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Adsorption of Phosphates from Aqueous Solutions on Alginate/Goethite Hydrogel Composite

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Abstract: The basic process to reduce the phosphate ions in aquatic environments is to move the phosphorus circulation processes on the water–sediment phase boundary towards depositing it in the solid phase through chemical precipitation or adsorption. Modern technologies for removal of phosphorus can be based on cheap and environmentally friendly natural polysaccharides modified with multivalent metals. In this study alginate/goethite hydrogel composite has been investigated for phosphate uptake from aqueous solutions. The composite was produced by a cross-linking reaction between sodium alginate and calcium chloride in six configurations of suspensions, which differed in goethite content. In all cases, spherical and durable capsules of alginate/goethite composite were produced. In laboratory tests, mechanical stability of the capsules at various temperatures and the coexisting ions of lake water were tested. Chemical composition of the aquatic environment had a strong influence on their mechanical stability. Static batch adsorption of phosphate studies were carried out for two adsorbents: goethite and alginate/goethite composite. The goethite gelation resulted in almost double growth of sorption capacity in the case of adsorption from deionized water and, on average, a 50% growth in adsorption from the environmental water compared to raw goethite. The alginate/goethite adsorbent removed phosphate in a wide pH spectrum—from 4 to 10. Results suggest that the proposed adsorbent has potential for the removal of phosphate from contaminated water.

Keywords: eutrophication; alginate-based composites; goethite; phosphorus removal; adsorption

1. Introduction

Excess phosphate ions in surface waters is the main reason for their eutrophication. In order to reduce the concentration of phosphates in treated waste waters and in degraded water reservoirs, chemical methods are applied. In aquatic environments, phosphorus is strongly bound chemically, mainly by multivalent metals, forming hard-to-dissolve salts and complex compounds. Apart from compounds of aluminum [1–3] and calcium [4–6], compounds of iron are the most frequently tested and used in chemical methods for inactivation of phosphate ions, for instance: $\text{Fe}(\text{OH})_3$, FeCl_3 [7,8], $\text{Fe}_2(\text{SO}_4)_3$ [9], or those in the form of mixes with, e.g., NO_3^- and Ca^{2+} in the Depox preparation [10]. Wastes containing iron were tested too, e.g., dust containing iron or ferric oxide (III) [11], as well as minerals containing iron, where goethite drew most of the attention [12–15]. Goethite ($\alpha\text{-FeOOH}$) is one of the most common and stable crystalline iron (hydro)oxides in natural systems. Goethite has a very large specific area of ca. $100 \text{ m}^2 \cdot \text{g}^{-1}$ and substantial sorption affinity and selectivity towards phosphate ions in aquatic environments, which was confirmed in many studies [12–15].

Chemical inactivation of phosphates by using hydroxides and salts of iron have many limitations. The basic problem is the high susceptibility of those compounds to changes in the redox potential and pH. Upon increases in pH, which generally accompany photosynthetic processes, the sorption affinity of iron compounds towards phosphate ions drops down, whereas solubility of their combinations with phosphorus grows; e.g., the optimal pH for creating durable complexes of $\text{FeOOH}_2\text{PO}_4$ is below 5–7 [16]. Solubility of compounds of iron with phosphorus also increases in oxygen-free conditions, as a result of reduction of Fe^{3+} to Fe^{2+} [17–20]. The upper limit of electric potential, below which oxidized forms decline, and the lower limit, below which reduced iron forms occur, are 300 and 200 mV, respectively. Additionally, in oxygen-free conditions, iron gets removed from the phosphorus–iron cycle, as the iron is permanently bound in the sediments, forming some hard-to-dissolve ferric sulfides with sulfur reduced to sulfide ions [21]. Therefore, during application of those compounds aeration and supplementation of coagulants are recommended [22]. Additionally, there is no possibility of more efficient regeneration of most of coagulants, and consequently, the reuse of phosphorus is not possible [23]. Coagulation and precipitation processes in natural waters are accompanied by co-precipitation and adsorption processes of different forms of phosphorus [24]. Tian et al. [25] recommended adsorption as one of the most effective removal processes for the low concentration of phosphorus. Modern technologies for removal of phosphorus should be based on such materials which do not pose a toxicological threat to the environment, can be recovered and reused, as well as facilitate separation of the deposited phosphorus and its reuse as, e.g., fertilizer [26].

One of the methods to eliminate most of the limitations observed in the process of inactivating phosphates using iron compounds can be applying them in the hydrogel form. Such forms can be obtained from cheap and environment-friendly biosorbents, including alginate that is extracted from sea algae [27]. Alginate is a natural, nontoxic, non-immunogenic, fully biodegradable anionic polysaccharide, which in its structure contains hydroxyl and carboxyl groups distributed along a backbone chain of polymer. The functional groups form a crosslinking bond with polyvalent cations (except magnesium), creating an alginate gel with large specific areas [27]. The structures may serve as a stable matrix for other types of adsorbents (mostly in powder form) that are too fine in particle size and too difficult to separate from aqueous solution. The adsorbents are entrapped in alginate gel beads (with an “egg-box” structure) to form heterogeneous beads [28]. Calcium alginate-based composites are fabricated as adsorbents for both inorganic and organic contaminants like dyes, heavy metals, and antibiotics [29]. In the case of alginate with modification by Fe^{3+} , some adsorbents were produced for purifying water from oxygen anions containing Se^{4+} , Cr^{6+} , and As^{5+} [30,31]. The literature refers to two similar formula obtained for adsorption of phosphate ions from the aquatic phase alginate/zirconium sulfate matrix, which has better sorptive qualities than powdered zirconium sulfate [32] and alginate/ Fe^{3+} beads [33].

