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Phosphate adsorption from natural waters and evaluation of sediment capping using modified clays

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ABSTRACT

The aim of this study was to investigate the efficiency of Fe-modified bentonite as adsorbent for phosphate removal from natural waters with an additional estimation of sediment capping effectiveness preventing phosphorus release from eutrophic lake sediments. A modified inorganic bentonite (Zenith/Fe) based on natural Zenith-N, was prepared by embedding Fe in its interlayer space. Its morphology and structure was thoroughly characterized and adsorption isotherms were evaluated in a wide range of pH. The initial phosphate concentration was 0.1 mg/L, and represents a eutrophic natural ecosystem. The results showed that Zenith/Fe was effective at removing phosphate from aqueous solution at pH values from 5 to 9. The maximum adsorption capacities (q_m) calculated from the Langmuir model were 11.60, 14.45, 14.14, 11.20, and 9.98 mg/g for pH range from 5 to 9, respectively. Adsorption kinetics showed that most phosphates (more than 80% at pH 6) are adsorbed during the first 1 h. The adsorption rate of phosphates fits pseudo-second-order kinetic models for all pH values considered. Moreover, Zenith/Fe is likely to be effective in the adsorption of phosphates in natural environments in the presence of strong reducing conditions. In addition, the application of Zenith/Fe as a P-inactivation agent resulted in about 68% reduction of the phosphate flux from the sediments under anoxic conditions. Thus, Zenith/Fe is a very good adsorbent for phosphorus removal and potential lake restoration.

Keywords: Bentonite; Eutrophication; P-inactivation agents; Phosphorus; Restoration

1. Introduction

Eutrophication is one of the most widespread environmental problems responsible for the deterioration of the water quality in worldwide scale. It is still the first and foremost problem of surface waters and the most visible example of human alteration of the biosphere [1,2]. More than 40% of water bodies in many regions of the world are considered to have eutrophication problems. One gram of phosphorus is required for every 7 g of nitrogen for the formation of organic matter [3]. Therefore, the excess of bioavailable phosphorous is the key nutrient which causes

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eutrophication of water bodies and results in increased cyanobacterial growth.

The Water Framework Directive (WFD) (2000/60) was adopted in December 2000 to protect and improve the surface waters quality in EU. The main target of the WFD is to achieve a minimum good ecological status in all water bodies by the year 2015. A recent study of over 14,000 lakes less than 1 ha in size in Great Britain revealed that 51% are likely to require P- reduction measures to meet the Water Framework Directive and achieve "good status" by the year 2015 [4,5]. Therefore, regional water action plans have been adopted to explore possibilities for the lakes to meet the criteria of "moderate, high," or "good" ecological condition [6–8].

Lake sediments are considered a source for nutrients and therefore play a decisive role in eutrophication. Phosphorus can be found in lake sediments in various forms. Some forms are practically bound in the sediments, while others are implicitly mobile leading to release of phosphorus under specific conditions [8,9]. Inorganic phosphorus which occurs in its readily soluble form as orthophosphate anion can be found in sediments either as part of a mineral or as precipitated phosphate salt [9,10]. Internal P loads derive from the release of phosphate sequestered by oxidized iron species and the composition of organic matter in the lake sediments releasing biologically available (bioavailable) P as soluble phosphate into the water column during periods of anoxia, usually in summer [5,10].

Lake restoration efforts were traditionally focused on reducing nutrient inputs from the catchment, such as sewage discharges and diffuse runoff from agricultural land. Catchment remediation works including restricting stock access to the lake, enhancing riparian buffer zones, and installing constructed wetlands on the main inflow have been previously used [11]. However, the in-lake concentration is still high enough to maintain eutrophic conditions. Thus, even in cases where this action has been quite successful, the recovery of the waterbody may still be very slow due to internal nutrient loads. According to Kagalou et al. [12], after a short-term recovery, the eutrophication status of the lake remains eight years later (1996–2004), suggesting the importance of the internal loading process. Internal loading is expected to enhance the eutrophication and reduce the lake's response time to external reductions in phosphorus load by a decade or longer.

