Towards a zerocost-biorefinery using a new nutrient recovery model library and global sensitivity analysis

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Outline

- Introduction
- Objectives
- Model development and validation
- Global sensitivity analysis and process optimization
- Conclusions
INTRODUCTION
Why recovering nutrients?

Haber Bosch process: \( N_2 \rightarrow NH_4 \)

P-mining: Apatite → Ortho-P

K-mining: Potash → \( K_2O \)

Waste(water), slurry and sludge processing

Agriculture, industry and households

Bioavailable nutrients

Non-bioavailable nutrients

Waste Water Treatment Plant (WWTP) → Water Resource Recovery Facility (WRRF)

Volatilization, leaching, run-off, soil fixation

\( NH_4 \rightarrow N_2 \)

Ortho-P → Fe/AlPO

\( K_2O \rightarrow ? \)

\( S \rightarrow H_2S \)

Resources ↓

Demand ↑

80% N, 25-50% P

80% N, 25-50% P

\( NH_4 \rightarrow N_2 \)

\( Ortho-P \rightarrow Fe/AlPO_4 \)

\( K_2O \rightarrow ? \)

\( S \rightarrow H_2S \)
Nutrient recovery processes

- Precipitation → struvite, calcium phosphates
- Ammonia stripping → NH₃
- Acidic air scrubbing → ammonium sulfates
- Concentration → H₂O, N-K concentrates
- Biomass production and harvest → biomass

⇒ Mainly physicochemical unit processes!
Points of attention

• The nutrient recovery process must have equivalent treatment efficiency as conventional treatment

• The process must be cost-effective

• The process must be simple to operate and maintain

• There must be a market for the recovered nutrient products
Problem: Optimal combination different for each waste flow

Question: What is the optimal combination of unit processes and operating conditions?

- Given: Particular waste stream
- Optimal:
  - Maximal resource recovery (nutrients, energy)
  - Minimal energy and chemical requirements

Approach = Mathematical models
Modeling challenges

⇒ Insights in chemical speciation required for fertilizer quality optimization

SeLow - Sustainable energy Low waste
Modeling challenges

- Reactor model
- Chemical speciation model
- Physico-chemical model
- Biochemical model

Fast reactions
- Species pH

Slow reactions
- Species pH

Numerical solution?!
Modeling challenges

Existing WWTP models → WRRF models

⇒ Lack of models to adequately put together optimal treatment trains for nutrient recovery and to select the optimal operating conditions
OBJECTIVES
Project: Industrial Innovation Scholarship (BMP, 2013-2015)

• Ph.D. Céline Vaneeckhaute (2015): Nutrient recovery from bio-digestion waste: From field experimentation to model-based optimization

• Supervisors: Peter Vanrolleghem (modelEAU), Evangelina Belia (Primodal), Filip Tack & Erik Meers (Ghent University)
Specific research objectives:

1. To develop generic models for the best available resource recovery systems including:
   - detailed chemical speciation
   - biological and physicochemical reaction kinetics
   - interactions between three phases (liquid-solid-gas)

2. To apply the models as a tool for optimization of single processes and treatment trains in order to:
   - maximize resource recovery (nutrients, energy) + product quality
   - minimize energy and chemical requirements
MODEL DEVELOPMENT AND VALIDATION
Model development

Generic nutrient recovery model library

NRM = Nutrient Recovery Model

SeLow - Sustainable energy Low waste
Model development

Numerical solution

- Reactor model
- Chemical speciation model
- Physico-chemical model
- Biochemical model

Fast reactions
- Species pH

Slow reactions
- Species pH

PHREEQC
- Interface
  - Tornado/(West)

SeLow - Sustainable energy Low waste
Model development

**Important findings & contributions**

- **Geochemical databases incomplete:**
  - Extended database for nutrient recovery, e.g., \((NH_4)_2SO_4, AlPO_4, \ldots\) \((Nutricover.dat)\)

- **Speed-up of model simulations:**
  - Selective database reduction
    - Speed X 4-5
  - Tight model coupling
    - Speed X 10

⇒ Highly efficient and practically implementable models!
Model calibration & validation

Experimental results

Simulation results
Model validation: NRM-Prec

Process lay-out

Struvite = MgNH₄PO₄·6H₂O

Source: adapted from Ostara (2015)
Model validation: NRM-Prec

Lab-scale experiments

MgCl$_2$:6H$_2$O → Different Mg:P ratios

Digestate sample

Reactor

Centrifuge

Precipitate

Effluent

Struvite (MgNH$_4$PO$_4$:6H$_2$O)

Detailed characterization

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Model validation: NRM-Prec

Experimental vs. simulation results (12 h)

<table>
<thead>
<tr>
<th>Mg:P</th>
<th>Digestate 1</th>
<th>Digestate 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% P-recovery</td>
<td>% P-recovery</td>
</tr>
<tr>
<td></td>
<td>Experim.</td>
<td>Original PHREEQC</td>
</tr>
<tr>
<td>1:1</td>
<td>41</td>
<td>95.60</td>
</tr>
<tr>
<td>2:1</td>
<td>44</td>
<td>97.91</td>
</tr>
</tbody>
</table>

⇒ Very good prediction of P-recovery at steady state
⇒ Importance of a detailed chemical solution speciation and accurate input characterization!
Scenario analyses: NRM-Prec

