

IMPACT OF CHITOSAN CROSS-LINKING ON RB 5 DYE ADSORPTION EFFICIENCY

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Abstract

In this work, the effect of cross-linking of chitosan beads on the removal efficiency of dye RB 5 from aqueous solutions was defined. In the studies not crosslinked chitosan as well as chitosan cross-linked with a chemical cross-linking agent - glutaraldehyde and ionic cross-linking agent - pentasodium tripolyphosphate were used. The scope of the research included the determination of pH at which the adsorption process proceeded efficiently, study time, in order to designate the time, after which the reaction equilibrium is reached and to determine the kinetics of the adsorption process and constants in the Langmuir 2 equation. The work sets maximum sorption capacity of the sorbent non-crosslinked and two crosslinked sorbents. Based on these results, it was found that the highest removal efficiency of dye RB 5 was obtained for chitosan crosslinked with ion agent - pentasodium tripolyphosphate. The maximum sorption capacity of the sorbent amounted 1125.7 mg / g d.m. of chitosan.

Key words: cross-linked chitosan, dye RB5, adsorption,

Received: 08.02.2016

Accepted: 13.05.2016

1. Introduction

Colored industrial wastewater can occur in a variety of industries including: textile, paint, pulp-paper, food, leather, pharmaceutical and cosmetic. Textile industry produces 280 thousand tons of colored wastewater annually [1]. In order to achieve the desired color is used approximately 100 thousand various coloring substances, global production of which exceeds 800 thousand tons per year [2].

In the industry, the common sorbents include activated carbons, gels of silicic acid and aluminum oxides. However, they are relatively expensive. It is therefore appropriate to search for a widely available, cheaper substitute to conventional sorbents [3-5].

Chitosan has a high efficiency in the sorption of color impurities from aqueous solutions. Absorptive capacity of chitosan can result from many processes, such as hydrogen bonding, ion exchange, physical adsorption (the action of van der Waals forces) and chemisorption [6].

Chitosan is dissolved in acidic solution and loses the ability to bind contamination [7]. Because the dyeing process is usually carried out at a pH of 3 - 4 - waste water from the paint industry is usually acidic [8]. This limits the use of chitosan in the sorption process to the conditions of low pH. The cross-linking of chitosan provides a solution to this problem. The cross-linking process affects the behavior of the sorbent effectiveness at a constant level in a wide pH range. It also improves its mechanical strength and regenerative properties [9]. Typically, the production of chitosan comprises treating the purified chitin with a concentrated alkaline solution (NaOH or KOH at a concentration of 40 - 50 wt.%) at a temperature of 100 °C or higher.

The study examined the effectiveness of sorption with the popular textile dye Reactive Black 5 (RB 5) on a chitin sorbent- chitosan in the form of beads, non-crosslinked and crosslinked with two agents- glutaraldehyde and pentasodium triphosphate.


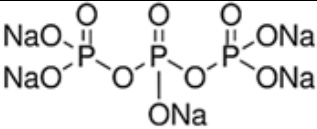
2. Materials and Methods

2.1. Characteristics and preparation of adsorbents

In the study chitosan in the form of flakes having a deacetylation degree DD = 85%, viscosity of 100 mPa/s and a dry matter content of 86.8%, originating from the German company Heppe was used.

The crosslinking agents (Table 1), glutaraldehyde 25% and pentasodium triphosphate (p.a.) were purchased from Sigma - Aldrich.

Table 1. The crosslinking agents used in the studies

	Crosslinking agents	
	GLUTARALDEHYDE	PENTASODIUM TRIPOLYPHOSPHATE
Structural formula		
Molar mass	100,1 g/mol	367,86 g/mol
Nature of cross-linking process	Covalent crosslinking (permanent)	Ion crosslinking (reversible)

In order to prepare the sorbent, 25 g of d.m. chitosan flakes, 50 g of acetic acid (99.5%) and 925 g of distilled water was added to a beaker with a capacity of 2 dm³. The content of the beaker was stirred mechanically until homogenous mass was formed, and then left to stand for 24 h to vent. The concentration of the thus prepared mixture was 2.5% chitosan. The solution was added dropwise to a 2M NaOH solution and as a result beads with a diameter of 2.0 - 2.2 mm formed. During gelation of the sorbent NaOH solution was stirred with a magnetic stirrer (300 r.p.m.).

Prepared chitosan beads were kept in a solution of NaOH for 24 h and then washed with distilled water until neutral. Thus prepared, ready-to-use sorbent was kept in distilled water at 4 ° C.

