

# The Removal of Reactive Dyes from Binary Mixtures Using Chitin

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## Abstract

The adsorption of reactive dye mixtures onto chitin modified with 5N KOH was investigated. Three binary mixtures were tested. Each mixture contained Blue D-5RN and either Yellow D-5GN, or Red D-8B or Black DN as the second dye. The tests were conducted without pH adjustment and after pH adjustment to 3.0. The results were based on the constants determined from double Langmuir isotherm.

The maximum adsorption capacity of Blue D-5RN (control sample) in the samples without pH adjustment accounted for 97 mg/g d.w., and in the sample with pH adjustment (pH=3) – for 205 mg/g d.w. The adsorption capacity of a mixture of Red D-8B and Blue D-5RN reached 93 and 196 mg/g d.w., respectively, and in a mixture containing Yellow D-5GN – 103 and 214 mg/g d.w., respectively.

The dye competition in a mixture was evaluated comparing 7 constants in Langmuir equation for mixtures and Blue D-5RN in a mixture.

The adsorption capacity of Blue D-5RN in a mixture was found to be by ca. 8.8 % lower than the adsorption capacity of a dye mixture in the samples without pH adjustment and by ca. 9.4 % lower compared to the samples with adjusted pH. An explicit decline in  $K_1$  value was also observed, depending on the type of the second dye and pH. Blue D-5RN and Red D-8B characterized by a high similarity of chemical structure competed for active sites more strongly. It was confirmed by a higher (ca. 9-fold and 2.1-fold –pH=3) decrease in constants K determined for Blue D-5RN in a mixture. The experimental data showed that in the samples with pH=3, the competition for active sites between dyes was weaker.

**Keywords:** adsorption, reactive dyes, modified chitin, binary mixtures, Langmuir isotherm

## Introduction

Adsorption is one of the most effective physical processes applied for the removal of colour and treatment of textile effluent. Therefore, different chemical and biological adsorbents have been extensively studied in the last few years [1, 2, 3].

The estimation of an adsorbent usability is usually based on the analysis of its adsorption capacity. Lambert [4] tested three inorganic adsorbents (activated bauxite, fullers earth and synthetic clay). The result indicated that

the maximum adsorption capacity of synthetic clay and active bauxite was comparable to that of activated carbon and amounted to approximately 100 mg/g dry weight. Fuller's earth was characterized by a low maximum adsorption capacity – to about 20 mg/g dry weight for Blue 71. In the research of Poots [5], peat with particle size of 250-355  $\mu\text{m}$  demonstrated the maximal adsorption capacity of 18.0 mg/g dry weight, whereas the adsorption capacity of peat with particle diameter of 750-1000  $\mu\text{m}$  reached 11.9 mg/g dry weight.

Among synthetic sorbents, the product of condensation of glyoxal, urea and formaldehyde, called "cucurbituril," shows high efficiency of dye adsorption. This

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sorbent is characterized by a high adsorption capacity of reactive dyes, i.e. Blue 19, Blue 2, Yellow 17, Orange 16, Purple 5, Red 123 [3], and of direct ones such as Red 79, Red 80, Yellow 33 and Blue 71 [6].

Al-Degs [1] obtained high removal efficiency of activated carbon Filtrasorb 400 (F-400) towards three remazol dyes, namely Remazol Golden Yellow, Remazol Red and Remazol Black B. The adsorption capacity data showed the highest values of 1111 mg/g dry weight for Remazol Golden Yellow (dye containing single azo group). The maximum adsorption capacity of Remazol Red (diazo) and Remazol Black B (diazo) onto activated carbon was over 2-fold lower – 400 and 434 mg/g dry weight, respectively.

McKay [2] tested adsorption of four dyes onto bagasse pith, a cheap waste product from the sugar industry. They proved that the adsorption capacity depends on dye type. The maximum adsorption capacity of basic Blue 69 and basic Red 22 onto pith was 158 and 77 mg/g dry weight, respectively, whereas it was lower (23 and 22 mg/g dry weight) in respect to acid Red 114 and acid Blue 25.

It is thought that cellulose-containing adsorbents prepared (e.g. from eucalyptus bark [7], maize cob [8] or bagasse pith [2]) are likely to demonstrate a strong adsorption affinity to basic dyes. They adsorb basic dyes through coulombic attraction and ion-exchange processes. The adsorption of acid dye can be hindered by the negative surface charge acquired by the adsorbent on contact with water [9].

