_L coefficient determines the shape of the isotherm: unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [57].

2.5.2. Freundlich Model

The Freundlich (1906) isotherm equation describes the well adsorption on heterogeneous surfaces (non-uniform energy) and microporous adsorbents [59]. It is used for description of reversible adsorption and is not confined to the formation of a single layer. The Freundlich model can be described based on the following Equation (7):

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (7)$$

where k_F —Freundlich constant ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$), $1/n$ —parameter characterizing the energy heterogeneity of the adsorbent surface, C_e —equilibrium DY50 concentration (mg/L), q_e —amount of DY50 adsorbed at equilibrium (mg/g).

The values of the Freundlich parameters were calculated from the plots $\log q_e$ vs. $\log C_e$.

The value $1/n > 1$ indicates a weak bond between the adsorbate and adsorbent molecules while a value of $1/n < 1$ points out to a strong adsorption bond as a result of strong intermolecular attractions in the adsorbent layers [58].

2.5.3. The Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

To investigate the dye adsorption mechanism by the anion exchanger, the attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FT-IR) technique was used (Cary 630, Agilent, Santa Clara, CA, USA). The spectra of anion exchangers before and after DY50 sorption were recorded in the range of 600–3500 cm^{-1} .

2.6. Desorption Experiments

Samples of resins A21, A23 and A24 (0.5 g), loaded with DY50 (50 mg/g), were shaken with 50 mL of various regenerant solutions: 1 M NaOH, 1 M HCl, 1 M NaCl and their mixture with 50% v/v methanol. The suspensions were stirred for 3 h at a constant speed (180 cycle/min) and amplitude ($A = 8$). The concentration of desorbed dye was determined by absorbance analysis. The dye desorption rate (% D) was calculated from the Equation:

$$D = \frac{m_{des}}{m_{ads}} \times 100\% \quad (8)$$

where m_{des} —mass of DY50 desorbed (mg), m_{ads} —mass of DY50 adsorbed (mg).

3. Results and Discussion

3.1. Effects of Initial Dye Concentration and Phase Contact Time

Kinetic sorption studies of DY50 on A21, A23 and A24 anion exchangers of different matrices were estimated using varying phase contact times (1–240 min) for three different initial dye concentrations (100 mg/L, 300 mg/L, 500 mg/L) at room temperature with a constant mass of anion exchanger 0.5 g and a volume of dye solution (50 mL). An increase in the initial dye concentration from 100 to 500 mg/L causes an increase in the amount of dye adsorbed by the anion exchanger (q_t) as presented in Figure 3.

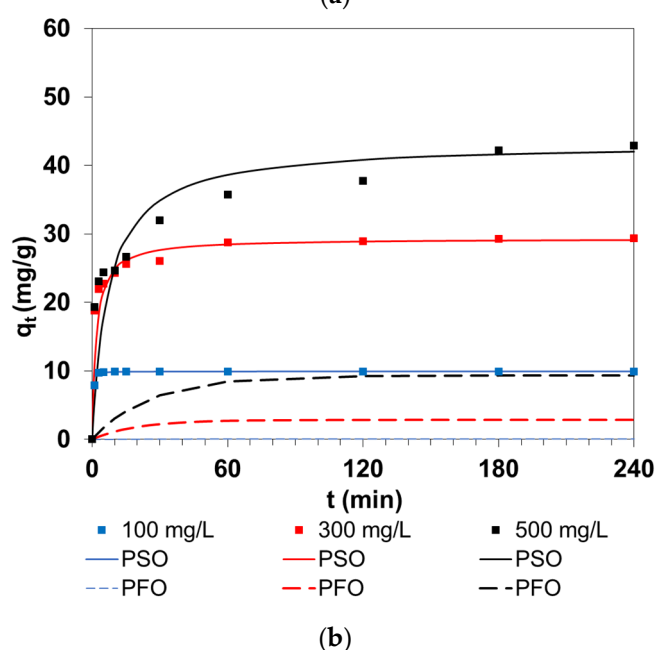
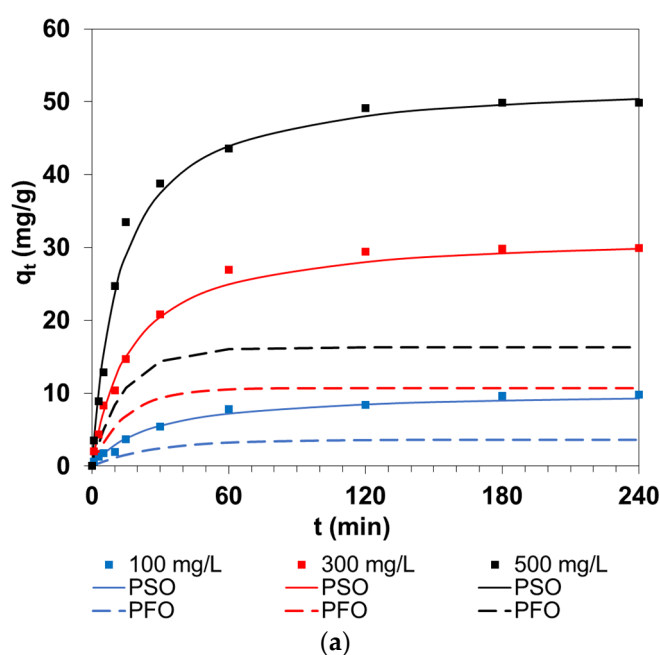


Figure 3. Cont.

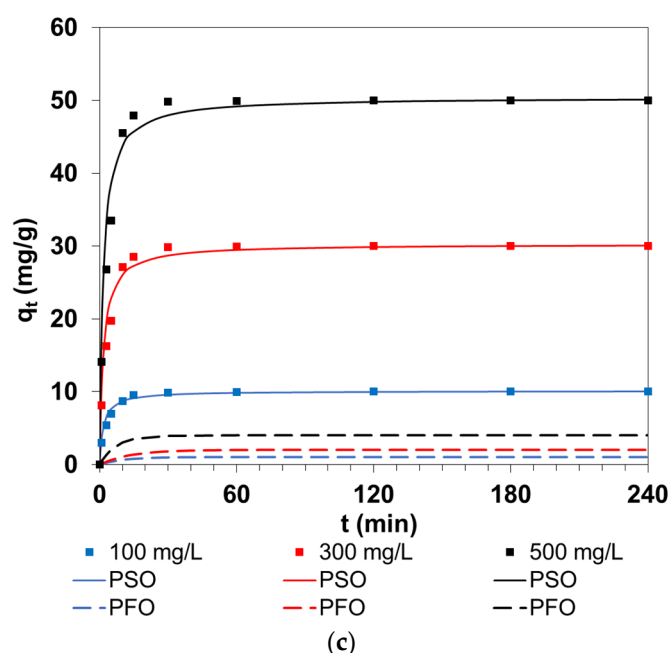


Figure 3. Influence of phase contact time and initial concentrations of DY50 on the amount of dye adsorbed by (a) A21, (b) A23 and (c) A24 resins and the fitting of experimental data to the kinetic models.

