Phosphorus removal by a fixed-bed hybrid polymer nanocomposite biofilm reactor

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Abstract

Eutrophication is one of the main challenges regarding the ecological quality of surface waters, phosphorus bioavailability being its main driver. In this context, a novel hybrid polymer nanocomposite (HPN-Pr) biofilm reactor aimed at integrated chemical phosphorus adsorption and biological removal was conceived. The assays pointed to removal of 1.2mgP/g of reactive phosphorus and 1.01mgP/g of total phosphorus under steady-state conditions. A mathematical adsorption-biological model was applied to predict reactor performance, which indicated that biological activity has a positive effect on reactor performance, increasing the amount of reactive phosphorus removed.

Keywords: eutrophication; phosphorus adsorption; hybrid nanocomposite

Introduction

The leaching of surplus fertilisers from agriculture and the discharge of phosphorus (P)-rich wastewaters are among the most significant anthropogenic pressures on river basins.[1,2] As a consequence, severe loss of ecosystem biodiversity occurs and water abstraction is at risk when toxins are released following cyanobacteria blooms.[3] The eutrophication of aquatic environments, such as lakes or rivers, has been noted since the 1950s, and the phenomenon is far from being solved, affecting 53% of European lakes and many others around the world.[4] The European Water Framework Directive (WFD-2000/60/EC) aimed to restore water body quality by 2015, but derogations have been claimed when eutrophication is the main pressure. Currently, even when external P sources are eliminated, slow recuperation is observed due to the redissolution of P

accumulated in sediments.[5,6] Furthermore, polyphosphates may also have a crucial role, since they gradually hydrolyse into phosphates. [2,7,8]

The search for and development of technologies for P removal started in 1950s, with the aim of reducing the amount of P arriving at the water surface. Nowadays, chemical precipitation is the main commercial process used to remove P from eutrophic mediums and wastewater. It is based on the direct application of salts like aluminium, iron or calcium, industrial byproducts and

mineral clays to the water. [3,9,10] Nevertheless, direct application of chemicals has recognised drawbacks, such as possible contamination by heavy metals, tight control of the pH to avoid dissolution of the precipitates, chemical overdose to guarantee the desired degree of removal due to parallel reactions and the possibility of increasing turbidity for long periods.[11-15] Moreover, most commercial products have been developed to precipitate P and not to recover it.

P recovery has become an important issue because the main source of P is phosphate rock, a non-renewable source like oil, which is becoming scarce and expensive.[16,17] Consumption of phosphate rock grows by 2.7% per year, increasing from 17.8 t in 2008 to 19.8 t in 2012.[18]

To overcome some of the disadvantages of the commercial materials, a new polymeric material was developed (HPN-Pr). According to previous results, it is stable, does not provoke any chemical contamination or change in pH and can be design to be introduced locally into the water body without dissolution or loss of physical shape.[19] Moreover, after water treatment, it is possible to recover the adsorbed P , thereby contributing to the sustainability of this non-renewable nutrient, and regenerate the material to be used again.

Even though biological P-removal is a well-established process in wastewater treatment plants and in natural mediums, such as lake and rivers, there has been a considerable lack of research.[20] Therefore, the aim of this study was to assess the efficiency of a new bioreactor using HPN-Pr media for both chemical adsorption and the biological removal of P from natural water. The specific goals of the study were: (1) to evaluate the effect on pH and the efficiency for polyphosphate removal, and (2) to test the HPN-Pr bioreactor performance regarding the elimination of soluble reactive phosphorus (SRP) and total phosphorus (TP).

Materials and methods

HPN-Pr synthesis

HPN-Pr is a hybrid nanocomposite containing 1.4% aluminium that results from a reaction between polypropylene grafted with maleic anhydride (PP-g-MA, Polybond 3200 supplied by Crompton) and aluminium isopropoxide $[Al(Pr-i-O)_3$, acquired from Sigma Aldrich] using a solgel process in an extruder at 180°C. The density of the nanocomposite was initially of 0.93 g/dm^3 and was increased to 1.2 g/dm^3 by the addition of antimony trioxide (Sb_2O_3). The HPN-Pr was milled in pellets 3 mm long. A more detailed description of the synthesis process and properties of HPN-Pr can be found in the references.[21,22]

Reactor operation I: pre-feasibility studies without biofilm

Effect of pH on phosphate removal by HPN-Pr

Experiments were done in a column 260 mm long and 30 mm in diameter filled with 50 g of HPN-Pr. The fixed-bed porosity, determined by the gravimetric method, was 0.4. Synthetic water containing 200μ gP/L was prepared with potassium dihydrogenophosphate (KH_2PO_4, Merck), initial pH values of 5,6,7 and 8 , and was passed in upflow mode at a rate of 0.5 mL/min over 15 days. Empty bed hydraulic retention time (the time that the water is inside the column), calculated taking into account the column volume, material porosity and flow rate, was 2.5 h . The experiments were performed in duplicate and stopped when the equilibrium concentration in the liquid phase was reached. The P removal capacity (C/C_0) was expressed as the ratio between the P concentrations at outlet (C) and inlet (C_0).

Table 1. Characterisation of Cávado river water quality.

pH	SRP (μg/L)	Total P (μg/L)	Carbon TC (mg/L)	Carbon TOC (mg/L)	TSS (mg/L)	VSS (mg/L)
6.56 $\pm$ 0.02	266 $\pm$ 1	267 $\pm$ 11	232 $\pm$ 11	214 $\pm$ 16	0.60 $\pm$ 0.03	0.50 $\pm$ 0.04

Polyphosphate removal by HPN-Pr at pH 6

A polyphosphate solution containing 100μ gP/L with an initial pH of 6 was passed upflow through the column at rate of 0.5 mL/min. The experiments were carried out in duplicate and pentasodiumtripolyphosphate ($Na_5P_3O_{10}.6H_2O$, Sigma Aldrich) was used as polyphosphate source.

Reactor operation II: start-up operation with biofilm growth

Water characterisation

The Cávado River provided the feed water used in these experiments. The Cávado watershed is an intense agricultural region in northern Portugal where eutrophication is reported. The average water pH was 6.6 and the TP and SRP concentrations were 267 and 265μ gP/L, respectively. Total carbon (TC), total organic carbon (TOC), total suspended solids (TSS) and volatile suspended solids (VSS) were determined according to Standard Methods.[23] The water sample collected was stored at 4°C for one day before use. Table 1 presents the water quality characterisation.

Column reactor set-up

The experimental bioreactor set-up consisted of two connected acrylic columns as depicted in Figure 1. The first column was 300×50 mm and the second 260×30 mm (length $\times$ diameter). Both columns were filled with 400 g of HPN-Pr. The operation conditions were the same as those used in the experiments described above and the total hydraulic retention time in both columns was 10.4 h . The bioreactors were run until equilibrium state was reached, which took 50 days. Samples were taken daily during the first 30 days of operation and twice a week afterwards until the end of the 50-days experiment. The biofilm formed on the surface of the HPN-Pr was quantified as total solids (TS) and its bacterial diversity was assessed by DGGE patterns of partial 16S rRNA gene amplicons.

