Advances on Catalytic-Photocatalytic Ozonation

DEPARTAMENTO DE INGENIERÍA QUÍMICA Y QUÍMICA FÍSICA

INSTITUTO UNIVERSITARIO DEL AGUA, CAMBIO CLIMÁTICO Y SOSTENIBILIDAD

UNIVERSIDAD DE EXTREMADURA

Badajoz 2015

Spain

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1st Summer School of Advanced Oxidation Processes,
Fisciano, Italy, May 2015

CATALYTIC OZONATION

Types of ozone reactions in water

The ozone involving advanced oxidation processes

The heterogeneous catalytic ozonation

The Photocatalytic ozonation process

Ozone mechanisms of reactions

Direct ozone reactions

•Oxygen and electron transfer reactions

* Cycloaddition reactions

* Electrophilic substitution reactions

Indirect ozone reactions

•Ozone decomposition in free radicals (hydroxyl radical)

H_2O_2

•Ozone indirect oxidation reactions

Ozone involving AOPs

O_3/H_2O_2

$$O_3 + HO_2^- \xrightarrow{k=2.8x10^6 M^{-1}s^{-1}} HO_2\cdot + O_3^-\cdot$$

O_3/UV(254nm)

$$O_3 + H_2O \xrightarrow{h\nu} \boxed{H_2O_2 + O_2}$$

$$H_2O_2 \xrightarrow{h\nu} 2HO\cdot$$

O_3/Catalysts (in research and development)

$$O_3 \xrightarrow{Catalyst} Different\ routes \longrightarrow Molecular\ reactions\ or\ HO\cdot$$

O_3/UV/Catalysts (in research and development)

$$O_3 \xrightarrow[Radiation]{Catalyst} Different\ routes \longrightarrow h^+\ and\ /\ or\ HO\cdot$$

CATALYTIC OZONATION PROCESSES

HOMOGENEOUS PROCESSES

HETEROGENEOUS PROCESSES

HETEROGENEOUS CATALYTIC OZONATION PROCESSES

NON-PHOTOLYTIC CATALYTIC OZONATION PROCESSES

PHOTOCATALYTIC OZONATION PROCESSES

WORKS ON
Non-photolytic heterogeneous catalytic ozone processes

Synthesis and Characterization of catalysts ⟶ Physical and chemical properties

Application ⟶ Influence of variables (pH, scavengers, concentrations, etc)

Mechanism: ⟶ Adsorption, surface or bulk reaction, desorption steps
Type of reactions: direct or Hydroxyl radicals

Kinetics: ⟶ Mass transfer and chemical steps, reaction rates

Activity and stability: Repetition of experiments, time duration

TYPE OF CATALYSTS

Metal oxides and Supported metal oxides :

TiO_2, Al_2O_3, Fe_3O_4, MnO_2, FeOOH, SiO_2, etc

CeO/Al_2O_3, Fe_3O_4/SiO_2, PdO/CeO, TiO_2/Al_2O_3, Fe_3O_4/Al_2O_3, TiO_2/SiO_2, Co_2O_3/Al_2O_3, MnO_2/Al_2O_3, RuO_2/Al_2O_3, etc

Carbon materials with or without metal oxides:

Activated carbon, carbon fibers, Multiwall carbon nanotubes, etc

MgO/AC, CeO_2/AC, CuO/MWCNT, etc

Others of miscellaneous nature:

Ceramics, zeolites, perovskites, perfluorinated alumina, etc

GENERAL CATALYTIC OZONATION EFFECTS

Increase of ozone decomposition

Increase of organic removal rates

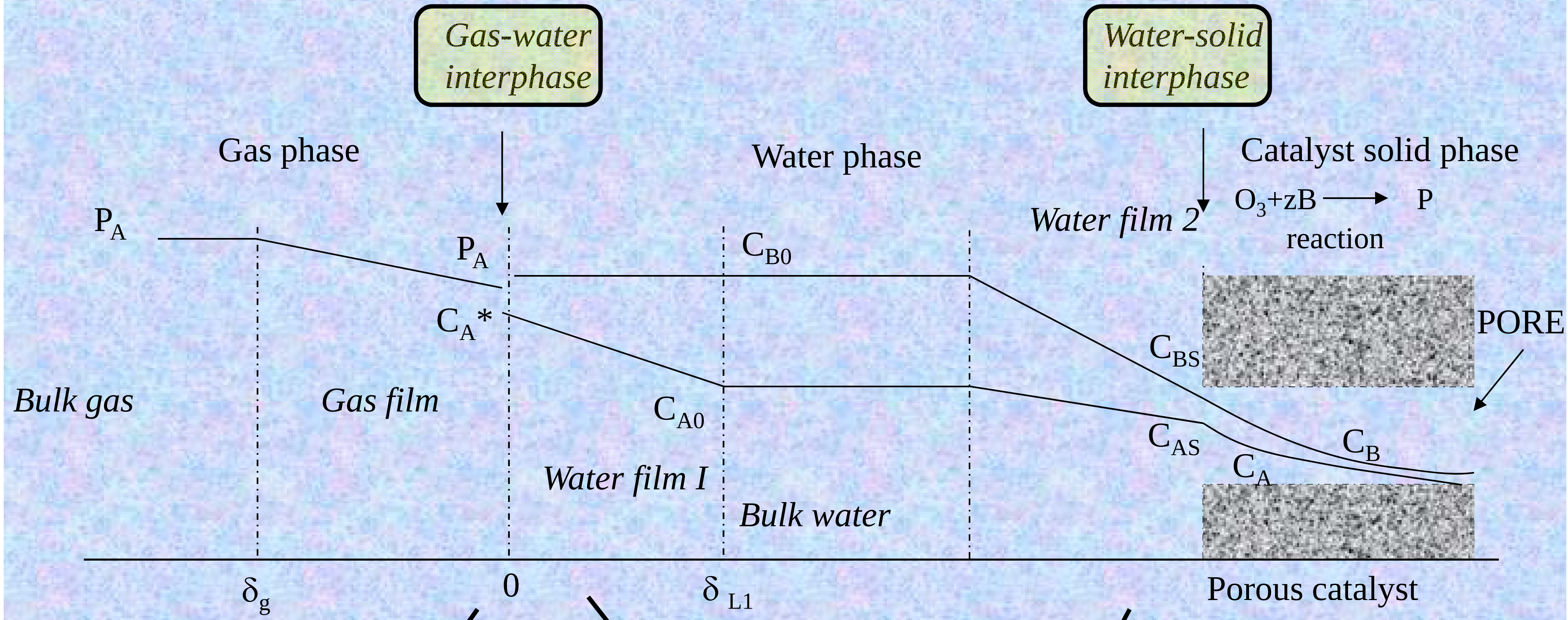
Significant increase of TOC removal

Negative or no influence of HO scavengers

Negative effect of pH, in some cases

Increase efficiency of ozone utilization

KINETICS
Mass transfer and chemical reaction steps



Constant concentration zone

Gas external diffusion

Water external Diffusion

Constant concentration zone

Water-solid external diffusion

~~Pore internal diffusion~~ and surface reactions

→ Adsorption, Reaction, Desorption

O_3 sparingly dissolved in water

High gas flow rate
High speed of agitation

D_p < 100 μm

MECHANISMS

Steps of the mechanism and nature of reactions

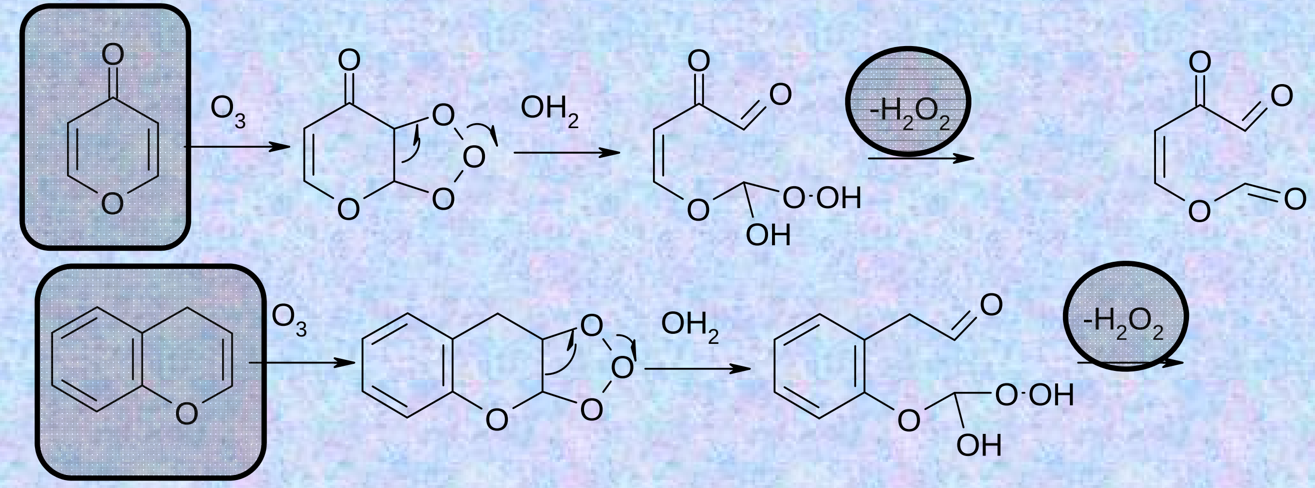
LHHW or ER Mechanisms:

1. Ozone and target compound adsorption on active sites, surface chemical reaction and product desorption

2. Ozone or target compound adsorption on active sites, reaction between adsorbed species and the other in solution

3. Hydroxyl radicals formed through LHHW or ER mechanisms and their reaction with compoundsin bulk water

ACTIVATED CARBON CATALYTIC OZONE DECOMPOSITION



Possible reactions of ozone with 4-pyrone and 4H-chromene activated carbon surface oxygen groups

Activated carbon acts as promotor of ozone decomposition

Photolytic heterogeneous catalytic ozone processes

PHOTOCATALYTIC OZONATION

COMBINATION OF OZONE-RADIATION AND CATALYST (SEMICONDUCTOR)

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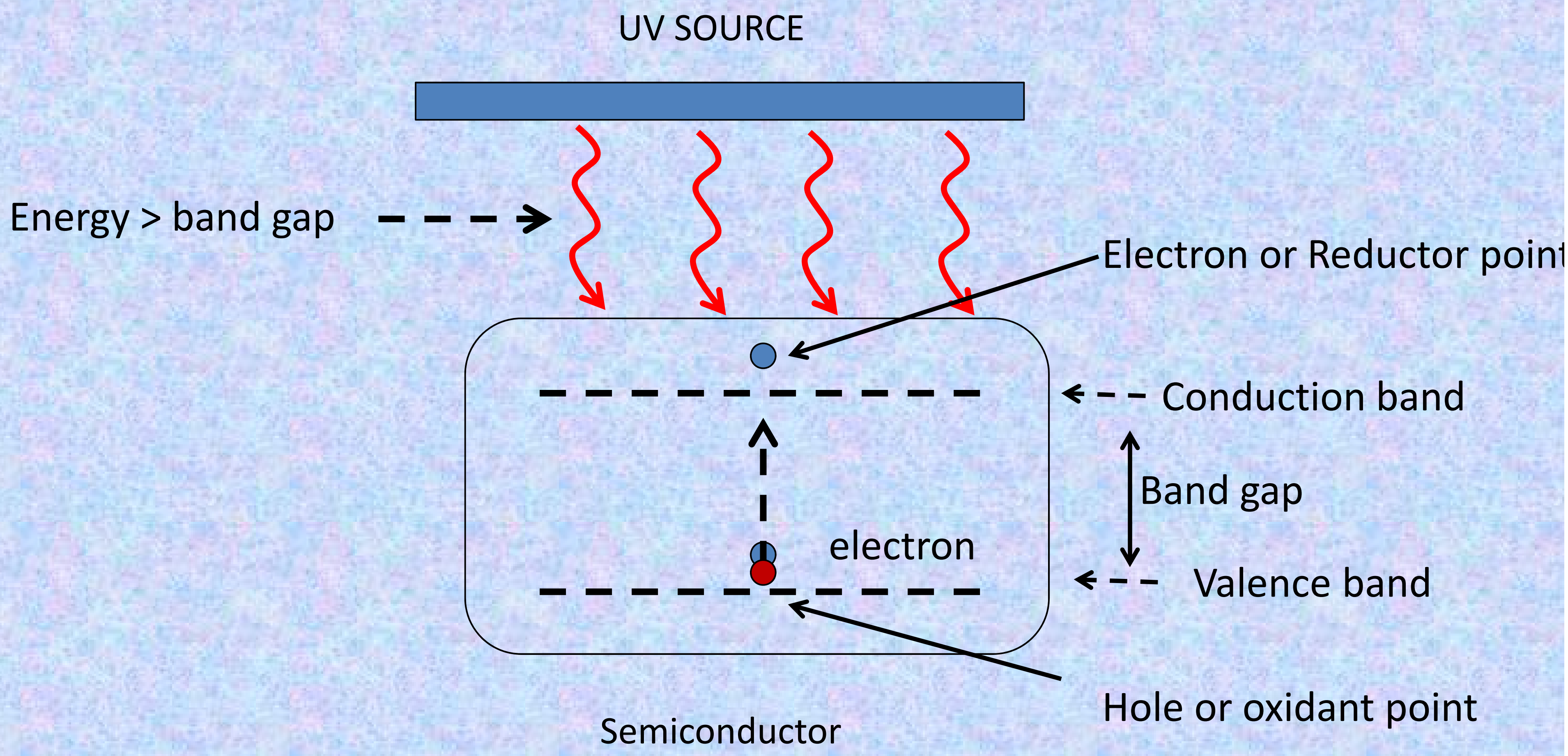
SOLAR PHOTOCATALYTIC OZONATION

