Interreg
North Sea Region
NuReDrain
European Regional Development Fund

EUROPEAN UNION

Webinar II: Recovery of phosphorus by chemical treatment

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Introduction

- Water flows from agriculture, e.g.,
  - Drainage water originating from tile drained agricultural fields
  - Greenhouse effluent

→ contain phosphate amounts of unused fertilizers

→ above the standard limits for surface water

Proposed solution:

Adsorption technology using Al and Fe based P-adsorbing materials: Iron Coated Sand (ICS), Vito A and B, DiaPure.

Relevant research question:

What about the saturated adsorption material: should it simply be disposed of as solid waste? When is recovery/regeneration recommended?

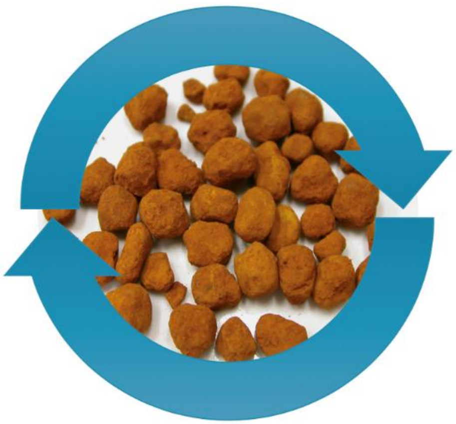
Integration of P-adsorbing material in a circular process

Introduction

Prospects for P-recovery:

- The main objectives:
  - **Regeneration of the saturated sorbents** making it reusable in several adsorption/desorption cylces and
  - **Recovery of phosphorus** by precipitation or used directly with irrigation water as fertilizer .

- The reusability of the granules is as important (or even more) than recovering phosphate
- Different desorption reagents: inorganic and organic acids, chelating agents and alkaline solutions, are already proposed in the literature
- A desorption process using an **alkaline** solution is proposed without harming the adsorbing material.

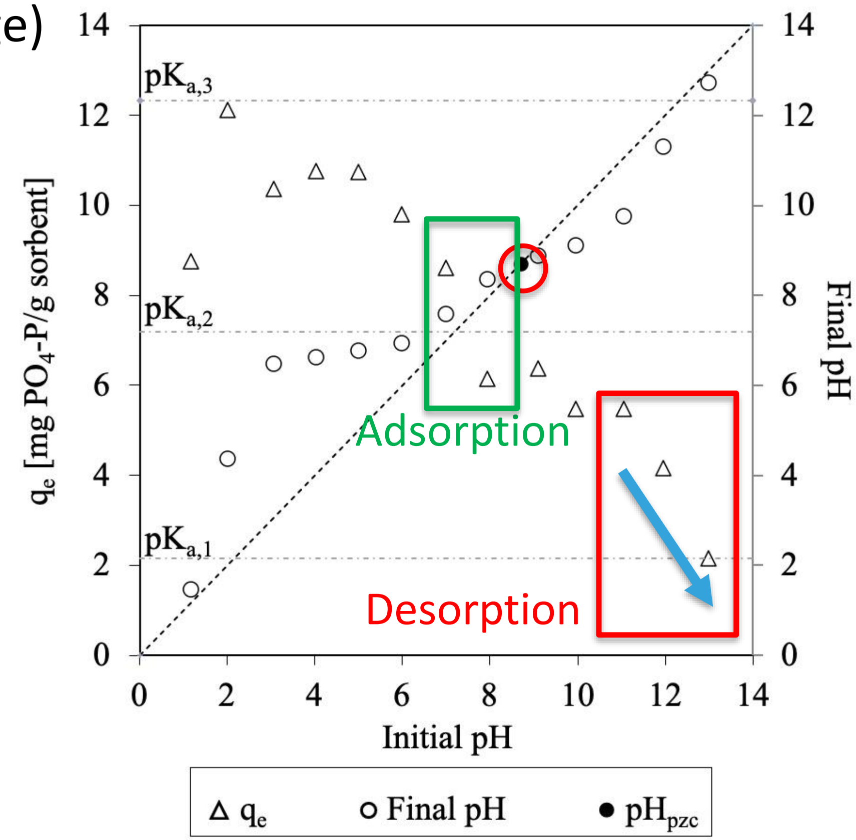


Integration of P-adsorbing material in a circular process

Introduction

Theoretical basis:

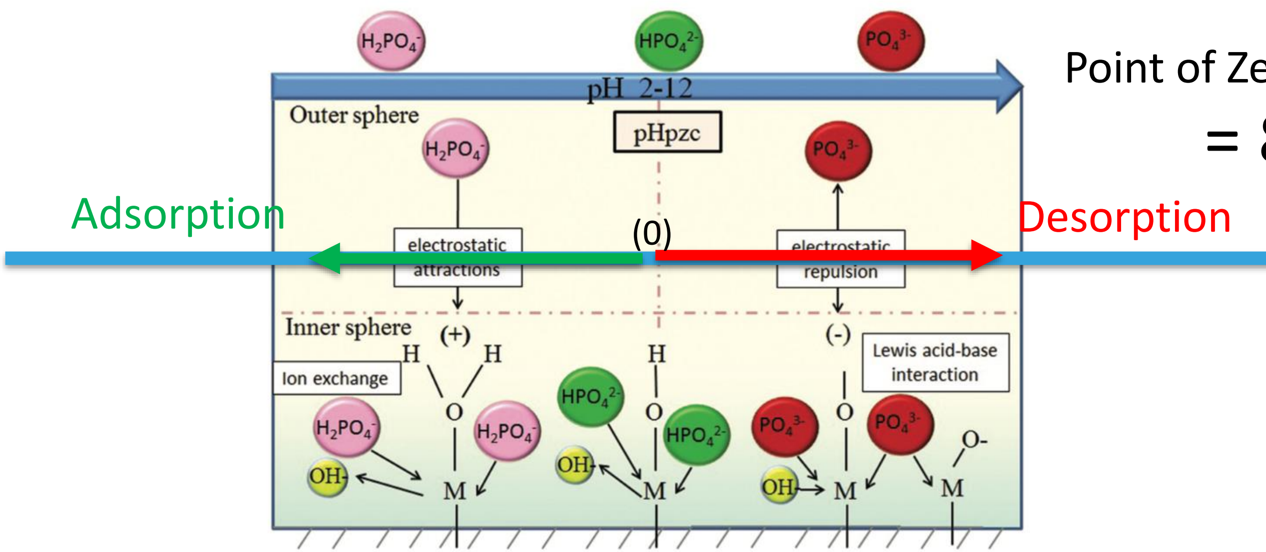
- The influence of initial pH on the adsorption capacity q_e for ICS
- Adsorption/desorption are **balancing processes** until an equilibrium is reached!
- pH 8.7 = pH_{PZC} (Point of Zero Charge) = final pH is equal to the initial pH
- pH range 1 - 8.7: high q_e
- pH range 8.7 – 13: low q_e
- pH>11 the q_e drops considerably



