We deliver Phosphorus made in Europe

We cooperate to close P-cycle

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School of Life Sciences

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University of the Highlands and Islands
Oilthigh na Gàidhealtachd agus nan Eilean

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Arriving at a Sustainable Future

Biosorbents produced from waste crab carapace, oyster and mussel shell: Potential for phosphate removal and recovery from wastewater

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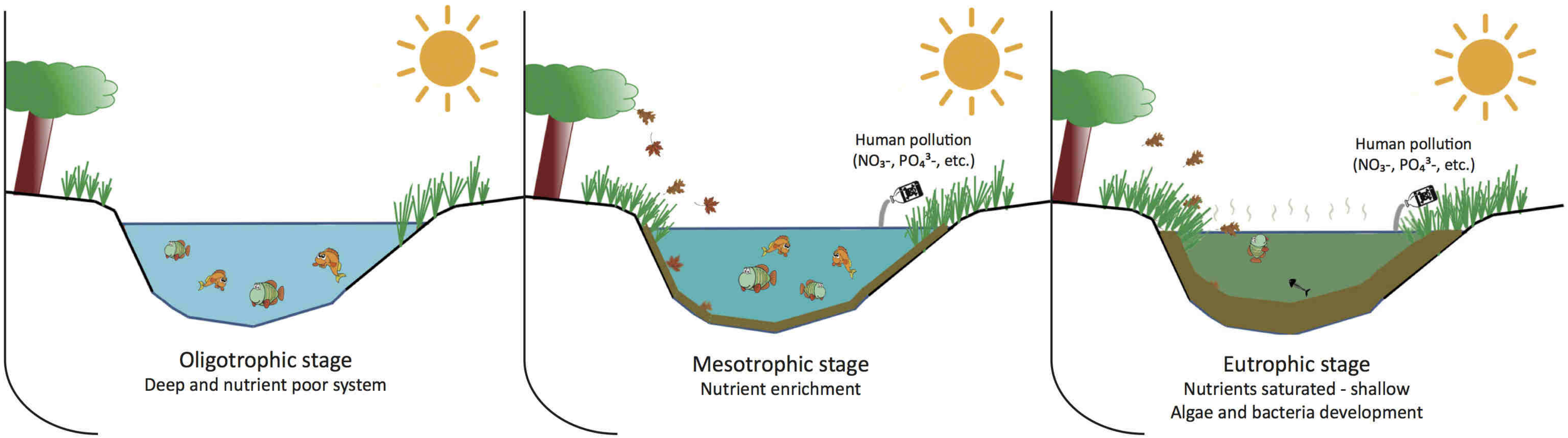
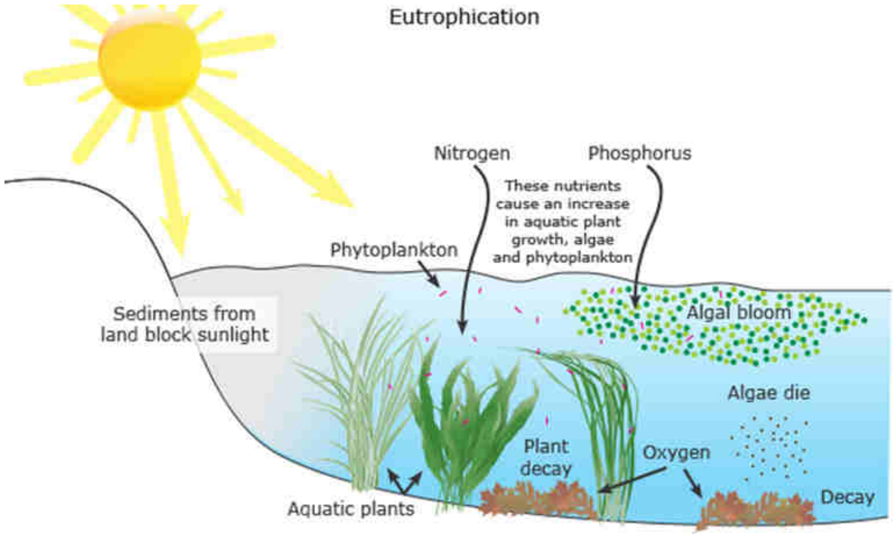
Introduction
Phosphorus





