Photoelectrocatalytic Treatment and By-Product Formantion

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Istanbul University at a Glance

- **The Oldest University of Turkiye (Established in 1453)**
- **Academics**
  Faculties: 20
  Schools: 3
  Vocational Higher Schools: 6
- **Students:**
  Associate Degree: 9000 Students
  Undergraduate: 65000 Students
  Graduate: 14500 Students **Total: 88500 Students**
- **Nobel Prizes: (Orhan Pamuk)**
  1 Nobel Prize in Literature
- **Campuses:**
  12 Campuses

Coloboration with Industry

- EPA Treatment Coop. (SMEs), Istanbul
- ENTA Treatment Coop.(SMEs), Istanbul
- Sunholding Research Center Inc. (Textile) Izmir.
- Yunsa Inc. (Textile Industry) Cerkezkoy, Istanbul
- Akin Textile Inc. Luleburgaz
- TISAN Inc. Izmir. www.tisan.net , the garbage container Truck" (SMEs)
- GUMUSSU Treatment Camp. (Denizli, Turkiye)
- Karboy Textile, Kahramanmaras, Turkiye
- 5 Other Textile Industries

Organization

http://rr.istanbul.edu.tr/

International Projects

TUBITAK “Deposition of TiO_2 ve Metal Doped TiO_2 Nanoparticles for the self-cleaning and antibacterial cotton textile; Funded by TUBITAK 260.000$

LEONARDO DA VINCI, Community Vocational Training Action Program, WASTE TRAIN: Vocational Training, Education, Conveying Information on up to data Waste Management Practices Makers/Staff Involved Waste Management. *Partner 550.000 €*

MIUR Italy Collobration Project, -Evaluation of Advanced Oxidation Processes for Wastewater Treatment and Disinfection, and Reuse. MIUR Project (Italy, Greece, Turkey, Morocco), *Partner 80.000 €*

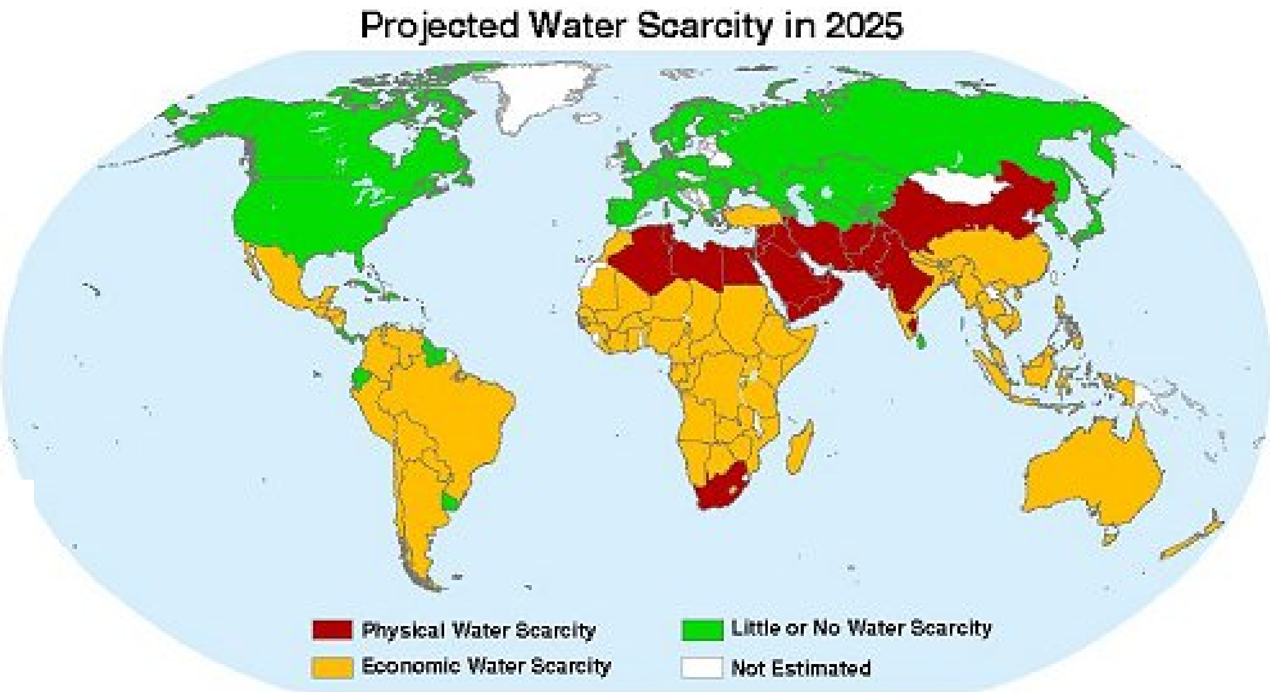
NATO Collaborative Linkage Grant, (€ 15.400, # EST.CLG.980506), “Evaluation of alternative water treatment systems for obtaining safe drinking water in three countries”

Cost action, ICTAG C-075, “Environmental Pollution Effects and Best Available Integrated Technologies for Textile Industry Preparation, Dyeing and Finishing Process Chemicals”, 80.000 $

Industrial Projects

- ***SERTAS Alaminium INC., EPA Treatment Company (SME),*** "Recovery of liquors and metals from Aluminum Industry for zero discharge".
- ***Sunholding Research Center Inc.*** Izmir. "Application of Advanced Oxidation and Membrane Separation Treatments for the Reuse of Salt and Textile Process Wastewater: 480.000$.
- ***Yunsa Textile Inc.*** Cerkezkoy, Istanbul, "Development of Selfcleaning Properties on the wool textile" 84.000$.
- ***Akin Textile Inc. Luleburgaz***. "Integrated Membrane Treatment for treatment and reuse of the segregated dyeing and mercerizing process waters" 850.000$.
- ***Gumussu Treatment Inc. (SME)*** "Integrated Membrane Treatment for the Advanced Treatment of the Biologically Treated Wastewaters and Reuse of Membrane Brine in Textile Processes" 240.000$
- ***TISAN Inc. Izmir (SME)*** "Development of wastewater treatment and reuse system for the garbage container washing truck" 240.000$.

Water Shortage



New water resources: Polluted water and treated wastewaters

- Remaining refractory organics
- High TDS level is not suitable for potable, industrial and agricultural uses.
- Still not safe (due to the pathogens, micropollutans, many different toxic chemicals)
- Hazardous By-Products (Bromate, THM, HAAs......)
- The cost of advanced treatment system is high

Solutions??

Today, it is critical:

to reduce salinity (Desalination)

to decrease refractory organic levels of waters/wastewaters (advanced treatment)

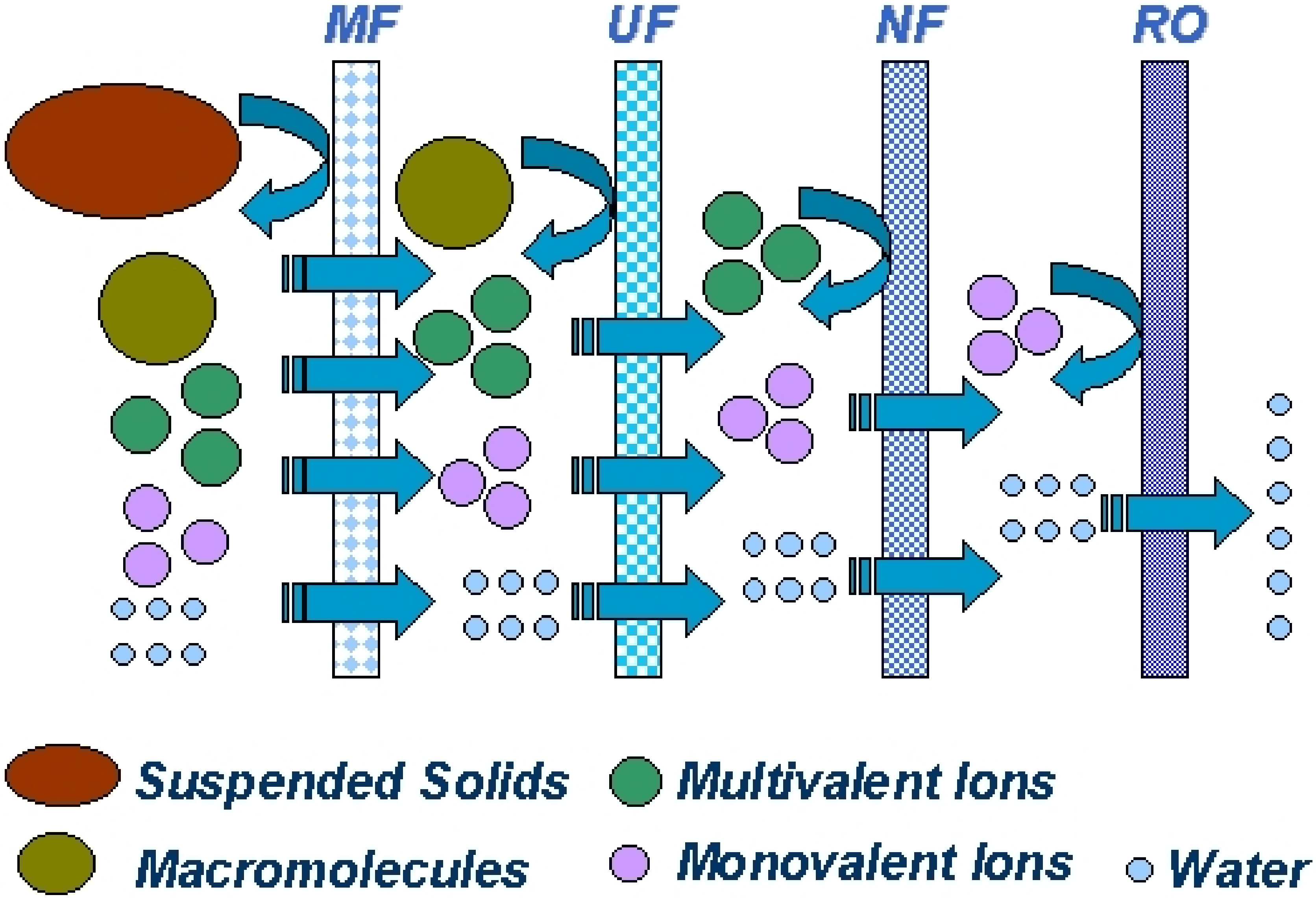
to reduce treatment cost

to develope energy free treatment and disinfection Tech. (Solar Systems)

