Phosphorus retention in subsurface constructed wetlands: investigations focused on calcareous materials and their chemical reactions

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Abstract Phosphorus removal from wastewater has been of growing interest for some decades to avoid eutrophication in surface water. In subsurface constructed wetlands precipitation and adsorption are the main mechanisms responsible for P uptake. Two media (calcite and recycled crushed concrete (RCC)) were examined in batch and continuous systems. Batch experiments show attractive sorption capacities, however experiments carried out in open reactors pointed out some limitation in retention capacities and effluent quality. RCC is sensitive to a strong dissolution leading to a quick phosphorus precipitation but induces high conductivity and pH values in the treated water. Calcite efficiency depends on the carbonate equilibrium of the solution. Microscopic observations of the calcite surface show crystal growth of phosphorus precipitate. Crystallisation seems to be the main P uptake once a material's surface is covered.

Keywords Adsorption; calcareous material; constructed wetlands; phosphorus retention; surface precipitation

Nomenclature

c: P concentration (mg L^{-1})
d: effective grain size (mm)
d_X: mesh diameter allowing $X\%$ of the material mass to go through (mm)
$K_d=\%_c$: distribution coefficient (m^3 of solution kg^{-1} of soil)
M: Total mass sample used to determine the particle size distribution (g)
m_i: grain mass collected on sieve number i (g)
pH_{ZPC}: pH of zero point of charge
q: P mass adsorbed on material (mg P g^{-1})
S: specific area (m^{-1})
T: Temperature in °C
ε: Porosity (%)

Introduction

Phosphorus is the main factor involved in eutrophication of surface water, so its removal from wastewater has been of growing interest for the past ten years in CW. In France, the most common CWs are vertical reed bed filters which are known to achieve high quality effluents in terms of organic matter and nitrification, but phosphorus removal remains poor. In horizontal subsurface constructed wetlands, surface reactions in the liquid-solid interface are promoted thanks to saturated conditions. It would be therefore preferable to design horizontal flow reed beds as a 2nd stage treatment. The use of specific media to improve precipitation and adsorption has been widely studied (Drizo *et al*., 1997; Zhu *et*

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al., 1997; Brix *et al.*, 2000). Calcareous materials seem to have attractive capacities in P retention (Brix *et al.*, 2000) but could induce high pH release incompatible with a river ecosystem if discharge flow is significant when compared to that of the river. Calcareous materials are subject to the dissolved carbonate equilibrium leading to dissolution or precipitation of the solid phase (Stumm and Morgan, 1996). If the solution is under-saturated, material dissolution will induce Ca^{2+} release and pH increase. Moreover, when materials contain lime, pH, and Ca^{2+} release, will be strong. These mechanisms are of great importance on P-Ca reactions that could occur in the system. The aim of this paper is to describe experiments that allow a better understanding of phosphate retention on two calcareous materials.

Background

P-Ca reactions mainly depend on adsorption/desorption and precipitation/dissolution mechanisms. The surface complexation theory has been reviewed in detail in a number of publications (Stumm and Morgan, 1996; Sposito, 1984). The central concept is that water molecules and dissolved species from chemical bonds with exposed lattice, bind ions at mineral surfaces. For calcite, the primary hydration surface sites are described as hydroxylated surface cation centres: $>CaOH^0$, where $>$represents the mineral lattice. This hydroxyl group can deprotonate ($>CaO^-$) or protonate ($>CaOH_2^+$). However surface anion sites lead to the appearance of a new type of site $>CO_3H^0$. In the absence of specifically adsorbing solutes other than H^+, densities of the charged surface sites (controlled by the pH solution) determine the surface charge of the oxide mineral. For calcite many studies relate that below a pH of 8.2 (Van Capellen *et al.*, 1993; Pokrosky *et al.*, 2000; Vdovic, 2001), $>CaOH_2^+$ and $>CO_3Ca^+$ are the main species and above, $>CO_3^-$ and $>CaCO_3^-$ become the predominant forms. Hence, the surface charge is characterised by a specific pH of zero point of charge (pH_{ZPC}) below which the surface is positively charged and above which it is negatively charged. This leads to opportunities of P retention by specific adsorption below the pH_{ZPC}. On natural calcite, organic matter, impurities or precipitation of a new phase on the surface may be responsible for variations in surface properties. Vdovic (2001) found negative surface charge on different natural calcite material over a great range of pH (from 6 to 10).

