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Remazol Black B removal from aqueous solutions and wastewater using weakly basic anion exchange resins

Research Article

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Abstract: In this study, the use of the weakly basic anion exchange resins of phenol-formaldehyde (Amberlyst A 23), polyacrylate (Amberlite IRA 67) and polystyrene (Lewatit MonoPlus MP 62) matrices for removal of the reactive dye Remazol Black B (RBB) from aqueous solution and wastewater were investigated. RBB sorption on the anion exchangers was a time dependent process. Color reduction percentiles of 75.2, 33.9 and 25.1% in wastewater treatment were found after 216 h of phase contact time with Lewatit MonoPlus MP 62, Amberlyst A 23 and Amberlite IRA 67, respectively. Inorganic salts and anionic surfactant action influenced RBB uptake by the anion exchangers. The amounts of dye retained by the anion exchangers increased with a rise in temperature. The maximum sorption capacities calculated from the Langmuir model were 66.4, 282.1 and 796.1 mg g^{-1} for Amberlite IRA 67, Amberlyst A 23 and Lewatit MonoPlus MP 62, respectively. Regeneration of phenol-formaldehyde and polystyrene resins were possible using 1 M NaOH, 2 M KSCN, 1M KSCN in 40-60% methanol as well as 1 M NaOH in 60% methanol.

Keywords: *Anion exchanger • Reactive dye • Remazol black B • Sorption • Textile wastewater*

1. Introduction

Reactive dyes contain in their molecules reactive atoms or group of atoms capable of forming covalent bonds with ionized hydroxyl cellulose groups. For the first time they appeared commercially in 1950 and their intensive development took place between 1956-1972 [1]. Despite an increase in the production of synthetic fibers, development has steadily decreased. As reactive dyes are available in a wide range of colours and owing to simple applicative methods as well as good resistant properties of decolorization, they have become common in cellulose dyeing. They are classified according to reactive groups or systems through which they bind with fibers. The two most common groups are triazine dyes containing one or two chlorine atoms as the active system reacting with cellulose according to nucleophilic substitution. The other are those containing β-sulfoethyl-sulfone group transforming into the vinylsulfone group in the colorization process, reacting with the fiber through nucleophilic addition. The disadvantage of dyes in both groups is the fact that during application in the basic medium some amount of dye reacts with water (undergoes hydrolysis) and the hydrolyzed form of the dyes is incapable of forming a covalent bond with cellulose. According to Epolito *et al*. [2] 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 by an intensive color that is difficult to remove. Moreover, due to the small affinity for fibers, they require application of a greater amount of electrolytes thus causing wastewater salination and resulting in an increased hazard for the environment [1,3,4]. 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 [5,6]. More than 80,000 tons of reactive dyes are produced and consumed every year [6]. The textile industry releases more than 0.2 million tons of salts into the environment each year according to EIPPCB (European Integrated Pollution Prevention and Control Bureau) estimations [5]. One can easily imagine the total amount of pollution generated.

The most widely used methods of dye removal from industrial effluents can be divided into three categories: chemical, physical and biological. Possible decolorization methods of textile wastes with associated advantages

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and disadvantages are listed in Table 1 [6-9]. Currently the main methods of textile dye treatment are by physical and chemical means with research concentrating on cheap and effective sorbents. However, it should be stressed that they are characterized by relatively low sorption capacity towards dyes compared with activated carbons or ion exchangers. For example, Eren and Acar [10] applied high lime fly ash for RBB removal from aqueous solutions. The equilibrium capacity was found to be 7.2 mg g^{-1}. According to Karcher *et al*. [11] cucurbituril, a cyclic condensation product of glycoluril and formaldehyde, seems to be an interesting material for RBB removal. Loading as large as 940 mg g^{-1} was obtained, however, salt concentration of 100 mmol L^{-1} and above decreases sorption efficiency due to the increasing solubility of cucurbiturial in the salt solution.

Of biodegradable sorbents applied for purification of sewages containing RBB, chitosan is of particular interest. The adsorption capacity of chitosan is particle size, pH and temerature dependent. The monolayer adsorption capacity increased from 91.5 to 130 mg g^{-1} with a temperature rise from 30 to 60^{o}C [12]. Gibbs *et al.* [13] found sorption capacity of chitosan for RBB in acidic solutions as large as 750-1000 mg g^{-1} and proved that sorption efficiency of chitosan significantly decreases when the sorbent is protonated before sorption (by acidic conditioning).

Activated carbon is a common sorbent for removal of RBB owing to its large surface area, developed porous structure and large surface reactivity. Al-Degs *et al.* [14-16] investigated the activated carbon Filtrasorb 400 for RBB removal by the batch and column methods. The monolayer adsorption capacity for RBB was equal to 278 mg g^{-1}. It was found that equilibrium adsorption capacities decreased in the multi-component systems (as compared to a single dye system) [15]. The column capacity calculated at 90% of column exhaustion was lower than carbon capacity obtained from equilibrium studies [15]. In studies performed by Choi *et al.* [17] the effect of cationic surfactant cetylpyridinium chloride (CPC) on RBB removal on activated carbon from aqueous solution was investigated. CPC contributes to sorption of RBB on the activated carbon in two ways. In simultaneous addition of CPC and RBB, the cationic surfactant formed CP-RBB complex, which has less negative charge density and is more hydrophobic than RBB. In precoated activated carbon by CPC, the sorbent has positive sites produced by adsorption of CPC. RBB could be adsorbed on activated carbon due to hydrophobic interactions and on the positive site due to electrostatic interactions. The Langmuir monolayer capacities determined for pure activated carbon, activated carbon with the simultaneous addition of CPC and RBB and precoated activated carbon by CPC, were equal to 99.2, 89.2 and 99.2 mg g^{-1}, respectively [17].

