EFFECT OF CROSS-LINKING WITH GLUTARALDEHYDE ON ADSORPTION CAPACITY OF CHITOSAN BEADS

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Abstract
The study was undertaken to analyze the effect of chitosan cross-linking with glutaraldehyde on the adsorption capacity of chitosan beads during adsorption of Reactive Black (RB5) and Basic Green (BG4) dyes. Analyses were conducted at three pH values: pH 3.0; 5.0 and 9.0. Results obtained were evaluated with the use of four models of adsorption isotherms − Freundlich, Langmuir, Double Langmuir and Redlic-Petreson. The cross-linking of beads with glutaraldehyde turned out to be beneficial for the anionic dye RB5. Compared to the non-cross-linked beads, a comparable adsorption capacity (over 500 mg/g d.m.) was obtained at pH 3.0 and pH 5.0. In the case of the cationic dye, chitosan cross-linking reduced the quantity of adsorbed dye, irrespective of the pH value of the adsorption process.

Key words: *adsorption, dyes, chitosan beads, crosslinking chitosan beads, glutaraldehyde.*

1. Introduction

One of the most effective methods for dye removal from wastewaters is the process of sorption. In this respect, chitosan is gaining an increasing interest as one of the sorbents. It is produced via deacetylation of chitin which is one of the most abundant biopolymers in nature. The annual global production of chitin by live organisms is estimated to reach even 10^{11} tons [1]. Potentially, 120,000 – 200,000 tons of chitin may be produced annually from wastes from the global processing industry of marine invertebrates [2]. For this reason, chitin as well as its derivative – chitosan are claimed to be easily available and cheap sorbents. Chitosan is characterized by a high effectiveness of dyes sorption from aqueous solutions [3 - 6]. Its sorption capacity may result from many processes including ionic exchange, formation of hydrogen bonds, physical adsorption (van der Waals forces) [5] and chemical adsorption (chemisoprtion) [7].

A drawback of chitosan is that it dissolves and loses its capability to bind sorbates in acidic solutions [3, 8]. The process of staining is usually conducted at pH 3 - 4, therefore post-production wastewaters have mainly acidic pH [4], which significantly reduces the possibility of applying chitosan as a sorbent under conditions of low pH. A solution to this problem may be the cross-linking of chitosan. This process affects the maintenance of a stable effectiveness of a sorbent in a wide pH range and improves its mechanical resistance [9 - 11]. In addition, cross-linking may improve regeneration properties of a sorbent [12].

The aim of this study was to determine the effectiveness of dyes removal from an aqueous solution with the method of adsorption. Non-cross-linked chitosan in the form of beads and chitosan cross-linked with glutaraldehyde also in the form of beads were used as the adsorbent. Experiments were conducted with two dyes: anionic dye – Reactive Black 5 (RB5) and cationic dye – Basic Green 4 (BG4). New in the studies was, to determine the maximum sorption capacity of sorbents studied at various pH values.

Results were evaluated with four mathematical models: two di-parameter models – Freundlich and Langmuir, a three-parameter model – Redlich-Peterson, and a four-parameter model – a double Langmuir model.

2. Materials and methods

2.1. Dyes

Due to their common application, the following two dyes RB5 (anionic dye) and BG4 (cationic dye) were used in the study (*Table 1*).

2.2. Sorbent

Preparation of chitosan beads

Analyses were conducted with chitin of krill obtained from the Sea Fisheries Institute in Gdynia, with dry matter content of 95.64%, ash content of 0.32%, and deacetylation degree below 3%. Before sorption, commercial chitin was rinsed with distilled water and 6 N hydrochloric acid in order to loosen its structure and wash out calcium ions, magnesium

