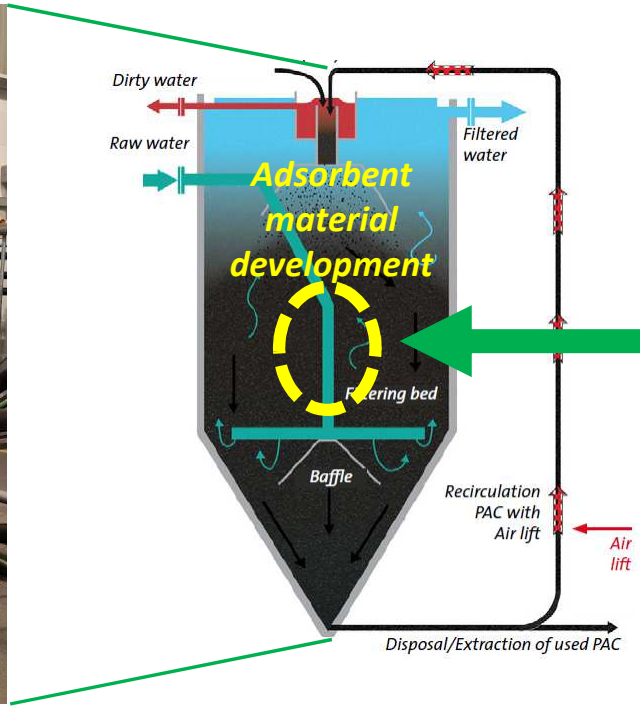
Development of a crab-carapace based adsorbent for FiltraFLO™-P

Phos4You FINAL CONFERENCE, 22nd – 23rd September 2021, Essen - Germany & online,

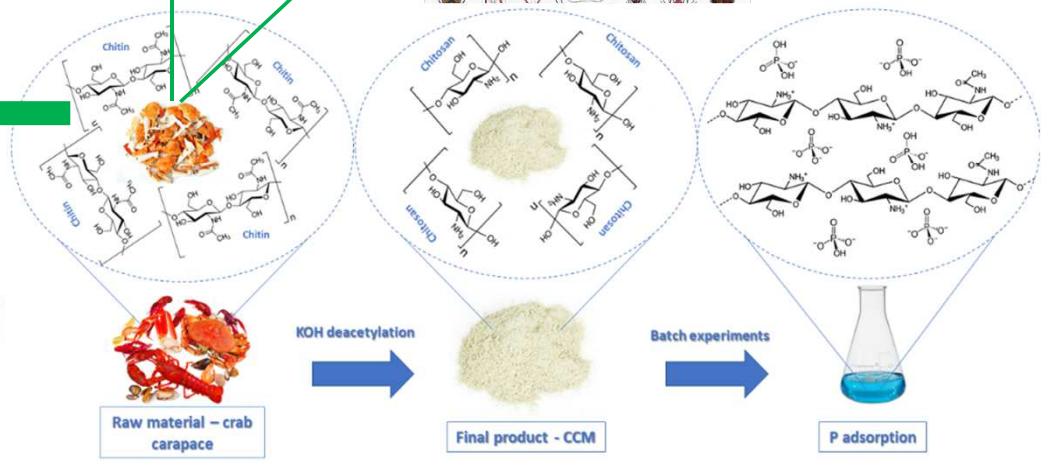
Dr Sabolc Pap, ERI, NHC, UHI

ERI contribution

One of 6 project process *demonstrators* – FiltraFLO™ (Veolia unit)



Over 4500 species
1.4 million tonnes

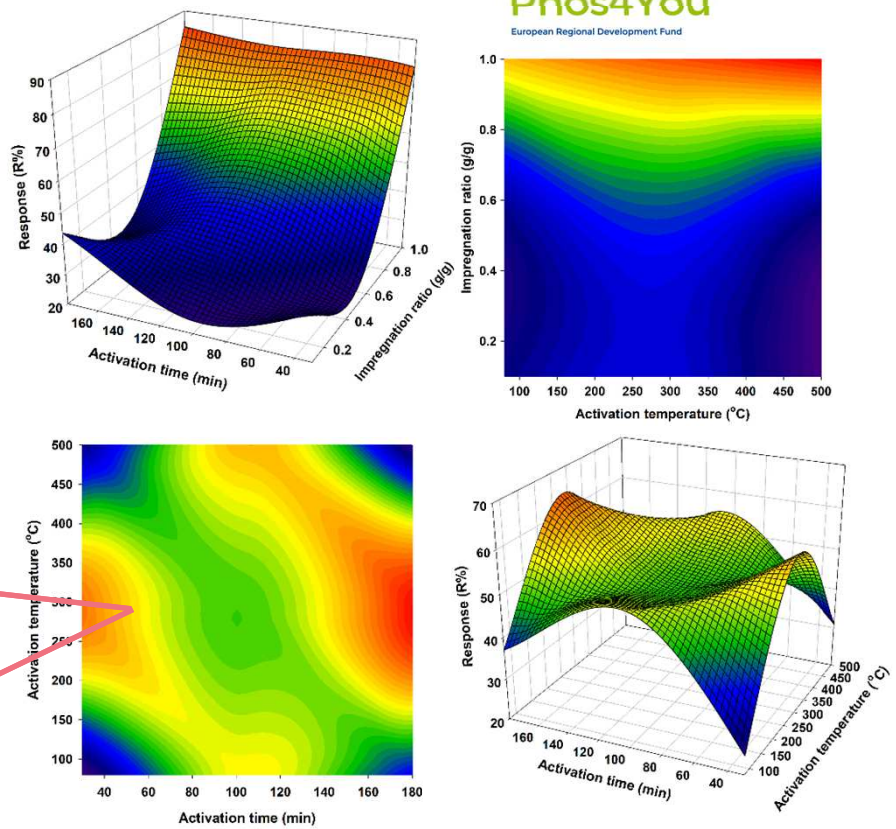


Chitosan-calcite adsorbent (CCM)

- Response Surface Methodology - Box-Behnken design (optimisation)
- Multi factor design

Veolia requirements

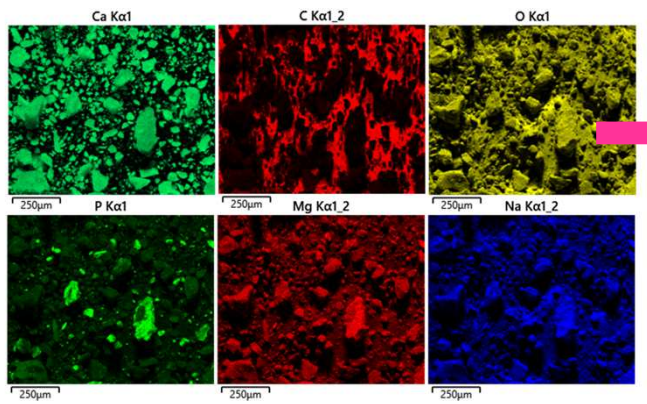
- Adsorption capacity > 10 mg/g
- Preparation cost ≈ 150 Euro/ton



