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Removal of C.I. Basic Blue 3 dye by sorption onto cation exchange resin, functionalized and non-functionalized polymeric sorbents from aqueous solutions and wastewaters

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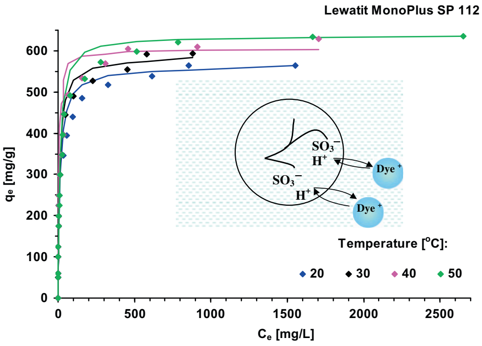
HIGHLIGHTS

- ▶ Cation exchanger and polymeric sorbents for Basic Blue 3 dye removal.
- ▶ Lewatit MonoPlus SP 112 is the most effective.
- ▶ Kinetic data were well described by the pseudo-second order model.
- ▶ Good adsorption characteristics of cation exchanger for basic wastewaters.
- ▶ Desorption using 1 M HCl in 90% methanol was quantitative.

GRAPHICAL ABSTRACT



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ABSTRACT

The adsorption behavior of the cationic dye C.I. Basic Blue 3 (BB3) from aqueous solution on the cation exchanger Lewatit MonoPlus SP 112 (SP 112), functionalized Dowex Optipore SD 2 (SD 2) and non-functionalized Amberlite XAD 1180 (XAD 1180) polymeric sorbents was investigated in order to identify the ability of these materials to remove textile dye from wastewaters. For this purpose a series of batch tests were carried out as a function of contact time (1 min-96 h), dye concentration (100, 500, 1000 mg/L), auxiliaries presence (NaCl, Na_2SO_4, surfactants) and adsorption temperature (20–50 °C). The adsorption capacity (Q_0) determined from the Langmuir isotherm model at 20 °C was found to be 560.7 mg/g for SP 112, 270.9 mg/g for SD 2 and 35.7 mg/g for XAD 1180. Q_0 increased with the temperature rise for the cation exchanger and non-functionalized polymeric sorbent. The inverse effect of the temperature on BB3 sorption on SD 2 was observed. Kinetic studies of the dye followed the pseudo-second order model rather than the pseudo-first order or intraparticle diffusion model. Total decolorization of basic dyes wastewater by means of SP 112 occurred after 1 h. Dye desorption from the cation exchanger reached 100% in four cycles of sorption–desorption using 1 M HCl in 90% CH_3OH. The working ion exchange capacities calculated from the breakthrough curves were equal to 205 mg/mL for SP 112, 3.5 mg/mL for SD 2 and 6.5 mg/mL for XAD 1180. These sorption properties of the polystyrene cation exchange resin Lewatit MonoPlus SP 112 recommend it as effective sorbent in the removal of organic ionic species like BB3 dye from aqueous solutions and industrial wastewaters.

1. Introduction

Cationic dyes are quarternary salts whose cations have the positive charge most often on the atom N (ammonium salts), rarely on C (carbonium), O (oxonium) and S (sulfone) [1].

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Table 1
Load of impurities carried in dyeing baths [6].

Depth of shade	Light shade	Medium shade	Deep shade
Dyes g/kg textiles	0.5–4	5–30	30–80
Organic auxiliaries g/kg textiles	0–30	0–30	0–35
Electrolytes NaCl, Na_2SO_4 g/kg textiles	90–400	600–700	800–1500
Inorganic auxiliaries g/kg textiles	50–250	30–150	30–150

The anions are most frequently Cl^-, SO_4^{2-}, HSO_4^- or $(COO^-)_2$. In some cases the kind of anion affects dye solubility. The first synthetic dyes (fuchsin, movein) were the dyes of colored cation. They formed colorless carbinol bases under the influence of alkalies. Hence comes their name basic dyes still used though they are salts not bases. These dyes colored protein and cellulose fibers with the tartrar emetic giving intense coloring but poorly resistant to light. At present cation dyes are a basic group used for coloring of polyacrylnitrile fiber wares. Dyeing is made in weakly acidic bath of pH 4.5–5. Dye binding with a fiber is of ionic character and is stable. The bounded dye hardly undergoes desorption [1].

In acrylic, nylon and silk dyeing processes a large volume of effluent is discharged. It was estimated that 1000 mg/L of dye was used in a typical dye bath and 100 mg/L of dye was left in the spent dye bath [2]. According to EPA[1] and OECD[2] the amounts of non-fixed basic dyes that may be discharged in the effluent were 1% and 2–3%, respectively [3]. Basic dyes are considered one of the most toxic substances [2]. They can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, they can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [4,5]. The chemical treatment of textiles requires the use, besides dyes, of a wide pallet of chemicals including even several hundreds of commercial products. These substances are mainly: sodium chloride, sodium sulfate and sodium hydroxide, detergents and other inorganic and organic auxiliaries. Therefore the textile wastewaters from dyer's factory are intensively colored, have high pH values and salinity. Moreover, they are characterized by a high coefficient of COD[3] with a very low one of BOD[4]. It causes that these wastewaters are not very susceptible to biological purification processes [6]. The auxiliaries remain in the wastewaters with the concentration close to the initial one (part of them is deposited on the textile products) as they are not used up but only create conditions suitable for the coloring process. The amounts of these substances of the dyeing baths are given in Table 1 [6].

Neglecting the aesthetic problem, the greatest environmental concern with dyes is their absorption and reflection of sunlight entering the waters, which interfere with the growth of bacteria limiting water impurities as well as hinder photosynthetic activity of aquatic organisms. It is evident, therefore, that removal of such colored agents from aqueous effluents is of significant environmental importance. One of the effective means of wastewaters purification after the dyeing processes is application of sorption methods. For this reason, many researchers have investigated for efficient adsorbents for basic dyes removal from wastewaters such as chitosan, activated carbons, agricultural wastes, sepiolite, peat or sawdust [2,7–16].

In the present study, the adsorption abilities of the cation exchange resin (Lewatit MonoPlus SP 112), functionalized (Dowex Optipore SD 2) and non-functionalized (Amberlite XAD 1180) polymeric sorbents for removal of C.I. Basic Blue 3 (BB3) from aqueous solutions and synthetic wastewaters were examined. Effects of initial dye concentration, phase contact time, auxiliaries addition and temperature on these sorbents with the batch method were investigated. Regeneration conditions were also presented. Column parameters were evaluated from the breakthrough curves, too.

2. Materials and methods

2.1. Adsorbents

Lewatit MonoPlus SP 112 (Lanxess, Germany) is a strongly acidic, macroporous cation exchange resin of the sulfonic functional groups with beads of uniform size (monodisperse, 0.65 mm ± 0.05) based on the styrene–divinylbenzene copolymer. The total ion exchange capacity is 1.7 eq/L. The operating temperature and pH range are equal to 120 °C and 0–14, respectively.

Amberlite XAD 1180 (Rohm & Haas, France) is a styrene–divinylbenzene copolymer of the surface area 500 m^2/g and the pore diameter 40–45 nm. The particle size of XAD 1180 is 0.2–1.9 mm. In order to remove organic and inorganic contaminants, Amberlite XAD 1180 resin was successively washed with methanol, 1 M HCl, 1 M NaOH and water.

Dowex Optipore SD 2 (Dowex Chemical Company, Germany) is the macroporous styrene–divinylbenzene copolymer with the tertiary amine groups (0.8 meq/g). The adsorbent has a high specific surface area of 800 m^2/g and an average pore diameter 50 nm.