PHOTOCATALYTIC OXIDATION DESCRIPTION



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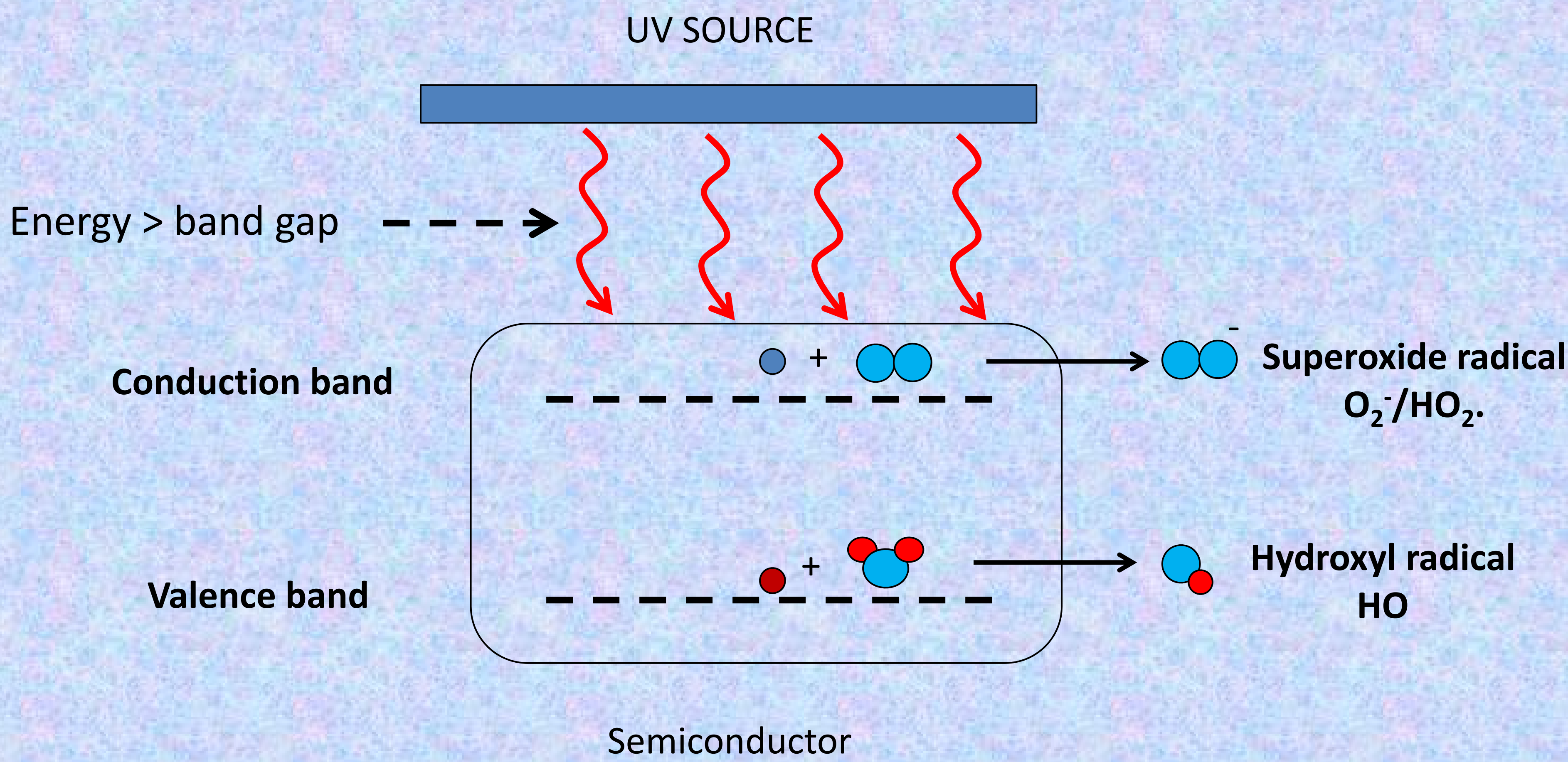

