

# The Adsorption of Reactive Dyes from Mixtures Containing Surfactants onto Chitin

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## Abstract

Adsorption of reactive dyes and surfactants onto chitin from mixtures containing surfactants at constant concentration and dyes at variable concentration was investigated in the present study. Two vinyl-sulfonate dyes (Scarlet R, Brilliantorange 3R); chlorotriazine dye (Black DN); anionic (Borutosol KRN, Siarczanol N-2) and non-ionic (Rokafenol N-8) surfactants were tested. The experiments were carried out without and with pH adjustment.

The research have proved that at pH 6.2 and in surfactants presence the adsorption of vinyl-sulfonate dyes onto chitin was lower than without surfactants (control sample). It was observed that the maximum adsorption capacity of chitin in mixtures of Scarlet R and surfactants was about 3-fold lower than without surfactants and in mixtures of Brilliantorange 3R and surfactants was from 2.5 to 4.1-fold lower than in control sample. At pH 3.0 the differences between maximum adsorption capacity of chitin for dyes from aqueous solutions and containing surfactants ranged from 2% (in mixture of Brilliantorange 3R and Borutosol KRN) to 23% (in mixture of Scarlet R and Siarczanol N-2). The maximum adsorption capacity of chitin for Black DN (chlorotriazine dye) in surfactants presence (from 140 to 290 mg/dm<sup>3</sup>) was higher at pH 6.2 as well as at pH 3.0 in comparison to control sample. Rokafenol N-8 was adsorbed the weakest onto chitin from among tested surfactants. At pH 3.0 for vinyl-sulfonate dyes the relationships between mass proportion of dye and surfactant adsorbed onto chitin ( $Q_{dye}/Q_{SAA}$ ) and initial concentration proportion of dye and surfactant in solution ( $C_{dye}/C_{SAA}$ ) was nearly linear. This indicates that dyes competed with surfactants of active sites of chitin.

SAA\* – Surface Active Agent (s)

**Keywords:** reactive dyes, surfactants, chitin, adsorption, Langmuir

## Introduction

The total dye consumption of the textile industry worldwide is in excess of 10<sup>7</sup> kg/year and estimated 90% of this ends up on fabrics. Consequently, approximately 1,000,000 kg/year of dyes are discharged into waste streams. Dye producers and users are interested in stability, fastness and con-

sequently produce dyestuffs, which are more difficult to degrade after use [1]. Therefore aqueous dyes pollution represents an important environmental problem.

Adsorption is a suitable method for the removal from wastewater of such contaminants, which are not biodegradable. Biological materials have shown potential for dye removal, but only low-cost biological materials with sufficiently high dye-binding capacity and selectivity for dyes are suitable for use in a full-scale biosorption

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process. Various materials have been examined for their biosorptive properties such as: peat [2], apple pomace, wheat straw, waste residues, corncobs, barley husks [3, 4], bleaching earth [5], chitosan and chitin [6,7].

Among the most promising types of tested biosorbents, chitin and its deacetylated form – chitosan have shown levels of dye uptake high enough to warrant further research. The adsorption capacity of chitin (deacetylation degree of 5%) without pH adjustment ranged from 66 (Brillantorange 3R) to 148 mg/g dry weight of chitin (Blau 3R). At pH 3.0 the adsorption capacity ranged from 160 (Ruby F-2B) to 294 mg/g dry weight (Blau 3R) [8].

Chitin, after cellulose, is the most common biomass. It is produced by a variety of marine animals [9,10], insects [11] and fungi [12]. Research of dye adsorption onto chitin and chitosan are quite numerous, describing dye removal from aqueous solution: anionic [13] or reactive [14-16].

However, textile industry wastewater contain other chemical substances among which surfactants are a very important group. Anionic surfactants can compete with dyes of active sites of chitin. This is why they can influence adsorption capacity of chitin. Non-ionic surfactants may have a large effect on adsorption due to surfactant-surfactant and surfactant-solvent interactions. It may cause surfactant aggregation in bulk and lead to an attraction of hydrophobic groups of dyes [17, 18].

In this study the effectiveness of reactive dye adsorption onto chitin was investigated. Two vinyl-sulfonate dyes (Scarlet R, Brillantorange 3R); chlorotriazine dye (Black DN); anionic (Borutosol KRN, Siarczanol N-2) and non-ionic (Rokafenol N-8) surfactants were used.

## Materials and Methods

### Chitin

Chitin used in the present work was extracted from krill and purchased from the Sea Fisheries Institute in Gdynia. Chitin flake characteristics were shown in Table 1.

### Chitin Preparation

In this research 10 g of raw chitin was poured with 100 cm<sup>3</sup> distilled water and left to expand for 24 h. Next,

Table 1. Chitin flake characteristics.

| Parameters                        | Chitin                 |
|-----------------------------------|------------------------|
| Deacetylation degree [%]          | 7.23                   |
| Dry weight [%]                    | 95.64                  |
| Ash [%]                           | 0.32                   |
| Swollen adsorbent hydratation [%] | 70                     |
| Elementar analysis [%]            | C= 43.9; N= 6.4; H=6.7 |

chitin was washed with 6 N HCl and distilled water until neutral pH was obtained. The aim of acid washing was the removal of calcium and magnesium ions from chitin. After that, chitin was poured over 5 N KOH solution and boiled for 3 hours at 100°C. The degree of deacetylation of chitin was 7.23%.

