Universität Stuttgart

4th International Symposium “Re-Water Braunschweig”

Phosphate recovery from wastewater with engineered superparamagnetic composite particles using magnetic separation

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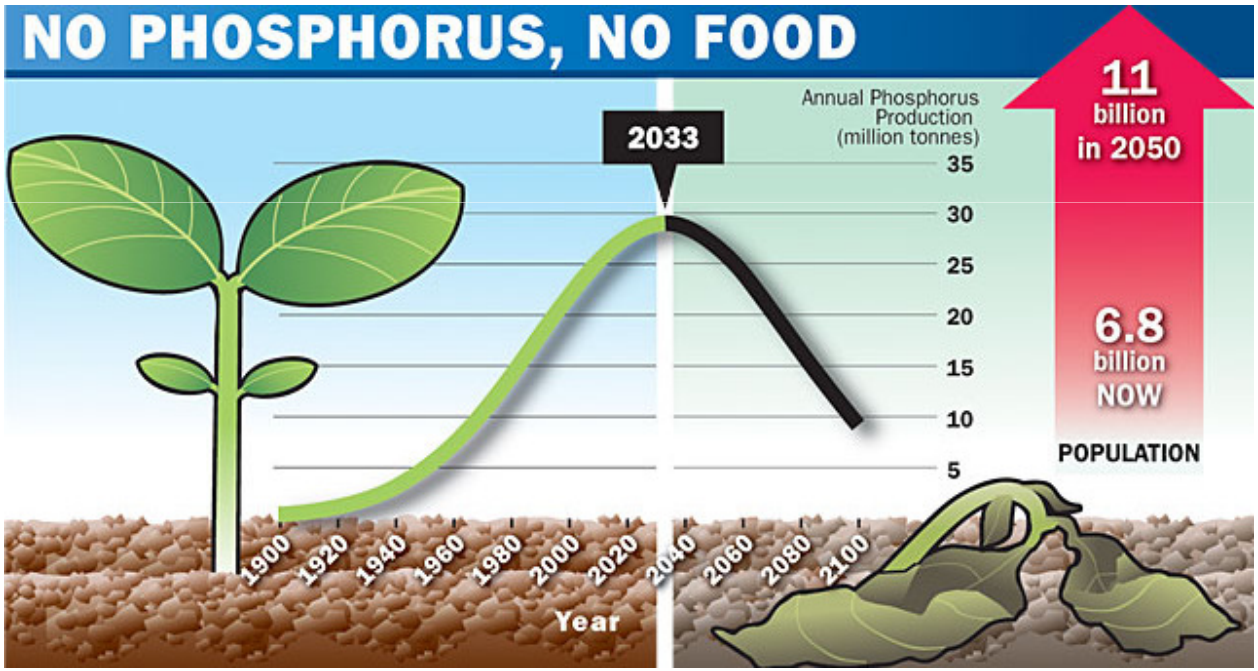
Good reasons for phosphorus recovery

- **Mineral phosphorus fertilizer is needed for food production, but phosphate rock resources are limited and quality decreases**