2.2. Dye

C.I. Basic Blue 3 dye (3,7-bis(diethylamino)phenoxazin-5-ium chloride; CAS: 33203-82-6) is known as Astrazon Blue FGRL. This cationic dye is the commercial product of Sigma–Aldrich (Germany) and was used without purification (dye purity 25%). Its physicochemical properties are listed in Table S1 (see Appendix A. Supplementary Material).

An accurately weighted quantity of the dye was dissolved in the doubly-distilled water to prepare stock solution. The experimental solutions of desired concentrations were obtained by successive dilutions. Dye concentration in the solutions was determined by the UV–Vis method at the maximum wavelength using a spectrophotometer Specord M-42 (Carl Zeiss, Germany).

2.3. Other chemicals

Sodium carbonate, chloride and sulfate, potassium rhodanate, hydrochloric acid, sodium hydroxide and methanol of analytical grade were purchased from POCh (Poland). The anionic surfactant sodium dodecyl sulfate (SDS) as well as the cationic one cetyltrimethylammonium bromide (CTAB) were obtained from Sigma Aldrich (Germany).

2.4. Batch equilibrium and kinetic experiments

Adsorption tests were performed in a set of Erlenmeyer flasks (100 mL) where 50 mL of BB3 solutions with the increasing initial concentrations were placed. Equal mass of 0.5 g of the sorbent was added to each flask and kept in an isothermal shaker at 20, 30, 40 and 50 °C for 24 h to reach equilibrium. The original pH of the solutions was used, which was around 4.3. Aqueous samples were taken from the solutions and the dye concentrations were analyzed. Each experiment was duplicated under identical conditions. The concentrations of BB3 in the supernatant solutions before and after adsorption were determined using a UV–vis

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[1] US Environmental Protection Agency.

[2] Organization for Economic Cooperation Development.

[3] Chemical Oxygen Demand.

[4] Biological Oxygen Demand.

spectrophotometer at 654 nm. The amount of dye adsorbed at equilibrium, q_e (mg/g) was calculated as:

$$q_e = \frac{(C_0 - C_e)}{w} \times V \tag{1}$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of BB3 before sorption and at equilibrium time, respectively, V (L) is the volume of solution and w (g) is the weight of dry sorbent.

Effects of auxiliaries addition on the dye uptake at equilibrium were studied by shaking the sorbent (0.5 g) with the 100 mg/L dye solution (50 mL) containing from 25 to 100 g/L of different salts (Na_2SO_4, NaCl) or from 0.1 to 1 g/L of surfactants (SDS, CTAB) at 20 °C. The dye concentration after sorption was measured spectrophotometrically at the maximum absorbance wavelengths depending on the system.

Effects of contact time and dye concentrations on the sorption of BB3 onto cation exchanger SP 112 as well as polymeric sorbents XAD 1180 and SD 2 were determined by the batch technique. A sample of 0.5 g sorbent was added under stirring of 180 cpm to 50 mL dye solution having the initial concentrations of 100, 500 and 1000 mg/L. After different contact times (1 min.-96 h), the supernatant solutions were taken for measurements of dye content. The amount of dye retained by the sorbents after time t was expressed by the calculation of q_t (mg/g) values.

The color removal of model textile wastewaters containing cationic dyes was studied using the batch method, too. In this experiment the dosage of 0.5 g of sorbent was shaken with 50 mL of the model wastewater solution containing Basic Blue 3, Astrazon Blue $FGRL_{200}$, Basic Yellow 2 and Basic Red 46 (each in the amount of 100 mg/L, pH 4.25) for 1 min to 72 h. During this experiment, small samples were withdrawn at various times in order to estimate the removal of dyes by the analysis of absorbance values at the maximum absorbance wavelength. The absorption spectrum of the textile wastewater at 0 h was 10 times diluted before recording, whereas the other samples were not diluted.

Desorption experiments were performed for 3 h by mixing the saturated cation exchange resin and polymeric sorbents with different solutions (0.1–1 M HCl, 0.1–1 M NaOH, 0.1–1 M KSCN, 0.1–1 M NaCl, 0.1–1 M Na_2CO_3, 0.1–1 M Na_2SO_4, 1 M KSCN (or 1 M NaOH or 1 M HCl) in 20–90% methanol, 20–100% methanol). The samples of sorbents was filtered and dye concentration was determined by UV–vis. The recycling of the sorbents were tested by successive sorption and desorption of dye under the standard experimental conditions in four cycles (the same volume of solutions for the sorption steps, i.e. 50 mL of the solution of the initial dye concentration 100 mg/L for 0.5 g of sorbent; and desorption steps, i.e. 50 mL of different eluting solutions and 0.5 g for the same amount of loaded sorbent). The desorption percentage (%) was calculated as:

$$\text{Desorption} = \frac{m_{\text{des}}}{m_{\text{ads}}} 100\% \tag{2}$$

where m_{des} is the mass of dye desorber (mg), m_{ads} is the mass of dye adsorber (mg).

The amounts of dye removed and recovered were compared in each step.

2.5. Column sorption experiments

The column sorption experiments were conducted using 10 mL of the swollen sorbents packed in glass columns (the inner diameter 10 mm). The feed solution of the dye of the initial concentration 100 mg/L was passed continuously downwards through the sorbents beds keeping the flow rate at 0.6 cm^3/min. The effluents were collected in fractions in which dye concentrations were determined by the UV–vis method at 654 nm. The sorption parameters such as the weight (D_w) and bed (D_b) distribution coefficients as well as the working (C_w) and total (C_t) ion exchange capacities were calculated according to the following equations [17]:

$$D_w = \frac{(U - U_0 - V_v)}{m} \tag{3}$$

$$D_b = \frac{(U - U_0 - V_v)}{v} \tag{4}$$

$$C_w = \frac{V_{b_p} C_0}{v} \tag{5}$$

$$C_t = \frac{U_t C_0}{v} \tag{6}$$

where U (mL) is the effluent volume at $C/C_0 = 0.5$, U_0 (mL) is the dead volume in the column, V_v (mL) is the void (interparticle) sorbent bed volume, m (g) is the dry sorbent mass, v (mL) is the volume of swollen sorbent, U_t (L) is the total effluent volume, V_{bp} (L) is the effluent volume to the breakthrough point, C_0 (mg/L) is the inlet dye concentration.

The degree of saturation or column efficiency η can be calculated as:

$$\eta = \frac{C_w}{C_t} \tag{7}$$

During the loading process of ion exchanger/sorbent bed, at any time the ion exchange takes place in only a portion of bed called exchange zone or mass transfer zone (MTZ). Exchange zone moves down through the ion exchanger/sorbent bed. The directions of moving of the exchange zone and the solution flow are the same. Ahead the exchange zone, ion exchanger/sorbent bed is exhausted whereas underneath it is still fresh. When the exchange zone reaches the end of the bed, dye ions leak into the effluent. Based on the column parameters and breakthrough curves, the time required for MTZ to move through its own length down the bed (t_z), the time required for MTZ to become established and move completely out of the bed (t_e) and the time needed for MTZ formation (t_f) were calculated according to the following equations:

$$t_z = \frac{V_z}{U_r S} \tag{8}$$

$$t_e = \frac{V_t}{U_r S} \tag{9}$$

$$t_f = (1 - F) t_z \tag{10}$$

where $V_z = V_t – V_{bp}$ (cm^3) is the distinction between the total volume (V_t) of effluent and that collected to the break point (V_{bp}), U_r (cm/min) is the linear flow rate, S (cm^2) is the total column cross-section area, F is the parameter measuring the symmetry of the breakthrough curve [18,19].

