Valorisation of bauxite residue as filter material to upgrade phosphorus removal in small wastewater treatment plants

Cristian Barca*, Aix-Marseille University, Laboratory M2P2, France

Pierre Hennebert, INERIS Aix-en-Provence, France

*cristian.barca@univ-amu.fr

Journées Scientifiques : "Bauxite Résidues"
Aix-en-Provence, du 08 au 09 juin 2021

Context: phosphorus pollution

Phosphorus (P) is an essential nutrient for biomass growth in aquatic ecosystems.

Excessive intake of P in water bodies may lead:

- **Abnormal growth of algae and aquatic plants (algal bloom);**
- **Degradation of water quality (eutrophication).**

Maine-et-Loire (France)

Lake Winnipeg (Canada)

Images from Internet

Context: phosphorus pollution

Phosphorus (P) is an essential nutrient for biomass growth in aquatic ecosystems.

Excessive intake of P in water bodies may lead:

- **Abnormal growth of algae and aquatic plants (algal bloom);**
- **Degradation of water quality (eutrophication).**

Treatment requirements for small and medium (10000-100000 P.E.) wastewater treatment plants (WWTP) in sensitive areas (directives 91/271/EEC and 2000/60/EC):

- **Total phosphorus concentration (TP): 2 mg P/L;**
- **Minimum percentage of reduction: 80%;**
- ➢ **National and local requirements are often stricter (even < 0.5 mg P/L)!**

Domestic wastewater in Western Europe (Comber *et al.*, 2013; Boutin *et* Eme, 2017):

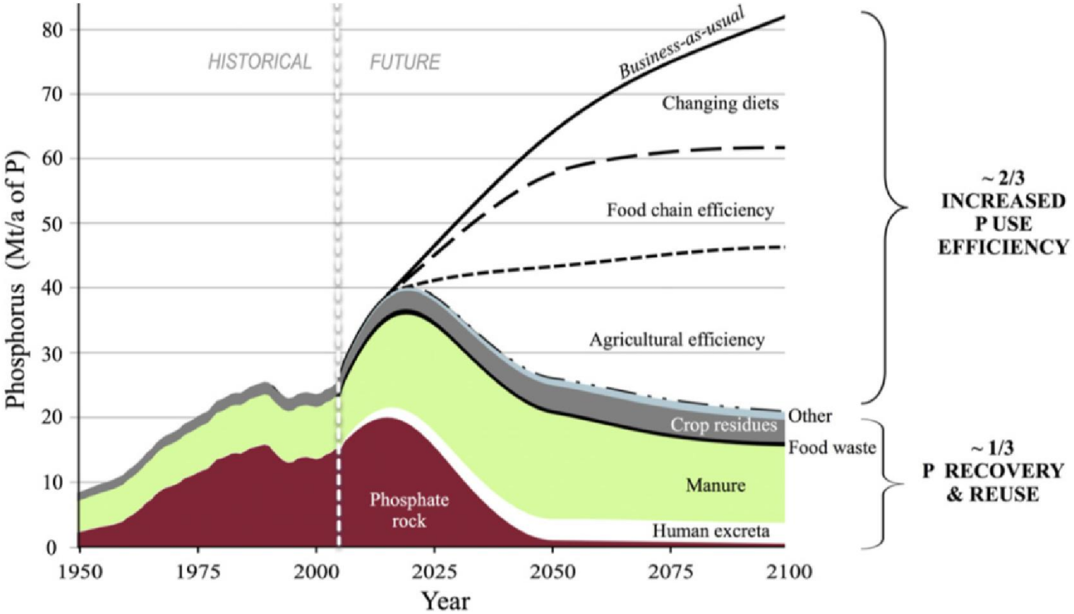
- ***Per capita* loadings of P: 2.0-2.6 g P *per capita per* day;**
- **TP concentration (fresh wastewater): 10-18 mg P/L ;**
- ➢ **The need to develop low cost techniques to treat P, especially for small WWTPs.**

Context: shortage of natural resources

Nowadays fertilizer production industry strongly depends on natural deposits of P such as phosphate rocks. Prospective studies indicate that (Cordell *et al.*, 2011):

- **The peak of P production from phosphate rocks will occur around 2020;**
- **P is very likely to become a critical resource by 2050;**

➢ **There is an urgent need to identify alternative renewable P resources.**



Scenario of long term phosphorus demand (Cordell *et al.*, 2011)

Context: shortage of natural resources

Nowadays fertilizer production industry strongly depends on natural deposits of P such as phosphate rocks. Prospective studies indicate that (Cordell *et al.*, 2011):

- **The peak of P production from phosphate rocks will occur around 2020;**
- **P is very likely to become a critical resource by 2050;**

➢ **There is an urgent need to identify alternative renewable P resources.**

P retention and recovery from domestic wastewater represents a promising strategy to (Tarayre *et al.*, 2016; Cieślik and Konieczka, 2017):

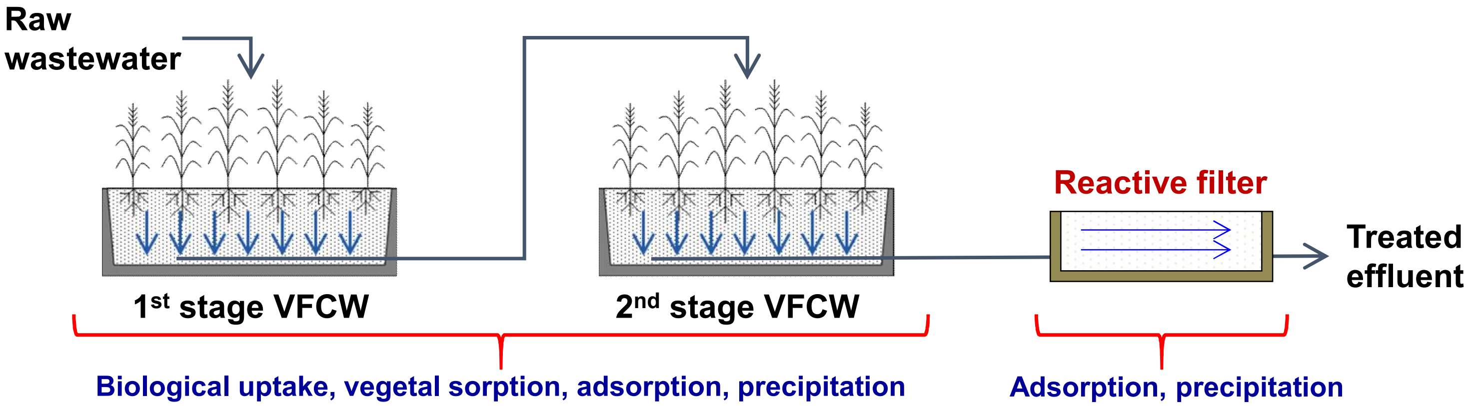
- **Reduce P supply to sensitive ecosystems (risk of eutrophication);**
- **Overcome the shortage of natural deposits of P (*e.g.* phosphate rocks);**

