

# THE INFLUENCE OF CHITIN AMINATION ON THE EFFECTIVENESS OF RB5 AND RY84 DYE SORPTION

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## Abstract

*This article presents the influence of chitin amination on the effectiveness of RB5 and RY84 dye sorption. For chitin and chitin modified by amination, the optimal pH of sorption and the maximum sorption capacity were determined in relation to two reactive dyes: Reactive Black 5 (RB5) and Reactive Yellow 84 (RY84), differing in the active group and molecular weight. Three sorption models were used to describe the experimental data: Langmuir, Langmuir 2 and Freundlich. The highest sorption capacity was obtained for aminated chitin for both tested dyes: 386.53 mg/g for RB5 and 261.56 mg/g for RY84. In the case of sorption on unmodified chitin, the sorption capacities were lower: up to 235.65 mg/g.d.m. for RB5 and 208.88 mg/g.d.m. for RY84. The modification of chitin by amination has a beneficial effect on the amount of dye adsorbed in the process. The adsorptive capacity increased by 1.6-times in the case of RB5 and 1.25-times in case of RY84.*

**Key words:** sorption, chitin, ammonification, dye

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## **1. Introduction**

Chitin is regarded as a material of high potential with the possibility of structure change in order to achieve desirable properties [1]. The literature describes various methods of chitin modification, aiming to improve its properties as well as to create new, better products. Physical parameters such as the size of the main surface and the diameter of pores and chemical parameters such as the addition of amino groups might be altered.

The purpose of this process is the improvement of sorption properties, as well as the increase in mechanical durability and resistance to acidic environments. The modifications are carried out using physical or chemical methods. Physical methods include obtaining chitosan in different forms, such as powder, nanoparticles, gel beads, membranes, sponges, 'honeycomb' structures and various types of fibres [2]. The ultrasound modification of chitin leads to an increase in the porosity of material, enables easier flow of the substance and, as a consequence, increases the number of locations to bond the dye. The adsorbent has the same functional group as before the modification, but a larger surface and an amorphous structure.

Chemical processes rely on crosslinking of the polymer structure with crosslinking agents such as glutaraldehyde, oxidised  $\beta$ -cyclodextrin, diglycidyl ether of ethylene glycol and epichlorohydrin [3].

Chitosan, as a product of the N-deacetylation of chitin, can also be a subject to various types of modifications and crosslinking. The modification of chitosan is easier due to the presence of free amino groups in its molecular structure, which increases its reactivity [4].

Dyes are chemical compounds with the ability to intensively absorb electromagnetic radiation in the visibility range, close to ultraviolet and infrared. They transform the absorbed energy and forward it to other materials. Dyes have diverse and complex chemical structures, which causes differences in their physicochemical and usable properties.

In the cellulose and textile industry, reactive (helactine) dyes appear to be the most useful; their advantage is their durability and the high quality colour of the dyed material. This group contains anionic dyes, the characteristic feature of which is the presence of azo groups in the molecular structure (-N=N-). Anionic dyes are firstly adsorbed on cellulose and then react with cellulose fibres. The reaction occurs through the creation of covalent bonds between the molecules of dye and fibres. However, hydroxyl ions present in the colouring bath compete with the cellulose bed in the alkaline environment. The result of that is the presence of 10–50% of the initial dye concentration in the wastewater [5].

The aim of the current work was to determine the effectiveness of reactive dyes Reactive Black 5 (RB5) and Reactive Yellow 84 (RY84) removal from aqueous solutions by sorption, with the use of two sorbents: chitin and chitin subjected to ammonification.

## **2. Materials and Methods**

### **2.1 Chitin**

The sorbents used in the research were from Heppel Medical Chitosan GmbH in Halle. The studies used chitin in the form of flakes with a deacetylation degree DD = 35%.

