



POLITECNICO DI MILANO

DIAR - Environmental Engineering Section

HETEROGENEOUS ELECTROPHOTOCATALYSIS ON NANOSTRUCTURED TiO_2 FOR REFRACTORY POLLUTANTS AND RESISTANT PATHOGENS REMOVAL FROM WATER AND WASTEWATER

SIDISA Summer School
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PROCESS FUNDAMENTALS

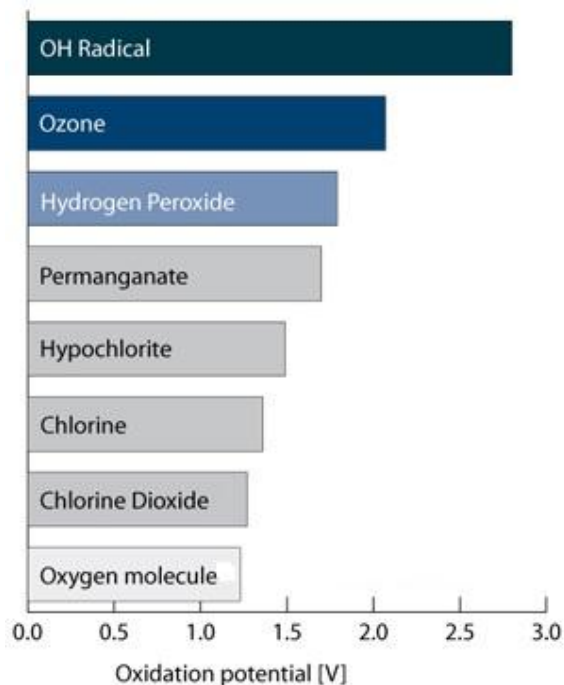
AIM OF THE PROJECT AND RESEARCH PLAN

MECHANISTIC PHENOMENA INSIGHT:
RADICAL SPECIES MEASUREMENT

OPTIMIZATION AND DEVELOPMENTS:
PHOTOELECTROCHEMICAL TESTS, CFD SIMULATIONS

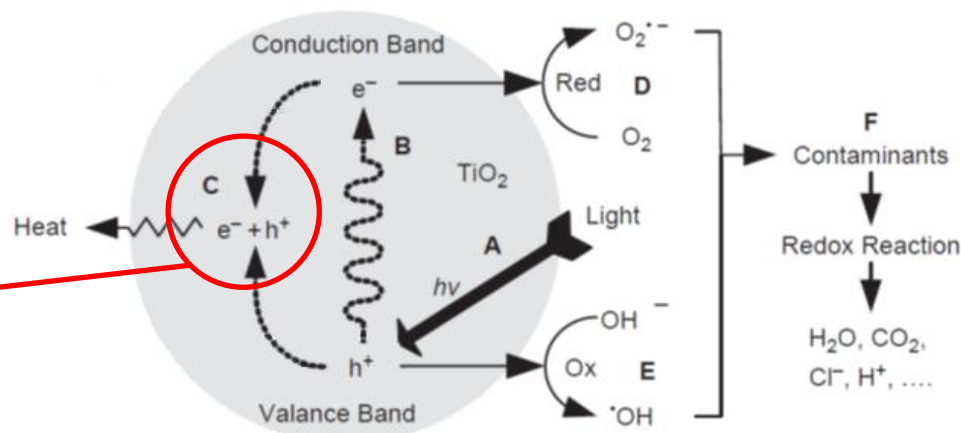
APPLICATION TO WATER AND WASTEWATER TREATMENT:
ORGANICS REMOVAL AND ECOTOXICITY

PROCESS FUNDAMENTALS: TiO_2 PHOTOCATALYSIS



**ELECTRON-HOLE PAIRS
RECOMBINATION:
MAIN PROCESS
DRAWBACK**

- **ADVANCED OXIDATION PROCESS (AOP)**
- **SEMICONDUCTOR BAND GAP: 3.2 eV**
→ UV RADIATION ($\lambda < 380 \text{ nm}$)
- **REACTIVE OXYGEN SPECIES (ROS)**
→ HYDROXYL RADICAL (OH^\bullet)
→ SUPEROXIDE RADICAL ($\text{O}_2^{\bullet-}$)
- **DEGRADATION OF POLLUTANTS INTO
LOWER MOLECULAR WEIGHT INTERMEDIATES
AND MICROORGANISMS STRUCTURE DAMAGING**



