

THE INFLUENCE OF CHITOSAN CONTENT IN HYDROGEL BEADS ON THE SORPTION EFFECTIVENESS OF REACTIVE BLACK 5 DYE

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Abstract

The influence of chitosan content in hydrogel beads on the sorption effectiveness of Reactive Black 5 (RB5) dye from aqueous solutions is presented in the following work. The dry mass of chitosan in the tested hydrogel chitosan sorbents was from 2 to 10%. The influence of pH (4–11) on the sorption effectiveness of RB5 on chitosan hydrogels as well as the sorption capacity of the tested chitosan sorbents in relation to RB5 were studied. The optimal pH of RB5 sorption was determined along with the pH at the potential at zero point charge (pH_{PZC}) of the tested sorbents. The maximum sorption capacity of the tested sorbents, depending on the amount of chitosan dry mass in the hydrogel beads, was determined. The obtained data was fit to Langmuir 1, Langmuir 2, and Freundlich models.

Keywords: sorption, chitosan, dye, hydrogel beads

Received: 25.03.2019

Accepted: 06.05.2019

1. Introduction

Substances of colour present in industrial wastewater are very problematic forms of pollution. Dyes that get into the aquatic environment not only worsen the visual qualities, but, above all, disrupt the biological balance of the ecosystem [1]. Many of them also show toxic and even carcinogenic effects [2–4].

Coloured industrial wastewater is created in many branches of industry, such as textile, cellulose paper, food, pharmaceutical, cosmetics, and dye industries. According to statistics, there are about 100,000 different coloured substances in the industry [5], and their annual global production exceeds 10^6 tons [6–8]. Demand for dyes and pigments increases annually. According to statistics from 2008–2013, an increase of 3.9% was observed [9].

Therefore, it is very important to look for new, innovative methods that allow for highly effective removal of hazardous coloured substances from wastewater [10].

Among the many technologies, the process of adsorption is considered one of the best options due to its ability to remove dyes from coloured aqueous solutions and its fairly uncomplicated mechanism, inexpensiveness, versatility, efficiency, speed, convenience, and non-toxic by-products. [11–14]

Chitin is the most widespread biopolymer in nature after cellulose. Chitin is the main component of arthropod shells. It also partly forms fungal cell walls and some seaweed and bacteria. According to literature data, the annual global production of chitin by living organisms is 10^{11} tons [15]. Chitin is used in agriculture and other industries. Due to its biocompatibility and biodegradability, it is increasingly used as a biomaterial in biomedicine, pharmacology, and biotechnology [16]. This polysaccharide is also known as an effective adsorbent in the process of absorption of reactive dyes [17] due to the presence of functional groups, such as acetamide, amine, and hydroxyl [18].

Chitosan is obtained as a result of enzymatic or chemical deacetylation of chitin. Replacement of acetamide groups with amino groups causes a change in its physical and chemical properties. Chitosan, as one of the few biopolymers, has a basic character due to the presence of free $-NH_2$ groups. Due to the presence of amino functional groups, chitosan has a high adsorptive capacity towards anionic dyes [19–21].

The main advantage of these biopolymers, especially chitosan, is the high efficiency of removing contamination in the form of anions [22,23]

Chitosan flakes are usually physically modified by their conversion into gel beads, membranes, and films. All of these modifications lead to increased porosity, expansion of chitosan polymer chains, increased surface area, decreased crystallinity, improved access to internal sorption sites, and, consequently, increased adsorption capacity [24]. The adsorption properties of chitosan hydrogel beads depend on many parameters, such as the concentration of chitosan, the acid concentration, and the temperature during the production of beads.

This paper presents the effect of chitosan content in hydrogel beads on the sorptive efficiency of Reactive Black 5 (RB5) dye from aqueous solutions.

2. Materials and Methods

2.1. Chitosan

The sorbents used in this research were from Heppe Medical Chitosan GmbH in Halle. The studies used chitin in the form of flakes having a deacetylation degree (DD) of 85%.

2.2. Preparation of the Sorbents

The study included 9 chitosan sorbents containing various amounts of chitosan in the chitosan bead. The parameters of the sorbents used in the tests are presented in Table 1.

