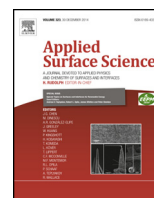




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A theoretical and experimental study on the P-adsorption capacity of Phoslock™

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ABSTRACT

The main objective of this study is to investigate the adsorption process from both experimental and modeling point of view of phosphate onto Phoslock™, an increasingly used worldwide restoration tool to control phosphorus from natural water ecosystems. Bench-scale batch experiments were performed to examine its efficiency as a phosphate adsorbent and detailed simulations were carried out, allowing for a deep insight of the removal process. The adsorption efficiency calculated by the simulations is 87.41%, being in excellent agreement with that experimentally measured (approx. 87%). However, it is important to notice the discrepancy between experimental measures and simulation estimates. Although the agreement is perfect for $T = 25\text{ }^{\circ}\text{C}$, it becomes more and more poor as temperature decreases, approaching approx. 10% difference for the low temperature of $10\text{ }^{\circ}\text{C}$. This inconsistency between experiments and model can be attributed to the internal inefficiencies of unit cell approach, which in particular overestimates the adsorption efficiency.

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1. Introduction

Phosphorous due to its excess bioavailability is the most important nutrient because it is responsible for the eutrophication of water bodies, resulting in increased aquatic plant and algal growth. Its release from the sediment into the lake water may be so intense and persistent that it prevents any improvement of water quality for a considerable period after the loading reduction [1,2]. Søndergaard et al., [3] indicated that highly P-saturated lake sediments are often slow to respond to reduced external loads because sedimentary stores of P can act as a buffer to changes in water column P concentrations. According to Kagalou et al. [4], after an instantaneous reduction of external load leading to an increase in the ratio of the internal nutrient concentration over the nutrient concentration of the inflow, a decrease in ratio may be expected again after some years when the P content in the top sediment layer has moved towards equilibrium with the concentrations in the overlying water column. The time needed for this recovery can vary largely between lakes, and may in some cases take decades [4].

The research in the use of Lanthanum for reducing phosphates has revealed that depending on the concentration and the rate of application it could be toxic to aquatic organizations [5]. This issue can be overcome by embedding La into the structure of clay minerals, such as bentonite, by taking advantage of their Cation Exchange Capacity (CEC). During the manufacturing of La-modified bentonite, lanthanum ions are exchanged with the bentonite internal surface random adsorbed exchangeable cations.

This gave birth to Phoslock™, developed by Commonwealth Scientific and Industrial Research Organization (CSIRO) during the 1990s [6]. Since then, Phoslock™ has demonstrated through a series of small and large scale laboratory as well as field trials that it can reduce the Soluble Reactive Phosphorous concentration (SRP) in the water column more than 97% within 24–36 h.

Phoslock™ forms a highly stable mineral known as Rhabdophane (LaPO_4) in the presence of P species such as orthophosphates which are common oxyanions. The rare earth element in the clay structure can either react with the phosphate anion in the water body or remain in that structure under a great range of environmental conditions [2,7]. Despite La ions could be toxic to some aquatic organisms, particularly cladocerans such as *Daphnia* [8,9], hence the potential liberation of La ions from the bentonite could mean a significant environmental risk [8], Phoslock™ has been classified as not hazardous [10]. A leachate experiment has shown the La could be released from the material, however in only insignificant quantities of 0.13–2.13 mg/L and provided Phoslock is applied in a worst-case scenario dose of 250 mg/L [11].

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Phoslock™ is applied in the treated water using two main application techniques. Spreading it in a granular form or as a thick suspension, a solid/water slurry through spray manifolds. As it settles through the water column it binds the orthophosphates permanently and rests on the sediment, acting as a capping material to prevent Phosphorous being released from the sediment [6,12,11,13].

Mathematical modeling is generally considered as a powerful tool in order to clearly understand physics and chemistry in phosphates reducing processes along with Phoslock™ use [14]. Furthermore, computational fluid dynamics (CFD) can be used to analyze complex systems involving fluid flow, heat transfer and mass transport processes. [15,16]. Although already applied in some research works, mathematical models regarding adsorption by Phoslock™ are quite fundamental, thus not allowing for a clear understanding of the processes/phenomena that actually take place.

