Photocatalysis in water treatment

Theodoros Triantis
Institute of Nanoscience and Nanotechnology
National Center for Scientific Research "Demokritos"

Water Pollution

Pollution means the direct or indirect introduction, as a result of human activity, of substances or heat into water which may be harmful to human health or the quality of aquatic ecosystems, which result in damage to material property, or which impair or interfere with amenities and other legitimate uses of the environment.
Framework Directive 2000/60/EC of EU in the field of water policy

Photograph: The Photolibrary Wales/Alamy Stock Photo

Sources of water pollution

Industrial waste →
- ✓ Organic solvents, toxic compounds
- ✓ Metals
- ✓ Heat exchange

Sewage & Wastewater →
- ✓ Detergents / Cleaning products
- ✓ Pharmaceuticals
- ✓ Byproducts of human metabolism

Agricultural / farming activities →
- ✓ Fertilizers
- ✓ Pesticides

Pollution with biogenic origin →
- ✓ Toxins and taste & odor compounds produced by cyanobacteria

Other sources →
- ✓ Petroleum spills, acid rain etc.

Water treatment processes

Need for water purification from organic pollutants

Physical methods

- ✓ Filtration
- ✓ Coagulation, Flocculation
- ✓ Activated carbon

▪ Partial removal of pollutants
▪ Not destructive
▪ Regeneration/disposal of the polluted residual material is needed

Conventional oxidation processes

- ✓ Cl_2 / HClO / ClO_2
- ✓ O_3
- ✓ H_2O_2
- ✓ Oxidation with $KMnO_4$

▪ All methods are able to degrade organic compounds
▪ Water quality parameters affect the process
▪ Formation of byproducts

Advanced Oxidation Processes

- ✓ Photolysis
- ✓ UV/H_2O_2
- ✓ UV/O_3
- ✓ Fenton
- ✓ Photo-Fenton
- ✓ TiO_2 Photocatalysis

Mode of Action

AOPs generate Reactive Oxygen Species (ROS) and sometimes other radicals as well, which react rapidly and non-selectively with a wide range of organic compounds

Advantages

▪ More effective than conventional methods
▪ Mineralization of pollutants can be achieved
▪ Environmental friendly methods

Research challenges (AOPs)

➢ New methods for the degradation of emerging contaminates are required
➢ Identification of transformation products and assessment of residual toxicity
➢ Synthesis of new materials with improved photocatalytic efficiency

Photocatalysis

Photocatalysis involves the activation of a photocatalytic material or substance by light photons, which in turn increases the rate of a chemical reaction without being consuming.

Advantages of Photocatalysis in Organic Pollutants Degradation

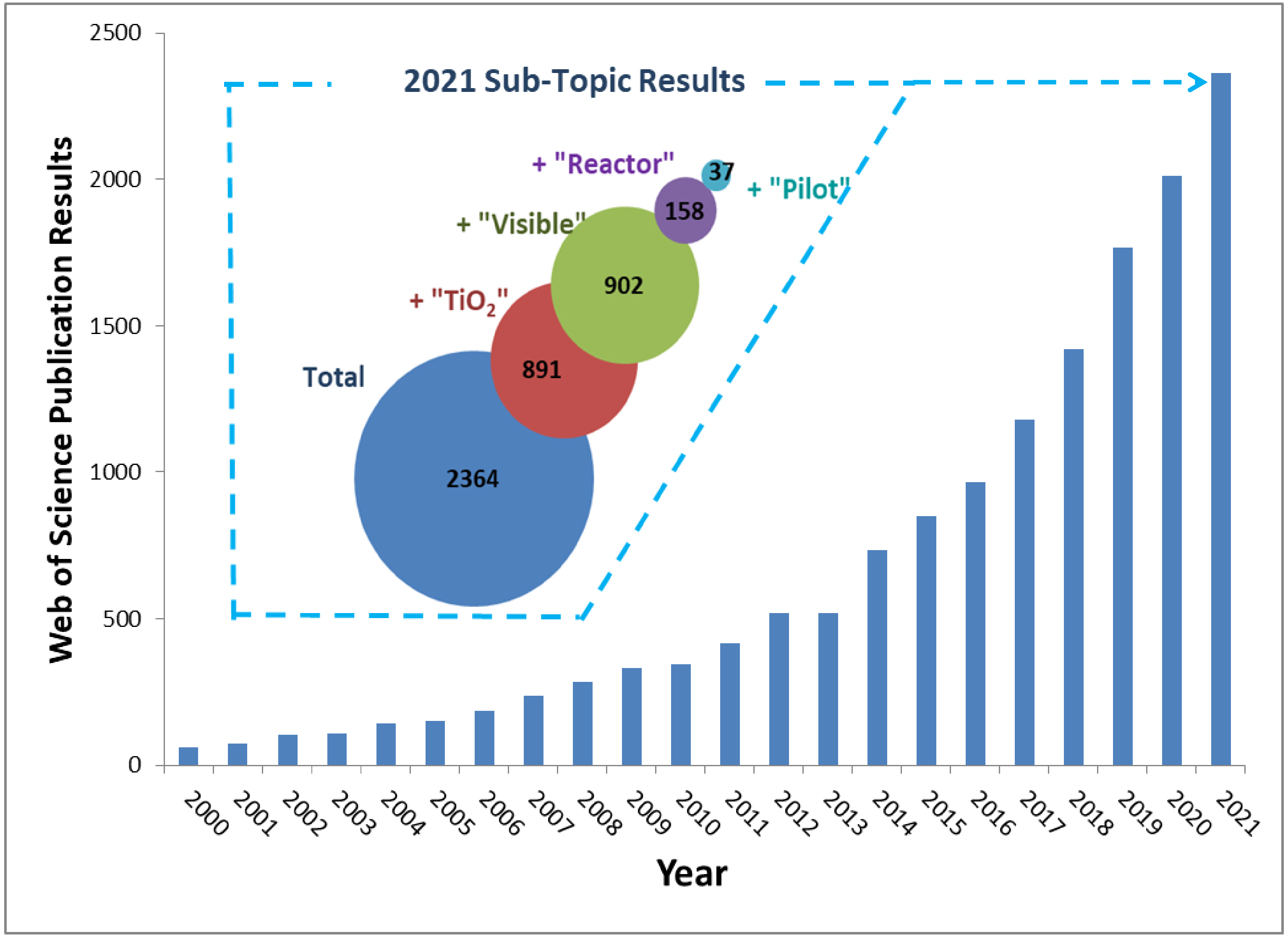
- ✓ Environmental friendly process
- ✓ Ambient temperature and atmospheric pressure
- ✓ Aquatic systems
- ✓ Use of O_2 as oxidant: No addition
- ✓ of other chemicals

Complete mineralization of organic pollutants to CO_2, H_2O and inorganic ions

High efficient process because of ROS production (especially hydroxy radicals)

