Full scale experience of granulated apatite filters for phosphorous retention in treatment wetlands.

L. Delgado Gonzalez, C. Gerbier, Stéphanie Prost-Boucle, S. Troesch, Pascal Molle

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L., Delgado-González*,, C., Gerbier*, S., Prost-Boucle*, S., Troesch**, P., Molle*.**

* Irstea, REVERSAAL Research Unit, 5 rue de la Doua, PB 32108, 69100 Villeurbanne Cedex, France, laura.delgado-gonzalez@irstea.fr; pascal.molle@irstea.fr
** Syntea, 12 rue Toussaint Fléchaire, 84510, Caumont sur Durance, France. S.troesch@ecobird.fr

Abstract: Phosphorous retention in full-scale granulated apatite filters is evaluated after several years of operation. Measurement campaigns have been carried out over two years to assess the saturation level of the media, the phosphorous retention kinetics and their hydraulic performances. Four filters have been selected: filter A has been monitored since its commission to evaluate the effluent's pH evolution due to lime dissolution. Three other hydraulically different filters, in operation for six years, are also studied: vertical up-flow (filter B); vertical down-flow (filter C) and horizontal flow (filter D). The pH-monitoring for filter A, has shown that 250m^3 of water per m^3 of granulated apatite is needed to fell under pH 8.5 (regulatory limit). Filter B shows the highest saturation level of 6gP/kg material taking into account the 37% of dead volume determined by tracer tests. Phosphorous concentration in the filter's outlet is already over the regulation threshold. Filters C and D present lower saturation levels but they seem to follow same tendency as filter B in terms of P retention performance. Estimated kinetic constants (KC* model) are lower than expected for all filters.

Keywords: Phosphorous removal; granulated apatite; apatite filters.

Session "Wetlands improvement: aeration, nutrient removal, fuel cells."

Introduction

Natural apatites have a great capacity for phosphate retention from wastewater (Molle *et al.*, 2011). Nevertheless these materials from rock phosphate mines are fine sands (0-2 mm) not suitable to ensure a secured flow rate through such filters. Accordingly, a granulated apatite product called Phosclean® has been developed and manufactured in a similar way than fertilizers pellets in order to control the particle size distribution (3-6 mm).

Currently, there are 20 full-scale granulated apatite filters (Phosclean® filters) for phosphorous (P) removal in France. They are usually associated with treatment wetlands (TW) to treat wastewaters of small and medium-size communities. Some of them are in operation for more than five years now, reason why some field experiences are being conducted under the project name of APPROVE (APatite for P Removal and Valorisation: an Evaluation) to assess the current performances, kinetics and saturation levels of some of these full-scale systems. The project is co-funded by Syntea SAS, the French Water Agencies Adour- Garonne and Rhône-Mediterranée-Corse and Irstea.

This paper will present field-feedback results from 4 different wastewater treatment plants (WWTP) with Phosclean® filters. WWTP A (filter A) has been monitored since its commissioning in 2017 to assess the effluent's pH evolution due to alkalinity release from the material's binder. Three other WWTPs (B, C and D) with hydraulically different Phosclean® filters in operation since 2012 are also monitored: vertical up-flow (filter B); vertical down-flow (filter C) and horizontal flow (filter D).

Material and Methods

Assessment of the treatment plants was performed using regulatory surveys carried out since the beginning of plants operations. As treatment plants have not the same capacity, the number of regulatory surveys is heterogeneous and not high enough to have a precise estimation of saturation levels and retention kinetics. Consequently, additional measurement campaigns have been carried out over the past two years.

Four-day campaigns have been done twice per year for each WWTP. Campaign measurements include 24h-flow proportional samplings at the inlet and outlet of the Phosclean® filter in order to evaluate P retention performance; as well as, online P-PO4 measurements at the outlet of the filter to monitor possible dynamics within a day. In order to estimate P retention's kinetic, some spot-samplings are also done at different hydraulic retention times inside the granulated apatite filter. Mayor parameters as pH, conductivity, redox potential, TSS, BOD, COD, N, TP, P-PO43- and mayor anions/cations were analysed for all the samples. For filter A, a flowmeter and an online pH probe at the outlet of the filter have been implemented for several months.

To assess hydraulic performance, fluorescein-tracer tests were carried out to precisely determine water retention times and the occurrence of any flow alteration (short-circuiting, dead volumes, etc). Finally, dynamic penetrometer measurements will serve to assess potential changes on the material density due to surface precipitation.

Phosphorous retention in the apatite filter is performed through adsorption and precipitation phenomena (Harouiya *et al.*, 2011, Molle *et al.*, 2011). The process is evaluated using the KC* model (Kadlec and Wallace, 2008) based on plug-flow and first order kinetic:

$$C = (C_0 - C^*)e^{-k_v \cdot t_s} + C^* \qquad [1]$$

Where C is the P outlet concentration for a given residence time t_s, C_0 is the inlet concentration, k_v is the volumetric retention rate and C* is the residual P concentration.

