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Biological WWTP
constituents of emerging concern (CEC)

Simone Pellizzari

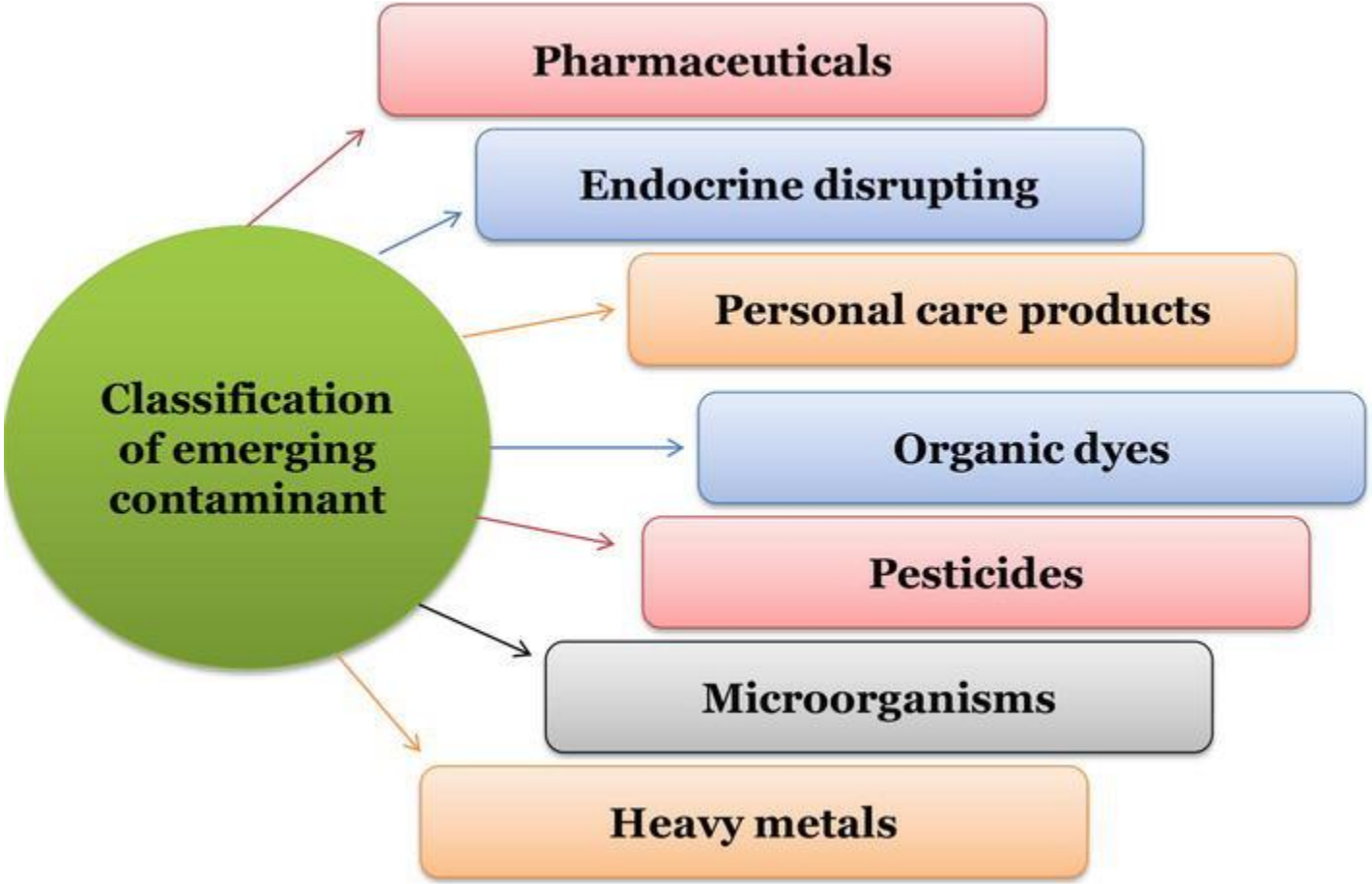
Emerging Polluttants Introduction

The term **emerging pollutants** primarily refers to those for **which no regulations currently require monitoring** or public reporting of their presence in our water supply or wastewater discharges.

The terms **constituents of emerging concern** (**CECs**), microconstituents, trace organic pollutants, and other similar terminologies **are often used** in the literature as terms for classes of chemicals that fall under the umbrella term emerging pollutants.

We **prefer** defining contaminants of emerging concern (**CEC**) as naturally occurring, manufactured or manmade chemicals or materials, **which have now been discovered or are suspected present in various environmental compartments** and whose toxicity or persistence are likely to significantly **alter the metabolism of a living being**.

Emerging Polluttants Classification



Emerging Polluttants
Many constituents

Many constituents described as emerging pollutants are:

- Pharmaceuticals or personal care products (**PPCPs**), including endocrine disrupting compounds (**EDCs**), that may enter the environment through excretion in human and animal urine and feces, through flushing of unused medications, household uses, or bathing, and result in nanogram per liter (ng/L) to microgram per liter (µg/L) concentrations in the environment. EDCs include a range of compounds, including natural and synthetic hormones, pesticides, phytocompounds, and industrial chemicals.