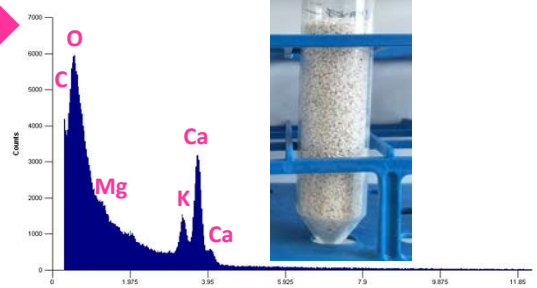
Pap, S., et. al., 2020. Synthesis optimisation and characterisation of chitosan-calcite adsorbent from fishery-food waste for phosphorus removal. *Environmental Science and Pollution Research*, pp.1-13.

CCM characterisation

- Proximate analysis (i.e., ash, moisture,…)
- ICP elemental analysis
- pH at point zero charge (pH_{pzc})
- pH_{sus} (acidity or alkalinity)
- Surface and porous characteristic (BET)
- Crystal structure (XRD)
- Morphology and pore structure (SEM)
- Surface elemental composition and mapping (EDX)
- Surface chemistry (FTIR)
- Thermal stability (TGA)
- X-ray photoelectron spectroscopy (XPS)

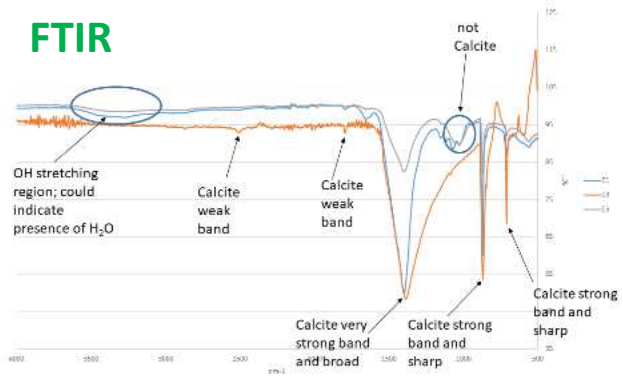


SEM mapping

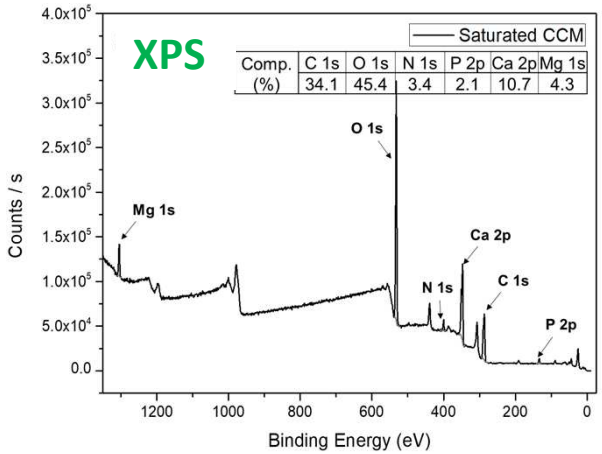


EDX

FTIR



XPS



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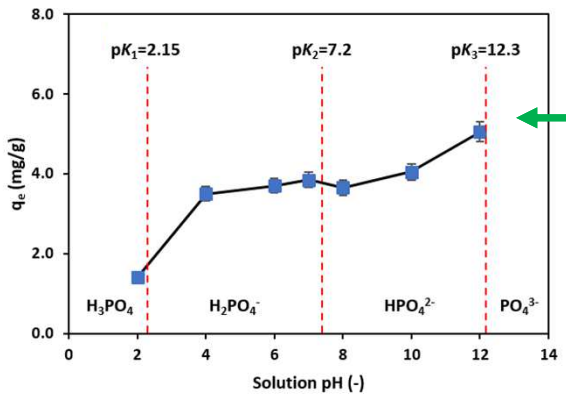
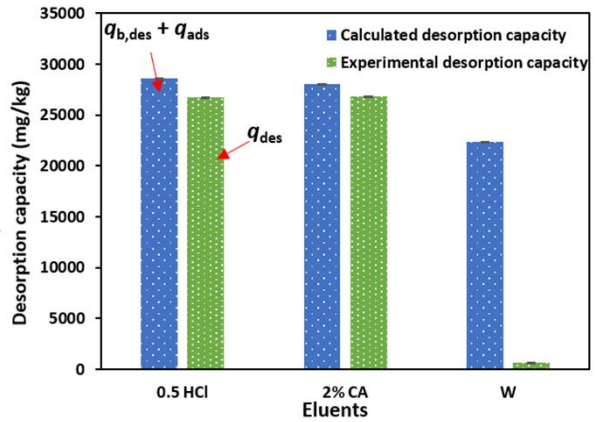
Batch adsorption studies

