Effect of ionic and covalent crosslinking of hydrogel chitosan beads on the adsorption efficiency of basic violet 10 and basic green 4 dyes from aqueous solutions

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Abstract

This work investigated the adsorption efficiency of Basic Violet 10 (BV10) and Basic Green 4 (BG4) dyes on ionically and covalently crosslinked chitosan hydrogel beads. The tested ionic crosslinkers were sodium citrate, sodium tripolyphosphate, and sulphosuccinic acid, while the covalent crosslinkers were glutaraldehyde, epichlorohydrin, and trimethylolpropane triglycidyl ether. The scope of the work included investigation of the effect of pH on the adsorption efficiency of dyes and the maximum adsorption capacity of crosslinked chitosan adsorbents. The maximum adsorption capacity of the non-crosslinked chitosan adsorbent was 2.94 mg/g and 44.32 mg/g for BV10 and BG4, respectively. Ionic crosslinking, regardless of the type of crosslinking agent, reduced the adsorption ability of hydrogel chitosan adsorbents in relation to cationic dyes (Q_{max} = 1.84-2.49 mg/g for BV10; 37.21-38.90 mg/g for BG4). Covalent crosslinking of chitosan slightly increased its adsorption capacity only for BV10 (Q_{max} = 3.59-3.81 mg/g for BV10; 39.15-40.62 mg/g for BG4).

1. Introduction

Chitosan is a polysaccharide derivative of chitin, one of the most abundant biopolymers in nature. In recent years, this biopolymer has gained popularity as a high-performance adsorptive material. Chitosan adsorbents can be in the form of a powder, flakes, or hydrogels. Chitosan in the form of hydrogel granules shows the highest adsorption capacity [1]. Hydrogel chitosan adsorbents have found a potential application in the removal of anionic dyes from coloured industrial wastewater. The adsorption capacity of the hydrogel chitosan granules for this type of dye can be >2000 mg/g [2]. The basic nature of chitosan is responsible for the high adsorption efficiency of anionic dyes. The surface of this material is rich in primary amines, which are the key adsorption centres for all anionic impurities [3]. The disadvantage of chitosan is the relatively low adsorption efficiency of cationic (basic) dyes, which can also be a component of production wastewater [4]. The adsorption capacity of chitosan adsorbents can be increased by modifying it by, for example, crosslinking. Depending on the crosslinking agent used, it is distinguished between crosslinking by covalent or ionic bonds [5].

Covalent crosslinking of chitosan is a chemical reaction that results in the formation of permanent covalent bonds between the crosslinking agent and the polysaccharide chains. The covalent crosslinking agent can be any compound having at least two functional groups capable of a condensation reaction with the functional groups of the crosslinked polymer. Popular covalent crosslinkers are glutaraldehyde and epichlorohydrin [6].

In the case of ionic crosslinking, electrovalent (ionic) bonds are formed between the crosslinking agent and the chitosan chains. The ionic crosslinking agent in the aqueous solution has a charge opposite to that of the modified polymer. The electrostatic attraction of the polymer chains to the ionic crosslinking agent produces an ionic crosslinking effect. In theory, an ionic crosslinking agent for chitosan can be any chemical having at least two functional groups that generate a negative charge in water, e.g. $-COO^-$, $-SO_3^-$, and $-O-PO_3^{2-}$. The most commonly used ionic crosslinkers are citrates and polyphosphates [7].

In this work, the influence of ionic and covalent crosslinking of chitosan on its adsorption capacity in relation to the popular cationic dyes Basic Violet 10 (BV10) and Basic Green 4 (BG4) was investigated. The ionic crosslinkers tested in the study were sodium citrate, sodium tripolyphosphate, and sulphosuccinic acid, while the covalent crosslinkers were: glutaraldehyde, epichlorohydrin, and trimethylolpropane triglycidyl ether.

2. Materials

2.1. Chitosan

The chitosan used in the research was obtained from Heppe Medical Chitosan GmbH in Halle (Germany). The specifications of chitosan are presented in Table 1.

2.2. Dyes

The dyes used in the research were purchased from the dye production plant 'Boruta-Zachem SA' in Zgierz (Poland). The characteristics of the dyes are summarised in Table 2.

2.3. Crosslinking agents

Six crosslinking agents (three ionic and three covalent) were tested in the research. The characteristics of the ionic and covalent crosslinkers used in the research are summarised in Table 3.

Ionic crosslinking agents:
– Trisodium citrate 2 hydrate> 99%, p.a. grade (POCH S.A., Poland),

– Sodium tripolyphosphate> 99%, p.a. grade (ACROS ORGANICS, Poland),
– Sulphosuccinic acid 70% water solution (Merck Sp.z o.o., Poland).
Covalent crosslinking agents:
– Glutaraldehyde solution 25% (POCH S.A., Poland),
– Epichlorohydrin 99% (ACROS ORGANICS, Poland)
– Trimethylolpropane triglycidyl ether >99% (Fluka Analytical, Germany)
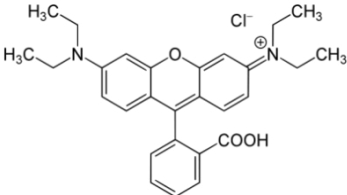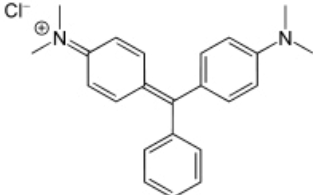
2.4. Other Chemical Reagents
The following chemical reagents were also used:
– Hydrochloric acid 37% (POCH S.A., Poland),
– Sodium hydroxide microgranules> 99% (POCH S.A., Poland),
– Acetic acid 99.9% (POCH S.A., Poland),
– Buffer solutions: pH 4.01 / 7.00 / 10.00 (POCH S.A., Poland).