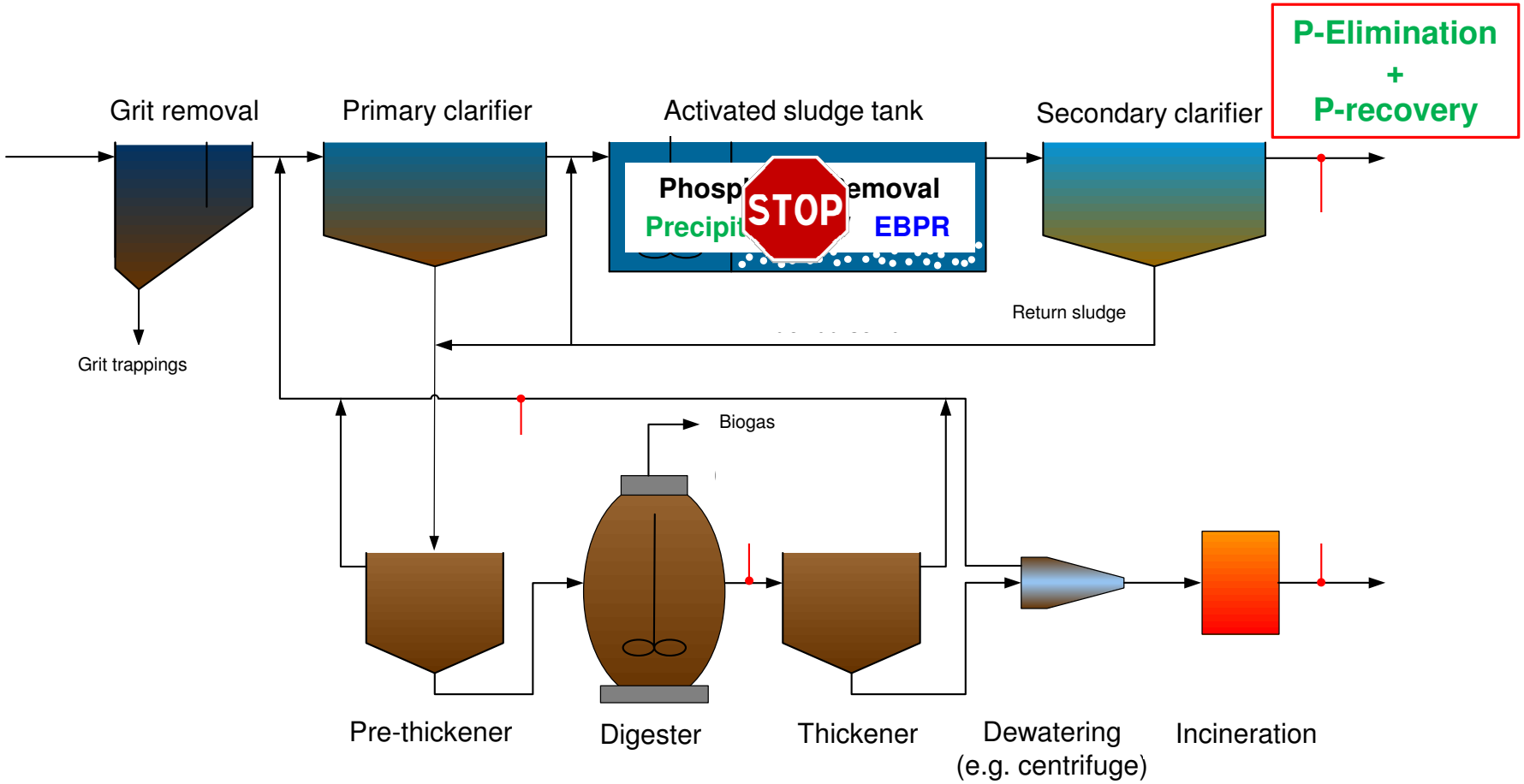


Source: rainharvest.co.za

More good reasons for phosphorus recovery

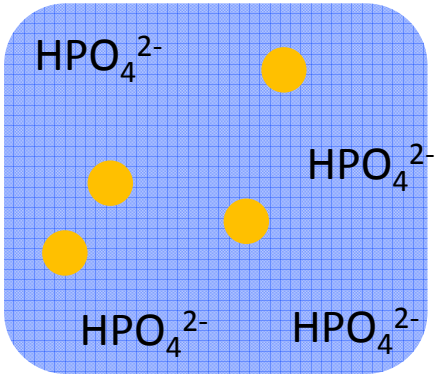
- **No direct application of P-rich sewage sludge or wastewater on soils, e.g. for food production; this is a highly controversial issue in terms of organic and inorganic pollutants, and fertilizing efficiency**
  - Solution: creation of a pure, unpolluted phosphorus product from wastewater
- **The highest potential for phosphorus recovery can be found within the municipal wastewater**
  - In Germany, between 20% and 40% of the „primary phosphorus“ used in fertilizers could be substituted by “secondary phosphorus” recovered from wastewater
    ⇒ sustainability
    ⇒ autarky

Which phosphorus-rich stream of a municipal WWTP to be used for P-recovery?

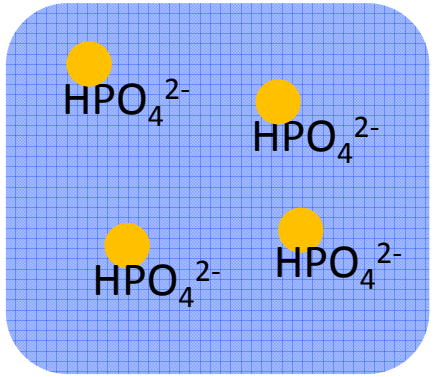


Basic idea for P removal *and* recovery from WWTP effluent

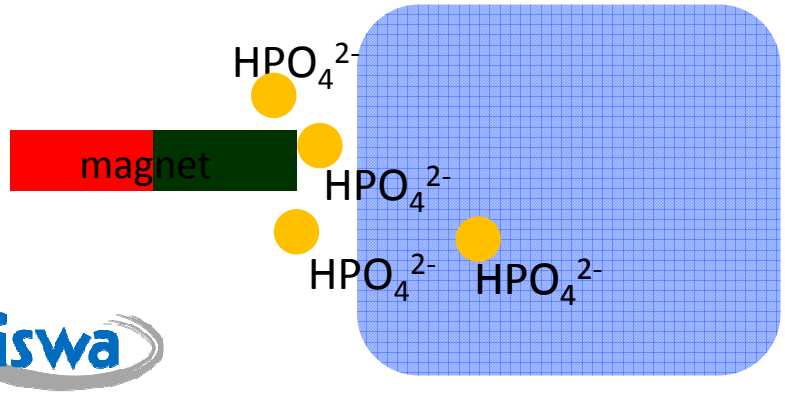
Wastewater containing phosphate + modifed particles



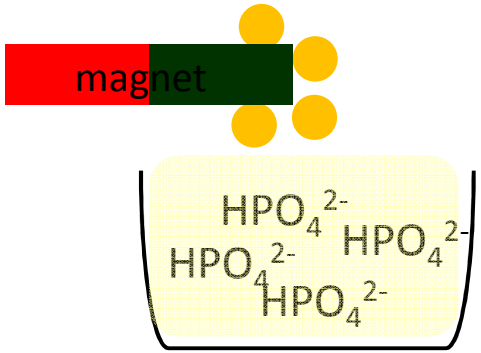
Phosphate (dissolved) adsorbs on particles



