

THE INFLUENCE OF SALINITY ON REACTIVE BLACK 5 DYE SORPTION EFFICIENCY ON HYDROGEL CHITOSAN SORBENTS

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Abstract

This study examined the effect of salt concentration ($\text{NaCl}/\text{Na}_2\text{SO}_4$) on the sorption efficiency of Reactive Black 5 (RB5) dye on chitosan hydrogel granules (CHs). The tested salt concentration was in the range of 0.0 to 0.5 mol/L. The scope of the research included the effect of salinity on RB5 sorption at different pH values (4–11), equilibrium time, and maximum sorption capacity (Langmuir 2 model).

At low pH (pH 4, $\text{pH} < \text{pH}_{\text{PZC}}$), the effectiveness of RB5 sorption on CHs decreased with increasing salinity. At higher pH (pH 9–11, $\text{pH} > \text{pH}_{\text{PZC}}$), an opposite trend was observed (the sorption efficiency of RB5 on CHs increased with increasing salinity). The concentration of salt in the solution did not have a major impact on the equilibrium time of sorption, which depended mainly on the initial pH of the solution (and ranged from 36 to 60 h). The relatively long sorption time resulted from the hydrogel structure of the sorbent used, which slowed the dye absorption ability.

The maximum sorption capacity of CHs in relation to RB5 at the optimum pH (pH 4) in the solution without the addition of salt determined after 60 h of sorption was 1.386 mmol RB5/g (1373.5 mg RB5/g). Under conditions of high salinity (0.5 mol $\text{Na}_2\text{SO}_4/\text{L}$), at pH 4, the capacity was 17.2% lower (1.148 mmol RB5/g to 1139.7 mg RB5/g), and at pH 11, it was 6.3% higher (1.474 mmol RB5/g to 1460.7 mg RB5/g).

Keywords: sorption, chitosan, RB5 dye, salinity, NaCl , Na_2SO_4

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1. Introduction

Sewage from the textile industry is characterized by a high concentration of coloured substances. Reactive dyes are the most common type of dyes present in industrial wastewater [1,2] due to the high popularity of use and low efficiency of staining materials (50–90%). The low capacity of reactive dyes for biodegradation limits the possibility of textile wastewater treatment with conventional biological methods, based on the technology of activated sludge or biological membranes [3].

It is common opinion that sorption is one of the best ways to decolourize liquid wastewater. Frequently, various forms of activated carbons are used as sorbents for binding dyes. Due to the relatively high price of conventional sorbents, cheaper alternatives are currently intensively searched. High hopes are associated with chitin and its chitosan derivative as raw materials for the production of efficient sorbents for dyes. As evidenced by numerous studies, properly prepared chitosan-based sorbents can exceed the commercial efficiency of activated carbons by many times [4,5]. For example, chitosan sorbents in the form of hydrogels show a capacity relative to reactive dyes at the level of $Q_{\max}=1500\text{--}2500\text{ mg/g}$ [6–8].

However, most of the studies conducted so far on the sorption capacity of chitosan are related to the sorption of dyes from their aqueous solutions (distilled water + dye + HCl/NaOH). In the case of real textile sewage, the sorption of chitosan dyes may be limited by a high concentration of salts (electrolytes), such as sodium chloride or sodium sulphate. These substances are commonly added to dyeing baths as aids to dye fabrics. Theoretically, chloride or sulphate ions can compete with anionic dyes for chitosan amine sorption centres. This problem seems to be important, especially due to the fact that concentrations of NaCl or Na₂SO₄ in textile sewage can reach up to 100 g/L and can many times exceed the concentration of dyes [9,10].

This study investigated the effect of wastewater salinity with sodium chloride and sodium sulphate on the effectiveness of Reactive Black 5 sorption on chitosan hydrogel.

2. Materials and Methods

2.1. Chitosan

Chitosan purchased from the German company Heppe Medical Chitosan GmbH in Halle was used as a raw material for sorbent production. Chitosan obtained from shrimp shells was in the form of flakes (0.5–3.0 mm) and it had a DD of 75%, 500 mPas, and a total content of heavy metals (Pb/Hg/Cd) did not exceed 25 ppm.

2.2 Reactive Black 5 Dye

Reactive Black 5 (RB5), a reactive dye popular in the textile industry, was purchased from the Boruta-Zachem SA dye production plant in Zgierz (Poland). RB5 belongs to the diazo dye class. It has characteristic vinyl-sulfone functional groups.

