JOURNÉE D'ÉTUDES – ECCOREV
Journée de restitution des projets lauréats de l'AOI 2016

Marseille, France, 23th May 2018

Phosphorus recovery from solid residues originated from wastewater treatment plants

Cristian Barca
Mathieu Martino
Nicolas Roche
Pierre Hennebert

Aix*Marseille université

Summary of the project

Project title: Phosphorus (P) recovery from solid residues originated from wastawater treatment plants (WWTPs)

Laboratories involved in the project:

- **Laboratory *Mécanique, Modélisation et Procédés Propres (*M2P2 UMR 7340), research team *Traitement des Eaux et Déchets* (TED);**
- **National Institute INERIS Aix-en-Provence, research group ARDEVIE .**

M2P2 UMR 7340 CNRS - Aix Marseille Universités - Ecole Centrale Marseille

INERIS maîtriser le risque pour un développement durable

Participants:

i. **Cristian Barca, MCF AMU M2P2-TED;**

ii. **Mathieu Martino, intern M2P2-TED (Jan-Jun 2017), PhD student M2P2 (2017-2020), research team *Procédés et Fluides Supercritiques* (FSC);**

iii. **Nicolas Roche, Pr. AMU CEREGE, research team *Environnement Durable*;**

iv. **Pierre Hennebert, Res. HDR INERIS-ARDEVIE.**

Introduction

This study aims at evaluating the potential of P recovery from two different solid residues originated from wastewater treatment plants (WWTPs):

- **A thermal pretreated sludge from an activated sludge plant (*technosables*);**
- **Bauxite residues used as filter media to retain P from wastewater.**

The main objectives of this study are:

i. **To determine the total P content of the residues;**

ii. **To evaluate the best operating parameters for P extraction;**

iii. **To determine rate constants and maximum capacities of P extraction;**

iv. **To describe and understand the main mechanisms of P extraction.**

Aix*Marseille université

Context: shortage of non renewable P resources

Phosphorus (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.* apatite rocks).**

Prospective studies indicate that (Cordell *et al.*, 2011; Sørensen *et al.*, 2015):

- **The peak of P production from phosphate rocks will occur around 2030;**
- **P is very likely to become a critical resource by 2050;**
- ➢ **There is a urgent need to identify alternative renewable P resources.**

Domestic wastewater represents a valuable source of P for the fertilizer production industry (Tarayre *et al.*, 2016; Cieślik and Konieczka, 2017):

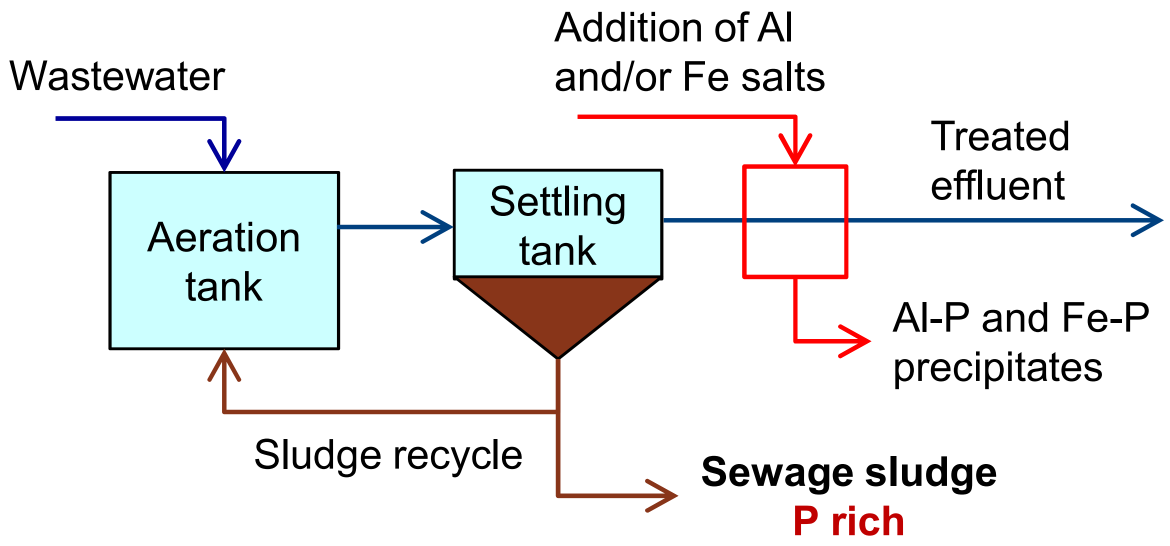
- ➢ ***Per capita* loadings of P (Comber *et al.*, 2013; Boutin and Eme, 2017): 2.0-2.6 g P *per capita per* day**
- ➢ **Maximum potential of P recovery from domestic wastewater: 0.7-0.9 kg P *per capita per* year**

