THE USE OF CHITIN AND CHITOSAN FOR THE REMOVAL OF REACTIVE BLACK 5 DYE

Paula Szymczyk[1*], Urszula Filipkowska[1], Tomasz Jóźwiak[1], Małgorzata Kuczajowska-Zadrożna[2]

*[1]Department of Environmental Engineering,
University of Warmia and Mazury in Olsztyn
ul Warszawska 117, 10 – 719 Olsztyn, Poland
e-mail: paula.szymczyk@uwm.edu.pl*

*[2]Department of Biotechnology in Environmental Protection,
University of Warmia and Mazury in Olsztyn
ul. Słoneczna 45G,10–709Olsztyn, Poland*

Abstract

In this study, we investigated the effectiveness of Reactive Black 5 dye adsorption onto chitin and chitosan flakes. Adsorption capacity of chitin and chitosan, optimal pH of the adsorption process and reaction equilibrium time were determined. Results achieved were described with Freundlich, Langmuir and double Langmuir models.

The pH value ensuring the highest dye adsorption effectiveness onto chitosan was pH 4. In turn, the highest dye adsorption effectiveness onto chitin was determined at pH 2, however considering that the pH value of industrial wastewater containing reactive dyes ranges from pH 3 to pH 4, further analyses with chitin were continued at pH 3. The time needed to reach the equilibrium concentration of dye was 360 min for chitin and 72 hours for chitosan.

The study demonstrated that chitosan is the most effective sorbent of RB5. Its maximum adsorption capacity of the reactive dye accounted for 696.99 mg/g d.m., compared to 131.56 mg/g d.m. determined for chitin. Higher effectiveness of RB5 removal by chitosan is result of more number of amine groups in the chemical structure of this polymer, compared to chitin.

Key words: adsorption, chitosan, chitin, Reactive Black 5 (RB5)

1. Introduction

According to statistical data, over 10,000 types of dyes are available in trade turnover. They may be divided into three basic groups: anionic dyes (direct, acidic, reactive) cationic dyes (alkaline) and non-ionic dyes [1]. Ca. $7x10^5$ tons of dyes are produced annually for the needs of the global textile, cellulose and tanning industries [2]. As a result of low susceptibility of some materials to dyeing and high solubility of dyes, from 10 to 50 % of dyes are released to wastewater during the dyeing process [3,4]. Owing to the presence of aromatic rings, dyes show very low susceptibility to biodegradation [5]. Conventional systems of wastewater treatment are characterized by low effectiveness of dyes removal, hence 10-15% of dyes are discharged to the natural environment with treated wastewater [6]. Even low concentrations of dyes – at 1 ppm – are noticeable in natural waters and significantly affect the natural environment. The problem of dyes in the aquatic environment is not only aesthetic in nature. Color compounds reduce oxygen diffusion in water and the access of light, thereby intensifying the process of eutrophication and contributing to depletion of freshwater resources [7]. Dyes may induce allergies, skin inflammations and irritation, as well as neoplasms and mutations in humans [8,9,10]. A severe environmental problem is also posed by toxic products of their degradation including, e.g., aromatic amines [11]. It seems advisable, therefore, to apply the most effective technology for industrial wastewater decolorization.

Many physical, chemical and biological methods of wastewater decolorization have been proposed in recent years, however only a few of them have been accepted by the industry [12]. One of the most effective turned out to be adsorption due to its high effectiveness and applicability for the removal of various types of dyes. The most commonly applied sorbent so far has been activated carbon owing to its high effectiveness of dyes removal from aqueous solutions [13]. Its use for dyes sorption from wastewater is, however, economically-unprofitable due to high costs of its production and recovery. For this reason, municipal wastewater treatment plants and industrial plants search for novel, inexpensive and effective technologies for dye removal.

