THE INFLUENCE OF THE DEACETYLATION DEGREE OF CHITOSAN IN THE FORM OF FLAKES ON THE EFFECTIVENESS OF NITRATES V SORPTION FROM AQUEOUS SOLUTIONS

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Abstract

The influence of the degree of deacetylation of chitosan from the range of DD = 75–90% on the effectiveness of sorption of nitrates from aqueous solutions was investigated. The scope of the research included: determining the effect of pH on the effectiveness of $N\text{-}NO_3$ *binding on chitosan sorbents and determining the sorption capacity of chitosan sorbents with different degrees of deacetylation after 5, 15, 30 and 60 minutes.*

The effectiveness of sorption of nitrates on chitosan sorbents increased in the series DD=75% < DD=85% < DD=90%. Regardless of the degree of deacetylation, the sorption effectiveness of nitrates on chitosan was the highest at pH 4. The amount of nitrate-related sorbents was the highest after 30 min of sorption. A process time which was too long resulted in desorption of nitrates. The maximum sorption capacity for chitosan with the degree of deacetylation DD = 75, 85 and 90% was 0.59 mg $N\text{-}NO_3/g$, *0.60 mg* $N\text{-}NO_3/g$ *and 0.87 mg* $N\text{-}NO_3/g$, *respectively.*

Key words: *sorption, chitosan, deacetylation degree, nitrate*

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1. Introduction

Post-production sewage from the fertiliser or explosives industry, due to the very high content of nitrates, is treated as particularly onerous. The increased concentration of $N\text{-}NO_3$ in municipal sewage may lead to the malfunctioning of conventional biological wastewater treatment plants based on activated sludge technology. Nitrates, which enter the aquatic environment along with untreated wastewater, may cause the eutrophication of rivers and lakes. They can also easily penetrate groundwater and contaminate underground seams of drinking water because nitrates have little ability to bind to soil particles [1, 2]. The consumption of water contaminated with nitrates may lead to methaemoglobinaemia [3] and may also be the cause of gastric cancer [4]. The development and application of effective technologies for the removal of nitrates from wastewater seems to be a priority.

Sorption is one of the simplest and most effective methods of removing nitrates from aqueous solutions [5, 6]. Due to the fact that sorption does not adversely affect the composition of treated wastewater, it is widely recognised as environmentally friendly. The effectiveness, as well as the sorption costs, depend mainly on the type of sorbent used.

In recent years, chitosan has gained great popularity as a sorbent. Chitosan is a polysaccharide, a deacetylated derivative of chitin, which is the main building block of arthropod shells. This material has already shown high suitability for the removal of dyes from aqueous solutions [7-9]. Chitosan, due to its alkaline nature and high affinity for anionic sorbates, can also be characterised by the high binding efficiency of nitrates from aqueous solutions [10-12].

The effectiveness of binding sorbates on chitosan sorbents depends on the degree of deacetylation of chitosan to a large extent [13]. For example, chitosan with the degree of deacetylation DD=90% may show a sorption capacity for dyes that was up to 160% higher than chitosan with DD=75% [14]. This study investigated the effect of the degree of deacetylation of chitosan in the range of DD=75–90%, on the effectiveness of the sorption of nitrates from aqueous solutions.

2. Materials

2.1. Chitosan

Chitosan with a deacetylation degree of 75, 85 and 90% was purchased from Heppe Medical Chitosan GmbH, Halle (Saale), Germany. The material specification given by the producer is presented in Table 1.

Table 1. Chitosan parameters, provided by the producer.

Basic parameters	Chitosan deacetylation degree (DD)		
	75%	**85%**	**90%**
Ash content	<1.0%	<1.0%	<1.0%
Content of heavy metals	<25 ppm	<25 ppm	<25 ppm
Viscosity	100 mPas	100 mPas	100 mPas
Raw material source	snow crab shells	snow crab shells	snow crab shells

2.2. Chemical reagents

The following chemical reagents were used in the research: potassium nitrate (KNO_3) P.F.A, hydrochloric acid (HCl) 35–38% PURE, and sodium hydroxide (NaOH), all purchased from POCH S.A. (Poland).

