

Phosphorous removal from water by polyolefins: effect of Al₂O₃ addition

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Abstract

Phosphorus is the main nutrient responsible for eutrophication of aquatic ecosystems, therefore it is important to develop new processes to remove phosphorus that avoid the formation of precipitates. Polyolefins with and without prior activation with aluminum oxide (Al₂O₃), processed as flat plates, were investigated for phosphate removal from an aqueous solution. The maximum amount of phosphorus removal was 0.042 µgP/cm² for PE (polyethylene), 0.049 µgP/cm² for PE-g-MA (polyethylene grafted with maleic anhydride), and 0.071 µgP/cm² for PE-g-MAe (PE-g-MA enriched in MA). Increasing polyolefins' polarity did not result in a significant increase in phosphate removal. Activated polyolefins with Al₂O₃ presented maximum amounts of phosphorus removal of 0.863 µgP/cm² for PE, 0.948 µgP/cm² for PE-g-MA, and 0.884 µgP/cm² for PE-g-MAe. As expected, addition of Al₂O₃ considerably increased phosphate removal. In kinetic experiments carried out with polyolefins activated with Al₂O₃ during 3 months a very high percentage of phosphorus removal was obtained for (> 90 %) as well as a very low remaining phosphorus concentration in solution (< 10 µgP/L).

As a conclusion, polyolefins activated with Al₂O₃ effectively removed phosphorous from aqueous solutions with low concentrations which indicate that this material might be used for in-situ remediation of eutrophic waters. The possibility to recover the material after use to recycle phosphate and the absence of precipitates' formation are two major advantages of this process.

Introduction

Phosphorus (P) is an essential nutrient for plant growth and has been intensively used as a fertilizer in agriculture. This practice contributed 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 (Ribero et al., 2008). Re-dissolution of phosphate accumulated in the 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 (Martins et al., 2008).

P inactivation is a lake restoration technique. Its purpose is to lower the lake's P content by removal of P from the water column (P precipitation) and/or by retarding P release from lake sediments (P inactivation). Remediation solutions have been tested for a long time but with limited success. A literature review on materials used for P removal, classified in appropriate groups, is given in Table 1.

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Table 1 - Literature review on adsorptive media for phosphorus removal

Aluminum	Calcium	Iron	Industrial by-products	Clay
<ul style="list-style-type: none"> • <i>Activated alumina</i> (7gP/kg)¹ • <i>Shale</i> (0.73 gP/kg)² • <i>Bauxite</i> (0.36 gP/kg)² • <i>Zeolite</i> (2.15 gP/kg)³ 	<ul style="list-style-type: none"> • <i>Wollastonite</i> (0.85 gP/kg)⁴ • <i>Limestone</i> (0.68 gP/kg)² • <i>Dolomite</i> (0.30 gP/kg)⁵ 	<ul style="list-style-type: none"> • <i>Iron oxide</i> (12.65 gP/kg)⁶ • <i>Iron coated sands</i> (1.50 gP/kg)⁷ • <i>Red mud</i> (0.58 gP/kg)⁸ 	<ul style="list-style-type: none"> • <i>Steel slags</i> (18 gP/kg)⁹ • <i>Blast furnace slags</i> (8.89 gP/kg)¹⁰ • <i>Coal fly ash</i> (8.81 gP/kg)¹⁰ 	<ul style="list-style-type: none"> • <i>Allophane</i> ($q = 5.620C^{0.264}$)¹¹ • <i>Phoslock™</i> (11-12 gP/kg)¹¹ • <i>Bentonite</i> (0.42 mgP/kg)¹²

1- Donnert and Salecker, 1999; 2- Drizo et al., 1999; 3- Sakadevan et al., 1998; 4- Hedström, 2006; 5- Pant et al., 2001; 6- Zeng et al., 2004; 7- Boujelben et al., 2008; 8- Huang et al., 2008; 9- Zhang et al., 2003; 10- Xu et al., 2006; 11- Yuan and Wu, 2007; 12- Pradas et al., 1992.

From all adsorbents shown in Table 1, activated alumina might be one of the most suitable materials to be used in phosphorus removal from natural waters with eutrophication problems. Activated alumina (aluminum oxide activated at 600 °C) has a very high surface area (300 m²/g) and is selective for phosphorus in the presence of nitrate and sulfate ions (Hano et al., 1997; Donnert and Salecker, 1999). The mechanism of phosphate removal by activated alumina is mainly ion exchange associated with chemical reaction, precipitation and formation of complexes (Narkis et al., 1981).

