

APPLICATION OF CROSS-LINKED CHITOSAN FOR PHOSPHATE REMOVAL FROM AQUEOUS SOLUTIONS

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Abstract

This study investigated the effectiveness of phosphate adsorption onto non-cross-linked chitosan beads [CHs], and onto chitosan beads cross-linked with glutaraldehyde [ALD-CHs] and epichlorohydrin [ECH-CHs]. The weight ratio of glutaraldehyde to chitosan was 1:2 (w/w), whereas that of epichlorohydrin to chitosan was 2:1 (w/w). The optimal pH value of the phosphate adsorption process was determined at pH 3 for cross-linked chitosan and at pH 4 for non-cross-linked chitosan. The time needed to reach the equilibrium concentration reached 60 min for both adsorbents. Experimental data were described with the heterogeneous Langmuir model (double Langmuir equation). The most effective adsorbent of phosphates was shown to be chitosan cross-linked with epichlorohydrin [ECH-CHs] - for which the adsorption capacity reached 139.4 mg/g d.m._{CHs}. In the case of the remaining adsorbents (chitosan [CHs] and chitosan cross-linked with glutaraldehyde [ALD-CHs]) the adsorption capacity was lower and accounted for 44.38 mg/g d.m._{CHs} and 108.24 mg/g d.m._{CHs}, respectively.

Key words: *adsorption, phosphates, chitosan, cross-linked chitosan, glutaraldehyde, epichlorohydrin.*

1. Introduction

Phosphorus present in wastewaters originates from detergents, food residues and faeces, as well as contaminants generated by industrial plants which manufacture, e.g., artificial fertilisers, matches and synthetic washing agents. In Western Europe alone, the mean content of phosphorus in wastewaters exceeds 250,000 tonnes annually [1].

Environment pollutions originating from municipal and industrial wastewater treatment plants pose a severe problem as they cause strong contamination of rivers, waters and ground waters [2 - 4]. Treated wastewaters containing too high quantities of biogenes (including phosphorus) when discharged to natural water bodies cause enhanced eutrophication [5 - 7].

In the natural environment, phosphorus occurs in the form of phosphates, polyphosphates and organic phosphorus [1]. In turn, phosphates with a small admixture of organic phosphorus predominate in wastewaters. The concentration of phosphorus in crude household and industrial wastewaters usually falls within the range from 3 to 15 mg/l [4]. In response to the deteriorating condition of surface waters, stricter regulations have been implemented regarding the quality of discharged wastewaters. According to the Regulation of the Minister of Environment, the concentration of phosphorus in treated wastewaters may range from 5 to 1 mg P/l depending on the unitary number of inhabitants [8]. One of the most effective methods for the removal of phosphorus compounds from wastewaters is precipitation with calcium or the salts of iron and aluminium. These methods are, however, relatively expensive and additionally lead to water salinity and the formation of high quantities of deposits [6, 9]. For this reason, municipal wastewater treatment plants and industrial plants search for novel, inexpensive and efficient technologies for the removal of biogenic compounds [10].

An alternative method for phosphate removal may be adsorption. Recently, increasing attention has been focused on the use of chitosan as an adsorbent. It is synthesised chemically from chitin [13]. According to data in the literature, the annual global production of chitin from live organisms can reach as high as 10^{11} tonnes [11], whereas from the processing of marine invertebrates, this reaches between 120,000 and 200,000 tonnes [12]. The high adsorption capacity of chitosan is due to the presence of free amine groups, which are revealed as a result of deacetylation, as well as to chitosan affinity to water and its crystallinity. The adsorption capacity of chitosan may result from many processes, including ionic exchange, the formation of hydrogen bonds, physical adsorption (van der Waals forces) [14] and chemical adsorption (chemisorption) [15]. Chitosan is biodegradable, non-toxic, stable, has a high adsorption capacity and – importantly – is cheap. Owing to these advantages, it is increasingly often applied for the removal of heavy metals, dyes and other toxic compounds that lead to the contamination of water [16 - 18].