2.1.1 Cross-linking of the adsorbent

The prepared chitosan beads were placed in glutaraldehyde solution. The concentration of glutaraldehyde was chosen on the basis of the active groups of the crosslinking agent to chitosan amino groups of 1:1 ratio and amounted 0.28 g of glutaraldehyde per 1 g of chitosan (Fig. 1b). Sorbent was crosslinked for 24 hours, the process proceeded under conditions of continuous stirring in a room temperature. In order to remove the unreacted cross-linking agent, cross-linked chitosan beads were washed with distilled water.

Cross-linking of chitosan with a solution of pentasodium tripolyphosphate was conducted with the ion charge ratio of the crosslinker to the amino groups of the chitosan (1:1) (Fig. 1c). Agent was used in an amount of 0.86 g / g of chitosan.

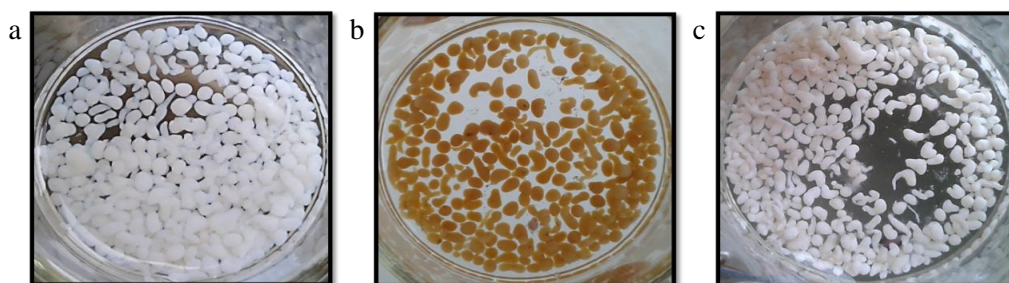


Figure 1. Adsorbents a. Non-crosslinked chitosan (CHS), b chitosan cross-linked with glutaraldehyde CHS-GLA), c. pentasodium tripolyphosphate crosslinked chitosan (CHS-TPP)

2.2 Characteristics and preparation of dyes

Experiments were conducted with dye Reactive Black 5 produced by ZPB “Boruta”SA in Zgierz. The structure of reactive dye is presented in Table 1.

A stock solution of dye was prepared by weighing 5.00 g of pure powdered dye. The dye was quantitatively transferred into a 1000 cm³ measuring flask which was then filled up with distilled water. Dye concentration in the solution reached 5000 mg/dm³. The stock solution was used to prepare working solutions.

Table 2. Characteristics of the dyes

Structural formula	Name	λ_{\max}	Molecular weight
	Reactive Black 5	600 nm	991 g/mol

2.3 Determination of the optimal pH value of adsorption process

In order to determine the optimal pH value of the adsorption process, aqueous solutions were prepared with dye concentration of 100 mg/dm³ and pH from 1 to 11. Adsorbent in the quantity of 0.1 g d.m. and 100 cm³ of dye solutions with pH from 1 to 11 were added to each of the conical flasks (250 cm³). Next, the flasks were placed on a magnetic stirrer, and the concentration of adsorbate in the solution was determined after 2 h of adsorption.

2.4 Determination of the effect of time on adsorption

For each of the three chitosan sorbents a beaker of 2 dm³ was prepared, to which 2g of sorbent was weighed. Solutions of the dye concentrations of 500, 1000 and 2000 mg /dm³ were poured into the beaker, then placed into a multi-position magnetic stirrer. In certain time intervals (0, 5, 10, 20, 30, 45, 60, 90, 120, 180, 240, 300, 360, 480, 600, 720 min) samples were made and residual dye concentration using spectrophotometric method was measured.

2.5 Determination of the maximum adsorption capacity

In order to determine the adsorption capacity of chitin flakes, 0.1 g d.m of the sorbent was weighed into 250 cm³ Erlenmeyer flasks and 100 cm³ of the working solution of the dye at concentration from 100 to 4000 mg/dm³ and optimal pH value was added. Flasks thus prepared with solutions and sorbents were set on a shaker (150 r.p.m). Badania zostały przeprowadzone przy temperaturze 20°C

2.6 Analytical methods

The concentration of dye left in the aqueous solution was determined spectrophotometrically in each sample. Samples to be analyzed were collected (10 cm³), decanted and centrifuged for 15 min at 10,000 rpm. To assay dye concentration, the solution was adjusted to pH 6. The concentration of the remaining dye was determined acc. to standard curves in a UV-VIS Spectrophotometer SP-3000.