In the case of the dye solution of 100 mg/L concentration, the time needed for its removal is quite short, being 10 min, 30 min and 180 min for A23, A24 and A21, respectively. At the initial stage, adsorption is rapid, which indicates the presence of many readily accessible ion exchange sites on the surface of the anion exchanger. When the adsorption of the outer surface reaches saturation, the DY50 anions enter the pores of the anion exchanger and are adsorbed in the inner surface of the particle. After this time, the equilibrium is reached without a significant change of q_t values. With an increase in the amount of dye in the aqueous phase, the time needed to reach equilibrium increases; at the dye concentration of 500 mg/L it is equal to 70 min, 190 min and 220 min for A24, A23 and A21, respectively. DY50 sorption on A23 was slow compared to that on A21 and A24. For the initial concentrations of DY50 at the level of 100, 300 and 500 mg/L, q_t was 9.9 mg/g, 29.3 mg/g and 43.2 mg/g, respectively. A similar phenomenon was observed by Wawrzekiewicz [37] in the process of C.I. Direct Red 75 sorption on the weakly basic (Amberlite IRA67) and strongly basic (Amberlite IRA458) anion exchangers of polyacrylic matrix from an aqueous solution. The time needed to reach equilibrium lengthened with the increasing concentration of dye in the water phase and for the initial concentrations of 100 mg/L, 500 mg/L and 1000 mg/L it was 30 min, 60 min and 120 min using Amberlite IRA67 and 40 min, 60 min and 120 min using Amberlite IRA458.

3.2. Kinetic Parameters of Sorption

Knowledge of adsorption kinetics allows for direction of the entire adsorption process so that its effectiveness is as high as possible. The mechanism of DY50 adsorption on AA21, A23 and A24 was described using the three most common models: pseudo-first order, pseudo-second order and intraparticle diffusion. These equations are based on the definition of the amount of substance adsorbed by a mass unit of adsorbent in a unit of time. Based on the calculated kinetic parameters, listed in Table 2, it is possible to determine which model is most compatible.

Table 2. The parameters determined from the pseudo-first order, pseudo-second order and intra-particle diffusion models in the DY50-A21, DY50-A23 and DY50-A24 adsorption systems.

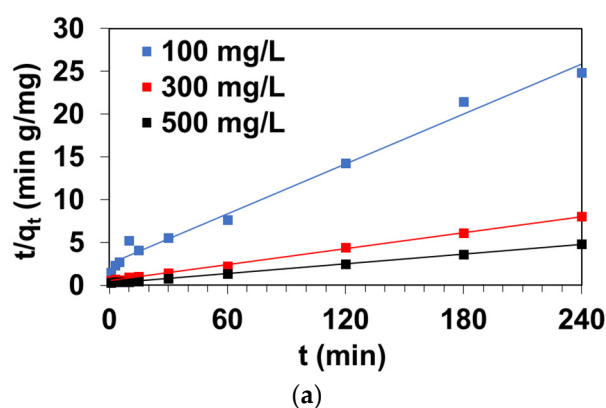
Resin	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	PFO			PSO			ID	
			q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg·min)	R^2	k_i (mg/g min ^{0.5})	R^2
A24	100	10.0	2.38	0.0435	0.779	10.12	0.0609	0.999	0.441	0.809
	300	30.0	4.65	0.0334	0.715	30.28	0.0201	0.999	1.106	0.946
	500	50.0	9.19	0.0608	0.907	50.44	0.0128	0.999	1.732	0.924
A21	100	9.8	8.3	0.0163	0.915	10.3	0.0038	0.999	0.923	0.874
	300	29.9	24.6	0.0297	0.991	31.9	0.0019	0.999	4.397	0.987
	500	49.9	37.5	0.0311	0.989	52.9	0.0015	0.999	5.612	0.874
A23	100	9.9	0.2	0.0137	0.257	9.9	1.1945	0.999	0.560	0.529
	300	29.3	6.5	0.0219	0.917	29.3	0.0188	0.999	0.668	0.789
	500	42.9	21.5	0.0169	0.944	43.2	0.0032	0.999	3.184	0.998

3.2.1. Pseudo First-Order Model

The Lagergren equation was not used to describe the DY50 sorption kinetics on anion exchange resins of different matrices such as A21, A23 and A24 due to the small values of the determination coefficients R^2 being in the range 0.779–0.907 for A24, 0.915–0.989 for A21 and 0.257–0.944 for A23. In addition, the calculated equilibrium capacities were much lower than those determined experimentally (Figure 3 and Table 2). Moreover, the graph $\log(q_e - q_t)$ vs. t was not linear.

3.2.2. Pseudo Second-Order Model

Figure 4 shows the linearized form of the pseudo-second order kinetic dependence for DY50 sorption from a solution of different initial concentrations on A21, A23 and A24. If the kinetics of the sorption process is described by means of the pseudo-second order model, the plot t/q_t vs. t gives a linear relationship from which q_e and k_2 can be calculated and it is not necessary to know any parameter beforehand. In the case of the pseudo second order model, the k_2 constant decreases as the concentration of dye in the aqueous solution increases. Based on the data presented in the Table 2 and Figures 3 and 4, it can be concluded that the PSO model received the best fit to the experimental data. This is indicated by not only high values of the determination coefficient R^2 (0.999), but also by the values of $q_{e,exp}$, which are very similar to those calculated from the PSO equation. Applicability of PSO model for description of experimental data in the DY50-cotton fiber [60] and DY50-natural clay and organoclay adsorbents systems was described in paper by Ismail et al. [60] and Khodaeer [61] and is also summarized in Table 3.

**Figure 4.** Cont.

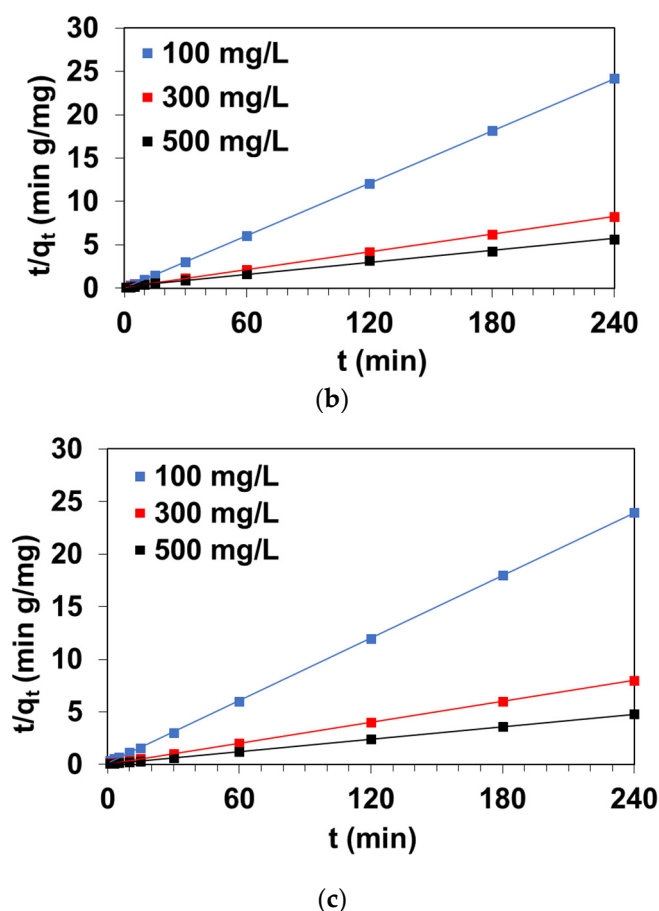


Figure 4. The t/q_t vs. t dependences determined from the linear form of the PSO model in (a) DY50—A24, (b) DY50—A24 and (c) DY50—A24 systems.

