

THE INFLUENCE OF CHITOSAN FLAKE DEACETYLATION DEGREE ON ORTHOPHOSPHATE SORPTION EFFICIENCY FROM AQUEOUS SOLUTIONS

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Abstract

The article presents the effectiveness of orthophosphate sorption from aqueous solutions depending on the deacetylation degree of chitosan flakes.

The first stage of the research was to determine the pH value at which the sorption process was the most effective (from the pH range 2–11). In the second stage, research was carried out to determine the maximum sorption capacities of chitosan with deacetylation degrees of 75%, 85% and 90% in relation to PO_4^{3-} . The highest effectiveness of orthophosphate removal on chitosan, regardless of its deacetylation degree, was obtained at pH 4. At pH 2 and 3, the chitosan flakes dissolved. This study showed that the sorption effectiveness of phosphorus compounds depends on the deacetylation degree of chitosan. Along with the increase in deacetylation degree, the sorption capacity of chitosan also increases in relation to orthophosphates. It is related to the higher number of amino groups in the structure of chitosan, which are responsible for the sorption of pollutants in the form of anions. The maximum sorption capacity of chitosan-DD = 75% in relation to biogen was 5.13 mg/g, chitosan-DD = 85% was 5.65 mg/g, and chitosan-DD = 90% was 5.91 mg/g.

After 60 minutes, the desorption process had begun and was most likely caused by an increase in the pH of the solution. Due to chitosan's ability to neutralise the sample and the associated risk of desorption, the time of sorbent contact with sewage cannot be longer than 60 minutes.

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

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1. Introduction

Typical forms of phosphorus in aqueous solutions are orthophosphates, polyphosphates and organic phosphates. In natural waters, phosphorus occurs mostly in the form of orthophosphates [1]. Phosphorus is the basic nutrient for the growth of microorganisms in most ecosystems, but is also an indicator of the quality of surface water. The excess of phosphorus in natural waters is one of the main reasons for eutrophication [2]. The eutrophication process begins when the concentration of phosphates in water tanks is higher than 0.02 mg/l [3]. Eutrophication causes the depletion of oxygen, which subsequently leads to the death of fish and adversely affects other aquatic forms of life. The main sources of phosphorus which cause disturbances in aqueous environments are point sources, including municipal and industrial wastes and dispersed wastes such as agriculture [4]. The amount of phosphorus compounds from these sources should be controlled to prevent the eutrophication of lakes and other surface waters. Not only does accelerated eutrophication influence the life of organisms in natural waters, it also indirectly hinders economic progress, which largely depends on the availability of good quality water [5].

The sources of phosphorus in wastewater may be detergents, food leftovers, manure and industrial waste. For municipal sewage treatment plants, the most burdensome are industrial sewage, characterised by an increased content of nitrogen and phosphorus compounds [6]. Concentrated wastewater often causes the malfunction of conventional wastewater treatment plants; as a result, purified wastewater containing increased values of biogenic substances are directed to natural tanks. In order to reduce the water eutrophication process, some factories are obliged to pre-treat post-production sewage before discharging it into municipal sewage treatment plants [7].

There are several methods for the removal of phosphorus from wastewater, among which we can distinguish physicochemical and biological methods, such as reverse osmosis [8], electrodialysis, nanofiltration [9], and sorption [10].

The most commonly used method for the removal of phosphorus compounds from sewage is precipitation with calcium or iron and aluminium salts. However, these methods are relatively expensive and lead to the formation of large amounts of sediments and water salinity [11]. Therefore, it seems advisable to develop an effective and, at the same time, cheap method for the removal of phosphates from wastewater.

One of the most effective and safe methods for removing contaminants from wastewater is the sorption process. This technology is considered environmentally friendly. The effectiveness of sorption primarily depends on the type of sorbent used, and more specifically on the chemical structure of the sorbent. In the case of the removal of PO_4^{3-} ions from solution, the sorbent should have a positive charge in the solution, because electrostatic interactions between positively charged functional groups of the sorbent and PO_4^{3-} ions greatly support the sorption process.

