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Article

Combination of Slag, Limestone and Sedimentary Apatite in Columns for Phosphorus Removal from Sludge Fish Farm Effluents

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Abstract: Laboratory scale studies have repeatedly reported high P-retention in slag, a by-product of the steel manufacturing industry. Thus, it has emerged as a potential material to increase P-removal from constructed wetlands (CWs). However, several limitations were highlighted by field experiments, including the high pH of treated water and clogging. We hypothesized that the addition of sedimentary rocks to slag would preserve P-removal properties while reducing the pH of treated water. Four 2.5 L-columns were filled with 100% apatite (column A); a 50% weight each mixture of limestone with apatite (column B); 10% steel slag located at the inlet, plus 45% limestone mixed with 45% apatite (column C); and a mixture of steel slag (10%), limestone (45%) apatite (45%) (column D). A synthetic effluent (26 mg P/L) and a reconstituted sludge fish farm effluent containing 97 mg/L total suspended solids (TSS), 220 mg/L chemical oxygen demand (COD) and 23.5 mg P/L phosphorus (P) were applied sequentially during 373 and 176 days, under saturated flow conditions and 12–24 hours hydraulic residence time (HRT), respectively. Treatment performance, P-removal, pH and calcium (Ca²⁺) were monitored. Results indicated that columns that contained 10% weight steel slag resulted in a higher P retention capacity than the columns without steel slag. The highest P removal was achieved in column C, containing a layer of slag in the inlet zone, 45% apatite and 45% limestone.

Feeding the columns with a reconstituted fish farm effluent led to biofilm development, but this had little effect on the P-removal. A combination of slag and sedimentary rocks represents a promising filtration material that could be useful downstream of CWs to further increase P-removal.

Keywords: phosphorus retention; electric arc furnace steel slag; apatite; limestone; wastewater

1. Introduction

Over the last 10 years there has been a growing interest in using by-products of the steel and power plant industry to upgrade P-removal from constructed wetlands (CWs) [1-7]. However, apart from the investigation of a full scale filter for municipal wastewater treatment located in Auckland, New Zealand [7], the majority of studies have been limited to laboratory batch and column experiments, with a very limited number of field trials [8].

The results from these studies provided strong evidence that regardless of the type of steel slag used (e.g., electric arc furnace, blast furnace or iron melter slag), this material has a high affinity for phosphorus (P) [3-5]. However, the elevated pH of the steel slag effluent from laboratory studies [2,9,10] raised concerns about the use of this material for field applications. Weber *et al.* [11] and Drizo *et al.* [5] investigated long term performance (200 and 850 days, respectively) of an electric arc furnace (EAF) steel slag in P reduction from a dairy farm effluent in Vermont and showed that at 1 day hydraulic retention time (HRT) steel slag filter effluent pH was elevated only during the first 3 weeks of operation, after which the pH stabilized to less than 8.5. However, while agricultural effluents (dairy runoff, milk parlor, pig farms, silage leachate) are typically characterized by high to very high concentrations of P (15–2,000 mg P/L), fish farm sludge effluents contain lower (20 mg P/L) P concentrations.

P removal by any filtration material will depend on the type (e.g., dairy or residential wastewater or stormwater runoff) and flowrate (contact time between material and the wastewater) of the effluents that need to be treated [12]. In the case of steel slag, P-removal mechanisms are largely influenced by the type of material used and the manufacturing process [5]. Drizo *et al.* [5] recently pointed out that different steel-making practices and source materials, such as iron ore, coal, or steel scrap, can have a marked impact on a slag's performance and highlighted the fact that it is necessary to test the P adsorptive capability of individual slag materials. For example, Yamada *et al.* [13] and Sunahara *et al.* [9] suggested that Ca-P precipitation followed by seeded crystallization is a principal P removal process in basic oxygen furnace (BOF) steel slag. Pratt *et al.* [14] investigated P removal in iron smelter slag in New Zealand where it has been operating for 14 years and concluded that P-adsorption onto Fe metal oxides represents a major process of P removal.