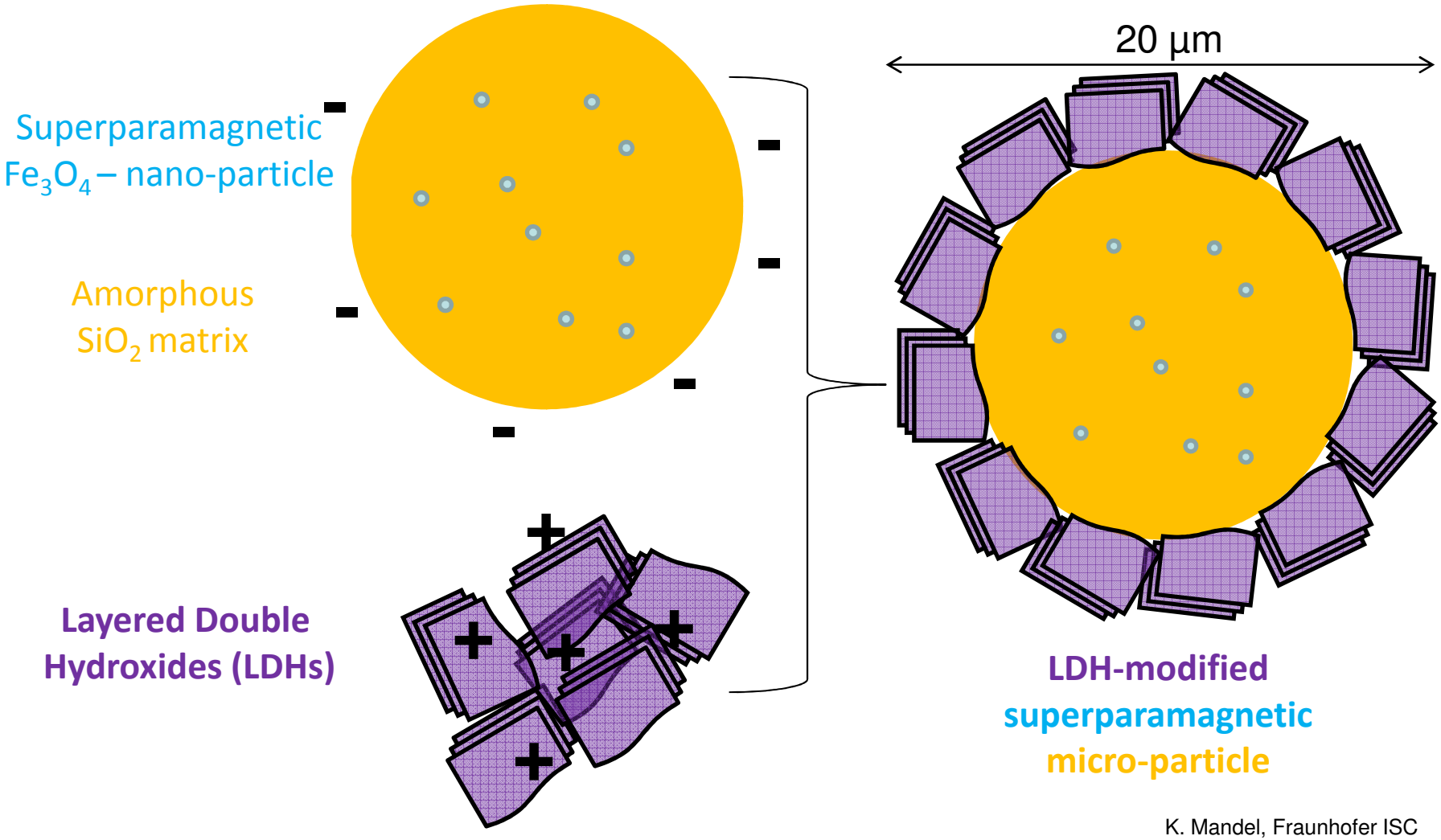
Magnetic separation of the particles



Washing of the particles -> phosphate ⇔ particles



Engineered superparamagnetic composite micro-particles



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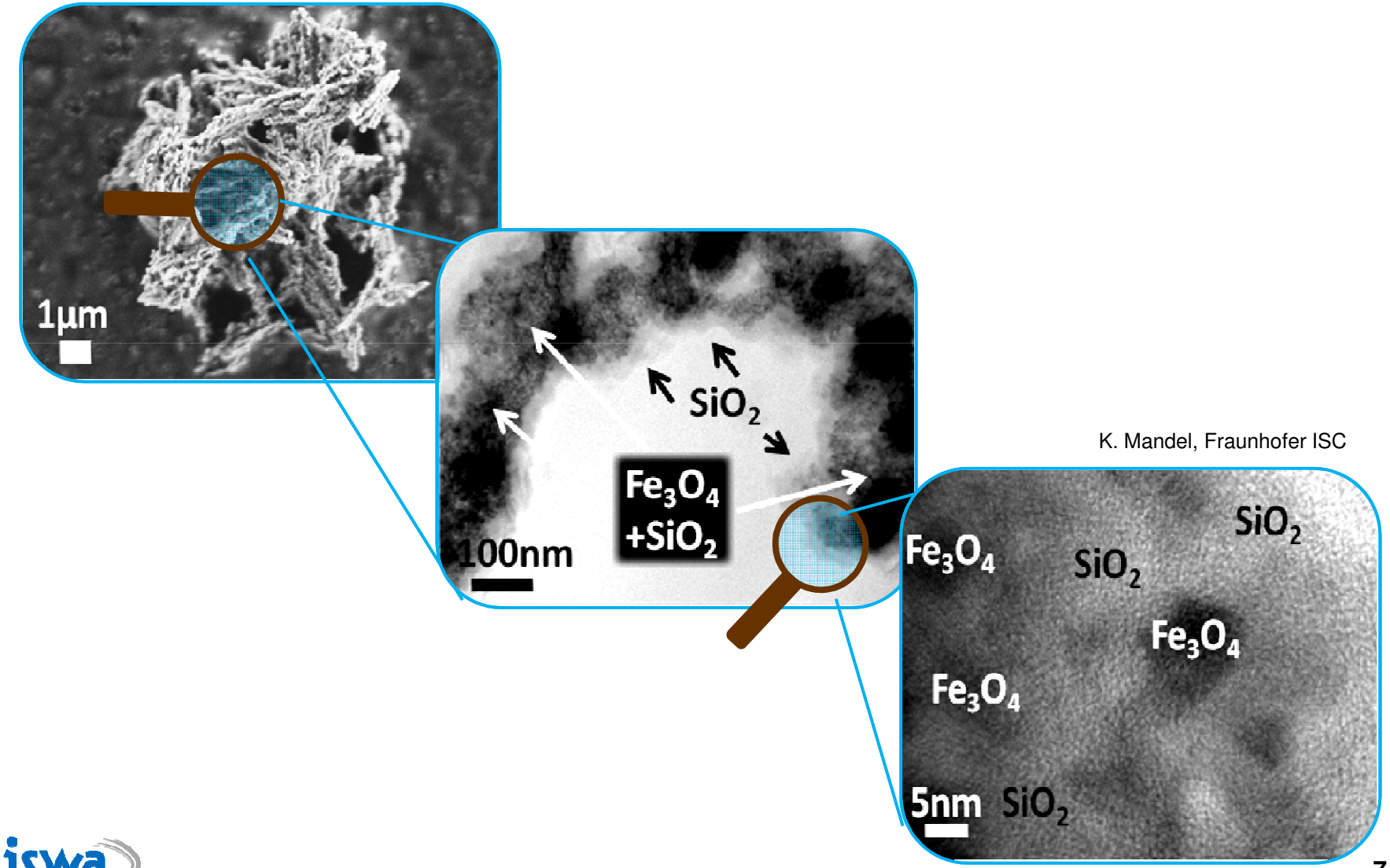
Structure of superparamagnetic composite micro-particles (1)



