

APPLICATION OF CROSS-LINKED CHITOSAN FOR NITRATE NITROGEN (V) REMOVAL FROM AQUEOUS SOLUTIONS

Tomasz Józwiak, Urszula Filipkowska,
Paula Szymczyk, Artur Mielcarek

*Department of Environmental Protection Engineering,
University of Warmia and Mazury in Olsztyn
ul. Warszawska 117, 10–719 Olsztyn, Poland
e-mail: urszula.filipkowska@uwm.edu.pl*

Abstract

This study was aimed at determining the possibility of applying non-cross-linked chitosan (CHs) as well as chitosan cross-linked with glutaraldehyde (CHs-GLA) and epichlorohydrin (CHs-ECH) for the removal of nitrates (V) from aqueous solutions. The scope of the study included determinations of: optimal pH value of nitrates sorption (from pH range of 2-11), equilibrium time of sorption process, and maximum N-NO₃ sorption capacity of the analysed chitosan sorbents. Kinetics of nitrates sorption was described with pseudo-first and pseudo-second order equations, and with the intraparticle diffusion model. Sorption capacity analysis was conducted with the heterogeneous Langmuir model, the double Langmuir model and the Freundlich model. The optimal pH value of N-NO₃ sorption onto CHs-GLA and CHs-ECH was pH 3, whereas onto CHs this was pH 4. The equilibrium time of sorption reaction was the same for all chitosan sorbents and reached 120 min. The maximum sorption capacity of CHs, CHs-GLA and CHs-ECH accounted for 12.71 mg N-NO₃/g, 34.99 mg N-NO₃/g and 38.47 mg N-NO₃/g.

Key words: adsorption, dyes, chitosan beads, cross-linked chitosan beads, glutaraldehyde.

1. Introduction

Post-production wastes from industries producing artificial fertilisers and explosive materials may contain significant quantities of nitrates (NO_3^-). An excess concentration of biogenes may disturb the functioning of conventional wastewater treatment plants. In addition, nitrates that penetrate into the aquatic environment may significantly accelerate the eutrophication process. The presence of NO_3^- in drinking water is claimed to induce methaemoglobinaemia in infants and increase the risk of the development of gastrointestinal tract cancers [1, 2]. The use of installations for the pre-treatment of post-production wastewaters containing high concentrations of nitrogen therefore appears to be necessary.

According to the World Health Organisation (WHO), the best available technologies for nitrate removal from aqueous solutions include: reverse osmosis, ionic exchange and electro dialysis [3]. A popular method of nitrate-containing water conditioning is chemical denitrification with the use of zero-valent iron (Fe^0) [4] or zero-valent magnesium (Mg^0) [5]. These methods are, however, very expensive and may generate noxious by-products [6].

A simple and relatively safe method for the removal of nitrates from water is sorption. Its effectiveness and costs primarily depend on the sorbent applied. Popular sorbents based on activated carbon are efficient but cost-ineffective in the process of wastewater treatment. Therefore, a search is underway for alternative sorbents that show high affinity to nitrates. So far, studies have been conducted regarding NO_3^- removal using agricultural wastes (straw, seed hulls, pomace from sugar cane) [7] and also various industrial wastes (gravel, sepiolite, bentonite) [8]. However, recently, increasing interest has been observed in the use of chitosan, a derivative of chitin, as a sorbent. Its acquisition from the waste of marine arthropods processing ensures its low price and high availability. Owing to its alkaline character, this biopolymer is a good sorbent of all anionic contaminants, and its stability in a wide range of pH values (pH 0 - 14) is assured by the process of chemical cross-linking.

In this study, we examined the effectiveness of nitrates removal from aqueous solutions onto three chitosan sorbents in the form of hydrogel beads: non-cross-linked chitosan (CHs), chitosan cross-linked with glutaraldehyde (CHs-GLA), and chitosan cross-linked with epichlorohydrin (CHs-ECH).

