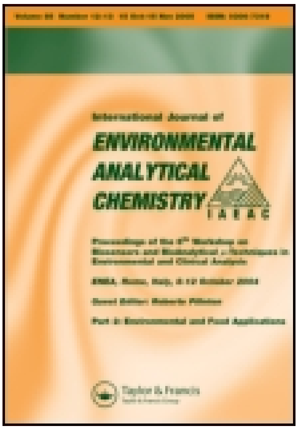

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Performance evaluation of phosphorus removal by apatite in constructed wetlands treating domestic wastewater: column and pilot experiments

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In constructed wetlands (CWs) treating domestic wastewater, good treatment performance is 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 person equivalent (pe), 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 has been studied by only a limited amount of work. Apatite materials appear to possess high and long-term removal capacity, thus a better knowledge is needed to determine the quality of apatite to be used and the P removal evolution with time and water quality. In this work the P removal rates were studied in two different scales (lab-experiments and pilot units) on different apatite qualities. Removal rate in the pilot units was smaller than the one found in lab-scale columns and the results suggested that a security coefficient might be applied while designing the 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 is not possible to remove the sludge and P is released back into water after organic matter mineralisation [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 (30–150 $\mathrm{kg\,ha^{-1}\,year^{-1}}$) [4]. To avoid eutrophication problems in surface waters the use of specific materials in CWs has been the subject of a large number of studies. These works have focused on a variety of substrates (iron, aluminium and calcium rich materials) tested in lab-scale and field trials [5,6]. The substrates include measurements of properties and sorption capacity of bauxite, shale,

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zeolite, fly ash, and clay aggregates [7]. Materials containing iron have been also investigated (magnetite, [8], steel slag [9,10]). Sorption of P by substrate rich in calcium and calcareous materials have been studied by several authors [11–16]. A number of recent publications have focused on the use of apatite materials ($Ca_5(PO_4)_3OH,F,Cl$) to promote irreversible sorption of P onto the material surface [17–19]. In these studies, the authors have observed a high and long-term capacity of apatite to remove phosphorus. The P removal was based on adsorption and/or precipitation mechanisms onto particle surface. Nevertheless, in the few works done on P removal by apatite [17–20], the materials were mainly evaluated in lab-scale experiments (batch and/or column) under controlled conditions. In this study six different apatite materials were tested in columns. Two qualities of these materials were tested in pilot units with conditions close to reality. In lab-scale columns, the objectives were to determine the removal rates versus apatite qualities and the influence of water ionic composition. In pilot units, fed with treated wastewaters in hydraulic controlled conditions, the objectives were to point out the removal rate evolution with time, scale transition effect and exhibit the reed effect on P removal. Other objectives were also sought as follows:

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

Apatite minerals are known to have a great stability and a particular crystalline structure allowing the 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 were characterised for their trace elements content. The trace elements concentrations in the influent and the effluent in column tests and pilot units were also compared to evaluate the ability of apatite to remove/release these elements.

2. Experimental

2.1 *Apatites tested*

P removal experiments were performed in the present study using five sedimentary apatites from Morocco and Algeria (Table 1) and compared to apatite 1 material studied by Molle

Table 1. Physical characteristics of tested materials.

	Particle size			Porosity %	Density $kg\,m^{-3}$	Geometric surface area $m^2\,kg^{-1}$
	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	0.19	9.21	47.54[a]	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

[a] HT 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.

et al. [18]. 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:

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

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.

The apatite materials studied were examined using X-ray powder diffraction (XRD) to determine mineralogical composition of materials. Moreover, the major elements composition was provided by X-ray fluorescence analyses (XRF). Trace elements were quantified by inductively coupled plasma mass spectrometry (ICP-MS). All physical, chemical and mineralogical properties of materials used are shown in Tables 1–3. Materials tested contain 40% to 95% of apatite mineral associated with other impurities. In this paper the term 'quality of apatite' will be used to mean percentage content of apatite mineral. A good quality of material is one with a high percentage of apatite mineral.