Table 1 Parameters of hydrogel sorbents

PARAMETERS OF HYDROGEL SORBENTS									
Content of chitosan in solution (before the gelation process) (%)	1.0	1.5	2.0	2.5	3.5	4.0	5.0	6.0	8.0
Content of chitosan in the hydrogel (%)	chs (3%)	chs (4.4%)	chs (4.8%)	chs (5.4%)	chs (6.6%)	chs (7.4%)	chs (7.9%)	chs (8.4%)	chs (9.3%)
	3.0	4.4	4.8	5.4	6.6	7.4	7.9	8.4	9.3
Hydrogel mass (mass of hydrogel per 1 g of chitosan) (g/g)	33.3	22.7	20.8	18.5	15.2	13.5	12.7	11.9	10.8

2.3. Characteristics and Preparation of Dyes

Experiments were carried out on RB5 dye produced by Industrial Dye Factory ZPB "Boruta" SA in Zgierz (Poland). The structure of the reactive dye is presented in Table 2.

Table 2. Characteristics of the dye

Reactive Black 5 (RB5)		
	Molar mass	991 g/mol
	λ_{\max}	600 nm
	Type	Anionic/reactive
Chemical structure	Class	Diazo

A stock solution of the dye was prepared by weighing 1.00 g of pure powdered dye. The dye was quantitatively transferred to a 1000 cm³ 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 the working solutions.

2.4. Determination of the Optimal pH of the Adsorption Process

The weighted amounts of the tested chitosan sorbents were placed in 250 mL Erlenmeyer flasks. Then, the working solutions, each with a concentration of 100 mg/L and a pH of 2–11, were added. The flasks with sorbents and dye solutions were placed on a shaker (150 rpm) for 120 minutes. Next, the samples were obtained (10 mL each)

with an automatic pipette. The concentrations of the dyes left in the solutions were determined using the spectrophotometric method on a UV–Vis spectrophotometer. After the end of the experiment, the change in the pH of the solution in relation to the initial pH was determined.

2.5. Determination of the Zeta Factor

To determine the pH_{ZPC} of the sorbents, 50 mL of 0.01 M KNO_3 solution with an initial pH (pH_0) of 3–12 was poured into each conical flask. Then, 1 g of each sorbent was added to each flask and the mixture was stirred for 24 hours. After this time, the final pH of the solution was measured. The pH_{ZPC} 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_0 with the axis of a graph on which the pH_0 was marked.

2.6. Determination of the Effect of Time on Adsorption

For each chitosan sorbent, three flasks were prepared, with a volume of 2 dm³, to which 2 g of each sorbent was weighted out. The flasks were filled with the dye solutions with a concentration of 500 mg/dm³ and then placed on magnetic stirrer. At specified time intervals (0, 10, 20, 30, 45, 60, 90, 120, 150, 180, 240, 300, 360, 420, 540, 720, 840, 1080, 1440, 2160, 2880, 3600, and 4320 min), the concentrations of dye remaining in the sample solutions were determined with the use of the spectrophotometric method.

2.7. Determination of the Maximum Adsorption Capacity

To determine the adsorption capacity of the 9 tested sorbents, they were weighed into 250 cm³ Erlenmeyer flasks and supplemented with 100 cm³ of the working solution of the dye at a concentration 500 mg/L and at the optimal pH value. Flasks prepared with solutions and sorbents were placed on a shaker (150 rpm). After 24 hours, samples were taken to determine the dye remaining in solution. The concentrations of the dye after shaking were determined by the colorimetric method using a UV–Vis SP 3000 spectrophotometer.

2.8. Analytical Methods

The concentration of dye left in the aqueous solution was determined spectrophotometrically in each sample. Samples for analysis were collected (10 cm³), decanted, and centrifuged for 15 min at 10,000 rpm. To analyse the dye concentration, the solution was adjusted to pH 6. The concentration of the remaining dye was determined according to standard curves in a UV–Vis SP-3000 spectrophotometer. The wavelength at which absorbance of RB5 was measured was 600 nm.

2.9. Calculation Methods

The effectiveness of dye adsorption from the solution was analysed based on changes in dye concentration in the solution. The quantity of adsorbed basic and acid yellow was calculated from the following formula (1):

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

where Q is the mass of adsorbed dye (mg/g.d.m.), C_0 is the initial concentration of dye (mg/L), C_s is the dye concentration after adsorption (mg/L), and M is the mass of the adsorbent (g.d.m.).

The following three different adsorption models were used to determine the maximum sorption capacity.

Homogeneous Langmuir model (2):

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

where q_e is the equilibrium amount of dye absorbed (mg/g.d.m); q_{\max} is the maximum sorption capacity [mg/g.d.m], K_c is the constant in the Langmuir equation [L/mg], and C is the concentration of dye remaining in the solution (mg/L).