## 2.2 Ammonification of chitin

The chitin flakes were placed in a beaker and then the solution of epichlorohydrin (in the ratio 1g/1g chitin) was added. They were maintained for 24 hours at a high temperature (60°C) in a water bath. Afterwards, the chitin was rinsed with distilled water in order to get rid of the excess epichlorohydrin. The next step was to place the obtained sorbent in the beaker on a magnetic stirrer and then add ammonia water with a concentration of 25% NH<sub>4</sub> (in the ratio 2g/1g chitin) for 24 hours. The prepared sorbent had 31.36% of ammonium.



Figure 1. Chitin



Figure 2. Aminated chitin

## 2.2 Characteristics and preparation of dyes

Experiments were conducted with Reactive Black 5 and Reactive Yellow 84 dyes produced by ZPB "Boruta" SA in Zgierz (Poland). The structures of the reactive dye are presented in Table 1.

Table 1. Characteristics of the dyes

Reactive Black 5 - (RB 5)	Reactive Yellow 84 - (RY84)
991 g/mol	1701 g/mol
$\lambda_{max}$ - 600 [nm]	$\lambda_{max}$ - 356 [nm]
acid charakter (anionic - reactive)	acid charakter (anionic - reactive)
Class – diazo dye	Class – diazo dye
vinylsulfonic groups	chlorotriazine groups
Application: dyeing of cotton, viscose, wool, polyamide fibers	Application: dyeing of: polyester, cotton, artificial silk

A stock solution of dye was prepared by weighing 1.00 g of pure powdered dye. The dye was quantitatively transferred into a 1000 cm<sup>3</sup> measuring flask which was then filled with distilled water. The dye concentration in the solution reached 1000 mg/L. The stock solution was used to prepare working solutions.

### **2.3 Determination of the optimal pH of adsorption process**

The weighed amount of chitin and ammonified chitin sorbents were placed in 250 ml Erlenmeyer flasks. Then, working solutions with a concentration of 100 mg/l and pH of 2–11 were added. The flasks with sorbents and dye solutions were placed on a shaker (150 rpm) for 120 minutes. After that, the samples were taken (10 ml each) with an automatic pipette. The concentrations of dyes left in the solutions were determined using spectrophotometric methods on a UV-VIS spectrophotometer. After the end of the experiment, the change in pH of the solution in relation to the initial pH was defined.

### **2.4 Determination of the maximum adsorption capacity**

In order to determine the adsorption capacity of chitin flakes and modified chitin flakes, the sorbent was weighed into 250 cm<sup>3</sup> Erlenmeyer flasks and supplemented with 100 cm<sup>3</sup> of the working solution of the dye at concentrations from 50–1000 mg/L and optimal pH value. Flasks thus prepared with solutions and sorbents were set on a shaker (150 rpm). After 24 hours, samples were taken to determine the dye remaining in solution. The concentration of each dye after shaking was determined by colorimetric methods using a UV-VIS SP 3000 spectrophotometer.

### **2.5 Determination of zeta factor**

In order to determine the p<sub>H<sub>ZPC</sub></sub> of sorbents, 50 ml of 0.01 M KNO<sub>3</sub> solution with an initial pH (pH<sub>0</sub>) from 3–12 was added to the conical flask. To each flask, 1 g of sorbent was also added and then the mixture was stirred for 24 hours. After this, the final pH of the solution was measured. The p<sub>H<sub>ZPC</sub></sub> value was determined based on the curve. The zero point was located at the intersection of the curve, defining the relation of ΔpH to pH<sub>0</sub> with the axis of a graph on which the pH<sub>0</sub> is marked.

### **2.6 Analytical methods**

The concentration of dye left in the aqueous solution was determined spectrophotometrically in each sample. Samples for analysis were collected (10 cm<sup>3</sup>), decanted and centrifuged for 15 min at 10,000 rpm. To assay the dye concentration, each solution was adjusted to pH 6. The concentration of the remaining dye was determined acc. to standard curves in an SP-3000 UV-VIS spectrophotometer. A wavelength at which absorbance was measured was determined for each of the dyes examined (Table 1).

### **2.7 Calculation methods**

The effectiveness of dye adsorption from the solution was analysed based on changes to the concentration in solution.