2.2 *Column experiments*

The apatite materials (BT, HT_1, HT, AM and AT_2) were tested in vertical downward flow columns of 9 cm of inner diameter (Figure 1(a)). All columns consist of 20 cm high layers of apatite, equipped with five sampling ports to study the 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 $16\,mg\,P\,L^{-1}$) and maintained in hydraulic saturation conditions as in horizontal flow constructed wetlands (HFCW). To test the impact of biomass development on removal capacity, the BT an HT materials were also tested in columns (BT_Bio and HT_Bio) using wastewater (40 to $100\,mg\,COD\,L^{-1}$). The inlet pH of all synthetic solutions was 7.6 ± 0.2. The columns samples were taken regularly and analysed for calcium, phosphorus,

Table 2. Mineralogical characteristics of materials.

	Mineralogical composition % (W/W) of materials					
	Apatite	Calcite	Quartz	Ankerite[a]	Dolomite	Clay
BT	41.8	50.4	4.8	–	3.0	0.0
HT_1	60.2	35.1	0.0	–	4.7	0.0
HT	46.3	39.5	10.1	–	2.5	1.5
AM	95.4	3.2	1.3	–	0.0	0.0
AT_2	58.1	0.0	0.2	41.7	0.0	0.0

[a] $CaFe\,(CO_3)_2$.

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	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

$mg\,kg^{-1}$	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[a]	152.0	196.0	106.0
HT	9.5	31.5	321.0	21.3	3.8	<LQ[a]	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	<LQ[a]	82.1	40.1

[a] Limit of quantification.

alkalinity and pH to observe the temporal evolution of the effluent composition. More details on column test of apatite 1 material were given in the work by Molle *et al.* [18]. Experiments lasted 90 days for BT, HT$_1$, HT, AM and AT$_2$ and 550 days for apatite 1 materials.

2.3 *Pilot units*

2.3.1 *Pilot units description*

BT and HT materials were tested in three similar pilot units (HFCW) at the Bagnols plant (Rhône, France). The pilot units consist of tanks, with dimensions 1.5 m long, 1 m wide and 0.4 m deep. The pilot units were fed with treated wastewater (except for P, Table 5) from the outlet of the Bagnols plant (trickling filter) (Figure 1(b)). One pilot unit (HT + r) was planted with *Phragmites australis* to study the reeds effect on P removal.

2.3.2 *Pilot units monitoring*

The monitoring of pilot units 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 analysed for COD, BOD, SS, Ca, nitrogen and phosphorus forms. Moreover PO_4-P analyses for inlet and outlet were 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 was determined by tracer experiments using a GGUN-FL30 Fluorometer. The apparatus was designed to provide continuous monitoring of uranine tracer concentrations. Tracer experiments were performed in the space of one week approximately, and the results were used to detect dead zones in pilot scale.

