European Twinning for research in Solar energy to (2) water (H2O) production and treatment technologies
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Sol2H2O

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Fast Track School #1

Solar-driven water production & water treatment technologies and brine treatment processes

PALERMO, 10-11.01.2024

Sol2H2O

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Solar water treatment, integration of technologies for WW regeneration

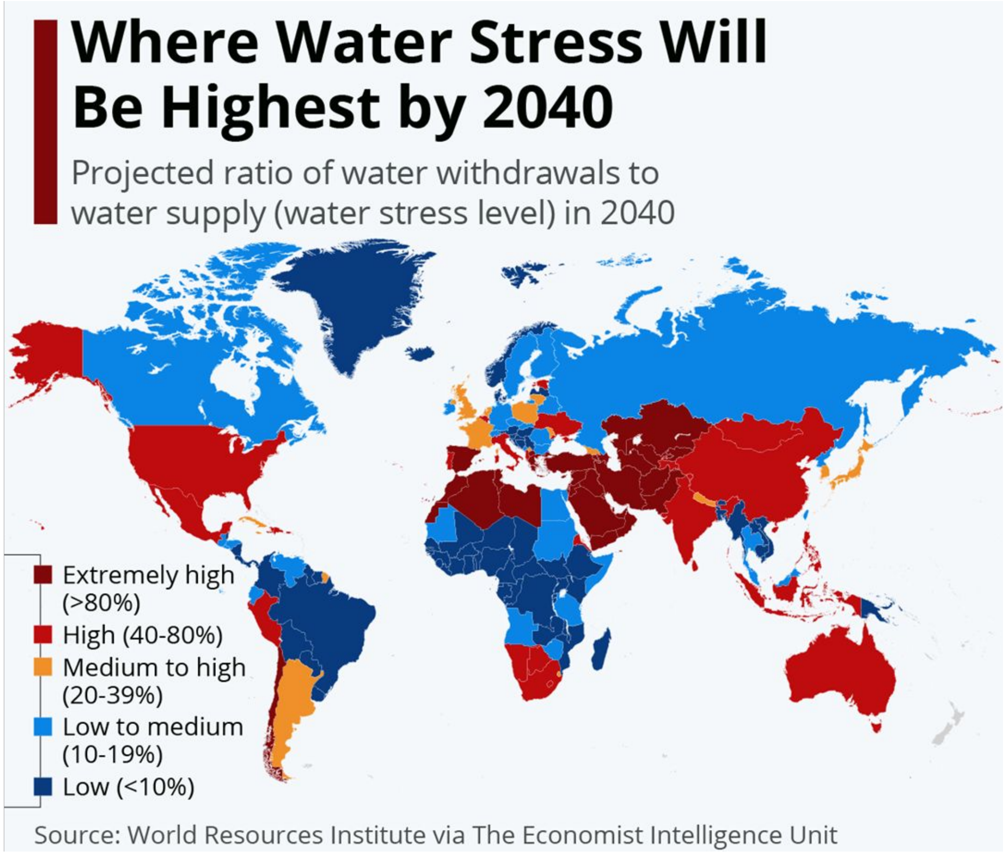
PALERMO, 10-11.01.2024

Outline

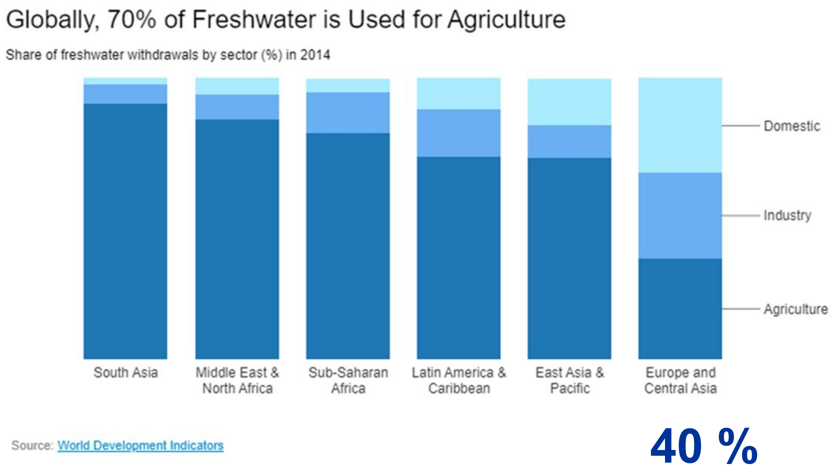
- Introduction & Motivation
- New EU regulation on water reclamation
- AOPs & photochemical processes
- Simultaneous water decontamination & disinfection
- Key messages

Introduction and Motivation

Exponential increase of population: **The world population has already crossed the 8 billion mark at the end of 2023 and it is expected to increase to 9.7 billions in 2050**



Introduction and Motivation



By **2050**, feeding a planet of **9 billion people** will require an estimated 50% increase in agricultural production and a 15% increase in water withdrawals.

