INFLUENCE OF FUNCTIONAL GROUPS OF POLYSTYRENE-DIVINYLBENZENE ADSORBENTS ON THE EFFECTIVENESS OF ACID DYE REMOVAL

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Abstract

For removal of C.I. Acid Red 18 (cochineal red A, ponceau 4R) from aqueous solutions, polystyrene Amberlyst A 21 and Lewatit VPOC 1064 were used. C.I. Acid Red 18 sorption was performed using static and dynamic methods. The parameters of the Freundlich and Langmuir isotherm models were calculated. The sorption rate constants were determined based on the pseudo-first-order, pseudo-second order and intraparticle diffusion models. The working and total exchange capacities, and bed and weight distribution coefficients were designated in the column system.

Key words: acid red, polystyrene adsorbents, dye removal

Introduction

Among the organic pollutants of the aquatic environment an important group are dyes and pigments. They are emitted into sewage from various industries including paint, textile, cosmetics, and paper. Dyes present in water, even in low concentrations, can stain significant areas of water giving it an unsightly appearance. They hinder the penetration of sunlight and thus inhibit photosynthesis and the development of biocenosis (1, 2). Textile wastes are a mixture of both organic and inorganic substances. They may contain not only significant amounts of dyes but also auxiliary agents (e.g. salts, acids, alkalis, surface active substances) as well as specific impurities (e.g. fats, waxes, casein, bleaching agents, starch) (3). These substances end up in sewage in the amount in which they are introduced into a dyeing bath and what is more, they do not wear out in the process of fiber dyeing as opposed to dyes. Table 1 shows the amounts of chemicals and auxiliaries (except dyes) contained in textile wastewater released into the environment in Europe.

Table 1. Content of auxiliaries in textile wastewaters in Europe (4).

Type of auxiliaries	Residue in sewage after the dyeing process
Carboxylic acids	15000-20000
Natural fibers contamination	50000-100000
Surfactants and detergents	20000-25000
Fats, esters, waxes	25000-30000
Dressings	80000-100000
Salts	200000-250000

The amount of unbound dye remaining in the dyeing bath depends inter alia on the type of dye, type of dyed fiber and dyeing method. The content of dyes in textile sewage after the dyeing process is from 2 to 50% depending on the type of dye used (5, 6). Table 2 shows the effects of the type of dye on the degree of its binding to fibers.

Table 2. The amount of dye entering textile sewage from dyeing baths (4).

Types of dye	Residual in sewage after the dyeing process (%)
Basic	2-3
Direct	5-20
Vat	5-20
Acid	7-20
Sulfur	20-40
Reactive	20-50

Acid dyes belong to one of the most numerous groups of dyes. They are most often used in the form of sodium salts of sulphonic acids, less frequently in the form of salts of carboxylic acids. The group of these dyes belongs to strong electrolytes, which in aqueous solutions are completely dissociated into coloured anions. Their permanent bond with fiber can be achieved by adding acids to the dye bath. In terms of chemical structure, they are azo dyes (mono- and diazo) (7). Azo dyes are the most important class of synthetic organic dyes used in the textile industry and therefore they can be considered as common industrial pollution. They are produced in large quantities and get into the environment during production processes. They are intended for dyeing wool and leather, and are also used in so-called household chemistry for colouring shampoos and lotions for baths, dishwashing liquids, toilet blocks as well as for coloring wood and paper (8). Cabrera and co-workers (9,10) obtained cochineal red A from dried and milled insects, and for its removal they used weakly basic anion exchangers of gel (Amberlite IRA 67) and macroporous (Amberlite IRA 96) structures. The determined sorption capacities were 0.318 kg and 0.271 kg cochineal

for 1 kg of Amberlite IRA-67 and 1 kg of Amberlite IRA-96, respectively. The modified clinoptilolite was used by Mirzaei et al. (11) for C.I. Acid Red 18 removal from aqueous solutions. The maximum adsorption capacity equaled 11 mg/g and was calculated from the Langmuir isotherm equation. In addition, kinetic studies showed that the adsorption was in agreement with the Elovich model. The proposed mechanism for removing the dyes are electrostatic interactions. Moreover, an attempt was made to remove C.I Acid Red 18 on a material based on titanium dioxide (As500). The monolayer capacity determined from the Langmuir equation was 24.92 mg/g. The time necessary to achieve the state of dynamic equilibrium was 180 minutes. In the case of dye solutions at a concentration of 100 mg/L and with increasing concentrations in the system, the period of equilibrium time increased. Experimental data were best described by the pseudo-second order model (12). Due to the complex structure of molecules, dyes are difficult to decompose by physical, chemical, and biological methods, as a result of which small amounts of toxic or carcinogenic products may be formed. One of the effective methods for removing dyes from water and sewage, both in the range of low and high concentrations, is their adsorption on porous synthetic sorbents (e. g. active carbons, ion exchange resins) (13). In connection with the above, the aim of the paper was to evaluate the effectiveness of Lewatit VPOC 1064 (VPOC1064) and Amberlyst 21 (A21) in the sorption process of C.I. Acid Red 18 (AR18, Fig. 1a) from aqueous solutions.

