Development of Permeable Reactive Barrier for Phosphorus Removal

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Abstract

Permeable reactive barriers were developed for phosphorus removal. The barrier consists in an organic-inorganic hybrid material, which allows water and others species to flow through it, while selectively removes the contaminants. Polyethylene oxide (POE) and aluminium oxide (Al_2O_3) were used as the organic and the inorganic parts, respectively. The hybrid material was obtained by sol-gel reaction, using aluminium isopropoxide as inorganic percursor in order to attain Al_2O_3. The hybrid material produced was characterized by FT-IR spectroscopy and thermogravimetry. The previous tests for phosphorus removal have shown the effectiveness capacity of the developed material to remove it.

Introduction

Phosphorus is an essential nutrient for plants growth and has been intensively used as a fertilizer in agriculture. However, this characteristic also contributed to the eutrophication of aquatic ecosystem (e.g. lakes, rivers and marshes) causing algal blooms, which leads aesthetic problems, undesirable odor, taste of potable water and lower oxygen concentration in the water [1,2]. The sources of phosphorus can be divided in two categories: first point sources, which are discharge located and well known from factories

of municipal sewage systems and second disperse sources, which cover run-off from rural and urban landscapes [2]. When these two sources are controlled, sediments and organic compounds also provoke algal blooms, whereas under certain environmental conditions (temperature, redox potential, pH , dissolved oxygen concentration, bacterial activity) these could release the accumulated phosphorus [3]. In natural waters, phosphorus occurs in two main forms: orthophosphate ($H_2PO_4^-, HPO_4^{2-}, PO_4^{3-}$) and polyphosphate (polymers of phosphoric acid). Polyphosphates can convert into ortho forms by hydrolyze in aqueous solution [4].

Chemical and biological precipitations methods 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 concentration of phosphorus due to thermodynamic and kinetic limitations and generally generates large quantities of flocks that settle to the sediment bottom of the aquatic systems [5, 6, 7]. Potential problems with sediment capping are ebullition of sediment gases, bioturbation and wave action [8].

The used of permeable reactive barriers (PRBs) for phosphorus removal is a new approach, which overcomes the limitations of the previous methods. PRBs are organic-inorganic compounds that form hybrid materials type I, which do not have covalent bonds between organic and inorganic phases but mainly hydrogen bonds between the two phases and are obtained by sol-gel reactions, through the reaction between a polymer and a metal alkoxide in the presence of a solvent [9]. Hybrids materials are not prepared direct dispersion of the metal oxide. Instead, the metal alkoxide is used as the precursor of the metal oxide, which is dispersed at molecular level by dissolution in an organic solvent, such as alcohol. Then, through a sol-gel process the metal alkoxide is converted in metal oxide, in the presence of an organic polymer which is also dissolved [10]. Since aluminium oxide (Al_2O_3) is very efficient on phosphorus removal, it was selected as the inorganic constituent.

The sol-gel process allows to obtained single phase material, substantially homogeneous, in which the polymer and the inorganic constituent forms a interpenetration network. The PRBs must have mechanical strength to maintained barrier integrity (both wet and dry), be able to incorporate selective sequester agent without this leach from barrier and remain active [11].

Thus, the objective of the present study was to develop and test PRBs composed of Al_2O_3 immobilized onto polyethylene oxide (POE) to remove phosphate from water. This new approach to the eutrophication problem prevents the dispersion of materials into aquatic systems with the consequent increase of water turbidity, avoids water contamination with other ions and metals and eliminates the formation of flocks that settle to the sediment at the bottom of the aquatic system.

Material and Methods

Materials. The commercial polyethylene oxide (POE), aluminium isopropoxide ($Al(OC_3H_7)_3$) and aluminium oxide (Al_2O_3) were supplied by Aldrich Chemical Company and used as received. All the other reagents were provided also by Aldrich Chemical Company and used as received. Pure water was obtained using Milli-Q Synthesis water purification system.