The purpose of this work was to prepare an alginate/goethite composite and verify the influence of temperature and light on the mechanical stability of those matrixes. The most durable capsule types, alginate/goethite and raw goethite, were examined for their adsorption of phosphate from aqueous media under batch equilibrium. For both adsorbents, kinetics, adsorption isotherms, and pH influence were studied.

2. Materials and Methods

2.1. Preparation of Goethite and Alginate/Goethite Hydrogel Capsules

Goethite was produced in laboratory conditions, according to a method described by Kentzer and Buczkowski [14]. A 5.0 M NaOH (Chempur, Piekary Śląskie, Poland) solution was added dropwise to a 1200 mL mixed solution of 0.25 M $\text{Fe}_2(\text{SO}_4)_3$ (Chempur, Piekary Śląskie, Poland) in a beaker at room temperature. The solution was stirred magnetically during addition of the NaOH solution, and the addition of the NaOH solution was stopped after the pH reached 12. The suspension was further stirred for 1 h. The precipitate was separated by centrifugation, washed with deionized water until

neutral, and finally dried in air at room temperature. Goethite fractions with granulation of <0.1 mm were tested. The hydrogel capsules, containing goethite, were produced with the injection method. Nine grams of sodium alginate powder (Manugel DJX, Ayresshire, UK) was dispersed in 600 mL of deionized water to give 1.5% w/v alginate solution. This solution was mixed with a mechanic stirrer until a transparent, viscous solution was obtained. Then 2 (G2), 3 (G3), 4 (G4), 6 (G6), 8 (G8), and 10 (G10) g of the goethite were mixed with 100 mL of the above sodium alginate solution, in six beakers. Goethite was added in the amount which provided a spherical shape of capsules. Alginate/goethite composite was obtained by adding dropwise 20 mL of each goethite/alginate suspension into 400 mL of 0.155 M CaCl₂ (Chempur, Piekary Śląskie, Poland) solution using a syringe. After delivery of the last drop of the suspension, the formed capsules were stirred for 15 min and flushed twice for 10 min with distilled water.

2.2. Mechanical Stability of Capsules

Mechanic stability of hydrogel capsules was tested by measuring their maximum strength under compression. The measurements were taken with a strength-tester by Zwick/Roell, equipped with a moving head rated for 20 N. During the tests, the attack velocity of the head was 0.1 mm/s. Changes in the pressure force were recorded by an integrated computer system, making it possible to define a maximum resistance of polysaccharide membranes to compression. The tests of the capsule strength were conducted during their storage for 12 weeks in three kinds of water—deionized water (WD) and two environmental waters, taken from eutrophic polymictic inland reservoirs (W1 and W2), selected quality indexes of which are shown in Table 1. The water differed in hardness; W1 was hard water and W2 was soft water. The capsules were kept at two temperatures: 4 °C and 20 °C, exposed to daylight and with no light access (kept in the dark). The mechanical strength tests were conducted after 24 h and after 1, 2, 3, 7, and 12 weeks of storage.

Table 1. Selected quality indexes of the environmental water.

Water	pH	Hardness (mg CaCO ₃ dm ⁻³)	Conductance (μS m ⁻¹)	P_PO ₄ N_NO ₃ N_NH ₄			Contents of Metals (mg dm ⁻³)						
				(mg dm ⁻³)			Ca	K	Fe	Mg	Mn	Na	Zn
W1	7.53	126.7	369	0.371	2.469	0.457	15.8	3.9	0.03	11.0	0.009	17.7	0.026
W2	7.13	76.0	125	0.076	1.052	0.422	14.6	0.0	0.09	2.5	0.014	2.4	0.010

2.3. Analytical Methods

Phosphate concentration was measured by the molybdenum blue colorimetric method [34], using a two-beam spectrophotometer Techcomp UV/VIS 8500, at a wave-length of 890 nm. Total iron (Fe) content in the solutions was determined by atomic absorption spectroscopy, using a ThermoElemental, Solaar S spectrometer.

