Environmental assessment of a photocatalytic degradation of contaminated water

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Water: A rare and precious resource

Only 0.01% of the total freshwater usable to human (UN-Wat
Wastewater: human-made phenomenon

• The *excessive use* and *continued mismanagement* of freshwater resources for industrial growth are increasing the contamination of the wastewater.

• A wide range of *organic compounds* is detected in industrial and municipal wastewater.

• Some of these compounds pose severe problems in biological treatment systems due to their resistance to biodegradation.
Advanced Oxidation Processes (AOPs)

• AOPs is an innovative water treatment technology used for destroying recalcitrant organic compounds transforming them into biodegradable products (CO₂, H₂O).

• The main mechanism of AOPs functionality is the generation of highly reactive free radicals such as hydroxyl radicals (OH•).

• One of the most effective methods of AOPs is the use of UV ray and oxidant such as H₂O₂, O₃, and TiO₂.

H₂O₂ / UV
O₃ / UV
O₃ / H₂O₂ / UV
UV / TiO₂ (Photocatalytic oxidation)
Titanium dioxide photocatalyst

- TiO$_2$ is a metallic oxide well known for its unique photocatalytic properties and ability to degrade organic matters.
- TiO$_2$ is very stable both chemically and photochemically, relatively low cost, nontoxic and insoluble in water.
- TiO$_2$ nanoparticles thanks to their small particle size can lead to the increase of surface area of the catalyst and improve the photocatalytic activity (more catalytic reactions can occur at the same time).
**TiO$_2$ nanoparticles for wastewater treatment**

**Prototype phase**

- Cylindrical photoreactor having a substrate coated with nanoTiO$_2$ and activated with proper UV irradiation;

- Laboratory scale
  Reactor dimensions:
  - external glass tube $h=450$ mm, $\phi=56$ mm
  - internal quartz tube $h=400$ mm, $\phi=35$ mm

- UV-A lamp (15 W) is collocated inside the internal tube;

- O$_3$ has been blown through the bottom opening to enhance the oxidation process of nanoTiO$_2$;

- Photocatalytic support: aluminum oxide (Al$_2$O$_3$) microspheres coated with nanoTiO$_2$;
TiO$_2$ nanoparticles for wastewater treatment
Prototype phase

*Material Lab - Department of Industrial Engineering - University of Parma, Italy*

Methylene blue
$C_{16}H_{18}ClN_3S \cdot xH_2O$

- The photoreactor has been tested with synthetic wastewater sample;
- Mode of operation: batch mode or semi-continuous mode to ensure the adequate contact time for the photocatalytic degradation.
Life Cycle Assessment  ISO 14040/44

• The aim of this study is to assess the *environmental* and *human health* impacts of the scale up of the developed photoreactor and the related wastewater purification treatment.

[Flowchart diagram]

- Impact of potential nanoTiO$_2$ releases during all life cycle stages
- Benefits of purification of wastewater treatment

• Functional unit: volume of the synthetic wastewater sample = 6917 cm$^3$
  Photoreactor internal volume: 7170 cm$^3$; Total spheres volume: 253 cm$^3$

• Data quality:
  ✓ primary data supplied by the *Material lab, University of Parma - Italy* has been used;
  ✓ secondary data obtained by Ecoinvent database v3 have been adopted to model the background processes (as electricity and heat productions and transports);
  ✓ lab-scale data has been scaled up adopting a linear rate.
Life Cycle Assessment


**NanoTiO₂ suspension**
- Al₂O₃ microsphere
- Electrical energy
- Deionized water
- Methylene Blue

**Nanotitania application to Al₂O₃ microsphere**

**Photocatalytic degradation plant**
- Decontaminated water containing nantitania particles
- Reverse osmosis filtration
- Water conferred to surface water
- Electrical kiln
- nanoTiO₂ emissions in air and indoor 😞
- Emissions: ammonium, nitrate, sulfate, chloride
- Benefit derived from degradation of MB
- nanoTiO₂ emissions in water 😞

