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IRON-ALGINATE GEL BEADS USED FOR PHOSPHORUS REMOVAL FROM WASTEWATER

In this study, the applicability of activated filter medium prepared by the cross-linking of the bio-polymer sodium alginate doped with iron chloride for phosphorus removal was investigated. For the purpose of evaluating the effectiveness of such a removal, bench-scale studies were carried out on the phosphate solution and wastewater using a batch and column system. The static sorption on activated filter medium appeared to be more effective compared to the filtration process. The uptake of phosphate was attained within 90 minutes and uptake percentage was 88% for 10 g of beads and the initial phosphate concentration of 28.9 mg/dm³ in wastewater. Like other selective sorption processes, intra-particle diffusion was the primary rate-limiting step for dissolved phosphorus removal by iron-alginate beads.

1. INTRODUCTION

The presence of phosphates in water bodies and wastewater is the major cause of pollution of rivers and lakes which for their environmental significance should be under special protection. Thus removal of these contaminants is one of the fundamental goals in waste treatment. Commonly applied technologies consisting in phosphate precipitation do not always ensure adequate treatment of wastewater. Moreover, they result in production of large amounts of chemical sludge and cause secondary pollution and salination of wastewater. Therefore, intensive research is continued in order to develop effective and less costly phosphorus removal methods used as a tertiary wastewater treatment. The new method suitable for residual phosphorus removal, which fulfils the above requirements, is filtration using activated filter medium [1]. This kind of filter medium can be chemically activated and then chemical compounds, contained in porous absorbent grain, bind wastewater pollutants. Applying the filtra-

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tion with chemically activated filter medium without initial precipitation of dissolved phosphorus salts one avoids the production of sludge masses and any risk that may result from contamination by the coagulants through their dissolution. The adsorbent used in the investigation had a form of an iron hydroxide coated gravel [2]. The results of our study confirmed the higher efficiency of phosphorus compounds removal by activated filter materials than by inactivated filter media. Furthermore, the possibility of regenerating the material with small quantities of coagulant brought about a decrease in operating costs.

Different activated sorbents have been developed/identified and tested for their abilities to uptake phosphorus. Recently, SCOTT and FARRAH [3] and AYOUB et al. [4] reported promising results of removing orthophosphates with the use of iron and aluminium hydroxy (oxide) coated filter media. However, it should be emphasized that the complex process of phosphate adsorption by this kind of active filter medium proceeds only on its surface.

The efficiency of such a filtration depends mainly on the properties of material used as the medium, and particularly on contents and accessibility of chemical compounds responsible for phosphorus binding. KHADHRAOUI et al. [5] investigated phosphorus removal using calcium-based sorbent, and reported that modification of the physical structure by creating large pore sizes appeared to be effective in increasing their phosphorus uptake.

The aim of our study was to further improve the chemically activated medium, adapted to phosphorus binding. An increase in activated filter medium yield can be obtained by making use of a porous structure of absorbent that could provide the phosphorus reduction in wastewater not only on its surface but in the whole volume. A proper material, environmentally benign, satisfying the above assumption is sodium alginate. This natural polymer has recently been used as a matrice for immobilization of cells, enzymes, drugs and other substances [6]–[9].

Alginate gels are formed by forcing the alginate molecules to self-association. The gellification is accomplished by diffusion into the alginate droplet of divalent ions (i.e., Ca^{2+}), which connect two alginate molecules, creating ionic interchain bridges. This means that when multivalent ions are added to a sodium alginate solution they will replace the sodium ions from alginate and cause formation of the gel structure [10], [11]. Advantage has been taken of these specific properties of sodium alginate in immobilization of iron chloride in gel beads. The porous activated medium thus formed enables diffusion of phosphates inside its structure where the chemical binding with iron ions proceeds. The additional advantage of alginate gels is the possibility of reactivating them in a similar manner to that of ion exchange resins and activated carbon.

The objective of this study was therefore to evaluate the effectiveness of the new, activated in whole volume, filter bed, which consists of entrapped iron chloride in sodium alginate matrix.

