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**Phosphorus sorption 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 of P uptake. The use of calcareous media is attractive because of P-Ca interactions. Two medium (calcite and recycled crushed concrete (RCC)) were examined in batch and continuous systems. They show attractive sorption capacities using batch experiments, however experiments carried out in open reactors pointed out some limitation in retention capacities and effluent quality. RCC was sensitive to a strong dissolution leading to a quick phosphorus precipitation but inducing high conductivity and pH values in the treated water. Calcite efficiency depended on the material dissolution rate directly linked to the carbonate equilibrium of the solution. Microscopic observations of the calcite surface show crystal making of phosphorus precipitate. Crystal growth seems to be the main P uptake once materials surfaces are covered. Any experimental condition allows to reach an effluent concentration below 2 mgP.L⁻¹.

KEYWORDS

Phosphorus retention, constructed wetlands, calcareous material, adsorption, surface precipitation, kinetics.

NOMENCLATURE

b: Langmuir adjustable parameter representing the maximum sorption capacity

c: P concentration (mg.L⁻¹)

CU: uniformity coefficient (d_{60}/d_{10})

d: effective grain size (mm)

d_{10} : mesh diameter allowing 10% of the material mass to go through (mm)

d_{60} : mesh diameter allowing 60% of the material mass to go through (mm)

K: Langmuir adjustable parameter representing the magnitude of the initial slope.

$K_d = \frac{q}{c}$: distribution coefficient (m³ of solution. kg⁻¹ of soil)

M: Total mass sample used to determinate 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)

RCC: recycled crushed concrete

S: specific area (m⁻¹)

T: Temperature in °C

ϵ : Porosity (%)

INTRODUCTION

Phosphorus removal from wastewater has been of growing interest for decades to avoid eutrophication in surface water. Small communities wastewater treatment needs low operational cost and maintenance simplicity. It could be the situation with constructed wetlands. Among the different types of CW, the most common in France are the vertical reed bed filters which are known for performing high quality effluents in terms of organic matter and nitrification but phosphorus removal remains poor. In sensitive areas it is thus necessary to focus on this aspect and a research project has been set up to investigate on different medias' capacities to retain phosphorus. In horizontal subsurface constructed wetlands, surface reactions in the liquid-solid interface are promoted thanks to saturated conditions and, therefore, it would be preferable to design horizontal flow reed beds as a 2nd stage treatment. An other aim of the project but secondary, will also be to evaluate in which such a design, obviously fit for phosphorus removal, would allow denitrification at the same time, in relation with anoxic conditions established in the water saturated media.

The use of specific media is widely studied [1-3] to improve the principals P retention factors that are precipitation and adsorption. Different medias are known for reacting with phosphorus. In non-calcareous minerals the reaction is predominantly with solid phase constituents of Al and Fe. Calcareous materials seem to have attractive capacities in P retention [3] but could induce high pH release which would be incompatible with river ecosystem if discharge flow is significant compared with the river one.

Considering the precipitation, dissolution and adsorption reactions, carbonate minerals can affect the biogeochemical cycles of P. These reactions are controlled by chemical processes which takes place at the interface between the mineral lattice and the bulk solution.

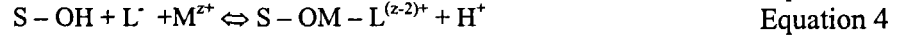
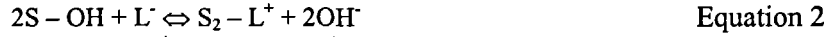
Calcareous materials are subject to the dissolved carbonate equilibrium in surrounding water and the solid phase can be partially dissolved or in opposite a new precipitate phase can appear [4] according to pH, temperature T or CO₂ partial pressure, carbonates and calcium concentrations values. For example, if the solution is under-saturated, material dissolution will induce Ca²⁺ release and pH increase. Moreover, when materials contain lime, pH increases as well as Ca²⁺ release, will be important. These mechanisms are of great importance on P-Ca reactions that might 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. Experiments were conducted in batch and open systems to determine kinetics parameters and evaluate the material retention capacities.

BACKGROUND

P-Ca reactions mainly depend on adsorption/desorption and precipitation/dissolution mechanisms. The surface complexation theory was reviewed in detail in a number of publications [4, 5]. The central concept is that water molecules and dissolved species from chemical bonds with exposed lattice, bound ions at mineral surfaces. For calcite minerals, the primary hydration surface sites are described as hydroxylated surface cation centers: $>\text{CaOH}^0$, where $>$ represents the mineral lattice. This hydroxyl group can deprotonate ($>\text{CaO}^-$) or protonate ($>\text{CaOH}_2^+$). However surface anion sites, lead to the appearance of a new type of site $>\text{CO}_3\text{H}^0$. In the absence of specifically adsorbing solutes other than H⁺, densities of the charged surface sites determine the surface charge of the oxide mineral. The relative distribution of the protonated surface sites is controlled by the pH solution. For calcite many studies relate that below a pH of 8.2 [6-8], $>\text{CaOH}_2^+$, $>\text{CO}_3\text{Ca}^+$ are main species and above, $>\text{CO}_3^-$, $>\text{CaCO}_3^-$ becomes the predominant form. Hence, the surface charge of oxides in water 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} . We can write the most important adsorption equilibria like:





Where S represents the lattice site, L the anion and M the metal cation. Equations 1 and 2 represent ligand exchange adsorption and equations 3 and 4, surface complex adsorption.