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

Oyster shells

Mussel shells

Biosorbent preparation and modification

Raw materials

0.01 M HCl

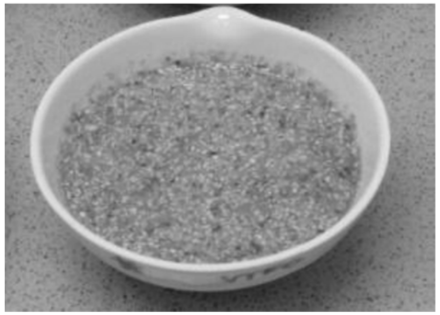
Pretreated biosorbent

600 °C 2h

Biosorbent after the thermal activation

KOH

Optimized conditions of thermo-chemical activation



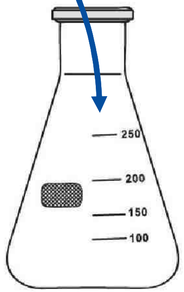
700 °C 1h

Final product

Phosphorus sorption experiments

agitation speed: 150 rpm
temperature: 20 ± 2 ºC

Biosorbent/P solution = 4 g/L



Biosorbents

Batch experiments

- 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^-, CO_3^{2-}, SO_4^{2-}, NO_3^-)

Sorption mechanisms

Characterization

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

Results and discussion

Influence of thermo-chemical treatment on P adsorption

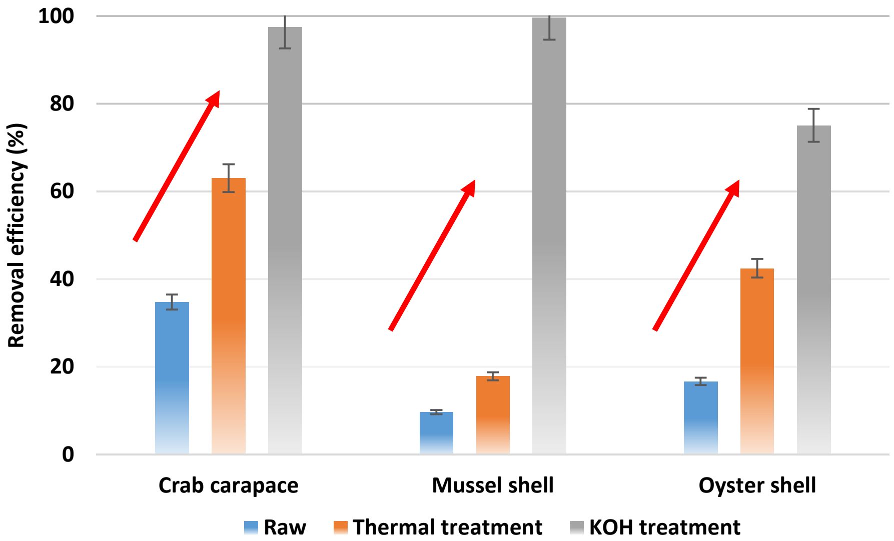


Fig 1. Removal efficiency of phosphorous onto crab carapace, oyster and mussel shell (initial concentration: 23.64 mg L^{-1}; initial pH: 7; agitation time: 120 min; agitation speed: 150 rpm; dose of sorbent: 500 mg; temperature: 20 ± 2 ºC)