The main objective of this study is to investigate the adsorption process from both experimental and modeling point of view of phosphate onto Phoslock™, an increasingly used worldwide restoration tool to control phosphorus from eutrophic waterbodies. Bench-scale batch experiments were performed to examine its efficiency as an adsorbent for phosphate removal from natural waters. Detailed simulations were carried out, allowing for a deep insight of the removal process. Phosphate uptake was evaluated vs. pH and adsorption kinetics. The effects of temperature and salinity (fresh, brackish and marine waters) on phosphate-uptake capacity were also investigated.

2. Experimental

2.1. Phosphate sorption experiments

Phosphate stock solution of 50 mg/L was prepared by dissolving 0.2197 g KH_2PO_4 (Merck, 99.5% purity quality) in 1.0L deionized water and dilutions of the stock solution were used in subsequent experiments. The adsorption isotherms were determined by batch equilibration of 0.02 g of Phoslock™ sample with 50 mL of aqueous phosphate solutions of varied initial concentrations (ranging from 0.05 to 5 mg/L). The experiments were carried out at room temperature ($25 \pm 1^\circ\text{C}$) and pH 7 for 3 h. After equilibration, the suspension was separated by centrifugation and the concentration in the supernatant (C_e) was measured by the molybdate blue spectrophotometric method [17] using a Lambda 25 UV/VIS spectrophotometer (Perkin-Elmer, Germany). The determination limit of the analytical method was 0.01 mg $\text{PO}_4^{3-}/\text{L}$.

The amount adsorbed (q_e) was calculated from the difference in concentration between the initial (C_0) and the equilibrium concentrations. Blank samples with no adsorbent were prepared and monitored as a control. Adsorption kinetic data of phosphate on Phoslock™ at contact times ranging between 15 and 250 min were studied using optimized conditions: pH 7, phosphate concentration 0.1 mg/L, adsorbent dose 0.02 g, and $25 \pm 1^\circ\text{C}$ temperature.

The effect of salinity on the phosphate uptake of Phoslock™ was determined by measuring the phosphate uptake of bentonites at salinities 0, 20 and 30 psu, adding NaCl at $25 \pm 1^\circ\text{C}$, pH 7 for 3 h.

To assess the effect of different temperatures, batch experiments were conducted at 5, 15, 25 and 35°C . Experiments were carried out in an orbital shaker batch at 15, 25, 35°C and a temperature controlled water bath in a cold room at 5°C for 3 h.

For the pH-edge experiments, a buffer system of 10 mM MES: (N-morpholino-ethanesulfonic acid), HEPES: (4-(2-hydroxyethyl) piperazine-1-ethanesulfonic acid) was used in all the samples [18]. This system presented a significant buffer capacity at pH range 5–8.5, with an average deviation from the adjusted pH value of

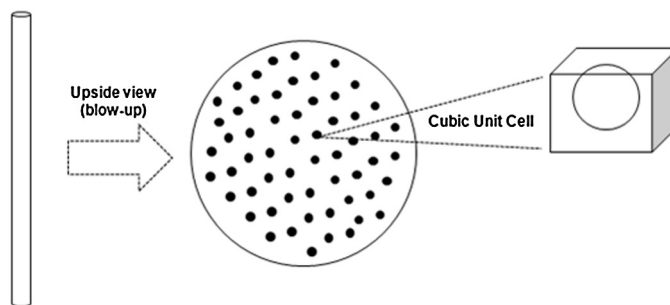


Fig. 1. Schematic representation of the modeling concept.

5%. Screening experiments indicated that under the above experimental conditions, the buffer molecules caused no interference on the adsorption phenomena. Prior to starting the experiment, the pH was adjusted from 5 to 9 at $25 \pm 1^\circ\text{C}$ and contact time 3 h, using 0.1 M HCl and NaOH solutions. All experiments were carried out in duplicates.

