Are we about to upgrade wastewater treatment for removing organic micropollutants?

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Contents

- Sorption
- Biodegradation
- Transformation products
- Predicting environmental concentrations
- Conclusion
Removal by sorption on activated sludge

Bacteria

Negatively loaded surface

Adsorption of a bivalent compound (e.g. Norfloxacain) or a positively loaded compound on the surface

Absorption of a hydrophobic compound (e.g. Tonalide) in the lipophilic membrane

Lipophilic cell membrane
Sorption of micropollutants

Sorbed concentration:

\[ C_{\text{sorbed}} = K_d \cdot SS \cdot C_{\text{soluble}} \]

\( K_d = \) Sorption coefficient [l/gSS]
\( SS = \) Suspended solids or sludge production [g/l]

Sorbed fraction:

\[ \frac{C_{\text{sorbed}}}{C_{\text{soluble}} + C_{\text{sorbed}}} = \frac{K_d \cdot SS}{1 + K_d \cdot SS} \]
Sorption of micropollutants on activated sludge

Pharmaceuticals

- Carbamazepine, Clofibric acid, Ibuprofen
- Diazepam, Roxithromycin
- Diclofenac, Iopromide
- Estradiol, Ethinylestradiol
- Norfloxacin
- Estrone
- Ibuprofen
- Diazepam, Roxithromycin
- Diclofenac, Iopromide
- Estradiol, Ethinylestradiol
- Norfloxacin
- Galaxolide, Tonalide

Sorption coefficient $K_{d,i}$ [L kg$^{-1}$ SS]

Sorbed share [%]

Primary sludge

Secondary sludge

Sludge prod.

100 gSS m$^{-3}$

200 gSS m$^{-3}$

100 gSS m$^{-3}$
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Conclusion
Full scale sampling

Kloten-Opfikon (Zurich-North)

CAS: 55,000 PE

MBR: 100 PE

Altenrhein
Lake Constance

CAS: 60,000 PE

BioFilter: 60,000 PE
Full scale sampling

Activated sludge floc

Kloten-Opfikon (Zurich-North)

CAS: 60,000 PE

BioFilter: 60,000 PE

CAS: 55,000 PE

MBR: 100 PE

CAS: 60,000 PE

BioFilter: 60,000 PE

100 μm
Full scale sampling

Submerged biofilm reactor

Kloten-Opfikon
Zurich-North

CAS: 55’000 PE

MBR: 100 PE

CAS: 60’000 PE

BioFilter: 60’000 PE
Full scale sampling

- **Kloten-Opfikon, Zurich-North**
  - CAS: 55'000 PE
  - MBR: 100 PE

- **50% wastewater to biofilter**: 0.5 – 1.5 h HRT
- **50% wastewater to CAS**: 6 – 20 h HRT

- **BioFilter**: 60’000 PE
Full scale sampling

Kloten-Opfikon
Zurich-North

CAS: 55‘000 PE
MBR: 100 PE

Liquid sample
Sludge sample

Altenrhein
Lake Constance

CAS: 60‘000 PE
BioFilter: 60‘000 PE
Comparison of elimination in MBR, biofilter and conventional plant

Most compounds:
- a) different treatment, comparable removal
- b) only partially removed
Batch experiment
Test degradation in lab
Batch experiment with municipal sludge

**Relative removal rate constant**

\[
\frac{\log C_t - \log C_0}{\Delta t} = k_{biol} \cdot SS
\]

**Reaction rate**

\[
[\mu g \cdot m^{-3}_{\text{Reactor}} \cdot d^{-1}]
\]

**Substance conc.**

\[
[\mu g \cdot m^{-3}_{\text{Reaktor}}]
\]

**Sludge concentration**

\[
[gSS \cdot L^{-1}]
\]

**Rate constant**

\[
[L \cdot gSS^{-1} \cdot d^{-1}]
\]
Modelling removal in the second biological step

removal [%]

July

Model fits most but not all compounds
Modelling removal in the second biological step