Context: P retention from wastewater

P retention from domestic wastewater in conventional treatment systems:

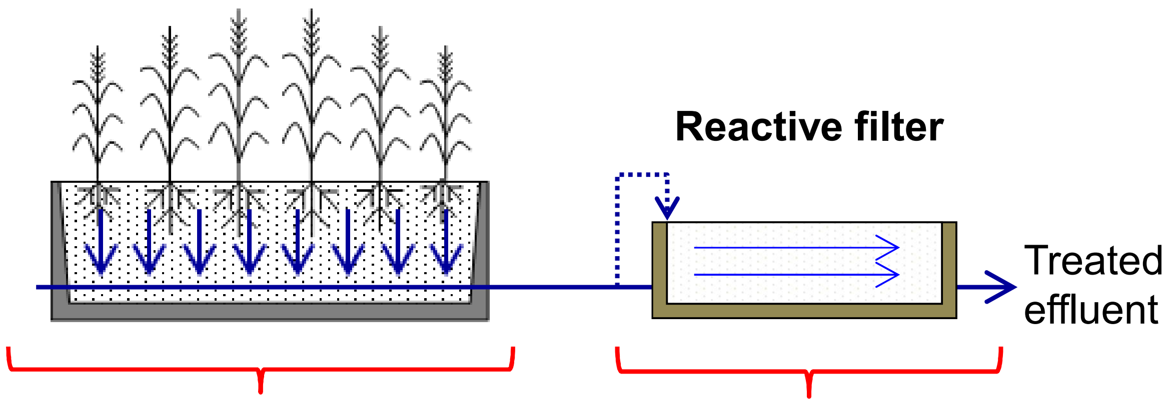
1. **Activated sludge WWTPs:**

- **Biological uptake: P is accumulated in sewage sludge;**
- **Chemical precipitation: precipitation of Al-P and Fe-P complexes.**



2. **Extensive systems (*e.g.* reed beds and constructed wetlands):**

- **P retention performances: < 20% (Molle *et al.*, 2008);**
- **Addition of reactive filters: P adsorption, precipitation, retention of precipitates (Barca et al., 2012 & 2014).**



Context: P recovery from wastewater

P recovery from sewage sludge (Cieślik and Konieczka, 2017):

i. **Direct use as a fertilizer:**
   - **Advantages:** **simplest and cheapest method;**
   - **Main limit:** **sludge can contain pathogens and heavy metals.**

ii. **Precipitation of struvite and hydroxyapatite from sludge leachates:**
   - **Advantages:** **recovery of high-quality P minerals;**
   - **Main limit:** **low P recovery efficiencies (< 40%).**

iii. **P recovery from sludge ashes after thermal valorization (*e.g.* gasification, incineration):**
   - **Advantages:** **high P recovery efficiency (> 60%);**
   - **Main limit:** **complex technology, sequential steps of (i) P extraction, (ii) metal purification, and (ii) P precipitation from the leachates.**

P recovery from saturated filter media:

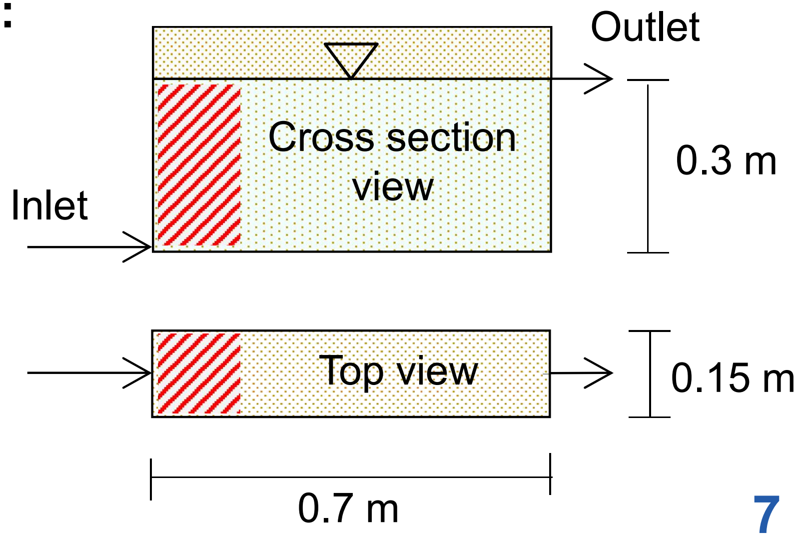
- **Only few studies (Bird and Drizo, 2009);**
- **Recovery process:** **direct re-use as soil amendment.**