PROCESS FUNDAMENTALS: ELECTROPHOTOCATALYSIS ON NANO TiO_2

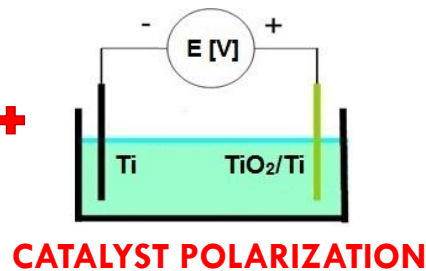
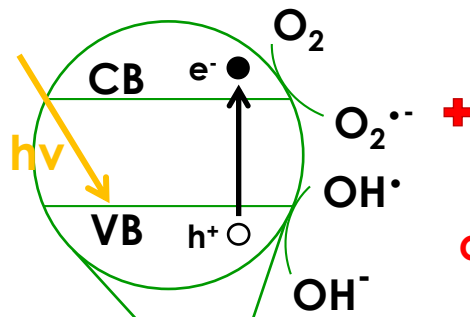
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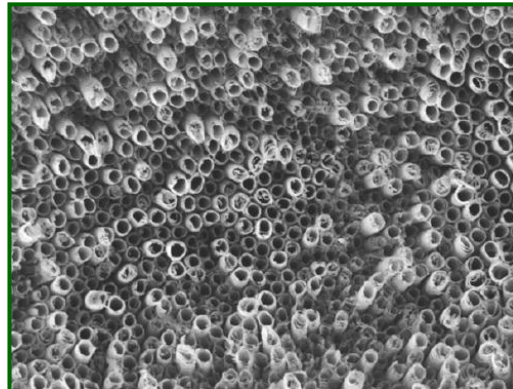
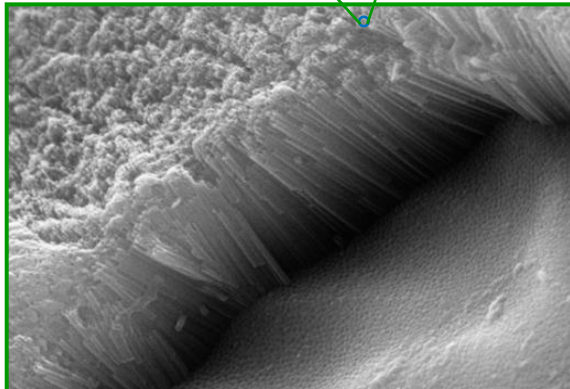
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THE PROCESS INTEGRATES PHOTOCATALYTIC DEGRADATION ON NANOTUBULAR TiO_2
AND ELECTROCHEMICAL POLARIZATION

TiO_2 PHOTOCATALYSIS



- NO OXIDANTS ARE REQUIRED TO GENERATE RADICALS
- THE CATALYST IS NOT A DISPERSED POWDER BUT IT IS DIRECTLY GROWN ON Ti SUPPORT (WIRE MESH) BY ANODIC OXIDATION
- A LIGHT POLARIZATION IS APPLIED TO THE TiO_2/Ti PHOTOANODE TO MINIMISE THE RECOMBINATION OF ELECTRON/HOLE PAIRS
- DISSOLVED OXYGEN IS REQUIRED



