Removal of phosphorus from water using active barriers: Al_2O_3 immobilized on to polyolefins

M. Oliveira [a*], D. Ribeiro [b], J.M. Nobrega [a], A.V. Machado [a], A.G. Brito [b] and R. Nogueira [b]

[a] IPC - Institute of Polymers and Composites, Department of Polymers Engineering University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal; [6] IBB - Institute for Biotechnology and Bioengineering, Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

Abstract

Phosphorus is known to contribute to eutrophication of fresh water systems, as generally it is the limiting nutrient controlling algae growth. Laboratory studies were conducted to develop and test active barriers composed of aluminium oxide immobilized on to polyolefins to remove phosphorus from water. For this purpose, flat plates of polyethylene and polyethylene grafted with maleic anhydride were prepared and tested. The adsorption mechanism of phosphorus on to aluminium oxide was described by the Freundlich isotherm. The optimum pH interval for phosphorus removal was between 5.2 and 7.8, which includes the pH of natural waters. The maximum phosphorus removal capacity was around 11.1μ g/cm^2 for both active barriers. Both barriers removed more than 90% of phosphorus from a 100μ g/L solution in a static batch experiment carried out for 90 d . The in situ implementation of the active barriers developed in the present study might be a valuable strategy to sequester phosphate and thus to control eutrophication in natural ecosystems, though further work is required to evaluate possible interferences coming from other substances present in the water.

Keywords: eutrophication; phosphorus removal; polyolefin; aluminium oxide

Introduction

Phosphorus (P) is an essential nutrient for plant growth and has been intensively used as a fertilizer in agriculture. This practice contributes to the eutrophication of aquatic ecosystems (e.g. lakes, rivers and marshes), causing algal blooms which ultimately lead to oxygen depletion and generally poor water quality [1]. Redissolution of phosphate accumulated in sediments, under certain environmental conditions (temperature, redox potential, pH , dissolved oxygen concentration, bacterial activity), might also be responsible for the occurrence of algae blooms, especially when external nutrient sources are controlled [2].

Remediation solutions aimed at decreasing the phosphorus (P) content of the water column (P precipitation) and/or delaying P release from sediments have been tested for a long time but with limited success. Chemical precipitation with aluminium, iron and calcium salts added to the water column has several disadvantages, namely it is inadequate to remove low concentrations of P, it contaminates water with high concentrations of sulphate and chloride ions, and generates large quantities of flocs that settle to the sediment at the bottom of aquatic systems [3-5]. Sediment capping also has some drawbacks since it may promote ebullition of sediment gases, bioturbation and wave action [6].

A literature review on materials used for phosphate removal, classified in appropriate groups, is presented in Table 1. Calcium compounds, composed largely of calcium carbonate ($CaCO_3$) in the form of calcite, present a phosphate removal capacity that is, in general, lower than those of aluminium and iron compounds. Literature studies reported that carbonate and phosphate ions compete for calcium, which inhibits the precipitation of calcium phosphate [7,8]. Moreover, phosphate removal with calcareous compounds induces an increase in water pH that might not be compatible with life in aquatic systems [9]. Phosphate removal with iron compounds occurs only under aerobic conditions, whereas under anaerobic conditions ferric phosphate compounds dissolve, as a result of the reduction of Fe^{3+} to Fe^{2+}, and phosphate is released into the water column [10]. Among the compounds presented in Table 1, industrial by-products present the highest removal capacity, which is strongly influenced by their content of metallic oxides such as those of Ca, Mg, Fe and Al [11]. An important disadvantage of these materials is

that they can contain heavy metals and thus contaminate the aquatic environment and increase the water pH [12,13]. Clay minerals have a tendency to disperse into very fine particles when applied to the water, which may increase turbidity for long periods. Moreover, the application of dispersible materials into aquatic systems for phosphate removal is not ideal because the immobilized phosphorus remains within the materials and could again be released [14]. Of all the compounds shown in Table 1, activated alumina (aluminium oxide activated at $600\ ^{\circ}C$, Al_2O_3) seems to be the most suitable material for removing phosphate from aquatic systems with eutrophication problems. Activated alumina has a very high surface area, is insoluble in water and is selective for P in the presence of chloride and sulphate ions [3,4].

The objective of the present study was to develop and test active barriers composed of aluminium oxide (Al_2O_3) immobilized on to polyolefins to remove phosphate from water. The concept of an active barrier, placed in situ to sequester phosphate and withdrawn from the system when its phosphate removal capacity is exhausted, is advantageous compared with conventional precipitation methods. This new approach to the eutrophication problem prevents the dispersion of materials into aquatic systems, so avoiding the consequent increase in water turbidity, avoids water contamination with other ions and

metals, and eliminates the formation of flocs that settle to the sediment at the bottom of the aquatic system.