Table 1. *Characteristics of the dyes examined.*

Dye			
	Reactive Black 5 - [RB5]		Basic Green 4 - [BG4]
Structural formula	NaO₃SO–CH₂–CH₂—SO₂—⬡—N=N— ... SO₃Na, HO, H₂N, NaO₃SO–CH₂–CH₂—SO₂—⬡—N=N— SO₃Na		(structure)
Molecular weight, g/mol	991		927
λ_{max}, nm	597		353
Other trade names	Begazol Black B, Diamira Black B, Levafix Black E-B, Remazol Black B,	Celmazol Black B, Intracron Black VS-B, Primazin Black BN, Sumifix Black B	Malachite Green, Aniline Green, Diamond Green B / Victoria Green B, Light Green N, Solid Green O

ions and lipid residues, next rinsed with distilled water until a neutral reaction of the filtrate. Afterwards, chitin was cooked for 3h in a water bath with 70% potassium base. After cooling, the chitin was again flushed with distilled water until a neutral reaction and filtrated off under vacuum. The resulting chitosan has a deacetylation degree of 50%. 50 g of chitosan dissolved in 5% acetic acid were instilled with a micropipette to 5% NaOH and left in the solution for 24 h. The size of the instilled beads was controlled by the size of the micropipette and was 3 mm. The resultant beads were filtrated, rinsed with distilled water and kept in distilled water until used.

Preparation of cross-linked chitosan beads
    Chitosan beads were fixed in a solution of a cross-linking agent − glutaraldehyde. The cross-linking agent to chitosan ratio reached 1 : 1 (w/w). The crosslinked chitosan beads will be rinsed with distilled water in order to remove the unreacted glutaraldehyde.

2.4. Analytical procedures
    Analyses were conducted for the effectiveness of adsorption of two dyes: anionic RB5 and cationic BG4, at three pH values: 3.0, 5.0 and 9.0, on two adsorbents – chitosan beads and chitosan beads cross-linked with glutaraldehyde. To this end, 0.1 g of sorbent/dm³ (1 g d.m. sorbent/dm³) was weighed into Elenmayer flask and 100 cm³ of a dye solution with a concentration from 1 to 1000 mg/dm³ was poured in. The pH value was adjusted with the use of 0.1 N solutions of HCl and NaOH. Thus prepared samples were shaken for 2 h, at the speed of "200" and vibration amplitude of "9".

2.5. Analytical methods
    In each of the samples, the concentration of dye left in the aqueous solution was controlled with the spectrophotometric method. Samples to be analyzed were collected (10 cm³), decanted and centrifuged for 15 min at 10,000 r.p.m. The concentration of the

remaining dye was determined acc. to standard curves in a UV-VIS Spectrophotometer SP-3000.

3. Results and discussion

The effectiveness of anionic dye RB5 and cationic dye BG4 adsorption from aqueous solutions onto two investigated adsorbents was analyzed based on a correlation between the quantity of adsorbed dye q_{max} (mg/g d.m.) and its equilibrium concentration in the solution C (mg/dm^3).

Four mathematical models were used to analyze the results.

Freundlich Model

It is an isotherm that characterizes adsorption on non-uniform surfaces. In the Freundlich's theory, the number of adsorbed molecules at the complete coverage of adsorbent surface cannot be higher than the number of active sites, and the layer formed isolates the action of adsorption forces, thus enabling the formation of subsequent layers.

$$Q = k \cdot C^{n} \tag{1}$$

where:
- Q – mass of adsorbed compound in mg/g d.m.,
- k – adsorption constant,
- C – concentration of adsorbed substance in the state of equilibrium in mg/dm^3,
- n – coefficient of separation that determines the ratio of adsorbed quantity to the quantity left in the solution in the state of equilibrium in dm^3/g d.m.

Langmuir Model

The Langmuir's equation assumes that active sites occur on the surface of adsorbent where sorbate molecules are subject to sorption. The binding of adsorbate molecules with the active site may be of physical or chemical nature. The adsorbed molecules form a monomolecular layer and no interaction occurs between them. The quantity of adsorbed substance depends on the sorption capacity of the monolayer (q_{max}) and on adsorption affinity of adsorbate to adsorbent (K_c)

$$Q = \frac{q_{max} \cdot K_c \cdot C}{1 + K_c \cdot C} \tag{2}$$

where:
- Q   – mass of adsorbed compound in mg/g d.m.,
- q_{max} – maximum adsorption capacity of adsorbent monolayer in mg/g d.m.,
- K_c – constant in Langmuir equation, an inverse of concentration at which half the maximum adsorption capacity is reached in dm^3/g d.m,
- C   – equilibrium concentration of adsorbed substance in mg/dm^3.