2.4. Adsorption Kinetic Measurements

Kinetics of adsorption of phosphate (V) ions (PO₄³⁻) was tested in WD and in two natural waters (W1, W2). Phosphate solutions (WD_P, W1_P, W2_P) with an initial concentration 10 mg PO₄ dm⁻³ were prepared by dissolving KH₂PO₄ in the waters concerned. Twenty-five milliliters of prepared solutions and 10 mg goethite or 10 capsules with alginate/goethite (containing 10 mg goethite) were put into 50 mL Erlenmeyer flasks. For each water type, 9 measurement series (repeated 3 times) were prepared. Changes in phosphate ion concentration were examined at different reaction times (1, 4, 7, 10, 24, 48, 96, 168, 264 h). At the same time, the content of phosphate ions was checked in referential tests in solutions without the capsules. The experiment was conducted at three temperatures (4, 10, and 20 °C).

2.5. Phosphate Adsorption Experiments

Phosphate adsorption characteristics were studied in a static batch system proposed by Naira et al. [35]. Using the deionized water (WD) and the two natural waters W1 and W2, solutions of KH_2PO_4 with different contents of PO_4^{3-} (1, 2, 4, 10, 20, 40, 80 $\text{mg PO}_4 \text{ dm}^{-3}$) were prepared. Similar to the previous experiment, some goethite or alginate/goethite capsules were added. Adsorption isotherms were determined at 20 °C, changes in the content of phosphate ions in the solution were tested at equilibrium (after 48 h for goethite and 264 h for alginate/goethite). The mixtures were shaken on a laboratory shaker for two hours at the beginning and at the end of the process of binding the phosphate. The experiment was carried out in triplicate.

2.6. Effect of pH

The effect of the initial pH on phosphate adsorption on the goethite and alginate/goethite composite was studied with a constant initial concentration WD_P of 10 $\text{mg PO}_4 \text{ dm}^{-3}$. The initial pH varied within the range of 4.0–10.0, and temperature was maintained at 20 °C. The pH was regulated using 0.1 M HCl or 0.1 M NaOH solutions. Similar to the previous experiment, some goethite or alginate/goethite capsules were added. The mixtures were shaken on a laboratory shaker for two hours at the beginning and at the end of the process of binding the phosphate ions. After equilibrium the phosphate concentration was measured.

2.7. Data Analysis

To determine the parameters of mathematical models describing the kinetics and the adsorption equilibrium, equations in the linearized form were used. Kinetic data of sorption of phosphate on goethite and alginate/goethite was described very well using the pseudo-second-order rate equation developed by Ho and McKay [36].

It can be expressed as follow:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (1)$$

where k_2 is the second-order rate constant of adsorption, q_e is the amount of phosphate adsorbed at equilibrium, and q_t is the amount of phosphate adsorbed at any time t .

The equilibrium data for the removal of phosphate in the present investigation were analyzed using the two-parameter model, Langmuir and Freundlich isotherms. The linear equations of Langmuir and Freundlich are represented as follows (Equations (2) and (3), respectively):

$$\frac{C_e}{q_e} = \frac{1}{(bQ_{max})} + \frac{C_e}{Q_{max}} \quad (2)$$

$$\log Q_e = \log k + \frac{(\log C_e)}{n} \quad (3)$$

where C_e is the equilibrium concentration of phosphate in the solution, q_e is the corresponding uptake capacity of the adsorbent, Q_{max} is the maximum adsorption capacity, b is the affinity constant, and k and n are Freundlich constants. Linear regression analysis has been used to determine the best-fit isotherm and the method of least squares has been used for finding the parameters of the equations. For the fitting of the isotherms and kinetic equation with the experimental data, the coefficient of determination, R^2 , was used [37].

The statistical analysis of the data was conducted at the significance level $\alpha = 0.05$.

3. Results

As a result of gelation of alginate in the six configurations of suspensions, that differed in goethite content, capsules containing from 2 to 10 g goethite per 1.5 mL alginate were produced. Regardless of the quantity of goethite applied, all the created capsules were spheroid.

A comparison of the maximum mechanical strength to compression (Figure 1) of capsules of different goethite contents after one day of keeping them in WD proved that, at 4 °C, the highest resistance to pressure was found in capsules with the highest content of goethite (G10), whereas at 20 °C the strongest were capsules containing 6 g goethite/1.5 mL⁻¹ alginate (G6). In most of the cases, after the end of the experiment, G6 capsules showed the highest mechanical strength and stability, so they were chosen as a subject for further studies on sorption capacities towards phosphate ions.