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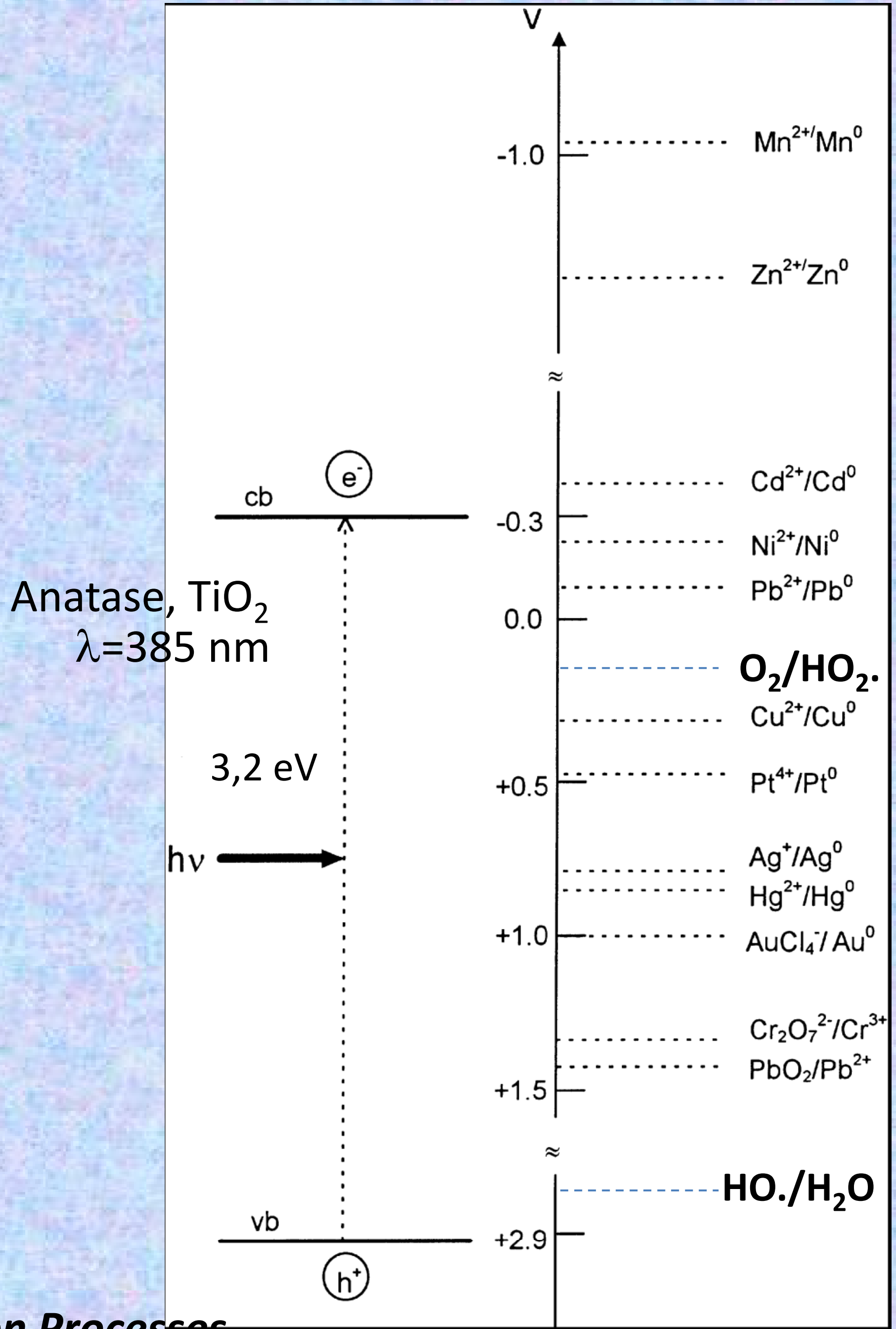
Redox Potentials of TiO_2 (Anatase)