Table 3. The kinetic and equilibrium parameters of DY50 sorption on various adsorbents based on the literature review.

Sorbent	Kinetic Studies	Equilibrium Studies	Ref.
Cotton fibre	PSO, $k_2 = 11.4 \times 10^2 - 12.95 \times 10^2$ g/mg min, $q_e = 0.684-0.965$ mg/g, $C_0 = 113.4$ mg/L, $T = 40-90$ °C, pH = 7.03, a.d. = 1 g/30 mL	Langmuir model, $q_e = 4.4-5.8$ mg/g, $T = 40-90$ °C, pH = 7.03, a.d. = 1 g/30 mL	[60]
Organoclay adsorbent	PSO, $k_2 = 0.087$ g/mg min, $q_e = 1.66$ mg/g, $C_0 = 50$ mg/L, $T = 25$ °C, pH = 3, a.d. = 0.2 g/50 mL	Freundlich model, $k = 0.617$ mg $^{1-1/n}$ L $^{1/n}$ /g, $n = 1.93$, pH = 3, a.d. = 0.2 g/50 mL	[61]
Sugarcane bagasse biomas	PSO, $k_2 = 0.0051$ g/mg min, $q_e = 18.8$ mg/g, $C_0 = 50$ mg/L, $T = 30$ °C, pH = 2, a.d. = 0.05 g/50 mL	Langmuir model, $q_e = 51.8$ mg/g, $T = 30$ °C, pH = 2, a.d. = 0.05 g/50 mL	[62]
Sugarcane bagasse biomas treated with polyethyleneimine	PSO, $k_2 = 0.012$ g/mg min, $q_e = 20.7$ mg/g, $C_0 = 50$ mg/L, $T = 30$ °C, pH = 2, a.d. = 0.05 g/50 mL	Langmuir model, $q_e = 68.4$ mg/g, $T = 30$ °C, pH = 2, a.d. = 0.05 g/50 mL	

Table 3. Cont.

Sorbent	Kinetic Studies	Equilibrium Studies	Ref.
Rice straw	No model, $q_e = 2.8\text{--}1.0\text{ mg/g}$, pH = 4–10, $C_0 = 100\text{ mg/L}$, $t = 8\text{ days}$, $a.d. = 0.5\text{ mg/50 mL}$	Freundlich model, $k = 0.28\text{--}0.77\text{ mg}^{1-1/n}\text{ L}^{1/n}/\text{g}$, $n = 1.34\text{--}1.86$, pH = 4–10, $a.d. = 0.5\text{ mg/50 mL}$	[63]
Radiation-modified maize starch/acrylonitrile	No model, $q_e = 2.8\text{--}1.2\text{ mg/g}$, pH = 4–10, $C_0 = 100\text{ mg/L}$, $t = 8\text{ days}$, $a.d. = 0.5\text{ mg/50 mL}$	Freundlich model, $k = 0.33\text{--}0.66\text{ mg}^{1-1/n}\text{ L}^{1/n}/\text{g}$, $n = 1.74\text{--}2.1$, pH = 4–10, $a.d. = 0.5\text{ mg/50 mL}$	
Marble powder	PSO, $k_2 = 0.81\text{--}35.31\text{ g/mg min}$, $q_e = 1.39\text{--}26.3\text{ mg/g}$, $C_0 = 10\text{--}60\text{ mg/L}$, $T = 25\text{ }^\circ\text{C}$, $a.d. = 2\text{ g/L}$	Langmuir model, $q_e = 50\text{ mg/g}$, $T = 25\text{ }^\circ\text{C}$, $a.d. = 2\text{ g/L}$	[64]
Amberlite XAD7 (PA non functionalized resin)	PSO, $k_2 = 0.015\text{--}2.34\text{ g/mg min}$, $q_e = 0.9\text{--}9.4\text{ mg/g}$, $C_0 = 10\text{--}100\text{ mg/L}$, $T = 25\text{ }^\circ\text{C}$, $a.d. = 0.5\text{ g/50 mL}$	Langmuir model, $q_e = 27.9\text{ mg/g}$, $T = 25\text{ }^\circ\text{C}$, $a.d. = 0.5\text{ g/50 mL}$	[48]
Amberlite IRA958 (PA with quaternary ammonium groups)	PSO, $k_2 = 0.020\text{--}0.036\text{ g/mg min}$, $q_e = 10\text{--}50\text{ mg/g}$, $C_0 = 100\text{--}500\text{ mg/L}$, $T = 25\text{ }^\circ\text{C}$, $a.d. = 0.5\text{ g/50 mL}$	Langmuir model, $q_e = 534.8\text{ mg/g}$, $T = 25\text{ }^\circ\text{C}$, $a.d. = 0.5\text{ g/50 mL}$	
Lewatit VPOC1064 (PS-DVB non functionalized resin)	PSO, $k_2 = 0.016\text{--}0.41\text{ g/mg min}$, $q_e = 0.9\text{--}6.8\text{ mg/g}$, $C_0 = 10\text{--}100\text{ mg/L}$, $T = 25\text{ }^\circ\text{C}$, $a.d. = 0.5\text{ g/50 mL}$	Langmuir model, $q_e = 19.4\text{ mg/g}$, $T = 25\text{ }^\circ\text{C}$, $a.d. = 0.5\text{ g/50 mL}$	[48]
Amberlite IRA900 (PS-DVB with quaternary ammonium groups)	PSO, $k_2 = 0.01\text{--}0.06\text{ g/mg min}$, $q_e = 7.7\text{--}39.1\text{ mg/g}$, $C_0 = 10\text{--}500\text{ mg/L}$, $T = 25\text{ }^\circ\text{C}$, $a.d. = 0.5\text{ g/50 mL}$	Langmuir model, $q_e = 487.2\text{ mg/g}$, $T = 25\text{ }^\circ\text{C}$, $a.d. = 0.5\text{ g/50 mL}$	
Amberlyst A23 Amberlyst A21 Amberlyst A24	PSO, see Table 2	$q_e = 284.3\text{ mg/g}$ $q_e = 610.9\text{ mg/g}$ $q_e = 666.5\text{ mg/g}$ Langmuir model, See Table 4	This study

Where PSO—pseudo-second order model, k_2 —pseudo-second order rate constant, q_e —equilibrium capacity, C_0 —initial DY50 concentration, T —temperature, $a.d.$ —adsorbent dosage, k_F and n —Freundlich isotherm parameters, t —equilibrium time, PA—polyacrylate, PS-DVB—polystyrene-divinylbenzene.

Table 4. The isotherm parameters determined from the Langmuir and Freundlich equations in the DY50-A21, DY50-A23 and DY50-A24 adsorption systems.

