We deliver Phosphorus made in Europe
We cooperate to close P-cycle
Biosorbents produced from waste crab carapace, oyster and mussel shell: Potential for phosphate removal and recovery from wastewater

Dr Szabolcs Papp

Environmental Research Institute, North Highland College
University of the Highlands and Islands, Scotland
Introduction
Phosphorus

Oligotrophic stage
Deep and nutrient poor system

Mesotrophic stage
Nutrient enrichment

Eutrophic stage
Nutrients saturated - shallow Algae and bacteria development

Eutrophication

Nitrogen
Phosphorus

These nutrients cause an increase in aquatic plant growth, algae and phytoplankton

Sediments from land block sunlight

Aquatic plants

Plant decay

Algae die

Decay

Oxygen

Phytoplankton

Interreg North-West Europe Phos4You

Phosphorus recovery and re-use – new approach

Phosphorus rich water → Biosorbents → Biochars → Clean water → Phosphorus recycling to soil
Research objectives

1. To investigate the effect of thermo-chemical activation on the sorption capacity of phosphorus onto three different biosorbent derived from crab carapace, mussel and oyster shell.
2. To optimize of phosphorus sorption
3. Determination of the phosphorus sorption mechanisms
Material and Methods

Biosorbents in this study

Crab carapace

Mussel shells

Oyster shells
Biosorbent preparation and modification

0.01 M HCl

Raw materials

Pretreated biosorbent

600 °C 2h

Biosorbent after the thermal activation

Optimized conditions of thermo-chemical activation

700 °C 1h

Final product
Phosphorus sorption experiments

Biosorbent/P solution = 4 g/L

- agitation speed: 150 rpm
- temperature: 20 ± 2 ºC

- Effect of pH (2-11)
- Effect of sorbent dosage (1-10 g/L)
- Sorption isotherms (1-300 mg/L)
- Sorption kinetics (1-1440 min)
- Effects of co-existing anions (Cl⁻, CO₃²⁻, SO₄²⁻, NO₃⁻)

- Proximate analysis (i.e. ash, moisture,...)
- pH at point zero charge (pHₚzc)
- Surface and porous characteristic (BET)
- XRD
- SEM-EDX
- FTIR

Sorption mechanisms
Results and discussion
Influence of thermo-chemical treatment on P adsorption

- KOH treated biosorbents were much more effective
- Specifically, the mussel shell removal efficiency was increased from 18 to 99 %.
- Improved surface chemistry and textural properties

Fig 1. Removal efficiency of phosphorous onto crab carapace, oyster and mussel shell (initial concentration: 23.64 mg L\(^{-1}\); initial pH: 7; agitation time: 120 min; agitation speed: 150 rpm; dose of sorbent: 500 mg; temperature: 20 ± 2 °C)
Effects of pH on P removal

- Highest removal efficiency on pH 2 for all biosorbents
- The form of phosphorus presents as $\text{H}_2\text{PO}_4^-$ at pH 2.15–7.20, and the main form changes to $\text{HPO}_4^{2-}$ when pH is between 7.2 and 12.33
- The surface of biosorbents are positively charged (pHpzc)
- Strong electrostatic attraction in acidic environment

**Fig 2.** Effect of pH on phosphorus removal (initial concentration: 20 mg/L; dose of sorbent: 200 mg; contact time: 120 min; agitation speed: 150 rpm; temperature: 20 ± 2 °C)
Effect of biosorbent dosage P removal

- The removal efficiency of phosphorus increased with the increasing biosorbent dosage
- Nearly 100% at the biosorbent dosage of 300 mg for crab carapace and mussel shell
- These findings are linked to the existence of many available active sorption sites on the surface
- 4 g/L (200 mg) the optimum dose for crab carapace and mussel shell
- 10 g/L (500 mg) for the oyster shell

Fig 3. Effect of sorbent dosage on phosphorus removal (initial concentration: 20 mg/L; initial pH: 7; contact time: 120 min; agitation speed: 150 rpm; temperature: 20 ± 2 °C)
Sorption kinetic

Fig. 5. Phosphorus adsorption kinetic (a) and pseudo-second-order model (b) onto biosorbents (initial concentration: 20 mg/L; initial pH: 7; agitation speed: 150 rpm; dose of sorbent: 1 g; temperature: 20 ± 2 ºC)