Mathematical simulation

Phosphate removal was hypothesised to occur sequentially, first by physio-chemical adsorption on the HPN-Pr support and then by biological metabolism. In order to test this hypothesis, a mathematical model was used based on the saturated soil compartment of AQUASIM.[24] The details needed for this model are presented in Table 2. The adsorption process was described using a Freundlich isotherm (Equation 1), where S is the amount of P adsorbed (g/kg), C is the equilibrium concentration (mg/L), K_f and α are the adsorption constants.

$$S = K_f \times C^\alpha \tag{1}$$

The biological consumption process is described by a Monod-type equation (Equation 2), where R is the specific grow rate of microorganism (h^{-1}), μ_{max} is the maximum specific grow rate (h^{-1}),

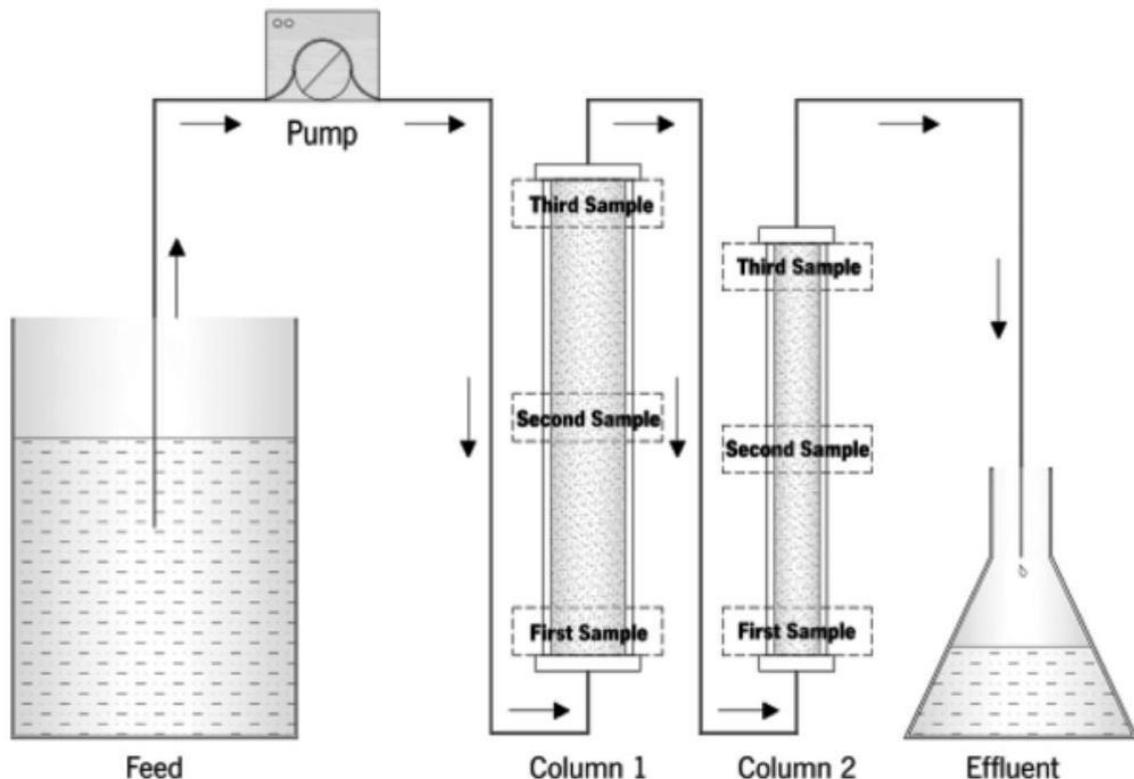Feed　　　　　Column 1　　Column 2　　Effluent

Figure 1. Scheme of the experimental set-up.

Table 2. Inputs parameters introduced into the AQUASIM model.

Variable	Value	Units	Description
Constants variables			
A1	0.00196	m^2	Cross-sectional area of column 1
A2	0.00071	m^2	Cross-sectional area of column 2
C_{in}	265	mg/m^3	Input concentration of P
Half saturation coefficient, K_m	55	$\mu g/L$	
Q_{in}	0,00003	m^3/h	Input flow rate
theta	0.4		Porosity
rho_s	1200	kg/m^3	Material density
L1	0.3	m	Column 1 length
L2	0.26	m	Column 2 length
Dynamic variables (State variables)			
C		mg/m^3	Concentration of P in water
S		mg/kg	Adsorbed P to hybrid polymer
P_bio		mg/g	Absorbed P by microorganism
Grid resolution	152	grid points	

K_m is the Monod constant and C is the limiting substrate concentration (g/L) :

$$R = \frac{\mu_{max} \times C}{K_m + C} \tag{2}$$

The parameters of the Freundlich isotherm, K and n, were calculated as $0.76 mg^{1-n}/L^n/g$ and 1.79 , respectively, with $R^2 = 0.986$. A more detailed description can be found in Oliveira et al.[19] The parameters of the Monod equation were estimated through the model adjustment to experimental data. The kinetic parameters are presented in Table 3.

The cross-sectional area of columns 1 and 2 was 511 and 259 cm^2 and the length was 300 and 260 mm , respectively.

Table 3. Kinetic data of Freundlich and Monod models.

Parameter	Value	Units
Adsorption constant, alpha	0.56 ± 0.02	-
Adsorption constant, K_F	0.76 ± 0.07	-
R^2, Freundlich model	0.986	
Maximum growth rate, μ_{max}	0.12	h^{-1}
Half saturation coefficient, K_m	55	$\mu g/L$

Analytical methods

The concentrations of SRP and TP were measured as phosphate using ascorbic acid method (Method 4500P-E) according to the Standard Methods (1998).[23] Polyphosphate was quantified as total P in samples that had been previously digested (Method 4500P-E).[23] To quantify TS and TP in the biofilm grown on the surface of HPN-Pr particles, ~ 1 g of the material was collected in each sampling port of the columns after 50 days of operation (Figure 1) and was shaken intensely in a vortex for 1 min to release the biofilm from the material. The TS of the biofilm suspension was measured using the gravimetric method according to the Standard Methods.[23] Total P was measured after digestion of the biofilm suspension as previously described.

The P adsorbed on the HPN-Pr was quantified after the biofilm removal step. Thus, the material was washed with 10 mL0.5MH_2SO_4 solution for 1 h as described in Oliveira et al. [19]. Afterwards, the solution was neutralised and P was measured as previously described.