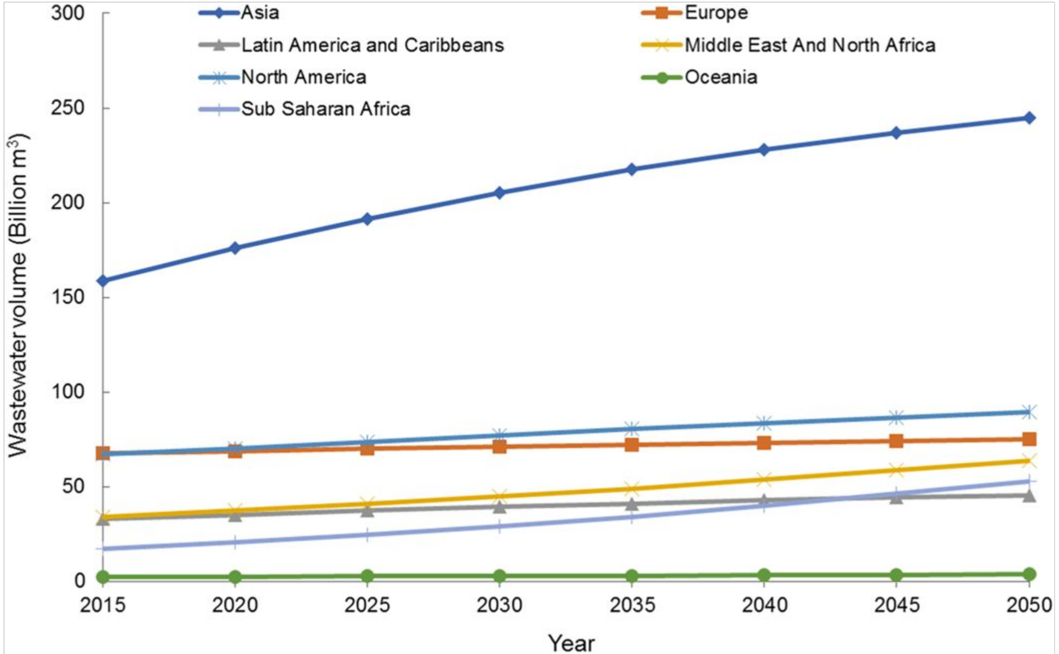
40 %

of the energy expenditures in small to medium-sized municipalities **go to pumping-moving-treating** of the urban water needed

Forecasts of global water demand in 2050 show a **400%** increase for the manufacturing industry and a **140%** increase for thermal power generation (OECD, 2012).
Water withdrawals for industrial use will have doubled by 2030, reaching a percentage of **22%** worldwide.

Introduction and Motivation: water reclamation, a global need

It is estimated an annual world production of **urban wastewater of 380 km^3**, that is 15% of water withdrawal for agriculture (42 millions ha).
World urban wastewater production is estimated to increase **24% in 2030 and 51% in 2050**.



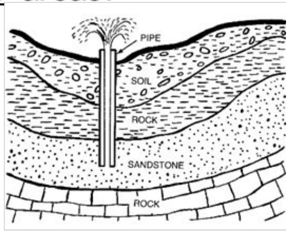
Nutrients in urban wastewaters:
16.6 Tg (Tg = million of metric tons) of nitrogen; 3 Tg for phosphorous and 6.3 Tg for potassium.
Total recovery of nutrients from urban wastewaters would compensate the 13.4% of the world demand for agriculture.

Introduction and Motivation: water reclamation, a global need

Benefits

- ✓ Environmental
- ✓ Social
- ✓ Economic

➢ It can improve the status of the environment both quantitatively, alleviating pressure by substituting abstraction, and qualitatively, relieving pressure of discharge from UWWTP to sensitive areas.



➢ Appropriate consideration for nutrients in treated wastewater could also reduce the use of additional fertilizers resulting in savings for the environment, farmers and wastewater treatment.