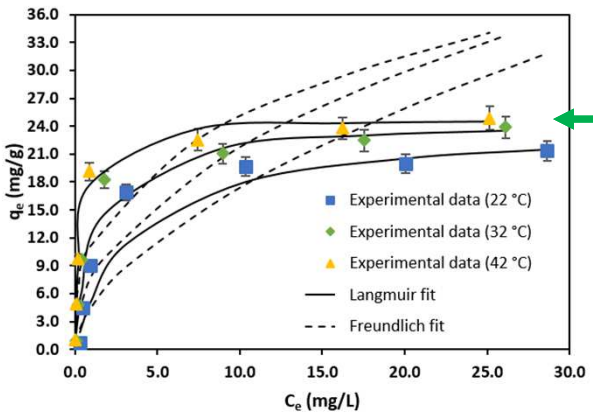


pH influence

Desorption potential

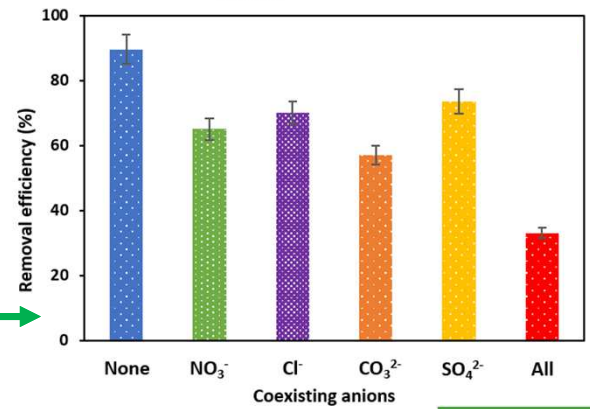


q_{max} = 21.36 mgP/g



Isotherm/thermodynamic study

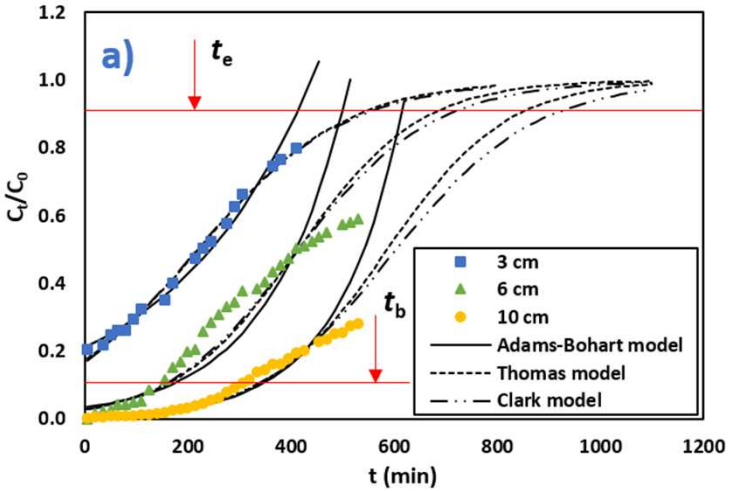
Coexisting anions

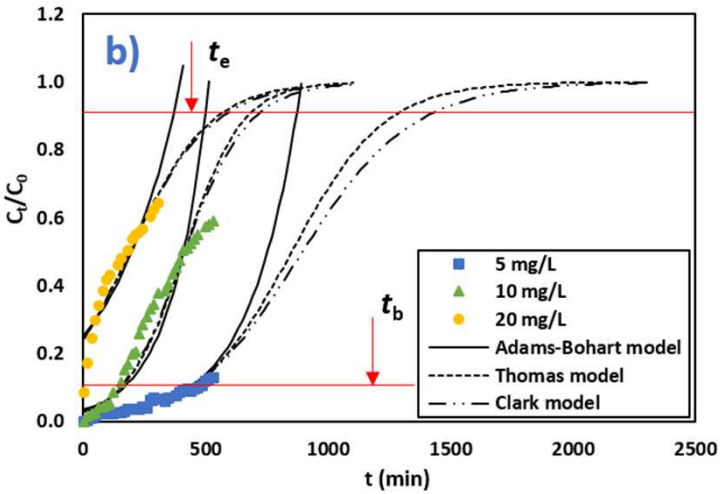


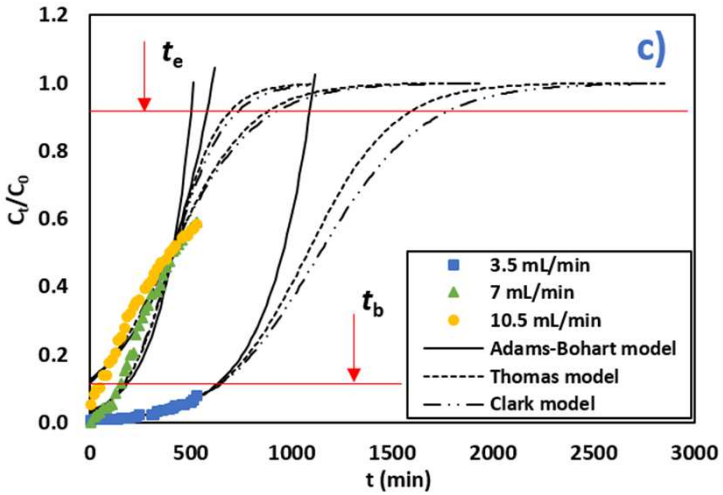
and many more…

Pap, S., et. al., 2020. Low-cost chitosan-calcite adsorbent development for potential phosphate removal and recovery from wastewater effluent. *Water Research*, 173, p.115573.

Dynamic column studies

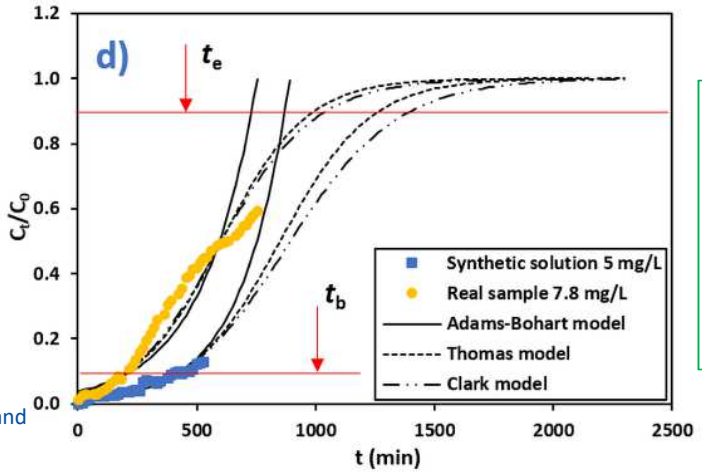






- **Bed height**
- **P inlet concentration**
- **Flow rate**

Optimal conditions

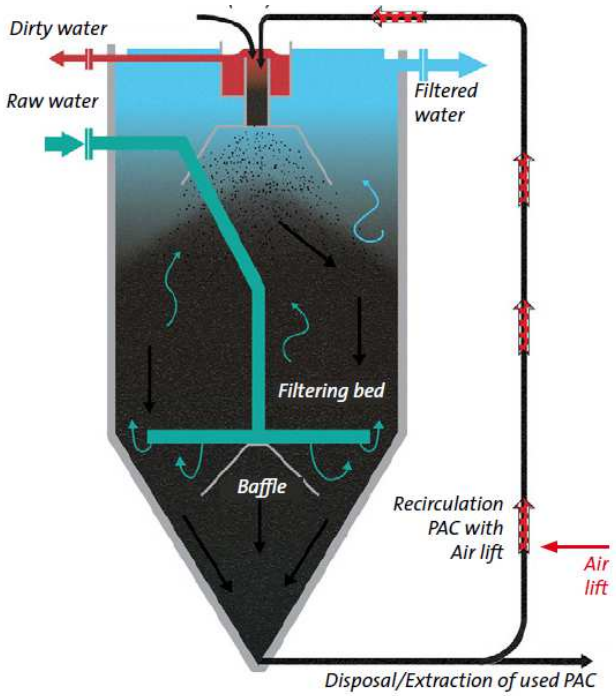


Secondary wastewater effluent

Pap, S., et. al., 2020. Low-cost chitosan-calcite adsorbent development for potential phosphate removal and recovery from wastewater effluent. *Water Research*, 173, p.115573.