2.2. Mathematical modeling

To adequately simulate the bed adsorption, a mathematical model, analogous to unit-cell approach [19,20] has been developed. By considering that all the grains fall towards bed's bottom under uniform velocity conditions, the active material actually acts like a "curtain" that falls with uniform velocity. Consequently, it is able to estimate the porosity of the model by using 2D approach, as follows

$$\varepsilon = \frac{S_{\text{void}}}{S_{\text{bed}}} = \frac{S_{\text{bed}} - S_{\text{grains}}}{S_{\text{bed}}} = 1 - \frac{S_{\text{grains}}}{S_{\text{bed}}} = 1 - \frac{\sum_{i=1}^{N_g} \pi R_i^2}{\pi R_{\text{bed}}^2} \quad (1)$$

where R_i is the radius of sphere i , R_{bed} is the radius of bed ($R_{\text{bed}} = 0.0631$ m) and N_g is the number of the grains. By assuming that grains' radii satisfy uniform distribution (that is, $R_i = R = \text{cons.}$), N_g can be calculated as follows:

$$N_g = \frac{m}{4/3\pi R^3} = 7, 156, 592 \text{ grains} \quad (2)$$

By assuming that the grains are homogeneously distributed on the surface without touching each other, it is easy to divide the whole surface in N_g cubic unit cells, each one containing one solid sphere located at its center. The conceptual idea behind this approach is that the unit cell is an adequate representative of the whole medium; therefore, processes occurring through the whole structure are sufficiently described by those occurring in the unit cell. The dimensions of the outer cube have to be adjusted so as the ratio of the solid volume to the volume of the liquid cubic envelope to represent exactly the solid volume fraction of the porous medium. The following Fig. 1 schematically depicts this modeling approach.

The void space (porous) is occupied by a Newtonian liquid mixture that flows under laminar flow conditions and contains a solute which can react heterogeneously on the solid/liquid interface. It should be mentioned that the inner sphere represents the surface (interface) where the heterogeneous catalytic reaction occurs. The outer cube represents the control volume. This reaction process can adequately represent a sorption mechanism under the pressure and temperature conditions specified by the phenomena that take place.

In the present study, it is assumed that Phosphate (PO_4^{3-}) flows through the liquid phase (void space) and approaches the liquid/solid interfaces of the lanthanum-modified bentonite, Phoslock™, through advection and/or diffusion. On these grains'

surfaces, adsorption of Phosphate takes place on at relatively low temperature. More precisely, the solid surface is assumed to be Lanthanum (La^{3+}), which reacts with Phosphate to produce LaPO_4 . The overall reaction is as follows:



Since the temperature is fairly low and there is only one liquid reactant, it is reasonable to assume that the reaction rate depends only on the PO_4^{3-} concentration and is of first order, given as [21]:

$$r_{\text{PO}_4^{3-}} = -k_c(T)C_{\text{PO}_4^{3-}} = -k_{c,0}e^{-E_a/RT}C_{\text{PO}_4^{3-}} \quad (4)$$

where k_c is the reaction rate constant, T is the temperature, $C_{\text{PO}_4^{3-}}$ is the phosphate concentration, E_a is the activation energy, and R is the universal gas constant.

The fundamental transport processes can be described by the following set of conservation equations at steady state [22]. Firstly, the continuity equation may be written as:

$$\nabla \cdot (\rho \underline{U}) = 0 \quad (5)$$

where \underline{U} is the velocity vector, and ρ is the fluid density. Due to the low Reynold's numbers, flow is considered laminar and can be described by the momentum equation, given as:

$$\nabla \cdot (\rho \underline{U} \underline{U}) = -\nabla P + \nabla \cdot \underline{\underline{\tau}} \quad (6)$$

where P is the pressure and $\underline{\underline{\tau}}$ is the shear stress tensor.