Desalination

- Membrane Based Processes
- Solar Desalination Systems

Types of Membrane



Membrane processes for solution

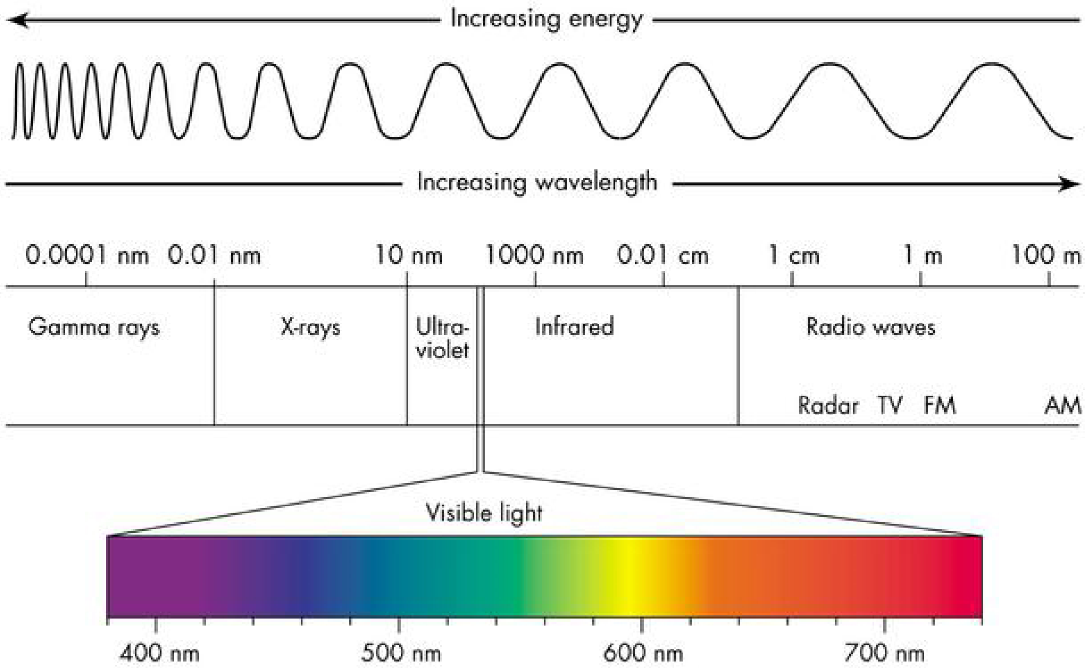
- Solar desalination is expensive
- Membrane treatment is the applicable solution. But
  – High energy cost of membrane system
  – Membrane fauling problems
  – Membrane brine

What should we do for an applicable UV/Solar system?

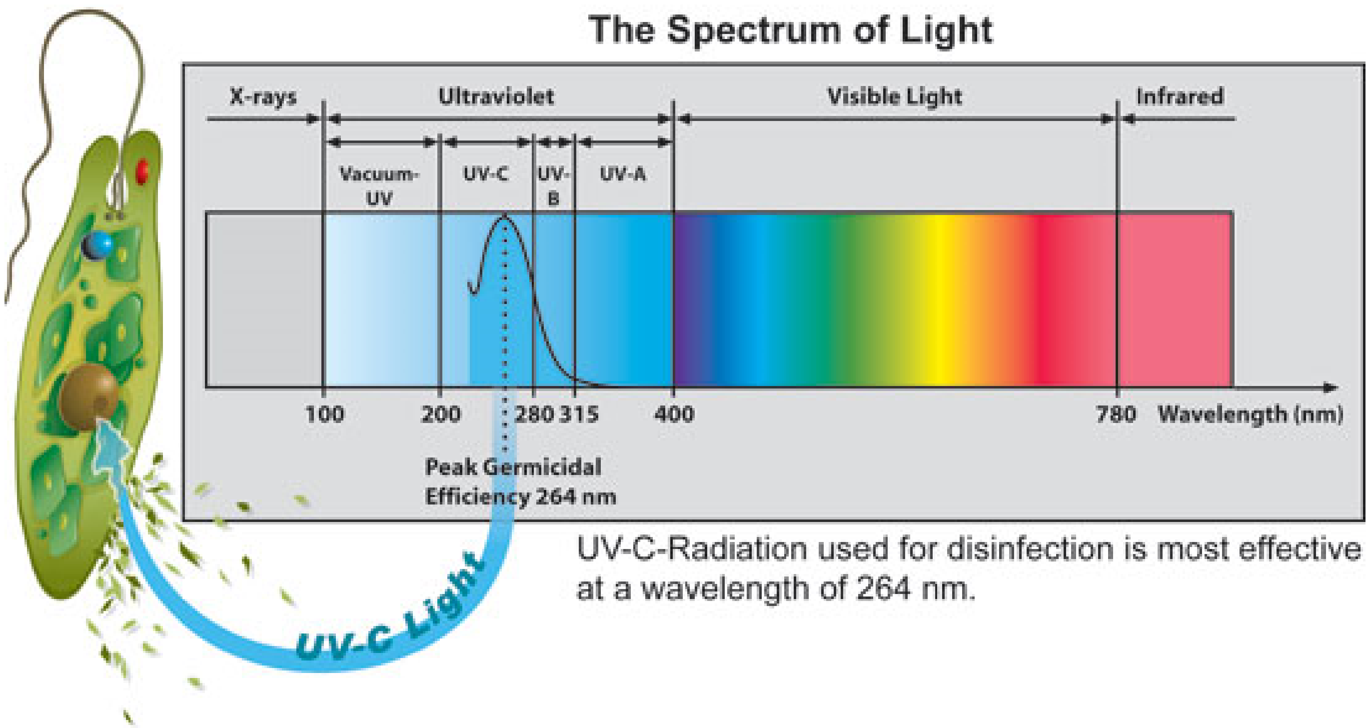
1. Enhancement of UV technologies
2. Development of efficient photocatalyst
3. Development of new photocatalytic systems

1. Enhancement of UV technologies

- Wavelength-Photolysis



Disinfection with photolysis



UV-C-Radiation used for disinfection is most effective at a wavelength of 264 nm.

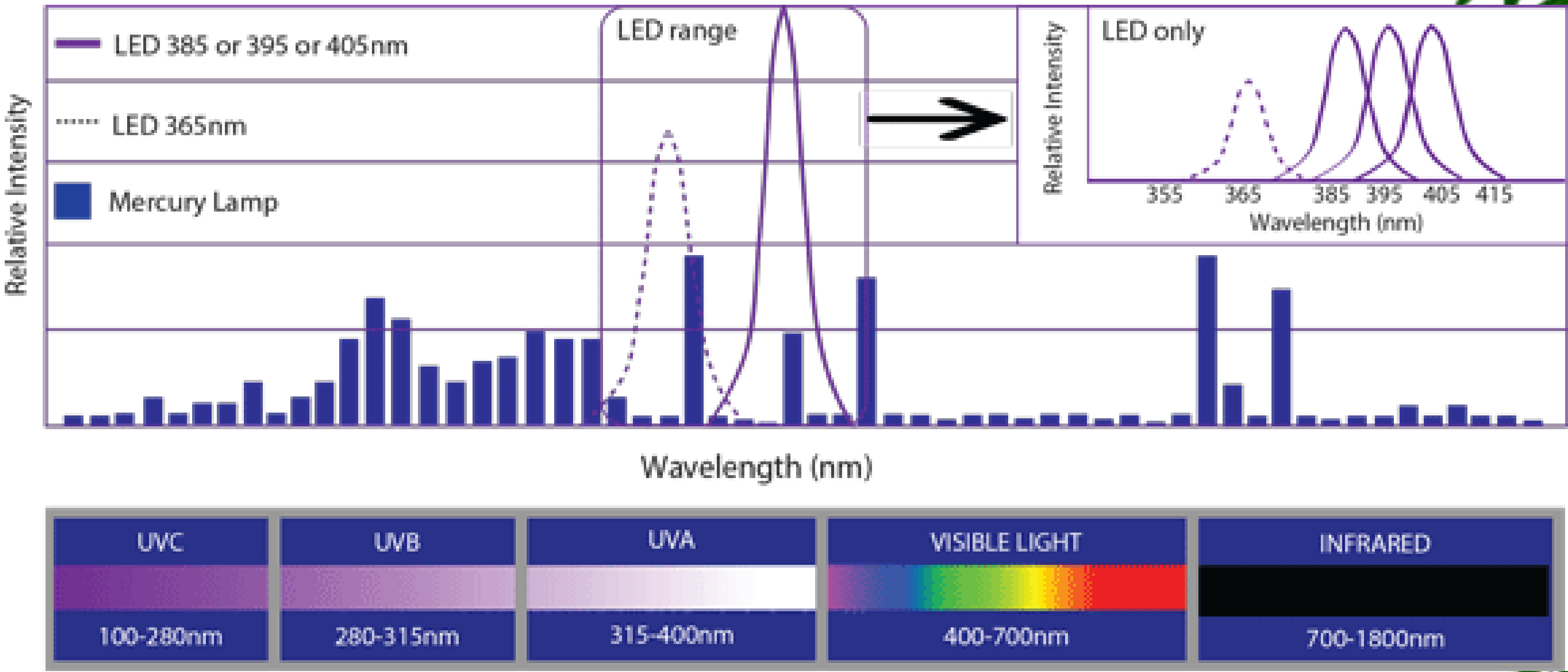
LED UV disinfection and Treatment

- One important aspect is to have low-energy consuming systems. In that regard, the UV disinfection using LEDs (Light-Emitting Diode) seems a promising technology.
- The market for water disinfection worldwide could be huge. LEDs are not yet competitive with legacy technologies, but there is hope that they could be within the decade