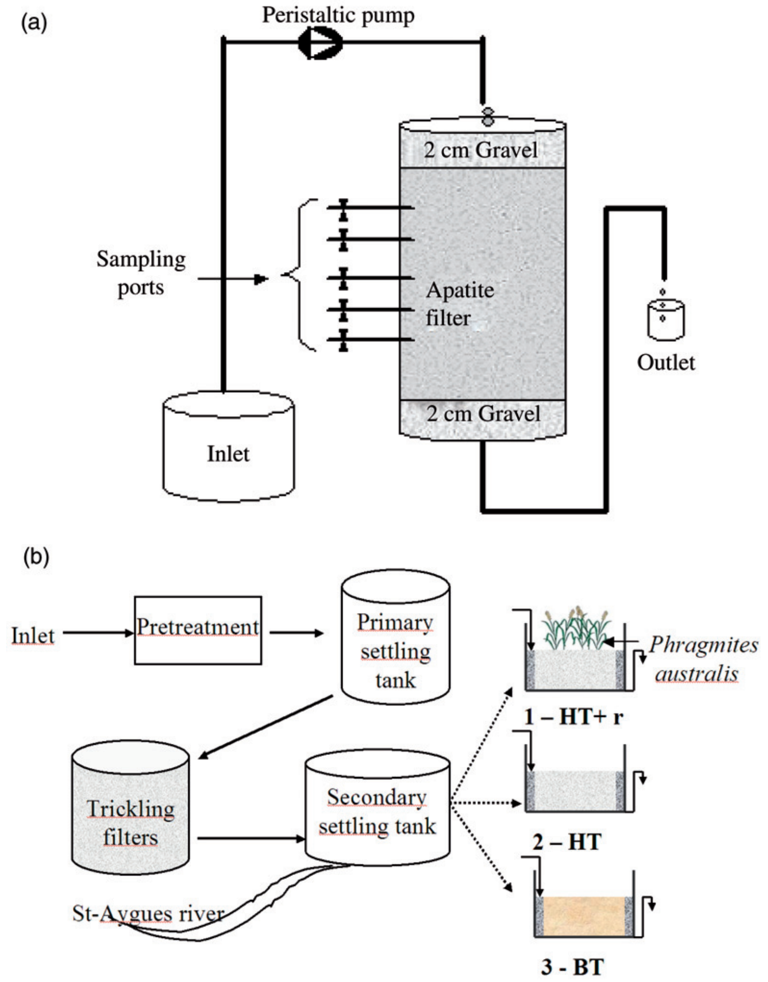

Figure 1. Schematic representation of: (a) column experiments and (b) pilots at Bagnols.

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	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. Trace elements concentrations of influent and effluent for AM column and pilot units (number of data: 1).

	AM column		Pilot units (first period)			
Element (μg.L^{-1})	Influent	Effluent	Influent	HT+r	HT	BT
Fe	0.63	1.18	–	–	–	–
As	0.96	3.12	2.94	3.31	3.24	1.33
Cd	0.02	0.20	0.06	0.49	0.40	0.48
Cr	0.14	0.26	0.43	0.11	0.17	0.09
Cu	28.9	0.80	16.90	13.30	17.00	17.00
Pb	<LQ[a]	<LQ[a]	0.67	0.22	0.25	0.21
Se	1.98	0.11	<LQ[a]	<LQ[a]	<LQ[a]	<LQ[a]
V	1.71	6.97	0.55	7.50	10.60	8.24
Zn	72.7	0.60	47.60	16.50	18.10	26.40
U	0.82	1.25	0.57	3.64	4.40	8.56
Hg	0.006	<LQ[a]	0.0088	0.0026	0.0035	0.0036

[a] Limit of quantification.

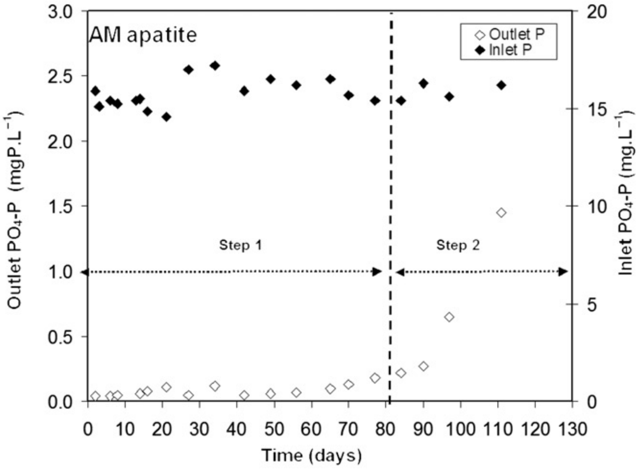

Figure 2. Evolution of P concentrations as a function of the time during the AM column experiment.

3. Results and discussion

3.1 *Phosphorus removal in column experiments*

As example, the evolution of P removal by AM material is shown in 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 during the experiment ($pH_{inlet} = 7.6 \pm 0.2$ and $pH_{outlet} = 7.4 \pm 0.3$).