2. Material and methods

2.1. Materials

Chitosan, in the form of flakes (DD = 85%), was purchased from Heppe Medical Chitosan GmbH, Halle (Saale), Germany. Sodium nitrate >99% and cross-linking agents: glutaraldehyde (25%) and epichlorohydrin (99%), were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Methods

2.2.1. Preparation of hydrogel chitosan beads

Chitosan (25 g d.m.) was dissolved in 975 mL of 5% acetic acid solution. Next, the solution with a chitosan concentration of 2.5% was instilled to 2 L of 2 M NaOH solution in

order to form beads. After 24 h, the hydrogel beads were filtered off and rinsed with distilled water to remove NaOH residues. The resultant beads (2.0 – 2.3 mm in diameter) were then stored in distilled water.

2.2.2. Chitosan cross-linking with glutaraldehyde (GLA)

The previously prepared beads (1 g d.m.) were placed in a 250-mL flask and poured into 200 mL of glutaraldehyde solution with a concentration of 0.7 g/L. The concentration of GLA was adjusted to ensure that the ratio of aldehyde groups of GLA to amine groups of CHs was 1:2 [9]. Next, the flask was placed on a shaker set at the speed of 120 r.p.m. After 24 h of cross-linking at 22°C, the CHs-GLA beads were rinsed with distilled water to remove non-reacted GLA.

2.2.3. Chitosan cross-linking with epichlorohydrin (ECH)

CHs beads (1 g d.m.) were placed in a flask (250 mL) and poured into ECH solution with a concentration of 1.3 g/L and pH 11. The ratio of functional groups of ECH to amine groups of CHs in the resultant solution reached 1:1. The flask was then placed in a water bath with a shaker (120 r.p.m). The cross-linking process proceeded for 24 h at 60 °C. Afterwards, CHs-ECH beads were rinsed with distilled water to remove non-reacted ECH.

2.2.4. Analyses of the effect of pH value on the effectiveness of nitrate nitrogen sorption

Experiments were conducted under static conditions onto 3 chitosan sorbents: CHs, CHs-GLA, and CHs-ECH. The pH value was adjusted with 1M solutions of HCl and NaOH. The process of nitrates sorption was conducted in 250 mL beakers placed on a multi-station magnetic stirrer. The most important parameters of these analyses are presented in Table 1.

2.2.5. Determination of reaction equilibrium time

The time necessary to reach sorption reaction equilibrium was determined after establishing the optimal pH value of the sorption process. Nitrates sorption onto CHs, CHs-GLA and CHs-ECH was conducted in 2500 mL beakers placed on magnetic stirrers. Samples (5 mL) were collected for analyses after 0, 1, 5, 10, 15, 20, 30, 40, 50, 60, 90, 120, 150, 180, 210, and 240 min. The other experimental parameters are presented in **Table 2**.

Table 1. Parameters of analyses of pH value effect on the effectiveness of nitrates sorption on chitosan sorbents.

Sorbent	Sorbent conc. [g/L]	Solution [mL]	Sorption pH [pH]	Sorbate conc. [mg N-NO ₃ /L]	Sorption time [min]	Stirring speed [r.p.m.]	Temp. [°C]
CHs, CHs-GLA, CHs-ECH	1	200	2, 3, 4, 5, 6, 7, 8, 9, 10, 11	10/ 50/ 100	60	120	22

Table 2. Parameters of determination of equilibrium time of nitrates sorption reaction onto chitosan sorbents.

Sorbent	Sorbent conc. [g/L]	Solution volume [mL]	Sorbate conc. [mg N-NO ₃ /L]	Stirring speed [r.p.m.]	Temp. [°C]
CHs,	1	2000	100	120	22
CHs-GLA,					
CHs-ECH					

Table 3. Parameters of determination of maximum sorption capacity of chitosan sorbents against nitrate nitrogen.

Sorbent	Sorbent conc. [g/L]	Solution volume [mL]	Sorbate concentration in successive solutions [mg N-NO ₃ /L]	Stirring speed [r.p.m.]	Temp [°C]
CHs,	1	200	5, 10, 25, 50, 100, 200, 300, 400, 500	120	22
CHs-GLA,					
CHs-ECH					

2.2.6. Determination of the maximum sorption capacity of chitosan sorbents

The maximum sorption capacity of CHs, CHs-GLA, CHs-ECH against nitrate nitrogen (V) was determined after establishing the optimal pH value and equilibrium time of the sorption reaction. The process of nitrates sorption onto chitosan sorbents was conducted in 250-mL conical flasks placed on a shaker. The main parameters of these analyses are provided in **Table 3**.