In order to reduce effluent pH while maintaining a high P-removal, Baker *et al.* [1] used a mixture of slag and Ca rich materials. Our study aimed at testing a mix of slag, limestone and sedimentary apatite to remove phosphorus from wastewater. We hypothesized that adding sedimentary rocks rich in calcium and apatite to slag would preserve P-removal properties, while reducing the pH of the treated

water and acting as a seed germ for P-crystallization at the same time. In addition, we tested the P removal from both a synthetic solution and a real wastewater effluent to assess the effect of COD, TKN and TSS on P removal processes.

2. Materials and Methods

2.1. Laboratory Scale Columns

Electric arc furnace (EAF) slag (5–10 mm), sedimentary limestone (2.5–5 mm) and sedimentary apatite rock (2.5–5 mm) were used in the column experiments. More details on the EAF slag are given in Drizo *et al.* [3,5] and Chazarenc *et al.* [15], while characteristics of sedimentary apatite from Cargill (Florida, USA) and limestone from Graymont (Quebec, Canada) are described in Bellier *et al.* [16].

Four identical lab scale columns of 2.5 L each (Figure 1), were filled with apatite, and different apatite, limestone and EAF steel slag mixtures as follows: column A: (100% apatite); B (50% limestone mixed with 50% apatite, w/w); C (10% EAF steel slag located at the inlet and 45% limestone mixed with 45% apatite, w/w); D also contained 10% EAF steel slag and 45% limestone and apatite, w/w, but the materials were completely mixed together). Weights of material and pore volumes are presented in Table 1.

Figure 1. Experimental set up. Lab scale experiment (section view).

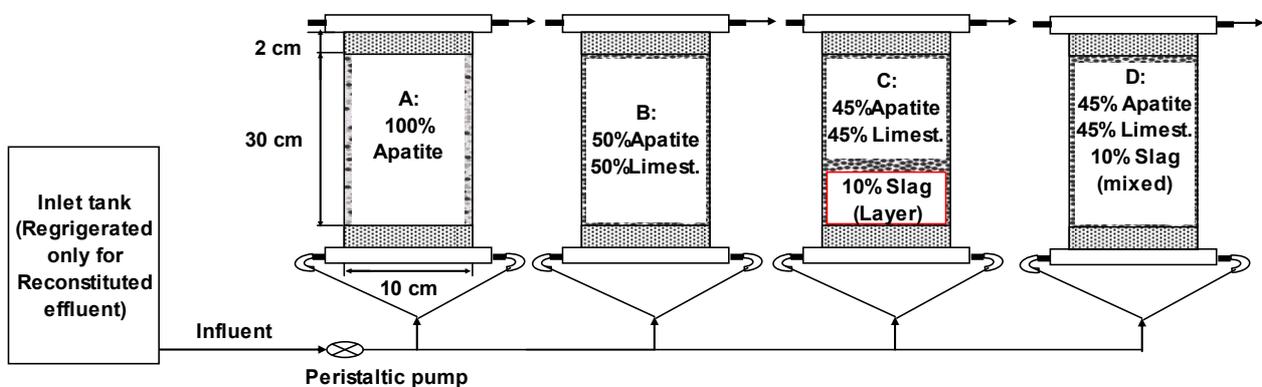


Table 1. Details on the three steps investigated and columns composition.

| | Residence time distribution (h) | Type of wastewater | Duration (days) | | Pore volumes (mL) | Total material weight (g) |
|----------|---------------------------------|------------------------|-----------------|----------|-------------------|---------------------------|
| Step I | 28 | Synthetic P solution | 0–55 | Column A | 313 | 3,360 |
| Step II* | 14 | Synthetic P solution | 56–373 | Column B | 250 | 3,400 |
| Step III | 28 | Reconstituted effluent | 374–547 | Column C | 293 | 3,715 |
| | | | | Column D | 314 | 3,655 |

* Columns were emptied, dried and rested to test P rejuvenation in the four different materials, according to Drizo *et al.* [3,5] between days 187–218.