2. MATERIALS AND METHODS

2.1. MATERIALS

Iron-alginate beads were prepared from commercially available alginic acid sodium salt (medium viscosity) purchased from Sigma Aldrich Chemie GmbH (Schnelldorf, Germany) and iron chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) purchased from POCH S.A. (Gliwice, Poland). Anhydrous calcium chloride manufactured by POCH S.A. (Gliwice, Poland) was used as the calcium salt for the formation of beads. Potassium diphosphate (KH_2PO_4) obtained from the same manufacturer was used as a source of phosphorus throughout the experiments, except when treated wastewater was taken as a test sample. The test batch of treated wastewater effluent was collected from the municipal wastewater treatment plant in Olsztyn. The composition of the wastewater of pH 6.9 was as follows: total suspended solids, 23.0 mg/dm^3 ; carbon oxygen demand (COD), $94.8 \text{ mg O}_2/\text{dm}^3$; nitrate-nitrogen, $1.0 \text{ mg NO}_3^-/\text{dm}^3$; nitrite-nitrogen, $0.013 \text{ mg NO}_2^-/\text{dm}^3$; ammonia-nitrogen, $61.0 \text{ mg NH}_4^+/\text{dm}^3$; chloride, $69.0 \text{ mg Cl}^-/\text{dm}^3$; sulfate, $50.0 \text{ mg SO}_4^{2-}/\text{dm}^3$; total iron, $0.88 \text{ mg Fe}^{3+}/\text{dm}^3$; phosphate, $28.9 \text{ mg PO}_4^{3-}/\text{dm}^3$ and total phosphorus, $32.6 \text{ mg PO}_4^{3-}/\text{dm}^3$.

2.2. FABRICATION OF IRON-ALGINATE BEADS

Based on a series of experiments the simplest and optimal preparation protocol of iron-alginate beads characterized by appropriate stability and efficiency of phosphorus compounds removal was established. The sodium alginate solution (2.2%) was made by dissolving sodium alginate in distilled water and heating the mixture in water baths at a water temperature of approximately 50°C . The alginate gel obtained was mixed with a previously prepared (neutralized to pH 6–7 by NaOH) aqueous solution of iron chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.25%). Spherical beads were made by adding the obtained mixture dropwise to gently stirred cold 0.05 M CaCl_2 solution with the help of a syringe of 1.5 mm in diameter. Calcium chloride was used as a source of calcium ions to initiate gellation. Beads were then maintained in the vortexed solution and allowed to solidify for 20 hours. The iron-alginate beads were separated from the solution by filtration. The excess of crosslinker solution was removed by rinsing it twice with distilled water until the Cl^- ions were undetectable. The beads were stored in the container with distilled water prior to use.

2.3. SORPTION EXPERIMENTS

For the purpose of evaluating the efficiency of phosphorus removal with iron-alginate gel beads, batch and column experiments were carried out using the phosphate solution and biologically treated wastewater.

Batch sorption experiments were carried out by mixing different amounts of absorbent (iron-alginate beads) with 50 cm³ of KH₂PO₄ solutions (series I, II, III, IV) and biologically treated wastewater (series V) at a constant speed of 100 rpm. The amount of PO₄³⁻ remaining in the solution (C_r), the total iron and pH of the solution were determined for definite time intervals. Additionally, for treated wastewater samples, carbon oxygen demand (COD), nitrate-nitrogen, nitrite-nitrogen, ammonia-nitrogen, chloride (Cl⁻), sulfate (SO₄²⁻), total iron (Fe³⁺) and total phosphorus concentrations were determined. The sorption experiments were also conducted for beads made of sodium alginate alone (without iron chloride) as a control sample.

