Removal of organic micropollutants by innovative processes: The SIAM system

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Organic micropollutants (OMPs)

- Heterogeneous group
- Largely consumed in modern societies
- Concentration in wastewater: ppb-ppt
- Bioactive compounds
- Effects: bioaccumulation, toxic, estrogenic and mutagenic
Concern about OMPs

EU legislation

<table>
<thead>
<tr>
<th>Directives</th>
<th>Priority substances under the Water Framework Directive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Directive on Environmental Quality Standards (2008/105/EC) EQSD</td>
<td>- Limits on concentrations of the 33 priority substances</td>
</tr>
<tr>
<td></td>
<td>- Diclofenac, estradiol and ethinylestradiol should be included in the first watch list of substances for which</td>
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<tr>
<td></td>
<td>Union-wide monitoring data should be gathered.</td>
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<td></td>
<td>- The first watch list shall contain maximum of 10 substances</td>
</tr>
<tr>
<td>Commission implementing decision (EU) 2015/495</td>
<td>- The watch list of substances include 4 pharmaceuticals (DCF and macrolides ERY, AZI, CLA) and 3 hormones (E1, E2, EE2)</td>
</tr>
</tbody>
</table>
State of the art of OMPs (bibliometrics)

Publication trends in OMPs in WWTPs (reporting period: 2000-2015)

Significant variability for OMPs removal in WWTPs

Operational conditions

Why?

Technologies

Biomass characteristics
Different OMP chemical structure

<table>
<thead>
<tr>
<th>Anaerobic conditions</th>
<th>Aerobic conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substituted pyrimidine</td>
<td>Electro-drawing groups</td>
</tr>
<tr>
<td>Straight-chain hydrocarbons</td>
<td>Hydroxyl group</td>
</tr>
<tr>
<td>Amide group</td>
<td>R - NH₂</td>
</tr>
<tr>
<td>Chlorine groups</td>
<td>R - Cl</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Biodegradable</th>
<th>Recalcitrant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straight-chain hydrocarbons</td>
<td>Hydroxyl group</td>
</tr>
<tr>
<td>Aromatic ether</td>
<td>Fused aromatic rings</td>
</tr>
<tr>
<td>Amine group</td>
<td>Chlorine groups</td>
</tr>
<tr>
<td>Fused aromatic rings</td>
<td>Heterocyclic N aromatic rings</td>
</tr>
</tbody>
</table>

Fernandez Fontaina et al., 2016; Musson et al., 2010; Field, 2002; Knockmus, 1996; Adrian et al., 1994; Bothling et al., 1994

OMPs removal mechanisms

- **Sorption**
  - Transfer to the solid phase
  - Adsorption (electrostatic interactions)
  - Acid dissociation constant
  - Absorption (hydrophilic interactions)
  - Octanol water coefficient

- **Volatilization**
  - Transfer to the gaseous phase
  - Stripping
  - Henry constant
  - Surface volatilization
  - Henry constant

- **Biotransformation**
  - Chemical reactions with bacteria
  - Metabolism
  - Henry constant
  - Cometabolism
  - Octanol water coefficient
  - Acid dissociation constant

\[
\frac{\Delta C}{\Delta t} = \frac{Q}{H} \cdot q_{air} \cdot \Delta t \cdot C_{eff} (mg L^{-1})
\]

\[
F_{biod} = k_{biod} \cdot VSS \cdot C_{eff} \cdot V
\]
Metabolism-cometabolism

- **Metabolism**: the primary carbon or nutrients source for growth and/or energy source
- **Cometabolism**: the presence of a primary substrate is necessary for inducing the enzymes for micropollutant removal

The role of redox potential: anaerobic and aerobic. Application to the treatment of urban wastewaters

1) The AnHMBR system


AnHMBR process

- Anaerobic treatment
  - Biogas production
  - Energy savings
  - Low sludge production

- Aerobic treatment
  - High effluent quality
  - High membrane fluxes

- Membrane filtration
  - Total retention of microorganisms
  - Elevated quality of effluent (reuse)

Reactors at lab-scale

- Anaerobic reactor
  - UASB reactor
  - Volume 4.5 L
  - Inoculum 40 gVSS L⁻¹
  - Influent Conc.: 1200 mg COD L⁻¹
  - COD load: 1200-2400 mg L⁻¹ d⁻¹

- Aerobic reactor
  - Conventional activated sludge
  - Volume 2 L
  - Inoculum 2 gVSS L⁻¹
  - Influent Conc.: 130 mg COD L⁻¹, 40 mg N-NH₄⁺ L⁻¹
  - COD load: 130-260 mg L⁻¹ d⁻¹

<table>
<thead>
<tr>
<th>Reactor</th>
<th>1º period</th>
<th>2º period</th>
<th>3º period</th>
<th>4º period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HRT</td>
<td>v_up HRT</td>
<td>HRT</td>
<td>v_up HRT</td>
</tr>
<tr>
<td>UASB</td>
<td>1 d</td>
<td>0.1 m h⁻¹</td>
<td>0.5 d</td>
<td>0.1 m h⁻¹</td>
</tr>
<tr>
<td>CAS</td>
<td>1 d</td>
<td>-</td>
<td>1 d</td>
<td>-</td>
</tr>
</tbody>
</table>