A synthetic effluent (using KH_2PO_4 and K_2HPO_4 with tap water to obtain a dissolved P concentration of 26 mg/L and pH of 7.4) and a reconstituted fish farm sludge containing 97 mg/L TSS,

220 mg/L COD and 23.5 mg P/L were applied sequentially during 373 and 173 days (Table 1). The hydraulic retention time considering the void volume was 24 or 14 hours during Steps I-III and II, respectively.

2.2. Sampling and Analysis

Effluent samples were collected from the outlet of each column using a closed bucket ($V_{\text{tot}} = 5 \text{ L}$) to minimize evaporation and atmospheric CO_2 dissolution. Outlet volume and inlet/outlet samples were typically measured and taken every third day, respectively. Alkalinity, pH and conductivity were measured just after sampling by using a pH probe, and an acid titration and conductivity probe, respectively, according to Standard Methods [17]. Orthophosphates and total phosphorus were measured using the Lachat QuickChem flow injection analysis method # 10-115-01-1-Q, derived from the automated ascorbic acid reduction method. TSS, COD and sCOD (soluble COD), Ca^{2+} and ionic measurements of tested materials were determined by atomic absorption spectroscopy, all according to Standard Methods [17]. Tap water was used to prepare the synthetic P-solution and the reconstituted effluent which resulted in an inlet Ca^{2+} concentration of 30 to 35 mg/L. Calcium phosphate supersaturation is required to generate Ca-P crystallization [18]. Thus, we monitored the concentration of Ca^{2+} at the inlet and outlet of the 4 columns to gain a better understanding of the P-removal mechanisms within the 4 selected materials. After 549 days of experiment, the columns were opened slag and media were sampled and the chemical composition of P-rich minerals were analyzed after loss on ignition (550 °C) using an atomic absorption spectroscopy method [17].