Double Lamgmuir Model

The double Langmuir model takes an account of the fact the adsorbent surface is energetically non-uniform and possesses four adsorption centers with different energy of adsorbate molecules binding. They are described by the Langmuir isotherm equation [13 - 15], and are characterized by constants: K_1, b_1 and K_2, b_2.

$$Q = \frac{b_1 \cdot K_1 \cdot C}{1 + K_1 \cdot C} + \frac{b_2 \cdot K_2 \cdot C}{1 + K_2 \cdot C} \tag{3}$$

where*:*

Q – mass of dye adsorbed on chitin in mg/g d.m.,

b_1 – maximum adsorption capacity of chitin at type I active sites in mg/g d.m.,

b_2 – maximum adsorption capacity of chitin at type II active sites in mg/g d.m.,

$q_{max} = b_1 + b_2$ – maximum adsorption capacity of adsorbent monolayer in mg/g d.m.,

K_1 – constant in Langmuir equation in dm³/mg, K_2 – constant in Langmuir equation in dm³/mg,

C – dye concentration in the solution in mg/dm³.

The total adsorption capacity (*b*) equals the sum of the maximum adsorption capacity determined for type I and type II active sites (b = b_1 + b_2). The K_1 and K_2 constants characterize adsorption affinity to, respectively, type I and type II active sites and correspond to an inverse of the equilibrium concentration at which the adsorption capacity equals over a half of the maximum capacity b_1 or b_2.

Redlich-Peterson Model

The Redlich-Peterson isotherm contains three parameters and involves the features of both the Langmuir and the Freundlich model [16, 17]. It can be described as:

$$Q = \frac{b \cdot C}{1 + K \cdot C^g} \tag{4}$$

where:

Q – mass of dye adsorbed onto chitin in mg/g d.m.,

b – constant in Redlich-Peterson equation in dm³/g d.w.,

K – constant in Redlich-Peterson equation in (dm³/mg)g,

g – constant in Redlich-Peterson equation,

C – dye concentration in the solution in mg/dm³.

At a low concentration, the Redlich-Peterson isotherm approximates to Henry's law and at a high concentration its behavior approaches that of the Freundlich isotherm.

In all applied models, constants were determined with the method of non-linear regression. The R^2 coefficient was adopted as measure of curve fit (at determined parameters) to experimental data.

