The Effectiveness of Surfactants Adsorption onto Chitin and Dye-Modified Chitin

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Abstract

Adsorption of anionic (Borutosol KRN, Siarczanol N-2) and nonionic (Rokafenol N-8) surfactants onto chitin and dye-modified chitin (Brillantorange 3R, Scarlet R and Black DN) was investigated. Experiments were carried out at pH 3.0 and pH 6.2. The Langmuir-Freundlich model was used to describe adsorption isotherms. It was proved that adsorption isotherms of SAAs* onto chitin were S-type. The adsorption was the most effective for anionic SAAs. It was stated that adsorption of SAAs onto dye-modified chitin depended on dye type, bound previously onto chitin and on pH adjustment. At pH 3.0, for vinyl dye-modified chitin (Brillantorange 3R, Scarlet R) the highest adsorption capacities at plateau region were stated for Borutosol KRN (320 and 330 mg/g d.w., respectively) and Siarczanol N-2 (290 and 310 mg/g d.w.). However, for Black DN-modified chitin, the mass of adsorbed anionic surfactants was distinctly lower – 120 mg/g d.w. for Borutosol KRN and 13 mg/g d.w. for Siarczanol N-2. The pH increase from 3.0 to 6.2 caused a drop in amount of SAAs adsorbed at plateau region.

Dye solubilization was demonstrated for dye-modified chitin. The amount of dissolved dyes in solution depended on pH adjustment as well as SAA type. At pH 3.0, for anionic SAAs dye solubilization increased clearly with the increase of SAA concentrations. Nonionic Rokafenol N-8 almost did not cause dye solubilization. At pH 6.2 dye solubilization was nearly independent of SAA concentration.

Keywords: surfactants, dye-modified chitin, adsorption, Langmuir-Freundlich, dye solubilization, SAAs* - surface active agents

Introduction

World production of textiles is running at about 30 million tons annually and shows an upward trend of approximately 3% a year [1]. Water consumption in textile industry comes to, on average, 100 m^3/t textiles [2]. It is estimated that about 10% of dye production is annually discharged in effluents from textile and associated industries. It corresponds to 1 mln kg/year [3]. Therefore,

removal of dyes from textile wastewater is an important environmental problem.

Adsorption is a method widely used in removal of contaminants from wastewater. In recent years, much research connected with dye removal has been carried out using various types of adsorbent. Among them are agricultural-waste residues such as apple pomace, wheat straw, corncob or barley husk [4,5], dolomite [6], peat [7], biosorbents, for example: *Spirodela polyrrhiza* [8], *Aspergillus foetidus* [9], yeasts [10], activated sludge biomass [11], tree fern [12], chitin [13,14] and chitosan [3,15]. The studies were applied

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to removal of single dyes from aqueous solutions. The equilibrium adsorption data usually were described by means of Langmuir or Freundlich equation. It could be used for comparison of adsorption behaviour for tested adsorbents or for various experimental conditions.

Among tested adsorbents, chitin and especially its deacetylated derivative chitosan, has shown high adsorption capacity, mainly with reference to reactive dyes. Wu et al. [16] obtained high maximum adsorption capacity of chitosan for Reacive Red 222 (1106 g/kg). Higher monolayer adsorption capacities for Reactive Blue 2 (2498 g/kg) and Reactive Yellow 2 (2436 g/kg) were stated by Chiou et al. [15] during dye adsorption onto cross-linked chitosan beads. It was observed that reactive dyes owing to their dyeing properties are commonly used in the textile industry.

Nevertheless, design operations of adsorption systems in textile wastewater treatment still encounter some limitations. The textile wastewater apart from dyes also contain numerous organic and inorganic compounds, among them surfactants. So far, relatively less attention has been paid to adsorption of dye-surfactant systems. Therefore, more and more research of modelling adsorption in a binary or ternary dye system have been developed [17]. The knowledge of dyes and surfactants coadsorption is important both in design systems of dyes and SAA removal from textile wastewater.

The interactions between surfactants and organic substances were investigated for nonionic SAAs and phenol and its alkyl-derivatives [18,19] or nonionic and anionic surfactants with atrazine [20]. For phenol, it was observed that nonionic surfactant can enhance its adsorption at the solid/liquid interface, whereas adsorption of atrazine was more efficient in anionic SAA presence. Klimiuk et al. [21] earlier investigated adsorption from mixtures containing dyes at concentrations ranging from 5 to 500 mg/dm^3 and SAAs at constant concentration of 100 mg/dm^3 onto chitin. The authors have proved that at pH 6.2 SAA presence influenced a decrease in maximum adsorption capacity of chitin for vinyl dyes, while at pH 3.0 it did not affect their adsorption. However, for chlorotriazine dye positive correlation was observed in both pH ranges. Chorro et al. [22] investigated adsorption of dodecyltrimethylammonium and dodecyldimethylammonium bromides on silica surface. In their opinion, even small amounts of impurities on adsorbent surface, to a large extent, can affect sorption mechanism of SAAs both from the qualitative (mechanism of adsorption) and the quantitative aspect (adsorption capacity).