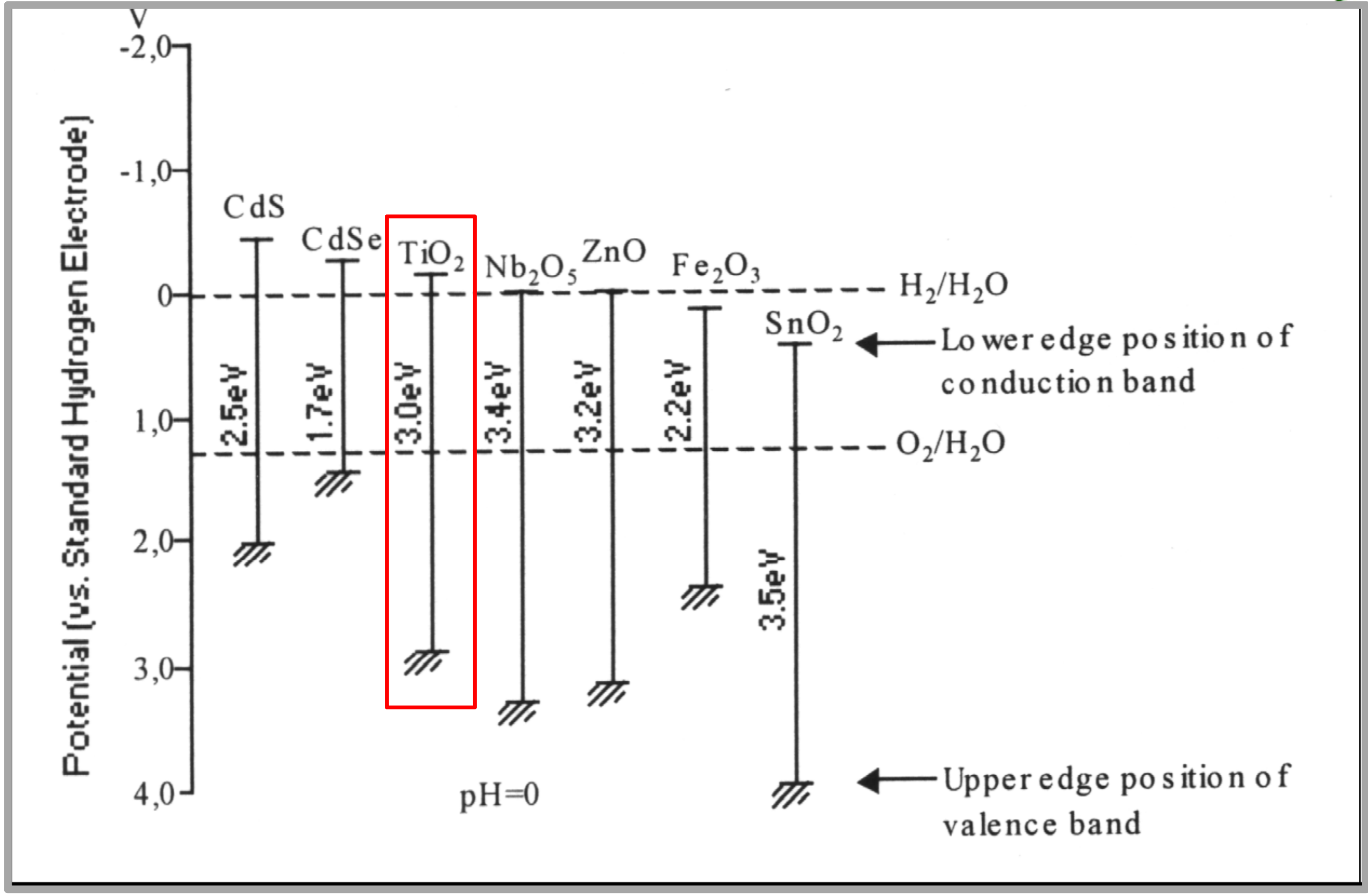
Basic advantages of LED Light

- **Energy efficient -** LED's are now capable of outputting 135 lumens/watt
- **Long Lifetime** - 50,000 hours or more if properly engineered
- **No warm-up period** - LED's light instantly – in nanoseconds
- **Not affected by cold temperatures** - LED's "like" low temperatures and will startup even in subzero weather
- **Directional** - With LED's you can direct the light where you want it, thus no light is wasted
- **Environmentally friendly** - LED's contain no mercury or other hazardous substances

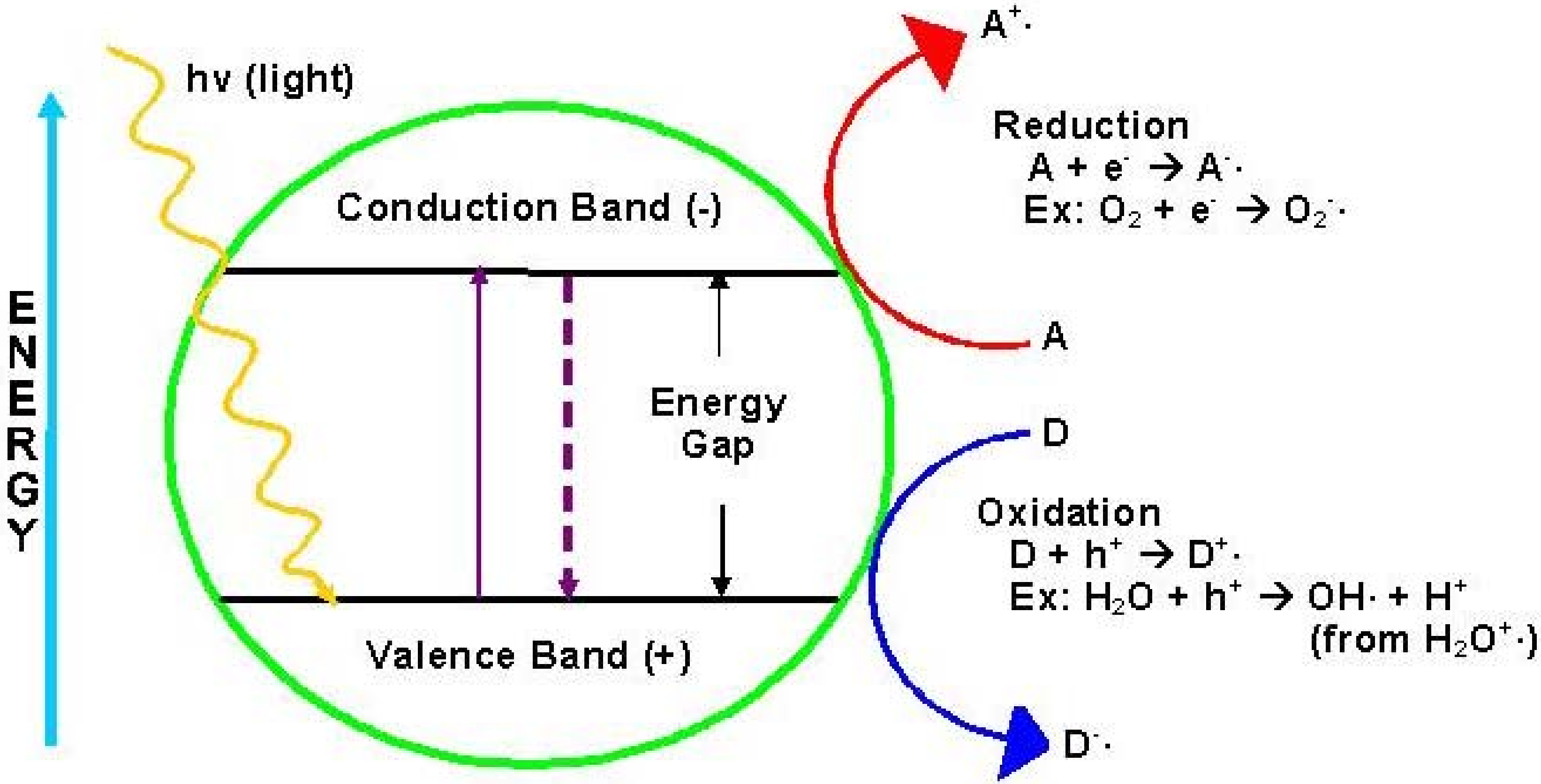
UV light Tech.



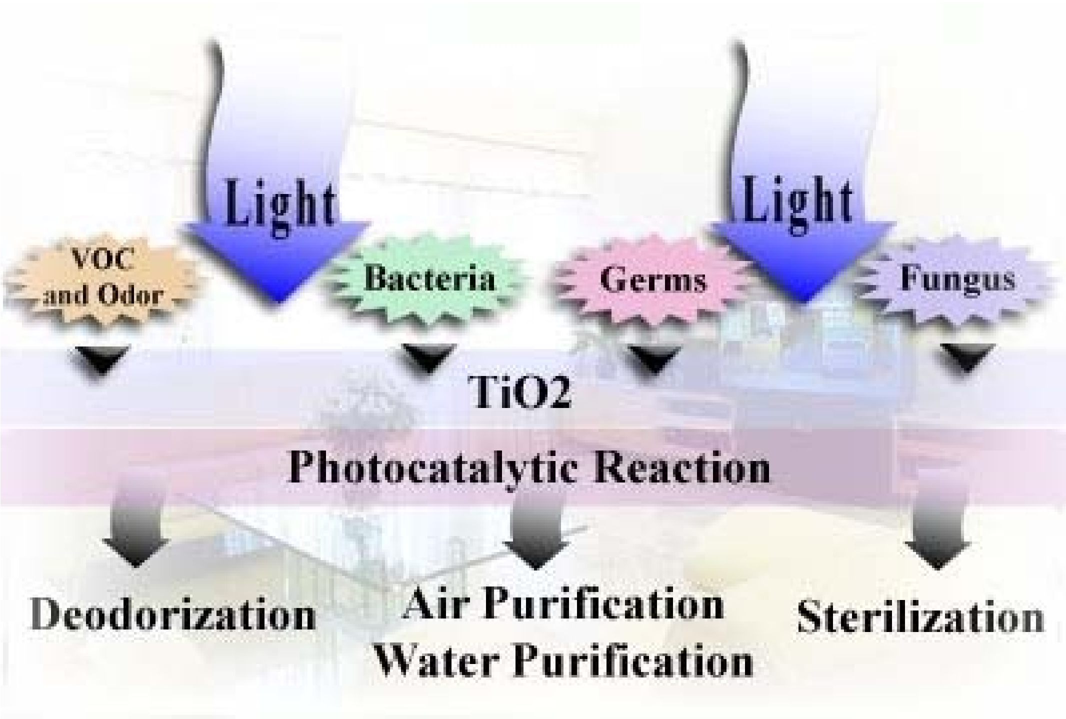
2. Development of efficient photocatalyst

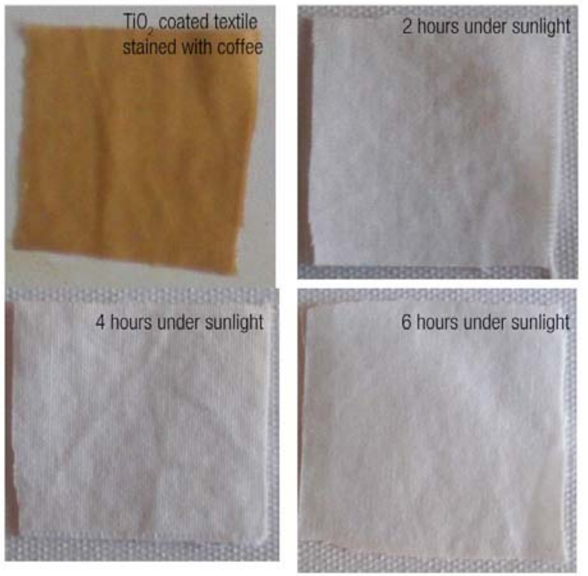


Photocatalysis



Photocatalysis can be used for?