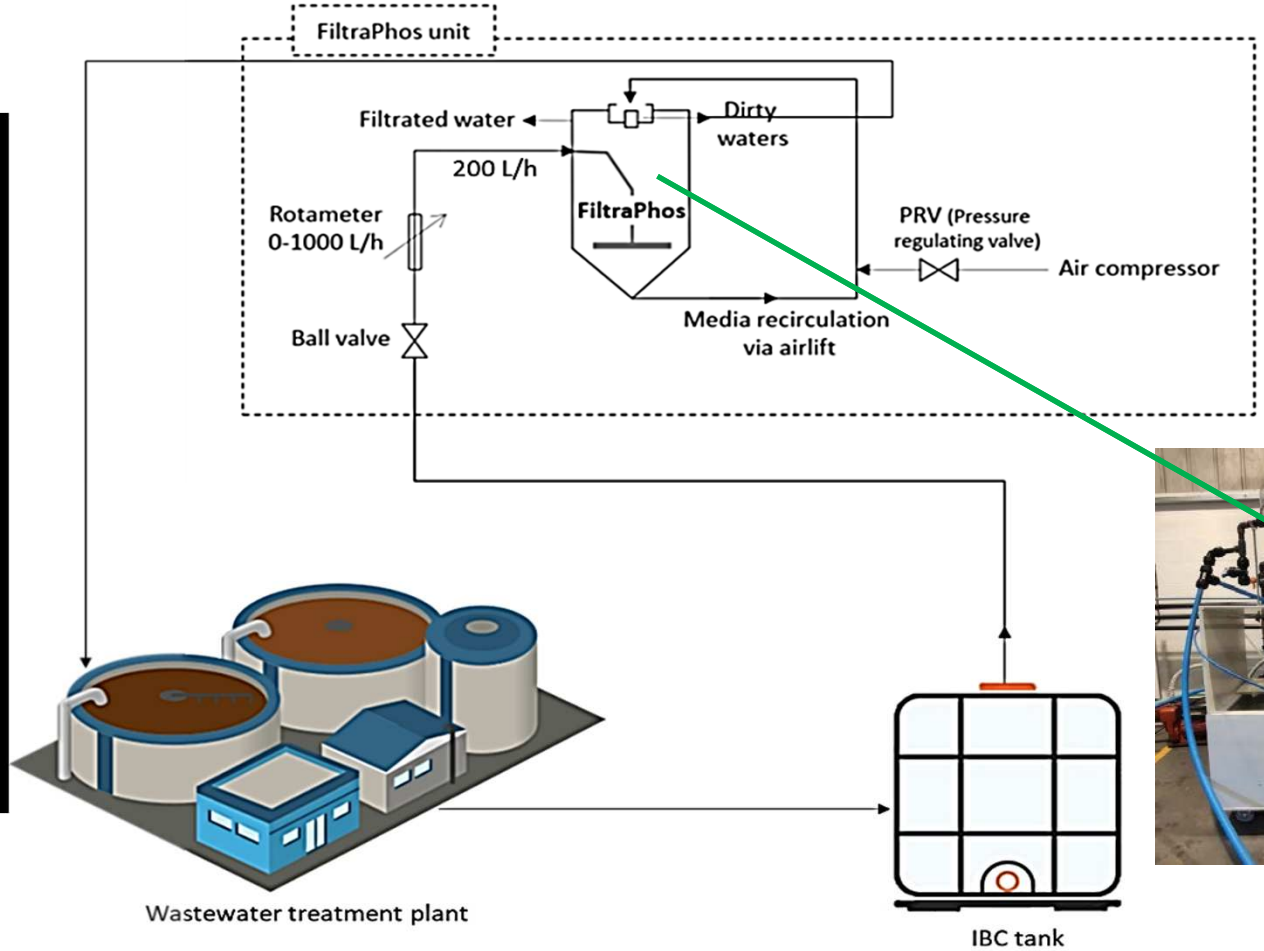
Pilot study with wastewater

Scottish Water Horizons Development Centre at Bo'ness

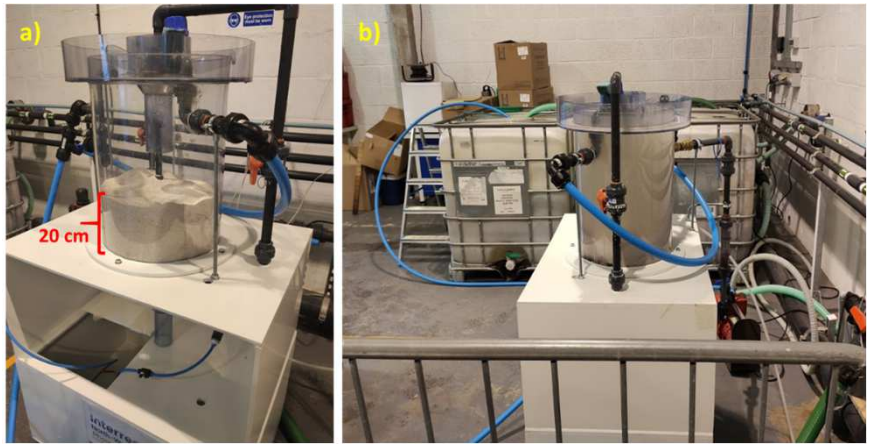


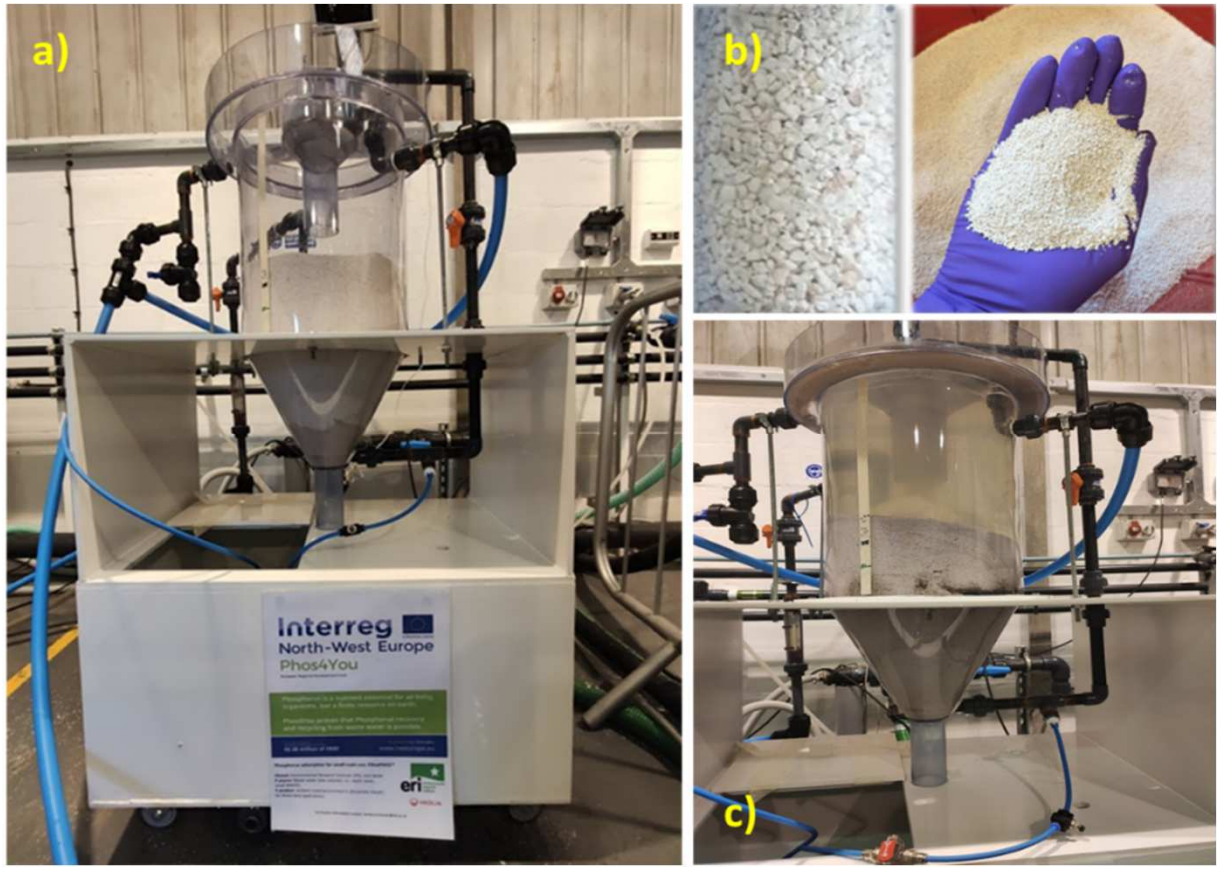
- Pilot trials during January-February 2020.
- Veolia™ Water Technologies designed FILTRAFLO™-P pilot reactor.