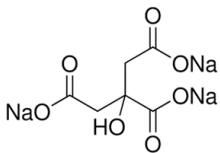**Table 1.** Specifications of chitosan used in the research.
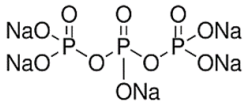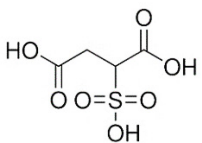
The appearance and form of chitosan	
	Flakes with a diameter of 1-2 mm
Degree of deacetylation (DD)	82.6%-87.5% (average of 85.0%)
Viscosity (in 1% acetic acid, 20°C)	351-750 mPas (average of 500 mPas)
Ash content (sulphated)	<1%
Heavy metal content	<25 ppm
Source of the raw material	Crab shells (waste products from the seafood processing industry)

Table 2. Characteristics of the dyes used in the study.

Name of the dye	Basic Violet 10 (BV10)	Basic Green 4 (BG4)
Structural formula		
Molar mass	479 g/mol	365 g/mol
λ_{max}	554 [nm]	618 [nm]
Type of dye	Basic (cationic)	Basic (cationic)

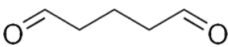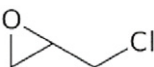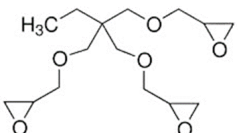| Dye class	Triphenylmethane	Triphenylmethane
Use	Dyeing of cotton, paper, and leather. Production of printing and painting dyes	Dyeing of wool, cotton, silk, leather, and paper
Other commercial names	Rhodamine B, Futramine D, Peltol D, Basic Red RB, Basazol Red 71 L, Violet B	Aniline Green, Malachite Green, Diamond Green B, Victoria Green B, Alkality Green, Conbasic Green D

Table 3. Characteristics of crosslinking agents used in the study.

Name	Type of cross-linking	Structural formula	Molar mass	Other use of the compound
Trisodium citrate (CIT)	Ionic		258.0 g/mol	Food additive (E 331) – as a flavouring or preservative and also as an acidity regulator. Others – descaler for boilers, cleaning of car radiators, buffering agent
Sodium tripoly-phosphate (TPP)	Ionic		368.0 g/mol	Food additive (E 451) – as a preservative, emulsifier, moisture absorber. Commercial detergent additive, chelating compound, tanning agent, anti-caking agent, flammability and corrosion reducing agent
Sulphosuccinic acid (SSA)	Ionic		198.0 g/mol	Most often used for syntheses. The derivative of this compound, sodium dioctyl sulphosuccinate, is used for medical purposes, as a laxative and also as a pesticide

Name	Type of cross-linking	Structural formula	Molar mass	Other use of the compound
Glutaraldehyde (GLA)	Covalent		100.0 g/mol	Preservative and fixative (e.g., in electron microscopy) Medical use – for the treatment of warts (10% solution) Disinfectant – mainly medical equipment
Epichlorohy-drin (ECH)	Covalent		93.5 g/mol	Syntheses – in the production of epoxy resins, synthetic glycerine Solvent for resins and paints Fumigant against insects
Trimethylol-propane triglycidyl ether (TTE)	Covalent		302.0 g/mol	Epoxy property modifier – hardening of epoxy polymers, increasing the solubility of aromatic epoxides, reducing the viscosity of epoxy solutions Additive for adhesives

2.5. Laboratory Equipment
The following equipment was also used:
– pH meter HI 110 (HANNA Instruments, Poland) – pH correction of solutions;
– magnetic stirrer MS-53M, (JEIO TECH, South Korea) – preparation of chitosan hydrogels;
– shaker SK-71 (JEIO TECH, South Korea) – dye adsorption experiments;
– water bath shaker JWE-357 (JW ELECTRONIC, Poland) – crosslinking of chitosan hydrogels;
– UV-VIS UV-3100 PC spectrophotometer (VWR, Canada) – determination of dye concentration in a solution.

3. Methods
3.1. Preparation of Chitosan Adsorbent in the Form of Hydrogel Beads (CHs)
Twenty-five grams (dry mass [DM]) of chitosan flakes was added to 975 g of 5% acetic acid in a 1 l beaker. The beaker contents were mixed with a magnetic stirrer until a homogeneous solution was obtained. The resulting solution was put into syringes and dripped through an injection needle (0.8 × 40 mm) into a beaker (2 l volume) with a 2 M sodium hydroxide (NaOH). Upon contact with the NaOH solution, the droplets of chitosan solution formed pale hydrogel beads with a diameter of 2.0-2.2 mm. The formed chitosan

beads were kept in the NaOH solution for the next 24 h and then washed with deionised water on a laboratory sieve until the effluent was a neutral pH. The prepared adsorbent was kept in deionised water at 4°C.