Results and discussion

Reactor operation I: pre-feasibility studies without biofilm

Effect of pH on phosphorus removal by HPN-Pr

The influence of pH on the P removal capacity of $HPN - Pr$ is depicted in Figure 2. The experimental results indicated that the P removal by HPN-Pr decreased slightly when pH increased, reaching $12 \pm 1 \mu gP/g$ at pH5.0,$11 \pm 2 \mu gP/g$ at pH6.0,$9.1 \pm 0.2 \mu gP/g$ at pH 7.0 and $8.30 \pm 0.06 \mu gP/g$ at pH 8.0 . This can be explained by the superficial charge, according to published results HPN-Pr has zero point charge around pH 7.5 .[18] Therefore, at higher pH, $HPN - Pr$ presents a negative surface charge and repulses the phosphates anions $(H_2PO_4^-, HPO_4^{2-}, PO_4^{3-})$.[25] Thus, pH values below the pH_{ZPC} are more favourable to P removal performance, because the HPN-Pr surface is positively charged and attracts phosphates anions.

Polyphosphate removal by HPN-Pr at pH 6

The HPN-Pr performance in eliminating polyphosphate is depicted in Figure 3. The polyphosphate removal capacity was $12.7 \pm 0.6 \mu gP/g$ and is strongly related to the Al^{3+} content of the HPN-Pr (1.4%) and specific mass transfer area. An adsorption capacity of $520 \pm 10 \mu gP/g$ was obtained in a previous study in which the Al^{3+} concentration was 3.3% and the particle size was much lower, at 0.2 mm .[26] Moreover, Razali et al. obtained a very high capacity of 23.5mgP/g using a by-product with $46\%Al_2O_3$ and $51\%Al^{3+}$ concentration.[27]

Reactor operation II: start-up operation with biofilm growth

Phosphorous removal test

Cávado river water was used to determine the bioreactor P -adsorption capacity with real water. The experimental results for TP and SRP are depicted in Figures 4 and 5.

TP removal was 1.04 and 0.98mgP/g in system 1 and 2, respectively. Therefore, the results show that HPN-Pr is unable to remove all P species (Figure 3), because these can come out in organic particles and increase the TP concentration after digestion. However, regarding   SRP   in
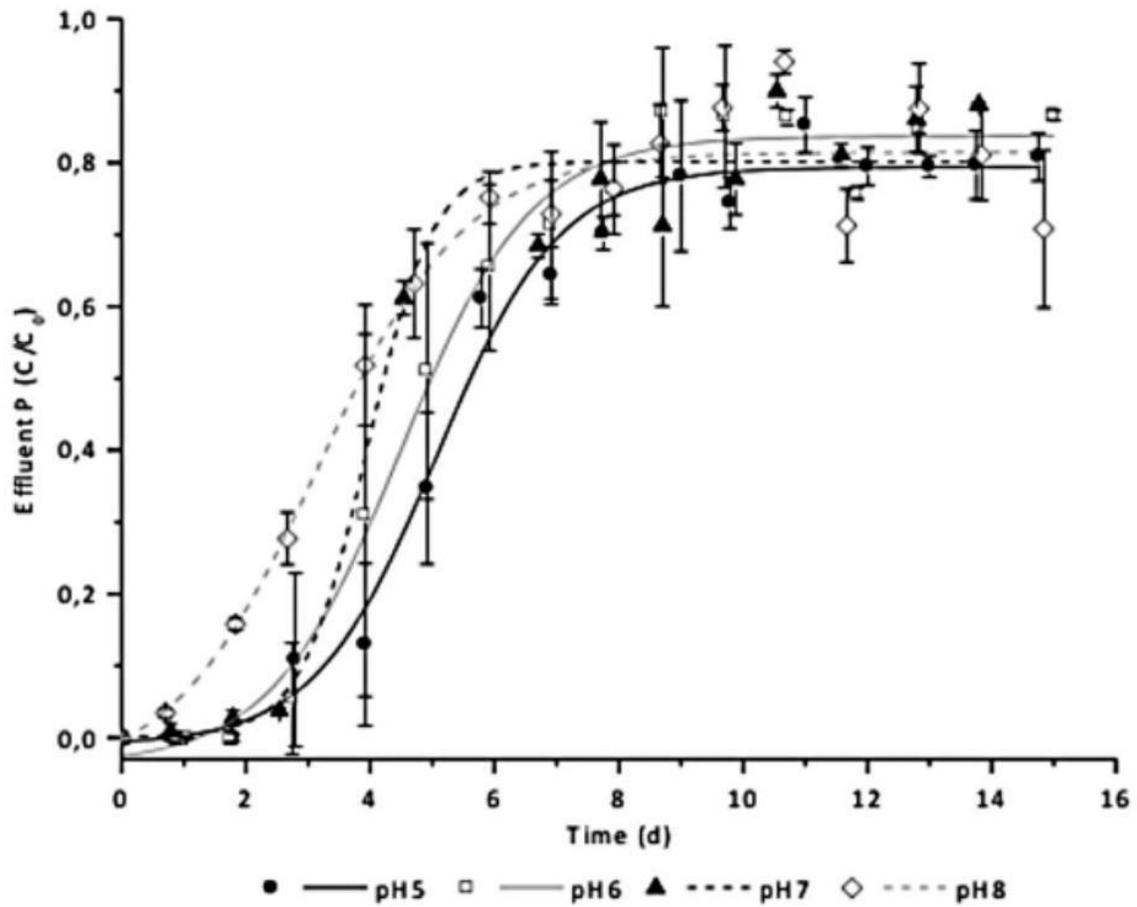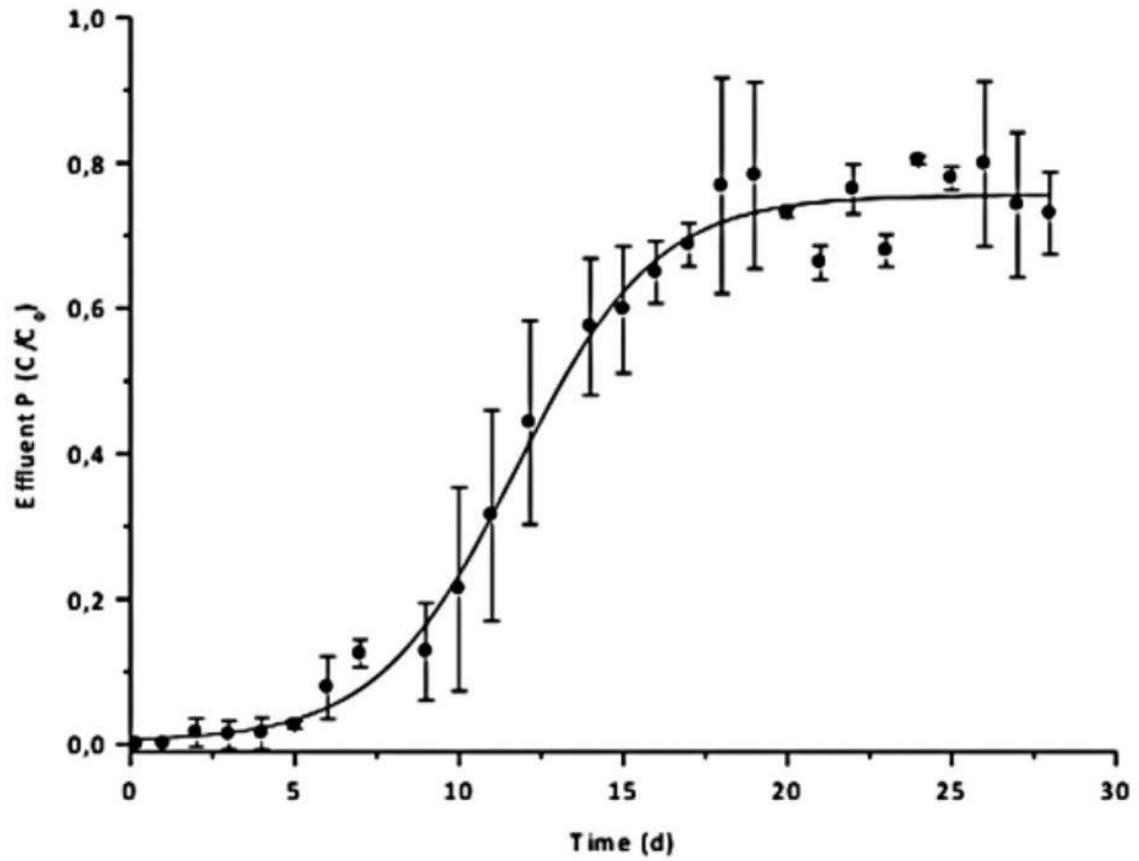
Figure 2. Phosphate removal capacity of $HPN-Pr$ at pH5,6,7 and 8.

