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Abstract

This study aimed at evaluating the potential use of carbonated bauxite residue (CBR) as filter substrate to upgrade phosphorus (P) removal in small wastewater treatment plants such as constructed wetlands. Comparative experiments of P removal were performed in two columns continuously fed with synthetic and real wastewater to investigate the behavior of CBR under aerobic (column A) and anoxic biotic conditions (column B). The effect of various parameters, including pH, temperature, addition of organic carbon, and dissolved oxygen concentration, was investigated. Also, a series of chemical extractions was performed to elucidate the main mechanisms of P removal achieved by CBR. Over 140 days of operation, columns A and B showed a total P removal performance of 98.5% and 91.6%, thus reaching a total P removal capacity of 0.63 mg P/g CBR and 0.61 mg P/g CBR, respectively. The results indicate that

aeration conditions and microbial activity can significantly affect the performance of CBR filters. Under aerobic conditions, precipitation of Ca-P complexes appears to be the main mechanism leading to P removal. Under anoxic biotic conditions, microbially driven mobilization of Fe from CBR may provide Fe ions for Fe-P precipitation, but also it may lead to Fe release from the filters. This study provides crucial information to evaluate the potential use of CBR at different steps of the wastewater treatment process. Overall, the results indicate that the use of CBR filters is particularly suitable as a tertiary treatment step to remove P from effluents with low organic load under aerobic conditions.

Keywords: wastewater treatment; phosphorus removal; bauxite residue; constructed wetland; reactive filter.

1 Introduction

Nowadays, improving phosphorus (P) removal performances in small wastewater treatment plants (WWTPs) such as constructed wetlands (CWs) represents a topical issue for researchers and professionals in the field of wastewater treatment [1]. Several strategies are currently being studied, including the enhanced P biological uptake by intermittent aeration [2], the use of electrochemical methods to intensify electron exchanges [3], the improvement of iron dosing strategies for efficient P removal [4], and the selection of wetland plants and substrate materials with high P sorption capacities [5,6]. During the last decade, the use of separate filter units filled with reactive materials having a high affinity for P binding has been proposed as a promising solution to upgrade P removal performances in CWs [7–10]. A large variety of reactive materials, including natural soils and sediments, industrial wastes and by-products, and manufactured adsorbent materials, have been tested for P removal [11–13]. Most of these materials present high contents of calcium (Ca), iron (Fe), and/or aluminum (Al), which are elements with a strong affinity for P binding [13,14].

Several international studies have demonstrated that bauxite residue, a Fe and Al oxide-rich waste from the aluminum industry, is an efficient filter material for P removal from wastewater [15–18]. According to Evans [19], aluminum industry produces about 150 Mt per year of bauxite residue worldwide, of which no more of 3-5% is reused in a productive way (*e.g.* cement and ceramic production) [20]. This indicates a very interesting potential market of bauxite residue valorization as filter substrate in CWs. Maximum P removal capacities ranged from 6 to up than 12 mg P/g bauxite residue [16,17], thus depending on the type and composition of bauxite residue and on the experimental parameters established for the experiments. The main mechanisms leading to P removal were anionic adsorption on functional sites (*e.g.* -OH) and precipitation of Ca-P complexes on the mineral surface of bauxite residue [17]. Due to its high alkaline nature [19], bauxite residue can produce high pH leachates (up to 13) [20], and therefore a pretreatment with gypsum was efficiently proposed by Cusack *et al.* [15] to neutralize its alkalinity and reduce pH leachates below 9. However, most of these studies were performed in batch and using synthetic P solutions, which did not contain all the components occurring in real effluents that may affect P removal performances (*e.g.* microorganisms and organic compounds, competing ions, suspended solids). Moreover, results from batch experiments usually cannot be directly employed to preview the behavior of field scale filters, as treatment performances and P removal mechanisms can differ under dynamic operating conditions. To the best of our knowledge, only a study in the literature has investigated P removal performances of bauxite residue in small-scale columns continuously fed with real effluents [21]. Furthermore, there is a lack of data in the literature concerning the effect of aeration conditions and microbial activity on the performance of bauxite residue filters.

This study aimed at evaluating performances and determining P removal mechanisms of carbonated bauxite residue (CBR) under aerobic and anoxic biotic conditions. Indeed, the organic content in wastewater and/or the addition of external organic carbon to the effluents,

which is often used as a strategy to enhance heterotrophic denitrification in WWTPs [22,23], may promote the establishment of anoxic biotic conditions in water saturated filters. Therefore, knowledge and understanding of the effect of different aeration conditions and microbial activity on the behavior of CBR are indispensable to evaluate its potential use as filter substrate at different steps of the wastewater treatment process in CWs. The novelty and importance of this paper are highlighted by the following two points:

(i) The first comparative investigation of P removal performances of CBR under aerobic and anoxic conditions in dynamic flow experiments. Two laboratory scale columns were filled with CBR and continuously fed with synthetic and real CW effluents. The effect of various parameters, including pH, temperature, addition of organic carbon, and dissolved oxygen concentration, on P removal performances was investigated.

(ii) An in-depth critical investigation of the P removal mechanisms achieved by CBR. A systemic approach, which involves the integration and analysis of the experimental results of water quality monitoring and chemical extractions from CBR, was followed to investigate mineralogical changes and to elucidate the main mechanisms of P removal achieved by CBR under aerobic and anoxic biotic conditions.

Overall, the results of this study allow evaluating the behavior of CBR under real operating scenarios, and they provide crucial information for the scale up of the filters from the laboratory to the field scale.

2 Materials and methods

2.1 *Bauxite residue collection and preparation*

The samples of bauxite residue used in this study were provided by the company ALTEO (Gardanne, France). Their main chemical composition was Fe_2O_3 (45-53%), Al_2O_3 (10-16%), TiO_2 (9-15%), SiO_2 (5-8%), CaO (3-8%), and Na_2O (3-5%) (data from ALTEO). Before

column experiments, bauxite residues were mixed with gypsum ($CaSO_4 \bullet 2H_2O$) at a dried mass ratio of 5% (mass of gypsum to mass of bauxite residue) and put in contact with the atmosphere to produce CBR. This was done to neutralize the NaOH content of bauxite residue by carbonation and calcium carbonate precipitation, according to equation (1), and to decrease the pH of CBR leachates below a value of 9 as described by Cusack *et al.* [15] and experienced in large scale on the storage site of ALTEO.

$$2NaOH + CaSO_4 \cdot 2H_2O + CO_2 \rightarrow CaCO_3 + Na_2SO_4 + 3H_2O \quad (1)$$

After carbonation, CBR was sieved and the fraction less than 2 mm was collected to perform column experiments. CBR samples were dried at 45 °C overnight to reduce their water content before the experiments. The temperature of 45 °C was selected in order to reduce the risk of changes in the mineralogical composition during drying [24]. The remaining water content of CBR was determined after heating at 105 °C until constant weight.

2.2 *Set-up of column experiments*

Two glass columns of total volume 0.59 L were filled with about 0.35 L of CBR each, thus corresponding to about 0.45 kg dried mass of CBR *per* column (columns A and B). The main details of the column design are shown in Fig. 1. During the full period of operation, the columns were continuously fed according to a vertical up-flow of about 12 mL/h, thus giving a theoretical hydraulic retention time based on the initial void volume (HRT_v) of around 24 h. During the first 54 days of operation, column A was fed with a synthetic solution of about 10 mg P/L and 40 mg N/L (prepared with tap water, KH_2PO_4, and KNO_3). These P and nitrogen (N) concentrations are in good agreement with the average outlet concentrations of vertical flow CWs in France (total-P 8 ± 3 mg P/L, phosphate-P 8 ± 2 mg P/L, total Kjeldahl-N 7 ± 7 mg N/L, ammonium-N 5 ± 6 mg N/L, and nitrate-N 56 ± 25 mg N/L, average values ± standard deviations of 151 plants) [25]. Then, from day 55 to 140, the column A was fed with the real

effluent of a vertical flow CW that treats the domestic wastewater of a small French municipality (1500 people equivalent, Rougiers, France). During the same periods of operation, the column B was operated identically to column A, but with the only difference that the feeding solutions were enriched with about 0.5 g/L of glucose. This was done to favor the establishment of anoxic metabolic conditions in column B. Column experiments were performed at the laboratory under room temperature conditions (22.7 ± 2.1 °C, average value ± standard deviation, 4 measures per week). Main composition and physical-chemical properties of the inlet solutions are summarized in Table 1.