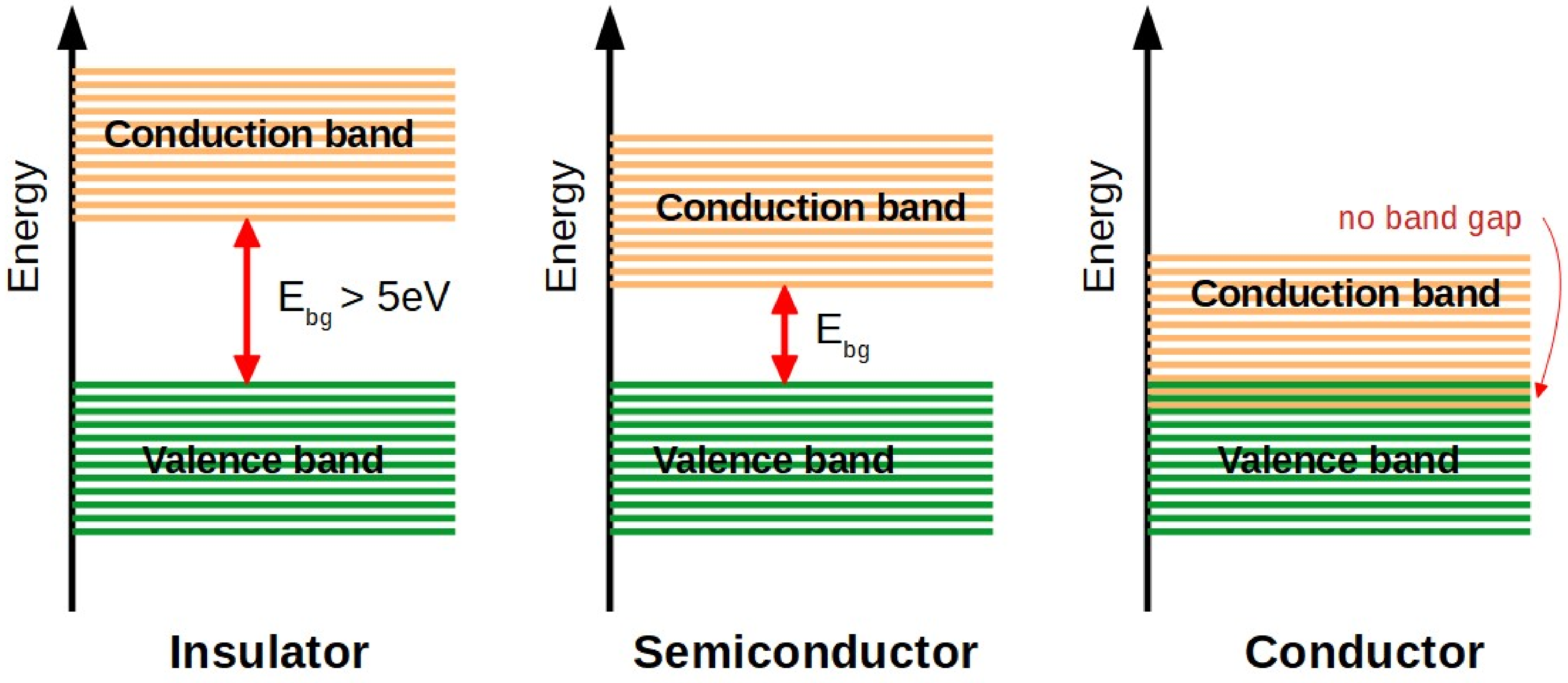
Degradation of plethora of organic pollutants such as: Phenols, chlorophenols, azodyes, pesticides, insecticides; cyanotoxins, T&O compounds

Publications trends in photocatalytic water treatment research



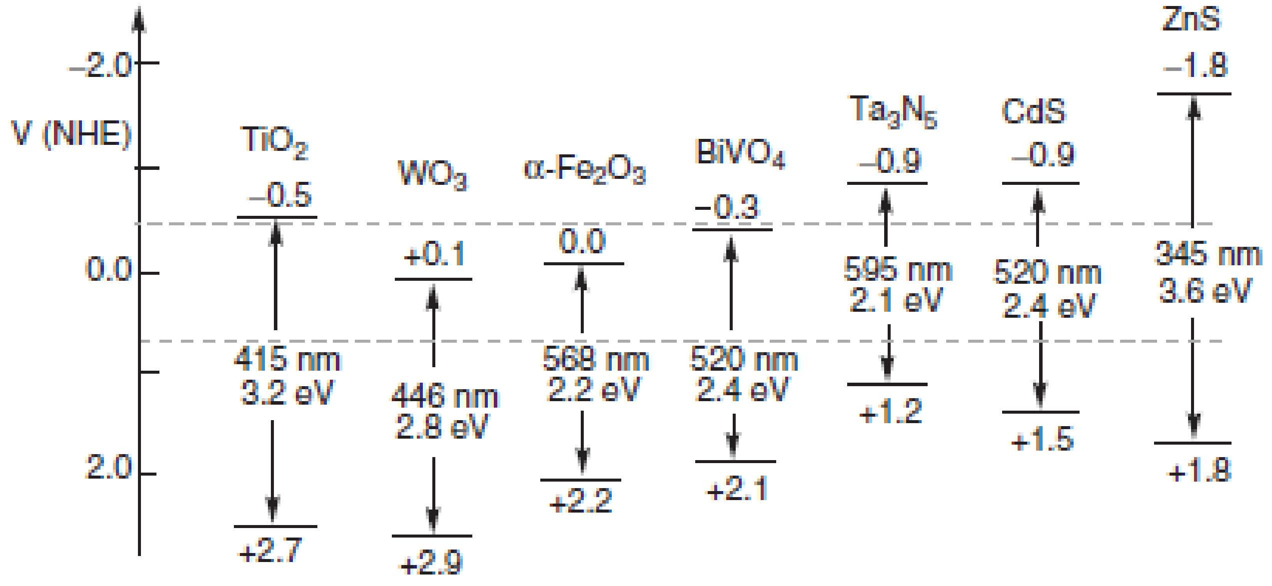
Search keywords:
Photocat* Water Treatment

Semiconductor Photocatalysts

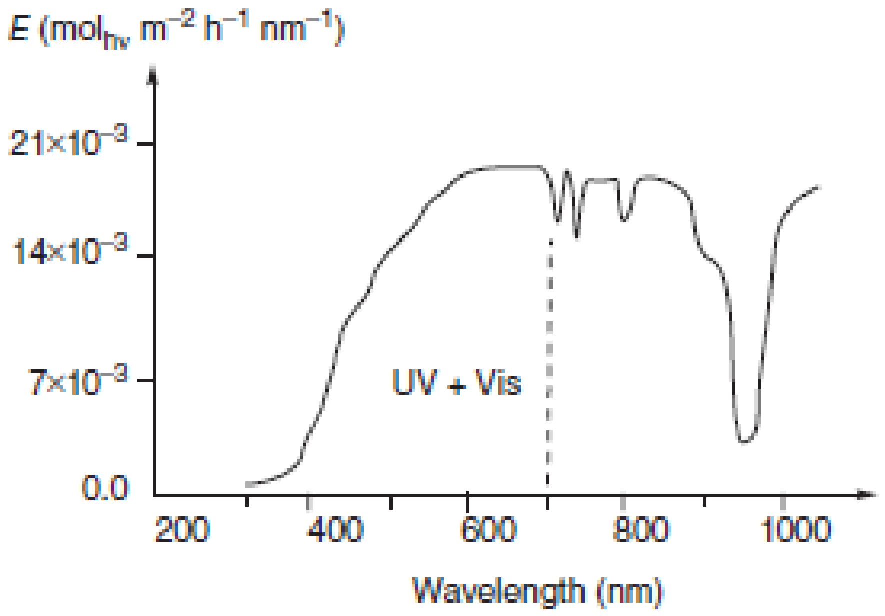


Schematic band diagram of insulators, semiconductors and conductors

Semiconductor Photocatalysts



Band edge positions of some semiconductor powders in contact with neutral water. The dashed lines indicate water-splitting potentials.



