Removal of emerging concern pollutants and treatment of turbid wastewaters

Optimization of the synthesis of NP-TiO_2 supported on a Persistent Luminescence Material

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Introduction

Photocatalysis

- TiO_2
- Photocatalysis for Environment
- Pros and cons

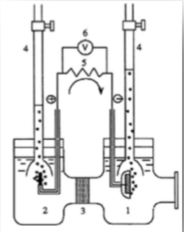
Optimization

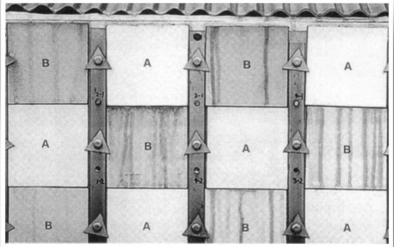
- Supporting Material
- Synthesis
- Characterization

Emerging Pollution

- Pharmaceuticals
- Photocatalytic activity

→ **Scale Up**





Clean Energy

Photo-catalysis

Building Materials

Personal care products

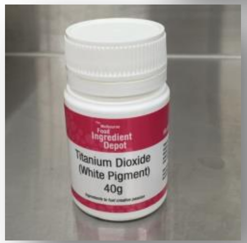
TiO_2

Filtration

Food additive

Sun screen

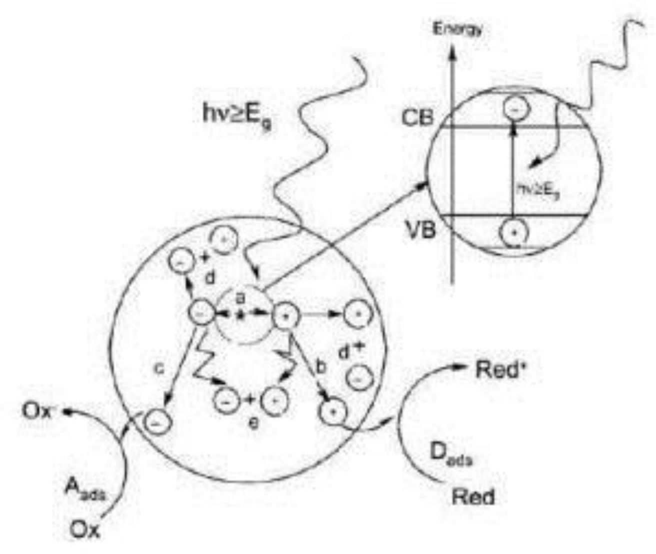
Paint



Carp, O. et al (2004). Photoinduced reactivity of titanium dioxide. *Progress in solid state chemistry*, *32*, 33-177

Diebold, U. (2003). The surface science of titanium dioxide. *Surface Science Reports*, *48*, 54-65

Photocatalysis for Environment



$$h\nu \underset{}{\overset{h\nu \geq E_g}{\rightleftarrows}} h^{+}_{VB} + e^{-}_{CB}$$

$$e^{-}_{CB} + O_2 \longrightarrow O_2^{\bullet}$$

$$h^{+}_{VB} + H_2O_{ads} \rightleftarrows H^{+}_{ads} + OH^{\bullet}_{ads}$$

$$h^{+}_{VB} + OH^{-}_{ads} \rightleftarrows OH^{\bullet}_{ads}$$

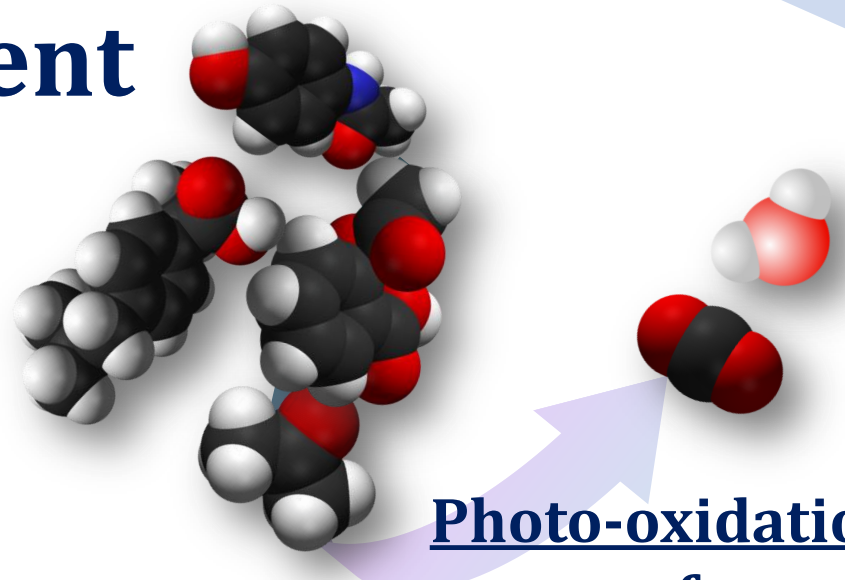
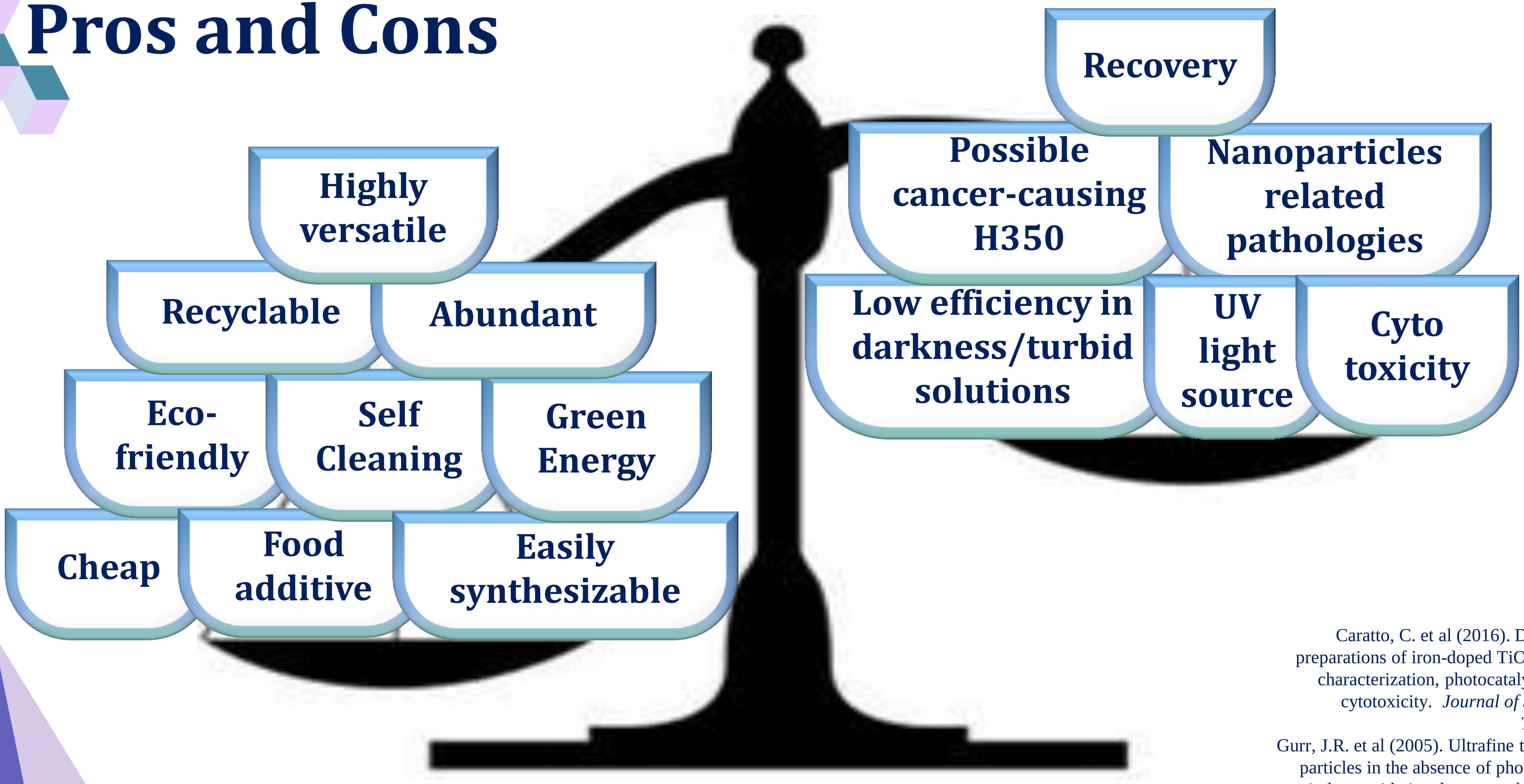