Stock phosphorus solution. A stock phosphorus solution with a concentration of 40mg/L was prepared by dissolution of 175.75mgKH_2PO_4 in 1 L of pure water and then used to prepare solutions with lower concentrations. Phosphate concentration was determined spectrophotometrically at a wavelength of 882 nm using the Ascorbic Acid method [12].

Determination of zero point charge ($\mathbf{pHH_{ZPC}}$) of $\mathbf{Al_2O_3}$. The pH_{ZPC} was determined by using 0.1 g of Al_2O_3 into eleven 100 mL Erlenmeyer flask containing 50 mL of 0.1 M sodium chloride solution, which was used as an inert electrolyte. The initial solutions pH was adjusted to 2,3,4,5,6,7,8,9, 10, 11 and 12 by either addition of chloridric acid or sodium hydroxide. The suspension was allowed to equilibrate during 24 h , in an isothermal shaker at 100 rpm and 22°C. Then the final pH value was measured.

Isotherm experiment of $\mathbf{Al_2O_3}$. Adsorption was measured by addition of 0.010,0.025,0.050, 0.075,0.100,0.300,0.400 and 0.500 g of Al_2O_3. The initial phosphorus concentration was 10mg/L in 100 mL of solution. Equation 1 was used to determine the amount of phosphorus adsorbed onto the Al_2O_3, where X is the amount of phosphorus adsorbed per kilogram of Al_2O_3(g/kg), C_0 is the initial concentration (mg/L), C is the equilibrium concentration (mg/L), V is the solvent volume (L) and M is the weight of Al_2O_3(kg).

$$X = (C_0 - C) \times V/M \quad (1)$$

Synthesis of hybrid materials. 300 mg of POE was dissolved into 10 mL of a 50/50(v/v) tetrahydrofuran/ethanol solution, by stirring at room temperature in a 50 mL round-bottomed flask. Then 336 mg of aluminium isopropoxide was added to this solution. The reaction was catalyzed with 150μ L of chloridric acid 50 mM and heated to 50°C under stirring during 30 min . After, the solution was dropped carefully to a Teflon ® mold, and aged during 12 h for solvent evaporation [11].

FTIR/TGA analysis. FTIR spectra were obtained on a Perkin Elmer 1600 Series FTIR using KBr pellets technique with 16 scans in the range of $4000 - 600\ cm^{-1}$. A Shymadzu 50 was used to perform the thermogravimetric analysis (TGA) using 10 mg of sample. The measurements were performed from 30 to 600°C, at 10°C/min, in a nitrogen atmosphere.

Phosphorus uptake by hybrid material. 0.100 g of hybrid polymer were placed in vials tubes with 50 mL of solution, which had 100μ g/L phosphorus concentration. The sealed vials were placed in a shaker at 100 rpm and 22°C. The initial and final pH values of the solutions were measured with an ORION pH meter model 420A. Aliquots of solution were taken regularly for phosphate analyses, which were carried using the Ascorbic Acid method with a Unican He λ los spectrophotometer [12].

Results

Zero point charge (pH_{ZPC}) is an important parameter to understand the surface chemistry of a material in aqueous solution; it is the value where the net surface charge of particles is zero. pH_{ZPC} of Al_2O_3 was determined before measuring its removal capacity. Fig. 1 depicts the pH_{ZPC} of Al_2O_3, which under the used conditions was 8.0. This value is consistent with literature values, which indicated a range from 8.0 to 9.4 [13]. The Al_2O_3 surface exhibits amphoteric properties and acts as a buffer in a pH range from 4 to 9 , where $pH_{equilibrium}$ remains almost close to the pH_{ZPC} for all $pH_{initial}$ values in this range.