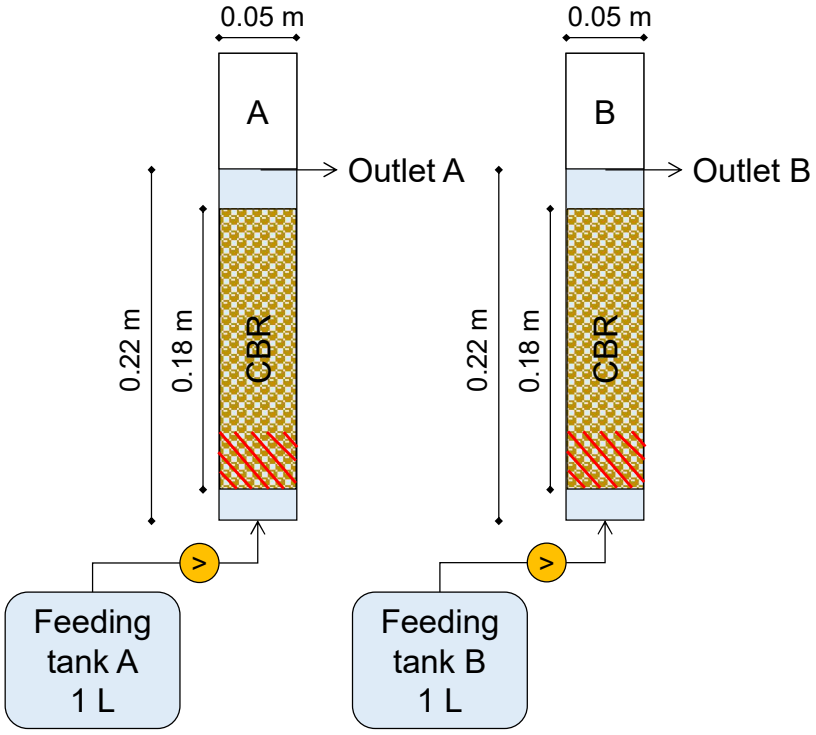


Fig. 1. Design of columns A and B (the dashed area shows the samples used for chemical extractions).

2.3 *Water quality monitoring*

Inlet and outlet values of pH, redox potential (Eh), and dissolved oxygen (DO) were measured twice per week by water probes. Water samples (about 40 mL) were collected from the inlet

and from the outlet of each column twice per week. Then, total phosphorus (TP), phosphate (PO_4-P), total N (TN), chemical oxygen demand (COD), Al, Ca, and Fe concentrations of the water samples were measured. TP concentrations were determined after persulfate digestion (EN ISO6878, 2004), whereas PO_4-P, Al, Ca, and Fe concentrations were determined after filtration (0.45 μm filters) of the water samples. Differences between TP removal efficiencies of columns A and B were tested by the non-parametric Mann-Whitney U test, and were considered significant at p-value < 0.05. Analytical and statistical methods are described in the supplementary information (SI).

2.4 *Chemical extractions*

A series of chemical extractions was performed to investigate the P content and chemical changes of CBR before and after column experiments, and hence to elucidate the main P removal mechanisms occurring in the columns. Samples of CBR were taken at the inlet-zone of the columns A and B after 140 days of operation (Fig. 1). Since this zone was exposed to inlet P-rich wastewater, these samples were likely to have had a high amount of P bound to their surfaces. Before the chemical extractions, the samples of CBR were dried overnight at 45 °C to reduce water content and to avoid mineralogical changes deriving from high-temperature drying [24].

Aqua regia extractions were performed according to standard methods (EN 13346, 2000; EN 13657, 2003) to determine the total P content of CBR before and after column experiments.

A series of chemical extractions was performed to quantify the amount of reactive amorphous and crystalline Fe (hydro)xides and Al (hydro)xides on CBR samples before and after their use in the columns. Indeed, speciation of reactive Fe and Al compounds in CBR may give useful information to better understand and describe the P binding mechanisms [26]. Amorphous Fe,

crystalline Fe, and Al (hydro)xides extractions were performed according to standard method ISO 12782-1 (2009), ISO 12782-2 (2009), and ISO 12782-3 (2009), respectively.

A sequential extraction protocol, adapted from Tiessen and Moir [27], was followed to quantify the fractions of P bound to different mineral compounds in CBR before and after column experiments. Four fractions of P were sequentially extracted from 1 g of CBR (dried mass equivalent) following the procedure described in Barca *et al.* [28]:

i. Bicarbonate extractable inorganic P: this fraction is defined as weakly bound P, as P extraction is mainly due to washing and ion exchange;

ii. Hydroxide extractable inorganic P: this fraction is primarily related to dissolution of Al and Fe bound P compounds that are soluble at high pH;

iii. Diluted acid extractable inorganic P: this fraction is defined as Ca bound P, as P extraction is mainly due to dissolution of Ca-P complexes at low pH;

iv. Hot concentrated acid extractable organic and inorganic P: this fraction represents P in stable residual compounds that need much more energy to be dissolved.

The detailed protocols of the chemical extractions are presented and discussed in SI. All chemical extractions were performed in duplicate or triplicate.

3 Results and discussion

3.1 *P removal performances*

The average values and standard deviations of inlet and outlet TP, PO_4-P, DO, pH, Eh, TN, COD, Fe, Al, and Ca of columns A and B over day 1-54 (synthetic solution feeding) and day 55-140 of operation (real effluent feeding) are summarized in Table 1. A slight COD release from column A was observed only during the first 3 weeks of operation, with outlet concentrations up to 52 mg COD/L. This was primarily attributed to the use of organic

flocculants (polyacrylamide) during the dewatering process of bauxite residue [19]. For both the columns, the average inlet TP concentration was 10.3 ± 0.5 mg P/L during the first period of operation (synthetic solution feeding) and 5.5 ± 1.5-1.7 mg P/L during the second period of operation (real effluent feeding). Results in Table 1 also indicate that PO_4-P represent more than 98% of inlet TP for synthetic solutions (day 1-54), and more than 89% of inlet TP for real effluents (day 55-140). The difference between TP and PO_4-P content in real effluents was primarily attributed to stable organic P and P content in microorganisms [29]. Over the full period of 140 days of operation, inlet and outlet DO concentrations of column A were 6.4 ± 1.0 mg O_2/L and 2.3 ± 1.4 mg O_2/L, respectively, whereas inlet and outlet DO concentrations of column B were 2.0 ± 3.2 mg O_2/L and 0.3 ± 0.4 mg O_2/L, respectively, with outlet DO stabilizing below a value of 0.3 mg O_2/L after day 28 of operation (Fig. S1.B). These results indicate that column A was operated under aerobic conditions during the full period of operation (day 1-140), whereas column B was operated under anoxic conditions, this especially during the second period of operation (day 55-140).

1 Table 1. Main water quality parameters at the inlet and at the outlet of columns A and B during
2 day 1-54 (synthetic solution) and day 55-140 (real effluent feeding): average values ± standard
3 deviations (number of measurements).