Lately, it has been possible to observe increasing interest in chitin and chitosan among unconventional sorbents. Chitin is, after cellulose, the most widespread biopolymer in nature. According to data in the literature, the annual global production of chitin by living organisms reaches up to 10^{11} tons [12]. What is more, 120,000–200,000 tons of chitin are obtained in the world annually from the processing of waste from marine invertebrates [13]. Chitosan, on the other hand, is obtained as a result of the deacetylation of chitin. As a result, chitosan is considered a sorbent that is both cheap and easily available. Chitosan sorbents due to the presence of amino groups are particularly effective against anionic impurities. However, the efficiency of removing

such contaminants is greatly affected by the degree of deacetylation of chitosan. With an increase in the degree of deacetylation, there is also an increase in the number of free amino groups, which are the main centres of sorption. According to Crini and Badot [14], it is the degree of deacetylation and pH that are the biggest factors affecting the sorption capacity of chitosan.

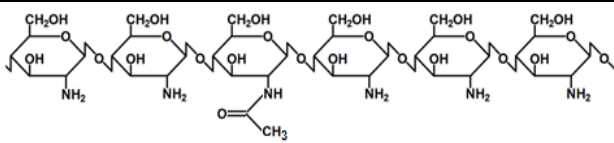
The main purpose of the research presented in this paper was to examine the effect of the degree of deacetylation of chitosan in the form of flakes on the effectiveness of removing orthophosphates from aqueous solutions using the sorption process. The scope of this research included: the effect of pH on the intensity of phosphate sorption and determination of chitosan capacity with a degree of deacetylation of 75, 85 and 90 % in relation to orthophosphates.

2. Materials and Methods

2.1 Chitin and chitosan

The sorbents used in the research were from Hepe Medical Chitosan GmbH in Halle. The chitin and chitosan specifications given by the manufacturer are shown in Table 1.

Table 1. Specification of chitosan

Specification of chitosan	Degree of deacetylation chitosan (DD)		
	75%	85%	90%
Structural formula			
Product	Hepe Medical Chitosan GmbH, Halle, Germany		
Viscosity	100 mPas		
Ash content in dry matter	< 1.0%		
Content of heavy metals	< 40 ppm		
Source of origin of raw material	exoskeletons of shrimps		

2.2 Chemical reagents

The following chemical reagents were used in the research: potassium hydrogen phosphate, hydrochloric acid, and sodium hydroxide. All of the mentioned reagents were purchased in POCH S.A., (Poland) and were characterised by the level of chemical purity: P.F.A.

2.3 Preparation of phosphate solution

In order to prepare a solution, 0.1433 g of potassium hydrogen phosphate (V) dried at 110°C was weighed on the analytical balance and placed into a beaker. Then, 700 cm³ of distilled water was added to dissolve the substrate. After mixing, the solution was quantitatively transferred into a volumetric flask (1000 cm³). The flask was then filled with distilled water to a volume of 1000 cm³ and the contents were mixed. The solution was kept in a dark room at a temperature of 4°C. The prepared solution contained 0.1 mg of orthophosphates in 1 cm³. The solution was used to prepare working solutions of P-PO₄. Adjustments to the pH of solutions were made with 0.1 and 1.0 M HCl and NaOH solutions.

2.4 Determination of the orthophosphate concentration in solution

The level of orthophosphate in solutions was measured by the ammonium molybdate spectrometric method in accordance with the Polish norm PN-EN ISO 6878: 2006.

2.5 Study on the influence of pH on the efficiency of orthophosphate sorption

Chitosan in the amount of 0.2 g d.m._{CHS} was weighed and placed into 300 cm³ conical flasks. Then, orthophosphate solutions (200 cm³) at a pH of 2–11 were added, and the flasks were placed on a shaker (150 rpm).

After 2 hours of the sorption process, samples (10 cm³) were taken to determine the concentration of nutrient left in the solution. The research parameters are summarised in Table 2.

Table 2. The research parameters upon the optimal pH for anion sorption

Sorbent concentration [g/dm ³]	Anions removed from the solution	Sorbate concentration [mg/dm ³]	Tested pH of the sorption [pH]	Sorption time [h]
1	PO ₄ ³⁻	1	2, 3, 4, 5, 6, 7, 8, 9, 10, 11	2

2.6 Determination the maximum sorption capacity

The adsorbent in the amount of 0.2 g d.m. was weighed and put into 250 cm³ conical flasks along with 200 cm³ of the solution of tested adsorbate at concentrations of 1, 2, 3, 4, 5, 6, 7, 8, 10, 15, and 20 mg PO₄³⁻/dm³. The solutions had an optimal pH which was determined to be 2.5. The flasks were then placed on a shaker (200 rpm). Samples in the amount of 10 cm³ were taken after 5 min, 15 min, 30 min and 60 min in order to mark the concentration of the remaining sorbate. Based on the results obtained, the maximum sorption capacity of chitosan sorbents was determined. The research parameters are summarised in Table 3.