A range of methods have been developed to reduce P release from sediments, the most common being: physical approaches, such as artificial destratification, oxygen injection, and dredging; and geochemical approaches as the application of active capping materials. The active barrier systems (or active capping agents) are generally chemical or geochemical materials capable of demobilizing contaminants by the adsorption or precipitation processes [11].

Nowadays there has been growing interest in finding inexpensive and effective clays as phosphorus adsorbents from natural water bodies. Several studies have been carried out on the adsorption of phosphates on activated aluminum oxide [13], hydroxides sludge [14], ferrihydrite [15], oxide tailings [11], titanium dioxide [16], and zeolite [17]. However, some materials have the capability to form hazardous species. Aluminum toxicity to living organisms (e.g. plants, fishes, etc.) has been demonstrated in several cases [18].

Bentonite, as one of the cheap clay minerals, has shown a great application potential in water treatment [19,20]. It is an aluminum phyllosilicate, consisting mostly of calcium montmorillonite, with permanent negative charge on its surface. Such structure enables bentonite to be intercalated by inorganic and/or organic cations and the resulting materials have high specific surface areas due to their small size [21]. Basically, the modification reactions are accomplished by replacing the interlayer cations (e.g. Na^+, K^+, and Ca^{2+}) with specific species (polymeric metal species) to alter the surface and/or structural characteristics of the clay [22].

The main objective of the present study was to examine the feasibility of using Fe-modified bentonite (Zenith/Fe) as potential material for phosphate removal from natural eutrophic waters. The adsorption of phosphate from artificial and natural aqueous solutions by using this modified clay was investigated in batch mode. One main parameter is the initial phosphate concentration aiming to represent a eutrophic natural ecosystem. In addition, sediment incubation experiments investigated the efficiency of Zenith/Fe as an active capping agent preventing the phosphate release from anaerobic sediments.

2. Materials and methods

2.1. Reagents

All solutions were prepared with analytical grade chemicals and purified water Milli-Q produced by Millipore Academic system with a conductivity of demineralized water of 18.2 μS/cm. The clay sample used in this work was a high Zn-containing batch of bentonite clay with a code name Zenith-N, from a mining site in Milos Island in Greece. $Fe(NO_3)_3.9H_2O$, $NaCO_3$, MES (*N*-morpholino-ethanesulfonic acid), and HEPES (4-(2-hydroxyethyl) piperazine-1-ethanesulfonic) acid were obtained from Sigma-Aldrich. The content of Fe in Zenith bentonite and the pillared material was determined by atomic absorption spectrophotometry (AAS) using a Perkin-Elmer Analyst

A700 Flame-Graphite Furnace AAS instrument. KH_2PO_4 and NaCl were also supplied from Merck.

2.2. Preparation of materials

$AlCl_3·6H_2O$ was added to aqueous solution of $Fe(NO_3)_3·9H_2O$, at Al/Fe molar ratio 4 then, 0.2 mol/L Na_2CO_3 was slowly added to the mixing solution followed by stirring at 60°C for 24 h. The resulting pillaring solutions were added dropwise to a 1% (w/w) Na-bent suspension under stirring for 12 h according to [23]. The slurry was then stirred for 24 h at room temperature, filtered, and washed repeatedly with deionized water until there was no chloride, verified by the $AgNO_3$ test. Following filtering, the solid was dried at 80°C, ground to 100 mesh, and kept in a sealed bottle.

2.3. Electron paramagnetic resonance spectroscopy

Electron paramagnetic resonance (EPR) spectra were recorded with a Brucker ER200D spectrometer equipped with an Agilent 5310A frequency counter at liquid nitrogen temperatures. The spectrometer was run under a home built software in LabView as detailed by Grigoropoulou et al. [24]. Adequate signal-to-noise was obtained after 5–10 scans.

2.4. Sampling

In the Aitoliko lagoon (Western Greece), the bottom water layer isolation in combination with the nutrient inflows and the consequent high primary productivity in the surface layer [25], leads to oxygen depletion and H_2S production in the monimolimnion. The permanent anoxic conditions in the hypolimnion, with the high concentration of H_2S in this layer, are the dominant factors of the system [26]. Sampling was conducted at the end of winter period (February 2010) at the deepest sampling site of anoxic Aitoliko lagoon. Sampling at this season of the year ensures the maximum retention of bioavailable phosphate into the sediments and simulates the expected time of application of the Zenith/Fe for a potential whole lake treatment.