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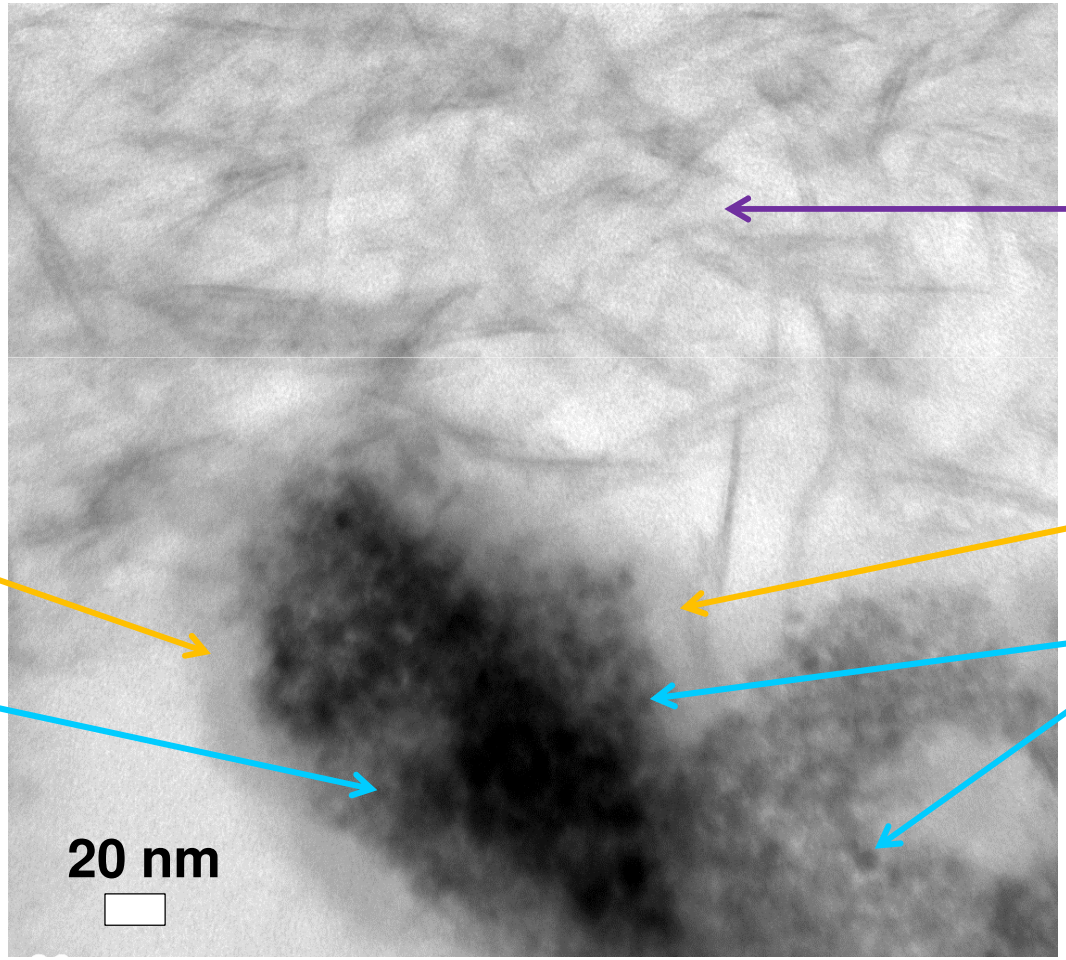
Structure of superparamagnetic composite micro-particles (2)



Layered Double Hydroxides (LDHs)

