Micropollutants removal by full-scale UV-C / sulphate radical based AOPs in the tertiary treatment of Toledo WWTP for water reuse

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Presenter: Ángel Encinas (FCC Aqualia)
SUMMARY

1. Introduction
2. Materials and methods
3. Results and discussion
4. Conclusions
1. Introduction

- Previously unknown
- Recent environmental concern
- Scarce scientific knowledge about their possible risks to human health
- Priority research lines: WHO, EPA, EC

Emerging Micropollutants (MPs)

- Trace level (ppb or ppt)
- Different nature: pesticides, Pharmaceutical & Personal Care Products (PPCPs) (perfumes, sunscreens), surfactants, antiseptics...

- Not regulated
- Candidates for future legislation
- Directive 2013/39/EU (modifies WFD & EQSD)
- Watch lists

Main sources:
- Domestic
- Agricultural / Livestock
- Industrial
- Hospital
1. Introduction

Advanced Oxidation Processes (AOPs)

Generation of high oxidant free radicals to degrade any kind of substances (chemical and biological)

- Hydroxyl radicals (HR-AOPs)

- Sulfate radicals (SR-AOPs)
1. Introduction

Objectives of the work

i. to assess the presence and removal of MPs in a municipal WWTP

ii. to apply selected photochemical AOPs at full-scale in the UV-C tertiary treatment of a municipal WWTP to evaluate the MPs removal efficiency

iii. preliminary economic assessment of operating cost and their feasibility of application
2. Materials and methods

Wastewater Treatment Plant (WWTP)

- TERTIARY TREATMENT
  - Secondary effluent
  - Coagulation
  - Flocculation
  - Decantation

- Rotofilter

- UV-C reactor
  - $V_{UV \text{ reactor}} = 140 \text{ L}$
  - $t_{UV \text{ contact}} = 4–18 \text{ s}$
  - $UV_{dosages} = 42–170 \text{ J/L}$

Tertiary treatment flow rates:
- 28 m$^3$/h
- 75 m$^3$/h
- 114 m$^3$/h

Reclaimed water

Estiviel WWTP (Toledo)
- 36,000 m$^3$/day
- 270,000 PE
- Activated sludge
- Tertiary treatment for gardens irrigation
2. Materials and methods

Micropollutants analysis

<table>
<thead>
<tr>
<th>Group</th>
<th>Compound</th>
<th>Abbrev.</th>
<th>Group</th>
<th>Compound</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medicines / antibiotics</td>
<td>Gabapentin</td>
<td>GBP</td>
<td>Pesticides / Flame retardants</td>
<td>Tris(2-chloroethyl) phosphate</td>
<td>TCEP</td>
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<tr>
<td></td>
<td>Sulfamethoxazole</td>
<td>SFX</td>
<td></td>
<td>N,N-Diethyl-m-toluamide</td>
<td>DEET</td>
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<tr>
<td></td>
<td>Metoprolol</td>
<td>METO</td>
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<td>Tris(1-chloro-2-propyl) phosphate</td>
<td>TCPP</td>
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<td>o-desmethyltramadol</td>
<td>ODT</td>
<td></td>
<td>Tris(1,3-dichloro-2-propyl) phosphate</td>
<td>TDCPP</td>
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<tr>
<td></td>
<td>Tramadol</td>
<td>TRA</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Norvenlafaxine</td>
<td>NVNF</td>
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<tr>
<td></td>
<td>Venlafaxine</td>
<td>VLX</td>
<td>Triphenylphosphate</td>
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<td></td>
<td>LIDOcaine</td>
<td>LDC</td>
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<td>Oxcarbamazepine</td>
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<td>CBZ</td>
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<td>Mirtazapine</td>
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<td>Tolytriazole</td>
<td>TT</td>
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<td>Synthetic fragrances</td>
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<td></td>
<td>IsocyClemone E</td>
<td>OTNE</td>
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<tr>
<td></td>
<td>Traesolide</td>
<td>ATII</td>
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<tr>
<td></td>
<td>Galaxolidone</td>
<td>HHCB-lactone</td>
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<tr>
<td></td>
<td>Tonalide</td>
<td>AHTN</td>
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<tr>
<td></td>
<td>Galaxolide</td>
<td>HHCB</td>
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</tbody>
</table>

- SPE: solid phase extraction *(SPE TELOS ENV cartridges, Kinesis)*
- GC–MS: gas chromatography *(HRGC Agilent 7890B)* coupled with mass spectrometry *(LRMS Agilent 5977B)*
- LC-MS/MS: liquid chromatography *(HPLC PE Series 200)* coupled with tandem mass spectrometry *(AB Sciex 2000)*
3. Results and discussion

MPs occurrence in secondary effluents from urban WWTP

Secondary effluent → Coagulation → Flocculation → Decantation → Rotofilter → UV-C reactor → Treated effluent