Double Langmuir model (3):

$$q_e = \frac{q_{\max_1} \cdot K_{c_1} \cdot C}{1 + K_{c_1} \cdot C} + \frac{q_{\max_2} \cdot K_{c_2} \cdot C}{1 + K_{c_2} \cdot C} \quad (3)$$

where q_e is the equilibrium amount of dye absorbed (mg/g.d.m), q_{\max_1} is the maximum sorption capacity of the sorbent (active site of the first type) (mg/g.d.m), q_{\max_2} is the maximum sorption capacity of the sorbent (active site of the second type) (mg/g.d.m), k_1 and k_2 are the constants in the Langmuir 2 equation (L/mg), and C is the concentration of dye remaining in the solution (mg/L).

Heterogeneous Freundlich model (4):

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

where q_e is the equilibrium amount of dye absorbed (mg/g.d.m), C is the concentration of dye remaining in the solution (mg/L), K is the constant's sorption equation [-], and n is the constant in the Freundlich equation [-].

The adjustment of experimental data to mathematical models was determined with the use of the correlation coefficient R^2 (54), as follows:

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

where R^2 is the correlation coefficient, which is a measure of data alignment to the model, q_{exp} is the experimental data for the adsorbed amount of dye (mg/g s.m.), and q_{cal} is the theoretical data resulting from the model for the adsorbed amount of dye (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 value of the optimal pH for solutions of colour was determined based on the changes in concentrations of adsorbed dyes after 2 hours of sorption. The research was carried out for 9 sorbents. The changes in the concentration of dyes depending on the pH are shown on the Fig. 1.

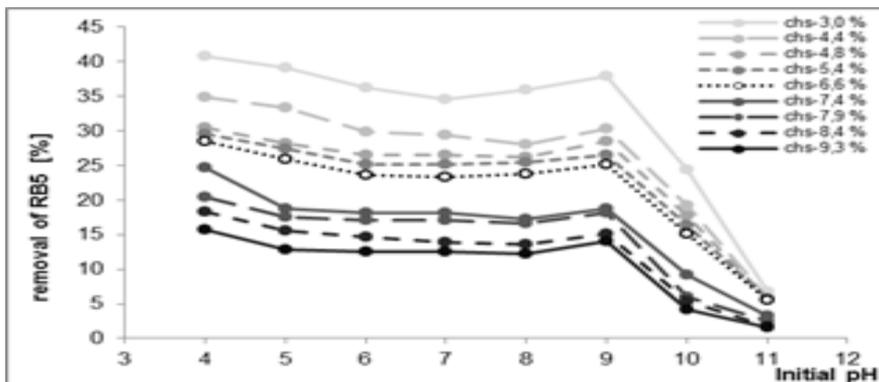


Figure 1. Effect of pH on the efficiency of RB5

The highest effectiveness of sorption of reactive dyes onto chitosan sorbents was achieved at an initial pH of 4 (Fig. 1). At pH 2–3, all the tested chitosan beads were completely dissolved and, for this reason, performing an analysis was impossible. For all tested sorbents varying in the chitosan content in the hydrogel bead, the same tendency was observed. The highest binding efficiency of the RB5 dye was found at the lowest tested pH of 4, and with the increase in the pH, the binding of the dye decreased. The lowest efficiency of RB5 removal for all sorbents, regardless of the amount of chitosan in the sorbent, was observed at pH 11. It was also observed that in the pH range of 4–9 the effectiveness of RB5 removal was slightly decreased or stable; only after the increase in pH to 10 and 11 there was a significant decrease in the effectiveness of RB5 binding. Taking into consideration the amount of chitosan in the hydrogel beads, the highest effectiveness of RB5 removal was observed for hydrogel beads containing 3% chitosan. The increase in the amount of chitosan in the hydrogel beads caused the decrease in the amount of removed RB5 (Fig. 1)

The pH of the solutions changed over the course of the sorption process. In case of chitosan (CHs) 3%, with the initial pH ranging from 4–9, the final pH of the solution ranged from 6.84 to 7.71. In case of CHs 9.3%, with the same initial pH, the final pH of the solution ranged from 6.01 to 8.25. (Fig. 2a)

The pH_{ZPC} value is related to the nature of the adsorbent and its possession of functional groups. The pH of the solution during adsorption was similar to the pH_{ZPC} of the tested sorbent. The pH_{ZPC} point value, determined for the all sorbents, was 7.54 (Fig. 2b).

