



Environmental assessment of a photocatalytic degradation of contaminated water

Martina Pini

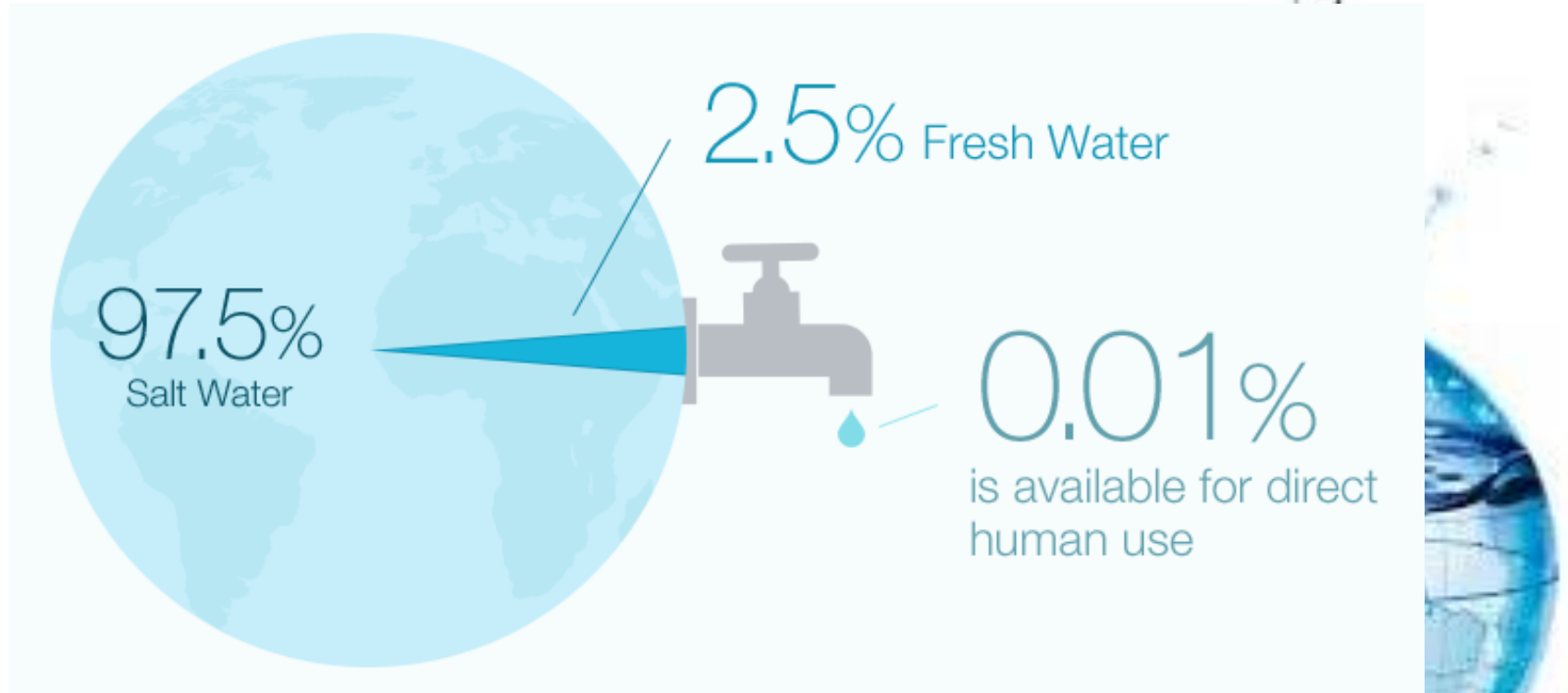
LCA WorkingGroup

Department of Science and Methods for Engineering

University of Modena and Reggio Emilia - Italy



Water: A rare and precious resource



Only 0.01% of the total freshwater
usable to human (UN-Wat



Wastewater: human-made phenomenon

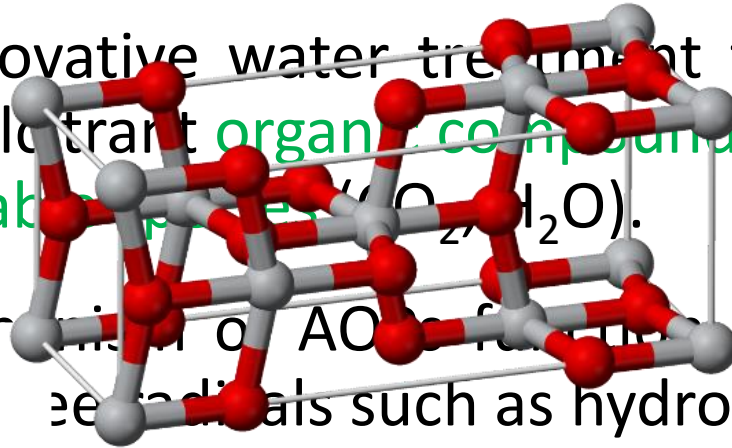
- The *excessive use* and *continued mismanagement* of freshwater resources for industrial growth are increasing the contamination of the wastewater.
- A wide range of *organic compounds* is detected in industrial and municipal wastewater.