Photo-oxidation of organic compounds

Heterogeneous photocatalysis → **Water Remediation**
Wastewater Bleaching

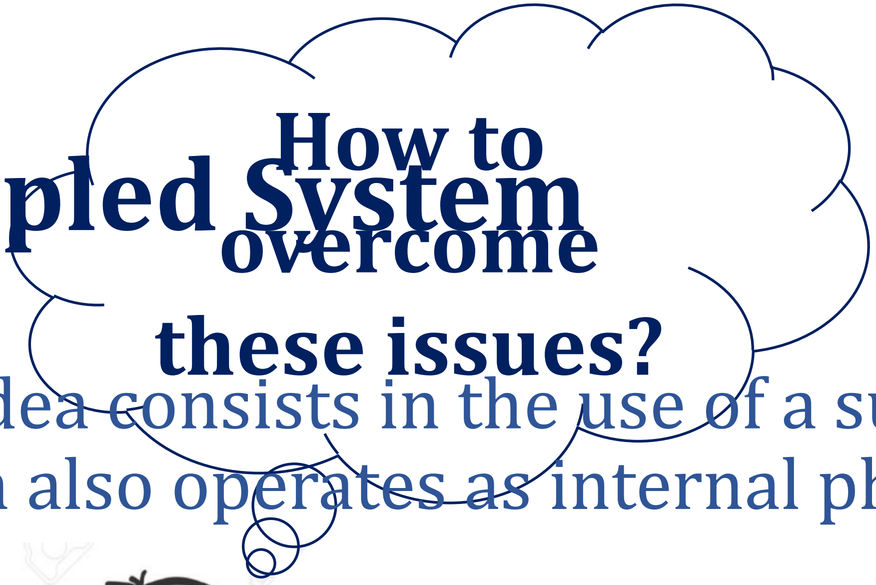
Pros and Cons



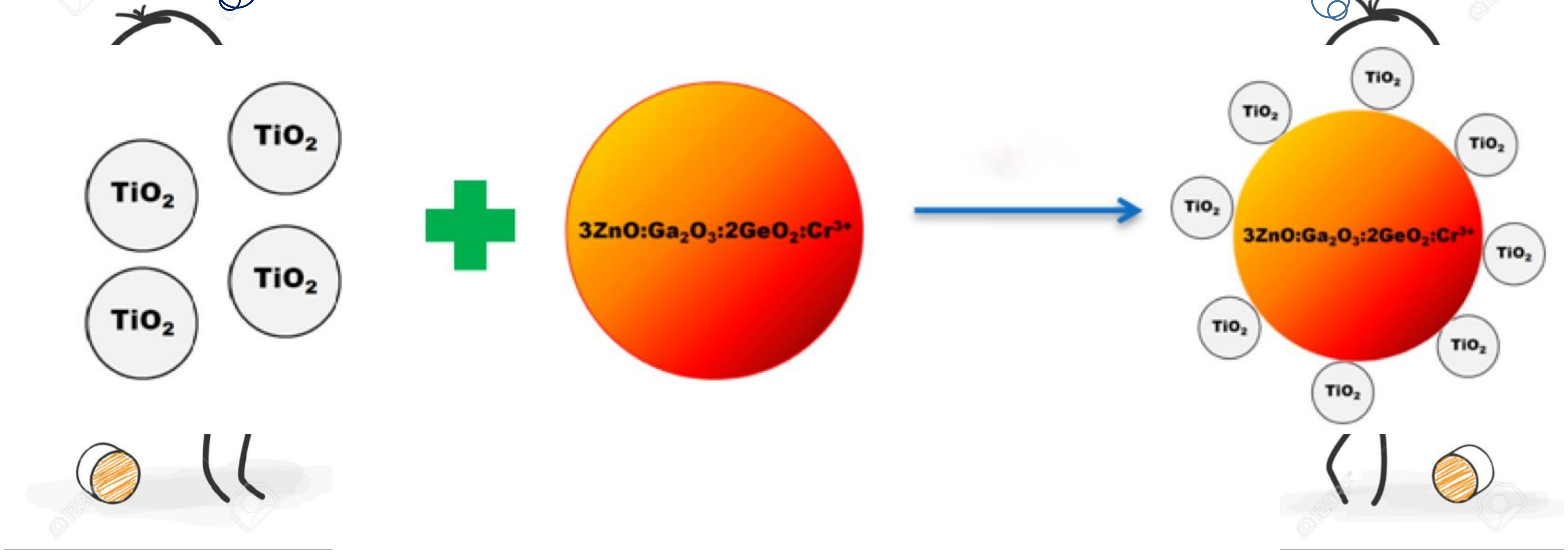
Caratto, C. et al (2016). Different sol–gel preparations of iron-doped TiO_2 nanoparticles: characterization, photocatalytic activity and cytotoxicity. *Journal of Sol-Gel Science Technology*, 1-8

Gurr, J.R. et al (2005). Ultrafine titanium dioxide particles in the absence of photoactivation can induce oxidative damage to human bronchial epithelial cells. *Toxicology*, *213 (1-2)*, 66-73

