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Adsorption of Reactive Dyes by Modified Chitin from Aqueous Solutions

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Abstract

The adsorption of reactive dyes onto chitin (deacetylation degree = 5%) was investigated from aqueous solutions at pH 3. Ten reactive dyes were examined, including 5 dyes from the helactine group, 3 dyes from the polactine group and 2 dyes from the remazol group. The K and b constants were calculated from the Langmuir equation that assumes the presence of two sites of different nature. It was found that the dye adsorption on chitin in type I and II sites differed in both the adsorption affinity and maximum adsorption capacity. Based on the dimensionless separation factor R_L it was found that the dye adsorption mechanism in type I sites was an ion exchange, whereas in the case of type II sites it was a physical adsorption. A correlation was found between dye adsorption on chitin and the number of sulfone groups in a dye molecule. However, neither molecular weight nor the number of aromatic rings was correlated with dye adsorption.

Keywords: adsorption, chitin, reactive dyes, Langmuir equation, Langmuir constants, dimensionless separation factor

Introduction

Worldwide annual textile production is currently 30 million tons with expected growth of 3% per annum [32]. Water consumption in the textile industry is on average 100 m^3 (per ton of product) [3]. The silk industry is the most water consuming (225 m^3/t), whereas the decorative fabric industry has four times less consumption (50 m^3/t) [28]. Besides, dye plants use great amounts of water - 225 m^3/t of dye [31].

The losses of reactive dyes are about 2% in the production processes and about 9% through dying and finishing operations in the textile industry [13]. As a result, from 40,000 to 50,000 tons of dye are discharged to surface water every year [14].

The treatment of wastewaters containing dyes is complex and expensive. Methods such as chemical and electrochemical oxidation, membrane processes, coagulation-flocculation, adsorption or ion exchange are recommended. Some of these have already been used in practice, whereas others have only been tested in laboratories or applied on a small scale. Adsorption is one of the most effective physical processes for colour removal. Activated carbon [1] is normally employed for this purpose, however, due to its high price it has not enjoyed wide-scale application. Therefore, other inexpensive and effective adsorbents have been tested.

A number of references outline the application of adsorbents such as fly-ash [10], kaolinite, bauxite and fuller's earth [16], bentonite [17], rice husk [18], eucalyptus bark [24], post-vanillin lignin V [19] and chitin [21]. They tested the effect of adsorbent particle size, effect of pH, process temperature or mixing speed on the process effectiveness [26], [27], [22], [23], [1], [18], [9].

Many authors have noted that dye adsorption onto biological adsorbents occurs through various mechan-

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isms. For example, cellulose-containing adsorbents prepared from eucalyptus bark, maize cob or bagasse pith are found to be efficient in binding basic dyes rather than acid dyes as a result of chemical and physical adsorption. Acid dyes are more weakly adsorbed in a reversible process involving physical adsorption [22]. Unlike cellulose, natural nitrogen-containing adsorbents such as chitin (and its derivatives) adsorb acid better than basic dyes [4]-

Currently, the world's production is over 40,000 structural dye units [7]. Reactive dye use equals 26% [6]. Due to the advantage of colouring and dyed fabric durability, reactive dyes have increasingly been used for dying and printing on both natural and regenerated cellulose fibres. Triazine and vinyl sulfone dyes are the most important moiety of reactive dyes. Vinyl sulfone reactive dyes contain a vinyl sulfone moiety -$SO_2CH=CH_2$, or more often a 2-sulfatoethylsulfone moiety -$SO_2CH_2CH_2OSO_2Na$ which is hydrolyzed into a previous one in the process of dying. Nationally produced triazine reactive dyes are known as helactine dyes [20]. Little is known about adsorption of various dyes, which belong to a defined group and dyes included in the defined groups of different chemical structures.

In this work, the adsorption of acid reactive dyes was determined using an adequately prepared krill chitin. The investigation included 10 selected reactive acid dyes including 3 groups: 5 helactine dyes with trichlorotriazine as a reactive moiety, 2 polactine dyes with chlorovinyl moiety and 3 remazol dyes with vinyl sulfone moiety. The dyes in each group had different molecular weights and chemical structures.

The constants K and b obtained from the Langmuir equation, as well as a dimensionless separation factor R_L was used as the criteria for the effectiveness of dye adsorption on chitin.

Experimental Procedures

Chitin Preparation and Characteristics

The krill chitin (polymorphic structure a, from the Sea Fisheries Institute in Gdynia) was used for the experiment. The chitin was prepared according to the methodology described by Stanley [29]. The adsorbent was waterlogged and left for 24 hours for expanding. Then the water was separated and the adsorbent was washed with a 6 N HCl solution. After washing with distilled water to reach a filtrate of pH 7 the chitin was boiled in a 5 N KOH solution at 100° C for 3 h. The average size of a chitin flake used for the experiment was 184-314 µm. The chitin flake characteristics are presented in Table 1.

Table 1. Chitin flake characteristics.

