

Phosphorus Removal from Eutrophic Waters with an Aluminium Hybrid Nanocomposite

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Abstract An excess of phosphorus (P) is the most common cause of eutrophication of freshwater bodies. Thus, it is imperative to reduce the concentration of P to prevent harmful algal blooms. Moreover, recovery of P has been gaining importance because its natural source will be exhausted in the near future. Therefore, the present work investigated the removal and recovery of phosphate from water using a newly developed hybrid nanocomposite containing aluminium nanoparticles (HPN). The HPN-Pr removes 0.80 ± 0.01 mg P/g in a pH interval between 2.0 and 6.5. The adsorption mechanism was described by a Freundlich adsorption model. The material presented good selectivity for phosphate and can be regenerated using an HCl dilute solution. The factors that contribute most to the attractiveness of HPN-Pr as a phosphate sorbent are its moderate removal capacity, feasible production at

industrial scale, reuse after regeneration and recovery of phosphate.

Keywords Eutrophication · Phosphorus removal · Hybrid nanocomposites · Aluminium

1 Introduction

Correll (1999), in his review work, reported that the excess of P is the most common cause of eutrophication in freshwater bodies, namely, lakes, reservoirs, streams and headwaters of estuarine systems (Correll 1999). The high input of P to water bodies that has been observed in the last decades results from two main sources: the growth of human population and inherent activities (point source of P) and the excessive use of fertilizers containing P to increase the production of crops (non-point source of P). Nowadays, the classification of the trophic state of freshwater bodies used in most European countries is based on the concentration of P and algal density present in the water column. In fact, a concentration of P of $30 \mu\text{g/L}$ may be enough to provoke the excessive growth of aquatic plants and algal blooms (Carmichael 1991; Selman and Greenhalg 2009; Zheng et al. 2011). Hickey and Gibbs (2009) reported that 51 % of the lakes in Great Britain with <1 ha required the implementation of P reduction measures to achieve the “good ecological status” prescribed by the Water Framework Directive until 2015 (Hickey and Gibbs

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2009). A study at global scale done by The Water Wheel reported that 54 % of the lakes and reservoirs in Asia are impaired by eutrophication, 53 % in Europe, 48 % in North America, 41 % in South America and 28 % in Africa (Nyenje et al. 2010).

Several processes have been used to remove P from eutrophied freshwater bodies. Examples include chemical precipitation with aluminium, iron, calcium and industrial by-products (Genz et al. 2004; Kõiva et al. 2010; Lewandowski et al. 2003; Lan et al. 2006) and adsorption with clays (Yuan and Wu 2007). Industrial by-products present a high removal capacity for P; however, they can contaminate the water with heavy metals. The use of aluminium and iron salts to precipitate P demands tight control of the pH to avoid dissolution of the precipitates; in addition, the parallel reactions that occur consume part of the chemicals, leading to the need of chemical overdose to guarantee the desired removal degree. Clay minerals have a tendency to disperse into very fine particles when applied to water bodies, which may cause an increase in turbidity for prolonged periods of time (Donnert and Salecker 1999; Hano et al. 1997; Miller 2005; Zeng et al. 2004; Zhang et al. 2009).

The present work investigated the removal of phosphate from water using a newly developed hybrid nanocomposite containing aluminium nanoparticles (HPN). The HPN results from a reaction between an organic and an inorganic component, the latter being the removal agent for P. HPNs were obtained by a sol–gel process. The chosen polymer was polypropylene grafted with maleic anhydride (PP-g-MA); two aluminium precursors, aluminium isopropoxide ($\text{Al}(\text{Pr-i-O})_3$) and aluminium acetylacetonate ($\text{Al}(\text{acac})_3$), were used. The experiments done in the present study comprised short-term batch tests to compare the P removal rates of the HPN with other materials and column experiments to assess the long-term attenuation capacity of the HPN under conditions of continuous P loadings.