Material & Methods: solid residues

Two different types of solid residues were tested for P extraction:

1. **Sludge residues from high temperature and high pressure water oxidation (*technosables*);**
   - **Sewage sludge from the Pioline WWTP (Aix-en-Provence, France, 175000 p.e.);**
   - **Treated by process Athos®:**
     T = 235 °C, P = 45 bar (VEOLIA, France).

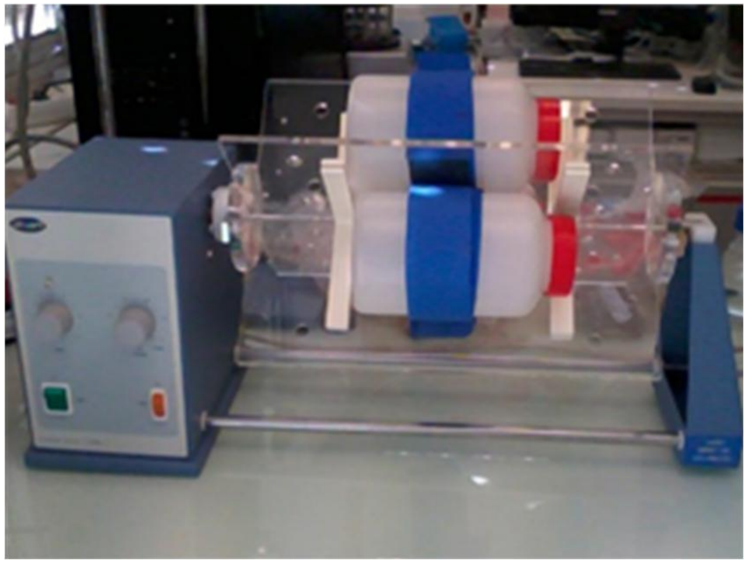
2. **Bauxite residues from a pilot scale filter after 6 months of operation at the IMT Atlantique (Nantes):**
   - **Feeding mode: continuous horizontal flow;**
   - **Inlet P concentration: 10 mg P/L;**
   - **Hydraulic retention time: 1 day;**
   - **P retention performances: > 95%;**
   - **Dashed area shows the samples used for the P extraction experiments.**



Material & Methods: characterisation of the residues

- *Aqua regia* extraction (EN 13657): to determine the total P content of the residues;

- Sequential extraction (adapted from Tiessen and Moir, 1993): to quantify four fractions of P in the residues:
  i. Bicarbonate extractable P (0.5 M $NaHCO_3$): weakly bound P;
  ii. Hydroxide extractable P (0.1 M NaOH): Fe and Al bound P;
  iii. Diluted HCl extractable P (1 M HCl): Ca bound P;
  iv. Concentrated HCl extractable P (~12 M HCl): P in stable compounds.



Material & Methods: P extraction experiments

- **24h equilibrium P extraction experiments (adapted from EN 12457(1-2)): to determine equilibrium P extraction capacities and best operating parameters:**
  - **Extractant solutions: 1 M HCl, 1 M citrate, 1 M acetate, and 0.1 M NaOH.**
  - **Liquid to solid ratio L/S (L/kg): 2, 5, 10, 20;**
  - **Volume of extractant solutions: 0.1 L;**
  - **Rotation speed: 5 rpm;**
  - **Contact time: 24 h.**

- **P extraction kinetic experiments: to determine rate constants (k) and maximum equilibrium capacities (q_e) of P extraction:**
  - **Extractant solutions: 1 M HCl and 1 M citrate at L/S ratio of 10;**
  - **Initial volume of extractant solutions: 0.7 L;**
  - **Duration of the experiments: 4 h.**

All the experiments were performed in duplicate and/or triplicate.