Unlike cellulose-containing, the biological nitrogen-containing adsorbents, such as chitin or chitosan, tend to demonstrate a significantly higher adsorption capacity for acid dyes. Šafařík [9] tested chitosan as an adsorbent and based on magnetic chitosan matrix – magnetic blue chitosan. The experiments were conducted for five polycyclic dyes (Acridine Orange, Congo Red, Neutral Red, Crystal Violet and Safranin O). In comparing the values of the maximum adsorption capacity for both sorbents, it can be concluded that the best adsorption onto magnetic blue chitosan was obtained for Crystal Violet (71.8 mg/g). Chitosan adsorbed Congo Red the best of all dyes (43.41 mg/g).

The available literature indicates that due to a highly complex structure of both dyes and adsorbents there have been no appropriate data so far that would enable modelling of the adsorption process. The fact that in waste water from the textile industry dyes occur generally as binary or multicomponent mixtures makes it even more complicated. Compared with single dyes, the adsorption of mixtures is likely to be of a complex character due to both the possibility of interactions between dyes in a solution and their capability of competing for active sites at the adsorbent's surface as well. In addition, the adsorption of an individual dye may effect a change in the surface charge of an adsorbent, and consequently decrease or increase the efficiency of binding other dyes occurring in a mixture.

In this work, the adsorption capacities for acidic reactive dyes were determined using chitin. The competitive

Table 1. Chitin flake characteristics.

Parameters	Chitin
Deacetylation degree [%]	5
Dry weight [%]	95.64
Ash [%]	0.32
Swollen adsorbent hydration [%]	70%
Elemental analysis [%]	C= 43.9, N= 6.4, H=6.7

adsorption of reactive dyes in binary mixtures was investigated to assess the efficiency of chitin in purifying real effluent containing dyes, depending on pH.

## Materials and Methods

### Chitin Preparation and Characteristics

Krill chitin (polymorphic structure  $\alpha$ ) from the Sea Fisheries Institute in Gdynia was used. The chitin was prepared according to the methodology described by Stanley [10]. The adsorbent was first waterlogged and left in water for 24 hours at room temperature to expand. Then the water was decanted, whereas chitin was treated with a 6 N HCl solution to remove ash and next washed with distilled water to reach a filtrate of pH 7. The washed chitin was boiled in a 5 N KOH solution at 100°C for 3 h. After cooling down, the chitin was washed again with distilled water to reach a filtrate of pH 7 and drained off in vacuum.

The average size of a chitin flake used for the experiment was 314×184  $\mu\text{m}$ . The size of the maximal and minimal flake was 756×434  $\mu\text{m}$  and 62×62  $\mu\text{m}$ , respectively. The chitin characteristics are presented in Table 1.

### Dye Preparation

The mixtures of chlorotriazine reactive dyes: Yellow D-5GN, Red D-B8, Blue D-5RN and Black DN (produced by "Boruta" SA in Zgierz), were investigated. The chemical structure of dyes is presented in Fig. 1.

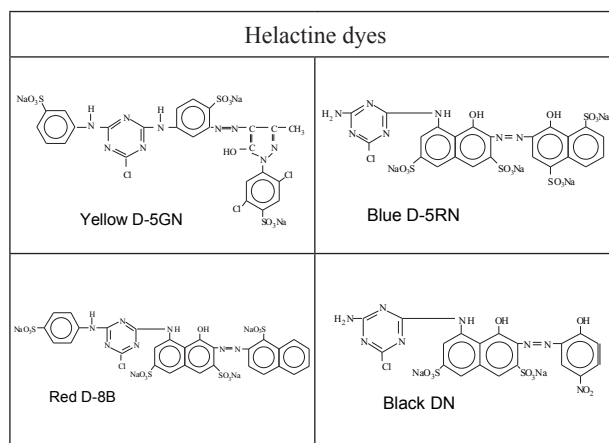


Fig. 1. Chemical structure of helactine dyes.

### Adsorption Analysis of Binary Mixtures of Dyes on Chitin

The tests were conducted with the use of chitin as an adsorbent, in the samples without pH adjustment (pH 6.2-6.3) and with pH adjustment to 3.0. Three mixtures of dyes were selected for investigations:

- Blue D-5GN and Yellow D-5DN (mixture 1),
- Blue D-5GN and Red DB-8 (mixture 2),
- Blue D-5GN and Black DN (mixture 3).