Materials and methods

Materials and preparation of active barriers

Polyolefins, namely high density polyethylene and polyethylene modified with 1.9wt% maleic anhydride (Total Petrochemicals, France), further referred to in the text as PE and PE-g-MA, respectively, were used to prepare active barriers, and functioned as polymeric matrices to support the reactive material. Aluminium oxide activated at 600°C (Sigma Aldrich, Germany), provided in pellets of 3 mm , was used as the reactive material to remove phosphate. Potassium dihydrogeno-phosphate (KH_2PO_4, Merck, Germany) was used as the phosphorus source.

Active barriers were prepared as flat plates (4.0 × 1.0 × 0.2 cm) by compression moulding of 60 g of polymer (PE or PE-g-MA) with 3 g of Al_2O_3 (previously crushed and sieved to an effective size in the range of 500μ m to 1 mm) in a hot plate press (Moore, England) at 200°C using a final pressure of 30 ton. As a result, Al_2O_3 was simply pressed into one the surfaces of the polymeric matrix. The active barrier containing PE as the polymeric matrix is further referred to in the text as Al-PE and the one containing PE-g-MA as Al-PE-g-MA.

P adsorption isotherm on granulated activated aluminium oxide

The extent of P removal from solution was studied using a batch contacting method. Granulated Al_2O_3, previously crushed and sieved to a granular size of 500μ m to 600μ m, was weighed in a range of weights from 10 mg to 500 mg . The weighed solids were contacted with 100 mL of solution containing 10mg/L P in sealed plastic Erlenmeyer flasks clamped into an orbital shaker at 100 rpm and 22°C for 14 d . Initial and final pH values of the solutions were measured using an Orion pH meter (model 420A). Experiments were carried out in triplicate. At equilibrium, the concentration of P in solution was analysed by the ascorbic acid colorimetric method using a Shimadzu spectrophotometer [21]. The amount of P adsorbed on the Al_2O_3 at equilibrium was calculated according to Equation (1), where X(g/kg) is the mass of P(g) removed per mass of Al_2O_3(kg), C_{ini} is the initial concentration of P(g/L), C_{eq} is the equilibrium concentration of P(g/L), V is the solution volume (L), and M is the mass of Al_2O_3(kg).

$$X = \left(C_{ini} - C_{eq}\right) \times \frac{V}{M} \tag{1}$$

Removal of P by active barriers

The P saturation potential for Al-PE and Al-PE-g-MA active barriers was assessed using a sequential batch contacting method. Both barriers were contacted with 100 mL of solution containing 100μ g/LP at 100 rpm

Table 1. Summary of literature review on materials used for phosphorus removal and amount of phosphorus removed (g/kg).

Aluminum	Calcium	Iron	Industrial by-products	Clay
[3] Acti. Alumina: 73	[16] Wollastonite: 0.85	[12] Iron oxide: 12.65	[11] Steel slags: 18	[14] Allophane: q = $5.620C^{0.264}$
[7] Shale: 0.7	[13] Limestone: 0.68	[18] Iron coated sands: 1.50	[20] Blast furnace slags: 8.89	[14] Phoslock ^{TM} : 11-12
[7] Bauxite: 0.36 [15] Zeolite: 2.15	[17] Dolomite: 0.30	[19] Red mud: 0.58	[20] Coal fly ash: 8.81	[18] Bentonite: 1.5×10^{-4}

and 22°C. The solution was replaced weekly until no changes in the concentration of P could be detected. The experiment was done for 14 weeks in triplicate. The concentration of P was measured both before and after the replacement step.

To simulate P removal in a natural water body characterized by a long hydraulic retention time, as for example a lake, an experiment was carried out in batch for 90 d under static conditions. Both Al-PE and Al-PE-g-MA active barriers were placed in plastic beakers with 100 mL of solution, containing 100μ g/LP, and sealed. Experiments were carried out in triplicate. Samples were collected regularly for P concentration analyses. The amount of P removed at equilibrium was calculated according to Equation (1), described above, with the exception that M was replaced by A, the area of the polymeric plate (cm^2).

Effect of pH on P removal

The point of zero charge is usually defined as the pH value at which a solid submerged in an electrolyte exhibits zero net electrical charge on the surface. To determine the point of zero charge $pH(pH_{pzc})$ of Al_2O_3, 0.1 g of the solid was placed in 50 mL of 0.1 M NaCL solution (used as an inert electrolyte) with initial pH in a range from 2 to 12 . The pH was adjusted by either addition of chloridric acid or sodium hydroxide. The experiment took place in sealed plastic Erlenmeyer flasks clamped into an orbital shaker at 100 rpm and 22°C. Chemical equilibrium was attained after 24 h and the pH was measured. Experiments were carried out in triplicate.