Anion Exchanger	$q_{e,exp}$ (mg/g)	Langmuir			Freundlich			
		R^2	Q_0 (mg/g)	b (L/mg)	R^2	n	$1/n$	k_F ($\text{mg}^{1-1/n}\text{ L}^{1/n}/\text{g}$)
A24	666.5	0.998	652.9	0.0834	0.726	6.661	0.150	239.5
A21	610.9	0.991	577.5	0.0460	0.308	3.526	0.284	84.3
A23	284.3	0.990	290.3	0.0035	0.799	1.889	0.529	4.8

3.2.3. Weber and Morris Intraparticle Diffusion Model

Figure 5 shows the applicability of intraparticle diffusion model in description of DY50 adsorption on A21, A23 and A24. The kinetic parameters calculated from the Weber-Morris equation are given in Table 2. The graphs illustrate multi-linearity, the adsorption data can be fitted with two or three straight lines. The first part of the graph can be attributed to the diffusion effect by the boundary layer while the second linear part is associated with intraparticle diffusion (diffusion into the polymer network) [65]. The slope of the second linear part is characterized by the speed parameter corresponding to the intraparticle diffusion. The values of intraparticle diffusion rate constants k_i increase in the range 0.441–1.732 $\text{g/mg}\cdot\text{min}^{0.5}$, 0.923–5.612 $\text{g/mg}\cdot\text{min}^{0.5}$ and 0.560–3.184 $\text{g/mg}\cdot\text{min}^{0.5}$ with the increasing initial concentration of DY50 from 100 to 500 mg/L for A24, A21 and A23, respectively. This may be associated with a driving force that increases with the increasing dye concentration in the solution and contributes to an increase in the dye diffusion rate. The values of determination coefficients R^2 are in the range of 0.809–0.946, 0.874–0.987 and 0.529–0.998 for A24, A21 and A23, respectively.

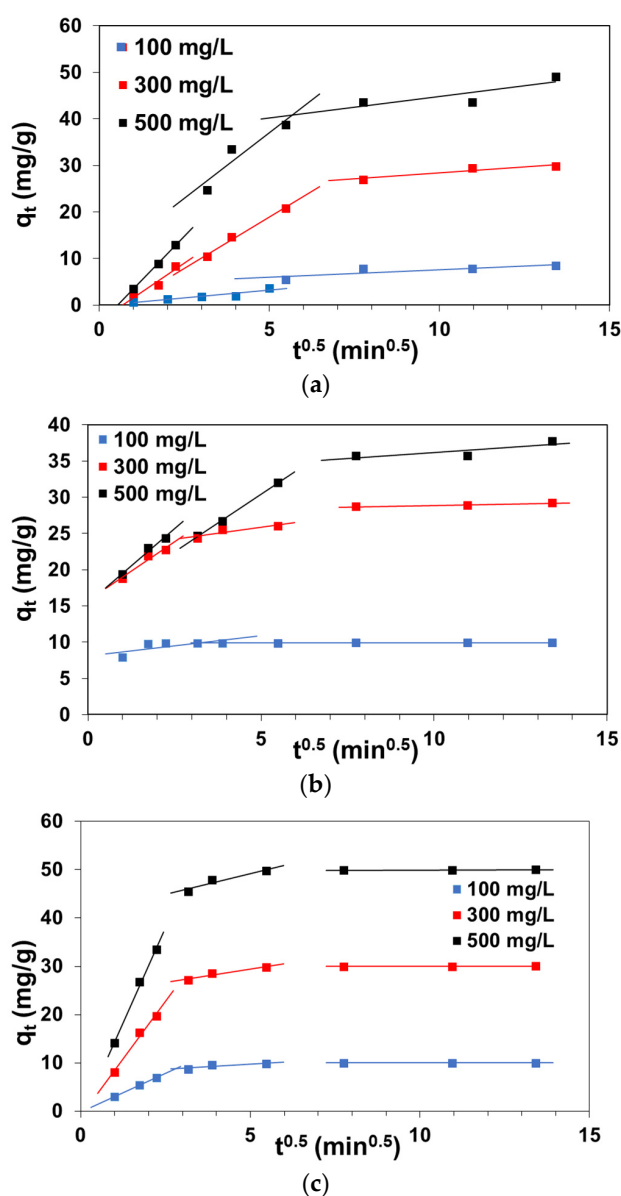


Figure 5. Intraparticle diffusion model applied for adsorption of DY50 on (a) A21, (b) A23 and (c) A24.

3.3. Effect of Salts and Surfactants Presence on DY50 Adsorption

Industrial wastewaters generated during various technological processes carried out in textile factories, paper and tanneries contain auxiliary agents such as salts, acids, bases, surfactants, oxidants and reducing agents. They get into the sewages in the amount in which they were used in the dyeing baths and do not wear out in the dyeing process of the fiber, as opposed to dyes. Depending on the type and nature of the fiber, as well as the intensity of coloration, the amount of dyes and auxiliaries used are different. The compositions of dyeing baths are summarized in Table 5 [66,67].

Table 5. Compositions of baths for dyeing with direct dyes.

Bath Components	Light Intensity	Deep Intensity
Dye	up 0.5%	0.5–3%
Na ₂ CO ₃	0.5–1%	1–2%
Na ₂ SO ₄	4–10%	10–30%
Surfactants	up 0.5%	0.5–1%

The main component of the dyeing bath is water characterized by a relatively high surface tension; therefore, it is necessary to introduce surfactants which reduce surface and interfacial tension [66,67]. The addition of surfactants will cause that water will moisten the fiber surface better, which will facilitate the dyes' contact with this surface. Interactions between the surfactant and the dye molecules in the aqueous solution are of great importance in the process of water treatment and reuse [66–70].

Therefore, it is necessary to assess the effects of various salt and surfactant amounts on the adsorption of dyes. The influence of auxiliaries on DY50 sorption efficiency on the A21, A23 and A24 anion exchangers was studied using the static method in the systems containing 0.5 g of anion exchangers and 50 mL of DY50 solution of 500 mg/L concentration while the concentration of salts and surfactants changed from 5 to 25 g/L of Na₂SO₄ or Na₂CO₃ and from 0.1 to 0.5 g/L of SDS or TX-100. The amount of dye adsorbed by the anion exchanger after 15 min of phase contact time was determined. In the studies a decrease of q_t was observed in the anion exchangers-DY50 systems with an increase of Na₂CO₃ concentration (Figure 6), however the least pronounced impact of carbonate presence on the uptake effectiveness can be observed for the anion exchange resin of polyacrylic matrix, i.e., A24. The decrease in the sorption capacity together with the increase of sulphate concentration in the system may be caused by competitive sorption of sulfate ions compared with the anionic form of the dye.

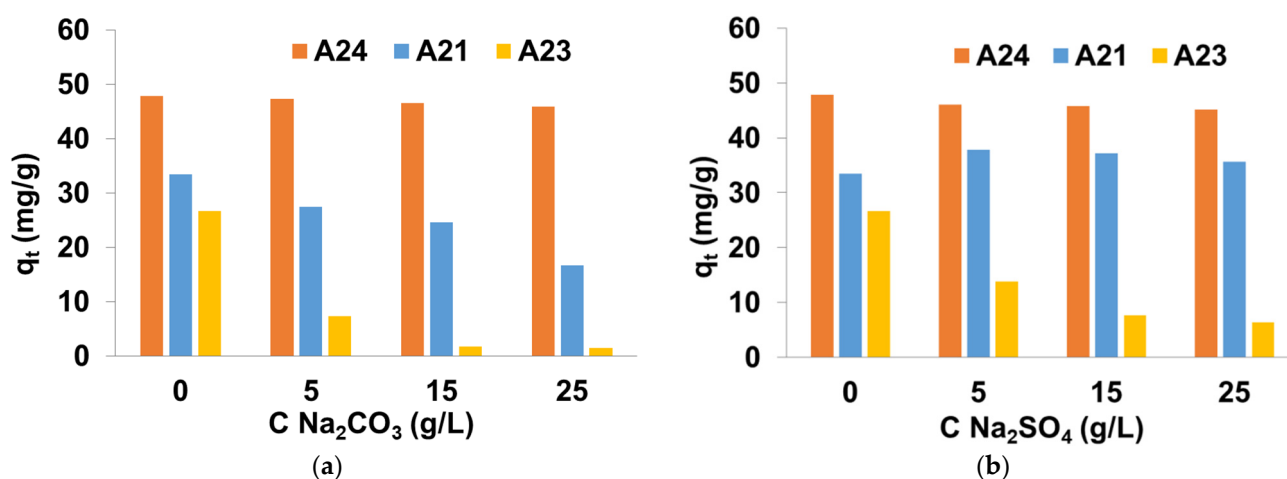


Figure 6. The effects of (a) Na₂CO₃ and (b) Na₂SO₄ presence on DY50 adsorption on A21, A23 and A24 anion exchangers.