Sediments were collected from an approximate depth of 25 m using a bottom grab sampler. Water samples for phosphate analysis were obtained from the water column 50 cm above the sediment sampling site. The main physicochemical characteristics of the water samples are given in Table 1. Water samples were collected, using a 2.51 Hydro Bios free flow sampler. All samples were brought to the laboratory in a portable fridge at 4°C within 2 h.

Table 1
Main physicochemical characteristics of water samples from Aitoliko Lagoon

Characteristics	Aitoliko Lagoon
Temperature	22°C
pH	6.9
Salinity	26.1 psu
Initial phosphate concentration	0.245 mg/L
REDOX potential	−410 mV (hypolimnion)

2.5. Phosphate sorption batch experiments

Phosphate stock solution of 50 mg/L was prepared by dissolving 0.2197 g KH_2PO_4 in 1.0 L deionized water; diluted stock solution was used in the experiments. The adsorption isotherms were determined by batch equilibration of 0.02 g of modified bentonite sample with 50 mL of aqueous phosphate solutions of varying initial concentrations (ranging from 0.05 to 5 mg/L). The experiments carried out at room temperature (25 ± 1°C) and pH varied from 5 to 9. For the pH adjustment, a buffer system of 10 mM MES, HEPES was used for all samples [22]. This system presented a significant buffer capacity at pH range 5–8.5 with an average deviation from the adjusted pH value less than 5%. Screening experiments indicated that under the conditions applied the buffer molecules caused no interferences on adsorption. Prior to starting the experiment, the pH was adjusted to values from 5 to 9 at 25 ± 1°C, using 0.1 M HCl and NaOH solutions. After 4 h of stirring, the suspension was separated by centrifugation and the concentration in the supernatant (c_e) was measured by the molybdate blue spectrophotometric method. The amount adsorbed (q_e) was calculated from the difference between initial (c_o) and equilibrium concentration. Blank samples without any absorbent were prepared and monitored as a control.

Adsorption kinetic data of phosphate on the modified bentonite Zenith/Fe for contact times ranging between 15 and 250 min were studied using (a) artificial aqueous solutions in optimum experimental conditions: pH 5–9, phosphate concentration 0.1 mg/L, adsorbent dose 0.02 g, and temperature 25 ± 1°C. (b) Natural aqueous solutions: 50 mg/L of natural water from Aitoliko lagoon, with initial phosphate concentration of 0.245 mg/L were added into conical flasks containing 0.02 g of Zenith/Fe (Table 2). All experiments were carried out in duplicates.

2.6. Column experiments

The sediment incubation experiments were carried out to estimate the efficiency of modified bentonite

Table 2
The constants of Langmuir, Freundlich, and R^2 for adsorption of phosphates on natural Zenith at pH 5–9

Model	Parameter	pH 5	pH 6	pH 7	pH 8	pH 9
Langmuir equation	q_m	11.60	14.45	14.14	11.20	9.98
	b	0.59	0.43	0.412	0.56	0.61
	R^2	0.99	0.99	0.99	0.99	0.99
Freundlich equation	K_f	4.27	4.48	4.42	4.11	3.88
	$1/n$	0.87	0.85	0.81	0.80	0.81
	R^2	0.99	0.99	0.99	0.99	0.99

Zenith/Fe as a sediment capping material for the reduction of phosphate flux under anaerobic conditions. Phosphate release measurements were conducted on well mixed wet sediments collected from the anoxic Atoliko lagoon. The sediments (5 cm of thickness) were transferred in two glass cylinders (1 L) with an internal diameter of 10 cm. About 700 mL of deionized water was added into each column. Ten grams of modified bentonite Zenith/Fe was carefully introduced into one column while the other acted as a control column simulating phosphate release from sediments under anoxic conditions. The columns were allowed to reconstitute under aerobic conditions for five days before starting the experiment. The dissolved oxygen was removed by N_2 introduction (for 2 h). The experiments were run in a controlled temperature room (25 ± 1˚C), under anoxic conditions and absence of light. The columns were monitored for 90 days and water samples were taken (0, 7, 14, 28, 48, 64, and 90 days) to determine phosphate concentration. The flux of phosphate released from sediments was calculated by [27]:

$$F_D = \frac{\sum_{i=1}^{n}[V_{i-1} \times (C_i - C_{i-1})]}{A \times t_n} \tag{1}$$

where F_D is the flux of phosphate release from the sediments during the whole period of incubation [mg/(m^{2}d)]; C_{i-1} and C_i are the phosphate concentrations (mg/L) at time t_{i-1} and t_i (d); n is the number of sample; t_n is the time of exposure (d); A is the surface area of the sediment (m^2).