In the present study, the investigations were undertaken on surfactants adsorption onto chitin and chitin modified by binding of vinyl dyes (Brillantorange 3R, Scarlet R) or chlorotriazine dye (Black DN) (so-called dyes-modified chitin).

The objective of this work was to explain in what manner dyes previously bound on chitin affect SAA adsorption. The experiments were carried out for three surfactants: Borutosol KRN, Siarczanol N-2 and Rokafenol N-8 at pH 3.0 and 6.2. Additionally, in this study the degree of dye solubilization was estimated.

Table 1. Chitin flake characteristics.

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

Materials and Methods

Materials

The chitin used in present work was extracted from krill and purchased from the Sea Fishing Institute in Gdynia, Poland. Chitin flake characteristics were shown in Table 1.

Chitin Preparation

In this research 10 g of raw chitin was poured with 100 cm^3 of distilled water and left to expand for 24 h. Next, chitin was washed with 6 N HCl and distilled water until the neutral pH was obtained. The aim of acid washing was the removal of calcium and magnesium ions from chitin. After that, chitin was poured with 5 N KOH solution and boiled for 3 hours at 100°C. The degree of chitin deacetylation was 7.23%. The chitin prepared in this way was used in further adsorption experiments.

Surfactants

In this experiment the following surfactants were used:
− anionic, represented by Borutosol KRN (polycondensate formaldehyde naphtalensulfonate acids sodium salts and carboxylic polyacids mixture) and Siarczanol N-2 (sulfonates of higher fatty alcohols mixture);
− nonionic, represented by Rokafenol N-8 (nonyl phenol polioxyethylene ether).

Experimental

The adsorption experiments were conducted in the following way. The samples containing the weight of chitin (1.5 g d.w./dm^3) and 100 cm^3 of surfactant solution with increasing concentrations from 5 to 500 mg/dm^3 were shaken (type 385c, Elpan firm) for 2 hours. The experiments were carried out with and without pH

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┌─────────────────────────────────────┐
│               CHITIN                 │
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Chitin modification with
reactive dyes
Initial concentrations:
pH 3.0 – 300 mg/dm³
pH 6.2 – 150 mg/dm³

Experiment 1

Experiment 2

Adsorption of SAAs
at pH 3.0 and 6.2
Concentrations: 5-500 mg/dm³

Adsorption of SAAs
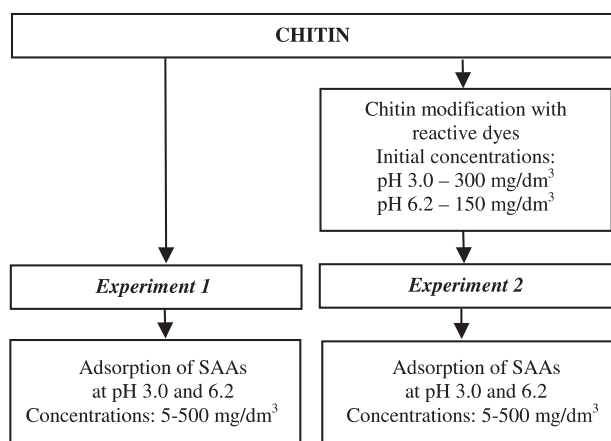at pH 3.0 and 6.2
Concentrations: 5-500 mg/dm³

Fig. 1. Experimental procedure.

adjustment (3.0 and 6.2, respectively). The solution pH was adjusted by 0.1N HCl. After shaking, the samples were left to settle for 10 min., decanted and centrifuged on centrifuge type MPW 210 at a rotation speed of 10,000 rpm for 10 min.

Two series were conducted. Experimental procedure was shown in Fig. 1. In experiment 1 chitin as described above was used, while experiment 2 used dye-modified chitin. The weighed portion of chitin was put into 200 cm³ Erlenmeyer flasks and poured with 100 cm³ of dye solution. The dye concentration in series at pH 3.0 was 300 mg/dm³ and in series at pH 6.2 was 150 mg/dm³. The samples were shaken for 2 hours. The dye-modified chitin was separated onto filter and transfered to flasks. Then surfactant adsorption tests were performed. 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. Brillatorange 3R was distributed by "Hoechst" Co., Łódź, Poland.

Analytical Methods

In order to measure the surfactant concentrations, supernatant was analyzed using a UV/Vis spectrometer (VSU 2-P) at the following wavelengths (λ): Borutosol KRN – 230 nm, Siarczanol N-2 – 220 nm, Rokafenol N-8 – 275 nm. To access a degree of dyes solubilization during surfactant adsorption onto dye-modified chitin, the samples were also analyzed for reactive dyes at the wavelengths (λ): Brillantorange 3R and Scarlet R – 490 nm, Black DN – 580 nm. Estimation of surfactants and dye concentrations in supernatant were calculated on the basis of analytical curves and conversion rates.

The pH solution was measured by using pH-meter type HI 8818.