Table 3. Parameters of research upon determining the maximum capacity of individual biogenes in the mixture

Sorbent concentration [g/dm ³]	Sorbent	Sorbate	Sorbate concentration [mg/dm ³]	Sorption time [min]
1	Chitosan-DD=75%	P-PO ₄	1, 2, 3, 4, 5, 6, 7, 8, 10, 15, 20	5, 15, 30, 60
	Chitosan-DD=85%		1, 2, 3, 4, 5, 6, 7, 8, 10, 15, 20	
	Chitosan-DD=90%		1, 2, 3, 4, 5, 6, 7, 8, 10, 15, 20	

2.7 Determination of the zeta coefficient

In order to determine pH_{ZPC} of sorbents, 50 ml of 0.01 M KNO₃ solution with an initial pH (pH₀) ranging from 3 to 12 was added to the conical flask. Then, 1 g of sorbent was also added to each flask and the mixture was stirred for 24 hours. After this time the final pH of the solution was measured. PH_{ZPC} value was determined based on the curve. The zero point for beech sawdust was located at the intersection of the curve defining the relation of ΔpH to pH₀ with the axis of a graph on which the pH₀ is marked [15].

3. Calculation methods

Two different adsorption models were used to determine the maximum sorption capacity.

Homogeneous Langmuir model (1):

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

where:

- q_e – equilibrium amount of the adsorbed nutrient [mg/g]
- q_{max} – maximum adsorption capacity of adsorbent monolayer [mg/g]
- K_c – constants in the Langmuir equation [dm³/mg]
- C – concentration of the nutrient remaining in the solution [mg/dm³]

Heterogeneous Freundlich model (2):

$$q_e = K \cdot C^n \quad (2)$$

where:

- q_e – equilibrium amount of the adsorbed nutrient [mg/g]
- C – concentration of the nutrient remaining in the solution [mg/dm³]
- K – sorption equilibrium constant in the Freundlich model
- n – parameter of heterogeneity

The adjustment of experimental data to mathematical models was determined with the use of the correlation coefficient R² (3):

$$R^2 = \frac{\sum(q_{\text{cal}} - \bar{q}_{\text{exp}})^2}{\sum(q_{\text{cal}} - \bar{q}_{\text{exp}})^2 + \sum(q_{\text{cal}} - q_{\text{exp}})^2} \quad (3)$$

where:

- R^2 – correlation coefficient – measure of data alignment to the model
- q_{exp} – experimental data – quantity of adsorbed nutrient [mg/g]
- q_{cal} – theoretical data resulting from the model – quantity of adsorbed nutrient [mg/g]

4. Results and discussion

4.1 The influence of pH on the effectiveness of P-PO₄ sorption

The effectiveness of nutrient sorption depended heavily on the pH of the solution. In the pH range from 4–11 the effectiveness of the P-PO₄ sorption on chitosan sorbents decreased along with the increase in the initial pH of the solution (Fig. 1a, 1b and 1c). A similar tendency was observed in the research upon the sorption of P-PO₄ at the goethite–water interface [16], layered double hydroxides [17] and nanoparticles of zirconium oxide [18]. The sorption abilities of chitosan in relation to pollutants in the form of anions mainly resulted from the electrostatic interaction between PO₄³⁻ ions and amino groups responsible for P-PO₄ sorption. In acidic environments there is an increase in the amount of protonated –NH₂ groups, which subsequently leads to an increase in the effectiveness of anionic nutrient sorption, which is also confirmed by the research presented in this work [19,20].

The effectiveness of phosphate removal from the solution at pH 4 with chitosan-DD = 75% was 46.3%, and for chitosan-DD = 85% was 50.5%, whereas for chitosan-DD = 90% the effectiveness was the highest and reached 54.2%. At pH 2 and 3, the chitosan flakes dissolved regardless of the deacetylation degree and lost their sorption abilities. The highest effectiveness of wastewater treatment at pH 4 as well as the ability of chitosan flakes to solubilise at lower pH was also proved by Saha et al. [21], who used chitosan flakes to treat colourful wastewater.