An alternative solution of dye removal from aqueous solutions seems to be their adsorption onto chitin or chitosan. Chitin is abundant in the natural environment and its acquisition does not involve high financial outputs. Chitin is acquired from waste products of seafood processing, whereas chitosan is a deacetylated form of chitin produced with cheap chemical reagents [14].
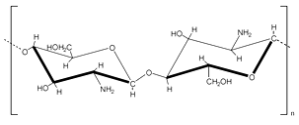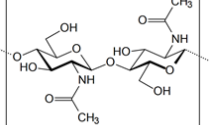
The main objective of this study was to evaluate the possibility of removing color substances in the process of adsorption onto biosorbents, namely chitin and its modified form – chitosan. Attempts were also undertaken to demonstrate differences in chitin and chitosan capabilities for adsorption of high and low concentrations of dyes.

2. Material and methods

2.1. Chitosan and chitin

Chitosan in the form of flakes (DD = 85%) and chitin in the form of flakes (DD < 15%) were purchased from BioLog company. Characteristics of adsorbents was presented in Table 1.
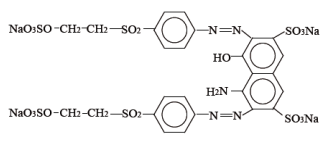
Table. 1 Characteristics of chitosan and chitin

	Chitosan	**Chitin**
Structural formula		
Degree of deacetylation	82.6 % - 87.5 % (average 85 %)	< 15 %

2.2. Dye

The study was conducted with anionic dye Reactive Black 5 (RB5), the structure and properties of which were presented in Table 2.

Table 2. Reactive dye RB5

Reactive Black 5 - [RB5]	
Structural formula of anionic dye	
Molecular weight	991 g/mol
λ_{max}	600 nm
Type of chromophore group	azo
Type of active groups	vinylsulfone

In order to prepare a working solution, 1 g of pure RB5 dye powder was weighed and transferred quantitatively into a 1 dm^3 measuring flask. The flask was then filled up with distilled water. Dye concentration in the resultant solution reached 1000 mg/dm^3.

2.3. Effect of pH value on dye adsorption

To determine the optimal pH value of the adsorption reaction, aqueous solutions were prepared with dye concentration of 200 mg/dm^3 and pH values of: pH 2, pH 3, pH 4, pH 5, pH 7, pH 9, pH 10, and pH 11. Next, 1 g d.m./dm^3 of the adsorbent and 200 cm^3 of adsorbate solutions were added to 250 cm^3 beakers. Afterwards, the beakers were placed on a magnetic stirrer and after 1-h adsorption, adsorbate concentration was determined in the solution. Parameters of these analyses were presented in Table 3.

Table 3. Parameters of solutions to analysis of the effect of pH value on adsorption process

Adsorbent type	Dye	Adsorbent concentration [g d.m./dm^3]	Adsorbate concentration [mg/dm^3]	pH value
Chitin	RB5	1	200	2, 3, 4, 5, 7, 9, 10, 11
Chitosan	RB5	1	200	2, 3, 4, 5, 7, 9, 10, 11

2.4. Determination of reaction equilibrium time

1 g d.m./dm^3 of the adsorbent and 2000 cm^3 of Reactive Black 5 solution with the concentration of 10, 200 and 1000 mg/dm^3 were added to 2500 cm^3 beakers. Samples (5 cm^3) were collected in specified time intervals in order to determine the concentration of dye left in the solution (C_e). Experimental parameters were presented in Table 4.

Table.4 Parameters of determination of adsorption equilibrium time

Adsorbent type	Removed anion	Adsorbent concentration [g d.m./dm^3]	Adsorbate concentration [mg/dm^3]	Sample collection times [min]
Chitin	RB5	1	10, 200, 1000	5, 10, 15, 20, 30, 40, 50, 60, 90, 120, 150, 180, 210, 240, 300, 360, 420
Chitosan	RB5	1	10, 200, 1000	5, 10, 15, 20, 30, 40, 50, 60, 90, 120, 150, 180, 210, 240, 300, 360, 420, 720, 1080, 1440, 2160, 2880, 3600, 4320

2.5. Determination of the maximum adsorption capacity

1 g d.m./dm^3 of adsorbent and adsorbate solution in the concentration from 5 to 2000 mg/dm^3 were added to 250 cm^3 conical flasks. Then, the flasks were placed on a laboratory shaker. The concentration of dye left in the solution was determined after the time determined in the preliminary studies. Analytical parameters were presented in Table 5.