## Dyes and Surfactants

In this experiment two vinyl-sulfonate dyes (Scarlet R, Brillantorange 3R) and chlorotriazine dye (Black DN) were used. Scarlet R and Black DN were provided by "Boruta" Co. in Zgierz, Poland. Brillantorange 3R was distributed by "Hoechst" Co., Lodz, Poland. Additionally, anionic (Borutosol KRN, Siarczanol N-2) and non-ionic (Rokafenol N-8) surfactants were used.

## Experimental

The adsorption tests were conducted in the following way. The samples, containing 1.5 g dry weight of chitin and 100 cm<sup>3</sup> mixture including various concentrations of each dye (5-500 mg/dm<sup>3</sup>) and constant concentration of each surfactant (100 mg/dm<sup>3</sup>), were shaken (type 385c, Elpan firm) for 2 hours. The experiments were carried out without and with pH adjustment (6.2 and 3.0, respectively). The solution pH was adjusted by 0.1N HCl. After shaking, the samples were left to settle for 10 minutes, decanted and centrifuged on centrifuge type MPW 210 at 10,000 rpm for 10 minutes.

### Estimation of Dye Concentration in Dye and Surfactant Mixture

For each tested dye the wavelengths ( $\lambda$ ) were estimated (Table 2). In order to measure dye concentration in aqueous solution, analytical curves and conversion rates were determined.

Surfactant absorbance values measured at wavelengths estimated for dyes were 0, which indicates that

Table 2. Dye and surfactant wavelengths.

| Dyes              | $\lambda$ (nm) |
|-------------------|----------------|
| Scarlet R         | 490            |
| Brillantorange 3R | 490            |
| Black DN          | 580            |
| Surfactants       |                |
| Borutosol KRN     | 230            |
| Siarczanol N-2    | 220            |
| Rokafenol N-8     | 275            |

Table 3. Dye and surfactant proportions in mixtures.

| Dye \ Surfactant       | 10 mg/<br>dm <sup>3</sup> | 20 mg/<br>dm <sup>3</sup> | 30 mg/<br>dm <sup>3</sup> | 40 mg/<br>dm <sup>3</sup> | 50 mg/<br>dm <sup>3</sup> |
|------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 10 mg/ dm <sup>3</sup> | 10+10                     | 10+20                     | 10+30                     | 10+40                     | 10+50                     |

surfactants did not influence dye absorbance values. However, dye absorbance values measured at surfactant wavelengths were different from 0. This means that dyes affected surfactant absorbance values. In order to estimate real surfactant concentrations in mixtures and to eliminate dye influence on the absorbance value, analytical curves were carried out.

The dye and surfactant mixtures were made in different proportions (Table 3). In each sample dye concentration was constant – 10 mg/dm<sup>3</sup>, but each surfactant concentration was varied between 10 and 50 mg/dm<sup>3</sup>. In general, 9 analytical curves were made (3 curves for each surfactant). On the basis of these curves, conversion rates were determined and in consequence the estimation of surfactant concentration in mixture was possible. The absorbance measurements were carried out at the wavelengths determined for single surfactants in aqueous solutions being included in the mixture.

### Analytical Methods

In order to measure dye and surfactant concentration solutions were analyzed by an UV/Visible spectrometer type VSU at the following wavelengths (Table 2).

Solution pH was measured using a pH-meter type HI 8818.

### Results and Discussion

Experimental data were analyzed on the basis of:

- adsorption isotherms of dyes  $Q = f(C)$ ,
- the mass of adsorbed surfactant ( $Q_{SAA}$ ) at various proportion of initial dye and surfactant concentration  $C_{dye}/C_{SAA}$ ,
- the ratio ( $r_{Q/C}$ ) between mass proportion of dye and surfactant adsorbed onto chitin ( $Q_{dye}/Q_{SAA}$ ) and proportion of initial dye and surfactant concentration in solution ( $C_{dye}/C_{SAA}$ ).

#### The Adsorption Isotherms of Dyes

The mass of adsorbed dye ( $Q$ ), depending on its concentration in solution ( $C$ ), is described by adsorption isotherms. Prior research conducted by Filipkowska et al. [19] indicates that for dye adsorption onto chitin the best degree of isotherms fitting to experimental data were obtained applying the two-surface Langmuir equation:

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

$Q$  – the amount of dye adsorbed onto chitin (mg/g d. w.)

$b_1$  – maximum adsorption capacity of chitin in active sites of the first type (mg/g d. w.)

$b_2$  – maximum adsorption capacity of chitin in active sites of the second type (mg/g d. w.)

$K_1, K_2$  – constant in Langmuir isotherm (dm<sup>3</sup>/g d. w.).

The usefulness of the two-surface Langmuir equation had been stated earlier by Sterritt, Lester [20, 21] during results interpretation of heavy metals adsorption by activated sludge and by Amacher et al. [22] in estimation of heavy metals adsorption in soils.