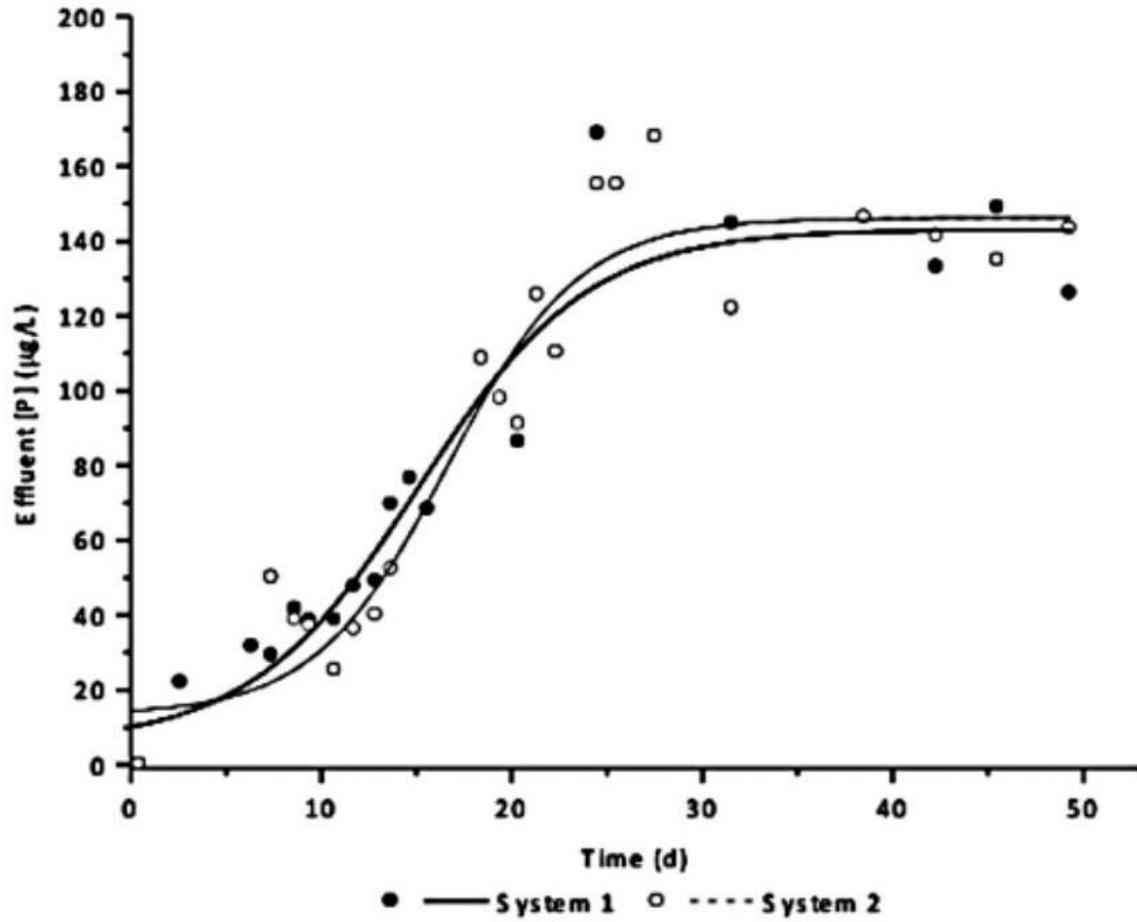Figure 3. Removal kinetic of polyphosphate by HPN-Pr at pH 6 with an initial [P] of 100μ g/L.