Materials and methods

Macroporous resins with a polystyrene matrix (Fig. 1b.) were used in the research: Lewatit VPOC 1064 (without the functional groups) and Amberlyst A21 (with the tertiary amino functional groups). Amberlyst A21 was prepared by washing with 1 M HCl and distilled water to remove impurities and convert the ionic form to chloride. In contrast, Lewatit VPOC 1064 was washed with 50% methanol with 4 M HCl at the ratio of 1:5 as well as with distilled water. Then both sorbents were dried at room temperature to a constant mass. The detailed information on the sorbents used is given in Figure 2.

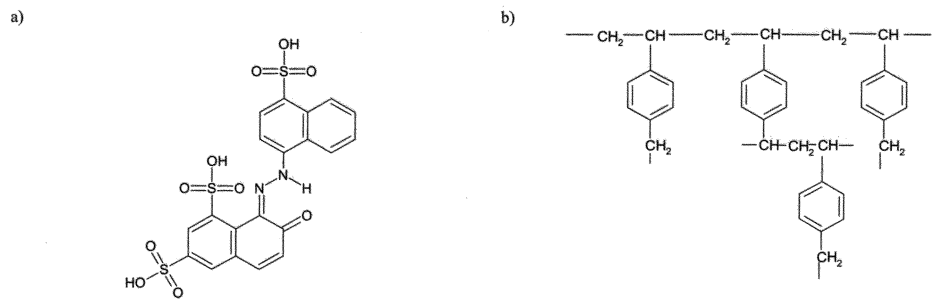

Figure 1. Structural formulae of dye (a) and polystyrene-divinylbenzene matrix (b) of the resins used.

Acetic acid, sodium chloride and sodium sulfate 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). C.I. Acid Red 18 (Sigma-Aldrich, Germany) is a synthetic azo dye. The molecular structure of C.I. Acid Red 18 ($C_{20}H_{11}N_2Na_3O_{10}S_3$, molecular weight 604.48 g/mol) is shown in Figure 1a. Solutions containing AR18 were prepared by dissolving a precisely weighed amount of dye in 1 liter of distilled water.

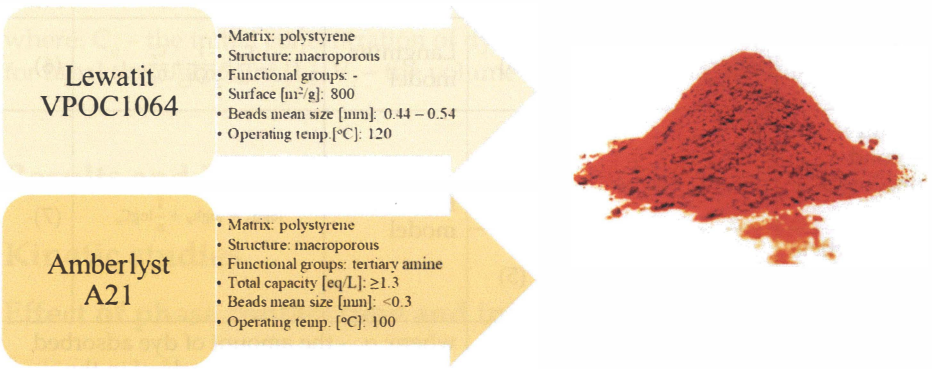

Figure 2. Physicochemical properties of the resins.

Static method

To perform laboratory tests using the static method, 100 ml conical flasks were used. The flasks were filled with 50 mL of a suitable dye solution and the resin of 0.5 g (± 0.0005). The flasks were then placed in a mechanical shaker (Elphin + 358S, Poland) with a vibration amplitude of 8 units at room temperature and stirred (180 cpm) from 1 to 240 min (kinetic test) or 24 h (equilibrium test). After shaking the sorbent was separated from the solution. The filtrate was analyzed using a spectrophotometer (Cary 60 UV-Vis, Agilent, USA) and then calculated:

– the amount of dye adsorbed at the equilibrium q_e [mg/g]

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

– the amount of dye adsorbed at the time t q_t [mg/g]

$$q_t = \frac{(C_0 - C_t)}{m} \cdot V \quad \text{for t = 1-240 min} \tag{2}$$

where: C_0 – the initial concentration of dye [mg/L], C_t – the concentration of dye after sorption time t [mg/L], V – the volume of solution [L], m – the mass of adsorbent [g].