3.2. Preparation of Crosslinked Chitosan Adsorbent

The process of hydrogel chitosan bead crosslinking consisted of bathing them in properly prepared working solutions of crosslinking agents. Two grams (DM) of hydrogel chitosan beads was weighed into conical flasks (300 ml capacity each), and then solutions of crosslinking agents (200 ml) were added to them (the solutions used the minimum doses of crosslinking agents that ensured full stability of the hydrogel adsorbent at pH 3-11). Then, the flasks were placed on a shaker with a water bath (150 rpm) for 24 h. After the allotted time, the crosslinked chitosan beads were drained and washed with deionised water on a laboratory sieve. The prepared crosslinked hydrogel chitosan adsorbent was kept in deionised water at 4°C. The most important parameters of chitosan crosslinking with individual crosslinking agents are summarised in Table 4.

Table 4. Conditions of the crosslinking process of chitosan hydrogel beads and abbreviated names of the crosslinked chitosan hydrogels.

Crosslinking conditions	CIT	TPP	SSA	ECH	GLA	TTE
Abbreviated name of the adsorbents	CHs-CIT	CHs-TPP	CHs-SSA	CHs-ECH	CHs-GLA	CHs-TTE
pH	4	4	4	10-12 ($\approx$11)	6-8 ($\approx$7)	6-8 ($\approx$7)
Temperature (°C)	25	25	25	60	25	25
Dose [g/g s.m.$_{CHs}$]	0.48	0.14	0.37	0.03	0.14	0.28
Time of the crosslinking [h]	24	24	24	24	24	24

Note. See Table 3 for details on the crosslinking agents.

A full description of the chitosan adsorbents used in the research (including the Fourier-transform infrared [FTIR] spectra analyses) is provided in our previous articles [2, 5].

3.3. Research on the Influence of pH on the Efficiency of Dye Adsorption

Chitosan adsorbent (0.2 g DM) was weighed and added to conical flasks (300 mL capacity each), followed by the addition of dye solutions (200 ml) with a concentration of 20 mg/l and a pH of 2-12. Then, the flasks were placed on a shaker (150 rpm). After 2 h of adsorption, samples (10 ml) were taken from the solution to determine the concentration of the remaining dye spectrophotometrically. The pH of the solutions after adsorption was also determined. Studies on the influence of pH on the adsorption efficiency of BV10 and BG4 were carried out for each tested chitosan adsorbent.

Because BG4 is a pH-sensitive dye, preliminary studies were carried out to evaluate the effect of pH on the extinction of dye solutions. A total of 11 test series (for pH 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) were performed, in which the changes in extinction of BG4 solutions over time were determined. The extinction value of dye solutions did not change for the pH range 3-7. Hence, the spectrophotometer (based on the curve made at pH 5) could only correctly determine BG4 concentration in solutions at pH 3-7. BV10 is not sensitive to pH changes; therefore, spectrophotometric measurements of this dye were possible using one measurement curve for the entire analysed pH range.

3.4. Research on the Maximum Adsorption Capacity of Hydrogels

Chitosan adsorbent (0.2 g DM) was weighed into a series of conical flasks (each with a capacity of 300 ml). Then, 200 ml of each dye solution with a concentration in the range of 1.0-500.0 mg/l and the most favourable adsorption pH (determined based on the tests described in Section 3.3) were added to the flasks. The flasks were then covered with parafilm to prevent evaporation of the solution and placed on a shaker (150 rpm). After 24 and 48 h, samples (10 cm³) were taken from the solutions to determine the concentration of the remaining dye spectrophotometrically. The capacities of all tested chitosan adsorbents were determined against the dyes BV10 and BG4.

3.5. Calculation Methods

The amount of dye adsorbed on the chitosan adsorbent was calculated from Equation (1):

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

where:
Q$_s$ – the mass of adsorbed dye (static conditions) [mg/g DM]
C$_o$ – initial concentration of the dye [mg/l]
C$_s$ – concentration of the dye after adsorption [mg/l]
V – the volume of the solution [l]
m – adsorbent mass [g DM]

Three adsorption isotherms were used to describe the experimental data from the research on the maximum adsorption capacity: Langmuir, in Equation (2); Langmuir 2 (dual-site Langmuir) in Equation (3); and Freundlich, in Equation (4).