Table 5. Parameters of analyses of the maximum adsorption capacity

Adsorbent type	Removed anion	Adsorbent concentration [g/dm^3]	Adsorbate concentration [mg/dm^3]
Chitin	RB5	1	5, 10, 25, 50, 100, 200, 500, 1000, 1500, 2000
Chitosan	RB5	1	5, 10, 25, 50, 100, 200, 500, 1000, 1500, 2000

2.6. Calculation methods

The quantity of adsorbed dye was calculated from the following formula (1):

$$Q_s = \frac{C_o - C_e}{m} \qquad (1)$$

where: Q_s – weight of adsorbed dye expressed per gram dry mass of RB5 (mg/g d.m.); C_o – initial concentration of dye (mg/dm^3); C_e – concentration of dye after adsorption (mg/dm^3); m – weight of sorbent expressed per gram dry mass of chitin/chitosan(g d.m.).

Data achieved were described with the following models: Freundlich model, Langmuir model and double Langmuir model.

The Freundlich model (2) is applied to describe adsorption onto energetically-heterogeneous surfaces. According to this model, the quantity of adsorbed molecules cannot be higher than the number of active sites, and the formed layer enables the formation of successive layers [15].

$$Q = C^n \cdot k \qquad (2)$$

where: Q – weight of adsorbed compound (mg/g d.m.); k – adsorption constant; C – concentration of adsorbed substance in the state of equilibrium (mg/dm^3); n – constant in Freundlich equation.

According to Langmuir model (3), there are no interactions between the adsorbed molecules and these molecules form a monomolecular layer. The

quantity of adsorbed molecules depends on the adsorption capacity of the monolayer (q_{max}) and adsorption affinity of adsorbate to adsorbent (K_c).

$$Q = \frac{q_{max} \cdot K_c \cdot C}{1 + K_c \cdot C}$$

(3)

where: Q – weight of adsorbed compound (mg/g d.m.); K_c – constant in Langmuir equation (dm^3/g d.m.); q_{max} – maximum adsorption capacity of adsorbent monolayer (mg/g d.m.); C – concentration of adsorbed substance in the state of equilibrium (mg/dm^3).

The double Langmuir model (4) assumes that the surface of adsorbate in energetically-heterogeneous and possesses active centers with different energy of adsorbate molecules binding. The active sites are characterized by the following constants: b_1, K_1 and b_2, K_2, whereas adsorption capacity equals the sum of the maximum adsorption capacity at type I and type II active sites (b_1+b_2) [16,17].

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

(4)

where : Q – real adsorption of sorbate onto sorbent (mg/g d.m); b_1 – maximum adsorption capacity of sorbent (type I active sites) (mg/g d.m); b_2 - maximum adsorption capacity of sorbent (type II active sites) (mg/g d.m); K_1; K_2 – constants in Langmuir equation (dm^3/mg); C – concentration of adsorbed substance in the state of equilibrium (mg/dm^3)

3. Results and discussion

Figure 1 depicts the effect of the pH value on the effectiveness of RB5 adsorption. Results obtained allow concluding that the effectiveness of RB5 adsorption onto chitin and chitosan flakes was decreasing along with the increasing pH value. The highest effectiveness of dye removal from aqueous solutions onto chitin was achieved at pH 2, whereas onto chitosan – at pH 4. Considering that the pH value of industrial wastewater ranges from pH 3 to pH 4, therefore further analyses with chitin flakes were continued at pH 3. The effectiveness of RB5 removal onto chitin at pH 3 was over 37%, whereas in the case of chitosan it reached almost 60% at pH 4.