2 Materials and Methods

2.1 Materials and HPN Synthesis

Two different HPNs were synthesised based on a sol–gel reaction in the melt. This reaction allows direct incorporation of aluminium nanoparticles into a polymeric

matrix. PP-g-MA, provided by Crompton, and two aluminium precursors ($\text{Al}(\text{Pr-i-O})_3$ and $\text{Al}(\text{acac})_3$), supplied by Sigma Aldrich and Acros Organics, respectively, were used. The HPN synthesised with $\text{Al}(\text{Pr-i-O})_3$ was named HPN-Pr, whilst the HPN synthesised with $\text{Al}(\text{acac})_3$ was named HPN-acac. The HPN was produced in the melt, in a batch mixer (Haake Rheomix OS600; volume, 60 mL), equipped with two rotors running in a counter-rotating manner. The rotor speed was 50 rpm and the set temperature was 180 °C. The following procedure was adopted: first, the polymer pellets were introduced into the hot mixer and melted, and then the aluminium precursor was added in a ratio 1:1 (maleic anhydride/precursor) and the mixing proceeded. After 10 min, the material was removed and crushed to a granular size between 100 and 300 μm . More detailed information on the synthesis and properties of HPN-Pr and HPN-acac can be found in Oliveira et al. (2012).

The density and the specific surface of HPN-Pr and HPN-acac were similar for both materials, 1.23 g/cm^3 and 2 m^2/g , respectively.

2.2 Reaction Extension and Chemical Properties of the HPNs

2.2.1 Reaction Extension

The incorporation of aluminium nanoparticles into the HPNs was determined by infrared analysis (Fourier transform infrared, FTIR). Thin films were previously prepared by compression moulding of the HPNs in a hot press at 180 °C. The FTIR spectra of the materials were recorded using a PerkinElmer 1610 in transmission mode between 400 and 4,000 cm^{-1} , with 32 scans and a resolution of 4 cm^{-1} .

2.2.2 Zero Point Charge

The zero point charge is usually defined as the pH value at which a solid submerged in an electrolyte exhibits zero net electrical charge on the surface, as explained by Kosmulski (2002) and Smičiklas et al. (2000). To determine the zero point charge pH (pH_{ZPC}) of the HPN-Pr and HPN-acac, 0.1 g of each material was placed in 50 mL of 0.1 M NaCl solution (used as an inert electrolyte) with initial pH in the range of 2.0–12.0. The pH was adjusted by either the addition of chloridric acid or sodium hydroxide using an ORION pH meter (model

420A). The experiments 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 then measured. Experiments were done in triplicate.

2.3 Phosphate Removal

2.3.1 Effect of pH on Phosphate Removal by HPNs

The effect of pH on phosphate removal by both HPN-Pr and HPN-acac was studied by a batch contacting method as follows: 0.04 g of each material was placed in contact with 50 mL solution containing 1,000 µg/L P with initial pH in the range of 2.0–11.0. The tests were performed in triplicate, at 22 °C, under 100 rpm for 5 days. The concentration of phosphate was measured in the beginning and at the end of the experiments by the ascorbic acid colorimetric method using a Shimadzu spectrophotometer (method 4500P-E, Standard Methods, Eaton et al. 1995). Potassium dihydrogenophosphate (KH₂PO₄, Merck) was used as the phosphate source.

2.3.2 Removal Capacity of Phosphorus by HPNs

The phosphate saturation potential of the HPNs was assessed by a batch contacting method. In this method, 0.04 g of each material was contacted with 50 mL solution containing 1,000 µg/L P with initial pH of 6.0. The tests were done in triplicate, at 100 rpm and 22 °C, for 5 days. The concentration of phosphate was measured daily as previously described.

At the end of the tests, the aluminium concentration present in the solution was determined by the electrothermal atomic absorption spectrometric method using a Shimadzu AA-6880F spectrometer (method 3500Al-B, Standard Methods, 1995). The HPN that released the lowest amount of aluminium was selected for further studies.

The capacity of the HPN-Pr to remove polyphosphate was tested by the batch contacting method. In this method, 0.04 g the HPN-Pr was contacted with 50 mL solution containing 1,000 µg/L of polyphosphate with initial pH of 6.0. The tests were done in triplicate, at 100 rpm and 22 °C, for 5 days. Pentasodiumtripolyphosphate (Na₅P₃O₁₀·6H₂O, Sigma Aldrich) was used as the polyphosphate source. The concentration of phosphate was measured by

the ascorbic acid colorimetric method after a digestion process, as previously described.