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

where:
Q$_s$ – mass of adsorbed dye (static conditions) [mg/g DM]
q$_{max}$ – maximum adsorption capacity in Langmuir equation [mg/g DM],
K$_c$ – constant in the Langmuir equation [l/mg]
C – concentration of the dye left in the solution [mg/l]

$$Qs = \frac{b_1 \cdot k_1 \cdot C}{1 + k_1 \cdot C} + \frac{b_2 \cdot k_2 \cdot C}{1 + k_2 \cdot C} \tag{3}$$

where:
Q$_s$ – the mass of adsorbed dye (static conditions) [mg/g DM]
b$_1$ – maximum adsorption capacity of the adsorbent (I type active sites) [mg/g DM]
b$_2$ – maximum adsorption capacity of the adsorbent (II type active sites) [mg/g DM]
k$_1$; k$_2$ – constants in the Langmuir 2 equation [l/mg]
C – concentration of the dye left in the solution [mg/l]

$$Qs = K \cdot C^n \tag{4}$$

where:
Q$_s$ – the mass of adsorbed dye (static conditions) [mg/g DM]
C – concentration of the dye left in the solution [mg/l]
K – the adsorption equilibrium constant in the Freundlich model
N – constant in the Freundlich model

4. Results and Discussion

4.1. Influence of pH on Cationic Dye Adsorption

The unmodified chitosan granules were dissolved at pH <4. Therefore, the results of the adsorption of dyes on CHs at pH 2-3 are not shown in Figure 1A. Ionically crosslinked chitosan hydrogels allowed for adsorption in the pH range of 3-12, while covalently crosslinked chitosan adsorbents ensured stability in the entire tested pH range (pH 2-12) (Figure 1).

BG4 is extremely sensitive to pH changes. These properties allow BG4 to be used as a pH indicator [8]. In a strongly acidic environment (pH <3), this compound changes colour from green to yellow, while in an alkaline environment (pH >10) it becomes colourless and precipitates in the form of a white suspension. However, the present research showed that the BG4 solution undergoes slow spontaneous discolouration even in a slightly alkaline environment (pH >7), which makes it impossible to correctly determine the content of the dye remaining in the solution. This dye remains stable (extinction does not change) at pH 3-7; therefore, the results of the research on the effect of pH on BG4 adsorption are limited to this range (Figure 1).

Adsorption of BV10 onto CHs occurred with similar efficiency over a wide pH range of 5.0-12.0. pH exerted a much greater effect on BG4 adsorption. This dye was adsorbed most effectively on chitosan hydrogels at pH 6.0. The adsorption efficiency of both cationic dyes onto CHs was the lowest at pH 4.0 (Figure 1A).

The effect of pH on the adsorption efficiency of BV10 on CHs-TPP was similar to that in CHs. The BV10 dye removal efficiency by CHs-TPP at pH 5-12 was comparable. The adsorption efficiency of BV10 was the lowest at pH 3. In the case of using CHs-CIT and CHs-SSA, the adsorption intensity of BV10 was similar for pH range of 3-12. Adsorption of BG4 on all ionically crosslinked adsorbents was most effective at pH 6. The dye adsorption efficiency against CHs-CIT, CHs-TPP, and CHs-SSA was the lowest at pH 3 (Figure 1B-D). At pH 2, the ionically crosslinked adsorbents dissolved.

The effect of pH on the adsorption of cationic dyes by covalently crosslinked chitosan was analogous to that of ionically crosslinked chitosan. Adsorption of BG4 on CHs-ECH, CHs-GLA, and CHs-TTE; CHs-CIT, CHs-TPP, and CHs-SSA; and CHs was most effective at pH 6. The adsorption efficiency of BV10 on covalently crosslinked chitosan adsorbents in the initial pH range of 4-12 was comparable (Figure 1E-G).

Based on the literature data, the optimal pH of adsorption of cationic dyes on chitosan adsorbents is usually 6-10 [9]. In this pH range, hydrogen bonds play an important role during adsorption, involving the hydroxyl and amine groups of the adsorbent, as well as the amine groups of the adsorbate. The low adsorption efficiency of cationic dyes at low pH (<5) results from the acquisition of a positive charge by the surface of chitosan adsorbents [10]. The protonated surface of the adsorbent at acidic pH repels the dye cations electrostatically and significantly reduces their adsorption. The similar effect of pH on the adsorption of BV10 and BG4 for all tested adsorbents (Figure 1) proves the negligible influence of the type of crosslinking agent on the adsorption mechanism.

pH 6 was the most favourable pH for BG4 adsorption on all tested chitosan adsorbents. As the adsorption efficiency of BV10 for chitosan adsorbents was comparable over a wide pH range, subsequent studies on BV10 and BG4 adsorption on chitosan adsorbents were carried out in solutions at pH 6.