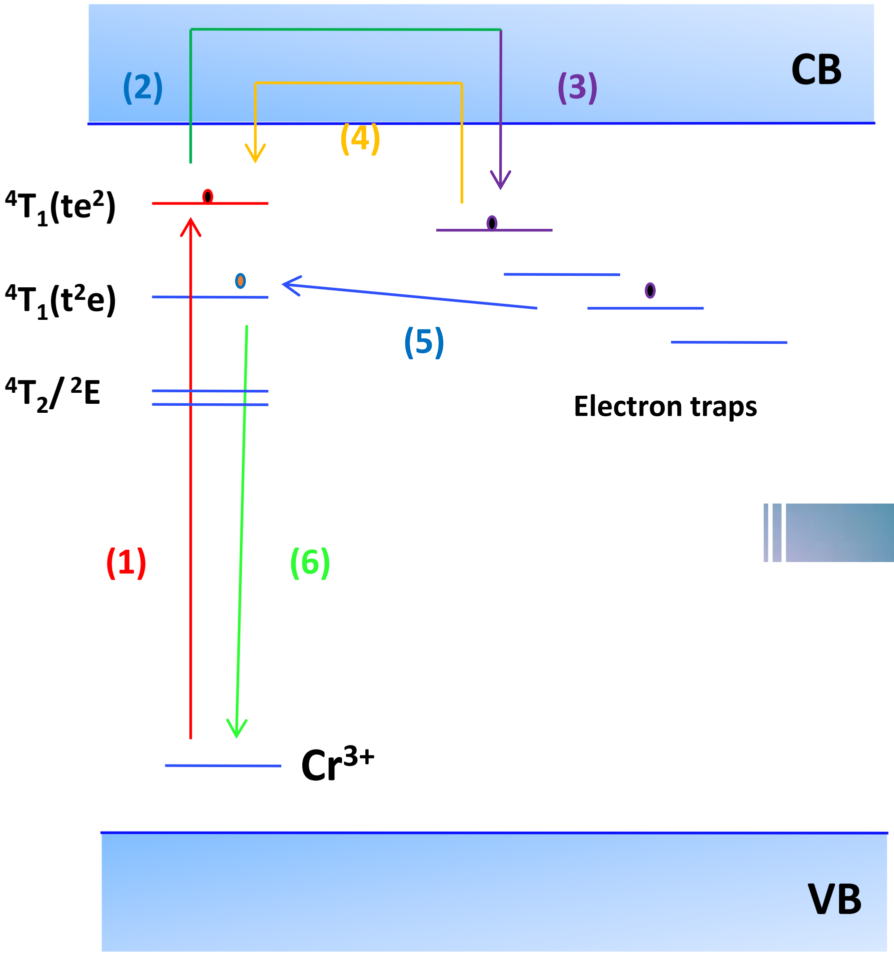
Coupled System



The idea consists in the use of a supporting material for TiO_2 which also operates as internal photons source.



Supporting Materials



$3ZnO:Ga_2O_3:2GeO_2:Cr^{3+}$

Persistent Luminescence "PeLM"

1. Excitation
2. e^- pass in conduction band.
3. e^- falls into a trap (lattice defects, vacancy, etc.)
4. e^- can return to luminescent centre by thermal release or
5. through athermal tunneling recombination mechanism.
6. Emission

Synthesis and Optimization

TiO_2
Sol-gel synthesis

- Titanium tetraisopropoxide	1
- 2-Propanol	2
- Water	5

Stirring at T_{room} for 4 hours

- Dried gel at 105°C for 12 hours
- Gel kept as it is

PeLM
Solid state synthesis

- ZnO	3
- Ga_2O_3	1
- GeO_2	2
- Cr_2O_3	0.5%

Grinding and mixing
Thermal treatment

900 °C for 2 hours
1100 °C for 2 hours

Experimental Design

Synthesis of the coupled system

Synthesis and Optimization

The syntheses of the coupled system were subjected to a chemometric approach in order to find the best experimental conditions.

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + bb_{123}x_1x_2x_3$$

Solid State Synthesis
Experimental 2^3 Factorial Design

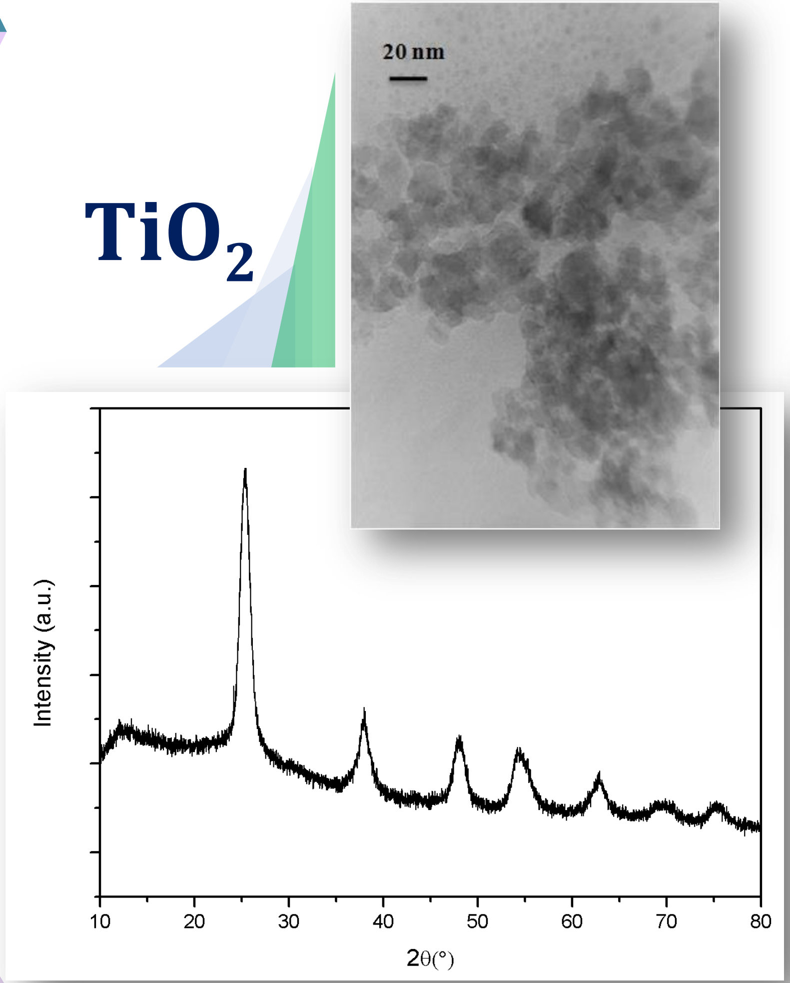
Variables	Level	
Codes	***+1***	***-1***
Weight ratio 'x_1'	*6*	*1*
Temperature 'x_2'	*550 °C*	*350 °C*
Time 'x_3'	*6 h*	*1 h*