SiO_2

Fe_3O_4

SiO_2

Fe_3O_4

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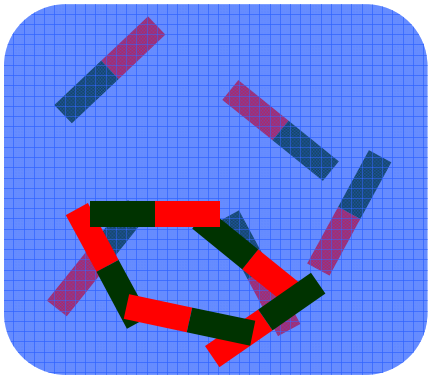
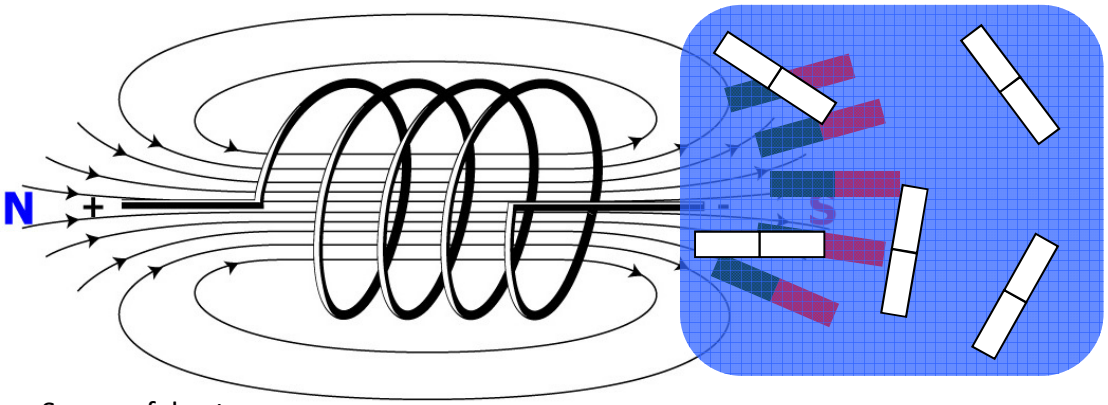
Why superparamagnetic nano iron oxide particles?

Ferromagnetic Fe_3O_4 particles µm-range



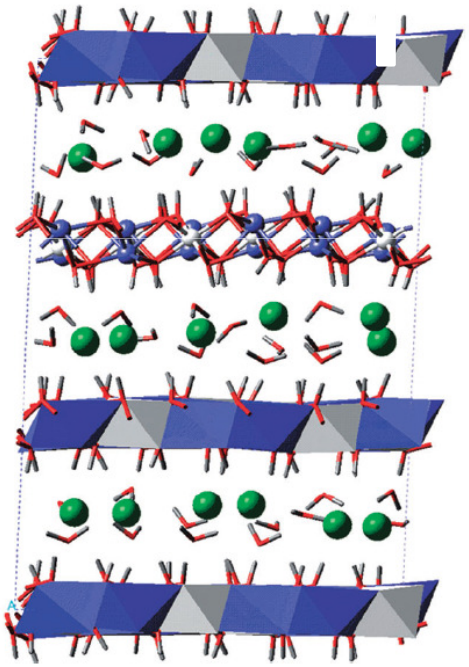
Superparamagnetic Fe_3O_4 particles <25 nm