A wave length at which absorbance was measured was determined for the dye examined (Table 1).

The effectiveness of dye adsorption from the solution was analyzed based on changes in its concentration in the solution.

The quantity of adsorbed Reactive Black 5 was calculated from the formula (1):

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

where:

Q_s – weight of adsorbed dyes (mg/g.d.m.),

- C_0 – initial concentration of dyes (mg/dm³),
 C_s – dyes concentration after adsorption (mg/dm³),
 m – weight of adsorbent (g.d.m.),
 V – volume of dye containing solution (dm³)

Experimental data were described using heterogeneous Langmuir sorption isotherm equation (double Langmuir sorption isotherm equation) (2).

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

where K_1 , K_2 , b_1 , b_2 are constants of isotherm and C are dye concentration in the solution after adsorption, Q mass of dye adsorbed by the biosorbent.

Program STATISTICA 12.0 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. Analyses of dye biosorption depending on the pH value

The figure 2 shows the effect of pH on the removal efficiency of dye RB 5 on three adsorbents tested. Studies have shown that the dye RB 5 adsorbed on non-crosslinked chitosan most efficiently at a pH of 4. Increasing the pH caused a reduction in the efficiency of dye binding. At a pH of 2 and 3 non-crosslinked chitosan beads became destroyed. In the case of GLA cross-linked chitosan most effective adsorption occurred at a pH of 2. Similarly to the non-crosslinked chitosan pH increases negatively affected the efficiency of adsorption. For TPP cross-linked chitosan highest efficiency of adsorption was observed at pH 3. Lowering the pH to 2 resulted in the destruction of the adsorbent, increase in reducing the effectiveness of binding dye RB5.

Taking into consideration actual pH of the wastewater from the dye industry and the possibility of comparing the efficiency of tested sorbents in the same conditions all further research was carried out at the pH 4.0.

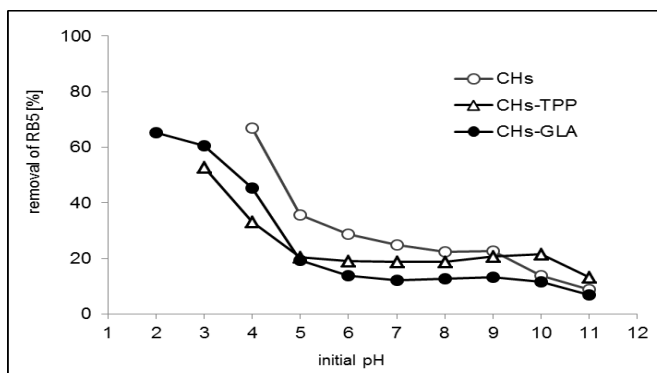


Figure 2. Comparison of the effect of pH on the sorption efficiency of the dye RB 5 (η) on non-crosslinked chitosan (CHs), chitosan cross-linked with glutaraldehyde (CHs-GLA) and chitosan cross-linked with pentasodium triphosphate (CHs -TPP) (temp. 20°C)

3.2 Influence of time on the efficiency of adsorption

Figure 3 shows the effect of time on the efficiency of dye binding RB5 on three adsorbents tested CHs, CHs-GLA and CHs-TPP. For each sorbent studies were performed using three primary dye concentrations – 500, 1000 and 2000 mg / dm³. The obtained data show that the RB5 adsorption time depended on the type of adsorbent. In the case of the cross-linked chitosan adsorbent with chemical agents - glutaraldehyde - dye adsorption efficiency after 10 hours for the initial concentrations of 500, 1000 and 2000 mg RB5 / dm³, was respectively 91.7, 67.7 and 37% and was higher in comparison with the efficiency of non-crosslinked chitosan (respectively 40.5, 25.2 I 14.4%). Cross-linking of the agent accelerated the process of sorption. A significant decrease in the amount of dye became visible in the solution after 2 hours of sorbing. Similar results were obtained with sorbing the dye solution on chitosan crosslinked with ion agent - pentasodium tripolyphosphate. Amount of dye in solution after 10 hours of sorbing decreased by 83, 61 and 37% of the initial concentrations of 500, 1000 and 2000 mg RB5 / dm³. Also in this case, in comparison to the sorption efficiency of RB5 on non-crosslinked chitosan, for each of the initial concentrations of the dye the adsorption efficiency of RB5 was higher.