*HRT = hydraulic retention time, v_up = upward velocity

*HRT v up HRT v up HRT v up

UASB 1 d0.1 m h⁻¹10.5 d0.1 m h⁻¹10.5 d0.5 m h⁻¹10.5 m h⁻¹

CAS 1 d-1 d-0.75 d-0.5 d-

*HRT: hydraulic retention time

*V_up: upward velocity
Removal mechanism in UASB and CAS units

UASB reactor HRT = 1 day CAS unit

Biotransformation

Comparison of oxidation rate (per liter of wastewater)
• 3 stage reactor:
  • Upflow anaerobic sludge blanket 120 L
  • Hybrid aerobic chamber 36 L
  • Membrane chamber 20 L
• Influent COD concentration: 1200 mg L⁻¹
• Influent organic load: 1700 mg COD L⁻¹ d⁻¹
• HRT: 13 h (UASB). 4 h (HMBR)
• VSS: 40 g L⁻¹ (UASB); 1-5 g L⁻¹ (HMBR)
• Membrane surface area: 0.9 m²
• Membrane pore size: 0.04 mm

Lower removals under aerobic conditions
Low COD concentration inlet
cometabolism
Lower nitrification
The role of redox potential: anaerobic and aerobic. Application to the treatment of urban wastewaters

2) The SIAM system

Introduction: UASB drawbacks

Anaerobic

Methane: Strong greenhouse gas

50-75% CH₄ (biogas)

25-50% CH₄ (dissolved) (1)

NH₄ & TSS

CH₄ GWP: 28 times higher than CO₂

Eutrophication problems

The SIAM process

Nitrite Dependent Anaerobic Methane Oxidation (N-DAMO)

Aerobic Methane Oxidation coupled to Denitrification (AMO-D)

Simultaneous CH₄ & N removal

Materials and methods

Biogas

Dissolved CH₄
21 mgCH₄·L⁻¹

Wastewater
TCOD: 841 mgO₂·L⁻¹
SCOD: 744 mgO₂·L⁻¹

Anaerobic
120 L

Anoxic
36 L

Aerobic
20 L

N₂
NO₂⁻
NO₃⁻
CH₄
NH₄⁺
NO₃⁻
Biological methane oxidation coupled to denitrification

- **Aerobic pathway (methanotrophs/heterotrophs)**
  
  \[ 5\text{CH}_4 + 5\text{O}_2 + 4\text{NO}_3^- + 4\text{H}^+ \rightarrow 2\text{N}_2 + 12\text{H}_2\text{O} + 5\text{CO}_2 \]

  1.3 g CH₄/g N (5.7 g-COD/g-N)

  *At low [O₂] reverse methanogenesis and HAc production*

- **Anaerobic pathway (N-DAMO bacteria)**
  
  \[ 3\text{CH}_4 + 8\text{NO}_2^- + 8\text{H}^+ \rightarrow 3\text{CO}_2 + 4\text{N}_2 + 14\text{H}_2\text{O} \]

  0.43 g CH₄/g N (1.71 g-COD/g-N)

- **Anaerobic pathway (N-DAMO arquea & bacteria)**
  
  \[ 2\text{CH}_4 + 8\text{NO}_3^- \rightarrow 2\text{CO}_2 + 8\text{NO}_2^- + 4\text{H}_2\text{O} \quad \text{(Arquea)} \]

  \[ 3\text{CH}_4 + 8\text{NO}_2^- + 8\text{H}^+ \rightarrow 3\text{CO}_2 + 4\text{N}_2 + 14\text{H}_2\text{O} \quad \text{(Bacteria)} \]

  0.71 g CH₄/g N (2.86 g-COD/g-N)

OMPs removal (SIAM)

- SIAM
  - Nitrification: 99%

OMPs removal:
- Anaerobic: NPX, SMX, TMP
- HMBR: BF-A, IBP, E1
- Both units: GLX, E2, EE2, ERY, ROX, TCS, FLX

Increased removal due to nitrification: IBP, ERY, ROX, hormones

High improvement of results
Influence of primary substrate

- **Kinetic assays** to determine biological kinetic coefficients of OMPs removal
- Influence of the type of primary substrate in OMPs removal
- Influence of the concentration of primary substrate in OMPs removal

**Primary substrates:**
- Nitrite + Methane (*methanotrophs*)
- Nitrite + Sodium Acetate (*heterotrophs*)
- Nitrite + Ammonia (*anammox*)
- Nitrite + Methanol (*methanotrophs + anammox*)

**Cometabolism: effect of primary substrate**

![Graphs showing % elimination of different substances](image)
Life SIAMEC project strategy (LIFE+ programme)

- Integrated anaerobic systems for wastewater reclamation at ambient temperature in European climates
  - To change of mainstream wastewater treatment concept from resource consuming processes into more sustainable treatment schemes
  - Anaerobic treatment of municipal and industrial wastewater
  - Reduce Energy consumption and Sludge production in WWTP
  - To produce reclaimed wastewater to be reused

Validation at pilot scale (Murcia, Spain)

http://www.life-siamec.eu/
Conclusions

- OMPs biotransformation was dependent on the nitrifying activity, the methanogenic activity and the heterotrophic activity.
- Most OMPs were more easily biotransformed under aerobic conditions. However, the anaerobic stage is crucial for OMPs biotransformation prone to be removed by reducing conditions.
- Sorption was only significant in the anaerobic reactors for the removal of lipophilic OMPs. The increase of upward velocity and HRT improved sorption.
- Biological processes need to be optimized not only in terms of macropolllutants, but also considering specifically the fate of OMPs, since the removal of these trace compounds are strongly affected by the main metabolic activities.

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Thank you for your attention!