Parameter	Column A		Column B	
	Day 1-54	Day 55-140	Day 1-54	Day 55-140
Inlet TP (mg P/L)	10.3 ± 0.5 (15)	5.5 ± 1.5 (25)	10.3 ± 0.5 (15)	5.5 ± 1.7 (25)
Outlet TP (mg P/L)	0.1 ± 0.1 (15)	0.1 ± 0.2 (25)	0.1 ± 0.1 (15)	0.9 ± 0.9 (25)
Inlet PO_4-P (mg P/L)	10.2 ± 0.6 (15)	5.4 ± 1.5 (25)	10.1 ± 0.6 (15)	4.9 ± 1.6 (25)
Outlet PO_4-P (mg P/L)	0.1 ± 0.1 (15)	0.1 ± 0.2 (25)	0.1 ± 0.1 (15)	0.6 ± 0.7 (25)
Inlet DO (mg O_2/L)	6.7 ± 1.4 (13)	6.2 ± 0.8 (25)	4.7 ± 3.7 (13)	0.7 ± 1.7 (25)
Outlet DO (mg O_2/L)	1.9 ± 1.9 (13)	2.6 ± 1.0 (25)	0.6 ± 0.7 (13)	0.2 ± 0.1 (25)
Inlet pH (-)	7.7 ± 0.2 (15)	7.6 ± 0.3 (25)	7.4 ± 0.3 (15)	6.4 ± 0.5 (25)
Outlet pH (-)	8.8 ± 0.3 (15)	8.0 ± 0.4 (25)	8.3 ± 0.4 (15)	7.2 ± 0.3 (25)
Inlet Eh (mV)	193 ± 11 (15)	176 ± 20 (25)	207 ± 12 (15)	242 ± 34 (25)
Outlet Eh (mV)	135 ± 16 (15)	156 ± 18 (25)	158 ± 19 (15)	197 ± 20 (25)
Intel TN (mg N/L)	37.0 ± 4.5 (8)	40.8 ± 16.4 (13)	35.1 ± 5.3 (8)	43.3 ± 19.6 (13)
Outlet TN (mg N/L)	15.0 ± 22.5 (8)	15.7 ± 9.9 (13)	7.4 ± 14.8 (8)	5.7 ± 3.1 (13)
Inlet COD (mg O_2/L)	< 10 (3)	< 10 (3)	490 ± 277 (8)	350 ± 56 (13)
Outlet COD (mg O_2/L)	42 ± 23 (5)	< 10 (4)	376 ± 370 (8)	120 ± 24 (13)
Inlet Fe (mg Fe/L)	< 0.01 (3)	0.02 ± 0.03 (10)	0.08 ± 0.09 (3)	0.11 ± 0.04 (10)
Outlet Fe (mg Fe/L)	0.28 ± 0.69 (7)	0.19 ± 0.17 (10)	0.08 ± 0.11 (7)	1.26 ± 0.61 (10)
Inlet Al (mg Al/L)	< 0.01 (3)	0.72 ± 1.80 (10)	0.08 ± 0.13 (3)	0.07 ± 0.22 (10)
Outlet Al (mg Al/L)	32.6 ± 3.9 (7)	5.8 ± 9.2 (10)	9.99 ± 8.38 (7)	0.52 ± 0.34 (10)
Inlet Ca (mg Ca/L)	92 ± 5 (7)	265 ± 63 (7)	120 ± 20 (7)	268 ± 8 (7)
Outlet Ca (mg Ca/L)	701 ± 662 (7)	82 ± 56 (7)	707 ± 778 (7)	264 ± 18 (7)

4

As shown in Fig. 2A, outlet TP concentrations of column A were always lower than 0.7 mg P/L with an average value of 0.1 mg P/L. This indicates very high P removal efficiencies of column A during the full period of operation (day 1-140). Over the first period of operation (day 1-55), column B showed outlet TP concentrations always lower than 0.2 mg P/L, thus showing very high P removal efficiencies (> 98%). However, a decrease in P removal performance of column B was observed during the second period of operation (day 55-140), when an average outlet TP concentration of 0.9 mg P/L and some massive releases of P (outlet TP > 2 mg P/L) were observed (Fig. 2B). The results from non-parametric Mann-Whitney U tests (SI) indicate that the differences between TP removal efficiencies of columns A and B were not significant during day 1-54 of operation (p-value = 0.528), whereas they were significant during day 55-140 of operation (p-value < 0.0001).

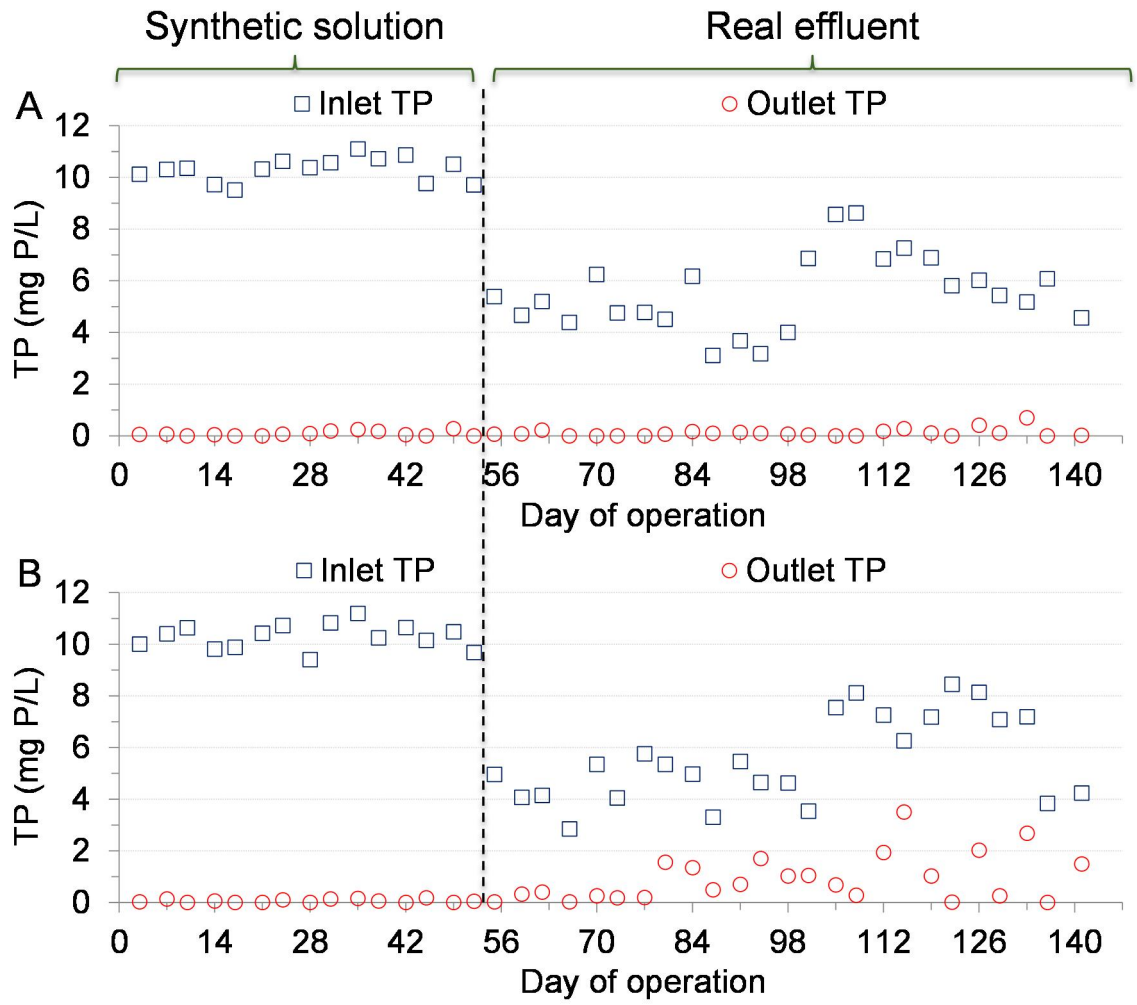


Fig. 2. Evolution of inlet and outlet TP concentrations: (A) column A; (B) column B.

