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Anion Exchange Resins as Effective Sorbents for Removal of Acid, Reactive, and Direct Dyes from Textile Wastewaters

Monika Wawrzekiewicz and Zbigniew Hubicki

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/60952>

Abstract

Coloured wastewaters are a consequence of batch processes in both dye-manufacturing and dye-consuming industries. Dyes are widely used in a number of industries, such as textile and leather dyeing, food, cosmetics, paper printing, gasoline, with the textile industry as the largest consumer. Dyeing as a fundamental operation during textile fibre processing causes the production of more or less coloured wastewaters, depending on the degree of fixation of dyes on substrates, which varies with the nature of substances, desired intensity of coloration, and application method. Dye bearing effluents are considered to be a very complex and inconsistent mixture of many pollutants ranging from dyes, dressing substances, alkalis, oils, detergents, salts of organic and inorganic acids to heavy metals. Thus after dyeing wastewaters are characterized not only by intensive and difficult for removal colour but also by high pH, suspended and dissolved solids, chemical and biochemical oxygen demands. Ion exchange is a very versatile and effective tool for treatment of aqueous hazardous wastes including dyes. The role of ion exchange in dye effluents treatment is to reduce the magnitude of hazardous load by converting them into a form in which they can be reused, leaving behind less toxic substances in their places or to facilitate ultimate disposal by reducing the hydraulic flow of the stream bearing toxic substances. Another significant feature of the ion exchange process is that it has the ability to separate as well as to concentrate pollutants. Taking into account high capacity and selectivity of ion exchange resins for different dyes, they seem to be proper materials for dyes sorption from textile effluents. The aim of the paper is to study the removal of the acid, reactive and direct textile dyes such as C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 on the commercially available anion exchangers (Lewatit MonoPlus MP 62, Lewatit MonoPlus MP 64, Lewatit MonoPlus MP 500, Lewatit MonoPlus M 500, Amberlite IRA 67, Amberlite IRA 478RF, Amberlite IRA 458 and Amberlite IRA 958) differing not only in basicity of the functional groups but also in composition and structure of the matrix. Comparison of the sorption parameters obtained by the batch method taking into account influence of phase contact time, dyes initial concentration and solution pH were discussed in detail. Desorption conditions depending on the dyes sorption mechanism were also presented. Influence of the auxiliaries typically present in textile ef-

fluents such as inorganic electrolytes and different surfactants on the amounts of dyes retained by the anion exchangers was presented. The adsorption behaviour of the polyacrylic Amberlite IRA 958 demonstrates that it can be a promising adsorbent for the textile wastewater treatment. The results obtained with raw textile wastewaters purification confirmed this statement.

Keywords: anion exchangers, dyes sorption, removal, textile effluents

1. Introduction

Wastewaters originating from the textile, cellulose, paper, chemical, tanning, food and cosmetic industries containing dyes are a hazardous source of natural environment contamination. They are troublesome in purification process due to complex structure of dye molecules. Even small amounts of dye are undesirable as they colour water making it look unaesthetic and disturb life processes in water. Most dyes do not undergo biodegradation, deteriorate light penetration into water and inhibit photosynthesis, increase chemical and biological demand for oxygen. Some dyes are toxic and sometimes even carcinogenic and mutagenic towards living organisms and they should be carefully removed [1]. Purification of wastewaters containing dyes becomes more and more important and is aimed at avoiding potential threat for the environment and legal consequences. Decolourization of these wastewaters before their reaching water outlets is a must. Conventional methods of wastewaters purification do not remove colour completely. Therefore it is advisable to work out a more effective methods of wastewaters purification which would reduce the amount of discharged impurities but also contribute to recovery of water and raw materials used in technological processes. The difficulties in elaboration of both simple and economical methods of dyes removal are due to frequent changes in technology of their production as well as the use of various dyes in technological processes. In the case of impurities whose creation cannot be prevented, there should be applied highly effective technologies for their rendering harmless which can be combined into multi-stage purification systems. Such possibilities are provided by adsorption processes using, among others, ion exchangers allowing not only to separate substances dissolved based on selective interactions but also to concentrate amounts of impurities and formed closed circulation of water in the technological process.

2. Dyes – Definition and classification

Dyes are commonly defined as organic compounds of natural or synthetic origin which absorb visible light selectively in the range 400–700 nm, being capable of dyeing various materials (fabrics, paper, leather, wood, plastic, food, cosmetics) [1]. Dye molecules possess chromophoric groups, e.g. $-N=N-$, $-NO_2$, $-NO$, $-CH=CH-$, owing to which these compounds selectively absorb electromagnetic radiation in the visible range and auxochromic one (e.g. $-NH_2$, $-OH$, $-OR$) responsible for dyes affinity for dyed materials [1, 2]. Dye molecules can also

contain other substituents which impart specific properties affecting their solubility or stability improvement.

There are two basic ways of dyes classification. Based on the chemical structure of dye molecule, there can be distinguished carbocyclic and heterocyclic dyes. Considering the occurrence of chromophore, carbocyclic dyes include, among others, azo, nitro, anthraquinone ones and heterocyclic dyes include xanthene, acridine, indigoid ones. Using the chemical classification of dyes is convenient while discussing methods of their synthesis, chemical structure, dependence between the structure and different properties. Technical classification of dyes is based on the way of dyeing taking into account their solubility and chemical properties (Table 1) [2]. It is useful in the case of different applications of dyes. Not all dyes are universal. The way of their application depends on different methods of dye bonding with the material. Thus dyes are divided into reactive, direct, acid, basic, ice, vat, mordant, suspended, sulfurous, oxidative, pigments and lakes. From a practical point of view, there are two groups of dyes. The first one are dyes soluble in water with a created coloured cation (basic dyes) or anion (acid, acid-chromic, reactive, direct, and metal complex dyes). The second group includes dyes insoluble in water (suspended and those formed on the fibre, e.g. ice, oxidative, mordant) as well as pigments. Among them, there are dyes whose salts dissolve in water (sulfur and vat ones) and those which dissolve in organic solvents, e.g. fatty dyes.

Class of dyes	Chemical character of dyes	Exemplary dyes	Kind of coloured material
Acid	Organic salts of sulfonic and carboxylic acids soluble in water	Anthraquinone, azo, triphenylmethane, nitro, xanthene	Protein fibres (mainly wool), polyamide fibres, paper, leather, cosmetics, food
Basic	Salts of organic bases soluble in water	Arylmethane, xanthene, azo, acridine, anthraquinone	Wool, natural silk, polyester and polyacrylnitrile fibres
Direct (substantive)	Salts of organic sulfonic acids soluble in water	Phthalocyanines, stilbene, oxazine, azo	Cellulose fibres (cotton, linen), leather
Reactive	Salts of organic bases and acids soluble in water	Azo, anthraquinone, formazine, oxazine	Cellulose and protein fibres
Mordant	Soluble in water, form complex with metals	Nitroso dyes, e.g. alizarin and its derivatives	Cellulose and protein fibres
Vat	Insoluble in water	Anthraquinone, indigo	Cellulose fibres
Sulfur	Insoluble in water	-	Cellulose fibres
Dispersive	Insoluble or sparsely soluble in water	Azo, anthraquinone, nitro, styrole	Synthetic mainly poliester, polyamide, polyacrylnitrile, acetic

Table 1. Technical classification of dyes

There is a special register called *Colour Index* for dyes first published in 1924. The dual classification system *Colour Index* includes: *Colour Index Generic Name (CIGN)*, e.g. Disperse Yellow 1, which is the name describing the kind of dye as regards its technical application and colour as well as chronological notation in the register and for the known and published chemical structure, so-called *Colour Index Constitution Number (CICN)* in this case C.I. 10345 [3]. Their largest use was recorded in 2008 in Asia, particularly in China and India (Figure 1) [4]. The yearly world production of dyes is 700, 000–1000, 000 tones, which corresponds to over 100, 000 commercial products whereby azo dyes constitute 70% [5-11].

Natural dyes such as indigo, woad, or madder lost their position due to dynamic development of textile industry in the XVIIIth century. In the second half of the XIXth century, there started a synthesis of intermediate products and new dyes not having equivalents in nature of various colours, shades, and high quality (resistance to chemical factors, light, friction).

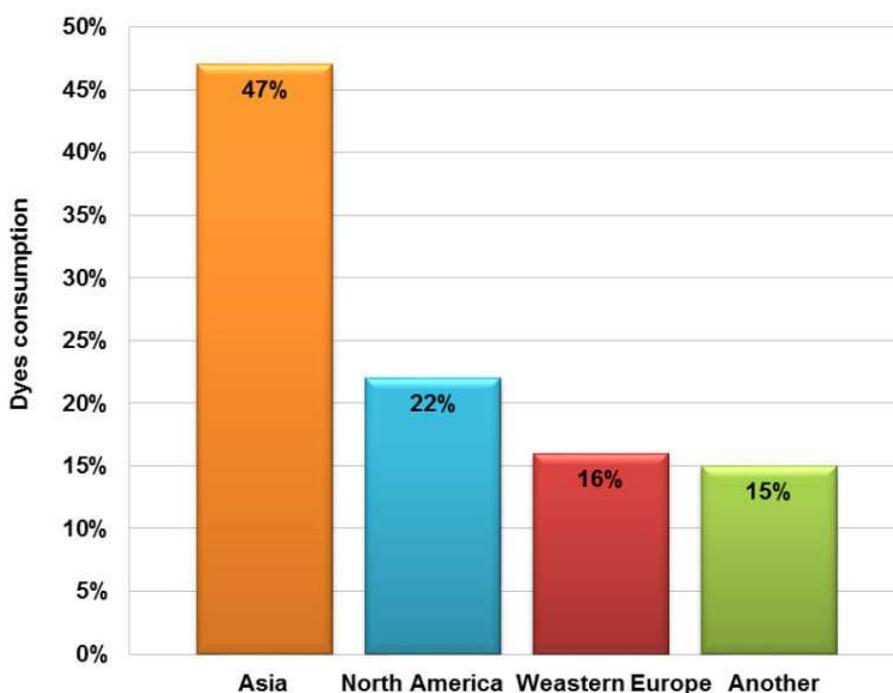


Figure 1. World dyes demand by the regions in 2008

The first synthetic dyes were fuchsine (prepared in 1855 by J. Natanson) and mowein (prepared in 1856 by W. Perkin) [1]. Development of dyes synthesis is promoted by their huge application in many fields of industry. The large tonnage consumer of dyes is textile industry. Moreover, they are applied in electronic industry for the production of liquid crystal and electrochromium visual indicators as well as in technology of optical recording, photographic (for creating coloured pictures), reprography (ink, non-carbon paper), food dyeing as well as for dyeing biological material, paper, leather, wood and cosmetics and also as indicators (e.g. redox, pH).

3. Sources of dyes in wastewaters and wastewater characterization

The basic sources of dyes in industrial wastewaters are complex technological processes in organic dye production plants, textile and paper plants as well as furrier and tanning ones. Waste products containing dyes from plastic production, food processing, petroleum, polygraphic, cosmetic, photographic and electronic industries are in somewhat lower amounts. Wastewaters from intermediate products and organic dyes production usually contain various chemical compounds which occur not only in the form of aqueous solutions but also in liquids, emulsions suspensions and pitch sparsely soluble in water. Besides residues of raw and intermediate materials such as benzene, aniline, phenol, amine, nitro compounds, alcohols, esters, salts, inorganic acids (mainly HNO_3 , H_2SO_4), they contain those of ready-made products or dyes. The weight amounts of unreacted substrates, by-products or auxiliary compounds largely exceed the amounts of the main product. They are characterized by intense colouring despite insignificant dye concentration as well as smell and taste due to the presence of nitro compounds. Some aniline dyes are distinctly visible even at the concentration about 40 mg/L [12]. Table 2 presents the characteristics of wastewaters from organic dyes production [12].