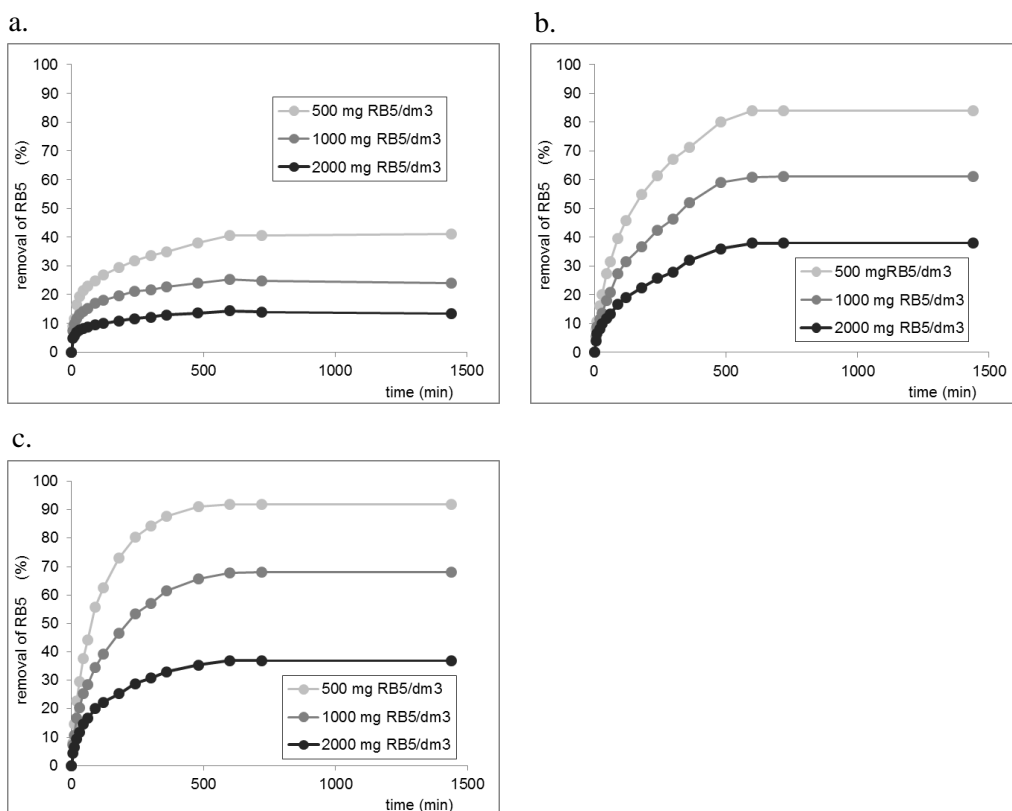


Figure 3. Influence of time on the dye adsorption efficiency of 5 RB: a) non-crosslinked chitosan, b) a GLA crosslinked chitosan, c) a TPP crosslinked chitosan (pH 4.0, temp. 20°C).

3.3. The maximum sorption capacity of the adsorbent

The maximum adsorption capacity was determined from the relationship between the amount of dye adsorbed on the adsorbents tested and the concentration of the dye remaining in solution. Figure 4 shows the experimental data and the adsorption isotherms. The applied double Langmuir model well described the adsorption data of dye RB5 obtained on all tested adsorbents. Determination coefficients are very high, within the range of 0.9992 to 0.9929. Calculations of tested adsorbents sorption capacity were made in the program Statistica v 12.5.