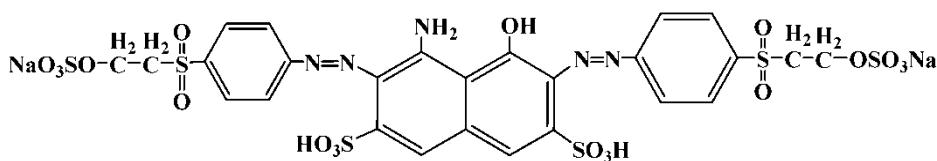


Figure 1. RB5 dye chemical structure.

2.3. Chemical Reagents

The chemical reagents used in the tests included HCl (35–38%), NaOH (>98.8%), CH₃COOH (>99.5%), NaCl (>99.5%), and Na₂SO₄ (>99.5%) (all AR quality or higher), which were purchased at POCH SA (Poland).

3. Methodology

3.1. Preparation of Chitosan Hydrogel Sorbents (CHs)

Chitosan in the form of flakes (25.0 g d.m.) was dissolved in 5% acetic acid (975 g). The resulting 2.5% chitosan solution was instilled with a syringe with a 0.8×40 mm needle into 2 M NaOH. In contact with the NaOH solution, drops of chitosan solution gelled, turning into bright granules. After 24 hours of gelation, the formed granules were strained on a laboratory sieve and washed with a large amount of distilled water until a neutral staining reaction was obtained (pH<7.5). The hydrogel granules were stored in distilled water at 4°C.

3.2. Research on the Effect of Salinity on RB5 Sorption Efficiency at Different pH Values

Chitosan (0.20 g d.m., each) was weighed into a series of conical flasks (300 mL). RB5 solutions containing NaCl/Na₂SO₄ (from 0 to 0.5 mol) were added to the flasks at pH 4–11. Then, the flasks were placed on a laboratory shaker (150 rpm, vibration amplitude of 2.0 cm) for 60 min. After the set time, samples (10 mL) were taken from the solutions for spectrophotometric determination of the concentration of the dye remaining in the solution (UV–Vis UV-3100PC spectrophotometer, VWR). The pH after sorption was also tested. The most important parameters of the experiment are summarized in Table 1.

Table 1. Research parameters on the effect of salinity and pH on the RB5 sorbent efficiency on CHs.

Salt type	Salt concentration (mol/L)	pH of tested solution	RB5 concentration (mmol/L)*	Sorbent dose (g/L)	Sorption time (min)	Stirring speed (rpm)	Temperature (°C)
NaCl	—	4, 5, 6, 7, 8, 9, 10, 11 ** (in every series)	0.05 (in every series)	1 (in every series)	60 (in every series)	150 (in every series)	22 (in every series)
	0.10						
	0.50						
	0.10						
Na ₂ SO ₄	0.50						

*0.05 mol RB5 ~ 49.6 mg RB5/L

**At pH<pH 4, non-crosslinked chitosan dissolves. Therefore, the pH range tested was pH 4–11.

3.3. Studies on the Effect of Salinity on the Equilibrium Time of RB5 Sorption on CHs

Hydrogel chitosan granules were weighed (1.0 g.d.m each) into laboratory beakers (volume 1000 mL). Next salt and dye solutions and optimal pH (pH determined on the basis of tests carried out in accordance with 3.2) were added to the beakers. Then, magnetic stirrers (40 × 8 mm, with a Teflon cover) were added to the beakers and the beakers were placed on a multi-station magnetic stirrer. Samples (5 mL) were taken from the solutions to determine the concentration of RB5 at defined time intervals. The test parameters are summarized in Table 2.

Table 2. Research parameters on the effect of salinity on the equilibrium time of RB5 sorption on CHs.

Salt type	Salt concentration (mol/L)	pH of tested solution	RB5 concentration (mmol/L)	Sorbent dose (g.d.m./L)	Sampling time (min)	Stirring speed (rpm)	Temperature (°C)
—	—	pH A*					
NaCl	0.02	pH A*	0.05 (in every series)	1 (in every series)	0, 10, 20, 30, 45, 60, 90, 120, 150, 180, 210, 240, 300, 360, 480, 720, 1440, 2880, 4320 (4320 min = 3 days)	150 (in every series)	22 (in every series)
	0.10	pH A*					
	0.50	pH A*					
		pH B*					
		pH A*					
Na ₂ SO ₄	0.02	pH A*					
	0.10	pH A*					
	0.50	pH A*					
		pH B*					

*pH A, optimal pH of RB5 sorption on CHs in solutions with the addition of salt.