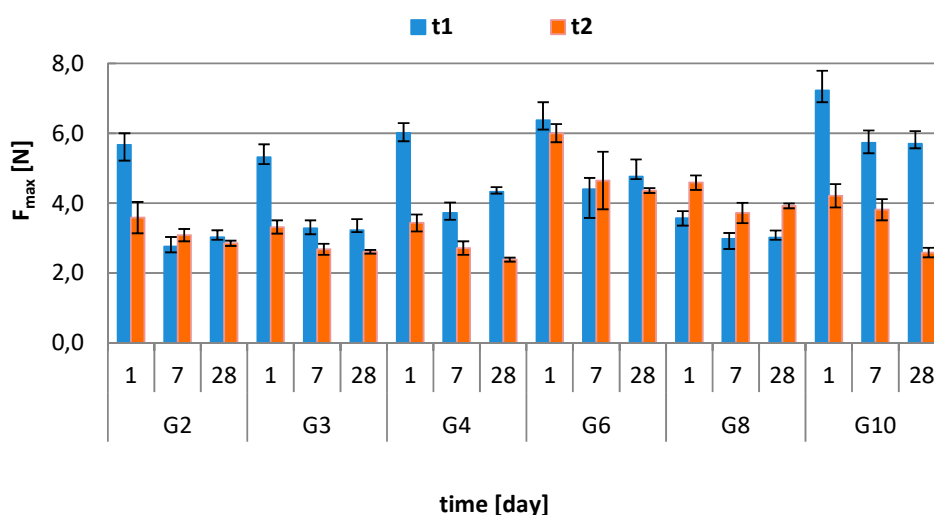


Figure 1. Maximum mechanical strength to compression of capsules of different goethite contents after keeping them in deionized water (WD), t1 = 4 °C; t2 = 20 °C.

A comparison of the maximum mechanical strength to compression of G6 alginate/goethite capsules after keeping them in WD and in natural waters (W1, W2) of different chemical compositions proved that in all cases, during the storage, reduction of stability was observed. The lowest stability was recorded for the capsules kept in water W1 (Figure 2).

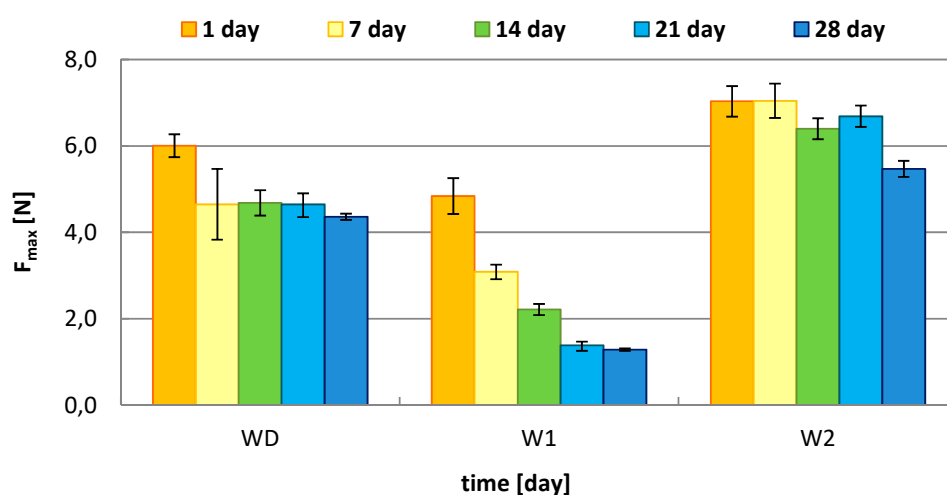


Figure 2. Maximum mechanical strength to compression of capsules containing 6 g goethite/1.5 mL⁻¹ alginate after keeping them in deionized water (WD) and in natural waters (W1, W2).

For both waters W2 and WD, after 7 and 28 days of storage, no significant changes in mechanical strength of capsules were obtained. Mechanical stability of capsules kept in waters W2 and WD was similar. Exposure to light did not affect the changes (Figure 3).

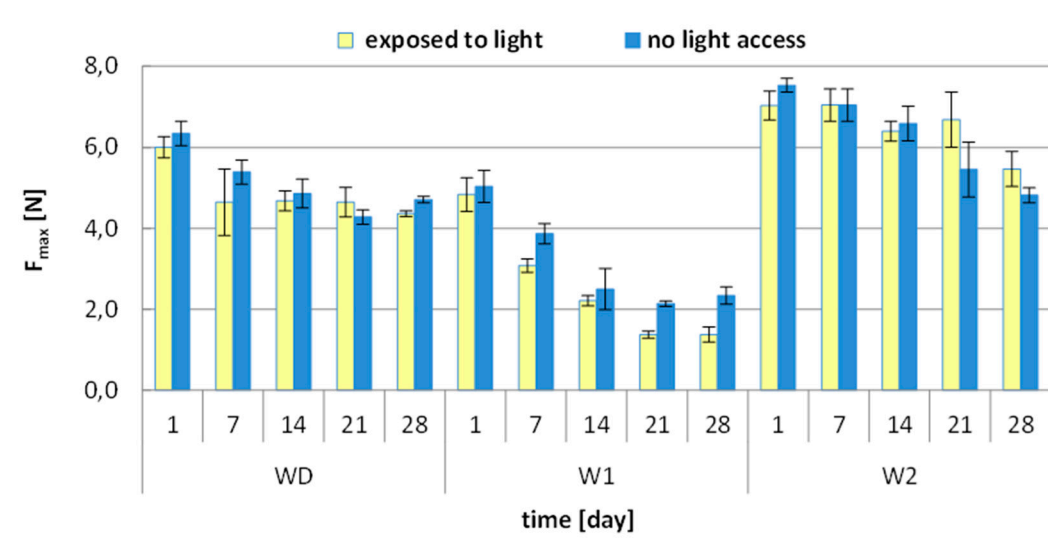


Figure 3. Effect of light on mechanical durability of capsules containing 6 g goethite/1.5 mL⁻¹ alginate.

