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N. Harouiya, S. Prost Boucle, C. Morlay, D. Esser, S. Martin Ruel, et al.. Performances evaluation of phosphorus removal by apatite in constructed wetlands treating domestic wastewater: Column and pilot experiments. WETPOL, Sep 2009, Barcelona, Spain. 17 p. hal-00619050

HAL Id: hal-00619050

<https://hal.science/hal-00619050>

Submitted on 5 Sep 2011

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Performances evaluation of phosphorus removal by apatite in constructed wetlands treating domestic wastewater: Column and pilot experiments

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Abstract

In constructed wetlands (CWs) treating domestic wastewater, good treatment performances are obtained on mains parameters except phosphorus (P) which can cause eutrophication problems. In order to improve P removal from wastewater with a low specific filter surface per people equivalent (p. e.), different materials have been tested: man-made and natural materials, industrial by-products, and a mixture of these materials. The P removal by natural apatite have been studied by a very few works. Despite apatite materials appears to possess high and long-term retention capacity, a better knowledge is needed to precise the quality of apatite to be used and the P removal evolution with time and water quality. In this work the P retention kinetics have been studied in two different scales (lab-experiments and pilots) on different apatite qualities. Retention rate in pilots is smaller than the one found in lab-experiments and the results suggested that a security coefficient might be applied while designing apatite filter.

Keywords: constructed wetlands; phosphorus removal; apatite; experiments scale; sustainable treatment.

1. Introduction

In constructed wetlands phosphorus can be assimilated by biomass and incorporated by organic matter [1]. But in such systems it's not possible to remove the sludge and P is released back into water after organic matter mineralization [2]. On the other hand phosphorus is used by reeds [3], however the quantity removed by plant assimilation can be neglected when using small surfaces (30 to $150 \text{ kg.m}^{-2}.\text{year}^{-1}$) [4]. To avoid eutrophication problems in surface waters many researches have been done to use specific materials in CWs. In the previous works several materials were tested as iron, aluminium and calcium rich materials [5-16].

The P removal by these materials is based on adsorption and/or precipitation mechanisms onto particle surface. Recently researches have focused on the use of apatite to promote irreversible sorption onto the material surface. Nevertheless, in the few works done on P removal by apatite [17-20], the materials have been only evaluated in lab-scale experiments (batch and/or column) under controlled conditions.

Apatite minerals are known to have a great stability and the particular crystalline structure allows substitutions of different elements [21-24]. This material has been proposed as an effective means for retaining metals and radionuclides [25-29]. For these reasons in this work besides the evaluation of apatite capacity to remove P in CWs, the materials have been characterized for metal content.

In this study five different apatite materials have been tested in column and pilot experiments. In lab-scale columns, the objectives were to precise retention kinetics versus apatite qualities and influence of water ionic composition. In pilots, fed with treated wastewaters in hydraulic controlled conditions, the objectives were to point out the retention rate evolution with time, scale transition effect and exhibit the reed effect on P removal. Other objectives were also sought as:

- Evaluation of the process sustainability and design optimization.
- The capability of column experiments to predict P retention.

2. Material and methods

2.1. Apatites tested

P retention experiments were performed in the present study using five sedimentary apatites from Morocco and Algeria (Table 1). Particle size distribution was determined using dry-sieving techniques [30], to calculate d_{10} , d_{60} (mesh diameter allowing, respectively, 10 or 60% of the material mass to pass through), and the uniformity coefficient ($UC = d_{60}/d_{10}$). Porosity

was determined from the amount of water needed to saturate a known volume of component (replicate number $n=3$) and the bulk density was measured by the volume of water displaced by a known mass of medium ($n=3$). Geometric surface areas in the present study were estimated from the particle size distribution, assuming spherical grains, according to:

$$S = \left(\frac{1}{\varepsilon} \right) \sum_{i=1}^{n-1} \frac{12}{(d_{i+1} + d_i)} \cdot \frac{m_i}{M} \quad (1)$$

Where d_i represents the sphere diameter, ε stands for the sample density, m_i correspond to the mass passing across d_i diameter, and M to the total mass of sample.

Physical, chemical and mineralogical properties of materials used are shown in Tables 1, 2 and 3.

Table 1 Physical characteristics of tested materials

	Particle size			Porosity %	Density $\text{kg}\cdot\text{m}^{-3}$	Geometric surface area $\text{m}^2\cdot\text{kg}^{-1}$
	d_{10} (mm)	d_{60} (mm)	UC (d_{60}/d_{10})			
BT	1.27	4.02	3.15	50	2414	0.73
HT ₁	4.44	9.21	2.09	46	2160	0.17
HT ₂	0.19	9.21	47.54 ⁽¹⁾	53	2243	1.48
AM	0.37	2.79	7.46	58	2392	1.76
AT ₂	2.14	3.85	1.80	54	2447	0.33

⁽¹⁾ HT₂ material contains 30 % of fine particles of clay that can be bonded to larger particles. As a consequence, particle size distribution is modified and real grain distribution is masked. In reality we observe apatite grains of 0.1 – 0.3 μm and coarser grains with impurities.