TiO_2 photocatalysis electon-hole reactions

- $TiO_2(e^- - h^+) \rightarrow e^- - h^+$
- e^- reactions;
  - $O_2 + e^- \rightarrow O_2^-$
  - $O_2 + 2e^- + 2H+ \rightarrow H_2O_2$
  - $H_2O_2 + e^- \rightarrow HO\bullet + OH^-$
  - $H_2O_2 + hv \rightarrow 2HO\bullet$
- h^+ reactions;
  - $H_2O + h^+ \rightarrow HO\bullet + H^+$
  - $OH^- + h^+ \rightarrow HO\bullet$

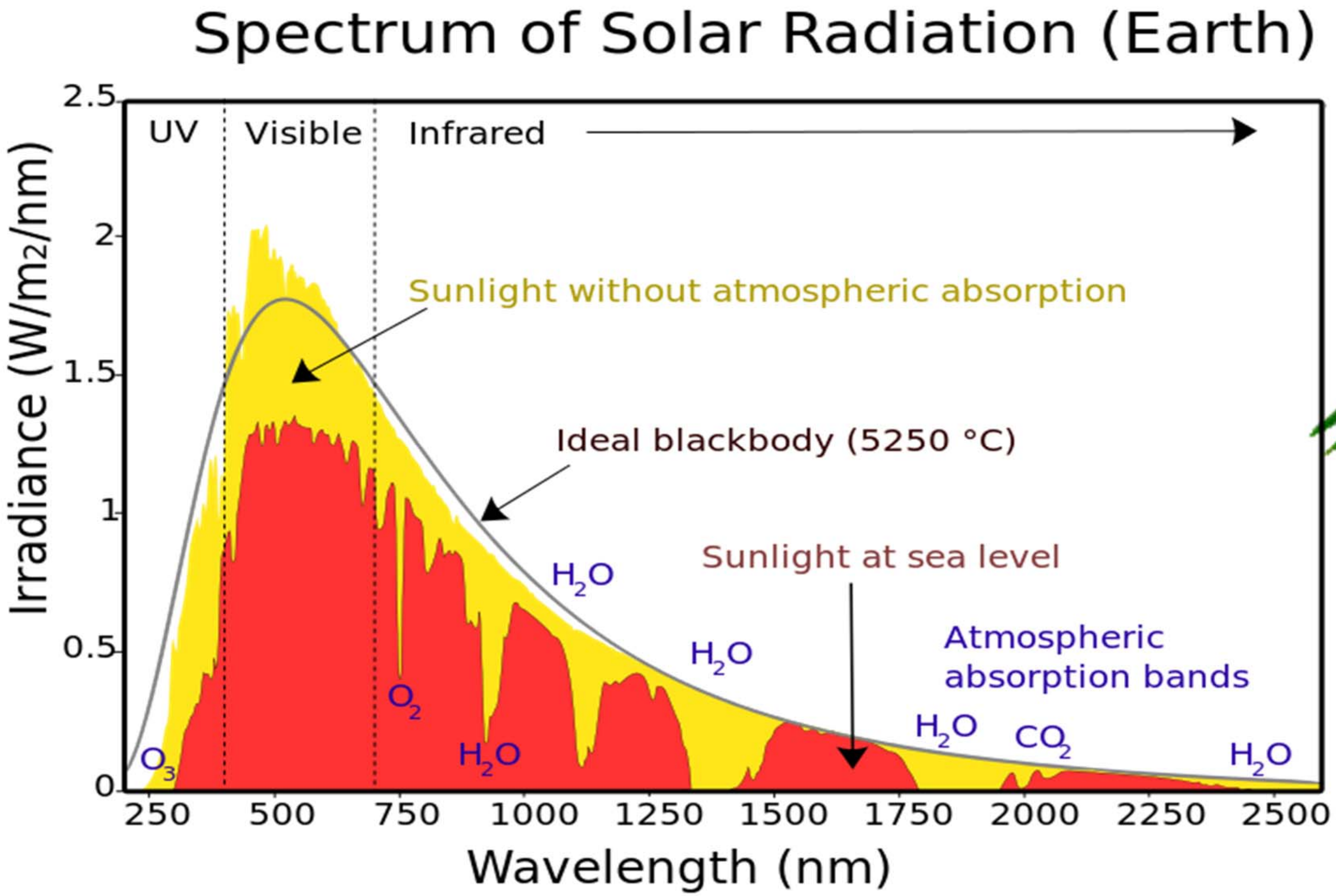
Why solar treatment is not applicable??

- Low quantum efficiency
- Separation of NPs from solution is difficult
- Recombination of elecron-hole pairs reduce photocatalytic efficiency
- Quenching of anode/cathode products decreases photocatalytic treatment.

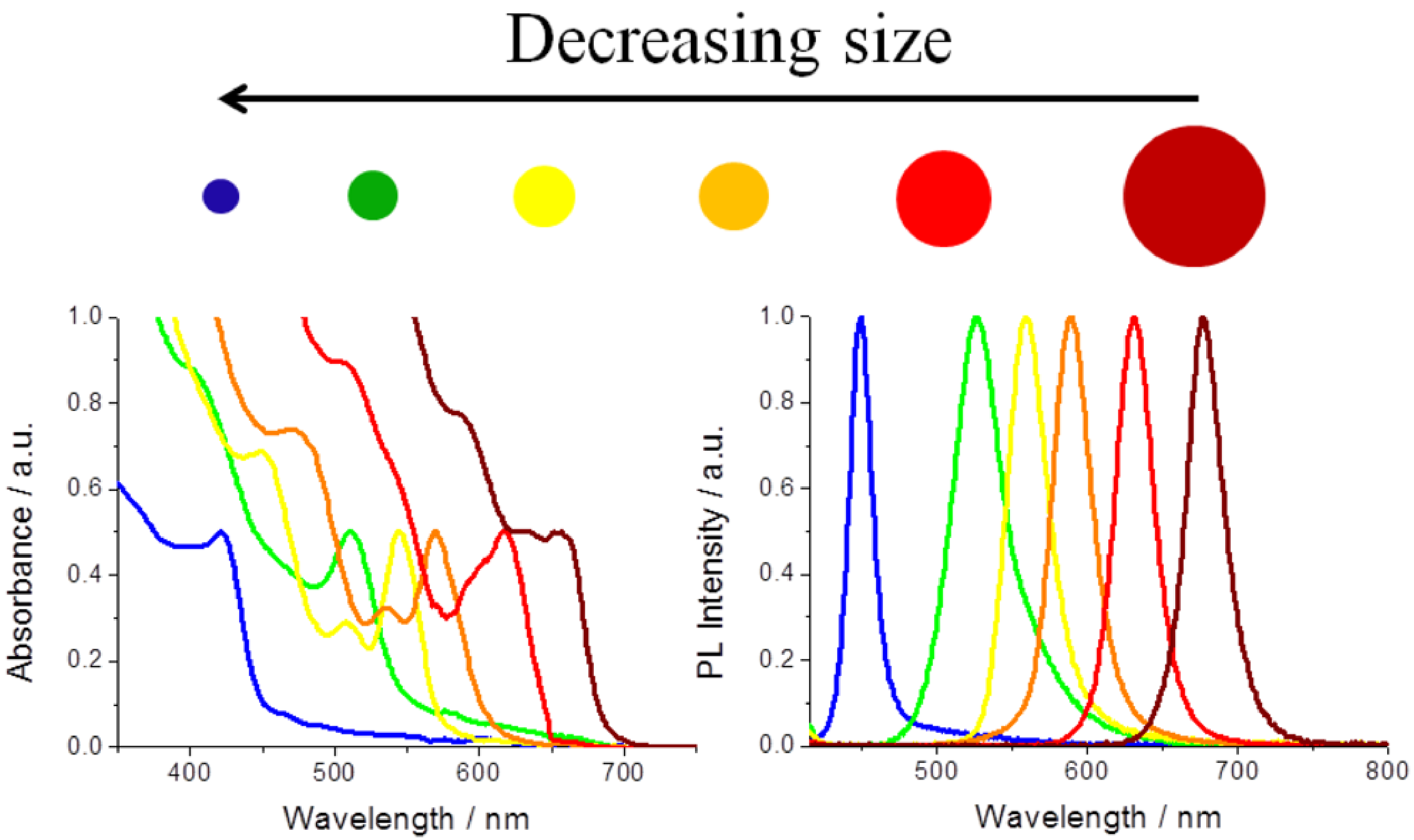
Lets do something but what?

- **Shift wavelength from UV to visible**
- **Increase quantum efficiency (Develope more efficient catalyst)**
- **Immobilization of NPs**
- **Decrease recombination of electron-hole pair** (photoelectrocatalytic system)
- **Decrease quenching of products (Seperation of hole-electron reactions, PEC cell)**
-

Sunlight?


Spectrum of Solar Radiation (Earth)
UV
Visible
Infrared
Sunlight without atmospheric absorption
Ideal blackbody (5250 °C)
Sunlight at sea level
Atmospheric absorption bands
O_3
O_2
H_2O
CO_2
Irradiance (W/m2/nm)
Wavelength (nm)
2.5
2
1.5
1
0.5
0
250
500
750
1000
1250
1500
1750
2000
2250
2500

Hybrid Catalysts: Absorption spectra of doped and differently sized nanocrystals (CdSe)



(Y. Yuan and M. Krüger *Polymers* **2012**, *4*(1), 1-19)

3. Development of new photocatalytic systems

- Immobilization of semiconductor
- Develope different reactor system

We are talking about

Photoelectrocatalytic (PEC) System

PEC process

- PEC process that first time introduced in 1972 by Fujishima and Honda for splitting of water
- In recent years, electron and hole reactions were separated in the PEC system for treatment of water (Vinodgopal et al., 1994; Selcuk et al., 2003).This provided great advantage for the disinfection and treatment of waters.