**pH B, optimal pH of RB5 sorption on CHs in solutions without the addition of salt.

3.4. Studies on the Effect of Salinity on CHs Sorption Capacity Relative to RB5

About 0.2 g d.m. CHs was weighed into conical flasks (300 mL). Then, salt and dye solutions with optimal pH (point 3.2) were added to the flasks and the flasks were placed on a shaker. After 24 and 60 h, samples were taken from the solutions for spectrophotometric analysis of the concentration of RB5 remaining in the solution (Table 3).

Table 3. Research parameters on the effect of salinity on sorption capacity of CHs

Salt type	Salt concentration (mol/L)	pH of tested solution	RB5 concentration (mmol/L)	Sorbent dose (g.d.m./L)	Sampling time (h)	Stirring speed (rpm)	Temperature (°C)
—	—	pH A*	0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.5 (in every series)	1 (in every series)	24, 60	150 (in every series)	22 (in every series)
NaCl	0.02	pH A*					
	0.10	pH A*					
	0.50	pH A*					
		pH B*					
Na ₂ SO ₄	0.02	pH A*					
	0.10	pH A*					
	0.50	pH A*					
		pH B*					

*pH A, optimal pH of RB5 sorption on CHs in solutions with the addition of salt.

**pH B, optimal pH of RB5 sorption on CHs in solutions without the addition of salt.

3.4. Calculation methods

The amount of adsorbed dye was determined from formula (1):

$$Q_s = \frac{(C_0 - C_s) \times V}{m} \quad (1)$$

where: Q_s is the mass of adsorbed RB5 (mmol/g.d.m), C₀ is the initial RB5 concentration (mmol/L), C_s is the concentration of the dye after the sorption process (mmol/L), V is the volume of solution (L), and m is the sorbent mass (g).

To determine the maximum sorption capacity, the Langmuir 2 model (Langmuir double isotherm) was used, which, in studies on the sorption of chitosan sorbents, has usually shown a better fit to experimental data than the Langmuir 1 or Freundlich models [11,12]. Langmuir double isotherm is shown in formula (2):

$$Q_s = \frac{b_1 \times k_1 \times C}{1 + k_1 \times C} + \frac{b_2 \times k_2 \times C}{1 + k_2 \times C} \quad (2)$$

where Q_s is the mass of adsorbed dye (mmol/g.d.m), b_1 is the maximum capacity of active type I sites in the monolayer (mmol/g.d.m), b_2 is the maximum capacity of active type II sites in the monolayer (mmol/g.d.m), k_1 and k_2 are the constants in the Langmuir double equation (L/mmol), and C is the RB5 concentration remaining in the solution (mmol/L).

4. Results and Discussion

4.1. Influence of Salinity and pH on the RB5 Sorption Efficiency on CHs

The effectiveness of RB5 sorption on CHs, in the case of a solution without salt, was the highest at pH 4 and in the pH 4–8 range as well as in pH 9–11 range, sorption efficiency of RB5 was decreased with increasing of pH (**Fig. 1**). The high sorption efficiency of RB5 at pH 4 was due to the strong electrostatic attraction between the chitosan amino protonates and the dye anions at low pH. At higher pH (pH 5–8), the number of protonated groups was already low, which translated into lower binding efficiency. At high pH (pH 10–11), CHs gained a negative charge, caused by partial deprotonation of functional groups, which caused electrostatic repulsion of the dye from the sorbent surface and resulted in a low sorption efficiency. A slight increase in the sorption efficiency at pH 9 is characteristic of RB5 sorption on chitosan-based sorbents [9,10] and is probably related to the presence of an amino group in the dye structure.

With the increase in salinity, the effectiveness of RB5 sorption at low pH decreased, which was most probably caused by competition of dye anions with chloride anions (in the case of NaCl) or sulphate anions (in the case of Na₂SO₄) for chitosan sorption centres (**Fig. 1**). At the same time, the increase in salinity resulted in an increase in the binding efficiency of RB5 on CHs at higher pH (pH 8–11). The sorption efficiency of RB5 binding to CHs was highest at pH 9 and at a NaCl concentration of 0.5 mol/L. In the case of a solution with sodium sulphate (0.1–0.5 mol/L), the RB5 sorption efficiency was the highest at pH 11. As a result, the pH had a completely opposite effect on the effectiveness of the dye sorption salt for solutions of RB5 with Na₂SO₄ (0.5 mol/L) than in the case of RB5 solutions without the addition of salt (**Fig. 1B**).