2.3.3 Phosphate Adsorption Isotherm on HPN-Pr

The extent of P adsorption from the solution was studied using a batch contacting method. The HPN that released the lowest amount of aluminium, HPN-Pr, was previously crushed to a granular size around 200 µm and weighed in the range of 10–300 mg. The weighed materials were contacted with 50 mL solution containing 10 mg/L P with initial pH of 6.0. Adsorption took place in sealed plastic Erlenmeyer flasks clamped into an orbital shaker at 100 rpm and 22 °C for 5 days. The tests were done in triplicate. At equilibrium, the concentration of phosphate in the solution was measured as previously described. The amount of P adsorbed on the HPN-Pr at equilibrium was calculated according to Eq. 1, where X (in grams per kilogram) is the mass of P (in grams) removed per mass of HPN-Pr (in kilograms), C_{ini} is the initial concentration of P (in grams per litre), C_{eq} is the equilibrium concentration of P (in grams per litre), V is the solution volume (in litres), and M is the mass of HPN-Pr (in kilograms).

$$X = (C_{ini} - C_{eq}) \cdot \frac{V}{M} \quad (1)$$

2.3.4 Column Test

A column test was performed to assess the long-term attenuation capacity of the HPN-Pr under a continuous P flow rate. A column of 90 and 35 mm (height and diameter, respectively) was packed with 17 g of HPN-Pr granules with sizes between 100 and 300 µm; the porosity of the bed was 0.19. A solution with 1,000 µg/L P was continuously pumped through the column at a flow rate of 1 mL/min for 4 weeks. The time required for the solution to cross the column was calculated using Eq. 2.

$$t = \frac{\pi \cdot r^2 \cdot h \cdot \theta}{Q} \quad (2)$$

where t is the residence time (in hours), r is the radius of the column (in centimetres), h is the height of the HPN-Pr in the column (in centimetres), θ is the porosity of the HPN-Pr bed inside the column, and Q is the flow rate (in millilitres per hour).

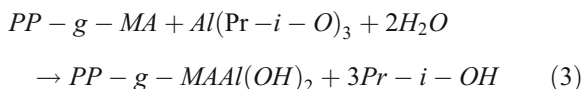
2.4 Regeneration and Recovery Study

The HPN-Pr was cut into small squares of 2×2 mm and saturated with phosphate. For that, 0.2 g of HPN-Pr was contacted with 50 mL solution containing 1,000 µg/L P with initial pH of 6.0. The experiments were done in triplicate, at 100 rpm and 22 °C, for 5 days. The concentration of phosphate was measured at the beginning and at the end of the batch tests. To recover the adsorbed phosphate and regenerate the HPN-Pr, the material was washed with 0.5 M NaOH or 0.5 M HCl for 10 s. The saturation and washing steps were repeated cyclically; in between, the material was washed with deionized water. As a comparison, the same procedure was done without the regeneration step. Finally, X-ray microanalysis mapping was performed on the HPN-Pr surface to evaluate its chemical composition. An energy-dispersive X-ray spectrometer (EDS) from Link eXL II attached to an electronic microscope (Oxford Instruments) was used.

3 Results and Discussion

3.1 Chemical Properties

The synthesis of HPN was based in a sol–gel reaction consisting of the incorporation of aluminium nanoparticles into a polymeric matrix via a hydrolysis condensation reaction, as illustrated in Eq. 3.



where PP-g-MA is the organic compound, Al(Pr-i-O)₃ the aluminium precursor, PP-g-MAAl(OH)₂ the final HPN-Pr, and Pr-i-OH a by-product of the reaction.

The FTIR spectra provided information on the hydrolysis condensation of the aluminium precursor and, thus, the new bonds formed. The spectra obtained for both HPNs are shown in Fig. 1. To evaluate the extension of PP-g-MAAl(OH)₂ formation, it is important to analyse two spectral ranges: 3,500–3,000 cm⁻¹, where the OH stretching mode appears, and 1,000–400 cm⁻¹, where the Al–O stretching mode occurs. In the spectrum of HPN-Pr, a very broad band appeared around 3,450 cm⁻¹ and another between 1,000 and 400 cm⁻¹. Conversely, the OH or Al–O stretching modes were not observed in the spectrum of

HPN-acac. These results suggested that the precursor containing smaller organic groups (Al(Pr-i-O)₃) promoted the formation of aluminium nanoparticles chemically bonded to the polymer backbone. On the contrary, Al(acac)₃ did not react with the polymer, as can be concluded by the presence of two bands at 1,520 and 1,580 cm⁻¹ characteristic of the organic group (acac) connected to the aluminium. HPN-acac consists of a physical mixture of polymer and aluminium precursor.