The effect of pH on P removal by Al-PE and Al-PE-g-MA active barriers was studied in batch. The barriers were contacted with 100 mL of solution containing 100μ g/LP with initial pH in a range from 2.0 to 9.0, at 100 rpm and 22°C for 7 d . Experiments were done

in triplicate. The concentration of P was measured at the beginning and at the end of the experiment.

Results and discussion

The literature review on materials used for phosphate removal (Table 1) suggested that activated aluminium oxide might be one of the most suitable materials to be used for the remediation of aquatic systems with eutrophication problems, because it has a high removal capacity and is insoluble in water. Therefore, in this study active barriers composed of aluminium oxide immobilized on to polyolefins (PE and PE-g-MA) were developed and tested for their ability to remove phosphate from water. Specifically, the mechanism of P removal, the maximum *P* removal capacity of the active barriers, and the effect of pH on P removal were assessed. The long-term P removal, under static conditions simulating a natural system, was also investigated.

P adsorption by granulated activated aluminium oxide

The adsorption isotherm of P on to aluminium oxide was determined to assess the adsorption mechanism. The results were fitted by the Freundlich model (Figure 1 and Equation (2)) with a correlation coefficient of 0.93:

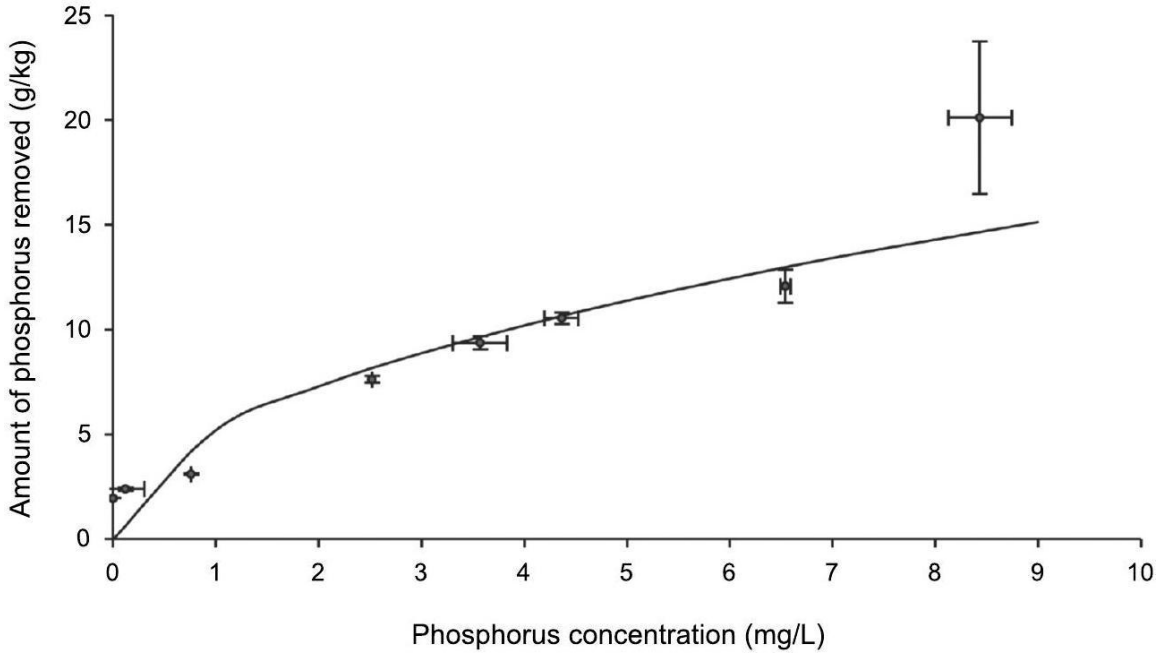

Figure 1. Phosphorus adsorption isotherm on to granulated Al_2O_3. The experiment was conducted at 22 $\pm$ 1 °C for 17 d at 100 rpm .

$$S = 5.1 \cdot [C]^{0.462} \quad (2)$$

where S is the amount of P adsorbed (g/kg), C is the equilibrium concentration (mg/L), $K = 5.2$ and $1/N = 0.49$. These results suggested that the adsorption of P on to Al_2O_3 followed a multilayer mechanism. Similar results were reported in the literature for the adsorption of P on to aluminium oxide hydroxide [22].