Precipitation requires the formation of stable nuclei, after which crystal growth can take place. In solution, some degree of supersaturation is required because crystal nuclei can only be formed after an energy barrier has been overcome (Anderson and Rubin, 1981). Supersaturation may be developed by increasing the calcium and phosphate content of the aqueous medium and/or its pH. Various calcium phosphate compounds may precipitate (Table 1). Once the nuclei exceed a critical size, they grow further on the active growth sites of the crystallites. In soils, minerals can catalyse the nucleation step of crystallisation. The energy barrier is reduced and surface precipitation is more likely to occur than precipitation in solution.

Making a specific distinction between both mechanisms is not easy when one realizes that the chemical bonds formed can be very similar and that existing solid phases can lead to

Table 1 Calcium phosphate compounds

Compound	Abbreviation	Composition	Ca/P
Dicalcium phosphate dihydrate	DCPD	$CaHPO_4.2H_2O$	1.00
Octacalcium phosphate	OCP	$Ca_4H(PO_4)_3$	1.33
Tricalcium phosphate	TCP	$Ca_3(PO_4)_2$	1.50
Hydroxyapatite	HAP	$Ca_5(PO_4)_3OH$	1.67

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surface precipitation. When no independent data on which to base a decision are available, the loss of substances from aqueous solution to the solid phases can be simply termed sorption. Prediction of maximum adsorption capacity is often determined by isotherm data via Langmuir modelisation:

$$q = \frac{bKc}{1 + Kc} \tag{1}$$

where b and K are adjustable parameters. b represents the value of q that is approached asymptotically as c becomes arbitrarily large, and is often interpreted as the maximum sorption capacity. K determines the magnitude of the initial slope that represents the affinity between ion and mineral to react. A precise way to determine these parameters is to plot the ratio $K_d = \frac{q}{c}$ against q. The Langmuir equation can be written in the linear expression:

$$K_d = bK - Kq \tag{2}$$

Such an approach should be taken with care, as it could lead to unrealistic estimates for P adsorption capacities in constructed wetlands (Drizo *et al*., 2000). Moreover if surface precipitation is a preponderant mechanism, P retention could continue for a long time, and this is not taken into consideration in Langmuir predictions. Processes involved in P retention should be identified in order to evaluate potential P removal, and to design filters correctly.

Materials and methods

Tested media

Natural calcite (Cal) and recycled crushed concrete (RCC) were examined in relation to their phosphorus removal capacities. The calcite studied is a natural calcite with less than 0.1% of organic matter. The concrete studied was obtained from heating concrete composed of 77% to 83% of $CaCO_3$, 2 to 4% of Al_2O_3 and 1.5 to 3% of Fe_2O_3. Calcium carbonates under high temperature turn to quicklime. Particle-size distributions were determined using dry-sieving techniques (European norm, 1997), to calculate d_{10}, d_{60} and uniformity coefficient ($CU = d_{60}/d_{10}$). Porosities were determined from the amount of water needed to saturate a known volume of component and the bulk density was measured by the water volume displacement of a known mass of medium. Specific area was evaluated from the particle size distribution, assuming spherical grains. Chemical and physical properties of calcite and RCC are shown in Table 2.

Batch experiments

Isotherms and kinetics were carried out with batch experiments at 22°C with a slow rotating shaker (25 rpm). In each test 20 g of materials were used in 1 L glass flasks containing 500 ml of distilled water, adjusted in pH with NaOH and conductivity with NaCl (pH = 7.0 ± 0.1 ; conductivity = 1,000 ± 100 μS cm^{-1}). For isotherms, P solutions were ranged from 0 to 500 mg P L^{-1} using KH_2PO_4 (contact time = 24 h). In kinetics experiments, contact time

Table 2 Chemical and physical characteristics of materials

| | Chemical composition %(W/W) of materials | | | | | Particle size | | | Porosity | Density | Specific |
	Ca	Mg	P	Fe	Al	d_{10} (mm)	d_{60} (mm)	CU	%	kg.m^{-3}	area m^{-1}
Cal 1	41	2.4	0	0	0	0.4	0.6	1.5	42	2,700	5,500
Cal 2						1	1.6	1.6	47	2,750	2,300
RCC 1	7.77	0.20	0.04	1.29	1.11	0.3	1.2	4	40	2,200	6,150
RCC 2						1.4	2.3	1.6	45	2,300	1,220

varied from 1 to 48 hours. Batch experiments were also focused on the characterisation of the P/calcite reaction mechanisms varying electrolyte concentrations (Ca^{2+}, pH, HCO_3^-, P). Orthophosphate P was determined using a phosphate molybdate method on the supernatant solution obtained from centrifugation.