On natural calcite, organic matter, impurities or precipitation of a new phase of the surface may be responsible for variations in surface properties. Vdovic [8] found negative surface charge on different natural calcite over a great range of pH (from 6 to 10).

Precipitation needs 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 [9]. Supersaturation may be developed by increasing the aqueous medium content in calcium and phosphate and/or pH. Various calcium phosphate phases may precipitate from saturated solutions (table 1). The status of the solution phase, quantified by the ratio between the ion activity product (IAP) and the solubility product of the crystalline product (K_{SO}), must be large enough to allow precipitation in solution [10]. 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 precipitation onto surface is much likely to occur than precipitation in solution. Among all the forms of solid calcium phosphates, apatites are the most thermodynamically stable.

Phases	Abbreviation	Composition	Ca/P
Dicalcium phosphate dihydrate	DCPD	CaHPO ₄ ·2H ₂ O	1.00
Octacalcium phosphate	OCP	Ca ₈ H(PO ₄) ₆	1.33
Tricalcium phosphate	TCP	Ca ₃ (PO ₄) ₂	1.50
Hydroxyapatite	HAP	Ca ₅ (PO ₄) ₃ OH	1.67

Table 1: Calcium phosphate phases.

Distinction between specific adsorption and precipitation is not evident after one realizes that the chemical bonds formed in both can be very similar and that existing solid phases can lead to 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 termed simply sorption.

Prediction of maximum adsorption capacities is often determined by isotherms data via Langmuir modelisation (eq 5).

$$q = \frac{bKc}{1 + Kc} \quad \text{Equation 5}$$

where b and K are adjustable parameters. b represents the value of q that is approached asymptotically as c becomes arbitrarily large often interpreted as the maximum sorption capacities. K determines the magnitude of the initial slope that is 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. Langmuir equation can be written in the linear expression:

$$K_d = bK - Kq \quad \text{Equation 6}$$

Such an approach should be taken with care, as it could lead to unrealistic estimates for P adsorption capacities in constructed wetlands [11]. Moreover if surface precipitation is a preponderant mechanism, P retention could occur for a long time, and not considered in Langmuir predictions. Processes involved in P retention should be known to evaluate correctly potentialities of P removal, and to filter design.

MATERIALS AND METHODS:

Tested media

Natural calcite (Cal) and recycled crushed concrete (RCC) were examined in relation with their phosphorus removal capacities. The calcite studied is a natural calcite of a pit rock from the south of France, with less than 0.1 % of organic matter. Concrete studied was obtained from heating concrete composed on 77 % to 83 % of CaCO₃, 2 to 4 % of Al₂O₃ and 1.5 to 3 % of Fe₂O₃. Calcium carbonates under high temperature turned to quicklime that could recombine with Al and Fe. This clinker was then mixed with alluvial sand.

Particle-size distributions were determined using dry-sieving techniques [12], to calculate d₁₀, d₆₀ and uniformity coefficient (CU = d₆₀/d₁₀). 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, according to:

$$S = (1 - \varepsilon) \sum_{i=1}^{n-1} \frac{12}{(d_{i+1} + d_i)} \cdot \frac{m_i}{M} \quad \text{Equation 7}$$

Chemicals properties of calcite and RCC are shown in table 2.

	Ca	Mg	P	Fe	Al
Cal	41	2.4	0	0	0
RCC	7.77	0.20	0.04	1.29	1.11

Table 2: chemical composition %(W/W) of materials

Particle size distributions show that a good uniformity is obtained in each sample tested. Characteristics are presented in table 3.

	Particle size			Porosity %	Density kg.m ⁻³	Specific area m ⁻¹
	d ₁₀ (mm)	d ₆₀ (mm)	Cu			
Cal 1	0.4	0.6	1.5	42	2700	5500
Cal 2	1	1.6	1.6	47	2750	2300
RCC 1	0.3	1.2	4	40	2200	6150
RCC 2	1.4	2.3	1.6	45	2300	1220

Table 3: physical characteristics of materials

Batch experiments

Isotherms and kinetics were carried out with batch experiments at 22°C with a slow rotating shaker (25 rpm) to avoid material alteration. 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 = 1000 ± 100 μS cm⁻¹).