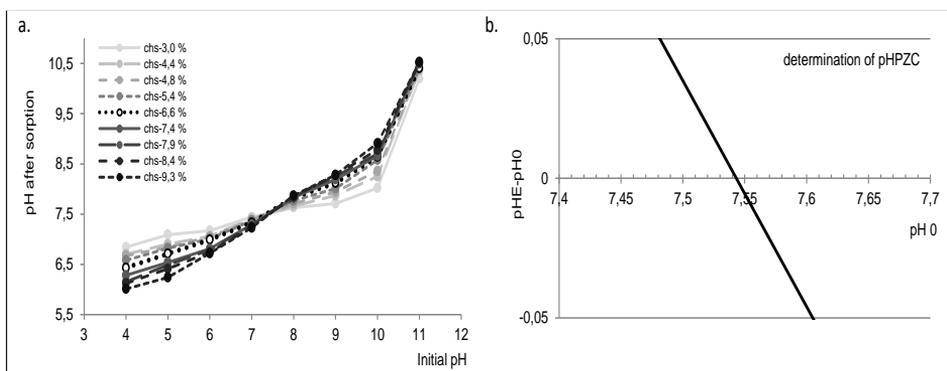


Figure 2. Determination of the pH_{ZPC} of the sorbents

The results of the analysis allowed for determination of the best pH for the tested chitosan sorbents and RB5, which was 4. This pH value was used in analysis of the sorption capacity of RB5 on the chitosan sorbents. The beneficial influence of a low pH value on the anionic dye sorption of chitosan sorbents has been shown in the literature [10,11]. This is due to the electrostatic interaction of the anionic dye with the negative charge and the positive charge of the chitosan adsorbent. At low pH values, protonation of the chitosan amino groups takes place, which attracts anionic dye as a result of electrostatic interaction. The increase in pH of the solution in which the adsorption is carried out is associated with the increasing amount of OH⁻ groups in the solution, which leads to a change in the adsorbent charge to negative and electrostatic repulsion of the negatively charged dye. The reduction of the RB5 adsorption capacity at high pH values may also result from the competition of the anionic dye with OH⁻ ions of the adsorbent active site.

3.2. Effect of Time on Adsorption

Fig. 3 shows the influence of time on the effectiveness of RB5 binding on the 9 tested sorbents (CHs 3% to CHs 9.3%). For each sorbent, the research was carried out with an initial dye concentration of 500 mg/dm³ and a time of 72 h (4320 min) (Fig. 3).

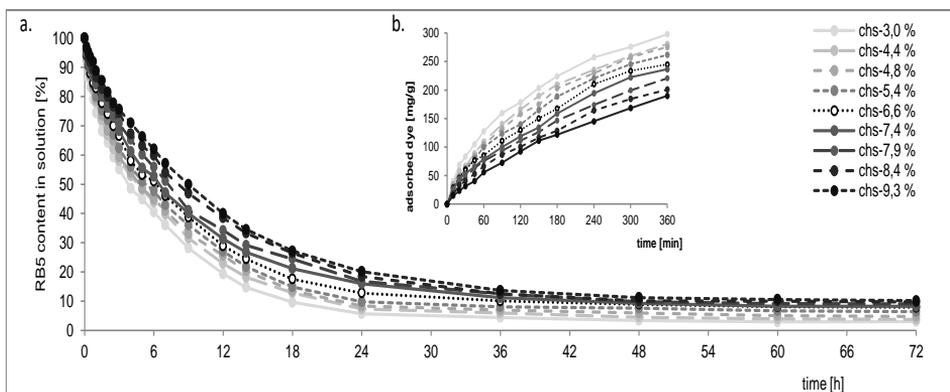


Figure 3. The influence of time of the effectiveness of RB5 removal

The equilibrium time of dye sorption on the tested hydrogels was relatively long and was obtained only after 60 h. In the initial sorption stage (lasting 18 h), the effectiveness of the dye sorption increased with decreasing concentration of chitosan in the hydrogel. Regardless of the sorbent type, the biggest decrease in the amount of RB5 dye left in the solution was observed during first 18 h. The increase in the amount of chitosan in the hydrogel beads increased the time of adsorption equilibrium. Higher efficiency of RB5 binding on hydrogels with lower chitosan content was caused by the supposedly relaxed hydrogel structure and easier access to sorption sites located in its deeper layers.