- 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

Effects of pH on P removal

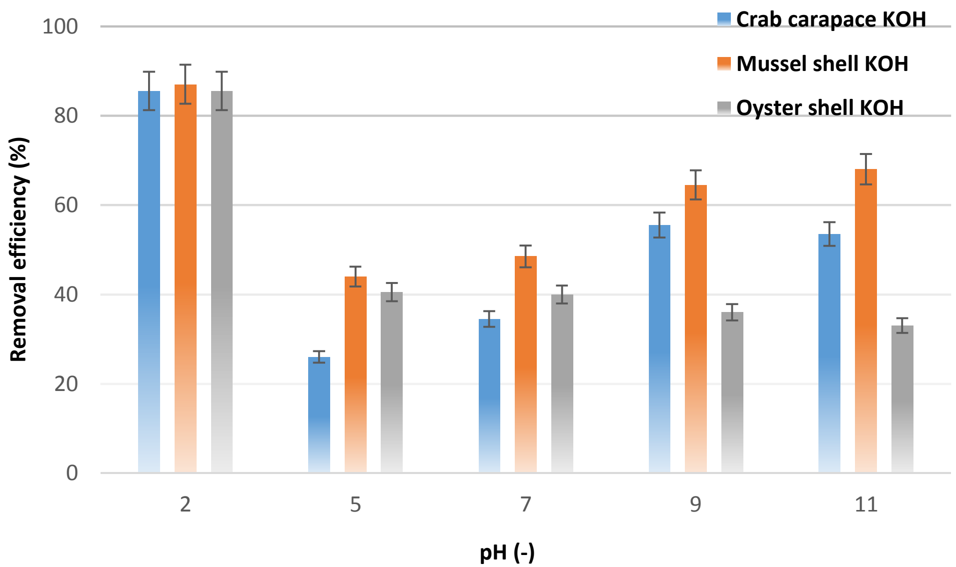


Fig 2. Effect of pH on phosphorus removal (initial concentration: 20 mg/L; dose of sorbent: 200 mg; contact time: 120 min; agitation speed: 150 rpm; temperature: 20 ± 2 ºC)

- Highest removal efficiency on pH 2 for all biosorbents
- The form of phosphorus presents as $H_2PO_4^-$ at pH 2.15–7.20, and the main form changes to 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

Effect of biosorbent dosage P removal

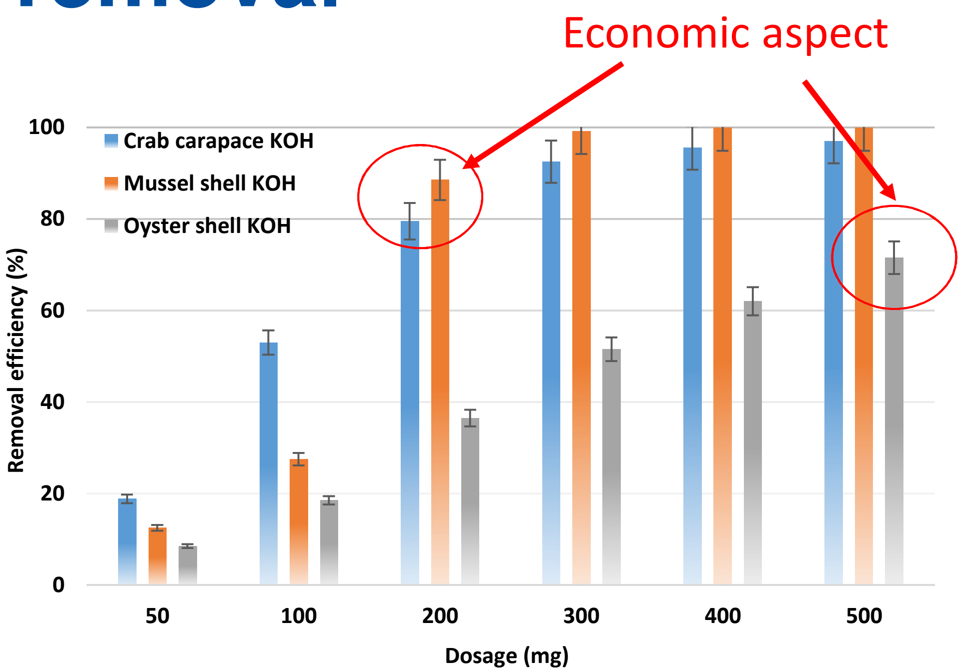


Fig 3. Effect of sorbent dosage on phosphorus removal (initial concentration: 20 mg/L; initial pH: 7; contact time: 120 min; agitation speed: 150 rpm; temperature: 20 ± 2 ºC)