Removal of P by active barriers

The maximum P removal of both Al -PE and Al-PE-gMA active barriers was $11.1 \pm 0.3\mu$ g/cm^{2}P from the 35μ g/cm^2 P theoretically available ($[100\mu$ g/L $\times$ 0.1 L $\times$ 14 weeks$]$ /4 cm^2). Although Al-PE and Al-PE-gMA active barriers removed almost the same amount of P , the initial removal rate of Al-PE-g-MA was higher than that of Al-PE, as depicted in Figure 2. The geometric surface area of the aluminium oxide layer deposited on top of the PE and PE-g-MA matrices was used in the calculation of the maximum P removal, instead of the available surface area. Experimental determination of the available surface area might have improved the accuracy of the results obtained, as aluminium oxide distribution might have not been homogenous. Also it is not straightforward to compare the maximum P removal obtained in this study with those reported in literature (Table 1) because previously explored strategies used granular adsorbing materials and consequently removal was listed per mass of material. Considering that the calculated amount of activated aluminium oxide in the adsorbing layer is 13.9mg/cm^2 the maximum P removal per mass of aluminium oxide would be around 1 g/kg. This value is lower than others obtained with granulated aluminium oxide (Table 1 and this study), and a possible explanation is that the removal of P on to the active barriers is limited by the surface area.

Long-term batch experiments (90 d) were carried out using the maximum concentration of P expected in natural waters, 100μ g/L, under static conditions. The experimental results showed that the concentration of P decreased faster in the first 30 d in the presence of Al-PE-g-MA than in the presence of Al-PE (Figure 3). The amount of P removed was $2.3 \pm 0.1\mu$ g/cm^2 for Al-PE and $2.5 \pm 0.1\mu$ g/cm^2 for Al-PE-g-MA, and the concentration of P at equilibrium for both barriers was lower than 10μ g/L.

Although the Al-PE-g-MA active barrier had a higher affinity to phosphate than the Al-PE, corresponding to a higher initial rate of phosphate removal, the presence of maleic anhydride in the polymer matrix did not contribute to a superior removal of P from solution in a long-term experiment. Because the extent of P removal was smaller than the maximal possible, these results suggested that the amount of P used in this experiment, and not the available surface area, was the limiting factor. Considering that the minimum P concentration needed to attain an algae bloom in a lake is about 20μ g g/L at the hypolimnion [1], the active barriers prepared in the present study can reduce the P concentration in water to values lower than 10μ g/L, the critical value for the algae growth, at a pH comparable to those found in natural ecosystems.

Effect of pH on P removal

The pH_{pzc} is an important parameter to understand the surface chemistry of a material in aqueous solution, and is defined as the pH value where the net surface charge of particles is zero. As depicted in Figure 4, the pH_{pzc} determined for aluminium oxide was around

8.0, which

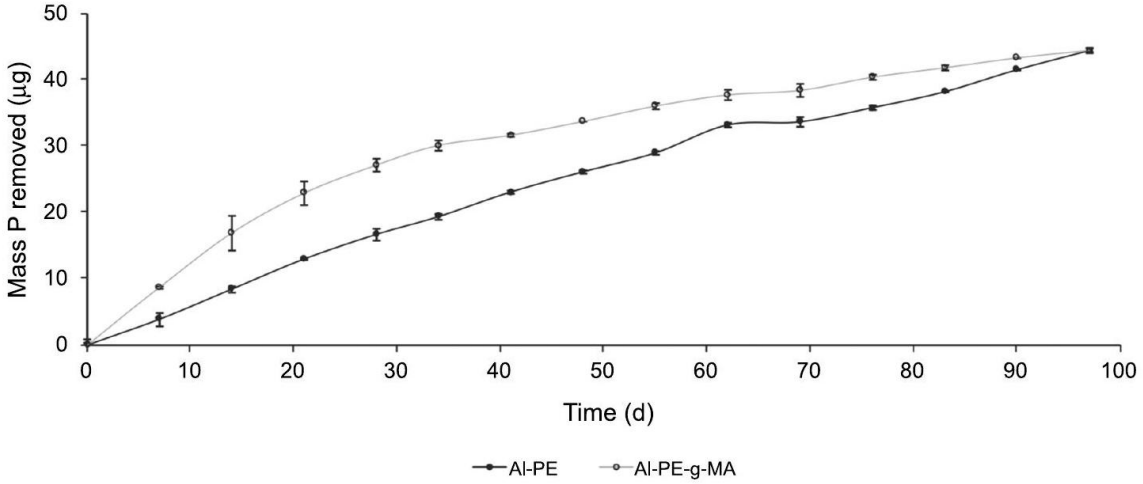

Figure 2. Cumulative phosphorus adsorption onto Al-PE and Al-PE-g-MA activated barriers. Experiments were conducted at 22 ± 1°C for 14 weeks at 100 rpm .

