
# Emerging contaminants in water/wastewater.

# Advanced oxidation processes.

**Aula 1** (semana 5)

# What are “**emerging** contaminants (ECs)”?

Chemicals that are being discovered in water/wastewater, that previously had not been detected or that are being detected at levels that may be significantly different than the expected.

# What are “**emerging** contaminants (ECs)”?

**<u>Emerging contaminants include</u>:**

- Pharmaceuticals
- Personal Care Products
- Endocrine Disrupting Compounds

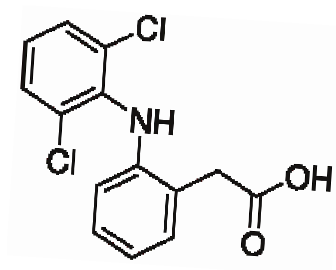
# Pharmaceuticals

- Human and veterinary substances taken in response to disease/maladies.
  - Cure disease
  - Alleviate disease associated symptoms
  - Prevent disease

# Pharmaceuticals

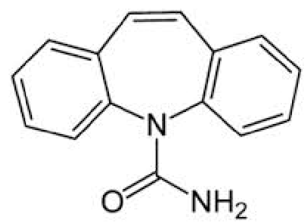
<u>Examples</u>:

- Diclofenac (antirheumatic)



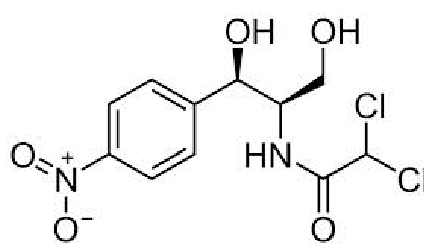


- Carbamazepine (antiepileptic)





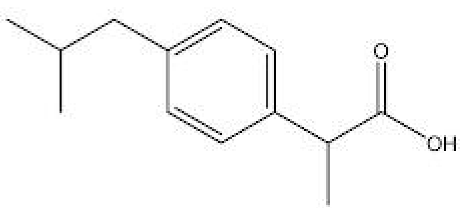
- Chloramphenicol (antibiotic)



# Pharmaceuticals

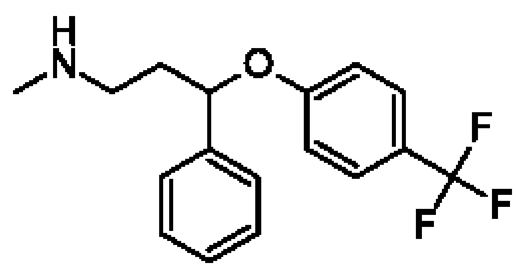
<u>Examples</u>:

- Ibuprofen (anti-inflammatory)


Molécula de ibuprofeno

- Fluoxetine (antidepressant)

# Personal Care Products


- Compounds used in our daily lives
  - Detergents, soaps, perfumes, aftershaves
  - Cleaning agents, disinfectants, sprays, deodorants
  - Bug sprays, sunscreens
  - Products are typically associated with hygiene


# Endocrine Disrupting Compounds

- Disrupt normal function of the endocrine system
- Mimic hormones;
- Active at very low levels;
- Concern about additive or synergistic effects caused by mixtures of EDCs;

# Endocrine disrupting compounds timeline

**Several studies pointed out that persistent, man-made chemicals were being transferred in the environment**

....

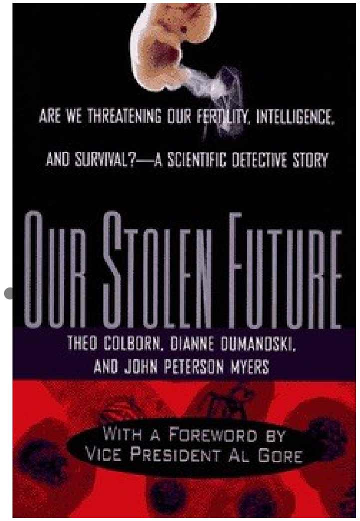
**1st time the term "endocrine disruption" was used**