Materials and Methods

Materials

Polyolefins, polyethylene (PE), polyethylene grafted with maleic anhydride (PE-g-MA), and PE-g-MA enriched in maleic anhydride were used as polymeric matrices to remove phosphorus from an aqueous solution. The maleic anhydride increases the polarity of the resulting polymeric matrix thus enhancing the contact between aqueous and solid phases. In addition, the polymeric matrices were loaded with Al₂O₃ (5.0 %) which was dispersed onto their surfaces. Polymeric plates (12 cm × 18 cm × 0.2 cm) were made in a hot plat press (Moore) at a temperature of 453.15 K and using a final pressure of 30 ton. They were divided into sections with variable dimensions. Al₂O₃, provided by Sigma Aldrich in pellets of 3 mm, was crushed and sieved to an effective size in the range of 500 µm to 1 mm.

Stock phosphorus solution

A stock phosphorus solution with a concentration of 40 mg/L was prepared by dissolving 175.75 mg KH₂PO₄ in 1 L of pure water and used to prepare solutions with lower concentrations. Phosphate concentration was determined spectrophotometrically at a wavelength of 882 nm using the Ascorbic Acid method (4500 - PE, in Standard Methods, 17th Edition 1989).

Kinetic experiments

Kinetic experiments were carried out to determine phosphate removal from a solution with an initial P concentration of 100 µg/L. Firstly, experiments were performed in glass beakers where 2.5 g of each material present as granules, PE (3 mm), PE-g-MAe (1 - 3 mm), and Al₂O₃ (0.5 – 1 mm), was placed in contact with 100 mL of a 100 µg/L P solution at 100 rpm and 22 °C during 7 d. Secondly, polymeric plates with similar areas, 10.5 cm² (4.0 cm × 1.0 cm × 0.2 cm), with and without prior activation with Al₂O₃, were placed in glass beakers containing 100 mL of a 100 µg/L P solution at room temperature for 16 d and 90 d without agitation. Samples were taken regularly and the phosphorus content was measured.

Influence of pH on P adsorption onto polymeric plates

Kinetic experiments with polymeric plates activated with Al₂O₃ were carried out as described previously at pH values of 2, 4, 5, 6, 7, 8 and 9, during 7 d, at 100 rpm and 22°C. The pH was adjusted by addition of either 2 M NaOH or 2 M HCl.

Determination of phosphorus uptake

The amount of phosphate removed, q (µg/cm²), onto polymeric matrix was calculated by the following equation:

$$q = \frac{(C_i - C_e) \cdot V}{A} \quad [1]$$

where C_i and C_e are initial and equilibrium phosphorus concentrations in solution (µg/L), V is the solution volume (L), and A is the area of polymeric matrix (cm²).

Results and Discussion

Kinetic experiments

Figure 1 depicts the concentration of phosphorus in solution obtained in assays carried out with granular polyolefins and Al₂O₃. Phosphorus removal was higher and faster in the presence of Al₂O₃. A decrease of 83 % in phosphorus concentration was observed for Al₂O₃ during the first day as compared to 40 % for PE and 43 % for PE-g-MA.