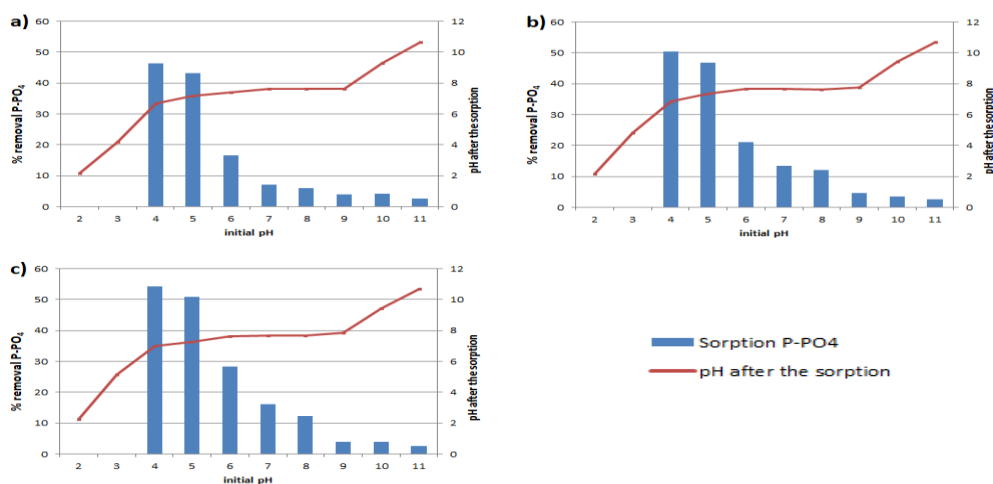


Figure 1. Effect of pH value on the effectiveness of P-PO₄ sorption onto a) chitosan-DD = 75 %, b) chitosan-DD = 85 % and c) chitosan-DD = 90 %

Above pH 5, the efficiency of phosphate sorption on chitosan gradually decreased, while the lowest sorption efficiency was recorded in the pH range from 9–11. Under alkaline conditions, the chitosan surface gains a negative charge and repulses PO_4^{3-} ions from the sorbent surface, limiting sorption. In addition, a significant decrease in sorption efficiency at a pH above 7 may be associated with increasing competition between $-\text{OH}$ groups and PO_4^{3-} ions for active sites [22, 23].

The deacetylation degree of the sorbent had a significant influence on the change in the pH of the solution during sorption. In the case of chitosan-DD = 75%, for the initial pH of the solution ranging from 5–9 after sorption, the pH of the solution was always higher than 7 and was between 7.16 and 7.62 (Fig. 1a), whereas for the initial pH = 4, the pH after sorption was lower than 7 and was 6.69. The pH_{ZPC} was around 7.24 (Fig. 2). Similar to previous sorbent results, also in the case of chitosan with the degree of deacetylation of 85%, for the initial pH of the solution ranging from 5–9 after the sorption process, the pH was higher than 7, ranging between 7.35 and 7.77 (Fig. 1b). Only in the case of the solution with an initial pH = 4 was the pH after sorption lower, equalling 6.86, with the aim of reaching a pH value close to the $\text{pH}_{\text{ZPC}} = 7.59$. (Fig. 2). In the case of the sorbent with the highest deacetylation degree, the pH of the solution after the process of sorption was always higher than 7 in the pH range of the initial solution from 4–9, ranging between 7.01 and 7.8, with the solution trying to reach $\text{pH}_{\text{ZPC}} = 7.81$. Chitosan's ability to neutralise the solution at an optimum pH of 4 is of great importance for the operators of wastewater treatment systems. The correction of the pH of the solution after the adsorption process is not required. The pH_{ZPC} values of chitosan increased with an increasing degree of deacetylation, which is indirect evidence that a higher degree of deacetylation of chitosan corresponds to a larger amount of free amino groups in the sorbent structure. The free amino groups of chitosan capable of being protonated are responsible for the basic nature of the sorbent.