- 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

Sorption kinetic

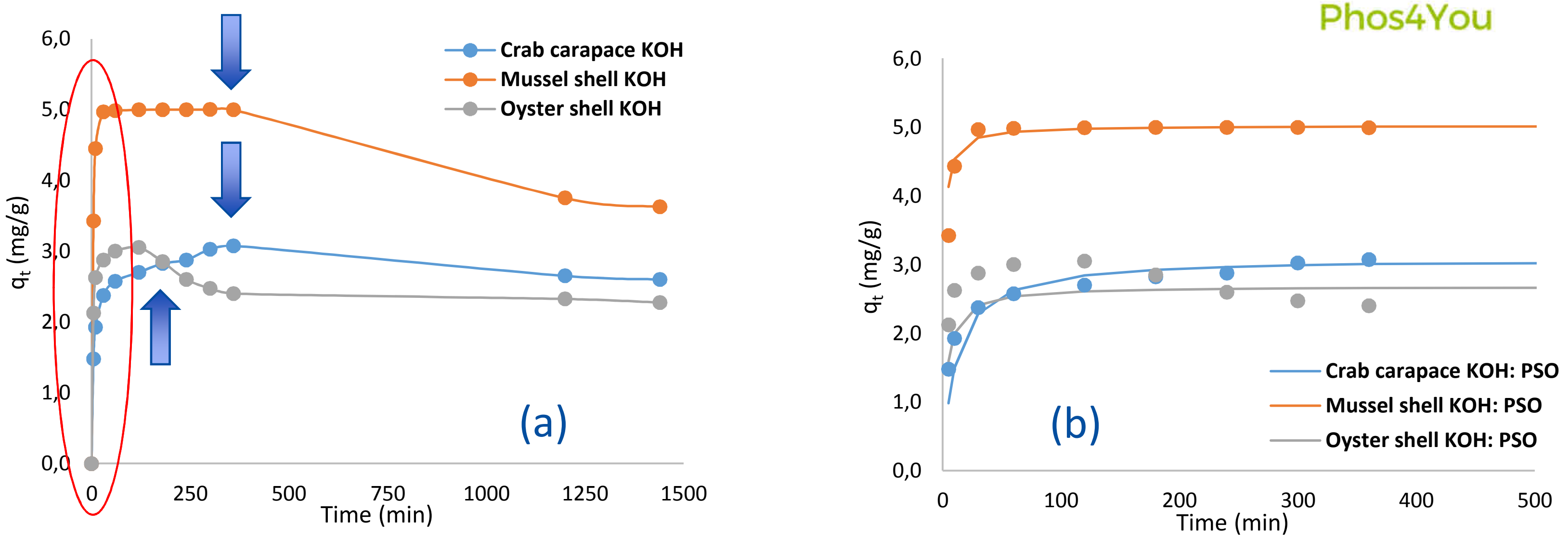


Fig. 5. Phosphorus adsorption kinetic (a) and pseudo-second-order model (b) onto biosorbents (initial concentration: 20 mg/L; initial pH: 7; agitation speed: 150 rpm; dose of sorbent: 1 g; temperature: 20 ± 2 ºC)

Table 1

Kinetic parameters for the adsorption of phosphorous onto biosorbents

	$q_{e, exp}$ ($mg\ g^{-1}$)	Pseudo-first order			Pseudo-second order		
		$q_{e, cal}$ (mg/g)	K_1 (1/min)	R^2	$q_{e, cal}$ (mg/g)	K_2 (g/mg min)	R^2
Crab carapace KOH	3.075	1.208	-0.009	0.924	3.099	0.030	0.998
Mussel shell KOH	4.999	0.285	-0.028	0.794	5.023	0.184	0.999
Oyster shell KOH	3.050	0.883	-0.049	0.964	2.683	0.108	0.998