In Figure 2 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 P L^{-1}. The adsorption seems to be the predominant mechanism, as proved by other previous studies [31].

Step 2: The outlet P concentration increased after a saturation level reached about 5 g of P kg^{-1} of material, as found by Molle *et al.* [18]. Probably the precipitation becomes the predominant phenomenon of P removal from this step. This points out how experiment duration is important to predict long-term P removal with such material.

In this study the presence of biomass in the influent for HT and BT experiments showed a loss of 10 to 20% of mass P removal efficiency. This results suggests that the influent characteristics in lab-scale tests is also essential to determine the real potential of apatite materials to remove P in CWs. Biomass development causes a decrease in surface availability for P sorption onto the apatite material.

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

Using the internal sampling system, the P concentration in the apatite was modelled using k-C* model (2). The model has been chosen because it is a simple way to model pollutant removal in HFCW. The P concentration (C) at time t can be obtained by the following expression:

$$C = (C_0 - C^*)\exp(-kt) + C^* \tag{2}$$

where C_0 is the inlet concentration of P, k the volumetric retention rate and C^* the residual P concentration.

Figure 3(a) presents the P concentration evolution as a function of hydraulic residence time in the AM apatite material. With an increasing distance from the inlet the most of the P was retained in the first part of apatite media.The removal rate k fitted was about $4.2 \pm 0.2\,h^{-1}$ in the beginning of the experiment (Figure 3(b)) and decreased with time and the saturation level attained, as presented by Figure 3(b).

The comparison of removal rate evolution for all materials tested in this study as given by Figure 3(b) shows that the value of k decreases systematically as adsorption mechanism reduces until it reaches a steady state once precipitation becomes the major mechanism involved in P removal. The k value for AM material was reduced gradually according the saturation level increase, but this reduction was not observed in Figure 2 before the 70 days. This observation was related to k value, witch remains sufficiently high ($>1.5\,h^{-1}$) to reach low outlet P concentrations. The P concentrations in the effluent began to rise at a saturation level of about 5 g of P kg^{-1} of material. The results of apatite 1 material [18] showed a good P removal performance and a saturation level of 13.9 g of P kg^{-1} of material at least. For this material quality a reduction of P removal capacity was observed at a saturation of about 4.9 g of P kg^{-1} of material [18]. The apatite 1 material possesses chemical characteristics close to those of AM material (good quality > 90% of apatite mineral) and the two materials present the same behaviour for P removal. For poor quality (40–60% of apatite mineral) the k values were lower than those of good quality material. For example, at saturation level of 1.45 g of P kg^{-1} of material the k value was about $4 \pm 0.1\,h^{-1}$ for AM material while it was $0.65 \pm 0.1\,h^{-1}$ for BT quality. Indeed, the removal rates were different between materials used and the differences observed could be related to material quality. This difference in k value is of great importance to determine the surface needed for P treatment in CWs.