Chitosan adsorbents showed the ability to change the pH of the adsorption solution. This is due to the fact that the pH of the solution always strives for the pH_{PZC} value of the adsorbent used (where PZC is the 'point of zero charge', the pH at which the net charge of the absorbent's surface is equal to zero). The pH_{PZC} values of chitosan adsorbents determined in our previous studies were CHs – 7.35; CHs-CIT – 4.50; CHs-TPP – 6.10;
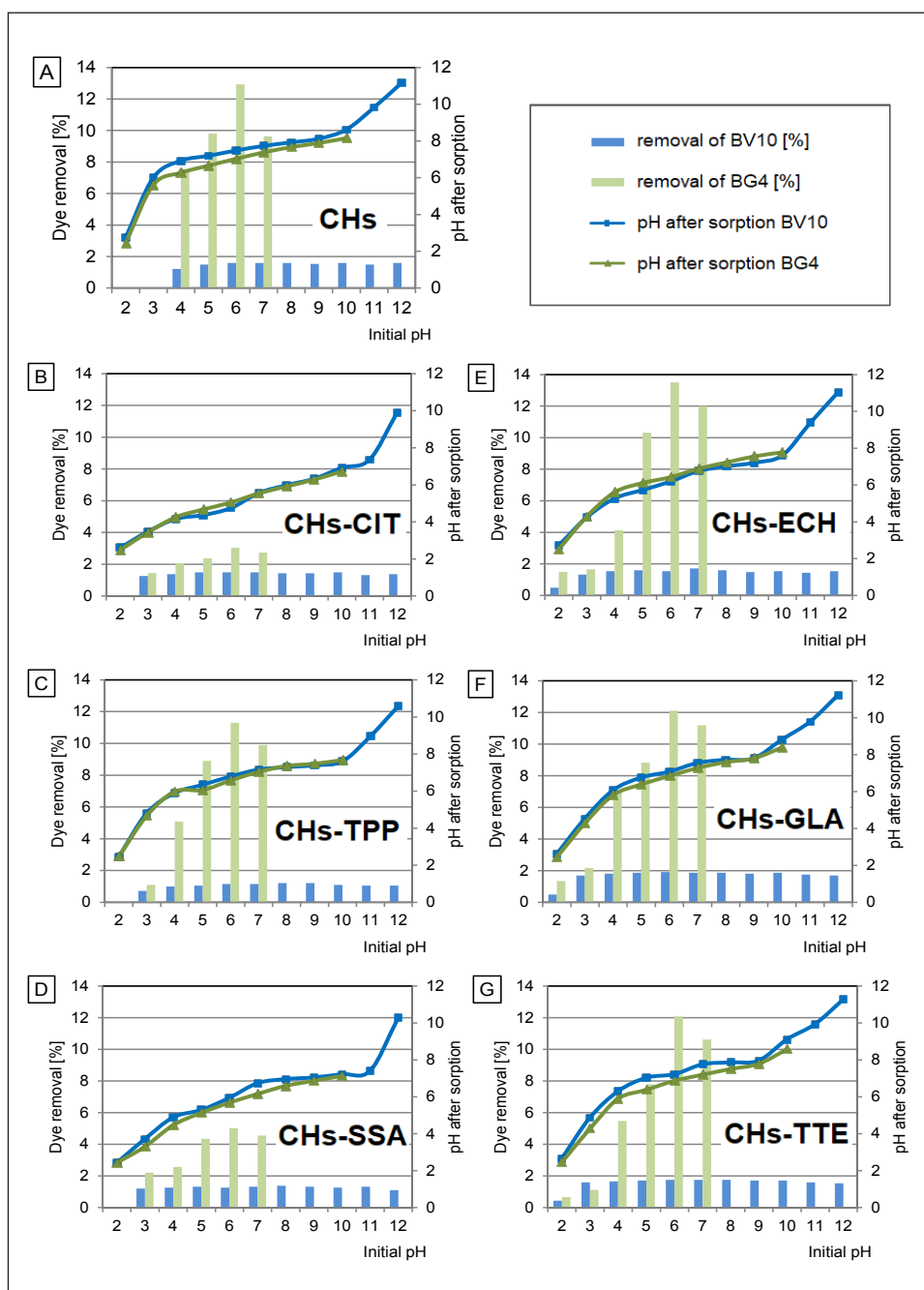
Figure 1. Influence of pH on the adsorption efficiency of BV10 and BG4 dyes and pH after adsorption on: CHs (A), CHs-CIT (B), CHs-TPP (C), CHs-SSA (D), CHs-ECH (E), CHs-GLA (F), and CHs-TTE (G). See Table 4 for details on the hydrogels.

CHs-SSA – 7.20; CHs-ECH – 6.45; CHs-GLA – 7.20; and CHs-TTE – 7.35. The ability of chitosan adsorbents to neutralise aqueous solutions is their unquestionable advantage. Assuming that adsorbents would be used to treat industrial wastewater, the problem of neutralising the wastewater pH before it is introduced into the sewage system or the next stage of treatment is solved.

4.2. Adsorption Capacity of Chitosan Hydrogel Adsorbents

Experimental data on the research on the adsorption capacity of chitosan hydrogel adsorbents in relation to cationic dyes were described with Langmuir 1, Langmuir 2, and Freundlich isotherms. In each research series, Langmuir 1 and 2 models showed a better fit to the data than the Freundlich model. In addition, the constants determined from Langmuir 1 and 2 models, such as Q_{max}, $k_1/k_2/K_c$, and the coefficients of determination (R^2), were the same. This suggests that only one specific mechanism or one type of active site plays a key role in adsorption of the BV10 and BG4 dyes on all tested chitosan adsorbents. Presumably, the cationic dyes are bound to chitosan mainly through hydrogen bonds between the amine groups of the adsorbent and adsorbate.

The preliminary studies found that the equilibrium time of adsorption of cationic dyes on the tested hydrogel chitosan adsorbents did not exceed 24 h. This was also confirmed by the Q_{max} values determined for 24 and 48 h of adsorption (Table 5).