➢ It is considered a reliable water supply, quite independent from seasonal drought and weather variability and able to cover peaks of water demand.

➢ Lower investment costs and energy compared to alternative sources such as desalination or water transfer, also contributing to reduce greenhouse gas emissions.

Introduction: Contaminants of emerging concern

EMERGING CONTAMINANTS

- Until recently unknown
- Commonly use
- Emerging risks (EDCs, antibiotics)
- Unregulated

WWTPs

INCOMPLETE REMOVAL

CONTINUOUS INTRODUCTION INTO THE ENVIRONMENT

NATURAL WATERS

(ng-µg/L)

Photochemical transformations

TRANSFORMATION PRODUCTS

Introduction: Microbial water contamination

Bacteria	Fungi	Viruses	Protozoa
E. coli	*Fusarium*	*Poliovirus*	*Acanthamoeba polyphaga*
Enterococcus sp	*Olphidium*	*Rotavirus*	*Cryptosporidium parvum*
Pseudomonas aeruginosa	*Aspergillus*	*Norovirus*	*Entamoeba sp.*
Salmonella typhi	*Candida*	*Bacteriophages*	*Giardia sp*
Vibrio cholera			

New challenge in UWW: Antibiotic Resistant Bacteria (ARB)

Definition: *Phenomenon by which a microorganism is no longer affected by an antimicrobial (previously sensitive), so that the usual medical treatments become ineffective and infections persist and can be transmitted to other people.* *WHO, Antimicrobial Resistance*

http://www.who.int/medicines/publications/global-priority-list-antibiotic-resistant-bacteria/en/

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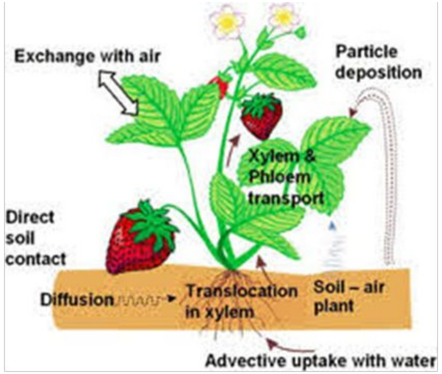
Reclamation of Wastewater: CECs and OMCs

OMCs translocation to plants and detection



Pharmaceutical	Plant	Spiked concentration	Study duration (days)	Mean concentration detected in plant (μg/g)		
				Roots	Stem	Leaves
Diclofenac	*Typha latifolia*	1 mg/L	1	0.2	Not reported	0.013
Fluoxetine hydrochloride	*Brassicaceae*	280 ng/mL	12 weeks	Not detected	0.49	0.26
Carbamazepine	Cucumber	4.14 μg/L	3 months	4.5[a]	1.9[a]	39.1[a]
	Scirpus validus	0.5–2.0 mg/L	21	3.3–19.0	Not reported	0.3–0.7
Naproxen	*Scirpus validus*	0.5–2.0 mg/L	21	0.2–2.4	Not reported	0.3–0.7
Diclofenac	*Medicago sativa* L.	10 μg/L	50	162.8[a]	Not reported	Not detected
Sulfamethoxazole	*Medicago sativa* L.	10 μg/L	50	52.5[a]	Not reported	3.5[a]
Trimethoprim	*Medicago sativa* L.	10 μg/L	50	311.9[a]	Not reported	23.5[a]
17α-Ethinylestradiol	*Medicago sativa* L.	10 μg/L	50	28.9[a]	Not reported	28.3[a]

[a] Concentrations are given in μg/kg.