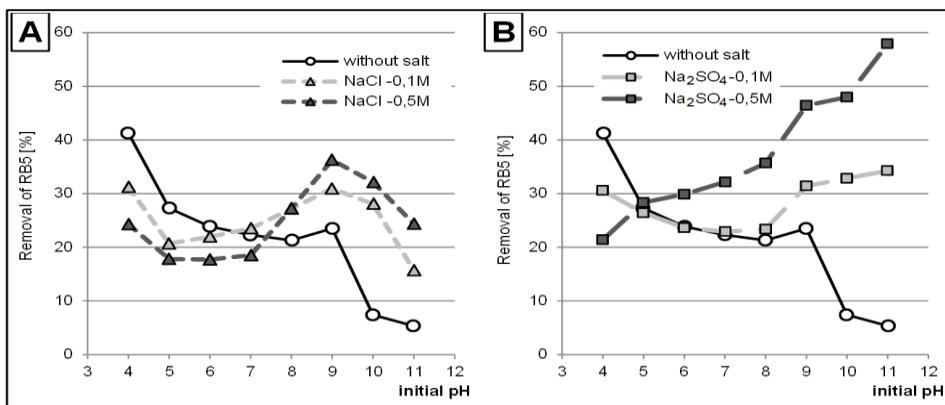


Figure 1. Influence of the presence of : A) NaCl, B) Na₂SO₄ and pH on the RB5 sorption efficiency on CHs.

The addition of salt neutralized the negative charge on the surface of the sorbent at elevated pH (pH 8–11) [13], causing the electrostatic barrier between the dye and the sorbent to be reduced, which enabled effective sorption of RB5. Presumably at pH 10–11, the main mechanism of RB5 sorption in the presence of electrolytes was chemisorption. The vinyl-sulfone group of RB5 and amine (a) or hydroxyl groups (b) of the chitosan group were involved in the condensation reaction of the dye with CHs.

- a) R_{RB5}—SO₂—CH₂—CH₂—SO₃Na + H₂N—R_{CHs} → R_{RB5}—SO₂—CH₂—CH₂—NH—R_{CHs} + NaHSO₃
- b) R_{RB5}—SO₂—CH₂—CH₂—SO₃Na + HO—R_{CHs} → R_{RB5}—SO₂—CH₂—CH₂—O—R_{CHs} + NaHSO₃

This process is widely used in industry when staining cellulosic (cotton) fibres or wool.

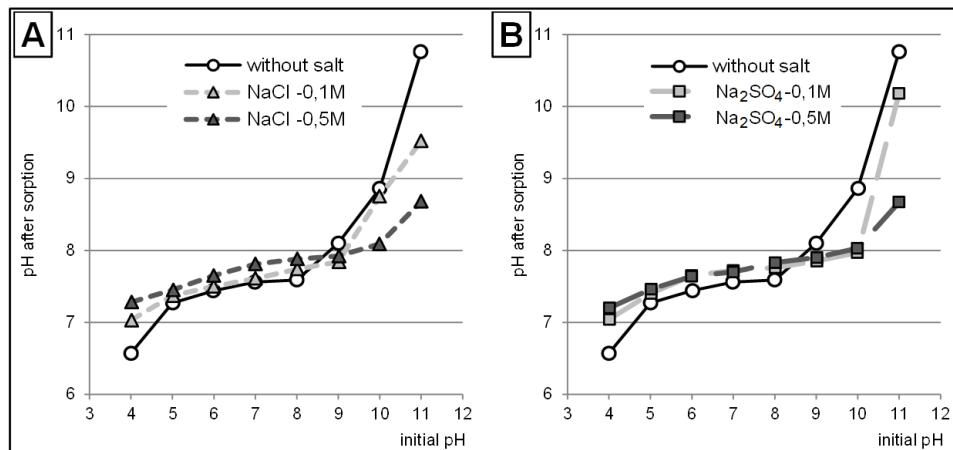


Figure 2. Changes in the pH of solutions after sorption using CHs at various concentrations of A) NaCl and B) Na₂SO₄.

Hydrogel chitosan granules had an effect on the pH of the dye solution (Fig. 2). The system aimed to obtain a pH close to the pH_{PZC} of the chitosan used ($pH_{PZC}=7.57$) (Fig. 3), which is a typical phenomenon during sorption [14]. Both the addition of NaCl and Na_2SO_4 intensified this process (Fig. 2A,B). This may be related to the neutralizing effects of electrolytes, which causes the surface of the sorbent at $pH>pH_{PZC}$ to bind a larger amount of hydroxyl ions and, at $pH< pH_{PZC}$, a greater number of hydronium ions.