Another alternative to activated carbon are the commercial anion exchange resins. They are characterized by excellent sorption capacity because of the functional groups bounded to the polymeric matrices, which in comparison with the polymeric sorbents additionally provide specific interactions with the pollutants and effectively improve adsorption performance toward highly water soluble dyes [18-21]. Not only do the anion exchangers demonstrate efficient regeneration property for the removal of dyes, but also it gives an important economic and environmental impetus. Anion exchange resins of various basicity and different matrices seem to be proper materials for dyes sorption from textile wastewaters owing to their high capacity and selectivity as presented in some papers [18-24]. Anion exchangers, especially styrene-divinylbenzene derivatives, are characterized by excellent physical strength and resistance to degradation by oxidation agents, hydrolysis and elevated temperature. Karcher *et al.* [19] confirmed the application of the strongly basic polystyrene anion exchanger Lewatit S6328A for RBB removal from textile wastewaters. Acrylic anion exchangers are also of significant importance because they are more resistant to fouling by organic compounds than their styrenic equivalents [25]. Strongly basic anion exchangers such as Amberlite IRA 958 and IRA 458 of the acrylic skeleton were used for RBB removal from aqueous solutions of different initial concentrations [19]. These resins turned out to be very efficient at adsorption of this dye.

In the present study, three commercial weakly basic anion exchangers were investigated as the potential sorbents for reactive dye removal from aqueous

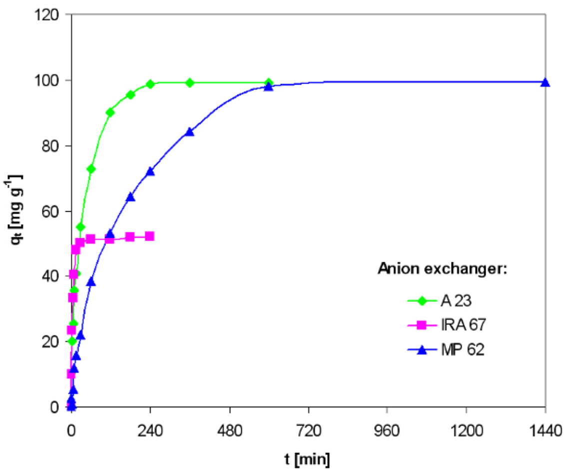


Figure 1. Influence of phase contact time on RBB uptake by Amberlyst A 23, Amberlite IRA 67 and Lewatit MonoPlus MP 62 in the system containing 1000 mg L^{-1} of dye.

Table 1. Advantages and disadvantages of the current methods of dye removal from industrial effluents [6-9].

Methods	Advantages	Disadvantages
Biological treatment	Low costs	Low biodegradability of dyes
Membrane processes	Removal of all types of dyes, all mineral salts and chemical auxiliaries	Concentrated sludge production
- Reverse osmosis	Good removal of hydrolyzed reactive dyes and mineral salts	High pressure
- Nanofiltration	Separation of organic compounds of low molecular weight and divalent ions from monovalent ones	-
- Ultrafiltration-microfiltration	Low pressure	Insufficient quality of the treated wastewaters
Adsorption	Effective removal of a wide range of dyes	Adsorbents requires regeneration or disposal
- Activated carbon	Good elimination of suspended solids and organic substances	High costs, blocking filter
- Low cost sorbents	Low costs of preparation and usage	Poor capacity
- Ion exchangers	High capacity for dyes	Difficult regeneration
Oxidation	Rapid process	High energy costs and formation of by-products
- Ozonation	Good decolorization	No reduction of the COD*, additional costs
- Fenton reagent	Effective decolorization of soluble and insoluble dyes	Sludge generation
Coagulation/flocculation	Economically feasible	High sludge production, costs

**COD = Chemical oxygen demand*

solutions and wastewater. The role of ion-exchange is to reduce the magnitude of the problem by converting hazardous waste into a form in which it can be reused, leaving behind a less toxic substance in its place, or to facilitate ultimate disposal by reducing the flow of stream bearing the toxic substance. Ion exchange is a very versatile and effective tool for the treatment of hazardous wastes. Although ion exchange has become widely accepted as a standard method for purifying water for certain applications, its actual use in treating hazardous textile effluents has not been nearly so widely investigated. There is a lack of information about application of weakly basic anion exchangers in RBB removal from wastewaters.

2. Experimental procedure

2.1. Sorbents and chemicals

Three weakly basic anion exchange resins of different matrices were applied in the sorption studies: Amberlite IRA 67, Amberlyst A 23 and Lewatit MonoPlus MP 62 (Table 2).