Parameters		Chitin
Deacetylation degree – DD	(%)	5
Dry weight of adsorbent	(%)	95.64
Ash	(%)	0.32
Swollen adsorbent hydratation	(%)	70
Elemental analysis	(%)	C = 43.9, N = 6.4, H = 6.7

Dye Preparation

Reactive dyes (according to the technical classification) commonly used in the textile industry were used in the experiment. The chlorotriazine dyes were represented by Polish dyes produced by BORUTA S.A. Dye Plant in Zgierz: namely Yellow D-5GN, Red D-B8, Ruby F- B, Blue D-5RN and Black DN; the chlorovinyl reactive dyes: Yellow 2R, Scarlet R (produced by BORUTA S.A), and the vinyl sulfone remazol dyes: Gelb GR, Brillantorange 3R and Blau 3R (distributed by HOECHST S.A. Lodz).

Figure 1 represents the chemical structure of helactine dyes and Figure 2 polactine dyes and remazols.

Analysis of Dye Adsorption on Chitin

Analysis was carried out at pH 3.0. In order to determine chitin adsorption capacity, 200 dm^3 conical flasks were filled with both 1.5 g dry weight/dm^3 of expanding chitin at 70% water content and 100 cm^3 of dye solution at the increasing initial concentrations: 50, 75, 100, 125, 150, 175, 200, 225, 250, 300, 400, 500 mg/dm^3. The pH of the dye solutions was adjusted to pH 3.0 with the use of 0.1 N HCl. The flasks were shaken at a constant speed agitation at 200 and the vibration amplitude of 9 at 20°C. The equilibrium time of 2 hours was found to be necessary for each system to attain equilibrium. The dye solution over the adsorbent was sampled after 1-minute sedimentation and separated in a MPW 210 centrifuge for 10 min. at 10,000 r.p.m.

Analytical Methods

The analyses of the effectiveness of dye adsorption on chitin included the following parameters: pH with the use of a HI 8818 pH-meter, chitin concentration as chitin dry weight according to the methodology by Hermanowicz [11].

The method of determination of chitin deacetylation and dye concentration is described below.

Determination of Chitin Deacetylation Degree

The chitin deacetylation degree was determined with the potentiometric titration with 0.1 M NaOH solution in the range of pH 2 - 12 at 20°C. The analysis was carried out with the use of METROHM 702 SM Titrino equipment in the Maritime Institute of Fisheries in Gdynia. A formula prepared in the same institute was used for calculations [33].

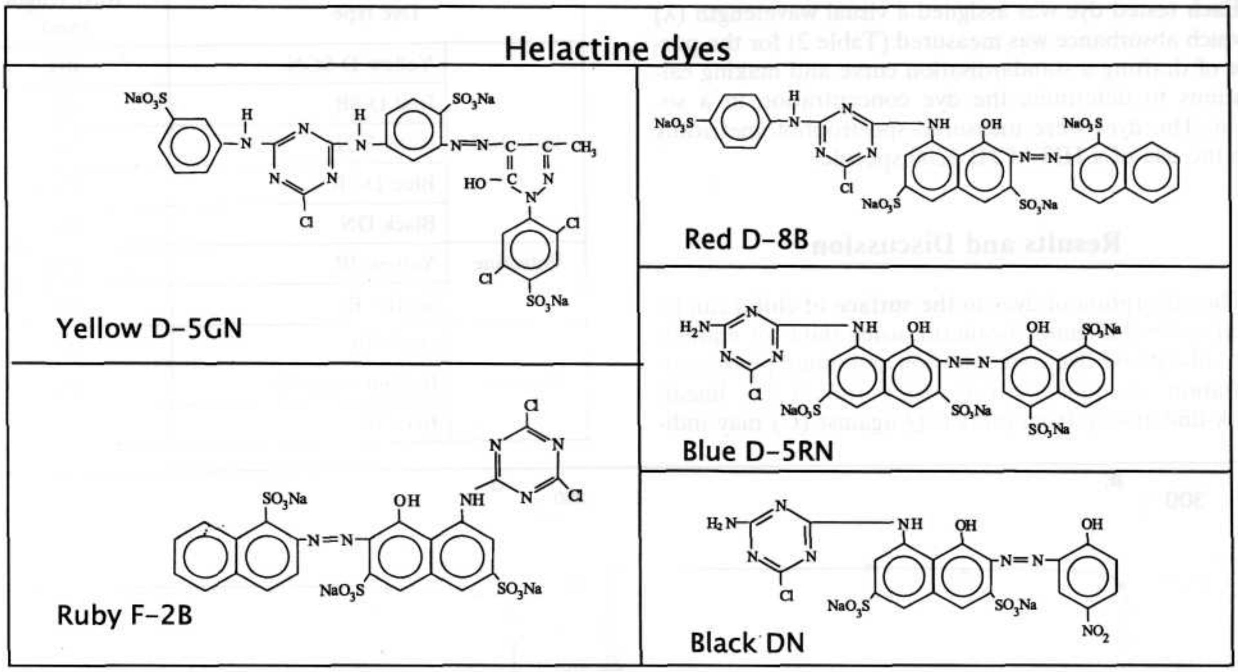


Fig 1. Chemical structure of the helactine dyes.