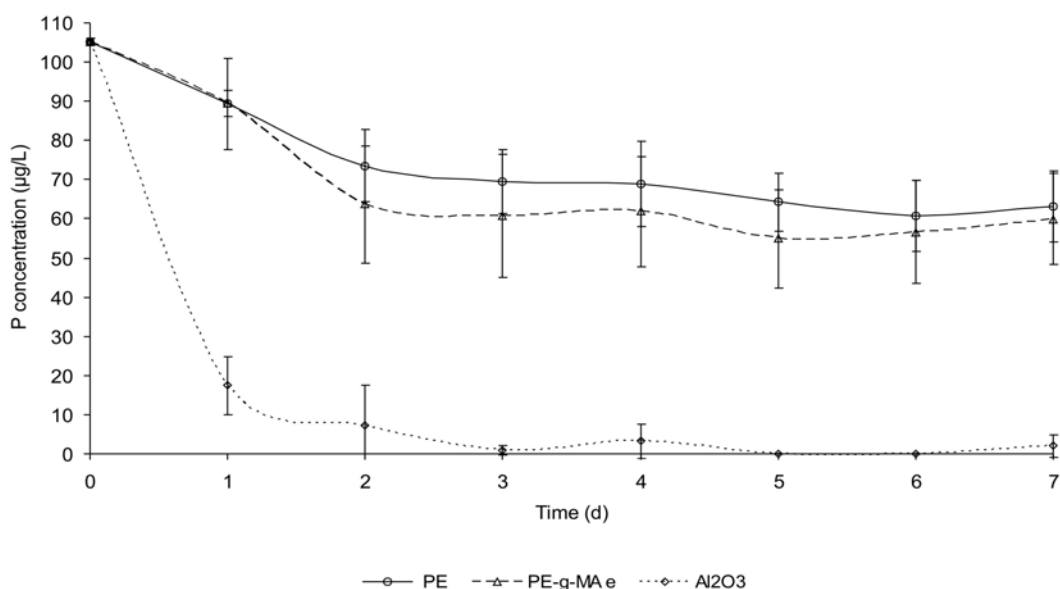


Figure 1 – Phosphorus in solution obtained in assays carried out with granular polyolefins and Al₂O₃.

Figure 2 depicts the concentration of phosphorus in solution obtained in assays carried out with polyolefin plates with and without previous activation with Al₂O₃. A limited affinity between polyolefin plates and phosphorus was observed after 16 d, as indicated by the low amount of P removed, respectively 0.042 µgP/cm² for PE, 0.049 µgP/cm² for PE-g-MA, and 0.071 µgP/cm² for PE-g-MAe. The amount of phosphorus removal was limited by the surface area available. Higher phosphorus removal were obtained for polyolefins activated with Al₂O₃, respectively 0.46 µgP/cm² for PE+5% Al₂O₃, 0.56 µgP/cm² for PE-g-MA+5% Al₂O₃, and 0.79 µgP/cm² for PE-g-MAe+5% Al₂O₃. The highest phosphorus removal was obtained in the case of PE-g-MAe. This result seems to indicate that polymers with higher polarities remove more phosphorus. During the first 19 h of contact phosphorus concentration decreased from 97 µg/L to 72

$\mu\text{g/L}$ and after 16 d a final concentration of $14 \mu\text{g/L}$ was achieved for PE-g-MAe+5% Al_2O_3 . A very high percentage of phosphorus removal was obtained as well as a low remaining phosphorus concentration in solution. By the end of the experiment the equilibrium phosphorus concentration was not yet reached. A new experiment was carried out for 90 d with the most promising materials, as depicted in Figure 3.

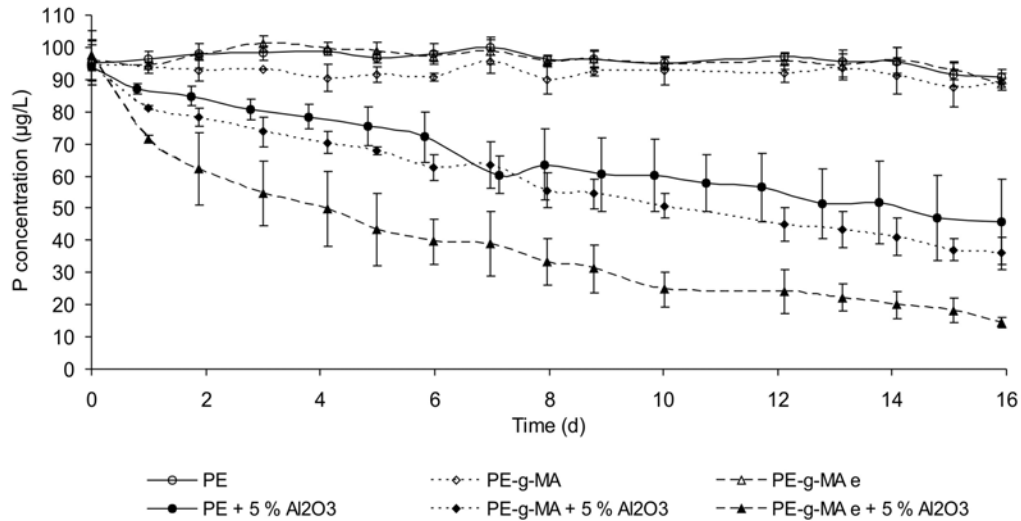


Figure 2 – Phosphorus in solution obtained in assays carried out with polyolefin plates with and without Al_2O_3 .

The maximum amount of phosphorus removed by polyolefin plates activated with Al_2O_3 was $0.86 \mu\text{gP/cm}^2$ for PE, $0.95 \mu\text{gP/cm}^2$ for PE-g-MA, and $0.88 \mu\text{gP/cm}^2$ for PE-g-MAe. Although the initially kinetics of phosphorus removal is faster for PE-g-MAe, phosphorus concentration remaining in solution after 90 d was below $10 \mu\text{g/L}$ in all cases, as depicted in Figure 3.