Table 2 Mineralogical characteristics of materials

	Mineralogical composition % (W/W) of materials					
	Apatite	Calcite	Quartz	Ankerite ⁽²⁾	Dolomite	Clay
BT	41.8	50.4	4.8	n.d. ⁽³⁾	3.0	0.0
HT ₁	60.2	35.1	0.0	n.d. ⁽³⁾	4.7	0.0
HT ₂	46.3	39.5	10.1	n.d. ⁽³⁾	2.5	1.5
AM	95.4	3.2	1.3	n.d. ⁽³⁾	0.0	0.0
AT ₂	58.1	0.0	0.2	41.7	0.0	0.0

⁽²⁾ $\text{CaFe}(\text{CO}_3)_2$ and ⁽³⁾ not determined

Materials tested contain 40 % to 95 % of apatite associated with other impurities. In this paper the term “quality of apatite” will be used to mean % content of apatite mineral. A good quality of material is one with a high percent of apatite mineral.

Table 3 Chemical composition of materials

(a) Major constituents						
% Mass	Ca	P	Si	Mg	Fe	Al
BT	36.3	8.4	3.1	0.5	0.3	0.4
HT ₁	35.3	10.1	3.3	0.2	0.3	0.2
HT ₂	32.3	8.2	6.5	0.5	0.6	1.0
AM	38.2	13.2	1.1	0.2	0.2	0.2

AT₂ 31.9 9.6 2.2 1.7 0.4 0.5

(b) Trace elements									
mg.kg⁻¹	As	Cd	Cr	Cu	Pb	Se	V	Zn	U
BT	11.4	76.8	182.1	6.4	2.3	3.2	115.5	109.9	61.5
HT ₁	11.6	34.5	196.0	18.9	3.3	<LQ ⁽⁴⁾	152.0	196.0	106.0
HT ₂	9.5	31.5	321.0	21.3	3.8	<LQ ⁽⁴⁾	242.0	237.0	78.9
AM	13.3	14.4	257.0	22.9	3.8	1.9	130.0	181.0	131.0
AT ₂	4.0	11.9	210.0	5.1	3.2	21.3	<DL ⁽⁴⁾	82.1	40.1

⁽⁴⁾ limit of quantification

2.2. Column experiments

The apatites materials have been tested in vertical downward flow columns of 9 cm of inner diameter (Fig.1a). All columns consist of 20 cm high layers of apatite, equipped with five sampling ports to study P removal evolution into the media and to have better model fitting. The columns were fed with synthetic solution (table 4) with known P concentration (inlet P concentrations ranged from 1 to 16 mg. l⁻¹) and maintained in hydraulic saturation conditions as in horizontal flow constructed wetlands (HFCW). The inlet pH of all synthetic solutions was 7.6±0.2. The columns samples are taken regularly and analyzed for calcium, phosphorus, alkalinity, and pH to observe the temporal evolution of effluent composition. Experiments have lasted 3 months for each material.

Table 4 Inlet water characteristics and hydraulic loads tested in column experiments

	Water	Flow rate/ cross section m.d⁻¹
BT	Tap water and wastewater	0.80-1.60
HT ₁	Tap water	0.85
HT ₂	Tap water and wastewater	0.80-1.60
AM	Tap water	0.80-1.15
AT ₂	Tap water	0.80-1.15

2.3. Pilots

2.3.1 Pilot-scale description

BT and HT₂ materials have been tested in three similar pilot-scale (HFCW) at Bagnols plant (Rhône, France). The pilots consist of 1.5m² tanks and 40 cm in depth filled up with apatite. The pilot units were fed with treated wastewater (except for P, table 5) from the outlet of Bagnols plant (trickling filter) (Fig.1b). One apatite pilot (HT+r) is planted with *Phragmites australis* to study the reeds effect on P retention.

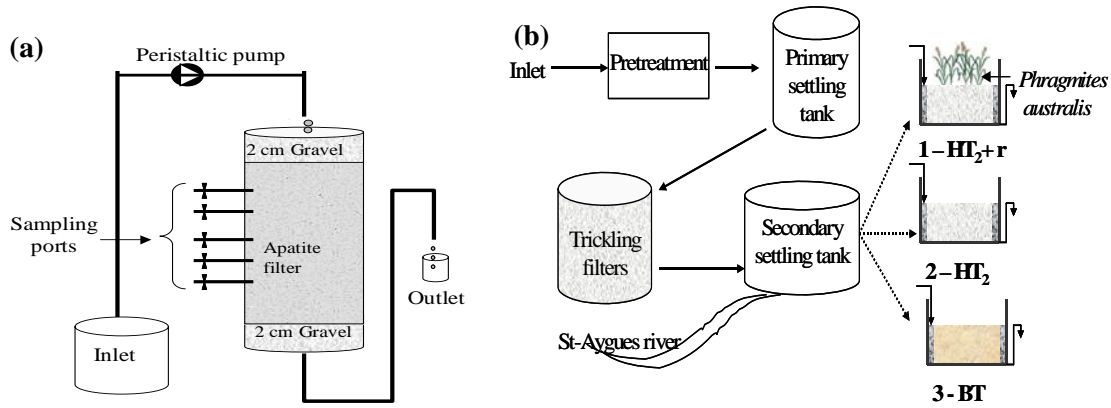


Fig. 1. Schematic representation of: (a) column experiments and (b) pilots at Bagnols