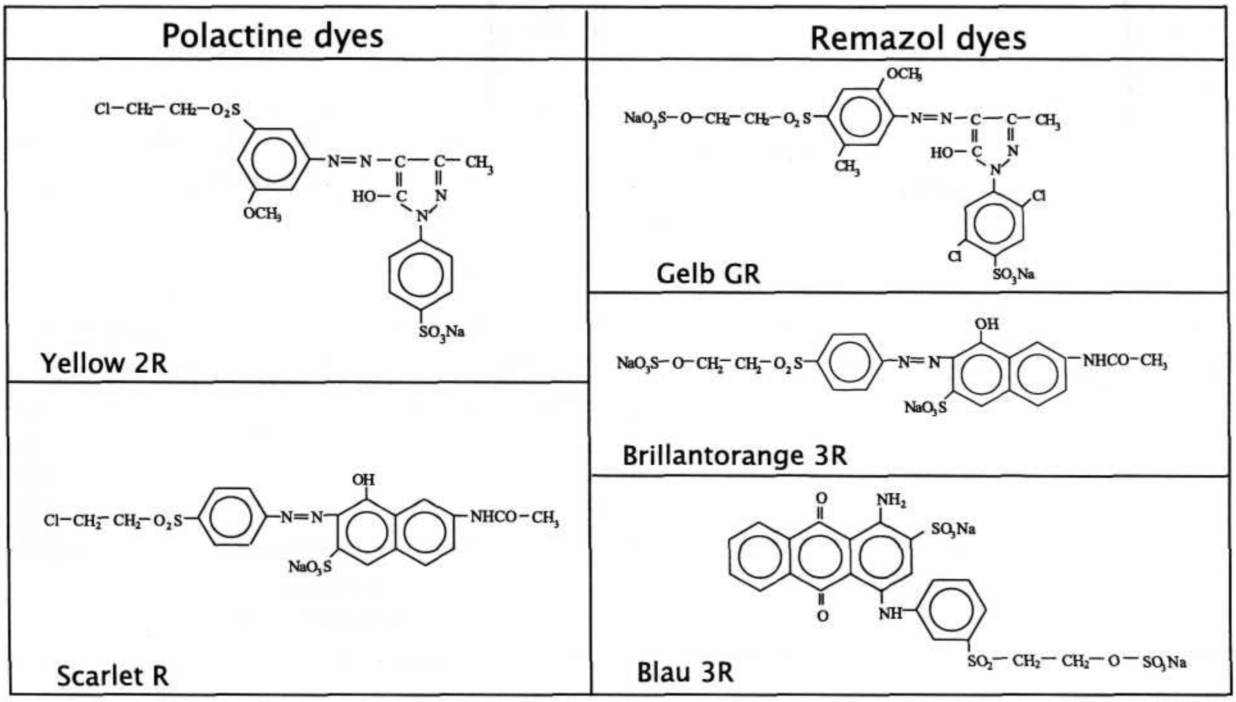


Fig 2. Chemical structure of the polactine and remazols dyes.