Indicator	Kind of produced dye			
	Pigment yellow 10G	Acid orange	Lake claret BLC	Azo Dyes
Reaction pH	4.3	8.8	4.7	2.6
COD (mg/L)	-	83,735	2269	19,410
Sulfates (mg SO_4^{2-} /L)	620	1887	16,527	5921
Chlorides (mg Cl^- /L)	975	153,500	17,750	20,500
Dry residue (mg/L)	11,910	393,600	49,400	377,800
Suspensions (mg/L)	3858	-	-	-

Table 2. Characteristics of wastewaters from organic dyes production plant

Amount and composition of wastewaters originated from textile plants depend on many factors, among others, on the kind of fibre or fabric, way of dyeing (kind of used dyes) as well as apparatus. Their largest amounts have arisen during chemical treatment of textile products. Textile plants in the three-shift (24 h/day and night) system equipped with 40 dyeing machines generate enormous amounts of effluents 2400–5200 m³/day and night assuming the average capacity of dyeing machine 200–6500 L and taking into account 7–10 fillings (baths) of the machine during one dyeing process [13].

Processes of chemical treatment of textile products are a separate branch of producing of above wares likewise mechanical treatment [14]. Their main aim is to give textile products suitable properties facilitating their further treatment and desirable usable features like shape stability,

resistance to outer factors' action (washing, friction, dirt, sweat) as well as surface appearance (smooth, creased, shiny, dull, colorful). The above mentioned properties of textile products are obtained during their treatment using various chemical substances: alkalis, acids, salts, surface active substances, oxidizers, reducers, dyes, thickeners, water, solvents and many others. The amounts of substances added to dyeing baths depending on colouring intensity are given in Table 3 [13, 15].

Depth of shade	Dyeing bath composition (g/kg textiles)			
	Dyes	Organic auxiliaries	Inorganic auxiliaries	Electrolytes NaCl, Na ₂ SO ₄
Light shade	0.5–4	0–30	50–250	90–400
Medium shade	5–30		30–150	600–700
Deep shade	30–80	0–35		800–1500

Table 3. Load of impurities carried in dyeing bath

These compounds are a main load in textile wastewaters; and besides dyes, they remain in wastewaters in the concentration close to the initial one (part is deposited on the textile product) as suitable dyeing conditions are created. The average water consumption in all processes of chemical treatment is from about 150 to over 300 liters per one kilogram of fibre causing formation of the same amount of strongly contaminated wastewaters [14]. Beside dyes and auxiliaries, textile industry wastewaters contain specific contaminations such as fat, wax, dextrin, starch, dressing or casein. Organization for Economic Cooperation Development estimated that 7–20% of acid dyes, 5–20% of direct dyes and 20–50% of reactive dyes were lost in the effluents in Europe [16-19]. A large percentage of pollution generated by the textile industry can be attributed to salts, sizing agents, preparation agents, detergents and organic acids [16], see Figure 2.

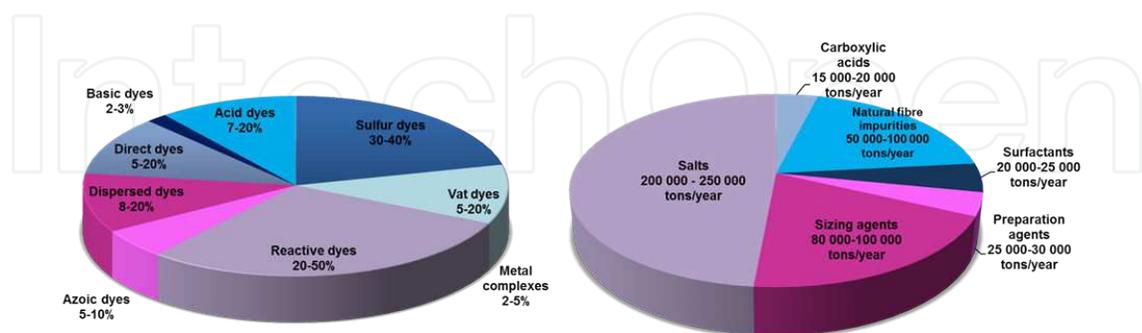


Figure 2. Percentage of non-fixed dyes and auxiliaries that may be discharged in the textile effluent (based on the data presented in the paper [16])

For example, reactive dyeing of 1 kg of cotton requires about 150 L of water, 0.6–0.8 kg of NaCl and about 40 g of reactive dye. One can easily imagine the total amount of generated pollution.

According to Epolito et al. [19] under typical dyeing conditions, up to 50% of the initial dye concentration remains in the spent dye bath in its hydrolyzed form. Thus after dyeing wastewaters are characterized not only by intensive and difficult colour removal but also by high pH, suspended and dissolved solids, chemical and biochemical oxygen demands. Typical characteristics of raw textile wastewaters are presented in Table 4 [12–14, 20, 21].

Indicator	Range of indicator fluctuations in the textile industry wastewater impurities			
	Cotton	Wool	Silk	Flax
Grade of dye	Reactive, vat	Acid	Acid, reactive, direct	Direct
Colour threshold*	1:10–1:250	1:10–1:300	1:8–1:400	1:2–1:150
Reaction pH	6.1–11.2	4.1–8.8	3.7–9.5	2.2–11
BOD (mg O ₂ /L)	50–620	60–455	50–700	30–1800
Permanganate value (mg O ₂ /L)	80–450	52–495	32–412	40–3600
Sulfates (mg SO ₄ ²⁻ /L)	50–690	32–423	70–520	35–150
Chlorides (mg Cl ⁻ /L)	80–650	44–530	40–1400	20–360
Sulfides (mg H ₂ S/L)	2.2–30	1–20	1–40	-
Total chromium (mg Cr/L)	-	1–5	-	-
Detergents (mg/L)	1–70	5–124	4–35	-
Fat (mg/L)	5–15	10–150	-	-
Dry residue (mg/L)	300–3500	478–2120	400–4100	400–2450
Total suspension (mg/L)	50–530	69–403	40–330	20–350
Temperature (°C)	30–50	25–50	36–40	25–45

*Colour threshold – given according to the platinum scale (e.g. in mg Pt/L) or in a descriptive way giving dilution extent at which specific colour disappears

Table 4. Composition of textile wastewaters

Wastewaters coming from tannery, besides impurities removed from leather (hair, blood, epidermis, fat tissue) contain significant amounts of chemicals: sulfuric acid and hydrogen chloride, lime, soda, sodium sulfide, chromium (III) compounds, detergents and organic solvents [14]. Water consumption in tanneries and furriery plants is from 30 to 81 m³ and from 8.5 to 400 m³, respectively, for 1000 leathers depending on their kind. Concentration of organic impurities from furriery plants is somewhat smaller than from tannery. Dyes contained in these wastewaters come from tanning, dyeing and rising of raw material and their concentration is 1 kg/m³ [21]. They constitute 17–32.5% of the total amount of wastewater generated by these plants [12]. The composition of wastewaters from the tannery and furriery plants is presented in Table 5 [21].

Wastewaters from paper factories containing dyes particularly aniline and sulfur ones are generated from the paper treatment process consisting in the addition of fillers and dyes to the bleached cellulose material. As a result of multi-stage purification of wastewaters from the cellulose plants, there is obtained a low value of BOD (biochemical oxygen demand) – 4 mg/L but COD (chemical oxygen demand) is maintained on the level 75 mg/L. These wastewaters contain a small amount of suspended matter – 5 mg/L, but they are characterized by intensive colour – 40 mg Pt/L [21].

Indicator	Tannery	Furriery plant
Reaction pH	7.8–9.8	3–10
Chlorides (mg Cl ⁻ /L)	1600–4000	30000
Sulfates (mg SO ₄ ²⁻ /L)	500–2000	1000
Chromium(III) (mg/L)	30–80	3000
Chromium(VI) (mg/L)	300–500	500
Surface active substances (mg/L)	60–200	2000
COD (mg O ₂ /L)	1000–9000	-
BOD (mg O ₂ /L)	500–4500	-

Table 5. Concentration of impurities in wastewaters from the tannery and furriery plants

4. Impact of dyes on natural environment

Wastewaters containing dyes are troublesome in purification processes due to a complex structure of dye molecules. Even small amounts of dyes (of a few ppm order) are undesirable; they colour water, making it look unaesthetic and disturb life processes in water. Most dyes do not undergo biodegradation, deteriorate penetration of light into water and inhibit photosynthesis processes, increase chemical and biological demand for oxygen. Some dyes exhibit toxic and even cancerogenic as well as mutagenic action towards living organisms and therefore they should be carefully removed [5, 17]. Most dyes have a harmful effect (directly or indirectly) on fish. Direct activity consist in colouring of water and changing its composition, which significantly deteriorates the living conditions of fish and plankton, but indirect activity consist in poisonous properties of many dyes. Studies of dyes toxicity for fish seem to be particularly interesting not only with respect for estimation of water purity but also for the fact that they are a valuable source of food for people. Based on the ETAD (Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers) tests made for 3000 commonly used dyes in 27 cases, the registered LC₅₀ (Lethal Dose₅₀) values were of the order 0.05 mg/L (compared with, e.g. for DDT [dichlorodiphenyltrichloroethane] the LC₅₀ value was 0.006 mg/L) [22]. It proved that 98% of studied dyes reveal LC₅₀ toxicity over 1 mg/L. High toxicity was found in C.I. Basic Violet 1 with LC₅₀ equal to 0.05 mg/L and C.I. Basic Yellow 37 with LC₅₀ equal to 0.8 mg/L [22].

5. Methods of coloured wastewaters purification

The dye removal technologies can be divided into three categories: biological, chemical and physical. Possible decolourization methods of textile wastes along with advantages and disadvantages are listed in Figure 3 [23]. Because of high cost and disposal problems, many of these conventional methods for treating dye wastewaters have not been widely applied on a large scale in the textile industry. At present, there is no single process capable of treatment, mainly due to the complex nature of effluents, combination of the above mentioned techniques provides effective treatment of coloured wastewaters [12, 13, 17]. According to Babu et al. [24], more than 100 references in the bibliographical review of textile wastewater treatment prove that combination techniques permit not only the reduction of suspended solids, organic substances and colour but also the recovery of process chemicals. Currently, the main methods of textile dye treatment are by physical and chemical means with research concentrating on cheap and effective sorbents such as sandy soils, hen feathers, bottom ash, rice husk ash, orange peel, sugarcane dust, etc. However, it should be stressed that they are characterized by relatively low sorption capacity towards dyes compared with activated carbons or ion exchangers and what is more they need to be dumped.



Figure 3. Advantages and disadvantages of the current methods of dye removal from industrial effluents

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

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

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

The internal structure of the resin beads, i.e. whether microporous (gel-type) or macroporous, is important in the selection of an ion exchanger. Macroporous resins, with their high effective surface area, facilitate the ion exchange process. They also give access to the exchange sites for larger ions, can be used with almost any solvent, irrespective of whether it is a good one for the uncross-linked polymer, and take up the solvent with little or no change in volume. They make more rigid beads, facilitating the ease of removal from the reaction system. In the case of the microporous resins, since they have no discrete pores, solute ions diffuse through the particle to interact with the exchange sites. Despite diffusion limitations on the reaction rates, these resins offer certain advantages: they are less fragile, requiring less care in handling, react faster in functionalization and application reactions as well as possess higher loading capacities [25].

Taking into account high capacity and selectivity of ion exchange resins for different dyes, they seem to be proper materials for dyes sorption from textile effluents. Applicability of the anion exchange resins in the removal of acid, reactive, direct dyes widely used in the textile industry, from aqueous solutions and wastewaters, was confirmed in some papers [2, 15, 20, 23, 25–28].

6. Experimental

In the paper, the results of the sorption of three textile dyes such as C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 on the commercially available anion exchangers are summarized and discussed based on the data presented in papers [2, 15, 20, 23, 25–31].