During dye adsorption onto chitin ion exchange is a dominating process in active sites of the first type (high  $K_1$  values). Apart from ion exchange, dyes can be adsorbed onto chitin as a result of hydrogen bonding or intermolecular interactions caused by van der Waals forces [23]. After adsorption of some amount of dye molecules, the chitin surface becomes more hydrophobic, which at high dye concentrations can result in forming hydrophobic bondings (small adsorption affinity values –  $K_2$ ). The maximum adsorption capacity of chitin ( $b$ ) equals the sum of maximum adsorption capacity in active sites of the first and the second types ( $b = b_1 + b_2$ ).

In present research it was stated that at low dye concentration the isotherms fitting to experimental data were not good enough. Better fitting of the curves to the data was obtained after modification of equation (1) to form (2):

$$Q = \frac{b_1 \cdot K_1 \cdot C^n}{1 + K_1 \cdot C^n} + \frac{b_2 \cdot K_2 \cdot C}{1 + K_2 \cdot C} \quad (2)$$

The  $K_1$  and  $K_2$  constants, maximum adsorption capacities ( $b_1$ ) and ( $b_2$ ), and  $n$  constant in equation (2) were determined on the basis of ( $C_i, Q_i$ )<sub>*i* = 1...n</sub> data by the non-linear regression method [24]. The results presenting a relationship between the mass of adsorbed dyes and adsorption isotherms showed in Fig. 1. In tables 4 and 5 the constants from equation (2) at pH 6.2 and 3.0, respectively, were presented.

On the basis of obtained results it can be observed that at pH 6.2 surfactant presence negatively influenced dyes adsorption. The pH decrease, depending on surfactant and dye type in the mixture, caused dye adsorption onto chitin to be comparable to and even higher than in the control sample.

Estimating surfactant influence on adsorption of each dye, it can be considered that Scarlet R adsorption onto chitin from mixtures containing dyes and surfactants was lower at pH 6.2 in comparison to adsorption from aqueous solutions containing single dye in the whole range of dye concentrations (Fig. 1a). The maximum adsorption capacity ( $b$ ) was not almost dependent on surfactant type (Table 4) and it was an average 3-fold lower than in control sample. At pH 3.0 the maximum adsorption capacity of chitin for Scarlet R was lower in Borutosol KRN and Siarczanol N-2 presence, while from the mixture with Rokafenol N-8 it was comparable with maximum capacity of chitin obtained for a single dye (control sample)

(Fig. 1b, Table 5). The adsorption of Brilliantorange 3R from the mixture containing both dye and surfactant at pH 6.2 (Fig. 1c) and at pH 3.0 (Fig. 1d) proceeded similarly to Scarlet R adsorption. This fact is probably a result of structural similarity both dyes.

Aksu [25] quoted for Brahim-Horn et al. (1992) [26], observed that the presence of surfactant in wastewaters may reduce the binding efficiency of the microorganisms and reported that high concentrations of Tween, a non-ionic surfactant, result in low adsorption and different dyes show different effects with the same concentration of Tween.

It was observed that surfactant presence in mixture disturbs Black DN adsorption in smaller range than adsorption of vinyl-sulfonate dyes described above. At pH

6.2 and at dye concentration below 200 mg/dm<sup>3</sup> the adsorption capacity of chitin in surfactant presence was lower in comparison with control sample. However, at high dye concentrations it exceeded the value of control sample (Fig. 1e). At pH 3.0 the maximum adsorption capacity of chitin for Black DN alone was not so high as for Black DN in a mixture of dye and surfactant (Fig. 1f). Black DN adsorption in Rokafenol N-8 presence at low concentrations range was small, therefore using Langmuir equations 1 and 2 to fit experimental data  $Q = f(C)$  was impossible.

Black DN is structurally different from the vinyl-sulfonate dyes because of triazine presence. According to Dupont et al. [27] adsorption of basic compounds as S-triazine onto soil can be due to partitioning from aqueous

Table 4. The constants from Langmuir equation based on data adsorption of dyes in aqueous solution and mixtures – pH 6.2.

| Dyes   | Coincidence coefficient | $K_1$ | $K_2$ | $b_1$ | $b_2$ | $b$ | n |
|--|-------------------------|-------|-------|-------|-------|-----|---|
| Scarlet R (control sample)                     | 0.0278                  | 1     | 0.014 | 40    | 55    | 95  | 1 |
| Mixture: Scarlet R and Borutosol KRN           | 0.239                   | 0.09  | 0.007 | 25    | 3     | 28  | 1 |
| Mixture: Scarlet R and Siarczanol N-2          | 0.0101                  | 0.08  | 0.008 | 25    | 4     | 29  | 1 |
| Mixture: Scarlet R and Rokafenol N-8           | 0.0024                  | 0.4   | 0.006 | 20    | 10    | 30  | 1 |
| Brilliantorange 3R (control sample)            | 0.0182                  | 1.2   | 0.024 | 20    | 46    | 66  | 1 |
| Mixture: Brilliantorange 3R and Borutosol KRN  | 0.0026                  | 0.04  | 0.001 | 25    | 1     | 26  | 1 |
| Mixture: Brilliantorange 3R and Siarczanol N-2 | 0.0067                  | 0.03  | 0.008 | 20    | 6     | 26  | 1 |
| Mixture: Brilliantorange 3R and Rokafenol N-8  | 0.0782                  | 0.04  | 0.001 | 15    | 1     | 16  | 2 |
| Black DN (control sample)                      | 0.0133                  | 4     | 0.03  | 49    | 47    | 96  | 1 |
| Mixture: Black DN and Borutosol KRN            | 0.0069                  | 0.9   | 0.006 | 20    | 120   | 140 | 2 |
| Mixture: Black DN and Siarczanol N-2           | 0.0226                  | 0.9   | 0.002 | 30    | 170   | 200 | 2 |
| Mixture: Black DN and Rokafenol N-8            | 0.0297                  | 0.4   | 0.004 | 30    | 120   | 150 | 2 |