- Some of these compounds pose severe problems in biological 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 (O_2 , H_2O).
- The main mechanism of AOPs is the generation of highly reactive radicals such as hydroxyl radicals (OH^\bullet).
- One of the most effective methods of AOPs is the use of UV light and oxidant such as H_2O_2 , O_3 , and TiO_2 .



OH• semi-permanently
Only photoenergy use

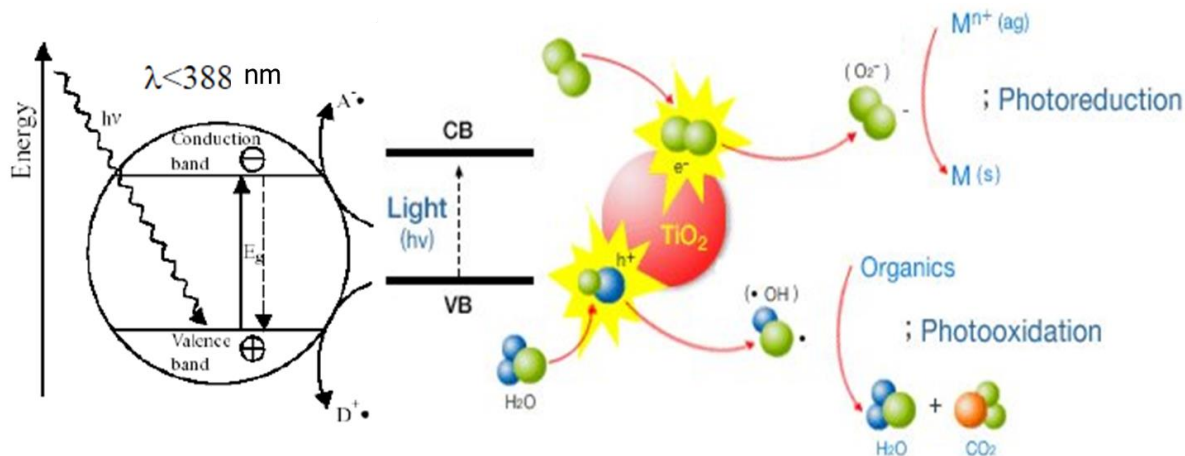
- H_2O_2 / UV
- O_3 / UV
- O_3 / H_2O_2 / UV
- UV / TiO_2 (Photocatalytic oxidation)





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).