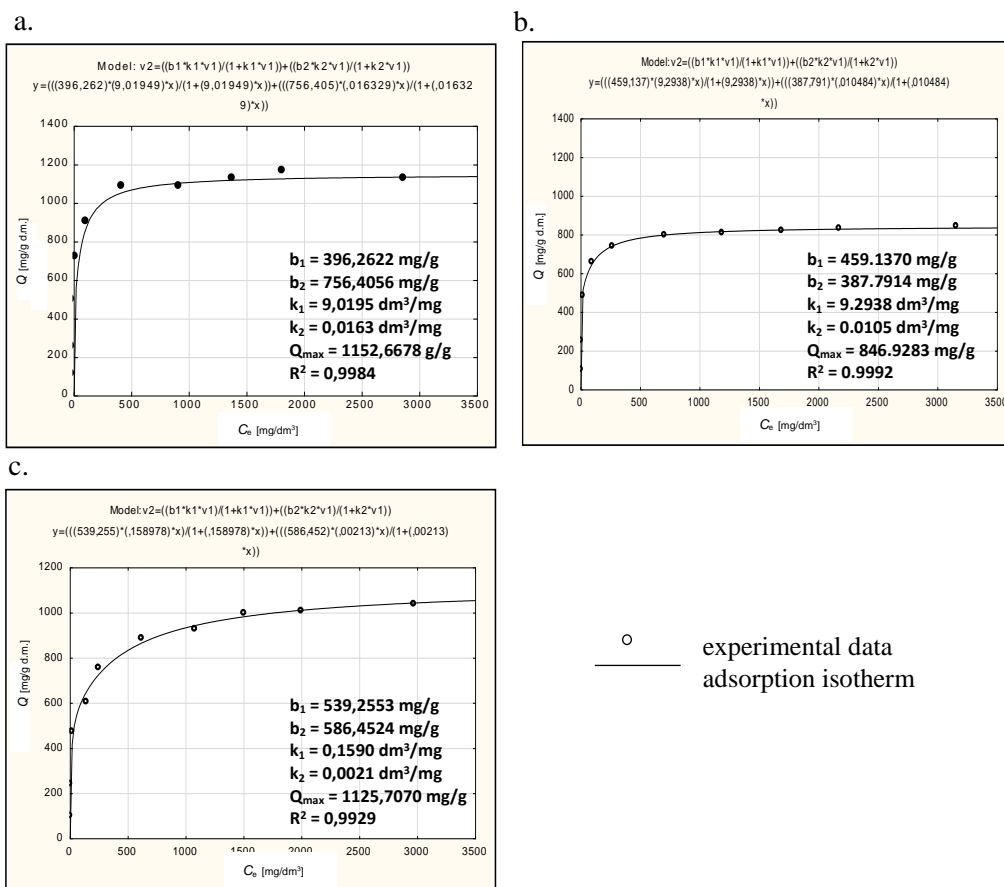


Figure 4. Langmuir 2 experimental data and adsorption isotherms a) chitosan not crosslinked, b) GLA cross-linked chitosan, c) TPP cross-linked chitosan (pH 4.0, temp. 20°C)

The obtained data show that the adsorption process was conducted in different ways depending on the applied adsorbent – non-crosslinked and crosslinked with various crosslinking agents. Constants obtained from adsorption isotherm show not only the amount of removed dye but also indicate the best fit of the adsorbent to the adsorbate.

Constants k_1 and k_2 describe the affinity of the adsorbate and the adsorbent. It can be seen that for all adsorbents constant k_1 is greater than k_2 . This may indicate that the binding

of anionic dye RB5 occurred in the active sites of the same kind. In the case of CHs and CHs-GLA, k_1 constant value is very high and amounts respectively 9.02 and 9.29 dm^3 / mg .

A similar, very high adsorption capacity, achieved for two tested adsorbents – non-crosslinked chitosan (CHs) and chitosan crosslinked with pentasodium tripolyphosphate (CHs-TPP), it amounted respectively 1152.7 and 1125.7 g/g d.m . In the case of the third adsorbent total adsorption capacity was slightly lower and amounted 846.9 g/g d.m .

4. Conclusions

The study determined the removal effectiveness of reactive dye Reactive Black on the three chitosan adsorbents in the form of beads: non-crosslinked and crosslinked by two agents - chemical GLA, and ion TPP. Based on the results it was found that chitosan is a very good adsorbent of reactive dyes, and its sorption properties can be increased by crosslinking. It has been observed that the pH, reaction time, and the type of crosslinking agent have a significant impact on the effectiveness of the adsorption process.

Analyzing the amount of the adsorbed dye RB5 the best adsorbents proved to be non-crosslinked chitosan – 1152.7 mg / g d.m and TPP crosslinked chitosan – 1125.7 mg / g d.m (pH 4.0).

However, taking into account the fact that waste water from the textile and the paint industry has a low pH it is preferable to use crosslinked chitosan. The use of cross-linking agent, regardless of its kind allowed to conduct an adsorption process at a lower pH without damaging the adsorbent. Crosslinking of chitosan also positively affected the time of the reaction reaching equilibrium. Regardless of the cross-linking agent it was shorter for sorbents cross-linked compared to non-crosslinked chitosan.

The system of removal of reactive dyes, e.g. Reactive Black 5 by adsorption method on chitosan crosslinked with ion agent - pentasodium tripolyphosphate, which has the best adsorption properties could be used in plants producing colored wastewater before discharging it into the drainage system, and a sewage treatment plant.

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

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