Simplified sketch of direct solar irradiance
3% UV (λ<400 nm), ≈47% visible (400-700 nm), 50% infrared

- Band edge positions depends on the nature of the liquid they are suspended in and the preparation methods
- Absorption of light with energy higher than that of the bandgap promotes electrons to higher-energy electronic states, which then relax to states located close to band edge
- Absorption of solar light requires the overlap of the SC absorption spectrum with the spectral composition of sunlight

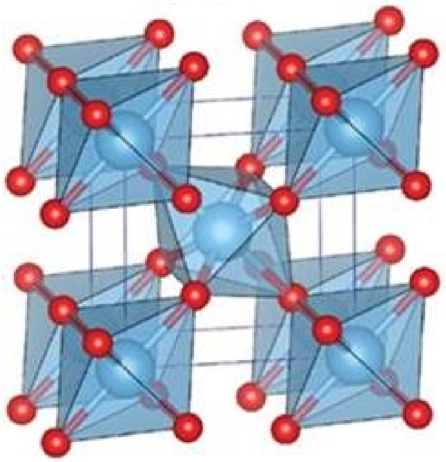
*Horst Kisch, **Semiconductor Photocatalysis**, Wiley-VCH Verlag GmbH & Co, Weinheim, Germany , 2015, pp. 1-249*

Titanium Dioxide (TiO_2)

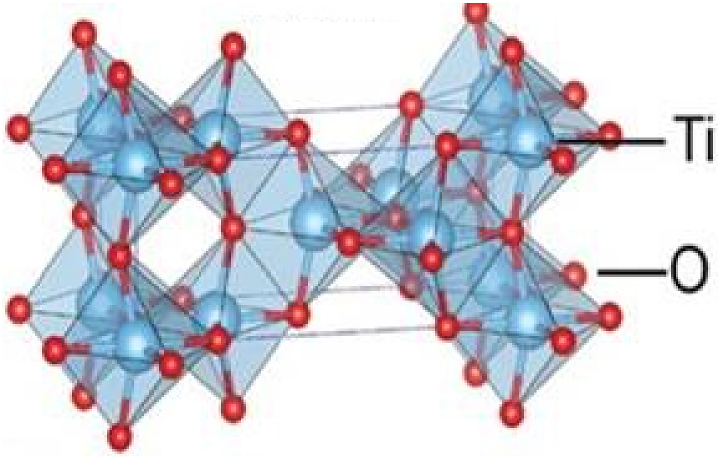
Why TiO_2

- Strong oxidizing power of valence band hole
- Excellent chemical and photochemical stability
- Availability / Low cost
- Low toxicity
- Band gap 3.2 eV
- Absorption of 5% of the solar light

❖ Phases of TiO_2: Rutile, Anatase and Brookite



TiO_2(rutile)
crystal structure: tetragonall
E_{Bg}≈3.1 eV (i.e., $\lambda < 400$ nm)
ρ= 4.23 g/cm^3



TiO_2(Anatase)
crystal structure: tetragonal
E_{Bg}≈ 3.3 eV (i.e., $\lambda < 376$ nm)
ρ= 3.78 g/cm^3

G. Zerjav et al. Journal of Environmental Chemical Engineering 10 (2022) 107722

Commercial TiO_2 materials

AEROXIDE® TiO2 P 25

AEROXIDE® TiO2 P 25 is a pure, hydrophilic titanium dioxide (TiO2) with a very high specific surface area. Due to its unique ratio of Anatase and Rutile crystalline structure it is suitable for many catalytic and especially photo-catalytic applications. In addition, it can be used as very efficient UV filter.

TECHNICAL DATA

appearance	white solid
delivery form	free-flowing powder
loss on drying	< 1.5 %
pH-value	3.5 - 4.5
SiO_2 content	< 0.2 %
specific surface area (BET)	35 - 65 m^2/g
tamped density	Approx. 140 g/l

Producer: Evonik Industries AG, Germany

KRONOClean® 7000

TiO_2-photocatalyst

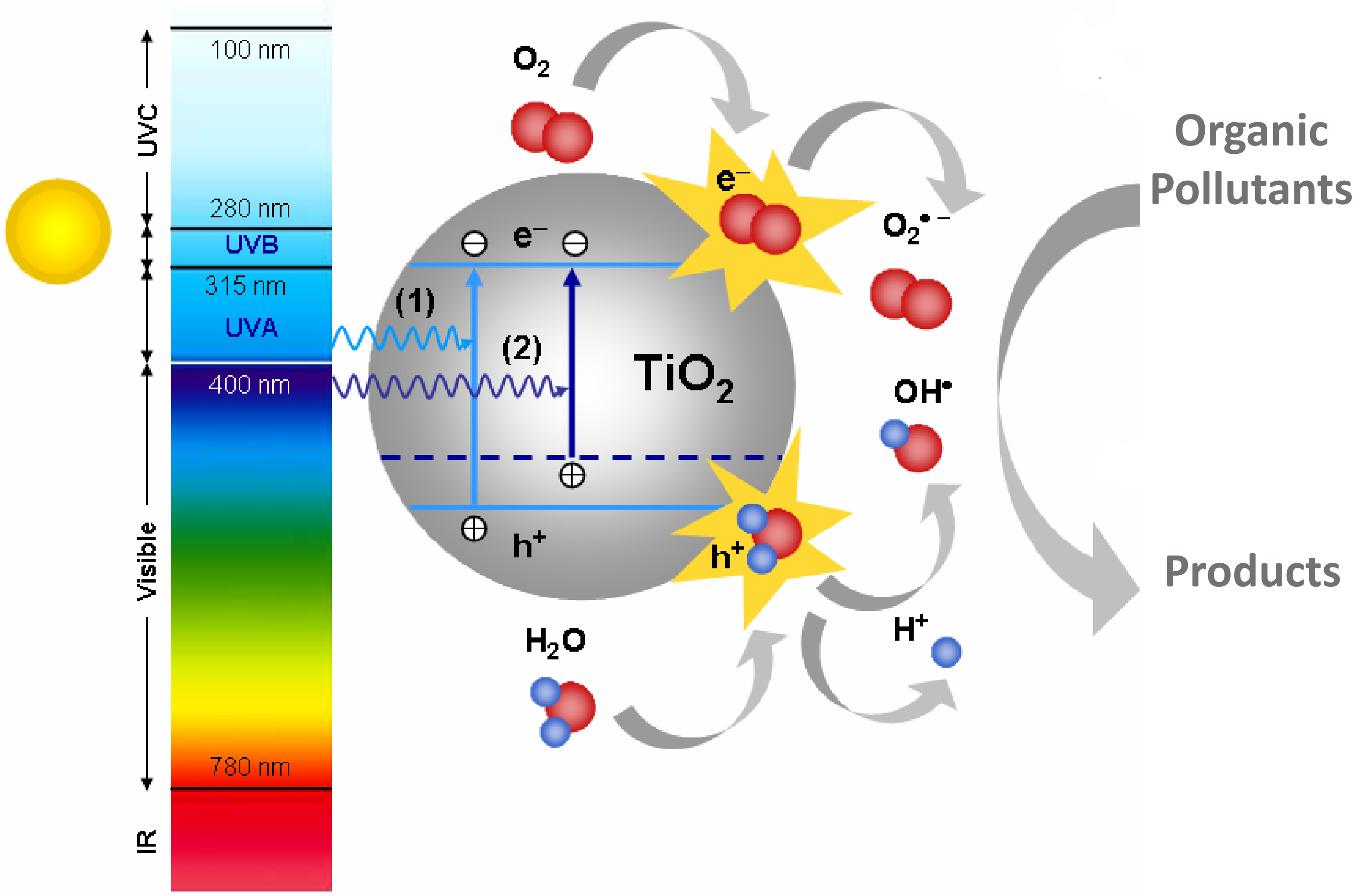
degrades pollutants with visible light and with UV radiation

Typical Product Characteristics

TiO_2-Content (DIN EN ISO 591)	> 87.5 %
Crystal modification	anatase
Density (DIN EN ISO 787-10)	2.9 g/cm^3
Crystallite size	approx. 15 nm
Specific surface area (BET)	> 225 m^2/g
Bulk density	350 g/l
Oil absorption[1]	~ 67 g/100 g
Water demand[1]	~ 210 g/100 g
Max. processing temperature	200 °C
Application pH-range	4 – 9