Introduction

Theoretical basis:

- Li et al. (2016): higher pH = the phosphate adsorption is affected by
  - the electrostatic repulsion (surface is negatively charged) and
  - increasing competitive effect of OH− ions for the active sites on the sorbent
  - =decreased adsorption capacity.

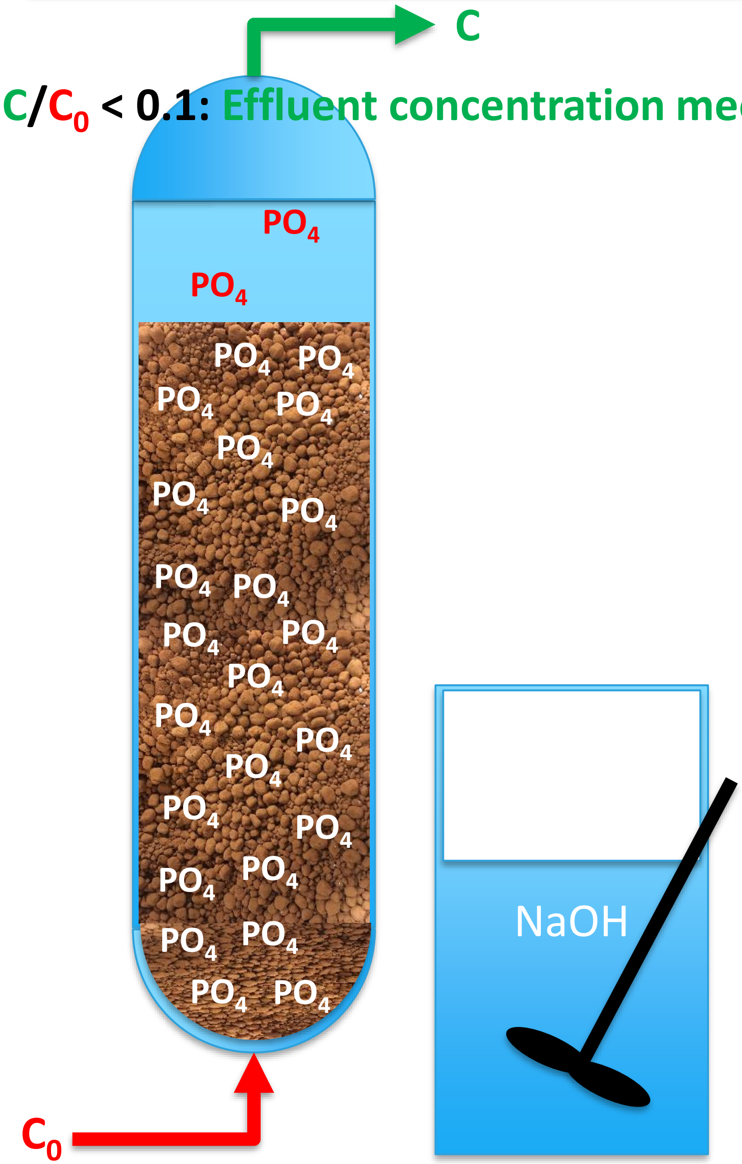


Point of Zero Charge = 8.7

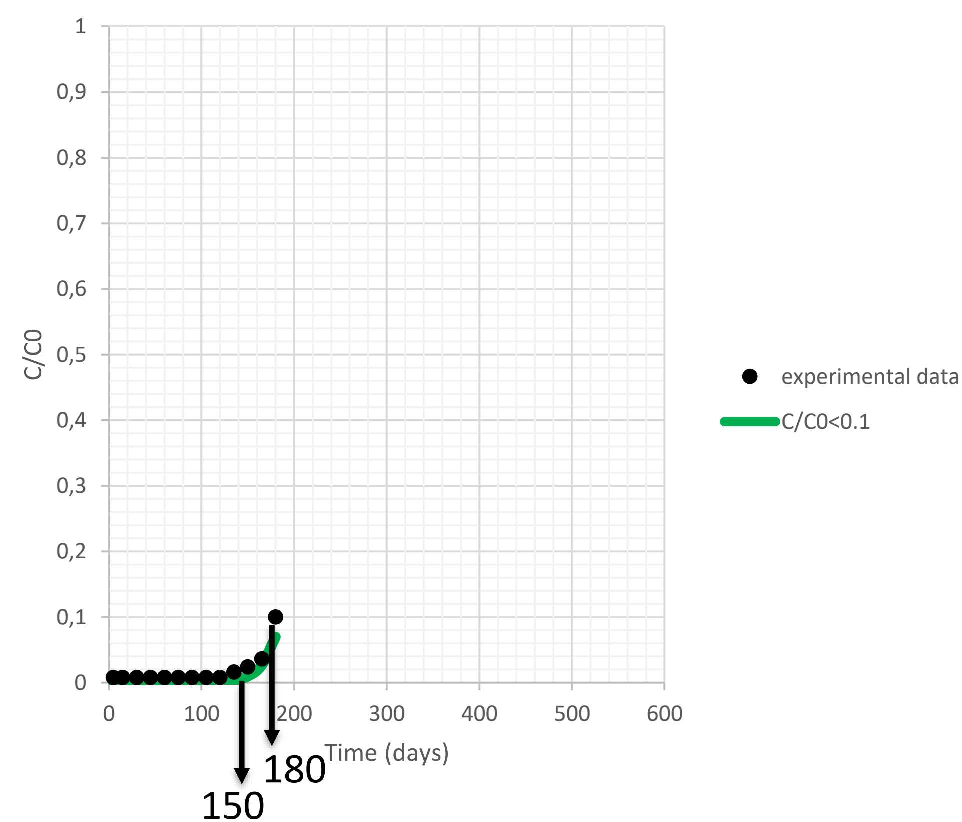
Li, M., Liu, J., Xu, Y., Qian, G., 2016. Phosphate adsorption on metal oxides and metal hydroxides: A comparative review. Environ. Rev. 24, 319–332.