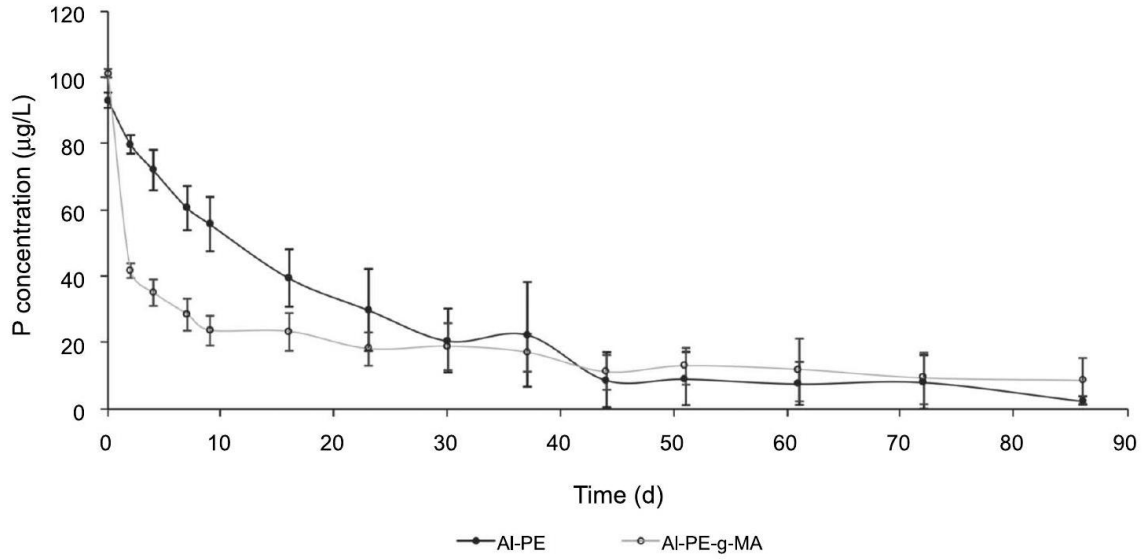

Figure 3. Phosphorus concentration profiles along time. Experiments were conducted at 22 ± 1°C for 90 d under static conditions.

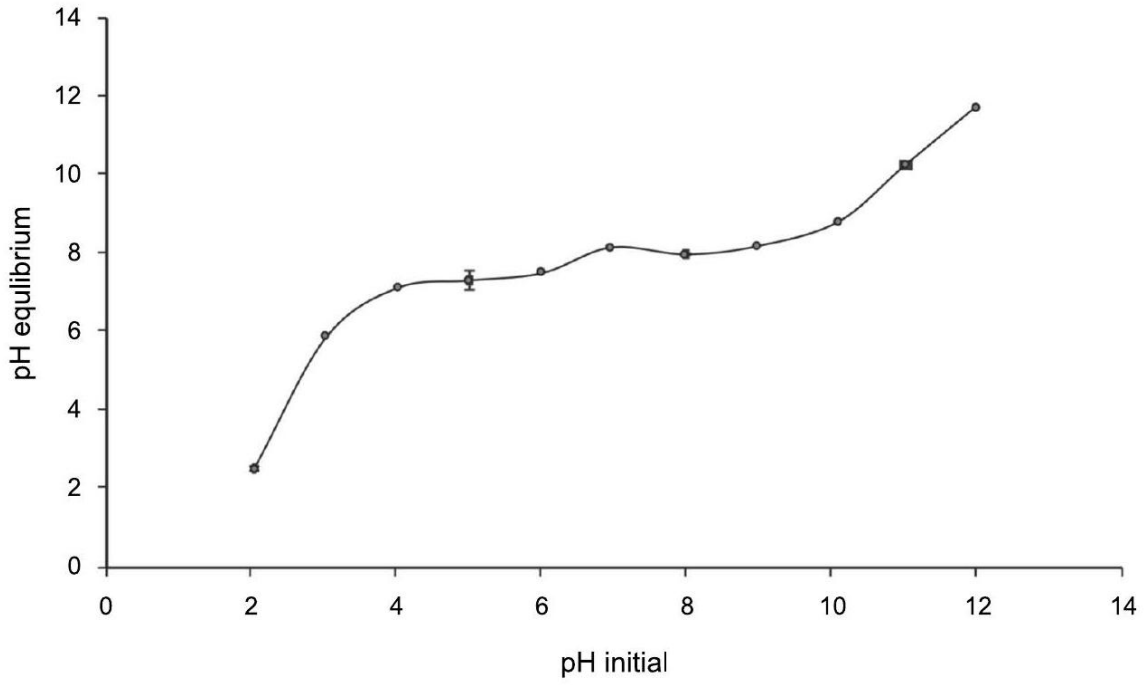

Figure 4. Point of zero charge for activated aluminium oxide.
is consistent with literature values [23]. Below the pH_{pzc}, the acidic water donates more protons than hydroxide groups, and so the aluminium oxide surface is positively charged (attracting anions). In contrast, above the pH_{pzc}, the aluminium oxide is negatively charged (attracting cations).