The concentration of Blue D-5RN in a mixture of dyes without pH adjustment was 5, 10, 25, 50, 75, 100, 125, 150, 200, 250 mg/dm<sup>3</sup>, and in those with pH adjustment – 5, 25, 50, 100, 150, 200, 250, 300, 400, 500 mg/dm<sup>3</sup>, respectively. The concentration of Yellow D-5DN, Red D-8B and Black DN in each mixture was constant and reached 50 mg/dm<sup>3</sup>.

Sorption studies were performed by the batch technique. The equilibrium isotherms were determined by the contact of the known mass of an adsorbent with dye solutions. To this end, 200 cm<sup>3</sup> conical flasks were filled with both 100 cm<sup>3</sup> of dye mixture at an appropriate concentration, without or with pH adjustment, and 1.5 g dry weight/dm<sup>3</sup> of chitin. The flasks were shaken at a constant agitation speed of 200 c.p.m., and the vibration amplitude of 9 at 20°C for 4 h (samples without pH adjustment), and for 2 h (samples with pH adjustment). After 1-minute sedimentation, the dye solution was decanted and separated in a MPW 210 centrifuge for 10 min at 10,000 r.p.m. Figure 2 presents the experimental procedure.

### Analytical Methods

The analyses of dye adsorption on chitin included the following parameters: pH measurements with the use of an HI 8818 pH-meter, chitin concentration as chitin dry weight according to the methodology by Hermanowicz [11]. The chitin deacetylation degree was analyzed according to Roberts [12]. The method for the estimation of dye concentration in a multicomponent solution was used

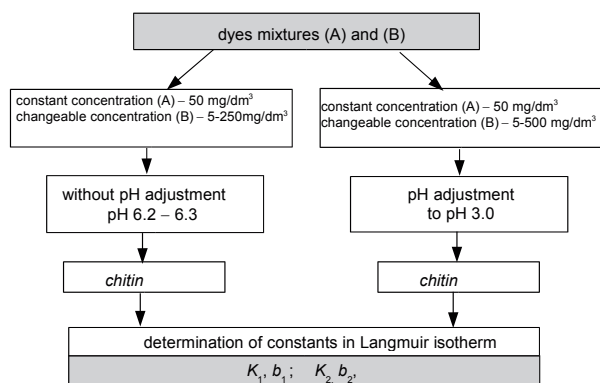


Fig. 2. The research assumptions to determine dyes adsorption on chitin from their binary mixtures.

A - dyes at constant concentration (Yellow D-5GN, Red D-8B or Black DN); B - Blue D-5RN.

Table 2. Wavelengths at which dyes absorbance was measured.

Dye type	Wavelength ( $\lambda$ ) [nm]
Helactine Yellow D-5GN	404
Helactine Red D-8B	521
Helactine Blue D-5RN	570
Helactine Black DN	580

following the work of Al-Duri [13]. The concentrations of dyes were measured spectrophotometrically with the use of an HITACHI 1200 specole. The method used to determine dye concentration is described below.

### Determination of Dye Concentration in a Binary Mixture

During the binary component competitive adsorption studies, standard solutions were prepared and the  $\lambda_{\max}$  (maximum adsorption value) was recorded for each dye. Wavelengths at which absorbance was measured are shown in Table 2. A pre-determined calibration curve was used to convert the optical densities into concentrations.

### A Mixture of Yellow D-5GN with Blue D-5RN

Blue D-5RN and Yellow D-5GN were mixed in 10 different proportions, namely 0.1, 0.2, 0.5, 1, 1.5, 2, 2.5, 3.0, 4.0 i 5.0 (in mixtures without pH adjustment), and 0.1, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, 10.0 (in mixtures with pH adjustment), respectively. Then the standardization curves were plotted from samples different in the proportion of Yellow D-5GN and Blue D-RN. In total, 10 standardization curves were drafted. Each standardization curve and conversion coefficients were useful for determining the dye concentration in a solution. Absorbance measurements were made at wavelengths specified for the solutions of single dyes that were included in the mixture (Tab. 2).