Figures 1 – 4 present experimental results and isotherms plotted from Freundlich, Langmuir, Langmuir 2, and Redlich-Peterson equations.
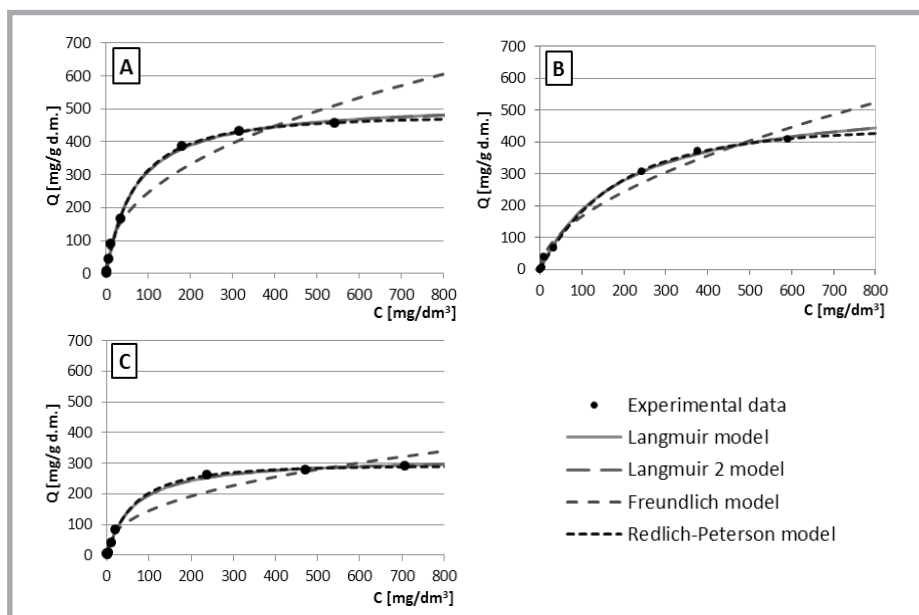
Figure 1. Experimental results and isotherms of RB5 dye adsorption on non-cross-linked chitosan beads: A. pH 3.0; B. pH 5.0, C. pH 9.0.
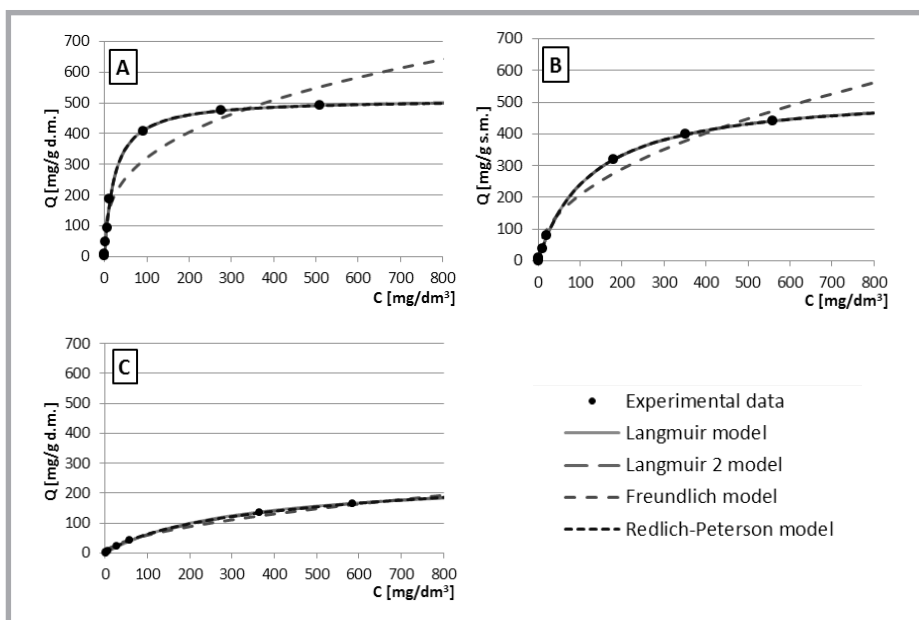
Figure 2. Experimental results and isotherms of RB5 dye adsorption on chitosan beads cross-linked with glutaraldehyde: A. pH 3.0; B. pH 5.0, C. pH 9.0.

Figure 3. *Experimental results and isotherms of BG 4 dye adsorption on non-cross-linked chitosan beads: A. pH 3.0; B. pH 5.0, C. pH 9.0.*