The maximum adsorption capacity of CHs against BV10 was 2.94 mg/g. The ionically crosslinked chitosan adsorbents showed a lower adsorption efficiency for BV10 than CHs. The maximum adsorption capacity of CHs-CIT, CHs-TPP, and CHs-SSA achieved after 48 h was 1.84, 1.89, and 2.49 mg/g, respectively (Table 5). The lower adsorption capacity of ionically crosslinked chitosan adsorbents in relation to BV10 could result from the compact structure of the adsorbent and worse availability of adsorption centres for the dye [2].

The maximum adsorption capacity of CHs-ECH, CHs-GLA, and CHs-TTE in relation to BV10 was greater than in the case of CHs and amounted to 3.66, 3.81, and 3.58 mg/g, respectively (Table 5). The greater adsorption efficiency of covalently crosslinked adsorbents could be due to the possibility of binding BV10 to fragments of crosslinking agents trapped in the chitosan structure. This is possible due to the surface structure of covalently crosslinked chitosan hydrogels, which are less compact and more permeable than the surface of ionically crosslinked adsorbents [5]. Moreover, covalently crosslinked chitosan adsorbents could have unreacted functional groups on their surface derived from crosslinking agents. These functional group could contribute to the chemisorption of BV10 based on their reaction with, for example, the carboxyl group of the dye, thus increasing the adsorbent capacity.

The ionically crosslinked chitosan adsorbents showed similar adsorption capacities for BG4. The maximum adsorption capacity of CHs-CIT, CHs-TPP, and CHs-SSA for a given dye was 37.21, 37.23, and 38.90 mg/g, respectively (Table 5). Compared with ionically crosslinked adsorbents, covalently crosslinked adsorbents showed slightly higher adsorption capacity in relation to BG4. The maximum adsorption capacity in relation to BG4 determined for CHs-ECH, CHs-GLA, and CHs-TTE was 40.62, 39.84, and 39.15 mg/g, respectively. Presumably, as in the case of BV10, it may be due to the possibility of dye adsorption on fragments of covalent crosslinking agents attached to the chitosan structure and the greater surface permeability of covalently crosslinked hydrogels [2].

The most effective adsorbent in relation to BG4 turned out to be unmodified chitosan (CHs), the maximum capacity of which was 43.17 mg/g (Table 6). The weaker efficiency of BG4 adsorption on covalently crosslinked chitosan adsorbents (CHs-ECH, CHs-GLA, and CHs-TTE) compared with CHs could result from worse accessibility to chitosan

Table 5. Adsorption constants of BV10 and BG4 determined from the Langmuir 1, Langmuir 2 and Freundlich models.

Sorbent	Dye	Time [d]	Langmuir 2 model						Langmuir 1 model			Freundlich model		
			Q_{max}	b_1	k_1	b_2	k_2	R^2	Q_{max}	K_c	R^2	k	n	R^2
CHs	BV10	1	2.94	1.52	0.031	1.42	0.031	0.991	2.94	0.031	0.991	0.30	0.4	0.940
		2	2.91	1.71	0.042	1.20	0.042	0.997	2.91	0.042	0.997	0.37	0.4	0.945
	BG4	1	43.17	22.1	0.005	21.08	0.005	0.998	43.17	0.005	0.998	1.06	0.6	0.986
		2	41.99	21.5	0.006	20.49	0.006	0.999	41.99	0.006	0.999	1.28	0.5	0.982
CHs-CIT	BV10	1	1.82	0.92	0.036	0.90	0.036	0.987	1.82	0.036	0.987	0.22	0.4	0.931
		2	1.84	1.01	0.057	0.83	0.057	0.991	1.84	0.054	0.991	0.3	0.3	0.934
	BG4	1	37.21	18.6	0.004	18.61	0.004	0.997	37.21	0.004	0.997	0.52	0.6	0.977
		2	37.01	18.5	0.004	18.50	0.004	0.995	37.01	0.004	0.995	0.67	0.6	0.975
CHs-TPP	BV10	1	1.81	0.90	0.038	0.90	0.038	0.988	1.81	0.038	0.988	0.21	0.4	0.923
		2	1.89	0.93	0.045	0.96	0.045	0.990	1.89	0.045	0.990	0.25	0.4	0.915
	BG4	1	36.35	18.2	0.006	18.17	0.006	0.998	36.35	0.006	0.998	0.98	0.5	0.969
		2	37.23	18.5	0.006	18.73	0.006	0.996	37.23	0.006	0.996	1.07	0.5	0.964
CHs-SAA	BV10	1	2.36	1.23	0.026	1.13	0.026	0.993	2.36	0.026	0.993	0.21	0.4	0.960
		2	2.49	1.30	0.029	1.19	0.029	0.992	2.49	0.029	0.992	0.24	0.4	0.940
	BG4	1	37.11	18.6	0.003	18.55	0.003	0.990	37.11	0.003	0.990	0.37	0.7	0.969
		2	38.90	19.5	0.003	19.45	0.003	0.994	38.90	0.003	0.994	0.42	0.7	0.977
CHs-ECH	BV10	1	3.66	1.79	0.038	1.87	0.038	0.994	3.66	0.038	0.994	0.42	0.4	0.926
		2	3.66	0.57	0.050	3.09	0.050	0.996	3.66	0.050	0.996	0.53	0.4	0.929
	BG4	1	40.62	20.3	0.006	20.3	0.006	0.998	40.62	0.006	0.998	1.03	0.6	0.975
		2	40.39	5.97	0.007	34.42	0.007	0.998	39.91	0.007	0.998	1.25	0.5	0.976
CHs-GLA	BV10	1	3.73	1.74	0.030	1.99	0.030	0.990	3.73	0.030	0.990	0.36	0.4	0.933
		2	3.81	1.8	0.034	2.01	0.034	0.987	3.81	0.034	0.987	0.4	0.4	0.915
	BG4	1	37.85	36.7	0.007	1.14	0.075	0.999	37.06	0.007	0.999	1.32	0.5	0.978
		2	39.84	38.2	0.006	1.67	0.148	0.999	38.21	0.008	0.998	1.45	0.5	0.982
CHs-TTE	BV10	1	3.54	1.71	0.031	1.83	0.031	0.996	3.54	0.031	0.996	0.34	0.4	0.948
		2	3.58	1.85	0.040	1.72	0.040	0.995	3.58	0.040	0.995	0.44	0.4	0.934
	BG4	1	38.59	19.3	0.007	19.3	0.007	0.994	38.6	0.007	0.994	1.12	0.5	0.957
		2	39.15	19.6	0.007	19.58	0.007	0.997	39.15	0.007	0.997	1.26	0.5	0.963