2.2.7. Analytical methods

The concentration of nitrate nitrogen (V) in solution was determined using the colorimetric method [PN73/C-04576/08], on a UV-VIS SP 2000 spectrophotometer.

The pH was measured using a HI-122 pH-meter.

2.2.8. Computational methods

The quantity of sorbed nitrate nitrogen (V) was computed from the following equation (1):

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

Sorption kinetics was described with the use of pseudo-first (2) and pseudo-second (3) order equations:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (2)$$

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (3)$$

Stages of nitrate nitrogen sorption onto chitosan sorbents were described with a simplified model of intraparticle diffusion (4)

$$q_t = k_d \cdot t^{0.5} \quad (4)$$

The maximum sorption capacity was determined using two various adsorption models.

Langmuir model (5):

$$q_e = \frac{q_{\max} K_c \cdot C}{1 + K_c \cdot C} \quad (5)$$

Freundlich model (6)

$$q_e = K \cdot C^n \quad (6)$$

The fit of experimental data to mathematical models was determined with the use of a correlation coefficient R^2 (7)

$$R^2 = \frac{\sum(q_{\text{cal}} - \bar{q}_{\text{exp}})^2}{\sum(q_{\text{cal}} - \bar{q}_{\text{exp}})^2 + \sum(q_{\text{cal}} - q_{\text{exp}})^2} \quad (7)$$

where:

- Q_s – weight of sorbed N-NO₃ [mg/g.d.m.]
- C_0 – initial concentration of N-NO₃ [mg/L]
- C_s – N-NO₃ concentration after sorption [mg/L]
- m – weight of sorbent [g.d.m.]
- q_e – equilibrium concentration of sorbed N-NO₃ [mg/g.d.m.]
- q – instantaneous quantity of sorbed N-NO₃ [mg/g.d.m.]
- k_1 – constant in pseudo-first order equation [1/min]
- k_2 – constant in pseudo-second order equation [g/(min·mg)]
- k_d – intraparticle diffusion rate constant [mg/g·min^{-0.5}]
- t – sorption time [min]
- q_{\max} – maximum adsorption capacity of adsorbent monolayer [mg/g.d.m.]
- K_c – constants in Langmuir equation [L/mg]
- C – concentration of N-NO₃ left in the solution [mg/L]
- K – sorption equilibrium constant in Freundlich model
- n – parameter of heterogeneity
- R^2 – correlation coefficient – a measure of experimental data fit to math. model
- q_{exp} – experimental data – quantity of sorbed N-NO₃ [mg/g.d.m.]
- q_{cal} – theoretical data resulting from the model – quantity of sorbed N-NO₃ [mg/g.d.m.]

3. Results and discussion

3.1. Effect of pH value on the effectiveness of N-NO₃ sorption

The effectiveness of N-NO₃ sorption onto CHs was found to increase along with a decreasing initial pH value and was highest at pH 4. At the optimal pH, the removal rate of N-NO₃ onto CHs reached 7.0%, 8.1% and 9.5% for initial nitrate concentrations of 10, 50 and 100 mg N-NO₃/L, respectively. Sorption on non-cross-linked chitosan at the initial pH value of 2 - 3 resulted in sorbent dissolution (*Figure 1.A*).

In contrast to CHs, the cross-linked chitosan sorbents (CHs-GLA and CHs-ECH) did not dissolve at pH 2 - 3. The sorption capability of CHs-GLA and CHs-ECH was the highest at pH 3. Along with pH increase, the effectiveness of N-NO₃ sorption onto