### A Mixture of RedD-8B with Blue D-5RN and Black DN with Blue D-5RN

Standardization curves and conversion coefficients for the mixtures of Red D-8B with Blue D-5RN, and Black DN with Blue D-5RN were determined in an analogous way as for the mixtures of Yellow D-5GN and Blue D-5RN.

## Results and Discussion

The adsorption isotherm for the tested dyes onto chitin was estimated using a plot of solid phase equilibrium concentration,  $Q$ , versus liquid phase equilibrium concentration,  $C$ . Data from the adsorption isotherm were modelled using the double Langmuir isotherm equation (1). The model takes into consideration that the surface of an adsorbent is energetically heterogeneous and contains adsorption sites of different energy of adsorbate binding [14].

It was assumed that chitin has two types of active sites [15]. Each type is described by the Langmuir isotherm (1).

$$Q = \frac{b_1 \cdot K_1 \cdot C}{1 + K_1 \cdot C} + \frac{b_2 \cdot K_2 \cdot C}{1 + K_2 \cdot C} \quad (1)$$

- $Q$  - equilibrium solid phase dye concentration [mg/g dry weight]  
 $b_1$  - maximum adsorption capacity of chitin for type I sites [mg/g dry weight]  
 $b_2$  - maximum adsorption capacity of chitin for type II sites [mg/g dry weight]  
 $K_1$  - constant in Langmuir isotherm [dm<sup>3</sup>/g dry weight]  
 $K_2$  - constant in Langmuir isotherm [dm<sup>3</sup>/g dry weight]

The total maximum adsorption capacity of chitin equals a sum of the maximum adsorption capacities obtained for type I and II sites ( $b = b_1 + b_2$ ).

Constants  $K_1$  and  $K_2$  and the maximum adsorption capacity ( $b_1$ ) and ( $b_2$ ) in the equation (1) were determined based on the experimental data ( $C_i, Q_i$ ) <sub>$i=1..n$</sub>  by non-linear regression with the use of APNIELIN software (author: S. Grabowski – University of Warmia and Mazury in Olsztyn). In order to evaluate the goodness of fit, the coefficient  $\phi^2$  was used [16].

### Adsorption of Reactive Dyes onto Chitin from Binary Mixtures

#### Samples without pH Adjustment

The adsorption isotherms for the binary mixtures 1, 2 and 3, and the adsorption isotherm for Blue D-5RN from a

single component solution (control sample) are presented in Fig. 3. The results indicate that the binary mixtures 1 and 3 were adsorbed slightly better compared to a control sample (Blue D-5RN). The total maximum adsorption capacity of chitin ( $b$ ) for the binary mixtures was comparable with the adsorption capacity for Blue D-5RN (Tab. 3).

The adsorption of Blue D-5RN from any mixture was lower than the adsorption of Blue D-5RN from a single component solution (control sample). With an increasing concentration of Blue D-5RN in a binary mixture, the amount of the second dye adsorbed onto chitin: Yellow D-5GN, Red D-8B or Black DN, decreased from 33.3 mg/g dry weight to about 18 mg/g dry weight (Fig. 3).

The total maximum adsorption capacity of chitin ( $b$ ) for the Blue D-5RN from a binary solution was lower by about 5-18 % with reference to that for Blue D-5RN in the control sample (Fig. 3). The adsorption affinity of dyes (constants  $K_1$  and  $K_2$ ) is presented in Table 4. Data compiled therein showed that the adsorption affinity of Blue D-5RN from a binary mixture was significantly lower both in relation to a binary mixture and control sample, especially to type I sites. In addition, it can be concluded that the second dye in the mixture competed with Blue D-5RN for active sites on the chitin surface.

Assuming that a decline in  $K_1$  and  $K_2$  for Blue D-5RN in a binary mixture is the factor of the ability for competition between dyes in mixtures, it can be stated that Red D-8B competed with Blue D-5RN most strongly. In the presence of Red D-8B, a 13-fold decrease in  $K_1$  for Blue D-5RN, and a 3.3-fold decrease in  $K_2$  in respect to the binary mixture 2 were observed (Tab. 4).