Determination of Dye Concentration

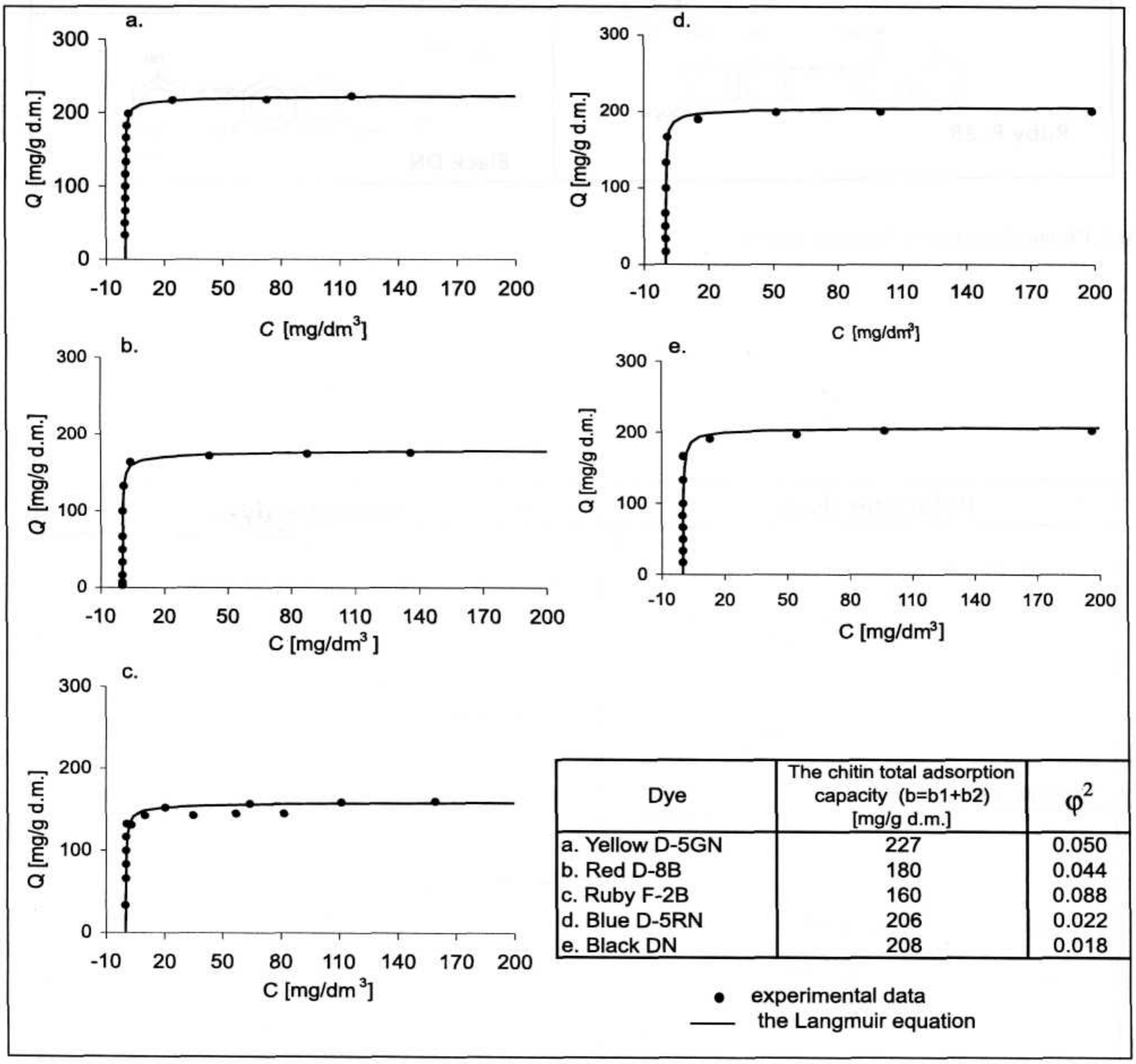
Each tested dye was assigned a visual wavelength (A.) at which absorbance was measured (Table 2) for the purpose of drafting a standardisation curve and making calculations to determine the dye concentration in a solution. The dyes were measured spectrophotometrically with the use of a HITACHI 1200 specole.

Results and Discussion

The adsorption of dyes to the surface of chitin can be described by Langmuir isotherm, using data for equilibrium solid phase dye concentration and liquid phase concentration. A plot of *C/Q=i(C)* should be linear. Break-line arising from plots *C/Q* against (C) may indi-

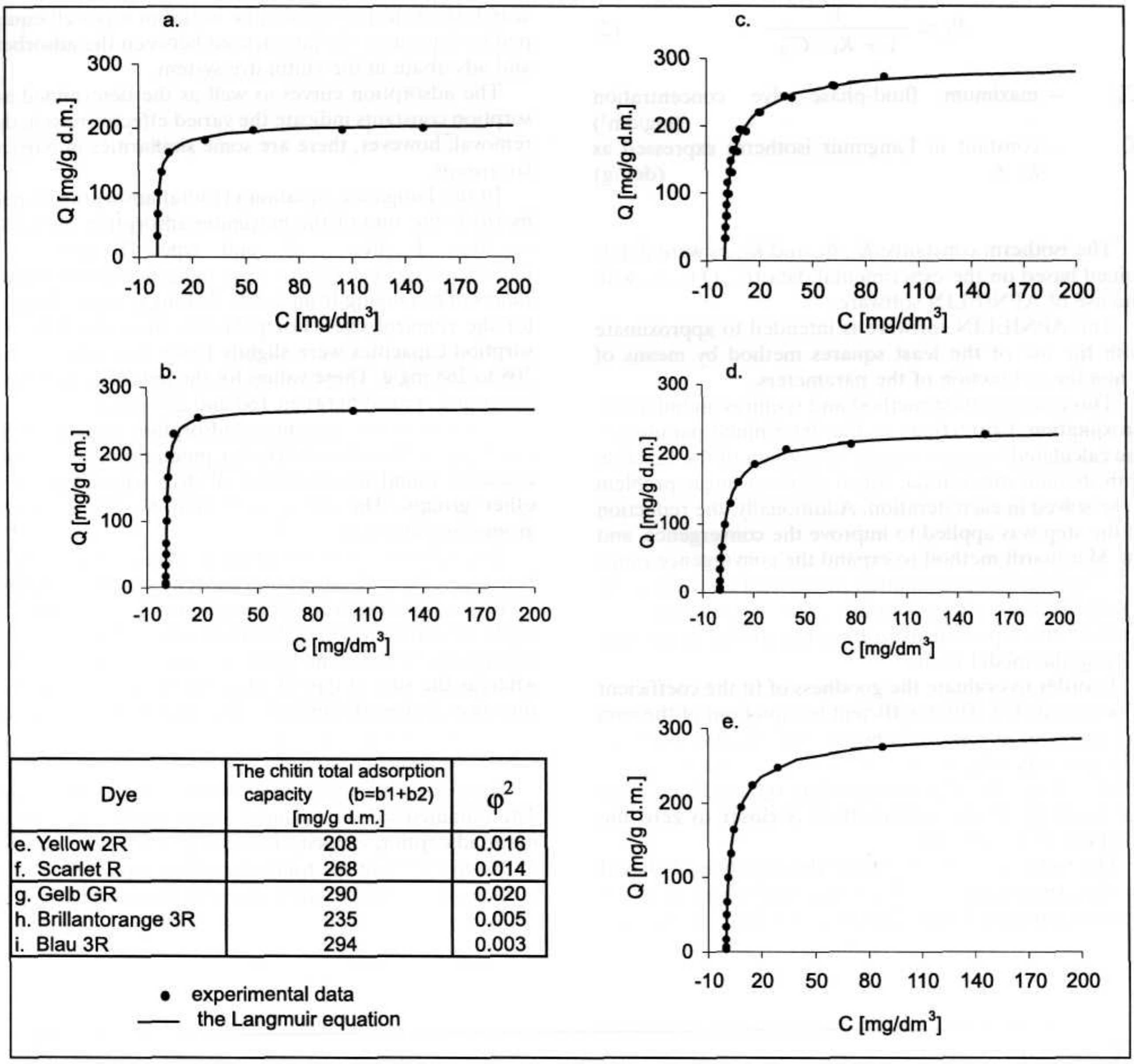
Table 2. Wave lengths at which dye absorbance was measured.