F is defined by:

$$F = \frac{S_z}{S_{\max}} = \frac{\int_{V_{bp}}^{V_t} (C_0 - C) dV}{C_0 (V_t - V_{bp})} \tag{11}$$

where S_z (mg) is the amount of solute removed by the exchanger from the breakthrough to the exhaustion, $S_{\max}$ (mg) is the amount of solute removed by the exchanger when it is completely exhausted [19].

3. Results and discussion

3.1. Equilibrium studies

The equilibrium sorption isotherms are one of the most important data to understand the mechanism of the sorption systems. Adsorption of dye, q_e (mg/g) at equilibrium was related to the dye equilibrium concentration C_e (mg/L) using:

(a) the Langmuir isotherm model

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{12}$$

where Q_0 (mg/g) is the Langmuir monolayer sorption capacity, b (L/mg) is the Langmuir adsorption constant; calculated from the intercepts and slopes of straight lines of plot of C_e/q_e vs C_e [20].

Langmuir isotherm is applied to homogeneous adsorption based on the following assumptions: (a) all the adsorption sites are identical; (b) each site retains one molecule of the given compound; and (c) all sites are energetical and sterical independent of the adsorbed quantity [21].

(b) the Freundlich isotherm model

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{13}$$

where k_F (mg/g) is the Freundlich adsorption capacity, $1/n$ is the Freundlich constant related to the surface heterogeneity; determined from the slope and intercept of the linear plot of log q_e vs log C_e [20].

Freundlich isotherm assumes heterogeneous surface with a nonuniform distribution of heat of adsorption [22,23].

3.1.1. Effect of temperature on sorption mechanism

Temperature is well known to play an important role during the adsorption processes. It can affect several aspects of adsorption, e.g. dye solubility, the swelling capacity of the sorbent and the equilibrium position in relation to the endo- or exothermicity of the adsorption phenomenon. In the present work, the effect of temperature on the amount of BB3 retained on Lewatit MonoPlus SP 112, Dowex Optipore SD 2 and Amberlite XAD 1180 at equilibrium was studied at four different temperatures: 20, 30, 40 and 50 °C (Fig. 1).

The values of Langmuir and Freundlich isotherm constants determined by the linear fit of Eqs. (12) and (13) are included in Table 2. The Langmuir isotherm model fits better than the Freundlich one (R^2 in the range 0.857–0.971). The Langmuir isotherm of BB3 on the investigated sorbents was found to be linear over the whole concentration range at four temperatures. The determination coefficients R^2 were extremely high ($\geqslant$0.984). These high degrees of correlation for the Langmuir relationship suggest that a single surface reaction with the constant activation energy is the predominant sorption step and possibly the predominant rate controlling step [24]. The computed maximum monolayer capacities Q_0 on the cation exchanger Lewatit MonoPlus SP 112 have very large values, 560.7 mg/g at 20 °C, 583.9 mg/g at 30 °C, 604.9 mg/g at 40 °C and 637.6 mg/g at 50 °C in comparison with data published by Bârsănescu et al. [16] for BB3 retention on the weak acid acrylic cation exchanger CM-60. A brief list of the maximum sorption capacities of various sorbents towards BB3, including the results obtained in this work, is presented in Table 3. The most part of the materials tested for BB3 sorption have been low cost sorbents. Karagozoglu et al. [13] proved that sepiolite (155.5–209.2 mg/g), fly ash (128.2–152.4 mg/g) and apricot stone activated carbon (181.5–201.6) were effective for BB3 removal from aqueous solutions. Nassar et al. [11] have investigated the sorption of BB3 on the cement kiln dust with the maximum capacity of 248.1 mg/g. The high value of the maximum adsorption capacity of 406 mg/g has been reported by Kumar and Sivanesan for the sorption of BB3 on the activated carbon [15]. Only the Q_0 values cited in the paper by Allen et al. [14] for the lignite demonstrate that this material has better sorption properties than the strongly acidic cation exchanger of the sulfonic groups.

The high values of the Langmuir constants b equal to 0.0771, 0.0945, 0.1041 L/mg at 20, 30 and 40 °C, respectively, indicate strong attraction between the sulfonic groups of the cation exchanger and the dye ions. However, the slight decrease of b value (0.0819 L/mg) at 50 °C shows that the binding force is weakened at higher temperatures. The high adsorption capacity of Lewatit MonoPlus SP 112 for the cationic dye BB3 indicates that the dye retention occurred by the combined effect of different adsorption mechanisms. To explain it not only conventional exchange of ions mechanism should be applied. It is proposed that the π–π interaction between the aromatic matrix of the resin SP 112 and the aromatic ring of the dye occurred.

The same dependence of the monolayer capacities Q_0 on temperature was noticed in the case of non-functionalized polymeric sorbent Amberlite XAD 1180. The values of Q_0 increased from 35.7 mg/g to 66.5 mg/g (R^2 = 0.999) with the temperature rise from 20 to 50 °C. Careful examination of BB3 adsorption on Amberlite XAD 1180 at 30 °C leads to the observations that the adsorption capacity value of 28.9 mg/g obtained at this temperature is lower than 35.7 mg/g obtained at 20 °C. Similar temperature effects on the dye loading on the strongly basic anion exchangers were reported by Greluk and Hubicki for the adsorption of Reactive Black 5 and Acid Orange 7 on Amberlite IRA-958 and Amberlite IRA 458, respectively [25–27]. Retention of BB3 cationic dye by the styrene–divinylbenzene non-functionalized resin Amberlite XAD 1180 confirmed that the sorption mechanism can involve interactions between the polymer network of the sorbent and the dye aromatic ring.

As shown in Fig. 1, the inverse effect of the temperature on BB3 sorption on Dowex Optipore SD 2 was observed in comparison with the results obtained for the dye sorption on SP 112 and XAD 1180 in the temperature range 20–50 °C. The increase in the temperature from 20 to 50 °C led to the decrease in the adsorption capacities of Dowex Optipore SD 2, from 270.9 to 247.5 mg/g. This indicates that adsorption of BB3 on this sorbent occurred favourably at low temperature and was controlled by the exothermic process. As reported in literature [25–29] with the increase in temperature, the interaction forces between the dye ions and the solution become stronger than those between the dye ions and the sorbent, consequently the dye is more difficult to adsorb [28,29]. The desorption step is also possible. According to Renault et al. [28] the adsorption capacities decrease with the increasing temperature, due to the enhanced magnitude of desorption step in the mechanism. The interactions established between the sorbent and dye are therefore reversible in this case. The decrease in the adsorption capacity of SD 2 for BB3 dye with the increasing temperature is consistent with the observations made for Acid Blue 25 adsorption on the ion exchanger starch adsorbent [28], for Methylene Blue adsorption on the coconut husk-based activated carbon [30] and for Congo Red sorption on the clay materials [31]. Retention of the dye by Dowex Optipore SD 2 may be attributed to the weak attraction of the tertiary amine functional groups of sorbent with the oxazine ring of dye.