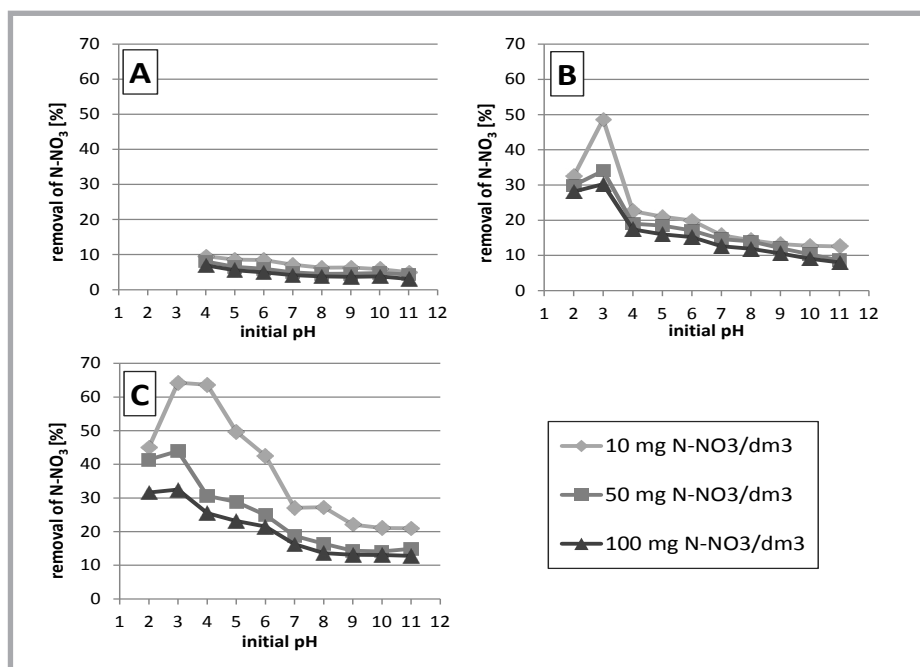


Figure 1. Effect of initial pH on effectiveness of N-NO₃ sorption onto: A – CHs, B – CHs-GLA, C – CHs-ECH.

cross-linked sorbents was observed to decrease. At optimal pH, the effectiveness of nitrates sorption onto CHs-GLA reached 48.6%, 34.0% and 30.2%, whereas that of nitrates sorption onto CHs-ECH reached 64.2%, 44.0% and 32.5% for initial concentrations of 10, 50 and 100 mg N-NO₃/L, respectively (**Figures 1.B, 1.C**).

The increased effectiveness of nitrates sorption at low pH was probably caused by protonation of amine groups of chitosan. Electrostatic interactions between positively-charged sorbent surface and negatively-charged sorbate (NO₃⁻) significantly enhanced the adsorption process. The positive impact of low pH on nitrates sorption was also observed in investigations with the use of activated carbon [10], sepiolite [11] and aluminium oxide [12] as sorbents. In the alkaline medium (pH > 7), OH⁻ ions may compete with NO₃⁻ ions, which significantly impairs their sorption.

A comparison of the effectiveness of N-NO₃ sorption onto CHs, CHs-ALD and CHs-ECH depending on pH value is presented in **Figure 2**. Amongst the analysed sorbents, CHs displayed the lowest sorption capability against nitrates (V). The sorption of nitrates (V) was significantly more effective upon the use of CHs-GLA; however, this processes required pH value adjustment to pH 3. The best sorbent of N-NO₃ turned out to be CHs-ECH, which shows high sorption capability in a wide range of pH values (pH 2 - 6).

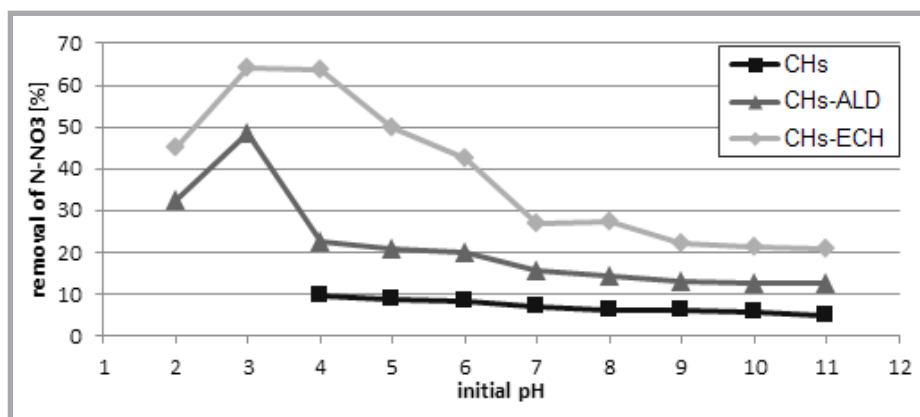


Figure 2. Comparison of the effectiveness of CHs, CHs-ALD and CHs-ECH sorbents at nitrates concentration of 10 mg N-NO₃/L.