Dye type		Wave length (nm)
Helactine	Yellow D-5GN	404
	Red D-8B	521
	Ruby F-2B	540
	Blue D-5RN	570
	Black DN	580
Polactine	Yellow 2R	470
	Scarlet R	490
Remazol	Gelb GR	416
	Brillantorange3R	490
	Blau 3R	570



Dye	The chitin total adsorption capacity (b=b1+b2) [mg/g d.m.]	φ²
a. Yellow D-5GN	227	0.050
b. Red D-8B	180	0.044
c. Ruby F-2B	160	0.088
d. Blue D-5RN	206	0.022
e. Black DN	208	0.018

Fig. 3. Equilibrium adsorption of helactine dyes by chitin.
The table includes total chitin adsorption capacity determined with the use of the Langmuir (1) equation and the goodness coefficient *q?* for the helactine dyes.



Dye	The chitin total adsorption capacity (b=b1+b2) [mg/g d.m.]	φ^2
e. Yellow 2R	208	0.016
f. Scarlet R	268	0.014
g. Gelb GR	290	0.020
h. Brillantorange 3R	235	0.005
i. Blau 3R	294	0.003

Fig. 4. Equilibrium adsorption of polactine and remazols dyes by chitin.
The table includes the total chitin adsorption capacity determined with the use of the Langmuir (1) equation and the goodness coefficient φ^2- for the polactine and remazol dyes.

cate the availability of more than one site type for the dye [30], [12], [2].

For chitin, the existence of two types of such sites was observed. In this situation it is assumed that each site's type can be described by the Langmuir isotherm equation. The double Langmuir isotherm is expressed as equation (1) where K_1 K_2 and b_1 b_2 are constants, namely adsorption affinity and maximum adsorption capacity. Total adsorption capacity *(b)* may be determined by summing adsorption capacities obtained for the first b_1 and second b_2 type of sites [8] (Figs. 3, 4).

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

Q - equilibrium solid phase dye concentration (mg/g)
b_1 b_2 - constant in Langmuir isotherm (maximum adsorption capacity) (^{m}g/g)
K_1, K_2 - constant in Langmuir isotherm (adsorption affinity) (dm^3/mg)
C - equilibrium liquid phase dye concentration (mg/dm^3)

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor R_L, which is defined by McKay [21]:

$$R_L = \frac{1}{1 + K_L \cdot C'_0} \qquad (2)$$

C'_0 – maximum fluid-phase dye concentration (mg/dm^3)

K_L – constant in Langmuir isotherm expressed as $K \cdot b$ (dm^3/g)

The isotherm constants: K_1 b_1, and K_2, b_2 were determined based on the experimental data $(C_i\ Q_i)_{i=1...,N}$ with the use of APNIELIN software.

The APNIELIN software is intended to approximate with the use of the least squares method by means of a non-linear function of the parameters.

This is an iteration method and requires an initial approximation. Corrections to the determined parameters are calculated by replacing the increment of the function with its total differential, which allows a linear problem to be solved in each iteration. Additionally, the reduction of the step was applied to improve the convergence, and the Marquardt method to expand the convergence range [5]. The initial approximation mentioned above is to be obtained either by transforming (e.g. by logarithmical operation) the equation describing the model or by simplifying the model itself.