Source: fehertamas.com

Layered double hydroxides (LDH) as selective phosphate ion exchangers

$[M^{2+}_{(1-x-y)}M^{3+}_{x}M^{4+}_{y}(OH)_2]$

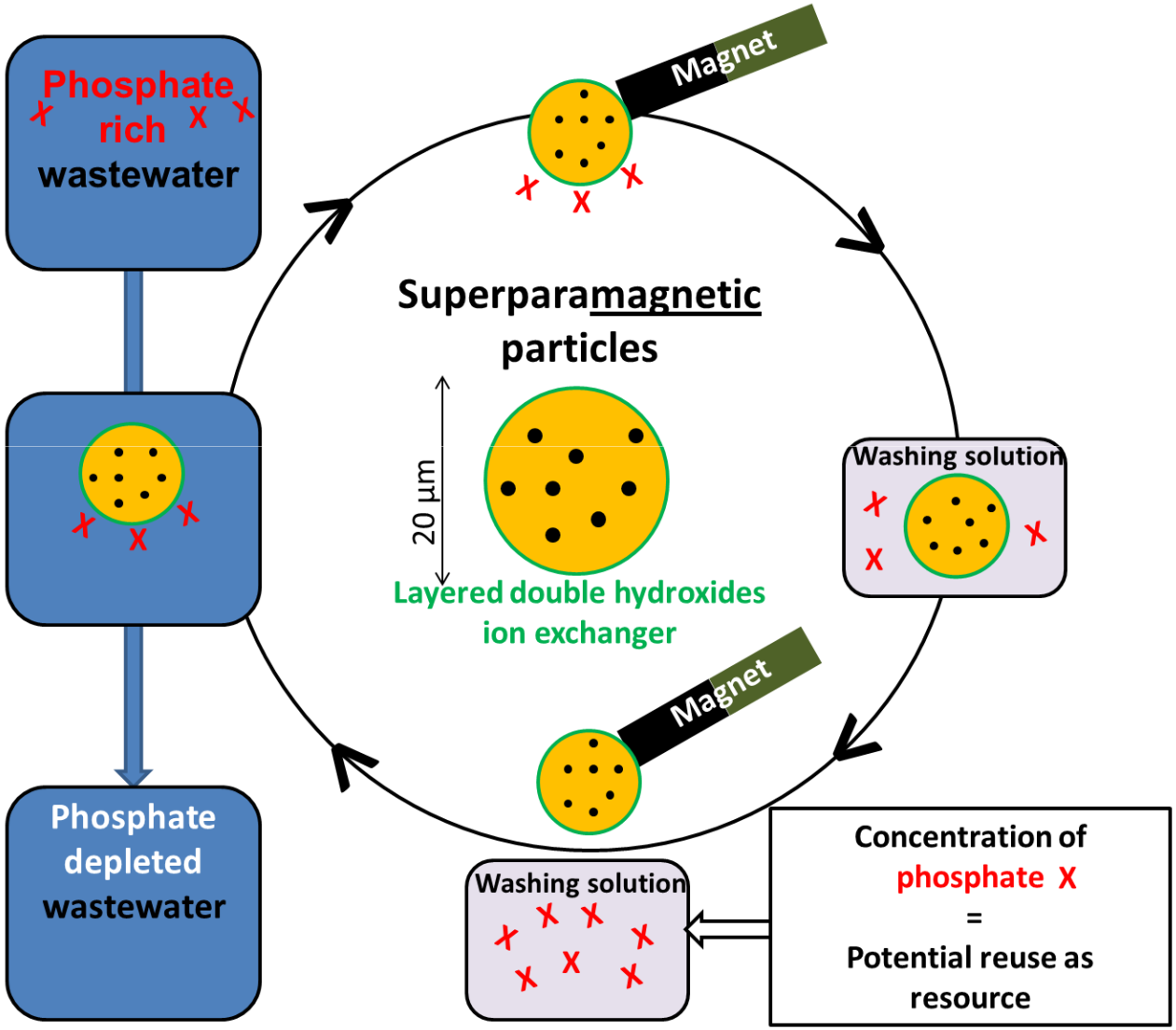


Source: Chem. Commun., 46 (2010), 5197-5210

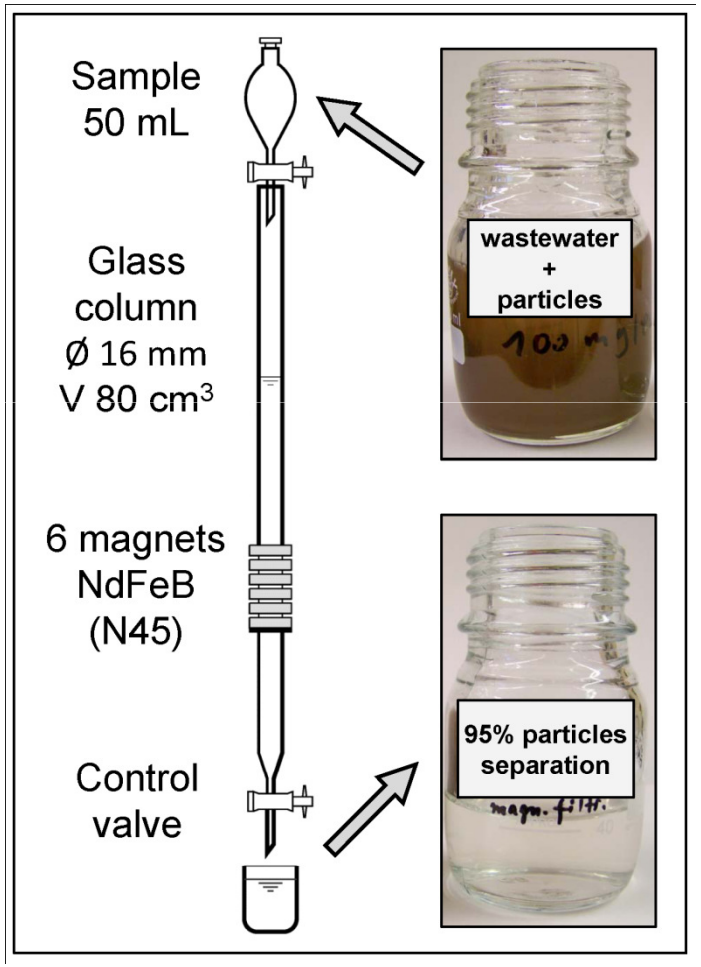
- May be exchanged reversibly with HPO_4^{2-}

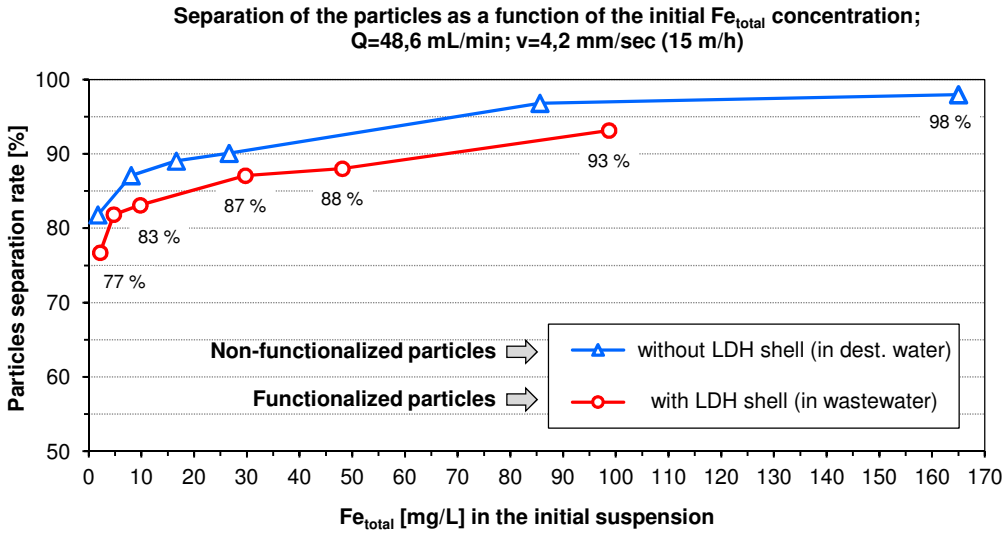
LDH Type	Determined formula
MgAl	$[Mg_{0.57}Al_{0.43}(OH)_2][Cl_{0.13}(CO_3)_{0.15}\cdot 1.27H_2O]$
MgAl-Zr	$[Mg_{0.67}Al_{0.15}Zr_{0.18}(OH)_2][Cl_{0.11}(CO_3)_{0.20}\cdot 1.18H_2O]$
MgFe-Zr	$[Mg_{0.69}Fe_{0.14}Zr_{0.17}(OH)_2][Cl_{0.07}(CO_3)_{0.205}\cdot 1.15H_2O]$
MgFe	$[Mg_{0.72}Fe_{0.28}(OH)_2][Cl_{0.10}(CO_3)_{0.09}\cdot 1.09H_2O]$