3. Methodology

3.1. Sorbent preparation for the research

Chitosan sorbent in the form of flakes was delivered by the manufacturer in hermetic packages. The material was only sieved through a laboratory sieve with a mesh diameter of 3 mm and then through a sieve with a mesh size of 2 mm. The chitosan fraction with a diameter of 2–3 mm was used for the research.

3.2. Research into the effect of pH on the effectiveness of nitrate sorption

Chitosan (0.25 g DM per flask) and nitrate solutions (250 mL) were weighed in the conical flasks (500 mL) and then a solution of 1 mg $N\text{-}NO_3$/L at a pH of 2/3/4/5/6/7/8/9/10/11 was added to the flasks. Then, the flasks were placed on a shaker (150 rpm/with a vibration amplitude of 30 mm) for 60 min. After the specified time, samples (25 mL) were taken from the flasks to determine the nitrates remaining in the solution. The pH of solutions after sorption was also examined.

3.3. Research on sorption capacity

Chitosan (1.0 g s.m.) was added to a series of conical flasks (1000 mL). Then, nitrate solutions (500 mL) at concentrations of 0.5/1.0/2.0/3.0/4.0/5.0/6.0/7.0/8.0 mg $N\text{-}NO_3$/L were added to flasks with an optimum pH determined to be 4.1, after which the flasks were placed on a shaker (150 rpm with a vibration amplitude of 30 mm). After 5/15/30/60 min, samples (25 mL) were taken from the solutions to determine the nitrate concentration in the solution.

3.4. Determination of nitrate concentration in solution

The $N\text{-}NO_3$ designation was performed in accordance with the Polish standard: PN82/C-04576/08. This method is based on the reaction of nitrates with sodium salicylate in the environment of concentrated sulphuric acid (VI).

3.5. Calculation methods

The amount of nitrate nitrogen adsorbed on chitosan was calculated from dependence:

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

where:

Qs – mass of sorbed $N\text{-}NO_3$ [mg/g.d.m.]
Co – initial concentration of $N\text{-}NO_3$ [mg/L]
Cs – $N\text{-}NO_3$ concentration after sorption [mg/L]
V – solution volume [L]
m – sorbent mass [g.d.m.]

To determine the maximum sorption capacity, the Langmuir (2) and Freundlich (3) adsorption isotherms were used.

$$\mathbf{Qs} = \frac{\mathbf{q_{max}}\cdot\mathbf{K_c}\cdot\mathbf{C}}{\mathbf{1}+\mathbf{K_c}\cdot\mathbf{C}} \qquad (2)$$

where:

Qs – mass of sorbed N-NO_3 [mg/g.d.m.]
C – the concentration of N-NO_3 remaining in solution [mg/L]
qmax – maximum sorption capacity in a Langmuir equation [mg/g s.m.],
Kc – constants in Langmuir equation [L/mg]

$$\mathbf{q_e = K \cdot C^n} \tag{3}$$

where:

q_e – mass of sorbed N-NO_3 [mg/g.d.m.]
K – sorption equilibrium constant in the Freundlich model
C – the concentration of N-NO_3 remaining in solution [mg/L]
n – Freundlich equation constant

4. Results and discussion

4.1 Effect of pH on nitrates sorption effectiveness on chitosan

At the initial solution pH of 2–3, the chitosan sorbent was dissolved. For this reason, the sorption effectiveness of N-NO_3 only for the initial pH range of 4–11 is shown in Figure 1A. Regardless of the degree of deacetylation, the sorption effectiveness of N-NO_3 on chitosan was highest at pH 4 and decreased with increasing pH, obtaining the worst result at pH 11 (Fig. 1A).

The high intensity of N-NO_3 sorption at low pH is due to the protonation of the chitosan amino groups (-NH_2 + H_3O^+ $\rightarrow$ NH_3^+ + H_2O). The positively charged amino groups attract the electrostatic ions of nitrates, which supports their sorption [11]. The amount of the-NH_2-protected groups and therefore the amount of nitrate-related sorbents decreases with increasing pH. At high pH, as a result of the deprotonation of functional groups, the sorbent gains a negative charge, which inhibits the sorption process of nitrates [10]. At pH 10–11, nitrate sorption may also be limited by competition with OH ions for chitosan sorption centres [12].