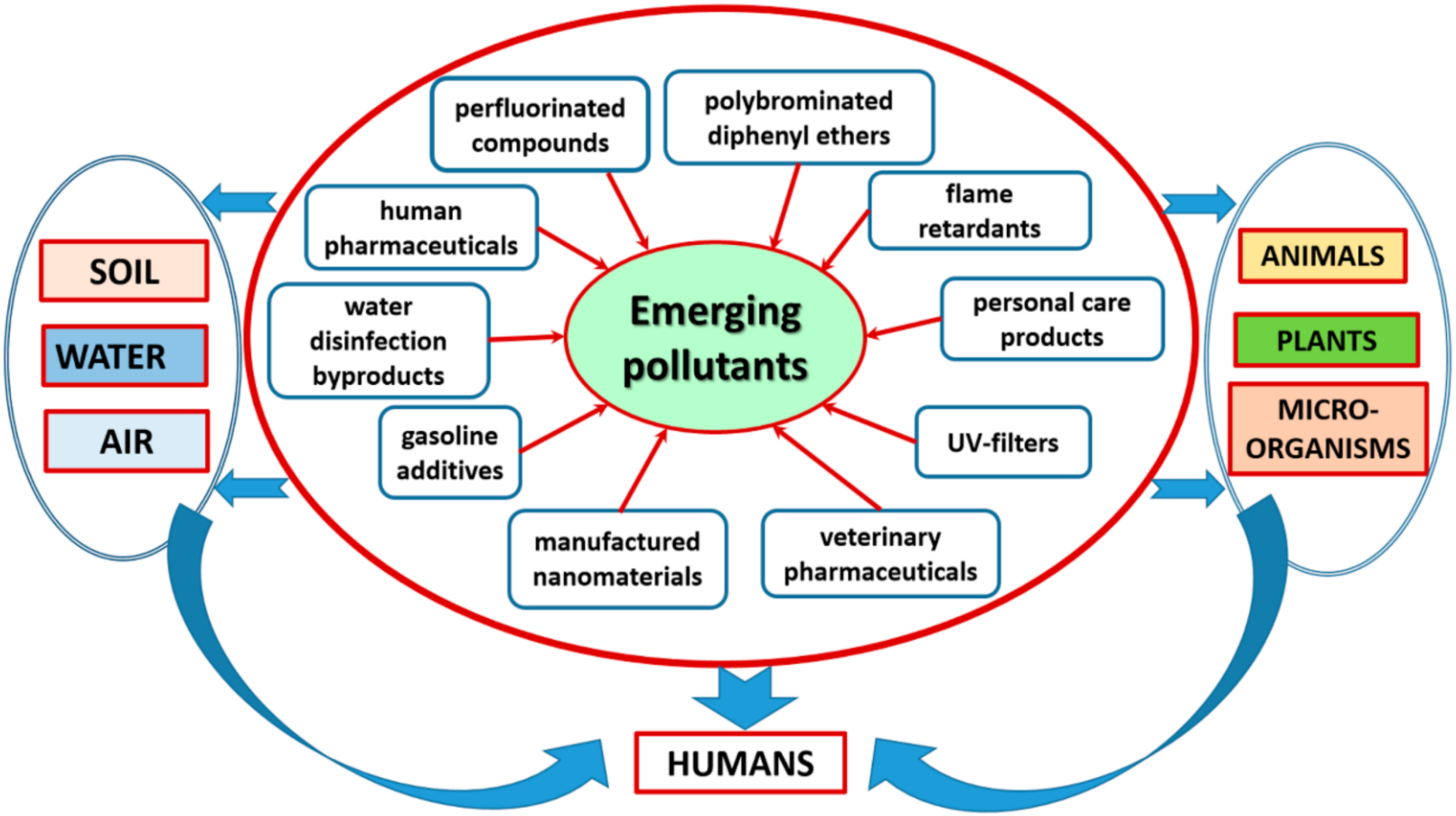
- Emerging organic compounds (**EOCs**) industrials (e.g.: MeBT), estrogens and illicit drugs, more than new 137 pesticides

Emerging Polluttants
Many constituents

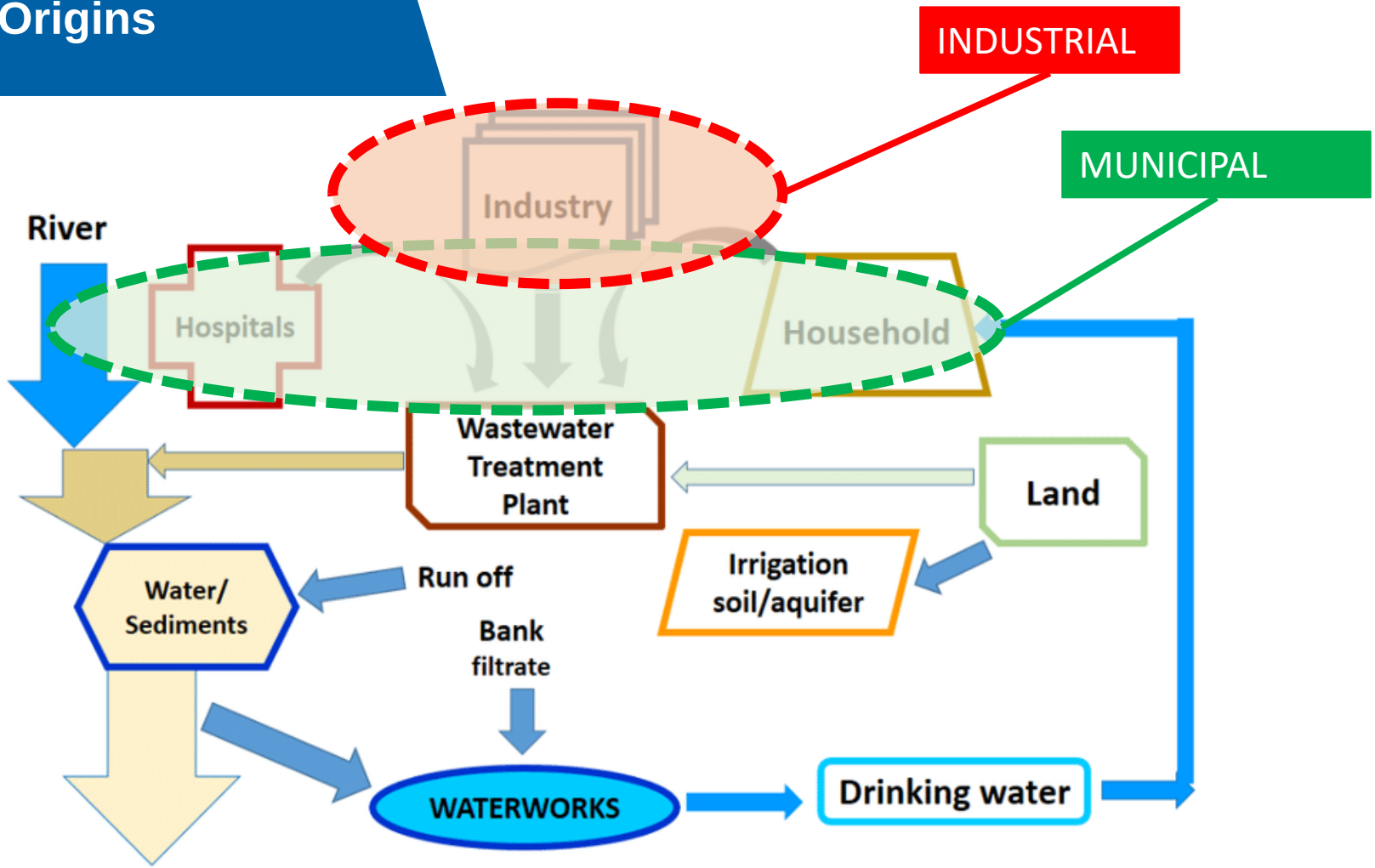
Many constituents described as emerging pollutants are:

- **Heavy metals**: Arsenic, Cadmium, Lead, Mercury, Lithium,
- Rare Earths are a group of 17 chemical elements of the periodic table, namely scandium, yttrium and lanthanoids. They are abbreviated to **RE** (Rare Earths), **REE** (Rare Earth Elements) or **REM** (Rare Earth Metals) and are also subdivided into light (**LREE**, from Lanthanum to Promethium), medium (**MREE**, from Samarium to Holmium) and heavy (**HREE**, from Erbium to Lutetium),
- **Pesticides**,
- **Genetically Modified Microorganism**,

Emerging Polluttants Impacts



Emerging Polluttants Origins



CEC
In municipal wastewater

Antibiotic resistance is a global threat to human and environmental health. Antimicrobial resistance is a property of microorganisms that jeopardizes the capacity to treat infectious diseases.

Endocrine-disrupting compounds (EDCs) are exogenous substances that cause adverse health effects in an intact organism, or its progeny, subsequent to the changes in endocrine function. These chemicals included **steroids** and **synthetic organic chemicals**. Therefore, the EDC removal performances of different treatment schemes.

The occurrence of more than 15 **pharmaceuticals** and **personal care** products in the influent and effluent from the wastewater treatment plant has been observed.

Molecules such **caffeine**, **N,N-diethyl-m-toluamide** and **chloramphenicol** were removed at a high rate.

Molecules as **Sulfamethoxazole** were removed to different extents varying from 99 to 100 %.

The occurrence and removal of others substances as: carbamazepine, metoprolol, trimethoprim (TMP), sulpiride , nonsteroidal anti-inflammatory drugs (**ibupro-fen**, **ketoprofen**, **naproxen**, **diclofenac**), antiepileptic (**carbamazepine**), and anti-microbial (**trimethoprim**),were observed in municipal WWTP

CEC
In industrial wastewater

There are several industrial chemicals well known as CEC:

- FRs, polychlorinated alkanes,
- Plasticizers, antioxidants,
- Perfluorinated and polyfluorinated alkyd substances (PFAS's family, mainly divided in PFOS and PFOA), over 4.700 in number well knowed at the moment,
- Organohalogen compounds such as polychlorinated naphthalenes (PCNs), chlorinated paraffins (CPs), and polychlorinated biphenyls (PCBs), chlorinate solvents,

More in general:

- Nano-plastics and Nano-particules

CEC
In industrial wastewater

Compounds								
Pharmaceuticals	**CAS**	**Use**	**PCPs**	**CAS**	**Use**	**Pesticides**	**CAS**	**Use**
17α-ethynylestradiol [ab]	57-63-6	Estrogen	OD-PABA	21245-02-3	UV filter	**Aldrin** [a]	309-00-2	Organochlorine pesticide
17-β estradiol [ab]	50-28-2	Estrogen	2-OHBP	117-99-7	UV filter	Ametryn	834-12-8	Triazine
Acetaminophen	103-90-2	Analgesic/anti-inflammatory	3-OHPB	13020-57-0	UV filter	Atraton	1610-17-9	Triazine
Albuterol	18559-94-9	Other PhACs	4-OHPB	1137-42-4	UV filter	Atrazineab	1912-24-9	Triazine
Amitriptyline	50-48-6	Psychiatric drug and stimulant	**4MBC**	36861-47-9	UV filter	Bifenthrin	82657-04-3	Pyrethroid
Amoxicillin	26787-78-0	Penicillin (antibiotic)	Benzyl salicylate	118-58-1	UV filter	Carbophenothion	786-19-6	Organophosphate pesticide
Ampicillin	69-53-4	Penicillin (antibiotic)	Bisphenol Ab	80-05-7	Plasticizer	Chlorpyrifos [ab]	2921-88-2	Organophosphate pesticide
Atenolol	29122-68-7	β-blocker (antihypertensive)	Cashmeran	33704-61-9	Other fragrances	Cyfluthrin (I-IV)	68359-37-5	Pyrethroid
Atorvastatin	134523-00-5	Lipid regulator	**Celestolide**	13171-00-1	Polycyclic musk	Cypermethrin (I-IV)	52315-07-8	Pyrethroid
Azithromycin	83905-01-5	Macrolide	**DEET**	134-62-3	Insect repellent	Deltamethrin I,II	52918-63-5	Pyrethroid
Bezafibrate	41859-67-0	Lipid regulator	**EHMC**	83834-59-7	UV filter	Dieldrin [a]	60-57-1	Organochlorine pesticide
Caffeine	58-08-2	Psychiatric drug and stimulant	Ethylhexyl salicylate	118-60-5	UV filter	Endosulfan Sulfate [a]	1031-07-8	Organochlorine pesticide
Carbamazepine	298-46-4	Psychiatric drugs and stimulants	Exaltenone	14595-54-1	Macrocyclic musk	Endrina	72-20-8	Organochlorine pesticide
Cefaclor	53994-73-3	Cephalosporin	**Galaxolide**	1222-05-5	Polycyclic musks	Endrin Ketone	53494-70-5	Organochlorine pesticide
Cefadroxil	50370-12-2	Cephalosporin	Habanolide	34902-57-3	Macrocyclic musk	Ethion	563-12-2	Organophosphate pesticide
Cefdinir	91832-40-5	Cephalosporin	Helvetolide	141773-73-1	Other fragrances	Fenvalerate I,II	51630-58-1	Pyrethroid
Cefquinome	84957-30-2	Cephalosporin	Homosalate	118-56-9	UV filter	Heptachlor	76-44-8	Organochlorine pesticide
Ceftiofur	80370-57-6	Cephalosporin	IRGAROL	28159-98-0	Insect repellent	Heptachlor Epoxide Isomer B	1024-57-3	Organochlorine pesticide
Chloramphenicol	56-75-7	Amphenicol	Mexenone	1641-17-4	UV filter	**Lindane** [b]	58-89-9	Organochlorine pesticide
Chlortetracycline	57-62-5	Tetracyclines	**MTCS** [b]	4640-01-1	Antibacterial	Metoxychlor	72-43-5	Organochlorine pesticide
Ciprofloxacin	85721-33-1	Quinolone (antibiotic)	Muscenone	63314-79-4	Macrocyclic musk	o,p′-DDT [ab]	789-02-6	Organochlorine pesticide
Clarithromycin	81103-11-9	Macrolide	Muscone	541-91-3	Macrocyclic musk	**p,p′-DDT** [ab]	72-54-8	Organochlorine pesticide
Clindamycin	18323-44-9	Lincosamides (antibiotics)	Musk ambrette	83-66-9	Nitro musk	**p,p′-DDE** [a]	72-55-9	Organochlorine pesticide