Concept of ad/desorption

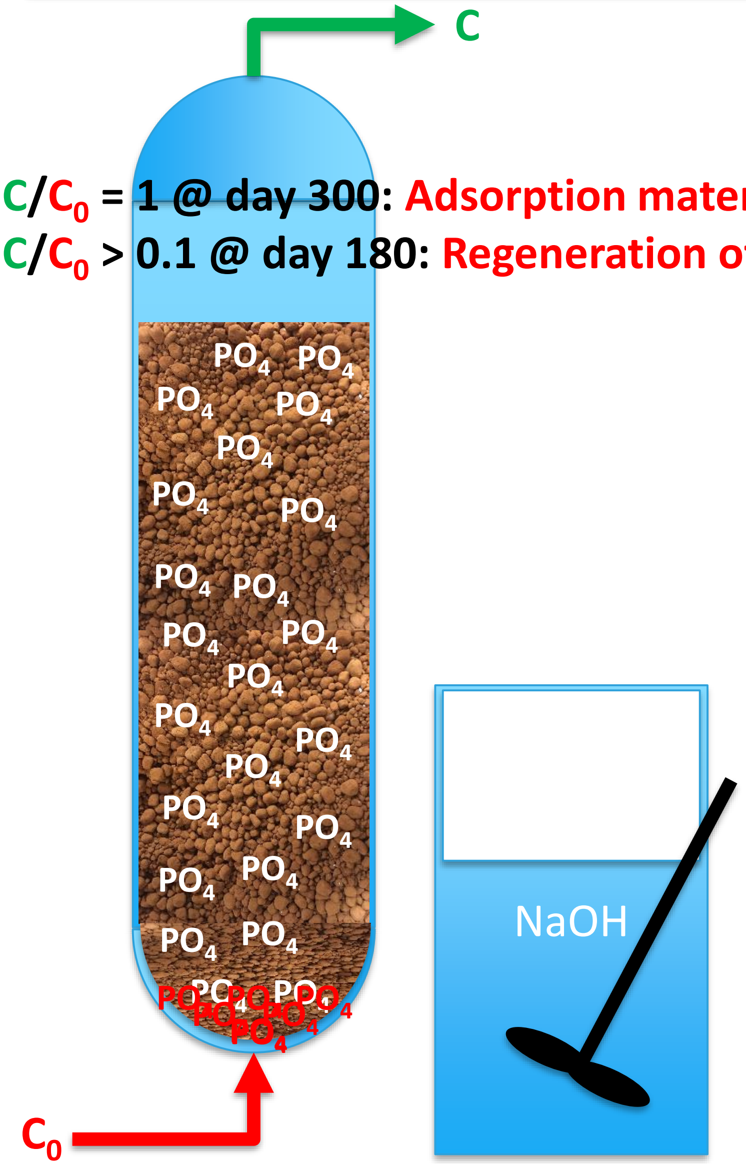
$C/C_0 < 0.1$: Effluent concentration meets the discharge limit