Sorption isotherms

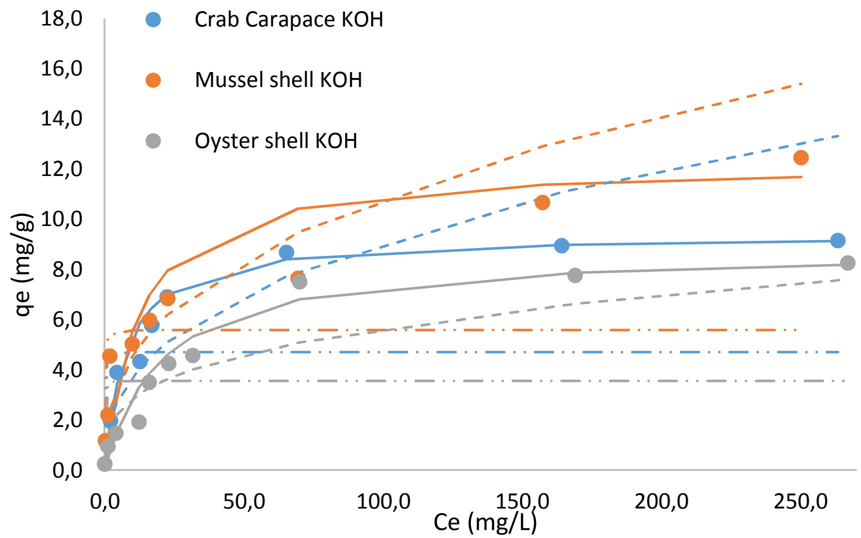


Fig. 4. Phosphorus adsorption equilibrium and their fitting by Langmuir, Freundlich and DR isotherm models (contact time: 120 min; initial pH: 7; agitation speed: 150 rpm; dose of sorbent: 200 mg; temperature: 20 ± 2 ºC)