Sampling points

High variability

< 4 µg /L

Secondary outlet occurrence of micropollutants

[ Micropollutant ] µg/L

5

4

3

2

1

0.5

0

25 m³/h

75 m³/h

115 m³/h

% Removal

0

10

20

30

40

50

60

70

80

90

100

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3. Results and discussion

AOPs applied

- Hydrogen peroxide ($H_2O_2$) photolysis: $HP / UV-C$
- Peroxymonosulfate ($HSO_5^{-}$) photolysis: $PMS / UV-C$
- Persulfate ($S_2O_8^{2-}$) photolysis: $PS / UV-C$

UV-C contact time = 4 – 18 s
3. Results and discussion

**H₂O₂ / UV-C**

- *R/D*: removal/dosage

- *R/D=130 (0.5 mM)* → 65%
- *R/D=154 (0.5 mM)*
- *R/D=180 (0.05 mM)* → 9%
- *R/D=1220 (0.05 mM)*

- UV-C contact time = 18 seconds

- [H₂O₂] = 0.5 mM

- UV-C contact time:
  - 18 seconds
  - 7 seconds
  - 4 seconds
3. Results and discussion

PMS / UV-C

UV-C contact time = 18 seconds

[0.05 mM]
[0.2 mM]
[0.5 mM]

48%  29%  20%

[PMS] = 0.5 mM
3. Results and discussion

**PS / UV-C**

**Hypothesis:**
- Not enough UV-C contact time for PS activation to generate $SO_4^\cdot$
- pH 3-5 (Deng et al., 2013)
3. Results and discussion

Classification of MPs abatement

- UV-C contact time: 18 s
- Oxidant dosages: 0.5 mM
3. Results and discussion

Physico-chemical parameters assessment

- Low turbidity: efficiency low affected by shadow effect
- Low nitrites: <0.1 mg/L \( \Rightarrow \) no \(-\)OH scavengers effect
- Applying AOPs:
  - Low TOC removal (mineralization level)
  - Low COD removal (organic matter reduction)
  - Highest TOC (15%) and COD (30%) removal: PS/UV-C

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Outlet secondary treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.17 ± 0.04</td>
</tr>
<tr>
<td>Conductivity (( \mu S/cm ))</td>
<td>985 ± 44</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>3 ± 0.46</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>6 ± 3</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>8 ± 3</td>
</tr>
<tr>
<td>COD (mgO_2/L)</td>
<td>27 ± 3</td>
</tr>
<tr>
<td>TN (mg/L)</td>
<td>7 ± 1</td>
</tr>
<tr>
<td>TP (mg/L)</td>
<td>0.76 ± 0.14</td>
</tr>
<tr>
<td>Ammonia (mg/L)</td>
<td>0.32 ± 0.49</td>
</tr>
<tr>
<td>Nitrates (mg/L)</td>
<td>6 ± 1</td>
</tr>
</tbody>
</table>

Competition of SR- in the degradation of MPs and organic matter
3. Results and discussion

Preliminary economic assessment

- Oxidant reagents cost (H₂O₂, PMS, PS)
- Electricity consumption of dosing pumps
- Electricity consumption of UV-C lamps

order = \log\left(\frac{100 - \% \text{ MPs removal}}{100}\right)

<table>
<thead>
<tr>
<th>UV-C contact time (s)</th>
<th>[Reagents] (H₂O₂, PMS, PS)</th>
<th>UV-C(^{a,b})</th>
<th>H₂O₂/UV-C</th>
<th>PMS/UV-C</th>
<th>PS/UV-C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>€/m³</td>
<td>€/m³-order</td>
<td>€/m³</td>
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<tr>
<td>18</td>
<td>0.05</td>
<td>0.017</td>
<td>0.017</td>
<td>0.189</td>
<td>0.072</td>
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<tr>
<td></td>
<td>0.2</td>
<td>0.023</td>
<td>0.026</td>
<td>0.164</td>
<td>0.243</td>
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<tr>
<td>18</td>
<td>0.5</td>
<td>0.012</td>
<td>0.035</td>
<td>0.102</td>
<td>0.585</td>
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<tr>
<td>7</td>
<td>0.5</td>
<td>0.004</td>
<td>0.026</td>
<td>0.164</td>
<td>0.576</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.003</td>
<td>0.025</td>
<td>0.365</td>
<td>0.574</td>
</tr>
</tbody>
</table>

**No reagents required**

Most demanding operating conditions: highest UV-C contact time and reagents dosages

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4. Conclusions

- SR-AOPs are efficient to disinfect and to remove MPs simultaneously, reaching total inactivation and high removal of micropollutants under the more demanding operating conditions. However, the required reagent’s dosages to microbial inactivation are around 50 time less than the required to remove MPs.

- Treatments showed very similar behaviour when they were applied at full-scale.

- Although the activation of PMS and PS with Fe(II) increased the efficiency of the treatments at lab-scale, the higher cost of the treatment not compensate their use at full-scale.

- The best option in terms of operating cost and efficiency is the photolysis of hydrogen peroxide.
GRACIAS POR SU ATENCIÓN