MAIN OZONE REACTIONS

$$O_3 + e^- = O_3.^-$$

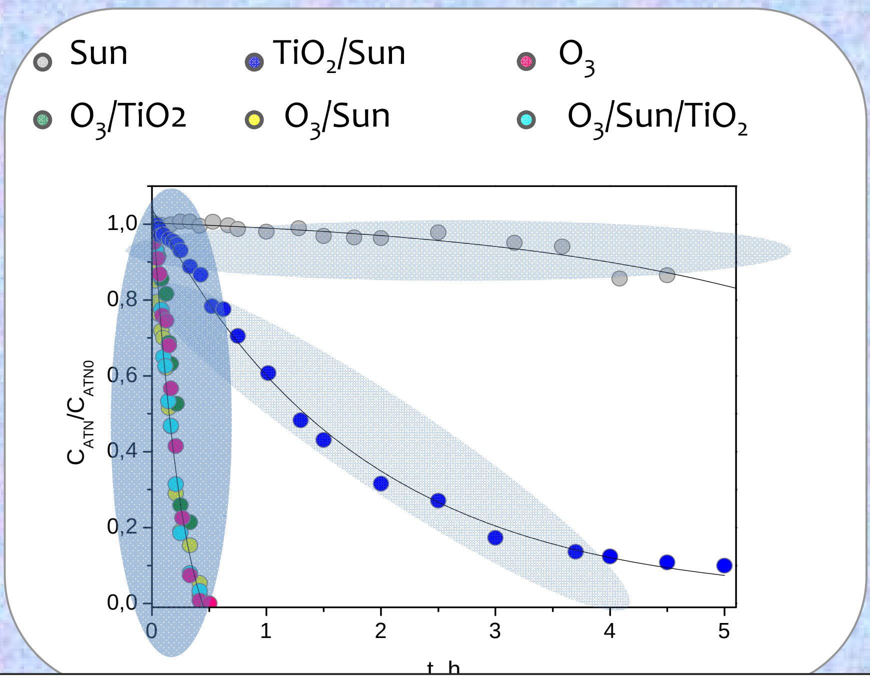
$$O_3 + O_2.^- = O_3.^- + O_2$$

$$O_3.^- + H^+ = HO. + O_2$$

SOLAR PHOTOCATALYTIC OZONACION

Urban wastewater from secondary effluent WWTP

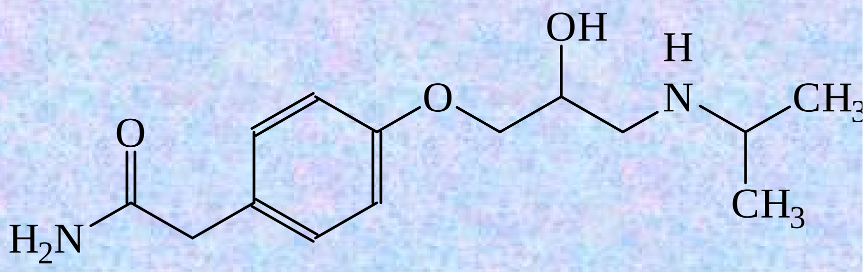
Emergent contaminant: ATENOLOL (beta-blocking)



Experimental conditions:

C_{Bo} = 0.5 mgL^{-1}; pH 7; Q_g = 45 Lh^{-1}; C_{O3ge} = 19 mgL^{-1}; C_{TiO_2} = 0.25 gL^{-1}, T = 16-30 °C; $\overline{UV}$ = 25-36 Wm^{-2}