L.M. Madikizela et al. / Science of the Total Environment 636 (2018) 477–486

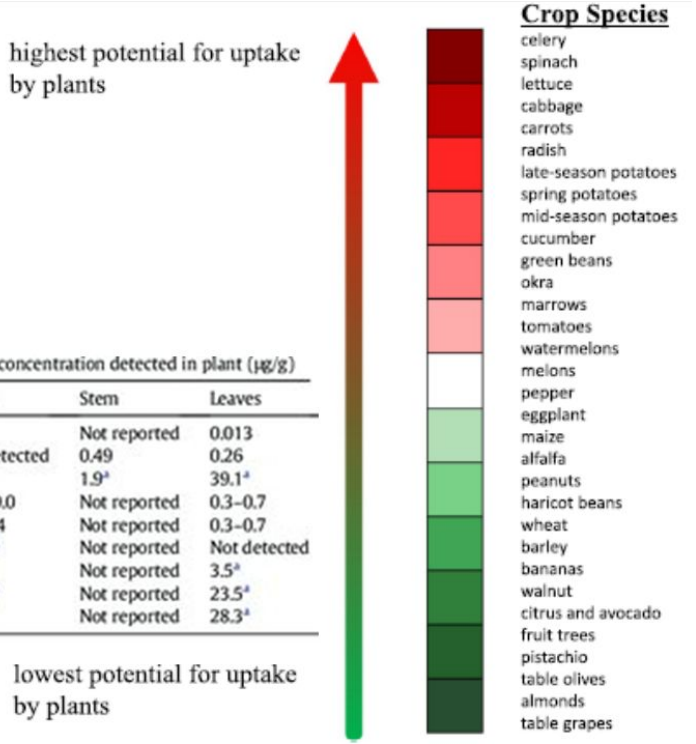


Fig. 2. Heat map showing the potential of the main crop species for CECs uptake. The highest potential for uptake is indicated with dark red; the lowest potential with dark green.

A. Christou et al. Environmental Research 170 (2019) 422–432

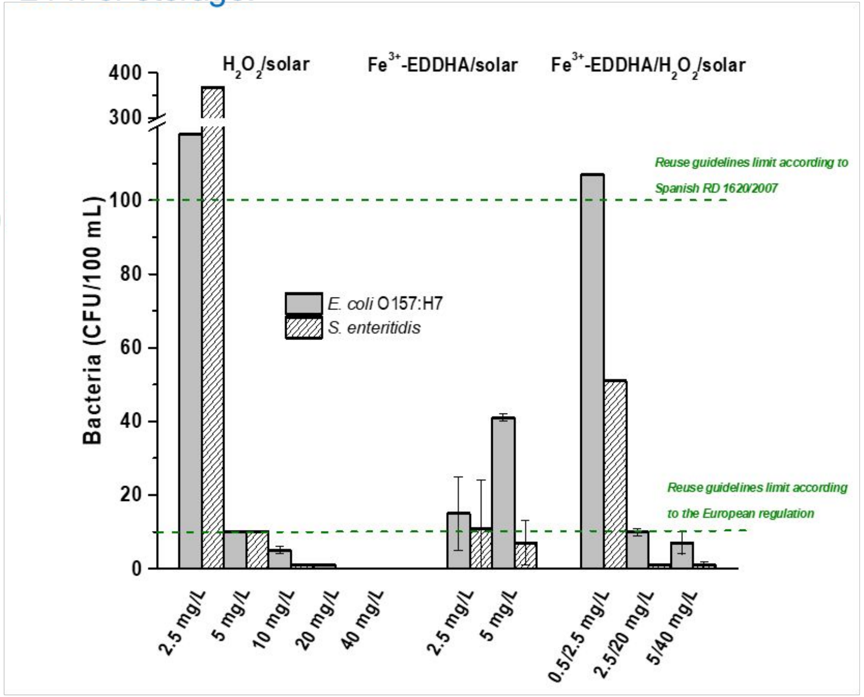
Reclamation of Wastewater: Pathogens

Regrowth during storage

INACTIVATION
OR
INHIBITION

?

Analysis of bacteria concentration in treated UWW after 24 h of storage.



S. Nahim-Granados, et al. Applied Catalysis B: Environmental 278 (2020) 119334

New EC regulation on water reuse

Table 1 Classes of reclaimed water quality and allowed agricultural use and irrigation method

Minimum quality c...		
A		
B		
C	Food crops consumed raw where the edible part is ...	Drip irrigation** or ...
D		

L 177/32 EN Official Journal of the European Union 5.6.2020

REGULATION (EU) 2020/741 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 25 May 2020

on minimum requirements for water reuse

(Text with EEA relevance)

Article 2

Scope

1. This Regulation applies whenever treated urban waste water is reused, in accordance with Article 12(1) of Directive 91/271/EEC, for agricultural irrigation as specified in Section 1 of Annex I to this Regulation.

2. A Member State may decide that it is not appropriate to reuse water for agricultural irrigation in one or more of its river basin districts or parts thereof, taking into account the following criteria:

(a) the geographic and climatic conditions of the district or parts thereof;

(b) the pressures on and the status of other water resources, including the quantitative status of groundwater bodies as referred to in Directive 2000/60/EC;

(c) the pressures on and the status of the surface water bodies in which treated urban waste water is discharged;

(d) the environmental and resource costs of reclaimed water and of other water resources.