Table 5. The constants from Langmuir equation based on data adsorption of dyes in aqueous solution and mixtures – pH 3.0.

| Dyes   | Coincidence coefficient | $K_1$ | $K_2$ | $b_1$ | $b_2$ | $b$ | n  |
|--|-------------------------|-------|-------|-------|-------|-----|----|
| Scarlet R (control sample)                     | 0.0234                  | 1.3   | 0.15  | 230   | 42    | 272 | 1  |
| Mixture: Scarlet R and Borutosol KRN           | 0.069                   | 2.8   | 0.1   | 218   | 22    | 240 | 1  |
| Mixture: Scarlet R and Siarczanol N-2          | 0.0983                  | 0.01  | 0.09  | 180   | 30    | 210 | 6  |
| Mixture: Scarlet R and Rokafenol N-8           | 0.3053                  | 0.1   | 0.06  | 190   | 120   | 310 | 5  |
| Brilliantorange 3R (control sample)            | 0.0126                  | 1.1   | 0.1   | 90    | 145   | 235 | 1  |
| Mixture: Brilliantorange 3R and Borutosol KRN  | 0.0372                  | 3     | 0.06  | 140   | 100   | 340 | 2  |
| Mixture: Brilliantorange 3R and Siarczanol N-2 | 0.0579                  | 2     | 0.03  | 140   | 50    | 190 | 2  |
| Mixture: Brilliantorange 3R and Rokafenol N-8  | 0.1562                  | 5     | 0.1   | 160   | 50    | 210 | 2  |
| Black DN (control sample)                      | 0.0183                  | 8.6   | 0.008 | 200   | 8     | 208 | 1  |
| Mixture: Black DN and Borutosol KRN            | 0.0313                  | 1.9   | 0.9   | 180   | 80    | 290 | 4  |
| Mixture: Black DN and Siarczanol N-2           | 0.539                   | 1.1   | 0.9   | 200   | 80    | 280 | 10 |

solution onto nonpolar surfaces as well as to interaction with specific charge-related soil sorption sites. As soil pH is decreased, the S-triazine molecules become protonated and these cations can be adsorbed by soil clay minerals in exchange for an exchangeable cation. The addition of acid also causes the same cation on the clay to be replaced by hydrogen and the result may adsorb the neutral molecule S-triazine.

Similarly, it can be supposed that protoionization of the amine group in Black DN molecules might lead to ion exchange between Black DN and anionic surfactants (Borutosol KRN and Siarczanol N-2), causing in this way an association of dye-surfactant. Additionally, hydrophobic interactions between surfactants and dye cannot be precluded. Dye-surfactant attraction to chitin results in an increase of dye and surfactant adsorption. Majed Abu-