ATENOLOL

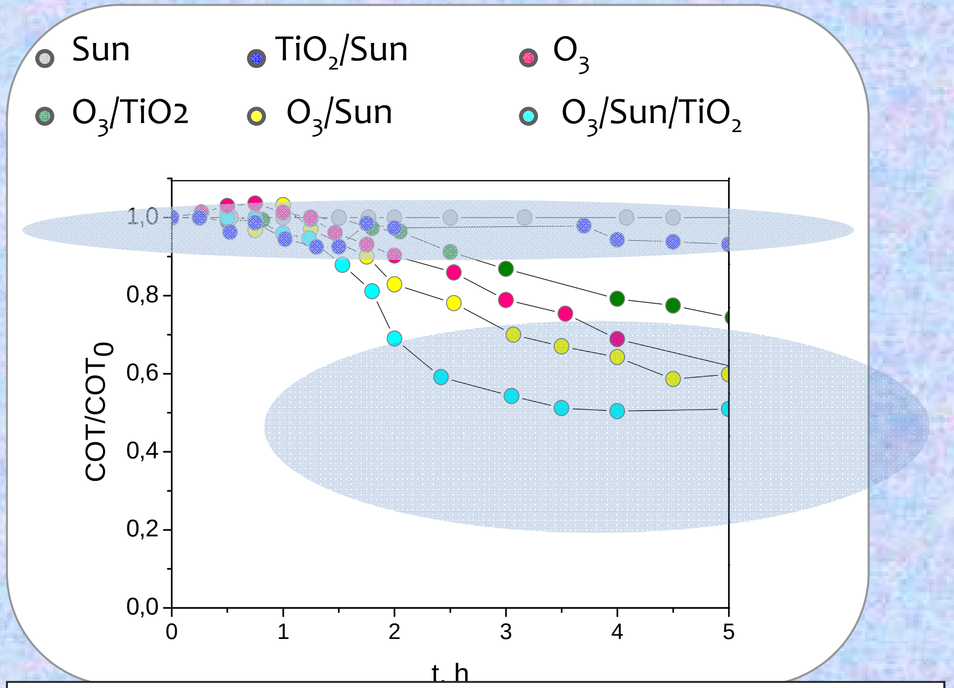


ATN

SOLAR PHOTOCATALYTIC OZONACION

Urban wastewater from secondary effluent WWTP

Organic mater removal: Mineralization: Total organic carbon



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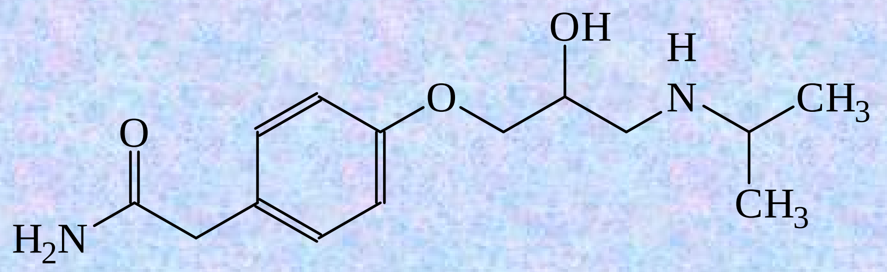
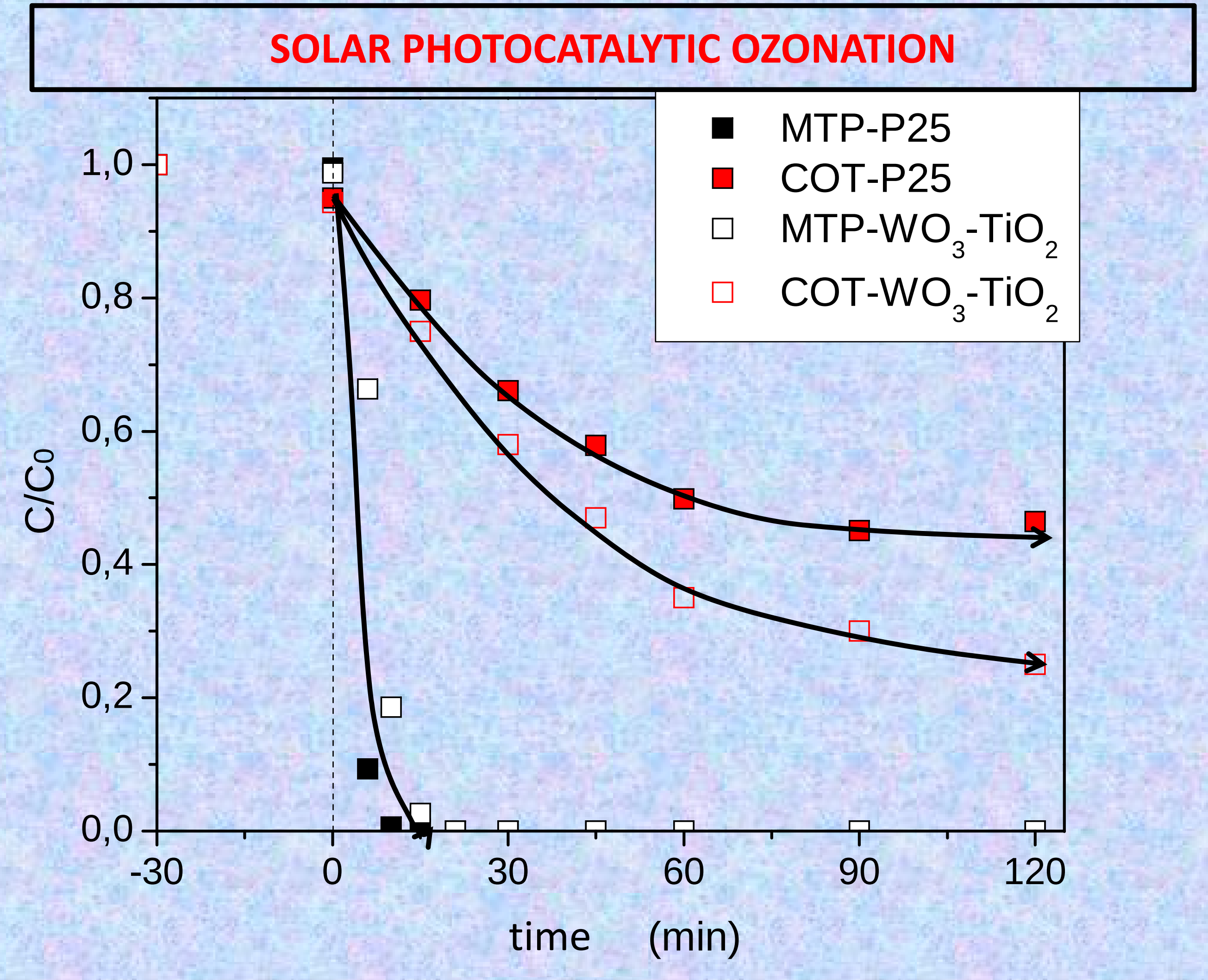