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Columns experiments

Phosphorus saturation was carried out in 95 mm diameter columns filled with media, and kept in hydraulic saturated conditions. A synthetic solution (pH = 7.0 ± 0.1; conductivity = $1,000 \pm 100$ μS cm^{-1}) was applied continuously at a flow rate of 1.35 L d^{-1}. Two P concentrations were used (20 and 200 mg L^{-1}) to evaluate differences in P saturation as a result of the sorption mechanisms involved. In order to attain saturation in a reasonable period, the volumes of media were 95 cm^3 for low P application and 285 cm^3 for high P application that correspond to hydraulic retention times of 5.6 h and 16.7 h respectively. The effluent of each column was collected daily and analysed for P concentrations. pH and conductivity were measured continuously. After saturation, columns were fed with a solution without phosphates to evaluate the reversibility of the sorption.

Pilot experiment

A horizontal subsurface pilot plant was built to evaluate P sorption onto calcite in conditions more representative of a full scale experiment (Figure 1). The pilot was composed of Cal 2 and not planted. Diluted urban wastewater (150 $\pm$ 50 mg COD L^{-1} enriched with KH_2PO_4 to reach 20 mg of Total P L^{-1}) was distributed on the pilot via gabion (gravel 5–10 mm). Effluent was collected and analysed for P concentration daily. P distribution in the system was evaluated via vertical sampling points evenly distributed on the surface and at different depths (0.1; 0.2; 0.3 m). The hydraulic load was about 25 L d^{-1} and corresponded to an average contact time of 55 h.

Analytical microscopy SEM and STEM

Scanning electron microscopy (SEM) as well as scanning transmission electron spectroscopy (STEM) were applied to characterise the microstructure and composition of the calcite surface before and after column experiments. Surface crystals were taken down by ultrasonic washing and analysed by STEM to evaluate the deposit composition.

Results

Batch experiments

Isotherm experiments are shown in Figure 2a. RCC led to dramatic pH and conductivity increases comparative to calcite material (about 12 for pH and 2,500 μS cm^{-1} for conductivity). No conductivity increase was observed in the calcite experiment and final pH was about 8.3. Plotting K_d as a function of q, it is obvious that the Langmuir correlation is not appropriate (Figure 3a and 3b). For the calcite graph, K_d is a curve convex to the q-axis. The
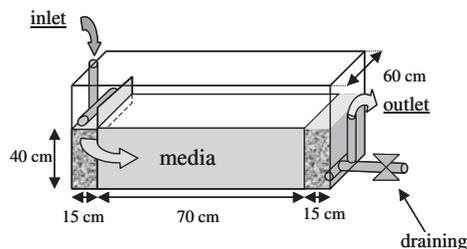
Figure 1 Schematic representation of pilot experiment

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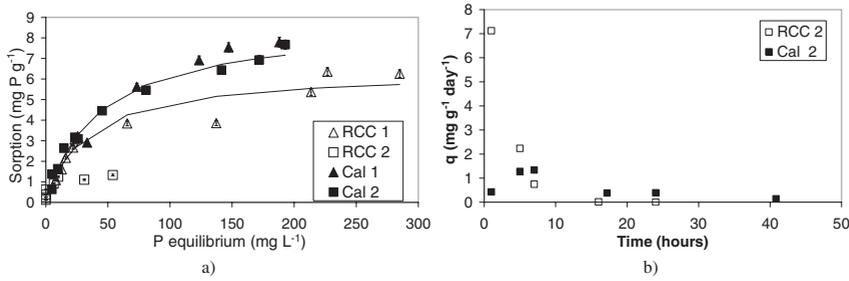
Figure 2 a) P sorption isotherms. b) Sorption kinetics. Initial P solution concentration: 30 mg L^{-1}
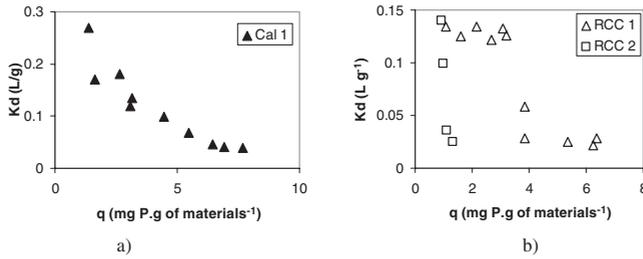