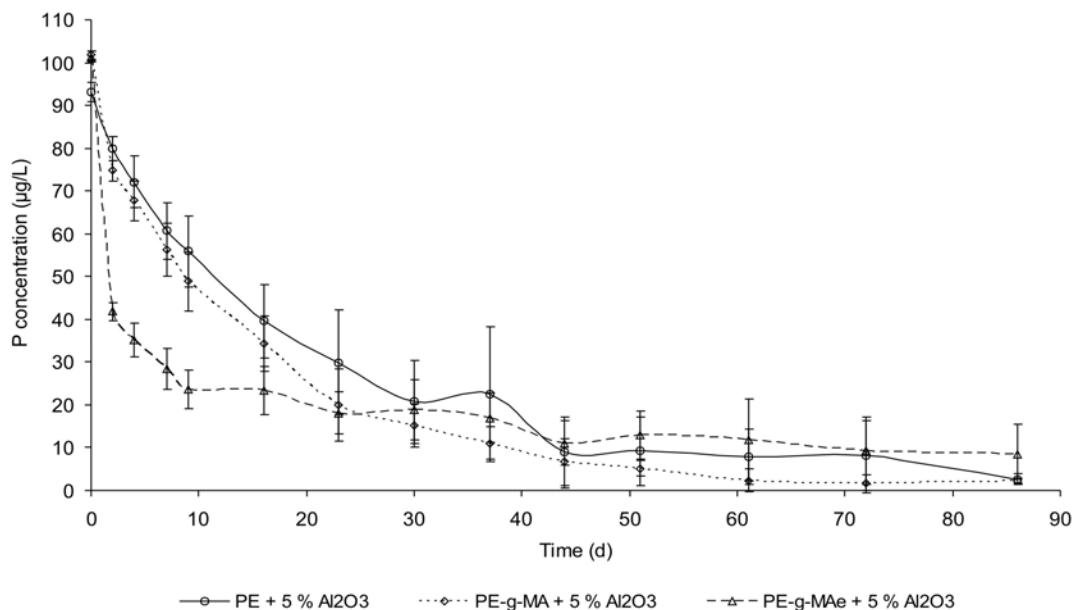


Figure 3 – Phosphorus in solution obtained in assays carried out with polyolefin plates activated with Al_2O_3 .

The amount of phosphorus removed by polyolefin plates activated with Al_2O_3 at different pH values is shown in Figure 4. The percentage of phosphorus removal of activated PE and PE-g-MA decreases with an increase of pH while PE-g-MAe presents a stable maximum removal between pH 5 and pH 8 seems to be the most promising one. Increasing PE's polarity shifts maximum phosphorus removal from acidic to neutral/basic pH values. These results seem to indicate that the interaction between pH and polarity is a key factor in phosphorus removal and that the mechanism responsible for phosphorus removal might be ion exchange.