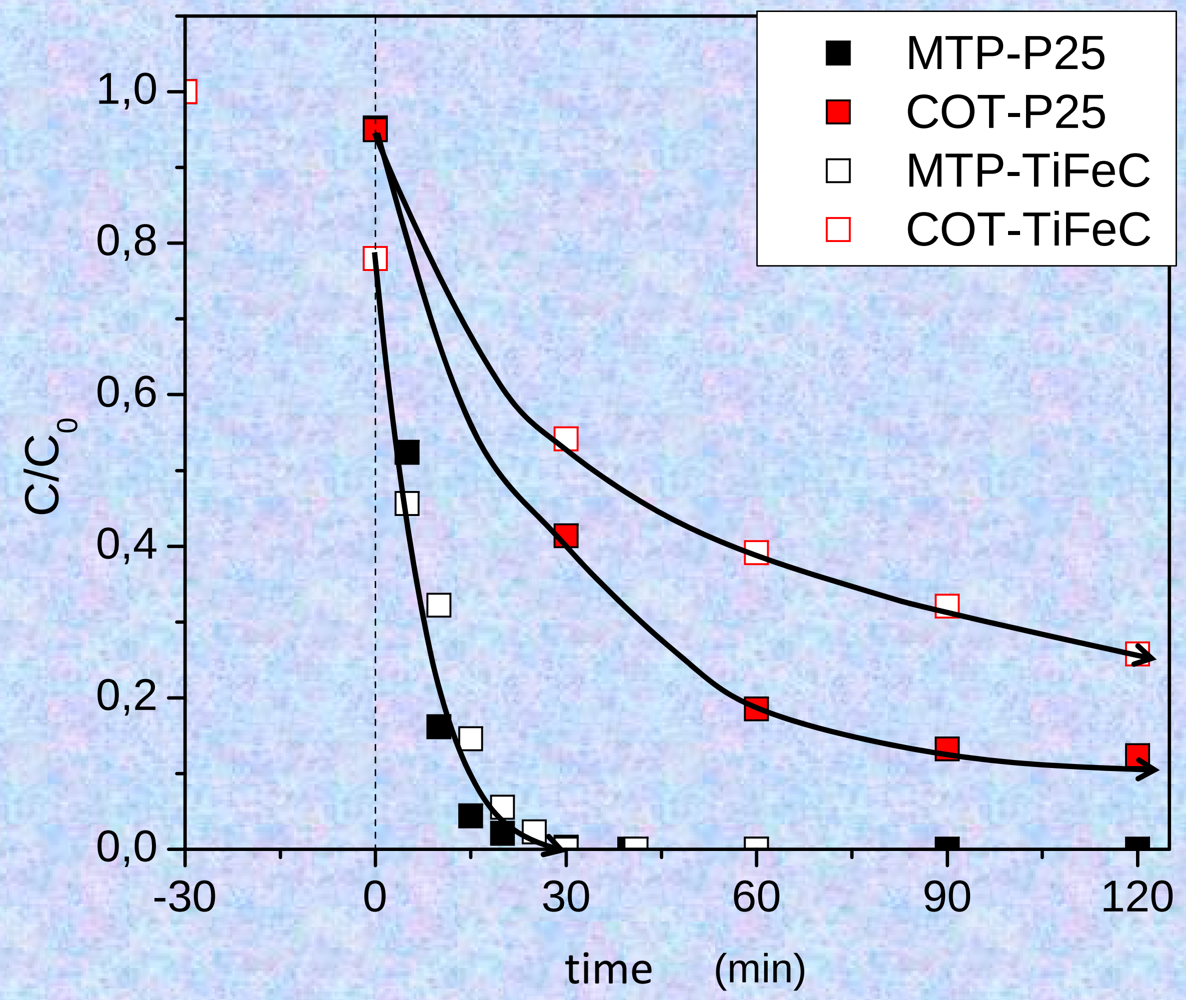
ATN

COUPLING SEMICONDUCTORS : TiO_2-WO_3



Changes of normalized MTP concentrations and TOC with TiO2 and WO3-TiO2 semiconductors. Conditions: C_{MTP}=2 mg·L^{-1} in wastewater, TOC_0=35 mg·L^{-1}, C_{CAT}=0.5 g·L^{-1}, Q_g=20 L·h^{-1}, C_{O3ge}=10 mg·L^{-1}, V_R=0.5 L, pH=8.3

SOLAR PHOTOCATALYTIC OZONATION



Changes of normalized MTP concentration and TOC with TiO_2 and TiFeC semiconductors.
Conditions: C_{MTP}=5 mg·L^{-1}, C_{CAT}=0.25 g·L^{-1}, Q_g=20 L·h^{-1}, C_{O3ge}=10 mg·L^{-1}, V_R=0.25 L, pH=6

THANK YOU FOR YOUR ATTENTION

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