

The Effect of pH and Chitin Preparation on Adsorption of Reactive Dyes

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Abstract

The effect of chitin preparation with HCl (*chitin A*) and with HCl and KOH (*chitin B*) and pH on the adsorption of reactive dyes (helactine, polactine and remazol) on chitin was investigated. The double Langmuir equation was appropriate to analyze the dependence between amount of the adsorbed dye on chitin (Q) and its equilibrium concentration (C). It indicated the presence of two types of active sites which differed in both the maximum adsorption capacity (b) and adsorption affinity (K). 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.

The adsorption capacity of the *chitin A* (deacetylation degree of 3%) for samples without pH adjustment ranged from 29 (Red D-8B) to 67 mg/g dry weight of chitin (Gelb GR). At pH 3.0 the adsorption capacity was higher from 1.9 to 2.3-fold. The most favourable effect of pH change was found for helactine dyes.

The adsorption capacity of the *chitin B* (deacetylation degree of 5%) was from 66 (Brilliantorange 3R) to 101 mg/g dry weight of chitin (Gelb GR). After pH adjustment to pH 3.0 the adsorption capacity ranged from 160 (Ruby F-2B) to 294 mg/g dry weight of chitin (Blau 3R). The most favourable effect of deacetylation degree increase was found in the case of helactine dyes in the samples without pH adjustment, and polactine and remazol dyes at pH 3.0.

Keywords: reactive dyes, modified chitin, deacetylation degree, Langmuir isotherm, pH, dimensionless separation factor

Introduction

Colour effluent is one of the main problems connected with wastewater from dye production and the textile industry. Therefore, the decolourization of wastewater has been a subject of research in recent years. Methods such as chemical and electrochemical oxidation, membrane processes, coagulation-flocculation, adsorption and ion exchange are recommended. Some of these have already been used in practice, whereas others have only been tested in a laboratory scale. In comparison with chemi-

cal oxidation or membrane processes, adsorption does not require large investment costs. However, due to the high price of adsorbents (as activated carbon) and difficulties in its regeneration it has not enjoyed wide-scale application so far. Hence, other inexpensive and effective adsorbents have been sought. Among them are biological adsorbents such as eucalyptus bark, maize cob, bagasse pith or chitin.

Dye adsorption on biological adsorbents is not recognized exactly. A number of references outline that cellulose-containing adsorbents prepared from eucalyptus bark [1], maize cob [2] or bagasse pith [3], are found to be efficient in binding basic dyes as a result of ion-exchange

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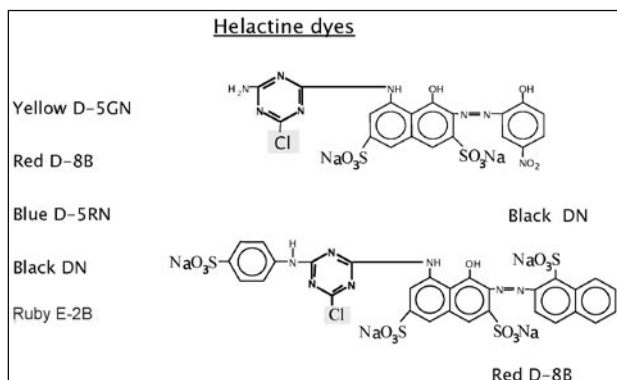


Fig. 1. Chemical structure of helactine dyes.

mainly. Acid dyes are more weakly adsorbed than basic dyes, in a process involving physical adsorption [3]. Unlike cellulose, biological nitrogen-containing adsorbents such as chitin or chitosan adsorb acid better than basic dyes. Among other things, reactive dyes belong to acid group.

Reactive dyes are the most often used dyes now and they occupy about 26% of the assortment applied [4]. Triazine and vinyl sulfone are the most important moiety of reactive dyes. In triazine dyes most often chlorine atoms are the groups capable of reaction, and triazine ring is their carrier. Vinyl sulfone dyes contain a vinyl sulfone moiety $-\text{SO}_2\text{CH}=\text{CH}_2$ or more often a 2-sulfatoethylsulfone moiety $-\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na}$ which is hydrolyzed into a vinyl sulfone moiety in the process of dyeing [5]. Nationally produced reactive dyes are known as helactine dyes [6]. Literature data results show that the efficiency of dye adsorption on chitosan such as Acridine Orange, Red Kongo, Crystalline Purple, Neutral Red or Safranin O included in the different groups has not been investigated until now [7].

In this work, the adsorption of 10 reactive dyes including three groups – helactine (5), polactine (2) and remazol (3) was determined. The effect of chitin preparation and pH was examined. For every dye the adsorption capacity and dimensionless separation factor R_L were calculated.

Experimental Procedures

Chitin Preparation and Characteristics

The krill chitin from the Sea Fisheries Institute in Gdynia was used for the experiment. Dry weight of chitin was 95.64%, and ash – 0.32%.

The chitin was prepared according to the methodology described by Stanley [8]. The way of proceedings after preparing chitin and its characteristics was the following:

- *chitin A* – 10 g of chitin was waterlogged in weight ratio of 1:10 and left for 24 hours at room temperature for expanding. Expanded chitin was filtrated to Büch-

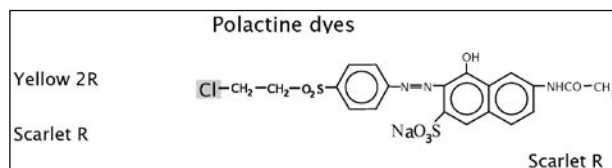


Fig. 2. Chemical structure of polactine dyes.

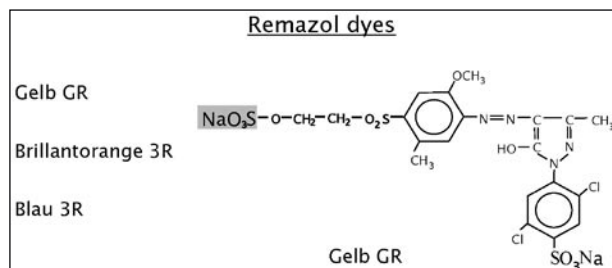


Fig. 3. Chemical structure of remazol dyes.

ner funnel and washed with a 6 N HCl solution. Then the chitin was washed with distilled water to reach a filtrate of pH 7 and drained off in vacuum. *Chitin A* contained about 70% of water, and its deacetylation degree was 3%. Amount of Ca^{2+} ions removed from *chitin A* was 25.7 mg/g dry weight, and Mg^{2+} ions 4.17 mg/g dry weight.

- *chitin B* – chitin after expanding was washed with a 6 N HCl solution and with distilled water to reach a filtrate of pH 7 and drained off in vacuum. Then the chitin was boiled in a 5 N KOH solution at 100°C for 3 h. After cooling down the chitin was washed with distilled water to reach a filtrate of pH 7 and drained off in vacuum. Hydration of *chitin B* was about 70%, and its deacetylation degree increased to about 5%.

The average size of a chitin flake used for the experiment was from 314 to 184 μm . The size of maximal flake was 756×434 μm , and minimal 62×62 μm .