CEC
The GMO's paradox

There are several and not-well knowned GMO (Industrial secret, Restricted informations, etc…)

- Antibiotical resistant genes as marker, Engineered cells for advanced medical therapy, Programmed microorganism for special pourpose (eg. «Fagae-technology in wwtp»)

BUT

GMO can play a **key-role** in CEC degradation

CEC Treatments

MBR (EMBR, HR-MBR, WRF-MBR)

MBBR (with selected biomass added)

TPPBR

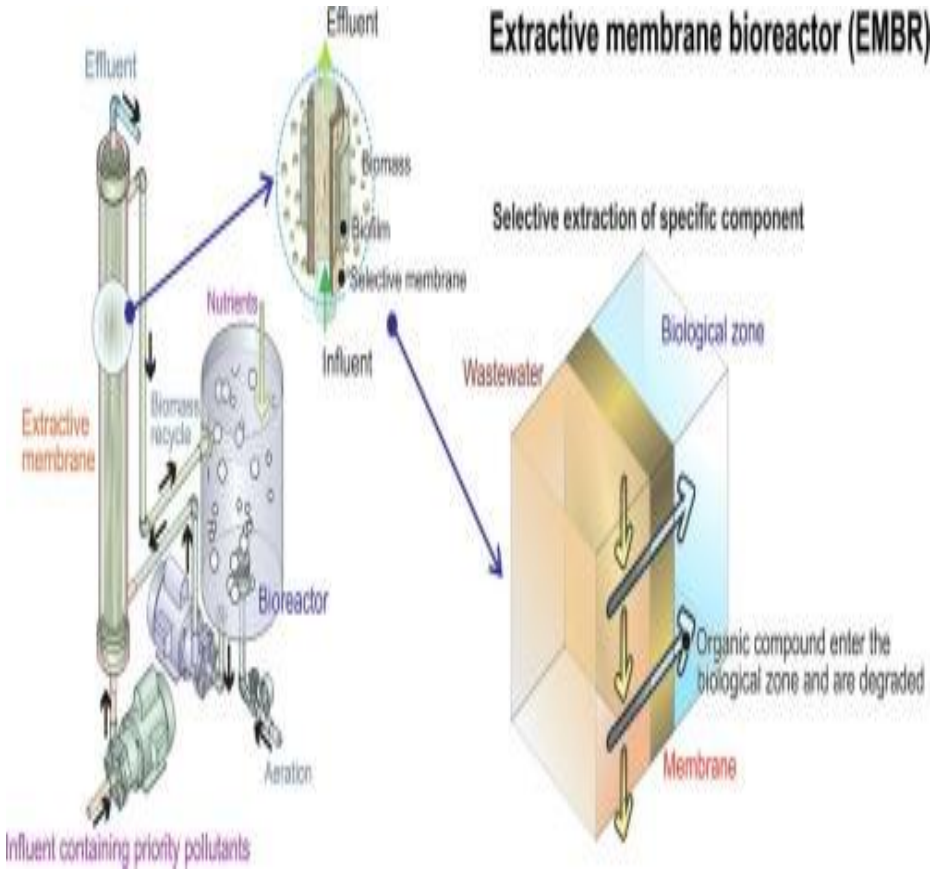
Fungae (selected and modified)

AOP's (Advanced Oxydation Process) as:

Photocatalisys
Photo-fenton
Ozone and **UV-Ozone**
Electrochemicals

Absorption technology (**Graphene's** derivates)

CEC Treatments



MBR (extractive configuration)