2.3.2 Pilots monitoring

The monitoring of pilots ran from April 2008 to September 2009 with continuous recording of inlet and outlet flow, pH, redox potential and meteorological conditions. Weekly samples of influent and effluent were taken and analyzed for COD, BOD, SS, Ca, Nitrogen and Phosphorus forms. Moreover PO₄-P analyses for inlet and outlet are performed continuously with a TresCon WTW online analyser. The P removal evolution into the apatite filter was performed by regular internal samples into the material. The hydraulic residence time, preferential-flow paths and dead zones in the pilots have been determined by uranine tracer experiments using a GGUN-FL30 Fluorometer. Tracer experiments were performed during 1 week approximately.

3. Results and discussion

3.1. P removal in column experiments

As example, the evolution of P removal by AM apatite is shown in the figure 2. The P concentration is presented as a function of time at the inlet and the outlet of the column (residence time = 3.3 hours in that case). A slight change of pH is observed ($\text{pH}_{\text{inlet}} = 7.6 \pm 0.2$ and $\text{pH}_{\text{outlet}} = 7.4 \pm 0.3$).

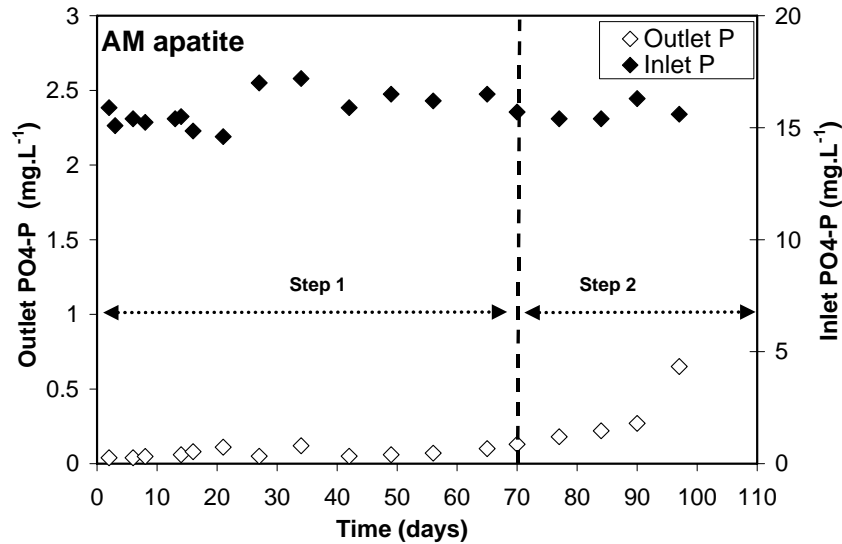


Fig. 2. Evolution of P concentrations as a function of the time during the AM column experiment

Two steps can be noted:

Step 1: For 70 days 99% of phosphorus was removed and the P outlet concentration did not exceed 0.1 mg. l⁻¹. The adsorption seems to be the predominant mechanism as proved by other previous studies [31].

Step 2: The outlet P concentration increased to reach lower but stable P retention kinetic. With AM, this period starts after a storage level of about 5 g of P. kg⁻¹ of apatite as found by Molle et al. [18]. The precipitation becomes the predominant phenomenon of P retention in this step. This points out how experiment duration is important to predict long term removal with such material.

3.2. *k-C** model and removal rates evolution

Using the internal sampling system, the P concentration in the apatite was modeled using *k-C** model [2]. The model has been chosen because it's a simple way to model pollutant removal in HFCW. The P concentration (*C*) at time *t* can be obtained by the following expression:

$$C = (C_0 - C^*) \exp(-kt) + C^* \quad (2)$$

Where *C*₀ is the inlet concentration of P, *k* the volumetric retention rate and *C** the residual P concentration.

The figure 3.a presents the P concentration evolution as a function of residence time in the AM apatite material. The majority of P was retained in the first part of the apatite and the retention rate *k* is about 4.2±0.2 h⁻¹ in the beginning of the experiment (Fig.3b). Retention rate for AM apatite decrease with time and with storage level of phosphorus in apatite material as presented by the figure 4.b.