The essential physicochemical properties of these resins (produced by Lanxess, Germany or Dow Chemical Company, USA) are given in Table 6 and Figure 4. The resins were washed with both 1 M HCl and distilled water in order to remove impurities and change the ionic form to the chloride one. The resins were dried at room temperature to the constant mass.

Molecular structures of the above mentioned dyes are presented in Figure 5. The dyes were purchased from Sigma-Aldrich (Germany) and used without further purification. These dyes were selected for the studies because they are extensively used in the textile industry. C.I. Acid Orange 7 is applied for fibers such as silk, wool and nylon using neutral to acid dye baths. Direct Blue 71 is used for cotton, paper, leather, wool, silk and nylon dyeing. Reactive dyes, e.g. RB5, are by far the best choice for dyeing of cotton and other cellulose fibers.

The other chemicals used were produced by Sigma-Aldrich (Germany) and were of analytical grade.

Commercial name	Functional groups	Matrix composition and structure	Total capacity (eq/L)	Operating temp. (°C)	Beads mean size (mm)
Lewatit MonoPlus MP 62	– N(CH ₃) ₂	S-DVB, m	1.7	70	0.47
Amberlyst A 23		PF, m	>1.8	80	0.47–0.74
Amberlite IRA 67		A-DVB, g	>1.6	60	0.55–0.75
Lewatit MonoPlus MP 64	– N(CH ₃) ₂ and – N ⁺ (CH ₃) ₃	S-DVB, m	1.3	70	0.59
Amberlite IRA 478RF		A-DVB, g	>1.15	35	0.78–0.98
Amberlite IRA 900	– N ⁺ (CH ₃) ₃	S-DVB, m	1.0	60	0.65–0.82
Lewatit MonoPlus MP 500		S-DVB, m	>1.1	45	0.63
Lewatit MonoPlus M 500		S-DVB, g	1.1	70	0.64
Amberlite IRA 458		A-DVB, g	1.25	35	0.6–0.9
Amberlite IRA 958		A-DVB, g	>0.8	80	0.63–0.85
Amberlite IRA 910		S-DVB, m	1.1	60	0.53–0.8
Lewatit MonoPlus M 600	– N ⁺ (CH ₃) ₂ C ₂ H ₄ OH	S-DVB, g	1.3	30	0.62

where: - weakly basic anion exchangers, - intermediate base anion exchangers, - strongly basic anion exchangers, S-DVB – styrene-divinylbenzene, A-DVB – acrylic-divinylbenzene, PF- phenol-formaldehyde, m – macroporous, g - gel

Table 6. Properties of applied anion exchangers

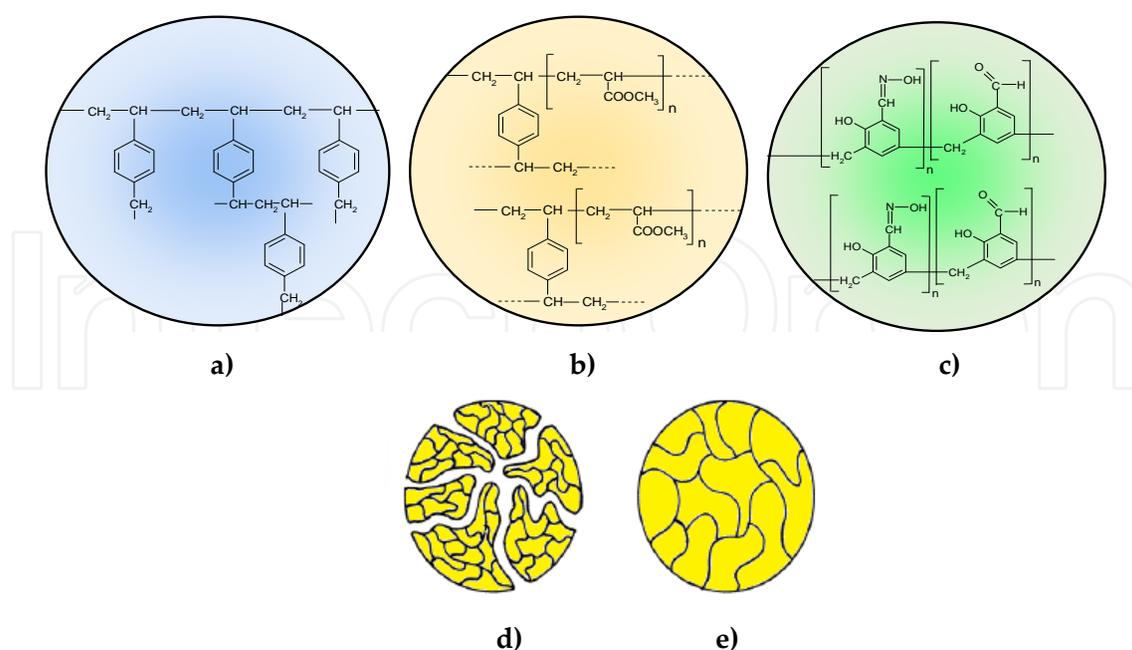


Figure 4. Composition of resin matrices: a) styrene-divinylbenzene skeleton, b) acrylic-divinylbenzene skeleton, c) phenol-formaldehyde skeleton, and their structure: d) macroporous, e) gel

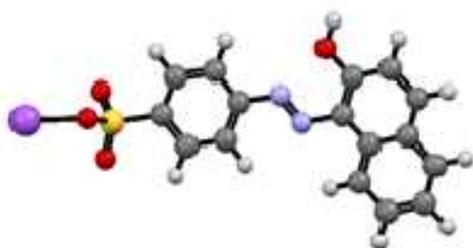
The sorption studies were performed by the batch method. The dye solutions (50 mL) were shaken with the dry anion exchanger (0.5 g) in conical flasks using a thermostated laboratory shaker Elphin (Poland) at 20°C. The experiments were conducted in the two parallel series with the reproducibility 5%. The amount of dye adsorbed after time t , q_t (mg/g), was calculated from Equation 1:

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

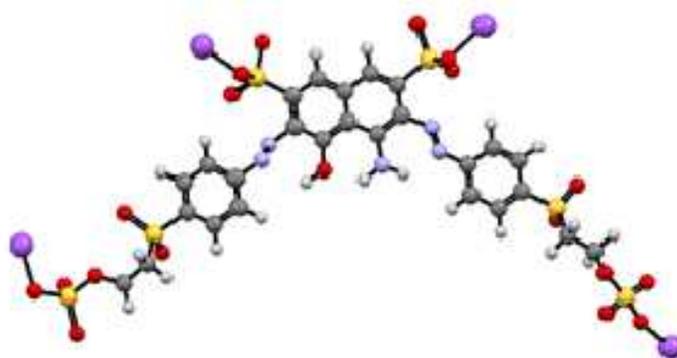
where: C_0 and C_t (mg/L) are the liquid-phase concentrations of dye at the time $t=0$ and after time t , respectively, V (L) is the volume of solution and w (g) is the mass of dry anion exchanger.

To test the influence of shaking speed on dye removal, preliminary experiments were carried out by varying the shaking speed from 140 to 200 rpm. The best results were obtained for the shaking speed 180 rpm. Therefore, 180 rpm was used in all batch experiments. To evaluate the kinetics of the sorption process, 50 mL solutions of 100 mg/L (or 500 mg/L or 1000 mg/L) dye concentration and 0.5 g of the anion exchanger samples were used. The shaking time was varied from 1 to 12 h, respectively (e.g. up to equilibrium). All the kinetic studies were carried out at the natural pHs (pH 4.98–5.83) of solutions (pH-meter; CX-742 Elmetron, Poland). The dyes concentration after the sorption was measured spectrophotometrically at the maximum absorbance wavelengths. Absorption spectra of raw textile wastewaters of different composition were recorded for the predetermined time interval of decolourization using a spectrophotometer Specord M-42 (Carl Zeiss, Germany).

C.I. Acid Orange 7; C.I. No 15510; MW = 350.32 g/mol
sodium salt of 4-(2-hydroxynaphthylazo)benzenesulfonic acid



C.I. Reactive Black 5; C.I. No 20505; MW = 991.82 g/mol
tetrasodium salt of 4-amino-5-hydroxy-3,6-bis((4-((2-(sulfooxy) ethyl)sulfonyl)phenyl)azo)-2,7-naphthalenedisulfonic acid



C.I. Direct Blue 71; C.I. No 34140; MW = 1029.88 g/mol
tetrasodium 3-[(E)-{4-[(E)-{4-[2-(6-amino-1-oxo-3-sulfonatophthalen-2(1H) ylidene)hydrazino]-6-sulfonatophthalen-1-yl}diazonyl]naphthalen-1-yl}diazonyl]naphthalene-1,5-disulfonate

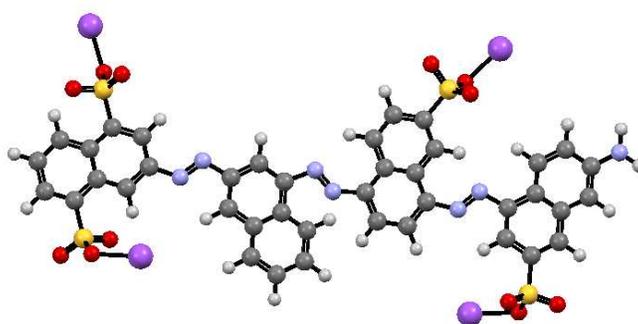


Figure 5. Dyes characteristics

Sorption isotherm studies were carried out analogously using dyes solutions of the increasing initial concentration at 20°C for 24 h. The effects of salts and surfactant additions on dyes' uptake at equilibrium were studied by shaking the anion exchanger (0.5 g) with the 100 mg/L dye solution containing different amounts of salts (Na_2SO_4 , Na_2CO_3 , NaCl) or surfactants

(sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB)). The dyes concentration after the sorption was measured spectrophotometrically at the maximum absorbance wavelengths depending on the system.

Regeneration tests for the anion exchange resin were conducted with different regeneration agents (1 M HCl, 1 M NaOH, 1 M KSCN, 1 M NaCl, 1 M Na₂SO₄, 1 M Na₂CO₃, 90% methanol, 1 M KSCN or 1 M NaOH or 1 M HCl in 90% methanol). The loaded resin containing 10 mg/g of dye was put into flasks in contact with 50 mL of different eluting agents. The flasks were agitated for 3 h and the dye concentrations in the solution were determined at the maximum absorbance wavelength in order to calculate the desorption percentage (%).

The above methods were described in detail in [2, 15, 20, 23, 25–31].

7. Results and discussion

7.1. Adsorption equilibrium and retention mechanisms

The equilibrium sorption isotherms are one of the most important data to understand the mechanism of the sorption. They describe the ratio between the quantity of sorbate retained by the sorbent and that remaining in the solution at the constant temperature at equilibrium and are important from both theoretical and practical points of view. The parameters obtained from the isotherm models provide important information not only about the sorption mechanisms but also about the surface properties and affinities of the sorbent. The best known adsorption models in the linearized form for the single-solute systems are:

a. the Langmuir isotherm

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (2)$$

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 .

The 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; (c) all sites are energetical and sterical independent of the adsorbed quantity [32].

b. the Freundlich isotherm

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (3)$$

where: k_F (mg/g) is the Freundlich adsorption capacity, 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 $\log C_e$.

The Freundlich isotherm assumes heterogeneous surface with a non-uniform distribution of heat of adsorption [33].

The applicability of isotherm equations was compared in this paper by judging the determination coefficients (R^2). The calculated constants of these models were largely dependent on the type of the anion exchanger (Tables 7–9). Not only the basicity of the resin but also the matrix composition and structure were the determining factors of sorption. It could be stated generally that the Langmuir isotherm model fits better than the Freundlich one. However, the comparison of the R^2 values indicates that the experimental data of C.I. Direct Blue 71 adsorption onto Amberlite IRA 67, Amberlite IRA 900 and Lewatit MonoPlus MP 62 were more appropriate for the Freundlich isotherm model. It could be in agreement with the aggregation tendency of the C.I. Direct Blue 71 dye, especially at high concentrations, and with the possibility of the dye uptake through many types of interactions. Similar observations were described for C.I. Basic Blue 9 sorption onto Purolite C 145 and Purolite C 107E resins by Suteu et al. [34].