The quantity of adsorbed basic and acid yellow was calculated using formula (1):

$$Q = \frac{C_0 - C_s}{m} \quad (1)$$

where:

$Q$  – mass of adsorbed dyes [mg/g.d.m.],

- $C_0$  – initial concentration of dyes [mg/L],  
 $C$  – dyes concentration after adsorption [mg/L],  
 $M$  – mass of adsorbent [g.d.m].

Three different adsorption models were used to determine the maximum sorption capacity.

Homogeneous Langmuir model (2) and double Langmuir model (3):

$$q_e = \frac{q_{\max} \cdot K_C \cdot C}{1 + K_C \cdot C} \quad (2)$$

where:

- $q_e$  – equilibrium amount of dyes absorbed [mg/g.d.m];  
 $q_{\max}$  – maximum sorption capacity of sorbent monolayer [mg/g.d.m];  
 $K_C$  – constants in Langmuir equation [L/mg];  
 $C$  – concentration of dyes remaining in the solution [mg/L].

$$q_e = \frac{q_{\max_1} \cdot K_{C_1} \cdot C}{1 + K_{C_1} \cdot C} + \frac{q_{\max_2} \cdot K_{C_2} \cdot C}{1 + K_{C_2} \cdot C} \quad (3)$$

where:

- $q_e$  – equilibrium amount of dyes absorbed [mg/g.d.m];  
 $q_{\max_1}$  – maximum sorption capacity of sorbent (active site of the first type) mg/g.d.m];  
 $q_{\max_2}$  – maximum sorption capacity of sorbent (active site of the second type) mg/g.d.m];  
 $k_1; k_2$  – constants in Langmuir 2equation [L/mg];  
 $C$  – concentration of dyes remaining in the solution [mg/L].

Heterogeneous Freundlich model (4):

$$q_e = K_F C^{1/n} \quad (4)$$

where:

- $q_e$  – equilibrium amount of dyes absorbed [mg/g.d.m];  
 $C$  – concentration of dyes remaining in the solution [mg/L],  
 $K$  – constants sorption equation [-];  
 $n$  – constants in Freundlich equation [-].

The adjustment of experimental data to mathematical models was determined with the use of the correlation coefficient  $R^2$  (4):

$$R^2 = \frac{\sum (q_{cal} - \bar{q}_{exp})^2}{\sum (q_{cal} - \bar{q}_{exp})^2 + \sum (q_{cal} - q_{exp})^2} \quad (5)$$

where:

- $R^2$  – correlation coefficient – a measure of data alignment to the model  
 $q_{exp}$  – the experimental data – sorbed amount of dyes [mg/g s.m.]  
 $q_{cal}$  – theoretical data resulted from the model – sorbed amount of dyes [mg/g s.m.]

The program STATISTICA 10.0 was applied to determine the fit of the curves (with the determined constant) to the experimental data with the use of non-linear estimation by the method of least squares, at a significance level of  $p < 0.05$ .

### 3. Results and discussion

#### 3.1. Effect of pH on the effectiveness of dye sorption

The optimal pH for solutions of colour was determined based on the changes to the concentrations of adsorbed dyes after 2 hours of sorption. The research was carried out for two dyes, RB5 and RY84, at a concentration of 100 mg/dm<sup>3</sup> and for two sorbents, chitin and ammonified chitin. The changes in the concentration of dyes depending on pH are shown in Fig. 3.