NANOTUBULAR SELF-ORGANIZED TiO_2/Ti

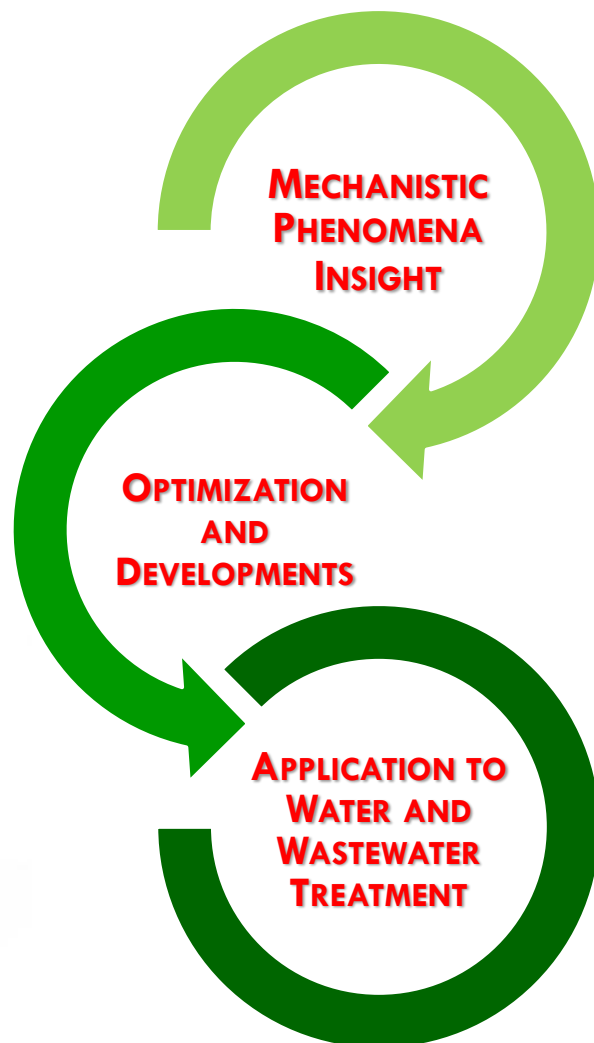
AIM OF THE PROJECT AND RESEARCH PLAN

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- PROCESS OPTIMIZATION:
PHOTOELECTROCHEMICAL
ASSESSMENT
- CFD SIMULATIONS
- REACTOR DESIGN
- LIFE CYCLE ANALYSIS



- IRRADIATION PHENOMENA
 - TiO_2/Ti PHOTOACTIVATION
 - RADICAL SPECIES GENERATION
 - ADSORPTION AND
DEGRADATION KINETICS
-
- ORGANICS REMOVAL
 - BY-PRODUCTS AND ECOTOXICITY
 - ADVANCED DISINFECTION
(RESISTANT PATHOGENS)
 - BENCHMARK TESTS (O_3 , H_2O_2 /UV)

MECHANISTIC PHENOMENA INSIGHT: RADICAL SPECIES MEASUREMENTS

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- SHORT LIFETIMES: 10^{-9} SECONDS
- LOW CONCENTRATIONS: $10^{-9} \div 10^{-11}$ MOL/L
- HIGH REACTIVITY: 2.80 V



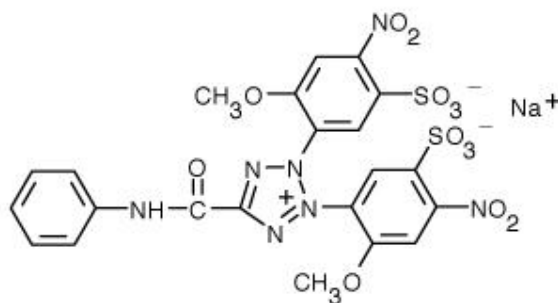
**DIFFICULT DIRECT
MEASUREMENT**

PROBE MOLECULES

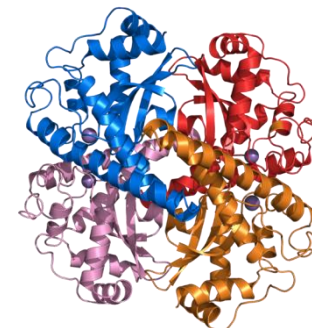
SPECIFIC CHEMICALS THAT REACT SELECTIVELY WITH REACTIVE OXYGEN
SPECIES GENERATING PRODUCTS THAT CAN BE MEASURED