For isotherms, P solutions were ranged from 0 to 500 mg P L⁻¹ using KH₂PO₄. The mixture was continuously shook for 24 hours. In kinetics experiments, contact time varied from 1 to 48 hours and different P concentrations were tested (30 and 100 mg P L⁻¹).

Batch experiments were also focussed on the characterisation of the P/calcite reaction mechanisms varying electrolyte concentrations (Ca²⁺, pH, HCO₃⁻, P) and particle diameter.

Orthophosphates P was determined using a phosphate molybdate method at the wavelength of 700 nanometres, on the supernatant solution obtained from centrifugation (3000 tr mn⁻¹, 20 mn).

Columns experiments

Phosphorus saturation was carried out on 95 mm diameter columns filled with media, and kept in hydraulic saturated conditions adjusting the outflow level just above the media surface. A synthetic solution (pH = 7.0 ± 0.1 ; conductivity = 1000 ± 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 different (95 cm³ for low P application and 285 cm³ for high P application that correspond to hydraulic retention times of 5.6 h and 16.7 h respectively).

Effluent of each column was collected daily and analysed for P concentrations as described below. pH and conductivity were measured continuously.

After saturation, columns were fed with a solution without phosphates to evaluate the reversibility of the sorption (pH and conductivity of the solution were unchanged).

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 (0.6 m wide, 0.7 m length and 0.4 m depth) was composed of cal 2 (see table 3) and not planted. Diluted urban wastewater (150 ± 50 mg COD L⁻¹ enriched with KH₂PO₄ 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, and oxydo-reduction potential, pH and conductivity were measured continuously. 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 which give an average contact time of 55 h.

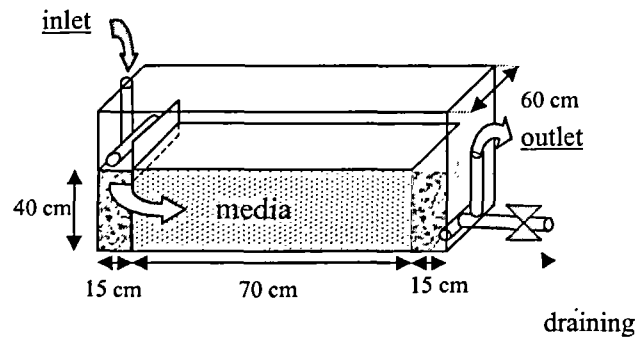


Figure 1: schematic representation of pilot experiment

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's experiments. Surface crystals were taken down by ultrasonic washer (1 minute) and analysed by STEM to evaluate the deposit composition.

RESULTS

Isotherms

Isotherm experiments are showed in figure 2. RCC lead to dramatic pH and conductivity increases comparatively to calcite material (between 11 and 12 for pH and about 2500 $\mu\text{S}\cdot\text{cm}^{-1}$ for conductivity). No conductivity increase was observed in calcite experiment and final pH was about 8.3.

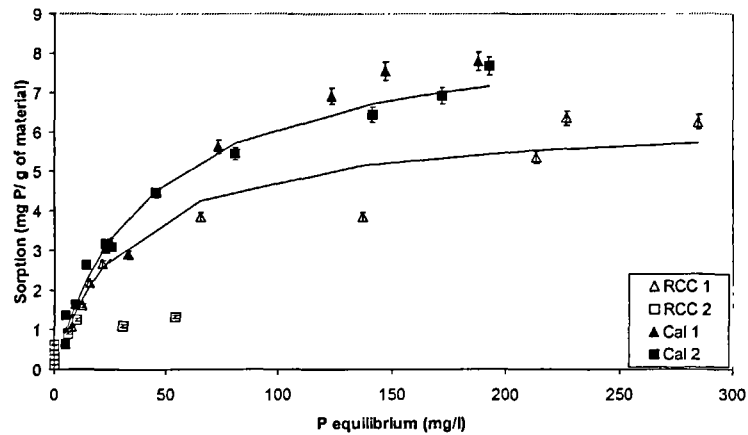


Figure 2: P sorption isotherms

Plotting K_d as a function of q for Langmuir parameters determination, it is obvious that the Langmuir correlation is not appropriate (Fig 3a and 3b). For calcite graph (figure 3a), K_d is a curve convex to the q -axis. These sorption isotherms can be fit to a two-term series of Langmuir equation [5]. RCC graph (fig 3b) shows a strong breakdown in K_d value when a precise material saturation is reached. This indicates the end of one P retention mechanism.

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

Langmuir modelisation could nevertheless be fitted by the least square roots method (fig 2) with correct correlation coefficient ($R^2 > 0.9$). Maximum predicted sorptions by Langmuir are respectively 8.75 and 6.39 mg P.g^{-1} for Cal 2 and RCC 2, i.e 13.8 and 6.2 gP.m^{-2} for respectively Cal 2 and RCC 2.