The reactive dye Remazol Black B is tetrasodium salt of 4-amino-5-hydroxy-3,6-bis((4-((2-(sulfooxy)ethyl)sulfonyl)phenyl)azo)-2,7-naphthalenedisulfonic acid ($C_{26}H_{21}N_5Na_4O_{19}S_6$, CAS numer 17095-24-8, C.I. 20505, MW=991.82 g mol^{-1}). The dye was purchased from Sigma-Aldrich (Germany) and used without further purification (dye content 55%). It is commonly used in cotton textile industry. The stock solution was prepared in distilled water and the working solutions were obtained by appropriate dilution.

Sodium sulfate and carbonate were purchased from POCh (Poland). The anionic surfactant sodium dodecyl sulfate (SDS), non-ionic surfactant (Triton X-100) as well as cationic surfactant cetyltrimethylammonium bromide (CTAB) were obtained from Sigma-Aldrich (Germany). All the chemicals used were obtained as research-grade chemicals.

2.2 Uptake experiments

Sorption experiments were carried out by shaking a known amount of the anion exchanger (0.5 g) with a 50 mL solution containing 1000 mg L^{-1} of dye. In separate series of experiments, the desired amounts of salts (5-20 g L^{-1} Na_2CO_3 or 10-100 g L^{-1} Na_2SO_4) or surfactants (1 g L^{-1} SDS, 1 g L^{-1} Triton X-100 or 1 g L^{-1} CTAB) were added, or pH values were adjusted with 1 M HCl or 1 M NaOH. The dye solution together with the anion exchanger was agitated on a laboratory shaker Elphin (Poland) at 180 cpm at room temperature. After equilibrating the solution was separated from the anion exchanger by decantation and concentration of

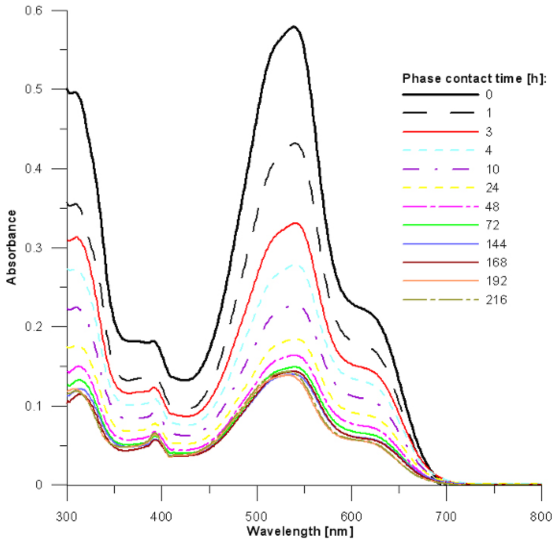


Figure 2. UV-Vis spectra of wastewater purified by means of Lewatit MonoPlus MP 62.

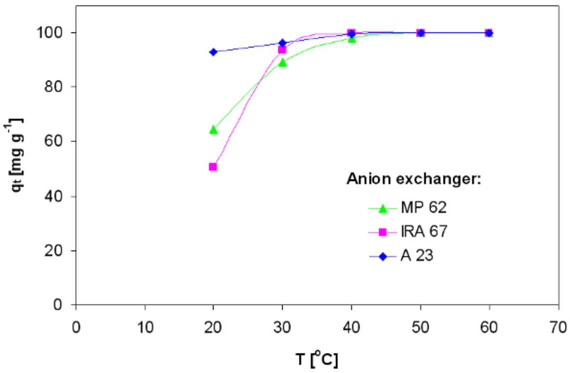


Figure 3. Effect of temperature on dye uptake by the weakly basic anion exchangers in the system containig 1000 mg L^{-1} of RBB after 3 h of phase contact time.

the dye was determined by the analysis of absorbance value at the maximum wavelengths (from 598 to 620 nm depending on auxiliaries addition in the system) using a spectrophotometer Specord M-42 (Carl Zeiss, Germany).

To test the influence of temperature on the dye uptake, the samples of 0.5 g of the anion exchanger were shaken with the solution containing 1000 mg of RBB per 1 L changing the temperature from 20 to 60°C. After 3 h the anion exchanger was separated from the solution and the dye concentration was measured spectrophotometrically.

Equilibrium isotherm studies were carried out analogously at the initial concentrations of dye in the range 800-10000 mg L^{-1} for 24 h.

Textile model wastewater was prepared as described in paper [26]. The composition of the wasterater was the following: 1000 mg L^{-1} of Remazol Black B, 1000 mg L^{-1} of Reactive Red 2, 1000 mg L^{-1} of Reactive Red 120 and 5 g L^{-1} Na_2CO_3. 50 mL of model wastewater were shaken with 0.5 g of the anion exchanger sample from 1 to 216 h. The UV-vis spectra of wastewater were recorded before and after sorption.

Regeneration tests for the anion exchange resins were conducted with different regeneration agents (1 M HCl, 0.1-1 M NaOH, 1-2 M KSCN, 1 M KSCN–methanol, 1 M NaOH (or 1 M HCl)– methanol). The loaded resins (0.5 g) were put into flasks in contact with 50 mL of different eluting agents. The flasks were agitated for 24 h and the dye concentrations in the solution were determined at maximum absorbance wavelength.