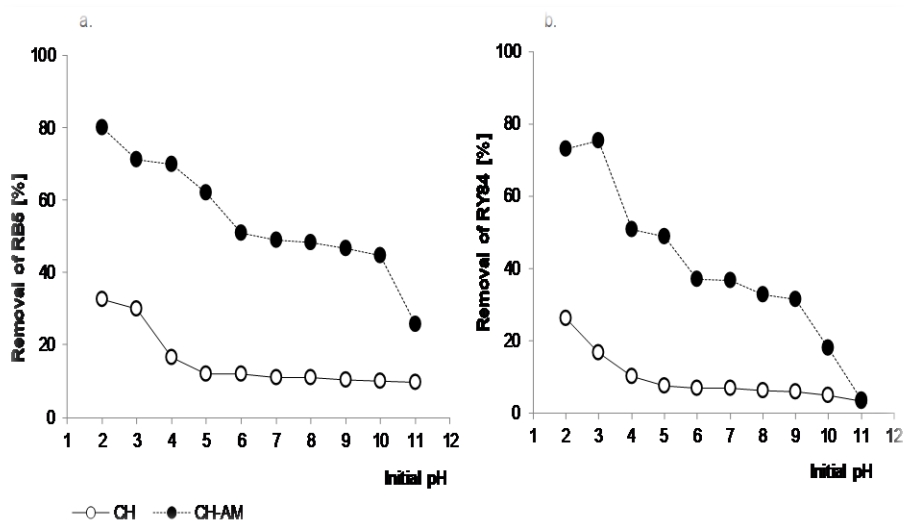


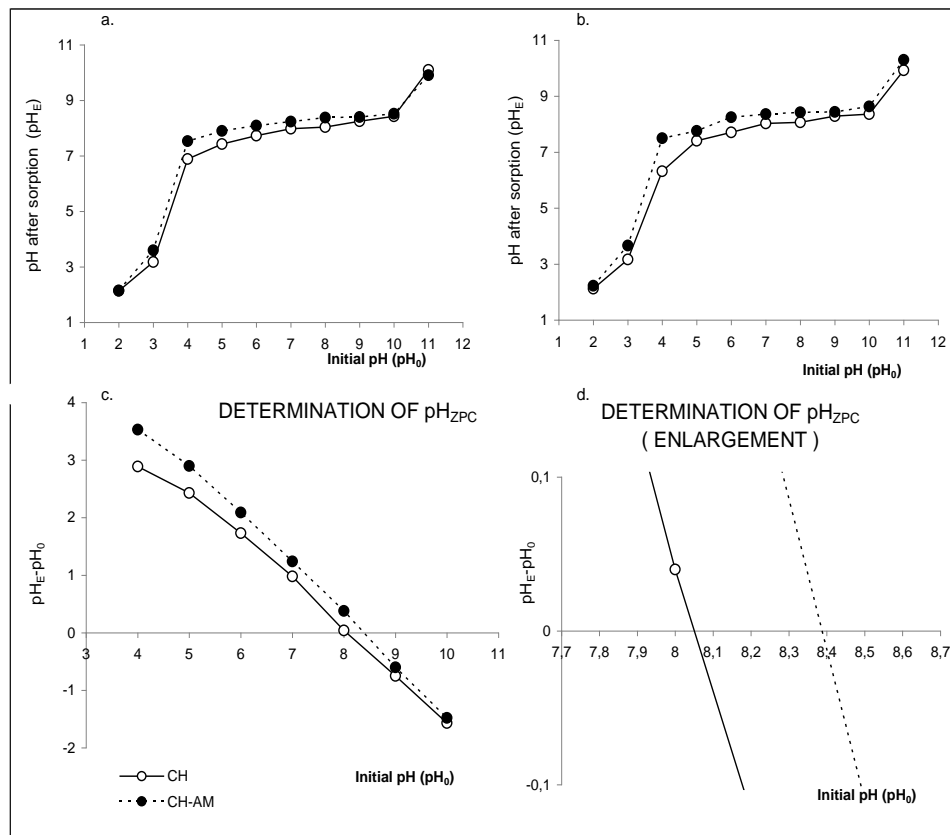
Figure 3. Effect of pH on the efficiency of dye sorption a. RB5, b. RY84

The effectiveness of RB5 sorption on CH and CH-AM was the highest at pH 2–3 and decreased with increasing pH by weight an initial pH of 4–11. The research has shown that the change in pH at which the sorption process was run influenced the amount of bound dye and depended on the tested sorbent. In the case of unmodified chitin, the pH change from 2–4 caused a decrease in the effectiveness of sorption, whereas the increase in the pH from 5–11 did not cause a significant decrease in the effectiveness of sorption. In the case of ammonified chitin, the sorption effectiveness was decreasing along with the increase in pH over the entire range examined. This tendency was observed for both of the tested dyes.