Dye Preparation

The chlorotriazine and vinyl reactive dyes were used in the experiment. The chlorotriazine dyes were represented by dyes produced by “Boruta” SA Dye Plant in Zgierz: namely Yellow D-5GN, Red D-8B, Ruby F-B, Blue D-5RN and Black DN. The vinyl dyes were represented by two vinyl sulfone dyes: Yellow 2R, Scarlet R (produced by “Boruta” SA Dye Plant in Zgierz), and three chlorovinyl dyes: Gelb GR, Brillantorange 3R and Blau 3R (distributed by “Hoechst” SA Łódź). Figures 1, 2 and 3 show the chemical structure of some helactine, polactine and remazol dyes.

Batch Experiments

The adsorption of each chitin was tested in samples without pH adjustment (pH 6.2 – 6.3) and with pH adjustment to pH 3.0. Dye concentrations in samples without

pH adjustment were: 5, 10, 25, 50, 75, 100, 125, 150, 175, 200, 225, 250 mg/dm³, and in samples of pH 3.0 - 50, 75, 100, 125, 150, 175, 200, 225, 250, 300, 400, 500 mg/dm³.

200 cm³ conical flasks were filled with both 1.5 g dry weight/dm³ of *chitin A* or *chitin B* (about 5 g/dm³ hydrated chitin) and 100 cm³ of dye solution (pH 6.2 – 6.3 and pH 3.0) at appropriate concentrations. The flasks were shaken at a constant speed agitation at 200 and a vibration amplitude of 9 at 20°C during the time needed to obtain equilibrium, i.e. 4 hours without pH adjustment and 2 hours 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 4 represents experiment characteristics.

Analytical Methods

The analysis of pH was carried out with the use of a HI 8818 pH-meter, chitin concentration as chitin dry weight according to the methodology described by Hermanowicz et al. [9].

Deacetylation degree of chitin was analyzed according to Roberts [10].

Determination of Dye Concentration

Each tested dye was assigned a visual wavelength (λ) at which absorbance was measured (Table 1) for the purpose of drafting a standardization curve and making conversion coefficients. Dye concentrations were measured spectrophotometrically using a HITACHI 1200 apparatus.

Results and Discussion

Equilibrium Isotherms

Dye adsorption was described using the relationship between amount of dye adsorbed on chitin (Q) and equilibrium dye concentration (C).

Commonly for this purpose the Langmuir equation is used, although double Langmuir equation, and BET model are also used.

- Langmuir isotherm assumes the homogeneity of active sites, i.e. the one-molecule adsorption layer forms on the adsorbent surface;
- double Langmuir isotherm assumes the presence of two types of active sites capable of binding the adsorbant molecules;

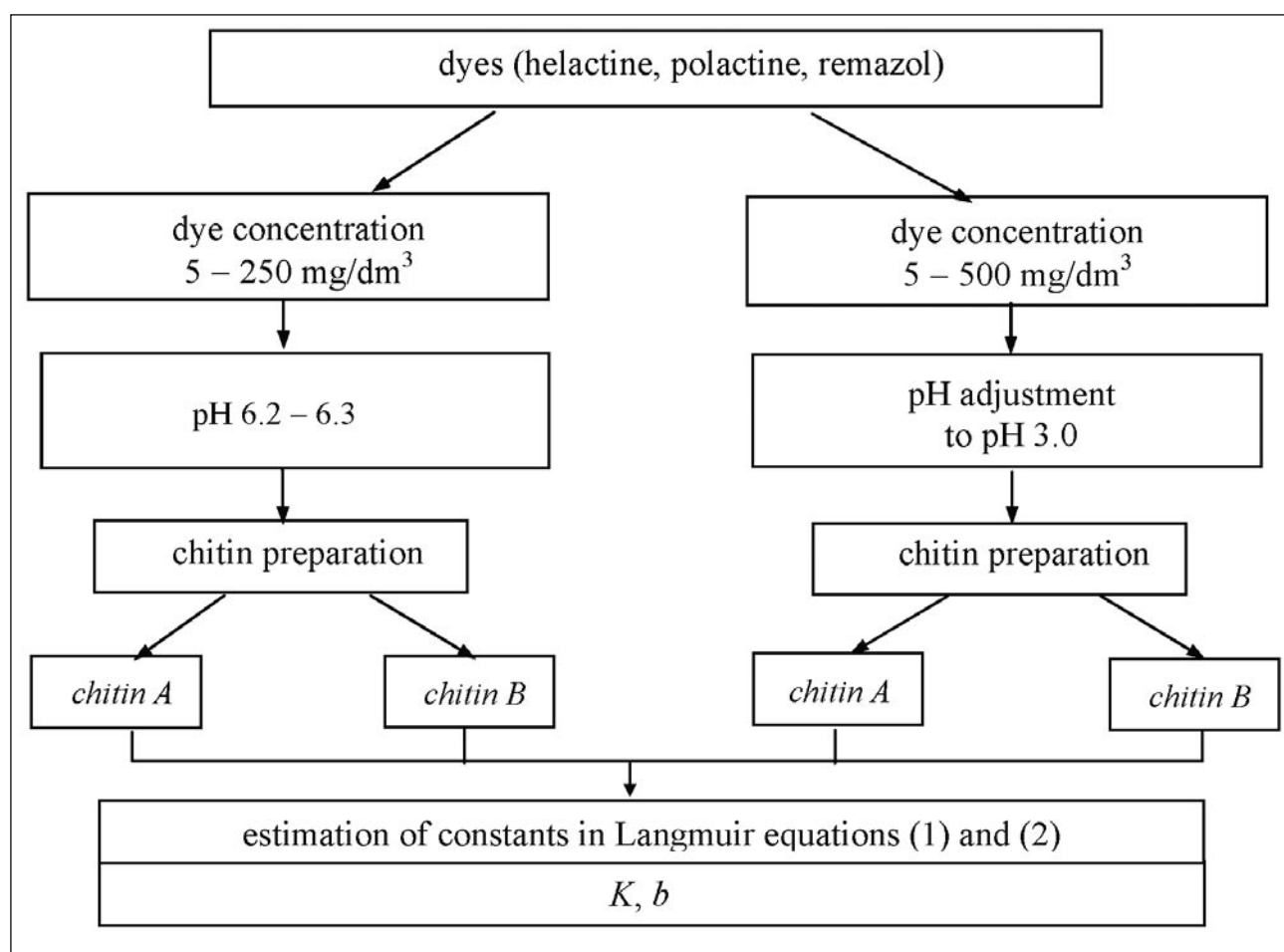


Fig. 4. Experiment procedure to determine the effect of chitin preparation and pH on the efficiency of dye adsorption.

Table 1. Wavelengths at which dye absorbance was measured.