3.1.2. Influence of auxiliaries on C.I. Basic Blue 3 equilibrium uptake

Wastewaters and industrial effluent waters from textile plants can contain not only large amounts of dyes but also many auxilia-

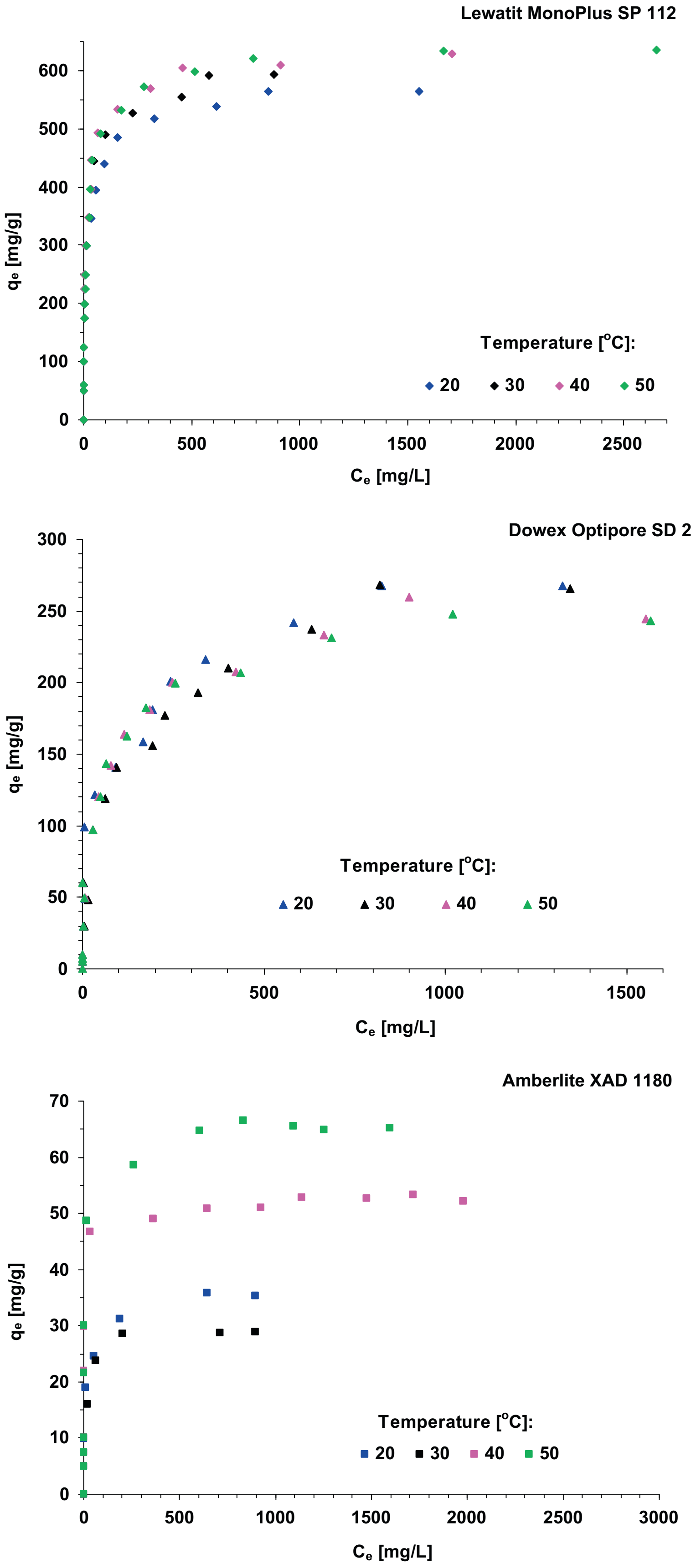

Fig. 1. Equilibrium adsorption data of C.I. Basic Blue 3 on Lewatit MonoPlus SP 112, Amberlite XAD 1180 and Dowex Optipore SD 2 at different temperatures (*conditions*: phase contact time: 24 h, volume: 50 mL, sorbent mass: 0.5 g, agitation speed: 180 cpm).

Table 2
Comparison of the Freundlich and Langmuir adsorption constants of C.I. Basic Blue 3 uptake on Lewatit MonoPlus SP 112, Dowex Optipore SD 2 and Amberlite XAD 1180 at different temperatures.

Temperature (°C)	Sorbent	Freundlich model			Langmuir model		
		n	k_F (mg/g)	R^2	b [L/mg]	Q_0 [mg/g]	R^2
20	Lewatit MonoPlus SP 112	3.89	122.3	0.893	0.0771	560.7	0.998
30		3.54	122.8	0.890	0.0945	583.9	0.997
40		4.04	131.6	0.857	0.1041	604.9	0.998
50		3.88	124.2	0.874	0.0819	637.6	0.998
20	Dowex Optipore SD 2	2.29	16.2	0.940	0.0160	270.9	0.984
30		2.41	19.9	0.905	0.0219	271.5	0.989
40		2.56	21.7	0.932	0.0284	251.0	0.995
50		2.57	21.7	0.927	0.0291	247.5	0.997
20	Amberlite XAD 1180	7.06	13.9	0.991	0.1133	35.7	0.999
30		7.84	13.0	0.926	0.2156	28.9	0.999
40		12.92	30.5	0.959	0.1627	52.7	0.999
50		11.36	35.7	0.971	0.1352	66.5	0.999

Table 3
Comparison of C.I. Basic Blue 3 uptake by different adsorbents.

Material	Sorption conditions			Ref.
	q_e (mg/g)	pH	T (°C)	
Chitosan based sorbent prepared from crab shells	166.5	3	25	[7]
Alleppo pine-tree sawdust	65.4	7	20	[8]
Etylenediamine modified rice hull	3.29	4.7	25	[9]
Wood activated charcoal	0.59–0.64	7	10–50	[10]
Cement kiln dust	248.1	–	–	[11]
Quartenised sugar cane bagasse	37.59	6–8	20	[12]
Activated sludge biomass	36.5	–	20	[5]
Palm fruit bunch particle	91.33	–	–	[2]
Sepiolite	155.5–209.2	–	30–50	[13]
Fly ash	128.2–152.4			
Apricot stone activated carbon	181.5–201.6			
Peat	556	–	18	[14]
Activated carbon	406	8	32	[15]
CM-60 weak acid acrylic resin	34.36–59.53	5.5	17–50	[16]
Lewatit MonoPlus SP 112	560.7–637.6	–	20–50	This study
Dowex Optipore SD 2	270.9–247.5			
Amberlite XAD 1180	28.9–66.5			

ries including inorganic salts and surface active substances. Therefore complex purification of dye-surfactant and dye- electrolyte type solutions is necessary whereby the relations between these compounds can have a significant effect on purification effectiveness. In his study, the presence of inorganic salts and surfactants such as NaCl, Na_2SO_4, SDS and CTAB in the solution during the dye adsorption on Lewatit MonoPlus SP 112, Dowex Optopore SD 2 and Amberlite XAD 1180 was examined because these substances are typically present in real wastewaters. The following systems were studied: 100 mg/L of BB3 in 25–100 g/L NaCl or Na_2SO_4 as well as 100 mg/L of BB3 in 0.1–1.0 g/L SDS or CTAB. Experimental dependencies of the BB3 dye sorption on the concentration of these substances are shown in Fig. 2. C.I. Basic Blue 3 uptake by Dowex Optipor SD 2 and Amberlite XAD 1180 was not influenced by the presence of NaCl and Na_2SO_4 even at relatively high salts concentration. The sorption of BB3 on Lewatit MonoPlus SP 112 was slightly reduced in the presence of both electrolytes. The amounts of BB3 retained by the cation exchange resin at equilibrium dropped from 10 mg/g to 8.3 mg/g and from 10 mg/g to 9.4 mg/g with the increasing amount of NaCl and Na_2SO_4, respectively. It is due to a competition between Na^+ cations and the cationic dye.