The pH of zero point charge (pH_{ZPC}) of the HPNs studied in the present work was derived from Fig. 2. In the pH interval from 5.0 to 9.0, the pH at equilibrium was similar to the pH_{ZPC}, suggesting that the surface of both HPNs exhibited amphoteric properties acting as a buffer in this pH interval. No significant differences in charge density were observed between both HPNs, and the pH_{ZPC} values obtained ranged from 7.0 to 8.0.

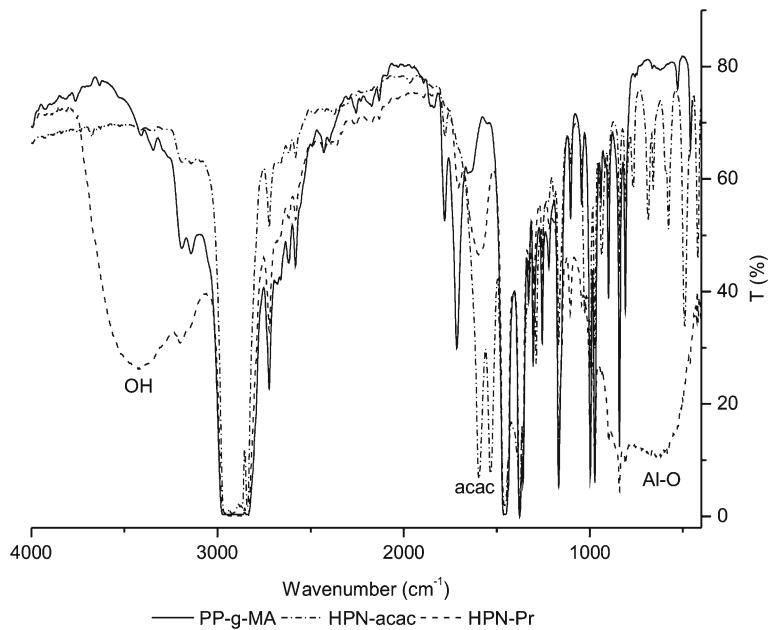
3.2 P Removal

3.2.1 Effect of pH on Phosphate Removal

The effect of pH in the removal capacity of phosphate by both HPNs is shown in Fig. 3. HPN-Pr presented a maximum removal capacity in the pH range from 2.0 to 6.5. For pH values near its pH_{ZPC} (7.0–8.0), a drastic reduction in the phosphate removal capacity was observed, which can be due to the change of the surface charge from positive (+) to negative (-). Also, at high pH values, a decrease in the phosphate removal capacity due to OH⁻ competition was expected. HPN-acac depicted a maximum phosphate removal capacity in a narrower pH range, between 6.0 and 8.5. Moreover, for pH values above the pH_{ZPC}, a reduction in the phosphate removal capacity was detected. A similar behaviour was described for Al(OH)₃ by Galarnau and Gehr (1997). Since HPN-acac consists of a physical mixture of polymer and aluminium precursor, the latter, when immersed in water, rapidly hydrolysed, forming Al(OH)₃. This might explain the different behaviour.

Taking into account that the pH values found in freshwater bodies range from 2.5 to 8.2 (Claret et al. 2003; MacLeod and Whitfield 1996; Markich and Brown 1998; Olías et al. 2004), the HPN-Pr (7.22 % oxide composition) has a broader application to remove phosphate compared to that of HPN-acac (2.84 % oxide composition).

Fig. 1 FTIR spectra of HPN-Pr and HPN-acac recorded between 400 and 4,000 cm^{-1}



3.2.2 Removal of Phosphorus by HPNs

The kinetic curves of phosphorus removal by both HPNs are depicted in Fig. 4. A clear difference can be observed between both materials; the HPN-acac removed all phosphate in <24 h, whilst the HPN-Pr only lowered the phosphate concentration from 1,000 to 400 $\mu\text{g/L P}$ in 5 days. The phosphate removal capacity was $0.80 \pm 0.01 \text{ mg/g}$ for HPN-Pr and $1.27 \pm 0.02 \text{ mg/g}$ for HPN-acac.