Figure 3 Graph of K_d against the amount adsorbed. a) Calcite 1, b) RCC 1 and 2

RCC graph shows a strong breakdown in K_d value when a precise material saturation occurs. This indicates the end of one P retention mechanism.

Kinetics (Figure 2b) show that P sorption on RCC is an instantaneous reaction whereas calcite kinetic shows an increase after a period of maturation.

Column experiments

Output P levels for both experiments are plotted in Figure 4. Phosphorus retention was total with RCC at the beginning with pH, Ca^{2+} and conductivity increases in effluent as presented in Table 3. So it was obvious that an important RCC material dissolution was effective during the experiment. Unlike RCC, calcite showed a P residual outlet concentration from the beginning of the experiment.
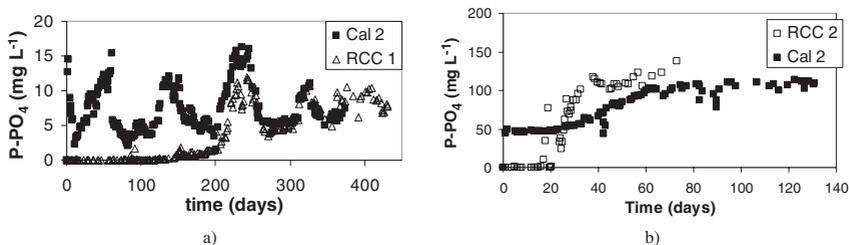
Figure 4 Breakthrough curve. a) $P_{inlet} = 20$ mg.L^{-1} b) $P_{inlet} = 200$ mg.L^{-1}

Table 3 Physicochemical characteristics of solution (*correspond to the period of increased P concentration in outlet)

	pH		Conductivity (µS cm^{-1})		Ca^{2+} (mg L^{-1})	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Cal 20 mg L^{-1}	7.0 ± 0.1	8.1 ± 0.3	$1,000 \pm 100$	$1,000 \pm 100$	0	7 ± 2
RCC 20 mg L^{-1}	7.0 ± 0.1	$11\text{--}12 \rightarrow 9^*$	$1,000 \pm 100$	$2,700 \pm 300 \rightarrow 1,300^*$	0	$110 \pm 30 \rightarrow 6 \pm 2^*$

In the 200 mg.L^{-1} experiment, for both media, at the breakthrough points sorption was still working and seems to be stable with time. With low phosphorus concentrations in the influent, calcite shows a great instability in its retention capacity which depends on the water quality. Each peak corresponds to the saturation of the laboratory demineralisation columns, and once regenerated, sorption became better. Decrease in P retention performances for RCC could be compared with changes in the physicochemical characteristics of the outlet solution (Table 3). In the second period RCC behaved as calcite. Degrees of saturation of RCC at the beginning of the breakthrough are respectively 1.25 and 0.95 gP.m^{-2} for the 20 and 200 mgP L^{-1} column experiments. For both media with respect to the effective retention observed at the end of each experiment, P uptake could continue. After experiments a washing of the media confirmed the irreversibility of the retention: less than 0.5% of the fixed P was released during one week of leachate studies on each material.

Pilot experiment
When using urban wastewater, a low P retention took place in the first centimetres of the filter but remained non-existent in the following part despite significant internal concentrations of reagents (5–10 mgP L^{-1} and 80 mgCa L^{-1}). No evolution of bulk solution concentration was found during this period, neither P, Ca, HCO$_3^-$ concentrations nor pH.

Analytical electron microscopy
Examination of the calcite surface by STEM and SEM experiments showed that the calcite employed in the column experiments is covered by crystals. The column fed with 200 mgP L^{-1} was covered with more crystals than the one fed with 20 mgP L^{-1}. Quantitative analysis of this deposit revealed that for both column experiments, the Ca/P molar ratio of crystals was the same (1.4).