Anion exchanger	Langmuir isotherm model			Freundlich isotherm model			Ref.
	Q_0 (mg/g)	b (L/g)	R^2	k_F	n	R^2	
Lewatit MonoPlus MP 62	79.9	0.03	0.993	43.2	9.2	0.896	[27]
Amberlyst A 23	80.2	0.03	0.996	39.7	8.6	0.872	This study
Amberlite IRA 67	168.2	0.002	0.996	41.2	7.3	0.892	[29]
Lewatit MonoPlus MP 64	586.5	0.68	0.999	168.8	5.6	0.794	[27]
Amberlite IRA 478RF	1279.2	0.166	0.999	213.0	2.95	0.996	[25]
Amberlite IRA 900	1289.7	0.007	0.999	207.6	0.421	0.943	[26]
Lewatit MonoPlus MP 500	979.0	0.17	0.993	157.7	2.5	0.956	[27]
Lewatit MonoPlus M 500	215.9	0.129	0.999	154.7	21.0	0.427	This study
Amberlite IRA 458	1211.3	0.066	0.999	198.6	0.221	0.842	[29]
Amberlite IRA 958	1370.4	0.063	0.999	161.7	0.345	0.872	[30]
Amberlite IRA 910	1012.6	0.015	0.998	159.1	0.521	0.900	[26]
Lewatit MonoPlus M 600	174.1	0.987	0.998	38.3	36.9	0.789	This study

Table 7. Comparison of the isotherms parameters for C.I. Acid Orange 7 sorption on the studied anion exchangers

Anion exchanger	Langmuir isotherm model			Freundlich isotherm model			Ref.
	Q_0 (mg/g)	b (L/g)	R^2	k_F	n	R^2	
Lewatit MonoPlus MP 62	796.1	0.049	0.990	183.5	4.96	0.925	[23]
Amberlyst A 23	282.1	0.204	0.999	125.6	8.77	0.937	[23]
Amberlite IRA 67	66.4	0.503	0.998	26.4	7.10	0.914	[23]
Lewatit MonoPlus MP 64	592.7	0.242	0.999	84.3	3.45	0.717	This study
Amberlite IRA 478RF	150.4	0.057	0.999	93.0	16.1	0.906	[25]
Amberlite IRA 900	1351.8	0.039	0.999	179.4	6.92	0.845	[31]
Lewatit MonoPlus MP 500	1170.5	0.416	0.996	312.1	3.24	0.955	This study
Lewatit MonoPlus M 500	17.4	0.099	0.998	3.83	3.69	0.789	This study
Amberlite IRA 458	1329.5	0.037	0.999	241.3	4.92	0.823	[30]
Amberlite IRA 958	1655.2	0.468	0.999	263.2	3.21	0.815	[30]
Amberlite IRA 910	1219.9	0.021	0.998	172.4	4.62	0.794	[30]
Lewatit MonoPlus M 600	4.6	0.236	0.896	0.15	1.2	0.629	This study

Table 8. Comparison of the isotherms parameters for C.I. Reactive Black 5 sorption on the studied anion exchangers

Anion exchanger	Langmuir isotherm model			Freundlich isotherm model			Ref.
	Q_0 (mg/g)	b (L/g)	R^2	k_F	n	R^2	
Lewatit MonoPlus MP 62	470.6	0.0003	0.874	1.47	0.86	0.931	[20]
Amberlyst A 23	456.2	0.079	0.994	22.2	2.69	0.645	This study
Amberlite IRA 67	90.9	0.005	0.909	1.02	1.57	0.998	[20]
Lewatit MonoPlus MP 64	420.4	0.021	0.997	24.2	2.35	0.510	[20]
Amberlite IRA 478RF	41.8	0.0047	0.974	4.67	3.6	0.969	[25]
Amberlite IRA 900	778.2	0.0001	0.828	0.21	1.18	0.901	[20]
Lewatit MonoPlus MP 500	523.6	0.0023	0.959	2.65	1.39	0.874	[20]
Lewatit MonoPlus M 500	2.02	0.165	0.692	0.14	1.06	0.509	[20]

Anion exchanger	Langmuir isotherm model			Freundlich isotherm model			Ref.
	Q_0 (mg/g)	b (L/g)	R^2	k_f	n	R^2	
Amberlite IRA 458	48.4	0.034	0.982	5.6	2.84	0.650	[20]
Amberlite IRA 958	1630.6	0.0001	0.987	0.65	1.26	0.965	[20]
Amberlite IRA 910	663.7	0.008	0.945	0.19	1.02	0.900	This study
Lewatit MonoPlus M 600	1.89	0.154	0.713	0.11	1.01	0.603	This study

Table 9. Comparison of the isotherms parameters for C.I. Direct Blue 71 sorption on the studied anion exchangers

Based on the values of the monolayer sorption capacities determined from the Langmuir isotherm model, the studied anion exchangers can be arranged in the following sorption effectiveness series as:

- for C.I. Acid Orange 7

Amberlite IRA 958 > Amberlite IRA 900 > Amberlite IRA 478RF > Amberlite IRA 458 > Amberlite IRA 910 > Lewatit MonoPlus MP 500 > Lewatit MonoPlus MP 64 > Lewatit MonoPlus M 500 > Lewatit MonoPlus M 600 > Amberlite IRA 67 > Amberlyst A 23 ≈ Lewatit MonoPlus MP 62

- for C.I. Reactive Black 5

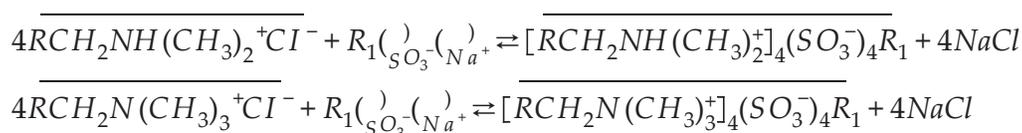
Amberlite IRA 958 > Amberlite IRA 458 > Amberlite IRA 900 > Amberlite IRA 910 > Lewatit MonoPlus MP 500 > Lewatit MonoPlus MP 62 > Lewatit MonoPlus MP 64 > Amberlyst A 23 > Amberlite IRA 478RF > Amberlite IRA 67 > Lewatit MonoPlus M 500 > Lewatit MonoPlus M 600

- for C.I. Direct Blue 71

Amberlite IRA 958 > Amberlite IRA 900 > Amberlite IRA 910 > Lewatit MonoPlus MP 500 > Lewatit MonoPlus MP 62 > Amberlyst A 23 > Lewatit MonoPlus MP 64 > Amberlite IRA 67 > Amberlite IRA 458 > Amberlite IRA 478RF > Lewatit MonoPlus M 500 ≈ Lewatit MonoPlus M 600

as far as their applicability is concerned in removal of these dyes.

Under experimental conditions, sorption of the dyes occurred between the sulphonic groups of dyes (e.g. $R_1(SO_3^-)_4(Na^+)_4$) and the functional groups of the weakly ($RCH_2NH(CH_3)_2^+Cl^-$) or strongly ($RCH_2N(CH_3)_3^+Cl^-$) basic anion exchangers in the chloride form [25]:



The dye anions ($R_1(\text{SO}_3^-)_4$) replaced exchangeable chloride anions which compensates positive electric charge of the tertiary amine or quaternary ammonium groups of the anion exchanger. The ion pairs are formed between these groups. Such interactions were revealed during the analysis of the ATR FT-IR spectra of the dye loaded anion exchangers, the absorption peaks at 1170–1047 nm and 1019 nm were attributed to the presence of $-\text{SO}_3^-$ and $-\text{S}=\text{O}$ groups [20]. In the FT-IR spectrum of the weakly basic anion exchanger Purolite A 847 with loaded azo- (Lanasyn Navy M-DNL) and phthalocyanine (C.I. Acid Blue 249) dyes, the vibrations at 1042 nm and 1032 nm related to $-\text{SO}_3^-$ groups were detected by Kaušpėdienė et al. [35]. Although ion exchange is a significant mechanism in dyes sorption, some extent of physical adsorption can also occur. The attachment through hydrophobic π - π interactions between the aromatic rings of the dye and the matrix of the anion exchanger ('like attracts like') is considered. These interactions play a more extensive role in the case of the polyacrylic resins like Amberlite IRA 958, IRA 458 or IRA 67 compared to those of polystyrene-based materials. High affinity of dyes for the anion exchangers can also result from the formation of H-bondings, which can be created between nitrogen of the quaternary ammonium groups of strongly basic anion exchange resins and nitrogen of the $-\text{NH}_2$ group of dyes as well as oxygen of the carbonyl group of the resins and the $-\text{NH}_2$ group of dye. Also oxygen atom of the carbonyl group of anion exchangers and oxygen atom of the hydroxyl group or nitrogen atom of the azo group of dyes through the water molecules could interact. Possible interactions between the anions of C.I. Reactive Black 5 and the strongly basic anion exchangers of polyacrylic matrices are shown in Figure 6. Kaušpėdienė et al. [35, 36] also observed that more than one interaction was involved in dyes sorption on Purolite A 847 of polyacrylic matrix: ion exchange and nonelectrostatic interactions. The studies on the sorption of dyes and organic compounds on the ion exchangers reported so far showed that the size of the sorbate molecules has a considerable effect on the sorption degree. Organic dye molecules of different positions of sulfonic groups as well as the number of other anionic groups and their charges can interact in a different way with anion exchangers. Of significant importance in the removal of dye anions by an anion exchanger is the resin structure. Concerning the exchange of large molecular weight species like dyes, the macroporous property becomes important in providing an easier diffusion path for uptake compared with the gel structure. Amberlite IRA 958 as the anion exchanger with the macroporous structure possesses significant porosity in comparison with that of gel Amberlite IRA 458 or IRA 67. Therefore, sorption capacity of Amberlite IRA958 is much more bigger than that of Amberlite IRA 458 of the same functional groups in the case of C.I. Direct Blue 71 sorption. Taking into consideration the strongly basic anion exchangers Lewatit MonoPlus M 500 and Lewatit MonoPlus M600 of polystyrene matrix and gel structure, a very low capacity is observed. Additionally, flat structure of the reactive and direct dyes can inhibit the interactions between the dyes and the anion exchangers. Also when the dye anions are too large, they are excluded because of resin structure ('sieve effect'). Besides, because large size dyes have the tendency to form aggregates in the solution rather than in the resin phase [25].

7.2. Influence of auxiliaries such as salts and surfactants

Auxiliaries such as inorganic electrolytes and surfactants are widely used in chemical treatment of fibers. They remain in wastewaters at a concentration close to the initial one. Depend-

ing on the class of dye, dyeing process requires application of other auxiliaries. Acid dyes are the most numerous group of those known. They occur in the form of sodium salts of coloured compounds containing 1–3 sulfonic or carboxylic groups. They belong to strong electrolytes, undergo complete dissociation in water into coloured anions. The condition of their binding with fibre is forming a sufficient number of the ammonium groups in wool which can be obtained by the addition of acids to dyeing baths, hence it is said ‘they dye in the acid bath’. Disposal of the carboxylic acids to the textile sewages in Europe amounts from 15, 000 to 20, 000 tons/year [16].

Acid dyes are divided into three groups differing in dyeing conditions. The first group includes so-called well equalizing dyes that is providing uniform level dyeing of a relatively small molecular mass. They are used for dyeing in acid bath of pH 2–2.5 with the addition of strong acids, e.g. H_2SO_4 .