Bauxite and shale, both argillaceous rocks, presented a phosphate removal capacity of the same order of magnitude of HPN-Pr, 0.36 and 0.73 mg/g , respectively. Previous studies showed that activated alumina, which is pure Al_2O_3 , presented a phosphate removal capacity of 7 mg/g , which is almost ten times higher than that of HPN-Pr (Drizo et al. 1999; Sakadevan and Bavor 1998). Xiong and Peng (2011), using ferrihydrite-modified diatomite (89.2 % SiO_2 and 4 % Al_2O_3), achieved a total phosphorus removal efficiency of 85 % under anoxic conditions with an initial phosphorus concentration of

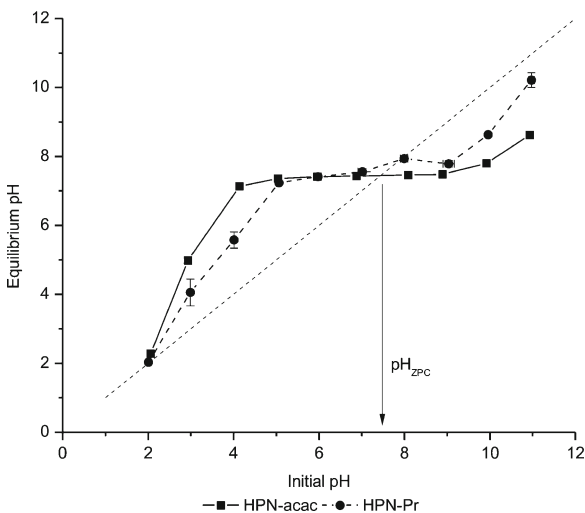


Fig. 2 Determination of point of zero charge for HPN-Pr and HPN-acac at $22 \pm 1 \text{ }^\circ\text{C}$ for 24 h under 100 rpm

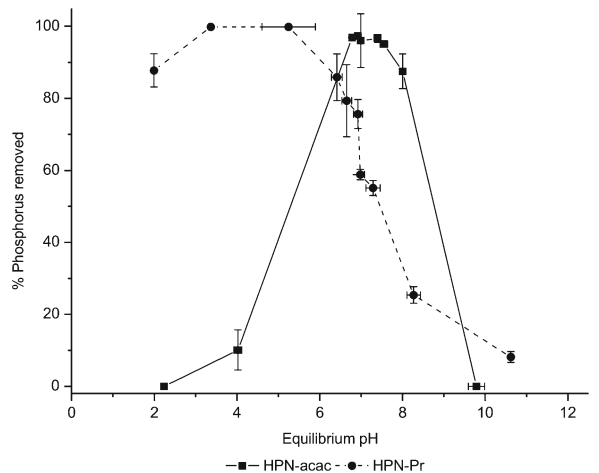


Fig. 3 Influence of pH on HPN phosphate removal capacity at $22 \pm 1 \text{ }^\circ\text{C}$ for 5 days under 100 rpm

113 $\mu\text{g/L}$. However, when comparing the phosphate removal capacity of HPN-Pr with other aluminium-based materials described in literature (Table 1), we need to keep in mind that only a fraction of the HPN is active to remove phosphate (8 %). Clipnotiolite, a zeolite based on SiO_2 (65.9 %) and Al_2O_3 (12.97 %), presented a phosphate removal capacity of 2.15 mg/g, which is higher than that of both HPNs developed in the present study (6.2 % for HPN-Pr and 3.9 % for HPN-acac; Sakadevan and Bavor 1998). This fact might be due to the very high porosity and, consequently, internal surface area of zeolites. Also, a mesoporous silica has been functionalized with Cu and Fe to remove phosphate from water (Chouyyok et al. 2010). The removal capacity of these sorbents is much higher than that of both HPNs, which is due, again, to their huge internal area (169 m^2/g). Although it is very advantageous to use sorbents containing very small pores to maximize the removal capacity, the tiny pores with a size of angstroms might be immediately blocked when used in natural systems, where solid particles that have higher dimensions than the pores are present (for example, bacteria have, on average, 1 μm), resulting in a fast decrease of the removal capacity. The approach followed in the present work was to produce a polymeric sorbent with a rough surface but without internal pores whose surface area can be improved and optimized via a 3D structure. Future studies will be dedicated to improve the design of the HPN-Pr.