The sorption parameters were calculated from the equations listed in Table 3. All experiments were conducted in two parallel series with the reproducibility ± 3%. The obtained results are presented as the mean value.

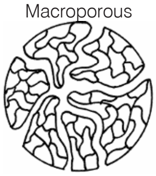
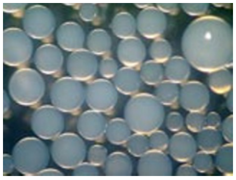
3. Results and discussion

3.1. The effects of phase contact time and resin structure

The influence of phase contact time on RBB uptake from the solution containing 1000 mg L^{-1} of the dye is shown in Fig. 1. The equilibrium was reached after 4 h, 6 h and 24 h of phase contact time for Amberlite IRA 67, Amberlyst A 23 and Lewatit MonoPlus MP 62, respectively. The amount of the dye uptake increased with the increasing phase contact time. The quantitative dye sorption was achieved using the macroporous anion exchange resins of the phenol-formaldehyde and styrene-divinylbenzene matrix. The values of q_t were equal to 99 mg g^{-1} and 99.2 mg g^{-1} for Amberlyst A 23 and Lewatit MP 62, respectively. Only 50% of the dye was sorbed from the solution by the polyacrylate anion exchanger Amberlite IRA 67. The amount of RB uptake by Amberlite IRA 67 was found to be 51.9 mg g^{-1} at equilibrium. It can be explained by the sieve effect. Since a large number of functional groups are available for sorption at the beginning and after a lapse of time, the remaining sites are difficult to be occupied. Not only are tertiary amine groups present in the surface layer of Amberlite IRA 67 but also those inside the matrix are responsible for sorption.

The anion exchangers under consideration possess the same functional groups (*i.e.*, tertiary amines). Therefore this indicates that their matrix plays a significant role in the sorption process. Macroporous resins, being highly cross-linked, possess quite a heterogeneous distribution of structurally dense and tortuous regions of high charge density. For this reason the affinity of a

Table 2. Anion exchangers characteristics.

Properties	Amberlyst A 23	Lewatit MonoPlus MP 62	Amberlite IRA 67
Functional groups	Tertiary amine		
Ionic form as shipped	Free base		
Skeleton	Phenol-formaldehyde	Polystyrene	Polyacrylic
Matrix structure	Macroporous 		Gel 
Physical form	Brown to grey granules 	Beige beads 	White beads 
Total ion-exchange capacity [eq L^{-1}]	>1.8	1.1	>1.6
Moisture holding capacity [%]	60-65	50-55	56-62
Harmonic mean size [mm]	0.47-0.74	0.47	0.55-0.75
Maximum operating temperature [°C]	80	70	60
Producer	Lenntech, the Netherlands	Lanxess, Germany	Lenntech, the Netherlands

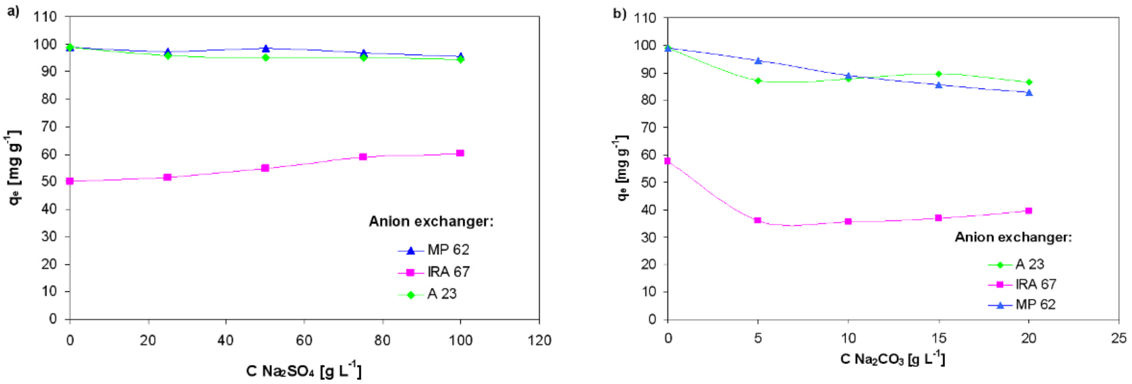


Figure 4. Influence of Na_2SO_4 (a) and Na_2CO_3 (b) additions on the dye uptake by the weakly basic anion exchangers.

macroporous resin for a given inorganic ion is usually greater than that for a gel resin, and sometimes the rate of exchange can be discernibly slower for macroporous resins when compared with gel equivalents. But where exchange of large, high molecular weight species like dyes are concerned the macroporous property becomes important in providing an easier diffusion path for the uptake and subsequent release of such species [27,28]. Greluk and Hubicki [20] pointed out that the concentration of RBB in solution strongly affects the dye sorption on the anion exchangers of the quarternary ammonium groups but they have not observed the influence of the matrix structure on RBB uptake. According to their observation, not only did the macroporous (Amberlite IRA 958) but also the gel (Amberlite IRA 458) strong base anion exchanger exhibited high affinity for RBB. The amounts of RBB uptake, from the solution of the initial concentration 500 mg L^{-1}, by macroporous Amberlite IRA 958 and gel Amberlite IRA 458 were found to be 49.99 mg g^{-1} and 49.98 mg g^{-1}, respectively.