**1991**

**1992**

**Turning point**

**1996**




**"Our stolen future" was published**

**"Chemically Induced Alterations in Sexual and Functional Development: The Wildlife/Human Connection".**

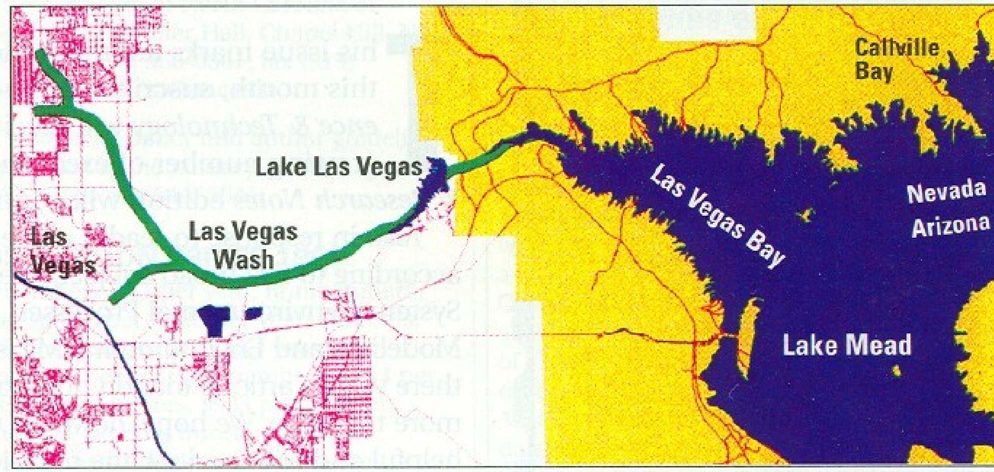
**Wingspread Consensus Statement**
**International scientists from different research areas shared their research on the nature and possible causes of these problems.**

8 A ■ JAN. 1, 1998 / ENVIRONMENTAL SCIENCE & TECHNOLOGY / NEWS

# Human estrogens linked to endocrine disruption

For the first time in North America, high levels of natural and synthetic hormones in municipal wastewater treatment plant effluent have been linked with endocrine disruption in fish. The study by researchers at Michigan State University's Department of Zoology indicates that human hormones, not industrial chemicals, in the effluent caused male fish to produce vitellogenin, a well-accepted indicator of endocrine disruption.

"This is a significant, if not a surprising, result," commented Gary Ankley, an EPA toxicologist who studies endocrine disrupters. The results were similar to findings published last year by U.K. researchers that identified hormones secreted in women's urine as the cause of vitellogenesis in caged fish exposed to sewage effluent in U.K. waters.