➢ **Maximum potential of P recovery: 0.7-0.9 kg P *per capita per* year.**

Context: P treatment in small WWTP

Most common treatment systems for small communities in France (< 2000 P.E.):

- **Two stage vertical flow reed planted constructed wetland (VFCW):**



Two stage VFCWs in France provide (Paing *et al.*, 2015):

- **High removal (> 90%): COD, suspended solid (TSS), and Kjeldahl nitrogen (TKN);**
- **Poor removal (< 30%): nitrate ($N\text{-}NO_3$) and total phosphorus (TP);**
- **Addition of separate filter units containing materials with high affinity for P binding.**

Context: reactive materials

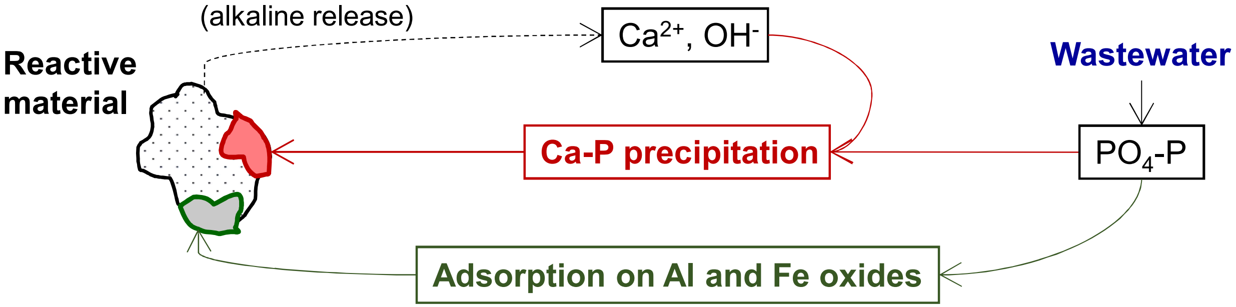
Reactive materials tested for P binding (Vohla *et al.*, 2011; Bacelo *et al.*, 2020):

- **Natural materials: limestone, zeolite, iron rich sand, etc.;**
- **Man made: Filtralite®, Phosphorite®, Polonite®, etc.;**
- **Industrial byproducts and waste: steel slag, fly ash, bauxite residue, etc.**

Most of these materials present high Ca, Al and/or Fe content.

Main mechanisms of P binding (Barca *et al.*, 2012):

- **Precipitation of Ca-P complexes followed by crystallization on mineral surface;**
- **Adsorption on Al and Fe oxides and hydroxides.**



Carbonated bauxite residue as filter material

Project BAUXFILTER (ALTEO, LabEx DRIIHM OHM-BMP, 2018-2019):

- **Laboratory M2P2, group Waste and Wastewater Treatment, Aix-en-Provence;**
- **INERIS-ARDEVIE, Aix-en-Provence;**
- **Company ALTEO, Gardanne (Provence, France).**

Bauxite residue: waste of aluminum industry (also known as red mud):

- **Worldwide production (Prajapati *et al.*, 2016): 90 million tons per year;**
- **Chemical composition (ALTEO): Fe_2O_3 (50%), Al_2O_3 (14%), CaO (5,5%), Na_2O (3,5%);**
- **High content of NaOH: high pH leachates;**
- ➢ **Carbonated bauxite residue (CBR): treated by addition of gypsum to reduce pH < 8.5.**

Bauxite residue storage area of Gardanne with Sainte-Victoire Mountain (Provence, France)

Vegetation growth on CBR, field-study (1000 m^2) (Hennebert *et al.*, 2017)

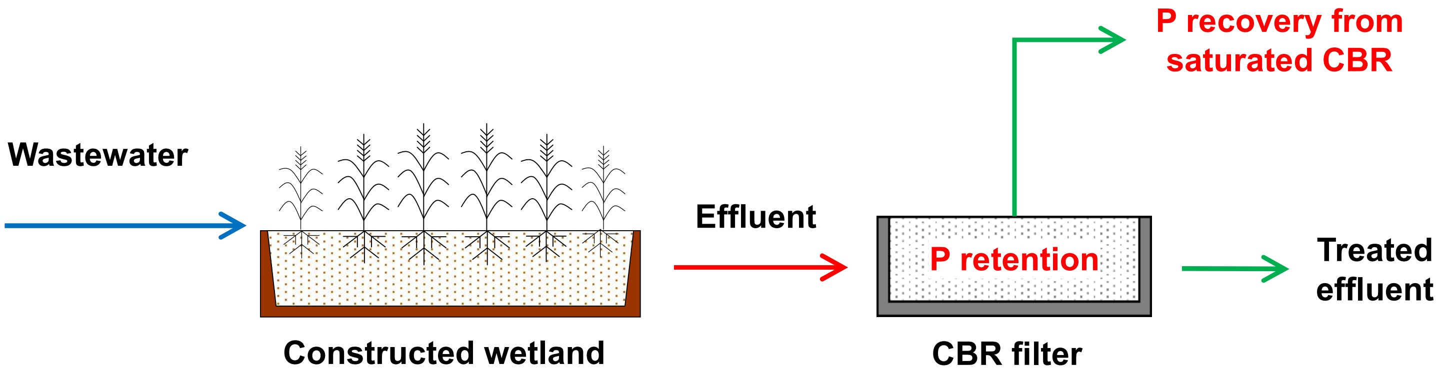
The project BAUXFILTER

Aim of the project:

➢ **Developing the use of CBR filters to remove P from the effluents of small WWTPs.**

Main challenges:

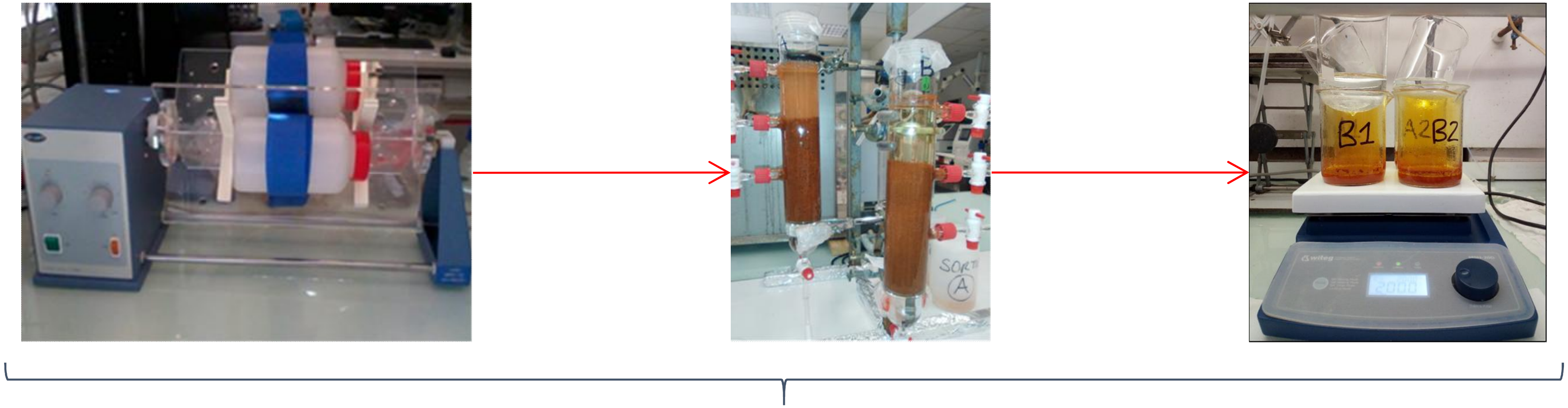
- **To reduce P supply to receiving waters;**
- **To valorize an industrial waste as filter material;**
- **To retain and recover P from wastewater.**