In order to evaluate the goodness of fit the coefficient φ^2 was used [15]. This coefficient is a quotient of the sum of squares of deviations between two experimental data (Q_i) and values ($Q(C_i)$) to the sum of squares of deviations between the experimental data (Q_i) and their average value Q. If the coefficient φ^2 is closer to zero the goodness of fit is better.

The isotherms obtained from the equation (1) based on the experimental data and the determined total adsorption capacity b are illustrated in Figs. 3, 4. Our research showed that the double isotherm was well equipped to determine the interactions between the adsorbent and adsorbate in the chitin-dye system.

The adsorption curves as well as the determined adsorption constants indicate the varied effectiveness in dye removal; however, there are some similarities in particular groups.

In the Langmuir equation (1) total adsorption capacity *(b)* is the sum of the maximum adsorption capacities on type I sites – b_1 and type II sites - b_2 ($b = b_1 + b_2$). The obtained data indicate that the highest values of *b*, ranging from 235 to 294 mg/g, were obtained for the remazol dyes. For polactine dyes, the total adsorption capacities were slightly lower and ranged from 208 to 268 mg/g. These values for the helactine dyes were lower and ranged between 160 and 227 mg/g.

Comparing the maximum adsorption capacities for chitin type I sites (b_1) and II, (b_2), greater ranges in values could be found in adsorption of dyes which belong to other groups. The obtained b_1 and b_2 values by dye groups are shown in Fig. 5.

The helactine dyes had high b_1 values ranging from 93.3% to 96.2% of adsorption capacity - *b*. On the other hand, the b_2 values were 20 times lower than i>! values. It could be concluded that the main role in the process of adsorption of helactine dyes is played by type I sites, whereas the role of type II sites was insignificant. Polactine dyes behaved similarly. The maximum adsorption capacity b_1 constituted from 72.1% to 96.2% of the maximum adsorption capacity *b*.

Remazols, however, were adsorbed in another way. The obtained values: b_1 and b_2 were similar. The maximum adsorption capacity for type I sites - b_1 was from 38.3% to 51.7% of the total adsorption capacity - *b*. The participation of both type I sites and II was significant in the process of adsorption in this dye group.

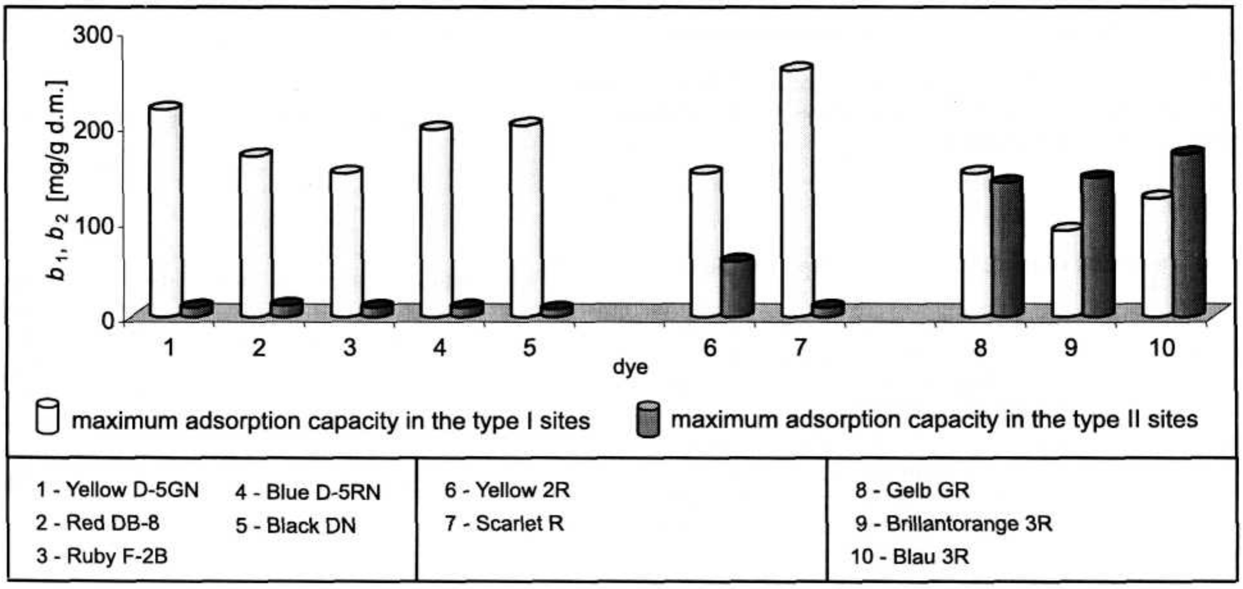


Fig. 5. The chitin maximum adsorption capacity in the sites both type I and II obtained from the Langmuir equation (1) for the helactine, polactine and remazol dyes.