Model fits most but not all compounds
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Removal of atenolol and psychoactive drugs in WWTP Frankfurt

- **Screen**
- **Grit removal**
- **Primary clarifier**
- **COD removal**
- **Clarifier 1**
- **Denitrification**
- **Clarifier 2**
- **Denitrification**
- **Receiving water**

**1. Biological step** (SA: 0.5d; HRT: 0.5h)

**2. Biological step** (SA: 15-20d; HRT: 4-5h)

**[c/c₀]**

- Codeine
- Dihydrocodeine
- Morphine
- Primidone
- Atenolol

< LOQ
Biological transformation
Example: Codeine

- used as analgesic and cough suppressant
- most widely used opiate in the world
- opium contains 0.2 to 6% codeine
- mainly produced from morphine by methylation of the hydroxy group at the aromatic ring

up to 90% is removed in WWTPs by primary degradation

formation of transformation products (TPs)?

capsule of the opium poppy (*Papaver somniferum* L.).
Codeine transformation products

TP 314, m/z 313
TP 332, m/z 331
TP 316, m/z 315
TP 300 (1), m/z 299
TP 264, m/z 263
TP 302, m/z 301

in most cases basic structure unchanged

typical reactions observed:
• double bond shift
• hydroxylation
• demethylation
Iopromide: potential aerobic degradation pathways

reaction I/II: oxidation prim./sek. hydroxyl moieties
reaction III: cleavage of amide-methylen bond
reaction IV: oxidative decarboxylation
reaction V: deacetylation

Source: Schulz et al. (2008) ES&T
Transformation products (TPs) of Iopromide in WWTP Frankfurt

Source: Schulz et al., ES&T, 2008
Transformation of iodinated contrast media

Conc. in µg/L

<table>
<thead>
<tr>
<th></th>
<th>WWTP effluent</th>
<th>surface water</th>
<th>groundwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iomeprol</td>
<td>(0.8)</td>
<td>(1.4)</td>
<td>(261)</td>
</tr>
<tr>
<td>sum of 12 TPs</td>
<td>(0.7)</td>
<td>(1.7)</td>
<td>(128)</td>
</tr>
<tr>
<td>Iopromide</td>
<td>(1.2)</td>
<td></td>
<td>(1.1)</td>
</tr>
<tr>
<td>sum of 9 TPs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iopamidol</td>
<td>(0.8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sum of 15 TPs</td>
<td>(0.5)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\text{transformation} \left( \frac{\text{conc. } \Sigma \text{ TP}}{\text{conc. ICM}} \right)
\]

dilution
Contents

- Sorption
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1) WWTP influent
2) WWTP effluent
3) Reed bed influent
4) Reed bed effluent
5) Effluent tertiary pond
Wetland van Cuijk

- 4 days hydraulic residence time
- 0.17 m$^3$·m$^{-2}$·d$^{-1}$ hydraulic loading

![Graph showing removal of Ibuprofen in wetland effluent compared to influent. The graph includes a line indicating 33% removal and a marker showing the influent concentration of Ibuprofen.]
Diclofenac: predicted concentrations in Swiss surface waters based on the dilution factor (environmental quality standard: 0.1 µg/L)

A simple model allows identifying hot spots for advanced treatment

- Consumption: 4 t/a
- 35% (Dicl. + meta) in wastewater
- Elimination in WWTP: Ø 25%
- No degradation in surface water

Data: Eawag/FOEN 2006/07
Basis: Vector25@swisstopo (2004)
DHM25@swisstopo (2004)

Ort et al. GWA 11, 2007
Conclusions

- **Sorption to sludge**: relevant for few compounds
- **Degradation** achieves only partial removal
  - First order kinetic does not always fit
- **Transformation products** of similar chemical structure often formed
  - Does elimination result in *detoxification*?
- **Wetlands** achieve little micropollutant removal
- **Environmental concentrations**: estimation based on consumption and dilution
  - Identify spots for advanced treatment
Thank you for your attention …

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