Fig. 3A shows the evolution of TP retained as a function of TP added at the inlet of each column (mg P/g CBR). Over the full period of 140 days of operation, column A showed a TP removal performance of 98.5% and it reached a TP retention capacity of 0.63 mg P/g CBR, whereas column B showed a TP removal performance of 91.6% and it reached a TP retention capacity of 0.61 mg P/g CBR. As shown in Fig. 3A, P removal performance of column B has started to decline during the second period of operation (day 55-140), when the column B was fed with a real CW effluent enriched with glucose to promote anoxic biotic conditions inside the column. Overall, these results suggest that the development of anoxic biotic conditions during the

operation of column B may account for its lower P removal performance, as described in the following sections.

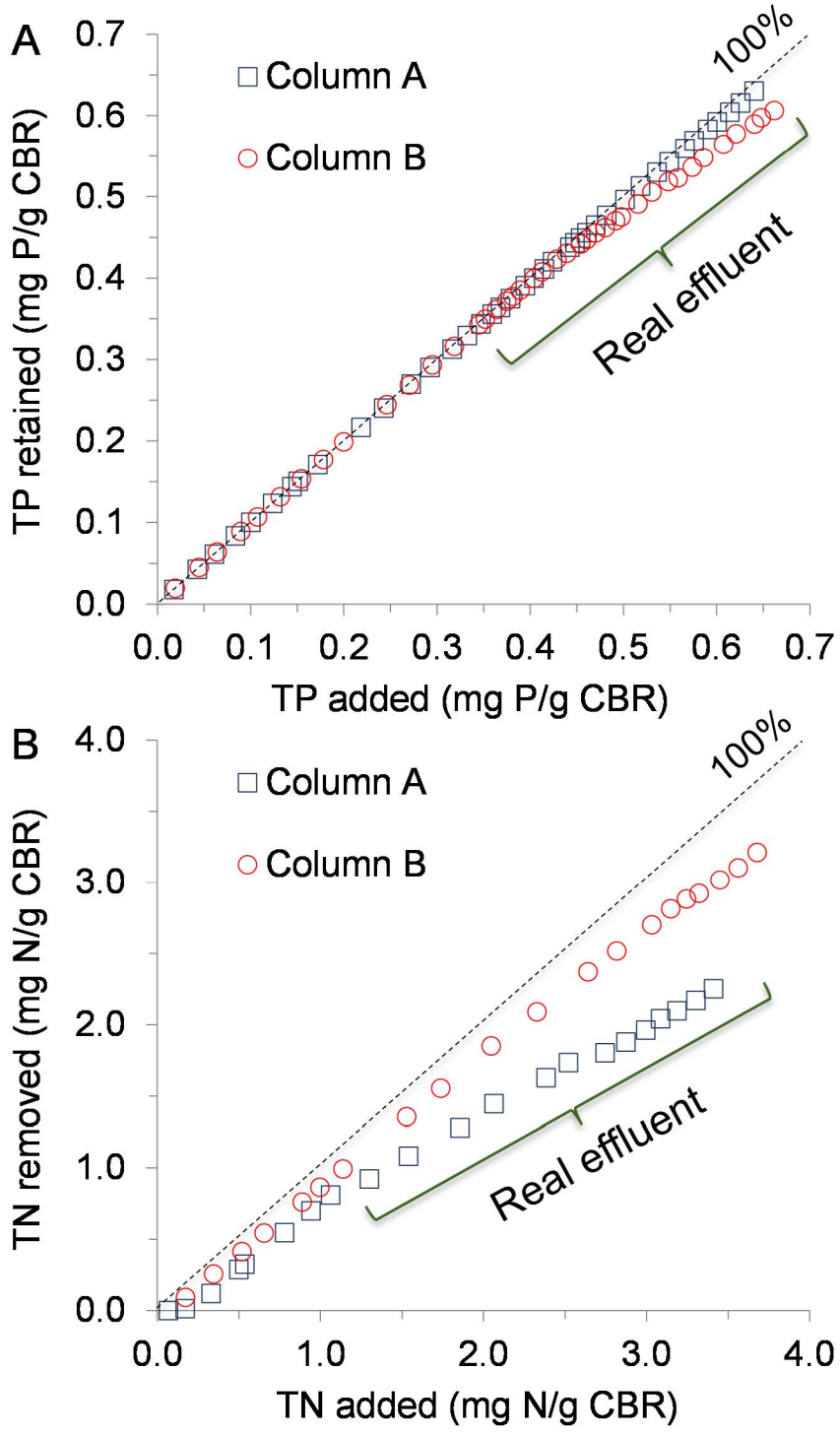


Fig. 3. Cumulated treatment performances of columns A and B over the full period of operation: (A) TP retained as a function of TP added; (B) TN removed as a function of TN added.

COD and TN removal were studied to investigate the main metabolic processes occurring in the columns. Fig. 3B shows the evolution of TN removed as a function of TN added to the inlet of the columns A and B (mg N/g CBR). Over the full period of 140 days of operation, columns A and B removed 66.1% and 87.3% of TN added to the inlet of each column, respectively. TN removal in column A was, most probably, primarily related to adsorption of nitrate (NO_3^-) on functional groups (*e.g.* –OH) at the surface of CBR [17], as already described by Cengeloglu *et al.* [30]. As shown in Fig. 3B, TN removal performance of column A started to decline after 55 days of operation, thus suggesting saturation of adsorption sites. Instead, column B showed a higher TN removal performance over the full period of operation. Most probably, glucose addition and low DO concentrations promoted heterotrophic denitrification in column B, thus improving TN removal performance. Inlet and outlet DO, COD, and TN concentrations of column B (Table 1) appears to confirm that TN removal was related to COD removal according to the metabolic pathways of heterotrophic denitrification. Indeed, several studies in the literature indicate that denitrification in CWs occurs when DO is below 0.5 mg O_2/L and the mass ratio of organic carbon to NO_3^- is higher than 2.86 g COD/g N [23,31]. Furthermore, the results of this study are in good agreement with the findings of previous pilot experiments [32], which have shown that the addition of methanol as a carbon substrate for denitrification improves the TN removal performance of Bauxsol pellets (seawater-neutralized bauxite residues) by a factor of 2. Over the full period of 140 days of operation, inlet and outlet Eh values for column B were 229 ± 32 mV and 182 ± 27 mV (Table 1), respectively. These results appear to confirm reduction of electron acceptors (*e.g.* NO_3^-) during water filtration trough the column B. Moreover, experimental Eh values varied in the range of values that promote denitrification in CWs [29,33].

Table 2 summarizes the main results of previous column studies that have investigated P removal performances of various types of untreated and treated bauxite residue. P removal

performances varied from 56% to 98%, thus confirming that bauxite residue is an efficient filter material to remove P from wastewater. However, it is difficult to compare the results of the different studies because of the large discrepancy on experimental parameters, such as type of bauxite residue, type of solution, inlet P concentration, and particle size. Comparative experiments of Herron *et al.* [34] have indicated that P removal performance increases from 28% to 98% with decreasing particle size from < 12 to < 2 mm, most probably because the lower particle size gives a higher specific surface available for P sorption. However, the lower particle size can also result in lower pore size between the grains, thus reducing the hydraulic conductivity of the filters [35]. In addition, various biological and physical-chemical phenomena, including biofilm growth, retention of suspended solids, particle segregation, precipitation and accumulation of precipitates, may further decrease the void volume and the pore size [36], thus affecting the long-term hydraulic and treatment performances of the filters and increasing the risk of clogging when treating real effluents. Therefore, Herron *et al.* [34] recommended the < 6 mm as optimum particle-size in field scale applications. It should be also noticed that many of the experiments were conducted for too short a period to evaluate long-term performances of the filters [21,34]. Despland *et al.* [32] observed that P removal performances of columns packed with Bauxsol pellets decreased from 95% to 80% and to 60% after 5 and 6 months of operation, respectively, thus suggesting saturation of P retention capacity. The results of our study indicate very high P removal performances over the full period of 140 days of operation (especially for column A, 98.5%), and no clogging phenomena were observed.

