APPLICATION OF CHITOSAN IONICALLY CROSSLINKED WITH SODIUM EDETATE FOR REACTIVE DYES REMOVAL FROM AQUEOUS SOLUTIONS

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Abstract

In this study, we investigated the effect of chitosan crosslinking with sodium edetate (SE) on its sorption capacity of Reactive Black 5 and Reactive Yellow 84 dyes. The first stage of the study allowed establishing conditions of chitosan crosslinking. The process of ionic crosslinking was effective only at pH 4 and at the optimal dose of sodium edetate ranging from 0.046 to 0.462 g/g $_{CHs}$. Process temperature in the range of 20-60^{o}C had no significant effect on the stability of crosslinked chitosan. Contrary to the non-crosslinked chitosan (CHs), chitosan crosslinked with sodium edetate (CHs-SE) was capable of dyes sorption at pH 3. Sorption of reactive onto both CHs and CHs-SE was the most effective at pH 4.

Chitosan crosslinking with SE had a positive effect on the effectiveness of RB5 and RY84 sorption. This effect was especially tangible within the first ten or so hours of sorption. After 24 h of the process, the sorption capacity of CHs-SE against RB5 and RY84 reached 1296.69 mg/g and 1883.62 mg/g, respectively. In the case of CHs, sorption capacity achieved after the same time was lower and accounted for 1025.55 mg RB5/g and 1539.67 mg RY84/g.

Key words*: crosslinking, chitosan beads, dyes sorption, sodium edetate*

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1. Introduction

Chitosan is a polysaccharide produced as a result of chitin deacetylation. Chitin – being a raw material for chitosan production – is acquired on the industrial scale from exoskeletons of marine crustaceans. Chitin exoskeletons of arthropods are produced in high quantities as waste during the processing of shrimps and crabs. Considering the above, both chitin and chitosan are claimed to be cheap and widely available materials.

Chitosan in the form of flakes or hydrogen beads has become a popular sorbent. The presence of amine groups capable of protonation in the structure of a given polysaccharide is the cause of the alkaline character of chitosan. The positive charge on the sorbent's surface has a beneficial effect on the binding of any anionic contaminants. Chitosan exhibits especially high effectiveness during the removal of acidic dyes from aqueous solutions. The sorption capability of chitosan regarding reactive dyes – being the most popular type of acidic dyes – may reach over 2000 mg/g [1]. High affinity of dyes offers the possibility of applying chitosan for the treatment of color wastewater from textile, tanning and dye industries. Appropriately modified chitosan could be a good substitute for commonly-applied activated carbon.

A drawback of chitosan is its instability in the acidic medium. At pH < 5, chitosan dissolves and loses its sorption abilities [2]. Stability of a chitosan sorbent during sorption at low pH may, however, be improved through the crosslinking process. Depending on the type of a crosslinking agent, the crosslinking of chitosan may be either covalent (chemical) or ionic.

During covalent crosslinking, a molecule of the crosslinking agent binds permanently with at least 2 chains of the polymer. This process results in the formation of a stable three-dimensional polymer network. Chitosan may be crosslinked covalently by any compound that possesses at least 2 functional groups capable of condensation reaction in the presence of amine or hydroxyl groups. The covalent crosslinking of polymers is an irreversible reaction[3]. The chemically-crosslinked chitosan is stable even at pH 1 [4], however the sorbent becomes more fragile and less resistant to mechanical damages [5,6].

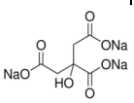
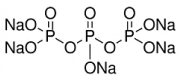
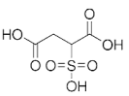
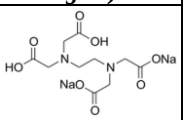
In turn, the ionic crosslinking of a sorbent requires introducing a compound into the system the electric charge of which in a solution is opposite to the charge of the polymer. The ionic compound that penetrated into the sorbent's interior, attracts electrostatically the neighboring chains which possess an opposite electric charge [7]. The ionically-linked polymer chains result in a compact structure of the sorbent and its increased resistance to solubilization.

Ionic crosslinking is less stable than the covalent one, and the resultant sorbent is not completely resistant to solubilization at low pH (e.g. pH 1-2). But still, an advantage of the ionic crosslinking is the easiness of process conduct and no need for the use of a catalyst [8].

In the case of chitosan, having a positive charge, the crosslinking agent could include any substance with at least two functional groups possessing a negative charge. The confirmed ionic crosslinking agents of chitosan include,

among others, citrates, oxalates, sodium polyphosphates and sulfosuccinates. Table 1 summarizes examples of ionic crosslinking agents of chitosan.