Dye type	Wavelength (λ) [nm]	Dye type	Wavelength (λ) [nm]
helactine Yellow D-5GN	404	polactine Yellow 2R	470
helactine Red D-8B	521	polactine Scarlet R	490
helactine Ruby F-2B	540	remazol Gelb GR	416
helactine Blue D-5RN	570	remazol Brillantorange 3R	490
helactine Black DN	580	remazol Blau 3R	570

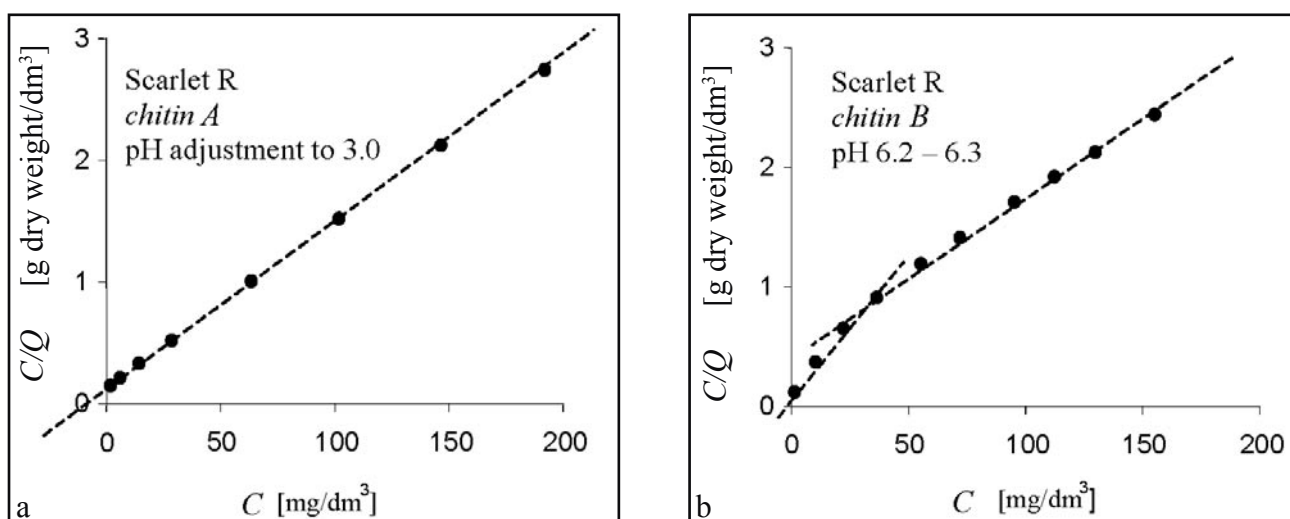


Fig. 5. Experimental data and linearized Langmuir equation plot. a – Langmuir equation (1) straight – line, b – Langmuir equation (2) – two straight lines.

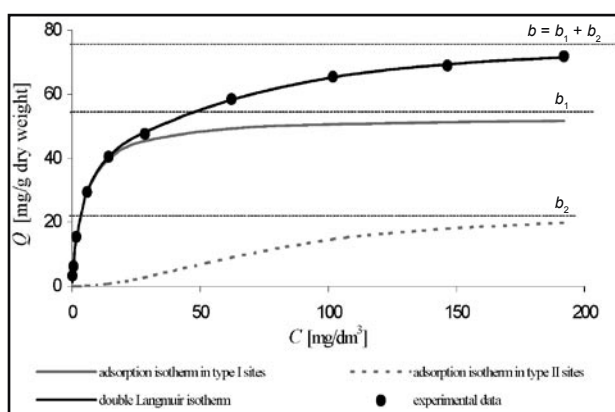


Fig. 6. The double Langmuir isotherms and the hypothetical adsorption isotherm in type I and II sites.

- BET model assumes multilayer adsorption as a result of the adsorption complexes forming.

The first two listed models were analysed, excluding BET model. From the literature data [11] it results that binding of dye molecules with sulfone groups to chitin

causes the repulsion of the next molecules in the solution, which exclude the forming of the following adsorption layers. Each tested dyes contained one or more sulfone groups. The helactine dyes in most cases contained three or four sulfone groups, remazol dyes – two, and polactine dyes one group.

Langmuir Isotherm

$$Q = \frac{b \cdot K \cdot C}{1 + K \cdot C} \quad (1)$$

Q - equilibrium solid phase dye concentration [mg/g dry weight];

b - maximum adsorption capacity [mg/g dry weight];

K - constant in Langmuir equation [$\text{dm}^3/\text{g dry weight}$];

C - equilibrium liquid phase dye concentration [mg/dm^3].

It was assumed that the adsorption can be described by Langmuir equation (1) when a plot of $C/Q = f(C)$ is linear (Fig. 5 a). The analysis of experimental data showed that in the case of some dyes after linearization $C/Q = f(C)$ the set of two lines of different slopes was obtained (Fig. 5 b).

On this basis it was assumed that some dyes could be adsorbed by chitin of more than one type of active sites of different energy of adsorbate binding. Each site type is described by the Langmuir equation. Then the isotherm is the sum of two Langmuir equations [12]. The equation was called the double Langmuir equation. The usability of the double Langmuir equation was earlier proved by Sterritt, Lester and Hughes, Poole [13,14] over the interpretation the results of metal adsorption by activated sludge, and by Amacher et al. [15] to evaluate the metal adsorption in soil.

Double Langmuir Equation

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

Q - equilibrium solid phase dye concentration [mg/g dry weight];

b_1 - maximum adsorption capacity for type I sites [mg/g dry weight];

b_2 - maximum adsorption capacity for type II sites [mg/g dry weight];

K_1 - constant in Langmuir equation for type I sites [dm³/g dry weight];

K_2 - constant in Langmuir equation for type II sites [dm³/g dry weight];

C - equilibrium liquid phase dye concentration [mg/dm³].

Each type of active site in double Langmuir equation is characterized by constants K_1 , b_1 and K_2 , b_2 . Total chitin adsorption capacity (b) may be determined by summing maximum adsorption capacities obtained for the first and second type of sites ($b = b_1 + b_2$). Constants K_1 and K_2 characterize the dye adsorption affinity to types I and II sites, and respond the inverse of the dye concentration, at which the chitin adsorption capacity equals half of the maximum capacity b_1 or b_2 (Fig. 6).

Constants K and b determined from the double Langmuir equation can be expressed in terms of a dimensionless separation factor R_L [16].

$$R_L = \frac{1}{1 + K_L \cdot C'_0} \quad (3)$$

C'_0 - the highest initial dye concentration examined [mg/dm³];

K_L - product of constants K and b determined from Langmuir equation [dm³/g].

The coefficient R_L value in double Langmuir equation was calculated for types I and II sites (R_{L1} i R_{L2}).

Determination of Constant K and b in Langmuir Equation

The constants K and b in Langmuir equation (1) and in double Langmuir equation (2) were determined based

on the experimental data $(C_i, Q_i)_{i=1..n}$ with the use of APNIELIN software (author: S. Grabowski – University of Warmia and Mazury in Olsztyn).

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 [17]. 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 coefficient φ^2 was used [18]. 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 \bar{Q} .

If the coefficient φ^2 is closer to zero the goodness of fit is better.

$$\varphi^2 = \frac{\sum_{i=1}^n (Q_i - Q(C_i))^2}{\sum_{i=1}^n (Q_i - \bar{Q})^2} \quad (4)$$

where:

$$Q = \frac{C_0 - C}{m} \quad (5)$$

where:

C_0 - initial dye concentration in the sample [mg/dm³];

m - chitin concentration in the sample [g dry weight/dm³].

Dyes Adsorption on Chitin

Experimental data show the dependence between equilibrium solid phase dye concentration on *chitin A* and *chitin B* and the equilibrium liquid phase dye concentration, and the isotherms obtained from Langmuir equation (1) and double Langmuir equation (2) in the samples without and with pH adjustment are presented in Figures 7, 8, 9 and 10. In the Tables the coefficient φ^2 values are presented, calculated with the use of the equation (4).