A drawback of chitosan is that it dissolves and loses the ability to bind adsorbates in acidic solutions, which limits its application as an adsorbent at low pH [17, 19]. This problem may be solved by the cross-linking of chitosan. The cross-linking process ensures the

chemical stability of chitosan and improves its mechanical resistance in a wide pH range, i.e. from pH 1 to pH 14 [20, 21, 23].

2. Materials and methods

2.1 Preparation of stock solution of phosphates

In brief, 3.871 g of sodium dihydrogenphosphate (V) (NaH_2PO_4) dried at 110 °C was dissolved in distilled water and the mixture was quantitatively transferred to a 1 dm³ flask and filled with deionised water.

2.2 Adsorbent

Preparation of chitosan beads

Chitosan in the form of flakes with deacetylation degree DD = 85% originated from BioLog company, which uses shrimp shells from the seafood processing industry. Chitosan flakes were dissolved in a 5% solution of acetic acid. The resultant solution was instilled to a 2 M solution of NaOH to form beads. The chitosan beads were left for 24 h in a solution of sodium hydroxide, and then rinsed with distilled water to reach neutral pH.

Preparation of cross-linked chitosan beads

The cross-linking of chitosan beads was conducted using two cross-linking agents – glutaraldehyde and epichlorohydrin.

The previously prepared chitosan beads were placed in a glutaraldehyde solution. The weight ratio of glutaraldehyde to chitosan was 1:2 (w/w). The cross-linking process lasted 24 h and was conducted under continuous stirring at room temperature. The cross-linked chitosan beads were rinsed with distilled water to remove the non-reacting cross-linking agent.

In the case of cross-linking chitosan beads in epichlorohydrin, the weight ratio of the cross-linking agent to chitosan reached 2:1 (w/w). The beads were placed in an alkaline solution of epichlorohydrin (pH 10). Then, the cross-linked chitosan beads (CHs+ECH) were rinsed with distilled water to remove the excess epichlorohydrin.

Determination of the optimal pH value of adsorption process

In order to determine the optimal pH value of the adsorption process, aqueous solutions were prepared with phosphate concentrations of: 10, 50, 100 mg $\text{PO}_4^{3-}/\text{dm}^3$ and pH2, pH3, pH4, pH5, pH6, pH7, pH8, pH9, pH10 and pH11. To each of the 10 conical flasks with the volume of 200 cm³, adsorbent was added in the cross-linked or non-cross-linked form in the quantity of 0.1 g d.m. (1 g/dm³) and 100 cm³ of adsorbent solutions with pH from 2 to 11. Next, the flasks were placed on a magnetic stirrer, and the concentration of adsorbate in the solution was determined after 2 h of adsorption.

Determination of reaction equilibrium time

In brief, 2 g d.m (1 g d.m./dm³) of non-cross-linked and modified chitosan beads and 2000 cm³ of orthophosphates solution at concentrations of 100 mg $\text{PO}_4^{3-}/\text{dm}^3$ were weighed

Table 1. Parameters of analyses of adsorption reaction equation

Adsorbent	Adsorbent concentration [g d.m./dm ³]	Phosphates concentration [mg/dm ³]	Sample collection time [min]
Chitosan cross-linked/non-cross-linked	1	100	0, 1, 5, 10, 15, 20, 30, 40, 50, 60, 80, 100, 120, 150, 180, 210, 240

into beakers with a volume of 2500 cm³. At specified time intervals (**Table 1**) samples (5 cm³) were collected in order to determine the concentration of anion left in the solution.

Determination of the maximum adsorption capacity

The adsorbent at a quantity of 0.2 g d.m. (1 g d.m./dm³) and 200 cm³ of the solution of the analysed adsorbate with concentrations of 10, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, and 1000 mg PO₄³⁻/dm³ were measured into conical flasks with a volume of 250 cm³. Next, the flasks were placed on a laboratory shaker. After the specified time determined in the preliminary study, analyses were conducted to determine the concentration of phosphates left in solution. The results obtained enabled determination of the maximum adsorption capacity of cross-linked and non-cross-linked chitosan.