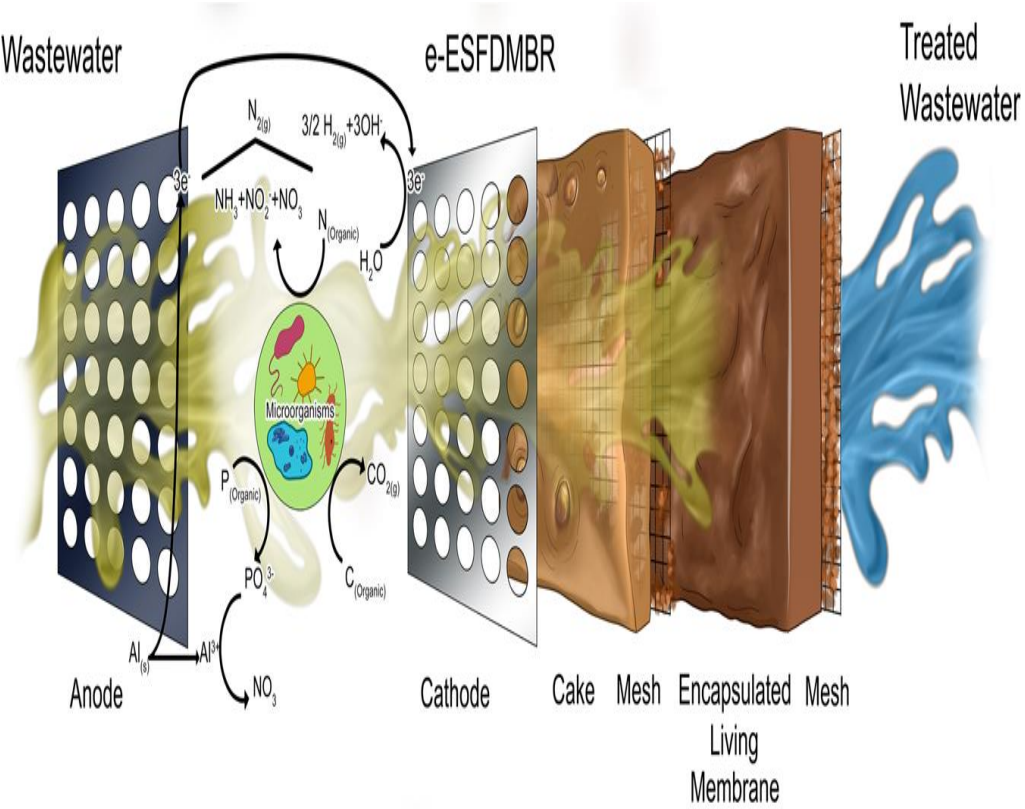
MBR has been developed into three types according to the configuration, namely membrane-aerated bioreactor (MABR), biomass separation MBR (BS-MBR), and **extractive** MBR (EMBR). **EMBR** was developed for biodegradation of toxic components in wastewater having a harsh condition which is usually hard to be treated by conventional biological processes. The **EMBR** configuration uses a selective membrane for removing or extracting specific pollutants from the wastewater stream resulting in a highly selective sorption process

CEC Treatments

MBR (High Rate Membrane's MBR)

High-rate processes have been investigated for the recovery of organic matter from municipal wastewater. High-rate membrane bioreactors (**HR-MBRs**) may simultaneously achieve the increased recovery of carbon and high effluent quality, although control of membrane fouling is extremely difficult. To address the severe fouling in HR-MBRs, the combination of granular scouring and frequent chemically enhanced backwashing was examined. The use of robust flat-sheet ceramic membranes enabled the application of those cleaning strategies.

CEC Treatments



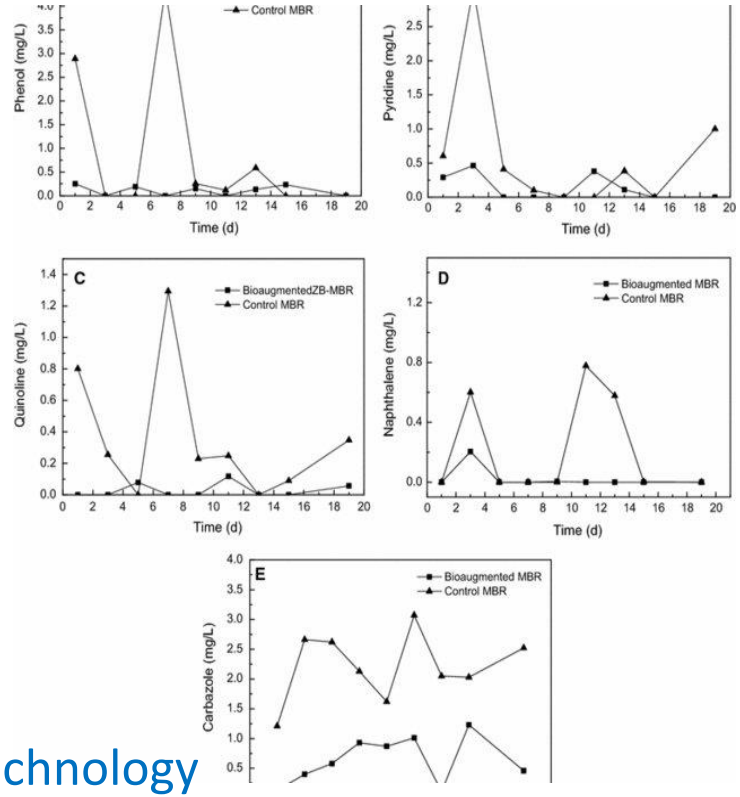
eMBR (**electrochemical** - MBR)

It is a membrane bioreactor (MBR) combined with electrochemical processes, which involved the enhancement of the conventional MBR with an important reduction of its main limitation which is the high fouling rate of the membrane, on the other a reduction of energy consumption normally brought about by electrochemical processes and an increase in removal efficiencies