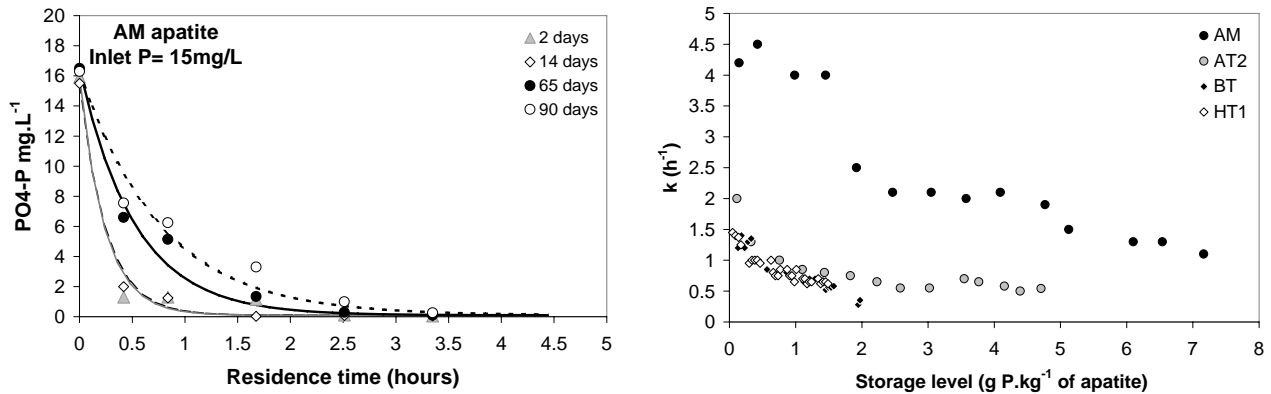


Fig. 3. (a) Variation of the phosphorus concentration with the reaction time for AM apatite. The symbols designate the P experimental data, the curves drawn through this data represent the P concentrations calculated from k-C* model and (b) Evolution of retention rates for all apatite materials studied as a function of P storage level per kilograms of apatite

The comparison of retention rate evolution for all materials tested in this study as given by the figure 4.b show that the retention rate k decreases systematically as adsorption mechanism reduces until it reaches a steady state once precipitation becomes the major mechanism involved in P removal. The stabilised k is about $0.9 \pm 0.1 \text{ h}^{-1}$ and $0.3 \pm 0.1 \text{ h}^{-1}$ for AM and BT materials respectively. Indeed, the retention rates are different between materials used and the differences observed could be related to material quality. This difference in k value is of great importance in determination of the surface needed for P removal.

3.3. Surface observations

The AM apatite surface before and after column experiments was observed using an Environmental Scanning Electron Microscopy (ESEM) equipped with a microanalysis instrument EDS (Energy Dispersive X-ray System).

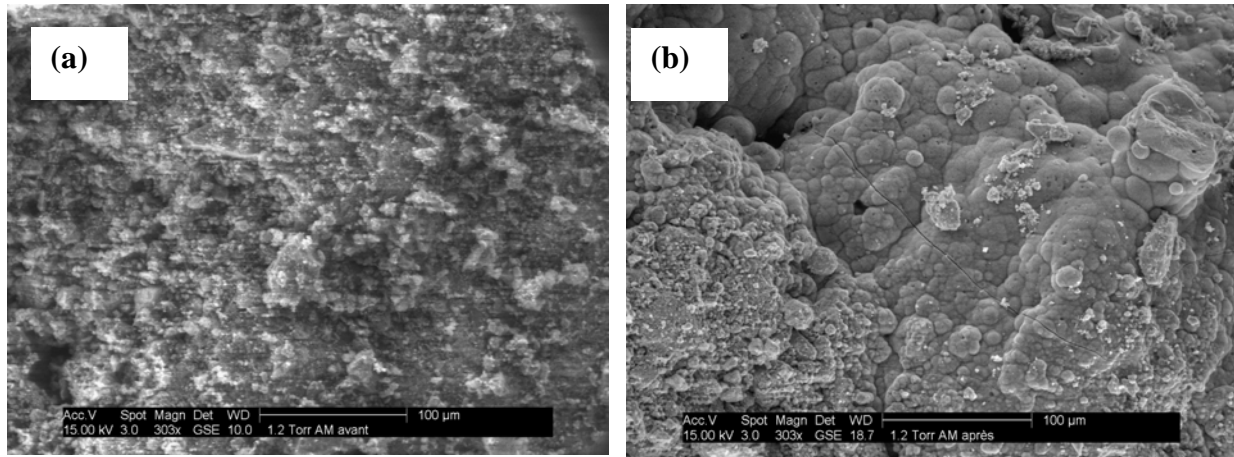


Fig. 4. Surface observation: (a) ESEM of AM apatite before experiment and (b) after experiment

Comparison of the photomicrographs illustrated in Figs. 4a and 4b shows a formation of precipitate at the apatite surface. Precipitate formed are rich in Ca and P with Ca/P molar ratio of 1.35 ± 0.06 . A presence of Zn in the precipitate was also observed and confirmed by water analyze performed in column experiments (about 99% of Zn was retained by AM apatite). If the Zn content is included as substitution of Calcium in the precipitate formed, the molar ratio ((Ca + Zn)/P) increase to 1.51 ± 0.04 . This composition obtained suggests a formation of tri-calcium phosphate (TCP) and the precipitate could be considered as a precursor for hydroxyapatite (HAP) phase. The formation of TCP as precursor of HAP precipitate could have an effect on the evolution of P removal rates as observed in 3.2.