Table 1. Examples of ionic crosslinking agents

Name of ionic crosslinking agent	**Trisodium citrate**	**Pentasodium tripolyphosphate**	**Sulfosuccinic acid**	**Sodium edetate *(not confirmed crosslinking agent)***
Structural formula				
Molecular weight	258 g/mol	368 g/mol	198 g/mol	336 g/mol
Ionic charge in aqueous solution	3 -	5 -	3 -	4 -

Considering its chemical structure, sodium edetate [SE] seems to be a potentially-effective ionic crosslinking agent. Owing to its relatively high negative charge, it is potentially capable of a strong interaction with positively-charged polysaccharide chains of chitosan. In this study, we investigated the possibility of applying sodium edetate as an ionic crosslinking agent as well as sorption capabilities of a chitosan sorbent modified with SE.

2. Materials and Methods

2.1. Materials

Chitosan used in experiments was purchased at BioLog Biotechnologie und Logistik GmbH, Landsberg, Germany. Parameters of chitosan provided by the producer were summarized in Table 2.

Sodium edetate > 98.0 % and other chemical reagents were purchased from Sigma-Aldrich (St.Louis, MO, USA).

Reactive dyes: Reactive Black 5 (RB5) and Reactive Yellow 84 (RY84), used in the study were purchased from the Dye Production Plant "Boruta" SA, Poland. The basic characteristics of the above dyes was provided in Table 3.

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Table 2. Specification of chitosan applied in the study

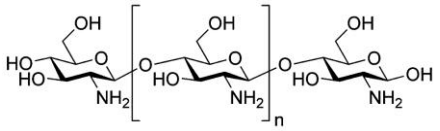
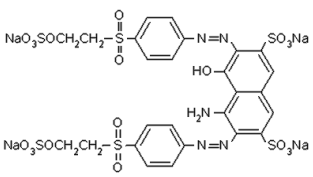
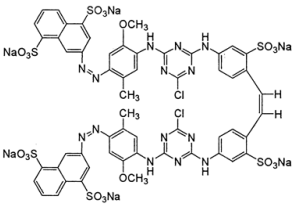
Structural formula		
Degree of deacetylation		82.6 % - 87.5 % (average 85.0 %)
Viscosity		351 – 750 mPas (average 500 mPas)
Content of dry matter		86.8 %
Content of heavy metals	**Pb**	20 ppm
	Hg	0.2 ppm
	Cd	0.5 ppm
Source of origin of raw material		Exoskeletons of shrimps

Table 3. Basic characteristics of dyes used in the study

Dye name	**Reactive Black 5 (RB5)**	**Reactive Yellow 84 (RY84)**
Structural formula		
Molecular weight	991 g/mol	1701 g/mol
λ_{max}	600 [nm]	356 [nm]
Character of dye	Acidic (anionic - reactive)	Acidic (anionic - reactive)
Characteristic functional groups	vinylsulfone	chlorotriasine

2.2. Methods

2.2.1. Preparation of chitosan sorbent in the form of hydrogel beads [CHs]

Chitosan (25 g d.w. [gram dry weight]) was dissolved in 975 g of an acetic acid solution (5%). The resultant mixture with chitosan concentration of 2.5 % was instilled (using 0.8 mm injection needle) into a 2 mol/dm^3 aqueous solution of sodium hydroxide. Chitosan solution in 2M NaOH was immediately subject

to the gelling process. The hydrogel beads formed were left in the solution of sodium hydroxide for 24 h. Afterwards, the chitosan beads were rinsed with high volume of distilled water to remove NaOH left on their surface. The resultant sorbent was stored in a solution of distilled water.

2.2.2. Crosslinking of chitosan sorbent with sodium edetate

The process of ionic crosslinking of chitosan consisted in the bath of hydrogel chitosan beads in a sodium edetate solution. Chitosan content in the crosslinking solution reached 10 g $_{d.w.}$/dm^3. The optimal dose of SE during crosslinking as well as pH value and temperature of the process were established during experiments described in points 2.2.3-2.2.4.. The crosslinking process lasted 24 h. Afterwards, the sorbent was filtered and rinsed with distilled water to remove the non-reacted SE. The resultant chitosan sorbent was stored in a solution of distilled water.