Hydrothermal Synthesis
Experimental 2^3 Factorial Design

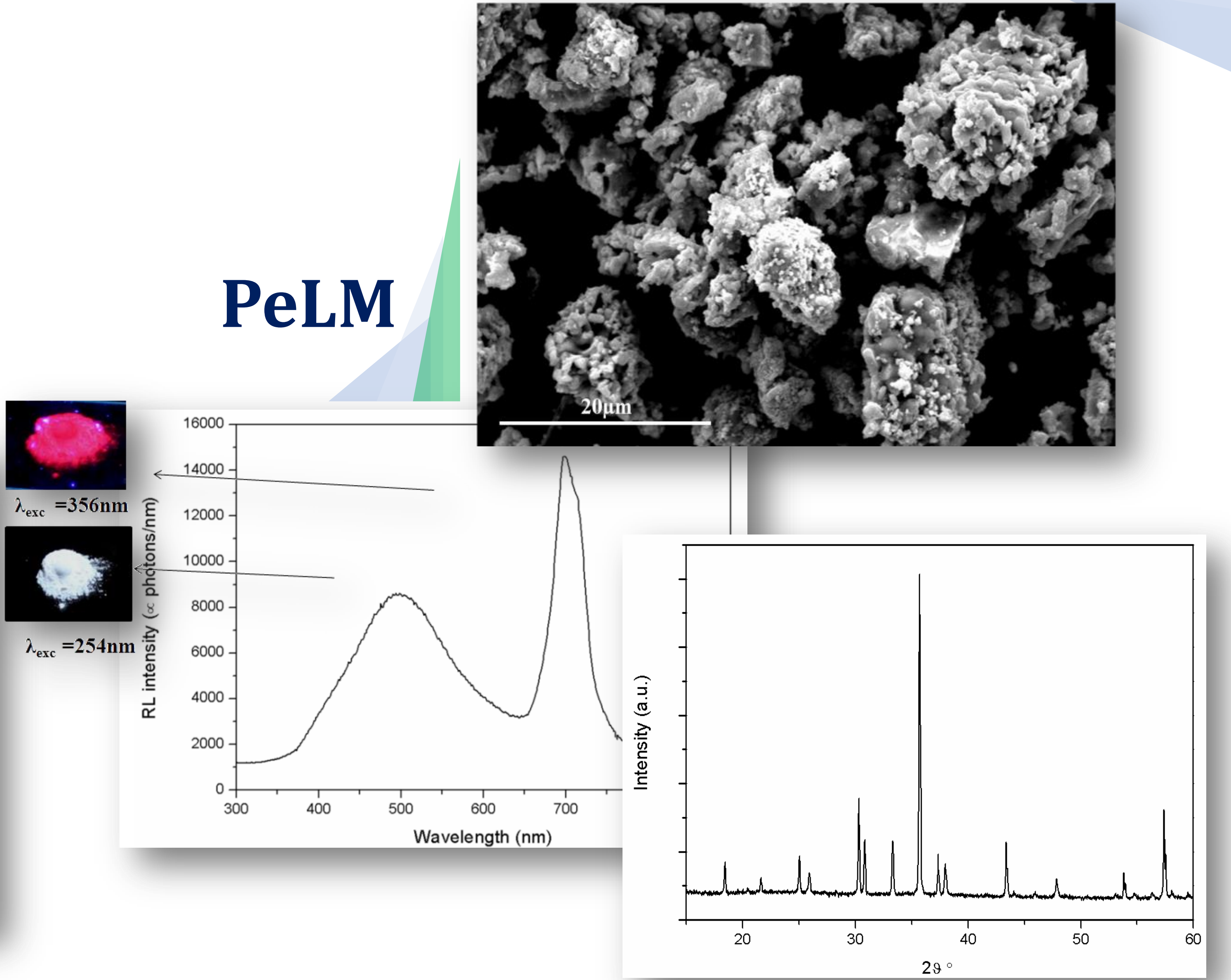
Variables	Level	
Codes	***+1***	***-1***
Filling volume 'x_1'	*75%*	*25%*
Temperature 'x_2'	*150 °C*	*100 °C*
Time 'x_3'	*6 h*	*1 h*