Producer: KRONOS Specialties GmbH, Germany

UV/TiO_2 photocatalysis – General concept

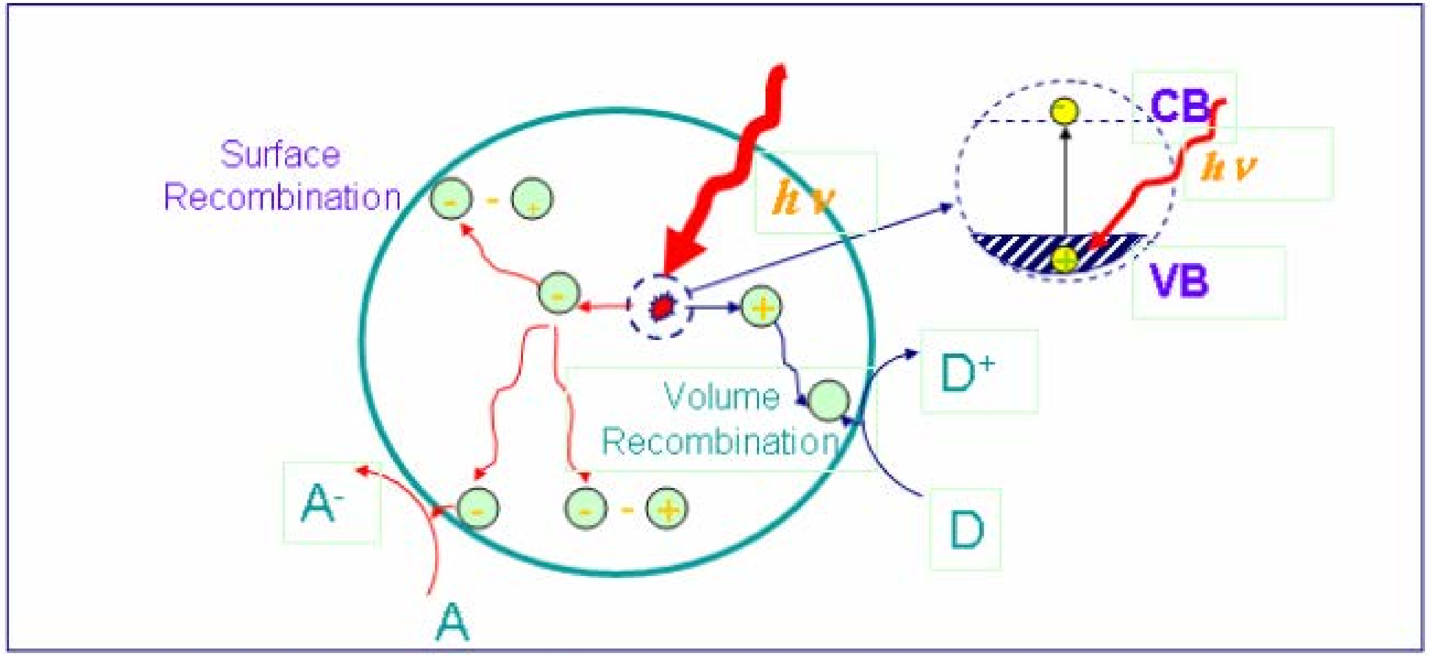


- Direct bandgap excitation of the semiconductor results in electron-hole separation
- Photogenerated holes as well as hydroxyl radicals oxidize the organic contaminant at the TiO_2 surface
- Electrons are scavenged by oxygen

M. R. Hoffmann et al., Chem. Rev. 1995, 95, 69-96

UV/TiO_2 photocatalysis – Primary reactions

Schematic photoexcitation in a solid followed by deexcitation events



$TiO_2 + h\nu \rightarrow h_{VB}^+ + e_{CB}^-$ (activation)

$e_{CB}^- + h_{VB}^+ \rightarrow$ heat (recombination)

$H_2O + h_{VB}^+ \rightarrow {}^{\bullet}OH + H^+$

$O_2 + e_{CB}^- \rightarrow O_2^{\bullet-}$

$O_2^{\bullet-} + H^+ \rightarrow {}^{\bullet}OOH$ pKa = 4.8

${}^{\bullet}OOH + {}^{\bullet}OOH \rightarrow H_2O_2 + O_2$

$H_2O_2 + e_{CB}^- \rightarrow {}^{\bullet}OH + OH^-$

$O_2^{\bullet-} + h_{VB}^+ \rightarrow {}^1O_2$

- Migration of electrons and holes to the semiconductor surface
- More efficient electron transfer if acceptor species are preadsorbed on surface
- Reactive oxygen species can be detected using EPR techniques and probe molecules

Linsebigler et al., Chem. Rev. 95(1995)735

Terms and Units used in Photocatalysis

Term	Symbol	Units (SI)	Definition / Notes
Irradiance (traditional term: Intensity, I)	E	$W\ m^2$	Radiant power, P, of all wavelengths incident from all upward directions on a small element of surface containing the point under consideration divided by the area of the element. Refers to a parallel and perpendicular beam not scattered or reflected by the target or its surroundings
Fluence rate	E_o	$W\ m^2$	Total radiant power, P, incident from all directions onto a small sphere divided by the cross-sectional area of that sphere.
Photon flux	q_p	$mol\ s^{-1}$	Number of *photons* (quanta of radiation, *N*p) per time interval. Common unit: einstein s^{-1} Einstein: 1mol of photons
Photon irradiance	E_p	$mol\ m^{-2}\ s^{-1}$	Number of photons per time interval (photon flux), qp, incident from all upward directions on a small element of surface containing the point under consideration divided by the area of the element
Quantum efficiency or yield	Φ (λ)		Amount of reactant consumed or product formed per amount of photons absorbed The term applies only for monochromatic excitation
Photonic efficiency (or apparent quantum yield)	ζ_p		Amount of reactant consumed or product formed per amount of incident photons

Photocatalytic reaction rate

(pseudo) first order kinetic model
Langmuir-Hinshelwood kinetic model

$$\mathrm{A}(fluid\ phase) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{A}(adsorbed\ phase) \quad (1)$$

$$\mathrm{A}(adsorbed) \xrightarrow[k_2]{} \text{Products} \quad (2)$$

$$r = -\frac{dC}{dt} = \frac{kKC}{1+KC}$$

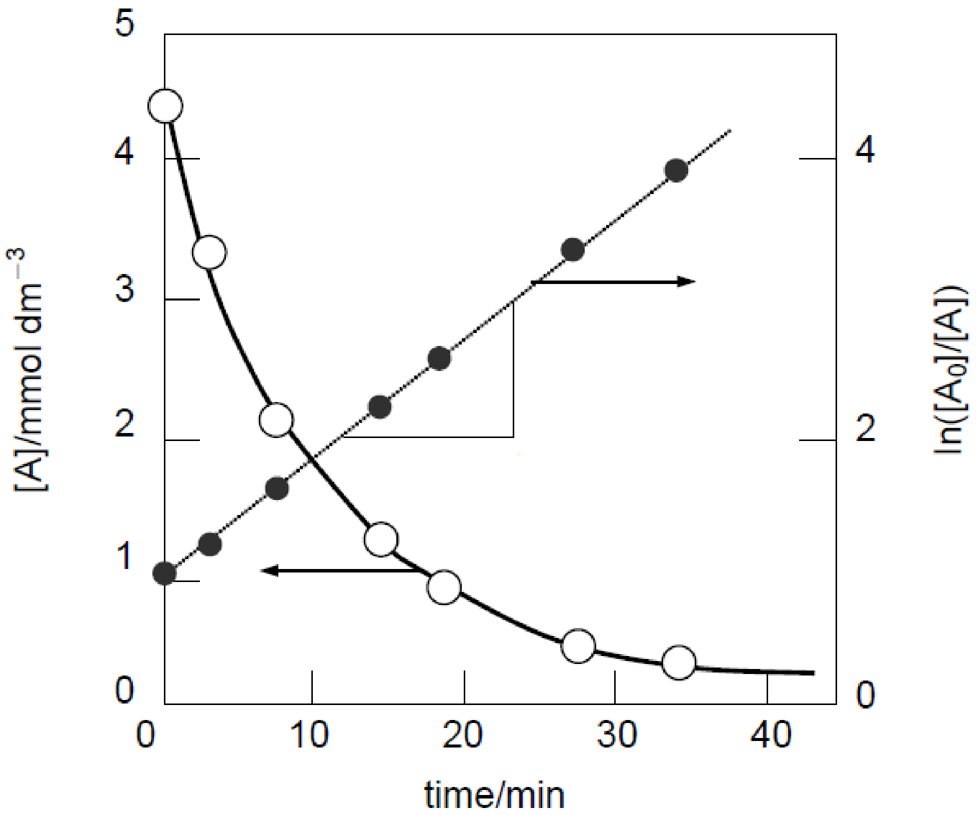
Where
r: reaction rate; k=rate constant;
$K=k_1/k_{-1}$= adsorption constant;
C=concentration of reactant A

