PHOSPHATE REMOVAL FROM AQUEOUS SOLUTIONS BY CHITIN AND CHITOSAN IN FLAKES

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Abstract

The article presents the effectiveness of phosphate adsorption on the flakes of chitin and chitosan. Studies performed determined adsorption capacity of chitin and chitosan, best among the tested adsorption pH and the equilibrium time. Langmuir model was used to describe the results. The highest removal efficiency of phosphorus compounds using chitin was obtained at pH 3 and with chitosan at pH 4. The study of phosphate equilibrium concentration time obtained for both sorbents was carried out at three concentrations of 1, 5 and 10 mg/dm³. The highest sorption efficiency of the phosphate using chitin was achieved after 20 minutes of the process and at the chitosan after 40 minutes. In the case of chitosan after the equilibrium time the effect of partial P-PO₄ release was observed, which could be related to the change in pH of the solution by the sorbent. Studies have shown that chitosan is a more effective absorbent for phosphorus compounds. The maximum adsorption capacity of chitosan with phosphate was 6.65 mg/g, and chitin - 2.09 mg/g.

Key words: *adsorption, chitosan, chitin, phosphate*

1. Introduction

Phosphorus (P) is an essential nutrient for the growth of microorganisms in most ecosystems, but an excess of phosphates in the water is one of the main factors causing eutrophication [1]. Eutrophication process begins when the concentration of phosphates in water reservoirs is greater than 0.02 mg/dm^3 [2]. This concentration becomes usually exceeded by the discharge of treated wastewater containing large amounts of nutrients into the natural reservoirs. This is often due to the malfunction of the conventional sewage treatment plant which is associated with wastewater with high concentration of nutrients delivered.

Detergents, food, feces and industry may be sources of phosphorus in the wastewater. Industrial wastewater, often characterized by a higher content of nitrogen and phosphorus compounds is the most burdensome for urban wastewater treatment plants. In order to reduce water eutrophication some industrial plants are required to pre-treat the post-production waste before discharging it to municipal treatment plants [3].

One of the most effective removal methods of phosphorus from wastewater is precipitation with lime or with salts of iron and aluminum. These methods, however, are relatively expensive and lead to the salinity of the water and to the generation of high quantities of sludge [4]. It seems appropriate, therefore, to develop an effective and also inexpensive method of removing phosphate from wastewater.

An alternative method for removing phosphate from the wastewater can be sorption. The costs of this process depend inter alia on price, availability and efficiency of the sorbent. The main factor influencing the performance of the sorption process is the chemical structure of sorbent and sorbate. Sorbent in the solution should have a positive charge in order to remove PO_4^{3-} ions from the solution. Electrostatic interactions between positively charged functional groups of the sorbent and PO_4^{3-} ions significantly enhance sorption process.

Chitin and chitosan have recently become increasingly popular among non-conventional sorbents. Chitin is one of the most common biopolymers in nature, whereas chitosan is obtained by chemical means from chitin. It is estimated that annual production of chitin by living organisms is about 10^{11} tons [5]. Therefore, chitin and its derivative - chitosan are considered to be adsorbents both cheap and easily available. Chitosan is obtained by enzymatic and chemical deacetylation of chitin. The exchange from acetamide to amine groups changes its physical and chemical properties [6]. High adsorption capacity of chitosan is associated with the presence of free amino groups, which are exposed as a result of deacetylation [7].

The main objective of the research was to assess the possibility of removing phosphorus compounds in the process of adsorption with adsorbents of biological origin - chitin and chitosan in the form of flakes. The scope of research included: the effect of pH on phosphate sorption intensity, sorbate and sorbent optimal contact time and determining chitin and chitosan capacity in relation to phosphates.

2. Materials and methods

2.1. Chitin and chitosan

Chitosan and chitin were purchased from Heppe Medical Chitosan GmbH in Halle. Characteristics of adsorbents were presented in Table 1.