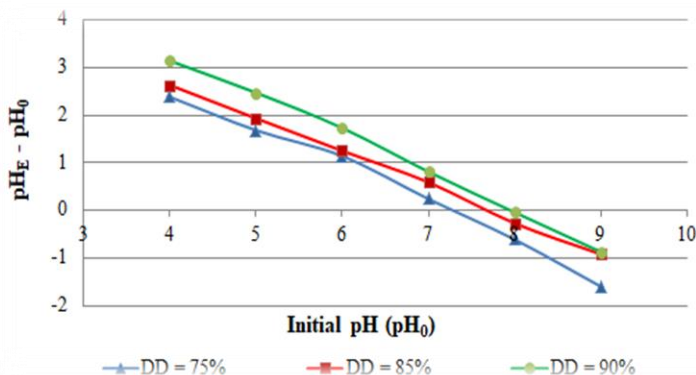


Figure 2. The pH of the solution before and after the sorption of phosphates, depending on the initial pH of the solution (method of pH_{ZPC} determination from chapter 2.7).

4.2 Maximum sorption capacity

Based on preliminary research, the study was carried out to determine the maximum sorption capacity of the sorbents. The obtained data were described by homogeneous Langmuir and Freundlich models. For both models, the constants were determined with the non-linear regression method. The measure of the curve fitting the experimental data was the coefficient of determination R^2 . In both cases, the best fit to experimental data

showed the Langmuir model, which indicates that the sorbent has a certain number of active sites located on its surface and that each of these sites is able to adsorb only one molecule of substance removed from the solution. Therefore, a monomolecular adsorbent layer is formed on the surface of the adsorbent [24].

In Figure 3 the sorption isotherms of P-PO₄ on chitosan flakes with deacetylation degrees of 75, 85, and 90% were shown, while Table 4 includes the matching factors and reaction constants.

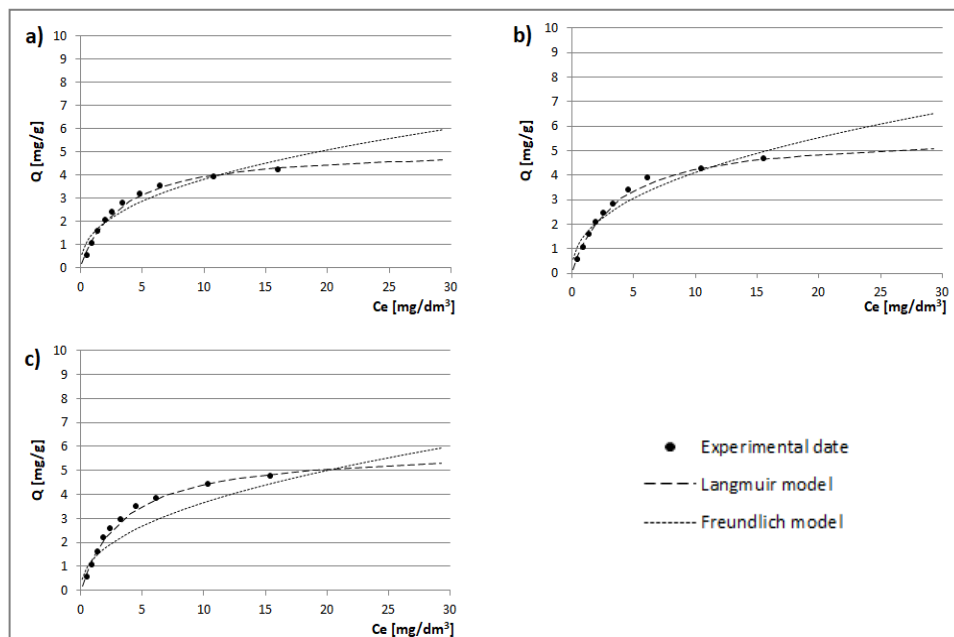


Figure 3. Experimental results and isotherms after 30 minutes of P-PO₄ sorption onto a) chitosan-DD = 75%, b) chitosan-DD = 85% and c) chitosan-DD = 90%

From the data shown in Table 4 and Figure 4, it can be seen that along with the increase in deacetylation degree of chitosan, there is also an increase in its sorption capacity in relation to phosphates. Maximum sorption capacity after 30 minutes for chitosan-DD = 75% was 5.3 mg/g, while for chitosan-DD = 85% it was 5.65 mg/g, and for chitosan with the highest deacetylation degree it was 5.91 mg/g. Different sorption abilities of chitosan sorbents in relation to phosphates resulted from varying amounts of amino groups in the sorbent structure, which are responsible for the process of anion sorption [25]. The higher the deacetylation degree of chitosan in the form of flakes, the greater the amount of -NH₂ groups and the higher the effectiveness of anion removal. The same conclusion was obtained by Piccin et al. [26], who investigated the effect of the degree of deacetylation of chitosan on the effectiveness of azobenzene FD&C Red No. 40 sorption (C.I. 16035). They proved that the increase in deacetylation degree from 42 to 84% resulted in an increase in the effectiveness of FD & C Red No. 40 removal by 40%. Increased sorption abilities along with the increase in the degree of deacetylation of chitosan has also been observed in studies on the sorption of dyes by Gonçalves et al. [27]. 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 the chitosan deacetylation degree. At low pH, a sorbent with a high degree of deacetylation probably has more phosphate-active sites than chitosan with a low degree of deacetylation [25]. In the majority of research series, the value of K_c coefficient increased along with an increase in the degree of deacetylation of chitosan. This may indicate a higher affinity of sorbate for the sorbent, which is caused by a larger number of amine groups in the sorbent responsible for the sorption of $P-PO_4$.