2.2.3. Determination of conditions of chitosan crosslinking (pH, temperature)

Non-crosslinked chitosan sorbent [CHs] (1 g $_{d.w.}$) was weighed into 5 conical flasks (vol. 200 mL). Next, SE solutions (100 mL – 4.62 mg SE/dm^3) with pH: 4, 6, 8, 10 and 12 were added to the flasks. The ration of SE ion charge to the number of amine groups of chitosan was at 1:1. Afterwards, the flasks were placed in a shaker (150 r.p.m.) in a room with a temperature of 20^{o}C. Analogous analyses were carried out at 60^{o}C. After 24 h of crosslinking, the sorbents were filtered and rinsed with distilled water.

Eventually, 10 types of chitosan sorbents differing in pH and temperature of crosslinking were obtained from the 2 above-described experimental series. Each of the sorbents, in the amount of 0.2 g $_{d.w. CHs}$ was weighed into 4 conical flasks with the volume of 300 mL. Next, a solution of RB5 dye (200 mL) with the concentration of 100 mg/dm^3 and pH 2,3,4 and 5 was added to the flasks. Then, the flasks were placed in a shaker (150 r.p.m.). After 60 min, samples were collected for the analysis of dye left in the solution.

2.2.4. Determination of the dose of sodium edetate during crosslinking

CHs in the amount of 1 g $_{d.w.}$ was weighed into 11 conical flasks with the volume of 200 mL. Then, SE solutions (100 mL) with concentrations of: 0.46 – 18.47 mg SE/dm^3 were added to the flasks. The concentrations of SE were adjusted
so as to ensure the ratio of the crosslinking agent ion charge to the number of amine groups of chitosan at 0.1. to 4.0. Afterwards, the flasks were placed on a shaker (150 r.p.m.) for 24 h. Temperature applied during crosslinking and pH value of the crosslinking agent were described in point 2.2.3.

Once the crosslinking process was completed, the sorbents were rinsed with distilled water. Each resultant sorbent was weighed in the amount of 0.2 g $_{d.w. CHs}$ into 4 conical flasks (300 mL). Then, RB5 solutions (200 mL) with the concentration of 100 mg RB5/dm^3 and pH 2, 3, 4 and 5 were added to the flasks, which were then placed on a shaker (150 r.p.m) for 60 min.

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Afterwards, samples (10 mL) were collected for the determination of the concentration of dye left in the solution.

2.2.5. Determination of the optimal pH value of dye sorption

Chitosan sorbent (0.2 g $_{d.w.\ CHs}$) was weighed into 10 conical flasks with the volume of 300 mL. Next, dye solutions (200 mL) with the concentration of 100 mg/dm^3 and pH 2-11 were added to the flasks that were then placed on a shaker (150 r.p.m.). After 60 min of sorption, samples were collected for determinations of the concentration of RB5 left in the solution. The optimal pH value of sorption of each sorbent was indicated by the highest effectiveness of dye sorption.

2.2.6. Determination of sorption capacity

Chitosan sorbent (0.5 g $_{d.w.\ CHs}$) was weighed into 8 conical flasks (vol. 1000 mL). Next, dye solutions with concentrations of 200 - 4000 mg/dm^3 and pH value 2-11 (see point 2.2.5) were added to the flasks. Afterwards, the flasks were placed in a shaker (150 r.p.m.). After 24, 168 and 336 h, samples were collected for analyses of the concentration of dye left in the solution.

2.2.7 Analytical methods

Concentrations of dyes in the solutions were determined with the spectrophotometric method using a UV-VIS SP 2000 spectrophotometer.

The pH values were measured with an HI-122 pH-meter.

2.2.8 Computational methods

The quantity of dye adsorbed on the sorbent was computed from the formula (1) :

$$\mathbf{Qs} = \frac{(\mathbf{Co}-\mathbf{Cs})\cdot\mathbf{V}}{\mathbf{m}} \qquad (1)$$

Sorption capacity of hydrogels was determined based on the double Langmuir model. Langmuir 2 model (Double Langmuir isotherm) (2):

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

Langmuir model assumes, that the sorbate formed the monolayer on the surface of the sorbent. In the theory of Langmuir, adsorbed molecules do not interact with each other and don't form a multilayer.Langmuir 2 model (double Langmuir equation) differs from the model Langmuir assumption that, the surface of the sorbent has at least two types of active sites with different degrees of affinity sorbent.