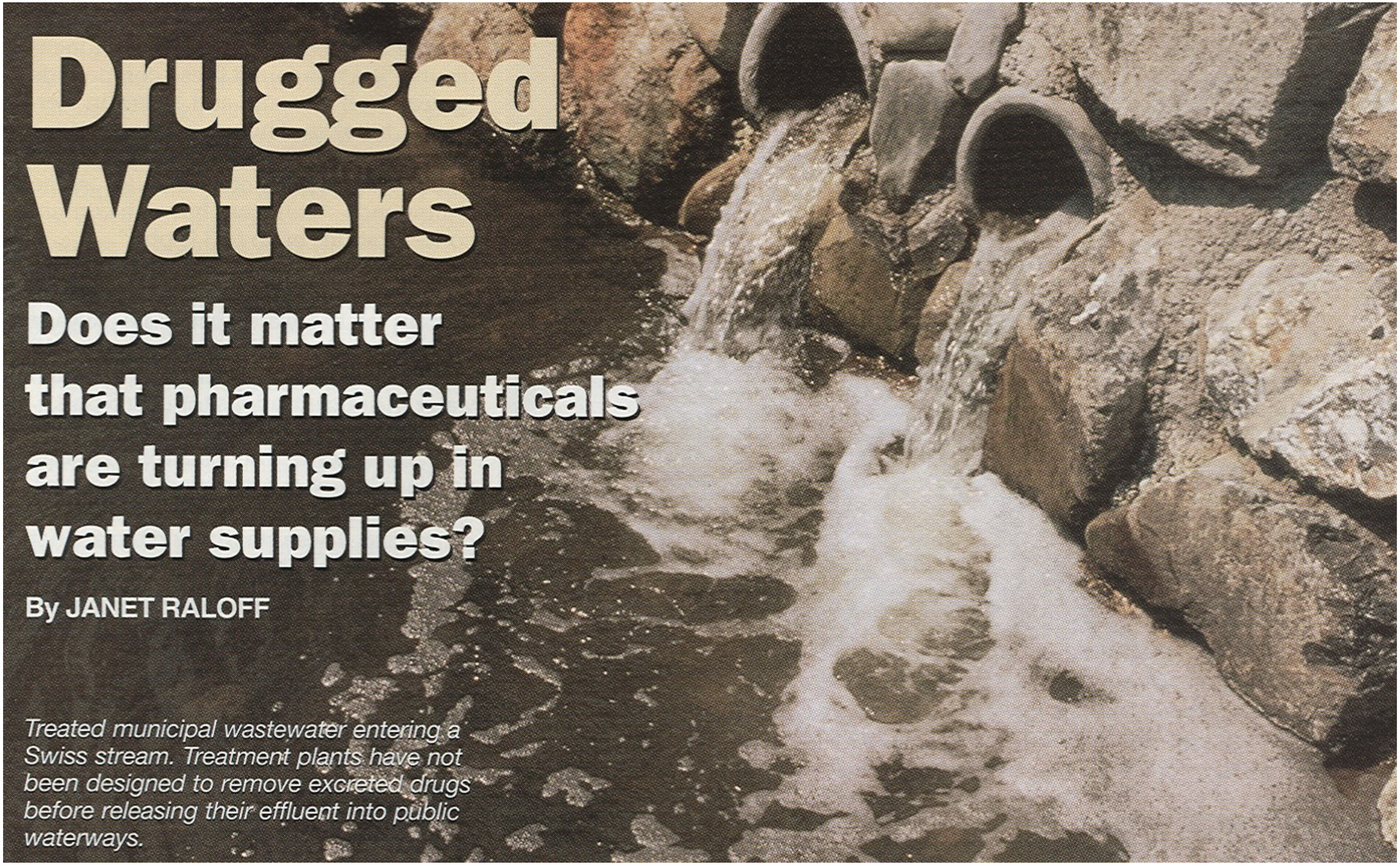



High levels of a female protein in male fish found in Lake Mead, Nev., led to a search for the cause in the effluent-dominated waters of the Las Vegas Wash. (Courtesy Shane Snyder, Michigan State University)

the compounds that were likely to act like estrogens in the fish. They also used an innovative method that involves solid-phase extraction and in vitro cellular bioassays to detect endocrine-modulating compounds in complex aqueous mixtures. Of the

the highest level of estrogenic activity in effluent downstream from a small plant (55,000 gal/day) with relatively few treatment processes.

Results from a companion Michigan State study, in which caged fish were exposed to Michigan wastewater effluent, suggest