3. Results and discussion

The efficiency of phosphate adsorption from the solution was analysed based on changes in their concentration in solution.

The quantity of adsorbed phosphates was calculated from the formula (1):

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

where:

Q_s – weight of adsorbed phosphates [mg/g.d.m.],

C_0 – initial concentration of phosphates [mg/dm³],

C_s – phosphates concentration after adsorption [mg/dm³],

m – weight of adsorbent [g.d.m.].

Experimental data were described using two models – the Freundlich model and heterogeneous Langmuir model (double Langmuir equation).

The Freundlich model (2) is applied to describe adsorption onto energetically heterogeneous surfaces. According to this theory, the quantity of adsorbed molecules at the total coverage of adsorbent surface cannot be higher than the number of active sites, and the layer formed isolates the action of adsorption forces, thereby enabling the formation of successive layers [23].

$$Q = k \cdot C^n \quad (2)$$

where:

Q – weight of adsorbed compound [mg/g d.m.],

k – adsorption constant,

C – concentration of adsorbed substance in the state of equilibrium [mg/dm³],

n – partition coefficient indicating the ratio of the quantity of adsorbed substance to the quantity of the substance left in the solution, in the state of equilibrium [dm³/g d.m.].

According to the Langmuir model (3), the adsorption of molecules may be chemical or physical in character. There is no interaction between the adsorbed molecules which form the monomolecular layer. The quantity of adsorbed substance depends mainly on the adsorption capacity of the monolayer (q_{max}) and adsorption affinity of the adsorbate to adsorbent (Kc).

$$Q = \frac{q_{max} \cdot K_c \cdot C}{1 + K \cdot C} \quad (3)$$

where:

Q – weight of adsorbed compound [mg/g d.m.],

Kc – constant in Langmuir equation [dm³/g d.m.],

q_{max} – maximum adsorption capacity of adsorbent monolayer [mg/g d.m.],

C – concentration of the adsorbed substance in the state of equilibrium [mg/dm³].

The double Langmuir model (4) takes into account the fact that the adsorbent's surface is energetically heterogeneous and possesses adsorption centres with different energy of adsorbate molecules binding. Each centre is described by the Langmuir isotherm equation and the active sites are characterised by respective constants: K_1 , b_1 and K_2 , b_2 . The double Langmuir equation was successively applied to interpret the results of metal adsorption by activated sludge and to evaluate metal adsorption in soils [24, 25].

$$Q = \frac{b_1 \cdot K_1 \cdot C}{1 + K_1 \cdot C} + \frac{b_2 \cdot K_2 \cdot C}{1 + K_2 \cdot C} \quad (4)$$

where:

Q – real adsorption of adsorbate on the adsorbent [mg/g.d.m],

b_1 – maximum adsorption capacity of adsorbent (type I active sites) [mg/g.d.m],

b_2 – maximum adsorption capacity of adsorbent (type II active sites) [mg/g.d.m],

K_1 ; K_2 – constants in Langmuir reaction [dm³/mg],

C – concentration of dye left in the solution [mg/dm³].

Figure 1 depicts the effect of pH value on the effectiveness of phosphates adsorption onto chitosan. The highest effectiveness of phosphates removal from aqueous solutions on non-modified chitosan was achieved at pH 4 and at the lowest initial concentration of phosphates reached 10 mg P-PO₄/dm³. Both a decrease and an increase in pH value diminished the effectiveness of phosphate anions removal by chitosan. The effectiveness of phosphates removal in the best conditions reached 30%.

Adsorption of phosphates onto chitosan cross-linked with glutaraldehyde was the most effective at pH 3. The effectiveness of phosphate removal from aqueous solutions with [ALD-CHs] reached 65% for the initial phosphate concentration in the solution at 10 mg P-PO₄/dm³, 41% for 50 mg P-PO₄/dm³ and 31% for 100 mg P-PO₄/dm³.