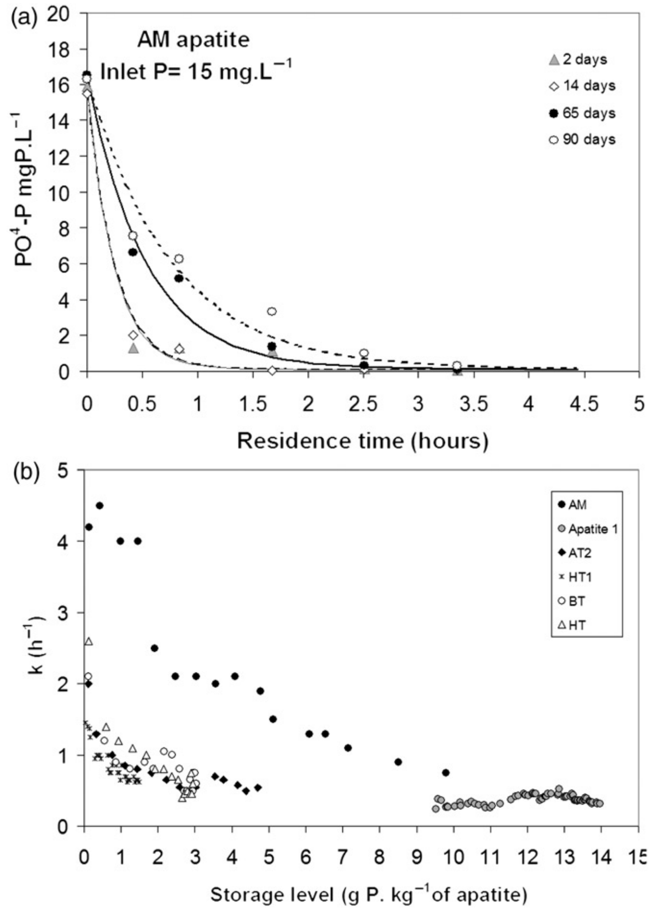

Figure 3. (a) Variation of the phosphorus concentration with the reaction time for AM apatite. The symbols designate the P experimental data, the curves drawn through this data represent the P concentrations calculated from k-C* model and (b) Evolution of retention rates for all apatite materials studied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

3.3 *Sorption/desorption observations*

3.3.1 *Phosphorus*

In order to study the Ca-P phases formed during the P removal tests, the AM material surface, before and after column experiments, was observed using environmental scanning electron microscopy (ESEM) equipped with a microanalysis instrument EDS (energy dispersive X-ray system). Comparison of the photomicrographs illustrated in Figure 4(a) and (b) 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. However, the molar ratios measured were lower than those of hydroxyapatite (HAP) phase (1.67).

3.3.2 *Trace elements*

As shown by the results presented previously in Section 3.2 above, the choice of apatite material quality is important for sustainable P treatment. However, the chemical

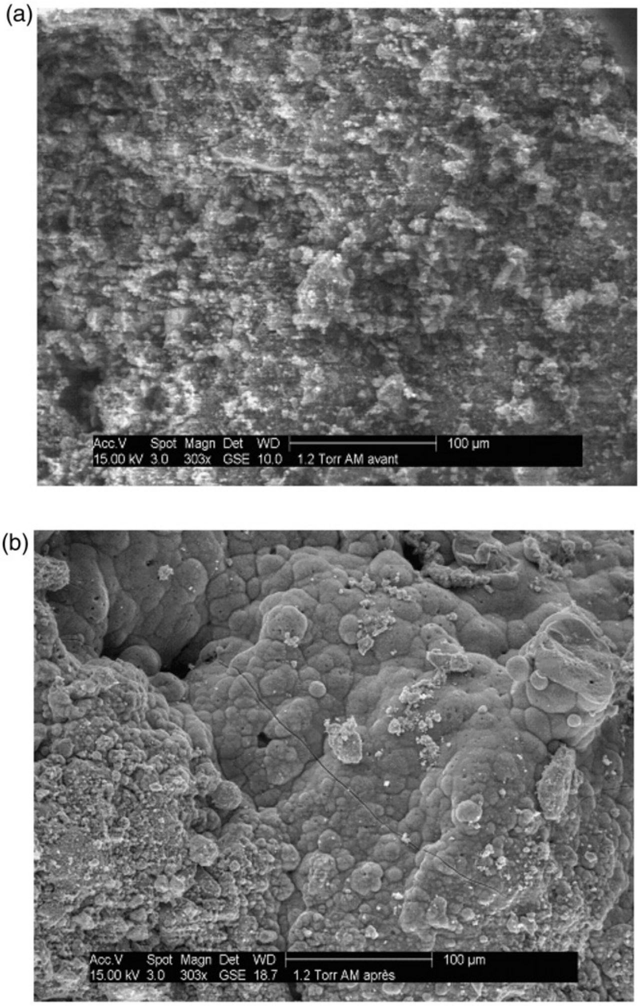

Figure 4. Surface observation: (a) ESEM of AM apatite before experiment and (b) after experiment.