Kinetics

P sorption on RCC is an instantaneous reaction whereas calcite sorption shows an increase after a period of maturation (fig 4). pH and conductivity modifications are the same as noticed before, and variations are similar to the sorption one.

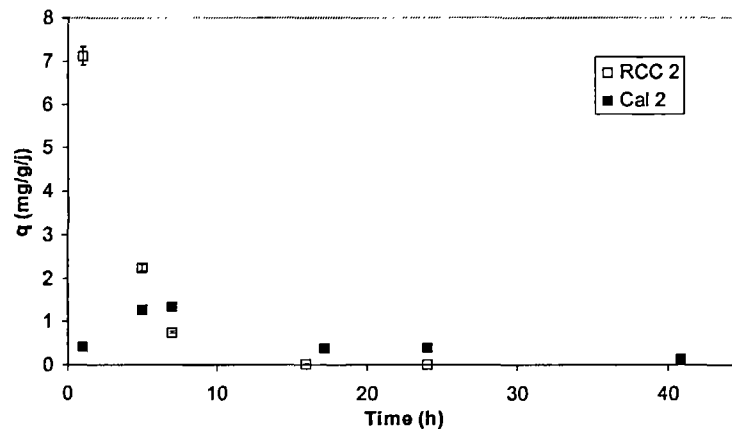


Figure 4: Sorption kinetics. Initial P solution concentration: 30 mg L^{-1} .

Column's experiments

Output P levels for both experiments (20 and 200 mg P.L^{-1} inlet concentration) are plotted in figure 5 and 6. As it was observed in batch experiments, the phosphorus retention was total with RCC material but during the retention period it appeared a pH, Ca^{2+} and conductivity increases in effluent as presented in table 4. So it was obvious that an important RCC material dissolution was effective during experiment.

	pH		Conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$)		Ca^{2+} ($\text{mg}\cdot\text{L}^{-1}$)	
	inlet	outlet	inlet	Outlet	inlet	Outlet
Cal 20 $\text{mg}\cdot\text{L}^{-1}$	7.0 ± 0.1	8.1 ± 0.3	1000 ± 100	1000 ± 100	0	7 ± 2
RCC 20 $\text{mg}\cdot\text{L}^{-1}$	7.0 ± 0.1	11-12 then 9*	1000 ± 100	2500 – 3000 then 1300*	0	110 ± 30 then $6 \pm 2^*$

Table 4: Physicochemical characteristics of solution.

*correspond to the increase P concentration outlet period.

Unlike RCC, calcite showed a high P residual outlet concentration from the beginning of the experiment. In the 200 $\text{mg}\cdot\text{L}^{-1}$ experiment, for both media, once the P output level increased, sorption always occurred and The P output level appeared to be stable.

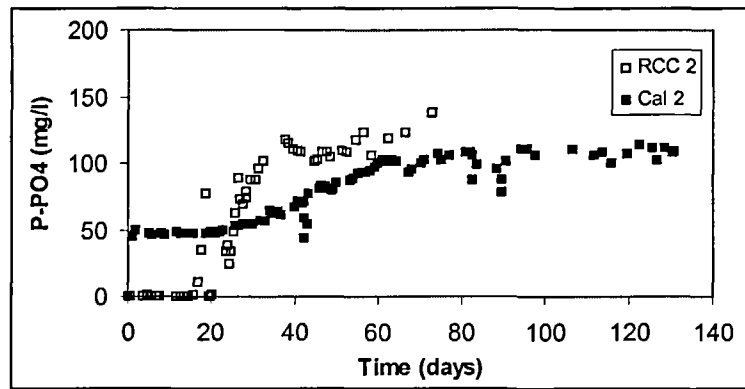


Figure 5: Breakthrough curve. $P_{\text{inlet}} = 200 \text{ mg}\cdot\text{L}^{-1}$

When low phosphorus concentrations were maintained in the influent, the calcite material showed a great instability in its retention capacity varied with the quality of the demineralised water used in influent preparation. Saturation of the laboratory demineralisation columns involved decrease of the water acidity and caused an increase in P outlet level, but once the demineralisation columns were regenerated, P removal became better. This latter observation was of great importance in the understanding of the P retention mechanism.

P removal on RCC was complete at the beginning. Decrease in P retention performances could be compared with changes in the physicochemical characteristics of the outlet solution. In the second period (P outlet concentration significant) RCC behaved as calcite, i.e. it depends on the water quality.