Results

Adsorption of SAAs onto Chitin

The adsorption isotherms are expressed in milligram of adsorbed surfactant per gram of chitin (Q) versus the surfactant concentration (C) at adsorption equilibrium. It was observed that the best fitting of experimental data corresponded to Langmuir-Freundlich equation (1):

$$Q = \frac{b \cdot K \cdot C^{n}}{1 + K \cdot C^{n}} \qquad (1)$$

Q – the amount of surfactant adsorbed onto chitin (mg/g d.w.)
b – maximum adsorption capacity of chitin (mg/g d.w.)
C – concentration of surfactant in solution (mg/dm³)
K, n – constants in Langmuir-Freundlich equation

The shape of isotherms was S or L-type, according to the classification of Giles et al. [23]. The isotherms were S-shaped when $n > 1$, and L-shaped for $n = 1$.
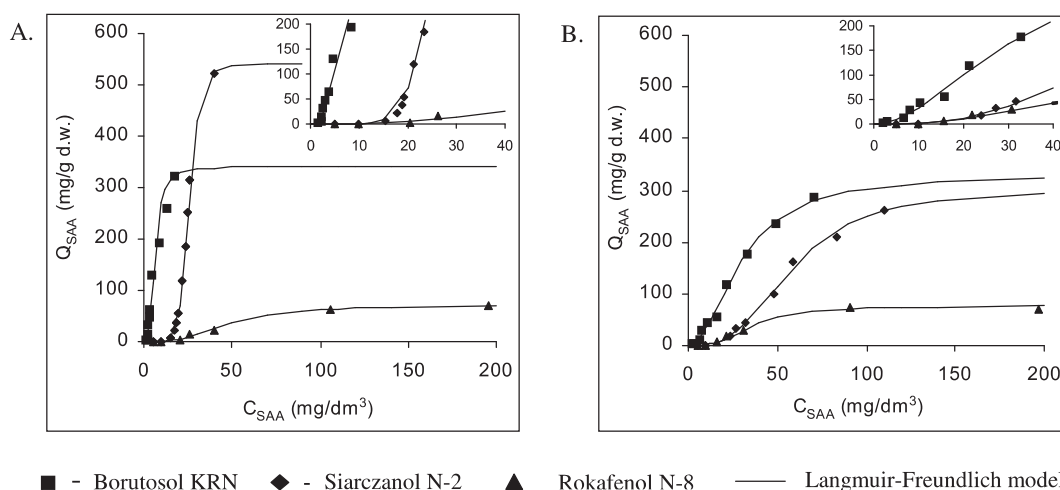

■ - Borutosol KRN   ◆ - Siarczanol N-2   ▲ Rokafenol N-8   —— Langmuir-Freundlich model

Fig. 2. Experimental data and isotherms of surfactants adsorption onto chitin: A – pH 3.0; B – pH 6.2.

Table 2. The mass of dyes bound onto chitin.

Reactive dye	Molecular weight of dyes [g/mole]	The mass of dye bound onto chitin [mole/g d.w.]	
		pH 3.0	pH 6.2
Brillantorange 3R	633	0.371	0.104
Scarlet R	549	0.488	0.173
Black DN	673.5	0.308	0.142

Table 3. The constants from Langmuir-Freundlich equation based on data adsorption of surfactants onto chitin and dye-modified chitin at pH 3.0 and 6.2.

Sample	SAA*	The constants from Langmuir-Freundlich equation							
		pH 3.0				pH 6.2			
		K	b	n	CC*	K	b	n	CC*
Chitin	Borutosol KRN	$4 \cdot 10^{-3}$	340	3	0.0502	$1.1 \cdot 10^{-3}$	330	2	0.0055
	Siarczanol N-2	$6 \cdot 10^{-12}$	540	8	0.0037	$6 \cdot 10^{-6}$	300	3	0.0115
	Rokafenol N-8	$8.7 \cdot 10^{-6}$	70	3	0.0071	$3 \cdot 10^{-5}$	76	3	0.0161
Brillantorange 3R-modified chitin	Borutosol KRN	$1.6 \cdot 10^{-2}$	320	1	0.0245	$6 \cdot 10^{-4}$	70	2	0.0104
	Siarczanol N-2	$2.1 \cdot 10^{-2}$	290	1	0.0246	$2.1 \cdot 10^{-5}$	34	2	0.0137
	Rokafenol N-8	$2.1 \cdot 10^{-2}$	100	1	0.0426	0.54	19	1	0.3032
Scarlet R-modified chitin	Borutosol KRN	$3.2 \cdot 10^{-2}$	330	1	0.0087	$8.3 \cdot 10^{-4}$	90	2	0.0325
	Siarczanol N-2	$2.1 \cdot 10^{-2}$	310	1	0.0293	$1.0 \cdot 10^{-21}$	50	10	0.0447
	Rokafenol N-8	$3.2 \cdot 10^{-2}$	21	1	0.0816	0.6	17	1	0.5653
Black DN-modified chitin	Borutosol KRN	$1.4 \cdot 10^{-2}$	120	1	0.0121	$1.5 \cdot 10^{-2}$	130	1	0.0135
	Siarczanol N-2	$1.3 \cdot 10^{-6}$	13	4	0.0336	$8.0 \cdot 10^{-5}$	90	2	0.0333
	Rokafenol N-8	$1.3 \cdot 10^{-7}$	85	4	0.0050	$9 \cdot 10^{-5}$	36	2	0.0223

CC* - coincidence coefficient, SAA* - Surface Active Agent

Experimental data and isotherms obtained from equation (1) for Borutosol KRN, Siarczanol N-2 and Rokafenol N-8 at pH 3.0 and 6.2 are presented in Figs. 2A, B.