composition of apatite materials can vary widely and contain a large range of trace elements. In this study the trace elements content were performed for four sedimentary phosphorites from Morocco (BT, HT_1, HT and AM) and one material from Algeria (AT_2), as summarised in Table 3(b). Trace elements concentrations showed a variation according to the material type and origin. Some of elements vary according to material (U,V, Zn and As) for Moroccan materials. For apatite material from Algeria, metals contents are generally lower than Moroccan materials. The trace elements contents of apatite materials analysed in this work were very similar to previous analyses of natural phosphates from Morocco and Algeria [31,32]. However, the material studied by these authors showed low content of Cr compared to AM material.

The behaviour of trace elements during column and pilot tests was studied in this work, as illustrated by Table 5. The comparison of the elements concentration between the inlet and the outlet in column test suggests sorption of Cu, Se, Zn and Hg by AM apatite material. In pilot units, the sorption effect was significant for Zn and Hg elements only. A slight release of some elements such as As, Cd and U was also observed in both column and pilot experiment; however, the concentrations of these elements remain lower than the water standards required for drinking water [34]. The significant reduction of Zn element in AM column (99%) and in pilot units (44–66%) is consistent with the results of surface analysis by ESEM. The X-ray microanalysis showed the presence of Zn in the precipitate. As is known, the apatite minerals have a particular structure allowing replacement of Ca, PO_4^{3-} ions by other anions and cations. Assuming that Zn was retained in Ca sites in the precipitate phase formed, the molar ratio ((Ca+Zn)/P) can be calculated using Zn content obtained by X-ray microanalysis. The new molar ratio ((Ca+Zn)/P) was about 1.51 ± 0.04 and this composition obtained suggests a formation of tri-calcium phosphate (TCP). This precipitate could be considered as a precursor for the HAP phase.

3.4 *Hydraulic and treatment performance in pilot units*

The pilot units were fed from April 2008. The hydraulic residence time in apatite media measured using uranine tracer ranged from 0.5 to 2 days, according to the hydraulic loads applied to each pilot units. Moreover, the dead volume resulted from tracer experiments was about 10% in pilot units. Samples into the apatite media also showed the presence of preferential-flow paths in the filter. The mean hydraulic loads received by the pilot units and all details on treatment performance for COD, BOD, SS, Ca, nitrogen and phosphorus forms are presented in Harouiya *et al.* [33] for the three periods studied. 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 unit (30–150 $\mathrm{kg\,Ha^{-1}\,Year^{-1}}$ [4]).

3.5 *Scale transition effect*

BT and HT materials were tested in pilot system in order to evaluate the scale factor effect and the biomass development on P removal rate. As presented in Table 6, the removal

Table 6. Comparison of removal rates between column experiments and pilot units at different saturation levels.

Materials	Saturation level ($\mathrm{g\,P\,kg^{-1}}$ of material)	k (h^{-1})
BT	0.95	1.00 ± 0.1
	1.31	0.85 ± 0.1
HT	0.96	1.00 ± 0.1
	1.34	0.90 ± 0.1
BT_Bio	1.16	0.70 ± 0.1
	1.70	0.55 ± 0.1
HT_Bio	1.14	0.65 ± 0.1
	1.54	0.60 ± 0.1
BT_Pilot unit	0.27	0.33 ± 0.04
HT_Pilot unit	0.44	0.33 ± 0.04

rates obtained in lab-experiments were different from those measured in pilot units, mostly for HT material. At saturation level of <1 g P kg^{-1} of apatite material, the removal rate in column system was of 1 ± 0.1 h^{-1} and decrease to 0.32 ± 0.04 h^{-1} in pilot units for both BT and HT materials. With wastewater and 10% of dead volume in pilot system, the removal rate was 2 to 3 times lower. For the same saturation level, in another and longer study on BT apatite carried out in real-scale HFCW at the Evieu plant [33], k value was of 0.29 ± 0.02 h^{-1}. In the Evieu plant, the dead volume measured was about 20%. The differences observed might be caused by the hydraulic conditions and biomass development in the system. In pilot units, hydrodynamic was less controlled than in lab-scale columns. Therefore, the P removal rates of BT and HT materials obtained in the full-scale plant and in the pilot units were smaller than those measured in columns: the k values in column tests have to be used carefully. Consequently, designers have to be aware of it and apply security coefficient (2 to 3) while designing the apatite filter.