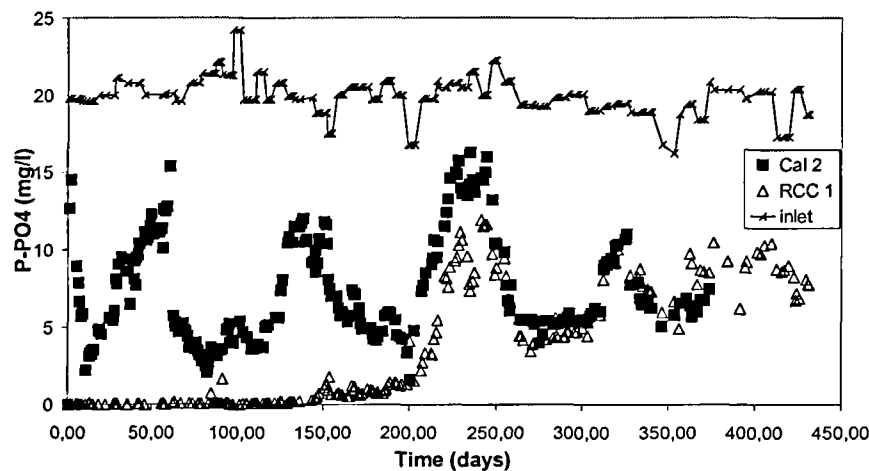


Figure 6: Breakthrough curve. $P_{\text{inlet}} = 20 \text{ mg}\cdot\text{L}^{-1}$

Degree of saturation of media are presented in table 5. With respect to the effective retention observed at the end of each experiments, P uptake could continue.

	20 mg.L ⁻¹ experiment		200 mg.L ⁻¹ experiment	
	Beginning of the breakthrough	End of experiment	Beginning of the breakthrough	End of experiment
Cal 2		4.12	0.56	5.26
RCC 1	1.25	2.25		
RCC 2			0.95	3.92

Table 5: media saturation of columns experiments (g P.m⁻²).

After experiments a washing of the media by clear water confirmed the irreversibility of the retention mechanisms: less than 0.5 % of the fixed P was released during one week leachate studies on each materials.

Pilot experiment

When using urban wastewater (close to carbonate equilibrium), P retention was firstly observed on the organic matter deposited onto the gabion surface and P removal was about 30 % and was stable over one year period. Then a low P retention took place in the first centimetres of the filter but remained inexistent in the following part of the filter despite of 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, HCO₃⁻ concentrations or pH.

Analytical Electronical microscopy

Examination of calcite surface by STEM and SEM experiments show that Calcite employed in column's experiments is covered by crystals (Figure 7). The column fed with 200 mgP.L⁻¹ was covered with more crystals than the one fed with 20 mgP.L⁻¹.

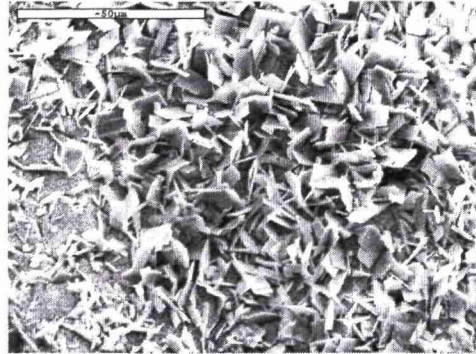


Figure 7: calcite surface by SEM (20 mgP.L⁻¹ column)

Quantitative analysis of this deposits are summarised in table 6.

	SEM		STEM	
	sheet thickness (µm)	Ca/P ratio	Ca/P ratio	Standard deviation
Pure Calcite		no P	no P	
Calcite 20	0.6	1.46	1.38	0.08
Calcite 200	0.1	1.1	1.47	0.1

Table 6: Composition of calcite crystals surface.

According to crystals ratio (STEM), precipitates seemed to be of the same nature for both media, but their structures were different (thinner sheet). Differences encountered in Ca/P ratio between the two methods could be explained by the multi undercoat formation in the calcite fed with 200 mgP.L⁻¹ which could be take into account by SEM analysis (Figure 8).

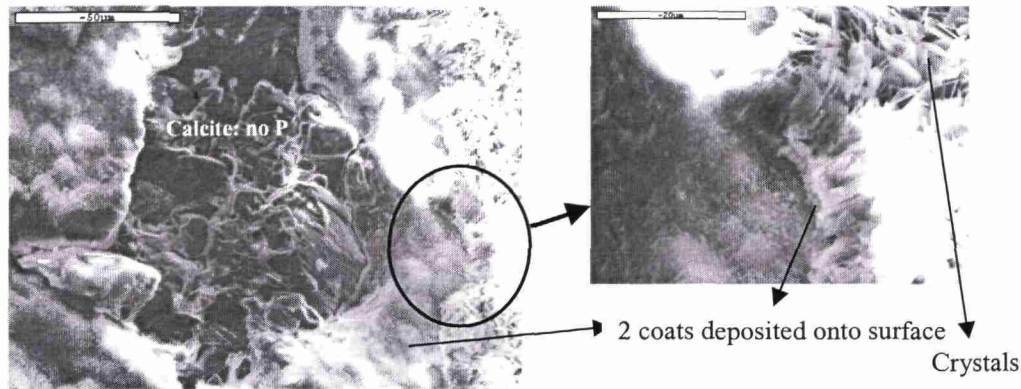


Figure 8: Different coats onto calcite surface (200 mgP.L^{-1} column)

Under the crystals two coats of P-Ca deposit are observed, with a smaller Ca/P ratio (1.1) which could have decreased the ratio value observed in SEM experiments.