If KC<<1 (milimolar concentration range)
the rate equation simplifies to first order

$$r = -\frac{dC}{dt} = kKC = k_{app}C \qquad \text{(first order)} \qquad (K_{app}=kK)$$

$\ln C=\ln C_o-kKt \Rightarrow \ln C=\ln C_o-k_{app}\,C \Rightarrow \ln C_o/C=k_{app}\,t$

If KC>>1 the reaction becomes zero order



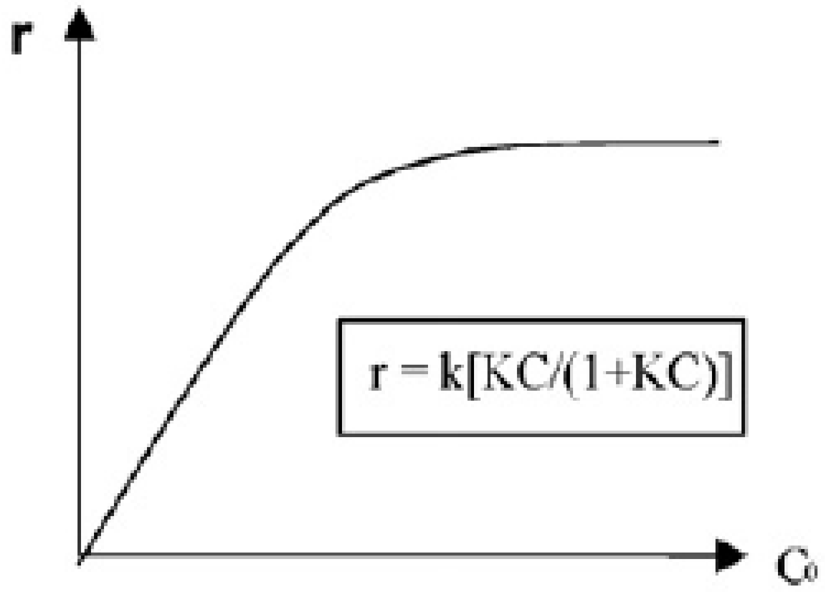
B. Ohtani, J. Photochem. Photobiol. C: Photochem. Rev. 11 (2010) 157–178

D.F. Ollis, Topics in Catalysis 35(3–4) (2005) 217-223. DOI: 10.1007/s11244-005-3827-z

Parameters influencing the photocatalytic degradation

Compound concentration

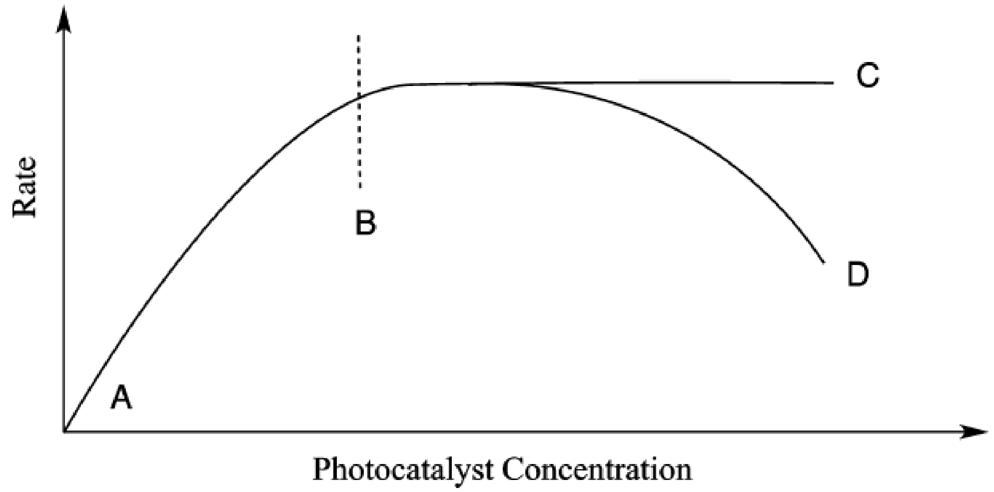
- Degradation rate increases with increase in substrate concentration till a certain level
- Increase of substrate concentration, increases the propability of reaction with reactive oxygen species
- Active sites on catalyst surface will be covered at high substrate concentrations. Further increase has no effect on reaction rate
- If substrate absorbs light, its increase in concentration can cause decrease in the reaction rate



J-M Herrmann, Applied Catalysis B: Environmental 99 (2010) 461–468

Parameters influencing the photocatalytic degradation

Catalyst loading



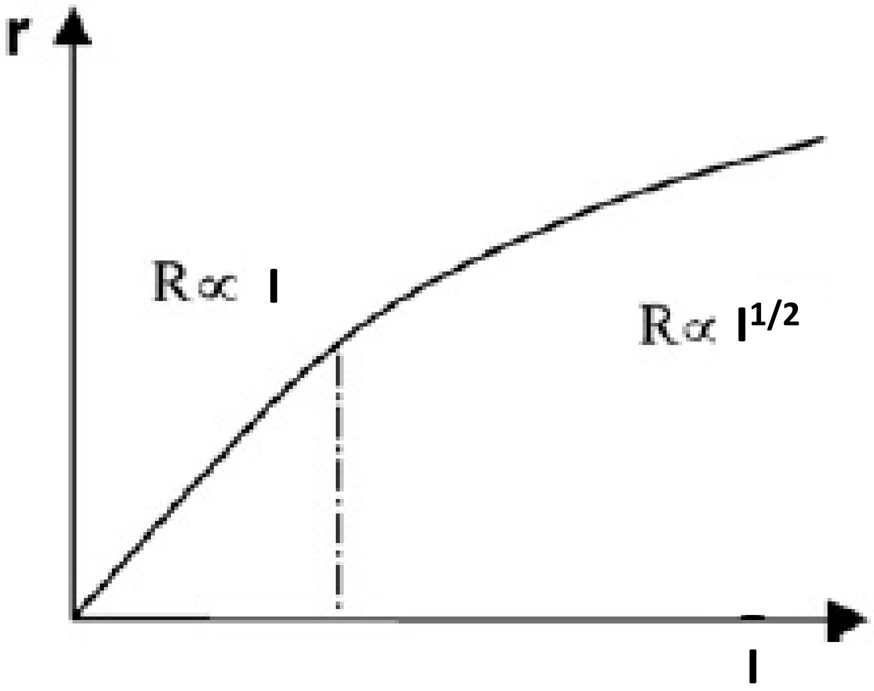
- Linear increase till a certain level of concentration
- Availability of catalyst active sites and light penetration affect the reaction rate
- Agglomeration and sedimentation of catalyst at high concentrations reduce the available surface for photon absorption
- High catalyst loading reduces the light penetration resulting in a rate decrease (trace BD)
- For TiO_2 materials with a surface area of 50-200 m^2/g the optimum catalyst concentration ranges from 0.5 to 3.0 g/L

H. Kisch, et al., Journal of Physical Chemistry Letters, 2015. ***6****(10): p. 1907-1910.*

Parameters influencing the photocatalytic degradation

Light intensity

- r is proportional to ***I*** below a max value (20 mW/cm^2) , above which the rate follows a square root variation
- Too high light intensities increase the production of electro – holes and subsequently their recombination rate
- For light intensities greater than a certain value (approx. 25 mW/cm^2), the rate is independent of light intensity