Figure 4. Profile concentration of total phosphate at the outlet of both systems over 50 days at an inlet [SRP] of 266μ g/L.
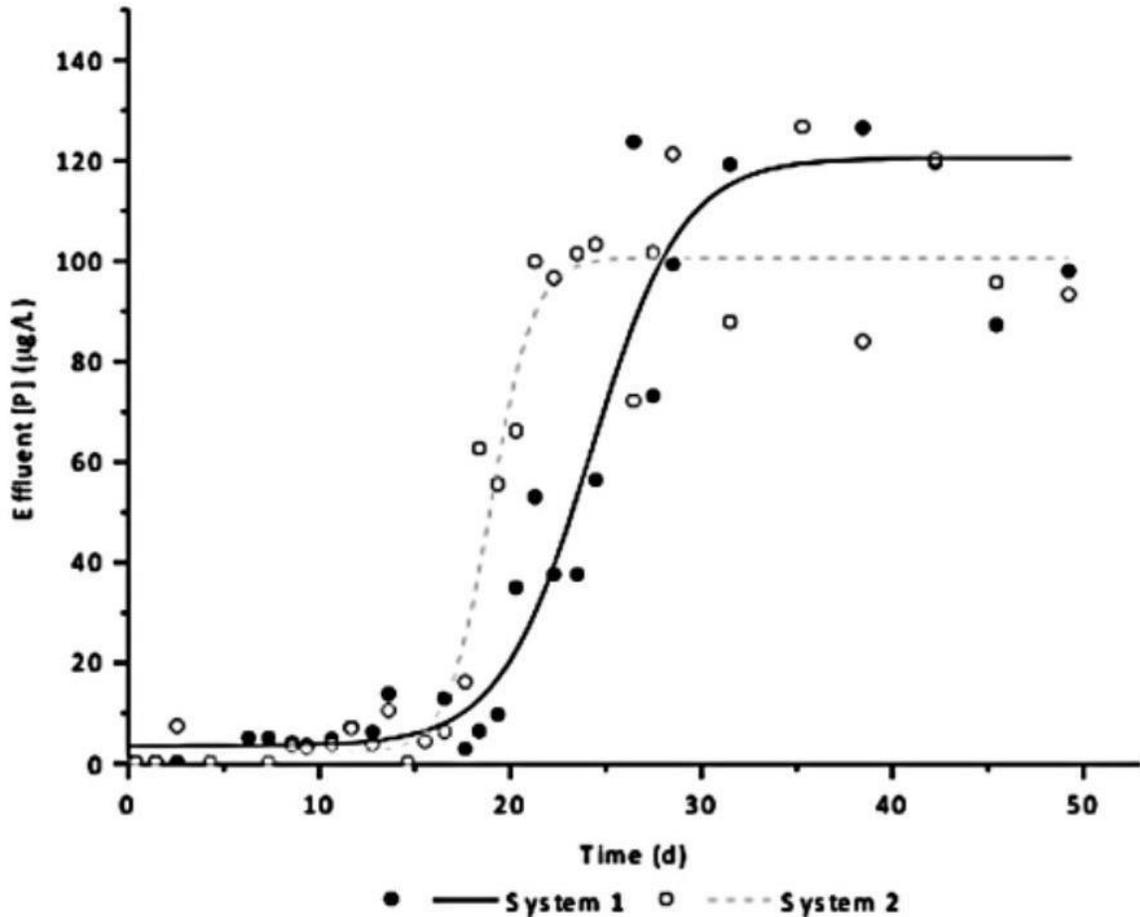
Figure 5. Reactive P concentration of phosphate at the outlet of both systems over 50 days.

Figure 5, HPN-Pr removal reached 100% during the first 12 days of operation. The amount of SRP removed was 1.36 and 1.04mgP/g for systems 1 and 2, respectively. Although the concentration of P at the outlet of both systems stabilised after 50 days of operation, the reactor was not saturated and maintained a removal capacity of 55% for system 1 and 62% for system 2 . This pattern might be explained by multilayer adsorption of P on HPN-Pr, as suggested by the adsorption isotherm and bioconsumption kinetics.[18,28]

Other published studies indicate that P removal depends on the type of adsorbent. Razali et al. removed 50.7mgP/g using aluminium sludge from a water treatment coagulation process.[27] Kabayama et al. removed 11.3mgP/g from a 1 mM disodium hydrogen phosphate aqueous solution passing through the column containing aluminium oxide hydroxide.[29] Drizo et al.
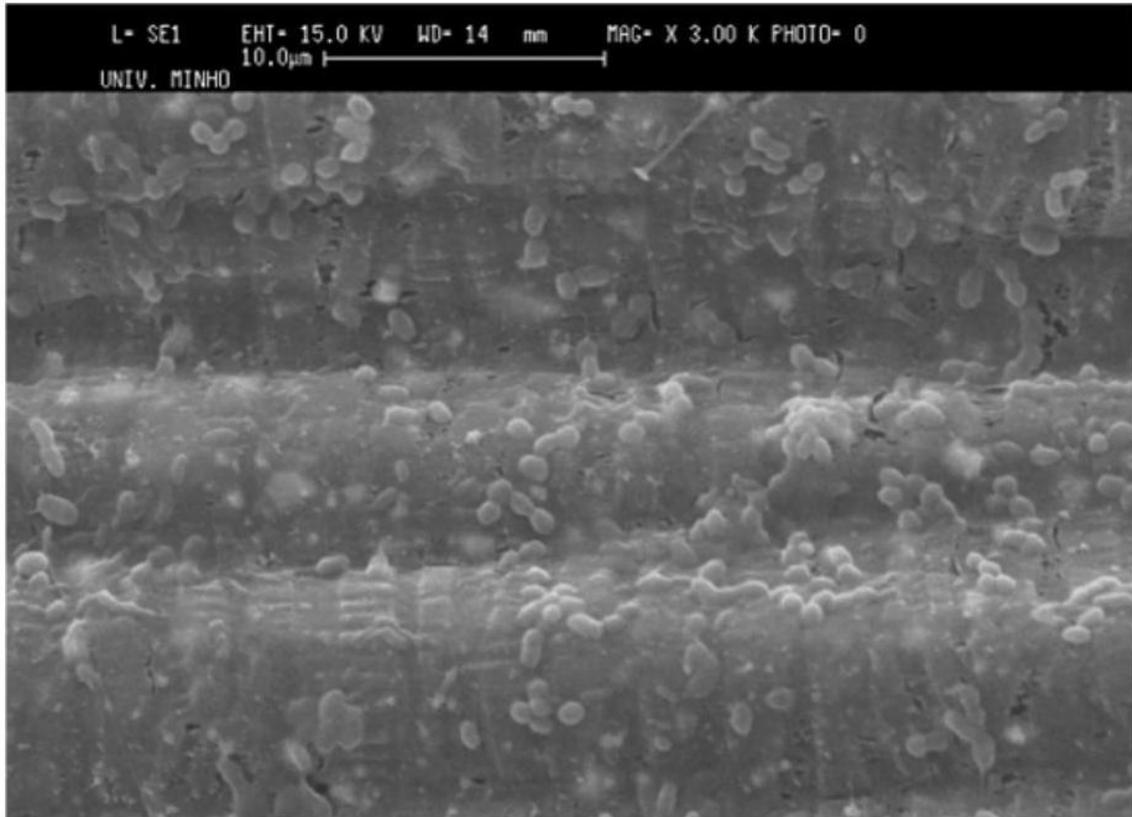
Figure 6. SEM of the HPN-Pr surface with biofilm. assessed P removal by shale and bauxite clays and obtained 0.73 and 0.35mgP/g, respectively. [30] Aluminium wastes from a water treatment plant adsorbed 0.48 and 0.14mgP/g, when used in aquaculture wastewater treatment.[31]

Biofilm assessment

As the bioreactor runs, a biofilm begins to form on HPN-Pr particles due to its rough surface. Figure 6 clearly shows ellipsoid bacteria similar to beans on the HPN-Pr surface. The biofilm becomes visible at the end of the second week when a change in particle colour from white to yellowish was noticed.

The DGGE band-pattern of the biofilm formed on HPN-Pr indicated the presence of several ribotypes, which reveals a high microbial diversity. This is in accordance with other studies that found similar microbial diversity in natural aquatic ecosystems.[32,33] Scanning electrom micrographs from the HPN-Pr surface confirm the presence of a well-established microorganism community (Figure 6).