Main objectives and approach

Multi-scale approach involving experiments at different scales of investigation:

- **I. Batch sorption experiments: kinetics and equilibrium capacities of P sorption;**
- **II. Lab-scale column experiments: P removal performance under dynamic conditions;**
- **III. Chemical extractions: main mechanisms of P removal achieved by CBR.**
- ➢ **Integration of results and design of a pilot scale filter.**



Batch sorption experiments

Column experiments

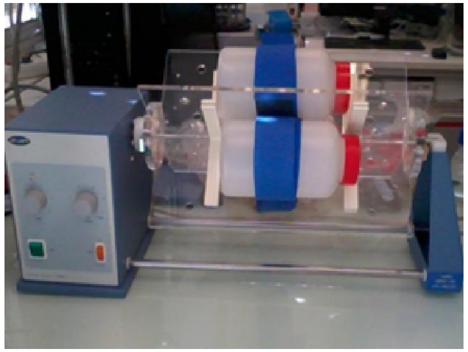
Chemical extractions

Integration of results

Material & methods: batch experiments

Batch kinetic experiments: **to determine the effect of different wastewater composition on equilibrium capacities and rate constants of P sorption:**

- **Ratio liquid to solid (ASTM D 4646): 20 L/kg;**
- **Initial volume of solutions: 0.7 L;**
- **Agitation mode: rotary agitation at 2.5 rpm;**
- **Room temperature: 20 ± 2 °C;**
- **Water samples taken at: 0.5, 1, 2, 4, 6, and 24 h.**



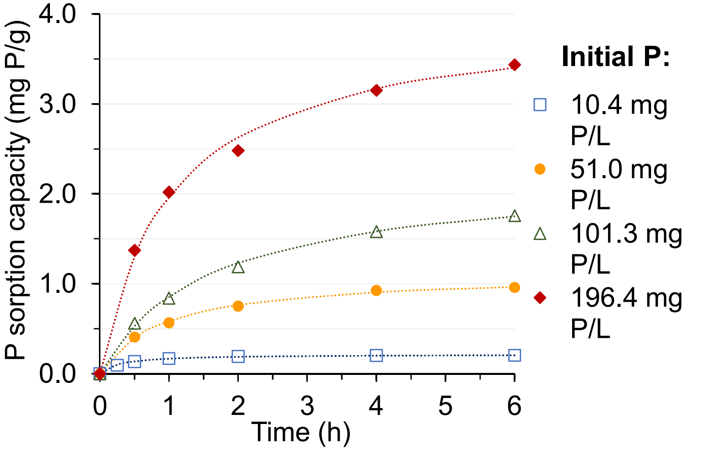
Solutions: 3 different water matrix at 4 different initial P:

- **Deionized water plus P: 10, 50, 100, and 200 mg P/L;**
- **Tap water plus 40 mg N-NO_3/L plus P: 10, 50, 100, and 200 mg P/L;**
- **Real wastewater* plus P: 10, 50, 100, and 150 mg P/L.**

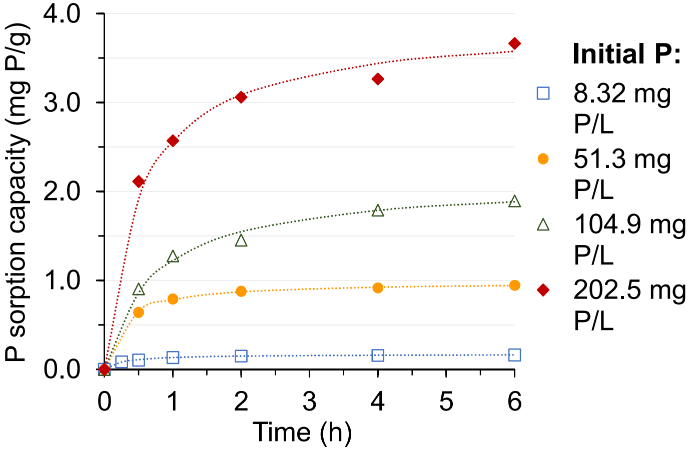
***Effluent from the two stage VFCW of Rougiers (Var, France), 1500 P.E..**

Results & discussion: batch experiments

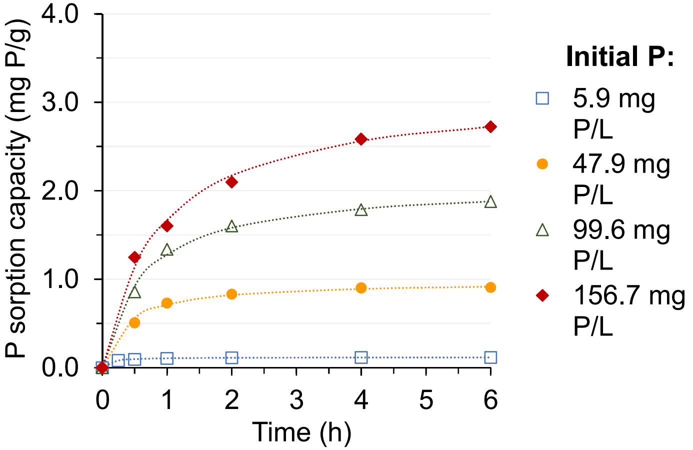
Deionized water + P



Tap water + N-NO_3 + P



Real wastewater + P



Pseudo 2nd order model (Ho and McKay, 1998):

$$\frac{dq_t}{dt} = k_2 \cdot (q_e - q_t)^2 \quad \Rightarrow \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

- q_e: equilibrium sorption capacity (mg P/g CBR);
- q_t : sorption capacity at time t (mg P/g CBR);
- k_2: rate constant of pseudo-second order (g mg^{-1} h^{-1}).

One or more reactants become limiting: process controlled by the reaction.