Figure 4. *Experimental results and isotherms of BG 4 dye adsorption on chitosan beads cross-linked with glutaraldehyde: A. pH 3.0; B. pH 5.0, C. pH 9.0.*
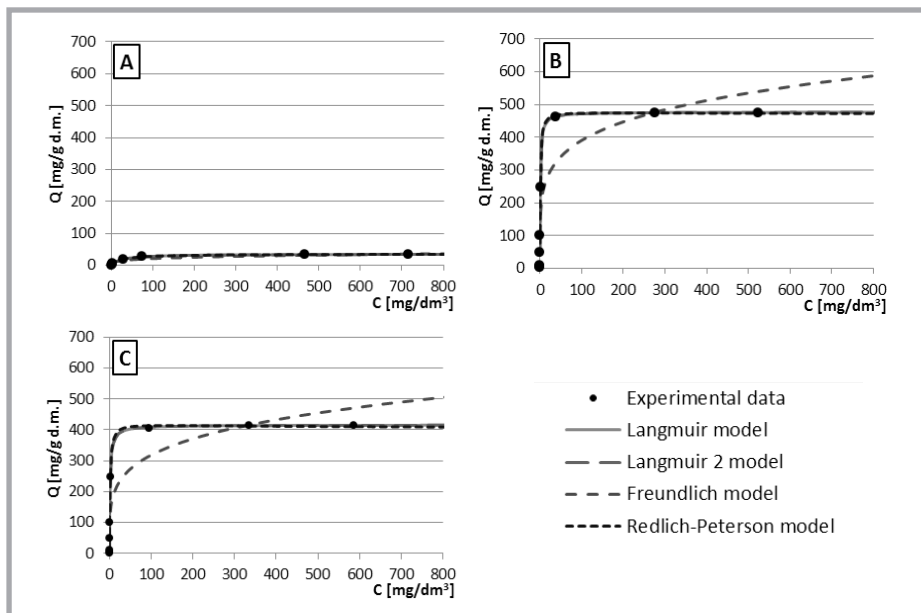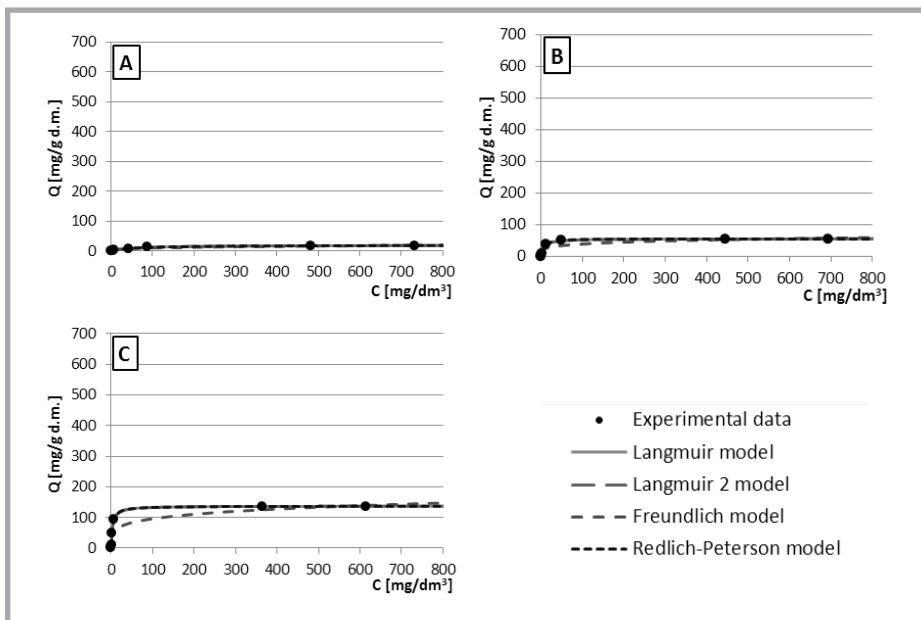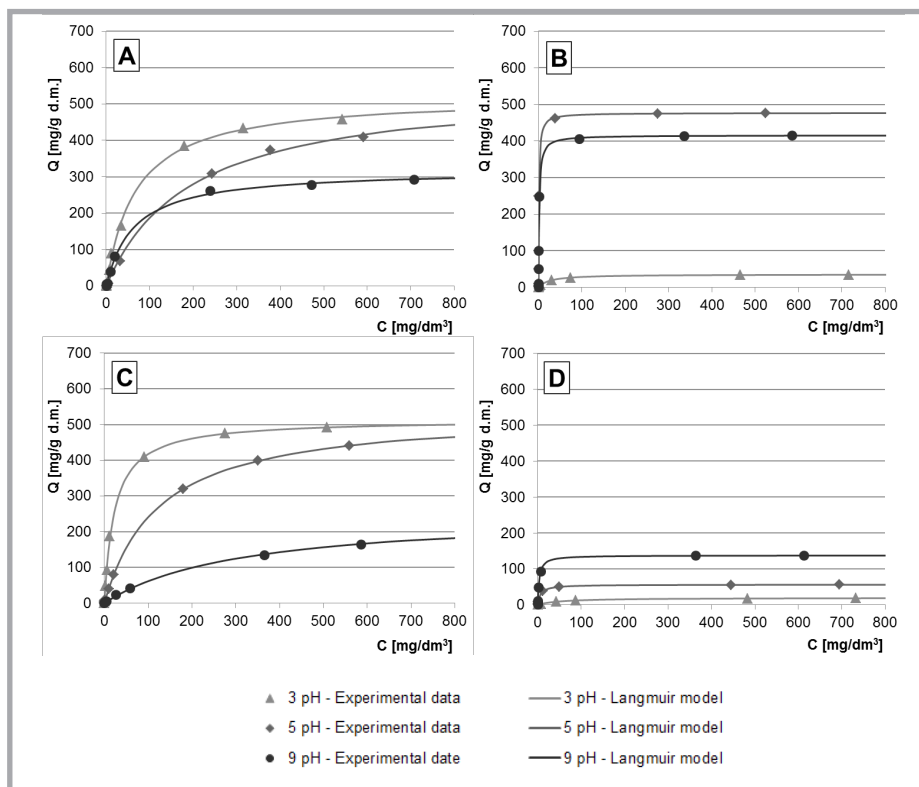
Figure 5. *Experimental results and Langmuir isotherms of dyes adsorption at different pH on chitosan sorbents: A) sorption of RB5 on non-cross-linked chitosan beads, B) sorption of BG4 on non-cross-linked chitosan beads, C) sorption of RB5 on chitosan beads cross-linked with glutar-aldehyde, D) sorption of BG4 on chitosan beads cross-linked with glutaraldehyde.*