Table 1

Initial composition of artificial wastewater used
in batch sorption experiments

Parameter	Initial artificial wastewater composition			
	Series			
	I	II	III	IV
P-PO ₄ [mgPO ₄ ³⁻ /dm ³]	0.5	1.3	6.0	8.9
Total Fe [mgFe ³⁺ /dm ³]	0.01	0.01	0.01	0.01
pH	6.8	7.0	7.0	7.2

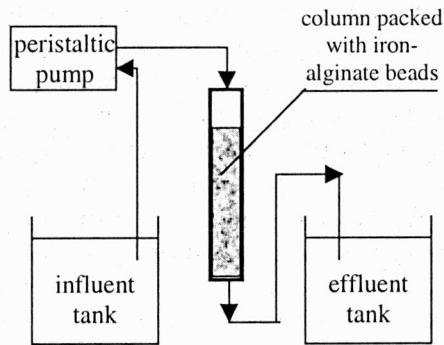


Fig. 1. Schematic diagram of the active filter system

Laboratory tests conducted on artificial wastewater (series I, II, III and IV) differ from each other in the pH and initial concentration of orthophosphates (C₀): in series I - C_{0I} = 0.5 mg PO₄³⁻/dm³, in series II - C_{0II} = 1.3 mg PO₄³⁻/dm³, in series III - C_{0III} = 6.0 mg PO₄³⁻/dm³, in series IV - C_{0IV} = 8.9 mg PO₄³⁻/dm³ (table 1). The phosphate reduction process was investigated for four quantities of iron-alginate beads: 10 g, 5 g, 3.3 g, 1.6 g. After the specified reaction times: 1, 5, 15, 30, 60 and 90 minutes

(which was found to be sufficient for attaining equilibrium), the beads were removed from the bottles to stop further reaction with phosphates, and the supernatants were analysed for PO_4^{3-} and pH was measured. For laboratory tests of treated wastewater (series V) 10 g of iron-alginate beads were used and the analysis of wastewater composition was carried out after 30, 60 and 90 minutes of contact time.

Each series was repeated three times. Results of all repetitions were presented as the average value.

Column sorption experiments were carried out by filtration of artificial wastewater through active filter system (figure 1). Experiments were conducted in 8 series differing from each other in the depth of the column filling, filtration rates and filtration manner. Each series was conducted on a separate filter. Each filter consisted of a 1.5 m long glass column with 0.01 m internal diameter packed with iron-alginate gel beads. The depth of the column filling was in the range of 0.1–1.0 m and filtration rates of 4–29 m/h were applied to the filters in individual series. A peristaltic pump was used to pump the test water from the influent storage tank in a gravitational or upflow mode, continuous or periodic manner through the columns. The effluent from the column was directed to a storage tank.

Data regarding operational parameters, such as phosphorus concentration, pH of influent and effluent were recorded during each experimental run at constant intervals until the breakthrough was achieved. Because it was noted from the batch experiments that the inactivated filter medium had no phosphorus sorbing capabilities, tests on inactive beads were discontinued.

The amount of ion removed was determined by calculating the difference of the concentration of ion in solution before (C_0) and after (C_r) absorption process. The sorption efficiency (E) of the activated filter medium was calculated using the following equation:

$$E(\%) = \frac{C_0 - C_r}{C_0} \times 100. \quad (1)$$

The amount of total Fe released from the beads was determined by calculating the difference of the concentration of total Fe in solution before and after the sorption process. The determination of the amount of Fe released from the beads allows evaluation of their operational stability. As the amount of iron released increased, the operational stability decreased.

Samples were analysed in duplicates for total phosphorus, nitrates, nitrites, ammonium, iron, sulfates, chloride using standard analytical procedures for Hach DR/2010 spectrophotometer [12]. Orthophosphate ion content was measured colorimetrically with ammonium molybdate and ascorbic acid at a wavelength of 710 nm using the spectrophotometer SEMCO S 91E, Polish Standard (PN-89/C-04537/03). Organic compounds expressed as total and dissolved COD [PN 74/C-04578/03] and total suspended solids [PN 73/C-04559/02] were measured according to HERMANOWICZ [13]. pH was measured using HANNA/HI 8818 pH-meter.

3. RESULTS AND DISCUSSION

Pretreatment or doping of polysaccharide, such as sodium alginate, with cations allows interaction between the biosorbent and anionic contaminants. In this study, alginate gel was treated with Fe^{3+} and Ca^{2+} to optimize both sorptive capacity for phosphate and the physical properties of the gel beads. Ca^{2+} ions act as primary gel forming cation providing a stable structure for the polymer network. The Fe^{3+} ions were included in the gel matrix and then partly replaced the Ca^{2+} to provide favourable sorption sites for phosphates. The criteria of the optimal choice of sodium alginate concentration of 2.2% and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ concentration of 1.25% were the high phosphorus reduction efficiency and the high operational stability which were determined in initial optimization experiments [14]. The iron-alginate beads had a diameter of 3.3 mm and average standard deviation was ± 0.33 . The influence on the phosphorus removal process was not investigated.