Complete concept of the P elimination/recovery



Magnetic separation of functionalized particles (1)

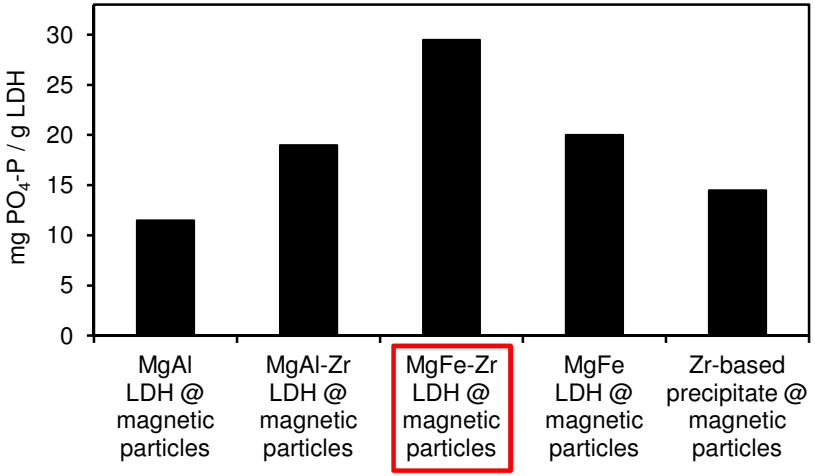




Magnetic separation of functionalized particles (2)

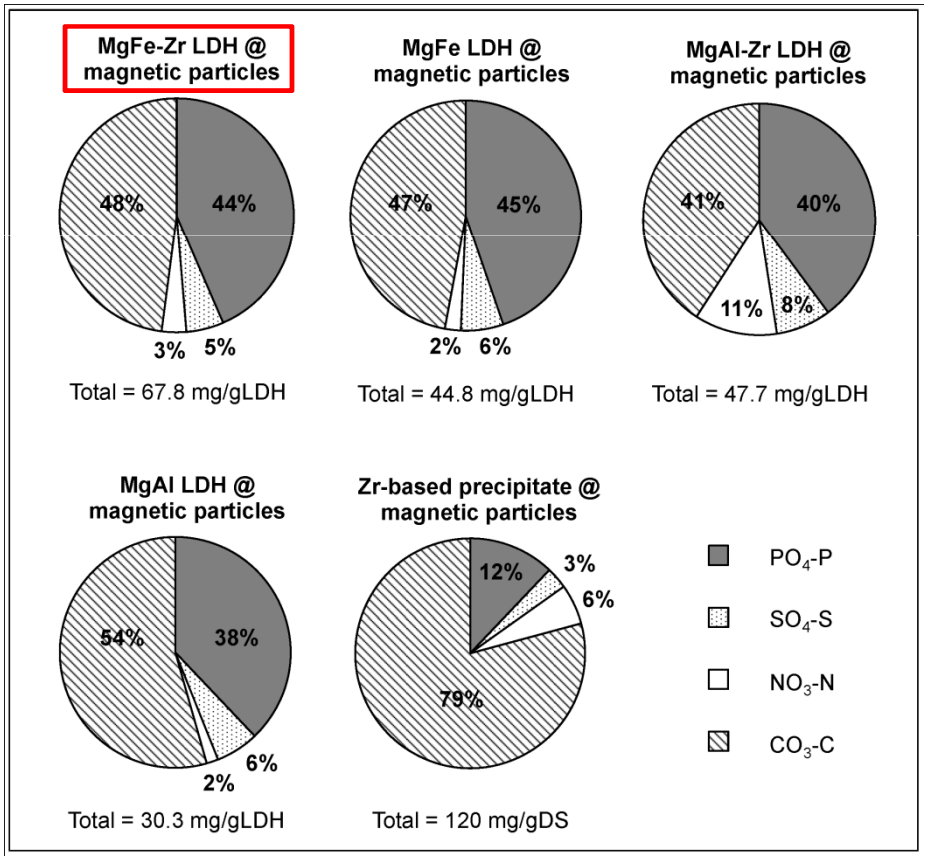
Phosphate adsorption capacity and selectivity of various LDH modifications on composite particles

Phosphate adsorption capacity of several LDH coatings deposited on superparamagnetic composite particles