In order to emphasize the influence of phase contact time on real wastewater purification by means of the anion exchangers, proper experiments were carried out. A simulated effluent from the textile industry containing 1000 mg L^{-1} of Remazol Black B, 1000 mg L^{-1} of Reactive Red 2, 1000 mg L^{-1} of Reactive Red 120 and 5 g L^{-1} Na_2CO_3 at pH 11.3 was equilibrated with the anion exchange resins from 1 h to 216 h.

Table 3. The sorption parameters obtained by the batch method.

The batch experiments		
Amount of dye uptake by anion exchanger after phase contact time t	$q_t = \frac{(C_0 - C_t)}{m} \times V$	C_0 – the initial dye concentration [mg L^{-1}] C_t – the dye concentration at time t [mg L^{-1}] C_e – the dye concentration at equilibrium [mg L^{-1}] V – the volume of the solution [L] m – the mass of the dry anion exchanger [g] K_F – the Freundlich constant related to the adsorption capacity [L g^{-1}] n – the Freundlich constant related to the surface heterogenity Q_0 – the Langmuir constant related to adsorption capacity [mg g^{-1}] b – the Langmuir constant [L mg^{-1}]
Amount of dye uptake by anion exchanger at equilibrium	$q_e = \frac{(C_0 - C_e)}{m} \times V$	
Freundlich isotherm equation	$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e$	
Langmuir isotherm equation	$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e$	

The UV-Vis spectra of the wastewater before and after sorption were recorded as presented in Fig. 2. The most effective anion exchanger in decolourization of the wastewater was Lewatit MonoPlus MP 62. Significant color reduction was observed during 72 h of phase contact time. It was noticed that the increase of phase contact time to 216 h did not enhance the purification yield. The absorbance value at the maximum wavelength after 216 h was reduced from 0.5740 to 0.1424. Summing up, 75.2, 33.9 and 25.1% color reduction was found after 216 h of shaking for Lewatit MonoPlus MP 62, Amberlyst A 23 and Amberlite IRA 67, respectively.

3.2. The temperature effect

The influence of temperature on RBB uptake by the weakly basic anion exchanger resins of various matrices was studied from the solution containing 1000 mg L^{-1} of dye with the contact time of 3h. The amounts of dye retained by the anion exchangers increased with temperature. Significant increase of q_t values from 50.5 to 99.9 mg g^{-1} and from 64.5 to 99.9 mg g^{-1} with the temperature increase from 20 to 60°C was observed for Amberlite IRA 67 and Lewatit MonoPlus MP 62, respectively. Slight dependence of temperature on the dye uptake using Amberlyst A 23 was spotted as shown in Fig. 3. The enhancement in adsorption with temperature may be attributed to the decrease in the thickness of the boundary layer surrounding the anion exchanger beads, so that the mass transfer resistance of sorbate in the boundary layer decreases.

3.3. The auxiliaries addition

The dyeing processes involve adding of large amounts of salts, such as Na_2SO_4 and NaCl, to enhance dye bath exhaustion, as well as Na_2CO_3 to adjust pH. Thus, it is important to examine their effect on the dye uptake by the anion exchangers. The influence of salt addition on dye uptake was studied from the system containing 1000 mg L^{-1} of RBB and different amounts of Na_2SO_4 (25-100 g L^{-1}) or Na_2CO_3 (5-20 g L^{-1}) and is shown in Figs. 4a-4b). The amount of dye retained by macroporous Amberlyst A 23 and Lewatit MonoPlus MP 62 was reduced with the increasing amount of sodium sulfate and sodium carbonate in the system, probably due to a competition between the salt anions and the anionic dye. The affinity of large organic anions for the resin is influenced not only by the ion charge but also by the structure of the ion and its size. However, in the case of the dye adsorption on polyacrylic gel Amberlite IRA 67, the effect of salt addition was meaningful. The retention of RBB by Amberlite IRA 67 drops when the system contains 5 and 10 g L^{-1} of Na_2CO_3 and then small increase of q_e values is observed with the increasing amount of carbonate up to 20 g L^{-1}. The increasing amount of Na_2SO_4 in the system from 25 to 100 g L^{-1}, the increase of the dye uptake from 50.9 to 60 mg g^{-1} was found. This suggests that van der Waals type intermolecular forces between the hydrocarbon structures of dye anion and the acrylic resin (“like attracts like”) can give the explanation [27,28]. The sorption enhancement is well documented for certain classes of chemicals, especially for low-polarity organic compounds, where the salting out effect reduces solubility of substances in the aqueous phase and promotes their sorption onto the hydrophobic part of sorbent [29].

Surfactants are present in real wastewater; therefore their influence on the dye uptake was studied. The amounts of RBB retained by Amberlyst A 23 in the presence of various kinds of surfactants are shown in Fig. 5. The presence of non-ionic surfactant (Triton X-100) and the anionic surfactant sodium dodecylsulfate (SDS) did not affect the sorption of RBB significantly. The sorption of RBB was sharply reduced in the presence of the cationic surfactant CTAB. The amount of dye sorbed by Amberlyst A 23 resin decreases to the value 3.6 mg g^{-1} in the system 1000 mg L^{-1} RBB – 1 g L^{-1} CTAB. Also noticed was the reduction of the amounts of dye sorbed at equilibrium to the value

Table 4. Langmuir and Freundlich isotherm parameters for the sorption of RBB on the weakly basic anion exchange resins at 25°C.