Table 2. Main results from column experiments that have tested P removal performances of treated and untreated bauxite residue: BP = Bauxsol Pellet; RMFC = Red Mud Filter Cake; UBR = Untreated Bauxite Residue; CBR = Carbonated Bauxite Residue.

Study	Experimental parameters							Experimental results	
	Volume (L)	Material	Size (mm)	Feeding solution	Inlet P (mg P/L)	Inlet flow (L/h)	Duration of experiments	P removal performance	P retention capacity (g P/kg material)
Despland *et al.* [32]	10	SBP	5 - 10	Secondary WWTP effluent	3.0 - 9.2	0.9	180 days	> 60%[a]	~ 2
Herron *et al.* [34]	1.15	RMFC	< 2	Synthetic P solution	6	14.5[b]	30 min	98%	25[c]
	1.15	RMFC	< 6	Synthetic P solution	6	29[b]	30 min	56%	N.A.
	1.15	RMFC	< 12	Synthetic P solution	6	44.6[b]	30 min	28%	N.A.
Cusack *et al.* [21]	0.03	UBR	< 0.5	Forest run-off	1.1	0.030	22.8 min[d]	95%	0.045[e]
	0.03	UBR	< 0.5	Dairy soiled water	10.6	0.030	5.8 min[d]	95%	0.27[e]
This study	0.35	CBR	< 2	Synthetic and real CW effluent	3.1 - 11.1	0.012	140 days	98.5%	0.63
	0.35	CBR	< 2	Synthetic and real CW effluent + glucose	2.8 - 11.2	0.012	140 days	91.6%	0.61

[a]P removal performances decreased below 95% after 30 days, and below 60% after 180 days of continuous operation;

[b]Based on article data;

[c]Maximum retention capacity from batch isotherm experiments (Langmuir equation);

[d]Filtration time to observe a breakthrough concentration of 5% of the inlet P concentration;

[e]Modelled maximum retention capacity as a function of filtration time.

3.2 *Alkaline and metal leaching from CBR*

Alkaline releases from both the columns were observed during the full period of operation, with average outlet pH values of 8.3 ± 0.5 and 7.7 ± 0.6 for columns A and B, respectively. These pH increases were secondarily attributed to release of residual diluted Na_2CO_3 and mainly to $CaCO_3$ dissolution from CBR, according to equation (2) [37], as already described in a recent study that has investigated the effect of gypsum treatment on the leaching behavior of CBR [15].

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^- \quad (2)$$

The highest outlet pH values (from 8.5 to 9.1) were observed during the first 2 months of operation (Fig. S2), then they stabilized around a value of 7.7 ± 0.1 and 7.2 ± 0.2 for columns A and B, respectively, after day 100 of operation. Over the full period of operation, column B showed lower outlet pH than column A. This was most probably related to the production of organic acids during the metabolic conversion of glucose in column B, which buffered the increase in pH due to $CaCO_3$ dissolution.

The evolution of Ca, Al, and Fe release rates (µg/ (g CBR · day)) from columns A and B was calculated by outlet to inlet mass balances using equation (3), where C_{outlet} indicates the outlet metal concentration (µg/L), C_{inlet} the inlet metal concentration (µg/L), M the dried mass of CBR in the column (g), and F the feeding flow (L/day).

$$Releaserate = \frac{(C_{outlet} - C_{inlet})}{M} * F \quad (3)$$

As shown in Fig. 4, positive values indicate metal release from CBR, whereas negative values indicate metal retention on CBR. Massive releases of Ca (> 1200 mg Ca/L) were observed from both the columns during the first 3 weeks of operation (Fig. S3), and they were most probably related to dissolution of $CaCO_3$ and/or unreacted $CaSO_4 \cdot 2H_2O$ from CBR (equation 1 and 2). Then, the data clearly indicate Ca retention in column A since

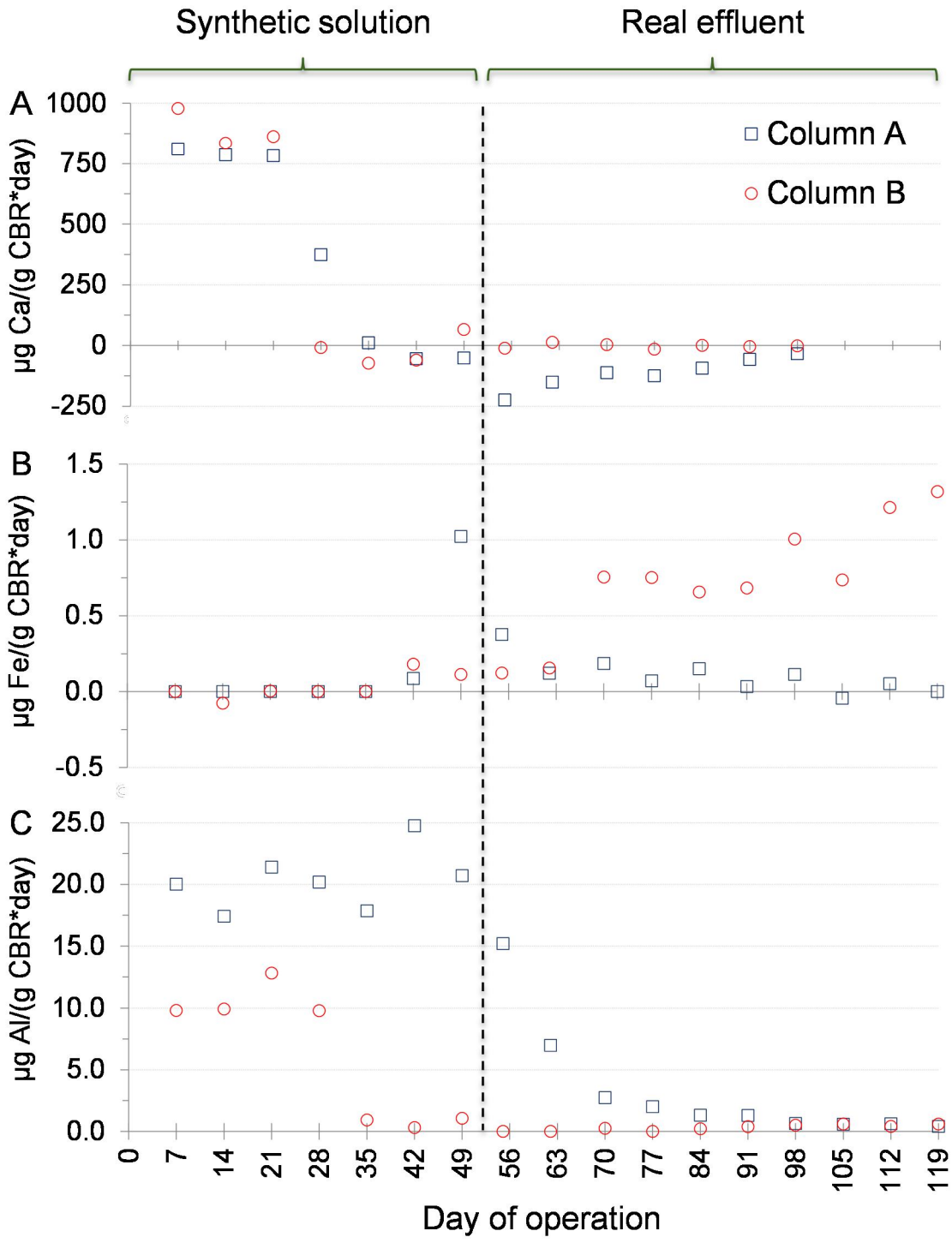
day 42 of operation, with outlet Ca concentrations always lower than inlet Ca concentrations. During the second period of operation (real effluent feeding), the molar ratio of Ca removed to P removed in column A varied from 10.8 to 56.0 mol Ca/mol P. These values are 6.5 to 56 times higher than Ca to P molar ratios of the most common Ca-phosphates in wastewater treatment systems (1-1.67 mol Ca/mol P) [38], thus suggesting co-precipitation of Ca-phosphates and Ca-carbonates under slightly basic conditions (inlet pH 7.6 ± 0.3, outlet pH 8.0 ± 0.4), as already found in previous studies [16,39]. Differently from column A, results from column B do not indicate Ca retention during the second period of operation (real effluent feeding), this although the Ca content of the real CW effluent was not a limiting factor for Ca-P precipitation, as indicated by the Ca to P molar ratios always higher than 34 mol Ca/mol P. Most probably, the lower pH values of column B (inlet pH 6.4 ± 0.5, outlet pH 7.2 ± 0.3) had the effect of limiting Ca-phosphate and Ca-carbonate precipitation compared to column A. Indeed, solubility of Ca-phosphate and Ca-carbonate drastically increases with decreasing pH below 8 [40]. However, the findings of Cusack *et al.* [21] indicate that P removal by surface precipitation of Ca-phosphates can happen at almost neutral pH and without requiring the consumption of Ca ions from the inlet wastewater, as the result of the interaction between PO_4-P ions present in the wastewater with Ca-compounds already present in the composition of bauxite residue.