The fit of experimental data to mathematical models was computed automatically also with the use of a determination coefficient R^2 :

$$\mathbf{R^2} = \frac{\Sigma(\mathbf{q_{cal}}-\overline{\mathbf{q}}_{\mathbf{exp}})^2}{\Sigma(\mathbf{q_{cal}}-\overline{\mathbf{q}}_{\mathbf{exp}})^2+\Sigma(\mathbf{q_{cal}}-\mathbf{q_{exp}})^2} \qquad (3)$$

where: *Qs* – weight of adsorbed dye (static conditions) [mg/g $_{d.w.}$]; *Co* – initial concentration of dye [mg/dm^3]; *Cs* – concentration of dye after sorption [mg/ dm^3]; *V* – solution volume [dm^3]; *m* - sorbent weight [g $_{d.w.}$]; *Q* – real sorption of sorbate on the sorbent [mg/g $_{d.m.}$]; b_1, b_2 – sorption capacity of the sorbent (type I and II active sites) [mg/g $_{d.w.}$]; K_1, K_2 – constants in Langmuir equation [dm^3/mg]; *C* – concentration of dye left in the solution [mg/dm^3]; R^2 – correlation coefficient – a measure of data fit to the model; q_{exp} – experimental data – quantity of adsorbed dye [mg/g $_{d.w.}$]; q_{cal} – theoretical data calculated from the model – quantity of adsorbed dye [mg/g $_{d.w.}$]

3. Results and discussion

3.1. Influence of pH and temperature on chitosan crosslinking and ability to dye sorption

Chitosan crosslinking with sodium edetate was feasible only at pH 4 (Table 4.). The chitosan sorbent crosslinked at pH 4 was capable of dye sorption at pH 3. At this pH value, the sorbent manifested signs of partial damage including gentle swelling or cracking of the surface, but ultimately preserved the form of hydrogel beads. Sorption conducted at pH 2 resulted in complete solubilization of the sorbent, which is typical of the ionically-crosslinked chitosan.

Table 4. Effect of conditions of ionic crosslinking of chitosan with sodium edetate on sorbents stability and RB5 sorption effectiveness at pH 2,3,4 and 5

		pH and temperature of crosslinking									
		pH 4		**pH 6**		**pH 8**		**pH 10**		**pH 12**	
		20°C	***60°C***	**20°C**	***60°C***	**20°C**	***60°C***	**20°C**	***60°C***	**20°C**	***60°C***
Sorption	**pH 2**	D	D	D	D	D	D	D	D	D	D
	pH 3	36.58*	28.74*	D	D	D	D	D	D	D	D
	pH 4	88.09	86.96	86.73	84.64	87.21	74.95	77.33	66.5	74.80	62.69
	pH 5	88.12	81.94	87.12	84.67	79.9	66.04	66.25	51.24	64.19	47.07

D – dissolution of sorbent; *- sorbent was partly damaged; XX.XX - % of RB5 dye removal

The crosslinking with SE at pH 6-12 was ineffective because the resultant sorbent, likewise the non-crosslinked chitosan, dissolved at pH < 4. According to literature data, relatively low pH of the crosslinking process (pH 5) is also applied during chitosan modification with sodium tripolyphosphate [9]. Any attempts of chitosan crosslinking in the solution with pH < 4 resulted in the dissolution of chitosan before its crosslinking. The crosslinking temperature had no significant effect on the stability of the resultant sorbent.

In a solution with the initial pH value of pH 4, the non-crosslinked chitosan hydrogel swelled significantly. Under these conditions, protonated

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polysaccharide chains were repulsing one another, thus loosening the spatial structure of hydrogel. Electrostatic interaction between the chains was, however, not strong enough to result in sorbent solubilization. This provided good conditions for the ionic crosslinking of the sorbent.

The crosslinking agent could penetrate to the interior of the loosened hydrogel structure, and therefore the crosslinking proceeded probably in the whole volume of the sorbent. In the case of chitosan crosslinking at pH 6-12, the sorbent's structure was more compact. Under these conditions, the capability of the crosslinking agent to penetrate sorbent's structure was curbed. Presumably, at pH 6-8 the crosslinking was only superficial which, however, failed to ensure sorbent stability at pH $\leq$ 3. At pH 10-12, the surface of hydrogel attained a negative charge, as a result of which the anionic crosslinking agent was electrostatically repulsed from chitosan. Probably for this reason, at pH 10-12 the crosslinking did not proceed even on sorbent's surface.

Although the chitosan crosslinked ionically by SE was capable of sorption at pH 3, the effectiveness of RB5 binding was relatively low. The effectiveness of RB5 dye sorption at pH 4-5 was the highest after chitosan crosslinking at pH 4. It is, probably, linked with the loosing of hydrogel structure during crosslinking in acidic pH. The extended surface and increased permeability of the hydrogel structure of chitosan resulted in greater accessibility of the dye to sorption centers. An opposite situation occurred during dye sorption onto chitosan crosslinked at pH 10-12. The structure of a chitosan hydrogel conditioned at alkaline pH was becoming compact, which impaired RB5 sorption especially at the early stage of the process.