Any decision taken pursuant to the first subparagraph shall be duly justified on the basis of the criteria referred to in that subparagraph and submitted to the Commission. It shall be reviewed as necessary, in particular taking into account climate change projections and national climate change adaptation strategies, and at least every six years taking into account river basin management plans established pursuant to Directive 2000/60/EC.

...ts for agricultural irrigation

	TSS (mg/l)g/l)	Turbidity (NTU)U)	Other
≤10	≤10	≤5	*Legionella* spp.: <1,000 cfu/l where there is risk of aerosolization
According to Council Directive 91/271/EEC[1] ((Annex I, Table 1)	According to Directive 91/271/EEC ((Annex I, Table 1)	-	Intestinal nematodes (helminth eggs): ≤1 egg/l for irrigation of pastures or forage
		-	
		-	

[1] Council Directive 91/271/EEC of 21 May 1991 concerning urban waste water treatment (OJ L 135, 30.5.1991, p. 40).

Has entered into force on June 2023

New EC regulation on water reuse

Table 4 Validation monitoring of reclaimed water for agricultural irrigation

Reclaimed water quality class	Indicator microorganisms (*)	Performance targets for the treatment chain (log_{10} reduction)
A	*E. coli*	≥ 5.0
	Total coliphages/ F-specific coliphages/somatic coliphages/coliphages(**)	≥ 6.0
	Clostridium perfringens spores/spore-forming sulfate-reducing bacteria(***)	≥ 4.0 (in case of *Clostridium perfringens* spores) ≥ 5.0 (in case of spore-forming sulfate-reducing bacteria)

(*) The reference pathogens *Campylobacter*, Rotavirus and *Cryptosporidium* can also be used for validation monitoring purposes instead of the proposed indicator microorganisms. The following log_{10} reduction performance targets should then apply: *Campylobacter* (≥ 5.0), Rotavirus (≥ 6.0) and *Cryptosporidium* (≥ 5.0).

(**) Total coliphages is selected as the most appropriate viral indicator. However, if analysis of total coliphages is not feasible, at least one of them (F-specific or somatic coliphages) has to be analyzed.

(***) *Clostridium perfringens* spores is selected as the most appropriate protozoa indicator. However sporeforming sulfate-reducing bacteria is an alternative if the concentration of *Clostridium perfringens* spores does not allow to validate the requested log10 removal.

Also risk assessment is required, but it´s not currently defined

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Solar treatments for water disinfection & decontamination

Advanced Oxidation Processes

Photochemical processes

TiO_2/UVA
(Carey et al., 1976)

$$TiO_2 \xrightarrow{h\nu} TiO_2(e^- + h^+)$$

$$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+$$

$$e^- + O_2 \rightarrow O_2^{\bullet -}$$

Photo-Fenton

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH$$

(J. Chem. Soc., 1894)

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + H^+ + {}^{\bullet}OH$$

(several authors, early 90s)

- **H_2O_2**
- **Persulfate**
- **Peroxymonosulfate**
- **Peracetic acid**
- **Chlorine**

- No generation of $HO^{\bullet}$ by solar wavelengths reaching the Earth´s surface
- High efficiency on water microbial inactivation
- Direct oxidation and complex microbial inactivation mechanisms

Ozone for water treatment

Disadvantages:

- **Solubility and activity:** When the ozone dosage is too low, some germs and bacteria may survive, which is why higher ozone concentrations are used. If the water being treated is rich in organic compounds or total suspended solids, then ozone will decay more rapidly, as it reacts with these contaminants.
- **High costs:** During corona discharge, around 85% of the energy is lost via heat waste, making ozone treatment extremely energy-intensive. Treating water with ozone is also energy-intensive because it requires high-class equipment, expensive technology, and an operator that knows how to work the complicated system.
- **Reactivity and toxicity:** Ozone's reactivity with metals can cause issues in wastewater treatment pipes and containers, therefore corrosion-resistant materials such as stainless steel must be used, which adds to plant construction costs. Because of the high toxicity, ozone levels need to be constantly monitored.
- **Reactivity and byproducts:** If the water contains bromide ions, ozone can react to form brominated compounds (like bromate ions/salts), which can cause human cancers. ozone leaves nothing behind; any ozone that doesn't react with the water contaminants is immediately broken down, leaving nothing to monitor after the disinfection process.