TiO₂ nanoparticles for wastewater treatment

Prototype phase

- Cylindrical photoreactor having a substrate coated with nanoTiO₂ and activated with proper UV irradiation;
- Laboratory scale
Reactor dimensions:
external glass tube h=450 mm, \varnothing =56 mm
internal quartz tube h=400 mm, \varnothing =35mm
- UV-A lamp (15 W) is collocated inside the internal tube;
- O₃ has been blown through the bottom opening to enhance the oxidation process of nanoTiO₂;
- Photocatalytic support: aluminum oxide (Al₂O₃) microspheres coated with nanoTiO₂;

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

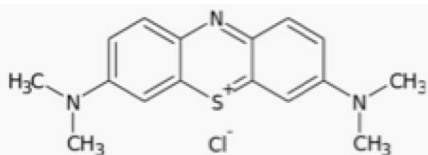




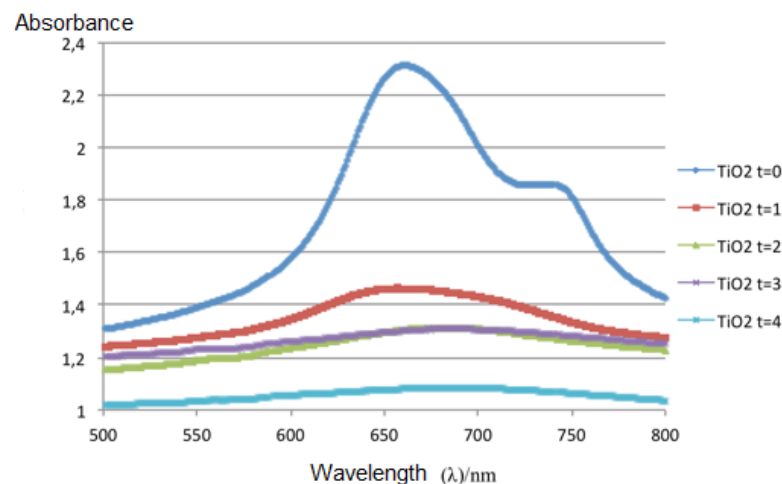
TiO₂ nanoparticles for wastewater treatment

Prototype phase

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



Methylene blue

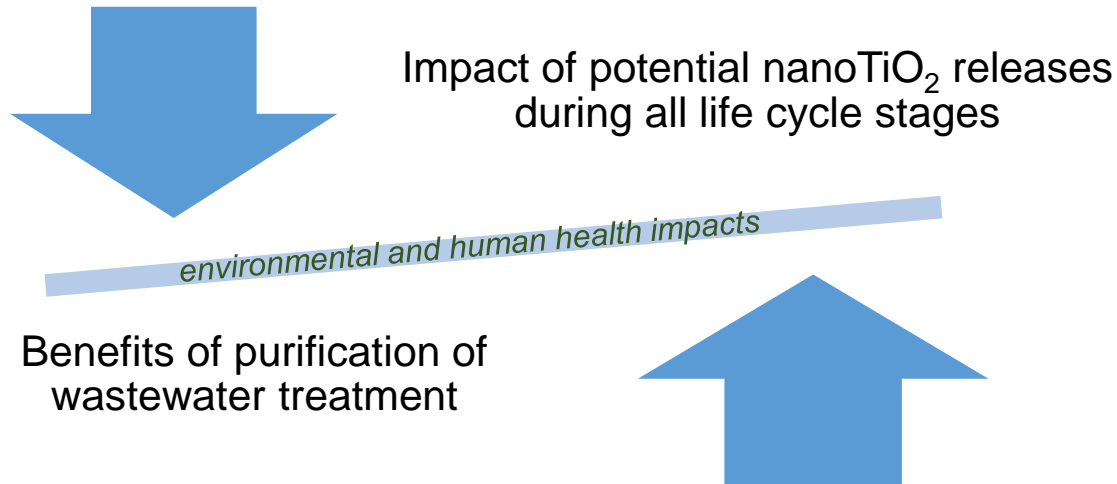


- The photoreactor has been tested with synthetic wastewater sample;
- Mode of operation: batch mode or semi-continuous mode to ensure the adequate contact time for the photocatalytic degradation.



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.