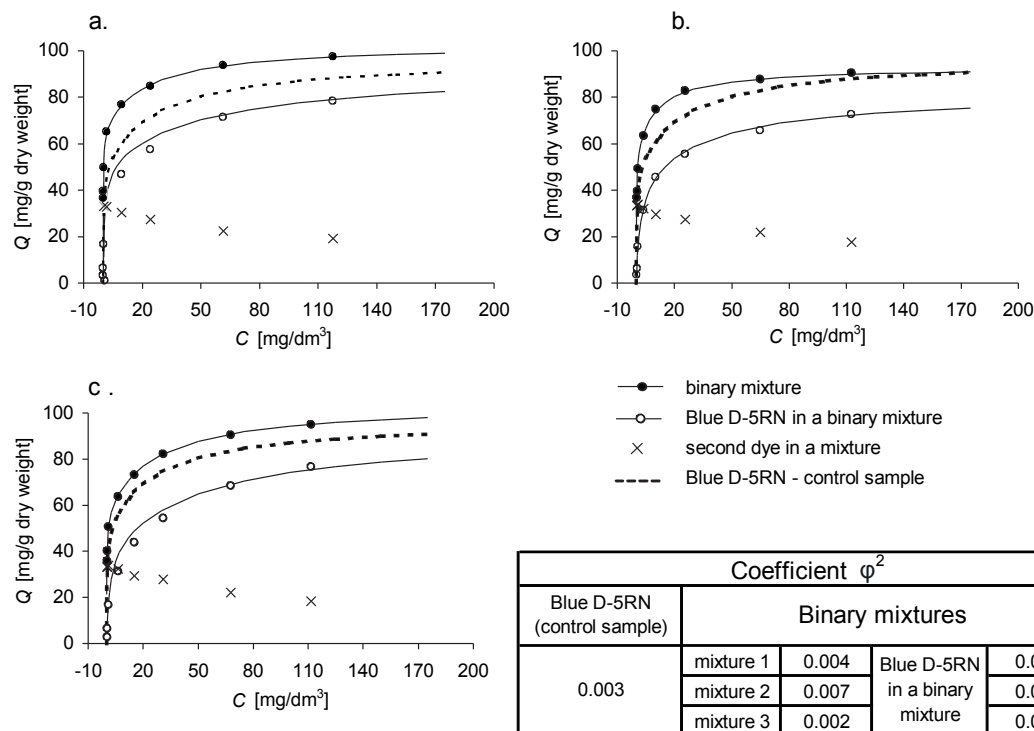


Fig. 3. Amount of equilibrium adsorption dye ( $Q$ ) depending on equilibrium liquid phase dye concentration without pH adjustment. In table there is the coefficient  $\phi^2$ ; a - mixture 1, b - mixture 2, c - mixture 3.

Table 3. Total adsorption capacity determined from the Langmuir isotherm (samples without pH adjustment).

Total adsorption capacity [mg/g dry weight] $b = b_1 + b_2$				
Blue D-5RN control sample	Binary mixture			
97	Yellow D-5GN Blue D-5RN	103	Blue D-5RN in a binary mixture	92
	Red D-8B Blue D-5RN	93		82
	Black DN Blue D-5RN	104		92

Table 4. Constants  $K_1$  and  $K_2$  determined from the Langmuir isotherm (samples without pH adjustment).

Constants $K_1$ and $K_2$ [dm <sup>3</sup> /mg]							
Blue D-5RN control sample		Binary mixture					
$K_1$	$K_2$	Mixture	$K_1$	$K_2$	Blue D-5RN in a binary mixture	$K_1$	$K_2$
4	0.404	Yellow D-5GN Blue D-5RN	8.8	0.05		1.4	0.02
		Red D-8B Blue D-5RN	6.5	0.10		0.5	0.03
		Black DN Blue D-5RN	6.0	0.04		0.7	0.02

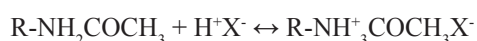
It was found that chitin adsorption capacity in relation to dyes in the binary mixtures with Blue D-5RN, both in the samples without and with pH adjustment, was ordered as follows:



In the case of single dye adsorption, the maximum adsorption capacity for Yellow D-5GN amounted to 101 mg/g dry weight, for Black DN to 97 mg/g dry weight, and for Red D-8B to 92 mg/g dry weight [15], and changed in the analogical way as the efficiency of their adsorption in the binary mixtures.