Discussion
The results presented above were analysed in accordance with a fundamental approach to point out the possible mechanisms of phosphorus retention in the studied conditions. The intensity of the phosphorus retention is very different with RCC and calcite materials. RCC, composed of quicklime, dissolves quickly and leads to important calcium concentrations and high pH values in solution leading to a strong precipitation. At a precise degree of saturation, dissolution decreases just like the P sorption rate. K_d curves and breakthrough of column experiments describe this sudden decrease in P sorption rate. K_d decrease corresponds to a surface coverage of 1.03 gP m^{-2} and 0.82 gP m^{-2} for RCC 1 and 2 respectively, which is in accordance with the surface coverage observed in column experiments at the breakthrough. The strong breakdown in the K_d value is explained by the surface lime consumption more than by a progressive decrease in dissolution due to surface coverage of precipitates. From this precise saturation, RCC behaves as calcite (Figure 4). Calcite behaviour shows great instability in P uptake while calcite isotherms are more attractive than the RCC ones. K_d curve for calcite is in accordance with two P sorption mechanisms (Sposito, 1984). Transition between both is in this case progressive. Further tests were carried out to get a better understanding of the mechanisms involved in P sorption with calcite and explain its instability.

Chemical reactions involved with calcite
As noticed in previous figures and comments, some precursor mechanisms seem to occur in P sorption with calcite (Figure 2b). Three different stages can be observed (Figure 5):
- Calcite dissolution without important P retention (about one hour).
- Substantial P decrease and little variation in pH and conductivity (from about one to 15 hours).
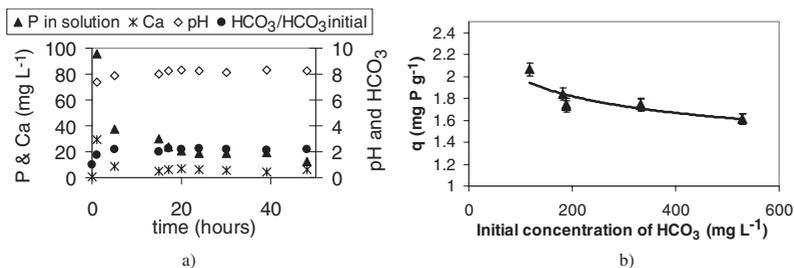
Figure 5 a) Chemical variations of solution during reaction. b) Effect of carbonate concentration on P sorption

- No variation in pH or conductivity and little P retention.

According to the fact that kinetics and intensity of sorption depend on the influent characteristics, more batch experiments were carried out to analyse the role of HCO_3^- and Ca^{2+} on P retention.

Carbonates impact on P sorption

A negative effect of carbonates on P sorption was observed (Figure 5b). That is in accordance with other studies like Millero *et al.* (2001), who ascribe the negative carbonate impact on P sorption as a competition between P and carbonates for adsorption sites. Considering calcite dissolution molar ratio observed in batch experiment without phosphorus, the Ca/P molar ratio that has reacted is about 0.49. This ratio indicates that precipitation is not the only mechanism involved in the P sorption. Adsorption might have occurred.

Calcium's role in P sorption

Ca addition promotes P sorption but not enough to reach greater values than those obtained in experiment without initial Ca (Figure 6a). A solution containing initially dissolved Ca is nearer to equilibrium than a solution without Ca, and therefore leads to minor calcite dissolution. With tap water (close to equilibrium), considering precipitation without calcite, and calcite dissolution, we can estimate the ratio Ca/P that had disappeared via sorption. The ratio was 0.36 and cannot correspond to a pure P-Ca precipitate.