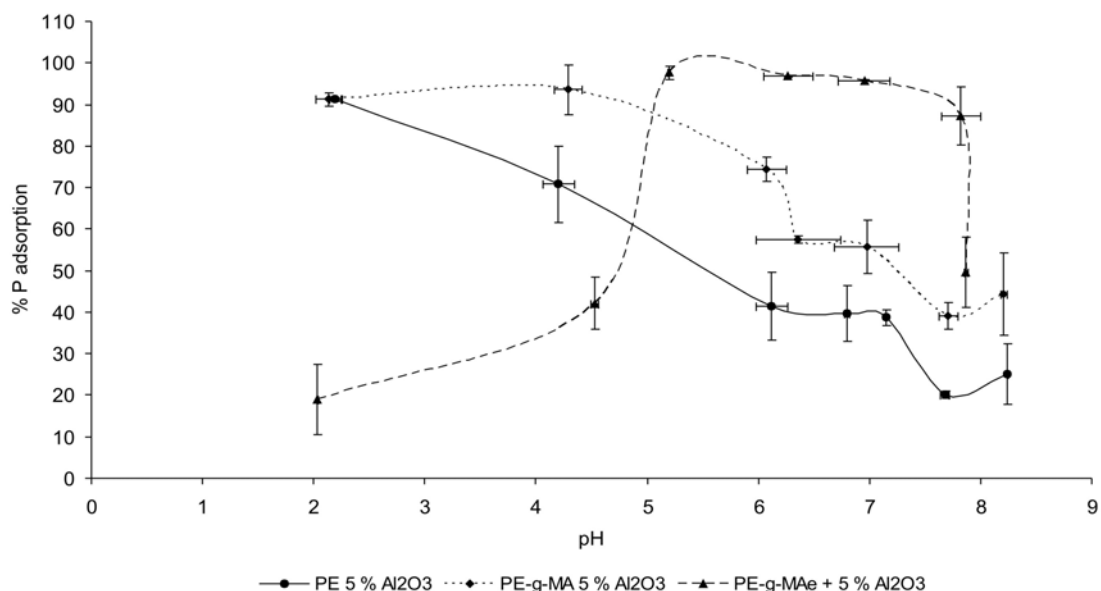


Figure 4 – Percentage of phosphorus removal as a function of pH in assays carried out with polyolefin plates activated with Al_2O_3 .

Conclusions

The present study indicates that polyolefins activated with Al_2O_3 remove efficiently phosphorus from low solutions with low concentrations. The maximum removal capacities obtained were $0.86 \mu\text{gP}/\text{cm}^2$ for PE, $0.95 \mu\text{gP}/\text{cm}^2$ for PE-g-MA, and $0.88 \mu\text{gP}/\text{cm}^2$ for PE-g-MAe. Furthermore, it was found that phosphorus removal efficiency depended on pH. The best results were obtained for PE-g-MA enriched in maleic anhydride that presented a maximum phosphorus removal in a pH interval between 5 and 8.

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References

- Boujelben, N., J. Bouzid, Z. Elouear, M. Feki, F. Jamoussi, A. Montiel (2008). Phosphorus removal from aqueous solution using iron coated natural and engineered sorbents, *Journal of Hazardous Materials* 151: 103-110.
- Donnert, D., M. Salecker (1999). Elimination of phosphorus from municipal and industrial waste water, *Water Science and Technology* 40: 195-202.
- Drizo, A., C. A. Frost, J. Grace, K. A. Smith (1999). Physical-chemical screening of phosphate removing substrates for use in constructed wetland systems, *Water Research* 33: 3595-3602.

- Hano, T., H. Takanashi, M. Hirata, K. Urano, S. Eto (1997). Removal of phosphorus from wastewater by activated alumina adsorbent, *Water Science and Technology* 35: 39-46.
- Hedström, A. (2006). Reactive filter materials for ammonium and phosphorus sorption in small scale wastewater treatment, PhD Thesis.
- Huang, W., S. Wang, Z. Zhu, L. X. Yao, V. Rudolph, F. Haghseresht (2008). Phosphate removal from wastewater using red mud, *Journal of Hazardous Materials*, article in press.
- Martins G., D. Ribeiro, D. Pacheco, J. V. Cruz, R. Cunha, V. Gonçalves, R. Nogueira, A.G. Brito (2008). Prospective scenarios for water quality and ecological status in Lake Sete Cidades (Portugal): the integration of mathematical modelling in decision processes. *Applied Geochemistry* (in press).
- Narkis, N., M. Meiri (1981). Phosphorus removal by activated alumina *Environmental Pollution Series B, Chemical and Physical Volume 2*, 327-343.
- Ribeiro D., G. Martins, R. Nogueira, J. V. Cruz, A.G. Brito (2008). Phosphorus Fractionation in lake volcanic sediments (Azores – Portugal). *Chemosphere*, 70 7.
- Pant, K., K. R. Reddy, E. Lemon (2001). Phosphorus retention capacity of root bed media of sub-surface flow constructed wetlands, *Ecological Engineering* 17: 345-355.
- Pradas, E. G., M. V. Sanches, A. G. Campo (1992). Effects of experimental variables on phosphate adsorption on bentonite, *Journal of Chemical Technology & Biotechnology* 3: 291-295.
- Sakadevan, K., Bavor, H.J. (1998). Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrate in constructed wetland systems. *Water Research* 32, 393–399.
- Xu, D., J. Xu, J. Wu, A. Muhammad (2006). Studies on the phosphorus sorption capacity of substrates used in constructed wetland systems, *Chemosphere* 63: 344-352.
- Yuan, G., L. Wu (2007). Allophane nanoclay for the removal of phosphorus in water and wastewater, *Science and Technology of Advanced Materials* 8: 60-62.
- Zeng, L., X. Li, J. Liu (2004). Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings, *Water Research* 38: 1318-1326.
- Zhang, H.C., Z. H. Cao, Q. R. Shen, M. H. Wong (2003). 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: 695-701.