SUPEROXIDE ($O_2^{\bullet -}$)



DETECTOR (SPECTROMETRIC METHOD): XTT



QUENCHER: SUPEROXIDE DISMUTASE (SOD)

OPTIMIZATION AND DEVELOPMENTS: PHOTOELECTROCHEMICAL TESTS

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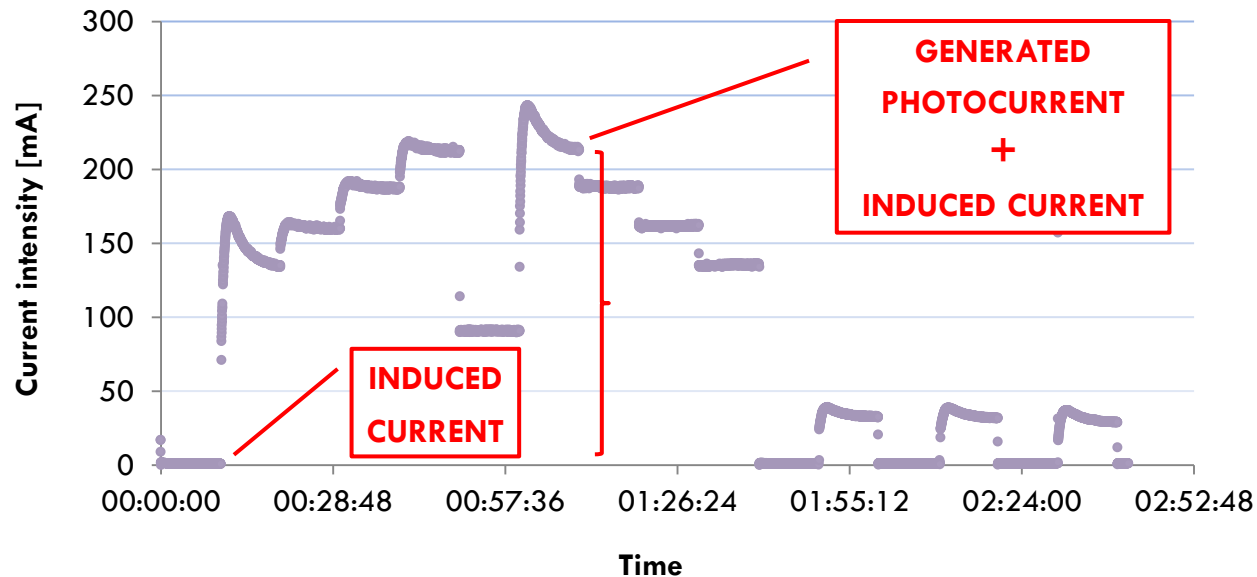


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EXPERIMENTAL SETUP ALLOWS GENERATED PHOTOCURRENT MONITORING:
 TiO_2/Ti PHOTOACTIVATION INDEX

GENERATED PHOTOCURRENT = TOTAL CURRENT – INDUCED CURRENT

HIGHER VALUES OF PHOTOCURRENT = BETTER CATALYST PHOTOACTIVATION



→ OPERATING PARAMETERS INFLUENCE ASSESSMENT: PROCESS OPTIMIZATION

OPTIMIZATION AND DEVELOPMENTS: CFD SIMULATIONS

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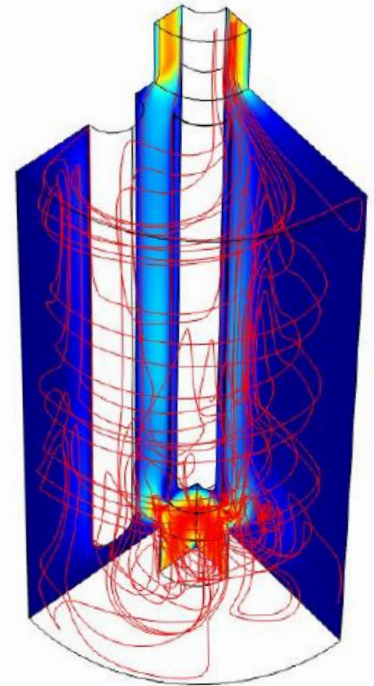
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NON-IDEAL REACTOR
HYDRAULIC BEHAVIOR