Results & discussion: batch experiments

Deionized water + P

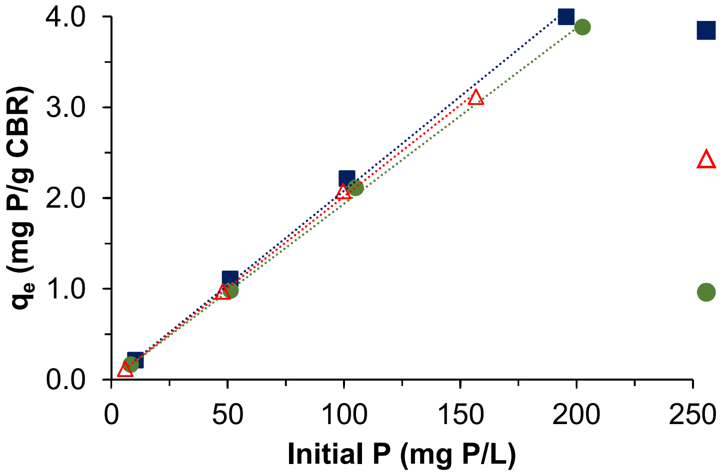
Initial P (mg P/L)	K_2 (g/(mg*h))	q_e (mg/g)	R^2 (-)
10.4	16.09	0.22	0.999
51.0	0.99	1.16	0.999
101.3	0.28	2.22	0.998
196.4	0.24	3.99	0.997

Tap water + N-NO_3 + P

Initial P (mg P/L)	K_2 (g/(mg*h))	q_e (mg/g)	R^2 (-)
8.32	21.48	0.17	0.999
51.3	4.01	0.98	0.999
104.9	0.65	2.12	0.997
202.5	0.50	3.88	0.995

Real wastewater + P

Initial P (mg P/L)	K_2 (g/(mg*h))	q_e (mg/g)	R^2 (-)
5.9	75.08	0.12	0.999
47.9	2.78	0.97	0.999
99.6	0.77	2.08	0.999
156.7	0.36	3.12	0.998



■ **Deionized water + P:**

$q_e = 0.0208 \cdot \text{Initial P}$ ($R^2 = 0.998$)

△ **Tap water + N-NO_3 + P:**

$q_e = 0.0194 \cdot \text{Initial P}$ ($R^2 = 0.999$)

● **Real wastewater + P:**

$q_e = 0.0202 \cdot \text{Initial P}$ ($R^2 = 0.999$)

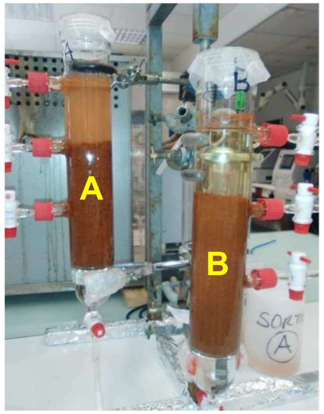
- **q_e increases according to the increase in initial P: saturation capacity not achieved;**
- **Different water matrix did not seem to significantly affect kinetics and capacity of P sorption.**

Material & methods: column experiments

Main objectives: to determine and describe the effect of aerobic and anoxic conditions on:

- **P removal performances;**
- **P removal mechanisms.**

Glass columns (0.5 L)

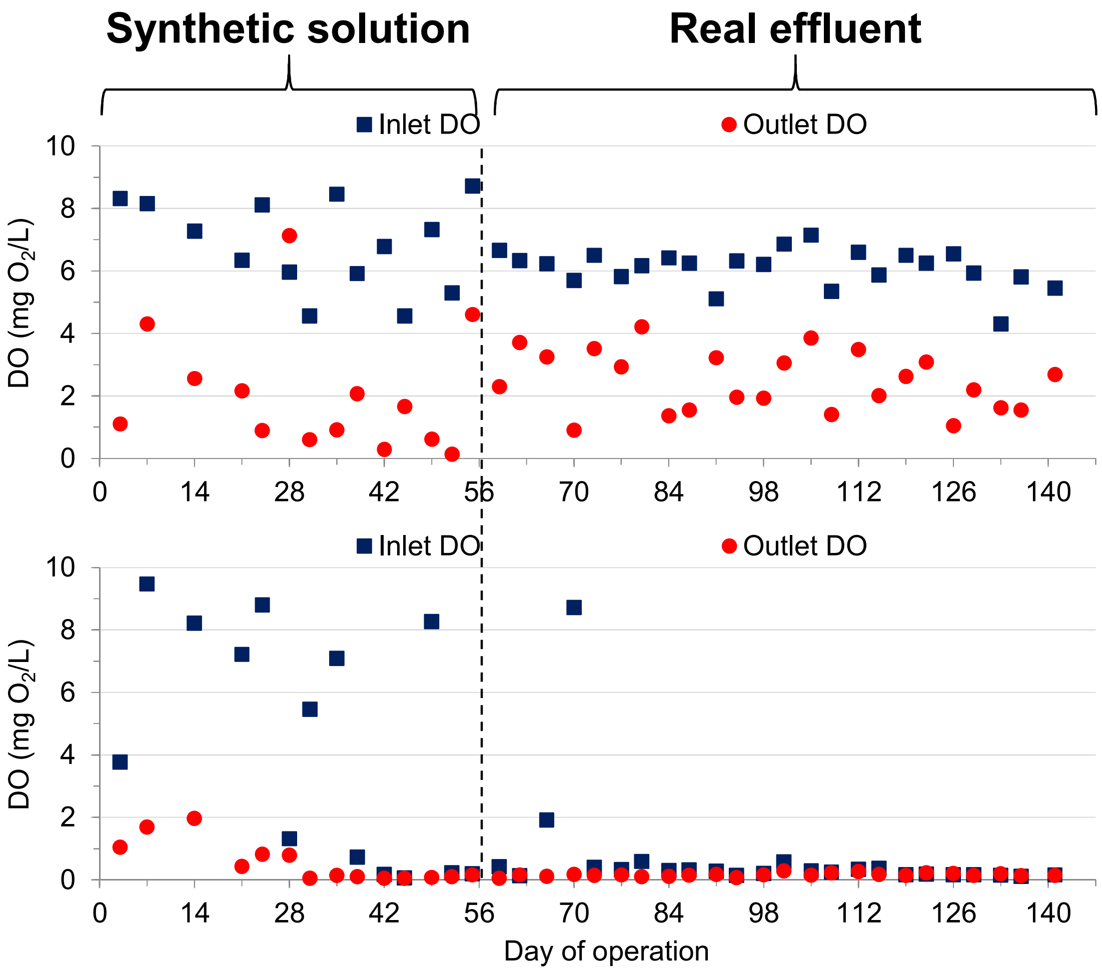


Two CBR columns were continuously fed according to a HRTv of 1 day for the full period of 5 months of operation:

- **Day 1 to 54: synthetic solution:**
  - **Column A: tap water + 10 mg P/L + 40 mg N/L (KNO_3);**
  - **Column B: tap water + 10 mg P/L + 40 mg N/L (KNO_3) + <u>500 mg COD/L</u> (glucose);**
- **Day 55 to 140: real effluent from a small WWTP*:**
  - **Column A: raw real effluent;**
  - **Column B: real effluent + <u>500 mg COD/L</u>.**

***Effluent from the two stage VFCW of Rougiers (Var, France), 1500 P.E..**

Results & discussion: DO concentrations



Column A: aerobic conditions

Synthetic solution (day 1-54):

- **Outlet DO: 1.9 ± 1.9 mg O_2/L**

Real effluent (day 55-140):

- **Outlet DO: 2.6 ± 1.0 mg O_2/L**

Column B: anoxic conditions

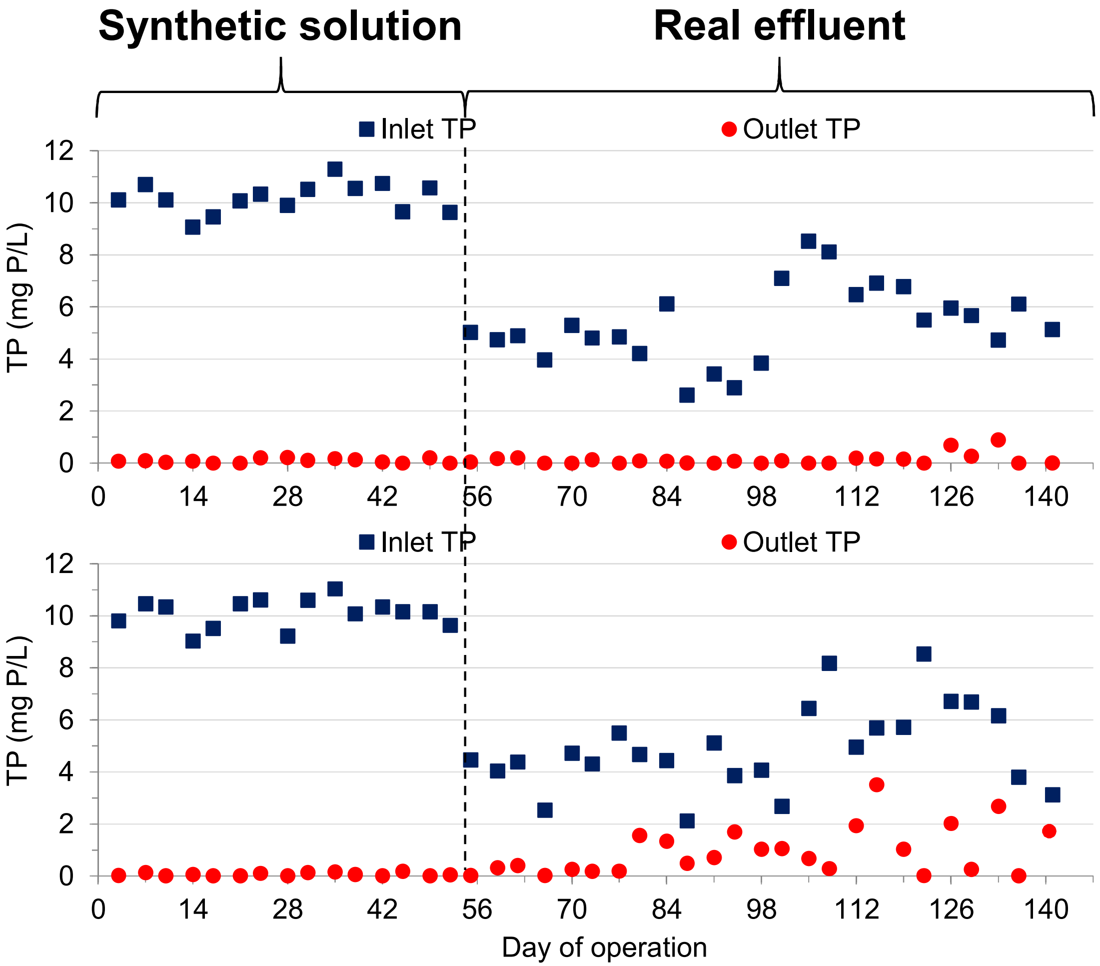
Synthetic solution (day 1-54):

- **Outlet DO: 0.6 ± 0.6 mg O_2/L**

Real effluent (day 55-140):

- **Outlet DO: 0.2 ± 0.1 mg O_2/L**

Results & discussion: TP removal



Column A: aerobic

Synthetic solution (day 1-54):

- **Inlet TP: 10.3 ± 0.5 mg P/L**
- **Outlet TP: 0.1 ± 0.1 mg P/L**

Real effluent (day 55-140):

- **Inlet TP: 5.5 ± 1.5 mg P/L**
- **Outlet TP: 0.1 ± 0.1 mg P/L**

Column B: anoxic

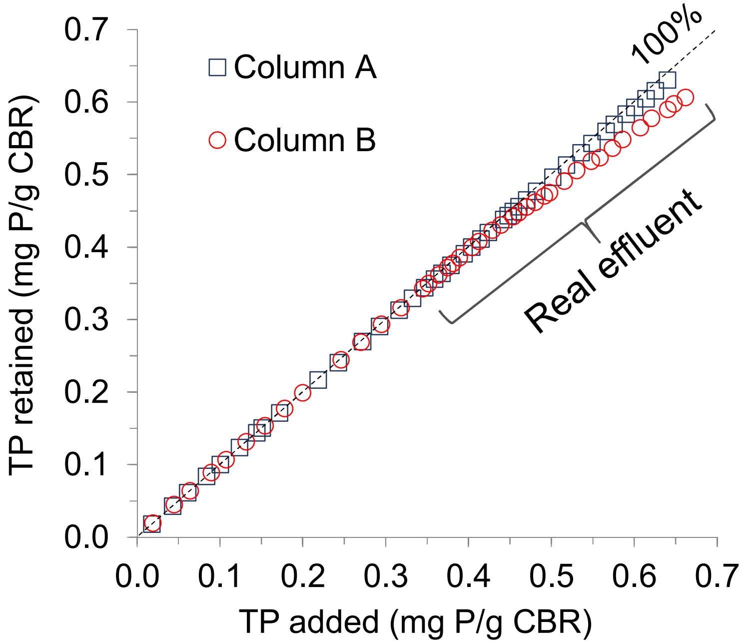
Synthetic solution (day 1-54):

- **Inlet TP: 10.3 ± 0.5 mg P/L**
- **Outlet TP: 0.1 ± 0.1 mg P/L**

Real effluent (day 55-140):