The parameters n and b determined from equation 1 should be mainly considered qualitatively in comparison with tested SAAs (Tab. 3). It was observed that for surfactants adsorbed onto chitin, n constants were always more than 1. The highest value ($n = 8$) was obtained for Siarczanol N-2 at pH 3.0. From experimental data it can be noticed that two-step adsorption with the first plateau was formed at a very low degree of chitin coverage (Figs. 2A, B).

Additionally, our own research has confirmed that pH increasing from 3.0 to 6.2 caused strong decrease in amount of adsorbed Siarczanol N-2 at plateau region and decrease of n value (Tab. 3). From isotherm shapes it also results that the amount of adsorbed SAAs at plateau region was higher for Siarczanol N-2 and Borutosol KRN than

for Rokafenol N-8 (Figs. 2A, B). The amount of Rokafenol N-8 adsorbed onto chitin at the isotherm plateau was comparable to 70 and 76 mg/m d.w. at two pH ranges.

Adsorption of SAAs onto Dye-Modified Chitin

The mass of dyes bound during chitin modification at pH 3.0 and 6.2 is shown in Table 2. The results indicate that Scarlet R, which was characterized by the smallest molecular weight, was adsorbed the most effectively onto chitin (0.488 mole/g d.w. and 0.173 mole/g d.w. at pH 3.0 and 6.2, respectively). The amount of Black DN, dye with the highest molecular weight, was approximately 37% and 18% lower in comparison with Scarlet R at two pH ranges, respectively.

Experimental data and adsorption isotherms of surfactants onto Brillantorange 3R and Scarlet R-modified chi-

tin were shown in Fig. 3. Analyzing the isotherm's shape, it can be stated that at pH 3.0 for all surfactants and at pH 6.2 for Rokafenol N-8 adsorbed onto chitin modified with both dyes *n* constants were equal 1 (Tab. 3). This means that adsorption isotherms were L-type.

Our own research has demonstrated that the amount of adsorbed SAAs onto dye-modified chitin at plateau region depended on type of dye and pH adjustment. However, at pH 3.0 for vinyl dye-modified chitin, the similarity in adsorption behaviour for Borutosol KRN and Siarczanol N-2 was stated. The capability of SAAs adsorption at pH 3.0 formed in the following order: Borutosol KRN ≅ Siarczanol N-2 >> Rokafenol N-8 (Tab. 3). At pH 6.2, for Brillantorange 3R-modified chitin, the highest quantity of adsorbed SAA at plateau region was no-

ticed for Borutosol KRN and much lower for Siarczanol N-2 and Rokafenol N-8, that can be written as: Borutosol KRN ≥ Siarczanol N-2 >> Rokafenol N-8 (Tab. 3). It was observed that for Scarlet R-modified chitin the order of SAA adsorption at pH 3.0 was analogical as for Brillantorange 3R-modified chitin. This fact might be connected with structural similarity of dyes, which were used in chitin modification.