Adsorption Phase: Day 0-180



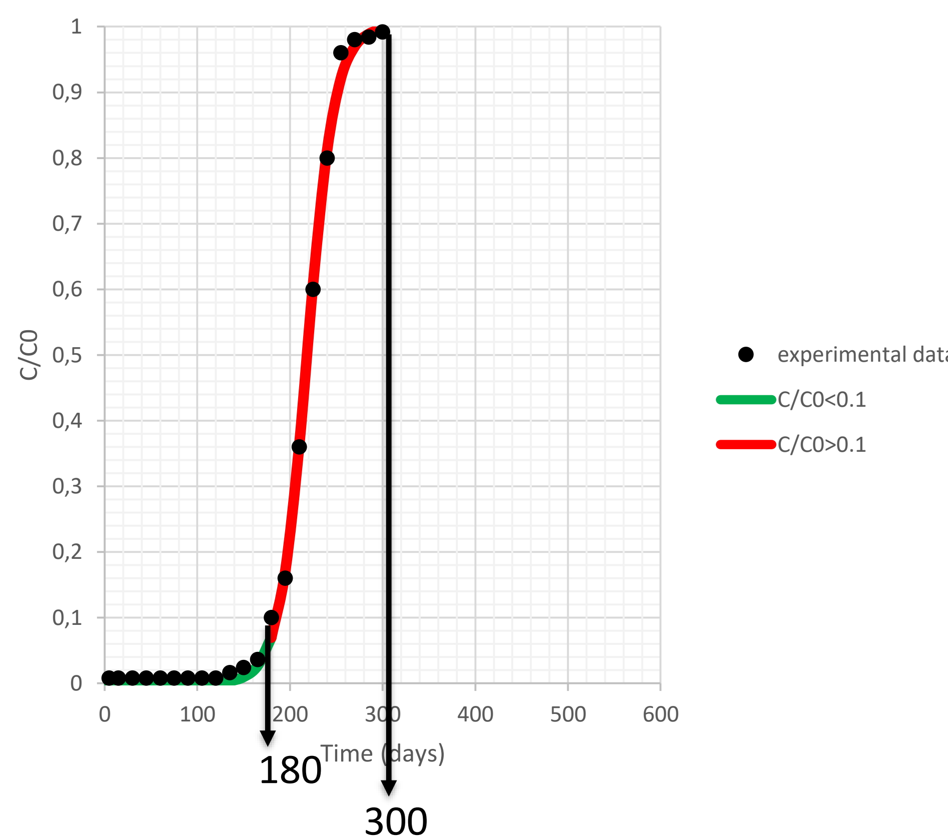
Concept of ad/desorption



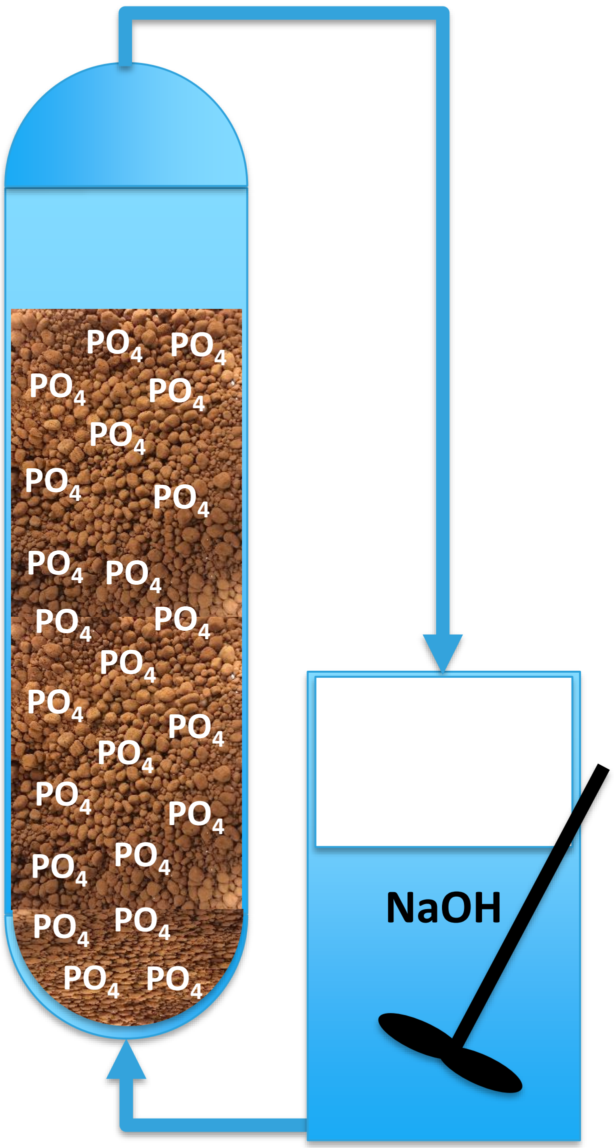
$C/C_0 = 1$ @ day 300: **Adsorption material (ICS) is completely saturated**