Anion exchanger	Freundlich model			Langmuir model		
	n	K_F [L g^{-1}]	R^2	b [L g^{-1}]	Q_0 [mg g^{-1}]	R^2
A 23	8.77	125.6	0.937	0.2036	282.1	0.999
MP 62	4.93	183.5	0.925	0.0494	796.1	0.990
IRA 67	7.10	26.4	0.914	0.5031	66.4	0.998

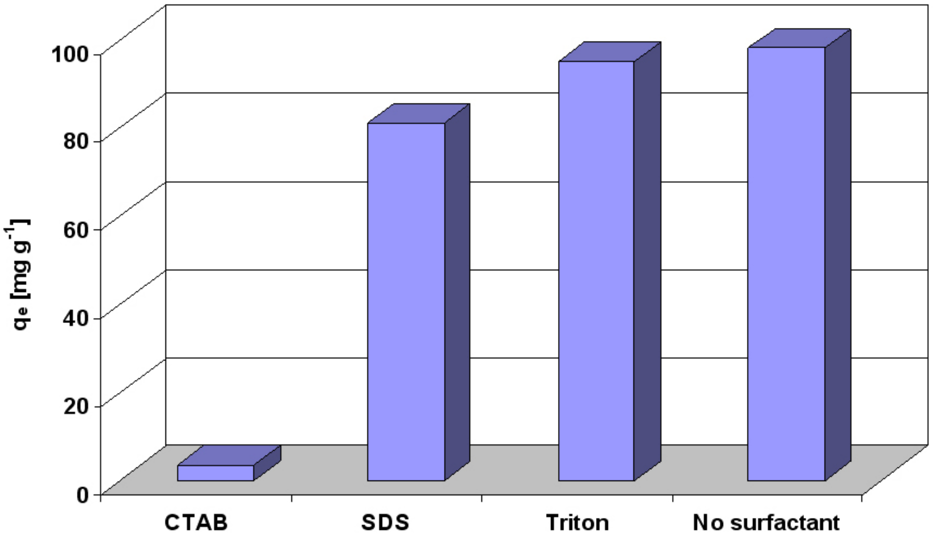


Figure 5. Effects of various surfactant additions on RBB sorption by Amberlyst A 23.

of 4.7 mg g^{-1} and 4.8 mg g^{-1} for Lewatit MonoPlus MP 62 and Amberlite IRA 67, respectively. It can be explained by the formation of the dye-surfactant aggregates. In aqueous solutions, a cationic surfactant and dye dissociate into ions and electrostatic attractive interactions can appear between the sulfonate group of dye and head group of surfactant. The formation of dye-surfactant complexes is a consequence of mutual influences of long-range and short-range interactions preventing their sorption by the anion exchangers [30-32].

3.4. Effect of solution pH

The pH value of the solution is a very important parameter controlling sorption processes. The weakly basic anion exchangers of tertiary amine functional groups such as Amberlite IRA 67, Amberlyst A 23 and Lewatit MonoPlus MP 62 are supplied in the free base form and function at low pH when the hydrogen ion concentration is sufficiently high to protonate the amine nitrogen atom. By equilibration with acid, the protonation of amine through the donor lone pair of electrons on nitrogen atom occurred as follows [29]:

$$\underset{\text{free base form}}{\overline{RN(CH_3)_2}} + HCl \xrightarrow{\text{acid addition}} \underset{\text{acid salt form}}{\overline{RNH(CH_3)_2^+Cl^-}}$$

The salt form of the resin may ion exchange with other anions in the external solution providing that pH is sufficiently low to sustain the protonated state of amine nitrogen atom. That is why the sorption proceeded due to the interactions between the dye anion and the functional groups of the anion exchanger in the acidic medium. With the increasing solution pH, hydroxide ions are so greatly preferred by the resin that ion exchange in strong alkali solutions is totally unfavourable, and the exchanger remains in the free base form:

$$\overline{RNH(CH_3)_2^+Cl^-} + NaOH \xleftrightarrow{\text{neutralization}} \overline{RN(CH_3)_2} + NaCl + H_2O$$

The relationship between the initial pH of RBB solution and the sorption capacity using weakly basic anion exchangers was studied in the system containing 1000 mg dye L^{-1} at different initial solution pH. As can be seen from Fig. 6, the amount of dye uptake at equilibrium by Amberlite IRA 67 at pH 3 and 5 was larger by 50% than at pH 11. Greluk and Hubicki [33], studying the adsorption of Acid Orange 7 dye on Amberlite IRA 67, also observed that the sorption of the dye was favourable at pH values 1-6 up to pH 10 where uptake of dye declined sharply with the further increase in pH. For the weakly basic anion exchangers of polystyrene and phenol-formaldehyde skeletons, pH had practically