Batch experiments. Phosphate partitioning into the solution and gel phase is shown as a function of time in figure 2. The shape of the curve is typical of sorption phenomena. The uptake attained equilibrium within 90 minutes and relatively large E value (56.5–90%) in the range of initial phosphate concentration of 0.5–32 mg/dm^3 was obtained using 10 g of beads. The quantities of orthophosphate that remained in solution phase, determined for defined time intervals, distinctly indicated that the sorption efficiency decreased with increasing contact time. With an increase in the number of active sites the sorbent attraction force decreases up to the moment the beads sorption capacity becomes used up. Kinetic data for phosphate sorption clearly indicate that sorption equilibrium is reached within 60–90 minutes. The uptake of phosphates was rather fast within the first 15 minutes, probably due to the adsorption on the surface, followed by a slow step controlled by mass transfer through gel matrices; the gel matrices are constructed of “egg-box” junctions and the diffusion of phosphate ions through them seems to be the rate-determining step [15]. It was observed that the phosphorus removal rate increased with an increase in the iron-alginate beads concentration (with increasing sorption surface) (figure 3) and an increase of the initial phosphate concentration (figure 2). Figure 4 shows that with the increasing phosphate concentration in a solution the uptake per unit of bead weight increased in a linear manner, with the effect being almost the same for the lower bead concentration, i.e., 1.6 g and 3.3 g. At a higher bead concentration the amount of phosphate adsorbed per unit weight of bead actually decreases. In the range of initial phosphate concentration used the phosphate concentration therefore does not appear to be the limiting factor. It can be noted from figure 3 that the phosphorus removal depends on the area of contact surface. The application of iron-alginate beads in large amounts caused an increase in the phosphorus removal efficiency (from 29.1% up to 85.8% in series IV), but the amount of phosphate adsorbed per unit of alginate bead weight was much higher when smaller amounts were used (figure 4). The lower phosphate sorption per unit of medium weight obtained when using large amounts of beads could be caused by the fact that orthophosphates occupy in the first place the surface active sites and then those located deep inside the gel bead as

a result of the internal diffusion process. A slight increase in pH of synthetic wastewater after the contact with activated medium was observed. The pH of treated artificial wastewater increased in all investigation series maximally by 0.2. This strongly suggests an ion exchange mechanism participating in complex phosphate uptake by iron-alginate beads.

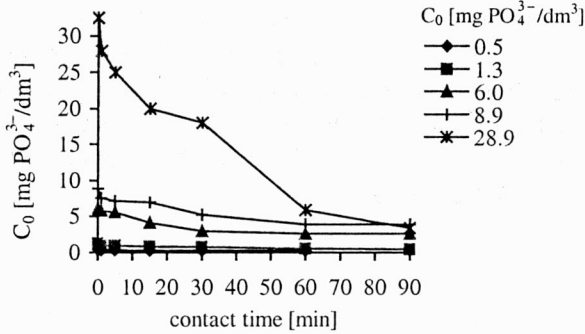


Fig. 2. Phosphate sorption kinetics depending on initial phosphate concentration (C_0)

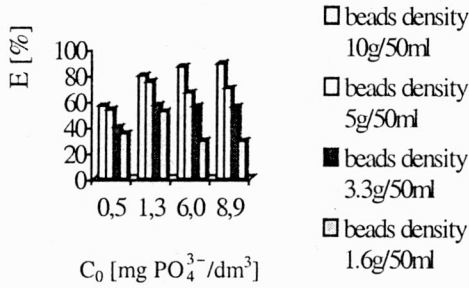


Fig. 3. Phosphate removal efficiency of iron-alginate beads depending on initial phosphate concentration and amount of activated medium