It is very difficult to explain interactions in such complex system as dye-surfactant-sorbent one. Prediction of the effect of surfactants on the solute sorption is not easy, as several simultaneous and competitive mechanisms may be operating during the sorption process. A more detailed discussion concerning removal of cationic dyes such as Basic Blue 9, Basic Green 4 and Basic Violet 3 by the iron humate sorbent, oxihumolite and chemically treated wood shavings in the presence of SDS and CTAB was presented in the papers by Janoš et al. [32–35]. No influence of SDS on the dye sorption by Dowex Optipor SD 2 and Amberlite XAD 1180 was observed (Fig. 2). Similar dependence was reported by Gupta et al. [36,37] for sorption of Basic Red 9 on carbon slurry or blast furnace slag. BB3 uptake by SP 112 resin was not affected by the SDS concentration in the range 0.1–0.5 g/L. The increasing amount of SDS in the system to 1.0 g/L decrease the q_e value to 6.9 mg/g for SP 112 resin. At higher surfactant concentrations, the well ordered aggregates-micelles are formed in the solution. The dye molecules may be incorporated into micelles (solubilized) forming water-soluble aggregates [35]. In other words, the anionic surfactant SDS and the cationic dye BB3 being compounds of opposite charge interact and form dye-surfactant aggregates causing the reduction of “free” dye cations in the aqueous phase and drop of the q_e value.

The cationic surfactant CTAB bearing the same charge as the dye affected only slightly the dye sorption on the investigated materials. Competition of adsorption sites between dye cations and CTAB was observed in the case of SP 112 resin. The same effect was observed for the sorption of Methylene Blue onto oxihumolite [33].

3.2. Kinetic studies

The rate at which dissolved dye is removed from the aqueous solution by solid sorbents is a significant factor for application in

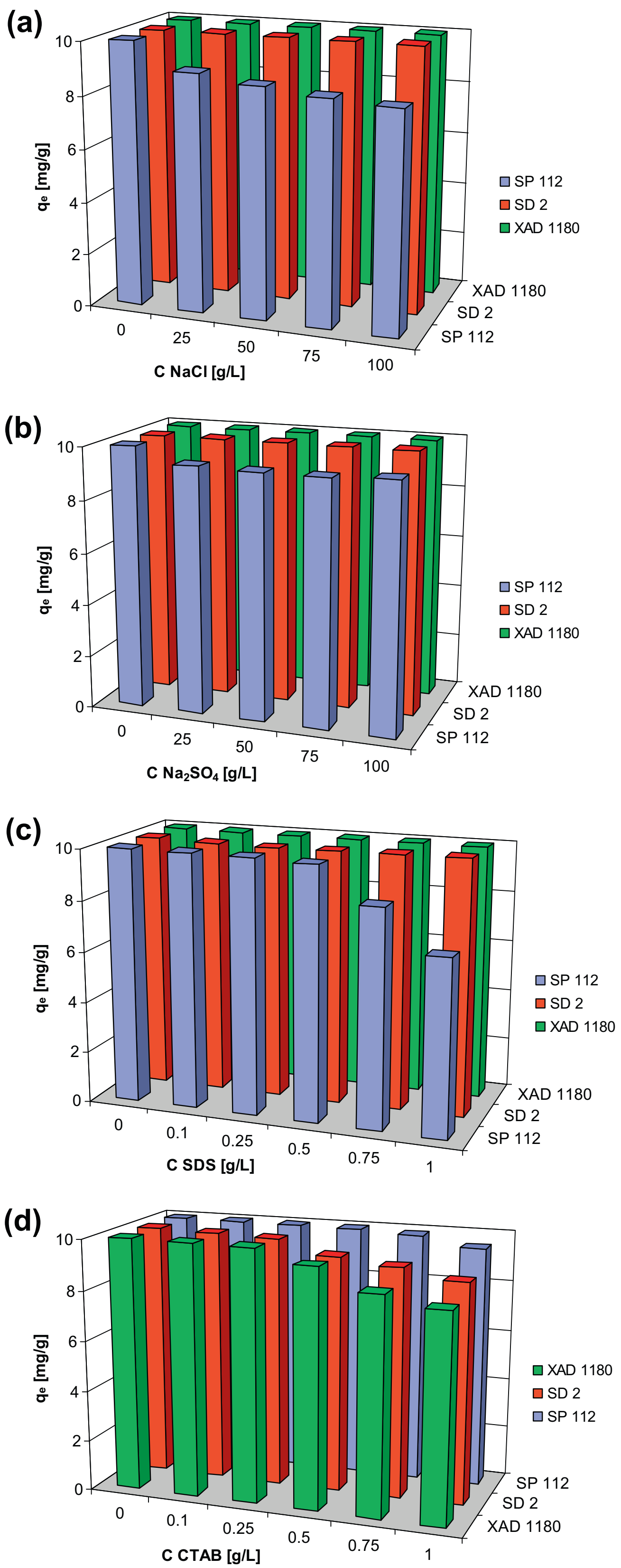

Fig. 2. Effects of NaCl (a), Na_2SO_4 (b), SDS (c) and CTAB (d) addition on C.I. Basic Blue 3 uptake from the system containing 100 mg/L BB3 by Lewatit MonoPlus SP 112, Amberlite XAD 1180 and Dowex Optipore SD 2 (*conditions*: salts concentration: 25–100 g/L, surfactants concentration: 0.1–1 g/L, phase contact time: 240 min, volume: 50 mL, sorbent mass: 0.5 g, agitation speed: 180 cpm).

wastewater quality control. It is essential to evaluate the adsorption kinetics using theoretical models in order to design and control the sorption process units [23]. The BB3 sorption kinetics on Lewatit MonoPlus SP 112, Dowex Optipore SD 2 and Amberlite XAD 1180 was tested using the pseudo-first order (PFO) and the pseudo-second order (PSO) equations as well as the intraparticle diffusion (ID) kinetic model as follows:

$$\text{(a)}\ \log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (14)$$

$$\text{(b)}\ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (15)$$

$$\text{(c)}\ q_t = k_i t^{0.5} + Ci \qquad (16)$$

where q_t and q_e (mg/g) are the amounts of the dye sorbed at time t and at equilibrium, k_1 (1/min) is the rate constant of the pseudo-first order sorption, k_2 (g/mg min) is the pseudo-second order rate constant, k_i (mg/g min$^{0.5}$) is the intraparticle diffusion rate, C_i is the intercept [38,39].

The values of k_1 and q_e were determined from the slope and intercept of the plot $\log(q_e - q_t)$ versus t, respectively. The k_1 parameter is the time-scaling factor the value of which decides how fast the equilibrium in the system can be reached. Eq. (14) can be interpreted by accepting the model in which the kinetics of sorption is determined mainly by the rate of the diffusional transport of solute. The pseudo-first order equation is usually not able to describe the kinetic data equally well as the pseudo-second order equation. From the intercept and slope of the plot t/q_t versus t the values of q_e and k_2 were evaluated. The initial adsorption rates h (mg/g min) were also calculated from the data of the pseudo-second order kinetics according to Eq. (17):

$$h = k_2 q_e^2 \qquad (17)$$

The pseudo second-order model predicts the adsorption behavior over the whole range of adsorption period and it is in agreement with the chemisorption mechanism being the rate-controlling step. Chemisorption (ion-exchange, electrostatic attractions) is commonly cited as the main mechanism for the adsorption of cationic species [40].

Determination coefficient (R^2) values were used to express the conformity between the experimental data and the theoretical ones.