Characterization

TiO_2

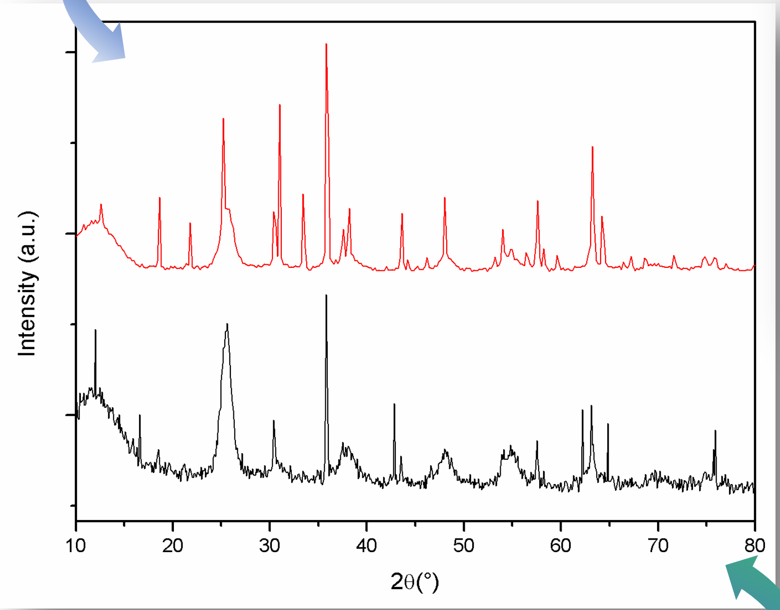


PeLM

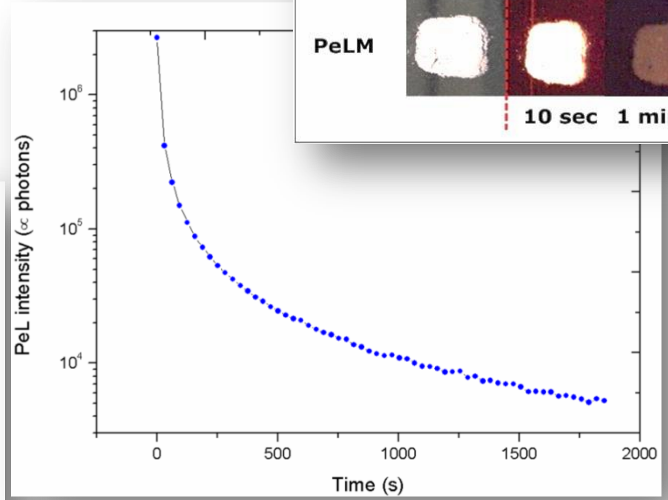


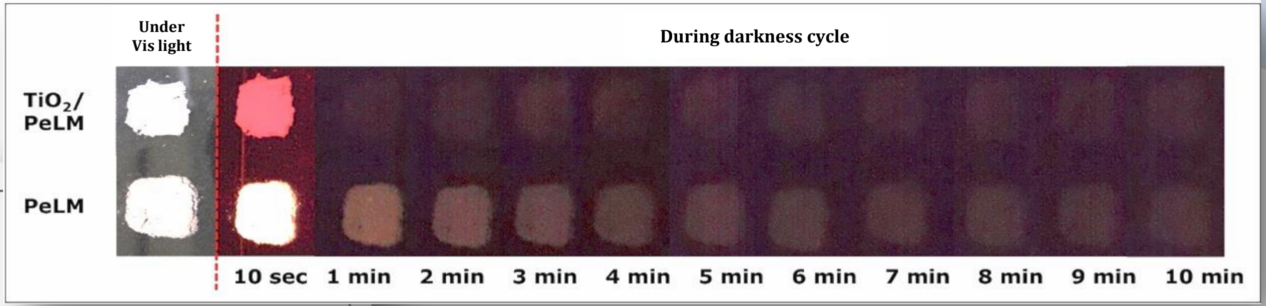
Characterization

Solid State



Hydrothermal

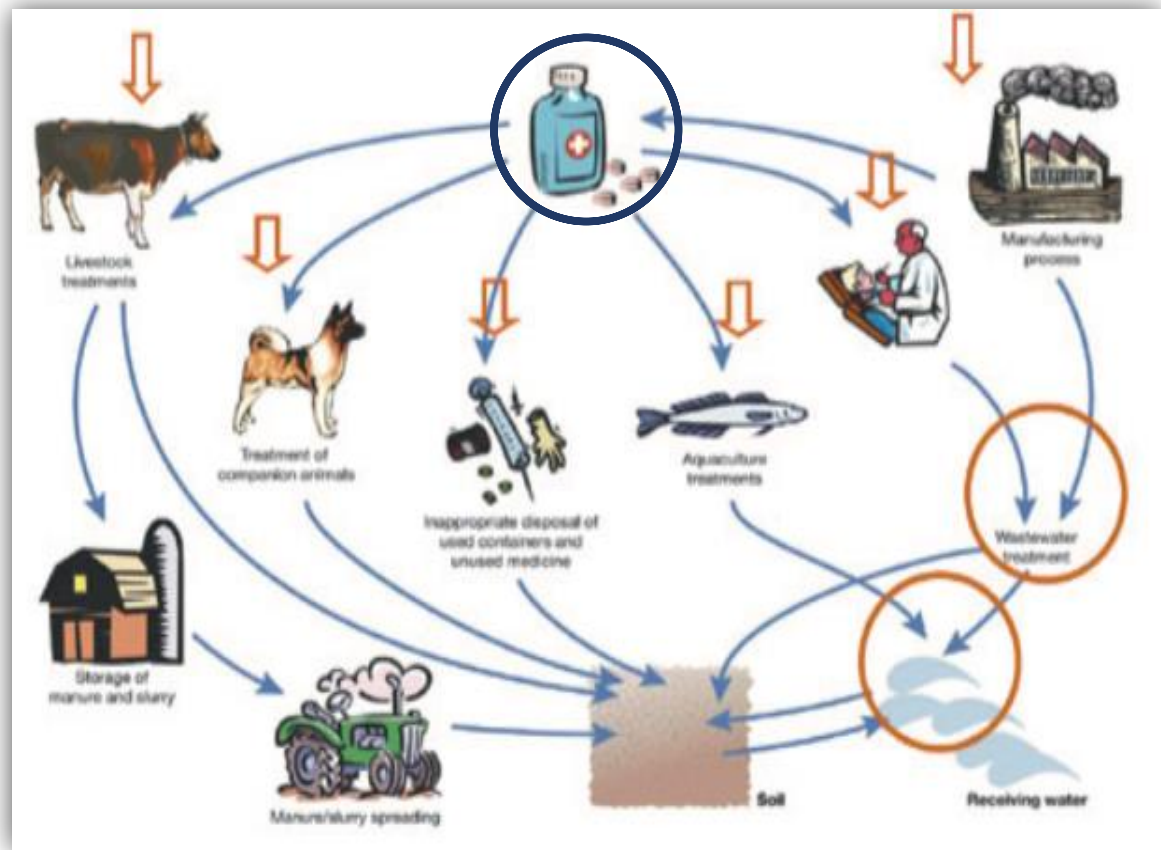


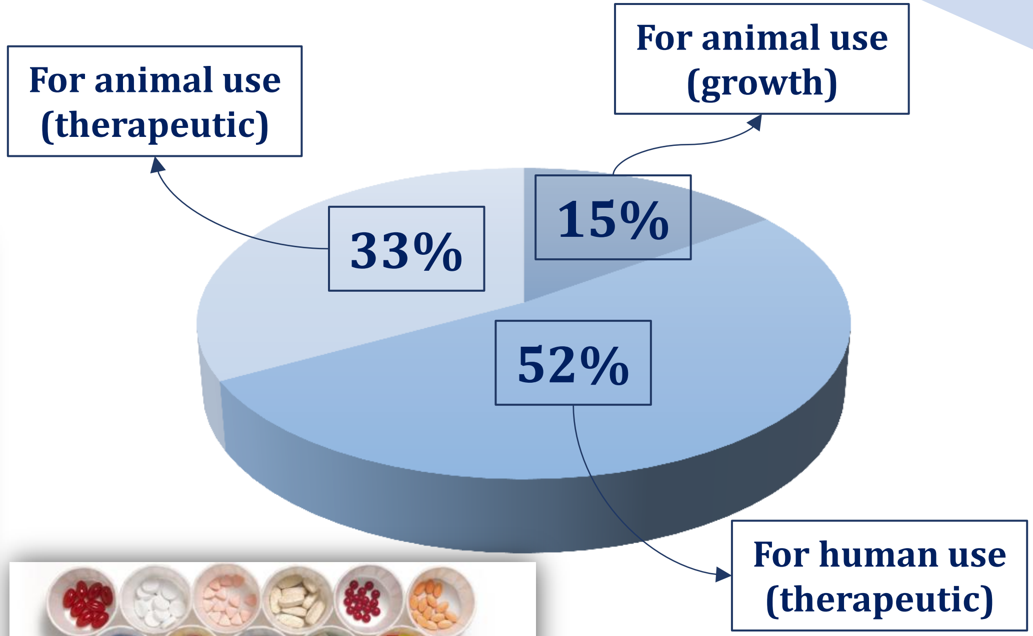


Coupled System

	Surface Area BET		Surface Area BET
TiO_2 solid state	**88.64 ± 0.01 m^2g^{-1}**	*TiO_2 + PeLM solid state*	**62.48 ± 0.01 m^2g^{-1}**
TiO_2 hydrothermal	**286.73 ± 0.01 m^2g^{-1}**	*TiO_2 + PeLM hydrothermal*	**225.61 ± 0.01 m^2g^{-1}**
PeLM	**4.49 ± 0.01 m^2g^{-1}**		

Emerging pollution





100,000/200,000 tonnes/year

Deblonde, T. et al (2011). Emerging pollutants in wastewater: A review of the literature. *International Journal of Hygiene and Environmental Health, 214 (6)*, 442-448

La Farrè, M. et al (2008). Fate and toxicity of emerging pollutants, their metabolites and transformation products in the aquatic environment. *Trends in Analytical Chemistry, 27 (11)*, 991-994

Zuccato, E. (2010). Gli interferenti endocrini nelle acque. *Atti Convegno*, 10-35

Photocatalytic Activity

Photocatalytic activity of the coupled system was evaluated as methylene blue degradation.