CEC Treatments

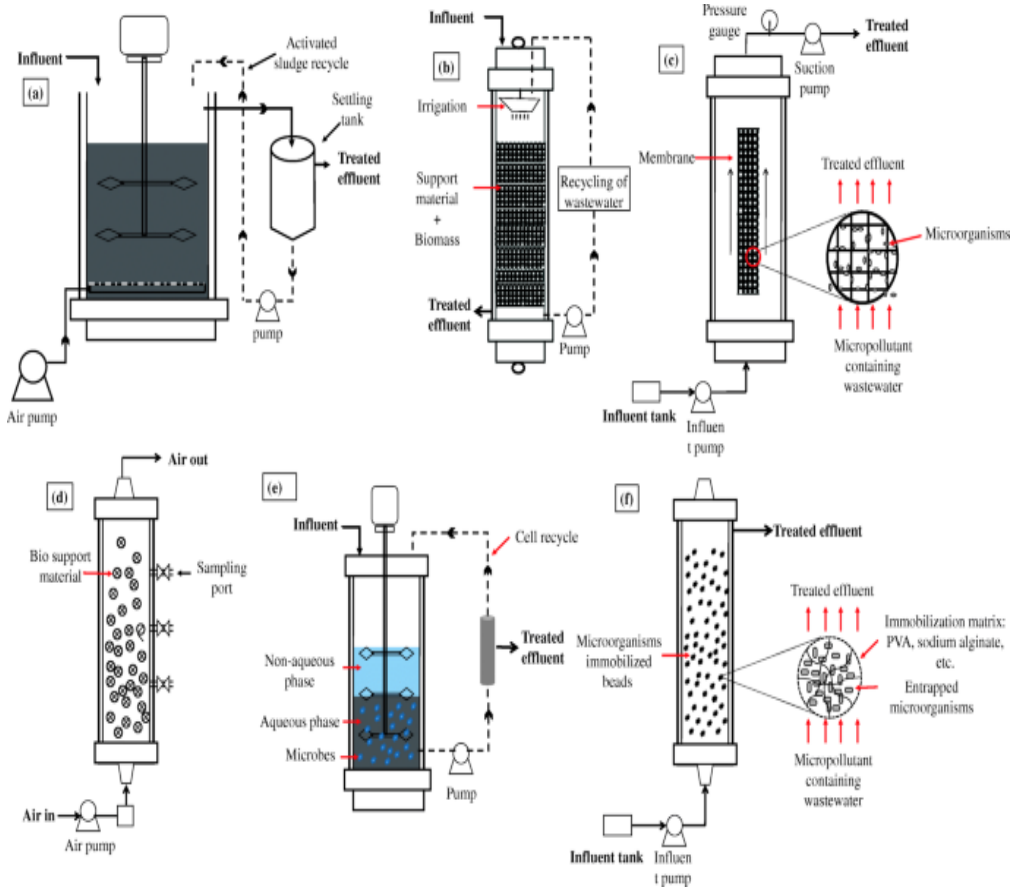
MBR (White-rot Fungi MBR)

The different MBRs configs are effective against Trace Organic micropolluttants (**TrOC**) and **Pharmaceuticals** products



NEW emerging technology

CEC Treatments



TPPBR

Two-Phase-Partitioning Biological Reactor (hybrid config.)

Sequencing biological reactor effective against the following CECs:

- Organic micropolluttants

NEW emerging technology

CEC
Treatments

Fungae (selected and modified)

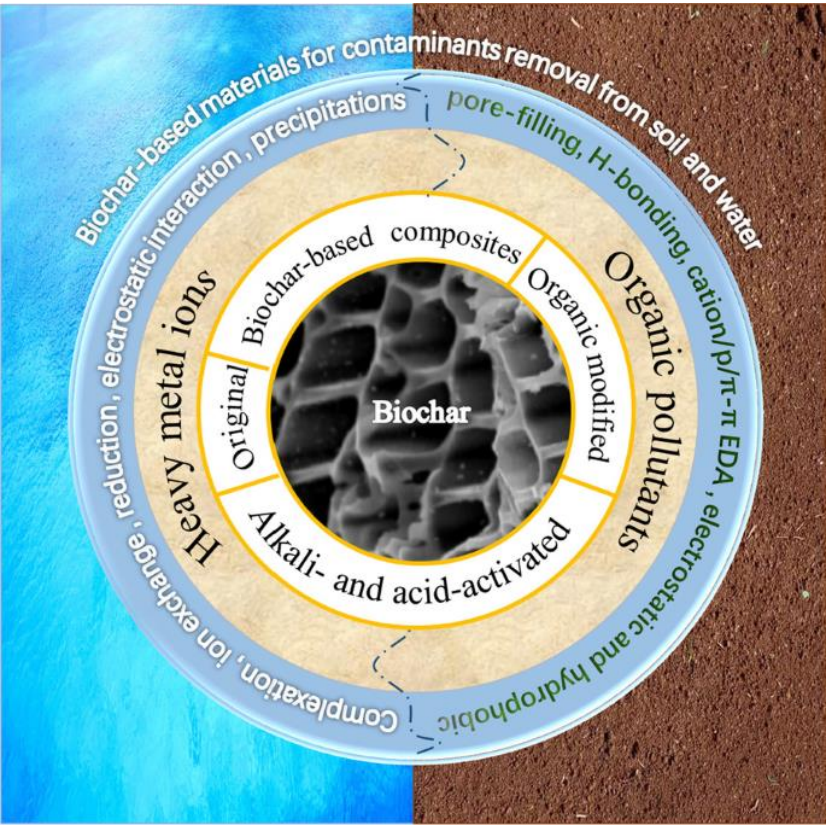
Bioremediation by fungi, also termed **mycoremediation**, has been more frequently observed in terrestrial than aquatic ecosystems.

- Fungae have the ability to break-down:
- Pesticides,
- Pharmaceuticals and PPCPs,
- Plastics, both conventional types and bioplastics,
- Mitigation of heavy metal pollution.