$C/C_0 > 0.1$ @ day 180: **Regeneration of ICS is needed**

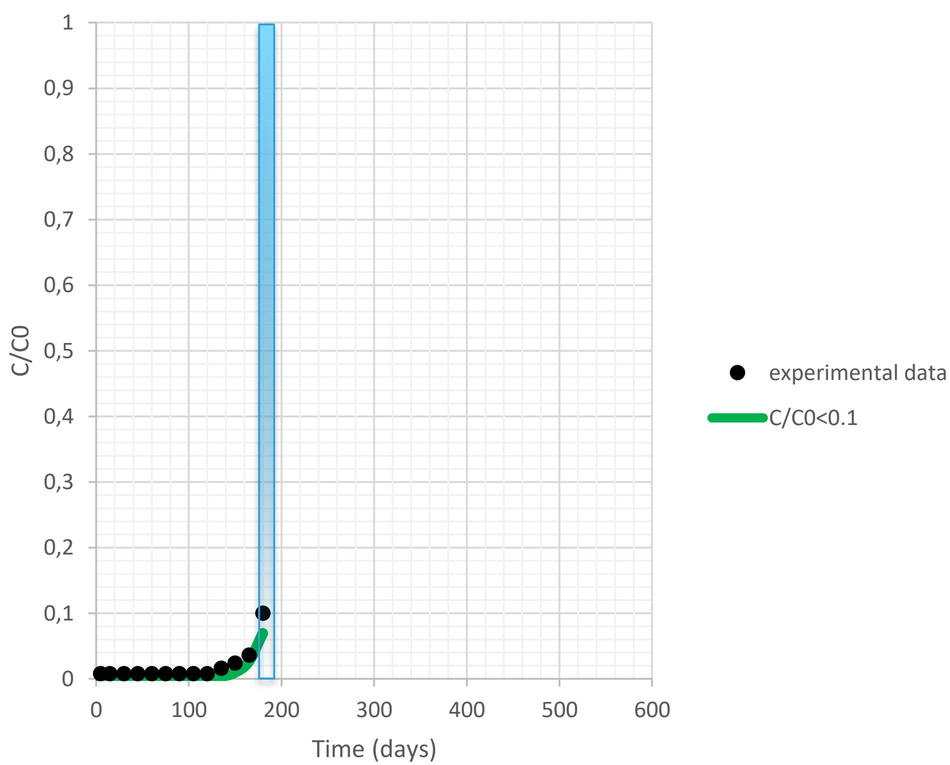
Adsorption Phase: Day 180-300



Concept of ad/desorption



Desorption Phase: Day 180



Concept of ad/desorption

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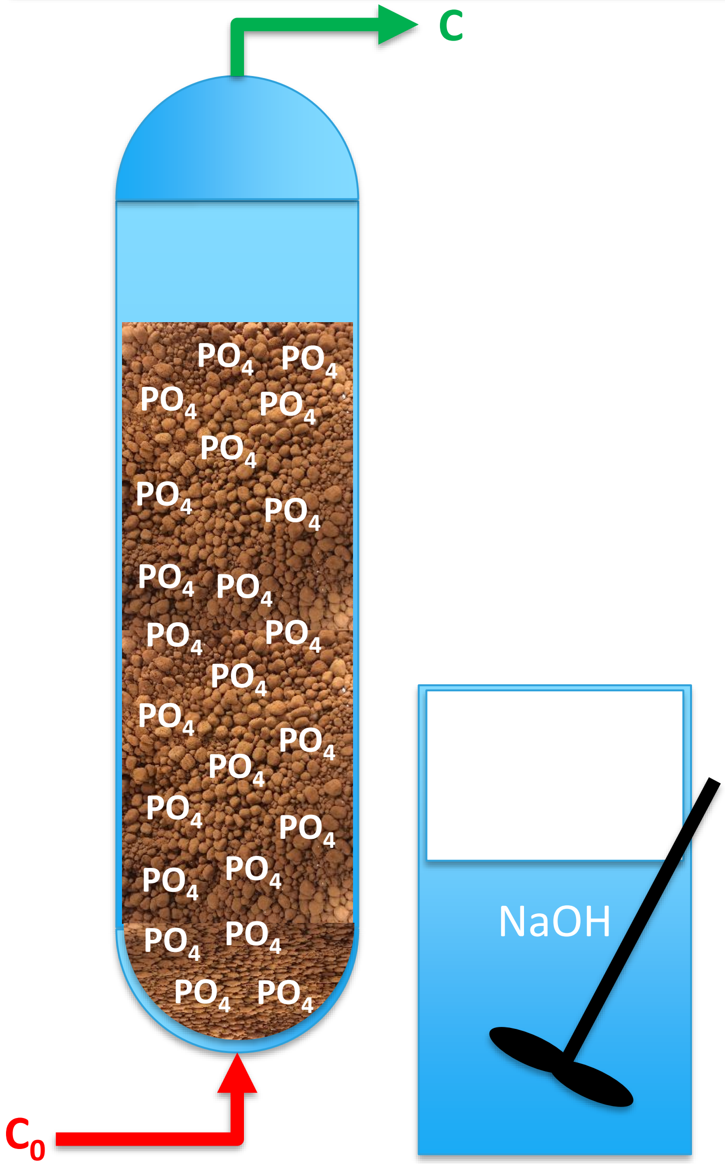
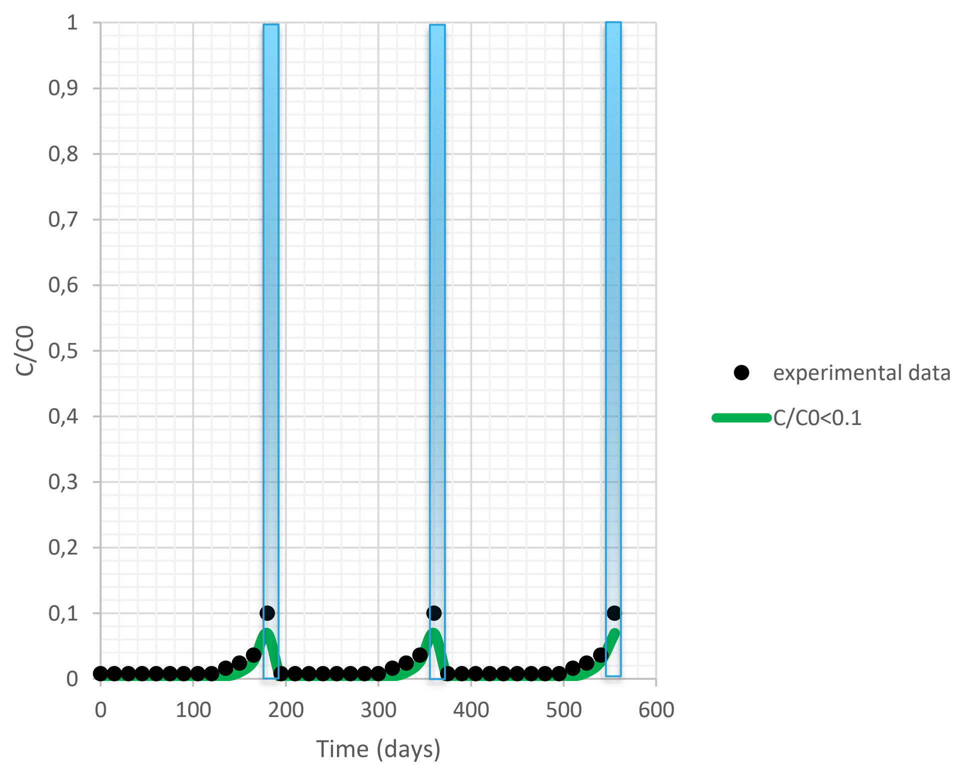


Regeneration of the saturated sorbent and recovery of phosphorus

Intermittent regeneration of ICS



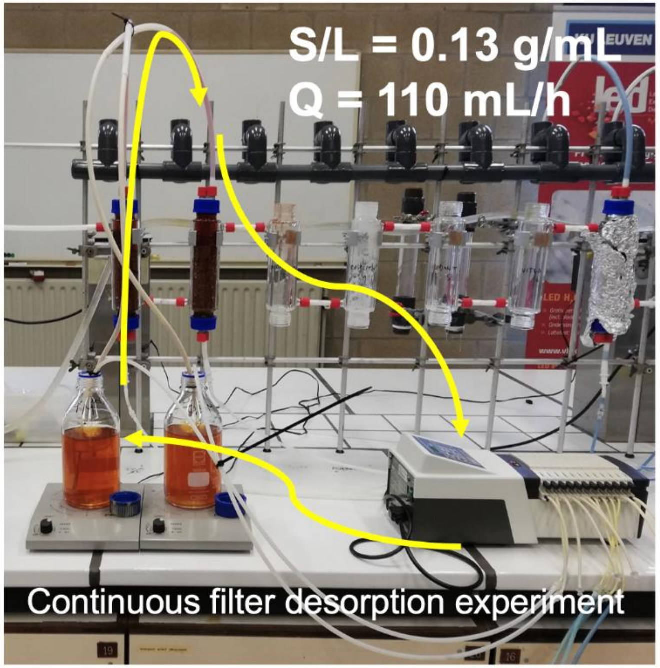
Materials & Methods

1. **Batch desorption experiments:** 5g of pre-dried saturated ICS was brought into contact with NaOH solution.