DISCUSSION

The raw results presented above were analysed in accordance with 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 concentration and high pH values in solution. pH values between 11 and 12 lead to an important precipitation as well onto the solid surface than in aqueous solution. From a precise degree of saturation, dissolution decreases just like the P sorption rate. K_d curves and breakthrough of column's experiments describe this sudden decrease in P sorption rate. This K_d decrease corresponds to a surface coverage of 1.03 gP.m^{-2} and 0.82 gP.m^{-2} for respectively RCC 1 and RCC 2. This is in accordance with the surface coverage observed in columns experiments (see table 5) when breakthrough appears. The strong breakdown in K_d value is explained by the accessible lime consumption more than by a progressive decrease in dissolution due to surface coverage of precipitates. From this precise saturation, RCC behaved as calcite (Fig 5 and 6).

Calcite behaviour showed great instability in P uptake while calcite isotherms were more attractive than the RCC ones. Physicochemical changes in solution with sorption are not as important and a maturation period appears in the P retention mechanism. K_d curve for calcite is in accordance with two P sorption mechanisms [5]. Transition between both is in this case progressive. 200 mg.L^{-1} column experiment confirms the two P retention rates. 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

As noticed in previous figures and comments, if P-Ca reaction were instantaneous with RCC, they were with calcite (figure 4) and some precursor mechanisms seem to occur (figure 9). Three different stages can be observed:

- Calcite dissolution without important P retention and important pH and conductivity variations (about one hour).
- Substantial P decrease in solution and little variations in pH and conductivity (from about one to 15 hours).
- No variation in pH or conductivity and little P retention.

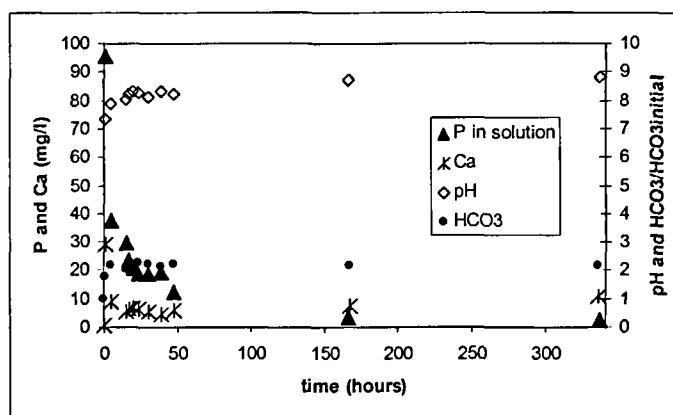


Figure 9: chemical variations observed in solution during P-water-calcite reaction.

According to fact that the kinetics and intensity of these phenomena depend on the influent characteristics, more batch experiments were carried on to analyse the role of H_3O^+ , Ca^{2+} and HCO_3^- ions in solution on P retention.. Their main parameters are presented in table 7.

N°	P-PO4 (mg.L^{-1})	P removal (%) 48h	Initial pH	Equilibrium pH 48 h	Ca^{2+} (mg.L^{-1})	HCO_3^- (mg.L^{-1})
1	0		7.5	8.1	0	667
2	0		7.2	8.3	0	159
3	101	88	7.0	8.2	0	120
4	102	91	7.0	8.2	0	181
5	101	80	7.0	8.2	0	333
6	104	73	7.0	7.8	0	529
7	100	88	7.0	8.8	0	188
8	104	50	7.5	8.5	0	501
9	103	33	8.2	9	0	577
10	80	62	7.3	8.4	8.3	240
11	87	88	7.0	8.4	18.4	215
12	76	83	7.3	8.6	10.6	207
13	76	98	7.0	7.7	42.7	30.5
14	90	93	7.02	7.7	55.6	303

Table 7: Solution characteristics of different batch experiments to evaluate P-Calcite reaction (Cal 1).

Calcite dissolution

Experiments 1 and 2 were conducted in a solution without P and Ca, whose characteristics were far from equilibrium condition. Calcite dissolution was studied and compared with dissolution in an equilibrated tap water, without P (experiment 14).