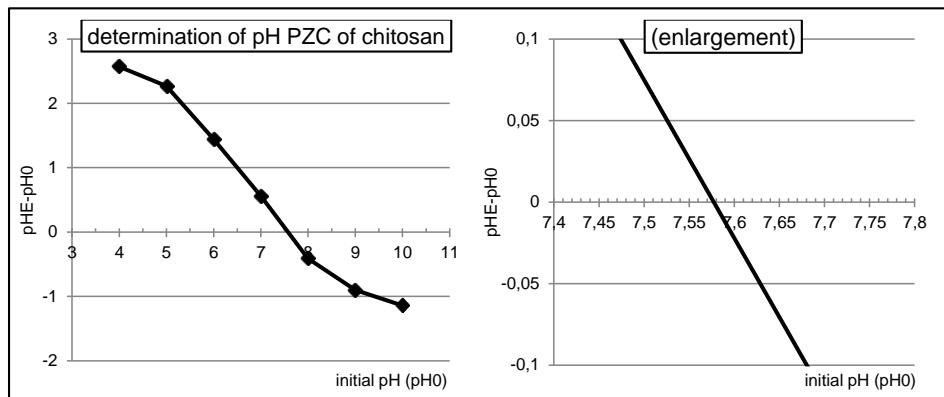


Figure 3. Determining the pH_{PZC} point for CHs.

4.2. The Influence of Salinity on the Equilibrium Time of RB5 Sorption on CHs

The amount of RB5 bound on CHs over time depended on the salinity and pH of the solution (Fig. 4A,B).

At an initial pH of 4, regardless of the type of salt, the effectiveness of sorption decreased with increasing salinity. However, at the optimal pH of RB5 sorption for high salinity solutions (pH 9 for 0.5 mol NaCl/L, pH 11 for 0.5 mol Na_2SO_4 /L), the dye binding rate on CHs was higher than for the optimal pH (pH 4) for uncommon solutions. This tendency can be seen particularly clearly in the first 30 minutes of the process (Fig. 5).

The system sought the sorption equilibrium fastest in the case of saline solutions with the optimum pH of sorption (pH 9 for 0.5 mol NaCl/L, pH 11 for 0.5 mol Na_2SO_4 /L). The sorption equilibrium time obtained in this series was 2160 min (36 h) (Fig. 4A,B). In the case of a series with an initial solution pH of 4, the equilibrium time was much longer (60 h) and was independent of the NaCl/ Na_2SO_4 concentration (Fig. 4A,B).

Shorter, and at the same time, more effective sorption of RB5 on CHs from saline solutions at high pH (pH 9 for NaCl/pH 11 for Na_2SO_4) probably results from more active sites on chitosan under specific conditions. At low pH ($< pH_{PZC}$), the main sorption centre of chitosan for anionic dyes is composed of displaced amino groups. At $pH>pH_{PZC}$ the binding of anionic dyes to chitosan is possible by chemisorption (in the presence of electrolytes), which is explained in section 4.1. Reactive vinyl-sulfone groups of RB5 are able to condense with chitosan, both with amine and hydroxyl functionality. In summary, the number of active sites involved in RB5 binding was higher under high salinity and high pH conditions (condensation of RB5 with $-OH$ and NH_2 groups) than in solutions with low pH (ionic interaction mainly from $-NH_3^+$).