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

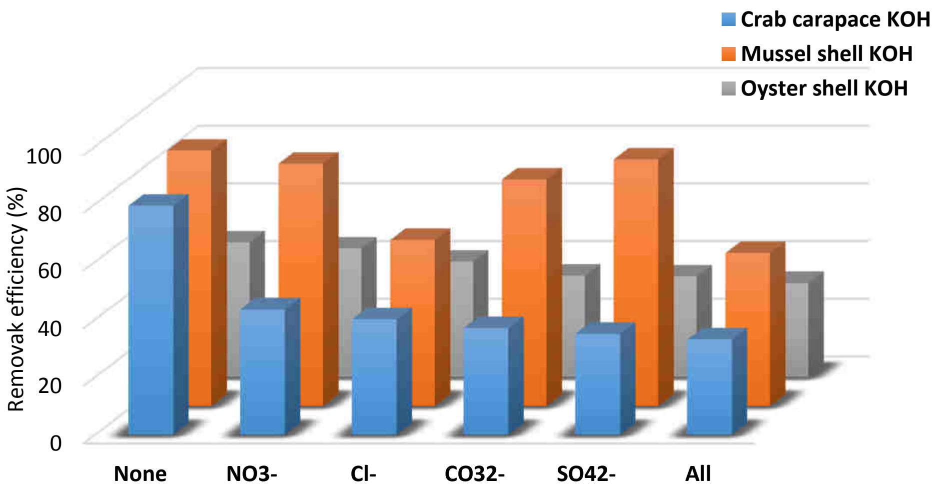
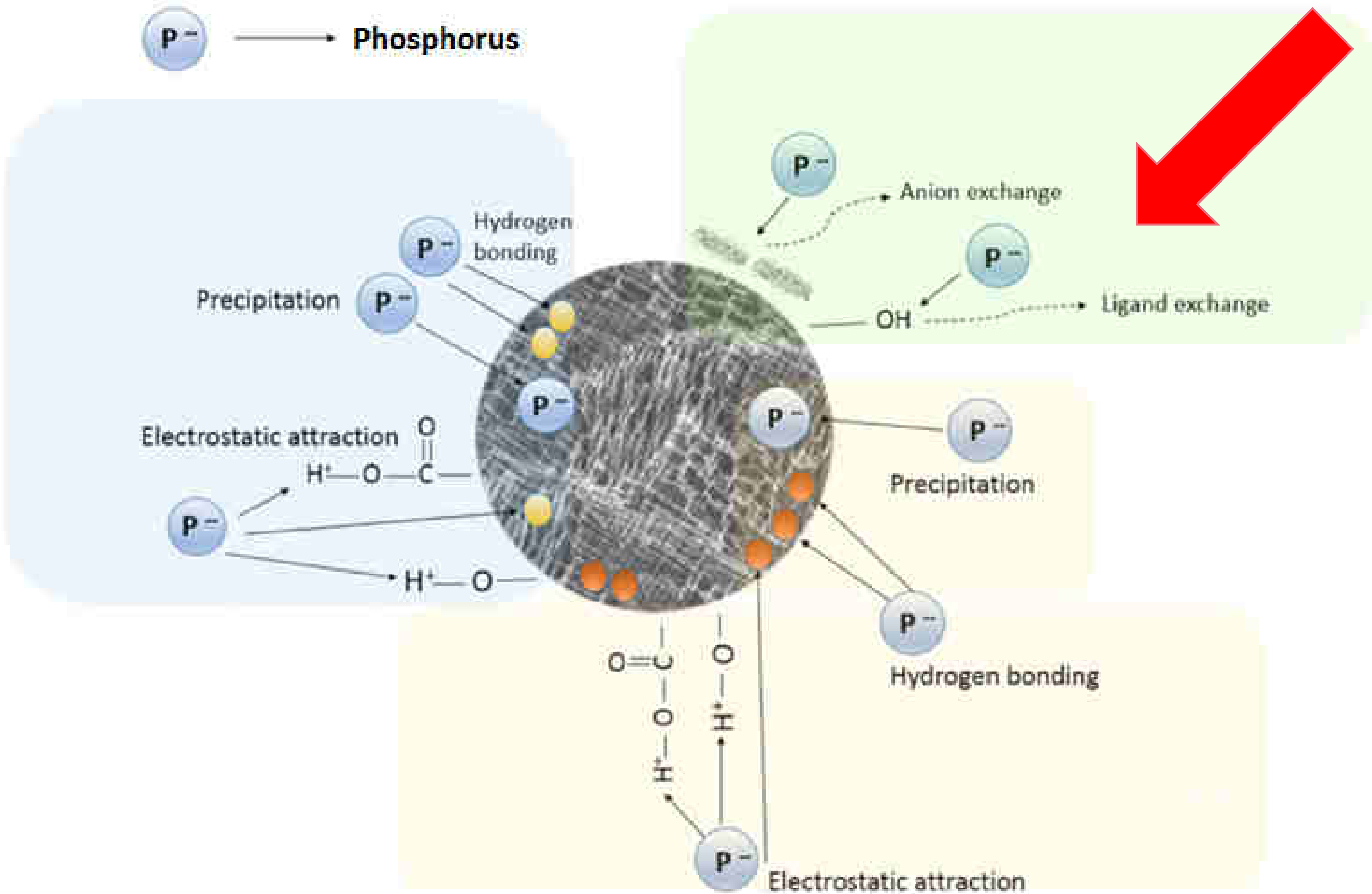


Fig. 6. Effect of coexisting anions on phosphorus adsorption (initial concentration of each anions: 20 mg/L; initial pH: 7; agitation speed: 150 rpm; dose of sorbent: 200 mg; temperature: 20 ± 2 ºC)

- 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

Postulated mechanisms for P sorption

Further research is needed



Summary

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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

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Future Perspective

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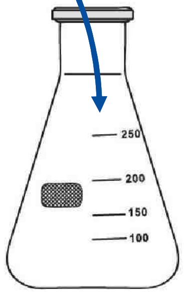

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Future work

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Thanks for listening

Any question

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