Results & Discussion: chemical characterisation

Aqua regia extraction

***Technosables*:**

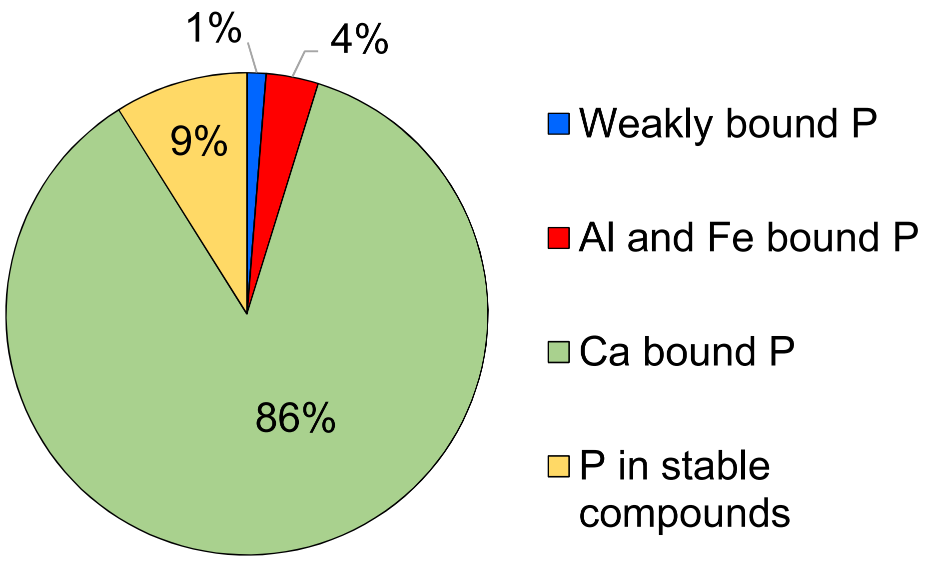
- **Main elemental composition (wt%):** **Ca 19.8%, Fe 16.3%, P 13.2%;**
- **Total P content: 131.9 ± 1.8 mg P/g.**

Bauxite residues from the pilot filter:

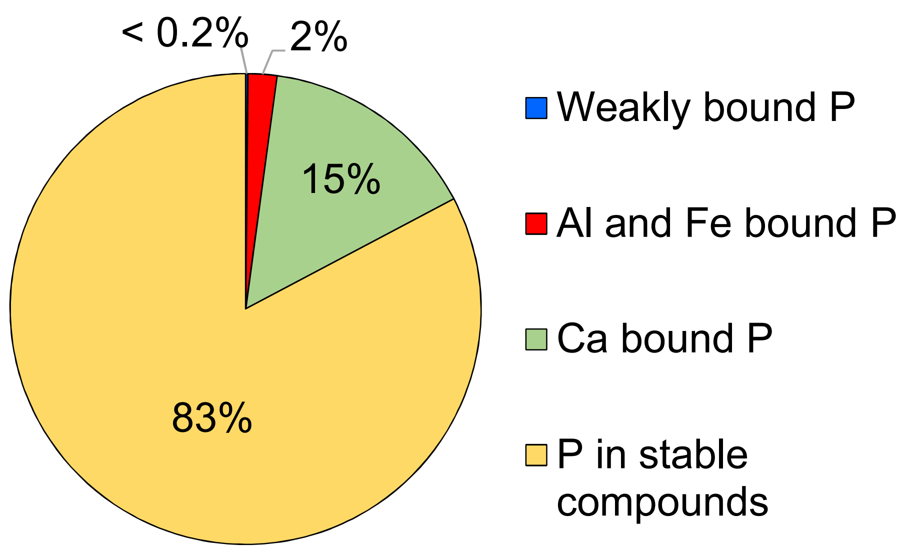
- **Main elemental composition (wt%):** **Fe 46.6%, Al 8.3%, Ca 3.5%;**
- **Total P content: 1.26 ± 0.04 mg P/g.**