The biofilm formed after 50 days was quantified as TS at three different columns heights, Figures 7 a and b . The data indicate that the biofilm concentration was proportional to bulk liquid carbon and macro-nutrients. However, the higher concentration of biofilm at the bottom of column 2 was due to the biofilm formed inside the pipe that connected the columns.

Phosphorus removal by adsorption on HPN-Pr particles and biofilm metabolism

The amount of P present in the biofilm and HPN-Pr particles was assessed as indicated in the Methods. To measure a concentration profile, samples were taken at three distinct points for each system (Figure 1). The desorption experiment quantified the P adsorbed by HPN-Pr particle surface and by the biofilm due to biosorption. The results indicated that both the biofilm and the polymeric material contributed to P removal. Moreover, the biofilm formed on HPN-Pr particles enhanced the removal performance. As seen in Figure 8, the highest amount of P was consumed at the bottom of the columns and this decreased along its length. These results are in agreement with the presence of a biofilm concentration profile along the reactor.
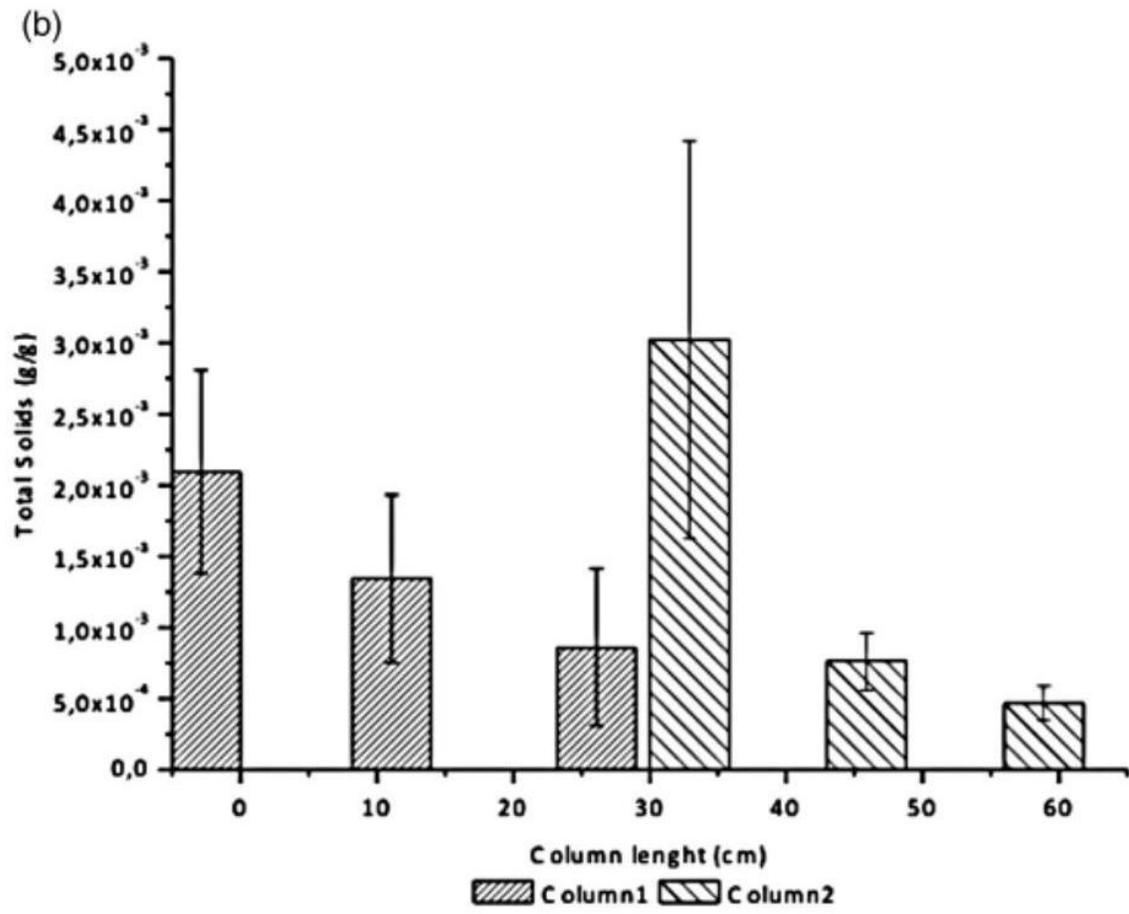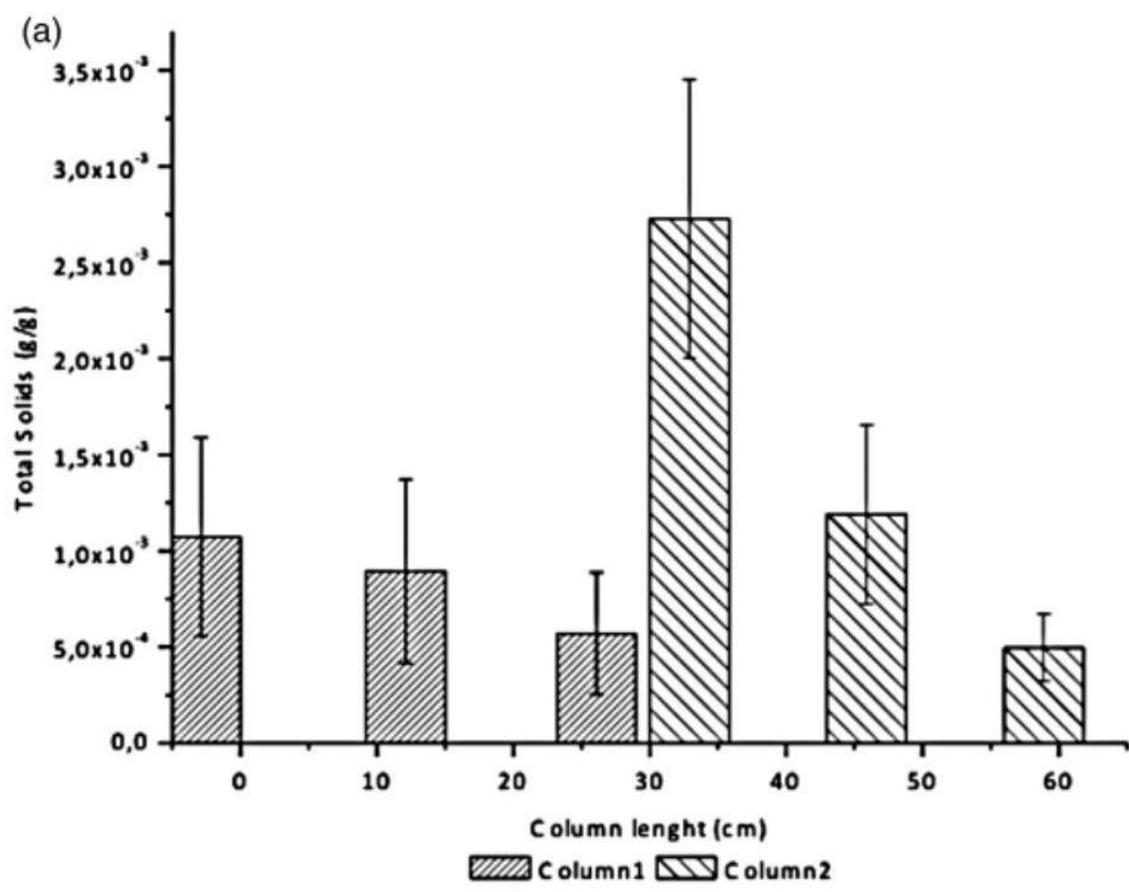
(a)