These comments point out that two mechanisms are involved in P sorption by calcite. Calcite dissolution due to under-saturated water allows Ca^{2+} and H^+ release and is responsible for the elapsing time before the P sorption becomes important. Then Ca^{2+} due to calcite dissolution or initially present in solution can react by adsorption until the pH of the solution reaches the pH_{ZPC} of the particle. We can note that in all calcite batch experiments, pH equilibrium is very close to the pH_{ZPC} observed in several works (Stumm and Morgan,
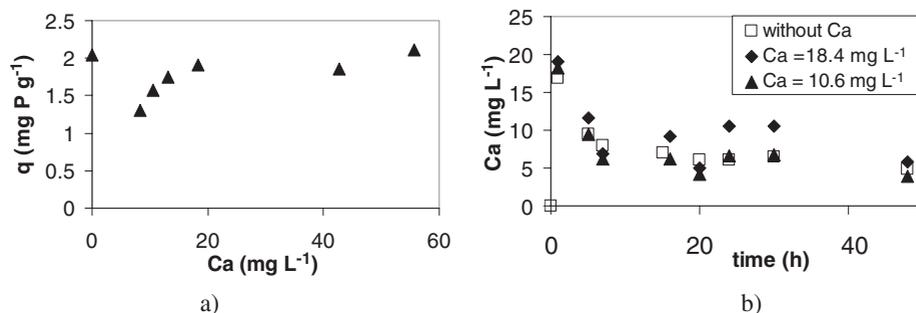
Figure 6 a) P sorption onto calcite for different initial Ca concentrations ($HCO_3^- = 250 \pm 50$ mg.L^{-1}), b) Ca solution evolution with time

1996; Van Capellen *et al*., 1993; Vdovic, 2001). Surface speciation could explain the first sorption mechanism. Below the pH_{ZPC} orthophosphates can neutralize the surface charge by surface complex formation if Ca^{2+} is present in solution.

$$S - OH + L^- + M^{z+} \Leftrightarrow S - L - M^{z+} + OH^- \qquad (3)$$

$$S - OH + L^- + M^{z+} \Leftrightarrow S - OM - L^{(z-2)+} + H^+ \qquad (4)$$

Above the pH_{ZPC} >$CaOH_2^+$ sites density decreases (Van Capellen *et al*., 1993). Surface charge and rate dissolution decrease, thus the P adsorption mechanisms are strongly limited. Sorption rates observed near the pH_{ZPC} in our experiment are very low. After that crystal growth by surface precipitation is more likely to occur than homogeneous precipitation. Song *et al*. (2001) have observed that homogeneous precipitation is favoured by high pH and Ca/P ratio. With pH = 8 and a Ca/P ratio = 1.67 (greater than in our batch experiments) less than 8% of the 20 mgP L^{-1} precipitate. We can compare these results with our pilot experiment where, in spite of a Ca/P ratio of 7, no P uptake is observed after the first 5 cm (pH = 7.5). For low P concentration, and neutral pH, homogeneous precipitation seems to be of minor importance. Heterogeneous precipitation becomes predominant as the surface coverage increases. Surface precipitation decreases the accessible mineral surface to water and therefore decreases dissolution mechanisms processes. Once the mineral surface is covered, P retention only becomes crystal growth. This is confirmed by microscopic analysis. Ca/P ratios of precipitates compounds onto calcite surface observed by STEM analysis, are between the theoretical value of OCP and TCP. In precipitating calcium phosphates, the compound that is formed initially is quite different from the final equilibrium phase, and intermediate compounds (OCP, TCP…) are often observed (Zoltek, 1974). In secondary effluent in which the total carbonate concentration is usually high, an imperfect carbonate apatite could be formed and affect the Ca/P ratio. More precise analysis is still needed to establish which precipitate is formed. The poor P leaching observed in column experiments after saturation indicates that this precipitate is relatively stable.

Conclusion

The P sorption mechanisms of both calcareous materials lead to point out that:

- Batch experiments and Langmuir estimations are not sufficient to define long term P removal in constructed wetlands.
- The choice of P inlet concentration in column experiments could lead to a wrong estimation of saturation capacities regarding the mechanisms involved with calcareous materials.
- Crystal growth seems to be the final P removal mechanism with calcareous materials.

Despite some good sorption capacities, RCC and calcite show limitations in constructed wetlands use. Calcite, as well as RCC (once lime is dissolved), show low P surface precipitation kinetics. RCC is responsible for high pH values which would not be compatible with discharge consents. Crystal growth could be promoted by other seed materials, closer to the obtained precipitate (hydroxyapatites). In order to use such a specific material as seed, more studies should be done to estimate i) the influence of biomass development on crystal growth rate and ii) the clogging risk induced by crystal growth.

Acknowledgements

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