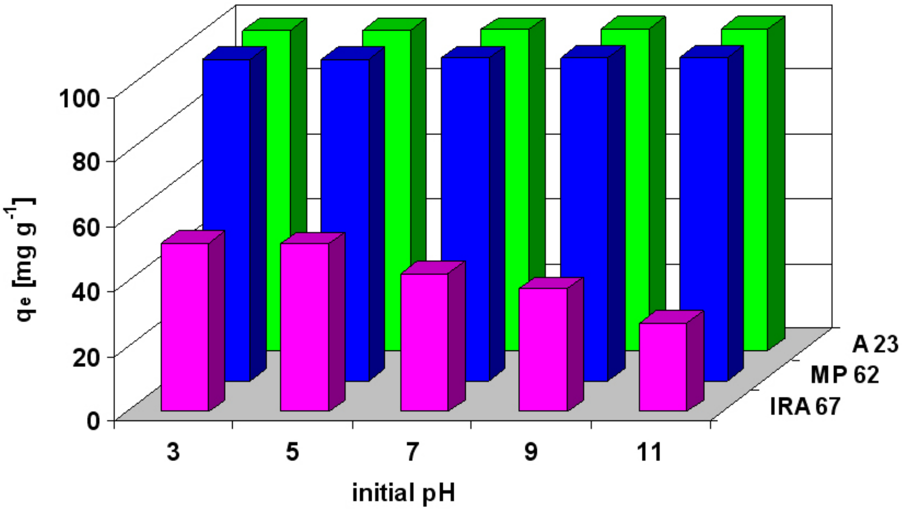


Figure 6. Influence of initial solution pH on dye (C_0=1000 mg L^{-1}) uptake by the weakly basic anion exchangers.

no effect on the dye adsorption. The difference between the amounts of dye sorbed at various pH values did not exceed 2%. The obtained results also indicate that the RBB sorption occurred not only by the ion exchange mechanism between the dye anion and the functional groups of the anion exchanger but also chemical and physical adsorption.

3.5. Isotherm studies

The adsorption isotherms were determined in order to evaluate the compatibility between the experimental data and the theoretical equilibrium capacity. In this study, the two most common isotherm models, the Langmuir and Freundlich (Table 3), were used to describe the RBB sorption on the anion exchangers of various skeletons. The Langmuir adsorption isotherm is most widely used for the adsorption of a pollutant from a liquid solution given the following hypotheses: monolayer adsorption (the adsorbed layer is one molecule thick); adsorption takes place at specific homogeneous sites within the adsorbent; once a dye occupies a site, no further adsorption can take place at that site; adsorption energy is constant and does not depend on the degree of occupation of an adsorbent's active sites; the adsorbent has a finite capacity for the dye (at equilibrium, a saturation point is reached where no further adsorption can occur); all sites are identical and energetically equivalent; the adsorbent is structurally homogeneous; there is no interaction between molecules adsorbed on neighboring sites [34,35]. The Freundlich isotherm is used for the description of multilayer adsorption with interaction between adsorbed molecules. The model predicts that the dye concentrations on the sorbent increases as long as there is an increase of the dye concentration in the solution (this is not restricted to the monolayer in the adsorbent). The model applies to adsorption onto heterogeneous surfaces with a uniform energy distribution and reversible adsorption [34].

The results listed in Table 4 confirmed that the Langmuir model is more suitable than the Freundlich adsorption isotherm. This suggests that the monolayer adsorption of RBB occurred on the anion exchange resins. The determination coefficients (R^2) ranged from 0.990 to 0.999. The monolayer sorption capacities were found to be 66.4, 282.1 and 796.1 mg g^{-1} for Amberlite IRA 67, Amberlyst A 23 and Lewatit MonoPlus MP 62, respectively. The macroporous anion exchangers such as Lewatit MonoPlus MP 62 and Amberlyst A 23 are characterized by significant porosity in comparison with gel Amberlite IRA 67, therefore their sorption capacities are larger. Not only matrix structure but also its composition plays an important role in the dye sorption. Taking into consideration the applicability of the weakly basic anion exchangers of various matrices in dye effluents treatment, they can be arranged as:
polystyrene > phenol-formaldehyde > polyacrylate.

3.6. Anion exchanger regeneration

The rational use of ion exchange technology with regard for all ecological and economic aspects involves regeneration. Regeneration of anion exchangers is an important part of water and wastewater conditioning cycles. Desorption parameters such as: the type of regenerate solution, its concentration, the regenerate feed rate, ion exchanger regeneration degree and the amount of regenerating solution must be taken into account in the macro scale technological scheme. According to Dulman *et al.* [22] many sorbents that