Schematic of the pilot process



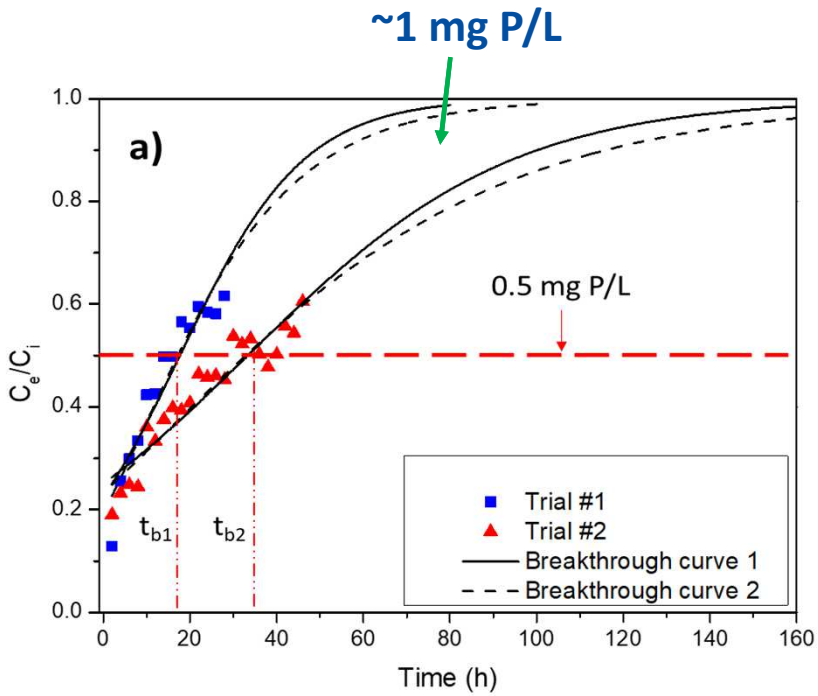
FILTRAFLO™-P pilot reactor

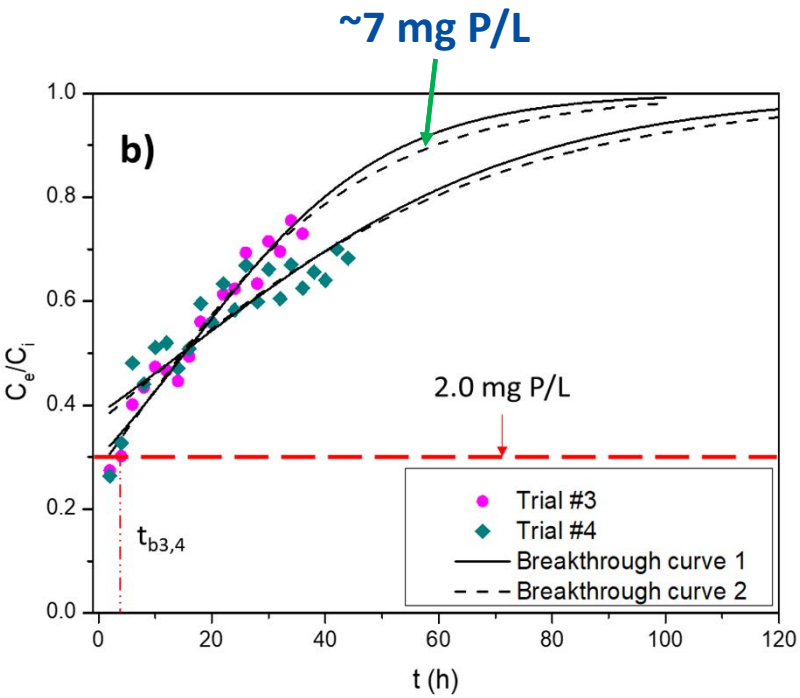




- Reactor designed by Veolia with CCM adsorbent developed by ERI
- 4 trials conducted within a 5 weeks
- 2 trial with low P concentration
- 2 trial with high P concentration