- **Inlet TP: 5.5 ± 1.7 mg P/L**
- **Outlet TP: 0.9 ± 0.9 mg P/L**

Results & discussion: TP retention capacity

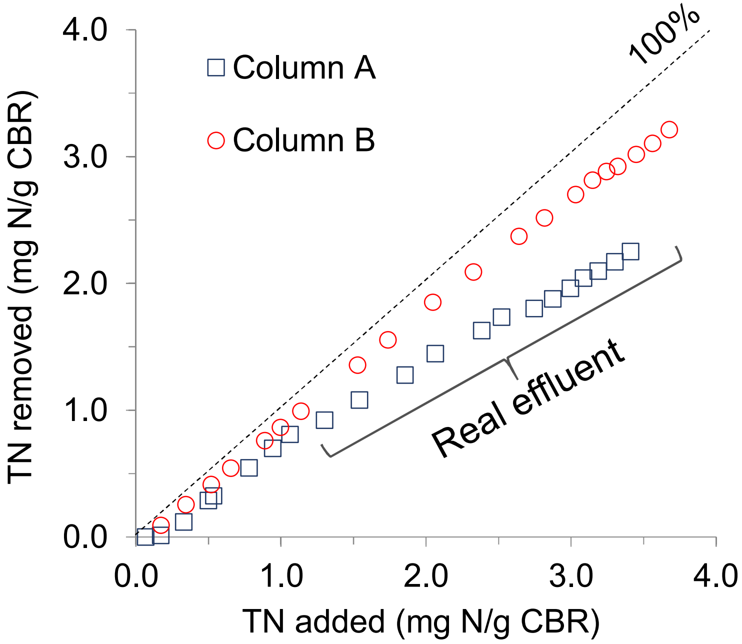


TP retention capacities over 140 days:

- **Column A: 0.63 mg P/g CBR**
- **Column B: 0.61 mg P/g CBR**

TP retention efficiency over 140 days:

- **Column A: 98 % → more efficient!**
- **Column B: 91 %**



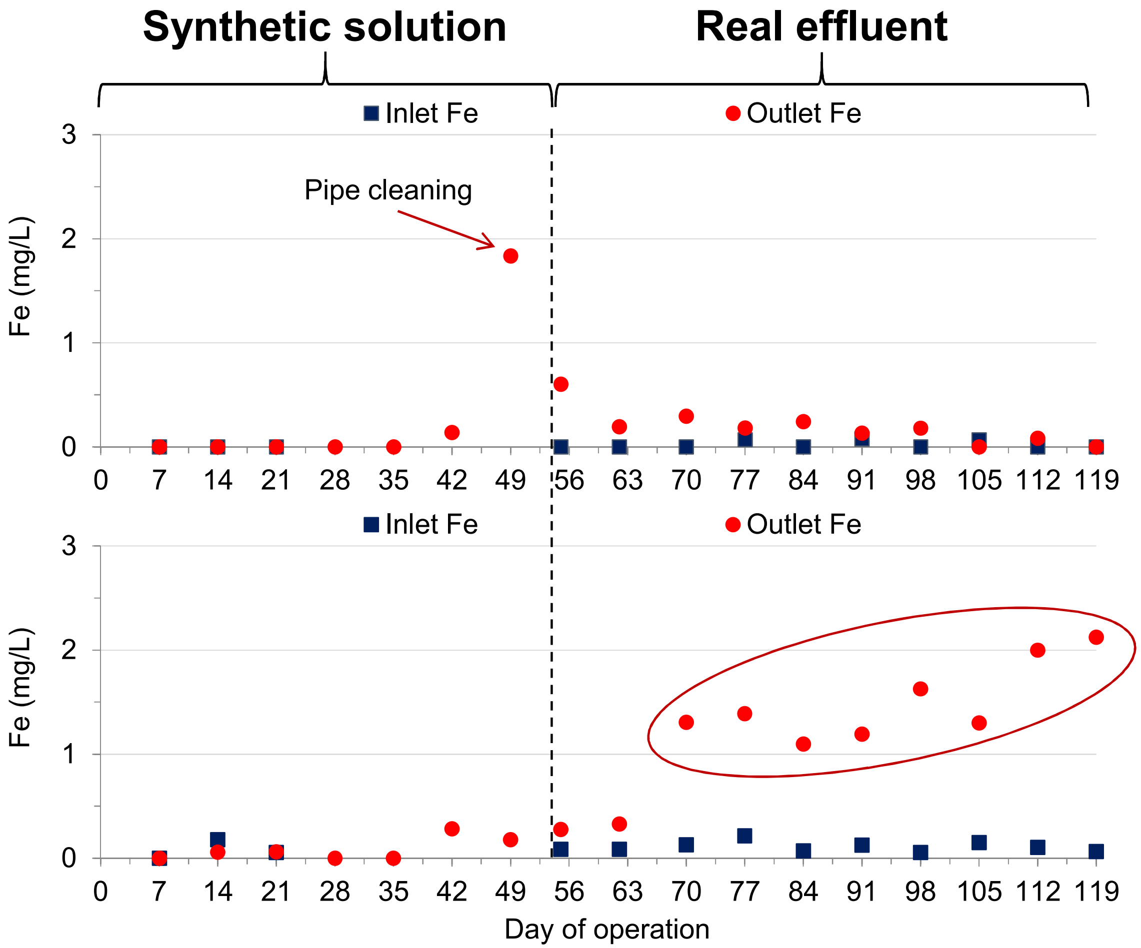
Average outlet TN over 140 days:

- **Column A: 11.9 mg N/L → removal 66 %**
- **Column B: 4.3 mg N/L → removal 87 %**

Column B shows higher TN removal:

- ➢ **Heterotrophic denitrification under anoxic conditions**

Results & discussion: Fe release



Column A: aerobic

Synthetic solution (day 1-54):

- **Outlet Fe: 0.28 ± 0.69 mg Fe/L**

Real effluent (day 55-120):

- **Outlet Fe: 0.21 ± 0.17 mg Fe/L**

Column B: anoxic

Synthetic solution (day 1-54):