To assess the feasibility of both HPNs to remediate eutrophic freshwater bodies without further contamination, the concentration of aluminium was assessed after a batch contacting test. The results revealed that $6.9 \times 10^{-3} \pm 1.9 \times 10^{-3}$ mg/L Al and 5.5 ± 0.4 mg/L Al were obtained with HPN-Pr and HPN-acac, respectively. As shown in the FTIR analysis and the pH test, the Al (acac)₃ precursor did not form covalent bonds with the

Table 1 Comparison of the phosphate removal capacity of HPNs with other materials describes in the literature

	Phosphate removed (mg/g)
HPN-Pr	0.80
HPN-acac	1.27
Bauxite	0.36
Shale	0.73
Alumina	7.00
Clipnotiolite	2.15

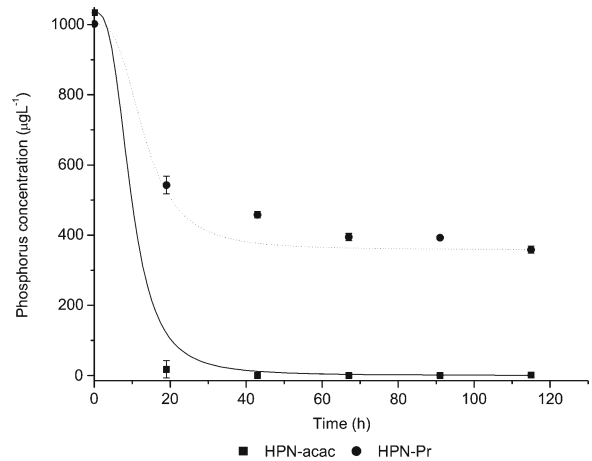


Fig. 4 Phosphorus concentration profiles along time for both HPNs at 22 ± 1 °C for 5 days under 100 rpm and initial pH of 6.0

polymer backbone and can easily hydrolyse into $\text{Al}(\text{OH})_3$, provoking water contamination with aluminium. Therefore, the application of HPN-acac in freshwater bodies to remove phosphate is not recommended due to the water contamination with aluminium. Thus, HPN-Pr seems to be an interesting solution to remediate eutrophic freshwater bodies due to its stability and reasonable capacity to remove phosphate.

Besides phosphate, polyphosphate is also present in water bodies and gradually hydrolyses into phosphate, contributing to the excessive growth of algae (Hongshan and Songqiang 2003; Hupfer et al. 2004). For this reason, the polyphosphate removal capacity of HPN-Pr was assessed from its concentration profile (data not shown). The amount of polyphosphate removed was 0.52 ± 0.01 mg/g P and occurred mainly in the first 71 h. This value was slightly lower compared to that of phosphate. This fact might be related to the size of the anions, orthophosphate (H_2PO_4^- , HPO_4^{2-} and PO_4^{3-}) being smaller and less complex than polyphosphate ($\text{P}_2\text{O}_7^{1-}$); thus, orthophosphate can more easily be adsorbed (Georgantas and Grigoropoulou 2007). Razali et al. (2007) reported a polyphosphate removal capacity of 7.4 mg/g for a by-product generated during the production of drinking water. This was to be expected because this sludge was mainly constituted of aluminium (46 % as Al_2O_3).

3.2.3 P Adsorption Isotherm on HPN-Pr

The adsorption isotherm of phosphate on the HPN-Pr was determined to assess the adsorption mechanism. The