The presence of SDS and TX-100 (0.1–0.5 g/L) in the dye solution resulted in an increase in q_t values using the phenol-formaldehyde resin A23 during sorption test as it is characterized by the highest value of the total capacity (1.8 eq/L as declared by the manufacturer), resulting in a larger concentration of the $-N(CH_3)_2$ functional groups compared to the other anion exchangers (A21, A24). The interactions between dye anion and a surfactant with the same charge contribute to electrostatic repulsion in the aqueous phase and favors adsorption of DY50 anion in the resin phase in dye-surfactant systems. The presence of these surfactants caused a decrease in the dye adsorption on the polystyrene A21 and polyacrylic A24 anion exchangers which suggests that competitive sorption of the anionic surfactant compared to the dye anions is more pronounced, as presented in Figure 7. Therefore, the type of anion exchanger matrix composition plays an important role in dye sorption from solutions containing auxiliaries such as surfactants. Notwithstanding this, the hydrophobic interactions between the DY50 and the SDS or TX-100 are dominate during DY50 adsorption on A23. The nonionic TX-100 could form aggregates with dye molecules that were less soluble in the aqueous phase and enhanced their adsorption in the resin phase [66].

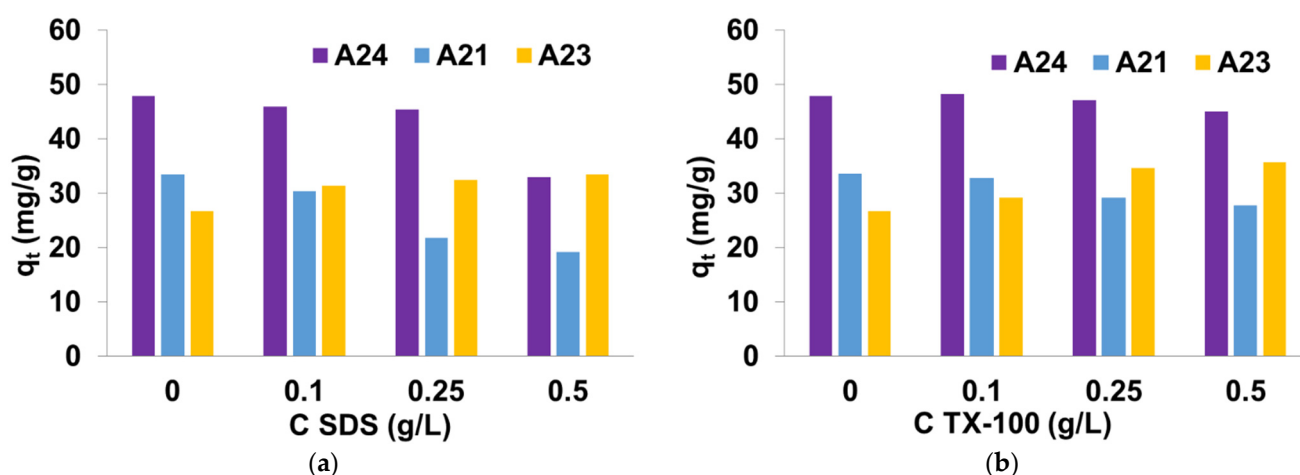


Figure 7. The effects of (a) anionic SDS and (b) non-ionic TX-100 surfactants presence on DY50 adsorption on A21, A23 and A24 anion exchangers.

Removal of organic compounds such as dyes in the presence of surfactants by anion exchangers is a complex process due to the several adsorption phenomena (ion exchange reaction, molecular interactions and driving forces) and significant impact of hydrophobic interaction [71–73]. The solute (dye, surfactants)-solvent (water) interaction is of great importance, too, in influencing the sorption affinity of organic compound such as dye [71]. The enhanced equilibrium uptake of organic compounds by the resins was broadly discussed considering enthalpy and entropy changes in terms of so-called entropy-assisted sorption, screening effect and de-solvation of molecules by Rahmani and Mohseni [71], Li and SenGupta [72,73] and Stevenson et al. [74].

3.4. Adsorption Isotherms

3.4.1. Langmuir Isotherm

It was found that the isotherms were linear over the entire range of tested concentrations, and R^2 values equaled to 0.998, 0.991 and 0.990 for A24, A21 and A23, respectively (Table 4). The Langmuir equation represents a better fit of experimental data than the Freundlich equation (Figure 8). The values of Langmuir parameters largely depended on the type of anion exchanger matrix. The monolayer adsorption capacity of A24 was found to be 666.5 mg/g and was larger compared to A23 ($Q_0 = 284.3$ mg/g). A high b value suggests a steep isotherm onset and indicates a high affinity of the anion exchanger for the

dye [14]. The b constants for A24, A21 and A23 were 0.0834, 0.0460 and 0.0035, respectively. The highest value was obtained for polyacrylic Amberlyst A24 suggesting strong direct dye binding. The dimensionless separation factor R_L calculated from Equation (7) for the Langmuir type adsorption process were in the range 0 and 1 as can be seen in Figure 8.