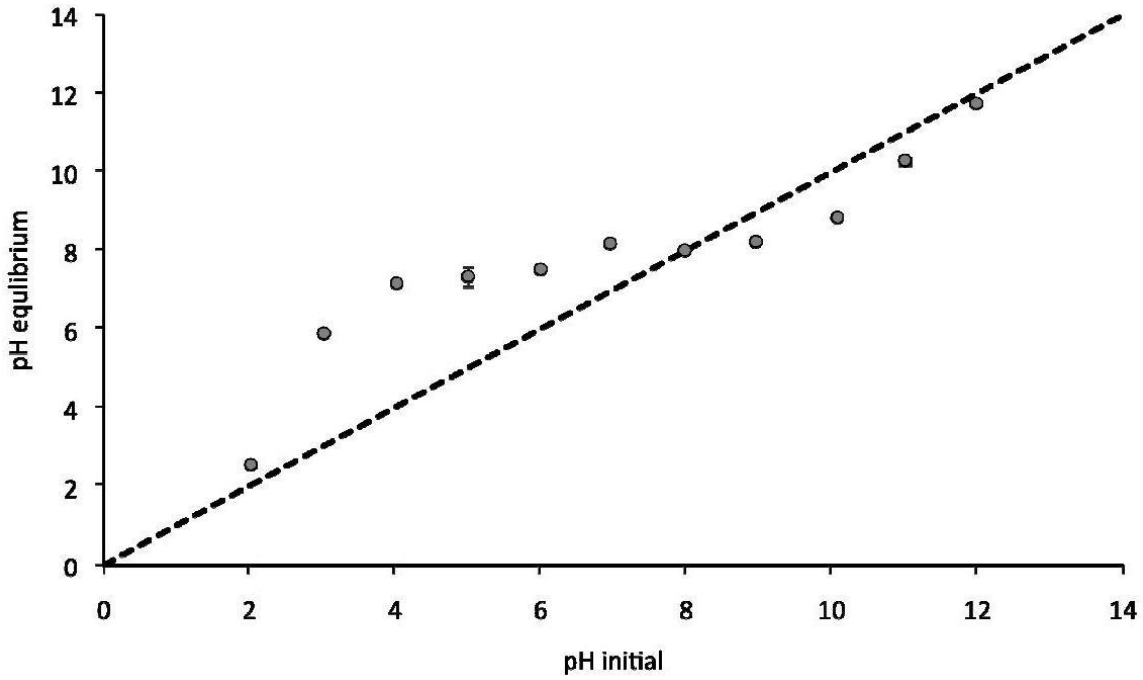

Fig. 1. Plot of $pH_{equilibrium}$ against $pH_{initial}$ for the determination of pH_{ZPC} of Al_2O_3.

Adsorption isotherm of phosphorus onto Al_2O_3 was measured and the results are shown in Fig. 2. The isotherm shows a curvilinear increase of adsorption with the phosphorus concentration. The data were fitted by Freundlich model with a correlation coefficient of 0.93 :

$$S = K[C]^{1/n} \tag{2}$$

($S = 5{,}1[C]^{0{,}462}$) where S is the amount adsorbed (g/Kg), C the equilibrium concentration (mg/L), K and $1/n$ are the adsorption constants. The constant $K = 5.1$ can be considered a hypotetical index of phosphorus adsorbed from a solution having a unit equilibrium phosphorus concentration and can be used to provide a measurement of the relative phosphorus capacity of the used material [14]. These results suggested that the adsorption of phosphorus onto Al_2O_3 followed a multilayer mechanism.