It was stated that for *chitin A* in all tested samples (Fig. 7 and 8) and for *chitin B* in the samples without pH adjustment (Fig. 9) the fit of isotherm from the double Langmuir equation (2) to experimental data was better. This is confirmed by lower values of the coefficient φ^2 .

In the case of *chitin B* after pH adjustment (Fig. 10) it was determined that the goodness of fit the isotherm to experimental data (φ^2) was dependent on the dye type and its affiliation to a given group.

- for dyes with vinyl group (polactine and remazol dyes), lower φ^2 values were obtained for the isotherm

described by the equation (2) by comparison with the equation (1), and the lowest φ^2 values were obtained for remazol dyes, where the participation of type II sites was the highest.

- in the case of helactine dyes, with the exception of Red D-8B, almost the identical goodness of fit both

Langmuir isotherm (1) and (2) to experimental data was proved. The coefficients φ^2 determined for Langmuir isotherm (1) and double Langmuir isotherm (2) amounted to: for Yellow D-5GN – $\varphi^2 = 0.051$ and 0.050 , Blue D-5RN – $\varphi^2 = 0.019$ and 0.022 and Black DN – $\varphi^2 = 0.018$ and 0.018 , respectively.

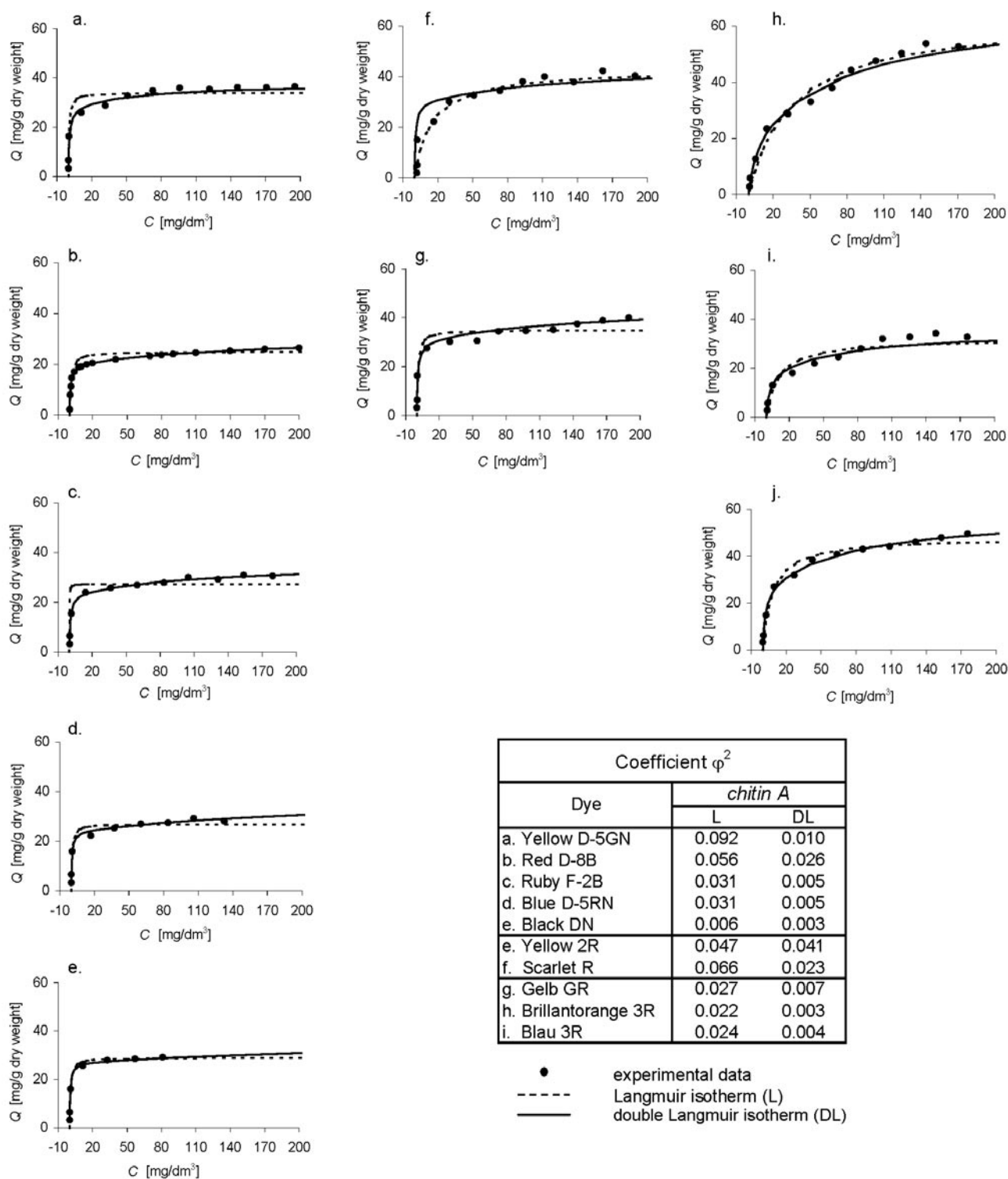


Fig. 7. Experimental data of the adsorption of reactive dyes on *chitin A* in the samples without pH adjustment and adsorption isotherms determined from equations (1) and (2). The Table presents coefficients φ^2 .

In order to estimate the chitin adsorption capacity the double Langmuir isotherm (2) for all tested dyes was finally accepted.

In the samples without pH adjustment the highest total adsorption capacity of *chitin A* of the deacetylation degree 3% was obtained for remazols – on average 54

mg/g dry weight, and the smallest for helactine dyes – on average 33 mg/g dry weight. The pH adjustment caused the increase in the chitin total adsorption capacity for tested dyes. The highest – 2.3-fold increase was noted for the helactine dyes and about 1.9-fold for remaining groups.