The influence of pH on the extent of P removal on to Al-PE-g-MA is depicted in Figure 5. The Al-PE-gMA barrier was used in this experiment because it presented a faster initial kinetics of P removal than AlPE . The results suggested that the amount of P removed by Al-PE-g-MA increased with pH in the range of 2.4 to 5.2. The removal of P was maximum in the pH interval between 5.2 and 7.8, decreasing abruptly for a pH value higher than 7.8. This behaviour can be explained by the different phosphate species present in solution at different pH values (Figure 6), which will affect the electrostatic interactions with aluminium oxide particles and consequently the P removal.

The maximum phosphate removal occurred for the ion pair $HPO_4^{2-}/H_2PO_4^{-}$ ($pK_a = 7.21$) and is the result of a strong electrostatic interaction of these two species with positive charges present on the aluminium oxide surface. As the pH decreases, the predominant species

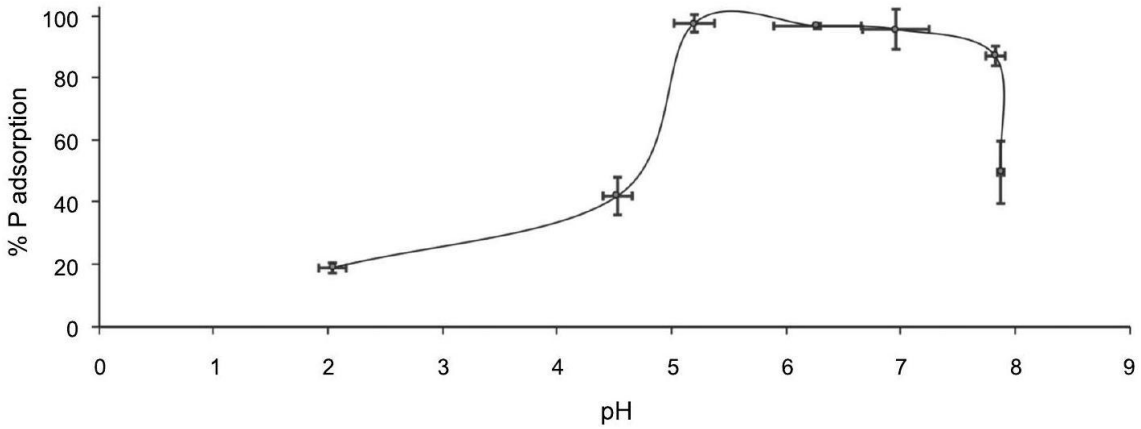

Figure 5. Influence of pH on the amount of phosphorus removed by Al-PE-g-MA.