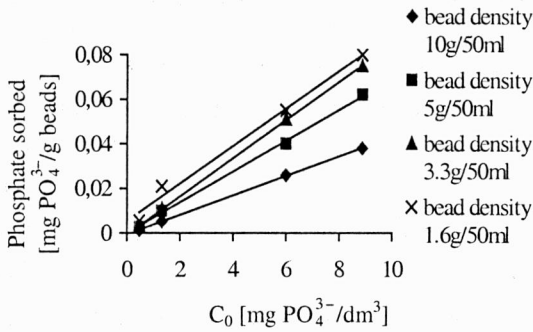


Fig. 4. Phosphate adsorber per unit of bead weight depending on initial phosphate concentration and amount of activated after 60 minutes of sorption experiments

In series when artificial wastewater was used, the amount of total iron, before and after sorption experiments, stayed unchanged ($0.01 \text{ mg Fe}^{3+}/\text{dm}^3$). It proved the sufficient operational stability of iron-alginate beads.

ZHAO and SENGUPTA [16] reported that dissolved chemicals such as sulfate, chloride, nitrate, bicarbonate and dissolved organic matter act as competing species relative to phosphorus. However, the results of the tests conducted on actual wastewater were as successful as the results obtained for phosphate water supply solutions (table 2). Significant sorption of 88.2% was achieved although the initial phosphate concentration was relatively high ($28.9 \text{ mg}/\text{dm}^3$) (figure 2). Moreover, iron removal of 94.3% was reported, which is due to high metal sorption capability of alginates proved by many researchers [17], [18].

Table 2

Wastewater composition after definite time of its reaction with 10 g of activated filter medium

Parameter	Wastewater composition after contact with activated filter medium			
	Contact time [min]			
	0	30	60	90
COD [$\text{mg O}_2/\text{dm}^3$]	94.8	87.0	86.4	85.4
Total P [$\text{mg PO}_4^{3-}/\text{dm}^3$]	32.6	8.7	5.7	5.7
P- PO_4 [$\text{mg PO}_4^{3-}/\text{dm}^3$]	28.9	18.0	5.9	3.4
N- NH_4 [$\text{mg NH}_4^+/\text{dm}^3$]	61.0	32.0	32.3	32.3
N- NO_2 [$\text{mg NO}_2^-/\text{dm}^3$]	0.013	0.013	0.012	0.011
N- NO_3 [$\text{mg NO}_3^-/\text{dm}^3$]	1.0	2.4	2.7	2.7
Total Fe [$\text{mg Fe}^{3+}/\text{dm}^3$]	0.88	0.12	0.11	0.05
SO_4^{2-} [mg/dm^3]	50	55	75	75
Cl^- [mg/dm^3]	69	119	111	85
Total suspended solids [mg/dm^3]	23	-	-	-

Chemical and biological treatment of N- NH_4 -containing wastewater is widely used. In the case of high concentration of N- NH_4 in the waste, air stripping process is the most common method. However, this treatment process is relatively expensive. Therefore, the phenomenon of N- NH_4 sorption on iron-alginate beads is very interesting as a 50% NH_4^+ ion removal was obtained (table 2). Of the various treatment methods for nitrate removal, ion exchange has been found to be very efficient [19]. However, the efficiency of NO_3^- ion removal with activated medium was generally low (table 2), supposedly, due to lesser physical sorption affinity of NO_3^- ion with partially charged ions. In an earlier study [20], a 58% NH_4^+ ion removal with refuse concrete, used as PO_4^{3-} sorbent, was reported. The activated medium as iron-alginate beads had lower COD removal efficiency (approximately 10%) than other natural sorbents (table 2). In an earlier study with refuse concrete

[21] as independent medium, COD removal of 24–30% was reported, which is due to higher organic matter adsorption capability of this material. Removal of organic matter by other treatment media is the possible result of higher affinity of carbon for their substrates.

The results suggest that the contact of the activated medium with synthetic wastewater did not exert any considerable effect on other qualitative parameters of wastewater. In applying iron-alginate beads, the impact of chloride and sulfate release on the environment should be taken into account, but is not likely to be a major issue.