In the pH range of 3 – 4 is ensured the highest effectiveness of dye adsorption process, physical adsorption - induced most probably by protonation of amine groups of adsorbents - is the predominating process [18]. Similar conclusions were suggested by Cheung et al. [2009], who investigated of chitosan capability for acidic dyes sorption. In their study, an increase in pH from 4 to 6 caused a tenfold decrease of the adsorption capacity [19]. According to Crini and Badot [20], the highest effectiveness of anionic dyes adsorption onto chitosan might be achieved at pH from 3 to 6, whereas below that pH range the OH$^-$ ions compete with anionic dyes for active sites of the adsorbent, which

significantly impairs the chemisorption process. It additionally explains the diminished adsorption observed in our study at alkaline pH.
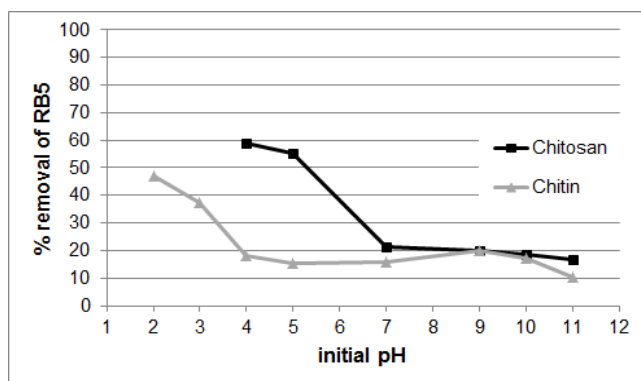

Figure 1. Effect of pH value on the effectiveness of RB5 dye adsorption onto chitin and chitosan flakes
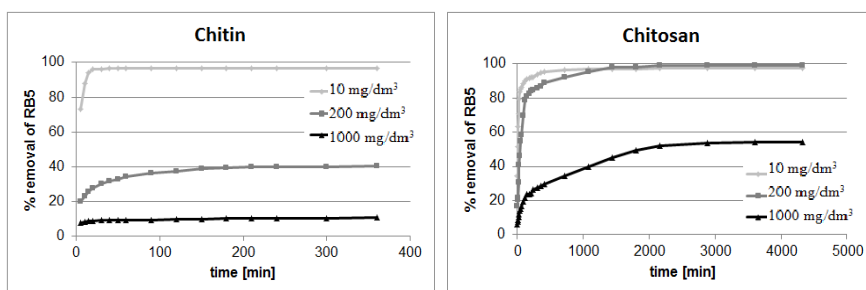

Figure 2. Time needed to reach the equilibrium of adsorption reaction of Reactive Black 5 dye onto chitin and chitosan and the effect of the initial concentration of dye on adsorption effectiveness, pH 3 for chitin and pH 4 for chitosan

Figure 2 presents equilibrium time of RB5 dye adsorption reaction at the earlier established pH value, i.e. pH 3 for chitin and pH 4 for chitosan, as well as the effect of the initial concentration of dyes on the adsorption process. Data presented in Fig. 2 demonstrate that the time needed to reach the equilibrium of the adsorption reaction reached 360 minutes for chitin and 72 hours for chitosan. Literature data confirm that reaction equilibrium time depends on the type of adsorbent, adsorbate and conditions of the process. The time needed to reach the equilibrium of RB5 sorption onto chitosan approximating 360 minutes was also confirmed by Akkaya et al. [21]. According to Gibbs et al. [22], adsorption of

Acid Green 25 onto chitosan ended after 1-2 h. In turn, Azlan et al. [23] demonstrated that the equilibrium time of Acid Red 37 reaction onto chitosan reached 100 minutes.