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Table 1. Characteristics of chitosan and chitin

	Chitosan	**Chitin**
Structural formula		
Deacetylation degree	82,6 % - 87,5 % (an average of 85,0 %)	< 15%
Origin of the material	Shrimp shells	Shrimp shells

2.2. Chemical reagents

In the study the following chemical reagents were used: potassium hydrogen phosphate, hydrochloric acid and sodium hydroxide. All the reagents were purchased in POCH SA (Poland) and characterized by a level of chemical purity: pure for analysis.

2.3. Preparation of the basic phosphate solution

In order to prepare the basic solution were 1.4325 g of potassium dihydrogen phosphate (KH_2PO_3) of potassium dried at 110°C weighed on an analytical balance and applied into a beaker. Next, ca. 700 cm^3 of distilled water was added to the beaker to dissolve the substrate. The solution was quantitatively transferred to a volumetric flask (1000 cm^3) after stirring. The flask was then supplemented to the mark with distilled water and the contents were mixed. The basic solution was stored in a dark room at a temperature of 4°C. Thus prepared solution contained 1 mg of orthophosphate in 1 cm^3. The basic solution served the preparation of working P-PO$_4$ solutions. Adjustments to the pH of the solutions were carried out using a 0.1 and 1.0 M solutions of HCl and NaOH.

2.4. Determination of the orthophosphate concentration in solution

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

2.5. Study on the pH Impact on the orthophosphate sorption efficiency

Chitin and chitosan in an amount of 0.2 g d.m. and then an orthophosphate solution (200 cm^3) at pH 2 - 11 was added the conical flasks of 300 cm^3. The flasks were placed on a shaker (150 r.p.m.). After 2 h of the sorption process, the solution samples were taken (10 cm^3) to determine the concentration of the P-PO$_4$ left in the solution (Ce). Study parameters are summarized in Table 2.

Table 2. Parameters of solutions to analysis of the effect of pH value on adsorption

Sorbent concentration [g/ dm^3]	Sorbate	Sorbat concentration [mg/dm^3]	Tested pH of the sorption	Sorption time [h]
1	P-PO$_4$	1	2, 3, 4, 5, 6, 7, 8, 9, 10, 11	2

2.6. Determination of the optimal sorption time

A sorbent in an amount of 2 g d.m. and 2000 cm^3 of a solution containing P-PO$_4$ at 1, 5, 10 mg/dm^3 and pH determined in the first stage of research were dispensed into the 2500 cm^3 beaker. At intervals samples of 5 cm^3 were collected in order to determine the concentration of nutritient left in the solution (Ce). Parameters of the experiment concerning the time of reaction are summarized in Table 3.

Table 3. Parameters of determination of adsorption equilibrium time

Sorbent concentration [g/dm^3]	Sorbat concentration [mg/dm^3]	Sample collection times [min]
1	1	0, 1, 5, 10, 20, 30, 40, 50, 60, 90, 120, 180, 240, 300
	5	
	10	

2.7. Determination of the maximum sorption capacity

Adsorbent in an amount of 0.2 g d.m. and a solution of 200 cm^3 of the tested adsorbate at a concentration of 0.5; 1; 2.5; 5; 7.5; 10; 12.5; 15; 20; 25 mg PO$_4^{3-}$/dm^3 were measured to the conical flasks of 250 cm^3. Solutions had optimal set out in point pH of 2.5. The flasks were placed on a shaker (200 rpm) for the time specified in paragraph 2.6. After a certain time, phosphate concentration left in the solution was marked. Based on these results, the maximum sorption capacity of chitin and chitosan was determined. Parameters of these studies are summarized in Table 4.

Table 4. Parameters of analyses of the maximum adsorption capacity

Sorbent concentration [g/dm^3]	Sorbent	Sorbate	Sorbate concentration [mg/dm^3]	Sorption time [min]
1	Chitosan	P-PO$_4$	0,5; 1; 2,5; 5; 7,5; 10; 12,5; 15; 20; 25	40
	Chitin		0,5; 1; 2,5; 5; 7,5; 10; 12,5; 15; 20; 25	20

2.8. Determination of zeta potential

In order to determine pH$_{ZPC}$ of chitin and chitosan, 50 ml of 0.01 M K$_3$PO$_4$ solution with an initial pH (pH$_0$) from 3 to 12 was added to the conical flask. To each flask was also added 1 g of sorbent and then the mixture was stirred for 24 hours. After this time the final pH of the solution was measured. Value of zeta potential will be determined on the basis of the curve. The zero point for sorbent will be located at the intersection of the curve defining the relationship ΔpH (pH $_{after\ sorption}$ − pH $_{initial}$) to pH$_0$ with the axis of a graph on which are marked pH$_0$ [8].