3.4. Hydraulic and treatment performances in pilots

The pilots were fed since April 2008 with residence time measured of about 2 days in the whole pilots. The mean hydraulic and organic loads received by Bagnols pilots and inlet wastewater characteristics are given in the table 5. Removal performances are similar in all pilots and achieve about 70% and 98% for COD and SS respectively.

Table 5 Mean hydraulic and organic loads applied on the pilots and inlet wastewater characteristics. Values for parameters are means/ (SD: standard deviation) of 34 samples

HL (m/d)		COD	SS	KN	TN	TP
	Inlet wastewater (mg. l^{-1})	67.8/(31.2)	19.7/(16.1)	6.2/(4.3)	21.8/(8.0)	4.2/(1.7)
0.18/(0.08)	HT+ r ($\text{g. m}^{-2}. \text{d}^{-1}$)/(SD)	11.6/(5.7)	3.1/(1.9)	1.0/(0.9)	3.6/(2.8)	0.7/(0.4)
0.18/(0.07)	HT ($\text{g. m}^{-2}. \text{d}^{-1}$)/(SD)	11.8/(5.3)	3.0/(2.2)	1.1/(0.8)	4.0/(2.3)	0.7/(0.4)
0.13/(0.05)	BT ($\text{g. m}^{-2}. \text{d}^{-1}$)/(SD)	8.3/(3.8)	2.2/(1.3)	0.7/(0.5)	2.5/(1.6)	0.5/(0.3)

Conversely total nitrogen removal in the pilots is low (<40%) and this result could be related to the longer time needed for nitrifying bacteria to develop in the beginning of experiments and insufficient amounts of organic carbon available for denitrifying bacteria. The total phosphorus removal is approximately 80% for HT₂ material and 98% for BT material. No

effect of reeds on phosphorus removal was observed in pilot experiments because the quantity removed by reeds is very negligible compared to P loads applied on the HT+r pilot (30 to 150 kg. ha⁻¹. year⁻¹ [4]).

3.5. Scale transition effect

BT and HT₂ materials have been tested in pilot system in order to evaluate the scale factor effect and the biomass development on P retention rate. As presented in table 6, the retention rates obtained in lab-experiments are different from those measured in pilots mostly for HT₂ material.

Table 6 Comparison of retention rates between column experiments and pilots

Materials	k (h⁻¹) in column-scale	k (h⁻¹) in pilot-scale
BT	0.3	0.3
HT ₂	0.6	0.3

The differences might be caused by the hydraulic conditions. In pilots, hydrodynamic is less controlled than in lab experiment. In another and longer study on BT apatite carried out in real scale HFCW at Evieu plant [31], k value decreases to 0.07±0.02 h⁻¹ after two years of experiments. Stabilised k value for all materials might be smaller than the one stated in table 6 and in figure 3.b. Therefore designers have to be aware of it and apply security coefficient while designing apatite filter. In real conditions the stabilised k values could be estimated two to three times less than values in lab-scale experiments.

3.6. Design recommendations

To evaluate the process sustainability and optimize the design of apatite filter. In the figure 5 is given the surfaces needed per p.e. to respect 2 or 1 mg P.l⁻¹ for the two extreme apatites studied in this work (AM and BT). In this figure the surfaces are calculated for an inlet P concentration of 10 mgP.l⁻¹ and a retention rates of 0.9±0.1 h⁻¹ and 0.3±0.1 h⁻¹ for AM and BT materials respectively.

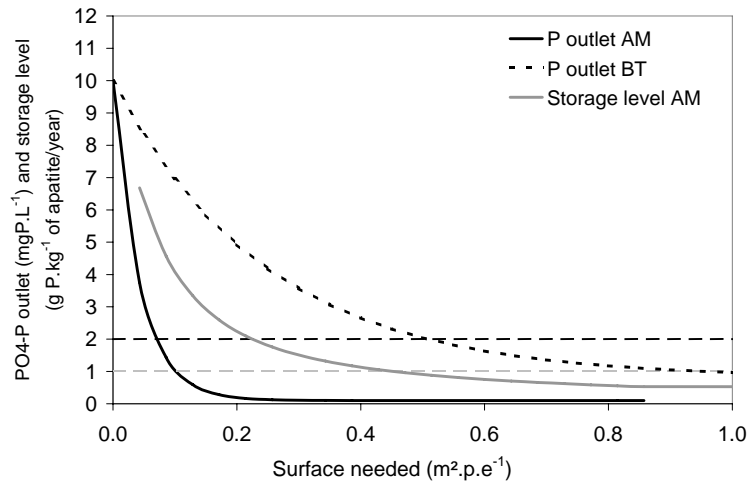


Fig. 5. Effect of apatite quality on surface needed for P treatment and on final saturation of the apatite filter

Using AM material a surface of 0.2 m²/p.e is sufficient to achieve 1 mgP.l⁻¹ in the effluent. However, due to hydraulic short-cutting it is not secure to use smaller surfaces and the best window in term of application is to use about 0.5 m².p.e⁻¹. It means that apatite materials like BT with poor quality are not suitable. The use of 0.5 m².p.e⁻¹ have also an important role to delay final saturation of the filter. The actual storage level reached for AM material in lab-experiments is about 7 g of P. kg⁻¹ of apatite. As presented by grey curve, if the filter accumulates 1g of P. kg⁻¹ of apatite per year using a surface of 0.5 m².p.e⁻¹, this level would be reached after 7 years and the filter could work at least 7 years with high P retention kinetics. The use of smaller filter surfaces would lead to earlier final saturation.