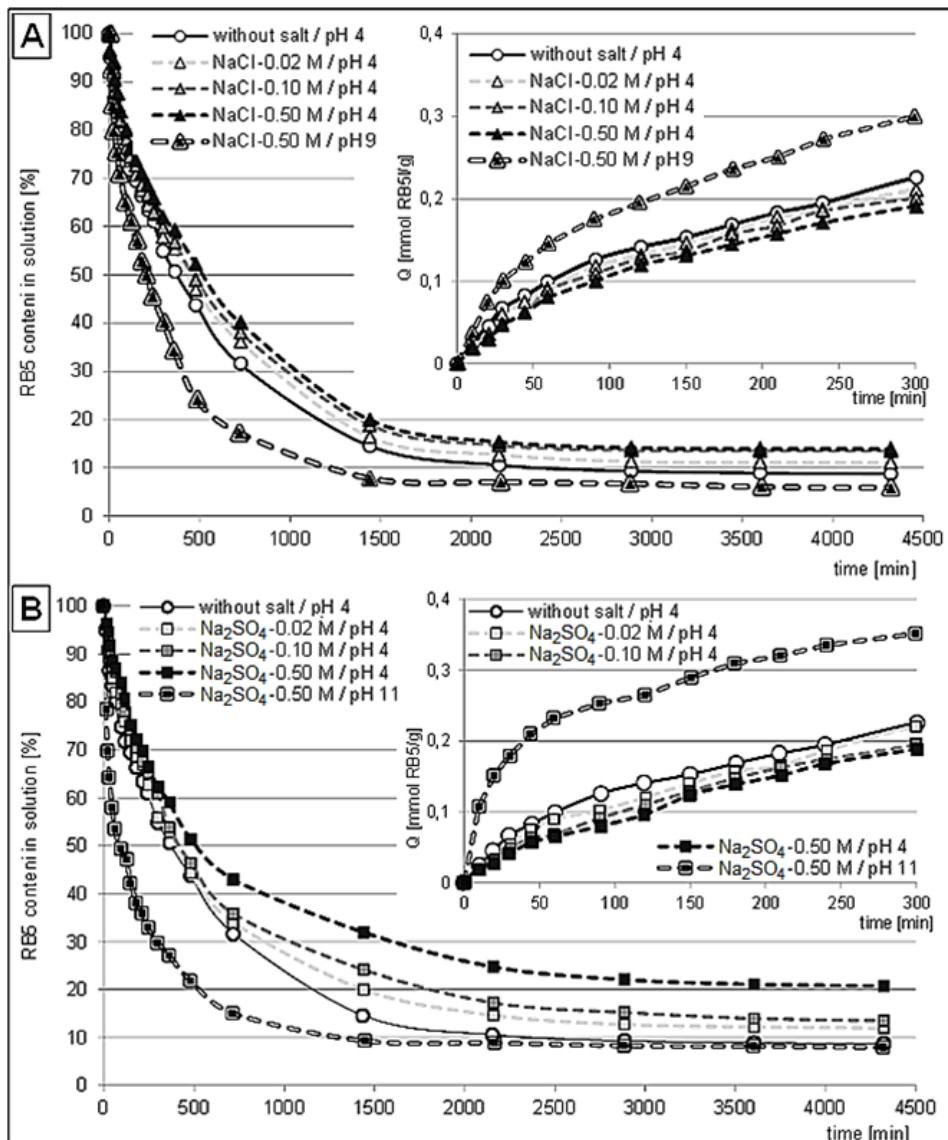


Figure 4. RB5 sorption on CHs over time at various concentrations of A) NaCl and B) Na₂SO₄.

The relatively long time to reach the sorption equilibrium time (>12 h = 720 min) probably resulted from the form of the chitosan sorbent used. Due to the hydrogel structure, the RB5 particles bound to the chitosan not only on the CHs surface, but also percolated the gel membrane and penetrated into it. Due to the interaction of RB5 with chitosan chains and the high concentration of both dye and polymer on the surface of the hydrogel granule, the process of penetration of RB5 into deeper layers of hydrogel granules was quite slow. This is explained by the long sorption equilibration time of RB5 observed in studies on CHs. Long equilibrium times for the sorption of dyes on hydrogels (>24 h = 1440 min) were also observed in studies on the sorption of dyes on cross-linked chitosan hydrogels [6,15].

4.3. Influence of Salinity on Sorption Capacity of CHs in Relation to RB5

Studies on sorption capacity of CHs in relation to RB5 were carried out for two sorption times, 24 h and 60 h. A time of 60 h guaranteed that the system obtained equilibrium (point 4.2). The results of the sorption capacity after 24 h of sorption were made for indicative and comparative purposes.

The experimental data were described by the Langmuir double isotherm (Langmuir 2 model) (Fig. 5). For the non-saline solution at pH 4, the maximum CHs sorption capacity (Q_{\max} , sum of b_1 and b_2) in relation to RB5 (calculated after 60 h) was 1.386 mmol RB5/g (1373.5 mg RB5/g). The addition of NaCl (at pH 4) affected the sorption capacity of the sorbent. The sorption capacity of CHs at pH 4 and 0.02 mol NaCl/L was 1.373 mmol RB5/g (1360.6 mg RB5/g) and at pH 4 and 0.5 mol NaCl/L was 1.307 mmol RB5/g (1295.2 mg RB5/g). A greater impact on the sorption capacity was observed in the case of the addition of sodium sulphate. At pH 4 and 0.02 mol/L Na₂SO₄/L, the CHs sorption capacity decreased to 1.315 mmol RB5/g (1303.2 mg/g), and at 0.5 mol Na₂SO₄/L was decreased to 1.148 mmol RB5/g (1137.7 mg RB5/g) (Fig. 5, Table 4).