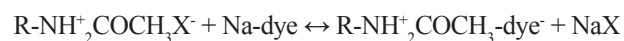
#### Samples with pH Adjustment

The pH value of the dye solution is of crucial importance to the entire adsorption process and particularly to the adsorption capacity. A charge (positive or negative) on adsorbent surface is proportional to the pH of the solution. Under acid conditions, chitin included acetamide groups and an insignificant number of amine groups. Both these groups are of a great significance to dye adsorption. Those groups are protonated according to the reaction:



Proton affinity to amine groups is higher than to acetamide groups [17]. The proton attachment by chitin en-

ables the adsorption of anion dyes (including all reactive dyes tested) by ion-exchange:



Experimental data and adsorption isotherms for binary mixtures 1, 2 and 3, and Blue D-5RN on chitin are shown in Fig. 4. It was observed that the total maximum adsorption capacity of chitin ( $b$ ) obtained for dyes in all samples (pH=3) was about 2-fold higher in comparison with the samples without pH adjustment.

The adsorption of a dye mixture was found to depend on the type of the second dye in the mixture. The adsorption of mixture 1 containing Yellow D-5GN was higher and that of mixtures 2 and 3 – lower, compared with the control sample.

The amount of equilibrium adsorption ( $Q$ ) for Blue D-5RN in a binary mixture was always lower compared to a control sample (Fig. 4). The amount of the second dye in the mixture (Yellow D-5GN, Red D-8B and Black DN) decreased with an increasing concentration of Blue D-5RN in the mixture, and the drop depended on its type.

The total maximum adsorption capacity of chitin ( $b$ ) for the Blue D-5RN in the binary mixtures is shown in Fig. 4 and Table 5. It was observed that constants  $K_1$  and  $K_2$  for mixtures 1, 2 and 3 were about 2-fold higher in comparison to a control sample (Tab. 6). In contrast to the samples without pH adjustment, the competition of Blue D-5RN with the second dye in the mixture (pH 3.0) was lower, which was proved by the  $K_1$  values obtained for



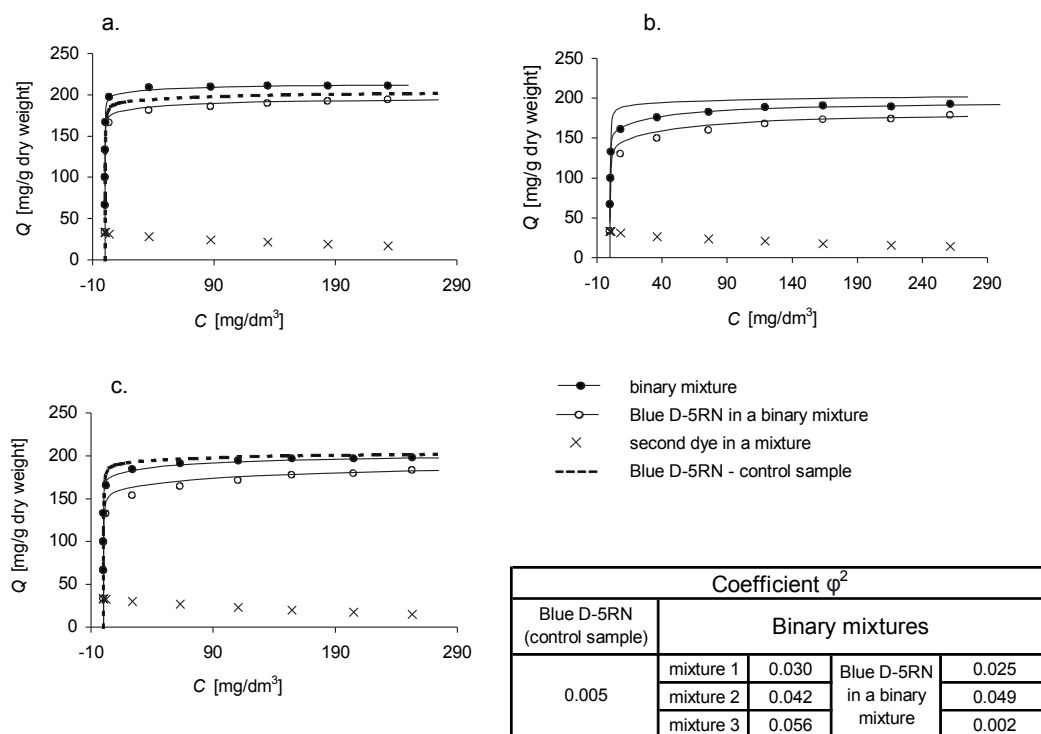


Fig. 4. Amount of equilibrium adsorption dye ( $Q$ ) depending on equilibrium liquid phase dye concentration with pH adjustment. In table there is the coefficient  $\phi^2$ ; a - mixture 1, b - mixture 2, c - mixture 3.