Methylene Blue

+

Catalyst

ISO: 10678:2010: 'Determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue'

60 min

-Continuous illumination

-Alternate light/darkness cycles

Sampling

Centrifuging for 10 min

Spectrophotometer

Percentage degradation

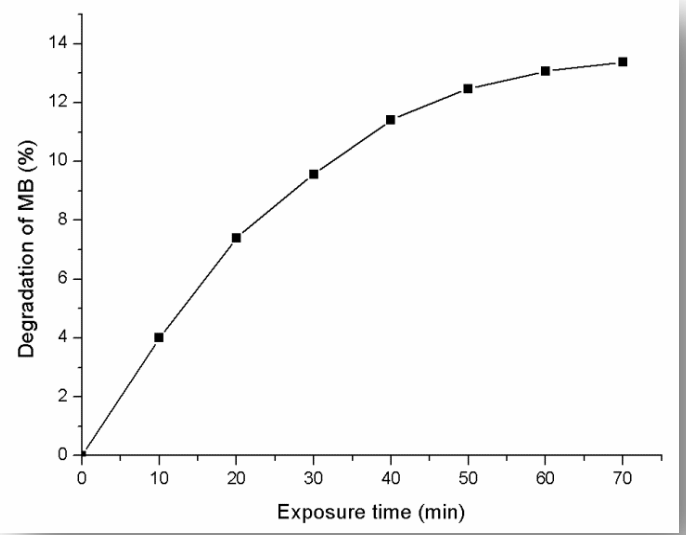
$$[(C_0 - C_t)/C_0] * 100$$

The best resulting samples were tested against Ofloxacin antibiotic

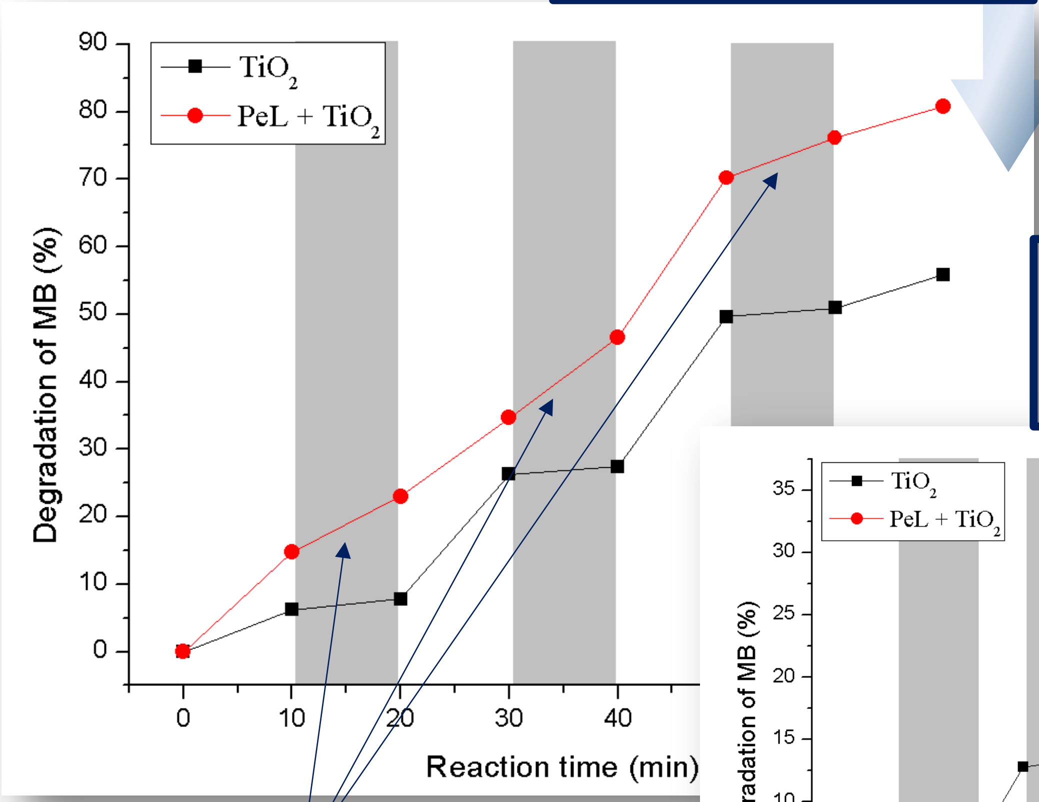
A. Mills, C. Hill, P.K.J. Robertson, J. Photoch. Photobio. A. 237 (2012) 7-23.