The effectiveness of the sorption of nitrates on chitosan sorbents increased along with the degree of deacetylation of chitosan. During the deacetylation, the acetyl group (in the form of CH_3COOH) is removed from the acetamide group, leaving the primary amine group (–$NHCH_3CO$ + H_2O $\rightarrow$ -NH_2 + CH_3COOH). Together with the degree of deacetylation, the number of protonisable amine functional groups, which are a potential sorption centre for anionic sorbates, is increased [13]. Therefore, the greater degree of deacetylation of chitosan means it has greater sorption potential relative to nitrates.

Chitosan sorbents affected the change in the pH of the solution during sorption (Fig. 1B). With the initial pH range of 4–9, the pH of the sorption was in the range from 6.4–7.4 (DD=75%), pH 6.6–8.1 (DD=85%) and pH 7.1–8.1 (DD=90%) at the end of the process. The reason for the observed changes in pH is the aim of the system to obtain a pH value of pH_{PZC} (PZC - Point of Zero Charge), characteristic for a sorbent. The pH_{PZC} of the tested chitosan sorbents were: pH_{PZC}=7.30 for DD=75%, pH_{PZC}=7.7 for DD=85% and pH_{PZC}=7.95 for DD=90% (Fig.1C).

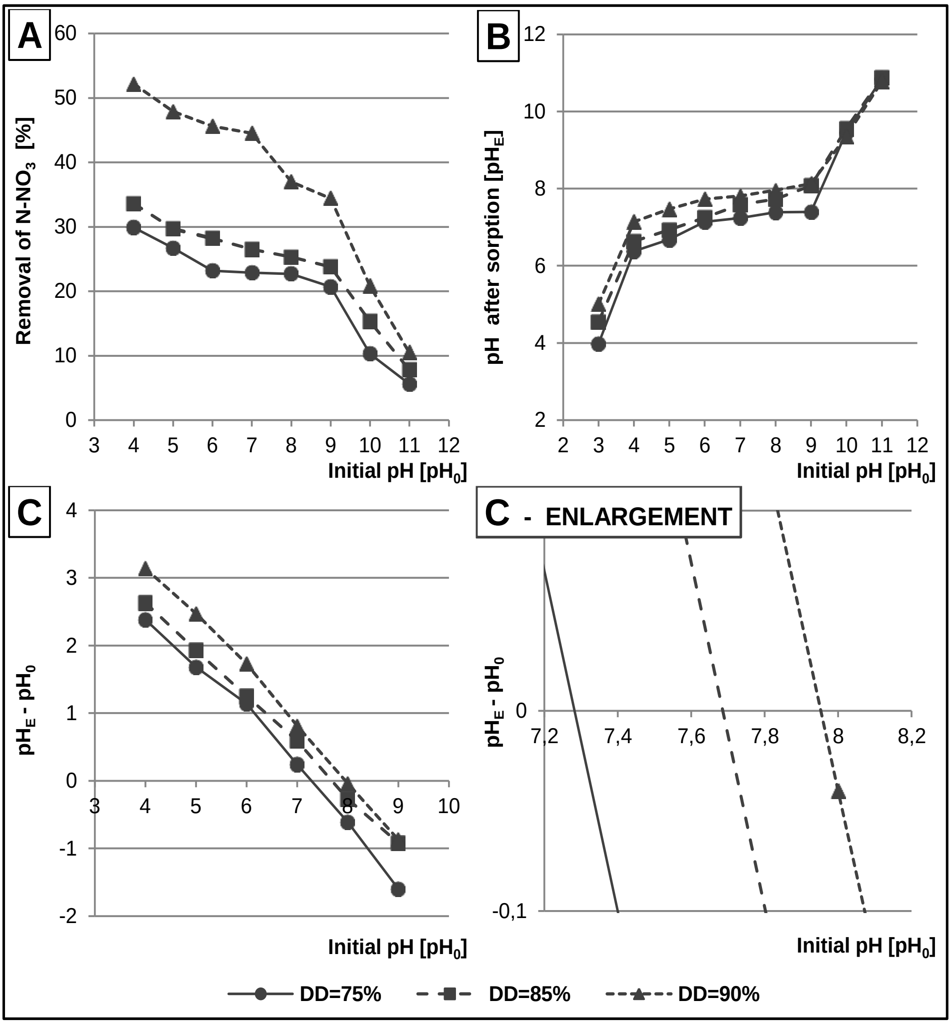

Figure 1. A) Effect of pH on the efficiency of N-NO_3 sorption on chitosan sorbent with DD=75/85/90%. B) Change in solution pH after sorption. C) Determination of pH_{PZC} of chitosan sorbents.

4.2. Sorption capacity over time