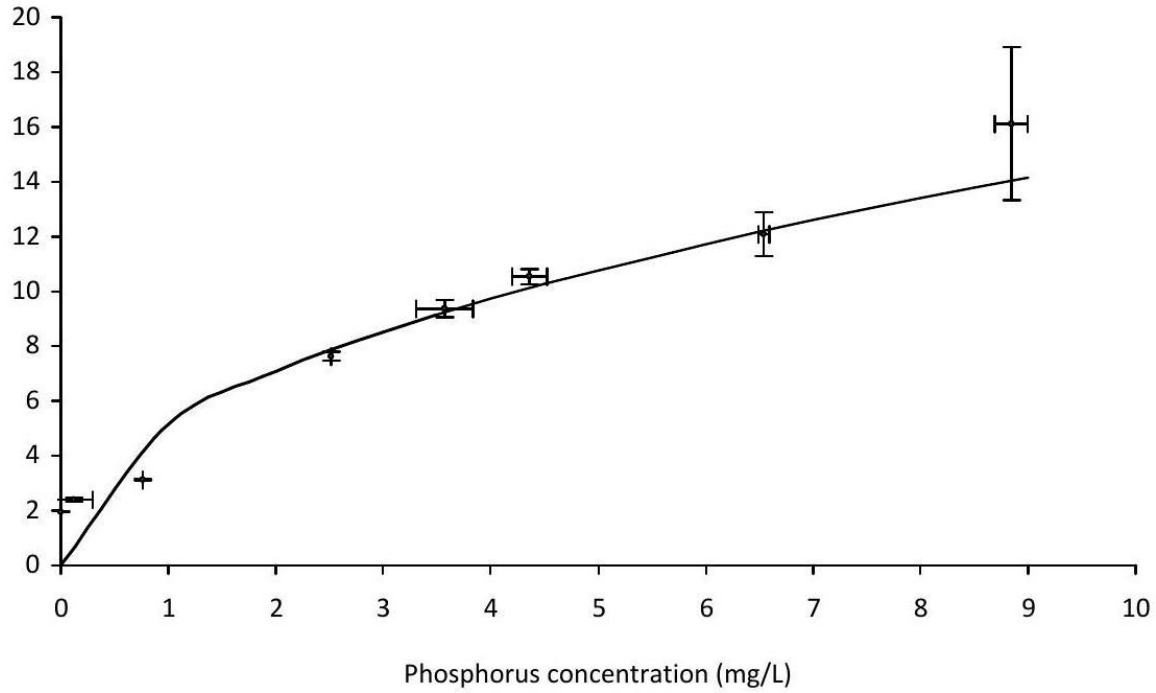

Fig. 2. Phosphorus adsorption isotherm onto Al_2O_3.

Fig. 3 shows the FTIR spectra obtained from the analysis of the hybrid material and Al_2O_3. The broad band between $500 - 1000\ cm^{-1}$ is characteristic of Al_2O_3, the O-Al-O bending mode appears in the range of $650 - 700\ cm^{-1}$ and Al-O stretching mode, a broad band between $750 - 850\ cm^{-1}$. It can be observed that these bands appear in both materials. The POE peaks appear at 2900, 1460 and $850\ cm^{-1}$, being C-H symmetric and asymmetric modes, CH_2 bending mode and CH_2 rocking mode, respectively.

The FTIR spectrum of Al_2O_3 depicts three signals due to adsorption of O-H groups. First the adsorption related to alanol groups (Al-OH), the stretching mode at $3400\ cm^{-1}$, second the bending mode of $\delta O - H$ at $1618\ cm^{-1}$, which indicated that the solid was hydrated, and the last bending mode of the first band at $1066\ cm^{-1}$[15,16,17].

The FTIR results prove that the hybrid material that was developed contains an inorganic part of Al_2O_3, which is the adsorption agent for phosphorus removal.