The first-order and second-order kinetic plots for a constant amount of Lewatit MonoPlus SP 112 and different BB3 concentrations are shown in Fig. 3. All the plots have good linearity with the determination coefficient higher than 0.982. The PFO fitting lines were close to the experimental data at the initial sorption period in the systems containing 100 mg/L of dye. After the first 5 min of sorption they deviated substantially from the experimental points in the solutions of initial dye concentration 500 and 1000 mg/L. The values of the rate coefficients found from these plots are given in Table 4. The comparison of q_e values obtained experimentally with those obtained from the applied kinetic equations for the used sorbents is also listed in Table 4. The PFO rate constants obtained for SP 112, SD 2 and XAD 1180 decreased with the increasing initial dye concentrations and were found in the range 0.364–0.075 1/min, 0.033–0.009 1/min, and 0.079–0.024 1/min, respectively. However, it was seen that the experimentally obtained q_e values did not match those determined from the PFO plots. The fitting lines of the pseudo-second order kinetics in the systems 100–1000 mg/L of BB3 were found to be closer to the experimental data in the whole sorption period for SP 112 and

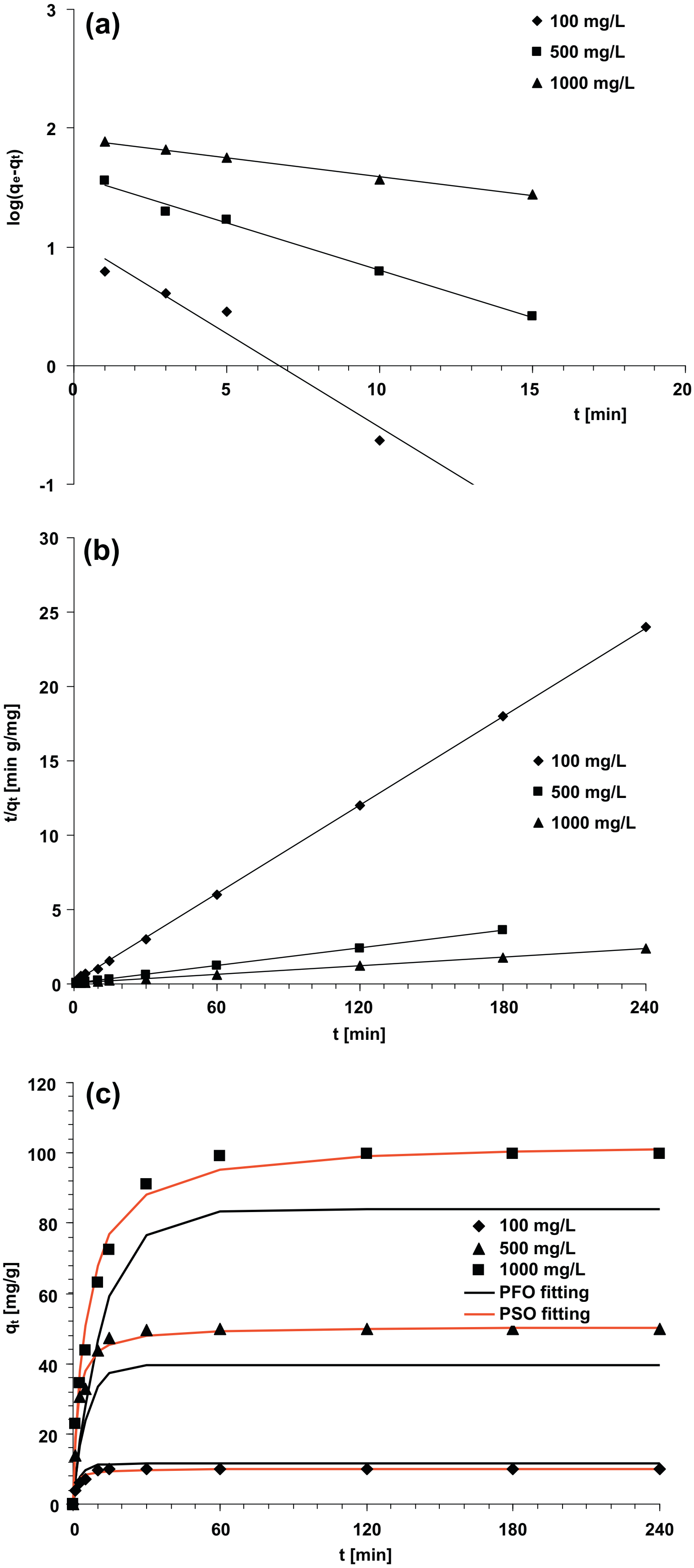

Fig. 3. PFO (a), PSO (b) plots as well as the fitting of PFO and PSO kinetic equations to the experimental data (c) for C.I. Basic Blue 3 sorption on the cation exchanger Lewatit MonoPlus SP 112 at different initial dye concentrations (*conditions*: initial dye concentrations: 100, 500 and 1000 mg/L, volume: 50 mL, sorbent mass: 0.5 g, agitation speed: 180 cpm).

Table 4
Comparison of the pseudo first-order, pseudo second-order and intraparticle diffusion rate constants as well as calculated and experimental values of q_e obtained at different initial dye concentrations for C.I. Basic Blue 3 sorption on Lewatit MonoPlus SP 112, Dowex Optipore SD 2 and Amberlite XAD 1180.

Sorbent	C_0 (mg/L)	$q_{e,\mathrm{exp}}$ (mg/g)	PFO			PSO				ID	
			q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg min)	h (mg/g min)	R^2	k_i (mg/g min$^{0.5}$)	R^2
Lewatit MonoPlus SP 112	100	10.0	11.5	0.364	0.982	10.1	0.101	10.2	0.999	1.41	0.786
	500	49.9	39.7	0.183	0.991	50.4	0.013	31.9	0.999	7.59	0.823
	1000	99.8	81.7	0.075	0.995	102.5	0.002	20.9	0.999	15.63	0.985
Dowex Optipore SD 2	100	10.0	8.2	0.033	0.992	10.1	0.007	0.716	0.999	1.06	0.993
	500	49.6	43.2	0.014	0.999	49.8	0.0005	1.106	0.999	2.86	0.991
	1000	98.3	82.7	0.009	0.977	99.0	0.0002	1.619	0.999	4.38	0.983
Amberlite XAD 1180	100	10.0	5.9	0.079	0.810	8.4	0.135	9.5	0.702	0.044	0.924
	500	42.0	32.4	0.021	0.742	22.8	0.026	13.6	0.746	1.187	0.983
	1000	55.0	45.1	0.024	0.891	31.8	0.011	10.7	0.912	1.825	0.951

SD 2. It is clear that the PSO kinetic model gave a better correlation ($R^2 = 0.999$) for the adsorption of the basic dye on SP 112 and SD 2 compared to the PFO model. Moreover, there is an excellent correlation between calculated q_e values and experimental q_e ones. The PSO rate constants k_2 values decrease with the increasing initial dye concentration, whereas the initial sorption rate h increases with an the increasing amount of the dye in the system. Bârsănescu et al. [16] confirmed the ability of the pseudo-second order model to describe the kinetics of BB3 uptake by the acrylic cation exchanger.