Experiments on the sorption capacity of the tested chitosan sorbents were carried out at the optimum pH of the sorption (pH 4), determined in section 4.1. In each research series, the Langmuir model showed the best fit to the experimental data (Tab. 2).

Regardless of the degree of deacetylation of chitosan, the maximum sorption capacity of the sorbents tested against nitrates was obtained after 30 min of sorption (Tab. 2, Fig. 2-3). The continued operation of the process resulted in desorption of the nutrient. The intensity of the sorption of nitrate from chitosans was highest in the first phase of sorption. The sorption capacity of chitosan with DD=75, 85 and 90% calculated after 5 min of sorption constituted 78, 88 and 93% of the maximum sorption capacity, respectively (obtained after 30 min) (Tab. 2).

Table 2. Constants designated from the isotherms: Langmuir and Freundlich

Sorption time [min]	**Deacetylation degree**	**Langmuir model**			**Freundlich model**		
		Q_{max} [mg/g]	K_c	R^2	k	n	R^2
5	**DD=75%**	**0.46**	1.1313	*0.981*	0.2419	0.2965	*0.968*
	DD=85%	**0.53**	1.0146	*0.981*	0.2640	0.3157	*0.968*
	DD=90%	**0.66**	1.3967	*0.961*	0.3659	0.2778	*0961*
15	**DD=75%**	**0.55**	1.2924	*0.967*	0.2984	0.2848	*0.967*
	DD=85%	**0.56**	1.4254	*0.993*	0.3142	0.2680	*0.957*
	DD=90%	**0.81**	2.2590	*0.959*	0.5215	0.2279	*0.882*
30	**DD=75%**	**0.59**	1.4018	*0.983*	0.3293	0.2728	*0.955*
	DD=85%	**0.60**	1.7194	*0.986*	0.3608	0.2465	*0.921*
	DD=90%	**0.87**	2.5028	*0.968*	0.5736	0.2168	*0.968*
60	**DD=75%**	**0.49**	1.4059	*0.970*	0.2920	0.2507	*0.946*
	DD=85%	**0.55**	1.4429	*0.984*	0.3135	0.2689	*0.966*
	DD=90%	**0.82**	2.5218	*0.970*	0.5394	0.2142	*0.873*