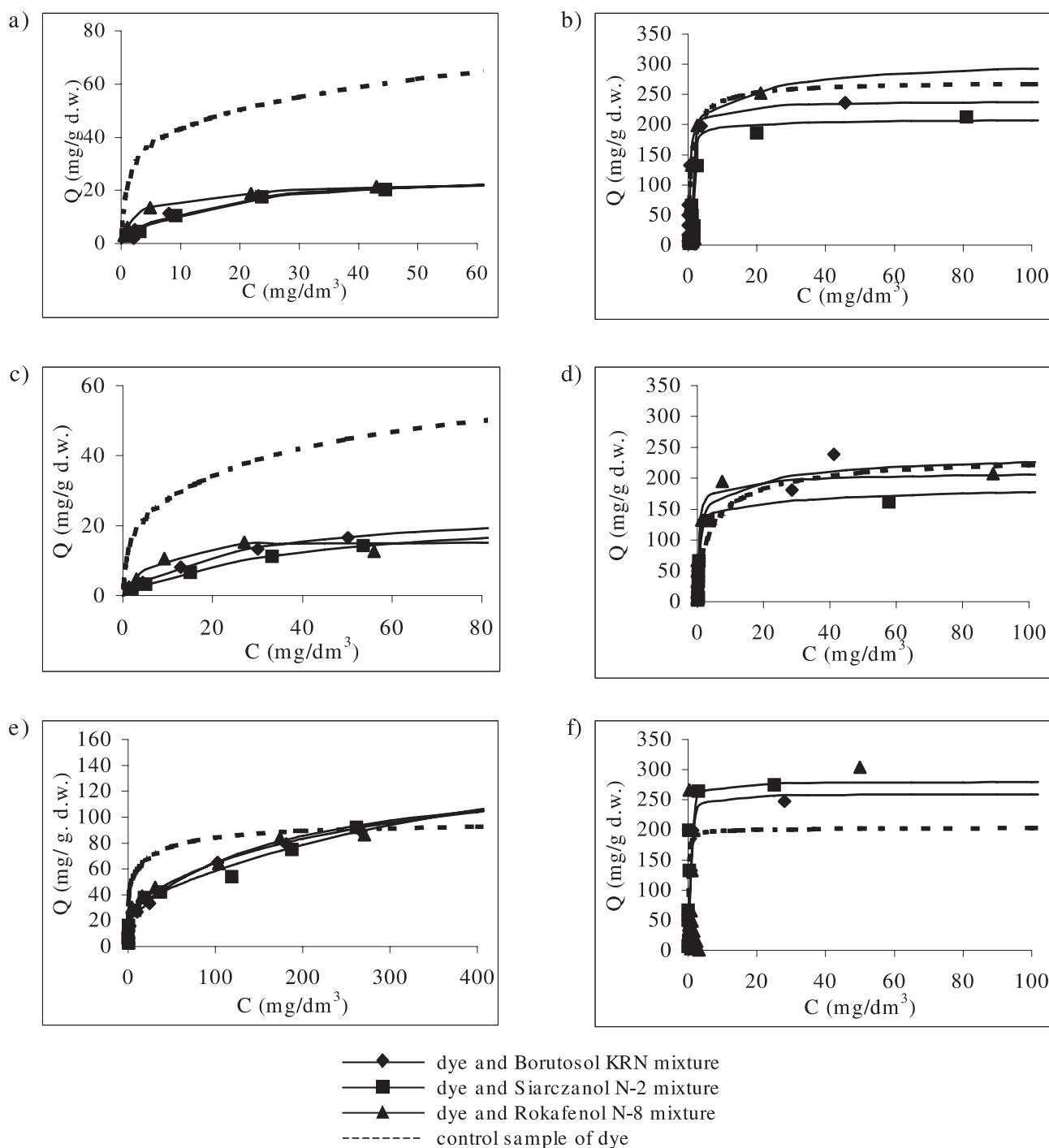


Fig. 1. The mass of adsorbed dyes depending on equilibrium concentration in samples at pH 6.2 (a, c, e) and pH 3.0 (b, d, f): a) and b) Scarlet R, c) and d) Brilliantorange 3 R, e) and f) Black DN.

Zreig [28] observed a favourable influence of surfactants on atrazine adsorption. Correspondingly with the increase in concentration of anionic Suphonic and non-ionic Rexol the increase in adsorption of atrazine in all soils was stated. The increase of atrazine adsorption in the presence of Rexol was caused by strong interaction between two hydrophobic molecules.

Atun et al. [18] studied adsorption of safranine-O on the hydrophilic and hydrophobic glass powder surfaces.

It was observed that safranine-O was adsorbed in different ways both as monomers and micelles depend on the types of surfaces. The adsorption isotherm of safranine-O on hydrophilic glass powder was S-shaped, which indicated the perpendicular orientation of adsorbate molecules on the surface. The striking increase in the apparent adsorption of safranine-O can be qualitatively rationalized in terms of much stronger attraction of highly positively charged micelles rather than monovalent