The pH adjustment from 3.0 to 6.2 had considerable, negative influence on the amount of adsorbed SAAs at plateau region, the strongest for anionic Siarczanol N-2. Adsorption of Rokafenol N-8 onto Scarlet R-modified chitin was insignificant in both tested pH ranges. It can be explained that Scarlet R-modified chitin caused repulsive interactions, preventing higher adsorption of Rokafenol N-8.
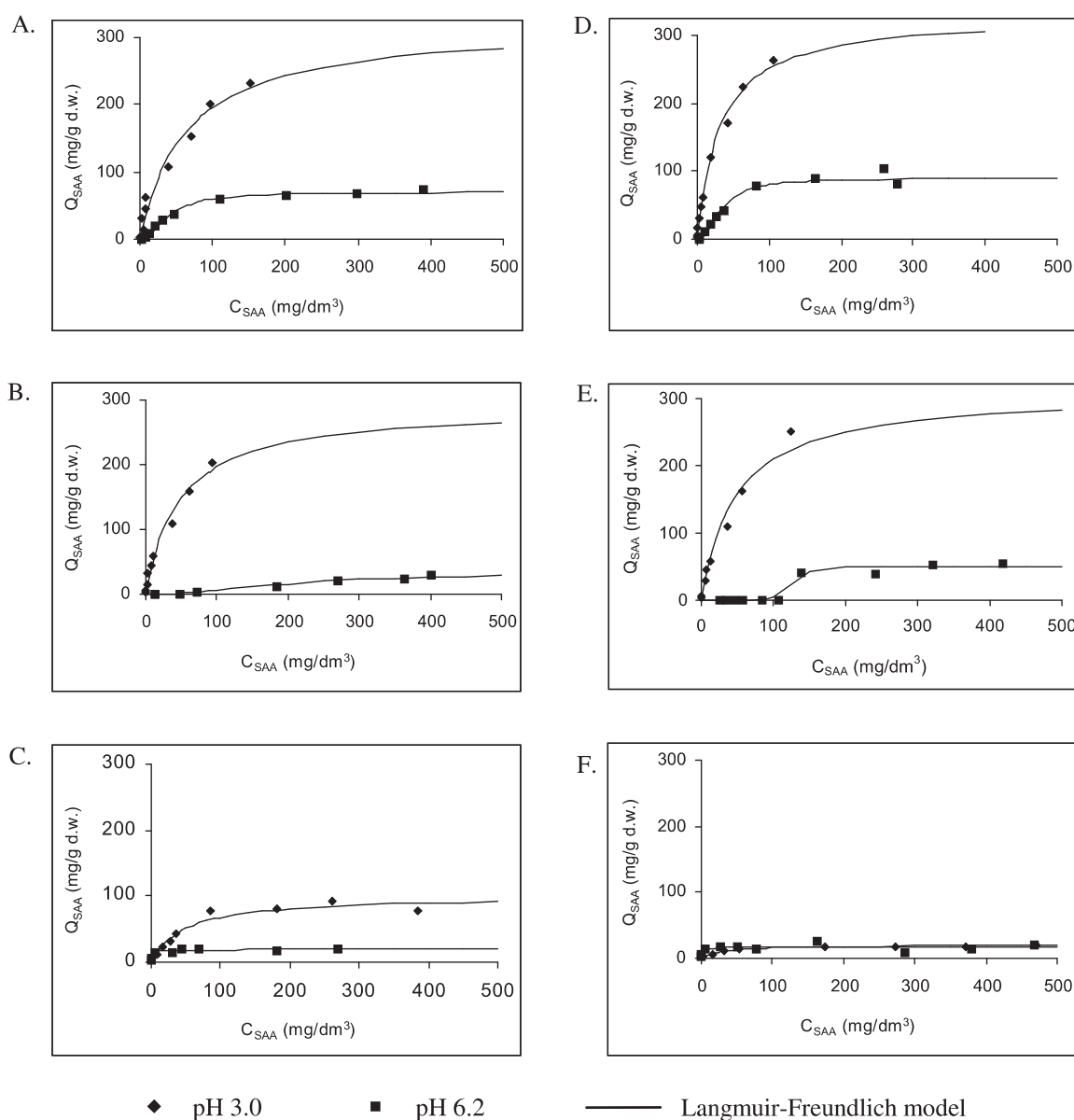

Fig. 3. Experimental data and isotherms of surfactant adsorption onto vinyl dyes-modified chitin at pH 3.0 and 6.2: A, D - Borutosol KRN; B, E - Siarczanol N-2; C, F - Rokafenol N-8.

The diversity of SAA adsorption behaviour was observed onto Black DN-modified chitin. In general, adsorption of SAAs onto Black DN-modified chitin proceeded weakly in comparison with vinyl dye-modified chitin. The amount of adsorbed SAAs at plateau region did not exceed 130 mg/g d.w. At pH 3.0 the amount of adsorbed SAAs at plateau region decreased as follows: Borutosol KRN > Rokafenol N-8 >> Siarczanol N-2 and at pH 6.2: Borutosol KRN > Siarczanol N-2 >> Rokafenol N-8. L-type isotherms were obtained only for Borutosol KRN in both pH ranges. Apart from this, the influence of pH on the amount of adsorbed Borutosol KRN was not stated (Fig. 4A). Additionally, n and b constants, determined from equation 1, were almost the same (Tab. 3).
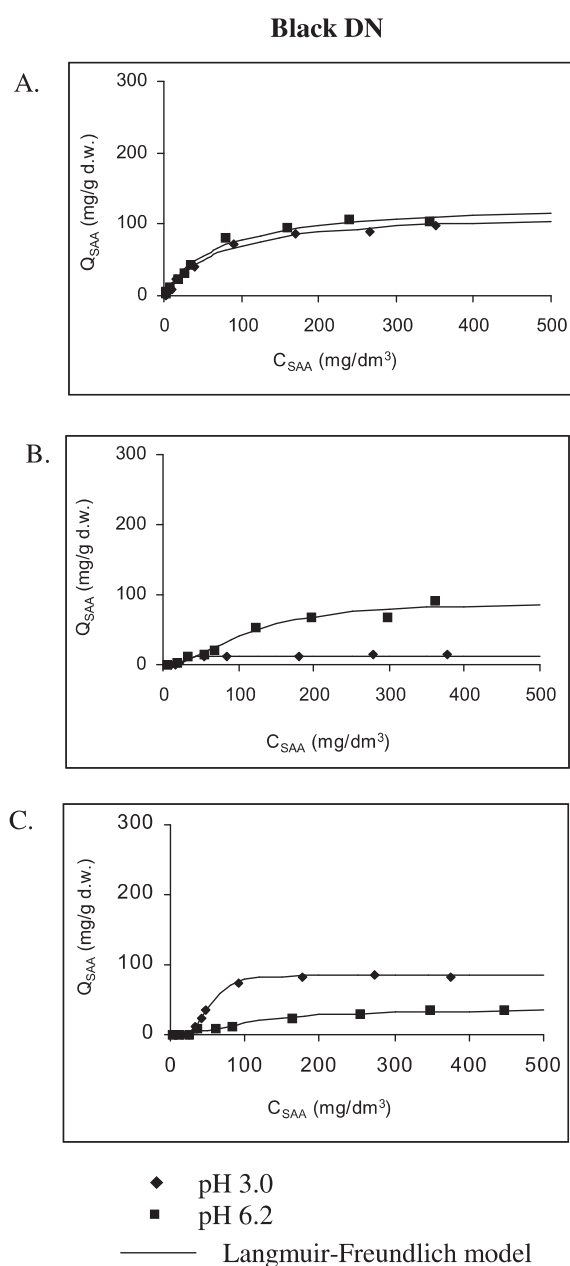
Black DN