Photocatalytic Activity

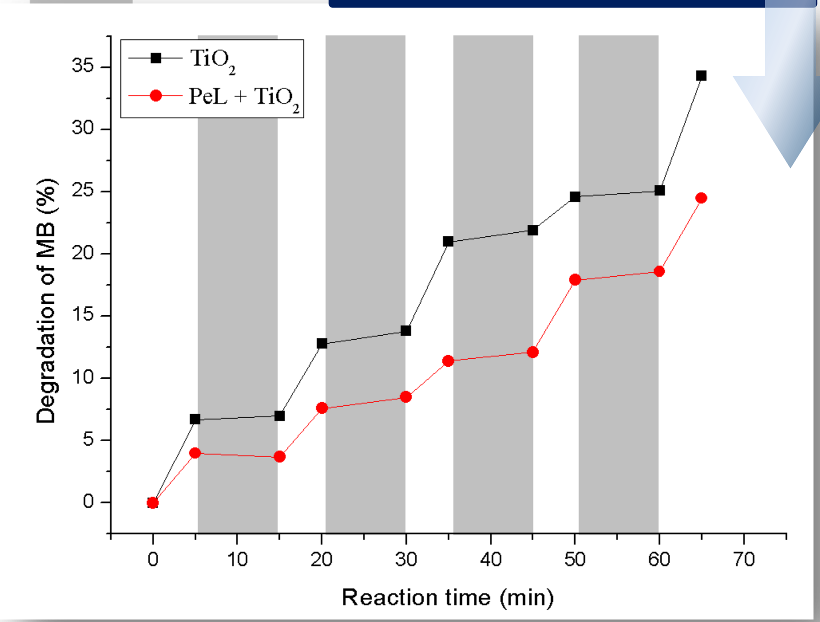
Methylene Blue Photolysis



Alternate
10 minutes light
10 minutes darkness



Alternate
5 minutes light
10 minutes darkness

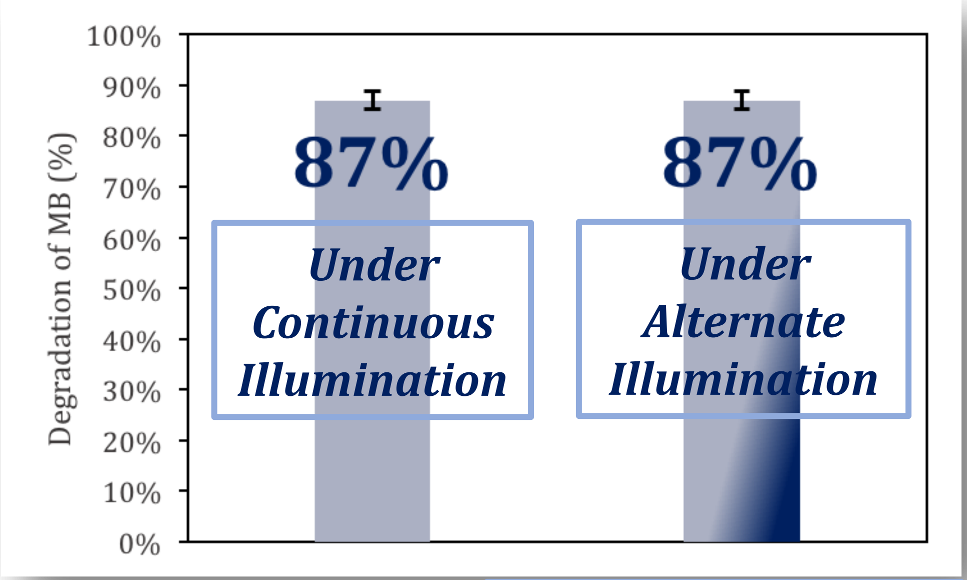


Photocatalysis continues during the darkness

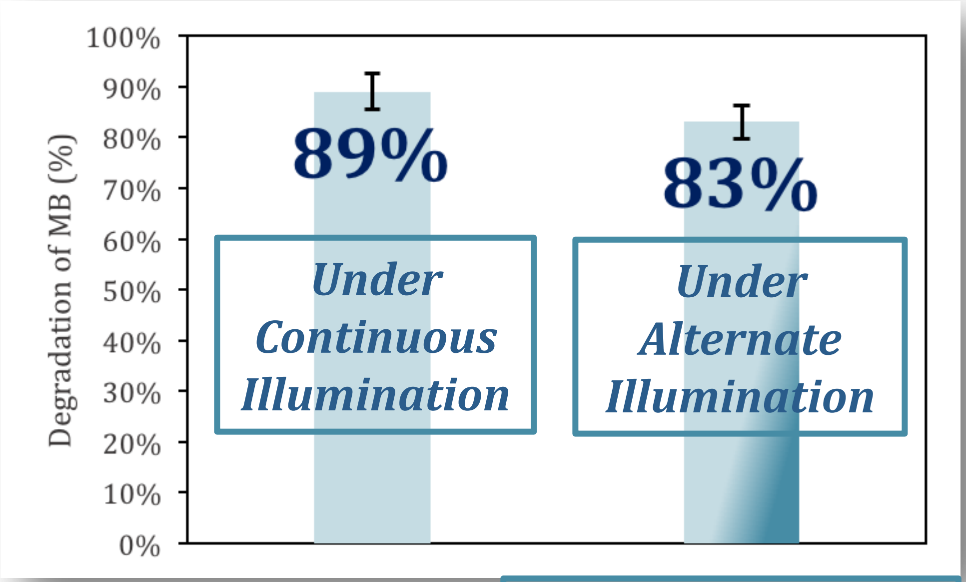
Photocatalytic Activity

Solid State

Variables	Optimized Sample
Weight ratio	***1***
Temperature	***350°C***
Time	***1 hour***



t= 60 min, n=3, RSD<5%

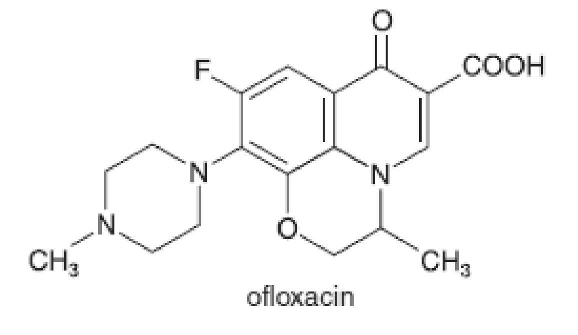


t= 60 min, n=3, RSD<5%

Hydro-thermal

Variables	Optimized Sample
Filling volume	***75%***
Temperature	***100 °C***
Time	***6 hours***

Photocatalytic Activity

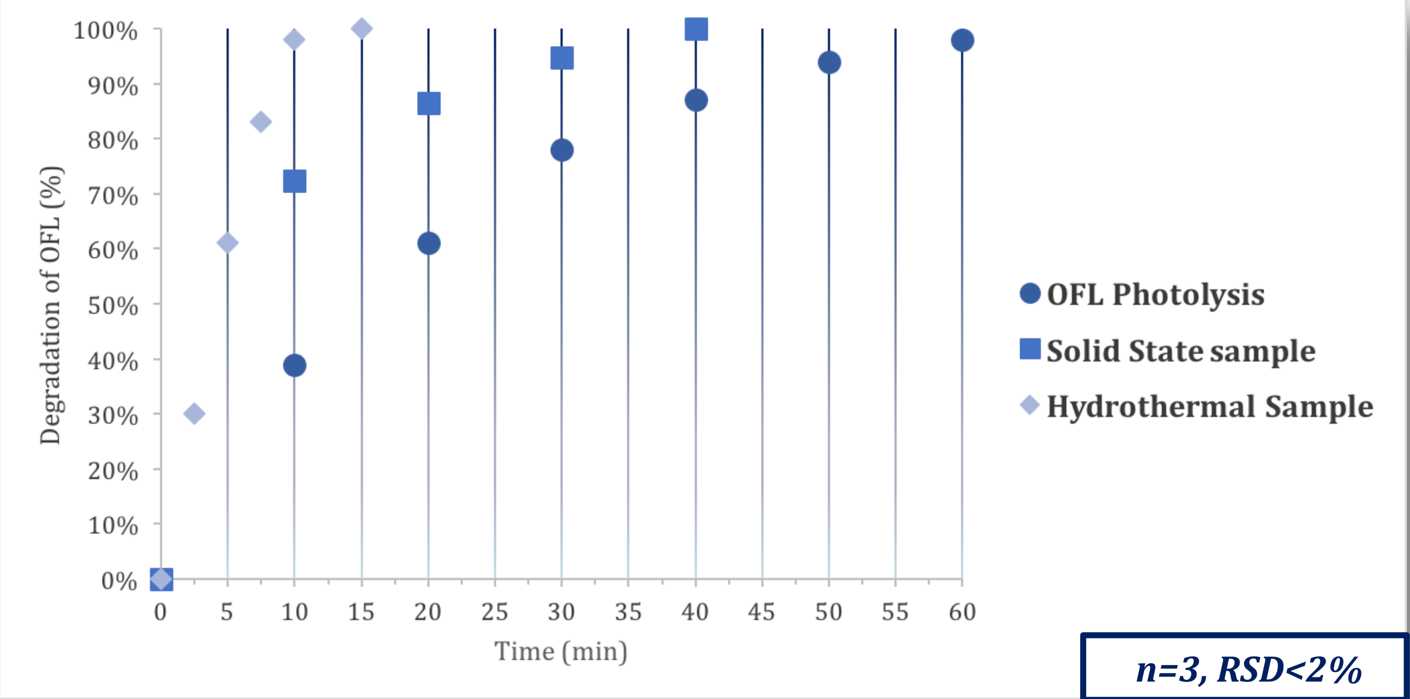


Samples were quantified by HPLC-UV
-LC-20AT solvent delivery
-DGU-20A 3 degasser
-SPD-20° UV detector
$\lambda_{analysis}$ 275 nm
Analytical Ascentis C18

Experiments performed under solar light

(462 Wm^{-2} VIS, 28 Wm^{-2} UV, Pavia, 45°11`N, 9°09`E)