Experiments conducted with the use of inactive filter medium showed that beads prepared only from sodium alginate did not remove phosphorus (data not shown). Therefore, alginate gel being an inert material played only the role of the carrier in the sorbent. The absence of phosphate uptake by inactivated beads demonstrates that phosphate accumulation in the pore volume of iron-alginate beads by passive diffusion is negligible compared with specifically bound PO_4^{3-} . This is consistent with the negligibly small water volume in the beads compared with the total solution volume in batch experiments.

Column sorption experiments. The effect of the activated filter media on the removal of orthophosphate from artificial wastewater at different depths of the media in the column and constant flow rate of 14 m/h is shown in figure 5. The phosphorus removal efficiency is slight for less than 1.0 m media depth in the column, with the average orthophosphate removal being in the range of 7–17% and the time to the breakthrough only 5–23 hrs. Best results were obtained when 1.0 m media depth in the column was used, the average orthophosphate removals being 20.5% and the filtration time lengthened up to 30 hrs. In the previous studies [14], two columns with 0.01 m and 0.02 m internal diameter packed with iron-alginate gel beads of different media depths and different amounts of particles were used. In the case where fewer beads were packed but the media depth was greater, the phosphorus removal efficiency was much higher. This confirmed the presumption that it is the media depth that plays major the role in filtration process rather than the amount of media particles.

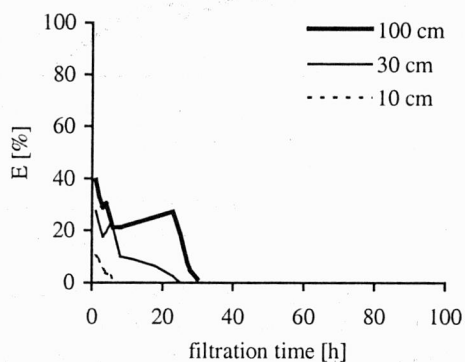


Fig. 5. Phosphate removal efficiency during filtration through activated filter medium at constant flow rate of 14 m/h depending on depth of the media in the column

A significant increase in phosphate removal efficiency with decreased flow rates has been reported to occur with medium of 1.0 m. Figure 6 illustrates that the most significant adsorption of PO_4^{3-} ion was observed with the flow rate reduction from 14 to 4 m/h. The average phosphate removal was two times higher (43.8%) but the filtration time to the breakthrough was still short (32 h). On the other hand, with an increase in flow rate from 14 to 29 m/h the phosphate removal efficiency remained at the level of 13.5% and the filtration time was 20 hrs.

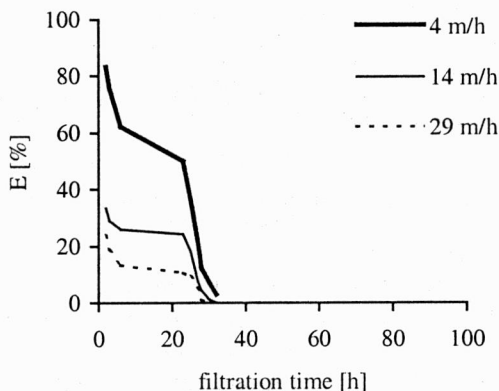


Fig. 6. Phosphate removal efficiency during filtration through activated filter medium at constant column depth of 1.0 m depending on filtration rates

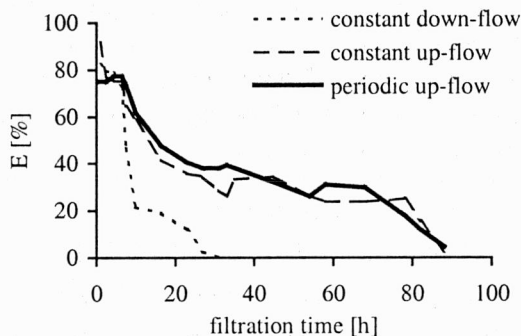


Fig. 7. Phosphate removal efficiency during filtration through activated filter medium at constant column depth of 1.0 m and flow rate of 4 m/h depending on filtration manner

All of the previous tests were conducted in a constant, gravitational flow mode through the columns. From figure 7 it can be noted that the phosphate removal efficiency is dependent on filtration manner. A significant increase in filtration time to the breakthrough (88 hrs) with changing the flow direction (upflow mode) has been reported to occur with the medium of 1.0 m and the flow rate of 4 m/h. The phospho-

phosphorus removal reached a maximum value of approximately 50% when the periodic up-flow system was used (2 minutes of operation and 10 minutes of standstill). A possible hypothesis for this behaviour is the slight stirring of the filter medium, due to which a better contact of wastewater with beads is achieved.