Fig. 4. Experimental data and isotherms of surfactants adsorption onto chlorotriazine dye-modified chitin at pH 3.0 and 6.2: A - Borutosol KRN; B - Siarczanol N-2; C - Rokafenol N-8.

For Siarczanol N-2 and Rokafenol N-8 adsorption isotherms were S-shaped ($n > 1$). However, Siarczanol N-2 was better adsorbed at pH 6.2, while Rokafenol N-8 at pH 3.0.

The Influence of SAAs on Dye Solubilization from Chitin

The results of solubilization of tested dyes, depending on pH adjustment at different types of SAA, are shown in Fig. 5.

On the basis of obtained data, greater regularities of behaviour in dyes solubilization were observed in experiments carried out at pH 3.0. At this pH the strongest capability of dyes solubilization was demonstrated for Siarczanol N-2. Solubilization by Borutosol KRN and Siarczanol N-2 proceeded in the following order: Black DN > Brillantorange 3R > Scarlet R. Concentrations of solubilized dyes increased with increasing SAA concentrations. Rokafenol N-8 in the whole range of concentrations caused slight dye solubilization, decreasing in order: Brillantorange 3R (on average 0.63 mg/dm^3) > Black DN (on average 0.32 mg/dm^3) > Scarlet R (on average 0.14 mg/dm^3) (Figs. 5A, C, E).

Dye solubilization at pH 6.2, to the greatest extent, was depended on dye type. For Brillantorange 3R-modified chitin, it was stated that the amount of solubilized dye did not depend on surfactant concentration. Furthermore, the capability of dye solubilization by Borutosol KRN and Siarczanol N-2 was nearly identical (on average 7.8 mg/dm^3) and slightly lower by Rokafenol N-8 (6.3 mg/dm^3) (Fig. 5B). In the case of Scarlet R, the amount of dissolved dye in solution increased in the following order: Borutosol KRN > Siarczanol N-2 > Rokafenol N-8. When it comes to Rokafenol N-8, it did not depend on surfactant concentration. However, for Borutosol KRN and Siarczanol N-2 a slight increase in concentration of solubilized dye with increasing SAA concentration was demonstrated (Fig. 5D).

The capability of Black DN solubilization at pH 6.2 by Rokafenol N-8 and Borutosol KRN was insignificant and oscillated around 1 mg/dm^3. Siarczanol N-2 revealed the best ability of dye solubilization. As a result, dye concentration increased clearly with increasing SAA concentration (Fig. 5F).

Nonionic Rokafenol N-8 showed weakest dye solubilization from chitin, independent of dye type and pH adjustment.

Discussion

In this study adsorption of SAAs onto chitin, effect of chitin modification by binding of reactive dyes on SAAs adsorption and dye solubilization from chitin at pH 3.0 and 6.2 were investigated.

It is evident that adsorption isotherms of SAAs onto chitin were S-type ($n > 1$). The adsorption of anionic

surfactants (Borutosol KRN, Siarczanol N-2) onto chitin was more effective than nonionic Rokafenol N-8. It is commonly accepted that adsorption of ionic surfactants proceeds as a result of electrostatic interactions between acetamid groups of chitin and negatively charged SAAs.

The model of ionic surfactants adsorption on oppositely charged surfaces is currently reported by many authors [22, 24-27]. Surfactant monomers initially adsorb onto charged sites electrostatically and they act as nucleation points for further surfactant adsorption. At low concentrations, the surfactants adsorb parallel to the hydrophobic surface, resulting in a high free energy of adsorption. As the reagent concentration increases further, the adsorbed surfactant molecules reorient to form a monolayer in which the hydrophobic portion of the surfactant adsorbed

in a vertical configuration, leaving the polyethylene oxide chains extended into solution. In our investigations, distinctly higher ability of anionic SAAs adsorption can be attributed to electrostatic interactions between SAAs and protonated acetamide groups of chitin. The highest values of n and b obtained for anionic Siarczanol N-2 onto chitin at pH 3.0 might confirm that the mechanism described above could be predominant.