   Variable parameters:
   - NaOH concentration (1-0.5-0.1- 0.01- 0.001M),
   - Desorption time (5min-48h)
   - Solid/liquid ratio (S/L= 0.03-1 g/mL)

2. **Continuous filter desorption experiment:** 1 liter of NaOH solution was recirculated over an adsorption column filled with 128 g of saturated ICS granules.

3. **Analysis of the samples: Liquids**: PO_4-P determination by ion chromatography after .45 µm filtration. **Solid grains**: SEM-EDX



Continuous filter desorption experiment

Results & Discussion
Batch experiments

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- The composition of 1 g of saturated ICS granules was determined by a complete destruction of the granules by Aqua Regia and ICP analysis:
  - Phosphorus: 15.30 +/-1.25 mg P/g DS **=1.5%P**
  - Iron: 590.7 +/-8.7 mg Fe/g DS **=59%Fe**

- **Figure 1**: A minimum desorption time of 24 hours and a NaOH concentration of 0.1 - 1M is necessary to ensure a sufficiently high desorption efficiency.

- **Figure 2**: The solid over liquid ratio (S/L expressed in g/mL) has a pronounced effect on desorption efficiency. An S/L lower than 0.10 g/mL is recommended.

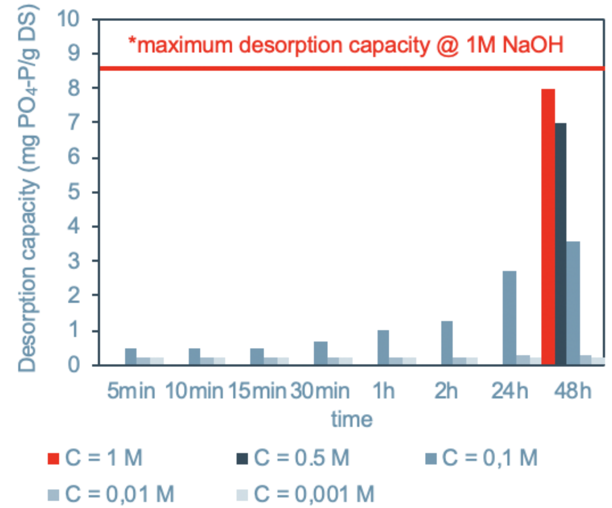


Figure 1: Influence of NaOH concentration and desorption time.

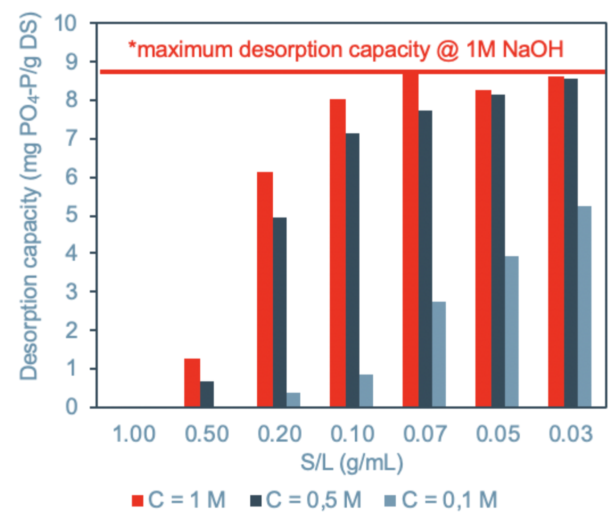


Figure 2: Influence of solid/liquid ratio.

Results & Discussion
Continious filter experiments

- **Figure 3:** Continuous desorption filter experiments show that only a concentration of 0.5 and 1M NaOH lead to a desired desorption of phosphorus from the ICS granule. At least 24 hours desorption time must be provided.

- **Figure 4:** During the first hour of the continuous desorption experiment only 0.4 mg P/g DS and 0.9 mg P/g DS can be leached for a NaOH concentration of 0.5 and 1M respectively. A concentration of 0.1M NaOH desorbed almost no phosphorus.

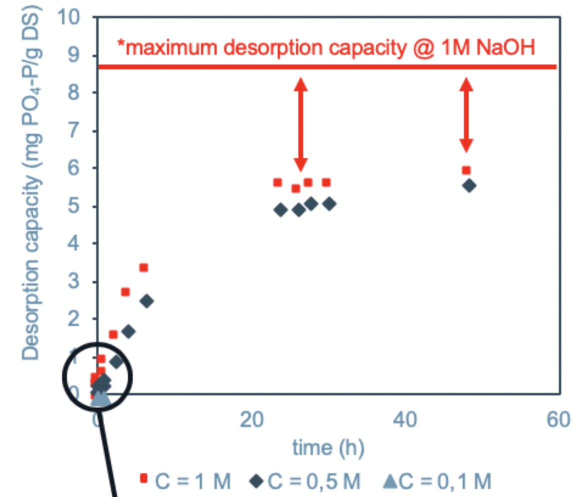


Figure 3: Continuous filter desorption experiment and the effect of the NaOH concentration on desorption capacity