- **Outlet Fe: 0.23 ± 0.07 mg Fe/L**

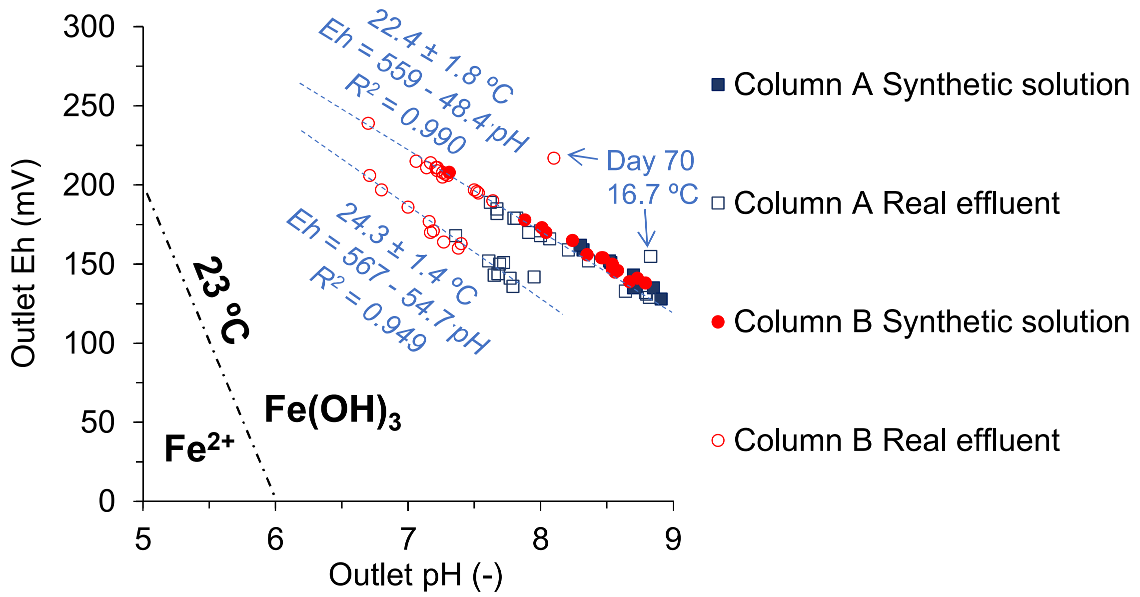
Real effluent (day 55-120):

- **Outlet Fe: 1.26 ± 0.61 mg Fe/L**

➢**Fe release from CBR**

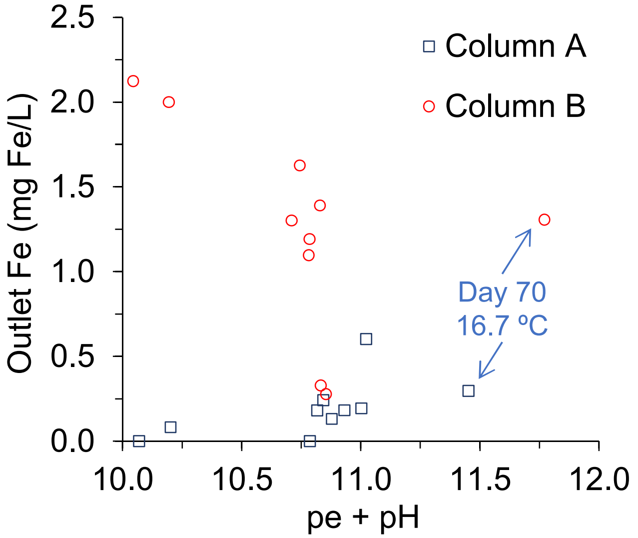
Results & discussion: Fe release

Simplified iron Poubaix diagram at 23°C: outlet Eh and pH values of columns A and B.



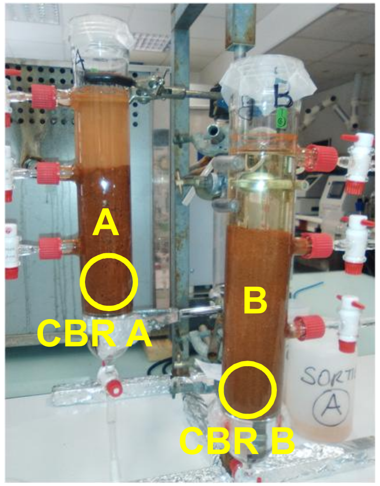
- **Linear correlation: Eh increases with decreasing pH;**
- **Eh and pH into the range of values that promote $Fe(OH)_3$;**
- ➢ **Eh and pH values alone cannot explain Fe mobilisation.**

Outlet Fe concentrations of columns A and B as a function of pe + pH (days 55-140).



- **pe + pH < 13.8: reducing media;**
- **Column B: outlet Fe increases with decreasing pe + pH below 11;**
- ➢ **Anoxic biofilm promoted Fe mobilisation.**

Material & methods: chemical extractions



Chemical extractions: to identify main mechanisms of P removal.

Three different samples of CBR:

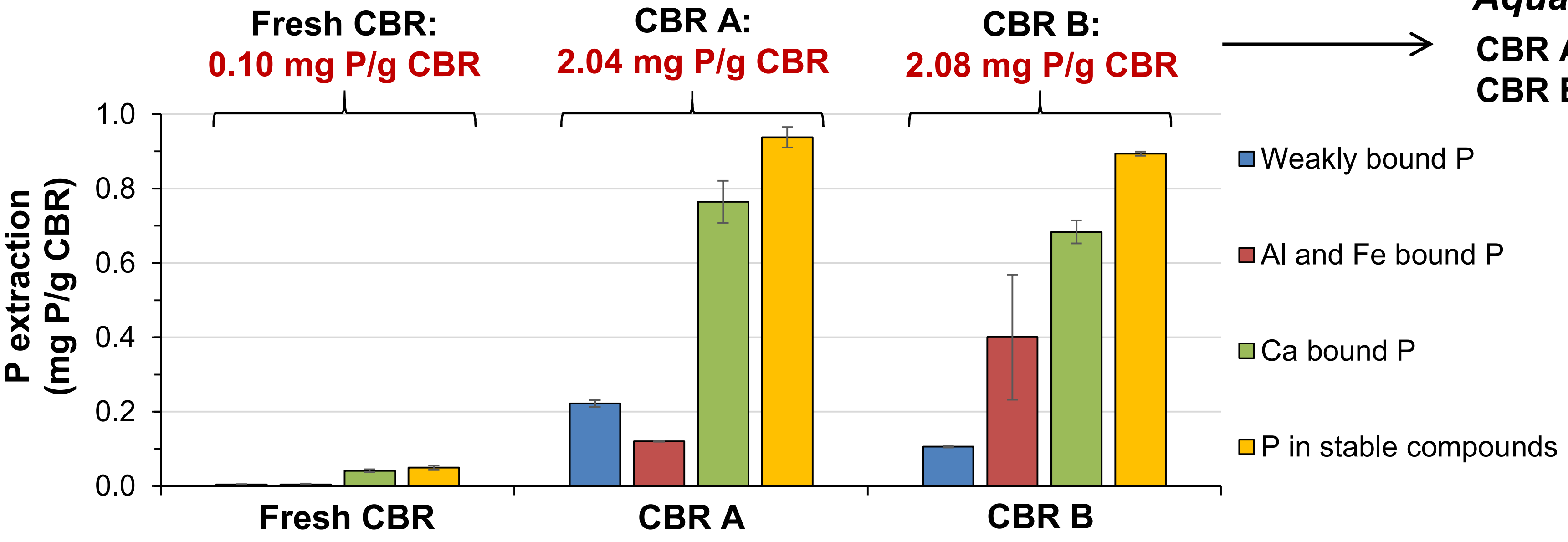
- **Fresh CBR: CBR before the use to treat water;**
- **CBR A: CBR from the inlet of column A;**
- **CBR B: CBR from the inlet of column B.**