J-M Herrmann, Applied Catalysis B: Environmental 99 (2010) 461–468

D.F. Ollis, et al., Environ. Sci. Technol. 25 (1991) 1523

Parameters influencing the photocatalytic degradation

Effect of pH

- pH relates with the ionization state of catalyst surface
- pH influences the adsorption / desorption of reactants/products
- The point of zero charge (pzc) of TiO_2 (Evonik P25) is at pH 6.8
- High pH favors the formation of OH radicals through oxidation by holes

($H_2O + h_{vB}^+ \rightarrow {}^\bullet OH + H^+$)

J-M Herrmann, Applied Catalysis B: Environmental 99 (2010) 461–468

Parameters influencing the photocatalytic degradation

Presence of oxygen or oxidants

- Oxygen facilitates the scavenging of electrons and formation of superoxide radical
- Hydrogen peroxide and peroxydisulphate increase the rate through generation of reactive radicals
- High H_2O_2 concentration scavenge holes and OH radicals

$O_2 + e_{CB}^- \rightarrow O_2^{\bullet-}$

$H_2O_2 + O_2^{\bullet-} \rightarrow {}^{\bullet}OH + OH^- + O_2$

$H_2O_2 + h\nu \rightarrow 2\,{}^{\bullet}OH$

$H_2O_2 + e_{CB}^- \rightarrow {}^{\bullet}OH + OH^-$

$S_2O_8^{2-} + e_{CB}^- \rightarrow SO_4^{2-} + SO_4^{\bullet-}$

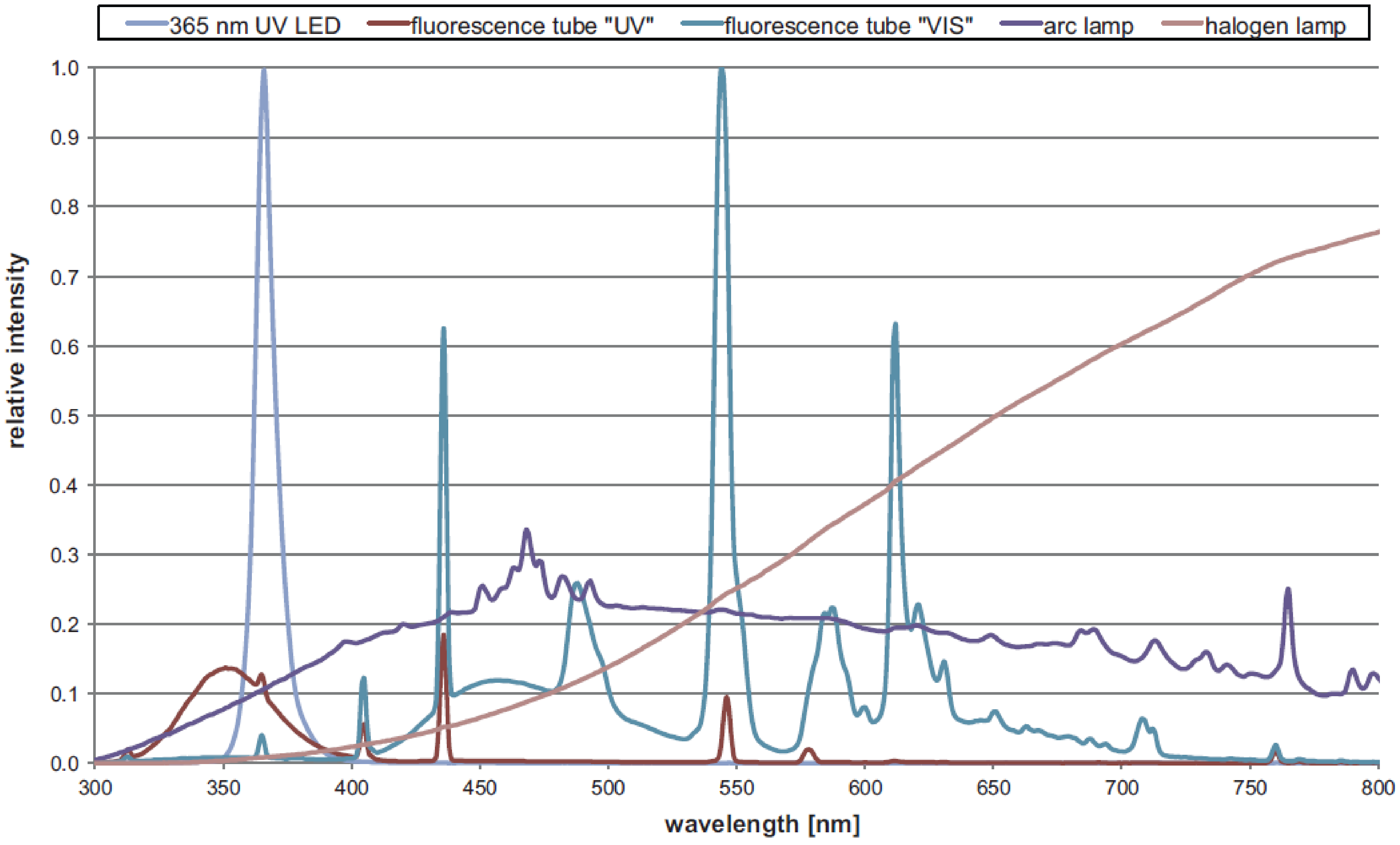
$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + {}^{\bullet}OH + H^+$

$H_2O_2 + 2h_{VB}^+ \rightarrow O_2 + 2H^+$

$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet-}$

T. Fotiou et al., Chemical Engineering Journal 261 (2015) 17–26
J-M Herrmann, Applied Catalysis B: Environmental 99 (2010) 461–468

Radiation sources widely used for photocatalysis analysis



365 nm UV LED (Omicron LED 250 mW 365nm.OEM);

Fluorescence tube“UV” (Vilber Lourmat (T-15L BL (15 W));

Fluorescence tube “VIS” (Philips (TLD Super 80));

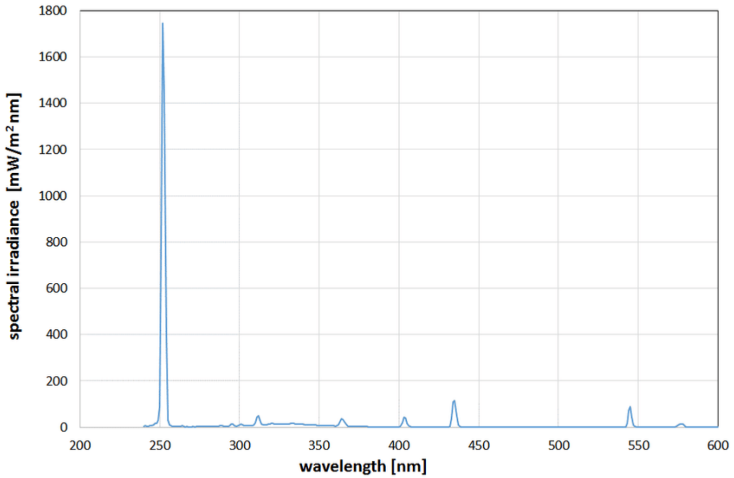
Arc lamp (L.O.T. Oriel GmbH (500 W Xenon/Hg(Xe));

Halogen lamp (Philips (R75Plusline Pro 150 T3Q/CL/CP 78 mm)