Measurements of the effluent pH showed minor changes (data not shown). The results for iron were also negative ($< 0.1 \text{ mg/dm}^3$). This indicated the absence of any release of iron from the activated filter medium, thus a high operational stability of the medium.

Summing up, the static sorption on activated filter medium appeared to be more effective compared to the filtration process. The weak PO_4^{3-} removal in the filtration process may be attributed to the limitation factor for effectiveness and rate of wastewater treatment such as internal diffusion process, which requires a longer contact time of wastewater with gel beads.

4. CONCLUSIONS

This paper describes phosphorus removal from artificial wastewater and biologically treated wastewater by the novel activated filter medium under different experimental conditions. Bench scale tests were conducted to investigate fundamental aspects of phosphorus removal from contaminated water and treated wastewater by use of biosorbent, which is environmentally benign. The phosphate ions were removed by physical-chemical sorption. The process is composed of a few stages. The first stage is an ion transport from solution phase to the absorbent surface. The second stage is the external diffusion process in pores of the gel bead external layer. The next one is the internal diffusion process inside the porous structure of gel beads, and after reaching the active sites the phosphate bonding takes place.

From the data collected in this investigation, the following conclusions can be drawn:

- Iron-alginate beads were found to be effective in removing phosphorus over a wide concentration range (from 0.5 to 29 mg/dm^3) through a static sorption process. Up to 90% removal of PO_4^{3-} from solution was achieved for an initial phosphate concentration of 8.9 mg/dm^3 after 90 minutes of contact time with 10 g of beads.

- Like other selective sorption processes, intraparticle diffusion is the primary rate-limiting step for dissolved phosphorus removal by iron-alginate beads.

- Removal depends on correct specification of the parameters of filtration technology and the nature of the filter bed. Phosphate removal efficiency during filtration through activated filter medium is dependent on depth of the media in the column, filtration rate and filtration manner.

- The equipment required to operate and maintain the system is readily available.

The ability of iron-alginate beads to take up phosphate ions from artificial wastewater has been clearly demonstrated. The relatively high rate of phosphorus removal

obtained after a short reaction time is a very interesting point for applications in water. Moreover, the alginate biopolymer is derived from kelp, so it is not only environmentally benign compared with other sorbent made from synthetic polymer, but the cost of large-scale production could be low enough for a single use. Additionally, the selenite, chromate and arsenic sorption capacity of iron-doped alginate beads was reported [17], [21], [22]. The findings from our study can be used as the basis for subsequent efforts in developing a removal strategy using iron-alginate gel sorbent. Further experiments should involve pilot studies of water and wastewater treatment.

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ZASTOSOWANIE ZIAREN ALGINIANOWO-ŻELAZOWYCH DO USUWANIA ZWIĄZKÓW FOSFORU ZE ŚCIEKÓW

Badano możliwość zastosowania wypełnienia aktywnego filtrów, utworzonego w wyniku sieciowania alginianu sodu połączonego z chlorkiem żelaza, do usuwania związków fosforu. Celem badań laboratoryjnych było określenie efektywności usuwania fosforu przez wypełnienie aktywne w warunkach statycznych i przepływowych. Sorpcja fosforu na wypełnieniu aktywnym w warunkach statycznych była efektywniejsza niż podczas filtracji. Usuwanie ortofosforanów ze ścieków trwało 90 minut, osiągając 88% efektywności dla 10 g ziaren alginianowo-żelazowych i początkowego stężenia fosforanów w ściekach 28,9 mg/dm³. Podobnie jak w przypadku innych selektywnych sorbentów, proces dyfuzji wewnętrznej był głównym czynnikiem limitującym szybkość usuwania rozpuszczonego fosforu na żelowym wypełnieniu aktywnym.