Photochemical processes: UV-C with oxidative agents

H_2O_2

$$H_2O_2 \xrightarrow{UVC} 2HO^{\bullet}$$

(Goldstein et al., 2007)

Chlorine

$$HClO \xrightarrow{UVC} HO^{\bullet} + Cl^{\bullet}$$

$$ClO^{-} \xrightarrow{UVC} O^{\bullet -} + Cl^{\bullet}$$

$$O^{\bullet -} + H_2O \rightarrow HO^{\bullet} + OH^{-}$$

(Chuang et al., Environ Sci Technol, 2017. 51(23) 13859-13868.)

Persulfate / Peroxymonosulfate

$$S_2O_8^{2-} \xrightarrow{UVC} 2SO_4^{\bullet -}$$

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

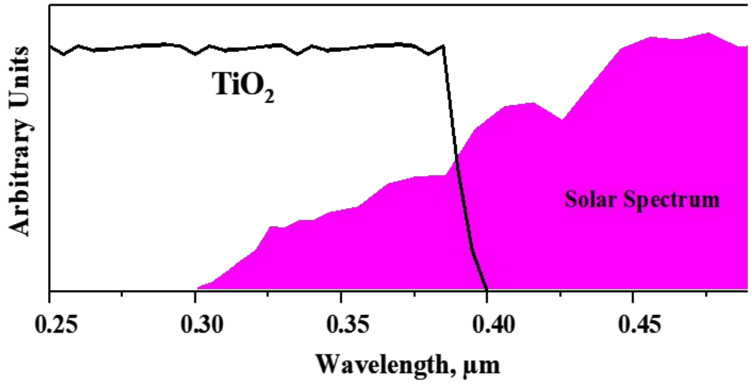
$$HSO_5^{-} \xrightarrow{UVC} SO_4^{\bullet -} + HO^{\bullet}$$

$$HSO_5^{-} + H^{\bullet} \rightarrow SO_4^{\bullet -} + H_2O$$

(Sánchez-Montes et al. Environ. Sci.: Water Res. Technol., 2020, 6, 2553–2566)
(Guerra-Rodríguez et al., Water 2018, 10, 1828)

- $SO_4^{\cdot -}$ has a high oxidation potential (2.5–3.1 V) comparable or even higher than $^{\cdot}OH$
- Reacts more selectively and efficiently with organic compounds that contain unsaturated bonds or aromatic π electrons
- Half-life of sulfate radicals is supposed to be 30–40 μs
- Chlorine radicals oxidation potential 1.5V. High half-life

Solar Heterogeneous photocatalysis: TiO_2



Linearly dependent on the energy flux but only ~5% of the whole solar spectrum is available for TiO_2 band-gap.

- 75% of solar collector efficiency and 1% for the catalyst means 0.04% original solar photons are efficiently used. This is a rather inefficient process.

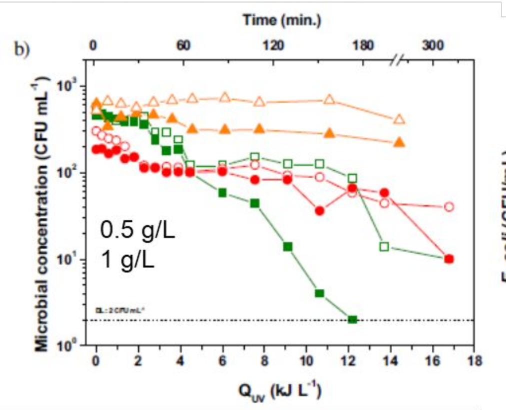
Mild catalyst working under mild conditions with mild oxidants.

- As concentration of contaminants and water ionic strength increase: slow kinetics and unpredictable mechanisms need to be solved.
- TiO_2 efficiency improved with the addition of powerful oxidants or when doped (with iron, nitrogen…) to undertake practical applications.
- Pure TiO_2 can utilize only UV and new catalysts able to work with the visible component of the solar spectrum are needed.