Conducted at three temperatures of 4, 10, and 20 °C, the studies on the kinetics of adsorption of phosphate ions on goethite and hydrogel alginate/goethite composite showed that in all cases the quantity of adsorbed phosphate ions increased with time (Figure 4). The adsorption process on goethite reached a state of equilibrium after 48 hours, for all solutions and temperatures. After that period, in water WD_P, 76.1% of phosphate ions were removed, and from natural waters W1_P and W2_P, 90.5 and 88.5%, respectively, were removed. Adsorption of phosphate ions on alginate/goethite composite proceeded at a slower pace, as the equilibrium was reached after 264 h. After that period, from solution WD_P 83.0% of phosphate ions were removed, and from the natural waters W1_P and W2_P 92.2 and 94.6%, respectively, were removed. In all the combinations in question, the rate of removing phosphates from the solutions increased only a little with an increase of temperature (Table 2).

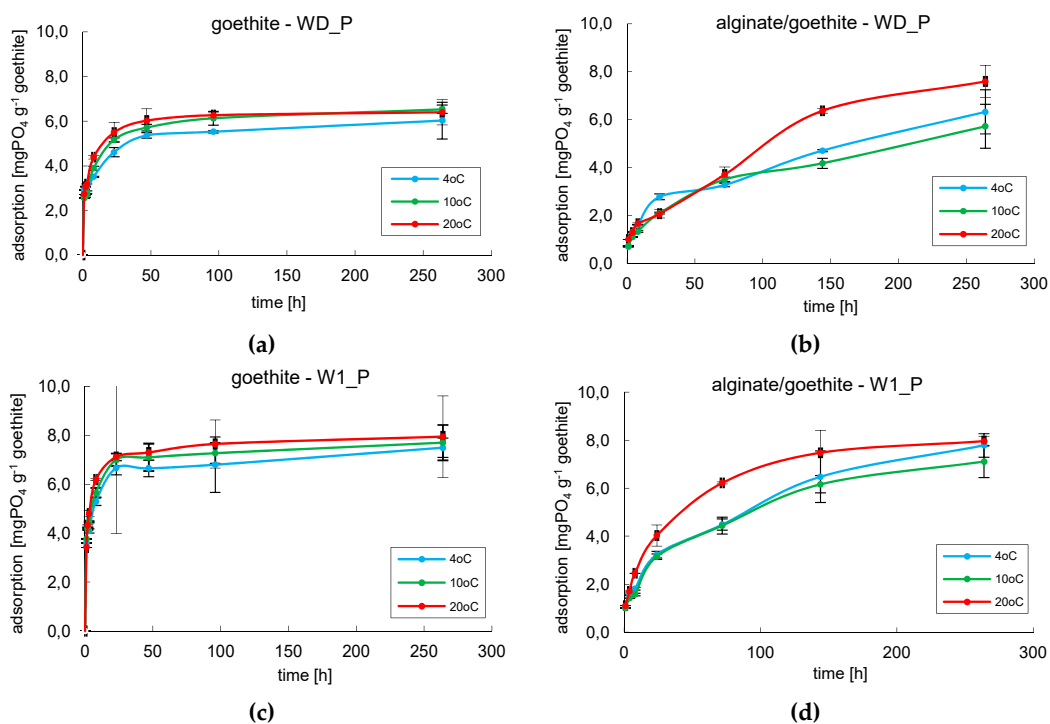


Figure 4. Cont.

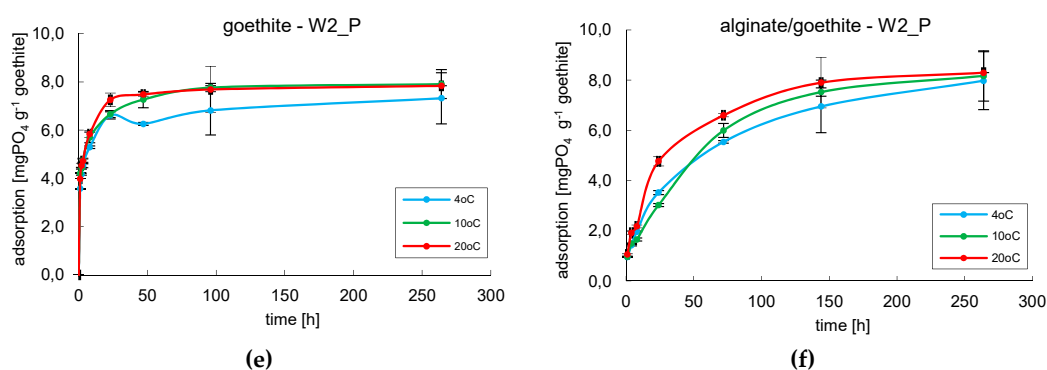


Figure 4. Adsorption kinetics of phosphate ions on goethite and on alginate/goethite composite. (a) adsorption on goethite in water WD_P, (b) adsorption on alginate/goethite composite in water WD_P, (c) adsorption on goethite in water W1_P, (d) adsorption on alginate/goethite composite in water W1_P, (e) adsorption on goethite in water W2_P, (f) adsorption on alginate/goethite composite in water W2_P.