Results and Conclusions

1. pH study

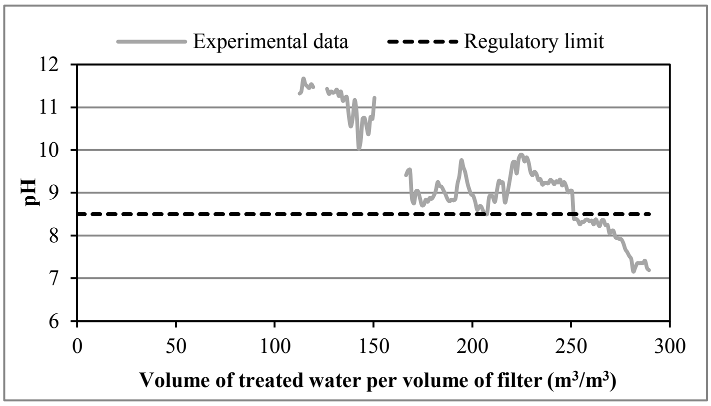

Figure 1. pH evolution for filter A.

Phosclean® granulated apatite uses a binder to agglomerate natural phosphate rocks so it can have the adequate size for filtration in WWTPs. This binder containing lime dissolves partially in contact with water increasing pH of the treated water as a result. The evolution of pH since the commissioning phase for filter A is presented in Figure 1. pH drops below the maximal regulation limit of 8.5 pH units after 250m^3 per m^3 of Phosclean® material.

2. Hydraulic performance

Hydraulic performance was studied by fluorescein-tracer tests. Results are shown in Table 1. Filter B presents constructive defects which leads to a 37% dead volume mainly localized at the first half of the filter as it was visually verified. The retention time determined is not representative of normal conditions because of rain occurrence during the test. A 30% of dead volume was also determined for filter C, however, none visual evidences of its localization were found in this case. For filter D, any dead volume was detected by tracer test but a short-circuit which has led to a hydraulic retention time (HRT) 10% lower than the theoretical HRT obtained. Nevertheless, it must be said that when the masse of tracer recovered is lower than 80%, results must be taken with care. This is especially important for filter D were spot-samplings have revealed that dead volumes are likely present in the filter.

Table 1. Results of fluoresceine tracer test for filters B, C and D.

	Filter B	Filter C	Filter D
Hydraulic load during tracer test	126 % of n.h.l.	45% of n.h.l.	55% of n.h.l.
Masse of tracer recovered	59%	100%	50%
Hydraulic residence time obtained by tracer test	6 hours	25 hours	56 hours
Theoretical hydraulic residence time	9 hours	36 hours	50 hours
Dead volume (percentage of filter's total volume)	37%	30%	Non dead vol.

*n.h.l: nominal hydraulic load.

Dynamic penetrometer measurements were also done at different spots in the filters and at different times to record an eventual evolution of media physical properties. This technique measures the resistance to soil penetration (shear strength) so it could account for density variations in the media due to disaggregation, compaction and/or crystallization of the granulated apatite.

Results for filter B show that the filtration bed is homogenous on the entire stretch, showing 1 to 2MPa of cone resistance on average in all its depth. For filter C, however, cone resistance increases gradually with depth (Figure 2), reaching maximal values of 4 to 8MPa on average for the different measurement campaigns done. These differences in between both vertical filters (B and C), may be due to wet and dry phase-alternation for filter C. Indeed, the outlet water of the TW by-passes the filter during winter season as no P regulation is requested for this period, drying up the filter as a result. Thus, different hypothesis for this increment in cone resistance could be considered: on one hand, as the filter dries slower at the deeper lawyers of the bed, crystallization phenomena onto the apatite surface could be exacerbated gluing the pellets against one another; on the other hand, the weight over the deeper lawyers of the granulated apatite, can lead to granulate disaggregation and its subsequent compaction during the drying period. The inside of the filtration bed is not readily accessible for visual inspection; however, both alterations of the media have been verified in other cases.