Additionally, heat transfer phenomena described by the energy conservation equation can be expressed as:

$$\nabla \cdot (\rho \underline{U} h_i) = -\nabla \cdot \underline{q} \quad (7)$$

where h_i is the enthalpy of i -th species (enthalpy of formation and sensible heat), and \underline{q} is the heat flux given by:

$$\underline{q} = -k \nabla T + \sum_{i=1}^{N_s} \underline{J}_i h_i \quad (8)$$

where k is the thermal conductivity (calculated by the kinetic theory of gaseous mixtures [22], N_s is the total number of gas species, and \underline{J}_i is the mass diffusion flux of the i -th species, expressed as:

$$\underline{J}_i = \rho \underline{U} Y_i - \rho D_i \nabla Y_i \quad (9)$$

where Y_i is the i -th species mass fraction, and D_i is the diffusivity of the i -th species in the mixture. Lastly, the species mass fractions are calculated using the mass conservation equation of species:

$$\nabla \cdot (\rho \underline{U} Y_i) = \nabla \cdot (\rho D_i \nabla Y_i) + \dot{\omega} \quad (10)$$

where $\dot{\omega}$ is the production/consumption rate of species i due to reactions.

To investigate the performance of the grains, the macroscopic adsorption efficiency, λ , is used and it is defined by the ratio of the solute adsorption rate divided by the rate of the upstream influx, and is given by:

$$\lambda = \frac{\iint_{S_{\text{inlet}}} (C_{\text{PO}_4^{3-}} - U) \underline{n} dS - \iint_{S_{\text{outlet}}} (C_{\text{PO}_4^{3-}} - U) \underline{n} dS}{\iint_{S_{\text{inlet}}} (C_{\text{PO}_4^{3-}} - U) \underline{n} dS} \quad (11)$$

where the first integral $\iint_{S_{\text{inlet}}} (C_{\text{PO}_4^{3-}} - U) \underline{n} dS$ is the total mass entering the volume of interest through the inlet surface, S_{inlet} , and the second integral $\iint_{S_{\text{outlet}}} (C_{\text{PO}_4^{3-}} - U) \underline{n} dS$ is the total mass exiting the volume of interest through the outlet surface, S_{outlet} . It should be noted that \underline{n} is the vector normal to the surface.

For the sake of simplicity, gravitational effects are neglected. The flow conditions are considered laminar. The fuel mixture at

Table 1
 Parameters used.

Quantity	Expression	Reference
Viscosity	$\mu_i = 2.6693 \times 10^{-5} \frac{\sqrt{MW_i T}}{\sigma_i^2 \Omega_{\mu}}$	[22]
Collision integral	$\Omega_{\mu} = \frac{1.16145}{(T^*)^{0.14874}} + \frac{0.52487}{e^{0.77320(T^*)}} + \frac{2.16178}{e^{2.43787(T^*)}}$	
Dimensionless temperature	$T^* = \frac{\epsilon T}{\epsilon}$	
Diffusion coefficient of the mixture by Bruggeman approach	$D_{i,\text{eff}} = \epsilon^r D_i$	[25]
Tortuosity	$\tau^2 = \frac{1}{1-(1-\epsilon)^{1/3}}$	[25]

the entrance is assumed to be homogeneous, considering no mass accumulation either at the entrance or exit. Typical calculations about mixture density, viscosity, thermal conductivity and mass diffusion coefficients were also employed. Furthermore, the specific heat is calculated by fittings to experimental JANAF curves [23]. To currently perform the simulations, the heterogeneous reaction characteristics were as follows [24]: $E_a = 2044.75$ kJ/mole, pH 7, $k_{c,0} = 6000$ m³/s kg while the inlet composition mixture is 20 mg/water L.

Regarding the boundary conditions, fixed pressure of 1 atm has been applied to the outlet surface, while normal velocity of 1.6×10^{-4} m/s to the inlet one, as experimentally measured. Furthermore, zero mass fluxes have been set to the walls and outlet, assuming zero accumulation. Finally, the inlet mixture is set to 273 K and zero heat fluxes have been also set to the walls and outlet.

For the solution of the nonlinear, strongly coupled conservation equations described previously, the finite-volume method was adopted allowing the SIMPLEC (Semi-Implicit Method for Pressure-Linked Equations Consistent) algorithm for the calculation of pressure. The parameters applied in the simulations are presented in the following Table 1. An HP Compaq 6000 Pro MT PC was used having the following characteristics: Intel® Core™2 Duo CPU E7500 at 2.93 GHz and 2 GB RAM memory. Given the required accuracy of at least 10^{-4} all the involved quantities, the convergence time was approx. 10 min, corresponding to a maximum number of 150 iterations.