NON-OPTIMIZED
PROCESS YIELDS

COMPUTATIONAL FLUID DYNAMIC
FOR MODELING AND SIMULATION
(FINITE ELEMENT SOFTWARE)



APPLICATION TO WATER AND WASTEWATER TREATMENT: ORGANICS REMOVAL AND ECOTOXICITY

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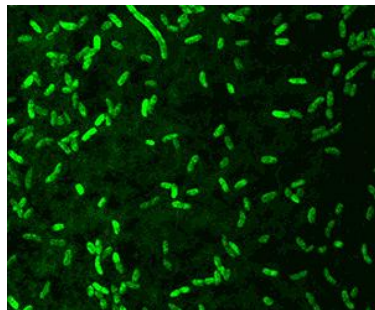
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WATER AND WASTEWATER CHARACTERISTICS:

- OPTICAL PROPERTIES
(TRANSMITTANCE, SUSPENDED SOLIDS)
- CATALYST POISONING OR COVERING COMPOUNDS
(OILS, METALS)

TARGET POLLUTANTS REMOVAL VS. OXIDATION BY-PRODUCTS

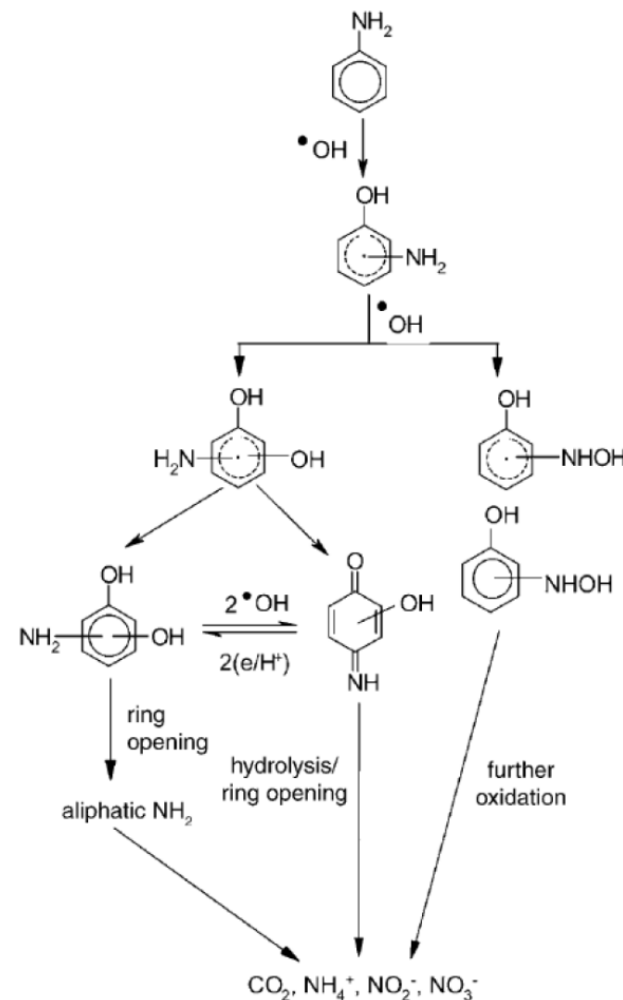
→ BIOLOGICAL AGGREGATE INDECES (MICRO-BIOASSAYS)



VIBRIO FISCHERI



DAPHNIA MAGNA





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THANK YOU