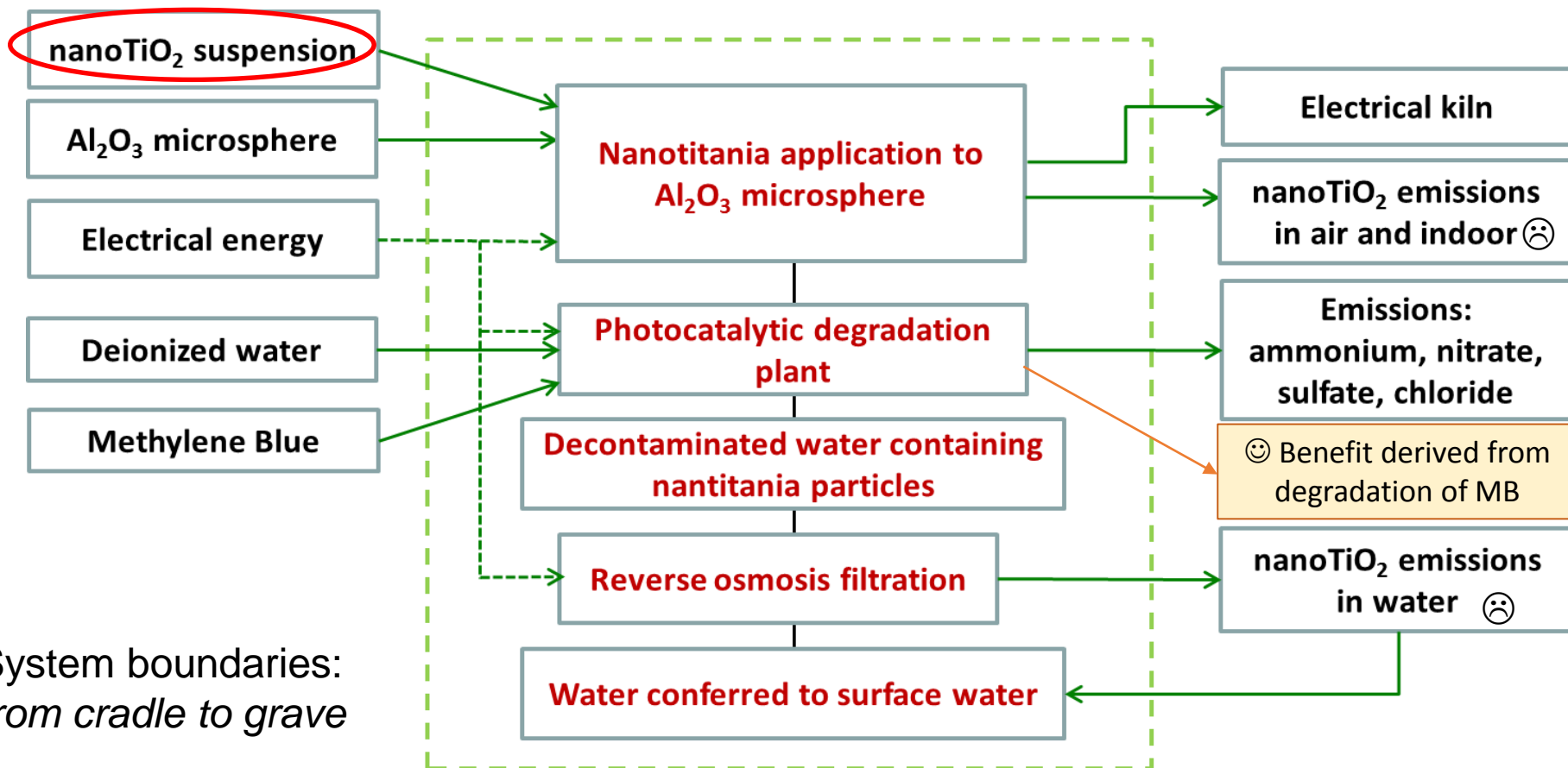


- Functional unit: volume of the synthetic wastewater sample= 6917 cm³
Photoreactor internal volume: 7170 cm³; Total spheres volume: 253 cm³
- Data quality:
 - ✓ primary data supplied by the *Material lab, University of Parma - Italy* has been used;
 - ✓ secondary data obtained by Ecoinvent database 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

Colorobbia S.p.A. Patent: US 2008/0317959 A1, Baldi G. et al. 2008
Pini et al., 2015. Green Chemistry 17 (1), 518 – 531.