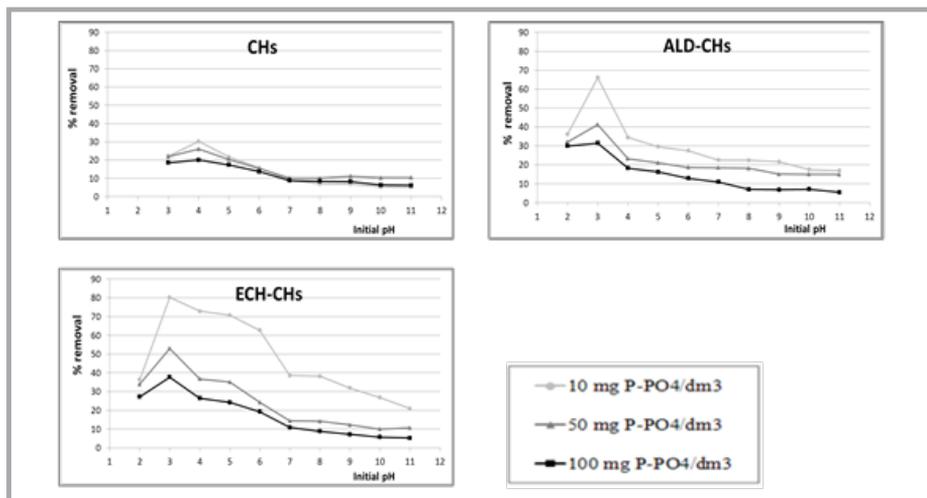


Figure 1. Effect of pH value on the effectiveness of phosphates adsorption onto non-cross-linked chitosan.

Figure 1 also shows the effect of pH value on the effectiveness of PO_4^{3-} anions removal with the use of chitosan modified with epichlorohydrin. The results obtained in this respect demonstrate that the most favourable conditions for the adsorption process occurred at pH 3. The highest effectiveness of phosphates removal, i.e. 80%, was obtained at the lowest initial concentration of phosphates, reaching 10 mg $\text{P-PO}_4/\text{dm}^3$ and pH 3.

Based on the results obtained it may be concluded that the effectiveness of phosphates adsorption onto chitosan decreases along with increasing pH value. For the cross-linked chitosan, the highest effectiveness was achieved at pH 3, whereas for the non-cross-linked chitosan this was reached at pH 4. In a pH range of 3 to 4, the predominating process was

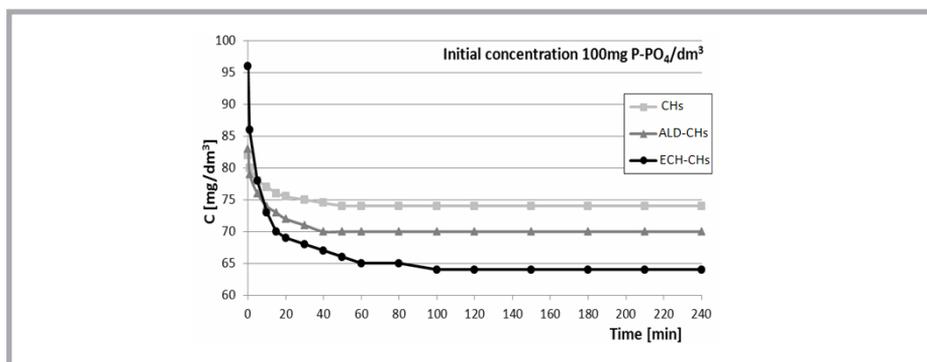


Figure 2. Determination of equilibrium time of P-PO_4 adsorption reaction onto chitosan adsorbents.

