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

Good reasons for phosphorus recovery

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

![Diagram showing the process of phosphorus elimination and recovery from a municipal wastewater treatment plant.](image-url)
Basic idea for P removal and recovery from WWTP effluent

Wastewater containing phosphate + modified particles

Magnetic separation of the particles

Phosphate (dissolved) adsorbs on particles

Magnet

Washing of the particles -> phosphate ⇔ particles
Engineered superparamagnetic composite micro-particles

Superparamagnetic Fe$_3$O$_4$ – nano-particle

Amorphous SiO$_2$ matrix

Layered Double Hydroxides (LDHs)

LDH-modified superparamagnetic micro-particle

K. Mandel, Fraunhofer ISC
Structure of superparamagnetic composite micro-particles (1)
Structure of superparamagnetic composite micro-particles (2)

Layered Double Hydroxides (LDHs)

SiO$_2$

Fe$_3$O$_4$

20 nm

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Why superparamagnetic nano iron oxide particles?

Ferromagnetic Fe₃O₄ particles  μm-range

Superparamagnetic Fe₃O₄ particles  <25 nm

Source: fehertamas.com
Layered double hydroxides (LDH) as selective phosphate ion exchangers

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

May be exchanged reversibly with \( \text{HPO}_4^{2-} \)

<table>
<thead>
<tr>
<th>LDH</th>
<th>Determined formula</th>
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<tbody>
<tr>
<td>MgAl</td>
<td>([\text{Mg}<em>{0.57}\text{Al}</em>{0.43}(OH)<em>2][\text{Cl}</em>{0.13}(\text{CO}<em>3)</em>{0.15}\cdot1.27\text{H}_2\text{O}])</td>
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<tr>
<td>MgAl-Zr</td>
<td>([\text{Mg}<em>{0.67}\text{Al}</em>{0.15}\text{Zr}_{0.18}(OH)<em>2][\text{Cl}</em>{0.11}(\text{CO}<em>3)</em>{0.20}\cdot1.18\text{H}_2\text{O}])</td>
</tr>
<tr>
<td>MgFe-Zr</td>
<td>([\text{Mg}<em>{0.69}\text{Fe}</em>{0.14}\text{Zr}_{0.17}(OH)<em>2][\text{Cl}</em>{0.07}(\text{CO}<em>3)</em>{0.205}\cdot1.15\text{H}_2\text{O}])</td>
</tr>
<tr>
<td>MgFe</td>
<td>([\text{Mg}<em>{0.72}\text{Fe}</em>{0.28}(OH)<em>2][\text{Cl}</em>{0.10}(\text{CO}<em>3)</em>{0.09}\cdot1.09\text{H}_2\text{O}])</td>
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Source: Chem. Commun., 46 (2010), 5197-5210
Complete concept of the P elimination/recovery

Phosphate rich wastewater

Superparamagnetic particles

Layered double hydroxides ion exchanger

Washing solution

Concentration of phosphate X = Potential reuse as resource

Phosphate depleted wastewater
Magnetic separation of functionalized particles (1)

Sample 50 mL

Glass column Ø 16 mm V 80 cm³

6 magnets NdFeB (N45)

Control valve

Separation of the particles as a function of the initial Fe_{total} concentration;
Q=48.6 mL/min; v=4.2 mm/sec (15 m/h)

Particles separation rate [%]

Fe_{total} [mg/L] in the initial suspension

INW1-UP (dest. Wasser)
CLDH 34 (Abwasser + H₃PO₄)

Functionalized particles
Non-functionalized particles

without LDH shell (in dest. water)
with LDH shell (in wastewater)
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 β[PO₄-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

- MgFe-Zr LDH @ magnetic particles: 48% PO₄-P, 44% SO₄-S, 3% NO₃-N, 5% CO₃-C
- MgFe LDH @ magnetic particles: 47% PO₄-P, 45% SO₄-S, 2% NO₃-N, 6% CO₃-C
- MgAl-Zr LDH @ magnetic particles: 41% PO₄-P, 40% SO₄-S, 11% NO₃-N, 8% CO₃-C

Total:
- MgFe-Zr LDH: 67.6 mg/gLDH
- MgFe LDH: 44.8 mg/gLDH
- MgAl-Zr LDH: 47.7 mg/gLDH

Total:
- MgFe-Zr LDH: 30.3 mg/gLDH
- MgFe LDH: 120 mg/gDS
Reusability of the particles – P-adsorption within 15 cycles of application

- Lab-scale experiment (1L); municipal wastewater; initial $\beta[PO_4^-P] = 10 \text{ mg/L}$
- 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

![Graph showing adsorption of PO$_4^-$-P (%) over adsorption cycles](image-url)
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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