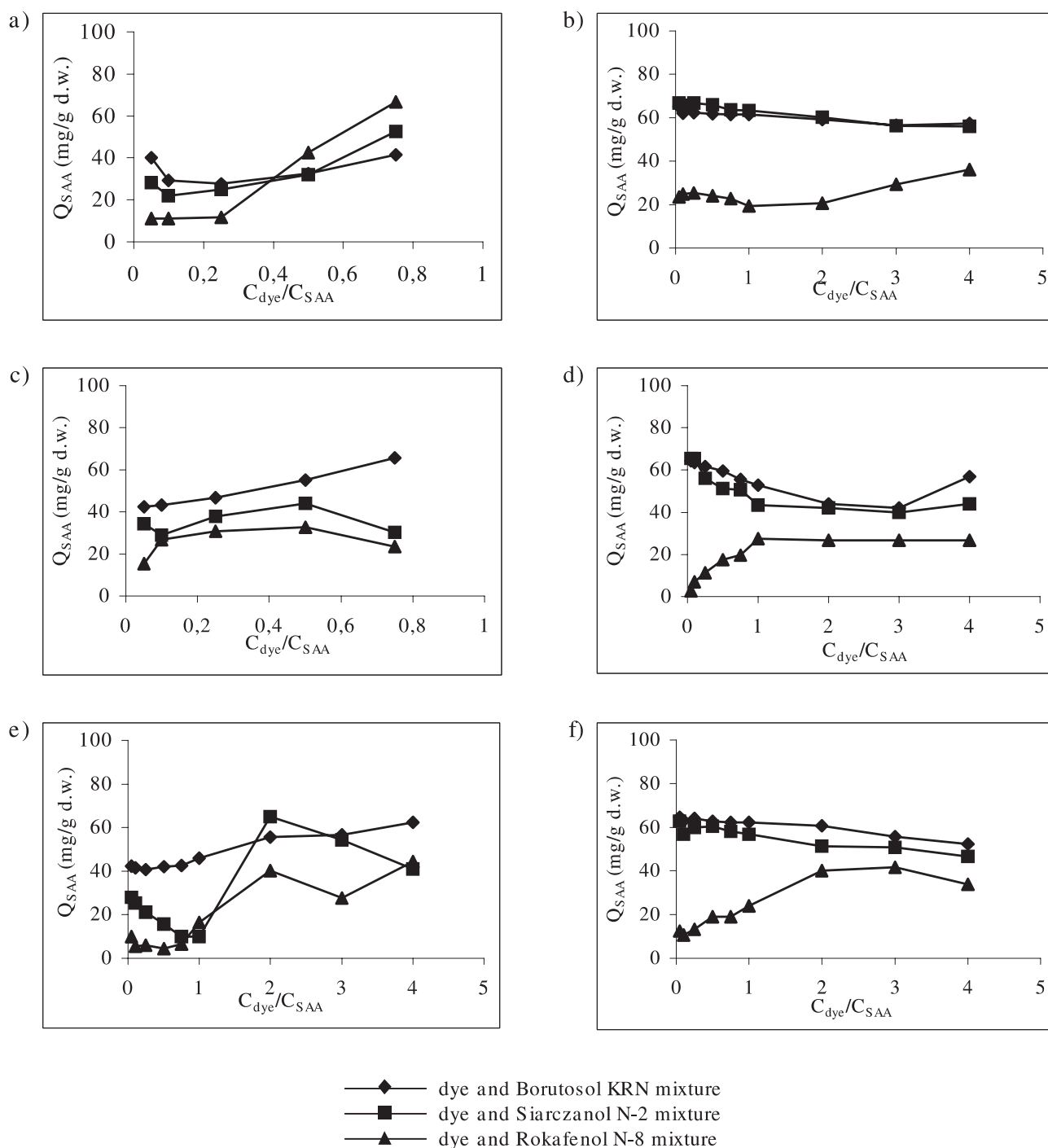


Fig. 2. The mass adsorbed SAA at different proportion  $C_{dye}/C_{SAA}$  in samples at pH 6.2 (a, c, e) and pH 3.0 (b, d, f): a) and b) Scarlet R, c) and d) Brillantorange 3 R, e) and f) Black DN.

monomers by the negatively charged hydrophilic glass powder. The adsorption isotherm of safranin-O on hydrophobic glass powder was L-shaped, which indicated that the adsorption was at least partly flatwise with the hydrophobic portion lying along the surface.

#### The Mass of Adsorbed Surfactant ( $Q_{SAA}$ ) at Various $C_{dye}/C_{SAA}$ Ratios in Solution

According to established assumptions, the dye concentration increased in the following samples, while surfactant concentration was constant. In such cases it can be accepted that an increasing dye concentration was a limiting factor, which affects surfactants adsorption in the samples. The results presenting the mass of adsorbed surfactants at various proportion of dye and surfactant initial concentration  $C_{dye}/C_{SAA}$  are shown in Fig. 2.

From obtained data it appears that at pH 3.0 Borutosol KRN and Siarczanol N-2 showed similar adsorption behaviour, regardless of dye type and clearly differences in surfactants adsorption at pH 6.2 depending on dye and surfactant type.

At pH 6.2 for Borutosol KRN and Siarczanol N-2 independently on adsorption initial conditions expressed as a proportion of Scarlet R and surfactant concentration (Fig. 2a); the mass of adsorbed surfactants started from  $C_{dye}/C_{SAA} = 0.1$  showed increasing tendency. A significant increase in Rokafenol N-8 adsorption from mixture with Scarlet R followed at  $C_{dye}/C_{SAA} > 0.25$ , the range at which adsorption approached the maximum value (Fig. 2a).

At pH 6.2 for mixtures with Brillantorange 3R quite significant differences in surfactants adsorption were stated. The highest values (from 42.6 to 65.6 mg/g d. w.) was obtained for Borutosol KRN, next for Siarczanol N-2 (on average 35 mg/g d. w.) and Rokafenol N-8 (on average 26 mg/g d. w.) (Fig. 2c). The mass of adsorbed surfactants (Borutosol KRN and Rokafenol N-8) at pH 6.2 in Black DN presence showed clear increasing tendency correspondingly with the increase of proportion between dye and surfactant concentration ( $C_{dye}/C_{SAA} > 1$ ).

At pH 3.0, the mass of adsorbed Borutosol KRN and Siarczanol N-2 were the highest at low  $C_{dye}/C_{SAA}$  values and it showed a slight decrease along with an increase of  $C_{dye}/C_{SAA}$  proportion (Fig. 2b, d, f). The amount of adsorbed Borutosol KRN and Siarczanol N-2, independent of dye type, was always higher than Rokafenol N-8.