Figure 2 shows also that, in most cases, the effectiveness of RB5 adsorption onto chitin and chitosan was decreasing along with an increasing initial dye concentration. In the case of chitosan, RB5 removal effectiveness reached ca. 98% at dye concentration of 10 mg/dm^3, 99% at 200 mg/dm^3 and 54% at 1000 mg/dm^3. In turn, the use of chitin enabled removing 97% of dye from the solution with the initial dye concentration of 10 mg/dm^3, 40% at dye concentration of 200 mg/dm^3 and 11% from the solution with the highest initial dye concentration, i.e. 1000 mg/dm^3. The same dependency was reported by Gaffar at el. [24], who claimed that it was caused by a limited number of active sites in the structure of adsorbents. Our study demonstrates also that the time of dye removal from the solution with a low initial concentration of this dye was several times shorter using chitin than when using chitosan. From the solution with the concentration of 10 mg/dm^3 chitin was able to remove ca. 90% of dye within 10 minutes, whereas chitosan reached the same dye removal effectiveness already after 90 minutes. These differences are, probably, due to the possibility of applying lower pH in the case of chitin because it is insoluble at low pH.

The preliminary studies enabled establishing the maximum adsorption capacity of both sorbents.

Constants were determined for Freundlich, Langmuir and double Langmuir models with the method of non-linear regression. A measure of curve fit to experimental data was the R^2 coefficient. Figure 3 presents experimental data described with the use of the three above models.
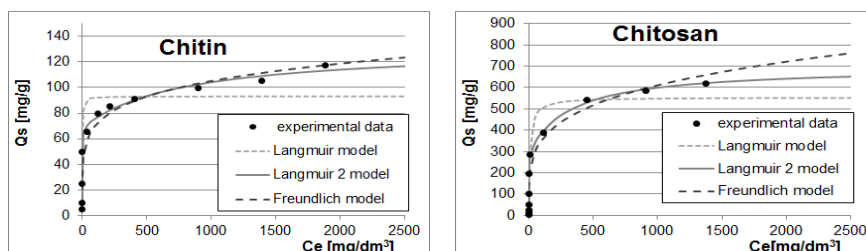

Figure 3. Comparison of the fit of Freundlich, Langmuir and double Langmuir model to experimental data

Based on results achieved, it may be concluded that the double Langmuir model was the best to describe Reactive Black 5 dye adsorption onto chitin and chitosan, which was indicated by the highest values of R^2 coefficient. The high coefficients of fit of double Langmuir model and Freundlich model indicate that the adsorption of RB 5 on both chitin and chitosan was not uniform. The binding could occur at energetically-heterogeneous sites (double Langmuir model) or a

few layers of dye molecules could be formed on surfaces of the adsorbents (Freundlich model). The fact that the active sites on the surface of chitin and chitosan are not homogeneous is additionally confirmed by a low coefficient of fit of the Langmuir model which assumes adsorbate binding in the form of a monolayer [25]. The R^2 coefficient values range from 0.96 to 0.99 in the Freundlich model indicates, probably, that the formed layer of adsorbed molecules enables the formation of successive layers of the dye [15]. Values of the fit coefficient for chitin and chitosan and reaction constants were presented in Table 6.

Table 6. Coefficients of fit and constants determined from double Langmuir equation, Langmuir equation and Freundlich equation.

Type of adsorbent	Constants in Langmuir equation		R^2	Constants in double Langmuir equation				R^2	Constants in Freundlich equation		R^2
	Q_{max}	K_c		b_1	K_1	b_2	K_2		k	n	
Chitin	91.1	0.879	**0.887**	69.14	1.314	62.4	0.0013	**0.961**	32.1	0.167	**0.910**
Chitosan	554.1	0.095	**0.932**	292.7	0.725	404.3	0.0032	**0.991**	115.9	0.241	**0.956**

Table 7. Constants determined from double Langmuir equation and total sorption capacity of chitin and chitosan against Reactive Black 5

	Sorption capacity (b_1+b_2) [mg/g d.m.]	Constants in Langmuir 2 equation				R^2
		b_1	K_1	b_2	K_2	
Chitosan	**696.991**	292.7	0.725	404.3	0.00318	0.991
Chitin	**131.562**	69.1	1.314	62.42	0.00129	0.941

Figure 4 presents results of experiments conducted with the use of double Langmuir, Langmuir and Freundlich isotherms for chitin and chitosan.