Table 2. Estimated pseudo-second-order kinetic model parameters for phosphate adsorption onto goethite and alginate/goethite composite.

Water	Temperature (°C)	Goethite			Alginate/Goethite		
		Adsorption at Equilibrium State q_e (mg/g)	Rate Constant of Adsorption k_2 (g/mg h)	R^2	Adsorption at Equilibrium State q_e (mg/g)	Rate Constant of Adsorption k_2 (g/mg h)	R^2
WD_P	4	6.10	0.034	0.998	6.49	0.005	0.943
	10	6.62	0.031	0.999	5.92	0.006	0.957
	20	6.49	0.052	0.999	8.33	0.003	0.918
W1_P	4	7.52	0.037	0.998	8.26	0.004	0.967
	10	7.75	0.047	0.999	7.58	0.005	0.978
	20	8.00	0.049	0.999	8.48	0.007	0.995
W2_P	4	7.35	0.040	0.999	8.55	0.005	0.988
	10	8.00	0.046	0.999	9.01	0.004	0.984
	20	7.94	0.062	0.999	8.85	0.006	0.996

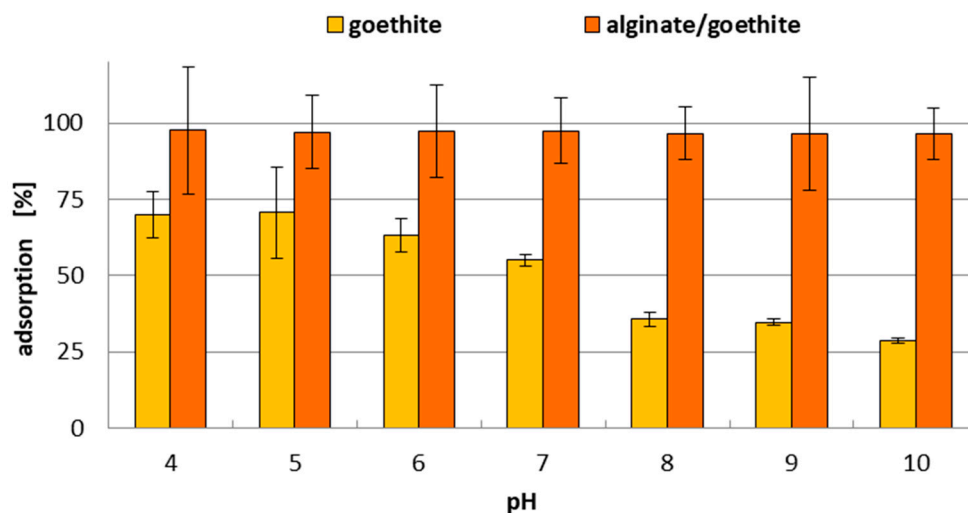
Phosphate ion adsorption isotherms onto the alginate/goethite composite and the goethite were estimated up as functions of quantities of phosphorus adsorbed by 1 g of goethite at equilibrium concentration of phosphorus in the solutions WD_P, W1_P, and W2_P. The process of adsorption of phosphate ions on the alginate/goethite beads and on the goethite was described mathematically with the Freundlich and Langmuir isotherm models. Results showed that the Langmuir equation gave a better fit than the Freundlich equation according to their determination coefficients, as in all cases the coefficients corresponding to the Langmuir equation were higher, $R^2 > 0.99$ (Table 3). The better fitting of the isotherm data to the Langmuir model indicates that removal of phosphate on the goethite and the alginate/goethite composites may involve monolayer adsorption processes. Parameters k and Q_{max} of the isotherms describing adsorption from natural waters W1 and W2 were higher than those calculated for adsorption process conducted from the distilled water. This indicates a higher sorption capacity of the adsorbents tested in waters containing other ions, which might affect the process of inactivating phosphate ions. The small differences between those parameters and, consequently, the limited effect of the water composition on the sorption capacity, were observed for the adsorption process on the alginate/goethite beads. The adsorbent presented a much higher sorption capacity than goethite, which, on average, for the alginate/goethite beads amounted to $36.01 \text{ mg P} \cdot \text{g}^{-1} \text{ goethite}$, whereas for the goethite it was $24.03 \text{ mg P} \cdot \text{g}^{-1} \text{ goethite}$. Values calculated in the Freundlich and Langmuir isotherms indicate that both adsorption intensity and the extent of adsorption of phosphate ions in the natural waters were higher on the alginate/goethite capsules than on goethite.

Table 3. Freundlich and Langmuir isotherms constants for phosphate adsorption onto goethite and alginate/goethite capsules.