The ionic crosslinking of chitosan at an increased temperature (60^{o}C) resulted in a reduced capability of the sorbent for RB5 sorption. It was especially noticeable at crosslinking pH of 8-12. Because high temperature has no positive effect on the stability and effectiveness of the sorbent, the heating of the crosslinking solution was found unnecessary.

Based on results from point 3.1, it was established that the ionic crosslinking of chitosan should be conducted at a room temperature and pH 4. These conditions were applied to prepare the crosslinked sorbent for further analyses.

3.2. Determination of the optimal dose of sodium edetate during chitosan crosslinking

The ionic crosslinking of chitosan with sodium edetate ensured sorbent stability during sorption at pH 3. The effect of chitosan crosslinking was noticeable already with a dose of 0.046 g SE/g_{CHs} (Table 5.).

The SE dose applied had a significant effect on the final pH value of the crosslinking solution and on the sorption effectiveness of the crosslinked chitosan. The final pH value of the solution was decreasing along with an increasing SE dose applied during crosslinking. Lower sorption pH is favorable for the sorption of anionic dyes. For this reason, in the SE dose

range of 0.046 – 0.462 g SE/g_{CHs} , the effectiveness of RB5 sorption onto crosslinked sorbent was increasing along with the applied dose of sodium edetate (Table 5., Fig. 1.).

A too high dose of sodium edetate applied during crosslinking caused sorbent damage. At the dose of 0.693 g SE/g_{CHs} , the outer layers of hydrogel were subject to slow partition, but not dissolution. The effect of mechanical damage on the outer layers of the sorbent was especially noticeable during RB5 sorption at pH 4-5. The dye was adsorbed both onto external layers of the sorbent and on powdery residues after the outer layers of hydrogel. The dose of 0.924 g SE/g_{CHs} resulted in complete damage of the sorbent, which made further experiments impossible (Table 5.).

Table 5. Effect of sodium edetate dose during chitosan crosslinking on sorbent stability and RB5 sorption effectiveness at pH 2, 3, 4 and 5

Ratio of the charge of crosslinking agent ion to the number of amine groups of chitosan		**Dose of sodium edetate per 1g d.m. of chitosan [g]**	**Sorption pH**			
			2 pH	**3 pH**	**4 pH**	**5 pH**
1 to 10	0.10	0.046	D	21.88 / 5.35*	75.98 / 6.80	71.22 / 6.95
1 to 8	0.13	0.057	D	22.46 / 5.25*	84.64 / 6.66	83.66 / 6.86
1 to 6	0.17	0.077	D	22.76 / 5.19*	89.11 / 6.41	84.55 / 6.69
1 to 4	0.25	0.115	D	30.20 / 5.12*	89.57 / 6.29	88.58 / 6.54
1 to 3	0.33	0.154	D	29.36 / 5.08*	89.04 / 6.25	89.07 / 6.43
1 to 2	0.50	0.231	D	31.38 / 5.03*	90.38 / 6.20	88.32 / 6.29
1 to 1	1.00	0.462	D	33.11 / 4.99*	89.18 / 6.17	89.46 / 6.23
1.5 to 1	1.50	0.693	D	25.44 / 4.75*	79.89 / 5.75*	73.12 / 5.79*
2 to 1	2.00	0.924	D	D	D	D
3 to 1	3.00	1.385	D	D	D	D
4 to 1	4.00	1.847	D	D	D	D

D – dissolution of sorbent; *- sorbent was partly damaged; XX.XX - % of RB5 dye removal/ pH after sorption

At doses of 0.046 – 0.462 g SE/g_{CHs} sodium edetate was attracting for polysaccharide chains of chitosan, thereby inducing the effect of ionic crosslinking. In case of higher doses (> 0.693 g SE/g_{CHs}) the chitosan chains which are coated with SE, probably undergo separation. It may be linked with complexation properties of sodium edetate. The separated polysaccharide chains

or local clusters of chains were easily detaching from the primary structure of hydrogel and migrated to the solution.

Results of analyses enabled establishing the optimal dose of SE during crosslinking at 0.462 g SE/g_{CHs}. This dose was applied during preparation of CHs-SE for the subsequent experimental series.