- PEC is also known to be a combination of photocatalytic and electrochemical process.
- In this system *insignificant* electrical potential is used to decrease hole-electron recombination in the bulk of photocatalyst.

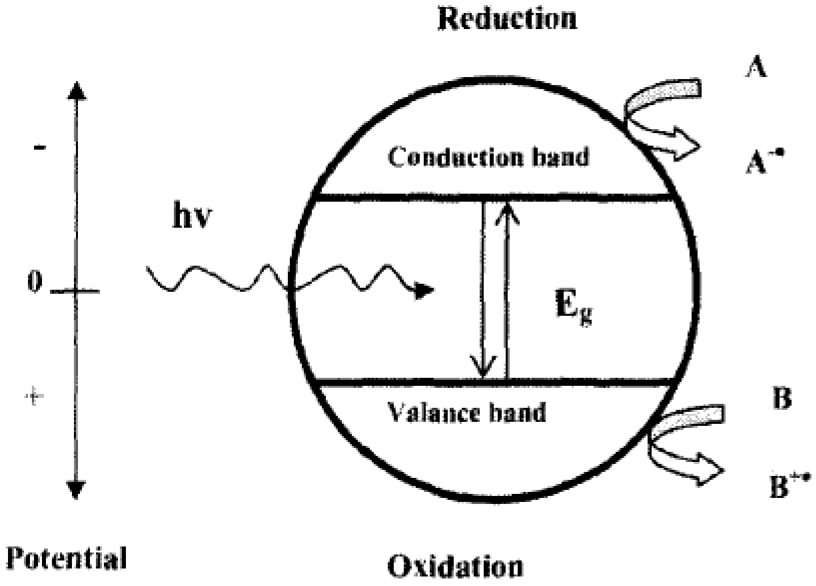


Fig. 1. Oxidation and reduction in the photocatalytic process (A, reducible and B, oxidizable species).

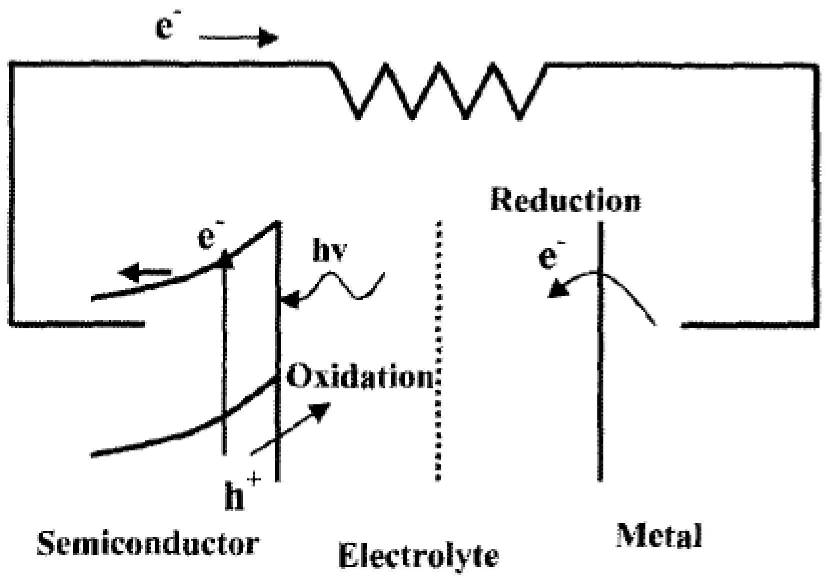


Fig. 2. Charge separation in the PEC system.

ELSEVIER

DESALINATION

Desalination 176 (2005) 219–227

www.elsevier.com/locate/desal

Effect of pH, charge separation and oxygen concentration in photoelectrocatalytic systems: active chlorine production and chlorate formation

Huseyin Selcuk[a]*, Marc A. Anderson[b]

PEC Reactor

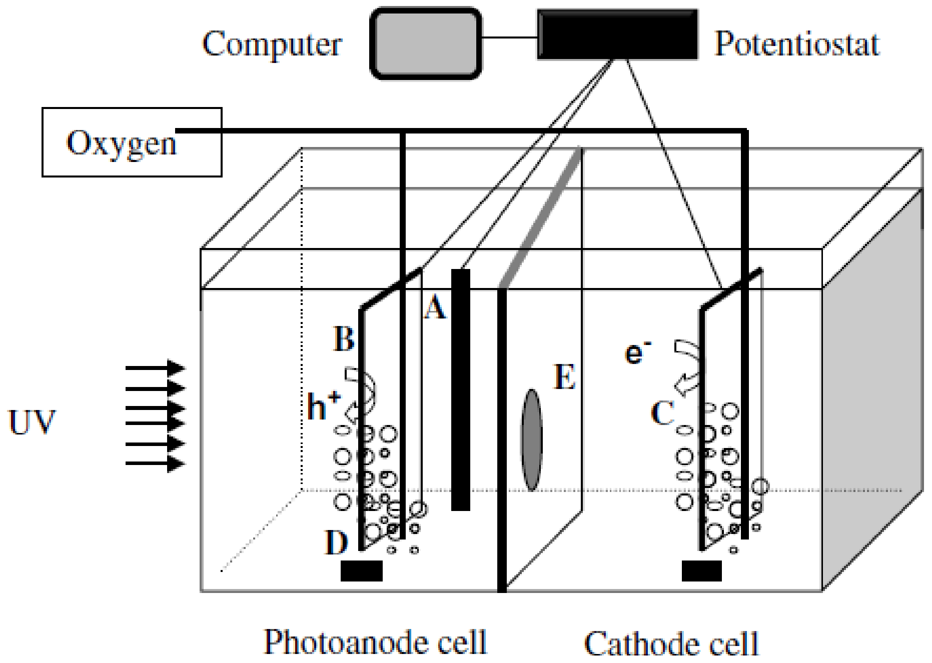


Fig. 1. Diagram for the reactor system for the photoelectrocatalytic reaction: (A) reference electrode (saturated calomel electrode); (B) photoanode TiO_2 coated electrode; (C) cathode electrode; (D) stirring bar; (E) Nafion 117 membrane.

TiO_2 photocatalysis electon-hole reactions

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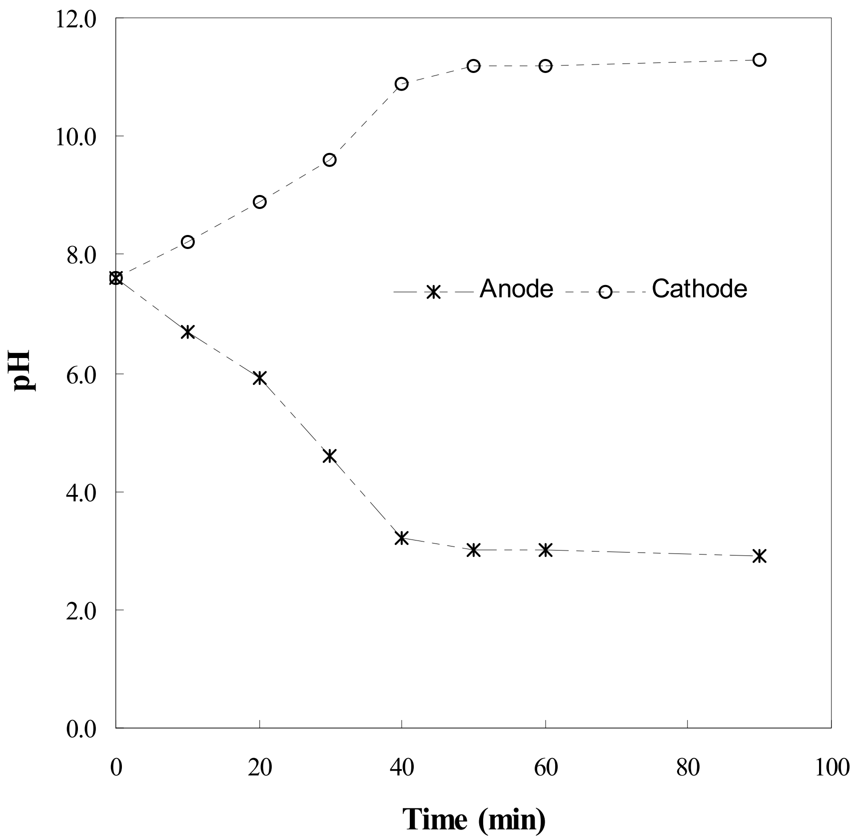
- h^+ reactions;
  - $H_2O + h^+ \rightarrow HO\bullet + H^+$
  - $OH^- + h^+ \rightarrow HO\bullet$