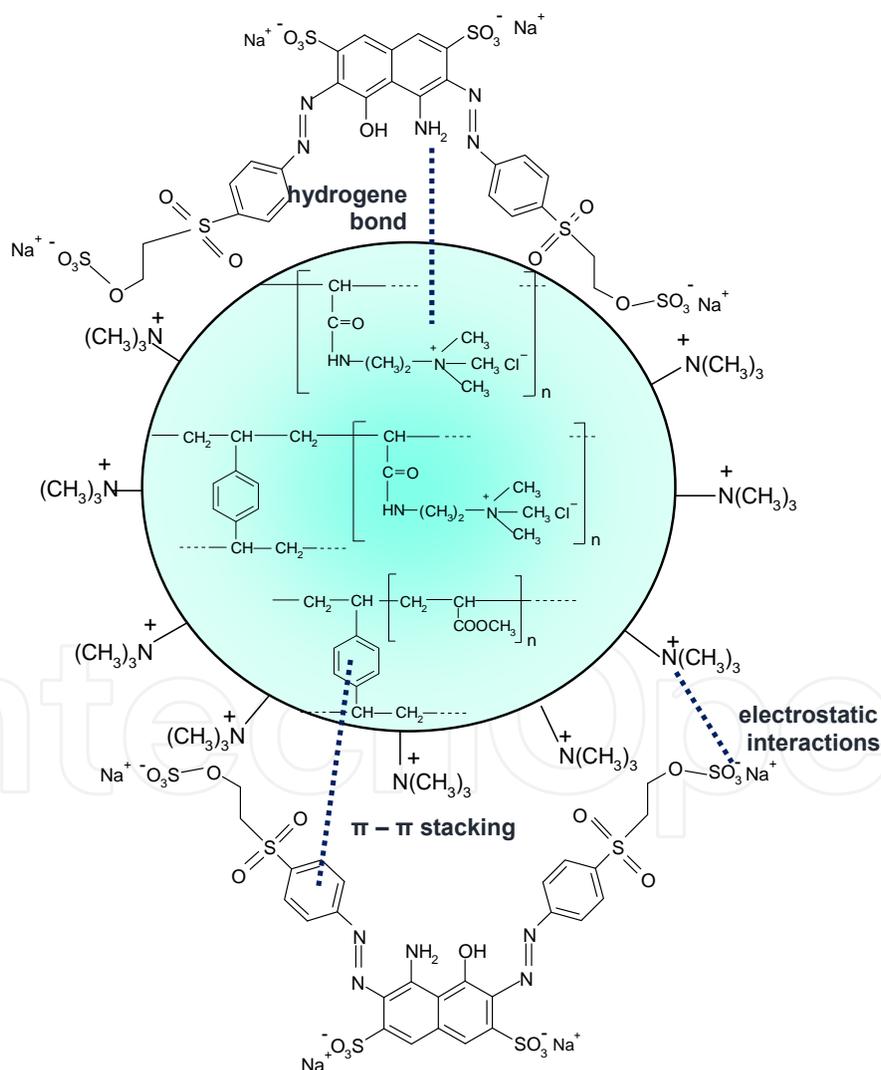


Figure 6. Mechanism of interactions between C.I. Reactive Black 5 and strongly basic anion exchanger of the polyacrylic matrix

The second group includes dyes of more developed molecules and greater affinity for wool. They are used for dyeing in the baths of pH 4.5–5 acidified with acetic acid. The third group has badly equalizing dyes of largely expended molecules and great affinity for wool. They are applied for dyeing in the baths of pH 5.5–6.5 in the presence of ammonium salts (sulfate, acetate), which decompose only at increased temperature acidifying the bath. Usually, sodium sulfate is added to the dyeing bath in the amount 10–20% in the proportion to the fibre and 1–2% of formic, acetic or sulfuric acid.

The influence of inorganic salts such as NaCl and Na₂SO₄ on the sorption of C.I. Acid Orange 7 from the solution of the initial concentration 100 mg/L was studied. The results indicate that the presence of these salts in the whole examination concentration of 1–25 g/L does not affect the dye adsorption significantly. In the case of the increasing amount of sodium sulfate in the solution from 1 to 25 g/L, the anion exchange capacities of the polyacrylic anion exchangers of the weakly basic functional groups Amberlite IRA 67 and of the intermediate base Amberlite IRA 478RF dropped from 9.98 mg/g to 9.2 mg/g and from 9.98 to 8.9 mg/g, respectively. The effect of Na₂SO₄ concentration on C.I. Acid Orange 7 removal using the strongly basic anion exchangers of the polyacrylic skeleton (Amberlite IRA 458 and Amberlite IRA 958) was insignificant. Similar observation of the effect of salts addition such as Na₂HPO₄ and NaH₂PO₄ was observed by Greluk and Hubicki [29]. In the presence of NaH₂PO₄ and Na₂HPO₄, the C.I. Acid Orange 7 retention by Amberlite IRA 958, in the system 200 mg/L dye and 0.1–2.0 g/L salts was not affected. Using weakly (Lewatit MonoPlus MP 62), intermediate (Lewatit MonoPlus MP 64) and strongly (Lewatit MonoPlus MP 500, Lewatit MonoPlus M 500, Lewatit MonoPlus M 600, Amberlite IRA 900 and Amberlite IRA 910) basic anion exchangers of the polystyrene–divinylbenzene matrix negligible influence of Na₂SO₄ addition in the range of 1–25 g/L on C.I. Acid Orange 7 uptake was observed. Quantitative removal of C.I. Acid Orange 7 of the initial concentration 200 mg/L from the system containing 0.1–2.0 g/L of NaH₂PO₄ and Na₂HPO₄ using strongly basic anion exchangers of type 1 Amberlite IRA 900 and of type 2 Amberlite IRA 910 was reported by Greluk [30].

The removal of C.I. Acid Orange 7 in the presence of sodium chloride even at relatively high concentration of 50 g/L was quantitative using all applied anion exchangers.

The removal of C.I. Acid Orange 7 from the solutions containing from 0.5 to 2.0 g/L of acetic acid was also studied. As shown in Figures 7 and 8, the amounts of the dye retained by the polystyrene and polyacrylic anion exchangers of various basicity decrease with the increasing amount of CH₃COOH in the system. The differences between the sorption capacities determined in the systems without the acetic acid and in the systems containing this acid do not exceed 15%. The same behaviour of the phenol–formaldehyde anion exchanger Amberlyst A 23 towards C.I. Acid Orange 7 was observed in the presence of the acid.

Direct dyes like the acid ones belong to strong electrolytes and are completely dissociated in water baths into coloured anions and sodium cations:



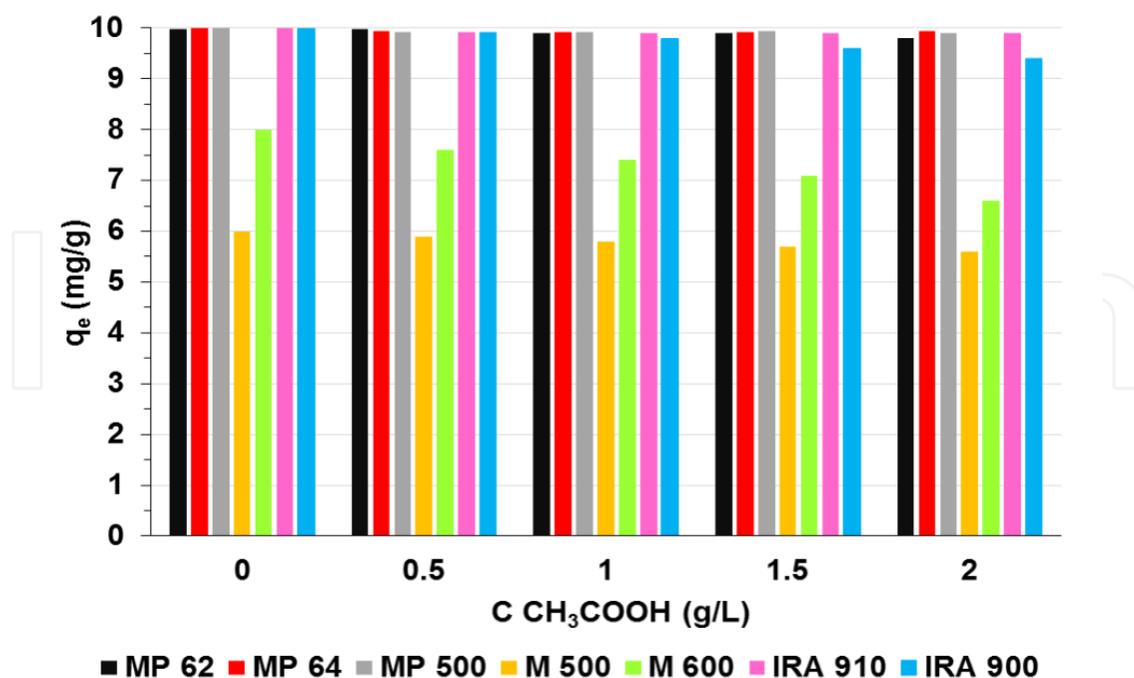


Figure 7. Influence of acetic acid concentration on C.I. Acid Orange 7 uptake by the anion exchangers of the polystyrene matrix

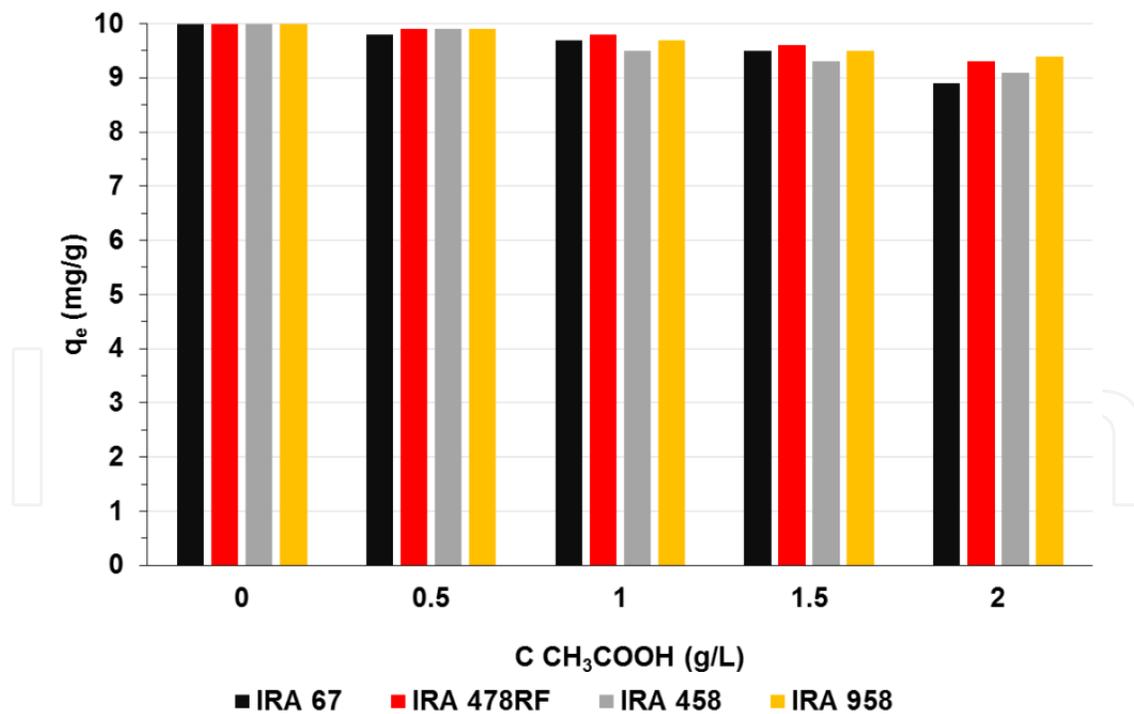
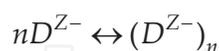


Figure 8. Influence of acetic acid concentration on C.I. Acid Orange 7 uptake by the anion exchangers of the polyacrylic matrix

where D^{z-} – the dye anion, z – the number of sulfonic groups.

Flat structure and large molecular mass (usually 600-1000) of direct dyes make their tendency to form associated ions (colloidal electrolytes):



where n – the association degree [14].