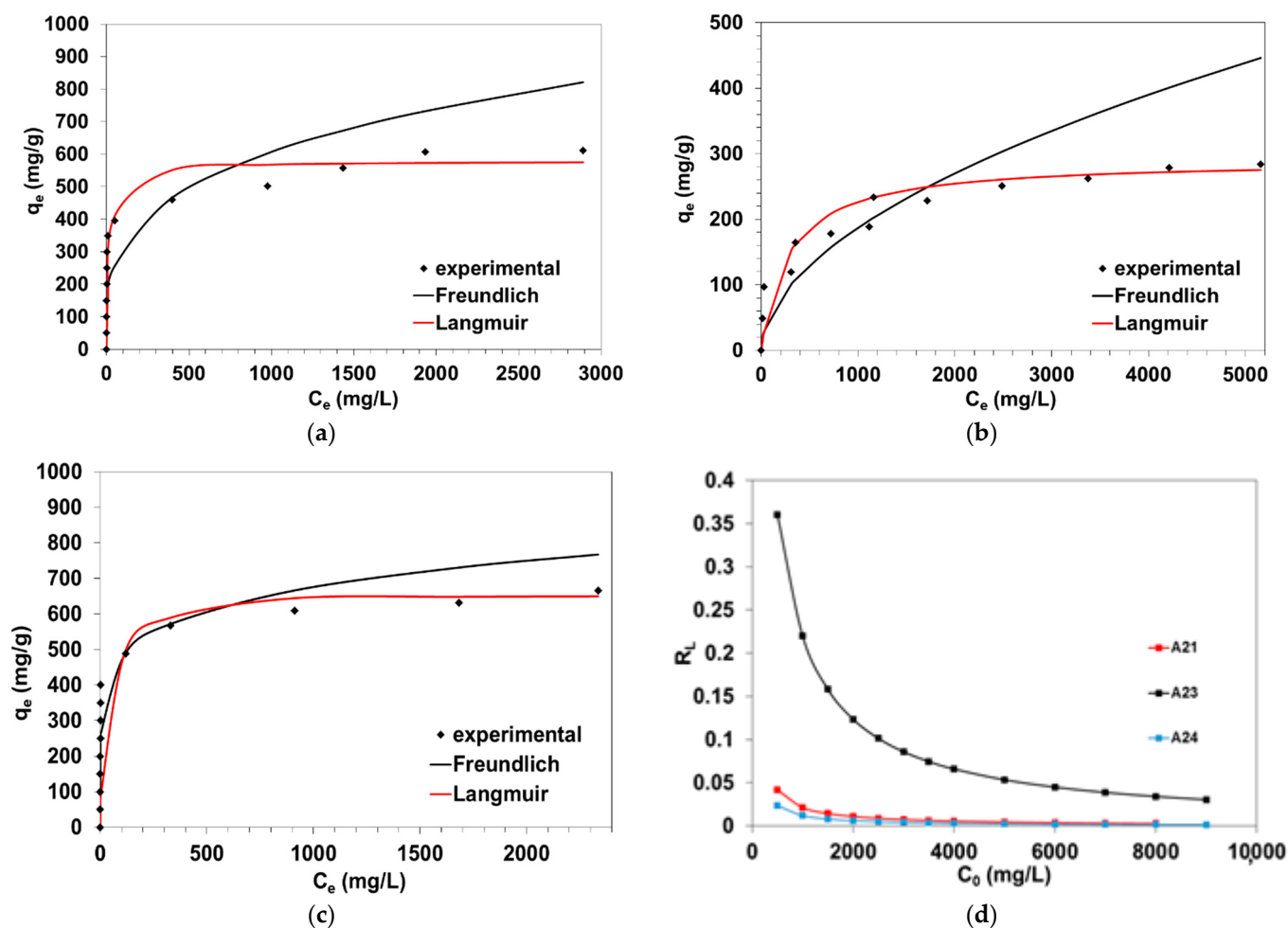


Figure 8. Fitting of the experimental data to the Langmuir and Freundlich isotherm models in the (a) DY50-A21, (b) DY50-A23 and (c) DY50-A24 systems as well as (d) the dimensionless separation factor as a function of DY50 initial concentration.

Research conducted by Wawrzkiecicz et al. [49] concerning DY50 removal using the polyacrylic (Amberlite IRA478, Amberlite IRA958) and polystyrene (Lewatit MonoPlus MP68, Amberlite IRA900) anion exchange resins of different basicity of functionalities as well as non-functionalized polymeric resins of polyacrylic and polystyrene matrices (Amberlite XAD7, Lewatit VPOC1064) confirm that this process depends on the composition and the structure of the anion exchanger. The highest sorption capacity towards DY50 was exhibited by the polyacrylic anion exchanger Amberlite IRA 958 of the quaternary ammonium functional groups and it was 534.8 mg/g. Moreover, in the case of adsorption of direct dyes on polyacrylic anion exchangers, one can also notice much greater efficiency of the adsorption process using weakly basic resins compared to strongly basic ones, which was confirmed in paper [37] describing adsorption of C.I. Direct Red 75 on the weakly and strongly basic gel resins of polyacrylic skeletons such as Amberlite IRA 67 and Amberlite IRA 458.

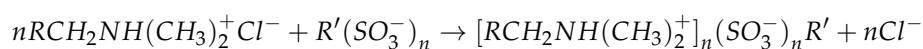
3.4.2. Freundlich Isotherm

The values of determination coefficients R^2 for the Freundlich isotherm are lower than for Langmuir isotherm and are equal to 0.726, 0.308 and 0.799 for A24, A21 and

A23, respectively. The values $1/n$ were smaller than 1, which indicates that the dye was preferably adsorbed (Table 4). In addition, k_F , that is the relative sorption capacity (approximate parameter of adsorption strength), was also determined. The highest k_F value was obtained for A24 being $239.5 \text{ mg}^{1-1/n} \text{ L}^{1/n}/\text{g}$. For A21 and A23, k_F were calculated as $84.3 \text{ mg}^{1-1/n} \text{ L}^{1/n}/\text{g}$ and $4.8 \text{ mg}^{1-1/n} \text{ L}^{1/n}/\text{g}$, respectively. The greater the value of the k_F parameter, the greater the adsorption capacity [64].

3.4.3. Adsorption Mechanism

The anion exchangers used for DY50 sorption have functional groups of the weak base nature, i.e., $-\text{N}(\text{CH}_3)_2$. Their sorption capacities declared by the manufacturer correspond to the functional group contents and are about 1.3, 1.6 and 1.8 eq/L for A21, A24 and A23, respectively. If the retention mechanism of DY50 occurred solely by anion exchange reaction, then A23 resin should exhibit the highest sorption capacity for DY50. However, the determined sorption capacity based on the isotherm models used is 290.3 mg/g (which is close to the experimentally determined value of 284.3 mg/g) and is the lowest among the studied resins. The mechanism of dye retention in the anion exchanger phase is a result of the formation of an ionic pair between the functional groups of the anion exchangers and the sulphonate groups of the dye to a considerable extent (Figure 9) and can be described by the following reaction:



where $\text{RCH}_2\text{NH}(\text{CH}_3)_2^+\text{Cl}^-$ —weakly basic anion exchanger in the chloride form, $\text{R}'(\text{SO}_3^-)_n$ —anionic form of dye of n sulphonate groups.