2.9. Computational Methods

The amount of P-PO$_4$ absorbed on chitin and chitosan was calculated from the equation (1):

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

where:

Qs – mass of P-PO$_4$ sorbed [mg/g]

Co – the initial concentration of P-PO$_4$ [mg/dm^3]

Cs – concentration of P-PO$_4$ after sorption [mg/dm^3]

V – volume of the solution [dm^3]

m – mass of the sorbent [g]

To determine the maximum sorption capacity two different models of adsorption were used.

The homogeneous Langmuir model (2):

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

where:

q$_e$ – equilibrium amount of P-PO$_4$ absorbed [mg/g]

q$_{max}$ – maximum adsorption capacity of adsorbent monolayer [mg/g]

K$_c$ – constants in Langmuir 2 equation [dm^3/mg]

C – concentration of adsorbed substance in the state of equilibrium [mg/dm^3]

The heterogeneous Freundlich model (3):

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

where:

q$_e$ – equilibrium amount of P-PO$_4$ absorbed [mg /g]

C – concentration of adsorbed substance in the state of equilibrium [mg /dm^3]

K – equilibrium sorption constant in the Freundlich model

n – heterogeneity parameter

Fitting of the experimental data for the mathematical models determined using the correlation coefficient R^2 (4):

$$R^2 = \frac{\Sigma(q_{cal} - \overline{q}_{exp})^2}{\Sigma(q_{cal} - \overline{q}_{exp})^2 + \Sigma(q_{cal} - q_{exp})^2} \tag{4}$$

where:

R^2 – correlation coefficient (a measure of data alignment to the model)

q$_{exp}$ – the experimental data (sorbed amount of P-PO$_4$) [mg/g]

q$_{cal}$ – theoretical data resulted from the model (sorbed amount of P-PO$_4$) [mg/g]

3. Results and Discussion

3.1. Effect of pH on the effectiveness of the P-PO$_4$ sorption

The efficiency of adsorption of P-PO$_4$ to a large extent depended on the pH of the solution. In the pH range of 4 – 11 effectiveness of the sorption P-PO$_4$ both for the chitin and for the chitosan decreased with increasing initial pH of the solution (Fig. 1a and 1b). A similar trend has been observed in studies of sorption of P-PO$_4$ at polymer – chitosan composite [9], iron oxide and aluminum containing balls [5] and oxygen furnace slag [10].

Sorption capacity of chitosan in relation to P-PO$_4$ is mainly due to electrostatic attraction between PO$_4^{3-}$ ions and amino groups capable of protonating. The amount of protonated -NH$_2$ groups that are responsible for sorption of P-PO$_4$ increases as the pH decreases. Therefore, the effectiveness of the adsorption of anionic nutrients on chitosan was highest in acidic solution [11, 12].