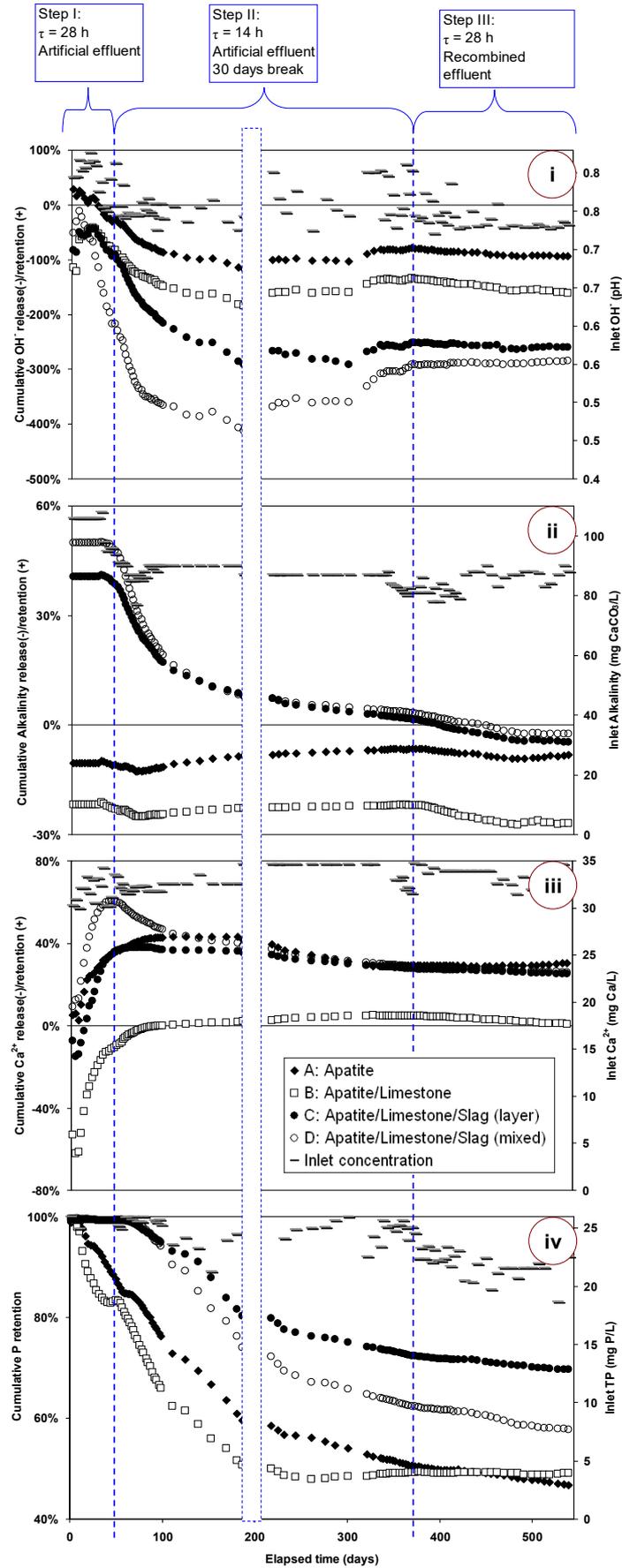
3. Results

3.1. Treatment Performance

During the first feeding period (Step I), P-retention by the apatite (column A) and a mix of apatite/limestone (column B) were lower than in the slag columns (C and D) and decreased rapidly [Figure 2(iv)]. The amount of cumulated OH^- released was similar in both slag columns and slightly lower for sedimentary rocks [Figure 2(i)].

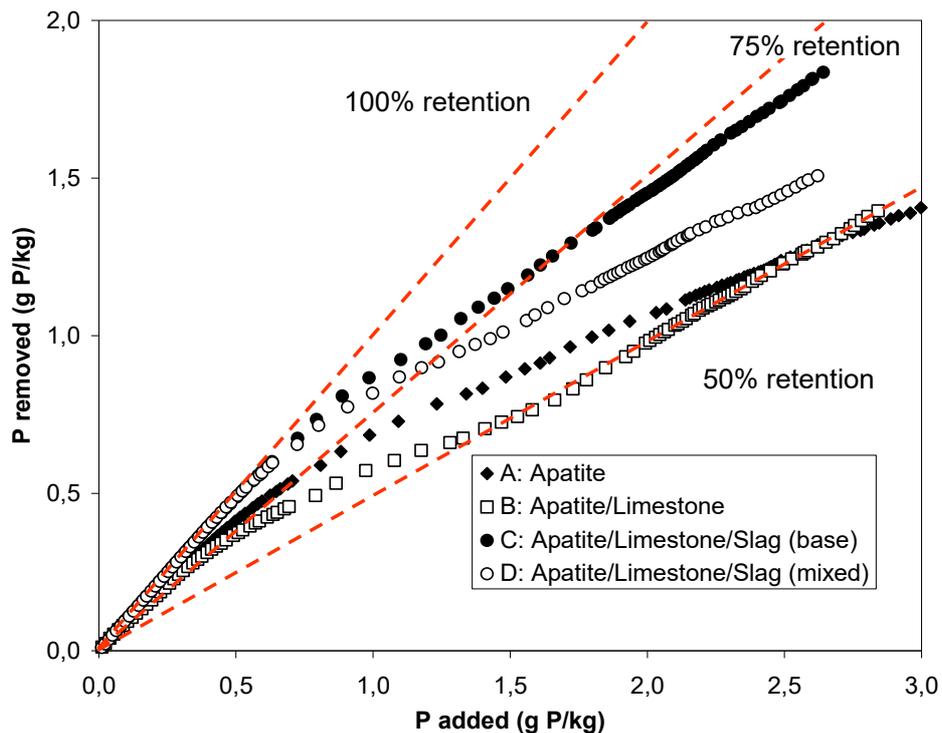
During the second feeding period (Step II), when the hydraulic retention time was reduced and a decrease in P removal was measured in all columns. The rejuvenation break had only a slight effect on the treatment performance of column A and was not significant for column B. After 300 days of experimentation. P-retention was close to 50% and remained relatively constant in column A, confirming the potential use of natural apatite as a reactive material [15]. The behavior of the two slag columns (C and D) was similar from the beginning of the experiment until day 100. From this point, the removal in column D (mixed media) decreased faster than in column C (slag upstream). Unlike in other studies on P removal with steel slag filters in which drying and resting of the material for the periods of 4-5 weeks resulted in P rejuvenation and a prolonged filter's P treatment efficiency [3,5], resting of the columns C and D in our study did not result in P rejuvenation.