The beneficial effect of low pH for the adsorption of anionic dyes on chitosan is confirmed by numerous studies, both by our group and other authors [8-13]. This is due to the electrostatic interaction of anionic dye with a negative charge and chitosan adsorbent with a positive charge. At a low pH, there is the protonation of chitosan amine groups that attract anionic dyes electrostatically. The increase in pH at which the adsorption is carried out is associated with the appearance of an increasing amount of OH<sup>-</sup> groups in solution, which consequently lead to a change in the charge of the adsorbent and the electrostatic repulsion of a negatively charged dye. A reduction of the efficiency of RB5 adsorption at high pH may also result from the competition of anionic dyes with the OH<sup>-</sup> ions for the active sites of the adsorbent.

Figure 4 shows the pH change in the dye solution after adsorption. Significant changes were observed after the adsorption reaction compared with the initial pH of the

solution. For the initial pH range from 4–10 for both the tested adsorbents and dyes, the pH after adsorption was in the range from pH 7–8.



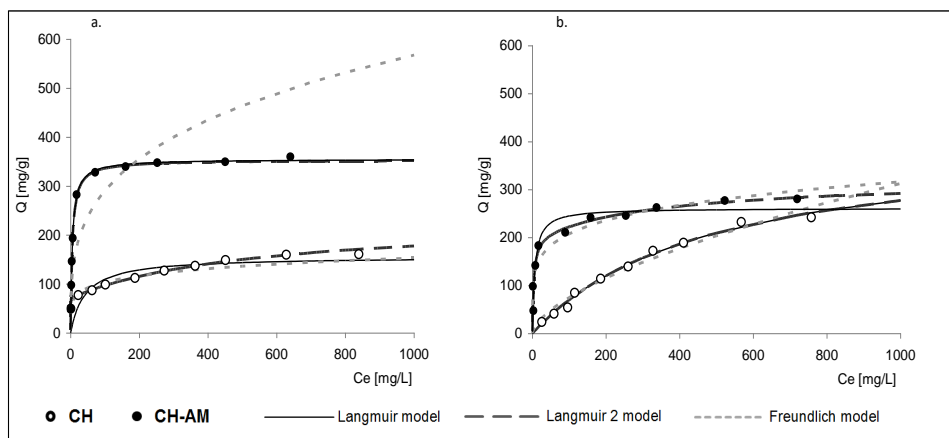
**Figure 4** Change in the pH of the solution after sorption a. RB5, b. RY84; and the determination of pH<sub>ZPC</sub> of the sorbents c. RB5, d. RY84.

The pH of the solution during adsorption always aimed to reach a level similar to the pH<sub>ZPC</sub> of the tested sorbent. The pH<sub>ZPC</sub> point value, determined for the CH and CH-AM was successively 8.05 and 8.39, and is related to the nature of the adsorbent and its possession of functional groups.

Adsorption capacity studies presented in the work were conducted at a pH of 3 with regard to the actual pH of the effluent colour range.

### 3.2 The maximum sorption capacity of the adsorbent

The experimental results of RB5 and RY84 dye adsorption from the aqueous solution and isotherms determined from Langmuir 2, Langmuir and Freundlich equations are presented in Figure 5.



**Figure 5.** Experimental results for RB5 and RY84 on a. chitosan (CH), b. aminated and adsorption isotherms determined from Langmuir, Langmuir 2, and Freundlich models

Based on the determination coefficient  $R^2$ , it can be stated that the results of the experimental adsorption for RB5 and RY84 on two tested adsorbents (the CH and CH-AM) are best described by the double Langmuir model (Table 2). This confirms that the binding of the tested dyes was in different active centres through the groups [6]. The groups could be in the form of amino and acetamide chitin groups.