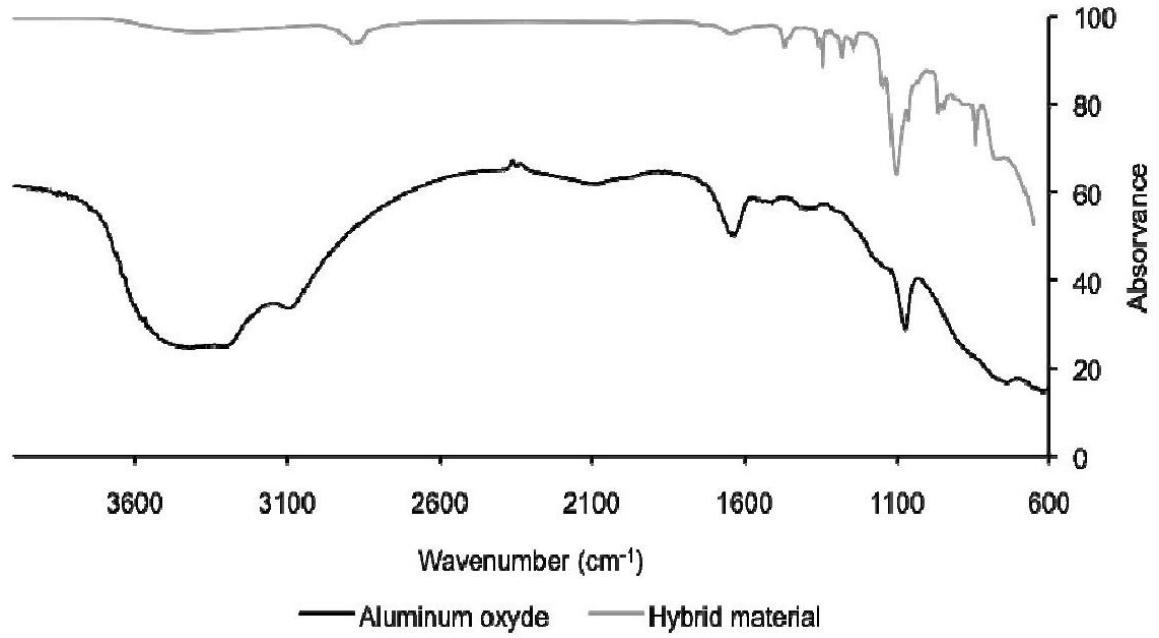

Fig. 3. FTIR spectra of the hybrid material and Al_2O_3.

Fig. 4 depicts TGA results of POE, POE and Al_2O_3 (physical mixed) and hybrid material in nitrogen atmosphere. The hybrid material shows three different zones of weight lost. The initial is due to evaporation of solvents used in the synthesis, second corresponds to POE degradation and the last is attributed to a structural arrangement of Al_2O_3. The POE shows only one zone, where all weight is lost, that corresponds to POE degradation. The physical mixture of POE and Al_2O_3 exhibits two zones, the first is due to POE degradation and the second to structural arrangement of Al_2O_3. In all cases the weight lost increases as the temperature increases. The behaviour of the hybrid material is in agreement with FTIR results, showing that all Al_2O_3 is incorporated in the polymer.