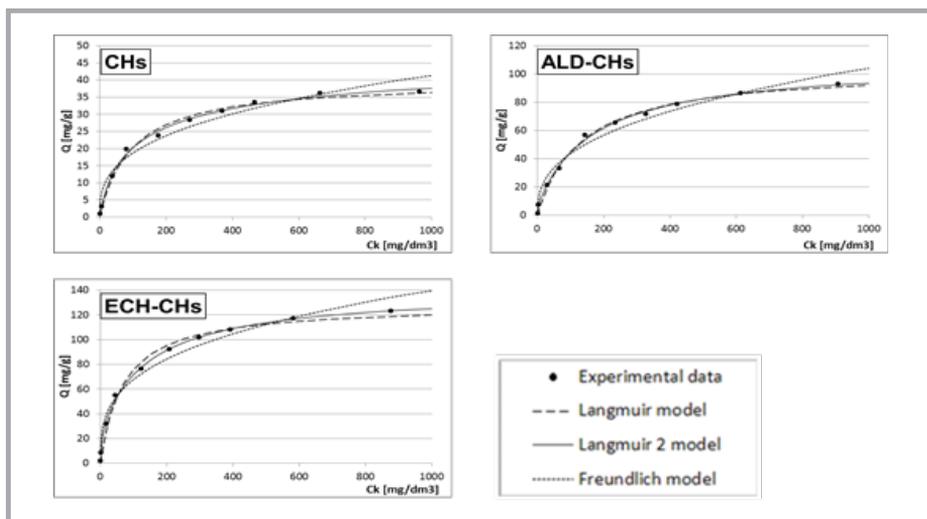


Figure 3. Comparison of the goodness of fit of the Freundlich model, Langmuir model and double Langmuir model.

the physical adsorption of PO_4^{3-} anions, most likely induced by the protonation of amine groups of chitosan [19]. Similar conclusions were drawn by Moharami et al., who examined the phosphorus adsorption capability of silty minerals. In their study, they applied calcite and kaolinite, with the highest effectiveness of phosphate removal being achieved in a solution with a pH range of 2 to 4. According to these authors, a decreasing pH value is accompanied by an increasing number of positive ions on the adsorbent's surface, meaning that it is only capable of adsorbing negatively-charged ions [26]. Data in the literature confirm that ca. 99.4% of amine groups contained in chitosan beads are subject to protonation at pH 3, whereas the protonation occurs in only 0.06% of the amine groups at pH 9.5 [27]. For this reason, at low pH, the amine groups of chitosan responsible for the adsorption process are more available to phosphates, and hence the highest effectiveness of their removal was recorded at pH 3 - 4 [16].

Figure 2 shows the equilibrium time of phosphate adsorption reactions for the previously established optimal pH 3 for the cross-linked chitosan and pH 4 for the non-cross-linked chitosan. Data presented in the Figure demonstrate that the reaction equilibrium was achieved after ca. 60 min for all adsorbents.

Considering the results shown in **Figure 2**, analyses were conducted to determine the maximum adsorption capacity for all adsorbents.

Constants in the Freundlich model and double Langmuir model were determined with the method of non-linear regression. The R^2 coefficient was adopted as a measure of curve fit to experimental data. **Figure 3** shows the experimental data achieved using three models.

Table 2. Constants and coefficients of the goodness of fit determined from double Langmuir equation, Langmuir equation and Freundlich equation.

Type of adsorbent	Constants in Langmuir equation		R ²	Constants in double Langmuir equation				R ²	Constants in Freundlich equation		R ²
	K _c	q _{max}		b ₁	K ₁	b ₂	K ₂		k	n	
CHs	0.0105	39,9	0.9928	22.2	0.0028	22.21	0.0230	0.9966	3.850	0.3434	0.9790
ALD-CHs	0.0076	104,2	0.9944	101.0	0.0058	7.20	0.6198	0.9976	7.707	0.3767	0.9874
ECH-CHs	0.0144	128,2	0.9910	110.6	0.0067	28.82	0.1926	0.9966	16.04	0.3131	0.9882