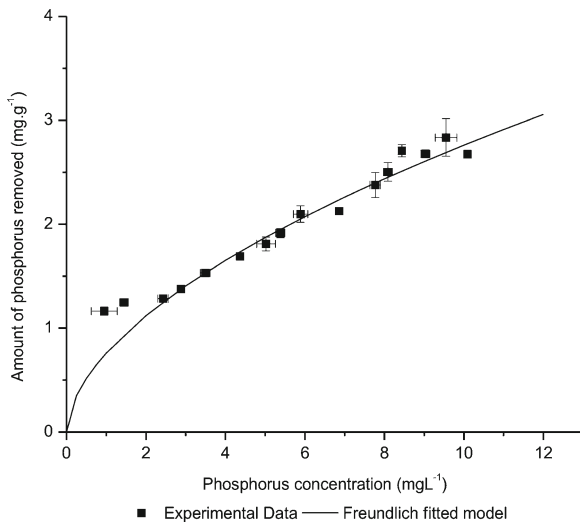


Fig. 5 Adsorption isotherm of phosphate onto HPN-Pr at initial pH of 6.0, 22±1 °C for 5 days under 100 rpm

experimental data were fitted using the Freundlich model (Fig. 5 and Eq. 4) with a correlation coefficient of 0.986.

$$S = 0.76 \cdot [C]^{0.56} \tag{4}$$

where *S* is the amount of P adsorbed (in milligrams per gram) and *C* the equilibrium concentration (in milligrams per litre). The values of the equation constants, *K* and *n*, calculated were 0.76 mg^{1-*n*}·L^{*n*}/g and 1.79, respectively. In general, it is considered that the adsorption capacity of the adsorbent improves with the increase of the *K* value (Kuroda 1987). The *K* value

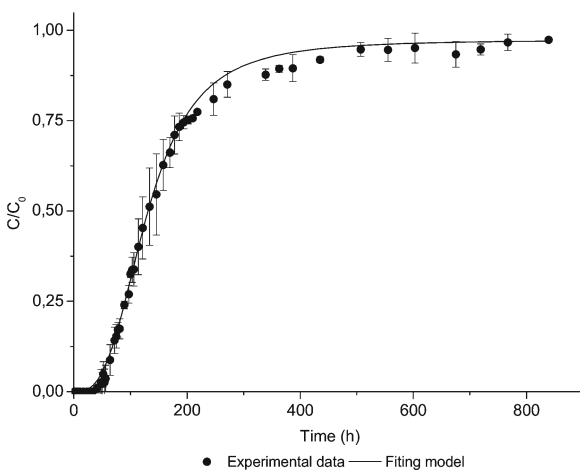


Fig. 6 Relative phosphate concentration (*C/C*₀) at the effluent of a column as a function of time for HPN-Pr at 22±1 °C for 4 weeks at 1 mL/min

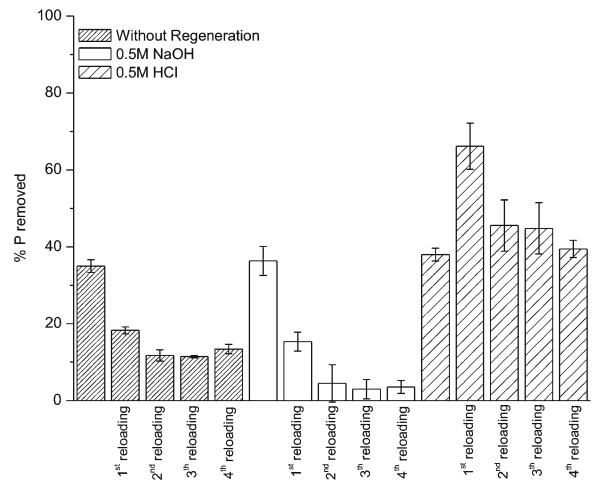


Fig. 7 Phosphate removal capacity of HPN-Pr with and without regeneration

obtained in the present study was higher than that reported by Kuroda for the adsorption of phosphate onto aluminium oxide (0.2). The *n* value obtained was higher than 1, indicating that P adsorption on HPN-Pr was a favourable process (Benyoucef and Amrani 2011).