Note. See Table 3 for details on the crosslinking agents. See Table 4 for details on the hydrogels.

adsorption centres. Moreover, compared with BV10, the chemisorption of BG4 on covalently crosslinked chitosan could be limited by fewer functional groups in the dye structure, resulting in lower efficiency of binding the dye from the solution.

The much higher adsorption efficiency of BG4 dye on chitosan adsorbents than BV10 may result from the dye's lower molar mass. With a smaller size, BG4 molecules showed a greater ability to penetrate the structure of hydrogels and occupy adsorption centres in the deeper layers of the adsorbent. In addition, the chemical structure of BG4 suggests that it is easier than with BV10 to form hydrogen bonds between the amine groups of the dye and chitosan.

Tables 6 and 7 summarise the adsorption efficiency of BV10 and BG4 on various unconventional adsorbents and selected types of activated carbons. The adsorption efficiency of BV10 and BG4 on the tested chitosan adsorbents compared with other unconventional adsorbents is relatively small. The following present much better adsorption efficiency for cationic dyes: plant biomass (e.g., leaves and stems of crops, fruit peels), industrial waste (sewage sludge, fly ash, tire scraps), and minerals based on aluminosilicates. However, the most efficient adsorbents for BV10 and BG4 are carbonised plant biomass and all kinds of activated carbons (Tables 6 and 7).

The low adsorption efficiency of BV10 and BG4 on chitosan hydrogels results from the basic nature of the adsorbent. The easily protonated amine and acetamide functional groups of chitosan mean that the adsorbent surface has a significant positive charge even at a neutral pH. This causes electrostatic repulsion of the dye cations, which translates into a generally low adsorption efficiency. The use of chitosan adsorbents to purify solutions from cationic dyes seems economically unjustified.

Table 6. Comparison of the adsorption capacity of various adsorbents in relation to Basic Violet 10.

Sorbent	Adsorption capacity [mg/g]	Time of adsorption [h]	pH of adsorption	Temp. (°C)	Source
CHs-TPP (ionically crosslinked granules)	1.81	24	6	25	This work
CHs-CIT (ionically crosslinked granules)	1.82	24	6	25	This work
CHs-SSA (ionically crosslinked granules)	2.36	24	6	25	This work
Powdered coffee	2.5	3	2	19	[11]
Fly ash washed with NaOH	2.5	72	6.2	30	[12]
CHs (non-crosslinked granules)	2.94	24	6	25	This work
CHs-TTE (covalently crosslinked granules)	3.54	24	6	25	This work
CHs-ECH (covalently crosslinked granules)	3.66	24	6	25	This work
CHs-GLA (covalently crosslinked granules)	3.73	24	6	25	This work
Unmodified activated sludge	4.6	2	6.5	25	[13]
Grapefruit peels	4.6	4	3	22	[14]
Lemon peels	5.7	4	3	22	[14]
Sugar cane fibre	10.4	-	-	25	[15]
BiFeO$_3$ (ceramics)	11.9	-	4	25	[16]
Sugar cane biomass	13.9	-	-	25	[17]
Coconut fibre	14.9	1.5	9.2	32	[18]
Cedar cones	17.2	8	5	25	[19]
Parthenium biomass	18.5	-	7	25	[20]
Activated sludge (anaerobic)	19.5	1.5	7	20	[21]
Banana peels	20.6	24	6-7	30	[22]