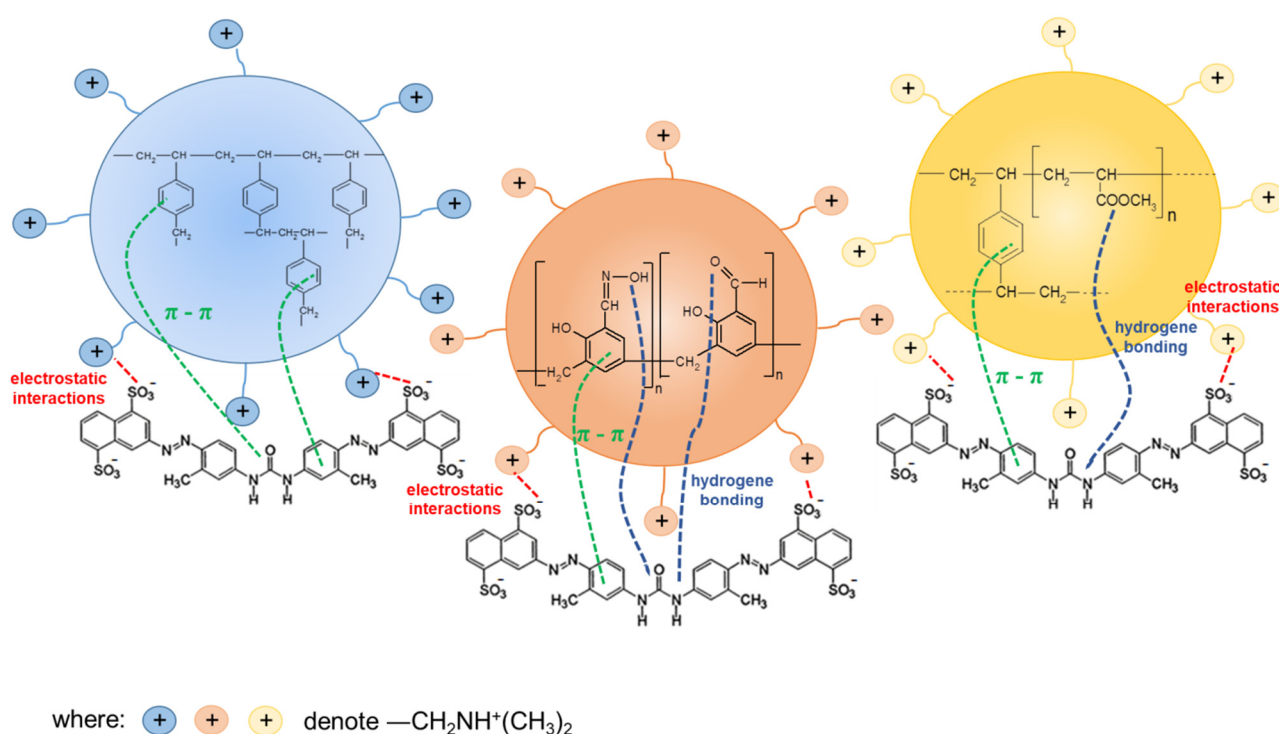


Figure 9. Proposed mechanism of DY50 interaction with the weakly basic anion exchangers of the polystyrene, phenol-formaldehyde and polyacrylic matrices.

However, the interactions between the delocalized electrons of benzene rings in the anion exchanger matrix and the delocalized electrons of dye aromatic rings (π - π type interactions), van der Waals and hydrogen bonds known as non-specific interactions can also be considered.

This suggests that the adsorption of dyes is dependent on the composition of the anion exchanger matrix. The q_e value of A24 possessing the polyacrylic matrix was found to be 666.5 mg/g. The polystyrene resin A21 adsorbed 610 mg of DY50 per gram, while the phenol-formaldehyde anion exchanger adsorbed dye in the amount of two times less. Resin of an acrylic matrix demonstrates beneficial exchange equilibria and kinetics towards large organic ions such as dyes compared with the styrenic ones [75]. A simplistic explanation for this lies with the greater hydrophilic nature of the aliphatic skeletal structure of the acrylic matrix, which in turn means van der Waals type interactions between the resin matrix and the hydrocarbon structure of an organic counter-ion (i.e., dye anion). The larger the organic anion the greater seems the affinity for an anion exchanger.

Another parameter that may influence the sorption capacity values is the matrix structure. Two of the studied anion exchangers, i.e., A21 and A23 have macroporous structure while A24 has gel structure. There are no actual internal macroscopic structural pores (holes or channels) in gel type resin and it can be likened to a dense electrolyte-gel within which the dissociated counter-ions are able to diffuse. The non-uniform distribution of crosslinking and functional groups in gel type resin implies the rise of regions showing different structural characteristics within a given resin bead, and consequently non-symmetrical strains within the structure. Additionally, during aqueous conditioning and rinses, some of the stresses and strains within a resin are induced which enhanced the hydrophilic nature. Macroporous resins, being highly crosslinked, possess quite a heterogeneous distribution of structurally dense and tortuous regions of high charge density therefore the rate of exchange can be discernibly slower when compared with gel equivalents [75]. Since macroporous resins possess real pores, the number of functional groups per unit dry weight of matrix is usually less than that for an equivalent gel product as reflected by their slightly lower dry weight capacities. This, in turn, can affect the dye retention capability. Slightly less important parameters affecting dye retention efficiency will be the physical features of the anion exchangers such as grain size, uniformity coefficient and sphericity [75].

Taking into consideration assumptions of the Langmuir and Freundlich models, calculated isotherm parameters, the flat structure of direct dye and properties of the anion exchange resins it can be stated that the adsorption of DY50 on A21, A23 and A24 has a complex nature. The mechanism of dye binding by anion exchangers depends on the chemical structure of the dye, the type and number of chromophore and auxochrome groups, as well as the structure and type of adsorbents.

For a more accurate analysis of DY50 retention by the A21, A23 and A24 anion exchangers there were recorded ATR-FT-IR. The spectra before and after DY50 sorption using the polystyrene (A21) and polyacrylic (A24) resins are shown in Figure 10. There were many bands characteristic for the anion exchangers matrix [76]. For example, the broad bands at 3374 cm^{-1} and 3271 cm^{-1} can be attributed to -OH stretching vibrations connected mainly with residual hydration water in A21 and A24, respectively. This band is particularly visible in the case of the polyacrylic anion exchanger, the matrix of which is more hydrophilic in comparison to the polystyrene anion exchanger, which is rather hydrophobic. There are low-intensity bands related to the stretching vibrations of the C-H in aromatic ring in the range $3100\text{--}3000\text{ cm}^{-1}$. The bands at $2800\text{--}3000\text{ cm}^{-1}$ refer to stretching vibrations of C-H in >CH- and $\text{-CH}_2\text{-}$. The stretching vibrations C-C of benzene rings and wagging or twist of methylene in amine functionalities can be found at $1420\text{--}1480\text{ cm}^{-1}$ and $1250\text{--}1350\text{ cm}^{-1}$, respectively. Vibrations at $1000\text{--}1100\text{ cm}^{-1}$ can be attributed to C-N stretching vibrations in -NH-CH_3 as well as -CH_3 rocking in $\text{-N(CH}_3)_2$. Bands at 1085 , 1145 and 1013 cm^{-1} are confirmation of a new symmetric and asymmetric vibration of the sulfonic -SO_3^- and -S=O groups in the analyzed spectra of the anion exchangers after DY50 sorption.

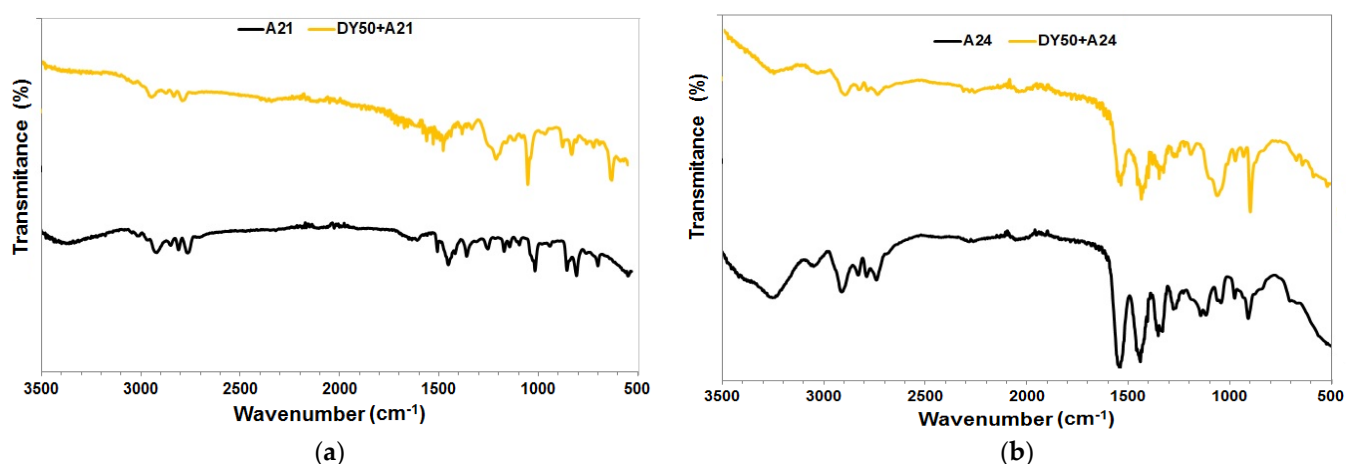


Figure 10. ATR-FT-IR spectra of (a) A21 and (b) A24 before and after sorption of DY50.