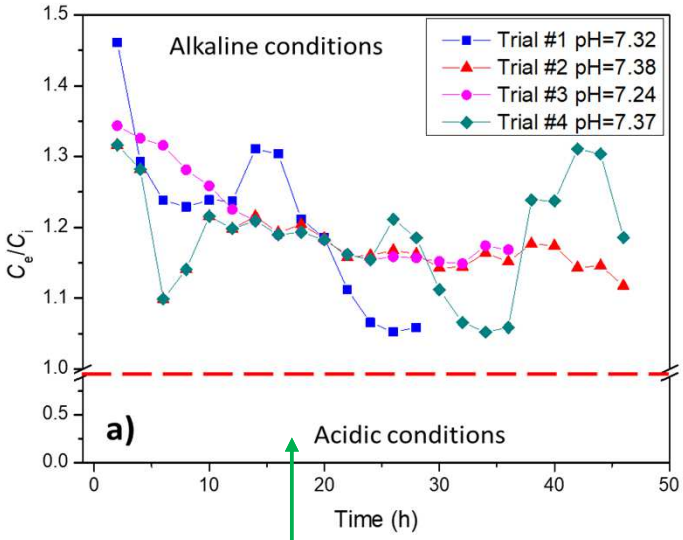
P recovery efficiency

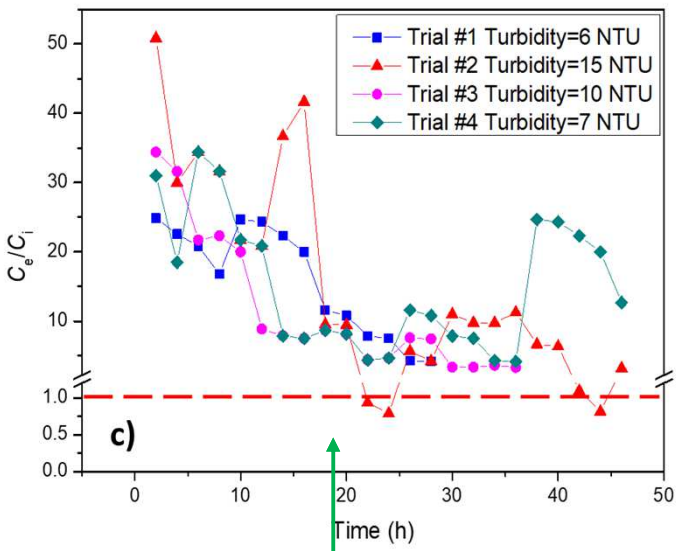


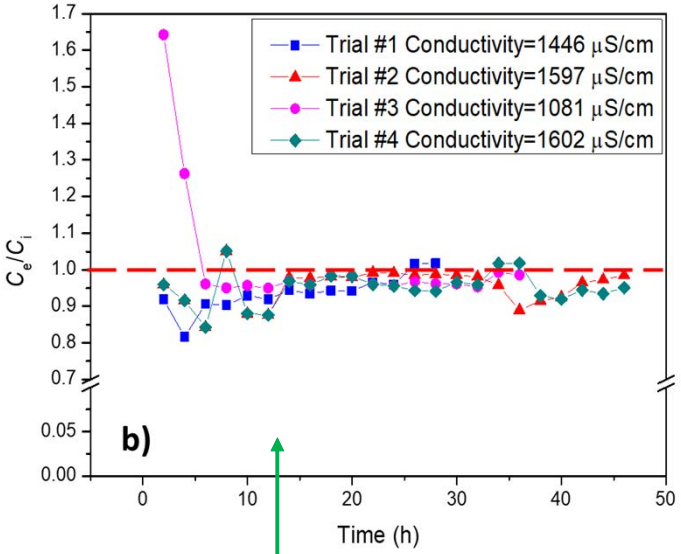


- P theoretical breakthrough curves (Bohart-Adams with solid line and Clark with dash line) for the field trials, low P concentration influents (a) and high concentration influents (b).
- The adsorption capacity were found from **300 mg/kg (trial #1)** and **363 mg/kg (trial #2)** to **1590 mg/kg (trial #3)** and **1859 mg/kg (trial #4)**.

Water quality parameters



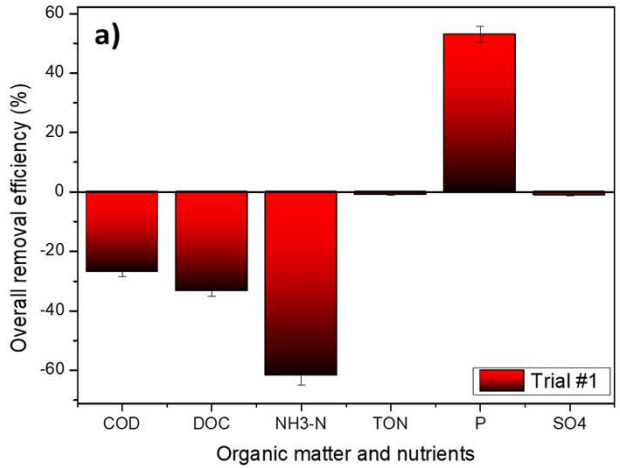


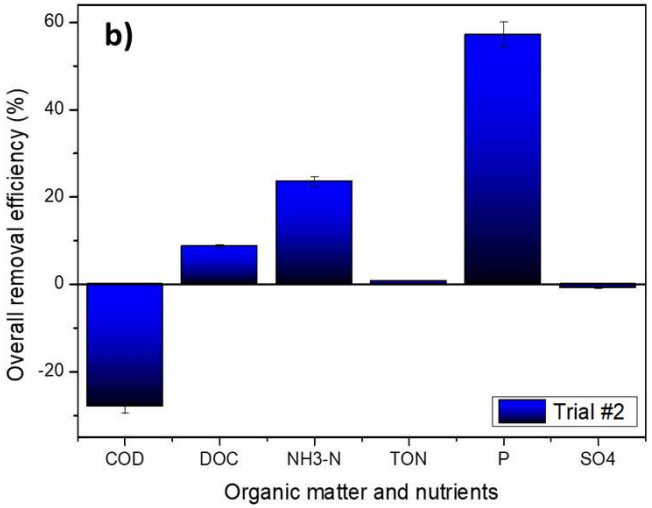


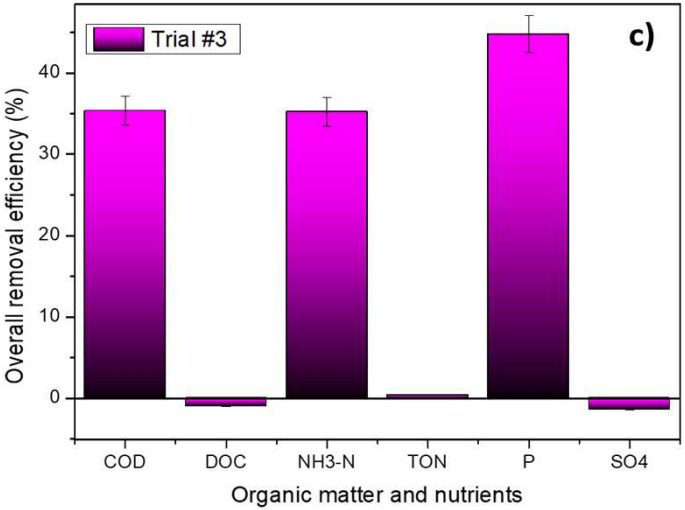
pH influence > **Turbidity** > **Conductivity** ≤