3. Results and discussion

3.1. Iron content

The initial iron concentration of the natural Zenith was 0.067 mmol/kg of material. The final Fe content in the modified Zenith/Fe product was 130 mol/kg of material. As shown by EPR spectroscopy (Fig. 1), Fe is dispersed in monomeric species in the Zenith/Fe material. This forms specific phosphate binding sites resulting in a significant phosphate capacity.

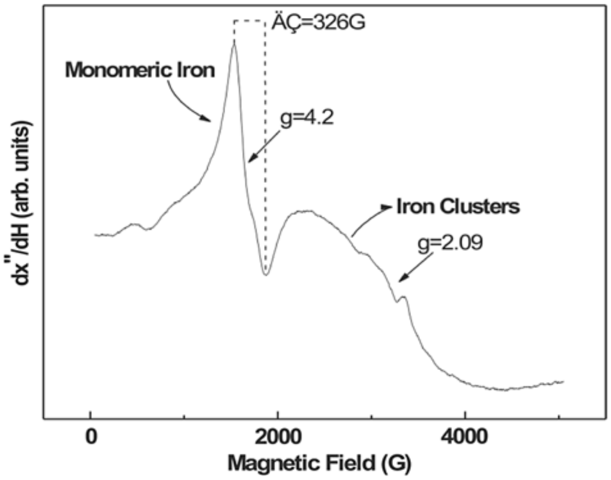

Fig. 1. EPR spectra of Zenith/Fe material.

3.2. Adsorption isotherms

The isotherm is meaningful to the design of adsorption systems, and its shape provides information about the homogeneity or heterogeneity of the adsorbent's surface. Two isotherm models including Langmuir and Freundlich as described in Eqs. (4) and (5) can express most of the adsorption data.

$$q_e = \frac{bq_mC_e}{1 + bC_e} \tag{2}$$

C_e (mg/L) and q_e (mg/g) are the equilibrium adsorbate concentrations in the aqueous and solid phases. Here, q_m (mg/g) is the maximum adsorption capacity and b is the Langmuir adsorption equilibrium constant.

The Freundlich isotherm model is an exponential equation which is a curve relating the concentration of a solute on the heterogeneous surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact.

$$q_e = K_f C_e^{1/n} \tag{3}$$

K_f is the Freundlich equilibrium constant indicative of adsorption capacity and $1/n$ is the Freundlich adsorption constant, the reciprocal of which indicates adsorption intensity.

The two models Langmuir and Freundlich have been considered to simulate the adsorption isotherms and establish the relationship between the amount of phosphate adsorbed on Zenith/Fe and the concentration of phosphate that remained in solution. Fig. 2 shows the changes in the equilibrium adsorption capacity of phosphates as a function of pH (5–9) and initial concentration. As shown in Fig. 2, the adsorption capacity of Zenith/Fe in the pH range 5–6 was higher compared to the respective adsorption capacity in higher pH values. The equilibrium adsorption capacity of Zenith/Fe changed slightly within the pH range 5–7 and decreased in solutions with higher pH values. The pH-dependent increase is due to the increasing adsorption of formed phosphate anions, with pKa 7.2, and with the positively charged surface sites of the clay. However, at pH values higher than eight, the bentonite surface becomes negatively charged with the subsequent drop of phosphate adsorption [22,28].

The phosphate uptake increases dramatically in all pH values when the phosphate concentration in the aqueous phase (C_e) increased from 0 to 2 mg/L. With further increase of the concentration, the increase of the phosphate uptake is less significant.

Table 2 summarizes the constants of the Langmuir and Freundlich adsorption isotherms for phosphate adsorption onto modified bentonite; all regression coefficient (R^2) values exceeded 0.99, suggesting that both models fit well the experimental results. The maximum adsorption capacities (q_m) calculated from the Langmuir model were 11.60, 14.45, 14.14, 11.20, and 9.98 mg/g, respectively for pH range from 5 to 9.