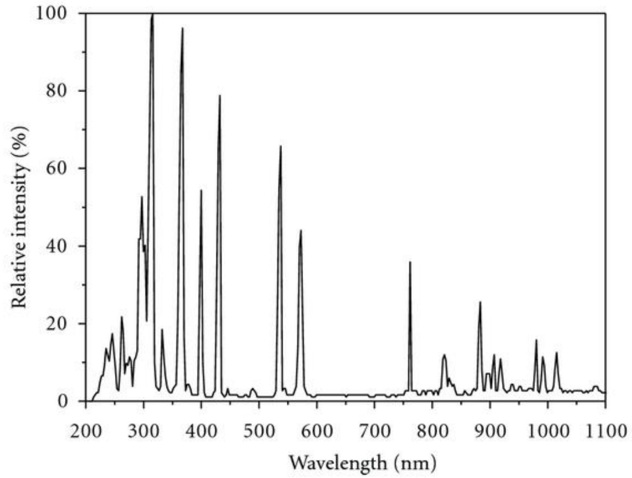
E. Blume, S.P. Bloess / Catalysis Today 230 (2014) 240–244

Mercury Lamps

Parameter	Low Pressure Mercury Lamp	Medium Pressure Mercury Lamp	High Pressure Mercury Lamp
Life time (h)	>5000	>2000	>3000
Output range	80% in a narrow range around 254 nm	Broad but not much below 250 nm	Strong below 250 nm
Energy Density	Low (~1 W/cm)	Moderate (~125 W/cm)	High (~250 W/cm)
Electrical energy to photon energy	High (~30%)	Moderate (~15% for 200–300 nm)	High (~30% for 200–300 nm)



Spectra of a low pressure mercury lamp



Spectra of a high pressure mercury lamp

J.R. Bolton, et al., 1995, The detoxification of waste water streams using solar and artificial UV light sources, ,in: Alternative Fuels and the Environment. F. S. Sterret, ed., Lewish Publishers. Boca Raton, FL. pp. 187-192.

Ferrioxalate actinometry

The method is based on the photochemical reduction of iron(III) to iron(II) during photooxidation of oxalic acid to CO_2

Ferrioxalate solution contains $(NH_4)Fe(SO_4)_2$ 0.005 M and $K_2C_2O_4$ 0.015 M in 0.1 N H_2SO_4

Addition of 1,10-phenanthroline in the irradiated solution facilitates the formation of a 1,10-phenanthroline -Fe^{2+} complex which exhibits a strong absorption at 510 nm

Calculations

$$n_{Fe^{2^+}} = \frac{6.023\ x\ 10^{20}\ x\ V_1\ x\ V_3\ x\ A_{510\ nm}}{V_2\ x\ l\ x\ \varepsilon_{510\ nm}}$$

$$Photon\ flux(number\ basis) = \frac{n_{Fe^{2^+}}}{\Phi(\lambda) x\ t\ x\ (1-10^{-A})}\ \text{(photons s}^{-1}\text{)}$$

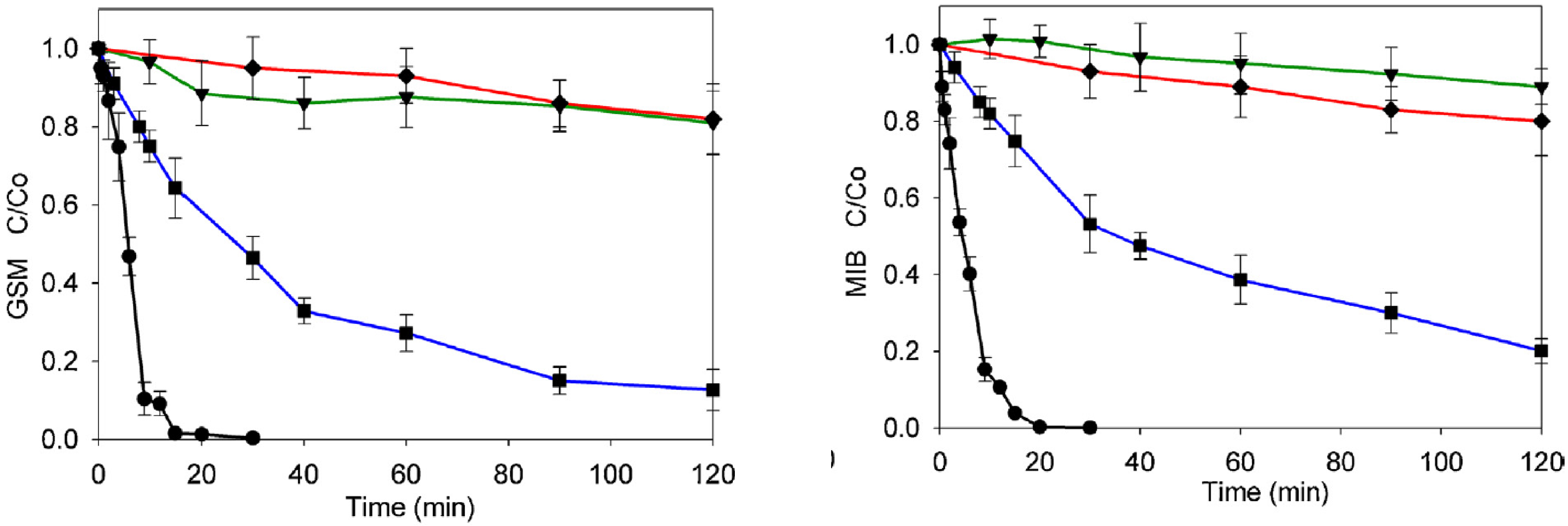
V_1: volume of actinometer solution irradiated (mL)
V_2: the volume of irradiated solution taken for analysis (mL)
V_3: the final volume to which the aliquot V2 is diluted (mL)
l : cell path length (cm)
ε_{510} : 1.11x 10^4 M^{-1} cm^{-1} (molar extinction coefficient of Fe^{2+} complex with 1,10-Phenanthroline at 510 nm)

$\Phi(\lambda)$: quantum yield of Fe^{2+} at wavelength of irradiation (1.25 at 253.7 nm & 1.26 at 366 nm)
t: irradiation time (sec)
N_A: Avogadro constant
A : solution absorbance at 510 nm

All above calculations apply for monochromatic irradiation. In case of polychromatic irradiation, eq. 2 should be modified.

J. Calvert and J. N. Pitts, Jr. Photochemistry, p. 783, John Wiley, New York (1966)

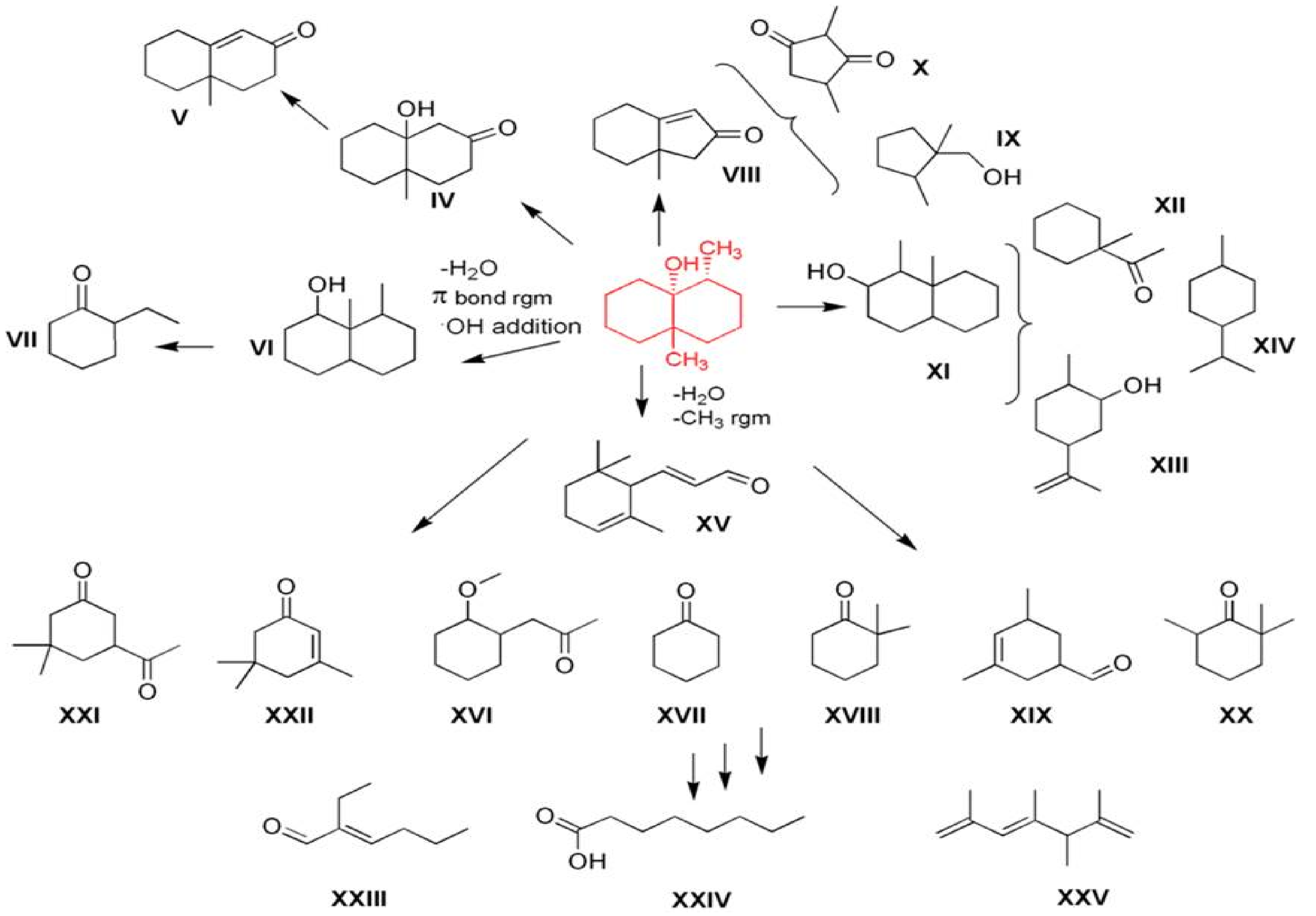
Photocatalytic degradation of Geosmin and 2-methylisoborneol using TiO_2