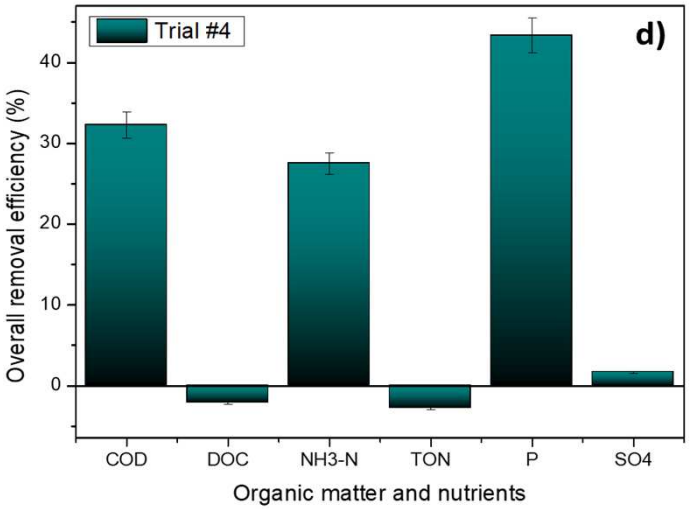
Organic matter and nutrients

- Overall P recovery more then 50%.





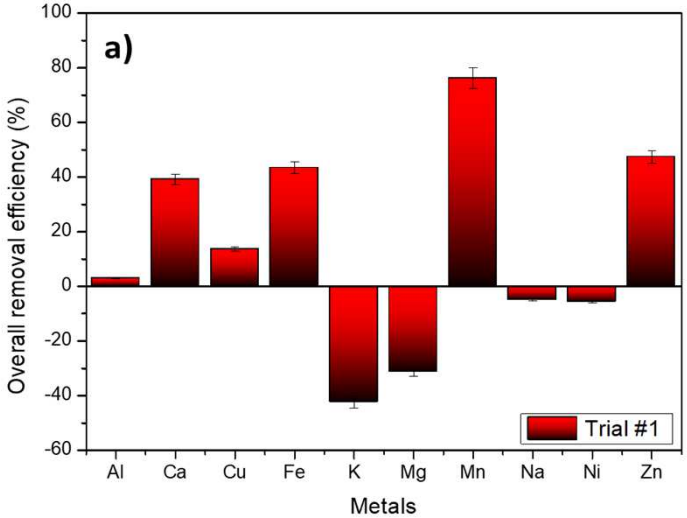


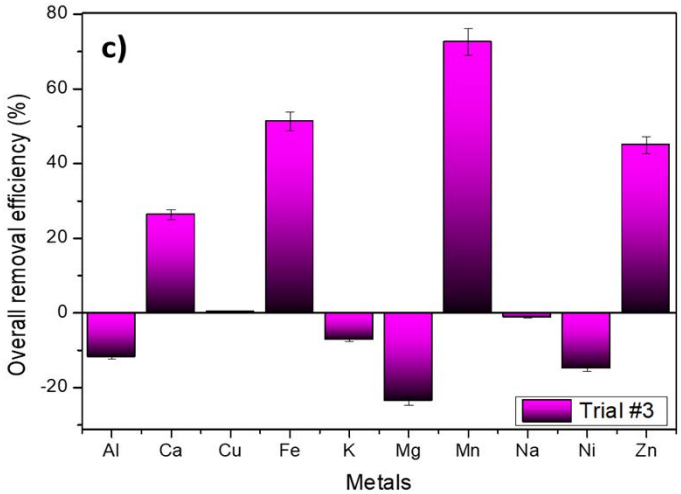


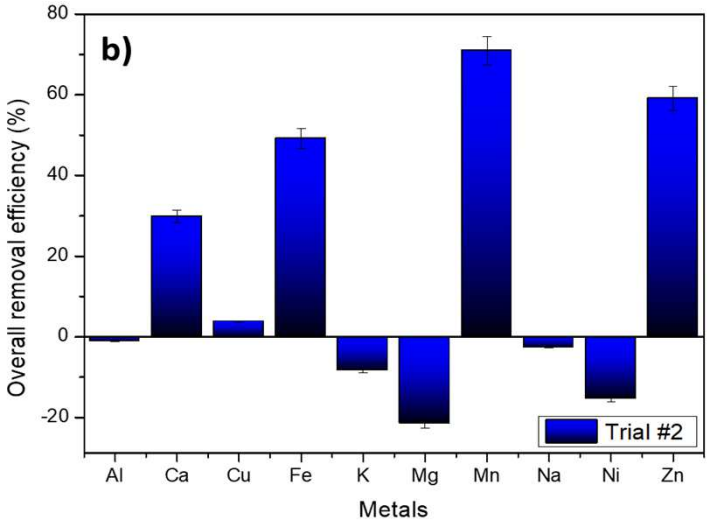
- Increase the organic carbon and nitrogen content of the material.

Macro- and microelements

- High removal efficiency for Ca, Cu, Fe, Mn and Zn.







- Alkaline earth and transition metal could strongly adsorb P.
- No detectable heavy metals.

Inorganics and microbiology testing

Interreg North-West Europe
Phos4You
European Regional Development Fund

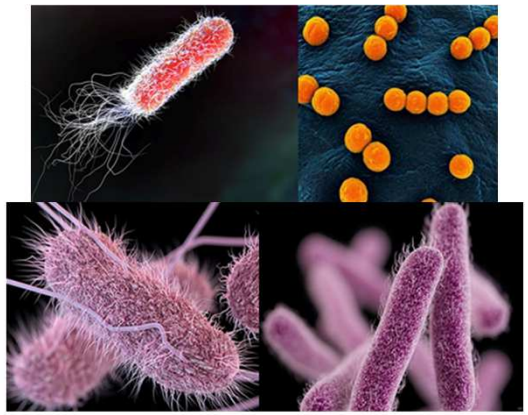
Methodology

Pretreatment: Ghent, Belgium
All tested in triplicate

HNO_3+H_2O_2 extraction: 0.25g sample overnight digested in 5 mL HNO_3, next day before the microwave treatment 1.5 mL H_2O_2 was added, after the treatment the samples diluted to 50 mL with MQ water and analysed on ICP-OES

Aqua Regia extraction: 0.25g sample overnight digested in 4.8 mL HCl, next day before the microwave treatment 1.2 mL HNO_3 was added, after the treatment the samples diluted to 50 mL with MQ water and analysed on ICP-OES