Sequential extraction

***Technosables*:**

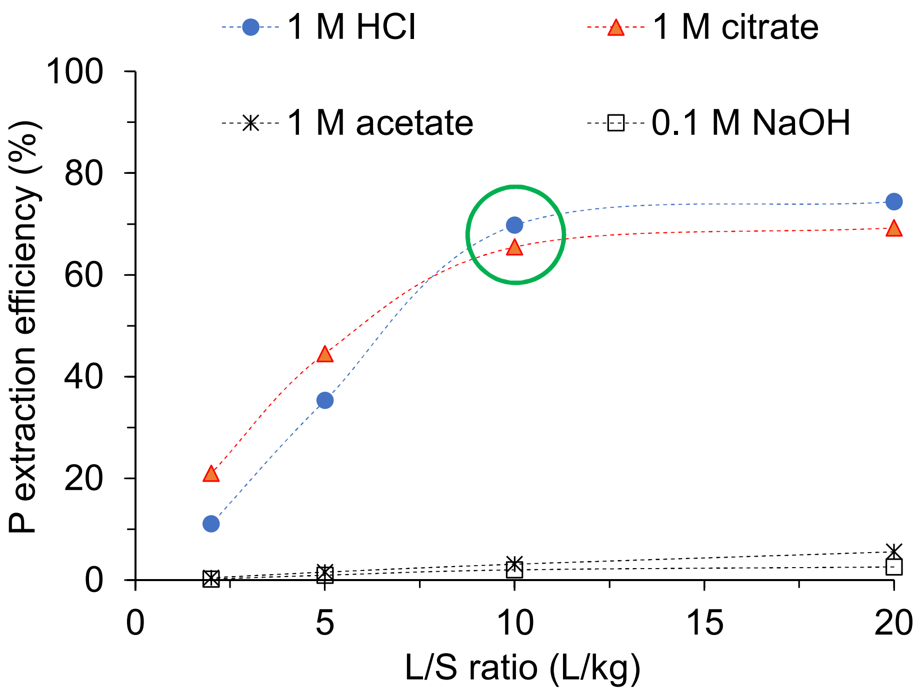


Bauxite residues from the pilot filter:



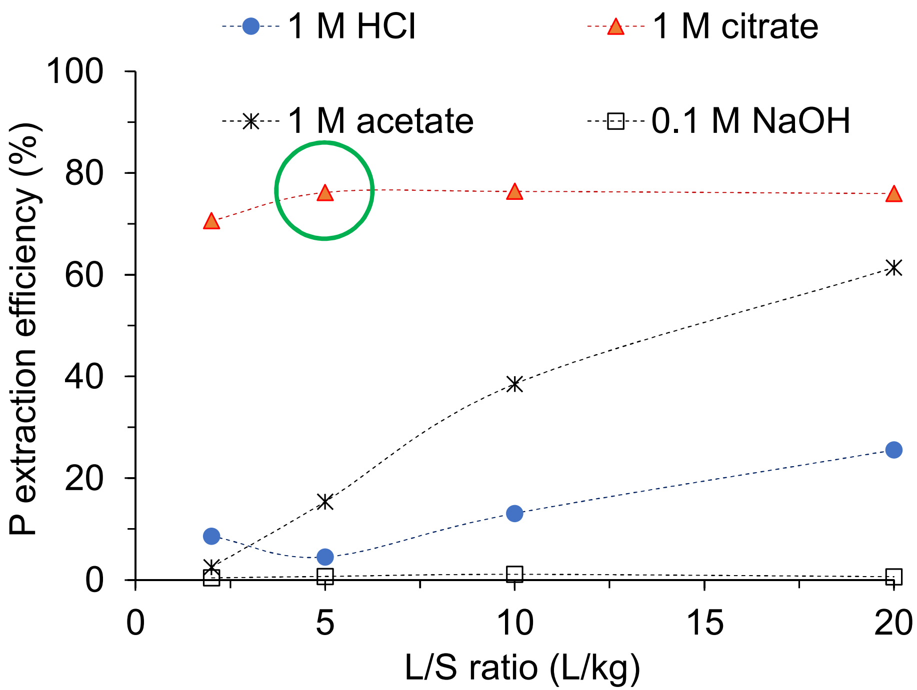
Results & Discussion: P extraction efficiency

***Technosables*:**



- **Best extractant solutions:**
  i. **1 M HCl and 1 M citrate;**
  ii. **L/S ratio of 10 L/kg;**
  ➢ **P extraction efficiency > 65%.**

Bauxite residues from the pilot filter:

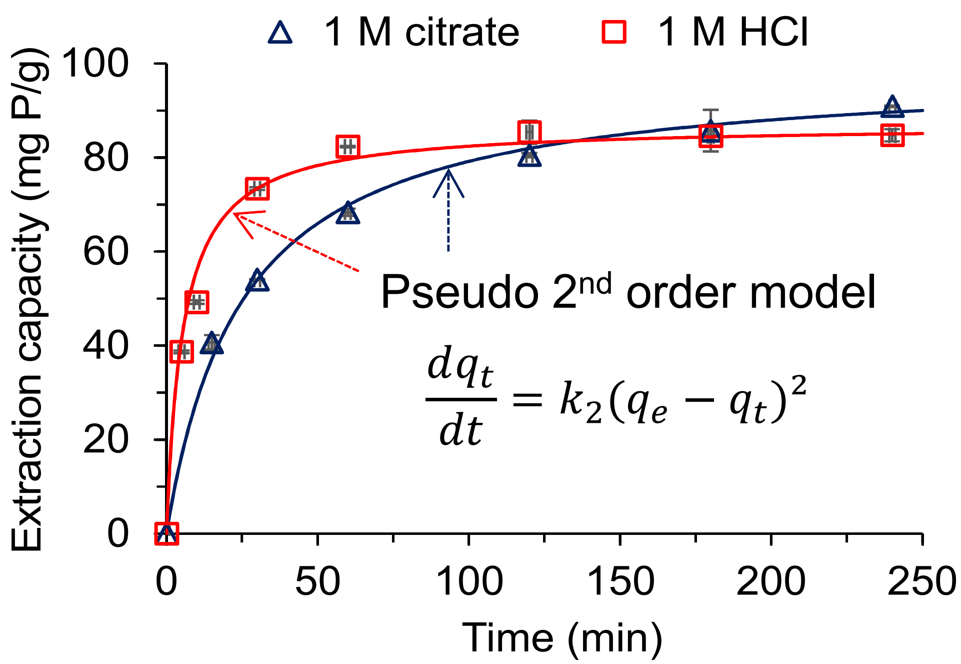


- **Best extractant solution:**
  i. **1 M citrate;**
  ii. **L/S ratio of 5 L/kg;**
  ➢ **P extraction efficiency > 75%.**

Contact time 24h

Results & Discussion: kinetics of P extraction from *technosables*

Kinetic experiments (L/S ratio 10)



P extraction efficiency after 1 h:

- **1 M HCl: 63%;**
- **1 M citrate: 52%.**

P extraction efficiency after 4 h:

- **1 M HCl: 65%;**
- **1 M citrate: 69%.**

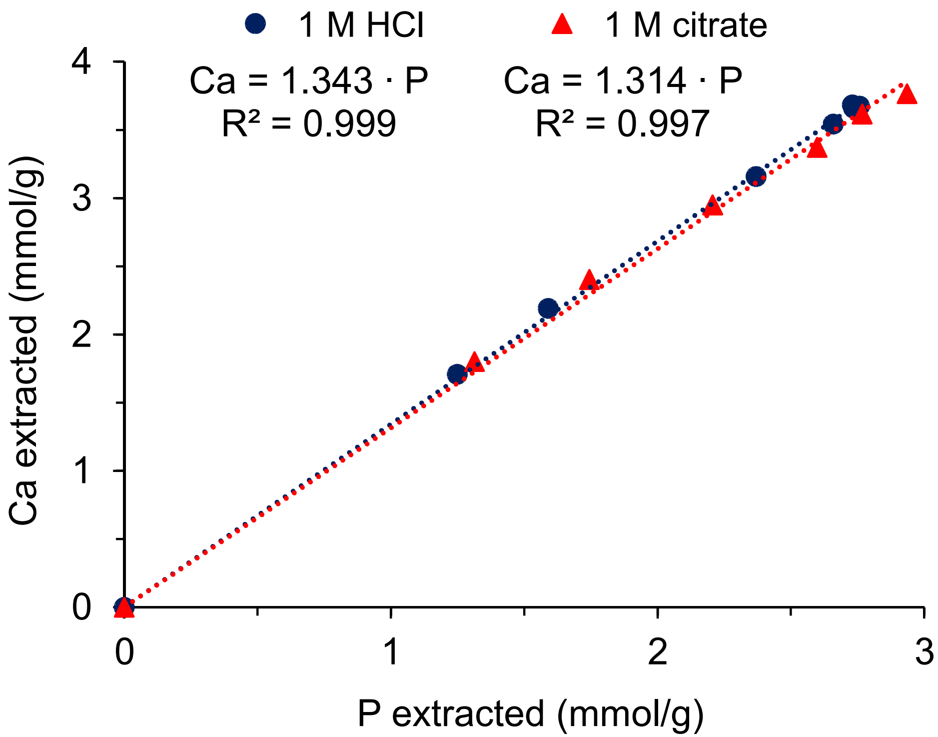
Pseudo 2nd order model (Ho and McKay, 1998)