4. Conclusions

Main conclusion, except confirmation of the good P removal potential of apatite in constructed wetlands, is the importance of apatite quality on long-term P removal. A better insight of processes in term of adsorption/precipitation, precipitate formed, impact of reeds and experiments scale allow to consolidate the design of apatite filters and its sustainability.

This work provides data in lab-scale experiments and in pilots for P removal by apatite. Apatite materials have a high retention capacity and the results of lab-scale experiments could be used to predict P removal in full-scale taking into account others factors as hydraulic conditions. A decrease in retention rates with time was observed for all materials and the apatite quality appears to be very important for sustainable P treatment. Using a good quality of apatite the surface needed for P treatment is about 0.5 m² to respect 1 mgP.l⁻¹ in the effluent.

Acknowledgements: the Authors would like to thank the Rhône-Alpes Chemicals and Environment competitiveness cluster “Axelera” in which this project takes place. We thank CERPHOS and FERPHOS groups for providing the apatite used in this study.

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FIGURES

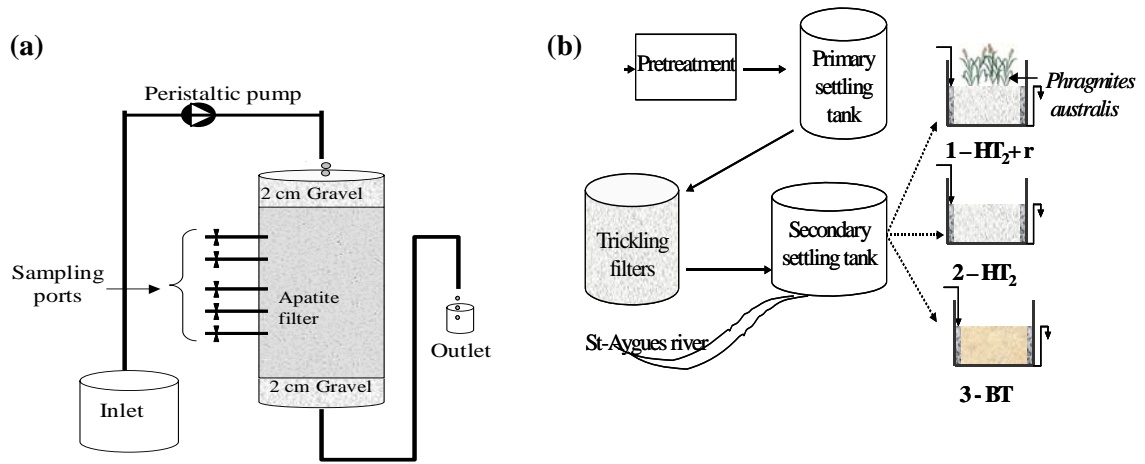


Fig. 1. Schematic representation of: (a) column experiments and (b) pilots at Bagnols

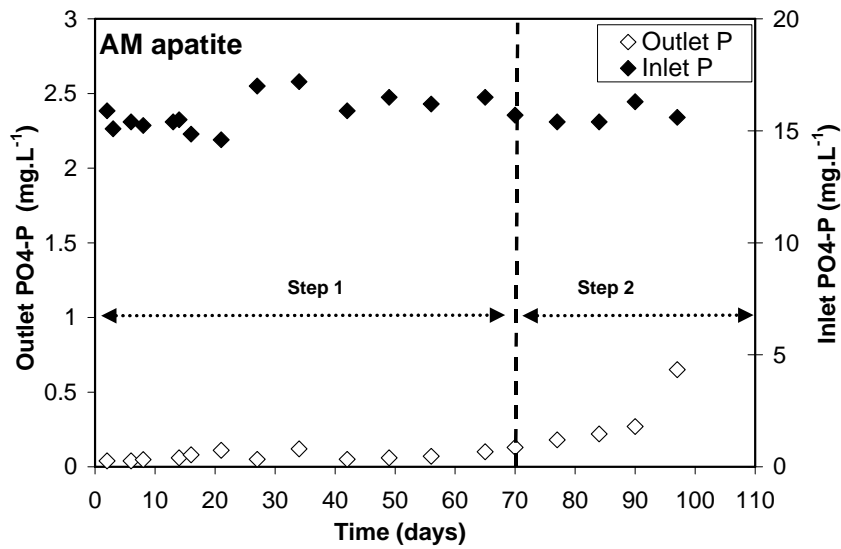


Fig. 2. Evolution of P concentrations as a function of the time during the AM column experiment