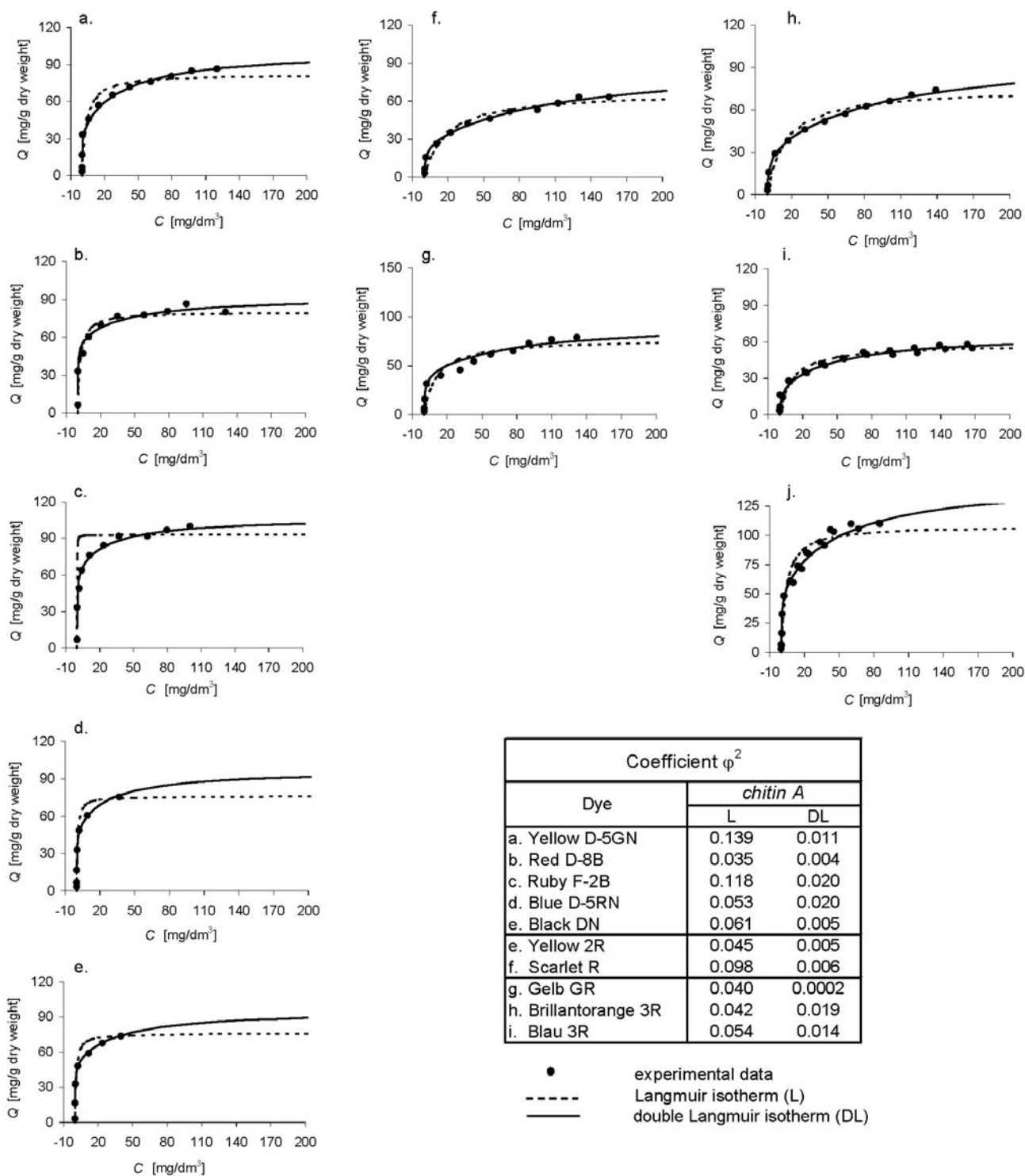


Fig. 8. Experimental data of the adsorption of reactive dyes on *chitin A* in the samples with pH adjustment and adsorption isotherms determined from equations (1) and (2). The Table presents coefficients φ^2 .

Similarly to the samples without pH adjustment, the highest total adsorption capacity of *chitin A* was noted for remazols (about 100 mg/g dry weight), the lowest for helactine dyes – about 76 mg/g dry weight.

Under acid conditions chitin included acetamide groups and insignificant amount of amine groups. Both

these groups have a great significance in dye adsorption. These groups are protonated according to the reaction:

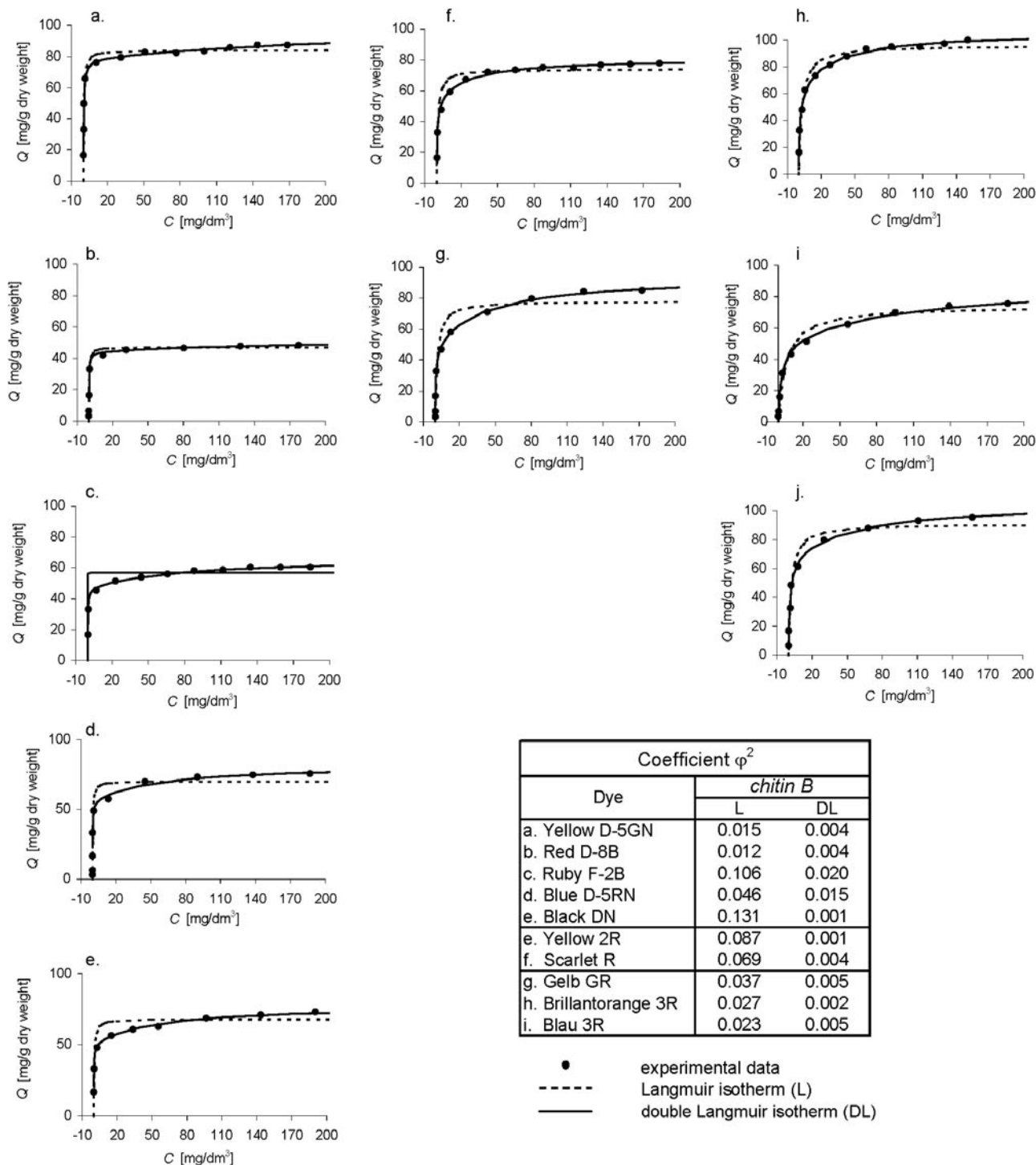
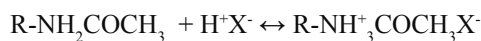
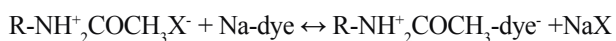


Fig. 9. Experimental data of the adsorption of reactive dyes on *chitin B* in the samples without pH adjustment and adsorption isotherms determined from equations (1) and (2). The Table presents coefficients ϕ^2 .