Comparison of the Langmuir isotherm for different pH is presented in ***Figure 5***.

Based on results obtained, it may be concluded that the adsorption of anionic dye RB5 and cationic dye BG4 dye on non-cross-linked and cross-linked chitosan beads is well described by three isotherms used for calculations –Langmuir, double Langmuir and Redlich-Peterson. This is indicated by very high values of the determined R^2 coefficients, which for these models were higher than 0.99 irrespective of the type of dye and adsorbent (***Tables 3 – 5***). Substantially worse fit to experimental data was obtained in the case of Freundlich model.

Constants determined from isotherm equations: two di-parameter ones: Freundlich and Lagmuir, one tri-parameter: Redlich-Peterson, and one four-parameter: double Langmuir were adopted as criterion of adsorption process efficiency. ***Tables 2 – 5*** present the constants determined from the model applied in experimental calculations.

Table 2. *Constants determined from Freundlich's equation.*

Dye	Sorbent	pH	Constants in the Freundlich model		R²
			k	n	
RB5	CHs non-cross-linked	3	35.096	0.4512	**0.9707**
		5	13.387	0.5484	**0.9798**
		9	22.230	0.4076	**0.9520**
	ALD-CHs	3	69.846	0.3316	**0.9386**
		5	23.285	0.4758	**0.9805**
		9	4.458	0.5633	**0.9938**
BG4	CHs non-cross-linked	3	6.488	0.2579	**0.9080**
		5	158.41	0.1959	**0.8711**
		9	114.63	0.2217	**0.8651**
	ALD-CHs	3	2.366	0.3095	**0.9516**
		5	15.933	0.1978	**0.8318**
		9	37.474	0.2049	**0.8915**

Table 3. *Constants determined from Langmuir's equation.*

Dye	Sorbent	pH	Constants in the Langmuir model		R²
			q_{max}, mg/g d.m.	Kc	
RB5	CHs non-cross-linked	3	599.84	0.0135	**0.9988**
		5	552.40	0.0051	**0.9980**
		9	319.62	0.0160	**0.9969**
	ALD-CHs	3	514.31	0.0432	**0.9981**
		5	538.31	0.0081	**0.9997**
		9	254.18	0.0032	**0.9992**
BG4	CHs non-cross-linked	3	35.54	0.0409	**0.9994**
		5	476.80	0.9378	**0.9963**
		9	415.74	0.6172	**0.9941**
	ALD-CHs	3	19.33	0.0186	**0.9971**
		5	56.10	0.1599	**0.9984**
		9	137.60	0.3132	**0.9995**

Experimental data indicate that the adsorption capacity of the analyzed adsorbents was influenced by both the type of dye and pH value.