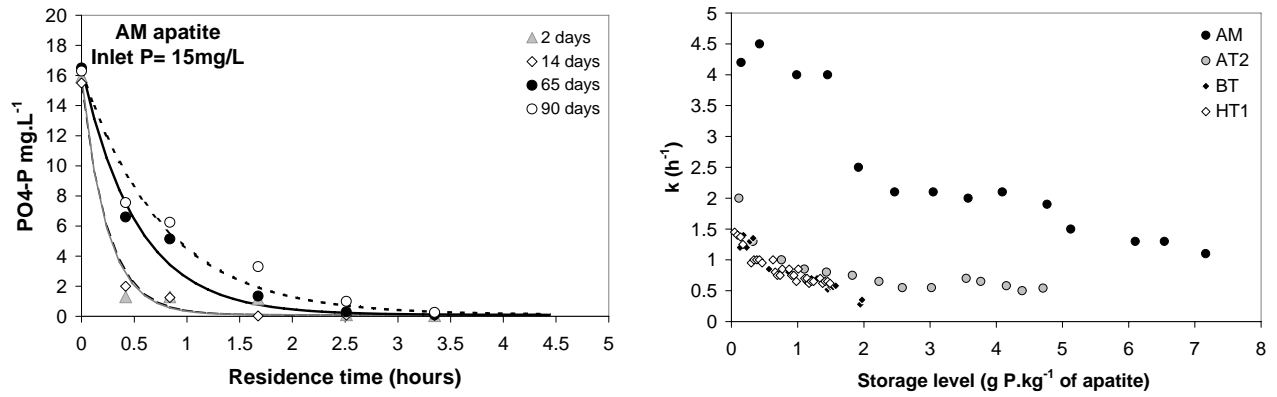


Fig. 3. (a) Variation of the phosphorus concentration with the reaction time for AM apatite. The symbols designate the P experimental data, the curves drawn through this data represent the P concentrations calculated from $k-C^*$ model and (b) Evolution of retention rates for all apatite materials studied as a function of P storage level per kilograms of apatite

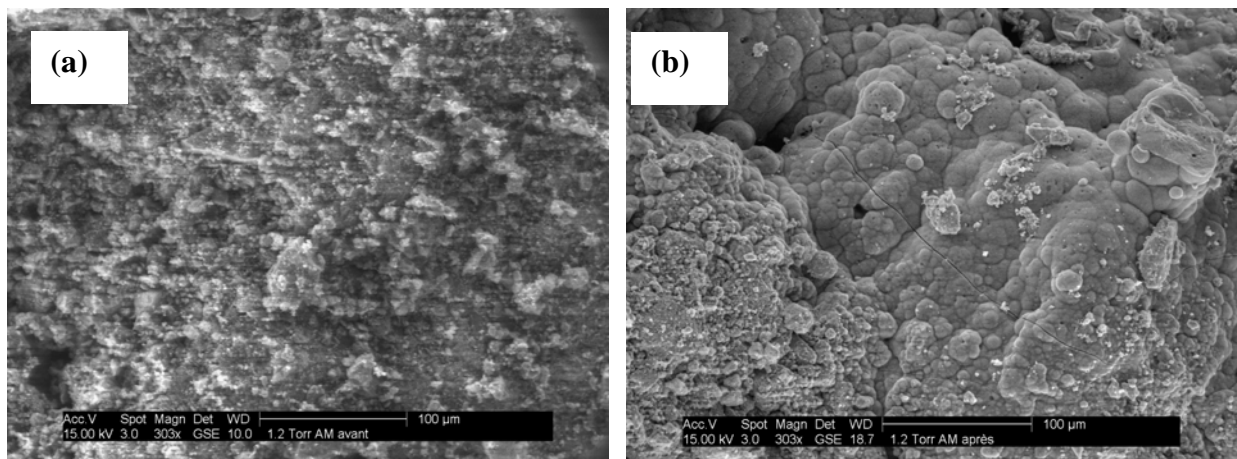


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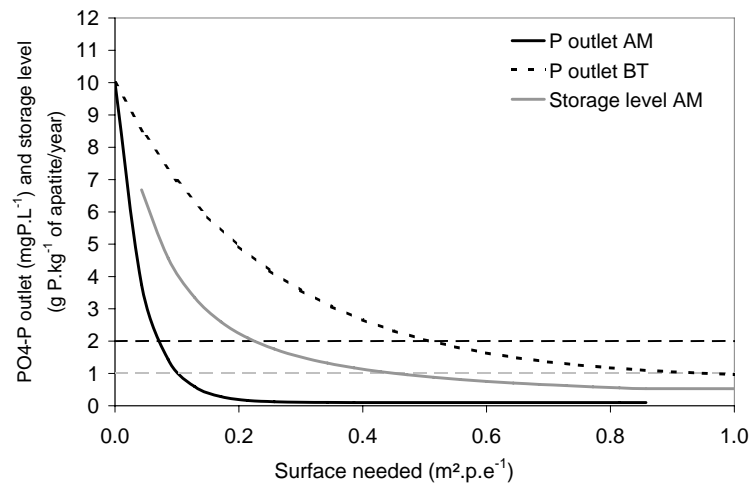