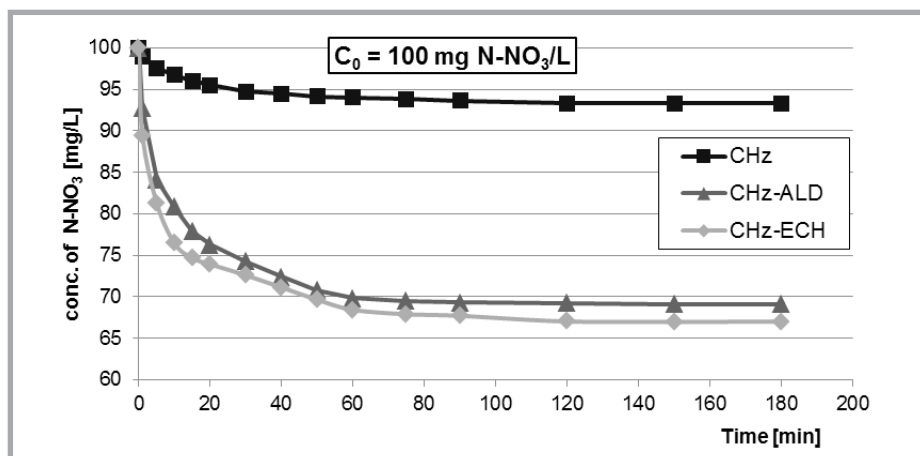


Figure 3. Changes in N-NO₃ concentration during sorption depending on the applied sorbent.

3.2 Kinetics of N-NO₃ sorption onto chitosan sorbents

The time necessary to reach reaction equilibrium in the N-NO₃ sorption process for all tested chitosan sorbents reached 120 min (Figure 3). The process of sorption was the most intensive in the first minutes of the experiment. Within the first 15 min, N-NO₃ sorption effectiveness onto CHs accounted for 59.7% (relative to the total amount of adsorbed N-NO₃), whereas it reached as much as 71.6% and 76.7% in the case of CHs-GLA and CHs-ECH, respectively.

3.2.1. Sorption kinetics

Kinetics of N-NO₃ sorption onto chitosan sorbents was described with the use of pseudo-first and pseudo-second order equations (Figure 4). Based on the coefficient

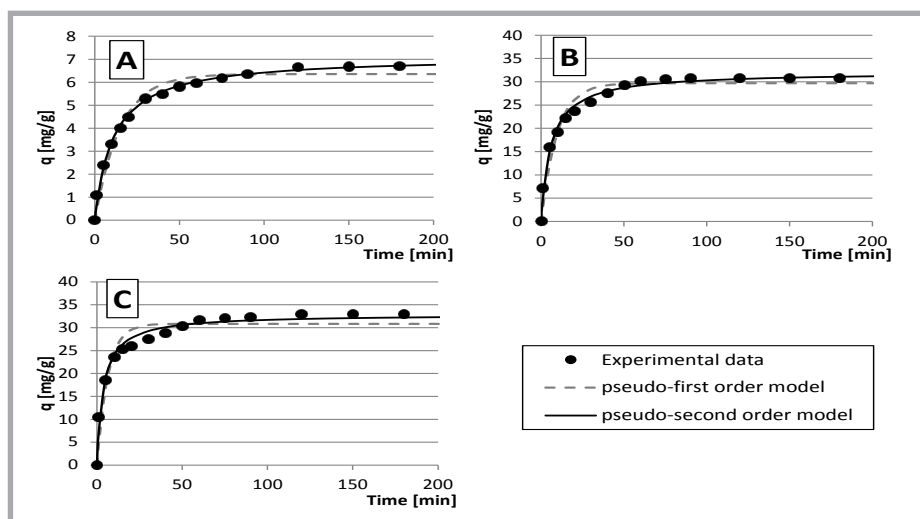


Figure 4. Kinetics of $N\text{-NO}_3$ sorption onto A – CHs, B – CHs-GLA, C – CHs-ECH; pseudo-first order and pseudo-second order model.