The Freundlich constant $1/n$ gives an indication of adsorption intensity. The values of $1/n$ were 0.87, 0.85, 0.81, 0.80, and 0.81 for pH values 5, 6, 7, 8, and 9 respectively; a value less than 1.0 indicates favorable adsorption of phosphate onto Zenith/Fe.

3.3. Adsorption kinetics

Adsorption kinetic data of phosphate on Zenith/Fe in contact times ranging between 15 and 250 min are presented in Fig. 3. The plots represent the amount of phosphorus adsorbed onto modified bentonite vs. time at different pH values varying between 5 and 9. As shown in Fig. 3, most phosphate ions were adsorbed during the first 1 h, then the rate of adsorption slowed down considerably and after 2 h was almost negligible. After approximately 2 h, equilibrium begins to establish itself for all the pH values investigated. In order to evaluate the mechanism of phosphate adsorption, pseudo-first- and pseudo-second-order models were applied. The pseudo-second-order kinetic model was based on the assumption that the adsorption follows second-order chemisorptions [29]. This model was used to describe the adsorption process and it is shown below [30]:

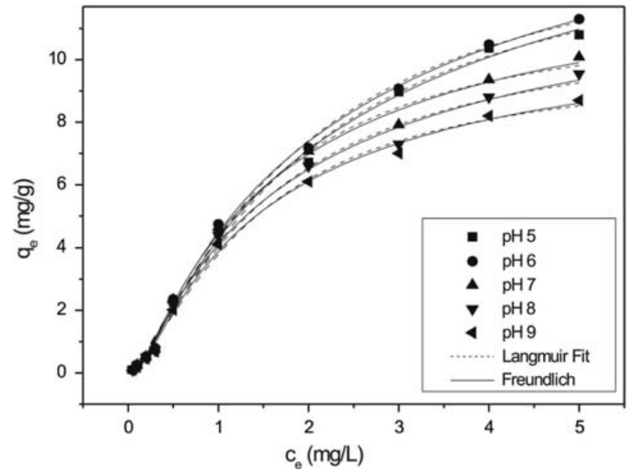

Fig. 2. The adsorption isotherms and Langmuir, Freundlich models fitting for phosphate adsorption onto natural Zenith-N. Phosphate concentration 0.1 mg/L, adsorbent dose 0.02 g, pH 5–9, and 25˚C temperature.

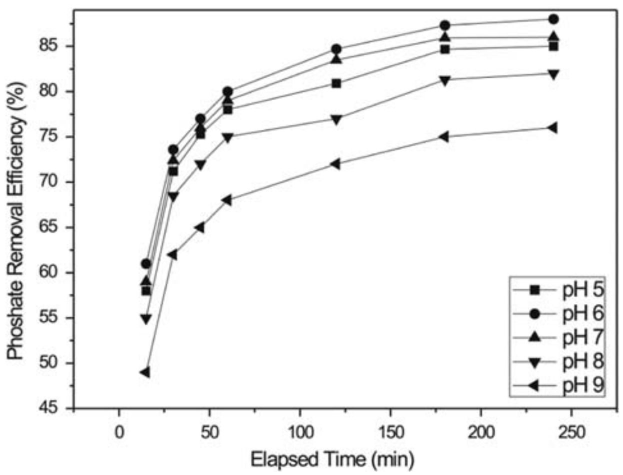

Fig. 3. Adsorption kinetics of phosphate by Zenith/Fe. Phosphate concentration 0.1 mg/L, adsorbent dose 0.02 g, pH 5–9, and 25˚C temperature.

$$\frac{dq_t}{dt} = K(q_e - q_t)^2 \tag{4}$$

In this equation, k [g/(min mg)] is the rate constant of the pseudo-second-order model. Also, q_t and q_e are the amounts of phosphates adsorbed onto the bentonite surface at time t and equilibrium, respectively. In the start of the adsorption, $q_t = 0$. So the equations are integrated to yield:

$$\frac{t}{q_t} = \frac{1}{Kq_e^2}\frac{1}{q_e}t \tag{5}$$

Rate parameters, k and q_e, can be directly obtained from the intercept and slope of the plot of (t/q_t) against t. The equilibrium concentration can be then calculated as the value of q_e that has been obtained from the fitting of Eq. (5).