Extractant	k_2 (g/(mg*min))	q_e (mg/g)	R^2 (-)
1 M HCl	0.0021	87.0	0.9996
1 M citrate	0.0004	99.0	0.9989

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

Results & Discussion: mechanisms of P and Ca extraction from *technosables*

Molar ratio of Ca extracted to P extracted (Ca/P)



Most recurrent Ca-P complexes (Valsami-Jones, 2001)

Name and formula	Molar ratio Ca/P	Solubility product (mol/L)
Brushite $CaHPO_4 \cdot 2H_2O$	1	$2.49 \cdot 10^{-7}$
Monetite $CaHPO_4$	1	$1.26 \cdot 10^{-7}$
Octacalcium phosphate $Ca_4H(PO_4)_3 \cdot 2.5H_2O$	1.33	$1.25 \cdot 10^{-47}$
Tricalcium phosphate $Ca_3(PO_4)_2$	1.5	$1.20 \cdot 10^{-29}$
Hydroxyapatite $Ca_5(PO_4)_3OH$	1.67	$4.7 \cdot 10^{-59}$

Direct correlation between Ca extracted to P extracted:

- **Molar ratio of Ca/P extracted (mean value ± SD): 1.34 ± 0.03;**

➢ **Dissolution of a mix of various Ca-P complexes.**

Self-assessment of the project

Duration of experimental work: 6 months (January-June 2017)

- **Main strengths and achievements:**
  - **Establishment of experimental protocols for:**
    1. **Physical-chemical characterization of the samples;**
    2. **P extraction experiments;**
  - **Complete description of capacity, kinetic, and mechanisms of P extraction from *technosables*.**

- **Weakness:**
  - **Poor P content of bauxite residues;**
  - **P saturation in pilot filter is not reached yet: continue filter operation and repeat the experiments when P saturation will be achieved:**
    1. **Physical-chemical characterization;**
    2. **P extraction experiments;**
    - **To determine capacity, kinetic, and mechanisms of P extraction from saturated samples of bauxite residue.**

Project outcomes and perspectives

This project has helped to develop research collaborations between the laboratory M2P2, INERIS-ARDEVIE and the company ALTEO (Gardanne, France).

Current projects focus on the development of reactive filters filled of bauxite residues to upgrade P removal in small wastewater treatment plants:

- **Project "Phosphorus" (M2P2-ALTEO), in progress:**
  i. **Duration: 6 months (February-July 2018);**
  ii. **Personnel: 1 master student;**
  iii. **Main objective: to describe performances of small-scale laboratory filters under different operating conditions (aerobic-anaerobic).**
- **Project "BauxFilter" (M2P2-INERIS), *appel à projets Observatoire Hommes Milieux Bassin Minier de Provence* (OHM-BMP 2018), selected:**
  i. **Expected duration: 6 months (February-July 2019);**
  ii. **Personnel: 1 master student;**
  iii. **Main objective: to describe performances of middle-scale laboratory filters with and without vegetation.**
- **Research contract (M2P2-INERIS-ALTEO), under final study: PhD thesis on field scale experiments under real operating conditions.**

Valorisation of the results

Internship report (1):

Martino M., Mise au point d'un procédé de récupération du phosphore à partir de résidus solides issus du traitement des eaux usées. Rapport de stage Master 2 en Génie des Procédés, spécialité Ecotechnologies et Procédés Propres, Faculté de Science, Université d'Aix-Marseille, 2017.

National conferences (1):

Barca C., Martino M., Chazarenc F., Roche N., Hennebert P., Phosphorus recovery from saturated samples of bauxite residue after their use as reactive filter material to treat wastewater. (Poster) 16ème Congrès de la Société Française de Génie des Procédés, Jul 2017, Nancy, France.

International conferences (1):

Barca C., Martino M., Chazarenc F., Roche N., Hennebert P., Phosphorus recovery from solid residues originated from wastewater treatment plants. (Oral presentation) International IWA conference on sustainable solutions for small water and wastewater treatment systems (S2small2017), Oct 2017, Nantes, France.

International peer reviewed journals (1):

Barca C., Martino M., Chazarenc F., Roche N., Hennebert P., Phosphorus recovery from solid residues originated from wastewater treatment plants. Under preparation.

Thanks for your attention