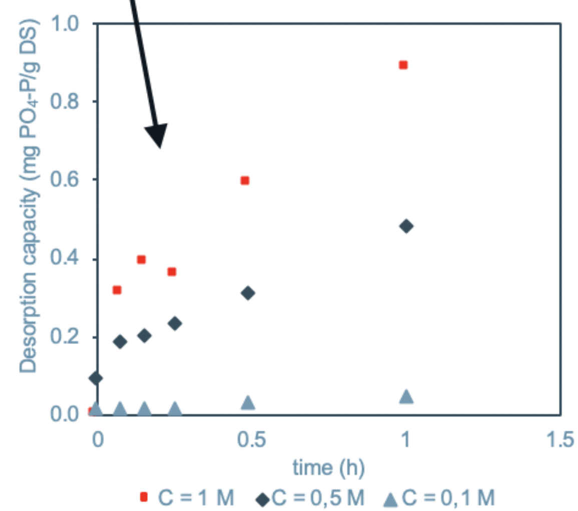


Figure 4: The progress of the desorption during the first hour of the continuous filter desorption experiment

Results & Discussion
SEM-EDX analysis

- Energy-dispersive X-ray (EDX) Analysis with a Scanning Electron Microscope (SEM) of saturated ICS from two column experiments.

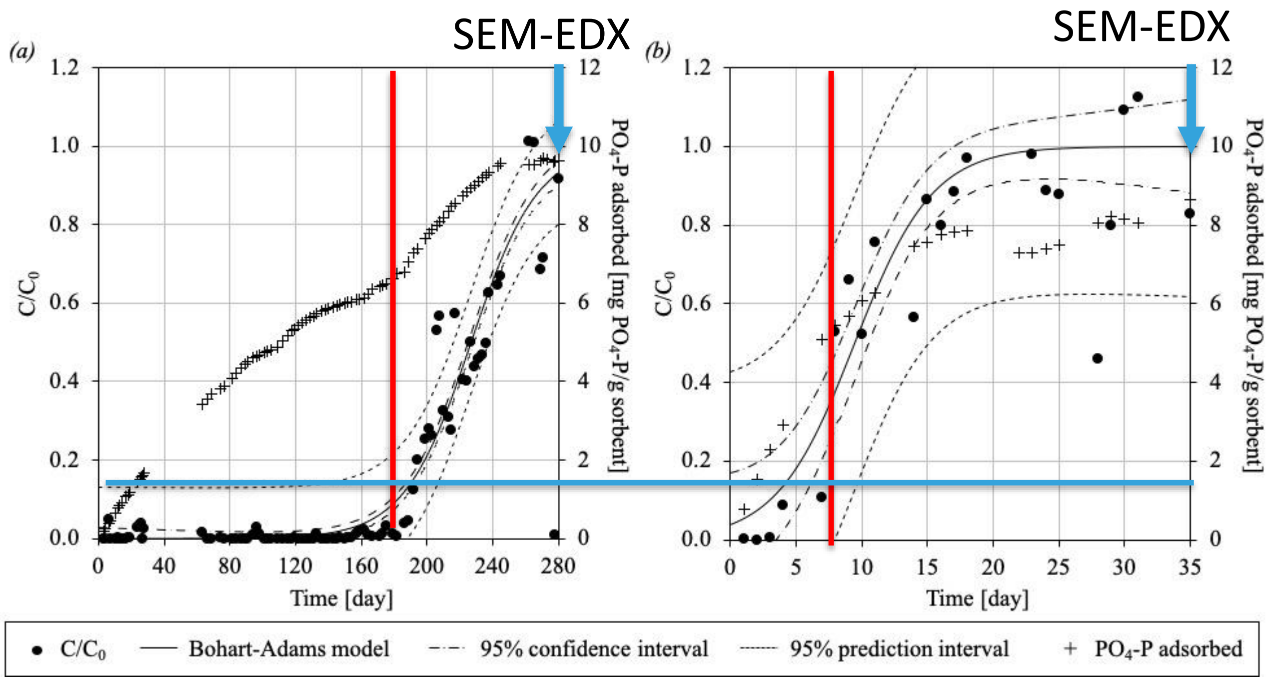


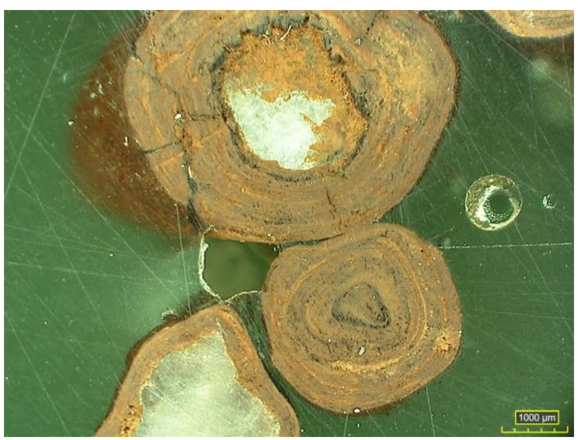
Figure 5: Adsorption column experiments on lab-scale (influent P concentration = 25 mg PO_4-P/L) with EBCT= 5.5 h (a) and EBCT= 0.5 h (b)

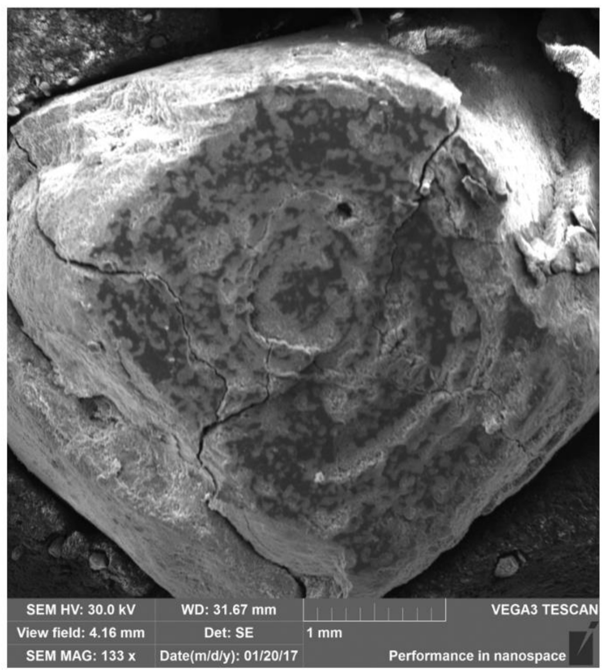
- **Figure 5:** The breakthrough curve of column experiments with an Empty Bed Contact Time (EBCT) of **5.5 h** and **0.5 h** results in a breakthrough time of **180 days and 7 days** respectively.