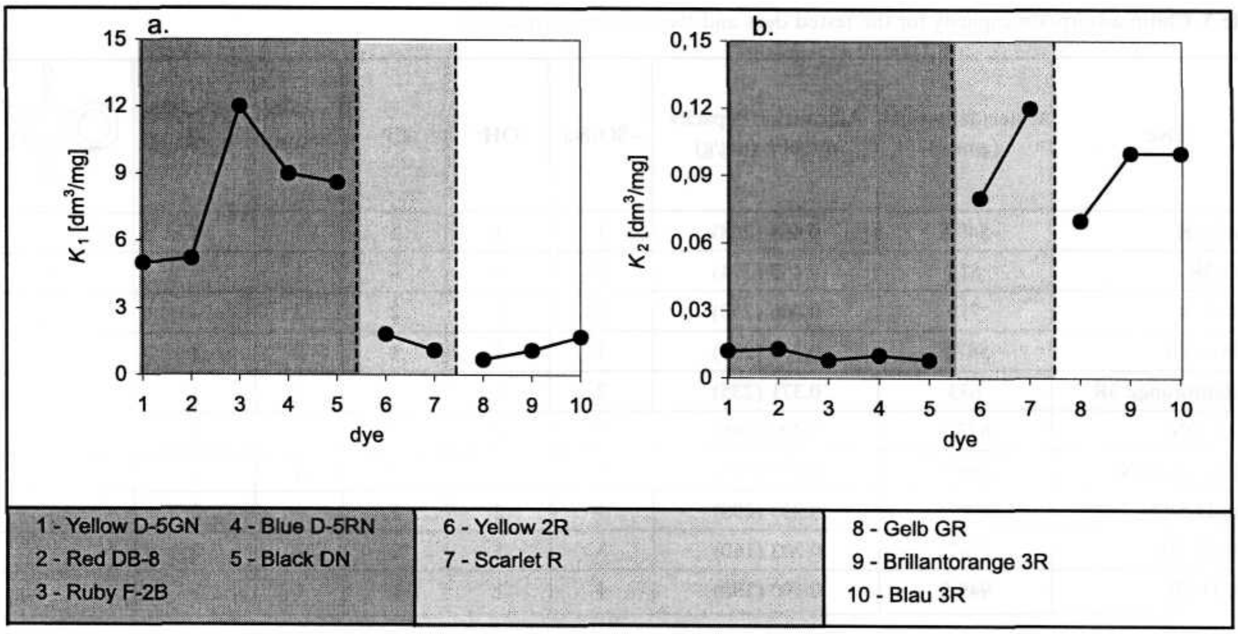


Fig. 6. The K_1 and K_2 constants obtained from the Langmuir equation (1) for the helactine, polactine and remazol dyes: a - sites type I, b - sites type II.

Based on the correlations between b_1 and b_2 it could be concluded that the adsorption of helactine, polactine and remazol dyes showed other adsorption mechanisms.

Figure 6 presents the Langmuir constants: K_1 and K_2 obtained from equation (1) for the examined dyes. Based on the obtained results, it could be concluded that the K_1 values for all dyes were considerably higher than the K_2 values.

The highest K_1 values (ranging from 12 dm^3/g - for Ruby F-2B to 5 dm^3/g - for Yellow D-5GN) were obtained for the helactine dyes. Therefore, it could be observed that the curves of adsorption on type I sites for these dyes resembled isotherm type L. The K_1 values for the polactine and remazol dyes ranged from 1.8 dm^3/g (Yellow 2R) to 1.1 drnVg (Scarlet R) and from 1.7 (Blau 3R) to 0.7 dnrVg (Gelb GR).

All the obtained values of the Langmuir equilibrium constant K_2 were considerably lower than K_1. The helactine dyes had lower K_2 values than the polactine and remazol dyes. The K_2 values for the particular dye groups ranged as follows: 0.0008 - 0.013 dm^3/g, 0.08 - 0.12 dm^3/g, 0.07 - 0.1 dm^3/g for the helactine, polactine and remazol dyes, respectively. The obtained K_1 and K_2 values indicate the higher adsorption affinity of reactive dyes to type I sites than to type II. The remazols had much greater affinities to type II sites than the helactine dyes.

The total adsorption capacities *(b)* expressed in mmole/g for reactive dyes (polactine, remazol and helactine dyes) are presented in Table 3.

Based on the experimental data it could be concluded that the amount of the adsorbed dyes on chitin ranged from 0.19 to 0.48 mmole/g, while the number of moles of amine groups in the adsorbent was 0.23 mmol/g.

Total adsorption capacity *b* (in mmol/g) for the helactine dyes was lower or similar to the number of amine groups in chitin. Additionally, the value of $b_1 = b$. It could be concluded that protonated amine groups are mainly responsible for the adsorption of the helactine dyes.

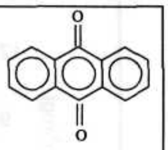
On the other hand, the polactine and remazol dyes had almost twice the total adsorption capacity *(b)* than the number of chitin amine groups (0.24 mmol/g). Moreover, the b_1 and b_2 values were similar. It was assumed that protonated-amine groups participated in the adsorption of these dye group as well as type II sites, whose adsorption was rather physical.