of correlation between experimental data ($q_{e,\text{exp}}$) and theoretical data, resulting from the applied model ($q_{e,\text{cal}}$), it was stated that the sorption process of nitrates onto chitosan sorbents was better described by the pseudo-order model. This model was also previously applied for the description of nitrates sorption onto activated carbon [10], aluminium oxide [12], and also onto wheat wastes [13] and beetroot wastes [14]. The computed kinetic parameters are collated in **Table 4**.

The intraparticle diffusion model indicates the occurrence of three stages of nitrates (V) sorption process onto chitosan sorbents (**Figure 5**). The first stage of sorption probably results from surface adsorption, in which an NO_3^- ion diffuses to the surface layer of sorbent. The second stage of sorption presumably involves the diffusion of nitrates to the sorbent interior, namely absorption. The last stage of sorption proceeds with the lowest rate and depicts sorbent saturation and reaches reaction equilibrium. Kinetic parameters of the intraparticle diffusion model are presented in **Table 5**. Significantly worse effects of NO_3^- sorption by CHs compared to CHs-GLA and CHs-ECH were probably due to the various pH values of the sorption process. Electrostatic interactions between NO_3^- and sorbent surface are stronger at pH 3 (sorption onto CHs-GLA, CHs-ECH) than at pH 4 (sorption onto CHs).

Table 4. Kinetic parameters of $N\text{-NO}_3$ sorption in pseudo-first order model and pseudo-second order model.

Sorbent	Pseudo-first order model			Pseudo-second order model			Exp. data
	k_1	$q_{e,\text{cal}}$	R^2	k_2	$q_{e,\text{cal}}$	R^2	$q_{e,\text{exp}}$
CHs	0.0667	6.36	0.9743	0.0128	7.13	0.9943	6.70
CHs-GLA	0.1049	29.70	0.9551	0.0053	32.10	0.9884	30.91
CHs-ECH	0.1573	30.84	0.9273	0.0081	32.90	0.9795	33.00

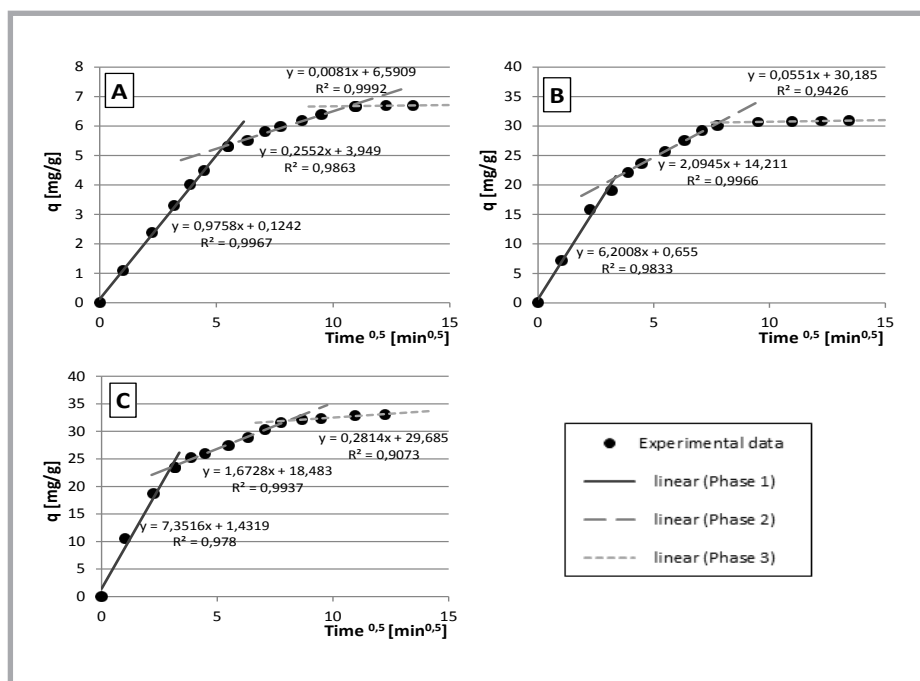


Figure 5. Intraparticle diffusion model for the sorption of $N\text{-NO}_3$ onto: A – CHs, B – CHs-GLA, C – CHs-ECH.