In order to understand better the dynamics of the adsorption process and its mechanism, the following equations were used: pseudo-first order (PFO) (14), pseudo-second order (PSO) (15) and intraparticle diffusion (ID) (16). The kinetic parameters of C.I. Acid Red 18 sorption on the polystyrene adsorbents were calculated. Adsorption isotherms were determined using the Langmuir (17) and Freundlich models (18) (Table 1).

Table 1. Kinetics and equilibrium parameters.

Kinetic parameters		No.	Equilibrium parameters		No.
Pseudo-first order (PFO) model	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$	(3)	Langmuir model	$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$	(6)
Pseudo-second order (PSO) model	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$	(4)	Freundlich model	$\log q_e = \log k_F + \frac{1}{n}\log C_e$	(7)
Intraparticle diffusion (ID) model	$q_t = k_i t^{1/2} + C$	(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 time t, respectively [mg/g], k_2 – the adsorption rate constant [g/mg min], C – the constant illustrating the effect of the boundary layer on the sorption process			where: q_e – the amount of dye adsorbed per unit mass of the adsorbent in the equilibrium state [mg/g], C_e – the equilibrium dye concentration [mg/L], Q_0 – the Langmuir constant associated with the maximum sorption [mg/g], b – the Langmuir constant associated with the sorption energy [L/mg], K_F [mg/g], n – the Freundlich constants		

The effect of salt (Na_2SO_4), acetic acid (CH_3COOH) and surfactants (SDS, Triton X-100) on the AR18 sorption process on the Lewatit VPOC1064 and Amberlyst A21 was studied using the following conditions:

- Na_2SO_4 concentrations: C = 0-25 g/L Na_2SO_4, C_0 = 500 mg/L AR18, t = 15 min, V = 50 mL, m = 0.5 g, A = 8, room temperature,
- CH_3COOH concentrations: C = 0-2 g/L, C_0 = 500 mg/L AR18, t = 15 min, V = 50 mL, m = 0.5 g, A = 8, room temperature,
- SDS and Triton X-100 concentrations: C = 0-0.5 g/L, C_0 = 500 mg/L AR18, t = 15 min, V = 50 mL, m = 0.5 g, A = 8, room temperature.

The dye concentration after the sorption process was measured spectrophotometrically at the maximum wavelength.

Dynamic method

Laboratory tests were carried out using the dynamic method with a specially assembled set consisting of an ion exchange column with a diameter of

1 cm connected to a glass container by means of a rubber hose with a squeeze which allows the speed of the solution to be adjusted through the column. 10 mL of swollen resin was placed in the columns. Prepared solutions of AR18 at the concentrations of 100, 300 and 500 mg/L at a rate of 0.6 mL/min were passed through the column bed. The concentration of the dye in the leak from the column was determined by the spectrophotometric method. Based on the breakthrough curves, the working capacity (q_r) was calculated:

$$q_r = \frac{C_0 \cdot V_p}{V_s} \tag{8}$$

where: C_0 – the initial concentration of dye [mg/L], V_p – the volume of solution for breakthrough point [L], V_s – the volume of sorbent in the column [mL].

Results and Discussion

Kinetic studies

Effect of phase contact time and initial dye concentration

Figure 3 shows the effect of contact time (from 1 to 240 min) on C.I. Acid Red 18 sorption using Amberlyst A21 and Lewatit VPOC1064. The effect of the phase contact time on AR18 sorption on the above sorbents was examined taking into account the change in the initial dye concentration in the range of 100-500 mg/L as a function of time at room temperature with a constant mass of sorbents (0.5 g). For the weakly basic anion exchanger Amberlyst A21 the phase contact time needed to reach equilibrium was shorter compared to that for Lewatit VPOC1064 and was 20 min in an aqueous solution containing 100 mg/L of dye whereas for the initial dye concentrations 300 mg/L and 500 mg/L it was 40 and 80 min, respectively. The amount of AR18 adsorbed at time t by Amberlyst A21 is 10.03 mg/g, 30.33 mg/g and 51.17 mg/g for the initial concentrations 100, 300 and 500 mg/L, respectively. The sorption of AR18 on Lewatit VPOC1064 was significantly slower. For the initial concentrations of dye 100, 300 and 500 mg/L, the amounts of AR18 adsorbed were equal to 6.63 mg/g, 12.88 mg/g and 16.70 mg/g, respectively. The time needed to reach equilibrium was 140 min, 160 min and 200 min.