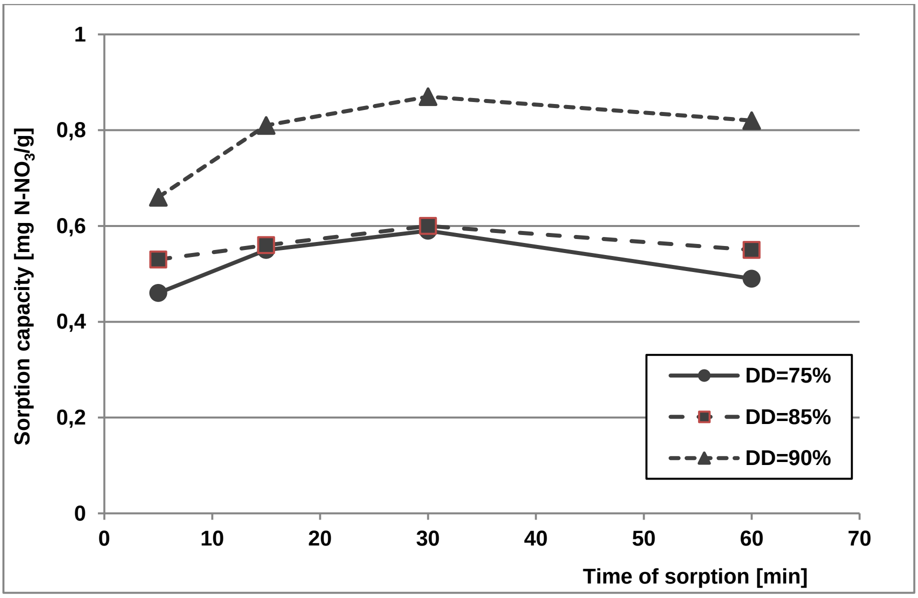

Figure 2. Chitosan sorption capacity with DD = 75/85/90% over time

A similar time (30 min), after which the amount of bound N-NO_3 on the sorbent was the highest, was also obtained in studies on the use of hydrogel chitosan sorbents to remove nutrients from the mixture of nitrates, nitrites and phosphates [11]. In the cited article, the phenomenon of desorption of nitrates was also observed, which intensified after 60 minutes of the process [11]. The main reason for the release of previously sorbed nitrate ions is most likely a change in the pH of the solution, caused by the aim of the system to obtain a pH close to the pH_{PZC} sorbent. With increasing pH, the amount of protonated chitosan amine groups responsible for the binding of nitrate ions to the surface of the sorbent is reduced, which results in the transfer of some of the N-NO_3 from the sorbent to the solution [12].