Tap water experiment showed that no dissolution occurs when a solution is close to equilibrium. With a solution far from equilibrium, a Ca and HCO_3^- release was observed as well as a pH increase until the solution reached equilibrium. Whatever the initial carbonates concentration was, dissolution released 1 mole of Ca^{2+} and 2 moles of HCO_3^- .

Carbonates impact on P sorption

Experiments 3 to 7, show the negative effect of carbonates on P sorption (figure 10). That is in accordance with other studies like Millero et al, [13] who ascribe the negative carbonate impact on P sorption as a competition between P and carbonates on adsorption sites. pH increase and Ca release are proportional to the sorption importance. Ca in solution, after one hour, disappears to reach a stable concentration after 7 hours of reaction.

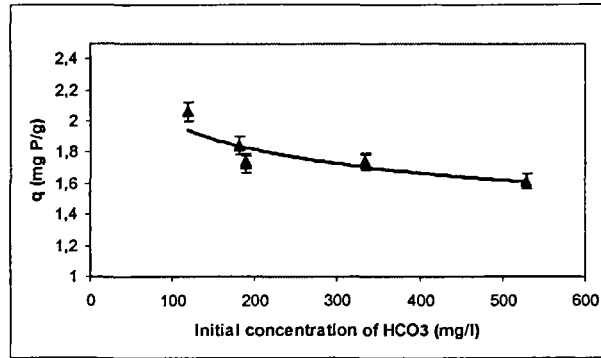


Figure 10: effect of solution carbonate concentration on P sorption.

Ca plays a role in P sorption. Supposing the same calcite dissolution molar ratio that was observed above, the Ca/P molar ratio that have 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 on P sorption

Experiments 10 to 14 are summarized in figure 11a and 11b. Ca adding promotes P sorption but not enough to reach greater values than the ones obtained in experiment without initial Ca (figure 10a). A solution containing initially dissolved Ca is nearer from equilibrium than a solution without Ca, and therefore leads to minor calcite dissolution. Whatever the Ca initial concentration was, its evolution was sensitively similar (figure 8 b). Ca initially in solution and Ca dissolved from calcite do not seem to have the same role in P sorption.

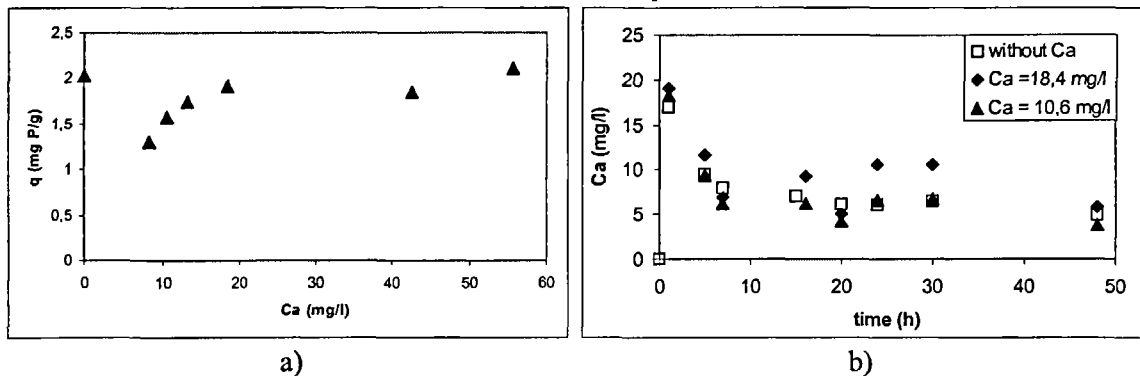


Figure 11a and 11b: a) P sorption onto calcite for different initial Ca concentrations ($\text{HCO}_3^- = 250 \pm 50 \text{ mg.L}^{-1}$), b) Ca solution evolution with time

P sorption onto calcite depends on the solution's saturation index of the solution that governs the calcite dissolution kinetics. Additional Ca in the solution allows a better sorption than if the solution was poor in calcium and close to equilibrium. This is showed in figure 12.

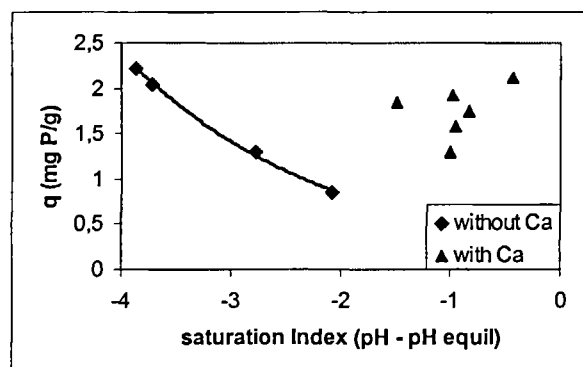


figure 12: Impact of equilibrium solution and Ca on sorption

The results obtained with tap water (close to equilibrium), which is more comparable to wastewater than demineralised water, are described below (experiment 14). Tap water without calcite leads to precipitation of P-Ca composed (ratio Ca/P = 3.15). Only 15 % of initial P disappears. This ratio is too important to be in accordance with the formation of calcium-phosphate solid phase alone (see table 1). Calcium should have precipitated with carbonates too. With calcite addition, considering the same amount of homogeneous precipitation, and the same dissolution stoichiometric (species dissolve with a molar ratio of $\text{HCO}_3^-/\text{Ca}^{2+} = 2$), as found above, we can estimate the ratio Ca/P that had disappeared via sorption.