After 140 days of column operation

1. ***Aqua regia* extractions (EN 13346, 2000): to determine total P content.**
2. **Sequential extractions (Moir *et al.*, 1993; Barca *et al.*, 2014): to quantify:**
   i. **Bicarbonate extractable P: weakly bound P;**
   ii. **Hydroxide extractable P: leachable Al and Fe bound P;**
   iii. **Diluted acid extractable P: leachable Ca bound P;**
   iv. **Hot concentrated acid extractable P: P in stable residual compounds*.**
3. **Amorphous Fe extractions (EN 12782-1, 2009): reactive Fe under amorphous form.**

***Mainly attributed to: recalcitrant Ca-P crystals and/or organic P.**

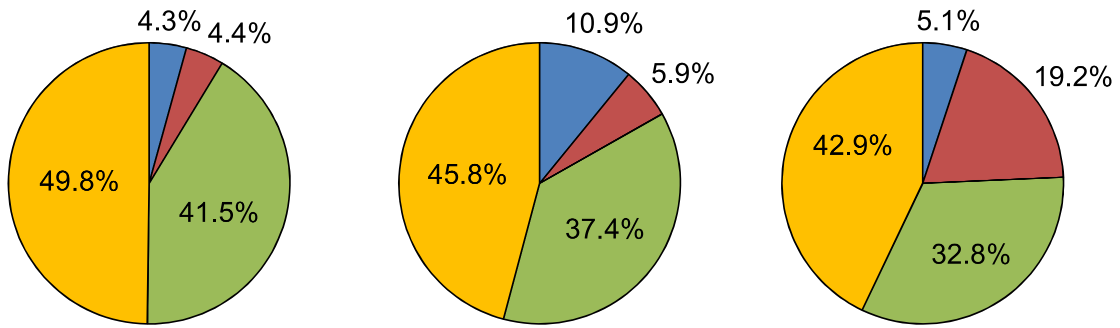
Results & discussion: P removal mechanisms



Aqua regia **extraction :**

CBR A: 2.3 mg P/g CBR
CBR B: 2.6 mg P/g CBR

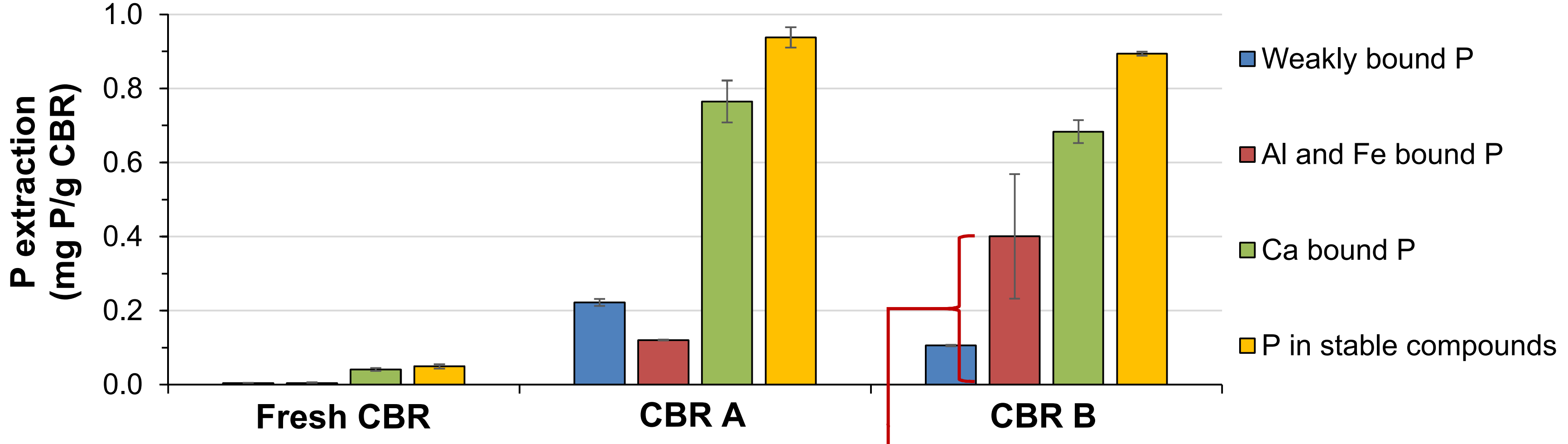
Sequential P extraction experiments



Al and Fe bound P on CBR B 3.3 times higher than CBR A:

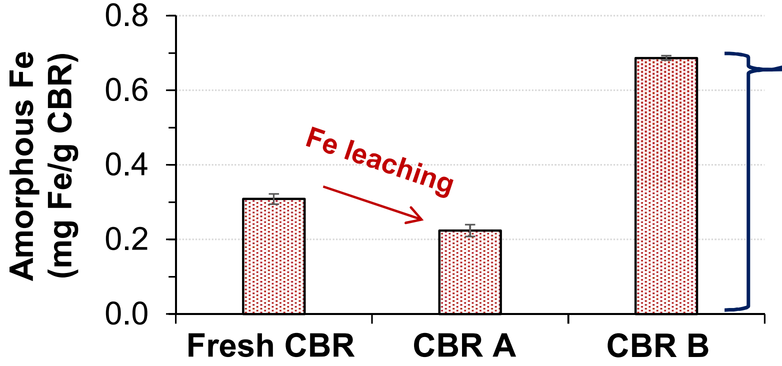
- **Anoxic (biotic) conditions promoted P binding to Al and/or Fe compounds**

Results & discussion: P removal mechanisms



Sequential P extraction experiments

Amorphous Fe extraction experiments:



0.40 mg P/g CBR

0.69 mg Fe/g CBR

Molar ratio Fe/P: 0.95 ⇨ **Stoichiometric molar ratio of Fe/P complexes: 1-1.5**

Amorphous Fe content of CBR B 3.1 times higher than CBR A:

- **Mobilization of stable Fe under anoxic (biotic) conditions:**
  1. **More Fe was available for P binding;**
  2. **Fe-release from column B (anoxic).**

Conclusions

CBR is an efficient material to remove P from wastewater:

- **High P retention capacity (> 4 g P/kg CBR);**
- **High P removal performance over the full period of 140 days of operation:**
  - **Column A (aerobic): 98.5%;**
  - **Column B (anoxic): 91.6.**
- **Almost neutral effluent pH (7-8);**
- **Good hydraulic conductivity.**

Main mechanism of P removal:

- **Precipitation of Ca-P complexes;**
- **P binding to Al and/or Fe compounds.**

Anoxic (biotic) conditions can promote mobilization of Fe from CBR.

➢ **The use of CBR filters appears to be particularly suitable as a tertiary treatment step to remove P from effluents with low organic load and under aerobic conditions.**

Thank you for your attention!

Barca *et al.*, 2021. https://doi.org/10.1016/j.jwpe.2020.101757