Analyzing the effect of phase contact time and the initial concentration of AR18 on the amount of dye absorbed by Lewatit VPOC1064 and Amberlyst A21, it can be concluded that the above-mentioned parameters had a significant effect on the q_t value. The time necessary to reach equilibrium was shorter using the resin with the tertiary amine functional groups - Amberlyst A21.

Pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models

The mechanism of adsorption of AR18 on Lewatit VPOC1064 and Amberlyst A21 was estimated using the most commonly applied kinetic models such as PFO, PSO and ID. They are based on defining the amount of substance adsorbed by the unit of adsorbent mass after conditioning time (q_t). Based on the calculated kinetic parameters (Table 3), it can be concluded that the best fit of experimental data was obtained for the PSO model.

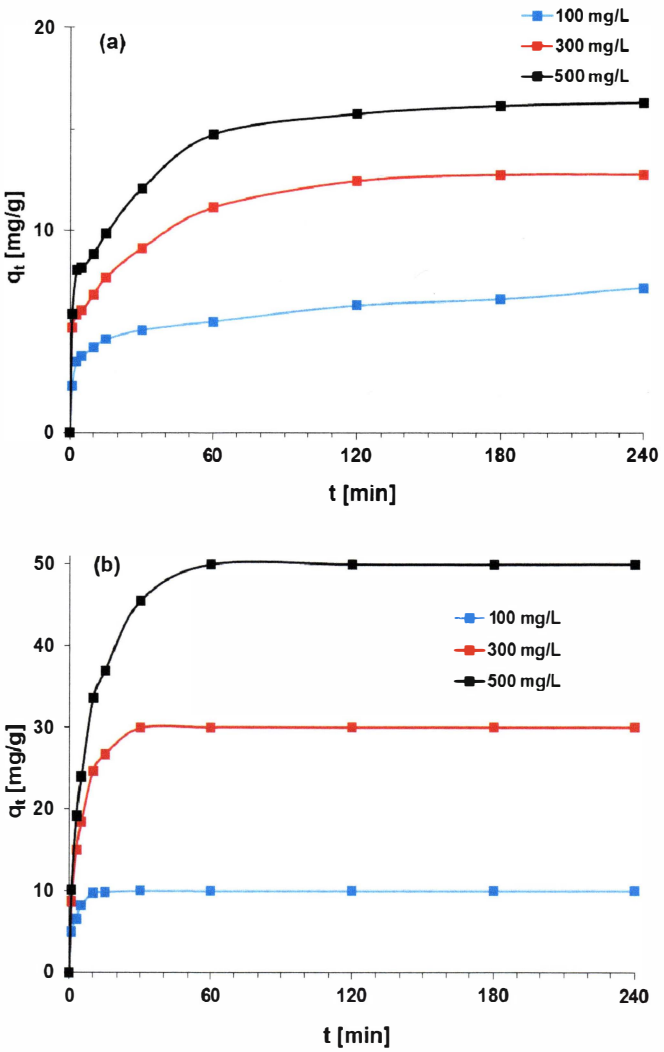

Figure 3. Influence of phase contact time and initial concentration on C.I. Acid Red 18 sorption on Lewatit VPOC1064 (a) and Amberlyst A21 (b).

Table 2. Kinetic parameters determined from the pseudo-first order kinetic, pseudo-second order, and intraparticle diffusion equations in the C.I. Acid Red 18 sorption process on Lewatit VPOC1064 and Amberlyst A21.

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_{int} [mg/g $min^{0.5}$]	R^2
Lewatit VPOC1064	100	7.20	3.65	0.0123	0.917	6.63	0.0254	0.998	0.560	0.880
	300	12.80	7.82	0.0262	0.991	12.88	0.0097	0.999	0.877	0.992
	500	16.30	8.88	0.0229	0.988	16.70	0.0087	0.999	1.239	0.954
Amberlyst A21	100	10.00	0.89	0.0489	0.615	10.03	0.1463	0.999	1.108	0.769
	300	30.00	5.03	0.0399	0.686	30.33	0.0159	0.999	4.701	0.913
	500	49.99	18.66	0.0419	0.798	51.17	0.0044	0.999	7.815	0.962

The pseudo-second order model is based on the solid phase capacity. If the kinetics of the sorption process is better described by the pseudo-second order model, then the t/q_t vs t graph gives a linear relationship from which q_e and k_2 can be determined and knowledge of any parameters is not necessary (Fig. 4.).