Association degree decreases with the increasing temperature. Alkalizing bath also promotes decomposition of associates; therefore, sodium carbonate is often added to the dyeing bath. Large negative charge of direct dye anions (2–4 sulfonic groups) causes that in the water bath they are repelled by the fibre surfaces of the negative electrokinetic potential ζ . The addition of electrolyte, most frequently sodium sulfate or sodium chloride, decreases the negative potential ζ facilitating the access of dye anions to the fibre surface. The dyeing bath contains (in the percentage of the dyeing product amount) from 0.5% to 2% Na_2CO_3 and 4–30% Na_2SO_4 depending on the method of dyeing and intensity of colour [14]. Removal of C.I. Direct Blue 71 from the systems containing 100 mg/L of dye and 1–25 g/L of NaCl and Na_2SO_4 on the weakly, intermediate and strongly basic anion exchangers was broadly described in the papers [20] and [25]. For the intermediate (Amberlite IRA 478RF) and strongly basic (Amberlite IRA 958 and IRA 458) anion exchangers of the polyacrylic matrix, the presence of NaCl and Na_2SO_4 in the whole examined concentration range of 1–25 g/L did not influence the adsorption capacities. The dye sorption was quantitative. The above mentioned anion exchangers have the same constitution of matrix, but different structure (gel or macroporous). Amberlite IRA 67 being of the same constitution of matrix and gel structure but of the tertiary amine functionalities exhibited insignificant drop of the sorption capacity with the increasing amount of electrolytes [20, 25]. It can be concluded that in the case of the polyacrylic anion exchange resins of different basicity, no significant influence of matrix structure was observed. Insignificant drop of the anion exchange capacities of Amberlyst A 23 towards C.I. Direct Blue 71 with the increasing amount of electrolytes was noticed, too.

The effect of the presence of NaCl and Na_2SO_4 on C.I. Direct Blue 71 sorption on the gelular polystyrene strongly basic anion exchangers of type I (Lewatit MonoPlus M 500) and type II (Lewatit MonoPlus M 600) was rather negligible. For Lewatit MonoPlus M 500, the increase in the amount of dye adsorbed at the equilibrium from 2.2 to 3.0 mg/g and from 2.2 to 2.8 mg/g was observed with the increasing NaCl and Na_2SO_4 concentration from 1 to 25 g/L, respectively. In the systems of the composition 100 mg/L – 1–25 g/L electrolyte – Lewatit MonoPlus M 600, the values of q_e ranged from 1.3 to 2.6 mg/g and from 1.3 to 2.4 mg/g with ranging concentrations of NaCl and Na_2SO_4 , respectively. Gel structure of both anion exchangers hindered diffusion of C.I. Direct Blue 71 anions to the pores and interactions with the $-\text{N}^+(\text{CH}_3)_3$ or $-\text{N}^+(\text{CH}_3)_2\text{C}_2\text{H}_4\text{OH}$ functional groups. The type of the functional groups of these strongly basic anion exchangers is of no significance as far as the removal of C.I. Direct Blue 71 is concerned.

A remarkable increase of adsorption capacities was observed during the dye uptake by the polystyrene anion exchangers of macroporous structure and different basicity of functional groups. The dye uptake by the weakly basic anion exchanger Lewatit MonoPlus MP 62 was increased in the presence of salts, the values of q_e increase from 5.86 mg/g to 9.9 mg/g with the increasing concentration of both electrolytes. The sorption enhancement of Lewatit MonoPlus MP 64 was observed from 1.9 to 9.97 mg/g and from 1.9 to 9.95 mg/g with the increasing concentration of NaCl and Na₂SO₄, respectively. At the equilibrium, the sorption capacities of Lewatit MonoPlus MP500 increase from 1.89 to 9.98 mg/g and from 1.89 to 9.95 mg/g with the increasing amount of NaCl and Na₂SO₄ in the range of 1–25 g/L, respectively. For Amberlite IRA 900 of the -N⁺(CH₃)₃ functional groups and Amberlite IRA 910 of the -N⁺(CH₃)₂C₂H₄OH functional groups, sorption capacities increased from 6.9 to 9.9 mg/g and from 5.9 to 9.2 mg/g with the increasing amount of NaCl in the solution. Similar dependences were noticed in the presence of Na₂SO₄, the addition of 25 g/L Na₂SO₄ enhanced the sorption yield of Amberlite IRA 900 and IRA 910 by about 36% and 30% compared with the systems without this salt.

Reactive dyes contain in their structure a system of atoms which can form covalent bonds with hydroxyl groups of cellulose. Hydroxyl groups of cellulose react with reactive systems in dye molecules according to the nucleophilic substitution mechanism (e.g. dyes with the symmetric triazine system) or nucleophilic attachment (residue of ethylsulfone sulfates). The alkaline medium (5–20 g/L Na₂CO₃) is the condition for the dye reaction with a fibre. To enhance it, the electrolyte in the form of sodium sulfate in the amount from 15 to 100 g/L depending on a dye is added to the bath [14]. The effect of sodium sulfate and sodium carbonate on the reactive dye adsorption on the anion exchangers was investigated in the salts concentration range 1–25 g/L with the constant initial C.I. Reactive Black 5 concentration of 100 mg/L.

Increasing amount of sodium sulfate and sodium carbonate in the system, insignificant decrease of the sorption capacities of Amberlite IRA 67, Amberlyst A 23, Lewatit MonoPlus MP 62 and Lewatit MonoPlus MP 64 were observed. Our previous studies revealed that in the 1000 mg/L C.I. Reactive Black 5 – 50–100 g/L Na₂SO₄ (or Na₂CO₃) system uptake of the reactive dye slightly increased by Amberlite IRA 67 [23]. C.I. Reactive Black 5 retention by the Amberlite IRA 478 RF, Amberlite IRA 458, Amberlite IRA 958 of the polyacrylic matrix and by Amberlite IRA 900 and IRA 910, Lewatit MonoPlus MP 500 of the polystyrene matrix was not affected in the presence of Na₂SO₄ and Na₂CO₃. It was reported by Greluk [30, 31] that the sorption capacities of Amberlites IRA 458 and IRA 958 devaluate about 2% in the presence of 100 mg/L of Na₂CO₃. The presence of NaCl in the range 25–100 g/L in the solution containing 200 mg/L of C.I. Reactive Black 5 caused significant decrease in the amount of the dye retained by Amberlite IRA 478RF according to Wawrzekiewicz [20]. The addition of Na₂SO₄ and Na₂CO₃ in the amount of 25 g/L enhanced adsorption capacities of Lewatit MonoPlus M 500 to C.I. Reactive Black 5 from 1.3 to 1.69 mg/g and from 1.3 to 1.72 mg/g, respectively. There was also noticed the increase of the amount of dye sorbed by Lewatit MonoPlus M 600 from the values 0.87 to 1.1 mg/g and from 0.87 to 1.2 mg/g with the increasing amount of sodium sulfate and sodium carbonate from 1 to 25 g/L, respectively.

Summing up, it could be stated that:

- Uptake of C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 by some anion exchangers of different matrices and functionalities was not affected by the presence of inorganic electrolytes such as NaCl, Na₂SO₄ and Na₂CO₃
- Insignificant decrease of the sorption capacities was observed with the increasing amount of above mentioned salts as a consequence of competition in sorption between the dye anions and the chloride, sulfate and carbonate anions. Decrease of the sorption capacities in some cases is reflected in the affinity series of the anions towards the weakly basic anion exchangers:

$F^- < ClO_3^- < BrO_3^- < HCOO^- < IO_3^- < CH_3COO^- < H_2PO_4^- < HCO_3^- < Cl^- < CN^- < NO_2^- < Br^- < NO_3^- < HPO_4^{2-} < SO_3^{2-} < SO_4^{2-} < C_2O_4^{2-} < CrO_4^{2-} < MoO_4^{2-} < WO_4^{2-} < S_2O_3^{2-} < I^- < SCN^- < ClO_4^- < salicylate < citrate < OH^-$

and towards the strongly basic anion exchangers:

$OH^- < F^- < ClO_3^- < BrO_3^- < HCOO^- < IO_3^- < CH_3COO^- < H_2PO_4^- < HCO_3^- < Cl^- < CN^- < NO_2^- < Br^- < NO_3^- < HPO_4^{2-} < SO_3^{2-} < SO_4^{2-} < C_2O_4^{2-} < CrO_4^{2-} < MoO_4^{2-} < WO_4^{2-} < S_2O_3^{2-} < I^- < SCN^- < ClO_4^- < salicylate < citrate$

- Increasing salts concentration in the system, enhancement of the reactive and direct dyes occurred. The salting out effect reduces solubility of the dyes in the aqueous phase and promotes their sorption onto the hydrophobic part of sorbent. Kind of salts has a great effect on salting out. This phenomenon depends on the size of ions, their effective charge and ability of hydrates formation.
- The affinity of large organic anions such as dyes anions for the resins is influenced not only by the anion charge but also by the structure of the anion and its size.
- The type of functional groups of the anion exchangers, matrix structure (gel or macroporous) and composition play an important role in the dyes solution treatment in the presence of salts. The sieve effect is of significance when the sorption of the dyes anions is considered in the presence of chloride, sulfate, and carbonate anions.

Wastewater and after-process water from textile plants can contain surface-active substances. Surfactants are often applied as wetting, penetrating, dispersing and leveling agents in dyeing processes. They increase the solubility of dyes in water, in order to improve the dye uptake and dye fastness. Many articles published recently about the treatment of textile wastewaters focused on dyes removal and often neglected the influence of surfactant. Effect of the addition of such surfactants as sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB) on the dye removal by the used anion exchangers was studied from the systems containing 100 mg/L of dye in the presence of 0.1–1 g/L SDS or CTAB.

Investigating the uptake of C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 by the applied weak, intermediate and strong base anion exchangers from the systems containing 100 mg/L of the dye in the presence of the cationic surfactant CTAB, major decrease in the sorption capacities with the increasing concentration of CTAB from 0.1 to 1 g/L was observed.

The attractive interactions between the dyes anions and positively charged head group of CTAB caused the formation of different types of aggregates (micelles) depending on the ratio of the dye to surfactant and decreasing concentrations of “free” dye anions in the aqueous phase at the same time. In case of anion exchangers’ interaction with dyes, these observations were described by Greluk and Hubicki [29, 31], Greluk [30] and Wawrzekiewicz [15, 20, 23]. Sorption of basic and acid dyes on different low-cost sorbents like chemically treated wood shavings, iron humate as well as oxihumolite in the presence of different surfactants was explained in detail by Janoš [37] and Janoš et al. [38-40].

The anionic surfactant SDS affected the dye sorption in three ways: no impact on the dyes uptake, decrease in the dyes uptake or enhanced dyes uptake as shown in Figure 9. The first mentioned behavior was observed during the sorption of C.I. Acid Orange 7 (100 mg/L) from the solutions containing 0.1–2 g/L SDS not only for the polystyrene anion exchangers but also for the polyacrylic ones (Figure 9 a) and b)).

Decreasing of the anion exchange capacities with the increasing amounts of SDS can be explained as a competition of adsorption sites between these species compared with dyes anions causing reduction of the dye uptake. For example, the sorption of C.I. Reactive Black 5 (Figure 9 c) and d)) was slightly reduced with the increasing amount of SDS in the system for the most of weakly and strongly basic anion exchangers of the polystyrene matrix. Both C.I. Reactive Black 5 and SDS are negatively charged and the interactions between the anionic SDS and the dye anions must be repulsive, independent of the surfactant concentration. Competition between these species of adsorption sites caused reduction of the dye uptake.

For the polystyrene anion exchangers of macroporous structure, i.e. Lewatit MonoPlus MP 62, MP 64, MP 500 and Amberlite IRA 900 a diverse trend was found (Figure 9 e) and f)) in the case of C.I. Direct Blue 71 sorption. Increasing the concentration of SDS in the range 0.1–1 g/L, enhancement of the dye anions sorption was observed. The surfactant can be adsorbed on the active sites or on the hydrophobic parts of the matrix of the anion exchangers in the form of relatively small poor ordered surface aggregates and interact with the aromatic rings or anionic groups of the dye.