Sorbent	Adsorption capacity [mg/g]	Time of adsorption [h]	pH of adsorption	Temp. (°C)	Source
Kaolinite	21.7	3	6.9	30	[23]
Acacia. nilotica leaves (microwave modified)	22.4	3	7	30	[24]
Fomes fomentarius biomass	25.1	48	7.5	20	[25]
Baker's yeast	25.2	1.2	6.5	25	[26]
Spent green tea leaves	26.7	4	3	22	[27]
Zeolite	32.6	200	8.5	30	[28]
Phellinus igniarius biomass	36.8	48	7.5	20	[25]
Spent coffee grounds	59.3	4	3	22	[27]
Jute powder	87.7	1	7	25	[29]
Carbonised vegetable wastes	91.1	0.5	-	25	[30]
Bentonite-Fe	98.6	-	7	25	[31]
Humic acids modified from Fe_3O_4	161.8	0.25	6	70	[32]
Montmorillonite	181.8	3	6.9	30	[23]
Coconut fibre	203.2	2.5	6.5	30	[33]
Oil palm husks	243.9	-	6.5	30	[34]
Activated carbon from agricultural waste	263.9	4	5.7	20	[35]
Worn tires	280.1	8.3	-	25	[36]
Rice husk activated carbon	479.0	-	-	25	[37]
Activated carbon from *Polygonum orientale*	500.0	4	5	15	[38]

Note. "-" information not provided.

Table 7. Comparison of the adsorption capacity of various adsorbents in relation to Basic Green 4.

Sorbent	Adsorption capacity [mg/g]	Time of adsorption [h]	pH of adsorption	Temp. (°C)	Source
Tamarind fruit shells	2.0	1.5	5	30	[39]
Bentonite	7.7	0.2	9	25	[40]
Hen feathers	10.3	2.5	5	30	[41]
Caulerpa racemosa marine algae	19.9	-	6	25	[42]
Luff cylindrical biomass	21.6	3	5	35	[43]
Compost	26.4	3	5	25	[44]
Caulerpa scalpelliformis alga	27.0	4	6	30	[45]
CHs-TPP (ionically crosslinked granules)	36.4	24	6	25	This work
CHs-GLA (covalently crosslinked granules)	36.7	24	6	25	This work

Sorbent	Adsorption capacity [mg/g]	Time of adsorption [h]	pH of adsorption	Temp. (°C)	Source
CHs-SSA (ionically crosslinked granules)	37.1	24	6	25	This work
CHs-CIT (ionically crosslinked granules)	37.2	24	6	25	This work
CHs-TTE (covalently crosslinked granules)	38.6	24	6	25	This work
Montmorillonite	40.5	24	6	25	[46]
CHs-ECH (covalently crosslinked granules)	40.6	24	6	25	This work
Sea clam shells	42.3	3	8	30	[47]
CHs (non-crosslinked granules)	43.2	24	6	25	This work
Lemon peels	51.7	51.7	-	32	[48]
Pineapple leaves	54.6	2.5	9	25	[49]
Coffee beans (skimmed)	55.3	-	4	25	[50]
Wicker (sawdust)	62.7	3.5	4-9	30	[51]
Activated slag	74.2	-	-	25	[52]
Sawdust modified with H2SO4	74.5	2	7	26	[53]
Clay soil	78.6	6	6	30	[54]
Zea mays biomass	81.5	0.5	6	50	[55]
The leaves of the *Platanus vulgaris* tree	85.5	24	5.0-5.5	25	[56]
Scobs	85.5	23	8	25	[57]
Rice husk activated carbon	92.6	0.5	5-6	25	[58]
Crosslinked corn starch	104.8	2	2.1	20	[59]
Activated carbon from apricot waste	116.3	1	-	30	[60]
Phitophora sp. (alga)	117.6	3	5	30	[61]
Jute fibre	136.6	6	8	30	[62]
Rice straw (carbonised)	148.7	-	5	30	[63]
Fly ash	170.3	4	7	25	[64]
Soybean husk	178.6	7	6	25	[65]
Sawdust modified with glutamate	196.1	4.5	6	25	[66]
Silica (TriSyl)	208.0	-	-	25	[56]
Powdered activated carbon	222.2	0.5	-	30	[67]
Activated carbon from tea leaves	243.9	3	4	15	[68]
Bamboo activated charcoal	263.6	4	5	30	[69]
Activated charcoal from durian skins	312.5	72	5	30	[70]
Activated carbon from rambutan rind	388.0	24	6.5-7.0	30	[71]

Note. "-" information not provided.

5. Summary

Ionic crosslinking, regardless of the type of crosslinking agent, reduced the adsorption abilities of hydrogel chitosan adsorbents in relation to cationic dyes. This outcome is likely related to the dense surface structure of ionically crosslinked chitosan beads, which makes it difficult for dyes to attach to active centres located in the top layers of the hydrogel. Covalent crosslinking of chitosan slightly increased its adsorption capacity only towards BV10, which can be explained by the dye's greater susceptibility to chemisorption than BG4. Among the ionically crosslinked chitosan adsorbents, CHs-SSA showed the highest adsorption efficiency of BV10 and BG4. However, due to the high production costs of a given adsorbent, a more economical solution would be to use CHs-CIT. Assuming that the wastewater contaminated with cationic dyes has a pH >4, the best solution would be to use CHs as the adsorbent. Adsorption of dyes from acid wastewater (pH <3) would require covalently crosslinked adsorbents such as CHs-ECH or CHs-GLA.

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7. References

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