In addition, the values of $q_{e.exp}$ are close to those calculated from the PSO equation and indicate that they fit this model perfectly. The values of determination coefficients R^2 during sorption of AR18 on Lewatit VPOC1064 were in the range of 0.998-0.999 while during sorption on Aberlyst A21 $R^2 = 0.999$. The PFO equation did not apply to the description of AR18 sorption kinetics on Lewatit VPOC1064 and Amberlyst A21 due to the lack of a linear dependence of $\log(q_e-q_t)$ vs t, confirmed by small R^2 values and differences between the determined sorption capacities ($q_{e,exp}$) and that calculated from the PFO equation (q_e). The studies also evaluated the usefulness of the intraparticle diffusion (ID) model due to the porosity of the resin. However, the kinetic parameters calculated from the ID equation based on the graphs q_t vs $t^{0.5}$ referring to the studied systems are characterized by very small values of the determination coefficients; therefore it was not applied in the description of kinetic data.

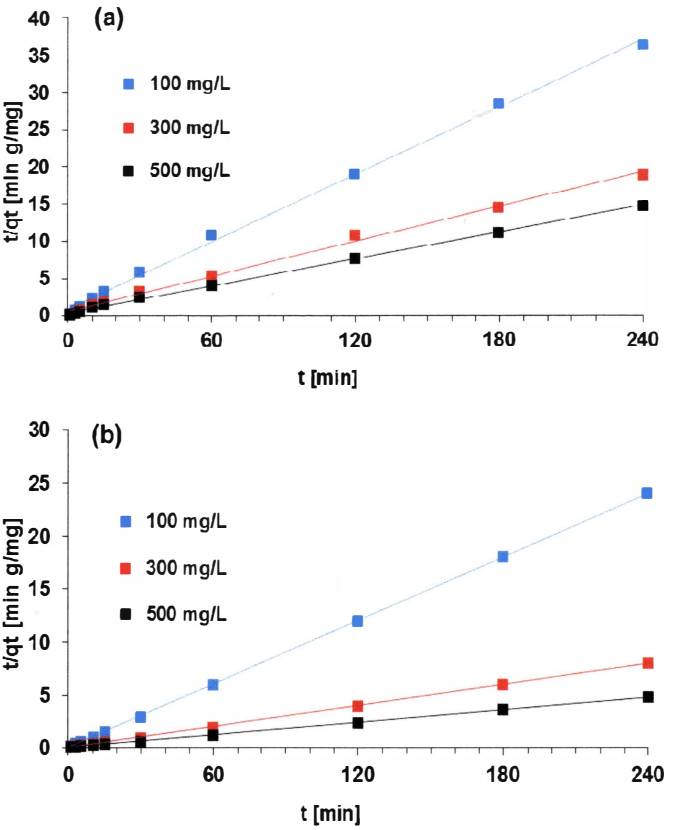

Figure 4. Dependence t/q_t vs t determined from the linear form of the PSO equation (AR18 - Lewatit VPOC1064 (a) and AR18 - Amberlyst A21 (b) systems).

Isotherms

To determine the balance between adsorbate concentration in the solid state and its concentration in the liquid phase, the adsorption isotherms were determined. The maximum sorption capacities of the resins in relation to AR18 were determined from the most popular adsorption models such as Langmuir and Freundlich (Fig. 5).

Based on the C_e/q_e vs C_e and $\log q_e$ vs $\log C_e$ the plots of isotherm parameters were determined and are given in Table 3. The best fit of the experimental data was obtained using the Langmuir model in the AR18-Amberlyst A21 system as evidenced by the high value of the determination coefficient R^2 (0.999). In the case of dye adsorption on the sorbent deprived of functional groups (Lewatit VPOC1064) a better match fit of the experimental data to the Freundlich

model was obtained. The value of the determination coefficient of R^2 was 0.690. Wawrzkiewicz et al. (19) removing C.I. Direct Yellow 50 with the aid of various sorbents confirmed that those without functional groups are better described by the Freundlich model.