Proton affinity to amine groups is bigger than to acetamide groups [11]. The proton attach by chitin enables the adsorption of anion dyes (including all reactive dyes tested) by ion-exchange:



Owing to the ability for ion-exchange the chitin can be compared to slightly basic anion exchangers, whose exchange capacity increases by increasing hydrogen ion concentration [19]. Low adsorption capacity under basic conditions can be explained by the slightly basic anion exchangers' affinity to hydroxide

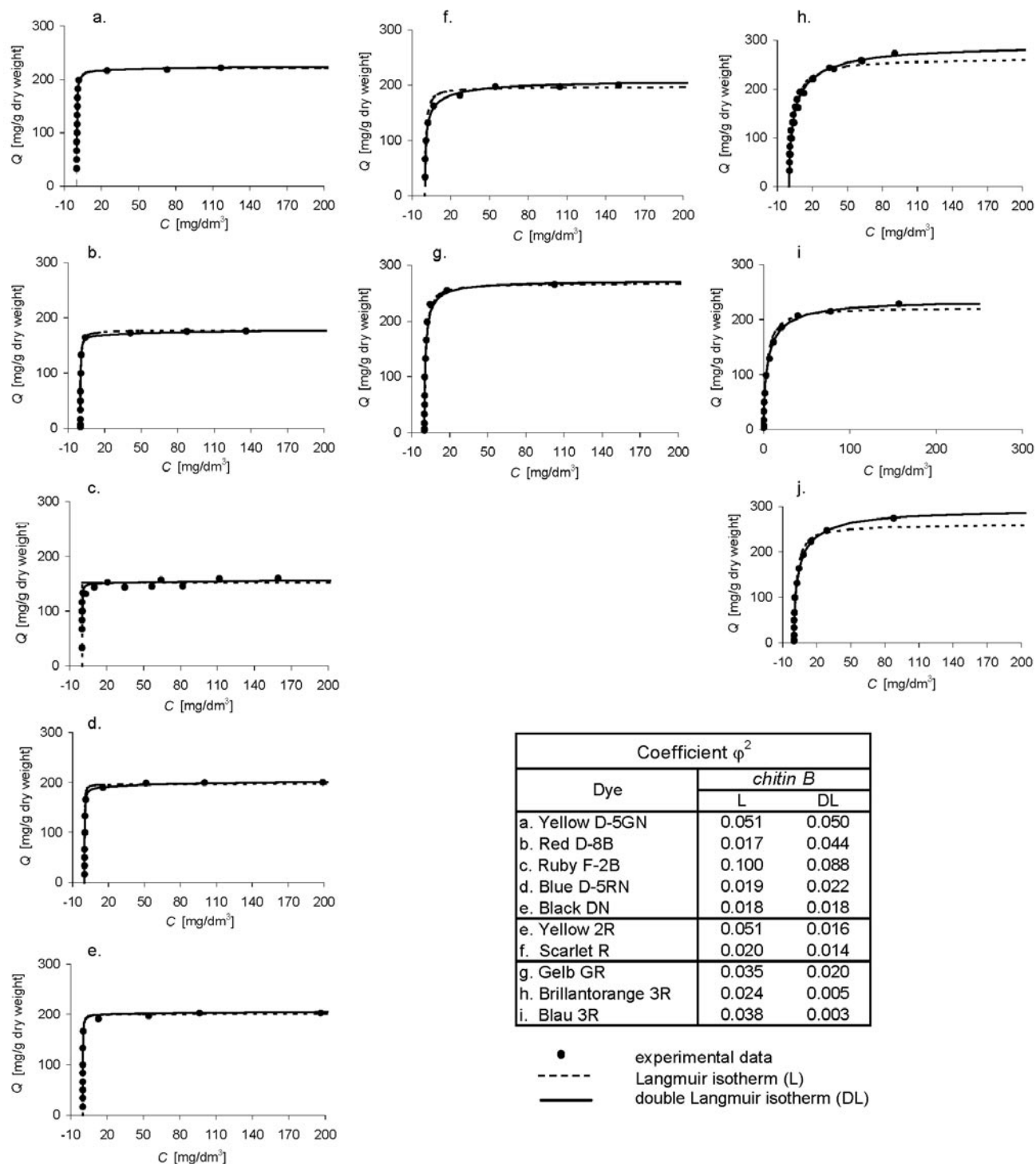


Fig. 10. Experimental data of the adsorption of reactive dyes on *chitin B* in the samples with pH adjustment and adsorption isotherms determined from equations (1) and (2). The Table presents coefficients φ^2 .

ions. This causes competition with negative ions of dye.

Research has proven that the increase in the chitin deacetylation degree improved the effectiveness of dye adsorption. The adsorption capacity of *chitin B* was the highest for remazol dyes and equaled about 105 mg/g dry weight, and the lowest for polactine dyes – on average 93 mg/g dry weight. So in comparison with *chitin A*, a 2- to 3-fold increase in an adsorption capacity was obtained.

The pH adjustment caused an increase in the adsorption capacity for all dyes examined. However, differently than for *chitin A*, the highest (about 2.6-fold increase) was noted for polactine and remazol dyes, lower (about 2-fold) for helactine dyes. In the samples with pH adjustment the total adsorption capacity for remazol dyes equaled to, on average, 273 mg/g dry weight, and for helactine dyes, on average, 196 mg/g dry weight.

Dye Adsorption on Chitin in Types I and II Sites

The maximum adsorption capacity b and Langmuir constant K can be expressed by the dimensionless separation factor R_L (3). Based on the R_L value both the isotherm shape and the adsorption mechanism can be predicted [16].

According to Al-Degs et al. [16] it was assumed that for values of $R_L \ll 1$ the adsorption can be described as a physical process, whereas for $R_L \cong 0$ the adsorption is characterized as a slightly reversible chemical reaction. The authors reported that for the separation factor $R_L \ll 1$ the adsorption mechanism is favourable.

The coefficient values obtained for type I sites R_{L1} and for type II sites R_{L2} of *chitin A* and *B* for helactine, polactine and remazol dyes are presented in Figures 11 and 12. It was proved that the dimensionless separation factor R_L values differed for the dye in dependence on particular types of sites, method of chitin preparation and pH. Within dye groups (in the case of particular way of chitin preparation and constant pH) the R_L values were quite similar.

Presented data indicate that in the samples with pH adjustment the R_{L1} values ranged from 0.0103 to 0.0179, and were the lowest for helactine dyes, and for remazol dyes – the highest from 0.0539 to 0.154 on *chitin A* for type I sites. For type II sites the reverse results were noted, i.e. the highest R_{L2} values were obtained for helactine dyes from 0.877 to 0.986, and the lowest for remazol dyes from 0.685 to 0.903 (Fig. 11a,b).