**System boundaries:** from cradle to grave

**Software:** Simapro 8

**LCIA Method:** USEtox™ modified
USEtox™ modified method

- **Human health CFs for TiO$_2$ nanoparticles**


- **Freshwater ecotoxicity CF for TiO$_2$ nanoparticles**


<table>
<thead>
<tr>
<th>Human health effect</th>
<th>Indoor CFs [cases/kg$_{emitted}$]</th>
<th>Outdoor CFs [cases/kg$_{emitted}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carcinogens</td>
<td>1.43E-2</td>
<td>1.34E-4</td>
</tr>
<tr>
<td>Non-carcinogens</td>
<td>5.87E-7</td>
<td>5.5E-9</td>
</tr>
</tbody>
</table>

Freshwater ecotoxicity CF = 0.28 PAF*day*m$^3$kg$^{-1}$
Ecodesign approach

- Application phase $\rightarrow$ 1% nanoTiO$_2$ emissions release in **air**
  - 99.97% retained by HEPA filter (High Efficiency Particulate Air)
  - 0.03% released into the production room
  - 95% retained by face mask filter (FFP3)

- Reverse osmosis filtration $\rightarrow$ 0.1% nanoTiO$_2$ emissions releases in **water**
  - 99.97% retained by filter
  - 0.03% released into water
Environmental results of the scale-up of photocatalytic wastewater purification treatment

**Impact category**

<table>
<thead>
<tr>
<th>Impact category</th>
<th>Total</th>
<th>( \text{Al}_2\text{O}_3 ) microspheres</th>
<th>nanoTiO(_2) application</th>
<th>Methylene Blue degradation</th>
<th>nanoTiO(_2) emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human toxicity, cancer (outdoor)</td>
<td>2,54E-08 CTUh</td>
<td>66,90%</td>
<td>15,60%</td>
<td></td>
<td>0,13%</td>
</tr>
<tr>
<td>Human toxicity, non-cancer (outdoor)</td>
<td>2,89E-08 CTUh</td>
<td>13,73%</td>
<td>41,52%</td>
<td></td>
<td>1,79 E-6</td>
</tr>
<tr>
<td>Ecotoxicity</td>
<td>4,1 CTUe</td>
<td>14,58%</td>
<td>49,84%</td>
<td>-1,45%</td>
<td>5,67 E-5</td>
</tr>
<tr>
<td>Human toxicity, cancer, indoor</td>
<td>6,14E-14 CTUh</td>
<td>/</td>
<td>100%</td>
<td></td>
<td>/</td>
</tr>
<tr>
<td>Human toxicity, non-cancer, indoor</td>
<td>2,51E-18 CTUh</td>
<td>/</td>
<td>100%</td>
<td></td>
<td>/</td>
</tr>
</tbody>
</table>

**Functional unit:** 6917,3 cm\(^3\)
Conclusions and next steps

- The life cycle assessment of the scale up of the cylindrical photoreactor to treat wastewater has been performed.
- The new freshwater and human health CFs developed following USEtox framework have been implementing in the USEtox method to carried out the LCIA results.
- Al₂O₃ microspheres production and nanoTiO₂ application are the life cycle stages with higher environmental loads.
- Standardization of nanoTiO₂ toxicological data and development of protocols for nanoparticle emissions measurement are urgently required.
- Due to the still uncertainty of toxicological effects of nanoTiO₂, during the scaling up phase a ecodesign approach has been use.
- Benefit derived from the Methylene blue degradation is higher than the damage of nanoTiO₂ emission in surface water (Ecotoxicity impact category).
- Next steps: adopting the Gavankar’s upscaling process for engineered nanomaterials


parametric analysis to model different nanoTiO₂ emissions scenarios
Thank you for your attention

In collaboration with Prof. Federica Bondioli and Dr. Maria Vittoria Grandi
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