# Drugged Waters

## Does it matter that pharmaceuticals are turning up in water supplies?

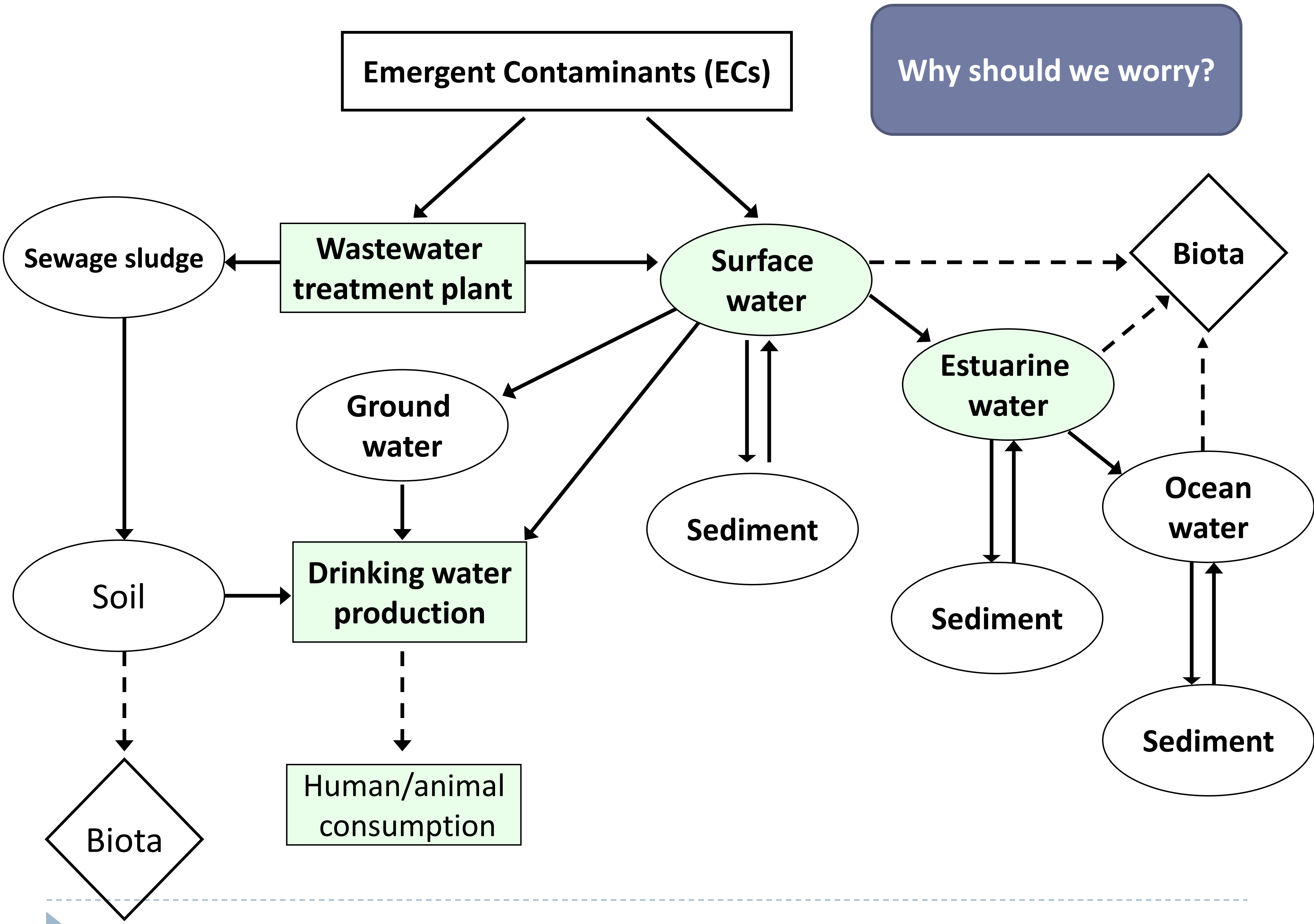
By JANET RALOFF

*Treated municipal wastewater entering a Swiss stream. Treatment plants have not been designed to remove excreted drugs before releasing their effluent into public waterways.*