3.5. Impact of Solution pH

The effect of the initial solution pH on the adsorption of DY50 on A21, A23 and A24 was investigated by shaking 0.5 g of the resin with 50 mL of a solution containing 500 mg/L of dye. The pH of the solution is a very important parameter controlling the sorption processes [77]. The ion exchange process depends on the acidity or alkalinity of the solution. A21, A23 and A24 are weakly basic anion exchangers for which the most effective working environment is the range of pH = 1–7. A slight decrease in sorption capacity with an increase in solution pH was noted in all cases, which can be explained by the protonation of functional groups at pH below 8–9 (Figure 11). This indicates that the mechanism of DY50 adsorption on the weakly basic anion exchangers is not only the result of interaction between resins functional groups and sulphonic groups of the dye.

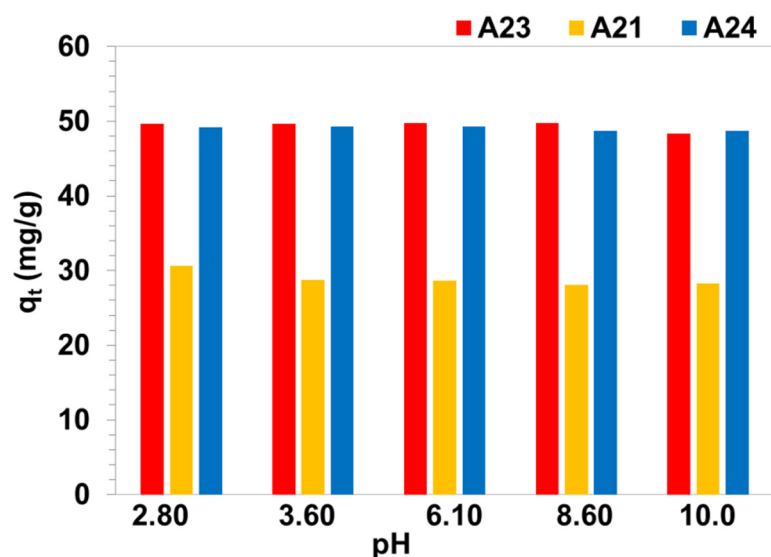


Figure 11. Influence of initial solution pH on DY50 uptake by the A21, A23 and A24 anion exchangers.

3.6. Desorption

Various reagents were tested in the experiments to find the most effective eluate: 1 M NaOH, 1 M HCl, 1 M NaCl, 50% *v/v* CH₃OH, 1 M NaOH + 50% *v/v* CH₃OH, 1 M HCl + 50% *v/v* CH₃OH and 1 M NaCl + 50% *v/v* CH₃OH. Figure 12 shows the results of DY50 desorption from the weakly basic anion exchangers A21, A23 and A24. The highest yield of reaction was observed during DY50 desorption from A23 and A24 using 1 M NaOH + 50% *v/v* CH₃OH (18.76% and 18.72% for A24 and A23, respectively). It is also acceptable to use

1 M NaOH for A23 (13.20%) or 1 M NaCl + 50% CH₃OH for A24 (14.56%). Regenerating agents such as 1 M NaCl, 1 M HCl or 50% CH₃OH turn out to be ineffective (Figure 12). Comparing the values of the desorption degree in aqueous and methanol solutions, it can be concluded that the use of methanol increases the desorption efficiency. The mechanism of DY50 sorption of the weakly basic resins occurs not only through ion exchange but also as a result of strong chemical adsorption. The same conclusions were drawn in case of C.I. Direct Red 75 removal from the weakly (Amberlite IRA67) and strongly basic (Amberlite IRA458) anion exchange resins as well as C.I. Reactive Black 5, Orange 16, Blue 15, Red 198 and Red 120 from weakly (MP62) and strongly (S6328a) basic resins [37,49,78].

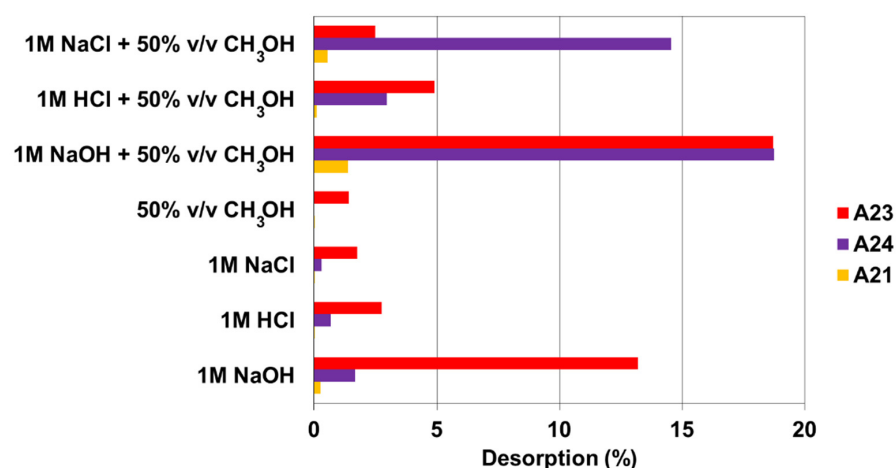


Figure 12. Desorption effectiveness of DY50 from the A21, A23 and A24 anion exchangers.

4. Conclusions

Applicability of the weakly basic anion exchangers of different matrices composition (polyarylic Amberlyst A24, polystyrene Amberlyst A21 and phenol-formaldehyde Amberlyst A23) in C.I. Direct Yellow 50 dye removal was investigated and described. Experimental parameters such as dye initial concentration, phase contact time and auxiliaries addition (Na₂SO₄, Na₂CO₃, SDS and TX-100) on dye removal efficiency are important parameters influencing the yield of dye removal. The largest sorption capacity for DY50 was exhibited by Amberlyst A24 ($Q_0 = 666.5$ mg/g) and Amberlyst A21 ($Q_0 = 610.9$ mg/g). Taking into account the composition of the matrix of anion exchange resins, the following series of sorbent usefulness can be presented:

polyacrylic > polystyrene > phenol-formaldehyde.

Kinetics sorption parameters were described by the pseudo-second order model and the equilibrium studies fitted well to the Langmuir equation. The resins regeneration can be performed with a yield of no more than 20% using 1 M NaOH/1 M NaCl in 50% v/v methanol. The anion exchangers can be considered as promising sorbents for removal of impurities such as dyes from aqueous solutions.

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