3.6 *Design recommendations*

To evaluate the process sustainability and optimise the design of apatite filter, Figure 5 gives the surface needed per person equivalent to achieve 2 or 1 mg P L^{-1} for the two extreme apatite materials studied in this work (AM and BT). In this figure the surface was calculated for an inlet P concentration of 10 mg P L^{-1} and a removal rate (including security coefficient) of 0.3 h^{-1} and 0.08 h^{-1} for AM and BT materials, respectively. The figure shows that the surface needed for P treatment is lower using a good quality of apatite material (>90% of apatite mineral). For example, a surface of 0.2 m^2 pe^{-1} is sufficient to achieve 1 mg P L^{-1} in the effluent for filter with AM material. However, due to hydraulic short-cutting, it is not secure to use the smaller surfaces and the best window in terms of application is to use about 0.5 m^2 pe^{-1}. It means that apatite materials like BT with poor quality are not suitable. The use of 0.5 m^2 pe^{-1} has also an important role to

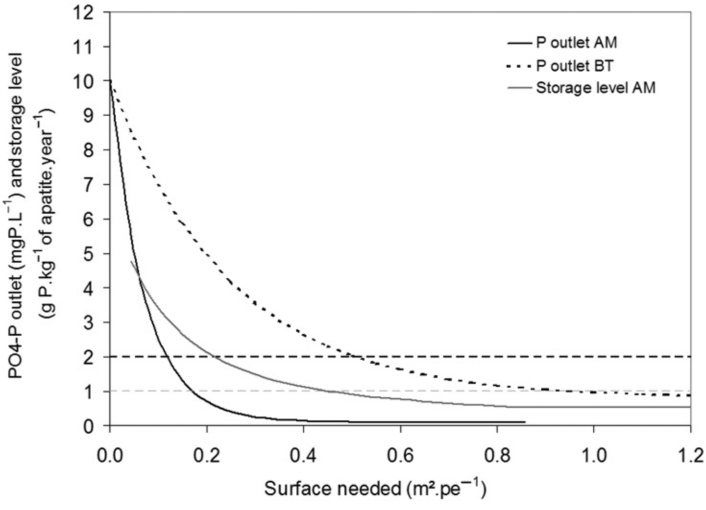

Figure 5. Effect of apatite quality on surface needed for P treatment and on final saturation of the apatite filter.

delay final saturation of the filter. The saturation level reached for AM material in lab-experiments was about 10 g of P kg^{-1} of material. As presented by the grey curve, if the filter accumulates 1 g of P kg^{-1} of apatite material per year, using a surface of 0.5 m^2 pe^{-1}, this saturation level would be reached after 10 years and the filter could work at least 10 years with high P removal rates. The use of smaller filter surfaces would lead to earlier final saturation.

4. Conclusions

As well as confirmation of the good P removal potential of apatite in constructed wetlands, another advantage is the importance of apatite quality on long-term P removal. A better insight of processes in terms of adsorption/precipitation, precipitate formed, impact of reeds and experiments scale allow one to consolidate the design of apatite filters and its sustainability. This work provides data in lab-scale experiments and in pilot units on P removal by apatite. The apatite materials have a high retention capacity and the results of lab-scale experiments could be used to predict P removal in full-scale operations, taking into account other factors such as hydraulic conditions. A decrease in removal 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 was about 0.5 m^2 to achieve 1 mg P L^{-1} in the effluent.

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