- **Digestate 1**: very high Fe and Al in influent → optimal P-recovery = 56.2%
- **Digestate 2**: low Fe and Al in influent → optimal P-recovery = 90.7%

**Main components precipitated**: Al, Ca, Fe, K, Mg, N, P

**Table: (Co-)precipitate**

<table>
<thead>
<tr>
<th>(Co-)precipitate</th>
<th>Digestate 1</th>
<th>Digestate 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeAl$_2$O$_4$</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>AlPO$_4$</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Fe$_3$(PO$_4$)$_2$·8$H_2$O</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

How to maximize nutrient recovery and guarantee fertilizer purity?
Scenario analyses: NRM-Prec

• Practical recommendations (if struvite is target):

  - Removal of CaCO$_3$ prior to precipitation (Huchzermeier et al., 2012)
  - Minimize the addition of Fe and Al upstream or implement struvite recovery upstream

Economic considerations:

- Mg ↑ ⇒ Costs ↑
- Particle size ↑ ⇒ Revenues ↑

K$_2$NH$_4$PO$_4$·6H$_2$O = Pure N-P-K fertilizer

MgKPO$_4$·6H$_2$O, Mg(OH)$_2$, Mg$_3$(PO$_4$)$_2$
= Pure Mg-P-K fertilizer
GLOBAL SENSITIVITY ANALYSIS AND PROCESS OPTIMIZATION
Model application for process and treatment train optimization

Feed composition & flow rate
Alkalinity addition
Influencing factors?
Heating
Mixing
Residence time

Tool for process optimization

Biogas volume & composition
Fertilizer quantity
Outputs?
Fertilizer quality:
- Nutrient content
- Nutrient use efficiency
- pH and salt content
- Dry weight and density
- Organic carbon
- Particle size distribution
- Metal content

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Global sensitivity analysis (GSA)

- Selection of factors with highest impact on model outputs (= objective for further study)

Acquired understanding

Optimal treatment train configuration
GSA results: NRM-AD

Effect of Fe on $H_2S$- and $CH_4$-production

$Fe \uparrow \Rightarrow H_2S$-inhibition of methanogens $\downarrow \Rightarrow CH_4 \uparrow$

Limit for corrosion risks (Deublein & Steinhauser, 2011) 0,0035 atm

$\Rightarrow$ Use of models for process and product quality optimization & control
$\Rightarrow$ Importance of species and precipitate modeling + input characterization!
GSA results: NRM-Prec

Effect of temperature on P-precipitation

\[ \text{Ca}_3(\text{PO}_4)_2: \beta = \text{stable at low temperature} \]

⇒ Struvite purity ↑ if temperature ↑

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GSA results: NRM-Strip

Process lay-out

Source: adapted from Colsen (2015)
GSA results: NRM-Strip

*Impact of chlorides on NH₃-recovery efficiency*

\[ y = -0.53x + 62.05 \]

\[ R^2 = 0.84 \]

- Chloride \( \uparrow \) ⇒ ionic strength \( \uparrow \) and pH \( \downarrow \)
- Importance of accurate phys-chem calculations!

⇒ Practical implication for treatment train:
  if preceding P-precipitation
  use Mg(OH)\(_2\)/MgO instead of MgCl\(_2\)
Treatment train configuration

OPTIMAL OPERATING CONDITIONS?

Consumables → Costs

Recovered products → Revenues

SeLow - Sustainable energy Low waste
Treatment train optimization

SeLow - Sustainable energy Low waste
Treatment train optimization

**Economic analysis**

### Variable costs & revenues

- Heat requirements ➔ worst & best case
- Chemicals
- Electricity
- Maintenance, material & labor costs
- Biogas production ➔ electricity and heat
- Fertilizer marketing ➔ worst & best case
- \( \text{CO}_2 \) emission reduction credits: 15 $ \text{ton}^{-1}

### Capital costs

- Technology providers
- CAPDET software
Treatment train optimization

Case-study

Financial benefits:

~ variable costs:
5 $ m\textsuperscript{-3} \text{ manure } y\textsuperscript{-1}
90 $ \text{ ton}^{-1} \text{ solids } y^{-1}

~ variable + capital costs:
2 $ m\textsuperscript{-3} \text{ manure } y\textsuperscript{-1}
40 $ \text{ ton}^{-1} \text{ solids } y^{-1}

ZeroCostWRRF (pay-back time: 7 years)

Note: If integration of nutrient recovery in existing WWTP
⇒ Need for overall optimization, e.g. aeration processes upstream, ...
CONCLUSIONS
Conclusions

- **WRRF modeling challenges:**
  - Integration of detailed chemical speciation and physico-chemical reaction kinetics in existing (biological) models
  - Generic models for nutrient recovery technologies?
  - Numerical solution?
Conclusions

• WRRF modeling advances:
  - Generic nutrient recovery model (NRM) library created
  - Efficient numerical solution strategy developed
  - Default parameters + proper input characterization → good agreement with steady state experimental results
  - Global sensitivity analysis → optimal treatment train configuration
  - Treatment train optimization → potential for ZeroCostWRRF

BUT if integration in existing WWTP:
need for overall optimization!
Acknowledgements
References


THANK YOU FOR YOUR ATTENTION

QUESTIONS ?