Table 5. Total adsorption capacity determined from the Langmuir isotherm (samples with pH adjustment).

Total adsorption capacity [mg/g dry weight] $b = b_1 + b_2$				
Blue D-5RN control sample	Binary mixture			
205	Yellow D-5GN Blue D-5RN	214	Blue D-5RN in a binary mixture	197
	Red D-8B Blue D-5RN	196		184
	Black DN Blue D-5RN	202		192

Table 6. Constants  $K_1$  and  $K_2$  determined from the Langmuir isotherm (samples with pH adjustment).

Constants $K_1$ and $K_2$ [dm³/mg]							
Blue D-5RN control sample		Binary mixture					
$K_1$	$K_2$	Mixture	$K_1$	$K_2$	Blue D-5RN in a binary mixture	$K_1$	$K_2$
7	0.013	Yellow D-5GN Blue D-5RN	13.5	0.024		11.1	0.02
		Red D-8B Blue D-5RN	13.0	0.030		5.3	0.02
		Black DN Blue D-5RN	15.9	0.028		5.7	0.01

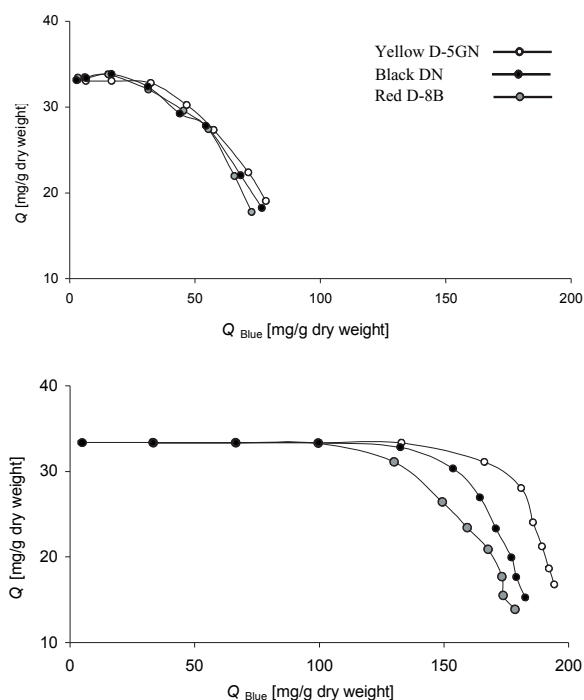


Fig. 5. The amount of adsorbed dye ( $Q$ ) - Yellow D-5GN, Red D-8B, and Black DN from their mixtures depending on the amount of adsorbed Blue D-5RN ( $Q_{Blue}$ ); a - samples without pH adjustment, b - samples with pH adjustment.

binary mixtures 1, 2, 3 and Blue D-5RN. In the samples without pH adjustment, the adsorption affinity of Blue D-5RN to type I sites differed by almost a quantity order, whereas in the samples with pH adjustment lower differences were noted (Tab. 4, Tab. 6).

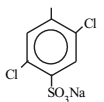
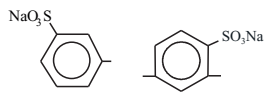
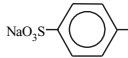
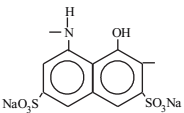
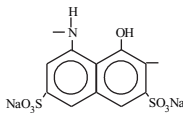
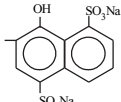
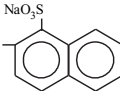
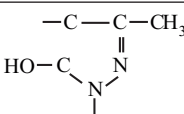
Fig. 5 shows the dependence between the amount of equilibrium adsorption of Blue D-5RN and the second dye (Yellow D-5RN, Red D-8B or Black DN) in a binary mixture.

In the samples without pH adjustment, an increase in the equilibrium adsorption of Blue D-5RN ( $Q_{Blue}$ ) was found to cause a decrease in the amount of the second dye adsorbed ( $Q$ ), whereas in the samples with pH adjustment at the identical amount of equilibrium adsorption of Blue D-5RN the amount of the second dye adsorbed remained constant (Fig. 5).