7.3. Effect of solution pH

The solution pH is a very important parameter during the adsorption process and is mainly influenced by two factors:

- Distribution of the dyes ionized species in the aqueous phase,
- Overall charge (functional groups and surface) of the adsorbent.

Weakly basic anion exchangers in the free base form ($\text{RN}(\text{CH}_3)_2$) function at low pH when the hydrogen ion concentration is sufficiently high to protonate the amine nitrogen atom. Protonation of the amine group through the donor lone pair of electrons on nitrogen atom occurred during equilibration with acid as described below [41]:

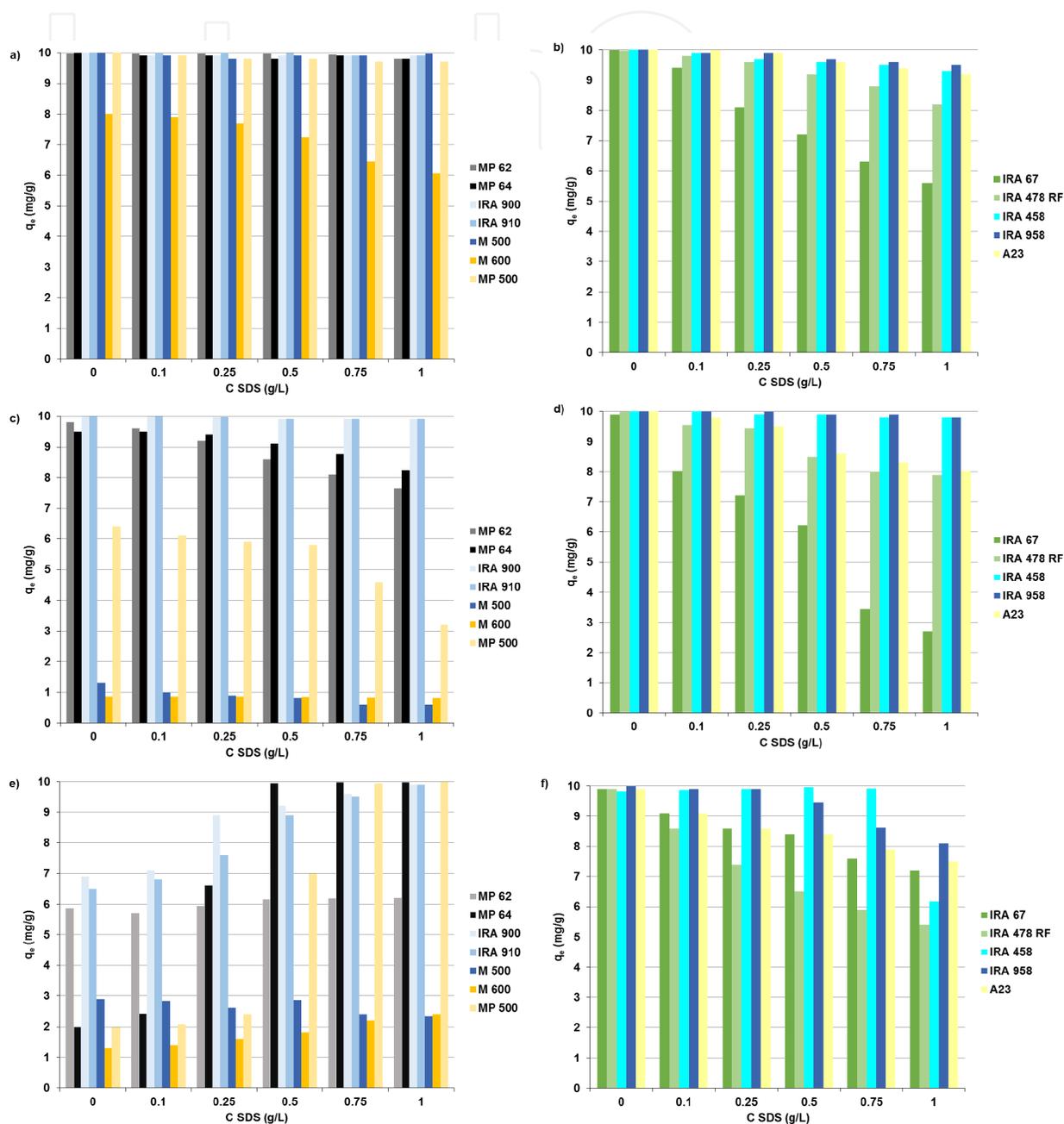
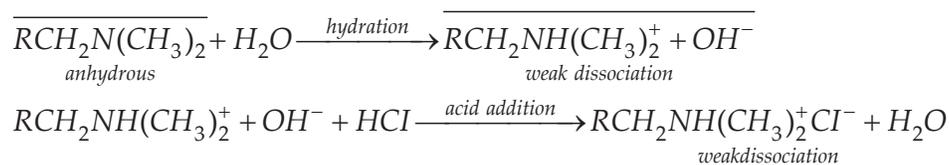


Figure 9. Influence of anionic surfactant sodium dodecyl sulfate (SDS) on uptake of C.I. Acid Orange 7 by the polystyrene anion exchangers (a) as well as the polyacrylic and phenol-formaldehyde anion exchangers (b), of C.I. Reactive Black 5 by the polystyrene anion exchangers (c) as well as the polyacrylic and phenol-formaldehyde anion exchangers (d) and of C.I. Direct Blue 71 by the polystyrene anion exchangers (e) as well as the polyacrylic and phenol-formaldehyde anion exchangers (f)

The resins were washed with 1 M HCl before the use taking the above into account. The relations between the initial pH of dyes solutions in the range of 1–12 and the sorption capacities of the anion exchangers were studied in the system containing 100 mg of dye per 1 L at 20°C. The decrease in the sorption capacities with the increasing initial solution pH was observed for the weakly basic anion exchangers because the capacity of the weak base anion exchange resin is a function of pH (it decreased with the increase of pH).

As the strongly basic anion exchangers function at any pH, there was observed no influence of solution pH of the dyes on their sorption on the strongly basic anion exchangers. As it was mentioned, formation of ion pairs due to the electrostatic attraction between the dye functional groups and the quaternary ammonium groups of strongly basic anion exchangers or the tertiary amine groups of weakly basic anion exchangers is probably a leading, though not the only one, mechanism of the acid, reactive and direct dyes retention. These dyes contain different groups such as -OH, -SO₃Na, -N=N-, -NH₂ that can participate in covalent, coulombic, hydrogen bonding or weak van der Waals forces. The occurrence of the double bond serves to enhance the interaction between the dyes and the anion exchangers macromolecule. The physical adsorption and π-π dispersion forces can arise from the aromatic nature of the resins and the dyes. A similar phenomenon was observed for the sorption of Acid Green 9 on the weak and strong base anion exchange resins [42], for the sorption of Sunset Yellow on the weakly basic anion exchanger Amberlite FPA 51 [43] and strongly basic Amberlite IRA 900 and IRA 910 [44] as well as for the sorption of Brilliant Yellow on Amberlite IRA 67, Amberlite IRA 458 and Amberlite IRA 958 [45].

7.4. Kinetic studies

To understand better the sorption process of dyes of various types of anion exchange resins, it is essential to determine the course of this process in time and the effect of different factors affecting their retention. The rate at which the dissolved dye is removed from the aqueous solution by solid sorbents is a significant factor for application in wastewater quality control, too. It is essential to evaluate the adsorption kinetics using theoretical models in order to design and control the sorption process units. Two common kinetic models, namely, the Lagergren pseudo first-order model (Equation 4) and the Ho and McKay pseudo second-order model (Equation 5) were fitted to the experimental data of dyes sorption on the anion exchangers:

$$\log(q_1 - q_t) = \log(q_1) - \frac{k_1}{2.303} t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \quad (5)$$

where q_1 and q_2 are the amounts of dye sorbed at equilibrium according to Equations (4) and (5), respectively (mg/g), q_t is the amount of dye sorbed at time t (mg/g), t is the time (min), k_1 is the constant rate of pseudo first-order adsorption (1/min), k_2 is the constant rate of the pseudo second-order adsorption (g/mg min) [46–50].

The values of k_2 and q_2 can be determined from the slope and intercept of the plot t/q_t vs. t , respectively. This dependence is defined as type 1 of the pseudo second-order expression or simply the pseudo second-order expression. Similarly, k_2 and q_2 can be calculated from the plots of $1/q_t$ versus $1/t$, $1/t$ versus $1/q_t$, q_t/t versus q_t and $1/q_2 - q_t$ versus t for type 2, type 3, type 4 and type 5 of the pseudo second-order expressions, respectively [51, 52].

The above mentioned equations were used due to the fact that the first one describes well the initial stage of dyes sorption, the second equation fits well experimental data in the whole range of process time for most adsorbate/adsorbent systems. Moreover, using these equations the dyes sorption process is considered as a chemical reaction (chemisorption) [46-52].

Kinetic behaviour of the anion exchangers towards C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 was examined in the systems of different initial dyes concentrations ranging from 100 to 500 mg/L (in most cases) or even 1000 mg/L [2, 15, 20, 23, 25-31]. It was noticed that the amounts of dyes uptake increased with the contact time, and at some point in time reached an almost constant value where the amounts of dyes retained by the anion exchangers were in a state of dynamic equilibrium with the amounts of dyes desorbed from the anion exchangers. For the initial dyes concentration of 100 mg/L, the time required to reach equilibrium differed from a few to dozens minutes or even 12 h depending on the type of dye, composition of resins matrices as well as their structure, hydrophilic character of the skeletons and type of functional groups as can be seen from the data presented in papers [2, 15, 20, 23, 25-31]. C.I. Acid Orange 7 of the smaller molar weight saturated faster the available anion-exchanging sites compared with C.I. Reactive Black 5 and C.I. Direct Blue 71. The studies on the sorption of dyes and organic compounds on the ion exchangers reported so far showed that the size of the sorbate molecules has a considerable effect on the degree of fixation [53-55]. According to Dragan and Dinu [55] investigating the interactions of azo dyes such as Ponceau SS, Crocein Scarlet MOO, Congo Red and Direct Blue 1, differing in either the position of sulfonic groups or the number of anionic groups, with quaternized poly(dimethylaminoethyl methacrylate) it was stated that the number of sulfonic groups, position of the anionic charges and the whole structure of the dyes determined the dyes removal by the sorbent [55]. From the papers of Wojaczyńska and Kolarz [53, 54] about sorption of Methyl Orange, Acid Orange 10, Acid Red 44 and Direct Blue 1 on the divinylbenzene weak base anion exchangers of mono- and diethanolamine functional groups, it can be found that the copolymer gel heterogeneity has a marked effect on the degree of sorption and its course [54]. With the constant anion exchange capacity, the sorption properties decreased with an increase in the gel heterogeneity [53]. The dyes with a higher content of sulfonic groups were sorbed mainly by the formation of aggregates in the anion exchanger phase whereas Direct Blue 1 dye because of large size has the tendency to form aggregates in the solution rather than in the resin [54].

As follows from the data included in papers [2, 15, 20, 23, 25-31], generally the Lagergren equation (PFO) is not applied for description of sorption kinetics of C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 on the chosen anion exchangers of different types. This results, among others, from the non-linear dependence $\log(q_e - q_t)$ vs t , confirmed by low values of the determination R^2 and significant differences between the values of sorption capacity obtained experimentally and that calculated from the Lagergren equation. Moreover, the condition $\log q_e = \text{intercept}$ is not satisfied which also indicates that the above equation is not

applied [56–59]. Only in one case it was observed that the pseudo first-order expression better predicts the sorption kinetics than the pseudo second-order one. The closeness of the pseudo first-order equilibrium capacity to the experimentally determined equilibrium capacity indicates the usage of the pseudo first-order model to describe the kinetics of C.I. Direct Blue 71 uptake by Amberlite IRA 478RF. Several authors have also shown the applicability of the PFO kinetics in describing the sorption of dyes onto anion exchangers [53, 54] and different adsorbents [60–67]. Numerous applications of the Lagergren equation in sorption of dyes and inorganic ions have also been reported in the paper by Ho and McKay [49].