#### The Ratio ( $r_{Q/C}$ ) Between the Mass Proportion of Dye and Surfactant Adsorbed onto Chitin ( $Q_{dye}/Q_{SAA}$ ) and Proportion of Initial Dye and Surfactant Concentration in Solution ( $C_{dye}/C_{SAA}$ )

The data analysis ( $Q_{dye}/Q_{SAA}$ ), depending on initial reaction conditions ( $C_{dye}/C_{SAA}$ ), allows us to estimate the competition between dyes and surfactants of active sites

of chitin. When the  $Q_{dye}/Q_{SAA}$  increases linearly with increase of the  $C_{dye}/C_{SAA}$ , the measure of competition is  $r_{Q/C}$  value, which numerically corresponds to the value of straight regression coefficient. When  $r_{Q/C} = 1$ , proportion between the mass of adsorbed dye and surfactant changes are identical as a proportion of dye and surfactant concentration in solution,  $r_{Q/C} > 1$  means preferable dye adsorption, while  $r_{Q/C} < 1$  means preferable surfactant adsorption (Fig. 3).

The results (Fig. 4) allow to state that in no experiment were ideal straight lines obtained, although at pH 3.0 in the experiment with dye mixtures with Borutosol KRN or Siarczanol N-2 the relationship between  $Q_{dye}/Q_{SAA}$  and  $C_{dye}/C_{SAA}$  was nearly linear.

At pH 6.2 the  $Q_{dye}/Q_{SAA}$  values for low  $C_{dye}/C_{SAA}$  appeared in region  $r_{Q/C} > 1$ , whereas along with the  $C_{dye}/C_{SAA}$  increase in region  $r_{Q/C} < 1$ . It was observed that the  $Q_{dye}/Q_{SAA}$  proportion decreased at maximum dye saturation of chitin correspondingly with the increase of surfactant adsorption from solution. Such a mechanism was evidently observed in the Black DN and Rokafenol N-8 mixture (Fig. 4e). At the  $Q_{dye}/Q_{SAA}$  proportion achieved maximum value at  $C_{dye}/C_{SAA}$  between 0.75 and 1, which corresponded with low Rokafenol N-8 adsorption. Dyes adsorption caused the chitin surface to become more hydrophobic, making the attraction of non-ionic Rokafenol N-8 possible. The  $Q_{dye}/Q_{SAA}$  was kept at  $r_{Q/C} < 1$  when  $C_{dye}/C_{SAA} = 1$ , and next along with increase of the  $C_{dye}/C_{SAA}$  (Fig. 4e).

It was observed that at pH 3.0 for all  $C_{dye}/C_{SAA}$  values, the experimental data ( $Q_{dye}/Q_{SAA}$ ) were kept at region  $r_{Q/C} > 1$ . Higher  $Q_{dye}/Q_{SAA}$  values obtained for Rokafenol N-8 were identical as for Borutosol KRN and Siarczanol N-2 proportion as  $C_{dye}/C_{SAA}$  caused that the amount of Rokafenol N-8 adsorbed from solutions containing each dye was small (Fig. 4b, d, f). There was nearly a linear relationship between  $Q_{dye}/Q_{SAA}$  and  $C_{dye}/C_{SAA}$  proportions for Borutosol KRN and Siarczanol N-2, indicating a competitive mechanism between dyes and surfactants of active sites of chitin. Similar results were obtained by Nevskaja et al. [29] during phenol and aniline adsorption from mixtures on both heated and unheated activated carbon. The authors have stated that more phenol than ani-

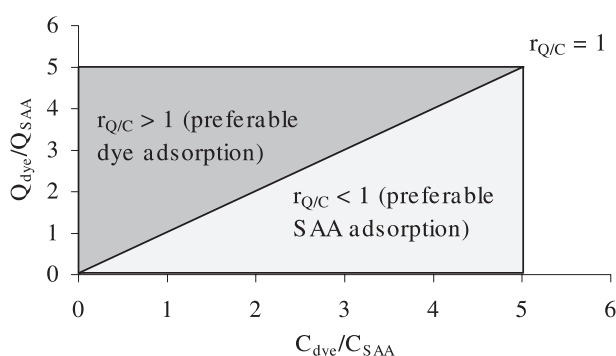


Fig. 3. Hypothetical diagram showing the ratio  $r_{Q/C}$ .

line was adsorbed. Furthermore, the total adsorbed amounts from the different mixtures (phenol + aniline) were very close to the adsorbed amounts of single compounds. This fact implies that the adsorption from mixtures has a competitive nature. From other experimental studies, research carried out by Snukiskis et al. [30] showed that during simultaneous adsorption of surfac-

tants and heavy metals (Pb, Ni, Zn) mixture in polyacrylic acid-functionalized cation-exchanger, the authors observed that in the presence of Pb (II) or Zn (II) the equilibrium sorption of ALM-10 (non-ionic surfactant) is lower than without metal. This is due to simultaneous and competing sorption of metal cations. The cosorption of metal (II) and surfactant leads to a decrease in the