Table 5. Constants of $N\text{-NO}_3$ diffusion rate determined from a simplified model of intraparticle diffusion.

Sorbent	First stage of sorption		Second stage of sorption		Third stage of sorption	
	k_{d1}	R^2	k_{d2}	R^2	k_{d3}	R^2
CHs	0.9758	0.9967	0.2552	0.9863	0.0081	0.9992
CHs-GLA	6.2008	0.9833	2.0945	0.9966	0.0551	0.9426
CHs-ECH	7.3516	0.9780	1.6728	0.9937	0.2814	0.9073

3.2.2. Maximum $N\text{-NO}_3$ sorption capacity of chitosan sorbents

The sorption capacity of the analysed chitosan sorbents was described with the Langmuir models and Freundlich model (**Figure 6**). Constants determined from these models are presented in **Tables 6** and **7**. For all sorbents, the best fit of experimental data was achieved for heterogeneous Langmuir and Langmuir 2 models.

The maximum $N\text{-NO}_3$ sorption capacity of CHs reached 12.71 mg $N\text{-NO}_3$ /g. A significantly higher sorption capacity was determined for the cross-linked chitosan sorbents CHs-GLA and CHs-ECH, i.e. 34.99 and 38.47 mg $N\text{-NO}_3$ /g, respectively (**Figure 7**, **Table 6** and **7**). **Table 8** provides a comparison of sorption capacities of various sorbents against nitrate nitrogen (literature data).

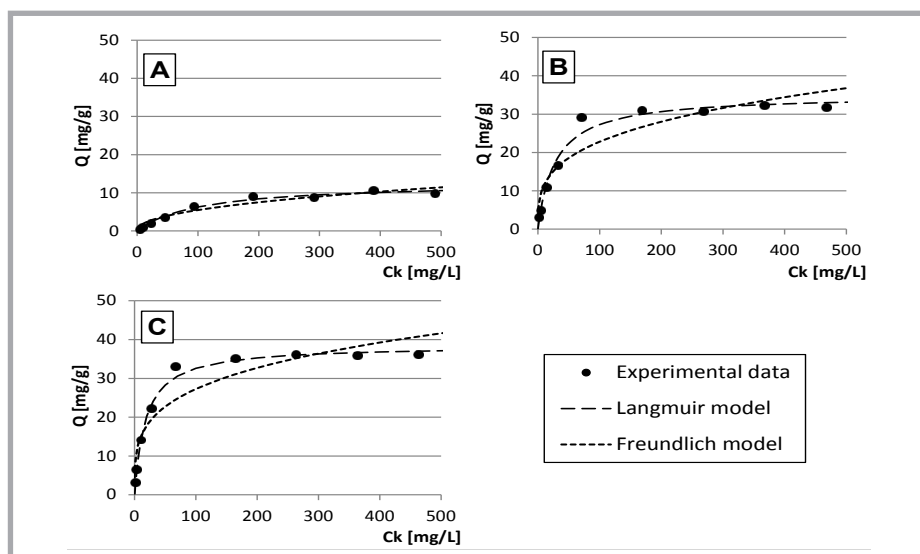


Figure 6. Isotherms of $N\text{-NO}_3$ sorption onto: A – CHs, B – CHs-GLA, C – CHs-ECH.

Table 6. Constants determined from the Langmuir equation.

Sorbent	Constants in Langmuir model		R ²
	q _{max} [mg/g d.m]	K _C	
CHs	12.71	0.0097	0.9835
CHs-GLA	34.99	0.0353	0.9788
CHs-ECH	38.47	0.0555	0.9933

Table 7. Constants determined from the Freundlich equation.