12.0
10.0
8.0
6.0
4.0
2.0
0.0
pH
0
20
40
60
80
100
Time (min)
Anode
Cathode

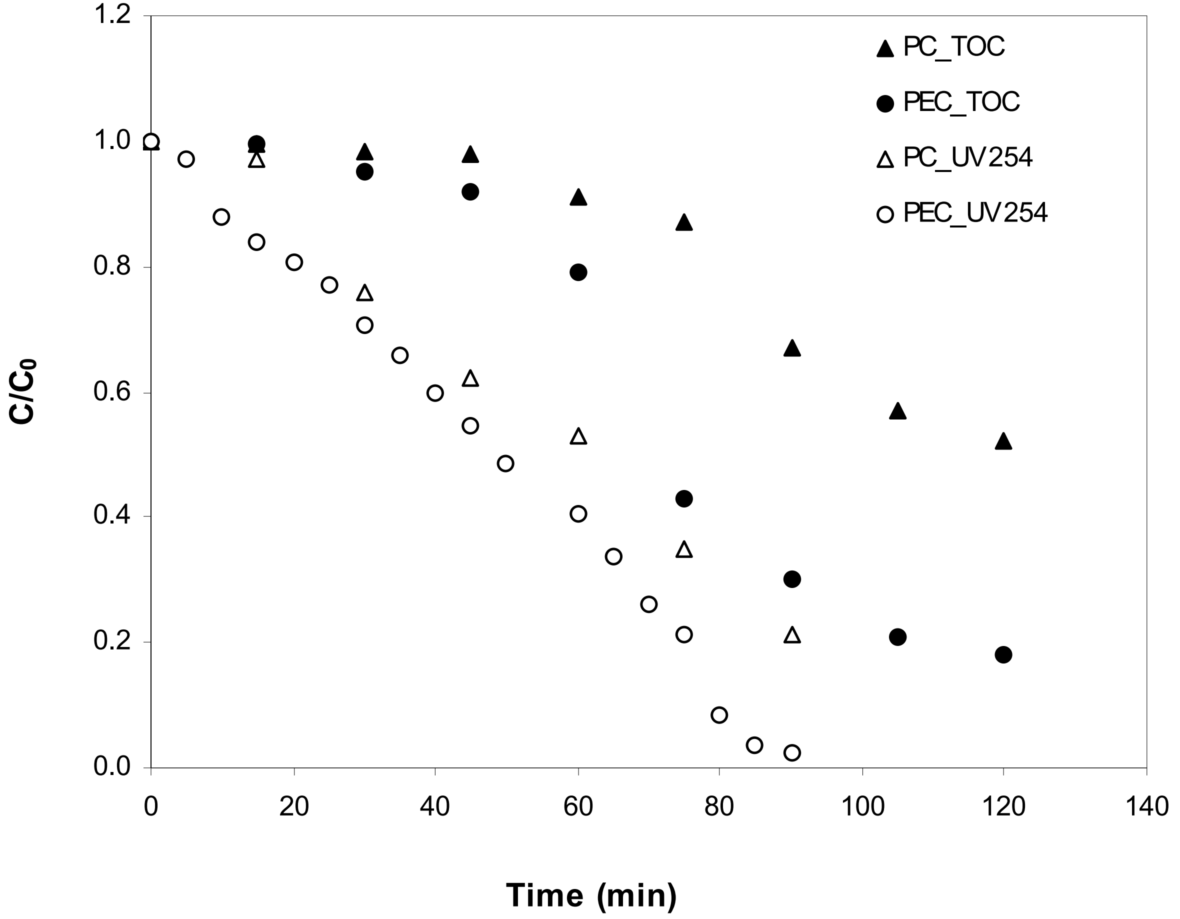
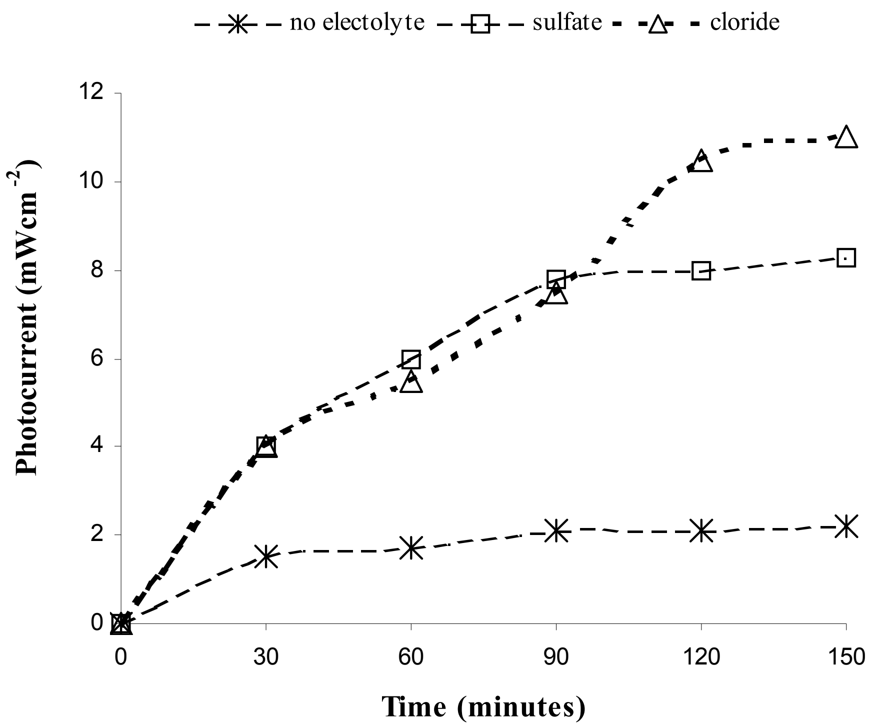


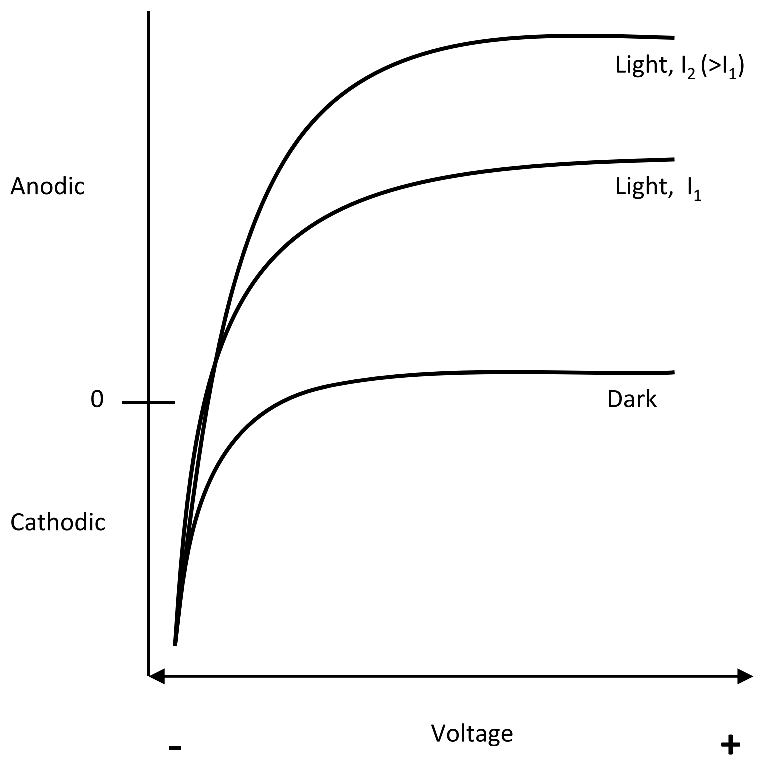
Figure: PEC and PC removal of 25 mgL^{-1} HA in 1.25x10^{-2} M NaCl solution using a titanium dioxide thin-film electrode.