P-PO$_4$ sorption for the chitin preferably occurred at pH 3.Efficiency of removing phosphate from the solution using chitin at pH 3 was 33%. In the case of chitosan sorption P-PO$_4$ was the highest at pH 4, and its efficiency was 56%. In the pH range of 2 – 3 chitosan petals underwent dissolution and lose the sorption ability. The highest efficiency of wastewater treatment at pH 4, and the ability to disintegrate chitosan flakes at a pH of 2 to 3 confirmed Pitakpoolsil et al. (2013), who have used chitosan for oil wastewater treatment [13].
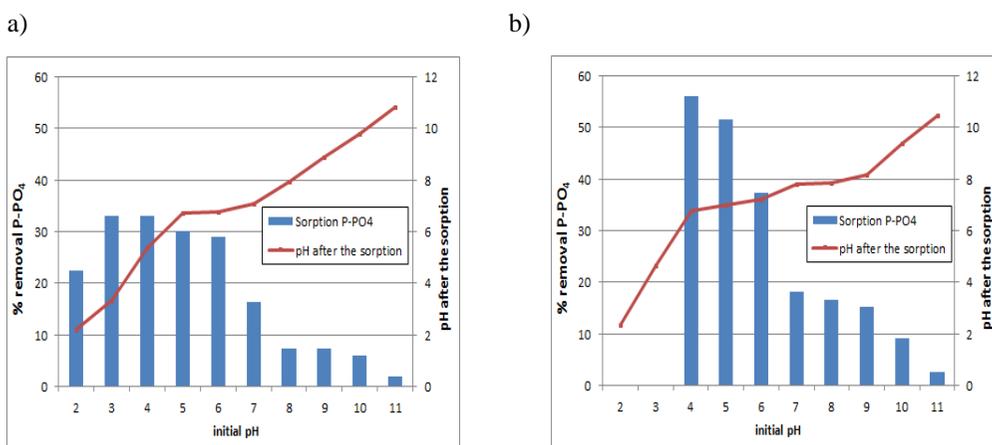
a)   b)

Figure 1. Effect of pH value on the effectiveness of P-PO$_4$ sorption onto **a)** chitin and **b)** chitosan

At pH greater than 5 the efficiency of phosphate adsorption on chitosan gradually decreased. The lowest efficiency of sorption was observed in the pH range of 8 – 11. In the alkaline conditions, chitosan surface attains the negative charge, as a result of which it repulses electrostatically the anionic P-PO$_4$ and prevents their sorption [14]. According to Crini and Badot low efficiency of sorption in the solution below pH 7 the OH$^-$ with PO$_4^{3-}$ ions for active sites of the adsorbent, which significantly impairs the chemisorption proces [15].

Type of tested sorbent had a large impact on the change of pH of the solution during sorption. In the case of chitin for the initial pH of a solution in the range of 5 – 7, after sorption pH of the solution determined the pH in the range 6.74 – 7.1 (Fig. 1a), while pH$_{ZPC}$ reverted to 7.2 (Fig. 2). In the case the initial pH of the chitosan solution in the range 4 – 8 after sorption determined the pH of the solution in the pH range of 6.75 – 7.86 (Fig. 1b). The system has always sought to achieve a pH close pH$_{ZPC}$ = 7.9 (Fig. 2). The ability of chitosan to neutralize the solution with optimal pH 4 is of great importance for sewage treatment systems exploiters. An adjustment of the pH of the solution after the adsorption process is not then necessary. However, in the case of chitin for the initial solution pH of 3 (highest sorption efficiency) after the sorption process pH of 3.33 is obtained (Fig. 1). Therefore treated wastewater would have to be neutralized before discharge into the natural reservoir.
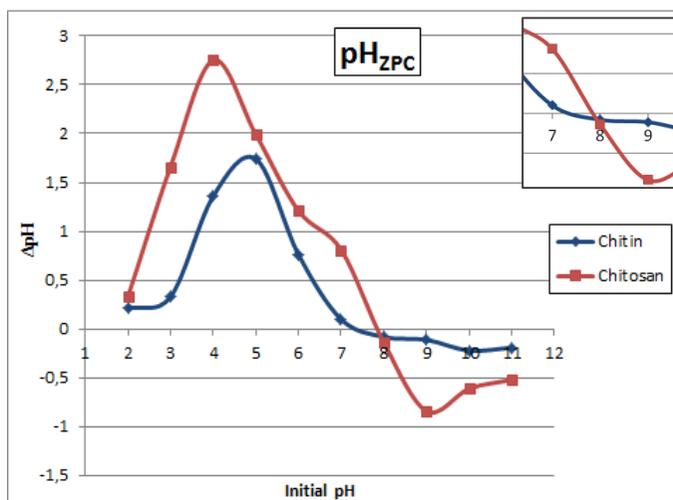
Figure 2. The pH of the solution before and after sorption of phosphates depending on the initial pH of the solution (the method of determining pH$_{ZPC}$ section 2.8)