Massive releases of Al from CBR were observed during the first period of operation (day 1-55) (Fig. 4C), with outlet Al concentration exceeding 30 mg Al/L and 15 mg Al/L for columns A and B, respectively (Fig. S4). These Al concentrations are several orders of magnitude higher than the maximum theoretical solubility of Al-hydroxides in water for pH ranging between 7-8 at 20 °C (0.3 mg Al/L, according to [41]). Therefore, they were

primarily attributed to washing out from the columns of colloidal fractions and/or very fine Al-CBR particles passing the 0.45 μm filters. Then, outlet Al concentrations stabilized below a value of 1 mg Al/L after day 98 and after day 49 of operation for columns A and B, respectively. Lower outlet Al concentrations of column B were most probably related to the more neutral values of outlet pH compared to column A (Table 1), as it is well known from the literature that Al-hydroxides present minimum solubility at pH ranging between 6-7 [41].

With the only exception of day 49, column A showed very few Fe releases during the full period of operation (Fig. 4B), with outlet Fe concentrations lower than 0.3 mg Fe/L (Fig. S5). The higher outlet Fe concentration on day 49 was most probably affected by a cleaning step of the outlet pipe that likely had the effect of mobilizing and washing out from the column some fine particles of CBR. Differently from column A, column B showed higher Fe releases during the second period of operation (real effluent feeding), with outlet Fe concentrations up to 2.1 mg Fe/L.

These results on metal release are in good agreement with the findings of Cusack *et al.* [21], who observed Al and Fe releases from bauxite residue in rapid, small-scale column tests with outlet Al and Fe concentrations up to 3.5 and 3 mg/L, respectively. Therefore, they recommended a washing step before packing bauxite residue to prevent excessive Al and Fe releases from the filters.



1

2 Fig. 4. Evolution of element release rates from columns A and B during the full period of

3 operation: Ca release rate (A), Fe release rate (B), and Al release rate (C).

4

3.3 *Iron mobilization in CBR*

The results of our study seem to indicate Fe mobilization from CBR in column B under anoxic biotic conditions, thus giving Fe releases up to 2.1 mg Fe/L. Both Eh and pH values are commonly used as key parameters to evaluate redox conditions and to interpret metal solubility data in soils [42,43]. The relationship between outlet Eh and pH for columns A and B during the full period of operation is presented in Fig. 5 (Pourbaix diagram, [44]). The results indicate a very good linear correlation between the experimental data ($R^2 > 0.949$), with Eh increasing with decreasing the pH. These Eh-pH relationships are in very good agreement with the findings of Husson *et al.* [42], who concluded that both Eh and pH should be interactively used as relevant primary parameters to characterize redox conditions in soils. As shown in Fig. 5, outlet Eh and pH values varied between the ranges of values that promote solid-phase Fe hydroxides ($Fe(OH)_3$) at 23 °C, which was the average temperature during column experiments (adapted from [45]). However, it should be noticed that theoretical Fe^{3+}/Fe^{2+} equilibrium conditions in Fig. 5 are established for $Fe(OH)_3$ solution in pure water. The presence of organic matter and/or microorganisms, and the related microbial activities, can play a key role in Fe mobilization from solid matrices [26,46–48]. Under anoxic conditions, microorganisms can use Fe^{3+} as a terminal electron acceptor to oxidize organic matter during the anaerobic respiration process, thus reducing Fe^{3+} to more soluble Fe^{2+}. Moreover, microorganisms can produce Fe^{3+} chelating molecules (*e.g.* siderophores) to improve the bio-availability of soluble Fe^{3+} compounds from crystalline Fe^{3+} minerals [46]. Overall, this microbially driven process of Fe^{3+} chelation and reduction can result in the mobilization of soluble Fe^{3+} compounds and release of Fe^{2+} ions. The results in Fig. 5 also suggest a shift from more oxidizing to less oxidizing conditions with increasing

temperature from 16.7 to 24.3 °C, probably because the increase in temperature has a positive effect on microbial activity and a negative effect on oxygen saturation concentration.

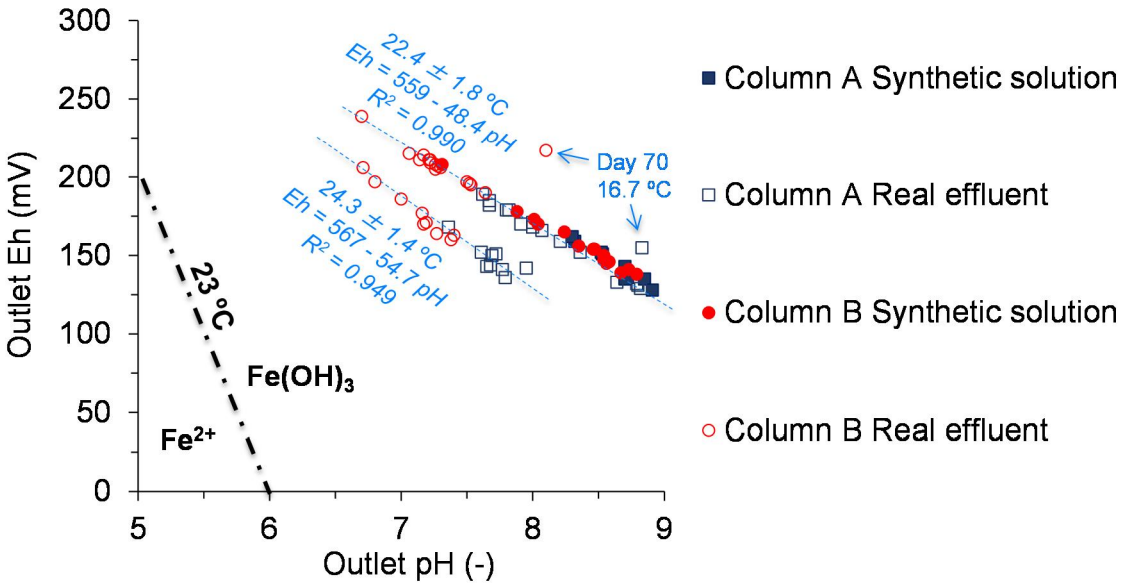


Fig. 5. Simplified iron Pourbaix diagram at 23 °C (adapted from [45]). Outlet Eh and pH values of columns A and B over the full period of 140 days of operation.