Solar photocatalysis: enhancement strategies

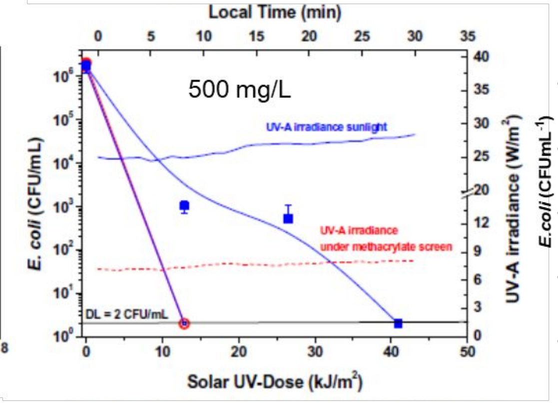
DOPED TiO_2 & OTHER SEMICONDUCTORS

Bismuth Vanadate/Ag



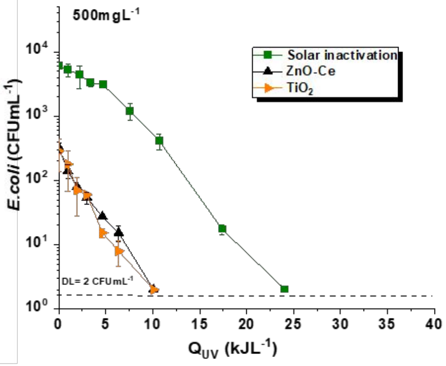
Catalysis Today 281 (2017) 124–134

TiO_2-Graphene oxides



Chemical Engineering Journal 261 (2015) 36–44

ZnO-doped with cations



IMMOBILIZATION OF THE CATALYST IN SUBSTRATES

Uncoated external, TiO_2 coated internal

- ➤ Lower microbial reduction efficiency than with suspended catalyst
- ➤ Scaling-up challenge

Dehaya et al., Applied Catalysis B: Environmental 128 (2012) 126– 134

Photochemical processes

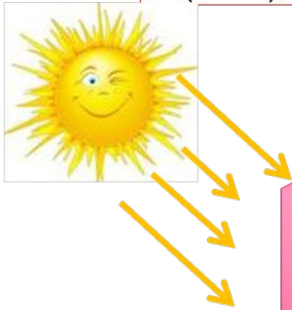
UV-C

- Low efficiency in CEC and OMC elimination.

In crop irrigation, regenerated wastewater is normally stored along hours/days before being used.

Free Chlorine (Chlorination)

- Low efficiency in CEC and OMC elimination.
- Generation of toxic by-products: trihalomethanes (THM), haloacetic acids.



UV-C/ free Chlorine

- **Low studied combination for CEC and OMC elimination.**
- **Effect of UVC in THM formation.**

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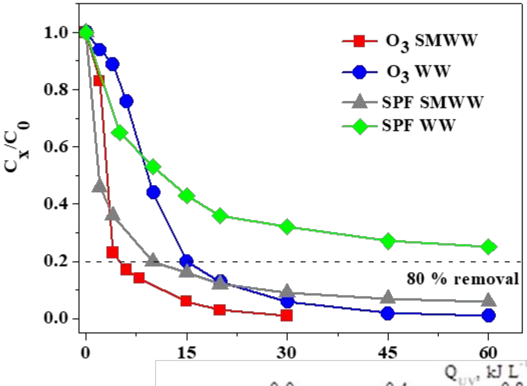
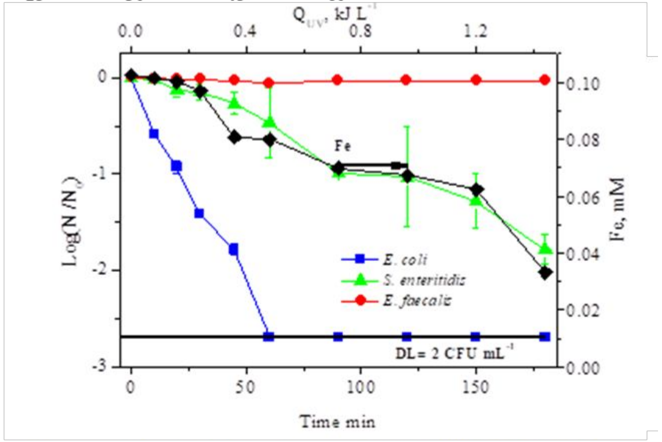
Simultaneous removal of CECs and Pathogens

Ozonation pilot plant

Raceway Pond Reactor





Science of the Total Environment 787 (2021) 147531
Science of the Total Environment 766 (2021) 144320

PANIWATER project

Assess the **efficiency of ozonation** for the treatment of **urban wastewater** (UWW), with three different O_3 doses. The parameters for the evaluation of the treatment were **degradation of organic microcontaminants (OMCs), disinfection, generation of disinfection by-products (DBPs) and toxicity.**

Municipal Urban Wastewater treatment plant "El Bobar" located in Almeria, South East of Spain.