3.2. Determination of reaction equilibrium time

Figure 3 shows the relationship between the amount of bound phosphorus on the duration of the reaction. The highest sorption efficiency of the phosphate chitin for all concentrations was obtained after 20 minutes of the process (Fig. 3a) and for chitosan after 40 min (Fig. 3b). At this time, in the case of chitosan, the concentration of P-PO$_4$ in the solution began to increase, suggesting that absorbed orthophosphates began to undergo desorption.

The phenomenon of releasing P-PO$_4$ may be related to changes in pH as a result of the neutralization by the sorbents. The solution in which the sorption takes place always tries to get pH close to pH$_{ZPC}$ of the sorbent (pH$_{chitin}$ ≈ 7.2; pH$_{chitosan}$ ≈ 7.9). The increase in the pH of the solution decreases the electrostatic forces of attraction between the centers of sorption of the sorbent and anionic orthophosphates. In the case of chitosan, the initial pH of the solution equal to 4 in the sorption process value close to pH of 6.75. In contrast, chitin does not have the ability to neutralize the solution with the optimal pH 3, and therefore the process of desorption occurs at a much lesser extent. Therefore sorption of phosphates on both chitin and chitosan should be performed at a specific time.

Equilibrium time reaction for the two sorbents was determined for three phosphates concentrations of 1, 5 and 10 mg /dm^3. For both chitin and chitosan highest efficiency was obtained for the lowest concentration. The percentage of removal of phosphate from a solution of 1 mg /dm^3 by chitin was about 31%, whereas by the chitosan was approximately 57%. The lowest phosphorus removal efficiency for both sorbents were obtained at a concentration of 10 mg /dm^3 – for 14.5% of chitin and 35% for chitosan (Fig. 3). Also, Nguyen et al. (2014) [16] and Filipkowska et al. (2015) [17] confirms that the lower the initial concentration of phosphorus in the solution, the faster and more efficiently sorption process occurs. This may be due to the high concentration of sorbate against a sorption capacity of the sorbent.
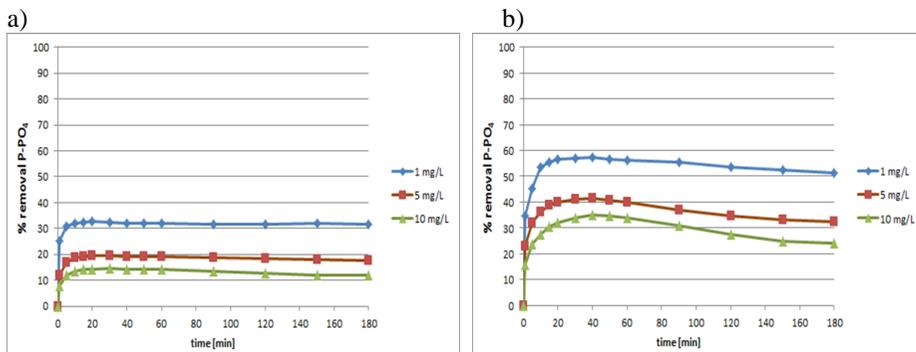
a)

b)

Figure 3. Determination of equilibrium time of P-PO$_4$ sorption reaction onto a) chitin and b) chitosan

3.3. Maximum sorption capacity

On the basis of preliminary tests, researches for determining the maximum adsorption capacity for both sorbents were conducted. The data obtained were described by the homogeneous Langmuir model and a Freundlich model. For both models constants were determined using nonlinear regression. The measure of curve fitting to the experimental data was the coefficient of determination R^2. In both cases best match to the experimental data showed Langmuir model, which may indicate the binding of phosphate by active sites on the surface of the sorbent. Therefore adsorbed molecules do not interact with each other and do not form a multilayer. The amount of contaminants removed depends on the maximum of the monolayer capacity of the sorbent (Q_{max}) and the affinity of the sorbent to sorbate (K_c) [18].