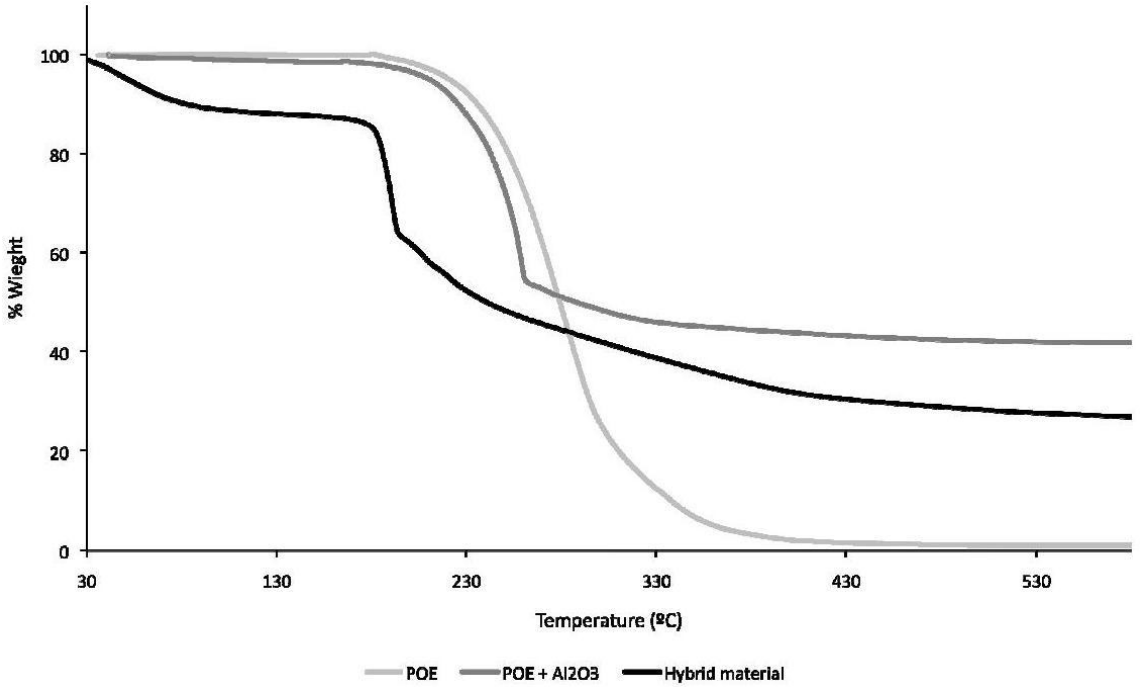

Fig. 4. TGA curves of POE, POE and Al_2O_3 and hybrid material.

Data on the efficiency of the developed hybrid material on phosphorus removal is given in Fig. 5, which shows the kinetic for phosphorus uptake. During the first seven days, phosphorus removal rate was considerably higher, removing about 80% of phosphorus present in solution, being constant after this. The phosphorus concentration at equilibrium was 20μ g/L, a value under the risk of eutrophication. This preliminary result demonstrates the efficiency of the developed material to remove phosphorus.

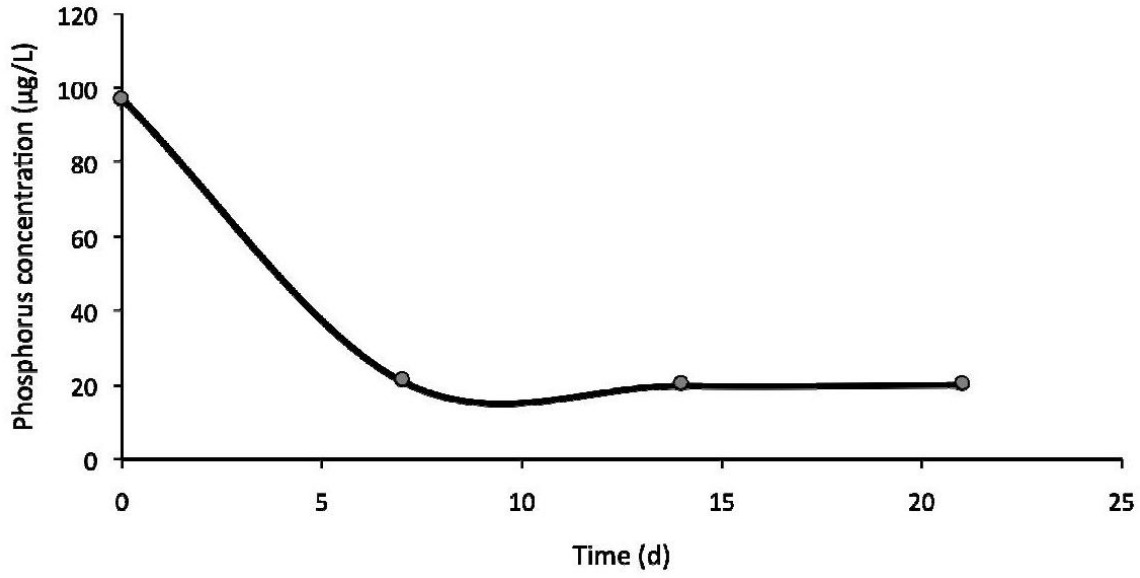

Fig. 5. Phosphorus uptake by hybrid material along the time.

Conclusion

The present study indicates that hybrid POE- Al_2O_3 is an attractive alternative technology for phosphorus removal from water. The FTIR and TGA results show that sol-gel process was successfully used to develop a hybrid material. The material developed was able to remove about 80% of phosphorus present in solution, only in seven days.

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