At the sorption pH optimal for high salinity, Q_{\max} for CHs was 1.442 mmol RB5/g (1429.0 mg/g) (for 0.5 mol NaCl/L, pH 9) and 1.474 mmol RB5/g (1460.7 mg RB5/g) (for 0.5 mol Na₂SO₄/L, pH 11) (Table 4).

Table 4. Constants determined from the Langmuir double isotherm (Langmuir 2 model) for RB5 sorption on CHs.

Sorpti on time (h)	Salt type	Salt concent ration (mol/L)	pH of solutio n	Q_{\max} (mmol/g)	Langmuir 2 model				
					b_1	k_1	b_2	k_2	R^2
24	NaCl	—	4	1.373	0.079	2059.0	1.294	6.13	0.9974
		0.02	4	1.369	0.095	386.41	1.275	5.24	0.9968
		0.10	4	1.356	0.735	11.37	0.621	2.41	0.9998
		0.50	4	1.307	0.753	4.89	0.554	4.89	0.9986
		0.50	9	1.439	0.295	22.44	1.144	22.2	0.9744
	Na ₂ SO ₄	0.02	4	1.280	0.715	6.81	0.566	6.80	0.9952
		0.10	4	1.250	0.644	5.86	0.606	5.86	0.9968
		0.50	4	0.996	0.731	5.01	0.265	5.01	0.9630
		0.50	11	1.473	0.901	12.43	0.572	7.42	0.9798
60	NaCl	—	4	1.386	0.177	596.58	1.209	7.14	0.9928
		0.02	4	1.373	0.196	343.23	1.177	5.90	0.9912
		0.10	4	1.354	0.067	2410.6	1.287	5.58	0.9953
		0.50	4	1.348	0.330	35.29	1.018	3.53	0.9986
		0.50	9	1.442	0.967	59.31	0.475	12.7	0.9629
	Na ₂ SO ₄	0.02	4	1.315	0.655	9.20	0.659	9.20	0.9959
		0.10	4	1.252	0.625	8.69	0.626	8.69	0.9921
		0.50	4	1.148	0.368	5.50	0.780	5.50	0.9759
		0.50	11	1.474	0.737	13.49	0.737	13.5	0.9854

The favourable effect of high pH (pH>pH_{PZC}) on the sorption process of RB5 on CHs from saline solutions are indicated by the k_1 and k_2 constants calculated from the model (sorbent-to-sorbent indexes). In the case of saline solutions (at high ionic strength), the values of k_1 and k_2 are higher in alkaline conditions than in solutions with low pH (Table 4).