MARCH 21, 1998 SCIENCE NEWS, VOL. 153

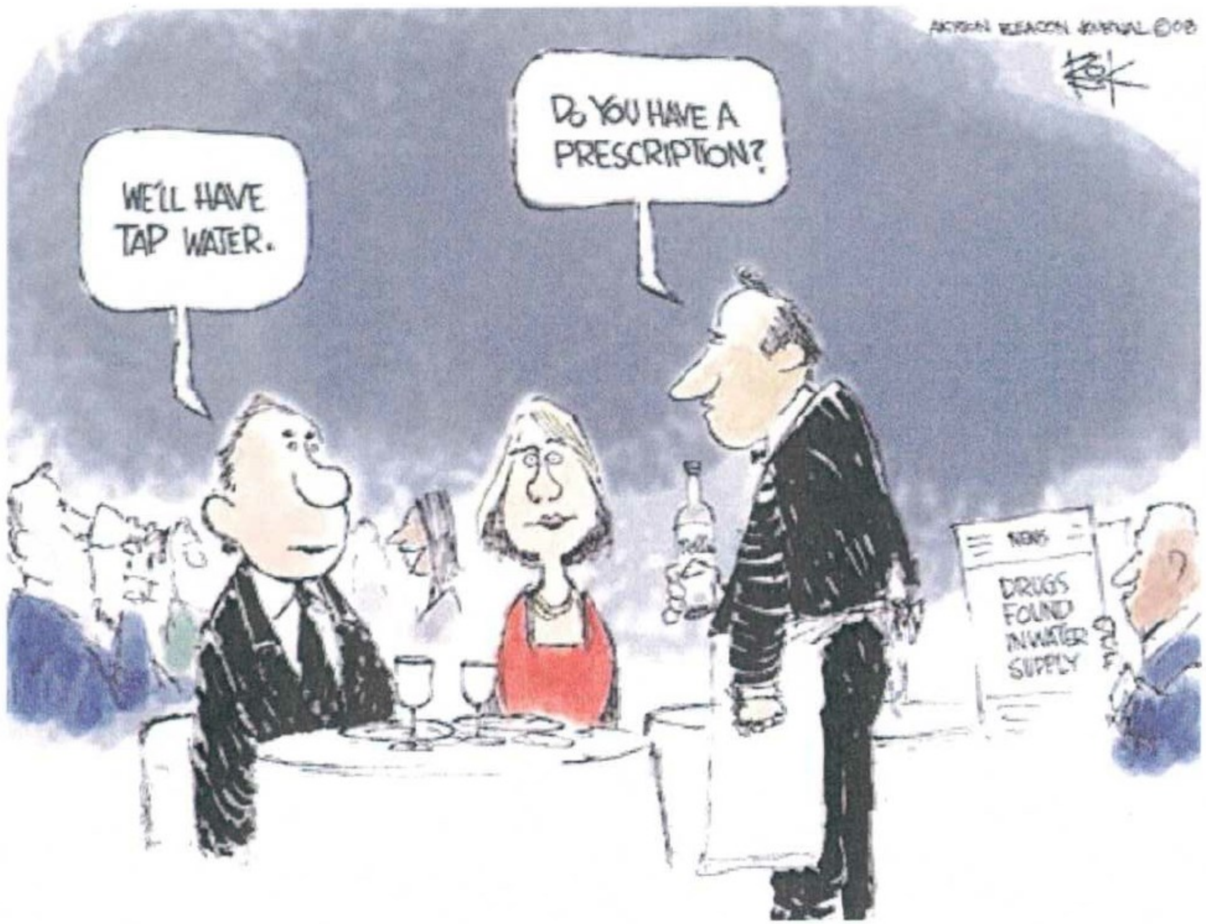
# Target Compounds

| Pharmaceuticals (20) | Potential EDCs (26) | Steroid Hormones (5) | Phytoestrogens (11) |
|---|---|---|---|
| Atenolol | Atrazine | Estradiol | Apigenin |
| Atorvastatin | Benzophenone | Estrone | Biochanin A |
| *o-Hydroxy atorvastatin* | BHA | Ethinylestradiol | Chrysin |
| *p-Hydroxy atorvastatin* | BHT | Progesterone | Coumestrol |
| Carbamazepine | a-BHC | Testosterone | Daidzein |
| Diazepam | b-BHC | | Equol |
| Diclofenac | g-BHC | | Formononetin |
| Dilantin | d-BHC | | Genistein |
| Enalapril | Bisphenol A | | Glycitein |
| Fluoxetine | Butylbenzyl phthalate | | Matairesinol |
| *Norfluoxetine* | DEET | | Naringenin |
| Gemfibrozil | Diazinon | | |
| Meprobamate | Dioctyl phthalate | | |
| Naproxen | Galaxolide | | |
| Risperidone | Linuron | | |
| Simvastatin | Methoxychlor | | |
| *Simvastatin hydroxy acid* | Metolachlor | | |
| Sulfamethoxazole | Musk ketone | | |
| Triclosan | Nonylphenol | | |
| Trimethoprim | ….. | | |



Emergent Contaminants (ECs)
Why should we worry?
Sewage sludge
Wastewater treatment plant
Surface water
Biota
Estuarine water
Ground water
Sediment
Ocean water
Soil
Drinking water production
Sediment
Sediment
Biota
Human/animal consumption