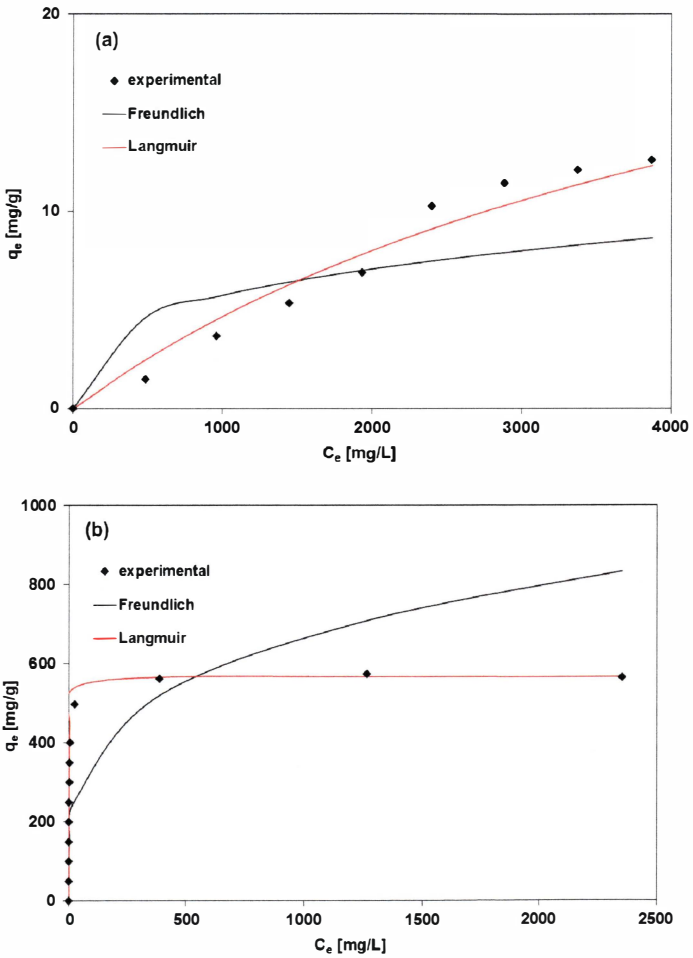

Figure 5. Adsorption isotherms of C.I. Acid Red 18 on the Lewatit VPOC1064 (a) and Amberlyst A21 (b) resins.

Table 4. Parameters determined from the Langmuir and Freundlich isotherms in the sorption process of C.I. Acid Red 18 by means of Lewatit VPOC1064 and Amberlyst A21.

Resin	Langmuir model			Freundlich model			
	R^2	Q [mg/g]	b [L/mg]	R^2	n	1/n	k_F [mg/g]
Lewatit VPOC1064	0.221	28.91	0.00019	0.690	3.29	0.303	0.705
Amberlyst A21	0.999	566.84	0.81365	0.233	3.81	0.262	109.018

Among the polystyrene resins used in the study the largest sorption capacity (Q_0) in relation to AR18 was found using Amberlyst A21, which amounted to 566.84 mg/g. Considering the presence or absence of functional groups it can be concluded that the Lewatit VPOC1064 adsorbent deprived of functional groups showed a much lower sorption capacity (Q_0 = 28.91 mg/g) compared to the adsorbent having functional groups – which leads to the conclusion that the presence of functionalities and their basicity increase the degree of adsorption in relation to the tested dye. Greluk and Hubicki (20) used anion exchangers with different basicity of functional groups to remove C.I. Acid Orange 7 from aqueous solutions. They observed that the strongly basic anion exchanger Amberelite IRA 458 exhibits much better sorption properties compared to the weakly basic Amberlite IRA 67 anion exchange resin as evidenced by the seven times higher Q_0 values 1211.3 mg/g and 168.2 mg/g, respectively.

Effect of sodium sulphate, acetic acid and surfactants presence on dye removal

Auxiliaries which include inorganic electrolytes (acids and salts) and surfactants are used in the processing of fibers. However, they remain in sewage at a concentration very close to the initial one in the dyeing bath. Depending on the type of dye, the dyeing process requires the use of other auxiliaries. Acid dyes belong to the most numerous group of dyes. The dyeing process using these dyes takes place in an environment of pH 4.5-5 acidified with acetic acid (21). Thus it is useful to study the effect of various concentrations of acetic acid, salts and surfactants on adsorption of AR18 (Fig. 6). The influence of auxiliaries on the effectiveness of sorption of AR18 on Lewatit VPOC1074 and Amberlyst A21 was studied using a static method in the system containing 0.5 g of resin and 50 mL of a dye solution (500 mg/L). The AR18 solutions additionally contained from 5 g/L to 25 g/L of Na_2SO_4, from 0.5 to 2 g/L of acetic acid and from 0.1 to 0.5 g/L of surfactants (SDS, Triton X-100). The amount of dye adsorbed by the resin was tested after 15 min of phased contact time.