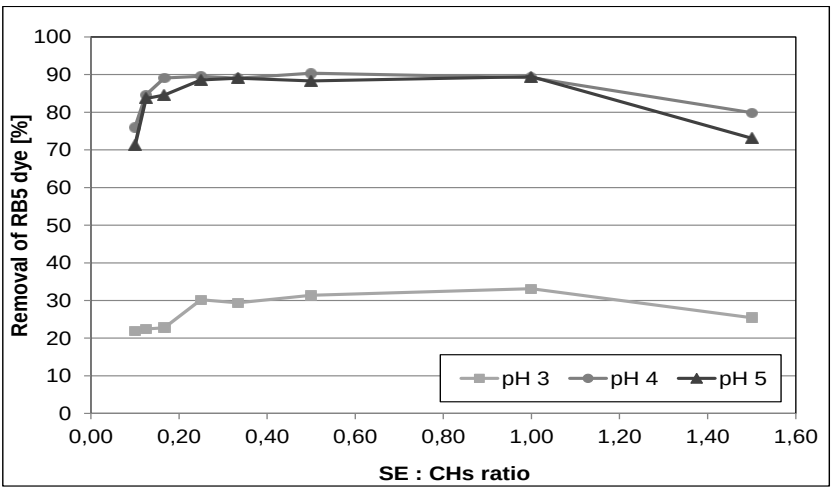

Figure 1. Effect of sodium edetate dose (ratio of SE ion charge to the number of amine groups of chitosan) during chitosan crosslinking on the effectiveness of RB5 sorption at pH 3, 4 and 5

3.3. Optimal pH of sorption of reactive dyes

The highest effectiveness of sorption reactive dyes onto chitosan sorbents was achieved at initial pH 4 (Fig. 2.). At pH 2-3, the non-crosslinked chitosan was completely dissolved, that why performing of analyses was impossible. The ionic crosslinking of chitosan wit SE allowed conducting the sorption process at pH 3, however the sorbent was partly damaged and sorption effectiveness was low compared to that determined at pH 4-5.

A the initial pH 4-12, the CHs-SE exhibited higher sorption capability than CHs, (Fig. 2-A). The initial pH of solutions was changing in the course of the sorption process. In the case of CHs, with the initial pH in the range of pH 4-9, the final pH of the solution ranged from 6.9 to 7.4. In the case of CHs-SE and the same initial pH, the final pH of the solution ranged from 6.0 to 7.0. It is indicative of SE effect upon decrease of pH_{ZPC} (pH of zero net proton charge) of the chitosan sorbent. It had, however, no negative impact on the sorption of anionic dyes.

Results of the above analyses allowed establishing the optimal pH were RB5 and RY84 dyes sorption onto chitosan sorbents is the highest, at pH 4.

This pH value was further applied in analyses of the sorption capacity of the chitosan sorbents. The beneficial effect of the low pH value on anionic dyes sorption onto chitosan sorbents was earlier confirmed in literature [10,11]. Low pH of the solution favors the protonation of the amino groups of chitosan. The positive charge of sorbent supports the sorption of anionic sorbates.

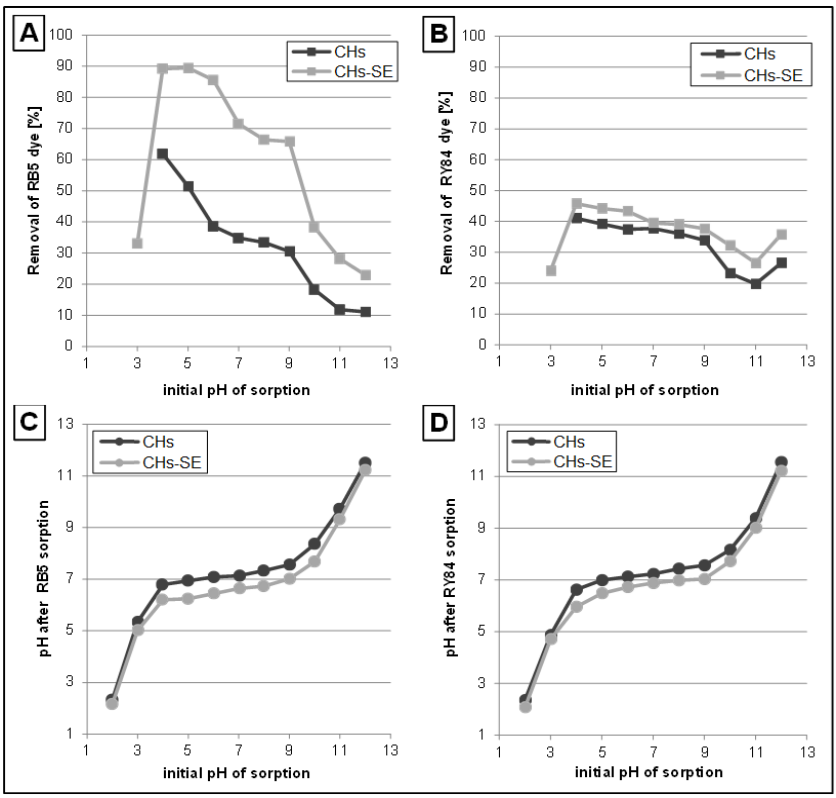

Figure 2. Effect of initial pH on the effectiveness of RB5 (A) / RY84 (B) sorption onto chitosan sorbents and on pH after RB5 (C) / RY84 (D) sorption