Generally, nonionic Rokafenol N-8 was weakly adsorbed onto chitin, regardless of pH adjustment. From literature review it follows that adsorption of nonionic surfactants involves a hydrogen bond between the oxygen atoms of their oxyethylenic chains and the hydroxyl groups or hydrophobic interaction at higher concentrations. Such mechanisms are now generally accepted for adsorption of
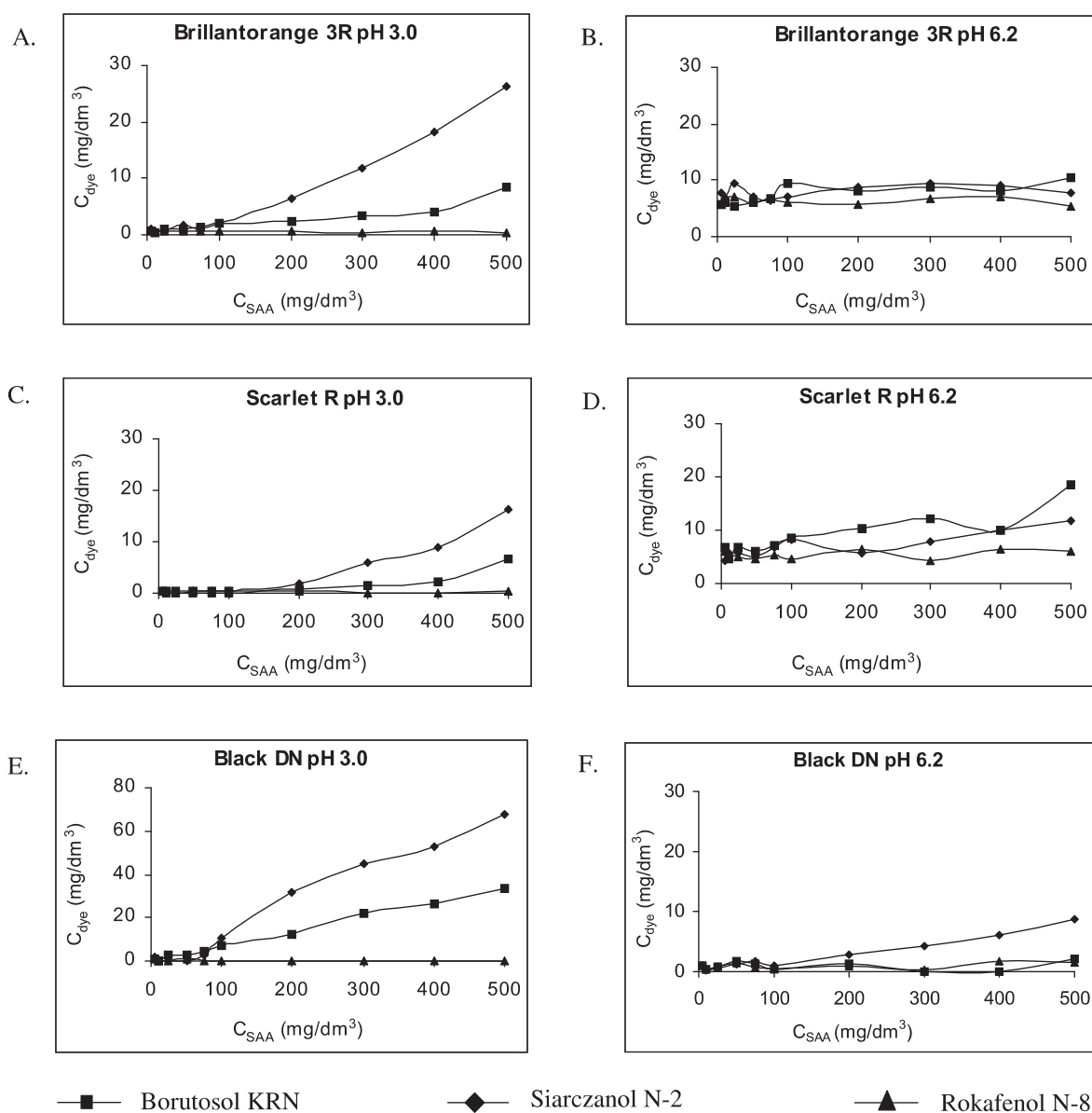

Fig. 5. Dye solubilization by SAAs: vinyl dyes: Brillantorange 3R: A. – pH 3.0, B. – pH 6.2; Scarlet R: C. – pH 3.0, D. – pH 6.2; chlorotriazyne dye: Black DN: E. – pH 3.0, F. – pH 6.2.

nonionic surfactants on silica [28,29] and quartz, kaolin, dolomite [30]. However, the hydroxyls must be free and sufficiently separated from other hydroxyls on the solid surface. According to Muzzarelli [31], the accessibility of hydroxyl groups on chitin is smaller in comparison with cellulose. It might result in small adsorption ability of nonionic Rokafenol N-8.

Chitin modification by binding of vinyl dyes caused a change of adsorption isotherm shapes from S to L-type at pH 3.0. Although at pH 6.2 isotherms were S-shaped, SAA adsorption at plateau region was clearly lower in comparison with chitin. The literature data indicate that S-shaped isotherms are obtained when longitunal axes of adsorbed molecules are perpendicular to the adsorbent surface. In L-type, longitunal axes of adsorbed molecules are parallel to the adsorbent surface. Nevskaia et al. [30] consider that S-shaped isotherms indicate interaction between hydrophobic moieties of surfactant molecules, whereas in L-shaped isotherms this kind of interaction is not present.