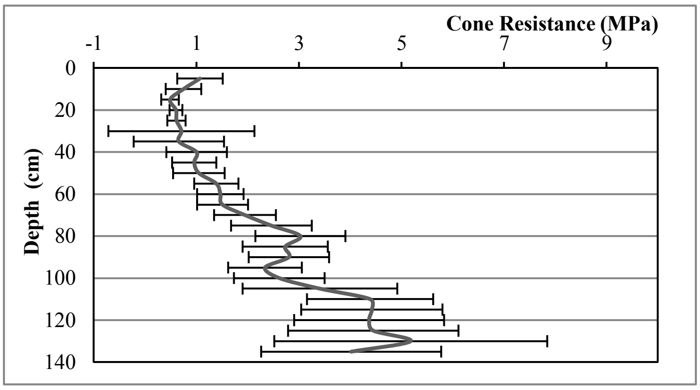

Figure 2 Mean cone resistance's evolution with depth at different localisations in filter C (Campaign of June 2017)

The great surface of filter D (5100m^2) plus some mismanagement observed during field campaigns has resulted in a quite heterogeneous media after six years of operation. The filtration bed shows high cone resistance at depths in between -10 and -30cm from surface at some regions far from the filter's inlet point. Indeed, the filter is expected to be hydraulically saturated; however, the water level was sometimes low drying up the more superficial lawyers of the filtration bed. Direct observation has revealed compaction and disaggregation phenomena of apatite granules at different spots in the filter.

3. Saturation and kinetics

Estimation of saturation conditions of the filtration bed has been done considering constant mean P inlet concentration and constant mean flow over the time. Figure 3 (left) shows that Filter B seems to approach its maximal saturation at 6gP/kg of material when taking into account the dead volume determined by tracer tests. This saturation is much lower than the one determined by Molle et al., (2011) with natural apatites, where the apatite filter still performed properly when reaching 14gP/kg of material. For filters C and D, the saturation level has reached 3.1 and 2.1gP/kg material, respectively during last campaigns. Filter's efficiency starts to decline as of 1.7 to 2.5gP accumulated per kg of material. This yield loss would be related to depletion of adsorption sites.

Sampling inside the filtering bed at different residence times is done to estimate the kinetic parameter k_v. Figure 3 (right) shows an example of experimental data fitting the model (Equation 1). For all the full-scale filters studied, the estimated k_v values are often lower than expected for a given saturation level of the media.

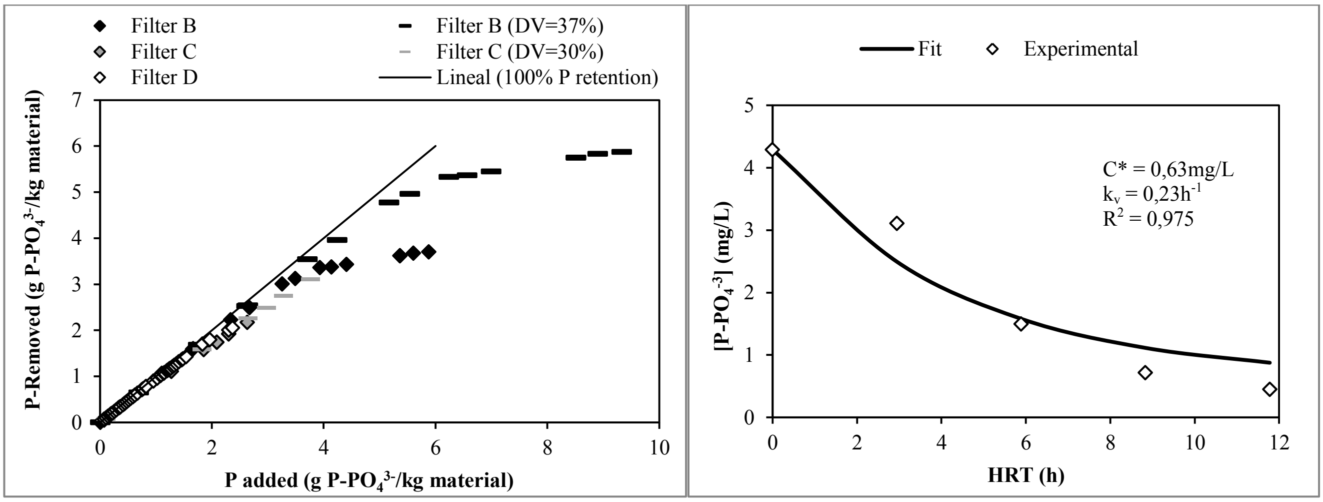

Figure 3. Left: Evolution of P retention efficiency of filters B, C and D (*DV: Dead volume); Right: Model fitting for filter C at an estimated saturation level of 2,7gP/kg material considering DV (Campaign of Octobre 2017)

Granulated apatite shows a weak P retention performance over the time leading to think that P retention is just done by means of adsorption onto the material and no precipitation mechanism is triggered off. Even though the occurrence of hydraulic malfunctions and the alteration of the physical properties of the granulated apatite sometimes observed, the fact that the binder used by Phosclean ® product covers apatite's surface, so that it cannot act like a seed for calcium phosphate precipitation, is the strongest hypothesis set up till now.

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