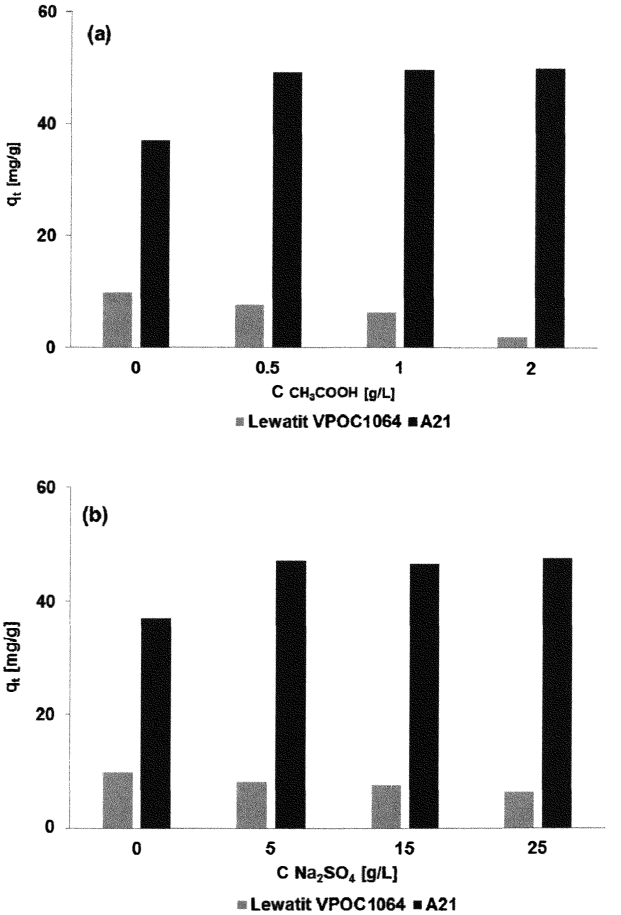

Fig. 6. The effect of salt and acid concentrations on the amount of C.I. Acid Red 18 adsorbed by the Lewatit VPOC1064 and Amberlyst A21.

The presence of acid in the system had an effect on the sorption process of AR18 on Lewatit VPOC1064 and Amberlyst A21. With increasing acetic acid concentration the values of q_t decrease during sorption on Lewatit VPOC1064, and q_t increases during sorption on Amberlyst A21 (Fig. 6a.). In the conducted studies, reduction of q_t values in the AR18-Lewatit VPOC1064 system and an increase of q_t in the AR18-Amberlyst A21 system with an increasing Na_2SO_4 concentration were observed (Fig. 6b.). The decrease in sorption capacity along with the increase in the concentration of salt or acid in the system may be caused by the competitive sorption of sulphate or acetate ions with the anionic form of the dye.

The effects of the SDS and Triton X-100 surfactants on AR18 sorption on Lewatit VPOC1064 and Amberlyst A21 were also studied (Fig. 7.). As the concentration of anionic surfactant (SDS) increases, q_t increases during sorption of AR18 on Lewatit VPOC1064 and Amberlyst A21. On the other hand,

the presence of non-ionic Triton X-100 caused a decrease in q_t values (9.81-1.59 mg/g) during sorption of AR18 on Lewatit VPOC-1064 and an increase in q_t (36.97-48.30 mg/g) during the sorption of AR18 on Amberlyst A21.

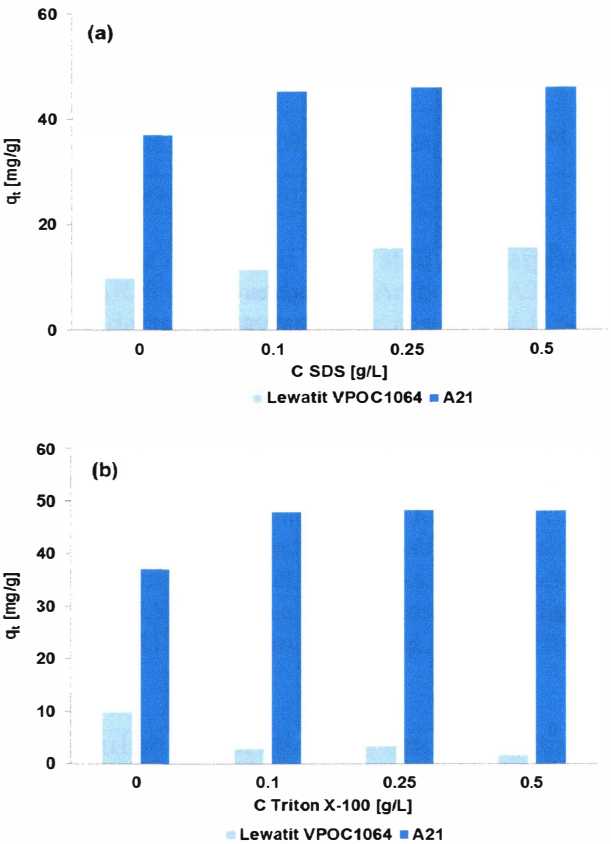

Figure 7. Effect of anionic SDS (a) and non-ionic Triton X-100 (b) surfactants on C.I. Acid Red 18 adsorbed by the Lewatit VPOC1064 and Amberlyst A21.