# Relevance to Human Health



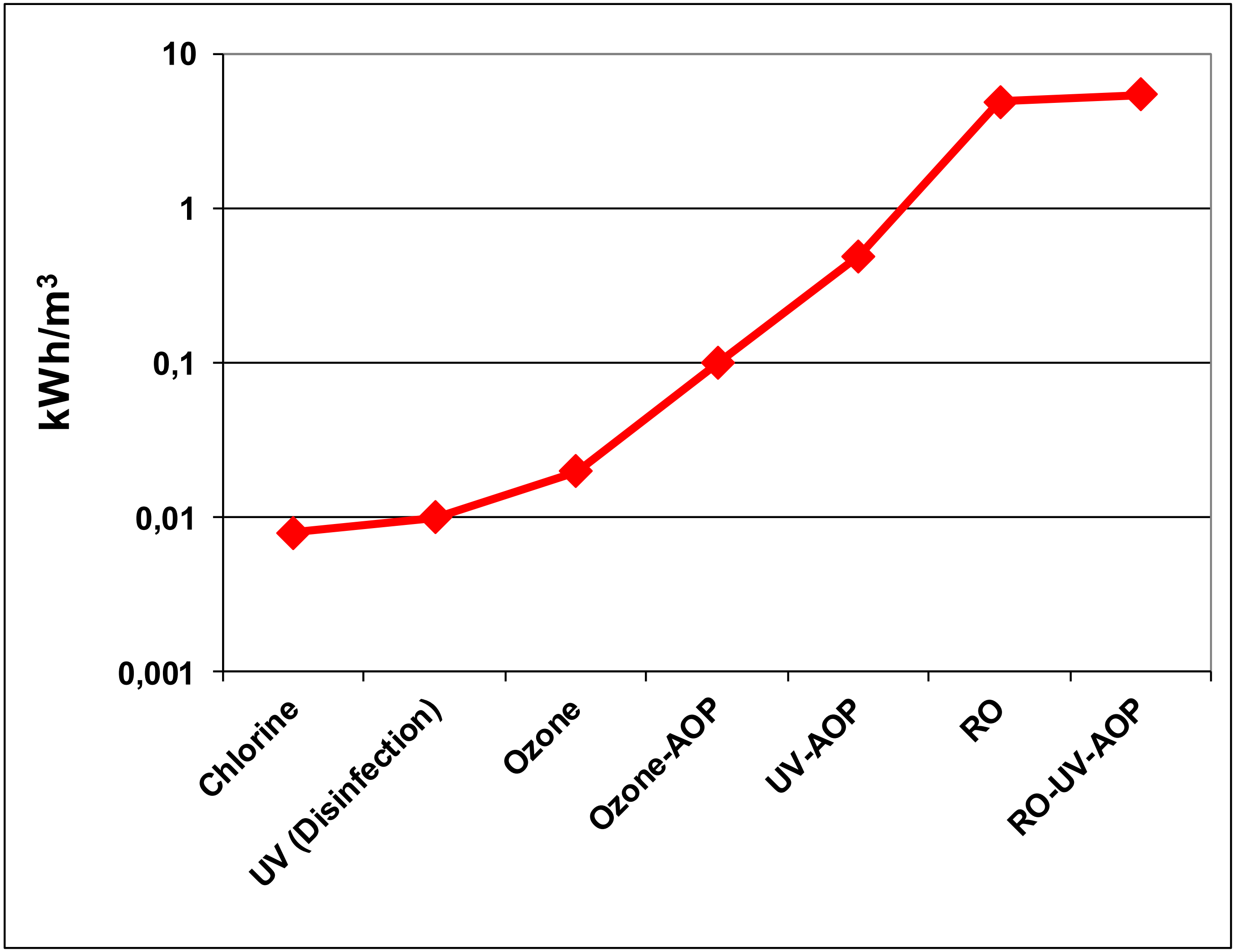
# And now?...

- How can we remove ECs?