Table 1
Kinetic parameters for the adsorption of phosphorus onto biosorbents

<table>
<thead>
<tr>
<th></th>
<th>$q_{e, \text{exp}}$ (mg g$^{-1}$)</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{e, \text{cal}}$ (mg/g)</td>
<td>$K_1$ (1/min)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Crab carapace KOH</td>
<td>3.075</td>
<td>1.208</td>
<td>-0.009</td>
</tr>
<tr>
<td>Mussel shell KOH</td>
<td>4.999</td>
<td>0.285</td>
<td>-0.028</td>
</tr>
<tr>
<td>Oyster shell KOH</td>
<td>3.050</td>
<td>0.883</td>
<td>-0.049</td>
</tr>
</tbody>
</table>
Sorption isotherms

**Fig. 4.** Phosphorus adsorption equilibrium and their fitting by Langmuir, Freundlich and DR isotherm models (contact time: 120 min; initial pH: 7; agitation speed: 150 rpm; dose of sorbent: 200 mg; temperature: 20 ± 2 °C)

| Table 2 | Langmuir, Freundlich and Dubinin–Radushkevich isotherm constants for phosphorous |
|---------|---------------------------------|-----------------|-----------------|-----------------|
|         | Crab carapace KOH | Mussel shell KOH | Oyster shell KOH |
| q_{max,exp} (mg/g) | 9.139 | 12.443 | 8.250 |
| Langmuir | q_{max} (mg/g) | 9.394 | 12.249 | 8.825 |
| | K_{L} (L/mg) | 1.222 | 1.002 | 0.425 |
| | R^2 | 0.998 | 0.975 | 0.982 |
| Freundlich | K_{F} (L/g) | 1.516 | 1.899 | 1.426 |
| | 1/n | 0.389 | 0.378 | 0.299 |
| | R^2 | 0.949 | 0.939 | 0.920 |
| Dubinin–Radushkevich | q_{DR} (mg/g) | 4.701 | 5.579 | 3.557 |
| | E (kJ/mol) | 4.446 | 4.027 | 7.337 |
| | R^2 | 0.808 | 0.867 | 0.756 |
Effects of co-existing anions on P removal

There often exist simultaneously some ions such as sulphate ($SO_4^{2-}$), nitrate ($NO_3^-$), chloride ($Cl^-$) and carbonate ($CO_3^{2-}$) in treated wastewater.

- Co-existing ion concentration – 20 mg/L of each
- No remarkable effect on the adsorption of P on oyster shell
- Higher competitions between other anions and P on crab carapace and mussel shell

Fig. 6. Effect of coexisting anions on phosphorus adsorption (initial concentration of each anions: 20 mg/L; initial pH: 7; agitation speed: 150 rpm; dose of sorbent: 200 mg; temperature: 20 ± 2 °C)
Postulated mechanisms for P sorption

Further research is needed
Summary

1. Improved removal efficiency with KOH treatment due to improved surface chemistry and textural properties
2. pH depend process - strong electrostatic attraction in acidic environment
3. Rapid adsorption in the first 5 min, which suggest electrostatic attraction
4. The adsorption rate slowed since that ion exchange and surface complexation controlled the following adsorption process
5. Desorption is appear after 6h for the crab carapace and mussel shell and 4h for oyster shell which means which points to the possibility of using these materials as fertilizer
6. Adsorption capacities are 9.14, 12.44 and 8.25 mg/g for crab carapace, mussel and oyster shells, respectively
Future Perspective

Biosorbent/P solution = 4 g/L
agitation speed: 150 rpm
temperature: 20 ± 2 ºC

- Effect of pH (2-11)
- Effect of sorbent dosage (1-10 g/L)
- Sorption isotherms (1-300 mg/L)
- Sorption kinetics (1-1440 min)
- Effects of coexisting anions (Cl⁻, CO₃²⁻, SO₄²⁻, NO₃⁻)
- P desorption kinetics
- Proximate analysis (i.e. ash, moisture,...)
- pH at point zero charge (pH_{pzc})
- Surface and porous characteristic (BET)
- XRD
- SEM-EDX
- FTIR

Batch experiments
Characterization
Future work
Acknowledgements

• Lisa Shearer
• Mark A. Taggart
• Barbara Bremner
• Stuart W. Gibb
• Organising committee and team

Thanks for listening
Any question