The mass of dyes adsorbed onto chitin at pH 3.0 decreased in the following order: Scarlet R > Brillantorange 3R > Black DN. Thereby, it can be concluded that Scarlet R-modified chitin was characterized by the smallest amount of bound dye molecules and the highest for Black DN-modified chitin. This phenomenon can be explained that the physical adsorption mechanism in small micropores is mainly pore filling, because the overlapping of pore wall potentials results in stronger binding of the adsorbate or enhanced adsorption. Larger molecules do not experience this adsorption phenomenon, even if there are multiple contact points between the adsorbate and adsorbent [32]. Musselman and Chander [33], investigating adsorption of nonionic surfactants on phtalocyanine and lampblack, did not preclude that decreases in adsorption plateau of nonionic SAAs could result from differences in the structures of both tested adsorbents. The presence of micropores in phtalocyanine pigment structure made penetration of larger surfactant molecules impossible, causing in this way a decrease in their adsorption density.

Our experimental data have shown that the amount of adsorbed Borutosol KRN and Siarczanol N-2 onto vinyl dye-modified chitin was high, and for Borutosol KRN it was comparable with chitin. However, small adsorption density was stated onto Black DN-modified chitin.

Theoretically, it can be assumed that for dye-modified chitin anionic SAAs could be adsorbed in active sites of chitin unoccupied by dye or as a result of dye-surfactant interactions. With regard to domination of the first mechanism, it might be expected that adsorption of anionic SAAs, which contain negatively charged sulfonate groups and compete with dyes of active sites of chitin, should be the highest for Black DN-modified chitin. This results from the smallest amount of Black DN moles adsorbed onto chitin at pH 3.0 (0.308 mole/g d.w.). However, from the research it follows that rather the chemical structure of bound dye used in chitin modification but not the number of active sites unoccupied by dye onto chitin affected SAA adsorption.

The experiments showed that dye solubilization was the greatest in anionic Siarczanol N-2 presence in comparison with nonionic Rokafenol N-8. At pH 3.0 and in anionic SAA presence the amount of dissolved dyes increased distinctly with increase of SAAs concentration in solution. Similar results were obtained by Doong et al. [34] for micellar surfactant solubilization of monocyclic aromatic compounds in soil system. The authors have obtained poor solubility of these compounds for Triton X-100 and better for anionic SDS, which increased linearly with the increasing concentration. The reason for such behaviour was the hydrophilic-hydrophobic balance. The hydration effect of Triton X-100 with the nonionic polar groups should be less significant than that of SDS, resulting in weaker interaction between nonpolar hydrocarbon group and aromatic compounds. Many investigators manifest the ability of surfactants to incorporate or partition organics within micelles [35,36].

From obtained data it results that solubilization degree also depended on type of dye used in chitin modification. Similarly, Choi et al. [37] reported that solubilization power is strongly dependent not only on the nature of the surfactant micelles but also on the structure of solubilized dye molecules. This was consistent with dye molecular size, suggesting that smaller molecules are solubilized more readily in micellar solutions.

In our research similar regularity was observed only at pH 6.2. Then, the smallest capability of solubilization was demonstrated for Black DN with the largest molecular weight, while the highest for Scarlet R with the smallest molecular weight. However, at pH 3.0 Black DN was solubilized by anionic SAAs, to a large extent, whereas at pH 6.2 Scarlet R.

Conclusions

1. Surfactant adsorption onto chitin was dependent on SAA type. Chitin has been shown to be a more effective adsorbent for anionic SAAs represented by Borutosol KRN and Siarczanol N-2 than for nonionic Rokafenol N-8 at both pH ranges. Adsorption isotherms were S-shaped and described by Langmuir-Freundlich equation.
2. Dye-modified chitin affected the shape of adsorption isotherms and amount of adsorbed SAAs at plateau region. At pH 3.0, adsorption isotherms of SAAs onto vinyl dyes-modified chitin were L-type. Binding of dyes caused a greater decrease in amount of adsorbed anionic SAAs at plateau region at pH 6.2 than at pH 3.0 in relation to chitin.
3. The effect of pH adjustment was dependent on procedure of chitin modification. At pH 3.0, adsorption of all tested SAAs onto chitin and vinyl dye-modified chitin was distinctly higher in comparison with adsorption at pH 6.2. However, for Black DN-modified chitin, the amount of anionic surfactants adsorbed at plateau region was greater at pH 6.2 than at pH 3.0.

4. Dye solubilization from dye-modified chitin was observed simultaneously with SAA adsorption. The concentration of dissolved dyes depended on pH adjustment and SAA type. At pH 3.0 it was changing, to a large extent, and increasing distinctly with an increase of anionic SAA concentration. In Rokafenol N-8 presence dye solubilization was insignificant. At pH 6.2, the influence of SAA concentration on dye solubilization was slight.

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