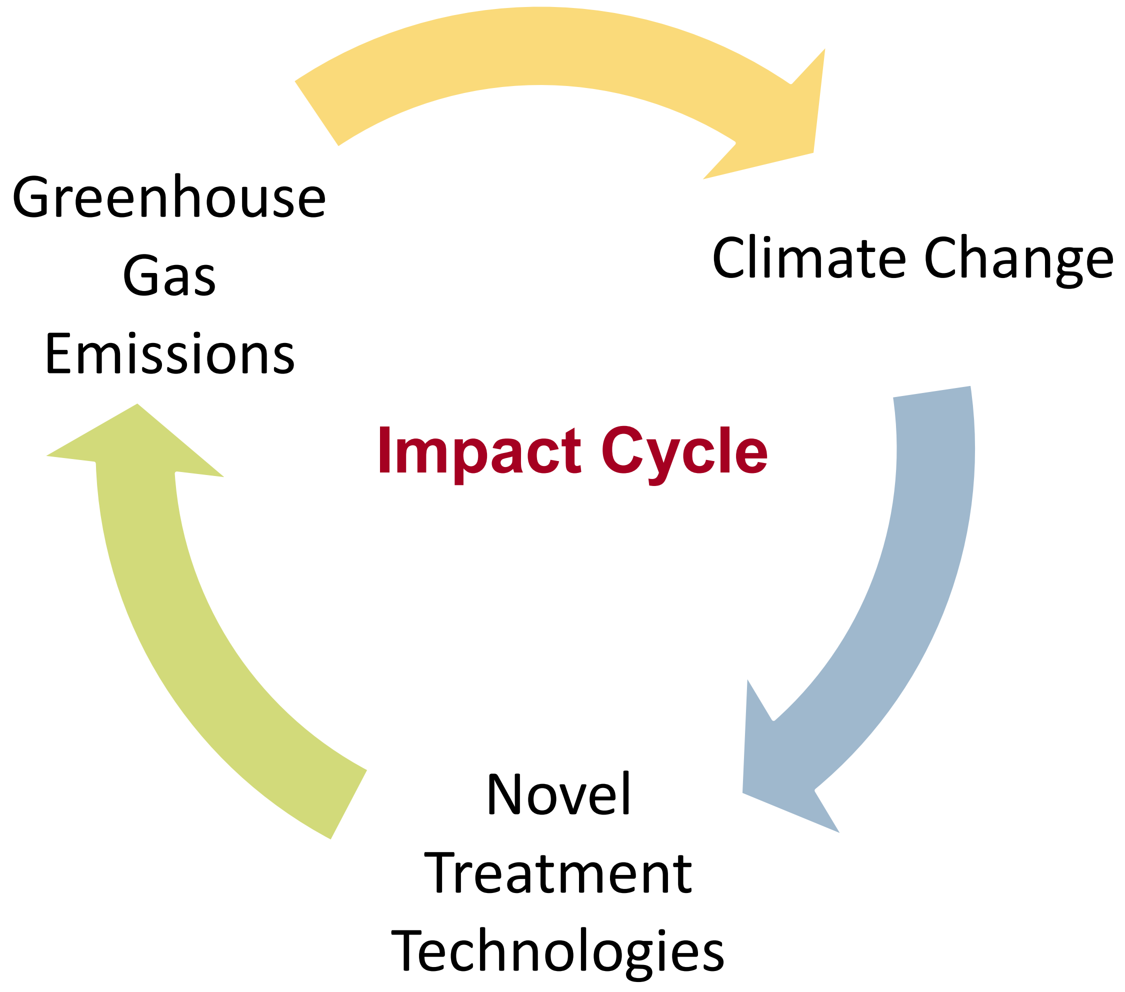
Any chemical can be removed from water/wastewater using highly sophisticated technology, but…

…its important to assess the operational costs associated and environmental aspects involved

# Energy per $m^3$ of Water treated and type of Process



# *Nexus* Water-Energy



# Advanced Oxidation Possesses (AOP)

Advanced oxidation processes (AOP) are based on insitu generation of free radicals, particularly the hydroxyl radical (·OH).

# Comparison of Oxidation Potentials

| | |
|---|---|
| Florine | 3.03 V |
| **Hydroxyl radical** | **2.80 V** |
| Atomic Oxygen | 2.42 V |
| Ozone | 2.07 V |
| $H_2O_2$ | 1.78 V |
| Perhydroxyl radical | 1.70 V |
| Permanganate | 1.68 V |
| Hypobromous acid | 1.59 V |
| Chlorine dioxide | 1.57 V |
| Hypoclorous acid | 1.49 V |
| Chlorine | 1.36 V |

# AOPs for Water and Wastewater Treatment

- Catalysis
- Electrochemical
- Fenton's Reagent
- Ferrate
- Ionizing Radiation
- Microwave
- Photo-Fenton's Reagent
- Photocatalysis
- Pulsed Plasma
- Supercritical water oxidation
- Ultrasound