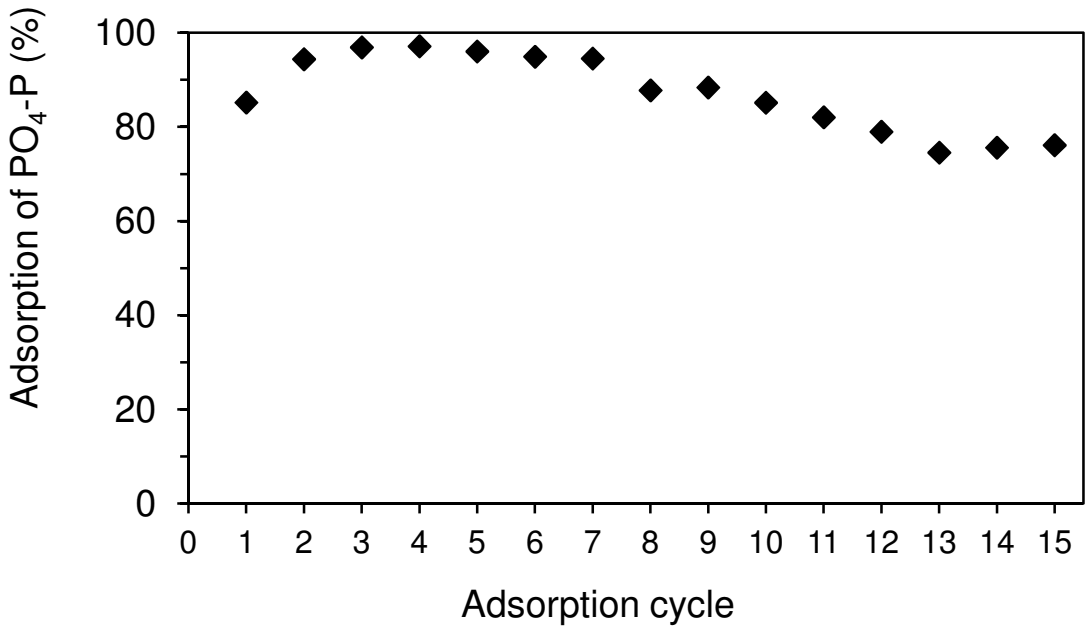
- LDH concentration = 200 mg/L (0.5 g/L particles)
- Initial ß[PO_4-P] = 10 mg/L
- pH = 7 – 8
- Contact time = 24 h
- Preferred LDH system: MgFe-Zr (30 mgP/gLDH)

Adsorption selectivity toward phosphate and competition of other common anions in municipal wastewater



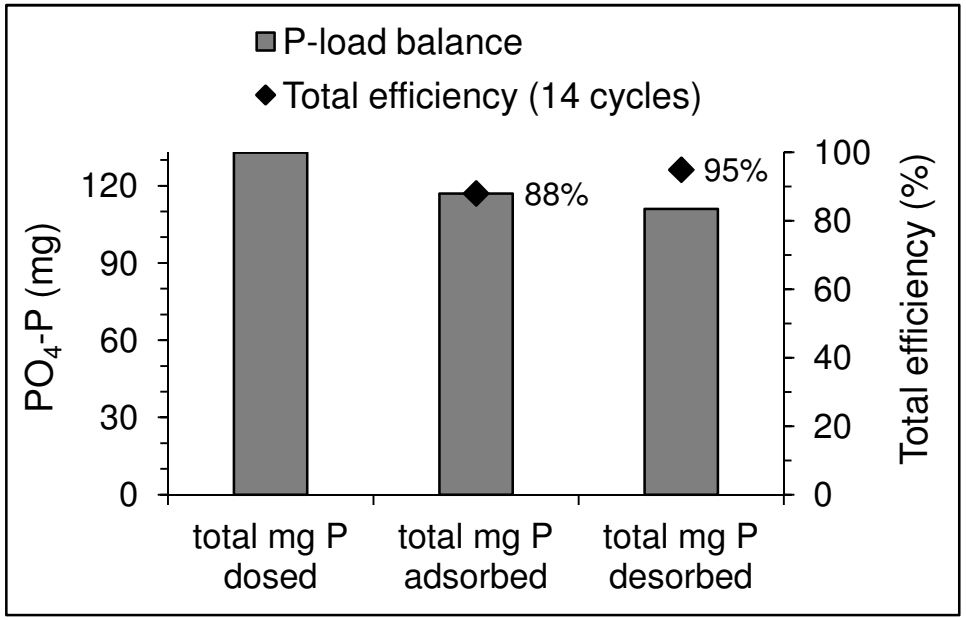
Reusability of the particles – P-adsorption within 15 cycles of application

- Lab-scale experiment (1L); municipal wastewater; initial ß[PO_4-P] = 10 mg/L
- 400 mgLDH/L (i.e. 1 g/L MgFe-Zr particles); contact time 1h
- > 75% PO_4-P adsorption efficiency even after 15 cycles of application



Reusability of the particles – P-desorption efficiency and total P-recovery

- Desorption solution 1M NaOH + 1M NaCl (pH 12.9); contact time 30 min
- 133 mgP dosed, 117 mgP adsorbed, 111 mgP desorbed
- 95% PO_4-P recovery, even after 14 application cycles (as total efficiency based on $P_{adsorbed}$)
- 11-times enrichment of the PO_4-P concentration in the desorption solution



Remark: Total efficiency and mass balance of phosphate recovery for the reactor with enriched desorption solution

Conclusions

- Using phosphate selective superparamagnetic composite particles is a feasible option for the elimination and recovery of phosphate directly from WWTP effluent
- The composite particles are well magnetically separable
- MgFe-Zr LDH showed the highest phosphate adsorption capacity and good selectivity for phosphate ions
- The reusability of the particles in municipal wastewater matrix was demonstrated for 15 adsorption/14 desorption cycles with insignificant drop in performance
  - 88% of the initial phosphate can be adsorbed
  - 95% of the adsorbed phosphate can be recovered

- Outlook:
  - An upscaling of the system appears to be very promising and will be subject to further research; e.g. use of a drum separator with permanent magnets
  - LDH system has to be enhanced for faster P-adsorption/desorption kinetics
  - Desorption at lower pH values; minimizing chemical usage

Thank you for your attention…

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