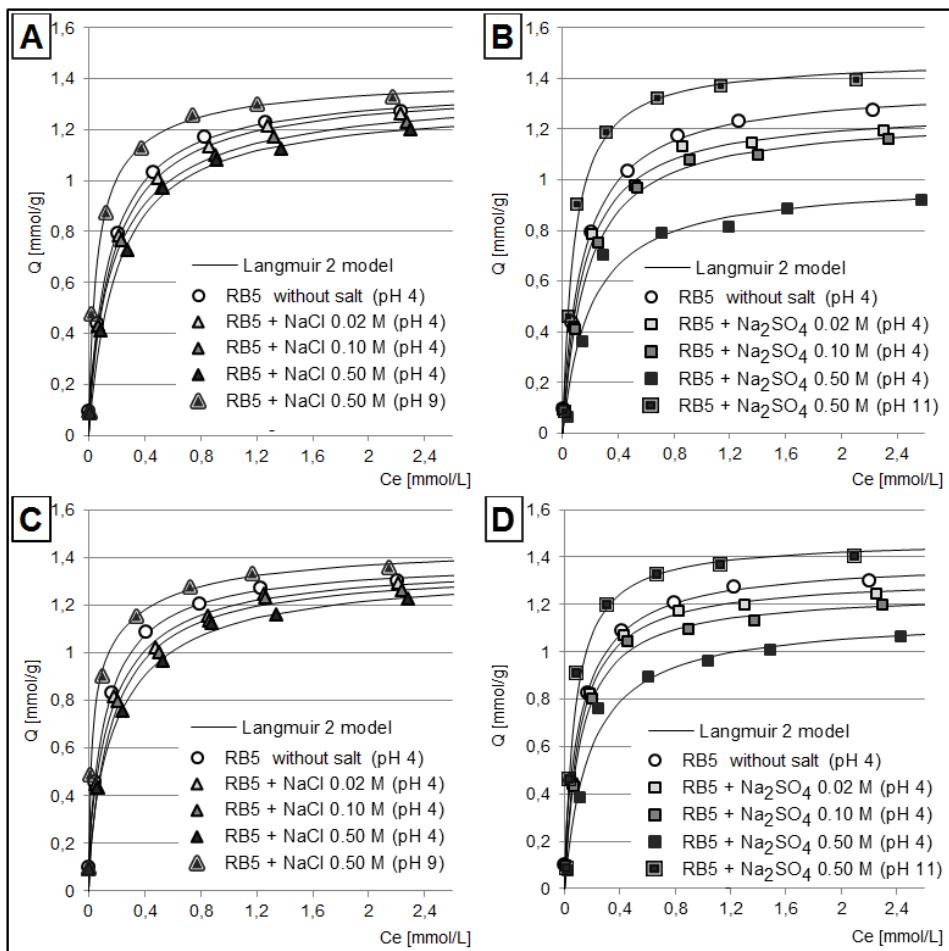


Figure 5. RB5 sorption isotherms on CHs (Langmuir 2 model) at various salt concentrations and also during various times of the process. A) NaCl (24 h), B) Na₂SO₄ (24 h), C) NaCl (60 h), D) Na₂SO₄ (60 h).

At pH 4, the deterioration of the sorption capacity of RB5 on CHs, along with the addition of salt to the solution, results from the competition of dye anions with chloride or sulphate ions with sorptive centres of chitosan ($-NH_3^+$ groups), as explained in section 4.1. The higher sorption capacity of CHs relative to RB5 in solutions with high salinity and high pH (in comparison with solutions without added salt, pH 4) results from the greater number of sorptive centres involved in the reaction. During chemisorption of the dye in alkaline conditions, apart from the amino groups, numerous hydroxyl groups are also involved, as explained in section 4.2.

The greater effect of sodium sulphate on the sorption capacity of CHs compared to sodium chloride may result from the higher molar mass of Na₂SO₄ (at the same molar concentration, the mass concentration of sodium sulphate is 143% higher than sodium chloride). The Na₂SO₄ electrolyte could also be influenced by the sulphate anion (sulfone groups present in the RB5 structure have a large share in the sorption processes of the dye).

4. Summary

The concentration of salt ($\text{NaCl}/\text{Na}_2\text{SO}_4$) in the solution (ionic strength) has a big influence on the sorption capacity of CHs in relation to RB5. This effect is largely dependent on the pH of the dye solution. At low pH ($\text{pH} < \text{pH}_{\text{PZC}}$), the sorption efficiency of the anionic dye on chitosan decreases with increasing salinity ($\text{NaCl}/\text{Na}_2\text{SO}_4$). This can be explained by the increased competition of dye ions with chloride or sulphate ions for the active sites of chitosan ($-\text{NH}_3^+$ groups). The reverse tendency is observed in alkaline conditions. At $\text{pH} > \text{pH}_{\text{PZC}}$, the effectiveness of RB5 sorption on CHs increases with increasing salinity. This is presumably due to the neutralizing effect of electrolytes, which reduce the negative charge of the sorbent surface at high pH, allowing the dye to overcome the electrostatic barrier and its binding to CHs. At low pH (pH 4), the salt concentration ($\text{NaCl}/\text{Na}_2\text{SO}_4$) in the solutions has no significant effect on the equilibrium time of the RB5 sorption (and is 60 h). The shorter sorption time (2160 min) (36 h) was observed in systems with high pH and high salt concentration (pH 9, 0.5 mol NaCl/L , pH 11, 0.5 mol $\text{Na}_2\text{SO}_4/\text{L}$), which probably results from more chitosan functional groups participating in the sorption (the ability for chemisorption under alkaline conditions).

The relatively long equilibrium time of RB5 sorption on CHs observed in all research series is probably associated with the hydrogel structure of the sorbent and its ability to slowly absorb the dye.

The salinity and pH of the solution also affect the sorption capacity of CHs. At the optimal pH (pH 4) in the solution without the addition of salt, the sorption capacity of CHs was $Q_{\text{max}} = 1.386 \text{ mmol RB5/g}$ (1373.5 mg RB5/g). Under conditions of high salinity (0.5 mol $\text{Na}_2\text{SO}_4/\text{L}$) at pH 4, the CHs sorption capacity was 17.2% lower compared to the system without added salt, while at pH 11, it was 6.4% higher. It follows that high efficiency of sorption of dyes on chitosan sorbents can be obtained regardless of the salinity of the solution, provided that the appropriate pH correction is applied.

5. Acknowledgements

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