3. Results and discussion

Fig. 2 shows the equilibrium adsorption capacity of phosphate as a function of initial concentrations. The experimental isotherm data (denoted as symbols in Fig. 2), can be described by the typical Langmuir-curve isotherm. In general, isotherm showed a rapid rise in the adsorption capacity with an increase in the equilibrium solution concentration, followed by a plateau at equilibrium, demonstrating typical Langmuir isotherm characteristics. In this type of isotherm, the initial slope does not significantly change with the increase of the solute concentration. From Fig. 2, the phosphate uptake increases dramatically with the equilibrium concentration increasing from 0 to 2 mg/L. With further increase of the equilibrium concentration, the increase of phosphate uptake is less significant. The mass of the adsorbed phosphorus at an initial concentration 0.1 mg P/L (which generally corresponding respectively to eutrophic waters) was 0.26 mg P/g Phoslock.

Adsorption kinetic data of phosphate on Phoslock™ in contact times ranging between 15 and 240 min are presented in Fig. 3. The plots represent the amount of phosphorus adsorbed onto Phoslock™ as a function of time. As shown, most phosphate is captured during the first 50 min of adsorption. As contact time increased, the removal rate decreased considerably and was almost negligible at 100 min. After approximately 120 min of adsorption, the sorption equilibrium begins to establish itself. The high

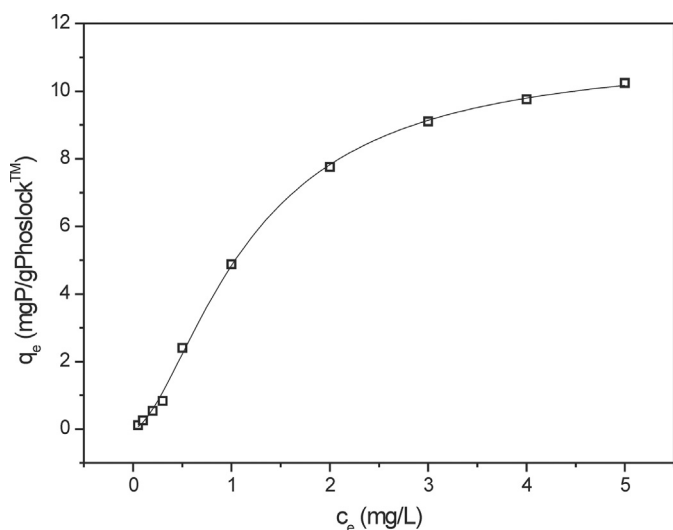


Fig. 2. The adsorption isotherms phosphate-uptake by Phoslock. Phosphate concentration of 0.1 mg/L, adsorbent dose 0.02 g, pH 7.0, and $T = 25^\circ\text{C}$.

adsorption rates observed at the beginning of the experiment were attributed to the very low saturation of adsorbed phosphate on the active surface (that is, the high concentration gradients, normal to this surface). The gradual decrease observed for longer time periods is connected with intraparticle diffusion processes.

Typical simulation results are depicted in Figs. 4 and 5, where the concentration of the reactant and the product within the unit cell are presented, respectively. It is clearly shown that the concentration gradients are towards the solid mass. As expected, areas where the reactant is of its lower concentration are characterized by the higher concentration of product and vice versa. Furthermore, the higher product concentration is observed in the stagnant point, where convection is negligible, thus eliminating the possibility for the material to escape from the volume of interest.

It is important to underline that the adsorption efficiency calculated by the simulations is 87.41%, being in excellent agreement with that experimentally measured (approx. 87%). The latter was expected as far as a “reverse engineering” process has been incorporated in the simulation procedure: by recognizing that the reaction rate (Eq. (4)) is one expression dependent on two-parameters (E_a and $k_{c,0}$), we fixed the value of the first one in a widely accepted