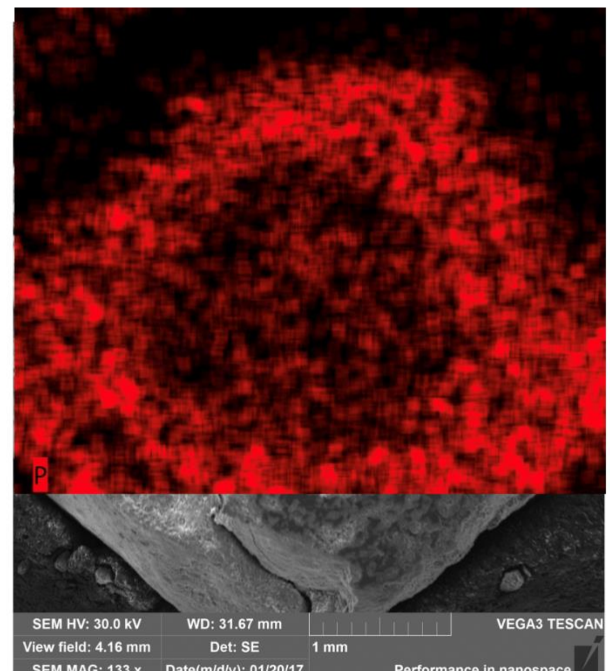
Results & Discussion
SEM-EDX analysis

- Energy-dispersive X-ray (EDX) Analysis with a Scanning Electron Microscope (SEM) of saturated ICS from two column experiments.
- **Figure 6:** SEM-EDX of saturated ICS of column experiment with **EBCT of 0.5 h**. The phosphate is mainly adsorbed at the outer layers of granules.

polished ICS granules embedded in a resin





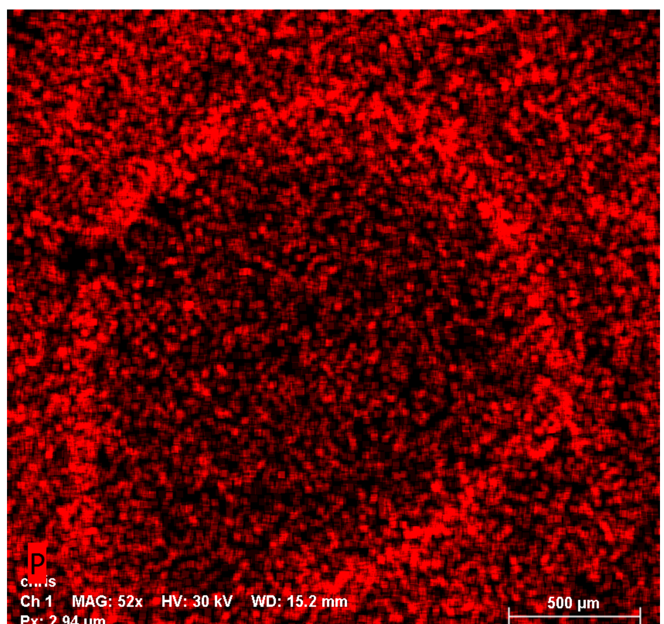


Results & Discussion
SEM-EDX analysis

- Energy-dispersive X-ray (EDX) Analysis with a Scanning Electron Microscope (SEM) of saturated ICS from two column experiments.

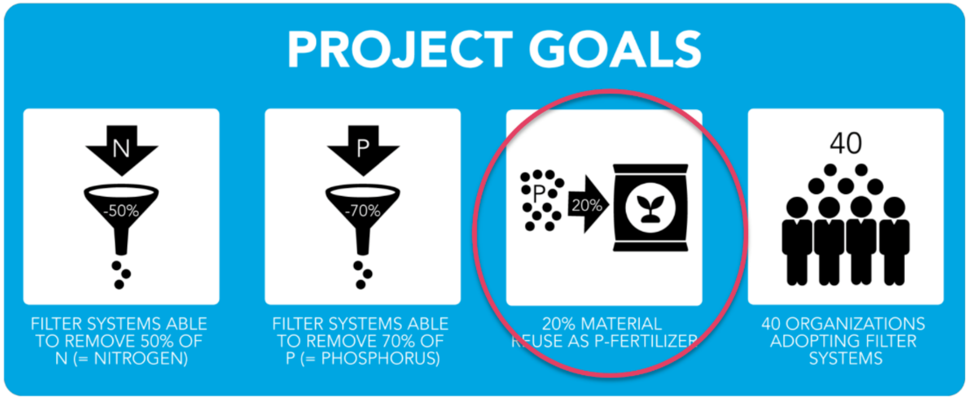
- Figure 7: SEM-EDX of saturated ICS of column experiment with **EBCT of 5.5 h**. phosphorous is accumulated at the sand core of the granule = phosphorous migrates towards the core of the granule.

Si – Fe – P analysis by EDX



Conclusions

- Optimal NaOH concentration = 0.5 M
- Optimal contact time = 24 hours or more
- Optimal S/L ratio = 0.10 - 0.05 g/mL
- P-desorption efficiency = 40% @ 0.5 and 1 M NaOH
- Leaching of Fe during the desorption process is a problem
- Desorption of P from the inner layers of the granule will be a problem



Future perspectives

- **What to do next?**
  - Investigating whether other adsorption materials are better suited for desorption: Vito materials and DiaPure?
  - Looking for ways to reduce desorption pH.
  - Carrying out continuous long-term column tests in which cycles of adsorption and desorption are completed → To do in the coming months.

Q & A