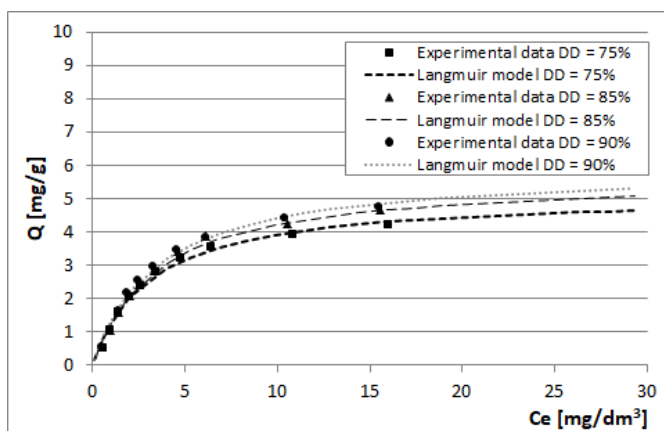


Figure 4. Experimental results and isotherms Langmuir of $P-PO_4$ sorption onto chitosan after 30 minutes

Table 4. Isotherms of $P-PO_4$ sorption onto chitosan

Time	Deacetylation degree	Langmuir model			Freundlich model		
		Q_{max}	K_c	R^2	k	n	R^2
		[mg/g]					
5 min	75 D	4.4792	0.2198	0.983	1.0190	0.4636	0.913
	85 D	4.8788	0.2138	0.985	0.7400	0.4700	0.917
	90 D	4.8704	0.2493	0.988	1.2275	0.4327	0.921
15 min	75 D	4.6628	0.2542	0.981	1.1679	0.4422	0.902
	85 D	4.9986	0.2696	0.993	1.3000	0.4348	0.926
	90 D	5.2788	0.2500	0.994	1.3015	0.4493	0.941
30 min	75 D	5.1317	0.3222	0.991	1.4813	0.4118	0.914
	85 D	5.6479	0.2942	0.989	1.5345	0.4279	0.913
	90 D	5.9056	0.2945	0.993	1.5807	0.4353	0.926
60 min	75 D	4.6404	0.3285	0.900	1.3688	0.4037	0.915
	85 D	5.0059	0.3130	0.992	1.4232	0.4150	0.919
	90 D	5.1175	0.3325	0.981	1.5081	0.4059	0.898

5. Conclusions

Sorption capacity depends on the construction of the sorbent and sorption parameters such as the pH of the process. The conducted research has shown that the effectiveness of the phosphate sorption increases along with an increase in the deacetylation degree of chitosan, because the higher deacetylation degree leads to more free amino groups, which are the main sorption centres for pollutants in the form of anions. The effectiveness of the P-PO₄ removal on chitosan also depended heavily on the pH at which the process was carried out. At low pH values, some of the functional groups of sorbent were protonated, which positively influenced the sorption of PO₄³⁻. Considering that, the pH at which the process of sorption ran the most effectively for all sorbents was set at pH 4. At a lower pH, the sorbents dissolved and lost their sorption abilities. The highest sorption capacities for all three sorbents were obtained after 30 minutes of sorption, whereas the process of desorption began after 60 minutes, probably caused by the increase in the pH of the solution. The results obtained were described with the use of a homogeneous Langmuir model, because it was characterised by the best fit to experimental data ($R^2 > 0.99$). The maximum sorption capacity for chitosan with the deacetylation degree of 75, 85 and 90% in relation to phosphorus compounds after 30 minutes was 5.15, 5.65 and 5.91 mg/g, respectively.

6. Acknowledgements

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7. References

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