$$P_{\text{sorption}} = P_{\text{initial}} - P_{\text{precipitated}} - P_{\text{equilibrium}} \quad \text{Equation 8}$$

$$Ca_{\text{sorption}} = Ca_{\text{initial}} + Ca_{\text{released}} - Ca_{\text{equilibrium}} - Ca_{\text{precipitated}} \quad \text{Equation 9}$$

$$Ca_{\text{released}} = 0.5\text{HCO}_3^-_{\text{appeared}} \quad \text{Equation 10}$$

The ratio was 0.36. This ratio cannot correspond to a pure P-Ca precipitate. Because of calcite dissolution, Ca released could have led to a larger amount of P precipitated than observed without calcite. Assuming that more precipitation took place, and according to the Ca/P ratio of possible homogeneous P-Ca precipitates, the sorption Ca/P ratio would have been smaller than 0.36 and therefore incompatible with a P-Ca precipitate.

These comments point out that two mechanisms are involved in P sorption by calcite. Microscopic analysis of deposition confirms the two P retention phenomena. P removal is sensible to carbonate equilibrium. Calcite dissolution due to under-saturated water allows Ca^{2+} and H^+ release that could react with P. Ca^{2+} addition (until 55mg.L^{-1}) in solution does not allow a greater sorption than the one observed with solution far from equilibrium. Song and co-workers [14] 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 our batch experiments) less than 8% of the 20mgP.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 centimetres (pH = 7.5). For low P concentration, and neutral pH, homogeneous precipitation seems to be of minor importance.

We can note that in all calcite batch experiments, pH equilibrium is very close to the pH_{ZPC} observed in several works [4, 6, 8]. Surface speciation could explain the first sorption mechanism. Below the pH_{ZPC} surface is positively charged and $>\text{CaOH}_2^+$ density is important [6,8]. Orthophosphates can neutralize the surface charge by ligand exchange, or by surface complex formation if Ca^{2+} is present in solution. Above the pH_{ZPC} $>\text{CaOH}_2^+$ sites density decreases because the sites concerned are progressively replaced by less protonated and, hence, more stable $>\text{CaOH}^0$ sites [6]. Surface charge and rate dissolution decrease. Thus the P adsorption mechanisms mentioned are strongly limited. Sorption rates observed near the pH_{ZPC} in our experiment are very low.

Dissolution rates observed in some experiments [4, 6], are about $10^{-6.5}\text{mmol.cm}^{-2}.\text{s}^{-1}$. These rates result in a quantity of about 1mg of calcium per g of material and per day in our batch experiment. It is in the same order of importance than P sorption observed in batch experiment with low P concentration where precipitation is restrained. We can assume that the elapsing time before the P sorption becomes important, is due to calcite's dissolution. Calcium addition (with the tested concentrations) does not allow a much better P retention. Dissolution mechanism is of great importance because of surface modifications with attractive sites. So the first mechanism in P sorption with calcite seems to be adsorption.

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. 200mg.L^{-1} column experiments, which accelerate the surface coverage, reveal an equal P removal after the breakthrough appearance for both materials. K_d curves tend to have the same

value for high material saturation. The sudden decrease of K_d value for RCC could be due to the lime consumption.

According to STEM analysis, Ca/P ratios of precipitates compounds onto calcite surface, are between the theoretical value of OCP and TCP. In precipitating calcium phosphates, the phase that is formed initially is quite different from the final equilibrium phase and intermediate phases (OCP, TCP...) are often observed [15]. 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 need to be done to distinct which precipitate is formed. The poor P leaching observed in columns experiments after saturation indicates that the 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 wrong saturation capacities estimation regarding to mechanisms implied with calcareous materials.
- Crystal growth seems to be the final P removal mechanism with calcareous materials.

Despite some good sorption capacities, RCC and calcite are not appropriate for P removal in constructed wetlands. Calcite, as well as RCC (once lime is used) make it impossible to respect the 2 mgP.L^{-1} levels, that will be surely require for small communities in sensitive areas. Furthermore RCC will be responsible for high pH value 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 a specific material as seed, some more studies should be done to estimate the lost of rate crystal growth due to biomass development in one hand, and the clogging risk by crystal growth in other hand.

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