It was established that the adsorption of each dye depended both on the amount of sites available on the chitin surface ( $b_1$  and  $b_2$ ), and on the proportion between dyes in the mixtures' concentrations.

In the samples with pH adjustment, the amount of active sites on chitin was about 2-fold higher compared with the samples without pH adjustment (2-fold higher maximum adsorption capacity). At a low concentration of Blue D-5RN in the mixture' concentration of dyes in the solution limited their adsorption. An increase in Blue D-5RN concentration in the mixture caused an increase

Table 7. Occurrence of chemical groups in the molecules of tested dyes.

Chemical group	Dye type		
	Blue D-5RN	Yellow D-5GN	Red D-8B
single aromatic rings	lack		lack
	lack		
condensed aromatic rings		lack	
		lack	
pyrazole ring	lack		lack

in its adsorption, whereas the amount of equilibrium adsorption of the second dye remained nearly constant. The amount of equilibrium adsorption of the second dye increased as long as the dye saturated all available active sites of chitin. Then, the amount of Blue D-5RN adsorbed approached the value close to the maximum adsorption capacity of chitin. From this moment, the second dye adsorption on chitin significantly dropped.

Maekawa [18] examined the adsorption of binary mixtures: Direct Blue 15 and Direct Yellow 12, with different affinity from the binary solution onto cellulose membrane. The following conclusion was drawn: the amount of equilibrium adsorption of each dye decreases by the presence of other dye; the extent of a decrease is getting higher with an increasing concentration of the other dye.

In our study, in the molecule of Blue D-5RN, similarly to Red D-8B, two condensed aromatic rings were the bases. Sulfone and hydroxyl groups also occurred and made the forming of negative ions easy. The molecule of Yellow D-5GN contained three single aromatic rings with chlorine and sulfone groups, and pyrazole (Tab. 7).

Along with an increase in the amount of Blue D-5RN removed, the highest adsorption drop was noted in the case of Red D-8B, and the lowest one in the case of Yellow D-5GN. As in the samples without pH adjustment, the adsorption capacity with reference to dyes in the binary mixtures with Blue D-5RN, both in the samples without and with pH adjustment, was ordered as follows:



In the case of single dye adsorption, the maximum adsorption capacity for Yellow D-5GN amounted to 227 mg/g dry weight, for Black DN to 208 mg/g dry weight, and for Red D-8B to 180 mg/g dry weight [15], and changed in the analogical way as the efficiency of their adsorption in the binary mixtures.

### Conclusions

Based on the results, the following can be concluded:

1. Biological adsorbent characterized by a complex chemical structure, including e.g. chitin, possess active sites with different energy of adsorbate molecules binding. The adsorption of dyes on chitin proceeded in the active sites of types I and II, different in terms of affinity and the maximum adsorption capacity. The constants derived from Langmuir equation, i.e. maximum adsorption capacity,  $Q$ , and equilibrium constants  $K_1$  and  $K_2$ , were assumed to be a measure of the adsorption capacity of a dye mixture.
2. The adsorption capacity of mixtures was not considerably different from that of a single dye (Blue D-5RN), which resulted from a high proportion of concentrations between Blue B-5RN and the second dye in the mixture, when  $Q \rightarrow b$ . Negligible differences in the capacity of a mixture might result from a differentiated adsorption capacity of an individual dye in the mixture.
3. The total adsorption capacities of the Blue B-5RN from any mixture was lower than the sorption from a mixture system for all dyes studied. It indicates that the dyes occurring in a mixture competed for active sites of chitin. The competition of the dyes was also proved by a drop in constants  $K_1$  for Blue DF-5RN in a binary mixture compared to the constants for mixtures and control samples.
4. The competition between dyes was found stronger when the number of active sites on chitin was small – the samples without pH adjustment. A 6.3- to 13-fold decrease in the  $K_1$  value for Blue D-5RN in a mixture was observed therein. In the samples with adjusted pH, a decrease in the  $K_1$  value for Blue D-5RN in a mixture was substantially lower – from 1.2- to 2.8-fold.
5. The pH for the adsorption solutions was hence increasing the positive charges on chitin. It results in attracting more negatively charged functional groups located on the reactive dyes during the adsorption process. In consequence, a 2-fold higher maximum adsorption capacity was observed at pH 3.0 in comparison with pH 6.2.

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