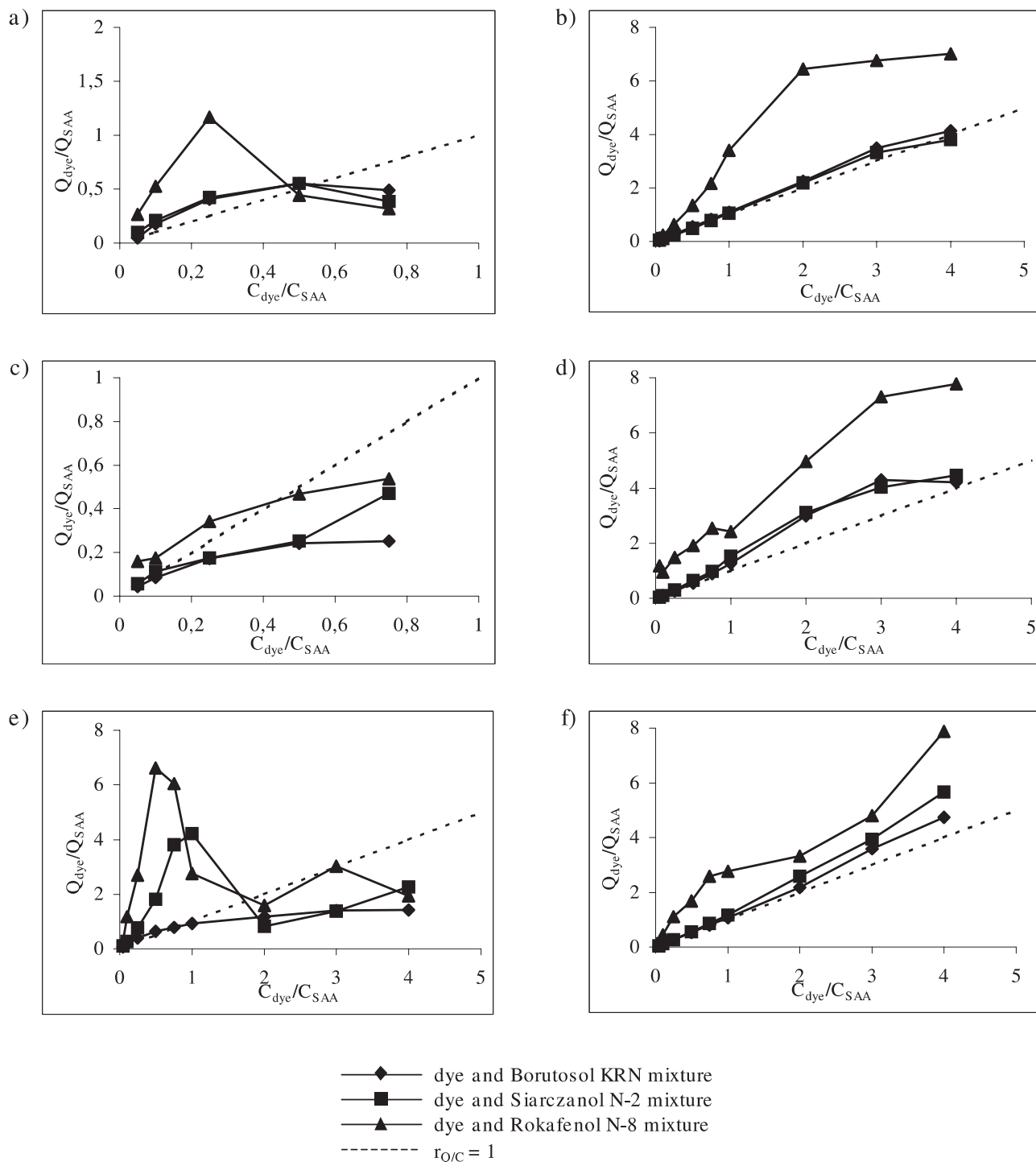


Fig. 4. Proportion of  $Q_{dye}/Q_{SAA}$  at different proportion  $C_{dye}/C_{SAA}$  in samples at pH 6.2 (a, c, e) and pH 3.0 (b, d, f): a) and b) Scarlet R, c) and d) Brilliantorange 3 R, e) and f) Black DN.



equilibrium sorption of both the metal (II) and the surfactant.

### Conclusions

1. From obtained data it results that surfactants influence on dye adsorption was depended most importantly on pH value and type of dye and less so on surfactant type. For Black DN (chlorotriazine dye), surfactants presence caused an increase of maximum adsorption capacity. For vinyl-sulfonate dyes at pH 6.2 negative influence of surfactants on adsorption was observed. The adsorption capacity was clearly lower in comparison with control sample. At pH 3.0 this negative influence was smaller.
2. Rokafenol N-8 was adsorbed the weakest from among tested surfactants. At pH 3.0 the differences between adsorption of Rokafenol N-8 (non-ionic surfactant) and Borutosol KRN and Siarczanol N-2 (anionic surfactants) were quite clear. In a significant number of experiments at pH 6.2 and along with the increase of dye concentration an increasing tendency of  $Q_{SA}$  was observed. At pH 3.0, except for Rokafenol N-8, the mass of adsorbed surfactants decreased correspondingly with an increase in dye concentration.
3. Accepting the ratio between proportion of dye and surfactant mass adsorbed onto chitin ( $Q_{dye}/Q_{SA}$ ) and proportion of initial dye and surfactant concentration in solution ( $C_{dye}/C_{SA}$ ) as a measure of competition, it can be stated that regardless of dye type, at pH 3.0 Borutosol KRN and Siarczanol N-2 competed stronger than Rokafenol N-8 of active sites of chitin.

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