Catalyst/OFL Ratio: **25:1**

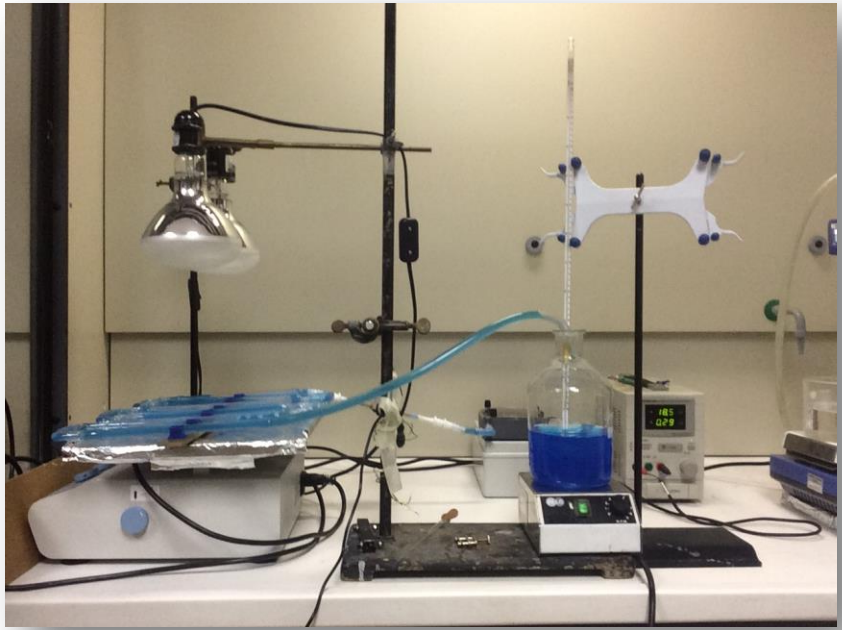


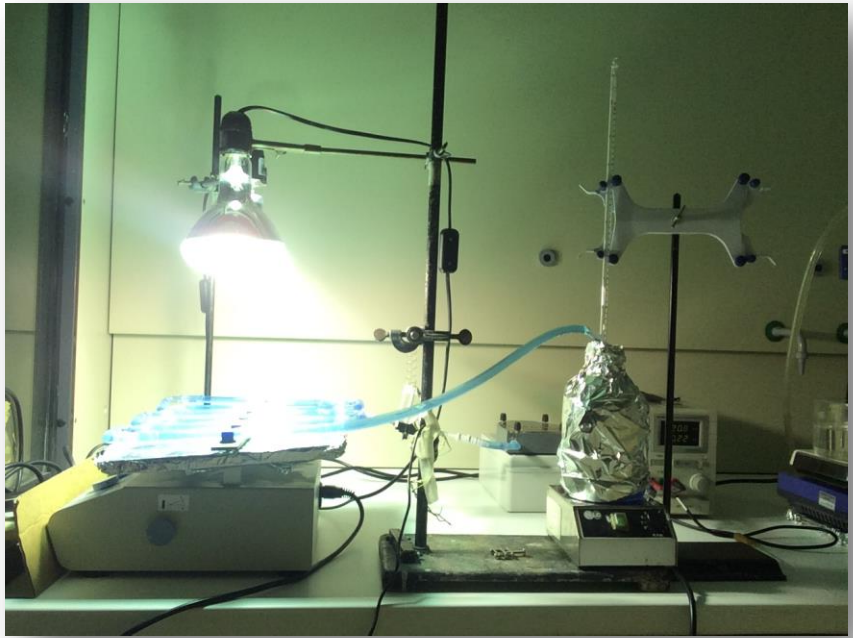
n=3, RSD<2%

Scale Up

A first scale up of **1:50** is under development.

Preliminary tests are currently underway in order to find the best working conditions towards an industrial scale up.



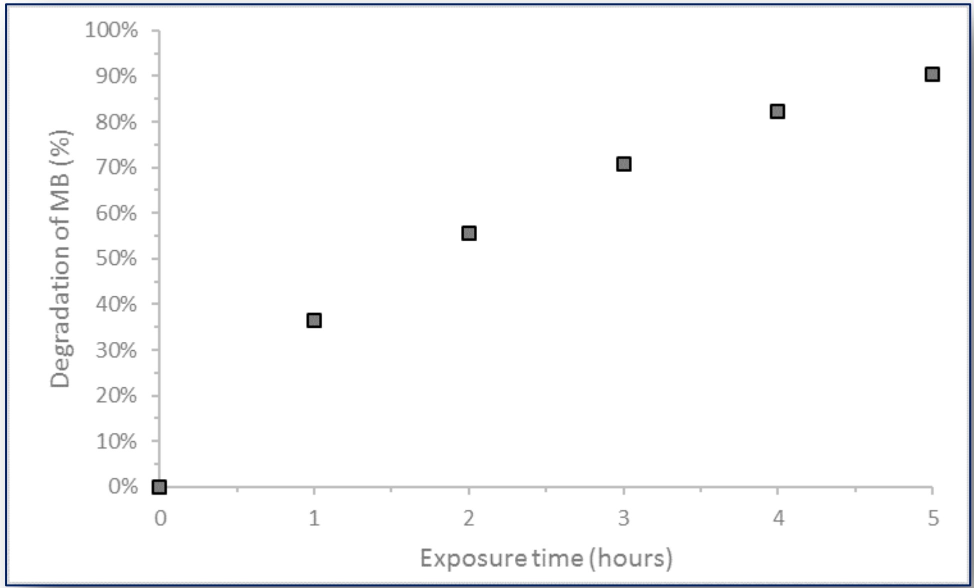


This first prototype will be used to treat turbid wastewater

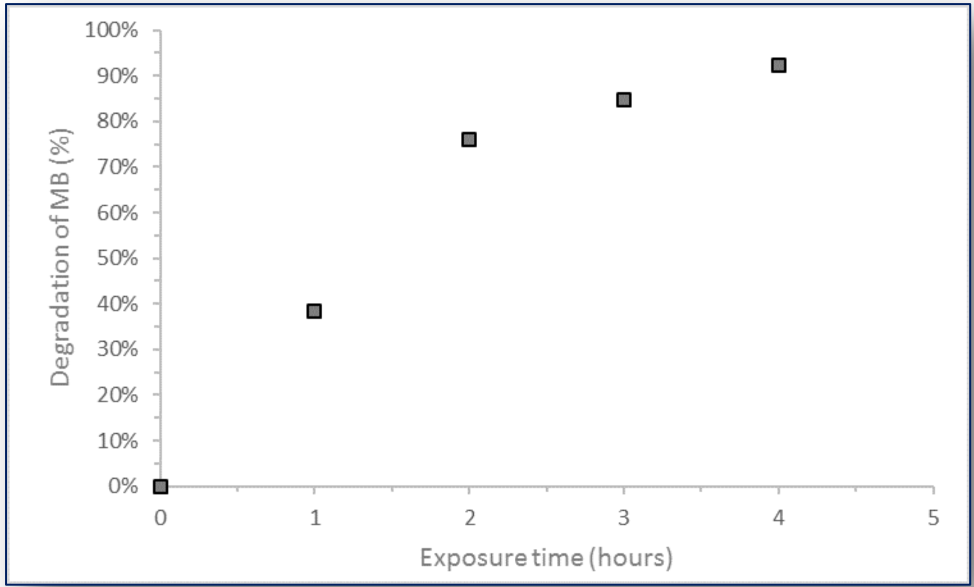
(e.g. olive vegetation waters)

Scale Up

Optimized Solid State



Optimized Hydrothermal



Flow Rate = ***70 mL/min***

Flask Capacity: ***1L***

Circuit Capacity: ***75 mL***

Catalyst/Dye Ratio: ***50:1***

Seesaw circuit

Conclusions

The solid state and the hydrothermal syntheses have been optimized

The coupled system resulted to be a very effective tool against emerging pollution

Photocatalytic activity has been extended even in darkness conditions and surface areas are kept to high values

An industrial scale up will allow this technology to become an effective tool for water depuration plants.

Thank you
for your attention

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