Figure 4 shows the P-PO$_4$ sorption isotherm on chitosan and chitin petals, while in Table 5 fitting coefficients and reaction constants were included.
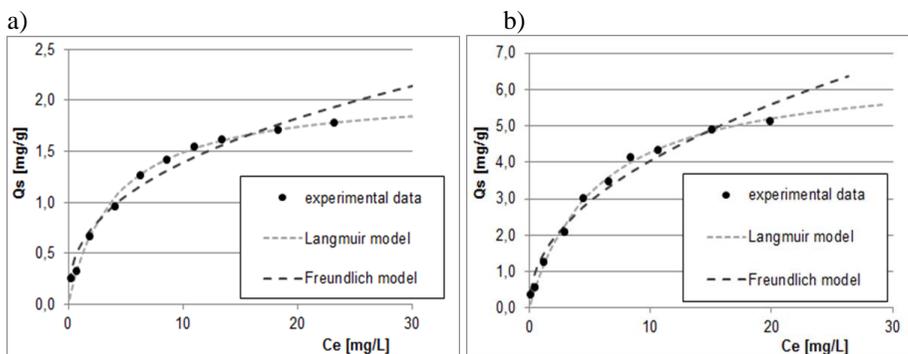
a)

b)

Figure 4. Experimental results and isotherms of P-PO$_4$ sorption onto **a)** chitin and **b)** chitosan

Data presented in Table 5 show that chitosan was has a higher sorption capacity relative to phosphate than chitin. The maximum adsorption capacity of the chitosan amounted to 6.64 mg/g, and for chitin – 2.09 mg/g. Differences in sorption capacity of chitin and chitosan with relation to phosphates result from the different chemical structure of the polymers. Chitosan has a higher efficiency of removing the P-PO$_4$, because on the surface there are more amino groups responsible for sorption of anions [19]. Literature data show that chitosan flakes have

greater sorption capacity with relation to P-PO$_4$ than aspen wood fibers [20] and activated carbons produced from cocoa hulls and corn cobs [21]. In contrast, Xiong et al. (2010), who removed the phosphorus compounds from aqueous solutions using peat, obtained similar sorption capacity [22].

Table 5. Constants determined from the Langmuir and Freundlich model

Sorbent	Langmuir model			Freundlich model		
	Q$_{max}$ [mg/g]	Kc [dm^3/mg]	R^2	n	K	R^2
Chitin	**2,09**	0,247	0.991	0,56	0,39	0.967
Chitosan	**6,64**	0,180	0.995	1,38	0,47	0.974

4. Conclusions

The sorption capacity may vary depending on the construction of sorbent and process parameters, ie. pH and time of the process equilibrium. The study showed that a better sorbent in relation to phosphate is chitosan. The efficiency of the removal of   P-PO$_4$ for chitin and chitosan to a large extent depended on the pH at which the process was carried out. At low pH (3 – 4 pH) part of functional groups of sorbents underwent protonation, which positively affected the sorption of anionic impurities. Therefore, the pH at which the sorption process took place most efficiently is set at pH 3 for chitin and pH 4 for chitosan. Equilibrium time of reaction for the two sorbents was determined on the basis of three concentrations of 1, 5 and 10 mg/dm^3. For both chitin and chitosan the highest efficiency was obtained for the lowest concentration. The time required to achieve equilibrium concentration of phosphate for all concentrations of the chitin was obtained after 20 minutes of the process, and for chitosan 40 minutes.

The results obtained were described by the homogeneous Langmuir model, as it characterized the best fit to experimental data ($R^2 > 0.99$). High values of the matching coefficient of Langmuir model isotherms to the experimental data obtained may indicate binding of phosphate by the active sites only on the surface of sorbent.

The maximum sorption capacity of chitosan in relation to phosphorus compounds is 6.65 mg/g, and chitin – 2.09 mg/g. Greatly improved efficiency of phosphates removal for chitosan is due to more amino groups responsible for the sorption process.

5. Acknowledgements

6. References

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