3.4. RB5 and RY84 dyes sorption capacity

Chitosan crosslinked with sodium edetate turned out to be a more effective sorbent than the non-crosslinked chitosan. The higher effectiveness of reactive dyes sorption onto CHs-SE compared to CHs was especially tangible at the initial stage of sorption covering the first 24 h (Fig. 3). The sorption capacity of CHs determined after this time reached 1025.55 mg/g for RB5 and 1539.67 mg/g for RY84 (Table 6). In the case of CHs-SE, the effectiveness of RB5 sorption after 24 h was higher by 26.4 % and that of RY84 by 22.3 %.

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The maximum sorption capacity of chitosan sorbents regarding RY84 was obtained after 168 h of sorption, when 1 g of CHs-SE adsorbed 2003.21 mg RY84 (Table 6). In the case of CHs, the maximum sorption capacity was lower by 19.0 %.

The sorption of RB5 onto CHs-SE was completed practically after 168 h. The sorption capacity of CHs-SE determined after this period reached 1640.49 mg/g. Within the successive 168 h, the calculated sorption capacity of CHs-SE increased only to 1678.23 mg (by 2.3%). After 168 h of sorption process, CHs achieved a similar sorption capacity (1668.99 mg/g). The sorption of RB5 onto CHs was completed already after 336 h, and sorption capacity reached 1946.19 mg RB5/g.

Table 6. Sorption capacity of chitosan sorbents for RB5/RY84 after 24, 168 and 336 h (pH 4).

Sorbent type	Dye type	Time after which sorption capacity was determined	Sorption capacity (b1 + b2)		Constants in Langmuir equation				R^2
			[mg/ g.d.w.$_{CHs}$]	[mmol/ g.d.w.$_{CHs}$]	K1	b1	K2	b2	
CHs	RB5	24	1025.6	1.035	0.5064	280.66	0.0005	744.9	0.999
		168	1669.0	1.684	4.1150	487.96	0.0056	1181.0	0.999
		336	1946.2	1.964	1.0829	875.13	0.0086	1071.1	0.998
	RY84	24	1539.7	0.905	0.0533	323.31	0.0012	1216.4	0.999
		168	1621.8	0.953	0.2606	792.26	0.0014	829.5	0.998
		336	1615.6	0.950	0.2244	913.90	0.0017	701.7	0.998
CHs-SE	RB5	24	1296.7	1.308	1.641	788.3	0.0011	508.4	0.978
		168	1640.5	1.655	9.445	978.4	0.0038	662.1	0.986
		336	1678.2	1.693	11.792	1023.0	0.0070	11.8	0.991
	RY84	24	1883.6	1.107	0.0023	941.6	0.0023	942.1	0.997
		168	2003.2	1.178	0.0025	1079.3	0.0025	923.9	0.996
		336	1938.9	1.140	0.0017	1269.9	0.0349	669.1	0.996

Differences in the effectiveness of particular dyes sorption may result from their different molecular weight, and thus also size. RB5 with lower molecular weight than RY84 was characterized by greater ability to penetrate the hydrogel structure. Owing to a relatively low weight, RB5 could penetrate into sorbent's interior and ultimately reach most of the free sorption centers. This was,