NEW emerging technology

CEC Treatments

GMO Microbes and **Nanosupports**

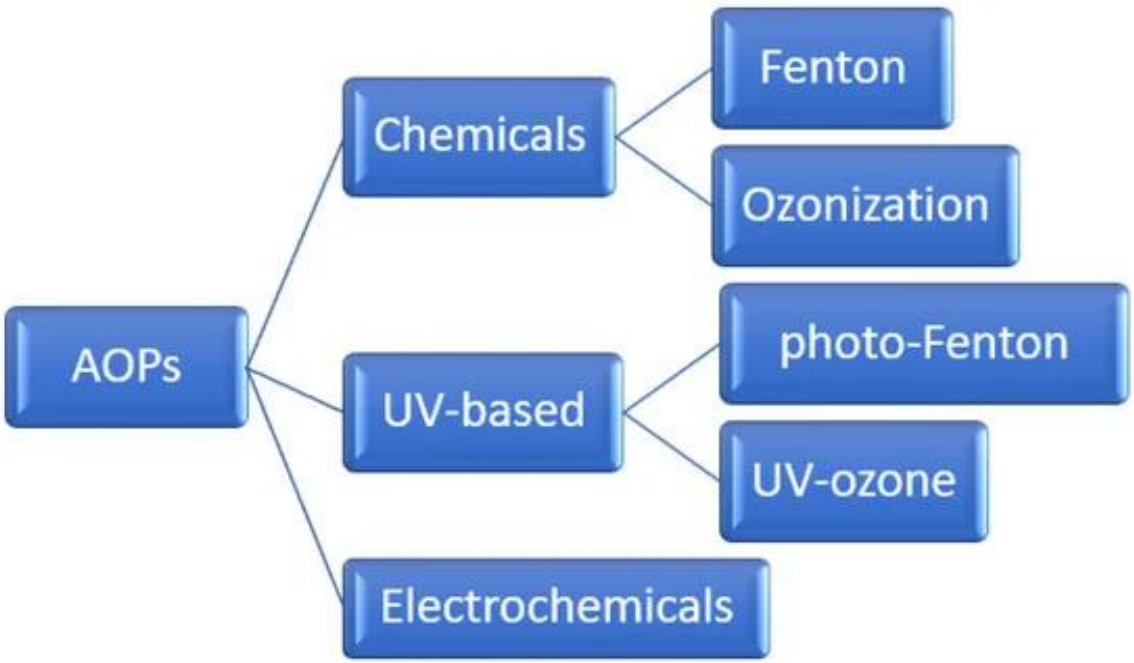


Naturally, existing microbes can be engineered using various techniques including, gene engineering, directed evolution, protein engineering, media engineering, strain engineering, cell wall modifications, rationale hybrid design, and encapsulation or immobilization process. The immobilization of microbes and enzymes using a variety of nanomaterials, membranes, and supports with high specificity toward the emerging pollutants is also an effective strategy to capture and treat the pollutants:

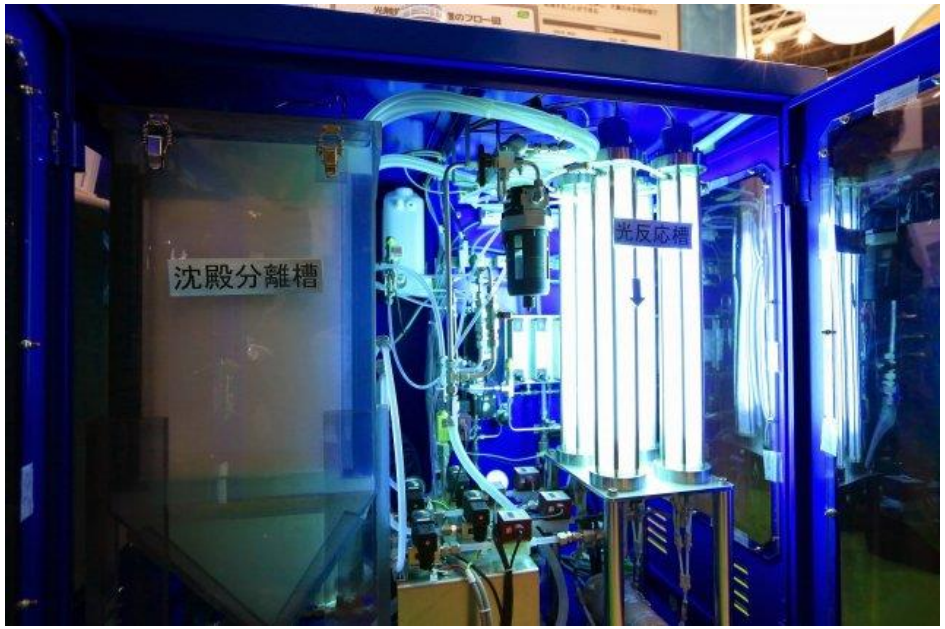
- PHA,
- Heavy Metals,
- REE,
- **NEW** emerging technology

CEC
Treatments

AOPs process resume



CEC
Treatments



Photocatalysis process

- Reduced graphene oxide (rGO)
- TiO_2, ZnO, $BiFeO_3$, $BiVO_4$, SnO_2, and CdO

Effective gainst paharma-molecules

Possibility to combination in other new/existing plant

CEC
Treatments

Contaminant	Type of Water	Hydrogen Potential (pH)	Catalyst Dose and Oxidant Dose	% Removal
Amoxicillin	Synthetic	3.5	$[H_2O_2]$ = 255 mg/L $[Fe^{2+}]$ = 25 mg/L	100%
Bisphenol A	Synthetic	3	Fe^{2+}/H_2O_2 = 0.012	100% (maximum)
Estrogens *	Activated sludge waste	3	Fe^{2+}/H_2O_2 = 0.167	70–98%
Paracetamol	Synthetic	3	H_2O_2/Fe^{2+} = 2	70.37%

Fenton process

Classical reactions, or Fenton reaction mechanisms, produce hydroxyl radicals (HO°) at pressure and room temperature at an acidic pH level in aqueous solution when hydrogen peroxide and ferrous ions come into contact.

Strong Radical Oxydation

CEC Treatments

Contaminant	Type of Water	Hydrogen Potential (pH)	Catalyst Dose and Oxidizer Dose	% Removal
Amoxicillin	Synthetic	3	$H_2O_2/Fe^{2+} = 20$	100%
Ampicillin	Synthetic	3	$H_2O_2/Fe^{2+} = 20$	100%
Cloxacillin	Synthetic	3	$H_2O_2/Fe^{2+} = 20$	100%
17α-ethinylestradiol	Wastewater with spike	3	$[Fe^{2+}] = 5$ mg/L $[H_2O_2] = 4.3–15$ mg/L	100%

Photo-Fenton process

The photo-Fenton process is AOP that generates hydroxyl radicals (HO°) through the use of hydrogen peroxide (H2O2), iron salts, and UV-visible light. In this case, the reactions are accelerated by light; the wavelength needed to perform the photo-Fenton AOP must be $\lambda < 580$ nm.