Photocatalytic degradation of GSM & MIB (1 mg L^{-1}) under UV-A (max= 365 nm) irradiation with TiO_2 (200 mg L^{-1}) in the presence and absence of scavengers. Conditions (♦) Photolysis, (●) No scavenger, (▼) KBr and (■) TBA (tert-butyl alcohol).

T. Fotiou et al., J. Photochem. Photobiology 286 (2014) *1–9;* http://dx.doi.org/10.1016/j.jphotochem.2014.04.013

Intermediate products of GSM photocatalytic degradation using TiO_2 and UV-A



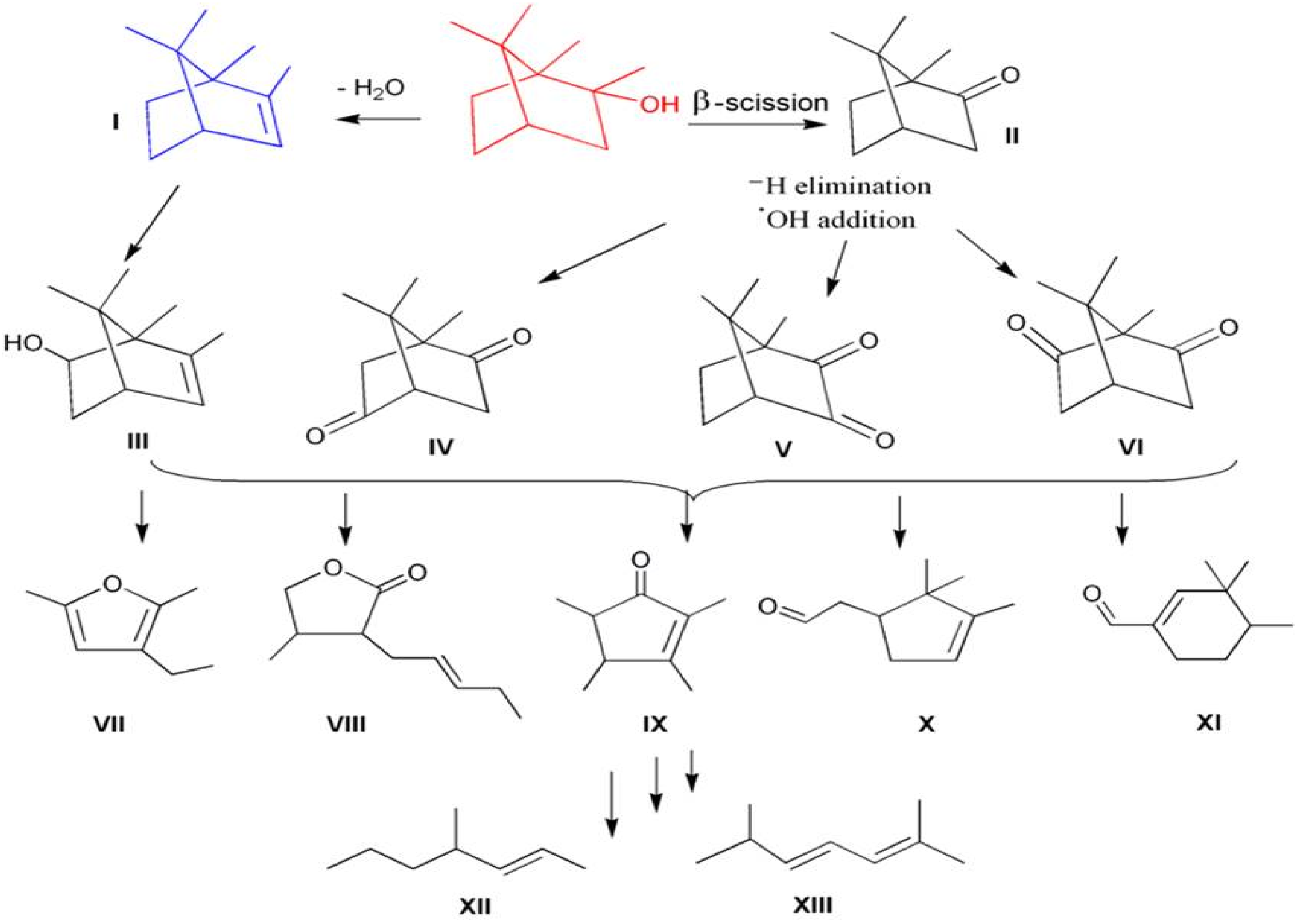
GSM: Geosmin

Identification of intermediate products using GC-MS

The presence of oxygenated degradation products suggests the involvement of OH radicals in the reaction mechanism

T. Fotiou et al., J. Photochem. Photobiology 286 (2014) *1–9;* http://dx.doi.org/10.1016/j.jphotochem.2014.04.013

Intermediate products of MIB photocatalytic degradation using TiO_2 and UV-A



Identification of intermediate products using GC-MS

MIB: 2-methylisoborneol

T. Fotiou et al., J. Photochem. Photobiology 286 (2014) *1–9;* http://dx.doi.org/10.1016/j.jphotochem.2014.04.013

Conclusions

- Light activation of TiO_2 involves the production of reactive oxygen species ($^{\bullet}OH$, $O_2^{\bullet-}$, $^1O_2$, $HO_2^{\bullet-}$) that react with solutes through oxidative or reductive pathways.

- Recombination of photogenarated electrons and holes decrease the photocatalytic activity.

- Many different parameters (e.g. initial concentration of substrate, catalyst loading, pH, incident irradiation, presence of oxygen, adsorption, etc.) influence the photocatalytic degradation of pollutants, so evaluation of the catalyst performance is a difficult task.

- The photon flux of the incident radiation in the photolysis cell can be calculated with ferrioxalate dosimeter, by measuring the production of Fe^{2+} by photometry

- Photocatalytic degradation of organic compounds involves a large number of known and unknown transformation products.

- TiO_2 photocatalysis can be effective for water purification from a plethora of organic pollutants belonging to different chemical classes.

Thank you for your attendance!!!