When analyzing the results, it may be observed that a decrease of pH value had a positive effect on the quantity of adsorbed RB5 anionic dye irrespectively of adsorbent type. This is in agreement with results of our previous studies and findings of other authors [18 - 24]. The sorption of anionic dyes are responsible amino groups of chitosan. At a low pH value, there are more protons available for the protonation of free amine groups $-NH_3^+$ of chitosan. It increases electrostatic affinity between negatively-charged anions of dyes and positively-charged adsorption sites. The attraction of anionic dyes influences an increase in adsorption. High adsorption capacities are due to electrostatic interactions between $-NH_3^+$ groups of chitosan and anionic dyes [25]. Glutaraldehyde causes blocking of the amino groups, and this can limit the sorption capacity of the sorbent. At pH value increase, the lower adsorption capacity results from the excess of OH⁻ ions competing with anionic dyes

Table 4. *Constants determined from double-Langmuir's equation.*

Dye	Sorbent	pH	Constants in the Langmuir 2 model					R^2
			(Q_{max}) $b_1 + b_2$, mg/g d.m.	b_1, mg/g d.m.	K_1	b_2, mg/g d.m.	K_2	
RB5	CHs non-cross-linked	3	620.86	536.05	0.0098	84.80	0.0519	**0.9992**
		5	552.41	369.92	0.0051	182.49	0.0051	**0.9980**
		9	319.61	159.99	0.0160	159.62	0.0160	**0.9969**
	ALD-CHs	3	514.32	251.48	0.0432	262.84	0.0432	**0.9981**
		5	538.32	367.05	0.0081	171.27	0.0081	**0.9997**
		9	280.77	18.22	0.0344	262.55	0.0022	**0.9999**
BG4	CHs non-cross-linked	3	35.64	15.82	0.0590	19.82	0.0303	**0.9995**
		5	476.80	225.57	0.9378	251.23	0.9379	**0.9963**
		9	415.74	181.99	0.6172	233.76	0.6172	**0.9941**
	ALD-CHs	3	19.53	0.9707	1.1474	18.56	0.0158	**0.9990**
		5	56.10	47.32	0.1599	8.78	0.1599	**0.9984**
		9	137.86	135.45	0.3228	2.41	0.0159	**0.9996**

Table 5. *Constants determined from Redlich-Peterson's equation.*

Dye	Sorbent	pH	Constants in the Redlich-Peterson model				R^2
			K_r	A_r	g	$b = K_R/A_R$, mg/g d.m.	
RB5	CHs non-cross-linked	3	8.899	0.0147	1.005	604.24	**0.9992**
		5	3.130	0.0055	1.011	569.07	**0.9985**
		9	4.646	0.0094	1.0679	494.26	**0.9976**
	ALD-CHs	3	22.035	0.0412	1.0034	534.83	**0.9982**
		5	4.317	0.0077	1.0069	560.64	**0.9997**
		9	1.020	0.0046	0.8273	221.74	**0.9999**
BG4	CHs non-cross-linked	3	1.488	0.0435	0.9943	34.21	**0.9994**
		5	438.522	0.8929	1.0057	491.12	**0.9964**
		9	245.385	0.5509	1.0124	445.42	**0.9944**
	ALD-CHs	3	0.390	0.0239	0.9747	16.32	**0.9972**
		5	8.277	0.1351	1.0143	61.27	**0.9988**
		9	43.546	0.3201	0.9982	136.04	**0.9996**

for the adsorption sites. As significant adsorption of anionic dyes may still be observed at alkaline pH, it may point to the occurrence of chemisorption. An opposite mechanism proceeds in the case of cationic dyes. An increase in BG4 dye adsorption effectiveness was achieved along with an increasing pH value of the adsorption process.

The adsorption of dyes was significantly affected by the type of adsorbent used. An overview of literature indicates that the type of a cross-linking agent determines properties of the modified adsorbent. The cross-linking reactions may be of homogenous or heterogenous nature and are the chemical modification of chitosan. They may be conducted by applying new functional groups onto structures of polymeric chains of chitosan using two or more functional cross-linking compounds. The degree of chitosan cross-linking depends on many factors including deacetylation of chitin, concentration of cross-linking, temperature

or reaction time [**5, 26**]. Such agents may include: glutaraldehyde, epichlorohydrin of gly-coethylene. The action of a cross-linking agent results in the formation of spatial networks, which diminishes the mobility of polymer chains by the formation of new links between these chains.