The experiment indicated a clear correlation between dye adsorption on chitin and a number of sulphonic groups in a dye molecule. The helactine dye molecules consisting of 3 or 4 sulphonic groups had the lowest adsorption effectiveness, while remazols containing one or two sulphonic groups were absorbed most effectively. Correlations with the number of aromatic rings: benzene or naphthalene were not found.

Muzzarelli [25] reports that dye affinity to chitin increases with the increase in the number of benzene rings and with the increase in molecular weight, however, it decreases with the increase in the number of sulphonic groups in the dye. Sulphonic groups have a negative affinity to chitin; thus, the repulsion of dye molecules to the chitin surface is becoming stronger as the number of sulphonic groups in the dye molecule increases.

The value of the dimensionless separation factor - R_L determined by equation (2) expresses the relation between maximum adsorption capacity *b* and Langmuir constant value *K*. Based on the R_L value both the isotherm shape and the adsorption mechanism can be predicted. The value of R_L indicates the shape of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L

Table 3. Chitin adsorption capacity for the tested dyes and their chemical structure.

Dye	Molecular weight (g/mol)	Adsorption capacity mmol/g (mg/g)	$-SO_3Na$	OH^-	Cl^-			
Scarlet R	549.5	0.488 (268)	1	1	1	1	1	–
Blau 3R	612	0.480 (294)	2	–	–	1	–	1
Gelb GR	715	0.406 (290)	2	1	2	2	–	–
Yellow 2R	547.5	0.380 (208)	1	1	1	2	1	–
Brillantorange 3R	633	0.371 (235)	2	1	–	1	1	–
Black DN	673.5	0.309 (208)	2	2	1	1	1	–
Yellow D-5GN	889.5	0.255 (227)	3	1	3	3	–	–
Blue D-5RN	8885.5	0.233 (208)	4	2	1	–	2	–
Ruby F-2B	787	0.203 (160)	3	1	2	–	2	–
Red D-8B	949.5	0.190 (180)	4	1	1	1	2	–

values for the helactine, polactine and remazol dyes are showed in Fig. 7.

The results indicate that the dimensionless separation factor values *(R_L)* differed significantly for the dye in dependence on particular types of sites. Within dye groups, the R_L values were quite similar (Fig. 7).

The R_{L1} values refer to dye adsorption on type I sites, whereas the R_{L2} to the adsorption on type II sites. For all the dyes, the R_{L1} values ranged close to zero. The R_{L2} values, however, were close to 1 for the helactine dyes, were 0.6 for the polactine dyes and 0.2 for the remazols. The results show that the highest differences between the values of dimensionless separation factors: R_{L1} and R_{L2} were found for the helactine dyes and the lowest for the remazols.

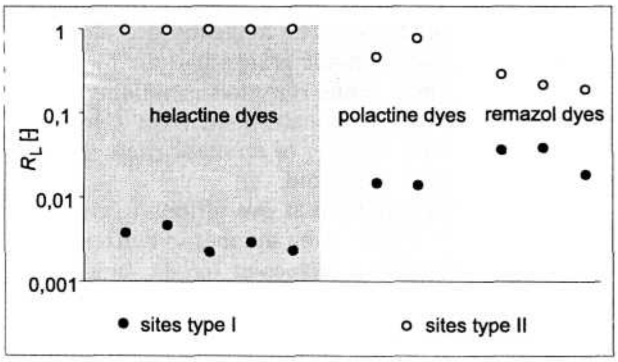


Fig. 7. Dimensionless separation factor values *(R_L)* for the helactine, polactine and remazol dyes.

It is possible to determine the sorption mechanism when the thermodynamic analysis are done. R_L values can be used only for preliminarily estimation, whether the adsorption is of physical or chemical character (Al-Degs [1]).

Based on the results it can be concluded that the dye adsorption on chitin type I sites was a chemical one, i.e. ion-exchange in the following decreasing order:

helactine dyes > polactine dyes > remazol dyes

Interactions between the dyes and the type II sites were a physical adsorption in the following increasing order:

helactine dyes < polactine dyes < remazol dyes

Conclusions

Based on the results the following can be concluded:

1. It was found that the dye adsorption on chitin occurred in both type I and II sites that differed in the adsorption affinity *(K)* and the maximum adsorption capacity *(b)*.
2. It was found that for all dyes the constant K_1 values in Langmuir equation were significantly higher than the values of K_2 ($K_1 \gg K_2$).
3. The dimensionless separation factor R_L in this experiment served as the criterion for the dye adsorption mechanism evaluation. Based on its value, it was found that the dye adsorption process in the case of type I sites revealed the characteristics of ion-exchange; however, in the case of type II sites - the characteristics of a physical adsorption.
4. The experiments showed a clear correlation between dye adsorption on chitin and the number of sulphonic groups in the dye molecule. However, the adsorption on chitin was neither correlated with the dye molecular weight nor with the number of aromatic rings: benzene and naphthalene.

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