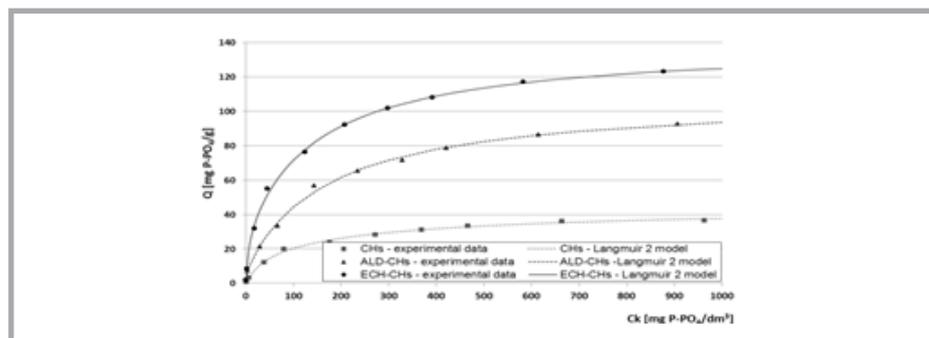


Figure 4. Results of experiments and double Langmuir isotherms for the three biosorbents analysed.

The results obtained enabled the conclusion to be drawn that the adsorption of phosphates onto non-cross-linked and cross-linked chitosan beads was well described by the double Langmuir model; this was indicated by very high values of the R² coefficient, exceeding 0.99. In contrast, considerably poorer goodness of fit was achieved in the case of the Freundlich model. Values of the goodness of fit coefficient for all biosorbents are presented in **Table 2**.

Figure 4 presents the results of experiments conducted with double Langmuir isotherms for non-modified chitosan and for chitosan cross-linked with epichlorohydrin and glutaraldehyde.

Biosorbents that contain nitrogen in their molecule, including chitosan, may bind anionic contaminants as a result of various processes, such as hydrogen bonding, ion-exchange adsorption and molecular interactions induced by van der Waals forces. All of these mechanisms contribute to the increased adsorption affinity of chitosan to phosphates. The sum of b₁ and b₂ constants from the double Langmuir equation is perceived to express the real adsorption capacity of adsorbents and also indicates in our study which of the adsorbents analysed ensured the highest effectiveness of phosphates removal. The maximum adsorption capacity of pure chitosan accounts for 44.38 mg/g d.m._{CHs}, that of chitosan cross-linked with glutaraldehyde for 108.24 mg/g d.m._{CHs}, and that of chitosan cross-linked with epichlorohydrin for 139.40 mg/g d.m._{CHs}. The study results confirm that none of the cross-

linking agent blocked the active sites; hence, the modified chitosan was characterised by higher adsorption capacity. Apart from that, the increase in the maximum adsorption capacity of chitosan cross-linked with epichlorohydrin may also result from the release of free functional groups by this compound because, when disrupted, the epoxide groups of epichlorohydrin release hydroxyl groups [28]. The modified chitosan was characterised by significantly higher adsorption capacities than the non-modified chitosan, as the optimal pH value of adsorption for [ECH-CHs] and [ALD-CHs], i.e. pH 3, enabled more intensive physical adsorption of phosphates than pH 4 (optimal for [CHs]).

4. Conclusions

Phosphates may be successively removed from aqueous solutions as a result of their adsorption onto cross-linked chitosan, especially chitosan cross-linked with epichlorohydrin. ECH is a beneficial crosslinking agent as it does not block active centres of chitosan that are responsible for phosphates adsorption.

The results achieved were described with a heterogeneous Langmuir model because it was characterised by the highest goodness of fit to experimental data ($R^2 > 0.99$).

The highest adsorption capacity at 139.4 mg/g d.m.-CHs was achieved for hydrogel beads cross-linked with epichlorohydrin. The optimal pH value of phosphate adsorption onto cross-linked chitosan is pH 3, whereas for the non-cross-linked chitosan it is pH 4, because the non-modified chitosan beads dissolve at pH lower than 4.

The time needed to reach the equilibrium concentration of phosphates was relatively short for all of the analysed chitosan adsorbents and reached 60 min.

5. References

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