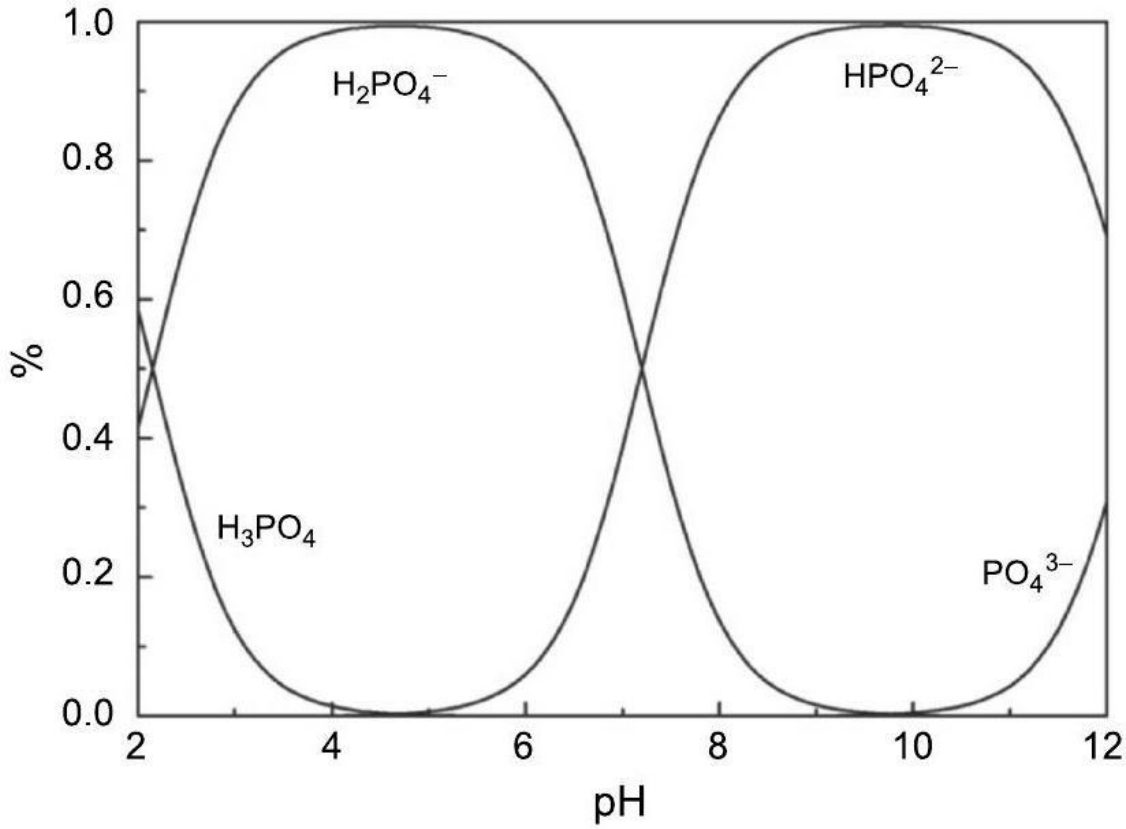

Figure 6. Speciation of phosphoric acid at low ionic strength [24].
are $H_2PO_4^-/H_3PO_4(pK_a = 2.12)$, resulting in fewer P ions available to interact with the aluminium oxide. The decrease in phosphate removal at pH higher than 7.8 is probably due to the accumulation of a net negative charge on the aluminium oxide surface (most Al oxides have a point of zero charge around pH 7 or 8). A limited number of studies investigated the effect of pH on phosphate removal by reactive materials. As examples, Tanada et al. [22] reported a maximum phosphate removal at pH 4.0 using aluminium oxide hydroxide. Huang et al. [19] and Zeng et al. [12] reported that red mud and iron oxide tailings presented a maximum phosphate removal at pH 2.0 and 3.2, respectively.

The reactive barrier developed in the present work, Al-PE-g-MA, is very appropriate as an in situ application because its maximum phosphate removal capacity occurs in a range of pH values that encompass the ones characteristic of aquatic ecosystems, as opposed to the studies mentioned above.

Compared with accepted or previously explored strategies to sequester phosphorus and thus to control eutrophication in natural ecosystems, this new approach prevents the dispersion of materials into aquatic systems and the consequent increase in water turbidity, avoids water contamination with other ions and metals, and eliminates the formation of flocs that settle to the sediment at the bottom of the aquatic system. Further work is required to evaluate possible interferences coming from other substances present in the water before of active barriers developed in the present study can be implemented in situ.

Conclusions

The present study suggested that active barriers composed of aluminium oxide immobilized on to polyolefins are an attractive alternative technology to remove phosphorus from water. The removal of phosphorus from aqueous solutions by aluminium oxide was described by a Freundlich adsorption isotherm. The maximum P removal capacity of the active barriers was 11.1μ g/cm^2. The extent of P removal depended on pH and the best results were obtained at a pH interval between 5.0 and 8.0. A considerable decrease in the concentration of phosphorus, from 100μ g/L to 10μ g/L (90% of removal), was achieved in long-term experiments under static conditions simulating a natural system (e.g. a lake). The major advantages of the active barriers proposed in the present study to remove phosphorus from natural ecosystems, compared with previously explored strategies, are that they prevent the dispersion of materials and the consequent increase in water turbidity, avoid water contamination with other ions and metals, and eliminate the formation sediments.

Acknowledgements

The authors acknowledge the Foundation for Science and Technology (FCT) Project SFRH/BD/39085/2007 and PPCDT/AMB/61155/2004 for the financial support.