System boundaries:
from cradle to grave

Software: Simapro 8

LCIA Method: USEtox™ modified



USEtox™ modified method



UNIVERSITÀ DEGLI STUDI
DI MODENA E REGGIO EMILIA



Materials Science & Technology

- Human health CFs for TiO₂ nanoparticles

Pini M, Salieri B, Ferrari AM, Nowack B, Hischier R (2016), “Human health characterization factors of nano-TiO₂ for indoor and outdoor environments”, *Int J Life Cycle Assess*, 21(10), 1452-1462. DOI: 10.1007/s11367-016-1115-8.

| Human health effect | Indoor CFs [cases/kg _{emitted}] | Outdoor CFs [cases/kg _{emitted}] |
|---------------------|---|--|
| Carcinogens | 1,43E-2 | 1,34E-4 |
| Non-carcinogens | 5,87E-7 | 5,5E-9 |

- Freshwater ecotoxicity CF for TiO₂ nanoparticles

Salieri B, Righi S, Pasteris A, Olsen SI (2015), “Freshwater ecotoxicity characterisation factor for metal oxide nanoparticles: A case study on titanium dioxide nanoparticle”, *Science of Total Environment*, 505, 494–502. DOI: 10.1016/j.scitotenv.2014.09.107.

Freshwater ecotoxicity
CF= 0,28 PAF*day*m³*kg⁻¹



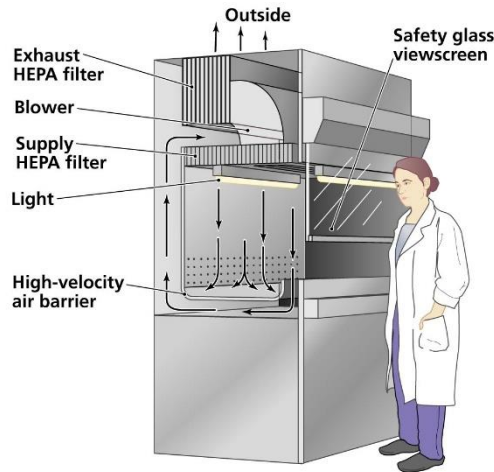
Ecodesign approach

- Application phase → 1% nanoTiO₂ emissions release in **air**

*EoL of HEPA and face mask filters:
landfill for residual materials*

99.97% retained by HEPA filter
(High Efficiency Particulate Air)

0.03% released into the
production room



95% retained by face mask filter (FFP3)