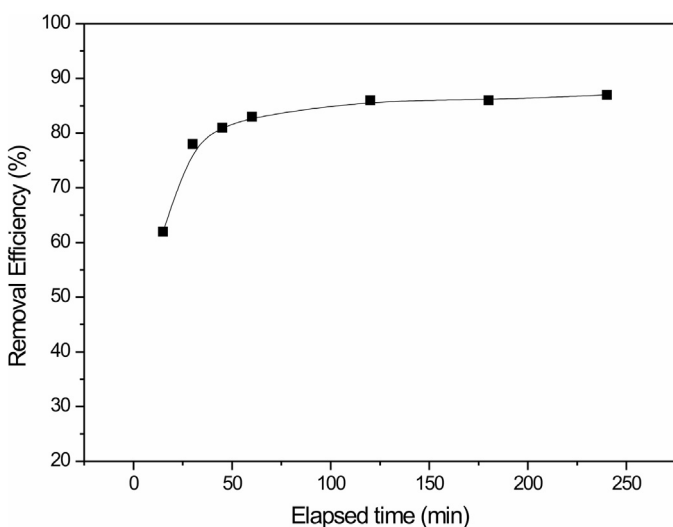


Fig. 3. Adsorption kinetics of phosphate-uptake by Phoslock. Phosphate concentration of 0.1 mg/L, adsorbent dose 0.02 g, pH 7.0, $T = 25^\circ\text{C}$.

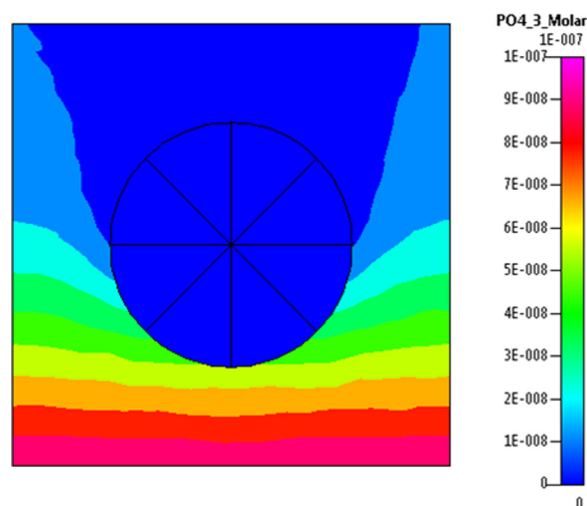


Fig. 4. Phosphate concentration within the unit cell.

value (namely $E_a = 2044.75\text{ kJ/mol}$, see [24]), and estimated the other one through the constraint of the agreement between experimental and theoretical values for λ in a tolerance $< 10^{-2}$.

The influence of temperature on phosphate adsorption was determined at temperatures ranging from 5 to 35°C . As shown in Fig. 6, high temperature is advantageous for phosphate adsorption on bentonites. Fig. 6 shows an increase in the adsorption capacity with an increase in temperature. This indicates that the adsorption reaction is of endothermic nature and the ion-exchange mechanism is favored at higher temperatures. Moreover, the increases in adsorption capacity of PhoslockTM at higher temperatures may be caused by the stronger diffusion and higher reaction rate.

It is important to notice the discrepancy between experimental measures and simulation estimates. Although the agreement is perfect for $T = 25^\circ\text{C}$ (as expected by the “reverse engineering” process), it becomes more and more poor as temperature decreases, approaching approx. 10% difference for the low temperature of 10°C . This inconsistency between experiment and model might be due to the internal inefficiencies of unit cell approach, which in particular overestimates the adsorption efficiency, as discussed in detail elsewhere [25]. On the contrary, modeling approach allows for a deep understanding and characterization of the processes occurs. By calculating the dimensionless Peclet and Damköhler numbers (whose definition and values are presented in Table 2), it is clear that the major driving force for mass transport is the

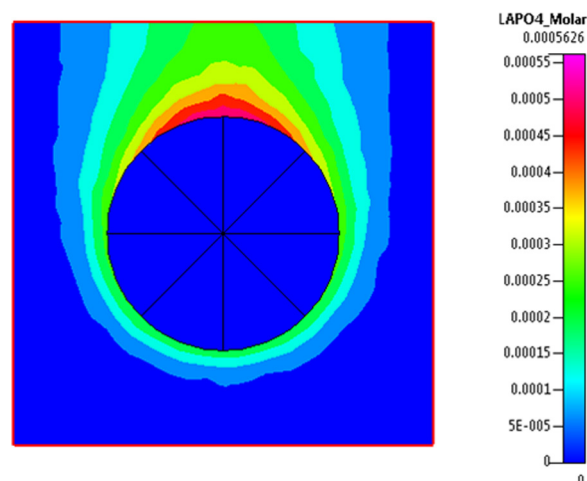


Fig. 5. LaPO_4 concentration within the unit cell.