Linear plots of t/q_t against t show the applicability of the pseudo-second-order equation for the system studied. As shown in Fig. 4, it is clear that the kinetics of phosphorus adsorption onto Zenith/Fe follows the pseudo-second-order model with correlation coefficients higher than 0.99 (data not shown).

Water samples were collected from the eutrophic and anoxic Aitoliko Lagoon to evaluate the removal of phosphate by modified bentonite from natural water bodies (Fig. 5). Phosphate removal efficiency of Zenith/Fe in natural waters increased with the increase of the reaction time until the equilibrium was reached after 3 h. After a reaction time of 4 h, the modified clay adsorbed ∼85% of phosphates compared with the yields obtained using artificial aqueous solutions.

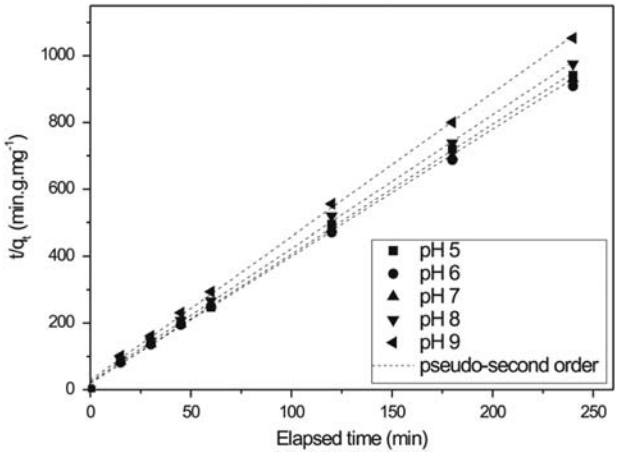

Fig. 4. Pseudo-second-order kinetics of phosphate uptake by Zenith/Fe (dotted line). Phosphate concentration 0.1 mg/L, adsorbent dose 0.02 g, pH = 5–9, and 25°C temperature.

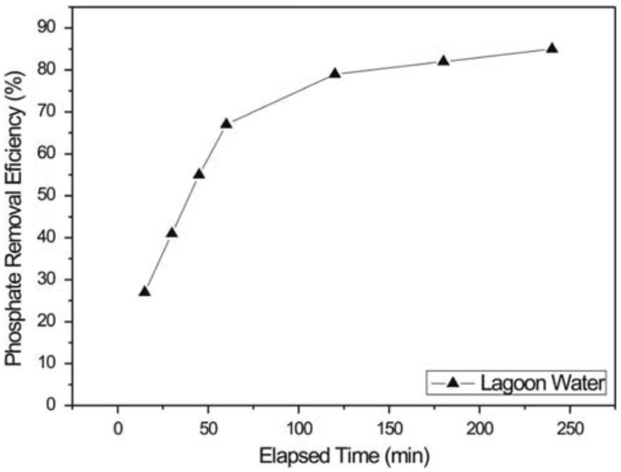

Fig. 5. Adsorption kinetics of phosphates by Zenith/Fe from natural water.

The phosphate removal efficiency as a function of time showed a decelerating trend than stock water samples, which is probably due to the strongly reducing conditions (Eh ~ -410 mV) that prevail in the hypolimnion of the lagoon (lack of dissolved oxygen–hydrogen sulfide production). However, around 85% removal was attained, suggesting the good performance of Zenith/Fe for remediation of natural waters.