Adsorbent	Solution	Freundlich Model*			Langmuir Model*		
		<i>k</i>	<i>1/n</i>	<i>R</i> ²	$\frac{Q_{max}}{(\text{mg P g}^{-1} \text{ goethite})}$	<i>b</i>	<i>R</i> ²
goethite	WD_P	6.08	0.37	0.98	18.2	0.75	0.99
	W1_P	10.2	0.25	0.95	27.0	0.41	0.99
	W2_P	11.2	0.28	0.99	27.0	0.82	1.00
alginate/goethite	WD_P	17.4	0.34	0.97	34.4	1.04	0.99
	W1_P	15.6	0.32	0.96	37.3	2.00	0.99
	W2_P	13.9	0.34	0.99	36.4	1.71	0.99

* Langmuir, $q_e = \frac{C_e b Q_{max}}{(1 + b C_e)}$; Freundlich, $q_e = k C_e^{1/n}$.

The amount of phosphate ions adsorbed from the solution of concentration $10 \text{ mgPO}_4 \text{ dm}^{-3}$ on goethite decreased along with the increasing pH value (Figure 5). The steady adsorption level of ca. 70% was observed only in an acidic environment, within the range of pH 4–5, and with a further growth of pH adsorption dropped down on average by 8% per one pH unit. In the case of adsorption of phosphate ions onto the alginate/goethite beads, no changes in adsorbed phosphate with a change in pH were observed. At pH 4 it was 97.6%, while at pH 10 it dropped to 96.3%.

**Figure 5.** Effect of pH on phosphate adsorption onto goethite and alginate/goethite beads.

4. Discussion

The chemical content of the aquatic environment the alginate/goethite capsules were stored in had a strong effect on their mechanic stability. For WD and natural water W2, after 7 and 28 days of storage, no significant changes in the mechanic strength of capsules were obtained. Similar results were found by LeRoux et al. [38] after 15 h of exposure of alginate gels to physiologic concentrations of NaCl. The compressive, equilibrium shear, and dynamic shear moduli decreased by 63, 84, and 90% of control values, respectively. The material properties exhibited no further changes after seven days of exposure to NaCl. The mechanic stability of the alginate/goethite composite was diminished the most in W1 water, which contained monovalent cations (sodium and potassium) and magnesium. In the natural water W1, the concentration of these ions was several times smaller and, in the case of potassium, its presence was not found. It is widely recognized that monovalent cations and magnesium do not induce alginate gel formation [39]. In addition, gels can be dissolved because of the release of divalent ions into the surrounding media due to exchange reactions with monovalent cations [40]. The degradation rate of the alginate gels is also strongly dependent on other environmental factors: the degree of oxidation, pH, and temperature [41].

According to the classification of Giles [42], for all the cases one group of type L isotherms was determined. That group includes those isotherms where no competitive action between the adsorbate and solvent occurs. The same form of isotherms was achieved by those authors, who studied phosphorus adsorption processes on goethite [13,15] and on other iron-containing adsorbents, e.g., the alginate/Fe³⁺ hydrogel beads [33], lignocellulose [43], wood biomass partially impregnated with carboxymethylcellulose, and FeCl₃ [44,45] or surfactant-modified natural zeolite [46]. As a result of studies on adsorption of phosphorus on a mix of iron oxide and gypsum, an S-type adsorption isotherm was obtained, characteristic for arrangements where the solvent is strongly adsorbed. Values calculated in Freundlich and Langmuir isotherms indicate that both adsorption intensity and the extent of adsorption of phosphate ions in the natural waters were higher on the alginate/goethite composite than on goethite.

Table 4. Freundlich and Langmuir isotherms constants for phosphate adsorption on adsorbents activated with iron ions.

Adsorbent	Adsorbate	Freundlich Model*			Langmuir Model*			Source
		<i>k</i>	<i>1/n</i>	<i>R</i> ²	<i>Q</i> _{max}	<i>b</i>	<i>R</i> ²	
Modified lingoellulosic	P	1.76	0.211	0.99	2.31	6.41	0.98	[43]
Iron oxide tailing	P	3.59	0.19	0.99	8.21	0.44	0.98	[11]
Wood fiber treated with ferrous chloride	PO ₄	0.15	0.54	0.97	3.00	0.02	0.96	[44]
Wood fiber treated with CMC**/Fe	PO ₄	1.3	0.27	0.99	4.30	0.19	0.99	[45]
Fe–Mn binary oxide	PO ₄	27	0.07	0.96	33.20	13.60	0.89	[47]
Synthetic goethite	P	17.3	0.11	0.99				[13]
Synthetic akaganeite	P	10	0.42	0.99				[13]

* Langmuir, $q_e = \frac{C_e b Q_{max}}{(1 + b C_e)}$; Freundlich, $q_e = k C_e^{1/n}$. ** Carboxymethyl cellulose.