References

[1] G. Martins, D. Ribeiro, D. Pacheco, J.V. Cruz, R. Cunha, V. Gonçalves, R. Nogueira, and A.G. Brito, Prospective scenarios for water quality and ecological status in Lake Sete Cidades (Portugal): The integration of mathematical modelling in decision processes, Appl. Geochem. 23 (2008), pp. 2171-2181.
[2] D. Ribeiro, G. Martins, R. Nogueira, J.V. Cruz, and A.G. Brito, Phosphorus fractionation in lake volcanic sediments (Azores - Portugal), Chemosphere 70 (2008), pp. 1256-1263.
[3] T. Hano, H. Takanashi, M. Hirata, K. Urano, and S. Eto, Removal of phosphorus from wastewater by activated alumina adsorbent, Water Sci. Technol. 35 (1997), pp. 39-46.
[4] D. Donnert and M. Salecker, Elimination of phosphorus from municipal and industrial waste water, Water Sci. Technol. 40 (1999), pp. 195-202.
[5] E.W. Shin and J.S. Han, Phosphate adsorption on aluminium-impregnated

mesoporous silicates: Surface structure and behaviour of adsorbents, Environ. Sci. Technol. 38 (2004), pp. 912-917.
[6] L.J. Thibodeaux and V.J. Bierman, The bioturbationdriven chemical release process, Environ. Sci. Technol. 37 (2003), pp. 252A-258A.
[7] A. Drizo, C.A. Frost, J. Grace, and K.A. Smith, Physi-cal-chemical screening of phosphate-removing substrates for use in constructed wetland systems, Water Res. 33 (1999), pp. 3595-3602.
[8] N. Miller, Locally available adsorbing materials, sediment sealing and flocculants for chemical remediation of lake and stream, Analytical & Environmental Consultants, Rotorua, 2005.
[9] L.J. Westholm, Substrates for phosphorus removal: Potential benefits for on-site wastewater treatment, Water Res. 40 (2006), pp. 23-36.
[10] Y. Ann, K.R. Reddy, and J.J. Delfino, Influence of chemical amendments on phosphorus immobilization in soils from a constructed wetland, Ecol. Eng. 14 (2000), pp. 157-167.
[11] H.C. Zhang, Z.H. Cao, Q.R. Shen, and M.H. Wong, Effect of phosphate fertilizer application on phosphorus (P) losses from soil in Taihu Lake Region. I. Effect of phosphate fertilizer rate on *P* losses from paddy soil, Chemosphere 50 (2003), pp. 695-701.
[12] L. Zeng, X. Li, and J. Liu, Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings, Water Res. 38 (2004), pp. 1318-1326.
[13] N. Boujelben, J. Bouzid, Z. Elouear, M. Feki, F. Jamoussi, and A. Montiel, Phosphorus removal from aqueous solution using iron coated natural and engineered sorbents, J. Hazard. Mater. 151 (2008), pp. 103-110.
[14] G. Yuan and L. Wu, Allophane nanoclay for the removal of phosphorus in water and wastewater, Sci. Technol. Adv. Mater. 8 (2007), pp. 60-62.
[15] K. Sakadevan and H.J. Bavor, Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrate in constructed wetland systems, Water Res. 32 (1998), pp. 393-399.
[16] A. Hedström, Reactive filter materials for ammonium and phosphorus sorption in small scale wastewater treatment, Ph.D. diss., Luleå University of Technology, 2006.
[17] K. Pant, K.R. Reddy, and E. Lemon, Phosphorus retention capacity of root bed media of sub-surface flow constructed wetlands, Ecol. Eng. 17 (2001), pp. 345-355.
[18] E.G. Pradas, M.V. Sanches, and A.G. Campo, Effects of experimental variables on phosphate adsorption on bentonite, J. Chem. Technol. Biotechnol. 3 (1992), pp 291-295.
[19] W. Huang, S. Wang, Z. Zhu, L.X. Yao, V. Rudolph, and F. Haghseresht, Phosphate removal from wastewater using red mud, J. Hazard. Mater. 158 (2008), pp 35-42.
[20] D. Xu, J. Xu, J. Wu, and A. Muhammad, Studies on the phosphorus sorption capacity of substrates used in constructed wetland systems, Chemosphere 63 (2006), pp. 344-352.
[21] A.D. Eaton, L.S. Clesceri, A.E. Greenberg (eds.), Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, Washington, DC, 1995, pp. 4-113-4-114.
[22] S. Tanada, M. Kabayama, N. Kawasaki, T. Sakiyama, T. Nakamura, M. Araki, and T. Tamura, Removal of phosphate by aluminum oxide hydroxide, J. Colloid Interface Sci. 257 (2003), pp. 135-140.
[23] A.G. Stack, S.R. Higgins, and C.M. Eggleston, Point of zero charge of a corundum-water interface probed with optical second harmonic generation (SHG) and atomic force microscopy (AFM): New approaches to oxide surface charge, Geochim. Cosmochim. Acta 65 (2001), pp. 3055-3063.
[24] Y. Xiaofang, W. Dongsheng, S. Zhongxi, and T. Hongxiao Adsorption of phosphate at the aluminium (hydr)oxides interface: Role of the surface acid-base properties, Colloids Surf. A 297 (2007), pp. 84-90.