- 0.2 gO_3/h L (25%).
- 0.3 gO_3/h L (50%).
- 0.4 gO_3/h L(100%).

- **OMCs**:UHPLC-QqQ-MS/MS.
- **DBPs**:HS-GC-QqQ-MS/MS.
- **Bromate and bromide:** IC.

- *Escherichia coli* and Coliforms.
- Plate counting Chromocult© agar media.

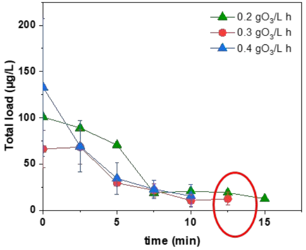
- Cytotoxicity.
- Phytotoxicity.
- Bacteria survival.

Microcontaminants

SFX, TMP, DCF, ACE, CBZ, CAF

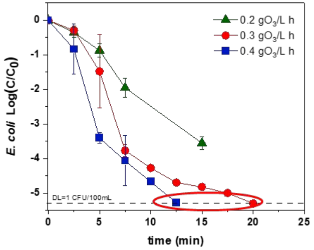
PANIWATER project

DEGRADATION OF OMCs



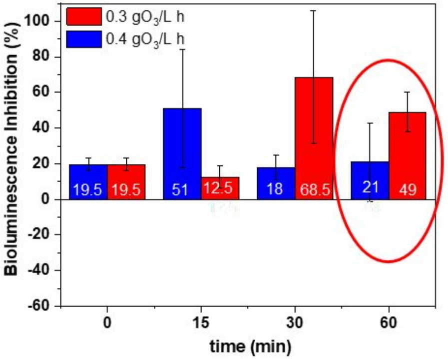
O_3 doses (gO_3/h L)	time (min)	O_3 Consumption (mg/L)
0.2	12.5	6.6
0.3	10.0	11.7
0.4	7.5	8.9

DISINFECTION

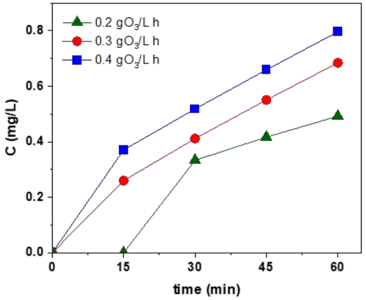


O_3 doses (gO_3/L h)	time (min)	O_3 Consumption (mg/L)
0.2	15.0	7.7
0.3	20.0	19.7
0.4	12.5	13.8

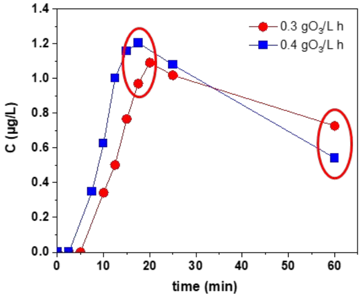
BACTERIAL SURVIVAL



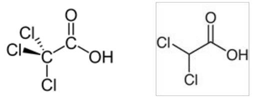
BROMATE



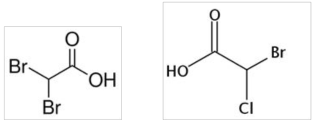
BROMOFORM



HALOACETIC ACIDS (HAAs)



Chlorinated HAAs = **Constant**



Brominated HAAs = **Increased**

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Key messages

- Water scarcity and bad water quality are problems affecting all over the world, which makes it crucial to find alternative water sources, such as municipal wastewater. Municipal wastewater treatment, jointly with desalination, mean a key strategy for trying to maintain high human life quality.
- A deep evaluation on the specific problem to be solved must be done just to focus on the optimum treatment option.
- Normally, different AOPs based technologies show highly efficiency as tertiary treatment for CECs & ARB elimination, but economic, health and life cycle assessments must support the final selection.
- Solar based AOPs are considered a sustainable and actual viable option for reducing contaminant impact on the Environment.
- Water quality parameters monitoring as well as contaminant transfer to crops must be carried out for ensuring a “safe reuse”. Risk Assessment studies are required

Sol2H2O

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