Figure 2. Evolution of inlet concentration (mg/L), pH and cumulative release/retention of (i): OH⁻, (ii): alkalinity, (iii): Ca²⁺, (iv): TP.



During the third feeding period (Step III), 1.6, 1.4, 1.3 and 1.3 g P/kg media were added and 0.6, 0.7, 0.8 and 0.6 were retained, respectively, by columns A, B, C and D (Figure 3). At the point of reconstituted fish farm effluent addition to the columns, P-removal efficiencies fell from 86 to 50 % in column A; 83 to 49% in column B, 99 to 72% in column C, and 98 to 62% in column D. During a 200 day period of feeding with reconstituted fish farm effluent, P removal efficiency decreased further to 46% (A), 49% (B), 69% (C) and 57% (D), respectively.

Figure 3. P removed as a function of P added.



In terms of TSS, COD and TKN removal (Table 2) all four columns achieved performances comparable to that of a saturated sand filter treating secondary/tertiary effluent with a 1 day retention time. The outlet pH was about 8.0 in all columns and P-removal was still higher than 75% in column C.

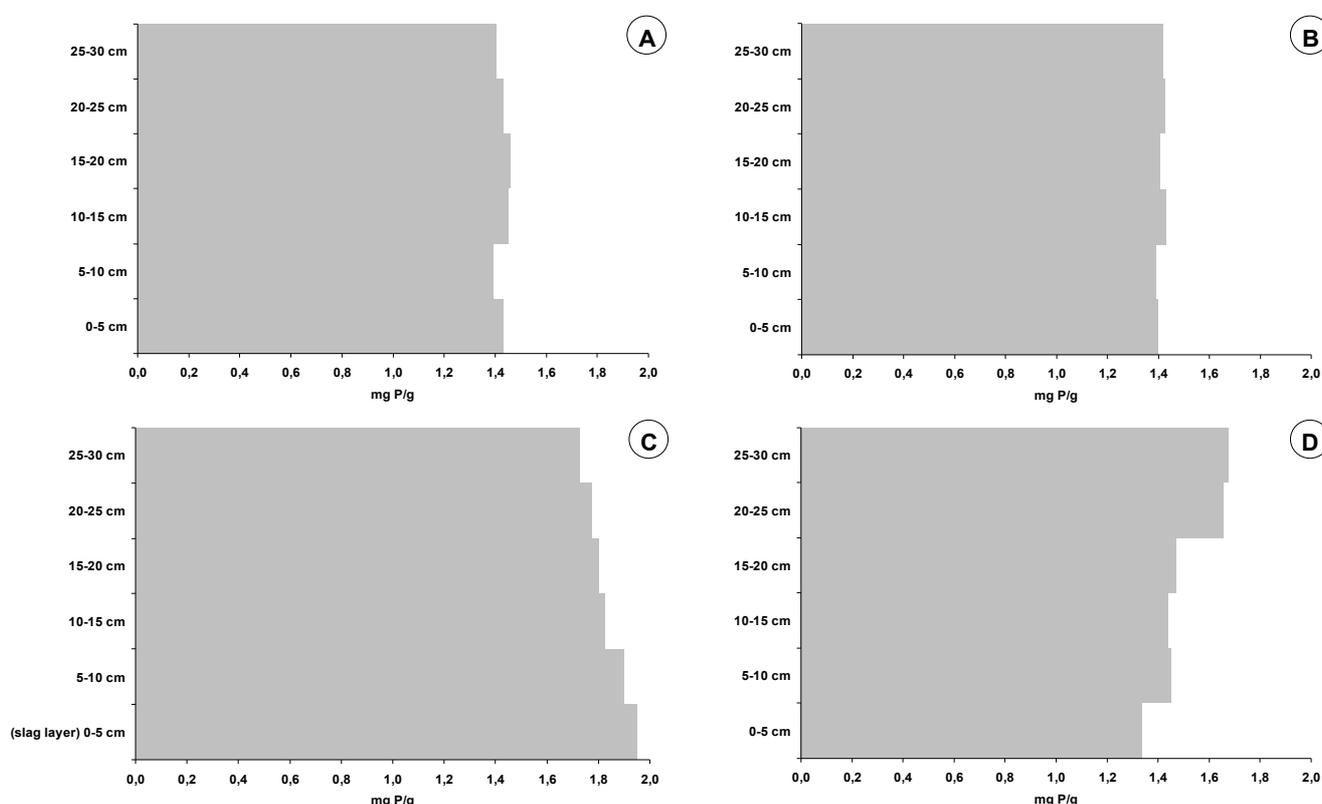
Table 2. Treatment performance observed during the reconstituted sludge fish farm effluent feeding step (Step III).