Variables of PEC Treatment

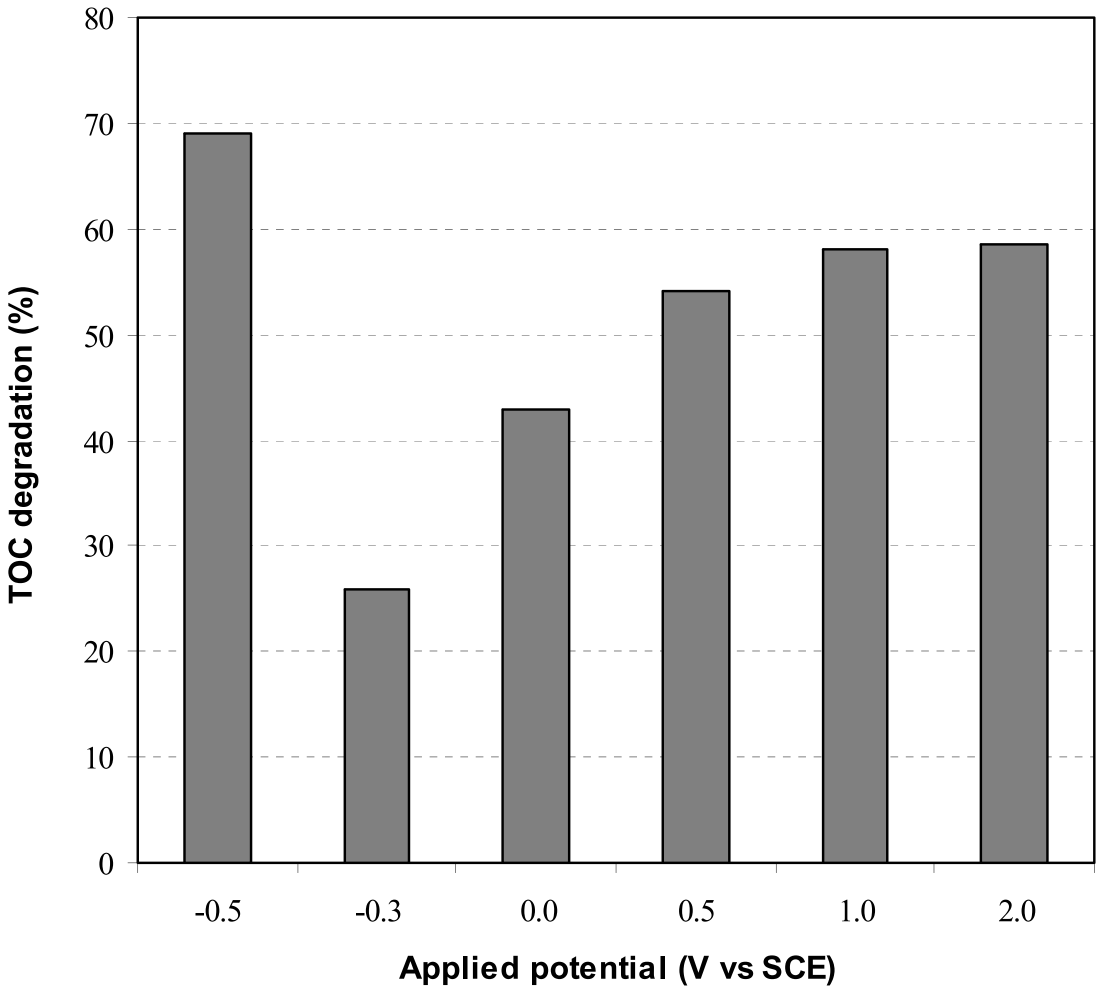
- Electrolyte



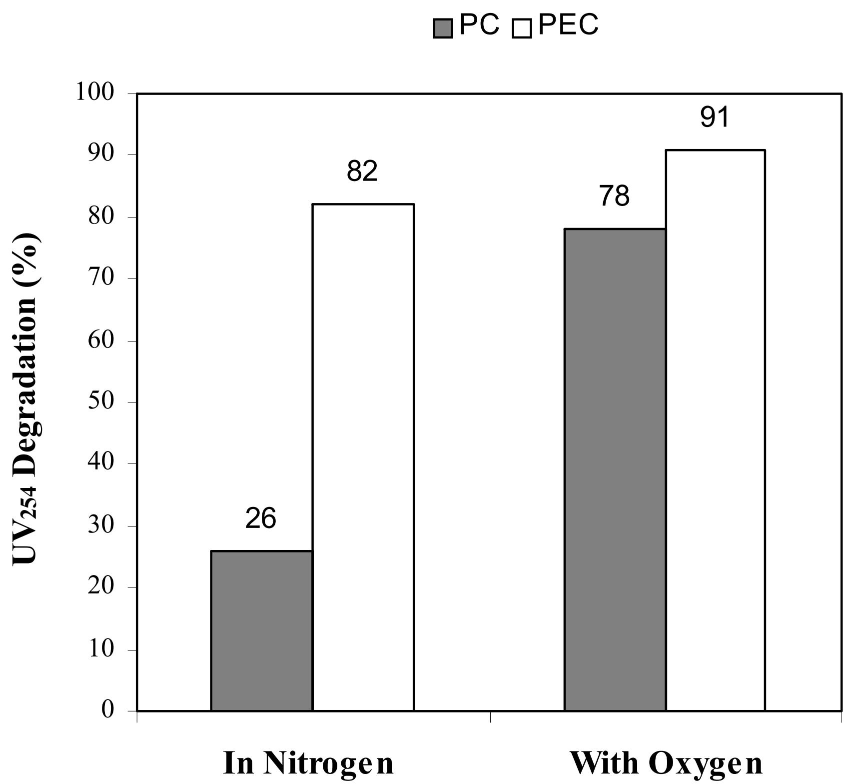
Light intensity



Applied potential



Oxygen



PC
PEC
UV254 Degradation (%)
100
90
80
70
60
50
40
30
20
10
0
26
82
78
91
In Nitrogen
With Oxygen

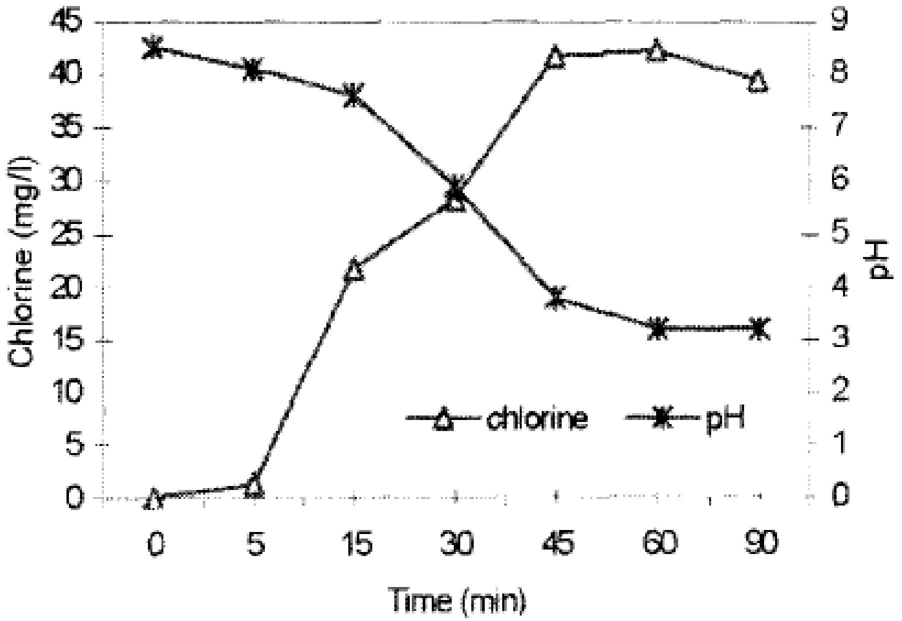
Chlorine generation in a PEC system

Selcuk H. and Anderson M. Desalination 176 (2005) 219-227

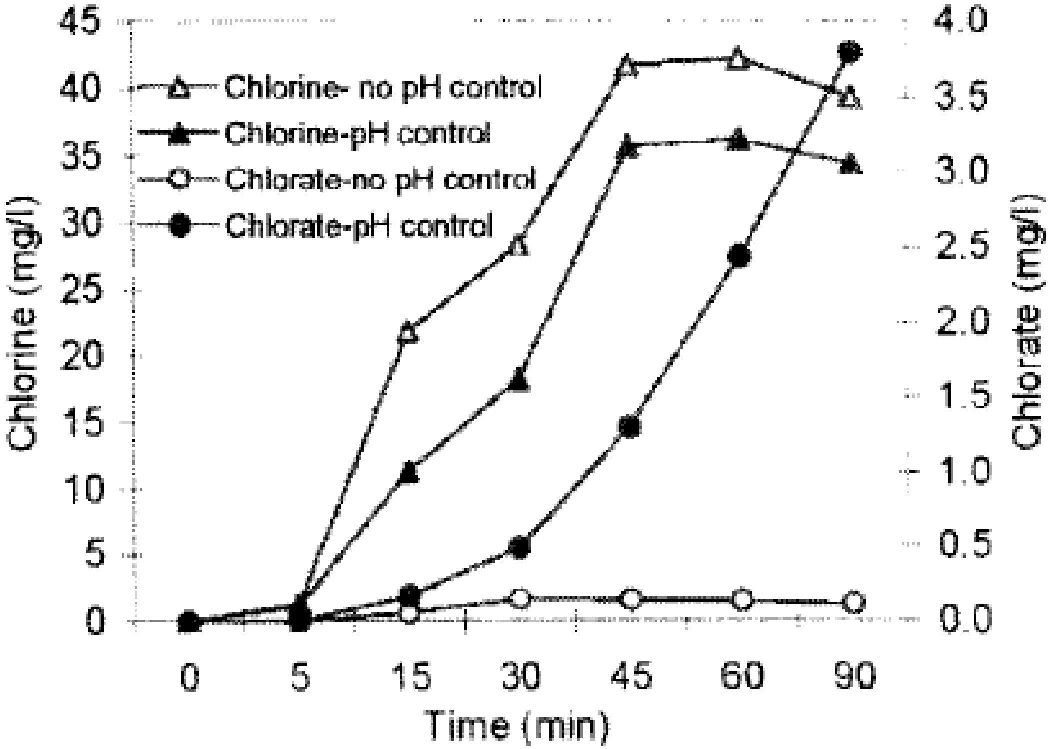
$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$Cl_2 + H_2O \rightarrow OCl^- + H^+ \qquad pK_h = 3.2$$

$$HOCl \rightarrow OCl^- + H^+ \qquad pK_a = 7.5$$

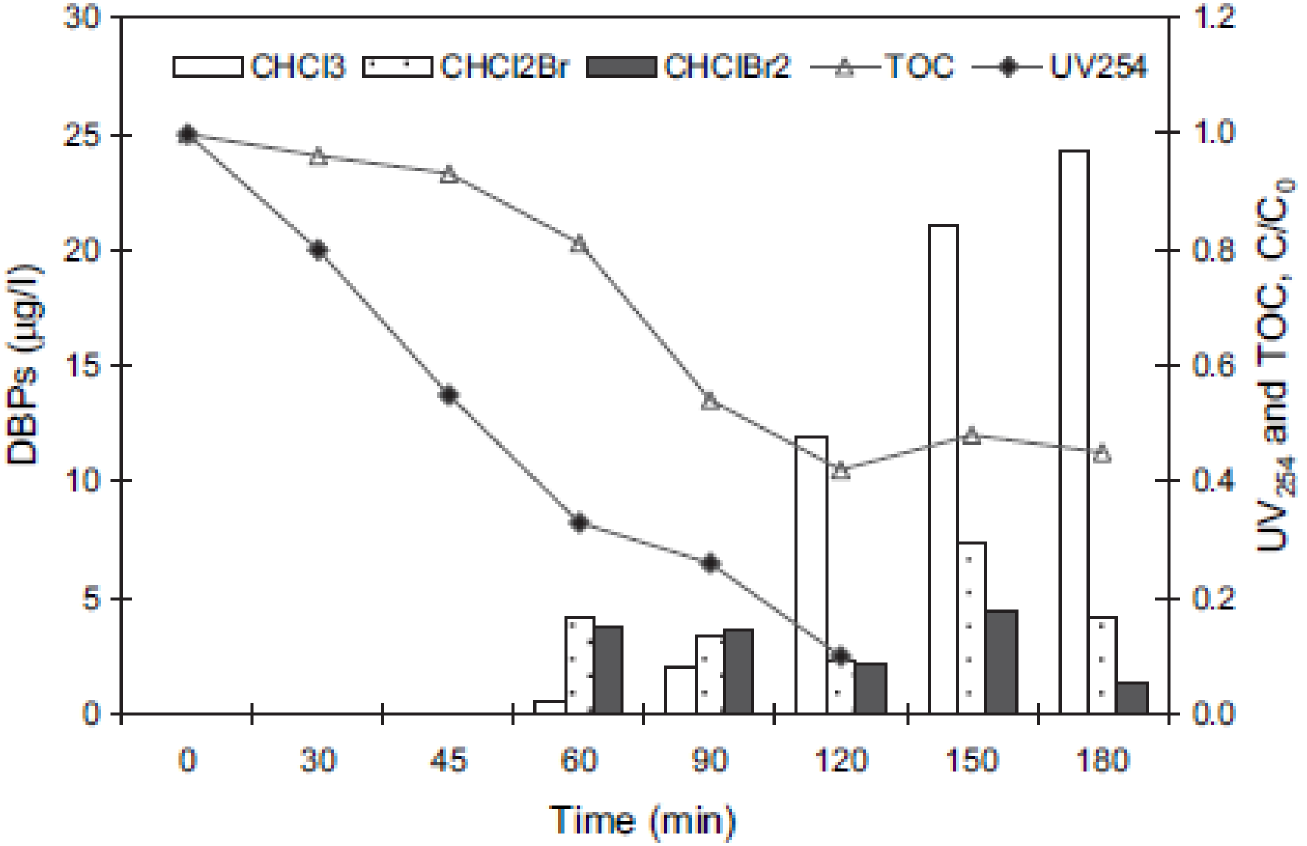


Chlorate Formation



Formation of THMs

Selcuk H., Water Research 44 (2010) 3966-3972



oxidation of halogens

$$2Br^- \rightarrow Br_2 + 2e^-_{CB}$$

$$Br_2 + H_2O \leftrightarrow HOBr + Br^- + H^+ \quad pK_h = 4.0$$

$$HOBr \leftrightarrow H^+ + BrO^- \quad pK_a = 8.8$$

$$Br^-_{aq} \rightsquigarrow (Br^-_{aq})^* \rightarrow Br^\bullet + e^-_{aq}$$

$$2Br^\bullet \rightarrow Br_2$$

$$3BrO^- \rightarrow 2Br^- + BrO_3^-$$

$$BrO^- + 2HOBr \rightarrow H^+ + Br^- + BrO_3^-$$

Ozone production- Formation of bromate

$$2OH_{ads} \rightarrow O_{ads} + H^+ + e^-$$

$$O_{ads} + O_2 \rightarrow O_3$$

$$O_3 + Br^- \rightarrow O_2 + BrO^- \quad k = 160\ M^{-1}\ s^{-1}$$

$$O_3 + BrO^- \rightarrow 2O_2 + Br^- \quad k = 330\ M^{-1}\ s^{-1}$$

$$O_3 + BrO^- \rightarrow BrO_2^- + O_2 \quad k = 100\ M^{-1}\ s^{-1}$$

$$BrO_2^- + O_3 \rightarrow BrO_3^- + O_2 \quad k > 10^5\ M^{-1}\ s^{-1}$$

$$^{\bullet}OH + BrO^- \rightarrow BrO^{\bullet} + OH^-$$
$$k = 4.0 \times 10^9\ M^{-1}\ s^{-1}$$