For Amberlite XAD 1180 the best correlation between the experimental values and the model developed by Weber and Morris were found. The values of R^2 are equal to 0.924, 0.983 and 0.951 for the initial dye concentrations 100, 500 and 1000 mg/L, respectively. The values of k_i evaluated from these linear parts of plots are also tabulated in Table 4. The data show that the rate of diffusion k_i increased with the rise in the initial dye concentration from 0.044 to 1.825 mg/g min$^{0.5}$. The plots of the amount of BB3 dye per unit weight of sorbent (q_t) against the square root of time ($t^{0.5}$) at all initial BB3 concentrations (Fig. 4) revealed that all the plots have the same general feature presenting multi-linearity, indicating that a few steps took place. The first, sharper portion obtained at the very beginning whose extent is related to the initial dye concentration

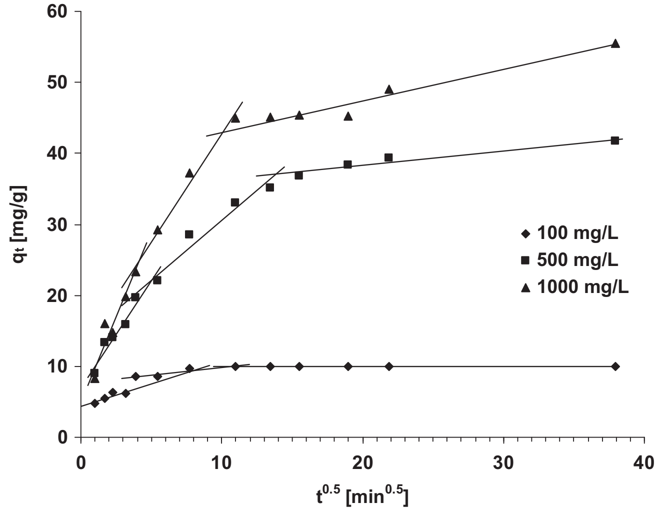

Fig. 4. Intraparticle diffusion model for C.I. Basic Blue 3 sorption on Amberlite XAD 1180 at different initial dye concentrations (*conditions*: initial dye concentrations: 100, 500 and 1000 mg/L; volume: 50 mL, sorbent mass: 0.5 g, agitation speed: 180 cpm).

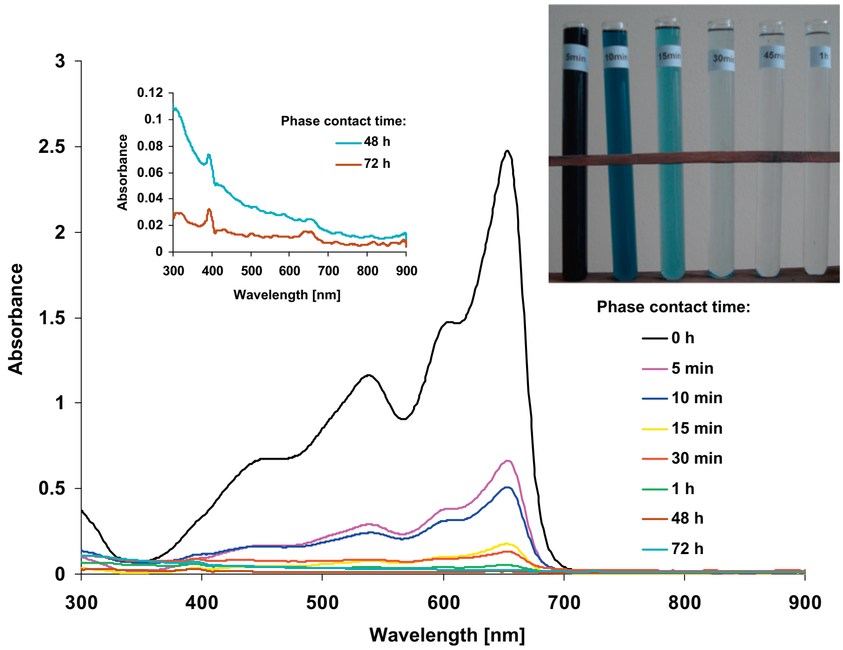

Fig. 5. Wastewater purification by means of Lewatit MonoPlus SP 112 at different phase contact times and the photo images of purified samples (*conditions*: wastewater composition: 100 mg/L Basic Blue 3 + 100 mg/L Astrazon Blue FGRL$_{200}$ + 100 mg/L Basic Yellow 2 + 100 mg/L Basic Red 46, pH 4.25; volume: 50 mL, sorbent mass: 0.5 g, agitation speed: 180 cpm).

Table 5
Desorption of C.I. Basic Blue 3 from Lewatit MonoPlus SP 112, Dowex Optipore SD 2 and Amberlite XAD 1180.

Lewatit MonoPlus SP 112		Dowex Optipore SD 2		Amberlite XAD 1180	
	Desorption (%)	Regenerant	Desorption (%)	Regenerant	Desorption (%)
Cycle 1					
1 M HCl – 90% CH_3OH	100	1 M HCl – 90% CH_3OH	100	1 M HCl – 90% CH_3OH	92.4
1 M KSCN – 90% CH_3OH	100	1 M HCl – 80% CH_3OH	100	1 M NaOH – 90% CH_3OH	36.6
1 M KSCN – 80% CH_3OH	100	100% CH_3OH	91	1 M KSCN – 90% CH_3OH	59.5
1 M KSCN – 60% CH_3OH	100	90% CH_3OH	90	90% CH_3OH	76.7
1 M KSCN – 40% CH_3OH	94	80% CH_3OH	92		
		60% CH_3OH	92		
Cycle 2					
1 M HCl – 90% CH_3OH	100	1 M HCl – 90% CH_3OH	100	1 M HCl – 90% CH_3OH	87.3
1 M KSCN – 90% CH_3OH	94.4	1 M HCl – 80% CH_3OH	100	1 M NaOH – 90% CH_3OH	45.2
1 M KSCN – 80% CH_3OH	98.1	100% CH_3OH	50.3	1 M KSCN – 90% CH_3OH	42.9
1 M KSCN – 60% CH_3OH	97.2	90% CH_3OH	46.3	90% CH_3OH	58
1 M KSCN – 40% CH_3OH	69.8	80% CH_3OH	52.3		
		60% CH_3OH	50.6		
Cycle 3					
1 M HCl – 90% CH_3OH	100	1 M HCl – 90% CH_3OH	77.1	1 M HCl – 90% CH_3OH	68.9
1 M KSCN – 90% CH_3OH	89.9	1 M HCl – 80% CH_3OH	73.1	1 M NaOH – 90% CH_3OH	17.9
1 M KSCN – 80% CH_3OH	95.4	100% CH_3OH	48.4	1 M KSCN – 90% CH_3OH	44.9
1 M KSCN – 60% CH_3OH	96.3	90% CH_3OH	48.8	90% CH_3OH	62
1 M KSCN – 40% CH_3OH	76.7	80% CH_3OH	51.6		
		60% CH_3OH	54.2		
Cycle 4					
1 M HCl – 90% CH_3OH	100	1 M HCl – 90% CH_3OH	69.2	1 M HCl – 90% CH_3OH	37.1
1 M KSCN – 90% CH_3OH	86.8	1 M HCl – 80% CH_3OH	58.4	1 M NaOH – 90% CH_3OH	11.6
1 M KSCN – 80% CH_3OH	100	100% CH_3OH	39.7	1 M KSCN – 90% CH_3OH	19.3
1 M KSCN – 60% CH_3OH	99.6	90% CH_3OH	39.4	90% CH_3OH	32.4
1 M KSCN – 40% CH_3OH	100	80% CH_3OH	44.3		
		60% CH_3OH	49.8		

is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second linear portion describes the gradual layer adsorption stage, where the intraparticle diffusion is rate limiting. The third portion is attributed to the final equilibrium stage for which the intraparticle diffusion started to slow down due to the extremely low dye concentration left in the solution. However, the linear plots of the second portion at each concentration did not pass through the origin, this is indicative of some degree of boundary layer control and this shows further that the intraparticle diffusion is not only rate-controlling step.

3.2.1. Color removal efficiency of basic wastewaters

The batch studies confirmed good sorption characteristics of Lewatit MonoPlus SP 112 in the model textile wastewater samples. Fig. 5 shows the absorbance spectra of model wastewater containing BB3 before and after its adsorption on this cation exchanger revealing the complete reduction of the major visible light absorbance peaks and the significant spectral change. The cation exchanger proves to be capable of color removal of basic dyes wastewater providing 98% color removal after only 10 min of adsorption process and reaching 99.9% color removal after 1 h. This percentage of color removal attained for the model textile wastewater is very high and suggests that Lewatit MonoPlus SP 112 with very good sorption characteristics could be a promising adsorbent for real textile wastewaters containing basic dyes. The spectral analysis of wastewaters purified by means of Amberlite XAD 1180 and Dowex Optipore SD 2 (figures not shown) reveals that the color removal of 95% was observed after 72 h of the phase contact time.