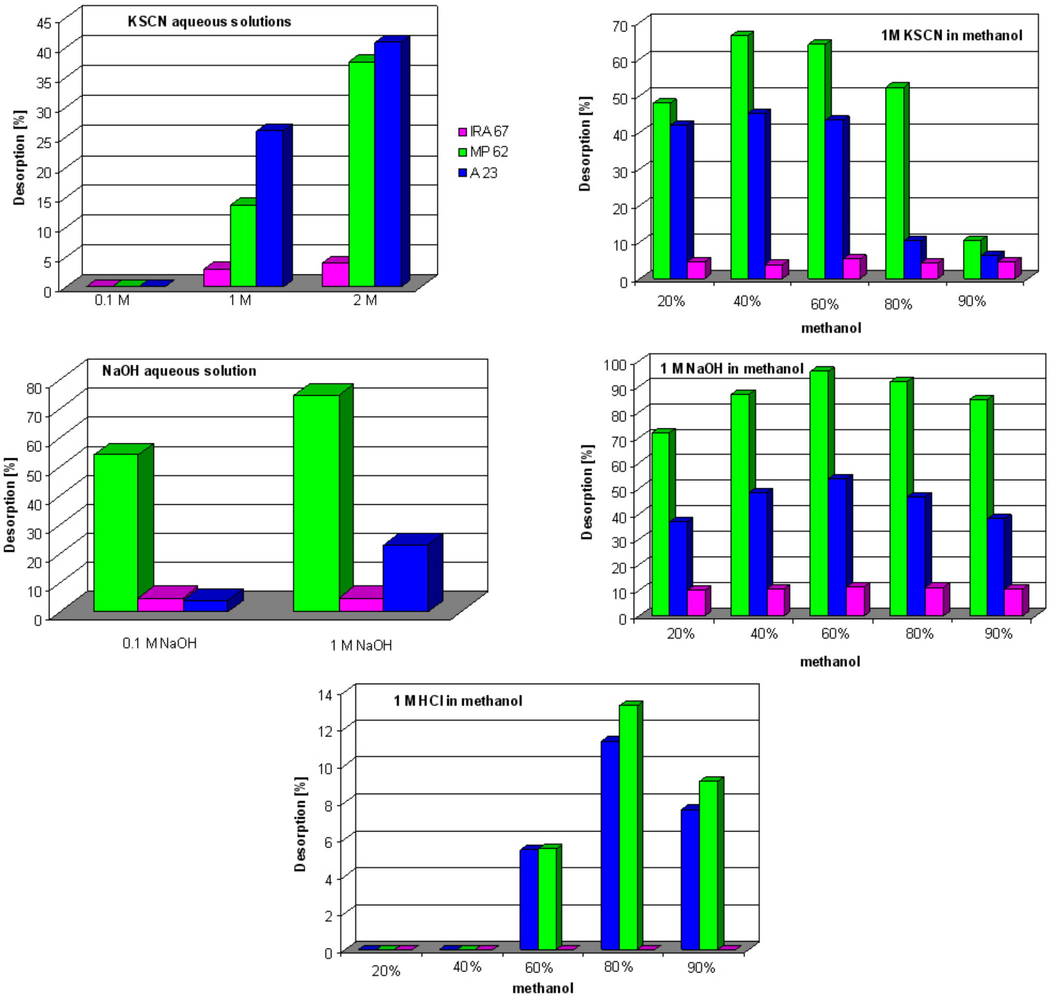


Figure 7. Desorption of RBB from the weakly basic anion exchangers by the batch method.

display acceptable sorption capacities for reactive dyes can be used only once and have to be disposed afterward, but commercial weak base resins with adsorbed dyes may be completely regenerated using alkaline methanol. In this paper, desorption process was carried out using different regenerating agents: 0.1-2 M KSCN, 0.1-1 M NaOH and 1 M HCl. Considering that the dye binding with the anion exchangers may not only be by ion exchange reactions but also by other binding forces such as hydrophobic interaction or hydrogen bonding, methanol was chosen for breaking these non-specific interactions (20-100% methanol, 1 M KSCN or 1 M NaOH or 1 M HCl in 20-90% methanol). As presented in Fig. 7, the mixtures of methanol with 1 M KSCN, 1 M HCl and 1 M NaOH greatly improved the dye desorption performance in most cases. Interestingly, methanol, when used alone, had no desorbing power whatsoever in all cases. From the polyacrylate anion exchanger Amberlite IRA 67 only 10% of dye was desorbed using eluents mentioned above. For polystyrene Lewatit MonoPlus MP 62 anion exchanger ~65%, 70% and 95% desorption were found using 1 M KSCN in 40-60% methanol, 1 M NaOH and 1 M NaOH in 60% methanol, respectively. The optimal desorption conditions found in this study for Amberlyst A 23 were the following: 2 M KSCN and 1 M KSCN in 20-60% methanol (~40% desorption) and 1 M NaOH in 60% methanol (~50% desorption). These results also indicate that RBB was retained by the weakly basic anion exchangers through more than one binding force: electrostatic interaction, hydrophobic interaction or hydrogen bonding. Similar observations were made by Karcher *et al*. [18,19] for RBB retention on anion exchangers and by Liu *et al*. [24] for Cibarcon blue 3GA and Cibarcon red 3BA – anion exchange membranes (SB6407 and DE81) system.

4. Conclusions

Removal of the reactive dye Remazol Black B (RBB) from the aqueous solutions and wastewater was studied using the anion exchange resins of various matrices (Amberlyst A 23, Amberlite IRA 67 and Lewatit MonoPlus MP 62). Significant decolourization of wastewater containing RBB and two different reactive dyes was achieved after 72 h of phase contact time when the polystyrene anion exchanger Lewatit MonoPlus MP 62 was used. The equilibrium data were fitted well using the Langmuir isotherm model. Taking into consideration the applicability of the weakly basic anion exchangers of various matrices in dye effluents, treatment can be arranged as:

Lewatit MonoPlus MP 62 > Amberlyst A 23 > Amberlite IRA 67.

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