(b)

Figure 7. Biofilm total solids distribution: (a) system 1; (b) system 2.

Mathematical modelling of P removal

The mathematical modelling was assessed using the Freundlich and Monod equations (3 and 4) and data from Tables 2 and 3:

$$S = 0.76 \times C^{0.56} \tag{3}$$

$$R = \frac{0.12 \times C}{55 + C} \tag{4}$$

P adsorption on HPN-Pr is much faster than biofilm formation. Biofilm growth is limited by P availability until HPN-Pr reaches saturation (Figure 9, $t = 400$ h). After this point, the P concentration in the bulk liquid triggers biofilm growth until it reaches the equilibrium (Figure 9,
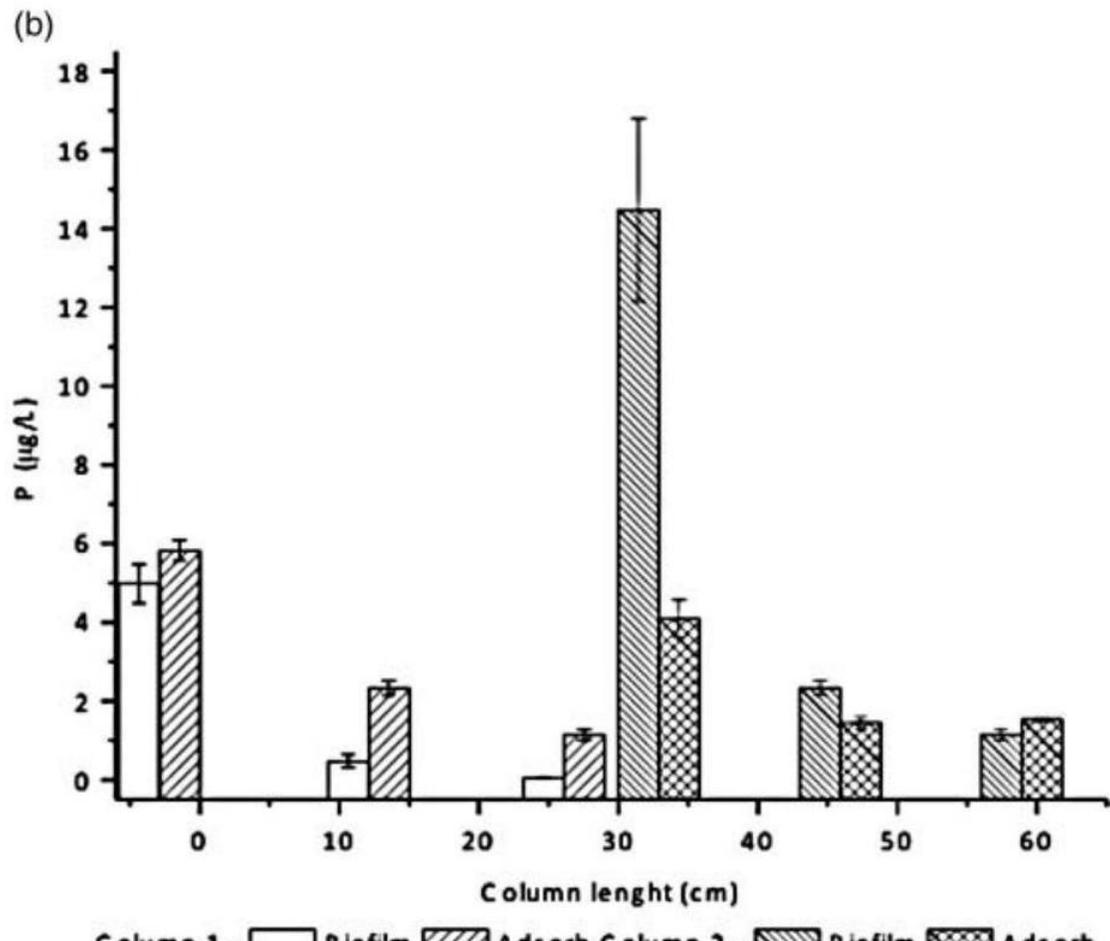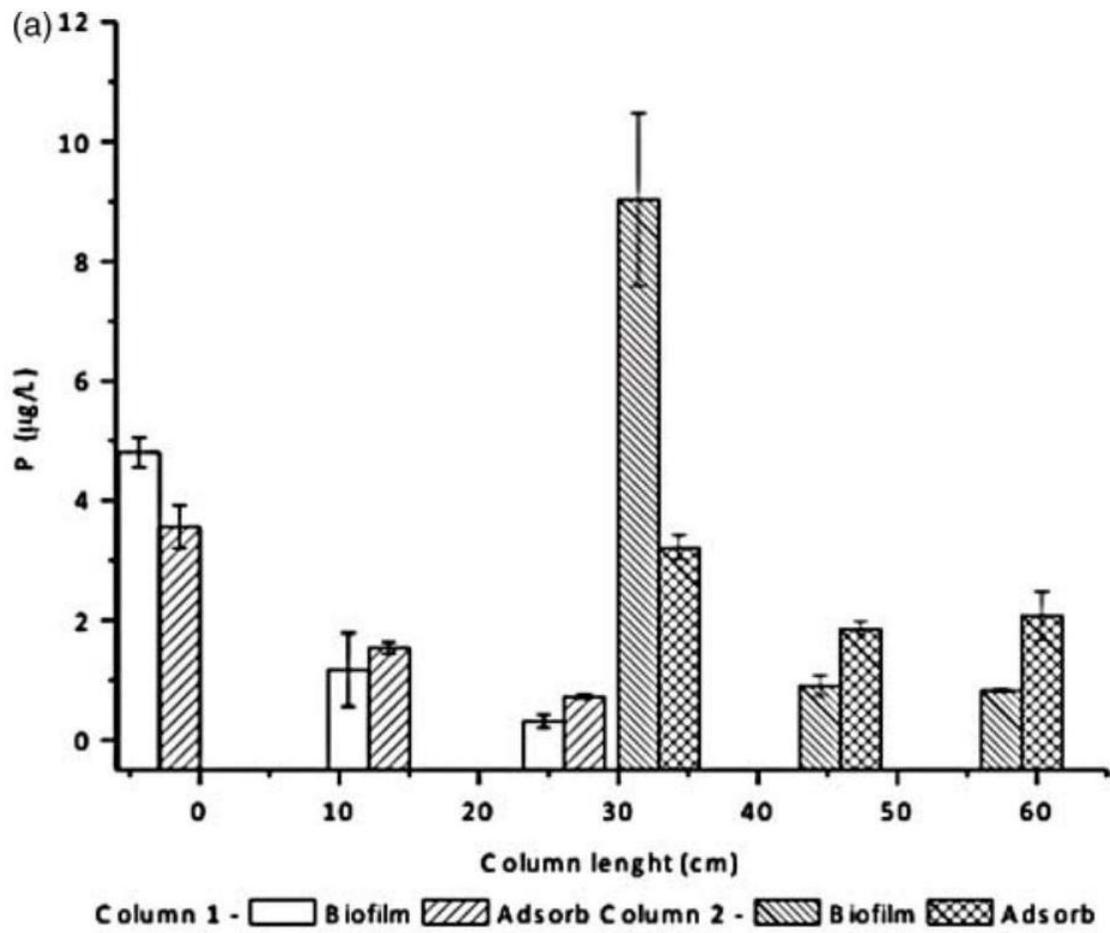
Figure 8. Distribution of the amount of phosphate in the biofilm and adsorbed to the HPN-Pr particles: (a) system 1; (b) system 2 . $t = 1200$ h). To compare the effects of P removal by adsorption and biomass growth, this process was inactivated in the model, allowing P removal to occur only by adsorption. The results are presented in Figure 9 (solid line).