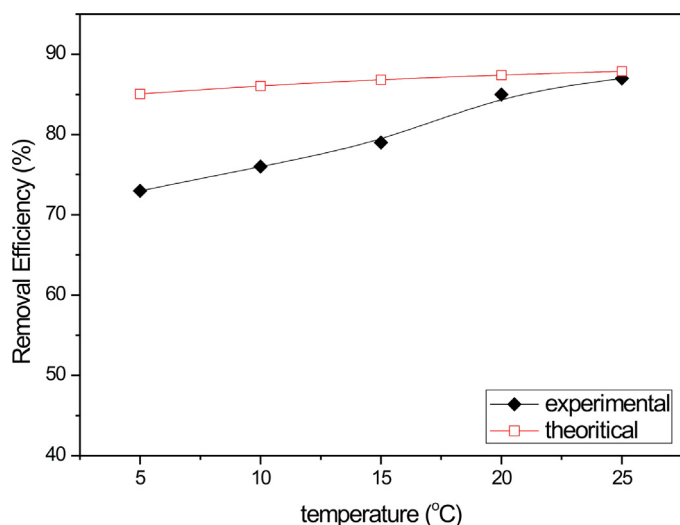


Fig. 6. Effect of temperature on phosphate-uptake by Phoslock.

Table 2

Dimensionless numbers controlling the process.

T (°C)	Peclet = convection/diffusion	Damköhler = reaction rate/diffusive mass transfer rate
5	10.90	210.60
10	9.54	220.49
15	8.48	230.48
20	7.63	240.55
25	6.94	250.71

influential reaction, while convection is significantly dominant over diffusion. This correlation implies a complex behavior defined through the competitive character between the transport processes: (a) the majority of phosphate molecules that approach the active surface are adsorbed (high Damköhler), and, (b) the number of phosphate molecules that escape from the volume of interest are significantly higher than those approaching the surface (high Peclet). The above result in slightly affect adsorption efficiency with temperature variation.

The influence of salinity on phosphate adsorption by Phoslock™ was studied at 0, 20 and 35 psu salinities. These values simulate salinities in fresh, brackish and marine waters, respectively. Fig. 7 illustrates that at salinity close to that of fresh water, Phoslock™ has the most prominent effect on phosphate ion removal, followed by brackish and marine water. Hence the phosphate adsorption

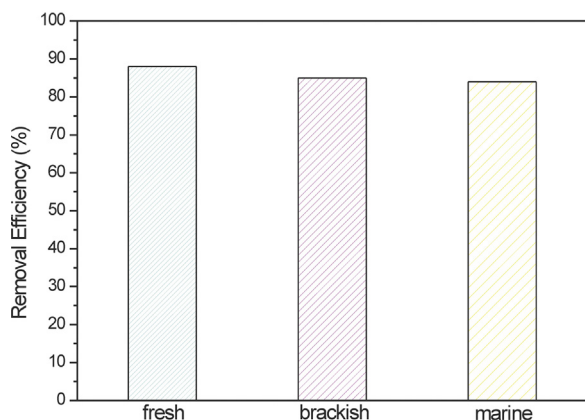


Fig. 7. Effect of salinity on phosphate-uptake by Phoslock.