3.3. The Maximum Adsorption Capacity

Experimental results of RB5 dye adsorption from the aqueous solution and isotherms determined from Langmuir 2, Langmuir, and Freundlich equations are presented in Fig. 4. Table 3 shows the constants from Langmuir 2, Langmuir, and Freundlich models.

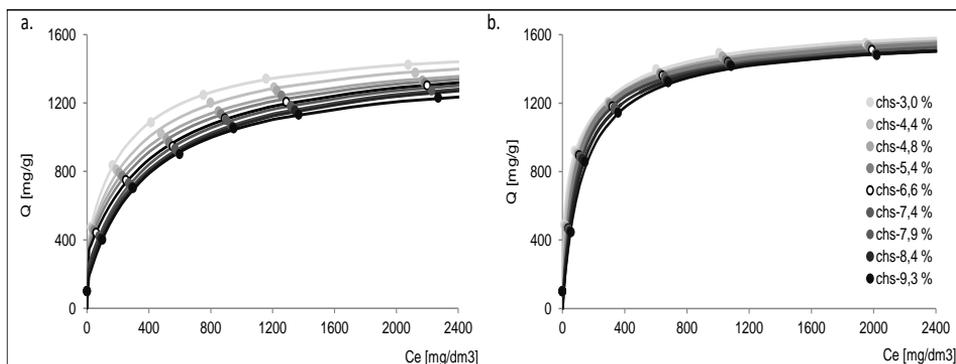


Figure 4. Experimental results of RB5 adsorption from the aqueous solution and isotherms determined from Langmuir 2, Langmuir, and Freundlich equations

Based on the obtained results, it should be stated that the best fit of experimental data to the model was obtained for the Langmuir 2 isotherm. The Langmuir model presumes that the sorbate creates a monolayer. Sorbate molecules binding with the active sites of the sorbent can have a physical (hydrogen or electrostatic interactions) or chemical (chemisorption) character. This theory says that the particles do not form a multilayer and do not interact with each other. Adsorbed particles, however, can move into the monolayer (changes the active sites), but they may also be replaced by the sorbate derived from outside the monolayers. The mass, which will be absorbed by a substance, depends on the maximum sorbent monolayer capacity (Q_{max}) and on affinity. The Langmuir 2 model differs from the Langmuir model because it assumes that the sorbent has two types of active sites on its surface, which have a different degree of sorbent affinity.

The amount of substance that will undergo sorption depends on the sorption capacity of the active sites of type I and II (b_1 and b_2) and the degree of affinity for the active sites of the sorbent to the sorbate (k_1 and k_2)

The results allow us to state that the amount of bound RB5 dye for all the tested sorbents, varying the amount of chitosan content in hydrogel beads, was comparable and ranged from 1672.6 mg/g for CHs 3% to 1608.8 mg/g for CHs 9.3 and, after 72 h of sorption, it was higher in comparison to the amount of RB5 bound after 24 h by about 7–13%.

The constants determined from the Langmuir 2 equation indicate, however, that even though the absolute sorption capacity of all tested sorbents was comparable, the mechanism of sorption depended on the amount of chitosan in the hydrogel beads and the time of sorption.

By analysing the constants determined from the Langmuir 2 equation, it is possible to notice that along with the longer sorption time, the method of RB5 dye binding changed significantly.

After 24 h of sorption, the amount of bound dye on the active sites of first type (q_{max1}) was lower in comparison with the amount of bound dye on active sites of the second type (q_{max2}). This dependency was observed for all the sorbents.

However, depending on the amount of chitosan in the hydrogel bead, the ratio q_{max2} to q_{max1} varied. For CHs 3%, it was 3.0, and for CHs 9.3 the sorption capacity in the second type of active site was 8.8 times higher than in the first type of active site. Such results may indicate that the binding of RB5 was of a weaker physical character.