The chemical notion of pe + pH, which involves both the Eh and pH parameters, can be used as an indicator of the electronic activity of a solution in the presence of living organisms [42,43,48]. The electronic potential (pe) at 25 °C can be calculated from Eh (mV) by using equation (4).

$$pe = \frac{Eh}{59} \quad (4)$$

According to Husson *et al.* [42], at 25 °C pure water is redox indifferent at pe + pH equal to 13.8. Then, pe + pH values higher than 13.8 indicate oxidizing media, whereas pe + pH values lower than 13.8 indicate reducing media. The Fig. 6 shows the relationship

between Fe concentrations and pe + pH values of the effluents from columns A and B during the second period of operation (real effluent feeding), when Fe release was observed at the outlet of column B. For column B, the results indicate a clear trend of increase in outlet Fe concentration with decreasing pe + pH below a value of 11, whereas no correlations were observed between outlet Fe concentrations and pe + pH values in column A. These results appear to confirm Fe mobilization from CBR in the presence of living microorganisms under anoxic conditions (column B).

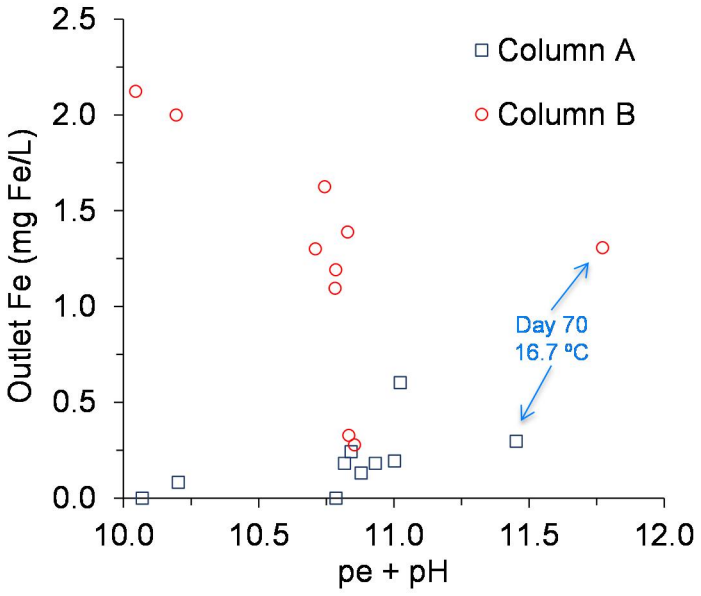


Fig. 6. Outlet Fe concentrations of columns A and B as a function of pe + pH during day 55-140 of operation (real effluent feeding).

Fig. 7 summarizes the results of amorphous Fe, crystalline Fe, and Al (hydr)oxide extractions from CBR before (Fresh CBR) and after their use as filter substrate in the columns A and B (CBR A and CBR B, respectively). The results indicate a relative increase in crystalline Fe and Al (hydr)oxides for both the columns after 140 days of

operation (Fig. 7B and C). These relative increases in crystalline Fe and Al (hydr)oxide contents were most probably related to the dissolution of more soluble Ca-compounds from CBR (*e.g.* $CaCO_3$ and residual gypsum), as already suggested by the high Ca releases observed during the first month of column operation (Fig. 4A).

As shown in Fig. 7A, the results indicate a slight decrease in amorphous Fe for column A after 140 days of operation, which was most probably related to washing out from the column of more mobile Fe compounds. Differently from column A, the content of amorphous Fe in column B (CBR B) increased by a factor 2.2 compared to fresh CBR, thus suggesting the conversion of crystalline Fe to amorphous Fe compounds under anoxic biotic conditions. The conversion of crystalline Fe to amorphous Fe compounds was already observed in soils in the presence of living microorganisms [26,47,48], and it was primarily attributed to microbial reduction of crystalline Fe^{3+} (hydr)oxides probably followed by the precipitation of amorphous Fe^{2+} complexes [47]. Li *et al.* [48] observed that a decrease of pe + pH from 11.06 to 8.29 was accompanied by a 110% increase of amorphous Fe content in rhizosphere soils. According to the authors, low pe + pH may promote the activity of Fe reduction bacteria to produce Fe^{2+}, which is re-oxidized to amorphous Fe oxides. However, this hypothesis still needs to be verified by further studies [48].

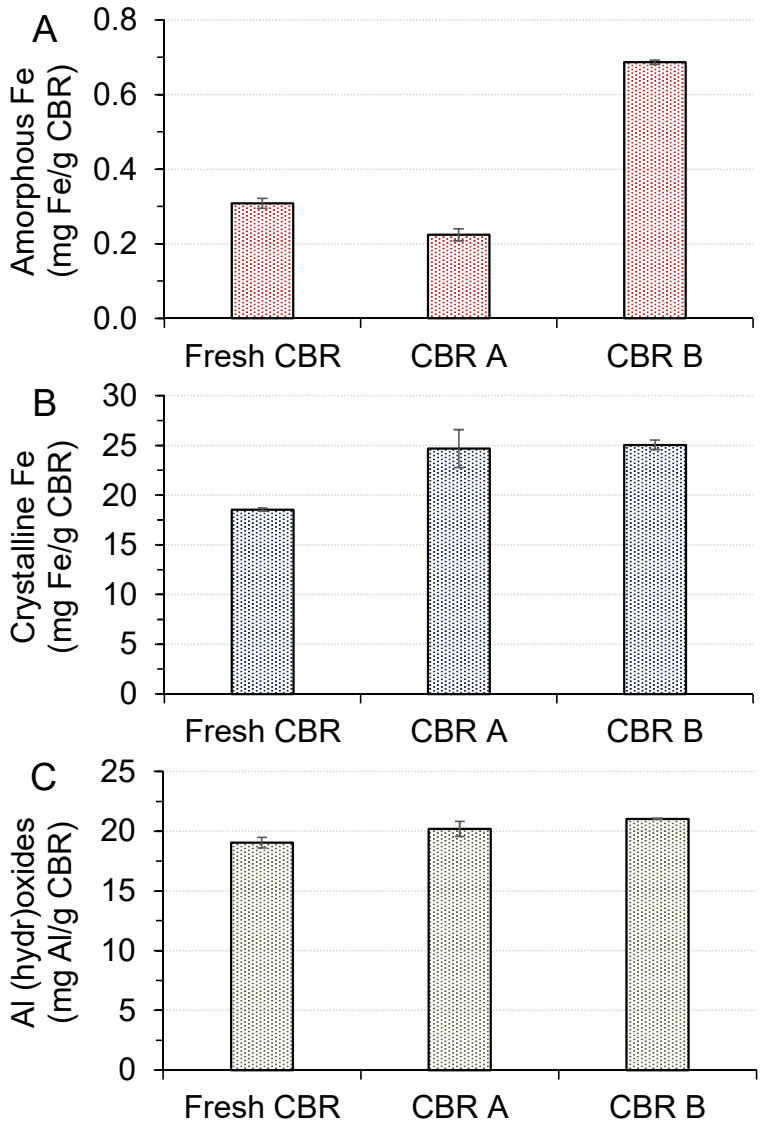


Fig. 7. Amorphous Fe (A), crystalline Fe (B), and Al (hydr)oxide extraction (C) from CBR before (Fresh CBR) and after 140 days of column operation (CBR A and CBR B). Average values from triplicate (amorphous Fe) and duplicate (crystalline Fe and Al (hydr)oxides) experiments, bars indicating the range min-max values.

3.4 *P removal mechanisms*

The results of sequential P extractions from CBR samples before (Fresh CBR) and after 140 days of column operation (CBR A and CBR B) are summarized in Fig. 8. The total

amounts of P extracted by sequential extractions was 0.10 ± 0.01 mg P/kg CBR, 2.04 ± 0.04 mg P/kg CBR, and 2.08 ± 0.21 mg P/kg CBR for Fresh CBR, CBR A and CBR B, respectively (average values ± standard deviations from duplicate experiments), thus confirming P retention on CBR during column experiments, and indicating a similar total amount of P extracted from CBR A and CBR B.