Column studies

Ion exchange reactions in industry are carried out in a column system under various conditions. Therefore it is quite important to determine the working ion-exchange capacity because the results obtained from such tests give the possibility of qualifying the adsorbent to be tested in a suitable technological process. On the basis of the breakthrough curves (Figs. 8 and 9), the working ion exchange capacities (C_w), weight (D_w) and bed (D_b) distribution coefficient were determined, the values of which are presented in Table 5:

$$D_w = \frac{(U - U_0 - V_v)}{m} \quad (9)$$

$$D_b = \frac{(U - U_0 - V_v)}{v} \quad (10)$$

$$C_w = \frac{V_{bp} \cdot C_o}{v} \quad (11)$$

where: U – the volume of the eluate for C/C_0= 0.5 [mL], U_0 – the dead volume of the column (liquid volume in the column between the bottom edge of the resin bed and the outlet of the column under the process conditions U_0=2 mL), V_v – the free volume (intergranular) in the resin bed (approx. 0.4 bed volume) [mL], m – the dry resin mass in the column [g], v – the swollen resin volume in the column [mL], V_{bp} – the column leakage volume [mL], C_0 – influent concentration [mg/L].

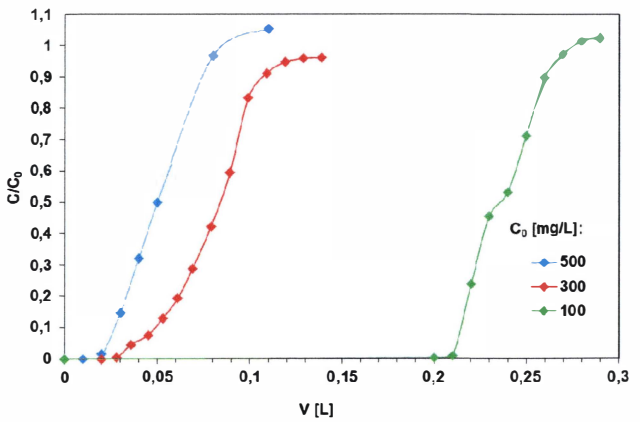

Figure 8. Breakthrough curves in the C.I. Acid Red 18 – Lewatit VPOC1064 system.

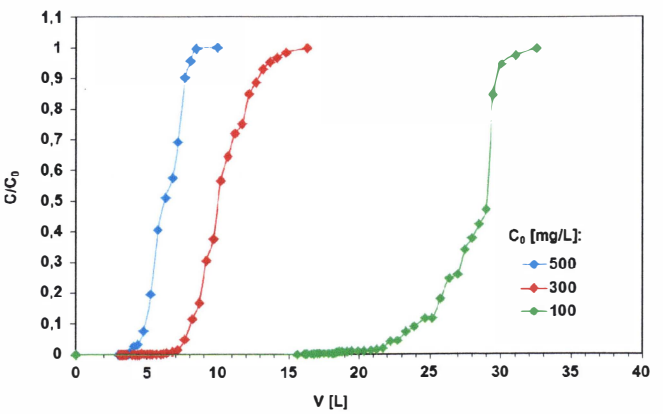

Figure 9. Breakthrough curves in the C.I. Acid Red 18 – Amberlyst A21 system.

Table 5. Comparison of the weight and bed distribution coefficients and working ion exchange capacities in the dye-resin systems.

Resin	C_0 [mg/L]	D_w	D_b	C_w [mg/mL]
Lewatit VPOC1064	100	76.1	22.9	2.1
	300	25.3	25.2	0.84
	500	14.3	4.3	0.5
Amberlyst A21	100	10102.4	2899.4	186
	300	3494.4	999.4	185.1
	500	2088.5	599.4	183.5

Conclusions

On the basis of the experiments it was found that polystyrene Amberlyst A21 of tertiary amine functional groups has a higher sorption capacity compared to the non-functionalized polymeric resin Lewatit VPOC1064. The Amberlyst A21 monolayer capacity determined from the Langmuir isotherm is 566.84 mg/g. The effectiveness of the dye sorption increases with the increasing contact time of the phases and the concentration of the initial dye until a plateau is reached. The kinetics of the AR18 sorption process on the resins was better described by the pseudo-second order model due to the high values of determination coefficients (the linearity of t/q_t vs t occured), and the sorption capacity determined experimentally ($q_{e,exp}$) is coincided with the capacities calculated (q_e) from the PSO equation. The presence of auxiliaries in the system, i.e. salts, acid and surfactants has an impact on the sorption of AR18 on Lewatit VPOC1064 and Amberlyst A21. The obtained results are of great application importance especially in dyes containing wastewater treatment technology.

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