Table 3. RB5 adsorption constants determined from Langmuir, Langmuir 2, and Freundlich models for the tested adsorbents

Langmuir 2							
Content of chitosan in the hydrogel (%)	Sorption time (h)	Q_{max} (mg/g)	b_1 (mg/g)	k_1 (L/mg)	b_2 (mg/g)	k_2 (L/mg)	R^2
3.0	24	1563.2	389.7	1.229	1173.5	0.004	0.9998
	72	1672.6	773.1	0.125	899.5	0.004	0.9950
4.4	24	1548.5	374.5	1.371	1174.0	0.003	0.9982
	72	1666.8	876.4	0.052	790.4	0.003	0.9943
4.8	24	1519.1	371.4	0.793	1147.7	0.003	0.9975
	72	1653.3	968.5	0.031	984.82	0.003	0.9943
5.4	24	1515.4	345.6	0.923	1169.8	0.002	0.9987
	72	1653.9	1320.1	0.017	333.7	0.001	0.9942
6.6	24	1512.7	307.7	6.852	1208.0	0.002	0.9993
	72	1650.1	1424.3	0.013	225.8	0.001	0.9930
7.4	24	1495.4	226.5	2.578	1268.8	0.002	0.9992
	72	1654.1	1432.9	0.012	221.3	0.001	0.9931
7.9	24	1489.0	238.4	1.158	1250.6	0.002	0.9993
	72	1644.8	1504.2	0.011	140.5	0.0003	0.9924
8.4	24	1478.5	205.7	0.494	1272.8	0.002	0.9997
	72	1630.6	1495.6	0.010	135.0	0.0005	0.9919
9.3	24	1413.4	144.3	2.192	1269.1	0.003	0.9996
	72	1608.8	1475.8	0.008	132.9	0.001	0.9921
Langmuir							
Content of chitosan in the hydrogel (%)	Sorption time (h)	Q_{max} (mg/g)	K_C (L/mg)	R^2			
3.0	24	1339.4	0.014	0.9615			
	72	1499.7	0.025	0.9666			
4.4	24	1305.7	0.011	0.9637			
	72	1521.1	0.018	0.9825			
4.8	24	1279.0	0.010	0.9612			
	72	1546.7	0.014	0.9891			
5.4	24	1342.9	0.007	0.9675			
	72	1552.6	0.013	0.9923			
6.6	24	1350.1	0.006	0.9722			
	72	1554.9	0.011	0.9922			
7.4	24	1335.7	0.005	0.9814			
	72	1555.0	0.011	0.9924			
7.9	24	1365.0	0.004	0.9823			
	72	1549.7	0.010	0.9922			
8.4	24	1326.5	0.004	0.9850			
	72	1559.9	0.009	0.9917			
9.3	24	1322.6	0.004	0.9863			
	72	1575.9	0.007	0.9920			

cont. **Table 3**

Freundlich				
Content of chitosan in the hydrogel (%)	Sorption time (h)	K	n	R^2
3.0	24	203.94	0.2715	0.9949
	72	344.31	0.2091	0.9711
4.4	24	177.80	0.2827	0.9969
	72	331.34	0.2118	0.9716
4.8	24	189.00	0.2619	0.9863
	72	297.30	0.2272	0.9629
5.4	24	174.12	0.2703	0.9882
	72	286.3	0.2311	0.9570
6.6	24	162.71	0.2758	0.9901
	72	283.8	0.2304	0.9550
7.4	24	106.6	0.3389	0.9933
	72	264.52	0.2384	0.9547
7.9	24	124.6	0.3073	0.9883
	72	267.00	0.2368	0.9507
8.4	24	86.26	0.3639	0.9951
	72	245.82	0.2472	0.9533
9.3	24	87.16	0.3596	0.9911
	72	224.33	0.2586	0.9552

This may suggest the influence of the bead structure on the type of bonding. The ch 3% structure of the bead contains less chitosan, which makes it looser, and the dye can more easily penetrate into the sorbent and bind it permanently this causes higher q_{max1} . In the case of sorbents with a higher chitosan content, it was more difficult for the dye to penetrate into the sorbent pores, binding with weaker van der Waals forces.

By analysing the values of q_{max1} and q_{max2} after 72 h of sorption, it is possible to notice a decisive influence of the amount of chitosan in the hydrogel bead on the amount of RB5 bound in the first and second types of active sites. For sorbents with the lowest tested amount of chitosan in the hydrogel bead, the sorption capacities in places of the first and second type were comparable. With the increase in chitosan in the hydrogel bead, an increase in sorption capacity was observed at places of the first type (q_{max1}) and a decrease in capacity at places of the second type (b_2) was also observed. For the sorbent with the highest amount of chitosan (CHs 9.3%) tested, the sorption capacity (b_1) was over 10 times higher than the capacity (q_{max1}). This may indicate a change in the mechanism of binding RB5 dye on the tested sorbents. Along with the prolongation of the sorption process, the total capacity did not change significantly, whereas the dye was bonded in a more permanent manner with the sorbent.