| | pH | TSS mg/L | COD | TKN mg N/L |
|--------------|-----------|-------------|----------|---------------|
| Inlet | 7.4 ± 0.2 | 97 ± 29 | 219 ± 90 | 15.3 ± 1.1 |
| A | 7.8 ± 0.3 | 6 ± 4 | 25 ± 16 | 9.1 ± 1.0 |
| B | 8.0 ± 0.3 | 6 ± 5 | 28 ± 19 | 7.7 ± 3.2 |
| C | 8.0 ± 0.3 | 6 ± 4 | 24 ± 13 | 10.2 ± 0.2 |
| D | 7.9 ± 0.3 | 6 ± 4 | 28 ± 19 | 8.5 ± 3.8 |

3.2. Overall P-Retention Capacity

P-removal efficiency was highest in column C, which achieved nearly 75% P removal (Figure 3). The amount of P retained (about 1.7 g P/kg material) for the amount of P added was comparable to values reported by Drizo *et al.* [12] and Weber *et al.* [11], who studied filters with 100% steel slag filters. The outlet pH of the slag columns was always below 8.5, meaning that the P-removal was achieved without generating an alkaline effluent requiring an acidification before disposal. Regarding the distribution of retained P in the column (Figure 4), it was more homogeneous in columns A and B. In columns C, the maximum amount of P was retained at the bottom of the column, in the slag layer, identified as the 0–5 cm layer in Figure 4. In column D, the P was retained mostly near the outlet.

Figure 4. P content in different layers after 549 days of experiment (mg P/g of reactive media in each column) A: apatite, B: 50% apatite + 50% limestone, C: ternary mix slag at the base, D: ternary mix (mixed). Columns (30 cm deep) were fed from the bottom (0 cm).



4. Discussion

4.1. P Removal Mechanisms

OH^- release by each column was measured every third day [Figure 2(i)]. During the first 100 days of the experiment the OH^- release was observed mostly in the slag columns due to lime dissolution. More OH^- release took place in column D than in the other columns. Since the amount of slag added in both columns C and D was the same, it suggests that the amount of OH^- reacting with Ca-P complex (including hydroxyapatite, HAP) was greater in column C.