$$^{\bullet}OH + HOBr \rightarrow BrO^{\bullet} + H_2O$$
$$k = 2.0 \times 10^9\ M^{-1}\ s^{-1}$$

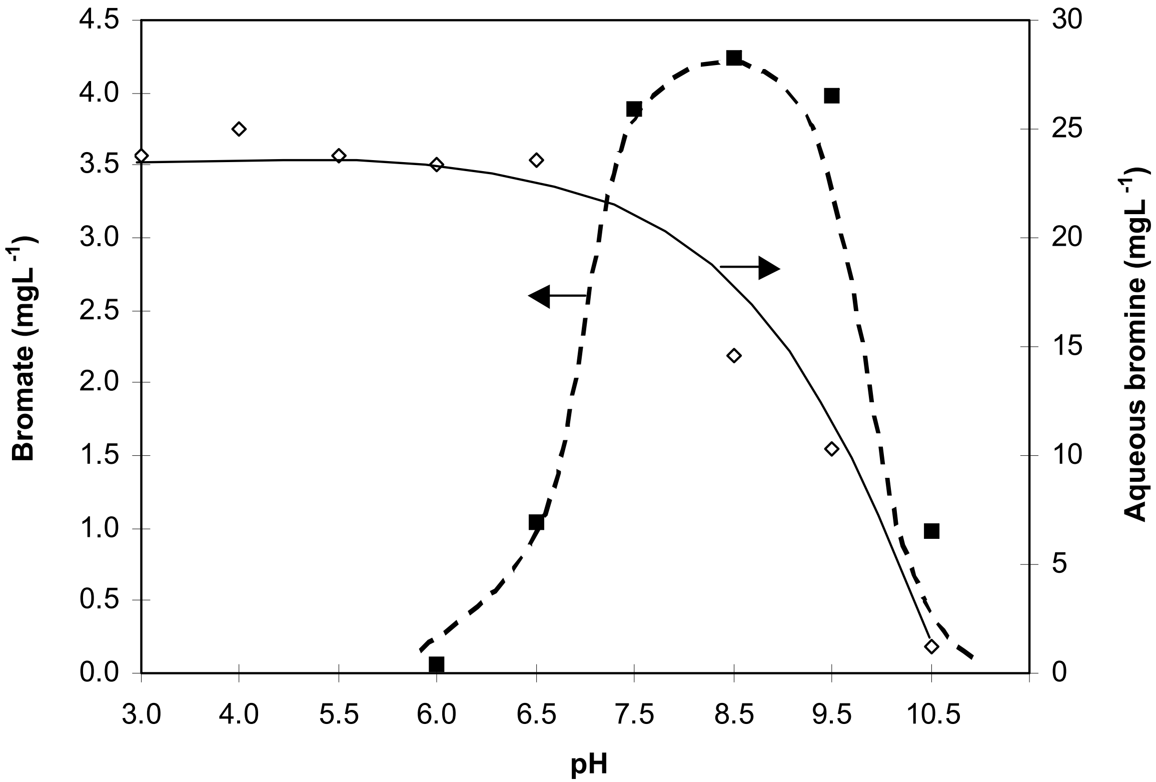
$$2BrO^{\bullet} + H_2O \rightarrow BrO_2^- + OBr^- + 2H^+$$
$$k = 4.9 \times 10^9\ M^{-1}\ s^{-1}$$

$$BrO_2^- + {^{\bullet}OH} \rightarrow BrO_2{\bullet} + OH^-$$
$$k = 2.0 \times 10^9\ M^{-1}\ s^{-1}$$

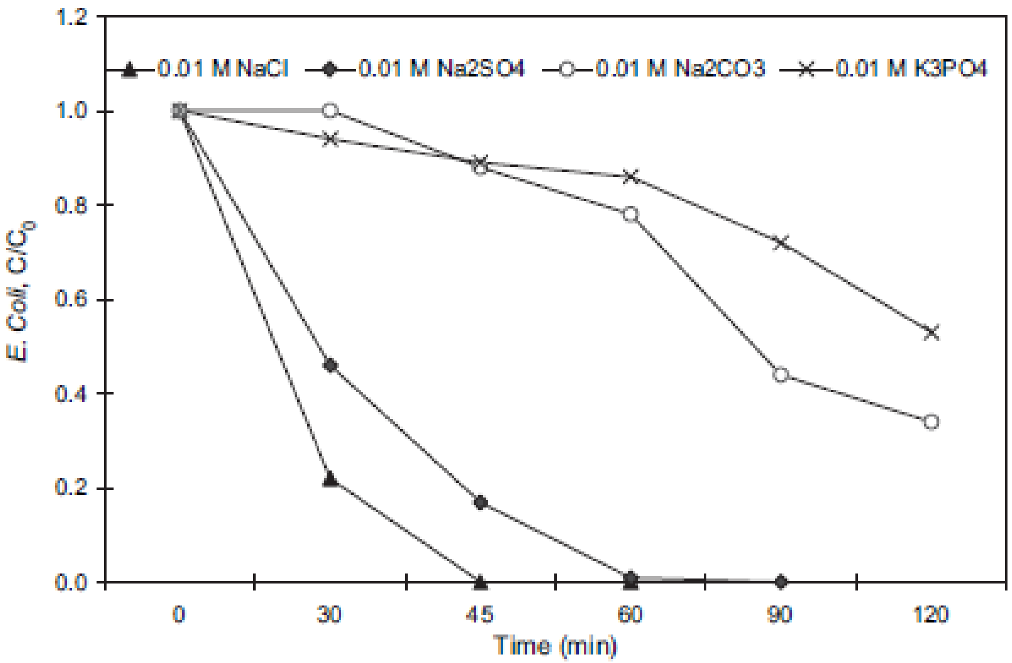
$$2BrO_2{\bullet} \rightarrow Br_2O_4 \quad k = 1.4 \times 10^9\ M^{-1}\ s^{-1}$$

$$Br_2O_4 + OH^- \rightarrow BrO_3^- + BrO_2^- + H^+$$
$$k = 7.0 \times 10^8\ M^{-1}\ s^{-1}$$

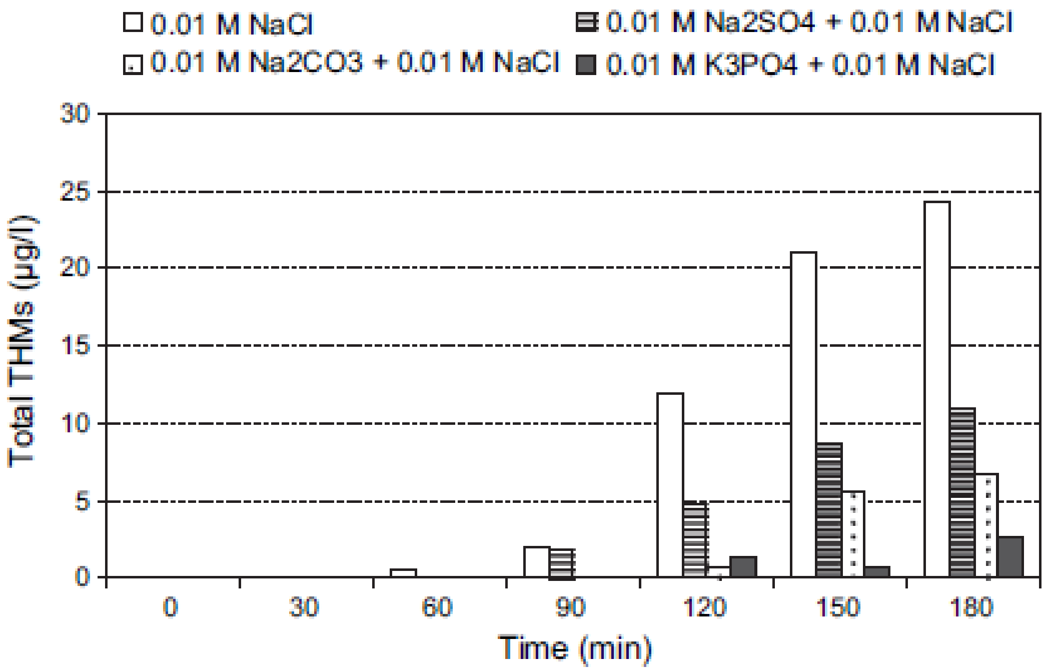
Formation of bromate in a PEC system



Effect of scavengers



Effects of radical scavancers



Conclusions

Anode peroducts	**Cathode products**
ozone	Hydrogen peroxide
Chlorine/chlorate/chlorinated organics	hydrogen
Bromine/bromate/brominated organics	
persulfate	

Possible Advanced oxidation	
Ozone+UV TiO2+UV persulfate+UV	H2O2+UV (OH radical generation)

Problems

- Nanofilms is stable under UV illumination but not under high saline solutions
- Unit efficiency of the immobilized photocatalys is lower than slurry system
- Tech. Readiness level is still low (labscale)