4. Conclusions

The effect of chitosan content in hydrogel beads on the sorption efficiency of RB5 dye from aqueous solutions was investigated. The tested range of dry matter of the biopolymer in the hydrogel ranged from 3.0 to 9.3%. The research included, among other factors, the effect of pH (pH 2–11) on the effectiveness of RB5 sorption, RB5

sorption kinetics, and determination of the maximum sorption capacity of the tested chitosan sorbents with respect to RB5.

RB5 sorption on hydrogels was most effective at pH 4, while it was the least effective at pH 11. Regardless of the chitosan content of the hydrogel, the sorbent at the initial pH value of 2–3 dissolved and lost its sorption properties. The equilibrium time of dye sorption on the tested hydrogels was relatively long and was obtained only after 60 h. In the initial sorption stage (lasting 18 h), the effectiveness of the dye sorption (mg/g d.m. chitosan) increased with decreasing concentration of chitosan in the hydrogel.

Higher efficiency of RB5 binding on hydrogels with lower chitosan content was caused by the supposedly relaxed hydrogel structure and easier access to sorption sites located in its deeper layers.

The sorption capacity determined after 24 h of sorption was the highest for the hydrogel with 3.0% chitosan content (1563.2 mg/g dm) and decreased with increasing biopolymer content in the sorbent, obtaining the worst result for a hydrogel with a chitosan content of 9.3% (1413.4 mg/g dm). Differences in the performance of the tested sorbents were lower when comparing the maximum sorption capacity, determined after the sorption equilibrium time. For example, for hydrogels with 3.0%, 6.6%, and 9.3% chitosan content, Q_{max} was 1672.6, 1650.1 and 1608,8 mg/g respectively. This suggests that RB5 uses most of the sorption sites present in the hydrogel, as well as the ability of chitosan hydrogels to absorb the dye.

This research has also shown that prolonging the sorption time influences how the RB5 dye is bound, causing it to have a more permanent bond with the sorbent.

5. Acknowledgements

This study was financed under Project No. 18.610.008-300 of the University of Warmia and Mazury in Olsztyn, Poland.

6. References

- [1] Genc A, Oguz A, (2010) Sorption of acid dyes from aqueous solution by using non-ground ash and slag. *Desalination*. 264: 78-83. doi.org/10.1016/j.desal.2010.07.007
- [2] Rai HS, Bhattacharyya MS, Singh J, Bansal TK, Vats P, Banerje UC; (2005) Removal of Dyes from the Effluent of Textile and Dyestuff Manufacturing Industry. *Crit. Rev. Env. Sci. Tec.* 35, 219-238. doi.org/10.1080/10643380590917932
- [3] Revanker MS, Lele SS; (2007) Synthetic dyes decolorization by white rot fungus, *Ganoderma* sp. *Bioresource Technology* 98(4), 775-780. doi.org/10.1016/j.biortech.2006.03.020
- [4] Machado F M, Bergmann C P, Fernandes T H, Lima E C, Royer B, Calvete T, Fagan S B; (2011) Adsorption of Reactive Red M-2BE dye from water solutions by multi-walled carbon nanotubes and activated carbon. *Journal of hazardous materials*, 192(3), 1122-1131. doi.org/10.1016/j.jhazmat.2011.06.020
- [5] Wang L, Li J; (2013) Adsorption of CI Reactive Red 228 dye from aqueous solution by modified cellulose from flax shive: Kinetics, equilibrium, and thermodynamics. *Industrial Crops and Products* 42, 153-158. doi.org/10.1016/j.indcrop.2012.05.031
- [6] Robinson T, McMullan G, Marchant R, Nigam P; (2001) Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology* 77, 247-255; doi.org/10.1016/S0960-8524(00)00080-8