3.2.4 Column Test

The removal of phosphate in a packed bed column with HPN-Pr along 30 days is depicted in Fig. 6. The residence time (*T*) determined was around 29 min. The removal efficiency of phosphate was 100 % during the first 40 h of operation. It decreased to 50 % at the end of 134 h, and the column reached complete saturation at 500 h. The removal capacity determined in the column test was 0.63 mg/g, which was lower than that obtained in batch assays. This result might be explained by the low porosity of the particles (0.19) and the very small HPN-Pr particles (100–300 μm). Since they are very small, they can be easily compacted; this would decrease the contact between the material and the solution, resulting in a lower removal capacity. Future studies will test materials with

Table 2 Aluminium and oxygen present on the surface of HPN-Pr before and after the acidic and alkaline regeneration steps determined by EDS

HPN	Al (%)	O (%)
Virgin	7.22	27.55
HCl regeneration	7.30	27.46
NaOH regeneration	3.65	23.37

higher granulometry. In a similar study with alum residues, 0.48 mg/g of P was removed from an aquaculture process water at pH 7.0 (Mortula and Gagnon 2009).

3.3 Regeneration Study

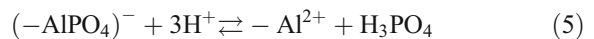
The regeneration of HPN-Pr and recovery of phosphate after the removal step is very important from the economical and environmental points of view. This process should be simple, fast and inexpensive. The removal capacity of HPN-Pr was regenerated by washing either with HCl or NaOH for 10 s. Four successive cycles of saturation and washing were made with the same HPN-Pr. The percentage of P removed in each cycle is depicted in Fig. 7.

Cyclic saturation of the HPN-Pr without intermediary regeneration steps revealed that the material continues to present adsorption capacity. This fact might be due to the existence of a phosphate concentration gradient between the solution and the solid phase. This result is in agreement with the Freundlich adsorption model that best described phosphate adsorption on HPN-Pr. According to the literature, the Freundlich model describes the adsorption process as a multilayer, where phosphate continues to adsorb after reaching the saturation in the presence of a concentration gradient (Genz et al. 2004; Zhang et al. 2011).

The regeneration of the saturated HPN-Pr with HCl was effective, whilst with NaOH was not successful. In the first alkaline washing step, the adsorption capacity of the HPN-Pr decreased significantly; it was maintained constant in the next washing steps, but considerably lower than that of the initial material. Conversely, an increase in the phosphate adsorption capacity was observed in the first acidic washing step. Between the first and the second washing steps, a decrease in the amount of phosphate adsorbed was observed, and then was kept almost constant and similar to the adsorption capacity of the initial HPN-Pr. The increase in the phosphate adsorption capacity observed in the first acidic treatment might be due to the removal of chemical groups connected to aluminium by weak bonds (e.g. OH), which would raise the adsorption capacity of HPN-Pr. The virgin HPN-Pr had an aluminium content around 7.2 %; the alkaline washing step caused a decrease in the amount of aluminium nanoparticles to 3.6 % (Table 2). This might have been caused by the breakdown of weak chemical bonds between aluminium atoms in the surface of the HPN-Pr. Conversely, the acidic washing did not

cause a variation in the percentage of aluminium in the surface of HPN-Pr, where 7.3 % was detected.

The phosphate species present in solution are dependent on pH (Oliveira et al. 2011). Around pH 7.0, H_2PO_4^- is the predominant species in solution (a weak acid with a $\text{p}K_a$ value of 7.2) and becomes a non-charged species in contact with an acidic solution (Awual et al. 2011). This might explain the fact that phosphate was desorbed when HPN-Pr was washed with HCl, the reaction being as follows:



4 Conclusions

The hybrid nanocomposites studied in the present work were revealed as new and effective materials to remove phosphorus from eutrophic natural waters. Whilst HPN-Pr removes 0.80 ± 0.01 mg P/g at the pH interval from 2.0 to 6.5, HPN-acac removes 1.27 ± 0.02 mg P/g at the pH interval of 6.0–8.5. However, determination of the aluminium concentrations in batch tests indicated that HPN-acac transferred higher levels of this ion to the solution, which makes this unviable for natural applications. HPN-Pr was shown to be chemically stable, with adsorption mechanism described by the Freundlich adsorption model. Moreover, HPN-Pr could be regenerated by washing it with 0.5 M HCl. Regeneration allows the recovery of phosphorus adsorbed by HPN-Pr, which can be again introduced on a commercial cycle, contributing this way to the sustainability of this mineral resource which, each time, is scarcer.

HPN-Pr is a material used to treat natural eutrophic waters preferentially by proper application; compared with other common phosphorus removal agents, it does not increase the water turbidity and sludge production or contaminate with toxic compounds.

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