Fig. 5. Effect of apatite quality on surface needed for P treatment and on final saturation of the apatite filter

TABLES

Table 1 Physical characteristics of tested materials

	Particle size			Porosity %	Density $\text{kg}\cdot\text{m}^{-3}$	Geometric surface area $\text{m}^2\cdot\text{kg}^{-1}$
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BT	1.27	4.02	3.15	50	2414	0.73
HT ₁	4.44	9.21	2.09	46	2160	0.17
HT ₂	0.19	9.21	47.54 ⁽¹⁾	53	2243	1.48
AM	0.37	2.79	7.46	58	2392	1.76
AT ₂	2.14	3.85	1.80	54	2447	0.33

⁽¹⁾ HT₂ material contains 30 % of fine particles of clay that can be bonded to larger particles. As a consequence, particle size distribution is modified and real grain distribution is masked. In reality we observe apatite grains of 0.1 – 0.3 μm and coarser grains with impurities.

Table 2 Mineralogical characteristics of materials

	Mineralogical composition % (W/W) of materials					
	Apatite	Calcite	Quartz	Ankerite ⁽²⁾	Dolomite	Clay
BT	41.8	50.4	4.8	n.d. ⁽³⁾	3.0	0.0
HT ₁	60.2	35.1	0.0	n.d. ⁽³⁾	4.7	0.0
HT ₂	46.3	39.5	10.1	n.d. ⁽³⁾	2.5	1.5
AM	95.4	3.2	1.3	n.d. ⁽³⁾	0.0	0.0
AT ₂	58.1	0.0	0.2	41.7	0.0	0.0

⁽²⁾ $\text{CaFe}(\text{CO}_3)_2$ and ⁽³⁾ not determined

Table 3 Chemical composition of materials

(a) Major constituents									
% Mass	Ca	P	Si	Mg	Fe	Al			
BT	36.3	8.4	3.1	0.5	0.3	0.4			
HT ₁	35.3	10.1	3.3	0.2	0.3	0.2			
HT ₂	32.3	8.2	6.5	0.5	0.6	1.0			
AM	38.2	13.2	1.1	0.2	0.2	0.2			
AT ₂	31.9	9.6	2.2	1.7	0.4	0.5			
(b) Trace elements									
$\text{mg}\cdot\text{kg}^{-1}$	As	Cd	Cr	Cu	Pb	Se	V	Zn	U
BT	11.4	76.8	182.1	6.4	2.3	3.2	115.5	109.9	61.5
HT ₁	11.6	34.5	196.0	18.9	3.3	<DL ⁽⁴⁾	152.0	196.0	106.0
HT ₂	9.5	31.5	321.0	21.3	3.8	<DL ⁽⁴⁾	242.0	237.0	78.9
AM	13.3	14.4	257.0	22.9	3.8	1.9	130.0	181.0	131.0
AT ₂	4.0	11.9	210.0	5.1	3.2	21.3	<DL ⁽⁴⁾	82.1	40.1

⁽⁴⁾ Detection limit

Table 4 Inlet water characteristics in column experiments

	Water	Flow rate/ cross section m.d⁻¹
BT	Tap water and wastewater	0.80-1.60
HT ₁	Tap water	0.85
HT ₂	Tap water and wastewater	0.80-1.60
AM	Tap water	0.80-1.15
AT ₂	Tap water	0.80-1.15

Table 5 Mean hydraulic and organic loads applied on the pilots and inlet wastewater characteristics. Values for parameters are means/ (SD: standard deviation) of 34 samples

HL (m/d)		COD	SS	KN	TN	TP
	Inlet wastewater (mg. l ⁻¹)	67.8/(31.2)	19.7/(16.1)	6.2/(4.3)	21.8/(8.0)	4.2/(1.7)
0.18/(0.08)	HT+ r (g. m ⁻² . d ⁻¹)/(SD)	11.6/(5.7)	3.1/(1.9)	1.0/(0.9)	3.6/(2.8)	0.7/(0.4)
0.18/(0.07)	HT (g. m ⁻² . d ⁻¹)/(SD)	11.8/(5.3)	3.0/(2.2)	1.1/(0.8)	4.0/(2.3)	0.7/(0.4)
0.13/(0.05)	BT (g. m ⁻² . d ⁻¹)/(SD)	8.3/(3.8)	2.2/(1.3)	0.7/(0.5)	2.5/(1.6)	0.5/(0.3)

Table 6 Comparison of retention rates between column experiments and pilots

Materials	k (h⁻¹) in column-scale	k (h⁻¹) in pilot-scale
BT	0.3	0.3
HT ₂	0.6	0.3

Figures captions