A comparison between the calculated parameters of adsorption isotherms and parameters calculated by other authors (Table 4), who studied adsorption of phosphate ions on adsorbents containing iron, indicates the highest affinity for phosphate ions to exist in the alginate/goethite composite. The composite presented a much higher sorption capacity than goethite. Similar results were obtained for the removal of phosphate, dyes, and heavy metals on alginate-based composites. Alginate/zirconium sulfate composite has better sorptive qualities than powdered zirconium sulfate [32]. The adsorption capacity of magnetic nanoparticles/activated carbon/alginate beads was found to be higher than the non encapsulated adsorbents for methyl orange and methylene blue [48]. Vu et al. [49] found that the graphene oxide/Ca-alginate beads exhibited greater adsorption efficiency for Cr⁴⁺ and As⁵⁺ than activated carbon and carbon nanotubes. The entrapment of the (hydro)oxide in the calcium alginate gel matrix improved the As³⁺ and As⁵⁺ sorption by 60% [50]. An increased goethite capacity when the adsorbent is entrapped might be attributed to the presence of calcium alginate activated for phosphate adsorption by partial substitution of calcium by iron ions [30]. Fe³⁺ ions can bind to the binding sites in the alginate backbone and form spatially separated iron centers [51].

Increased pH resulted in a significant reduction of adsorption capacity of the goethite towards phosphate ions. The phosphate adsorption on the iron oxides and hydroxides tended to decrease with an increase of pH was recorded also by other authors for both goethite [12] and other adsorbents, including aluminum hydroxide [52] and iron oxide(III) [11]. The distribution of potentials and electric charges near the surface of metal oxides and hydroxides depends mainly on the adsorption and desorption of protons, pH has a significant effect on the characteristics of surface adsorbent particles. In aqueous solution, protonation and deprotonation might take place at the hydroxyl sites on the surface of the metal hydroxides. According to the pH_{PZC} value, the surface of goethite is positively charged at pH less than 8.2 favoring the adsorption of phosphate ions. The rapid decrease in phosphate removal at alkaline pH is attributed to the competition effect of hydroxyl ions [53]. Luengo et al. [54] used ATR-IR spectroscopy to study phosphate adsorption on goethite concluded that at pH 4.5 two surface complexes nonprotonated (FeO)₂PO₂ and protonated (FeO)₂(OH)PO to evolve in time rather independently. At pH 7.5 and 9.0 the dominated surface species is (FeO)₂PO₂. The presented results show that alginate/goethite composite removed phosphate ions efficiently within the broad range of

pH, from 4 to 10. It might be related to the presence of alginate. As the increasing pH, hydroxyl and carboxylate groups within alginate beads gradually dissociated and the surface charge on the beads becomes negative which enhanced electrostatic this groups interaction with the iron ions [30], which can bind phosphates.

Adsorption at the equilibrium state and the rate constant of adsorption of phosphate ions on the goethite increased with the temperature growth. This indicates that the adsorption of phosphate by the goethite most likely occurs through chemical rather than physical interactions. Similar changes were observed for adsorption of phosphorus in natural sediments [55] and on iron oxide [11]. Temperature had some effect on the process of removing phosphorus when using goethite forms in a study only at the initial phase of the process, and as soon as the system reached the adsorption equilibrium, such differences ceased. In most of goethites there is a fast initial adsorption process that takes place in a few minutes, followed by a slower process that may last for several days or even weeks. This two-step adsorption seems to be normal for phosphate adsorption on goethite [54]. The values of the rate constants obtained for goethite were always much higher than those obtained for the alginate/goethite composite. These results indicate that the decrease in adsorption rate is related to presence of the alginate gel. Other authors reported longer equilibrium times when studying arsenates sorption onto Fe^{3+} and Ni^{2+} (hydro)oxides entrapped in calcium alginate compared to their native form [50]. It might be that the phosphate was slowly adsorbed on the alginate/goethite capsules due to the quasi-solid structure of natural hydrocolloid materials, which would be expected to retard the transport of a phosphate due to the movement through the aqueous regions between the polymer chains [56]. Moreover, calcium alginate ($\text{pH}_{\text{pzc}} = 6.5$) is expected to be partially ionized at $\text{pH} > 6.5$. Therefore, the negative charge on the calcium alginate surface could render difficult the diffusion of phosphate species through the gel to the adsorbent surface.

The proposed adsorbent can be a subject of further application studies investigating the use of waste goethite for the removal of phosphate from contaminated water and wastewater. The resulting hydrogel products enriched with phosphorus could be used as raw materials for the production of phosphate fertilizers or as a multifunctional soil improvement increasing the content of phosphorus and iron in soil, retention capacity of water in soil, and the phosphorus availability.

5. Conclusions

As a result of gelation of alginate in six configurations of suspensions, that differed with goethite content (within the range 2–10 g), spheroid capsules were produced. The chemical content of the aquatic environment the capsules were stored in had a strong effect on their mechanical stability. It was found that the highest mechanical strength and stability was typical of capsules containing 6g goethite in 1.5 mL alginate. The maximum adsorption capacity of phosphate on the alginate/goethite composite was found to be higher than on non-encapsulated goethite. The gelation of goethite led to an almost double increase in this capacity upon adsorption from deionized water and to an increase of 50% on average upon adsorption from natural waters. Increased pH in aquatic environments brings about a significant reduction in sorption capacity of goethite towards phosphate ions, while the alginate/goethite adsorbent removes phosphate ions equally efficiently within a pH broad range, from 4 to 10.

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