CEC Treatments

Contaminant	Type of Water	Direct Ozonation (O_3). % Removal	Indirect Ozonation (HO°). % Removal	% Large-Scale Removal
Paracetamol	Wastewater	97%	3%	ND*
Estrogens *	Wastewater	17–99%	1–83%	87–96%
Ofloxacin	Wastewater	7%	93%	80–92%
Metformin	Wastewater	1%	99%	ND*

Ozone

Ozone as such (direct form) used as an oxidant is very selective and, therefore, potentially attacks groups that are rich in electrons, for example, amines and activated aromatic rings, among others On the other hand, ozone can be used to generate hydroxyl radicals (HO°) and indirectly carry out the oxidation of organic compounds because hydroxyl radicals (HO°) are formed by the decomposition of O_3 are non-selective oxidants, as compared to the O_3. So it is better, from an oxidative point of view, to use ozone (O_3) to generate hydroxyl radicals because they are not selective instead of using ozone (O_3) directly to carry out the oxidation.

CEC
Treatments

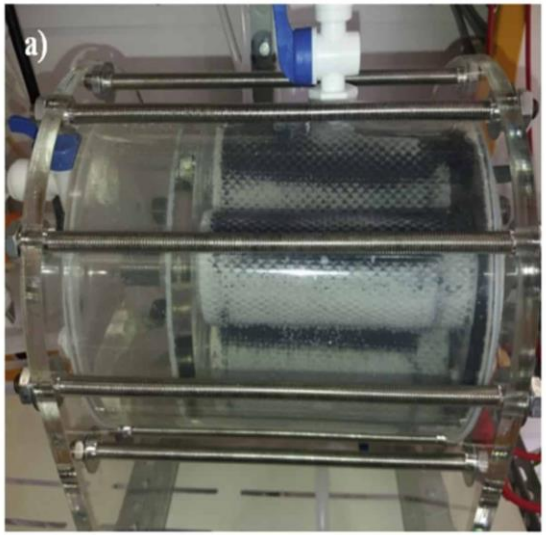
Contaminant	Type of Water	% Maximum Removal
Caffeine	Synthetic	95%
Mefenamic acid	Synthetic	60–80%
Ketoprofen	Synthetic	95% (mineralization)

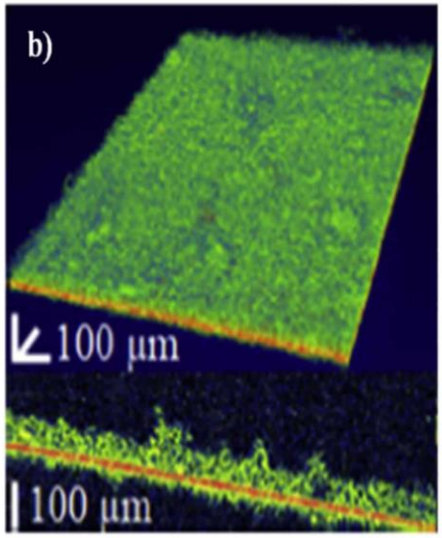
UV-Ozone

In UV-ozone AOP, the wavelength to be handled should be $\lambda < 300$ nm, so that dissolved ozone can be split and a fast reaction of atomic oxygen (O) with water (H_2O) takes place, and thermally excited hydrogen peroxide (H_2O_2) is generated (strong oxidant)

CEC Treatments

Electrochemicals process



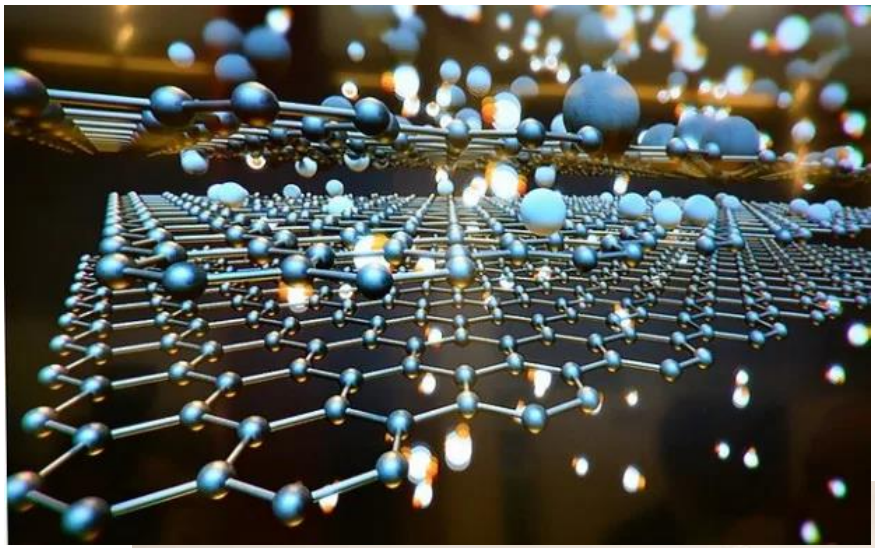


Contaminant	Type of Water	Important Notes	Electrochemical Method Used	% Removal
Paracetamol	Synthetic	pH independent	Anodic oxidation	100% (mineralization)
Ketoprofen	Synthetic	pH variable of minor importance	Anodic oxidation	100%
Tartrazine	Synthetic	-	Anodic oxidation	57.85–99.97%

Method for “in-situ” production of reactive oxygen species such as hydroxyl radicals (HO°). One of the most studied is the electrochemical anodic oxidation; in general, in this process, a high current density is applied to the anode in order to produce physiosorbed hydroxyl radicals on the anode surface M(HO°). The transfer of electrons, M(HO°) and M = O, or the combination of both, are part of the water cleaning process. However, the oxidation capacity depend on the electrochemical system used, the cell type, the electrodes, and the additional equipment, hydrodynamic parameters

NEW emerging technology

CEC
Treatments solutions



Graphene absorption
(nanotubes/nanopapers filters)
may be effective against:

- Organohalogen compounds,
- Pharma derivates,
- Pesticides,
- PPCPs

- Also hybrid-forms:
- Graphene + AlO_2

NEW emerging technology

Question time

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