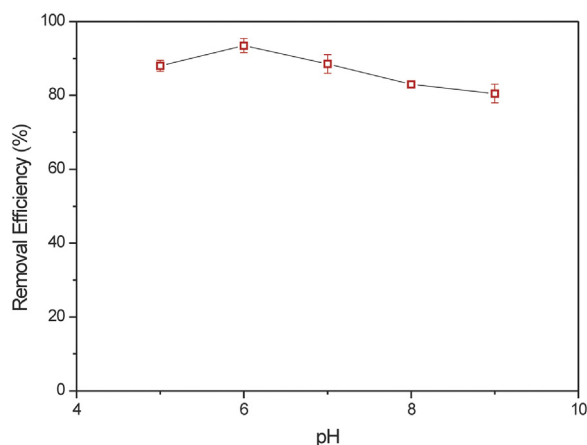


Fig. 8. Influence of pH on phosphate-uptake by Phoslock. Phosphate concentration of 0.1 mg/L, adsorbent dose 0.02 g, and contact time 3 h.

capacity followed the order: fresh water > brackish > marine water. The effect of salinity originates from the well-known ionic strength effects that are expected to suppress ion uptake by chargeable surfaces.

pH is considered as one of the most important parameters controlling the adsorption process at water-adsorbent interfaces [26–28]. The effect of pH on the removal of phosphate species, through adsorption onto Phoslock™, was examined in the pH region between 5 and 9 (Fig. 8). The phosphate adsorption efficiency of Phoslock™ is extremely increased in the same pH range of 5–9, and approaches a maximum (93%) at pH 6. At pH 9, the phosphate uptake efficiency drops a little extent (81%). The pH-dependent increase is due to increasing adsorption of formed phosphate anions, with pK_a 7.2, on the positively charges surface sites of the clay and the La^{3+} adducts. At pH over 8 the clay surface becomes negatively charged thus phosphate adsorption drops [24].

4. Conclusions

The current work was carried out to support the restoration of degraded lake and reservoir systems, and for this reason, the investigation of the adsorption process from both experimental and modeling point of view of phosphate onto Phoslock™ is of great importance. The findings can be summarized as follows:

1. The phosphate adsorption efficiency of Phoslock™ calculated by the simulations was 87.41% at 25 °C, being in excellent agreement with the experimental results (~87%).
2. However, a discrepancy between experimental measurements and simulation estimates was observed. Although the agreement is perfect for $T=25$ °C (as expected by the “reverse engineering” process), it becomes more and more poor as temperature decreases, approaching approx. 10% difference for the low temperature of 10 °C. This inconsistency between experiment and model can be attributed to the internal inefficiencies of unit cell approach, which in particular overestimates the adsorption efficiency. Accordingly to the cell approach, the medium is considered as an assemblage of unit cells gathered in a regular manner, thus one unit cell is the adequate representative of the whole medium, and therefore processes occurring through the porous structure are described sufficiently by those occurring in the unit cell. More precisely, sphere-in-cell models are based on the representation of the overall solid mass by a spherical or cylindrical solid body, which is embedded in a spherical or cylindrical liquid envelope, respectively. The boundary conditions imposed on the outer surface of the envelope is supposed

to adequately represent the interactions with the other grains of the swarm. Obviously, the thickness of the surrounding fluid layer is adjusted so the ratio of the solid volume to the volume of the liquid envelope to represents exactly the solid volume fraction of the porous medium. The main advantage of these models is that an analytical expression for the stream function can be obtained demanding significantly less effort than that needed for numerical investigations. The spherical shape corresponds to a formulation which leads to axially symmetric flow that has a simple analytical solution of closed form, and can thus be used readily for heat and mass transport calculations. Although this analytical solution is actually an approximation of the real flow field in a complex porous structure, it was sufficient for the engineering applications raised until the early 1980s. On the other hand, the model has one disadvantage in that the outer envelope is not space filling, a difficulty which must be dealt with when a scale-up from the single unit cell to an assemblage of particles is necessary. On top of this, a significant problem of unit-cell approach is that they are valid for high porosity values, a consideration which corresponds to an outer sphere of radius significantly higher than the inner one, i.e. porosity takes quite high values. In general, the lower the porosity the higher the erratic behavior is observed for this model. This behavior is due to the fact that high porosities, where analytical models are in principle applicable, correspond to a very low number of spheres for the numerical representation of the porous medium. It should be noted that at porosities lower than 0.8, the available analytical approaches become gradually less accurate and therefore less dependable [25].

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