The linear form of the second-order equation proposed by Ho and McKay (PSO) can be applied for description of sorption of C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 on ion exchangers of various types. In this case there are satisfied the following conditions: the dependence t/q_t vs t is linear, the determination coefficient reaches high values close to 1 and the calculated value of sorption capacity is largely consistent with the sorption capacity obtained experimentally. Comparison of quality of PFO and PSO equations fitting with the experimental data is presented for the system C.I. Reactive Black 5 – intermediate base anion exchanger Lewatit MonoPlus MP 64 in Figure 10.

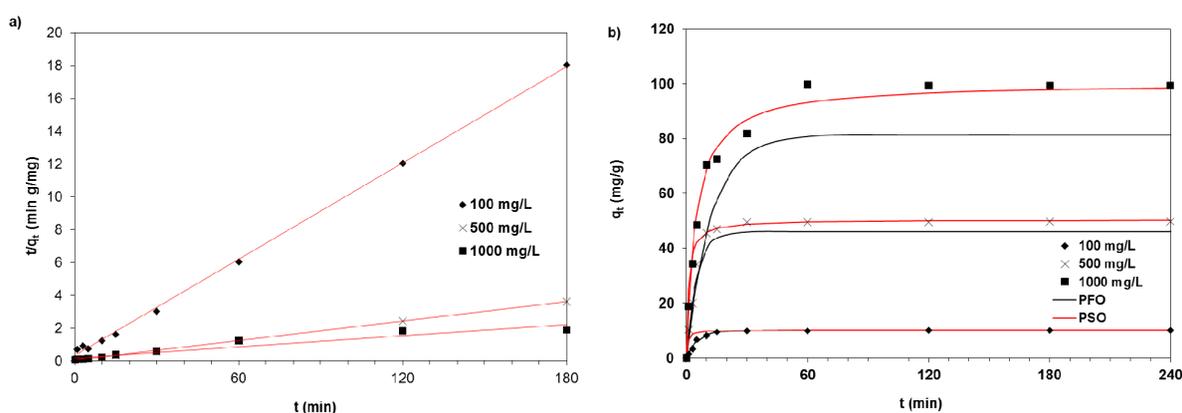


Figure 10. The pseudo second-order plot (a) and the fitting of the pseudo first-order and pseudo second-order equations (b) to the experimental data of C.I. Reactive Black 5 sorption on Lewatit MonoPlus MP 64 from the systems of different initial dye concentrations

In order to emphasize the influence of phase contact time on industrial effluents purification, suitable experiments were performed using the polyacrylic anion exchanger of the quaternary ammonium functionalities Amberlite IRA 958. Its effectiveness was confirmed in the batch experiments. The effluents from the textile industry containing different dyes and auxiliaries were shaken with 0.5 g of Amberlite IRA 958 from 1 to 144 h. The changes in absorbance values at the maximum wavelength in UV–vis spectra of the wastewater before and after sorption on Amberlite IRA 958 are presented in Figure 11. Analyzing the absorption values of untreated and purified wastewaters (Figure 11 a)), a significant colour reduction was observed after 12 h of phase contact time. The efficiency of decolourization exceeding 87% after only 1 h of contact time for the wastewater after the ozonation step is shown in Figure 11 b). The absorbance value at the maximum wavelength was reduced from 2.439 (before purification) to 0.1901

(after 12 h) in the case of wastewater containing Synazol Yellow KHL, SynazolBlue KBR and Synazol Red K3BS (Figure 11 c)). As shown in Figure 11 d), after 3 h of phase contact time the yield of decolourization was 88.3%, the increasing phase contact time to 144 h did not increase the adsorption efficiency significantly.

7.5. Desorption studies

The regeneration step is the key to the implementation of the anion exchange system on the commercial scale. Desorption studies help to evaluate the nature of adsorption process. Desorption experiments were performed using different regenerating agents such as 1 M NaCl, 1 M Na₂SO₄, 1 M Na₂CO₃, 1 M NaOH, 1 M HCl and even 1 M KSCN. As previously stated [2, 15, 20, 23, 25–31], the aqueous solutions mentioned above were ineffective for the dyes removal from the resin phase.

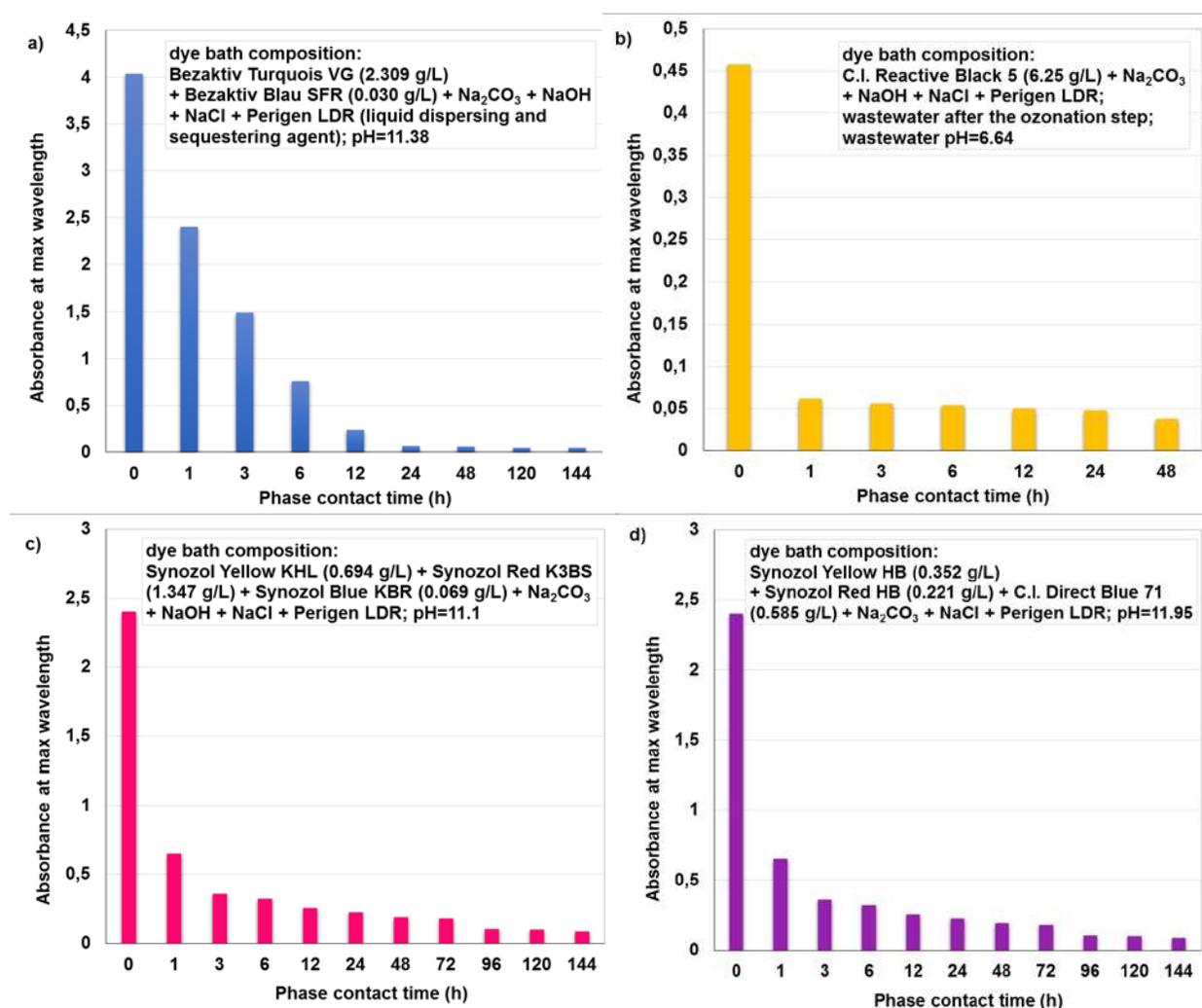


Figure 11. Influence of phase contact time on the purification of raw textile effluents of different compositions using Amberlite IRA 958: a) the absorbance values at max wavelength at 0 h and 1 h were recorded after ten times repeated dilution, b) and c) samples were not diluted before measurements, d) the absorbance values at max wavelength at 0 h was recorded after twice repeated dilution

Considering that the dye retention by the anion exchanger may not be only by ion exchanging but also by the hydrophobic interaction or hydrogen bonding, methanol was chosen for breaking these non-specific interactions. Regeneration of the anion exchangers using 10–90% methanol solutions was ineffective confirming that strong electrostatic attraction between the dyes and the anion exchange matrix is a predominant mechanism of adsorption. The mixtures of 90% methanol with 1 M KSCN, 1 M HCl or 1 M NaOH improved the dyes desorption from the anion exchangers in most cases. Greluk and Hubicki [28, 29, 31], Karcher et al. [68, 69], Liu et al. [70] and Wawrzkiwicz [20, 23, 25] confirmed that regeneration of the anion exchangers loaded with the acid, reactive and direct dyes was problematic and required usage of aggressive regenerants which could have negative impact on the cost of the process.

8. Conclusions

The possibility of the removal of C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 using weakly (Amberlite IRA 67, Lewatit MonoPlus MP 62, Amberlyst A 23), intermediate (Lewatit MonoPlus MP 64 and Amberlite IRA 478RF) and strongly (Amberlite IRA 458, Amberlite IRA 958, Amberlite IRA 900, Amberlite IRA 910, Lewatit MonoPlus MP 500, Lewatit MonoPlus M 500 and Lewatit MonoPlus M 600) basic anion exchangers of the polyacrylic, polystyrene and phenol–formaldehyde skeletons and different matrix structure from aqueous solutions and wastewaters were discussed [2, 15, 20, 23, 25–28, 34–36]. Not only the number of sulfonic groups, position of the anionic charges, whole structure of the dyes and their molecular weight but also type of the anion exchangers determined the dyes removal by these sorbents.

Based on the values of the monolayer sorption capacities towards C.I. Acid Orange 7 (1370.4 mg/g), C.I. Reactive Black 5 (1655.2 mg/g) and C.I. Direct Blue 71 (1630.6 mg/g), it seems that the macroporous anion exchanger Amberlite IRA 958 can be a promising adsorbent for the textile wastewater treatment.

The affinity series of the dyes for Amberlite IRA 958 of quaternary ammonium functionality can be presented as follows:

C.I. Reactive Black 5 > C.I. Direct Blue 71 > C.I. Acid Orange 7.

Its advantageous behaviour for the acid, reactive and direct dyes resulted from combination of such properties as positive charge of functional groups and large pores of hydrophilic polyacrylic matrix. The experimental data indicated that the amounts of dyes adsorbed on the anion exchange resins are influenced by many factors such as initial dye concentration, phase contact time, solution pH, auxiliaries presence (NaCl, Na₂SO₄, Na₂CO₃, CH₃COOH and surfactants) and their concentrations. The reversibility of adsorption depends on whether the predominant mechanism is a strong binding bond such as ionic bonding or weak binding forces such as van der Waals interactions or H-bonding and occurred with high yield using sodium hydroxide or hydrochloric acid (or potassium thiocyanate) in methanol. The adsorption behaviour of Amberlite IRA 958 demonstrates that it can be a promising adsorbent for the textile wastewater treatment.

Author details

Monika Wawrzekiewicz* and Zbigniew Hubicki

*Address all correspondence to: m.wawrzekiewicz@op.pl

Maria Curie-Skłodowska University, Faculty of Chemistry, Department of Inorganic Chemistry, Lublin, Poland

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