The adsorption capacity of sorbent was established based on the sum of b_1 and b_2 constants determined from double Langmuir equation. Data presented in Table 7 demonstrate that chitosan was characterized by higher sorption capacity of Reactive Black 5 compared to chitin. The maximum adsorption capacity of chitosan accounted for 696.99 mg/g d.m., whereas that of chitin – for 131.56 mg/g d.m. Literature data also demonstrate that chitosan is characterized by higher effectiveness of dye removal than chitin. It was confirmed by Prado et al. [26], who demonstrated that the sorption capacity of chitin against indigo carmine dye reached 1.24×10^{-5} and that of chitosan reached 1.54×10^{-4} mol/g. The differences in chitin and chitosan sorption capacity of Reactive Black 5 result from various chemical structures of these compounds. Better effectiveness of dye removal was achieved for chitosan because this polymer is constituted by

a higher number of amine groups that are responsible for the sorption of anions [26].

Figure 4. Experimental results of RB5 dye adsorption onto chitin and chitosan determined from double Langmuir, Langmuir and Freundlich equations
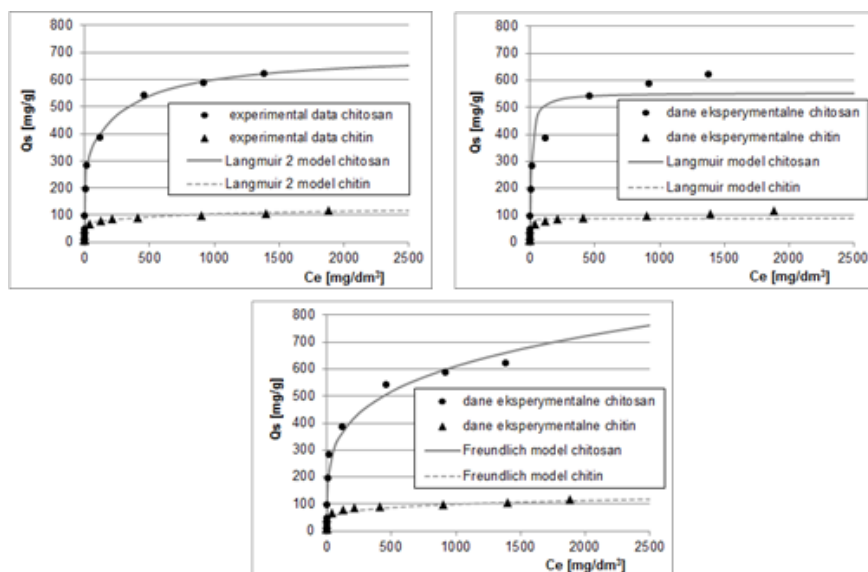
4. Conclusions

Based on results obtained in this study and literature data, it may be concluded that the sorption capacity depends on the structure of sorbate and process parameters, i.e. pH value and equilibrium time.

The study showed that chitosan is a better sorbent of Reactive Black 5 dye than chitin. The effectiveness of RB5 removal by chitin and chitosan was significantly influenced on the pH value of the process. At low pH values (pH 3 – 4), part of functional groups of the sorbents were subject to protonation, which had a positive effect upon the sorption of anionic dye. For this reason, the pH value which ensured the highest effectiveness of dye sorption was established at pH 3 for chitin and at pH 4 for chitosan.

The time needed to reach the equilibrium concentration of RB5 reached 360 minutes for chitin and 72 hours for chitosan.

The maximum adsorption capacity of chitosan accounted for 696.99 mg/g d.m., whereas that of chitin – for 131.56 mg/g d.m. The considerably higher effectiveness of nitrates removal onto chitosan is caused by a higher number of amine groups responsible for the sorption process.

High values of the fit coefficient of isotherms of double Langmuir model and Freundlich model to the achieved experimental data may point to the

sorption of Reactive Black 5 at energetically-heterogeneous sites and to the formation of several layers of dye molecules on the surface of the tested adsorbents.

5. Acknowledgements

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