**Table 2.** The correlation coefficient  $R^2$  for Langmuir, Langmuir 2, and Freundlich models and the tested sorbents

Dye	Sorbent	Double Langmuir model	Langmuir model	Freundlich model
		$R^2$	$R^2$	$R^2$
RB 5	CH	0.9983	0.9694	0.9907
	CH-AM	0.9965	0.9960	0.8540
RY 84	CH	0.9890	0.9890	0.9513
	CH-AM	0.9774	0.7790	0.9505

Table 3 shows the constants from Langmuir 2, Langmuir and Freundlich models.

**Table 3.** Reactive Black 5 and Reactive Yellow 84 adsorption constants determined from Langmuir, Langmuir 2, and Freundlich models for the tested adsorbents

Dye	Sorbent	Double Langmuir model					Langmuir model		Freundlich model	
		$q_e$ [mg/g]	$q_{max1}$ [mg/g]	$K_1$ [dm <sup>3</sup> /mg]	$q_{max1}$ [mg/g]	$K_2$ [dm <sup>3</sup> /mg]	$q_e$ [mg/g]	$K$	$k$	$n$
RB5	CH	234.65	71.27	7.4300	163.38	0.0019	181.94	0.0140	9.950	0.428
	CH-AM	386.53	353.05	0.2100	33.48	0.0001	355.27	0.2010	130.1	0.174
RY84	CH	208.88	100.42	0.0009	108.46	0.0030	208.88	0.0029	4.110	0.540
	CH-AM	261.56	151.24	0.0029	110.32	0.4700	147.85	0.1980	55.43	0.169



The enrichment of the sorbent with amino groups in a unitary chemical process that involves the introduction of the amino group  $-NH_2$  in place of the hydroxyl  $-OH$ , sulphone  $-SO_3H$ , ketone  $=C=O$ , and aldehyde  $-CHO$  groups, as well as halogen: Cl, Br and others. The sorbent amination might successfully increase the anionic dye sorption effectiveness by the introduction of  $-NH_2$  groups and strengthen the electrostatic effects between the sorbent and the dye [7].

The results from the experimental data show that the highest sorption capacity was obtained for aminated chitin; for the tested dyes, it was 386.53 for RB5 and 261.56 mg/g for RY84. In the case of sorption on unmodified chitin, the sorption capacities were lower: 234.65 mg/g d.m. for RB5 and 208.88 mg/g d.m. for RY84.

The amination of chitin also influenced how the dyes were bonded. The RB5 dye, with a chlorotriazine active group, showed very high affinity to unmodified chitin in the first type of active site: 7.43 dm<sup>3</sup>/mg. The modification of chitin caused a significant decrease in affinity to 0.21 dm<sup>3</sup>/mg in the active sites of the first type and a simultaneous increase in the amount of bonded dye from 71.27 to 353.05 mg/g. The analysis of constants determined from the double Langmuir and Langmuir models allow the proposal that the adsorption only happened in the active sites of one type. The constants determined from the double Langmuir model ( $q_{max1} = 353.05$  mg/g and  $K_1 = 0.21$  dm<sup>3</sup>/mg – first type active sites) and Langmuir model ( $q_e = 355.27$  mg/g and  $K_1 = 0.201$  dm<sup>3</sup>/mg) are comparable. The RY84 dye differed from RB5 due to the active group (vinylsulphone), and a molecular mass that was almost twice as high; it showed a significantly lower affinity to unmodified chitin, as well as to ammonified chitin, in comparison with RB5 in the active sites of the first type. Regarding the type of chitin, it is possible to notice that the amination of chitin influenced the increase in K constants regardless of the model describing the experimental data. This may indicate a change in the binding of RY84 to chitin with amino groups.

#### 4. Conclusions

The higher effectiveness of adsorption was obtained with the use of aminated chitin. The adsorption capacity increased 1.6-times in the case of RB5, and 1.25-times in the case of RY84 in relation to the adsorption capacity of chitin not subjected to modification. In the research, it was stated that the adsorption process of two tested dyes was more effective on ammonified chitin. The reason for that was the addition of amino groups to the structure of the chitin molecule. The adsorption of dyes was best described with the double Langmuir model.

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