Ca^{2+} retention was most probably a consequence of complex Ca-P precipitation and/or HAP precipitation and crystallization. In column A, Ca^{2+} retention occurred during the entire experiment and averaged 40%. In column B, Ca^{2+} release was observed at the beginning of the experiment (phases I and II), most likely linked to the dissolution of CaCO_3 , and then neither retention nor release were observed. This confirms that limestone plays a role in dissolving some Ca^{2+} into the column. In the slag columns, Ca^{2+} retention reached a maximum (60 % in column D) during the first feeding period [Figure 2(iii)]. This was associated with the max P-retention, supporting the hypothesis of HAP formation. Then a decrease of Ca^{2+} retention appeared, along with a decrease of P-retention.

It has been mentioned several times in the literature that the presence of alkalinity, either as HCO_3^- or CO_3^{2-} , can lead to a competitive reaction to that of HAP formation by removing available Ca^{2+} to form CaCO_3 [15,18,20]. In our experiment, alkalinity was released from columns A and B [Figure (2ii)], most probably due to CaCO_3 dissolution from the limestone. In slag columns, however, retention of alkalinity was first observed and it was larger in column D, which seemed correlated with the larger Ca^{2+} retention than in column C. The presence of slag in an upstream layer (column C) as opposed to being mixed with other materials (column D) resulted in a better long term P removal. This could be explained by the fact that a higher pH should have been reached in the slag layer, favoring the formation of more stable Ca-P precipitates and possibly of less CaCO_3 formation.

When feeding columns with a reconstituted effluent, good COD and TSS but poor TKN removal were observed, especially in column C. This was probably due to the Eh conditions in the slag layer having a negative impact on nitrification process [21]. Feeding the columns with a reconstituted fish farm effluent led to biofilm development, which was determined to be about 2 g of organic matter /100 g media in each column at the end of the experiment. This organic matter accumulation, however, had little effect on the P-removal, as indicated by the slight change in the slope of P-removal [Figure 2(iv)].

Emptying and resting of the columns C and D during 30 days did not result in P rejuvenation in the mixture of materials used in our study, possibly due to the resting period used being too short.

4.2. Influence of Sedimentary Rocks

P-retention by the apatite used (column A) rapidly decreased in comparison to the other media combinations used, reaching a low level of about 45% during the middle of step II [Figure (2iv)]. It was shown in a previous study [16] that the associated gangue of apatite from North America is systematically removed, which is most likely reducing the amount of calcium and hydroxide available and thus reducing the Ca-P nucleation performance. The use of untreated natural apatite showed a significant dissolution of calcium carbonate (5 mg Ca/L) leading to a pH increase from 7.0 to 8.0 and a good P retention (>14 mg P/g apatite [19]).

The addition of limestone was proposed to increase treatment performance of apatite [16], a hypothesis that is supported again by this study since the P removal was maintained at around 50% in column B, whereas in column A a net decrease below 40% was observed at the end of the study (Figure 3). The contribution of slag was clearly positive for P removal in both column C and D. It enabled to increase the overall capacity from 1.4 to 1.8–2.0 g P/kg media in column C, a range which is comparable to that observed in other studies [22], while maintaining the effluent pH below 8.0. The

presence of a slag layer at the upstream end of the column had a positive effect on P removal and enabled to reach a better removal performance, as confirmed by the analysis of the P content in each layer (Figure 3).

5. Conclusions

Our study confirmed that for phosphorus removal, the long term efficiency of sedimentary apatite (Cargill, North America) in a filtration media operated at a hydraulic retention time of 14 to 28 hours, can be slightly improved by adding limestone (50% global P removal in both cases) and significantly improved by adding electric arc furnace slag. The best results were obtained when the slag was located at the upstream end of the column (70% global P removal) instead of being completely mixed with the apatite and limestone (60% global P removal). After 18 months of operation, the media had accumulated 1.3 to 1.7 g P/g media without being saturated. In all cases the media used resulted in an effluent pH below 8, allowing its direct discharge into the environment. Despite feeding the columns during the last 6 of the 18 months of experimentation with a fish farm reconstituted effluent, the organic matter accumulation did not appear to affect much the P removal efficiency in any column.

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