Similar results were found for *chitin B*. The lowest R_{L1} values from 0.0022 to 0.0046 were obtained for helactine dyes at pH 3.0, and the highest for remazol dyes from 0.0186 to 0.0388. The R_{L2} values for helactine dyes varied from

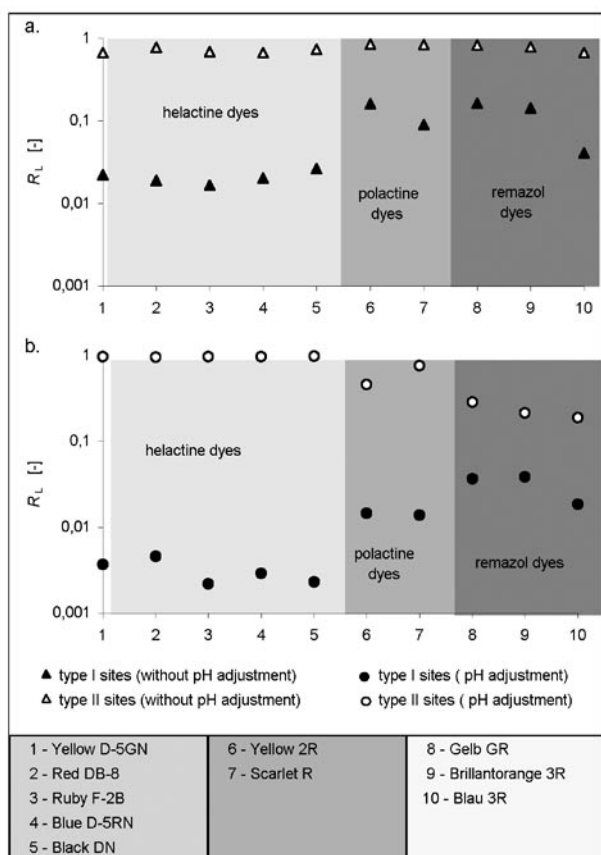


Fig. 11. The separation factor R_L for *chitin A* in samples a) pH 6.2 – 6.3, b) with pH adjustment for tested dyes.

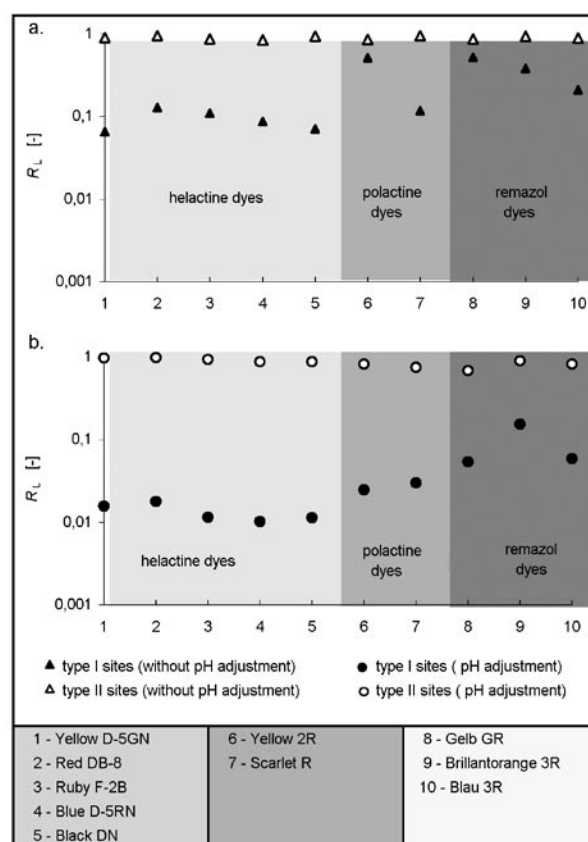


Fig. 12. The separation factor R_L for *chitin B* in samples a) pH 6.2 – 6.3, b) with pH adjustment for tested dyes.

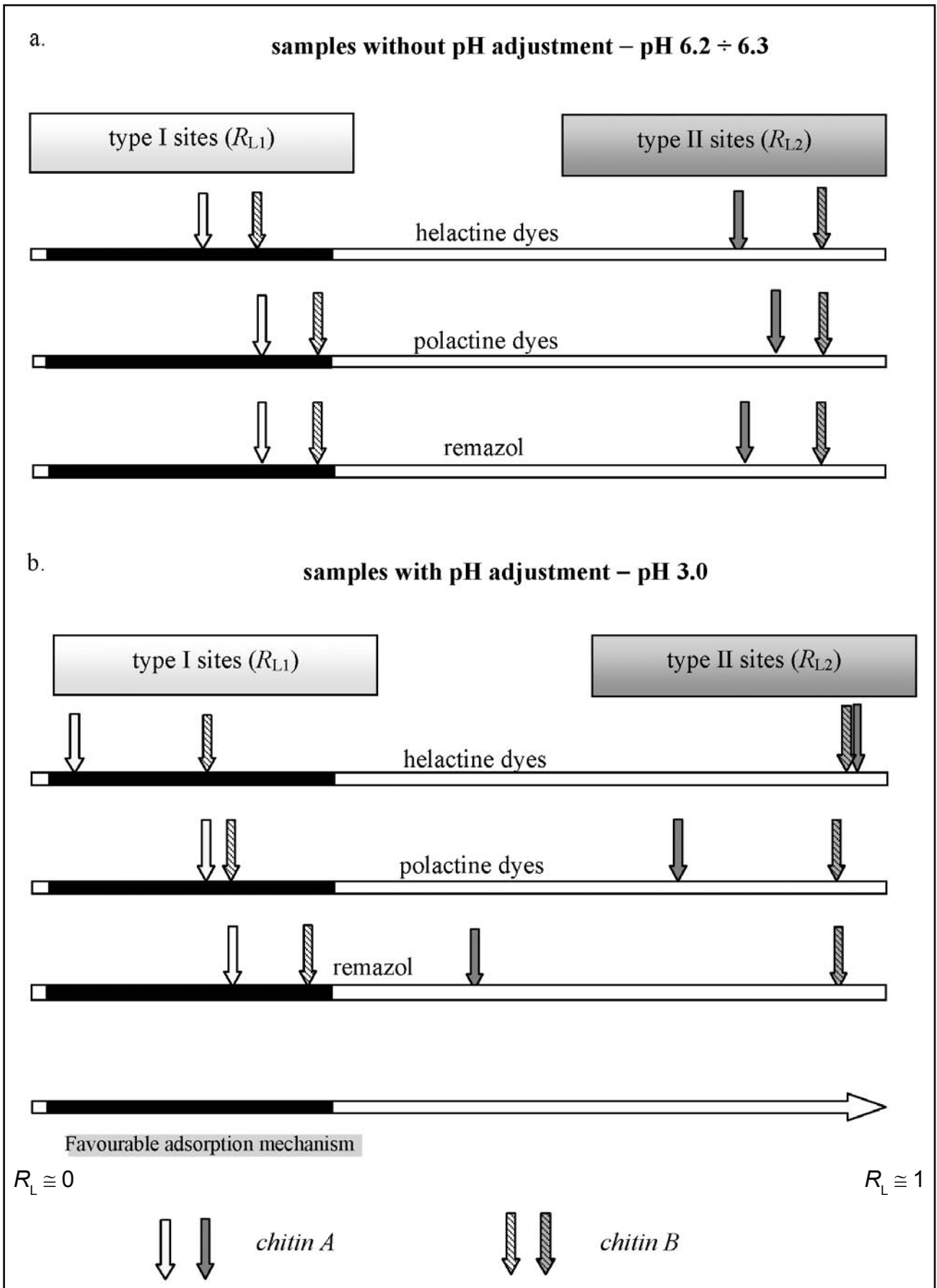


Fig. 13. The separation factor R_{L1} and R_{L2} calculated for helactine, polactine and remazol group dyes.

Table 2. The separation factor R_L values for different chemical and biological adsorbents.