The study demonstrated that the change in chitosan properties induced by the cross-linking with glutaraldehyde had a positive impact on the effectiveness of RB5 dye adsorption without causing a significant decrease in the adsorption capacity the anionic dye RB5 at pH 5.0. The achieved adsorption capacities of chitosan beads cross-linked at pH 3 and pH 5 were comparable and reached, respectively, 514 and 538 mg/g d.m. (**Tables 3, 4**) as well as 534.83 and 560 mg/g d.m. (**Table 5**). In the case of non-cross-linked beads, the adsorption at pH 5 was lower – 552.4 (552.41 and 569.07) mg/g d.m. than at pH 3.0 – 599.84 (620.86 and 604.24) mg/g d.m. (**Tables, 3, 4** and **5**).

An opposite tendency was noted in the case of the second analyzed dye – BG4. Cationic dyes may have affinity for the non-protonated amine groups and hydroxyl groups. For this reason, BG4 sorption on non-cross-linked chitosan was effective at pH 5 and 9 (476.8 and 415.74 mg/g d.w - **Table 3**). The cross-linking of chitosan beads with glutaraldehyde caused a decrease in the effectiveness of BG4 dye adsorption. Such an effect was noted in conduced experimental series irrespectively of the pH value. Because the amino groups in cross-linked chitosan is partly blocked by glutaraldehyde, for sorption BG4 are presumably responsible primarily the group -OH. The hydroxyl groups at high pH may undergo depro-tonation, or gain a negative charge, which has a positive effect on the sorption of cationic compounds. For this reason, the sorption BG4 on the glutaraldehyde cross-linked chitosan was efficiently at alkaline pH.

Chitosan cross-linking with glutaraldehyde affected also the mechanism of adsorption. This is indicated by the determined values of adsorption affinity K (Langmuir model and double Langmuir model). Irrespective of the type of adsorbent, the adsorption affinity determined for BG4 dye was higher compared to the affinity determined for RB5 dye.

The lower values of K constants for RB5, compared to the values obtained for BG4, confirm results of earlier investigations on the impact of the initial concentration of dye on the effectiveness of dyes adsorption onto non-cross-linked chitosan and chitosan cross-linked with glutaraldehyde [**27**]. In the case of the anionic dye RB5, a distinct dependency was found of dye removal effectiveness on the initial concentration of dye in the solution. At low initial concentrations, i.e. 1 and 5 mg/dm^3, the effectiveness of RB5 adsorption reached, respectively, 18.72 and 52.4% on average, and was lower compared to the effectiveness achieved at higher initial concentrations, i.e. 100 and 200 mg/dm^3 – ca. 80%. The cationic dye BG4 was characterized by high adsorption effectiveness at both low and high initial concentrations in the solution – 90 – 100%.

In analyzing the effect of chitosan cross-linking with glutaraldehyde, it may be observed that in the case of the anionic dye RB5 the determined values of K constants increased, whereas in the case of BG4 dye – decreased. Such a tendency was noted in the case of three applied models: constant K_C – Langmuir model, constant K_1 – double Langmuir

model, and constant A_R – Redlich-Peterson model. The higher values of adsorption affinity may point to stronger binding of adsorbent with adsorbate.

4. Conclusions

Results of the conducted study enable concluding that the effectiveness of the adsorption process depends on the type of dye and adsorbent as well as on pH value of the process. In the case of the anionic dye RB5, the highest adsorption effectiveness was achieved at low pH values, whereas an opposite tendency was observed for the cationic dye BG4 where an increase in pH value facilitated enhanced removal of dye.

The study demonstrated that the application of glutaraldehyde had a positive impact on sorption of the anionic dye. The adsorption capacity after chitosan cross-linking at pH 5.0 was higher than that of chitosan cross-linked at pH 3.0. An opposite tendency was noted for the cationic dye, in the case of which the adsorption capacity of chitosan after cross-linking decreased compared to the capacity recorded for the non-cross-linked chitosan beads.

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