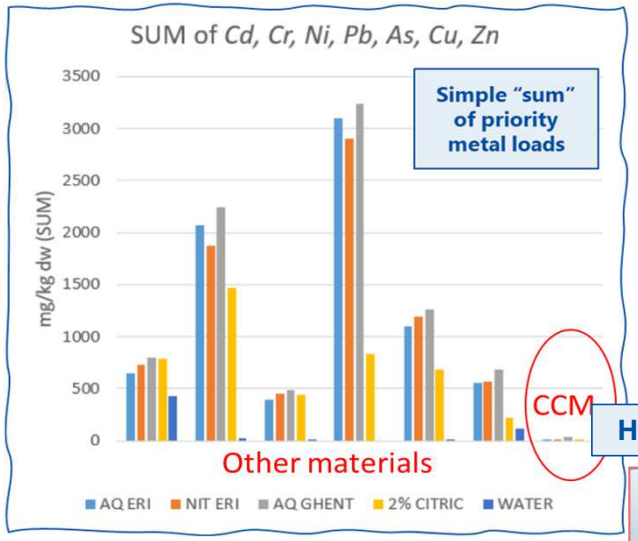
Water and 2% citric acid extraction: 0.5 g sample in 25 mL MQ water or 2% citric acid were shacked (170 RPM) for 24 h, next day first centrifuged for 10 mins, 9 mL sample were filtered with 0.45 µm nylon filter and acidified with 1 mL HNO_3 and analysed on ICP-OES



Salmonella spp.
Shigella spp.
E. coli
Enterococcus spp.
Aerobic Plate Growth

eri environmental research institute

Inorganics and microbiology testing, pot trials



- Certain elements are readily soluble in all/many products – i.e., S, Na, K – which 'may' be relevant within pot/field trials
- Others are far more recalcitrant (Al, Cr, Fe, Pb and As)
- No detectable levels of target bacterial pathogens – chitosan
- River sand 4 month growth of perennial ryegrass
- Plant P uptake increased in time and reached its maximum after 3rd plant cut
- Achieved higher plant dry matter compared to the unfertilised control

~2.5% of P_2O_5

HIGH

Product

LOW

	S	Na	K	Mg	Ni	P	Ca	Co	Zn	Mn	Cu	Cd	Al	Cr	Fe	Pb	As
1	81.4	71.0	99.4	90.6	68.2	99.7	77.8	44.7	65.9	62.0	12.7	44.0	18.1	11.2	1.9	~	~
2	31.2	76.1	81.2	38.3	33.8	1.6	5.1	16.2	3.9	3.0	20.3	~	~	1.9	1.3	~	~
3	43.0	90.1	77.3	30.0	29.7	1.7	4.9	20.7	~	0.3	15.0	~	~	0.0	~	~	~
4	66.7	23.8	28.0	~	~	~	0.3	~	~	~	~	~	14.8	2.3	~	~	~
5	20.3	36.7	8.3	12.1	~	8.1	0.1	~	~	0.1	4.3	~	~	~	~	~	~
6	67.8	3.0	0.7	1.0	~	0.3	0.8	~	~	~	~	~	0.5	~	~	~	~
CCM	28.9	15.2	14.0	5.5	~	0.1	0.1	~	~	~	~	~	~	~	~	~	~

HIGH → *Element solubility in water* → LOW

>20% marked in YELLOW

‘Take home messages’

- High P recovery potential was achieved even at low P concentrations
- Surface microprecipitation and inner-sphere complexation mechanisms
- Integration/combination with slow sand filtration
- Water polishing unit and P harvesting unit
- ~2.5% of P_2O_5, low heavy metal and organic pollutant content (well below legislative limits) and no detectable levels of target bacterial pathogens
- $CaCO_3$ content buffers against soil acidification
- Chitin/chitosan has antibacterial properties

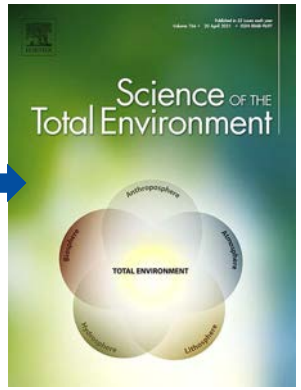
Publication

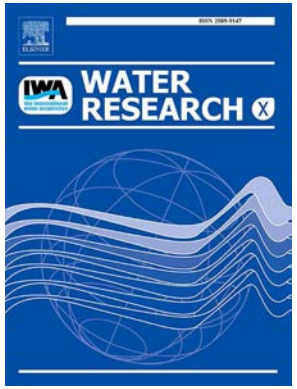
Pap, S., Kirk, C., **Bremner, B.**, Turk Sekulic, M., Gibb, S.W., Maletic, S., **Taggart, M.A.,** 2020. Synthesis optimisation and characterisation of chitosan-calcite adsorbent from fishery-food waste for phosphorus removal. *Environmental Science and Pollution Research*, 27, 9790–9802. https://doi.org/10.1007/s11356-019-07570-0

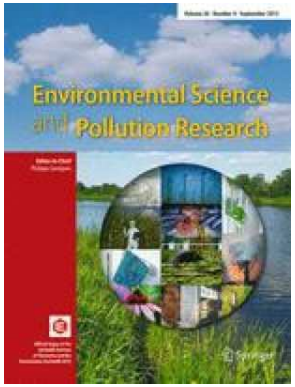
Pap, S., Kirk, C., **Bremner, B.,** Turk Sekulic, M., Shearer, L., Gibb, S.W., **Taggart, M.A.,** 2020. Low-cost chitosan-calcite adsorbent development for potential phosphate removal and recovery from wastewater effluent. *Water Research*, 173, p.115573. https://doi.org/10.1016/j.watres.2020.115573

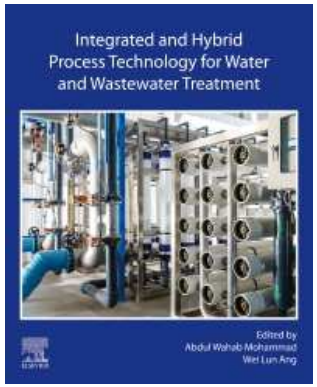
Pap, S., Turk Sekulic, M., **Bremner, B., Taggart, M.A.** 2021. From molecular to large-scale phosphorus recovery from wastewater using cost-effective adsorbents: an integrated approach. Elsevier book chapter in *Integrated and Hybrid Process Technology for Water and Wastewater Treatment.* https://doi.org/10.1016/B978-0-12-823031-2.00025-2

Mussel and oyster shell data – positive feedback from the reviewers









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Thanks for listening
Any questions?

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GHENT UNIVERSITY
GCU Glasgow Caledonian University
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VEOLIA
EGLV Emschergenossenschaft
EUPHORE
HVC
SNB
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