- [7] Husain Q; (2006) Potential applications of the oxidoreductive enzymes in the decolorization and detoxification of textile and other synthetic dyes from polluted water: a review. *Crit. Rev. Biotechnol.* 26: 201–221. doi.org/10.1080/07388550600969936
- [8] Gupta VK, Suhas AB; (2009) Application of low-cost adsorbents for dye removal – A review. *J. Environ. Manage.* 90, 2312-2342. doi.org/10.1016/j.jenvman.2008.11.017
- [9] *Word Dyes & Organic Pigments – Industry Study with Forecasts for 2013 & 2018*, Freedonia Group INC, 2009 Cleveland, USA.
- [10] Tan KB, Vakili M, Horri BA, Poh P E, Abdullah AZ, Salamatinia B; (2015). Adsorption of dyes by nanomaterials: Recent developments and adsorption mechanisms. *Separation and Purification Technology*, 150, 229–242. doi.org/10.1016/j.seppur.2015.07.009
- [11] Jain AK, Gupta VK, Suhas AB; (2003) Utilization of industrial waste products as adsorbents for the removal of dyes. *J. Hazard. Mater.* 101: 31-42; Ho Y.S., McKay G. Sorption of dyes and copper ions onto biosorbents. *Process. Biochem.* 38, 1047-1061. doi.org/10.1016/S0304-3894(03)00146-8
- [12] Ho YS, McKay G; (2003). Sorption of dyes and copper ions onto biosorbents. *Process. Biochem.* 38:1047-106 doi.org/10.1016/S0032-9592(02)00239-X
- [13] Ali I, Asim M, Khan TA; (2012) Low cost adsorbents for the removal of organic pollutants from wastewater. *Journal of Environmental Management*, 113, 170–183. doi.org/10.1016/j.jenvman.2012.08.028
- [14] Vakili M, Rafatullah M, Salamatinia B, Abdullah A Z, Ibrahim M H, Tan K B; (2014) Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: A review. *Carbohydrate Polymers*, 113, 115–130. doi.org/10.1016/j.carbpol.2014.07.007
- [15] Je J, Kim S; (2006) Antimicrobial action of novel chitin derivative. *Biochimica et Biophysica Acta* 1760, 104 – 109; DOI: 10.1016/j.bbagen.2005.09.012].
- [16] Akkaya G, Uzun I, Güzel F, (2007) Kinetics of the adsorption of Reactive dyes by chitin. *Dyes and Pigments* 73: 168-177 doi.org/10.1016/j.dyepig.2005.11.005
- [17] Dolphen R, Sakkayawong N, Thiravetyan P, Nakbanpate W; (2007) Adsorption of Reactive Red 141 from waste water onto modified chitin. *Journal of Hazardous Materials* 145, 250-255 doi.org/10.1016/j.jhazmat.2006.11.026
- [18] Begum HA, Mondal AK, Muslim T, (2012) Adsorptive Removal of Reactive Black 5 from Aqueous Solution Using Chitin prepared from Shrimp Shells, *Bangladesh Pharmaceutical Journal* 15 (2), 145-152 doi.org/10.3329/bpj.v15i2.12580
- [19] Annadurai G, Ling LY, Lee JF; (2008). Adsorption of reactive dye from an aqueous solution by chitosan: isotherm, kinetic and thermodynamic analysis. *Journal of Hazardous Materials*, 152, 337-346 doi.org/10.1016/j.jhazmat.2007.07.002
- [20] Dolphen R, Sakkayawong N, Thiravetyan P, Nakbanpate W, (2007) Adsorption of Reactive Red 141 from waste water onto modified chitin. *Journal of Hazardous Materials* 145: 250-255 doi.org/10.1016/j.jhazmat.2006.11.026
- [21] Begum HA, Mondal AK, Muslim T, (2012) Adsorptive Removal of Reactive Black 5 from Aqueous Solution Using Chitin prepared from Shrimp Shells, *Bangladesh Pharmaceutical Journal* 15 (2): 145-152 doi.org/10.3329/bpj.v15i2.12580
- [22] Józwiak T, Filipkowska U, Szymczyk P, Mielcarek A; (2016) Sorption of nutrients (orthophosphate, nitrate III and V) in an equimolar mixture of P–PO₄, N–NO₂ and N–NO₃ using chitosan. *Arabian Journal of Chemistry*. <https://doi.org/10.1016/j.arabjc.2016.04.008>.

- [23] Jóźwiak T, Filipkowska U, Szymczyk P, Kuczajowska-Zadrożna M, Mielcarek A, Zyśk M; (2016) The influence of chitosan deacetylation degree on reactive black 5 sorption efficiency from aqueous solutions. *Progress on Chemistry and Application of Chitin and its Derivatives*, 21, 83-92. DOI: 10.15259/PCACD.21.08
- [24] Vakili M, Rafatullah M, Ibrahim MH, Abdullah AZ, Salamatina B, Gholami Z; (2016) Preparation of Chitosan Beads for the Adsorption of Reactive Blue 4 from Aqueous Solutions, *Iranica Journal of Energy and Environment* 7 (2): 124-128
doi: 10.5829/idosi.ijee.2016.07.02.06