4. Sorbents regeneration

The desorption step is the key to the implementation of the ion exchange system. Regeneration of Lewatit MonoPlus SP 112, Dowex Optopore SD 2 and Amberlite XAD 1180 was performed in four cycles of sorption–desorption (Table 5). Sorption of the dye on SP 112 in all cycles was quantitative, while the decrease in the sorption in the amount of 8–10% was observed for SD 2 and XAD 1180. Several systems were tested for the recovery of dye loaded on the sorbents. The use of aqueous salt solutions such as NaCl, Na_2CO_3 and Na_2SO_4 as well as HCl and NaOH was ineffective, desorption did not exceed 25%. The methanol addition to 1 M KSCN and 1 M HCl greatly improved the dye desorption performance in most cases. The best results for SP 112 cation exchanger were obtained using 1 M HCl in 90% CH_3OH and 1 M KSCN in 40–90% CH_3OH. Desorption was efficient and reached 100% using 1 M HCl in 90% CH_3OH in four cycles of sorption–desorption (Table 5). Similar data were obtained for SD 2 sorbent in two consecutive cycles when the mixtures of 1 M HCl with 80% and 90% CH_3OH were used. For Amberlite XAD 1180 the most effective regenerants were 1 M HCl in 90% methanol as well as 90% methanol. The obtained data are in agreement with those known in literature [41–45]. The above results indicate that BB3 sorption is not entirely based on ion exchange mechanism, it was retained by the used sorbents through more than one binding force: electrostatic interaction, hydrophobic interaction or hydrogen bonding.

5. Column experiments

In the column studies, the concentration of dye in the effluent (C) or the relation between C and the initial dye concentration in the influent (C_0) is plotted as a function of the total volume of collected effluent, a characteristic '*S*' curve can be drawn. When the dye concentration in the effluent reaches 5–10% of its value in the influent, the exchange zone reaches the bottom of the bed. This point is known as the breakthrough point. The flow rate of feeding solution through the bed is continued until the concentration of dye in the effluent reaches the value of C_0. At this point, the exchange zone has moved out of the bed and the ion exchanger/

sorbent is exhausted. From the breakthrough curves (Fig. 6) the column parameters such as the weight and bed distribution coefficients as well as the working and total ion exchange capacities on Lewatit MonoPlus SP 112, Dowex Optipore SD 2 and Amberlite XAD 1180 were calculated. As follows from the data presented in Table 6, the cation exchanger Lewatit MonoPlus SP 112 was more effective for the sorption of the dye than the functionalized and non-functionalized polymeric sorbents. The values of D_w obtained for SP 112, SD 2 and XAD 1180 were found to be 6675.3, 905.5 and 571.7, respectively. The working ion exchange capacities were equal to 205 mg/mL for SP 112, 3.5 mg/mL for SD 2 and 6.5 mg/mL for XAD 1180. The biggest value of the total ion exchange capacity was determined for SP 112 and was found as 366 mg/mL. The time required for MTZ to move through its own length down the bed, the time required for MTZ to become established and move completely out of the bed and the time needed for MTZ formation were the longest for SP 112 resin and found to be 26833 min., 17500 min. and 3500 min., respectively. For SP 112 cation exchanger the bed symmetry coefficient F was calculated as 0.44 which is close to 0.5 for the symmetry S-shaped curve. The column efficiency η for SP 112 was 0.56. Based on the obtained column parameters, the studied sorbents can be arranged in the order: Lewatit MonoPlus SP 112 >> Dowex Optipore SD 2 > Amberlite XAD 1180 taking into account their applicability in BB3 removal from wastewaters by the dynamic method.

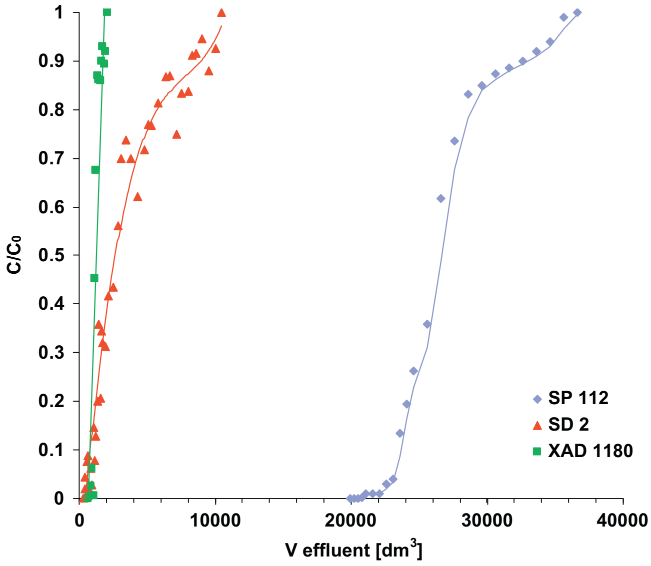

Fig. 6. Breakthrough curves of C.I. Basic Blue 3 on Lewatit MonoPlus SP 112, Amberlite XAD 1180 and Dowex Optipore SD 2 in the system containing 100 mg/L of C.I. Basic Blue 3 (*conditions*: volume of swollen resin: 10 mL, speed: 0.6 cm^3/min).

Table 6
Breakthrough curves parameters obtained for C.I. Basic Blue 3 (C_0 = 100 mg/L BB3) retention on Lewatit MonoPlus SP 112, Dowex Optipore SD 2 and Amberlite XAD 1180.

Sorbent	D_w	D_b	C_w (mg/mL)	C_t (mg/mL)	t_z (min)	t_e (min)	t_f (min)	η
SP 112	6675.3	2617.4	205	366	26833	61000	15026	0.56
SD 2	905.5	269.4	3.5	105	16917	17500	508	0.03
XAD 1180	571.7	118.4	6.5	21	2417	3500	749	0.31

6. Conclusions

Removal of C.I. Basic Blue 3 dye from aqueous solutions and wastewater was studied using the cation exchanger (Lewatit MonoPlus SP 112) and polymeric sorbents (Dowex Optopore SD 2 and Amberlite XAD 1180). The sorption experiments were carried out by means of batch and column methods. The presented process of removal of basic dye was affected by a number of operational parameters. The obtained results indicate that the cation exchange resin Lewatit MonoPlus SP 112 can be used as an effective, economic and favorable resin for the removal of BB3 not only from aqueous solutions but also from textile wastewaters.

In the case of the column method, SP 112 cation exchanger possesses the highest bed symmetry coefficient (close to 0.5) and column efficiency. Based on the breakthrough curve, the working and total ion exchange capacities of SP 112 were calculated as 205 mg/mL and 366 mg/mL, respectively.

Under the experimental conditions this resin possesses the highest monolayer sorption capacities, increasing from 560.7 to 637.6 mg/g with the temperature rise from 20 to 50 °C. The influence of salts addition on the q_e values determined for SP 112 was insignificant. At surfactants concentrations up to 0.5 g/L drop of the equilibrium capacities of the cation exchanger Lewatit MonoPlus SP 112 was observed. Kinetics data followed the pseudo-second order model. Only 1 h of phase contact time was sufficient for the total purification of the basic wastewater by means of SP 112 resin.

The above results indicate that the cation exchange sorption is promising treatment for the removal of BB3 dye from aqueous solutions and real textile streams.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2012.11.119.

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