Sorbent	Constants in Freundlich model		R ²
	k	n	
CHs	0.6592	0.4588	0.9488
CHs-GLA	5.8063	0.2970	0.8744
CHs-ECH	8.1170	0.2629	0.9338

4. Conclusions

Hydrogel chitosan beads may be successfully applied for nitrates sorption from aqueous solutions. The effectiveness of NO_3^- sorption onto chitosan sorbents increases along with a decreasing pH value. The lowest pH value at which CHs preserves its sorption capability is pH 4. Nitrates sorption at lower pH, i.e. pH 2-3, requires the use of cross-linked chitosan (CHs-GLA, CHs-ECH), which is resistant to dissolution at low pH. The cross-linking process may significantly increase the sorption capability of chitosan. The maximum $N\text{-NO}_3$ sorption capacities of the cross-linked chitosan are nearly

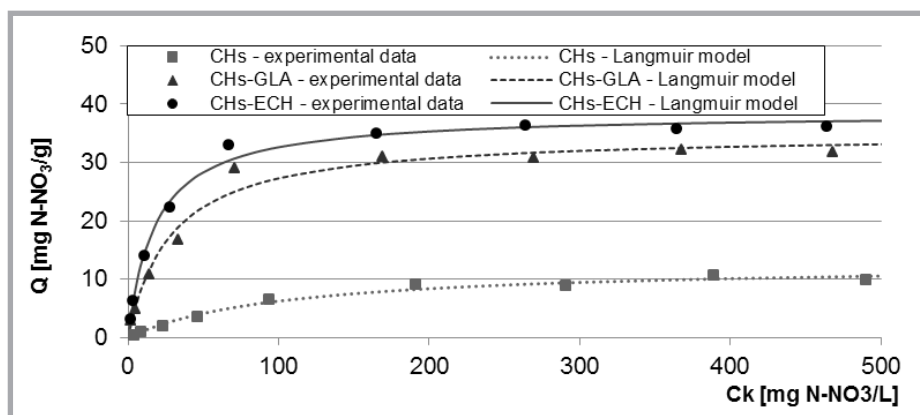


Figure 7. Comparison of isotherms of $N\text{-NO}_3$ sorption onto: CHs, CHs-GLA, CHs-ECH

Table 8. $N\text{-NO}_3$ adsorption capabilities of exemplary sorbents.

Type of sorbent	Maximum sorption capacity		Initial pH of sorption	Source
	[mg $N\text{-NO}_3$ /g]	[mmol $N\text{-NO}_3$ /g]		
Chitosan beads cross-linked with ECH	38.47	2.75	3.0	This work
Chitosan beads cross-linked with GLA	34.99	2.50	3.0	This work
Wheat residue modified with ECH	29.12	2.08	6.8	[13]
Pure alkaline lignin	25.20	1.80	-	[15]
Pure cellulose	18.76	1.34	-	[15]
Rice hull	18.48	1.32	-	[15]
Chitosan beads (CHs)	12.71	0.91	4.0	This work
Chitosan-coated zeolite	10.39	0.74	-	[16]
Mobil Composite Material No. 48	10.39	0.74	4.0	[17]
ZnCl ₂ -treated coconut granular activ. carbon	10.20	0.72	5.5	[18]
Sepiolite	5.71	0.41	2.0	[11]
Nano-alumina (AL ₂ O ₃)	4.00	0.29	4.4	[12]
Activated carbon from sugar beet bagasse	3.93	0.28	6.6	[10]
Raw wheat residue	2.02	0.14	6.8	[13]
Untreated coconut granular activated carbon	1.70	0.12	5.5	[18]
Commercial activated carbon	1.22	0.09	-	[19]
Wheat straw charcoal	1.10	0.08	-	[19]

3 times higher compared to these of the unmodified chitosan. An advantage of CHs-ECH over the remaining sorbents (CHs, CHs-GLA) is its high sorption effectiveness in a wide pH range (pH 2 - 6). Kinetics of nitrates sorption onto CHs, CHs-GLA and CHs-ECH is best described with the pseudo-second order model. The intraparticle diffusion model points to three stages of $N\text{-NO}_3$ sorption on chitosan sorbents. The equilibrium time of the sorption process for CHs, CHs-GLA and CHs-ECH reaches 120 min, whereas most of the nitrates are sorbed within the first 10 min of the process.

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