3.4. *Effect of capping agent on phosphate release from sediments*

The release of phosphate from treated and untreated sediments under anoxic conditions during 90 days of incubation experiments is presented in Fig. 6. The average flux from the sediments was

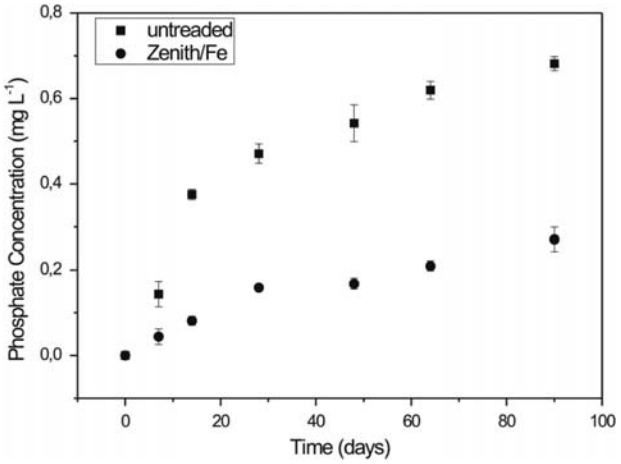

Fig. 6. Influence of Zenith/Fe on the phosphate release from sediments into the overlying water under anoxic conditions. Time of incubation: 90 days.

calculated using Eq. (1) and the obtained results are shown in Fig. 7. The concentration of total phosphorus (TP) in the overlying water increased from 0 to ~0.68 mg/L corresponding to an average phosphate flux of ~0.66 mg/(m^2d) (Fig. 7). The application of Zenith/Fe as a P-inactivation agent resulted in ~68% reduction of the phosphate flux from the sediments under anoxic conditions. This modified clay acts as a sink of phosphate, due to its tendency to chelate Fe and therefore P. Moreover, the potential dissolution of Fe^{2+} might be supported by the fact that treatment with Zenith/Fe resulted in the increased concentration of Fe^{2+} in the overlying forming Fe-bound P. Thus, adsorption of phosphates on Zenith/Fe and precipitation by dissolved iron species seem to be the main mechanisms contributing to the prevention of P release from the sediments.

Passive capping agents, such as sand, gravel, and clay, are designed to reduce the diffusion rate of nutrients into the overlying water [31]. The thicker the layer of passive material, the lower the P-diffusion rate, and hence the greater the reduction in sediment-water exchange of phosphates. Typical sediment capping thicknesses are >5 cm which limit this technique to smaller ponds and reservoirs owing to the large quantities of capping material required [32,33]. Zenith/Fe could serve as an active capping agent reducing the diffusion rate of phosphates from the sediments without disturbing the equilibrium of biotic and abiotic environment. If catchment input loads have also been subjected to remedial actions, the internal nutrient loads are likely to be reduced and the lake may become less eutrophic.

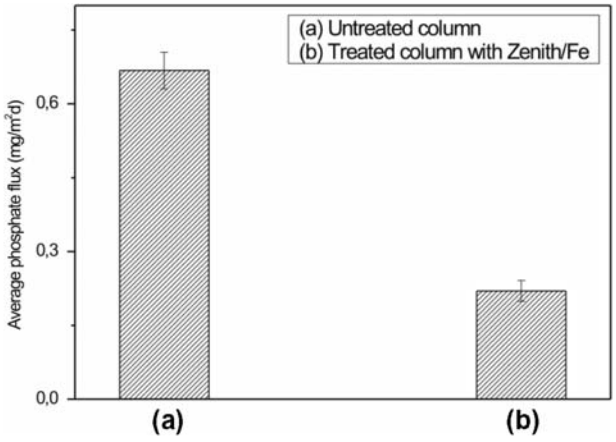

Fig. 7. Phosphate fluxes from untreated and treated sediments under anoxic conditions during 90 days of incubation experiments.

4. Conclusions

In this study, the performance of a modified bentonite Zenith/Fe as a potential restoration tool in eutrophic water bodies was studied through a number of batch experiments. Zenith/Fe was effective in removing phosphate from the water at pH values from 5 to 7; however, it seems effective in aqueous solution with higher pH values (8–9). The adsorption of phosphate on Zenith/Fe could be well described by pseudo-second-order kinetic and the data agree well with both the Freundlich and Langmuir adsorption isotherm models. The P fluxes from the sediments into overlying water under anoxic conditions were significantly reduced (in about ~68%). Natural bentonite is a low-cost and abundant element, readily available and its modification method is simple. Moreover, the nascent material is nontoxic and represents a natural component of aquatic environments. In addition, Zenith/Fe is likely to be effective in the adsorption of phosphates in natural environments with extreme reducing conditions (−410 mV). Although this approach is promising, it is necessary for further research to give more clarifying conclusions about its usability as a lake restoration tool in real environmental conditions.

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