Adsorbent	Dye	R_L [-]		References
“Cucurbituril”	Reactive Black 5 Reactive orange 96 Reactive Red 120	0.002 – 0.029		Karcher et al. [20]
Modified chitin (chitin B)	Yellow D-5RN Red D-8B Ruby F-2B Blue D-5RN Black DN	0.002 – 0.005	0.963 – 0.984	Data from this paper
	Yellow 2R Scarlet R	0,014 – 0,015	0,463 – 0,769	
	Gelb GR Brillantorange 3R Blau 3R	0.019 – 0.039	0.191 – 0.290	
Modified chitin (chitin A)	Yellow D-5RN Red D-8B Ruby F-2B Blue D-5RN Black DN	0.010 – 0.018	0.877 – 0.987	Data from this paper
	Yellow 2R Scarlet R	0.025 – 0.030	0.749 – 0.826	
	Gelb GR Brillantorange 3R Blau 3R	0.054 – 0.154	0.685 – 0.903	
Lignin V	Cation Red BLN Cation Blue GRL Astrazone Blue BG Astrazone Blue FGLN Reactive Blue DGR	0.011 – 0.587		Łebek, Wardas [21]
Chitosan non-modified	Acridine Orange Red Kongo Crystalline Purple Neutral Red Safranin O	0.020 – 0.959		Šafařík [7]
Activated carbon	Reactive Yellow Reactive Black Reactive Red	0.024 – 0.385		Al-Degs et al. [16]
Bagasse pith	Basic Blue 69 Basic Red 22 Acid Red 114 Acid Blue 25	0.157 – 0.844		Mckay et al. [3]
Maize cob	Telone Blue ANL Erionyle Red RS Maxilone Red BL-N Astrazone Blue FRR	0.397 – 0.890		El-Geundi [2]
Modified chitosan	Acridine Orange Red Kongo Crystalline Purple Neutral Red Safranin O	0.112 – 0.387		Šafařík [7]

0.963 to 0.984, and for remazol dyes from 0.191 to 0.290 (Fig. 12 a,b).

Based on the results the effect of chitin type and pH on the adsorption efficiency of particular dye groups was evaluated. The examined dye groups were systematized according to increasing R_L values. Black colour means

the values $R_L \ll 1$, which indicate favourable adsorption mechanism (Fig. 13).

The obtained results indicate that helactine dyes had a higher adsorption effectiveness in type I sites by comparison with polactine and remazol dyes both on *chitin A* and *chitin B*. The adsorption efficiency in type II sites differed

for particular groups.

Evaluating the effect of chitin preparation, it can be stated that in samples without pH adjustment by increase in deacetylation degree the similar increase in R_{L1} and R_{L2} values was obtained independently from dye affiliation to a particular group (Fig. 13a). In the samples with pH adjustment the strong decrease of the R_{L1} value was noted for helactine dyes by the increase in the chitin deacetylation degree, but the R_{L2} values were almost the same. It can be assumed that the adsorption on the chitin a large amount of dye molecules with three or four sulfone groups as a result of ion-exchange prevented their binding in the type II sites. As opposed to helactine dyes, the increase in the deacetylation degree caused a small decrease in the R_{L1} values for dyes containing vinyl sulfone groups, polactine and remazol dyes, and the significant drop of R_{L2} values. The change of deacetylation degree from 3 to 5% for remazol dyes caused the drop of the R_{L2} value from 0.9 to 0.2.

This indicates that the increase in deacetylation degree causes a diversity of adsorption efficiency depending on the dye affiliation to the group.

Assuming the R_{L1}/R_{L2} (pH 3.0) ratio as a criterion for the estimation of the effect of pH on the adsorption efficiency, depending on the chitin deacetylation degree, the dyes were ordered as follows:

• type I sites:

chitin A polactine dyes >> helactine dyes > remazol dyes

chitin B polactine dyes > helactine dyes >> remazol dyes

• type II sites:

chitin A remazol dyes \cong polactine dyes > helactine dyes

chitin B remazol dyes > polactine dyes > helactine dyes

In order to estimate the effect of pH in the case of *chitins A* and *B* at the deacetylation degree of 3 and 5%, it can be concluded that for type I sites the change of pH influenced most favourably the effectiveness of helactine dye adsorption, and the least favourable remazol dye adsorption. In the case of type II sites the change of pH influenced most strongly remazol dye adsorption, and the weakest helactine dyes, independently from the chitin deacetylation degree.

Research showed that among three groups of dyes, helactine dyes in type I sites had the lowest coefficient $R_L \ll 1$. Assuming that the dye adsorption on chitin type I sites was a ion-exchange, the following decreasing order of the adsorption can be stated: helactine dyes > polactine dyes > remazol dyes.

The adsorption mechanism on chitin type II sites was a physical adsorption in the following increasing order: remazol dyes > polactine dyes > helactine dyes.

Using both the literature data (constant K) and the maximum adsorbent capacity (constant b), the separation factor R_L values were calculated for chemical and biological adsorbents used for dye adsorption. Then the obtained data were compared with our own results (Tab. 2).

A comparison of R_L values indicates that krill chitin used in the experiment exhibits a high adsorption

capacity towards examined dyes. This is confirmed by the R_L values. The similar effectiveness to *chitin A* type I sites showed the synthetic adsorbent called customary "*cucurbituril*" containing nitrogen atoms. The effective adsorbents were also lignin V, activated carbon and chitosan. Cellulose-containing biosorbents turned out to be less effective in dyes removal.

Conclusions

Based on our results the following can be concluded:

1. Biological adsorbents of a complex chemical structure, e.g. chitin, have two active sites of different energy of the adsorbate binding. For this reason the Langmuir equation and the double Langmuir equation were examined in order to estimate the relationship between the equilibrium solid phase and the equilibrium liquid phase dye concentration. The double Langmuir equation turned out the better model to describe experimental data, except for the adsorption of helactine dyes on *chitin B* at pH 3.0.
2. Constants in the double Langmuir isotherm, i.e. maximum adsorption capacity b_1 and b_2 and K_1 and K_2 constants permitted to determine the dimensionless separations factors R_{L1} and R_{L2} . The dimensionless separations factor R_L informs the interaction between adsorbent and adsorbant. Research proved that the dye adsorption process for type I sites revealed the characteristics of ion-exchange, whereas in the case of type II sites - the characteristics of a physical adsorption.
3. Adsorption efficiency for chitin (prepared with NaOH) of the deacetylation degree of 5% at pH 3.0, for type I sites decreased in the following order: helactine dyes > polactine dyes > remazol dyes. The adsorption efficiency for type II sites was opposite: remazol dyes > polactine dyes > helactine dyes.
4. The increase in total adsorption capacity was noted by treating the chitin with NaOH similarly to pH decrease. The way of chitin preparation influenced strongest the adsorption of helactine dyes at pH 6.2-6.3, where a 3-fold increase in total adsorption capacity was noted at 1.67-fold increase in the deacetylation degree. For other dye groups this increase was from 2-fold (polactine and remazol dyes at pH 6.2 -6.3) to 2.7-fold (polactine and remazol dyes at pH 3.0).
5. Adjusting pH to 3.0 influenced the amide and acetamide groups' protonation. It caused an increase in total adsorption capacity for all tested dyes, apart from the method of chitin modification. The strongest effect of pH decrease on the adsorption was obtained for dyes with vinyl moiety and for *chitin B* treated with NaOH.

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