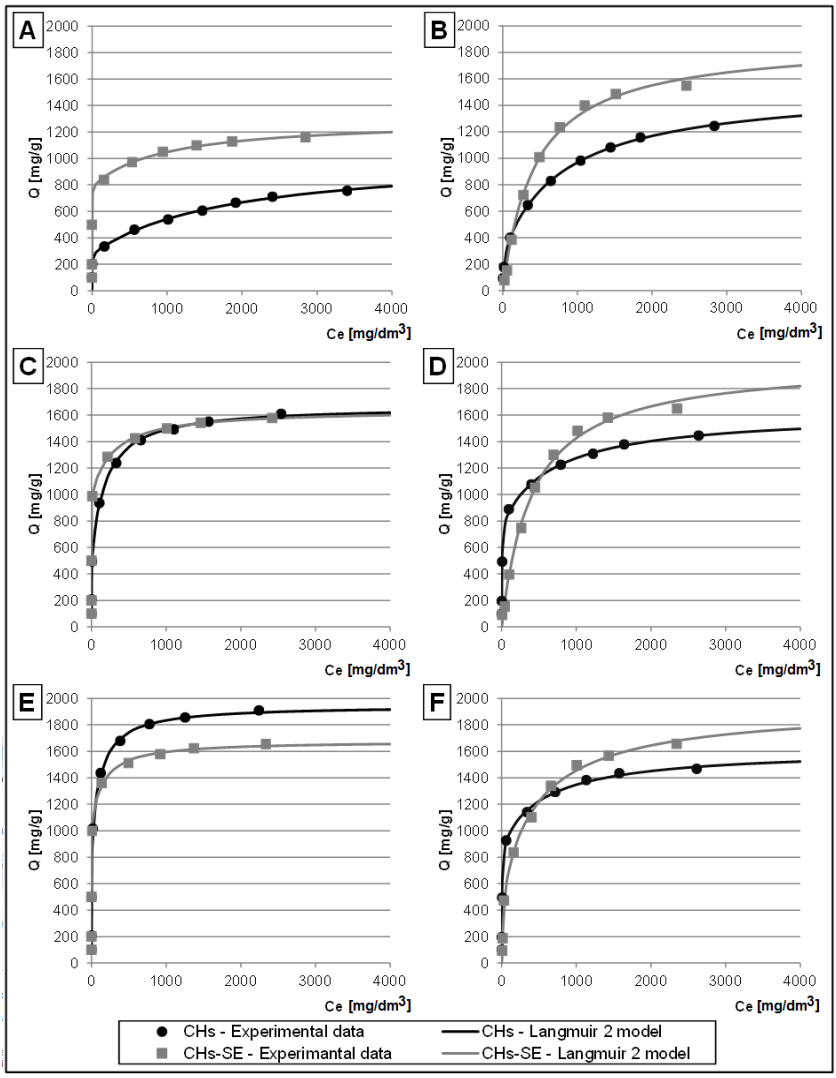

Figure 3. Comparison of isotherms of dyes sorption onto chitosan sorbents (Langmuir 2 model);
A) - Sorption of RB5 – after 24 h; B) - Sorption of RY84 – after 24 h;
C) - Sorption of RB5 – after 168 h; D) - Sorption of RY84 – after 168 h;
E) - Sorption of RB5 – after 336 h; F) - Sorption of RY84 – after 336 .

however, impaired in the case of CH-s-SE because of the presence of the crosslinking agent which linked the polysaccharide chains. Owing to large sizes, RY84 was probably attaching only to the sorption centers located in

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the outer layers of the hydrogel sorbent. The penetration of RY84 to hydrogel's interior was very curbed in the case of both CHs and CHs-SE. For this reason, successive sorption was either impossible or ineffective. It was indicated by the fact that both sorbents reached over 90% of the maximum sorption capacity against RY84 already within the first 24 h of the process.

4. Conclusion

Sodium edetate may be applied as an ionic crosslinking agent. Chitosan crosslinking with SE proceeds at the initial pH 4, at which the sorbent manifests the first symptoms of swelling. During chitosan crosslinking with sodium edetate, very high significance is ascribed to the dose of the crosslinking agent that should fit within the range of 0.046-0.462 g/g_{CHs}. Too high dose of SE during crosslinking may cause damage to the sorbent. At doses > 0.693 g/g_{CHs}, chains of chitosan coated with SE molecules began to repulse each other or to separate, which leads to sorbent damage. The temperature of crosslinking in the range of 20-60 ^{o}C has no greater impact on sorbent stability.

At pH <4, the non-crosslinked chitosan sorbent dissolves and loses its sorption capabilities. The properly crosslinked CHs-SE is capable to sorption of reactive dyes sorption at pH 3. In turn, at pH 2 the CHs-SE dissolves, which is typical of the ionic crosslinking. The optimal pH of RB5 and RY84 sorption onto both CHs and CHs-SE is pH 4.

CHs crosslinking with SE causes decreasing of sorbent pH_{ZPC}. It has no negative impact upon the sorption process of reactive dyes.

After 24 h of sorption, the CHs-SE exhibits higher sorption capability for anionic dyes than the CHs does. After this period, 1 g of CHs-SE may adsorb 1296.69 mg of RB5 or 1883.62 mg of RY84. In the case of CHs, the respective values are lower by 20.9 % and 18.3 %.

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