European Standard
EN149:2001+A1:2009

- Reverse osmosis filtration → 0.1% nanoTiO₂ emissions releases in **water**

99.97% retained by filter

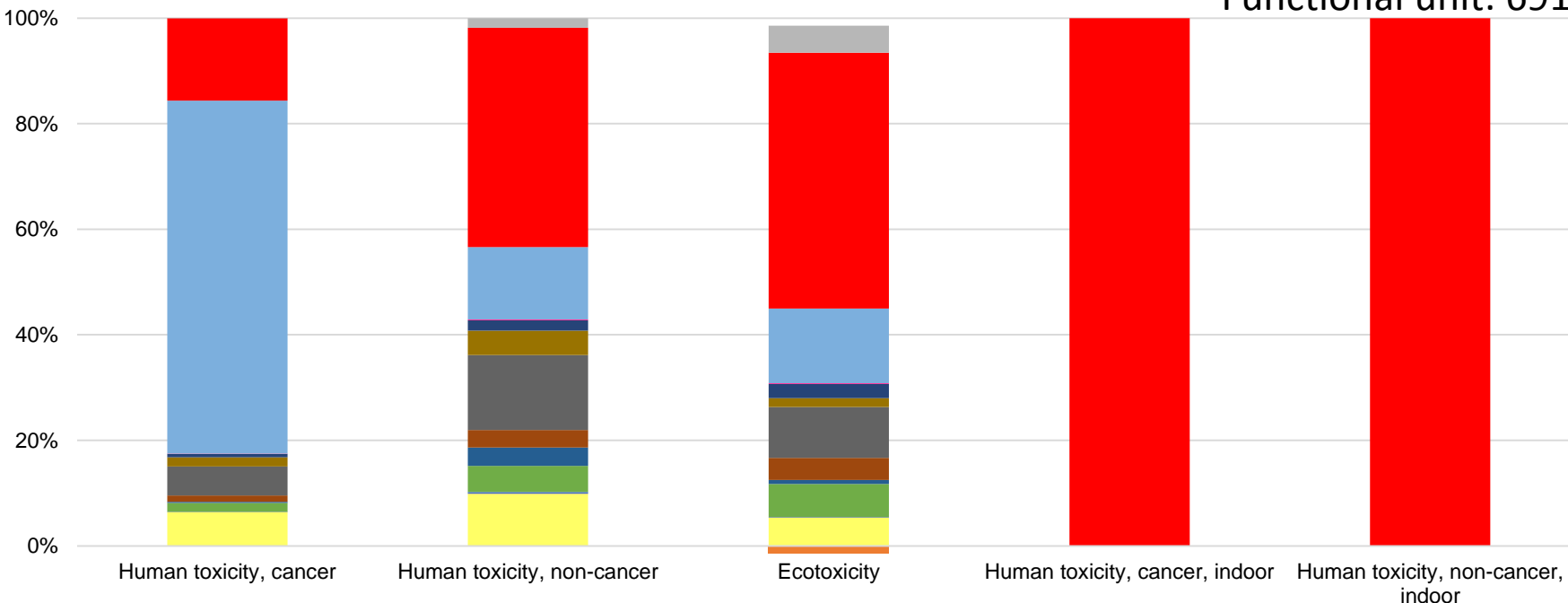
0.03% released into water





Environmental results of the scale-up of photocatalytic wastewater purification treatment

Functional unit: 6917,3 cm³



- Methylene Blue degradation
- Deionised Water
- Methylene Blue production
- Light bulb
- Electricity for light
- Pump
- Electricity for pump
- Compressed air
- Ozone liquid
- Reverse osmosis filtration
- Cylindrical photoreactor
- Al₂O₃ microspheres
- nanoTiO₂ application
- Residual material landfill of microspheres and nanoTiO₂ coating

| Impact category | Total | Al ₂ O ₃ microspheres | nanoTiO ₂ application | Methylene Blue degradation | nanoTiO ₂ emission |
|--------------------------------------|---------------|---|----------------------------------|----------------------------|-------------------------------|
| Human toxicity, cancer (outdoor) | 2,54E-08 CTUh | 66,90% | 15,60% | | 0,13% |
| Human toxicity, non-cancer (outdoor) | 2,89E-08 CTUh | 13,73% | 41,52% | | 1,79 E-6% |
| Ecotoxicity | 4,1 CTUe | 14,58% | 49,84% | -1,45% | 5,67 E-5% |
| Human toxicity, cancer, indoor | 6,14E-14 CTUh | / | 100% | | / |
| Human toxicity, non-cancer, indoor | 2,51E-18 CTUh | / | 100% | | / |



Conclusions and next steps

- The **life cycle assesement** 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.
- Al_2O_3 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
Gavankar et al., 2015. The Role of Scale and Technology Maturity in Life Cycle Assessment of Emerging Technologies - A Case Study on Carbon Nanotubes. J .Ind. Ecol. 19, 51-60.

parametric analysis to model different nanoTiO₂ emissions scenarios



Thank you for your attention

In collaboration with Prof. Federica Bondioli and Dr. Maria Vittoria Grandi
Department of Industrial Engineering – University of Parma, Italy



LCA Working Group

Department of Science and Methods for Engineering -
University of Modena and Reggio Emilia

www.lcaworkinggroup.unimore.it

Anna Maria Ferrari
Paolo Neri
Rosangela Spinelli
Elisabetta Zerazion
Camilla Tomasetta
Marco Cervino