It is possible to detect that, if P removal by biofilm does not occur, the concentration of reactive P will increase and reach saturation earlier (comparing dashed and solid lines in Figure 9). When HPN-Pr is fully saturated, the P concentration at inlet (250μ g/L of P) is the same as at the outlet (Figure 9, $t = 1200$ h), showing that this process could not remove more P. Thus, adsorption process is more important over a short-time perspective (until saturation), whereas biofilm growth
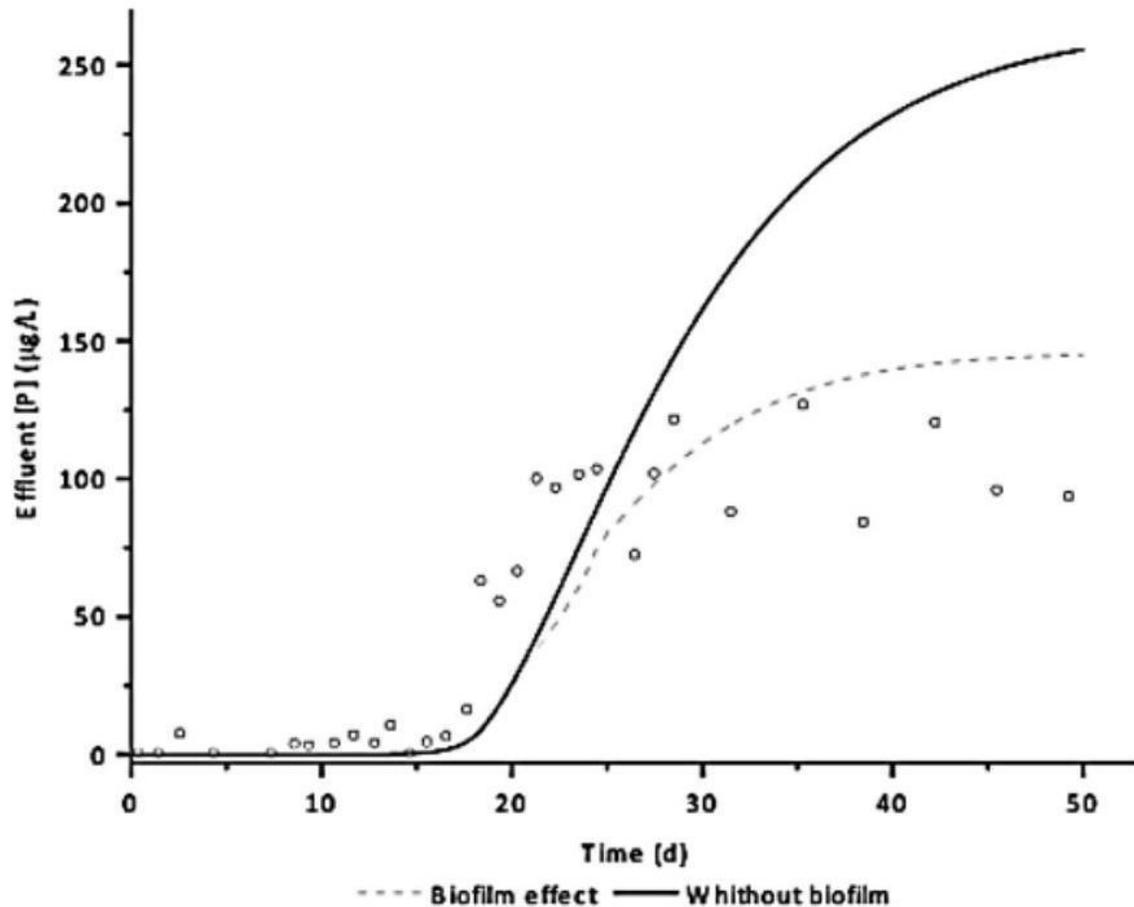

Figure 9. Predicted average values for phosphate removal by HPN-Pr in the presence and absence of biofilm obtained using AQUASIM model. has advantages over the long-term. However, one can anticipate that biofilm growth will reach a limit and biomass will tend to wash-out. In that case, reactive P will continue to be removed, but the organic P concentration may increase at the reactor outlet. Therefore, in order to prevent excessive biomass growth in the reactor, adsorption/regeneration cycles of HPN-Pr could be made for semi-continuous P removal and to recover the P that has been adsorbed. A future P removal application in wastewater treatment may be foreseen based in this hybrid technology.

Conclusions

The hybrid polymer nanocomposite biofilm reactor is a novel and promising integrated technology combining chemical adsorption and biological processes to eliminate P from natural waters. Removal performances of 1.20mgP/g of SRP and 1.01mgP/g of TP were obtained, reaching a saturation of around 50%. Moreover, this material allows P recovery and can be used several times, preserving the same efficiency.

A mathematical adsorption-biosorption model was applied to predict reactor performance. The model indicated that the biological activity has a positive effect on reactor performance, increasing the amount of SRP removed.

Acknowledgements

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