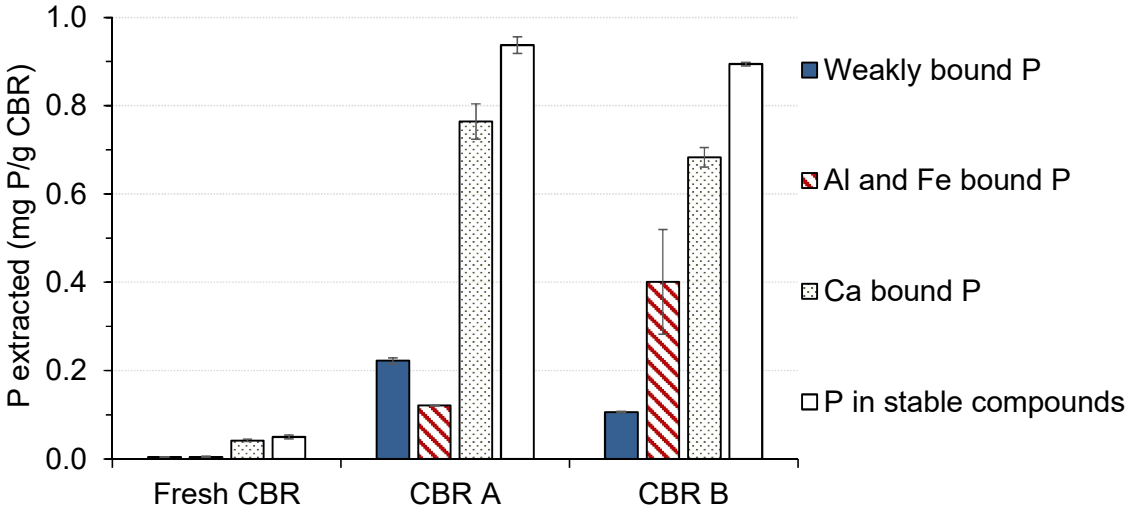


Fig. 8. Sequential extraction experiments: P fractions extracted from CBR before (Fresh CBR) and after 140 days of column operation (CBR A and CBR B). Average values from duplicates, bars indicating the range min-max values.

P in stable residual compounds represents the 45.8% and 42.9% of total P extracted from CBR A and CBR B, respectively, followed by Ca bound P that represents the 37.4% and 32.8% of total P extracted from CBR A and CBR B, respectively (Fig. 8). In the literature [27,28,49], P in stable residual compounds is mainly attributed to the most thermodynamically stable Ca-P crystals (*e.g.* hydroxyapatite) and/or organic matter that is not alkali extractable (organic P), whereas Ca bound P is mainly attributed to

amorphous Ca phosphates that can be dissolved with diluted acids (*e.g.* 1 M HCl). These results seem to confirm that Ca-P precipitation followed by the retention of Ca-P complexes into the columns was the main mechanism leading to P removal from wastewater, as already observed in previous column studies that have investigated P removal performances of Ca rich filter substrates (steel slag) [39,50,51]. Their findings indicated that Ca phosphates initially precipitate under amorphous forms, and later recrystallize into the most thermodynamically stable form of hydroxyapatite.

As shown in Fig. 8, Al and Fe bound P extracted from CBR B (0.40 ± 0.17 mg P/g CBR) was 3.3 times higher than Al and Fe bound P extracted from CBR A (0.12 ± 0.01 mg P/g CBR). The higher amorphous Fe content in CBR B appears to be correlated with the higher Al and Fe bound P in CBR B, when comparing Fe and P extraction data from CBR A and CBR B. Moreover, the molar ratio of Fe to P between the differences of (i) amorphous Fe in CBR B and A (Fig. 7), and (ii) Al and Fe bound P in CBR B and A (Fig. 8), is equal to 0.92 mol Fe/mol P. This value is close to the theoretical Fe/P ratios of the most common Fe-P complexes in wastewater systems (1-1.5 mol Fe/mol P). These results may indicate re-precipitation of mobilized Fe as amorphous Fe-P phases on CBR B at almost neutral pH (equation 5 and 6), as already observed and described in previous studies that have investigated the effects of microbial driven Fe mobilization in soils [26,47].

$$3Fe^{2+} + 2H_2PO_4^- \rightarrow Fe_3(PO_4)_2 + 4H^+ \quad (5)$$

$$Fe^{3+} + H_2PO_4^- \rightarrow FePO_4 + 2H^+ \quad (6)$$

The results of *aqua regia* extractions indicate total P contents of 2.66 ± 0.05 mg P/kg CBR and 3.00 ± 0.10 mg P/kg CBR for CBR A and CBR B, respectively (average values ± standard deviations from duplicate experiments). These values are 30% and 44% higher

than the total amounts of P extracted by sequential extractions for CBR A and CBR B, respectively. According to Tiessen and Moir [27], these differences may be related to highly recalcitrant inorganic P, but also to bicarbonate and hydroxide extractable organic P that were not taken into account in sequential extractions. Most probably, biological P uptake in column B may explain the higher difference between total P extracted by *aqua regia* and total amount of P extracted by sequential extraction for CBR B.

3.5 *Closing remarks and perspectives*

Overall, the results of this study indicate that aeration conditions and microbial activity affect the performance and P removal mechanisms of CBR filters as follows. Under aerobic conditions, Ca-P precipitation (probably followed by crystallization of Ca-P complexes) on the surface of CBR appears to be the main mechanism leading to P removal from wastewater. Under anoxic biotic conditions, microbially driven mobilization of Fe from minerals may (i) provide Fe ions for further Fe-P precipitation, but also may (ii) lead to Fe releases from CBR filters.

Vertical flow CWs represent one of the most employed wastewater treatment systems for small communities in France (less than 2000 people equivalent), with more than 2500 systems in operation in 2015 [25]. According to Paing *et al.* [25], French vertical flow CWs present high removal performances for COD and total suspended solids (TSS), whereas TP and TN removal performances are relatively low (mean values of 151 plants: 93%, 96%, 30% and 39% for COD, TSS, TP, and TN removal, respectively). Therefore, the use of CBR filters appears to be particularly suitable as a tertiary treatment step to remove P from the effluents of vertical flow CWs. The addition of external organic carbon and/or partial recirculation of raw wastewater at the inlet of CBR filters can further improve TN removal by coupling the processes of P retention and denitrification in a

single treatment step, but could also promote Fe mobilization and give a lower TP removal performance.

However, further studies are needed before full-scale application of CBR filters in CWs. In particular, long-term pilot experiments at the field-scale are required to evaluate the effects of seasonal variations of wastewater temperature and composition, and accumulation of solids and precipitates, on the hydraulic and treatment performances of CBR filters under real operating conditions.

4 Conclusions

The results of this study confirm that CBR is an efficient filter material to remove P from wastewater. Over 140 days of operation, column A showed a TP removal performance of 98.5% achieving a TP retention capacity of 0.63 mg P/g CBR, whereas column B showed a TP removal performance of 91.6% achieving a TP retention capacity of 0.61 mg P/g CBR, thus indicating higher P removal performance of CBR under aerobic rather than anoxic biotic conditions. The main mechanisms of P removal were related to the precipitation of Ca-P complexes, most probably followed by recrystallization under more stable forms (*e.g.* hydroxyapatite) on the mineral surface of CBR. The results of this study also indicate Fe mobilization from CBR under anoxic biotic conditions, thus (i) providing Fe ions that are available for further Fe-P precipitation, but also (ii) leading to Fe releases from CBR filters. Overall, the results of this study indicate that CBR filters can be successfully applied to remove P from effluents with low organic load in both aerobic as well as anoxic conditions, but aerobic conditions are recommended to prevent excessive Fe release from CBR.

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Supplementary information

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