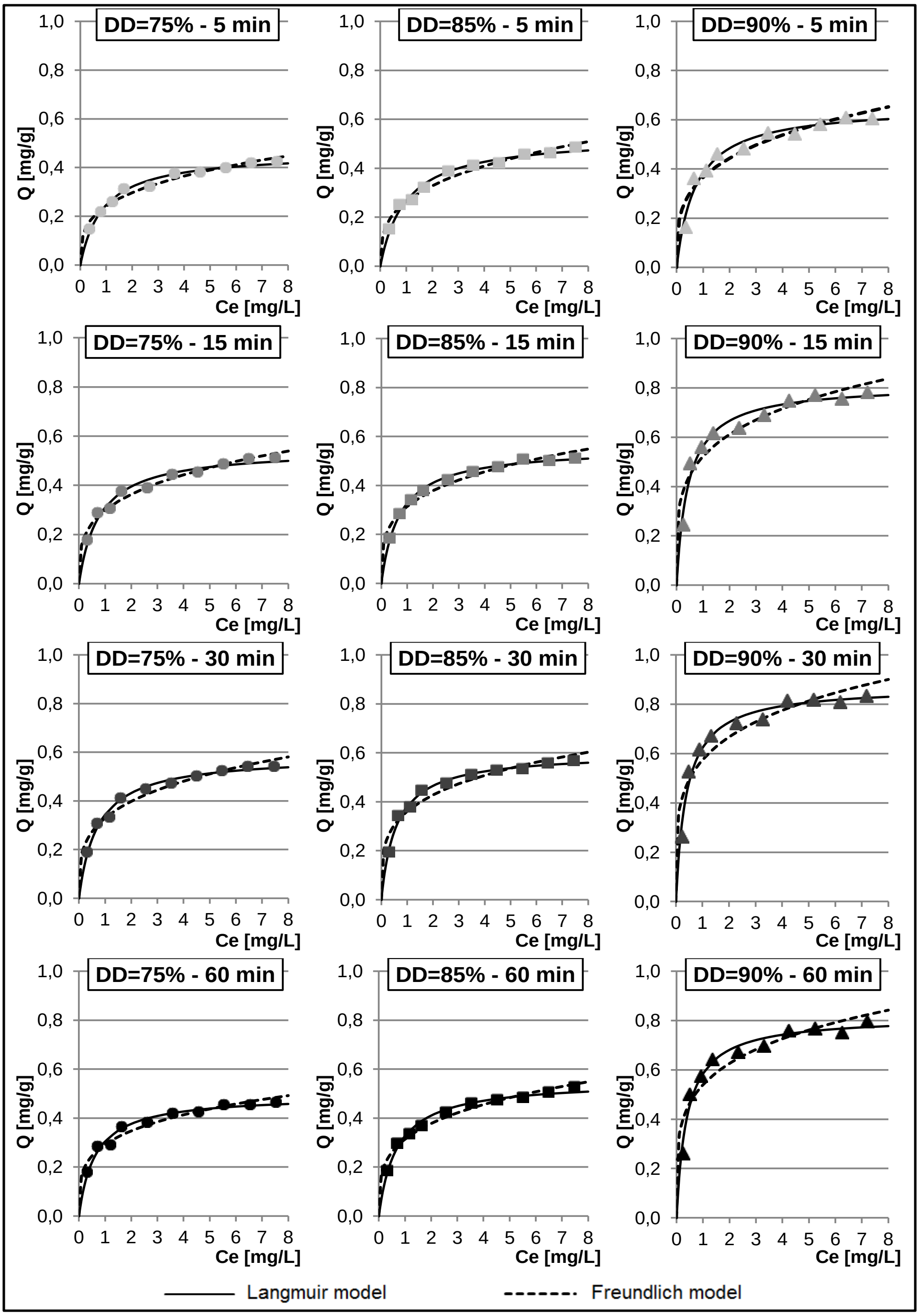

Figure 3. N-NO_3 sorption isotherms on a chitosan sorbent with DD=75/85/90% after 5, 15, 30 and 60 min

With the increase in the degree of deacetylation of chitosan, its maximum sorption capacity increased, which for DD=75, 85 and 90% was 0.59 mg N-NO_3/g, 0.60 mg N-NO_3/g and 0.87 mg N-NO_3/g, respectively (Tab. 2, Fig. 2-3). The higher degree of deacetylation also translated into a higher value of the Kc constant, indicating the degree of affinity of the sorbate for the sorbent.

The higher efficiency of the sorption of nitrates at a higher degree of deacetylation may result directly from a larger number of protonisable primary amine groups, as mentioned in Section 4.1. However, if the increase in the effectiveness of sorbitol nitrate on chitosan with the degree of deacetylation resulted only from a larger number of primary amine groups, the sorption capacity of chitosan with DD=90% should be greater than chitosan with DD=75% only by 20%. However, the research shows that the maximum capacity of chitosan with DD=90% relative to N-NO_3 is more than 47% higher than that of chitosan with DD=75%. Presumably, the degree of deacetylation may indirectly affect the spatial structure of the sorbent. At low pH, the positively charged chains of chitosan in the sorbent are repelled electrostatically, thanks to which the sorbent swells, increasing the access to sorptive centres located in its deeper layers. The electrostatic interaction between the chitosan chains is stronger relative to that of the degree of chitosan deacetylation. At low pH, a sorbent with a high degree of deacetylation probably has more nitrate-active sites than chitosan with a low degree of deacetylation [13, 14]. The influence of the degree of deacetylation on the availability of the deeper centres of sorption should be negligible at high pH, at which the sorbent structure is compact. This is confirmed by the results presented in Section 4.1 and Figure 1A, demonstrating the similar effectiveness of chitosan sorbents (with different degrees of deacetylation) at high pH.

5. Summary

The effectiveness of nitrate sorption on chitosan depends largely on its degree of deacetylation and grows in the series: DD=75% < DD=85% < DD=90%. The better sorption properties of chitosan with a higher degree of deacetylation results from the greater amount of primary amine groups, which are sorption centres for nitrates. The degree of deacetylation also has an indirect effect on the spatial structure of the chitosan sorbent. Probably at low pH, a chitosan sorbent with a higher degree of deacetylation is characterised by a more relaxed structure which is associated with a greater availability to deeper sorption centres.

Regardless of the deacetylation degree, nitrate sorption effectiveness on chitosan is highest at pH 4 and decreases with increasing pH, obtaining the worst result at pH 11. Sorption at lower pH (pH 2–3) results in the dissolution of the sorbent. The amount of nitrate associated with chitosan is the highest after 30 min of sorption. An excessively long process time results in desorption of nitrates, which is probably related to the change in pH of the system.

6. Acknowledgements

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