- UV
- UV/$H_2O_2$
- UV/$H_2O_2$/$O_3$
- Vacuum UV
- Wet Air Oxidation

## Hydroxyl radicals reaction mechanisms

a) **Hydrogen removal**

$$RH + HO^* \rightarrow R^* + H_2O$$

$$2\ HO^* \rightarrow H_2O_2$$

$$R^* + H_2O_2 \rightarrow ROH + HO^*$$

$$R^* + O_2 \rightarrow ROO^*$$

$$ROO^* + RH \rightarrow ROOH + R^*$$

## Hydroxyl radicals reaction mechanisms

b) **Electrophilic addition (or substitution)**

$$HO^* + X_2C = CX_2 \rightarrow X_2C\,(OH) - C^*X_2$$

c) **Electron transfer**

$$RX + HO^* \rightarrow RX^{+*} + H_2O$$

# AOPs for Water and Wastewater Treatment

## Hydroxyl radicals reaction mechanisms

d) **Radicals interaction**

$$HO^* + HO^* \rightarrow H_2O_2$$

$$H_2O_2 + HO^* \rightarrow HO_2^* + H_2O$$

# AOPs for Water and Wastewater Treatment

The **ultimate AOP aim is to mineralize** - convert constituents of an organic pollutant into simple, harmless and inorganic molecules.

- Carbon to carbon dioxide
- Hydrogen to water
- Phosphorus to phosphates or phosphoric acids
- Sulphurs to sulphates
- Nitrogen to nitrates
- Halogens to halogen acids

# AOPs for Water and Wastewater Treatment

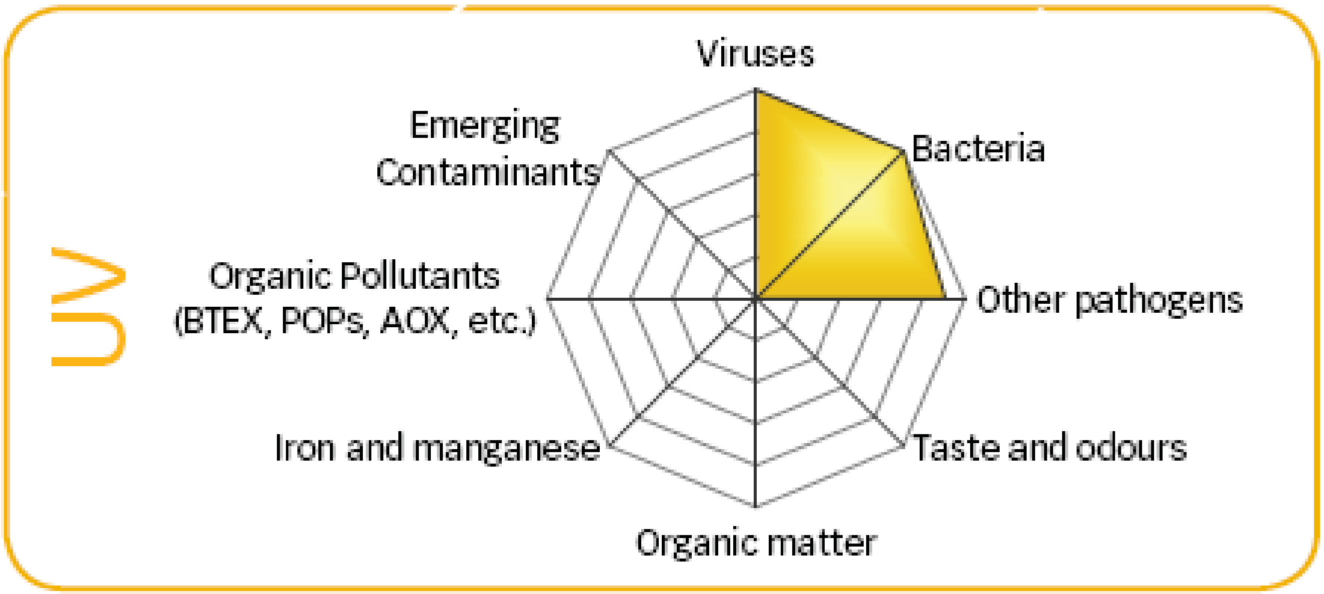
In some cases it is sufficient to partially oxidise the pollutant, enabling its following degradation by another process, e.g. biological oxidation.

Oxidation reactions can be classified according to their **extension** in:

- **Acceptable degradation** – change in compound's structure **decreasing** its **toxicity**
- **Definitive degradation** – conversion to $CO_2$
- **Unacceptable degradation** - change in compound's structure **increasing** its toxicity
- **Primary degradation** – change in compound's structure

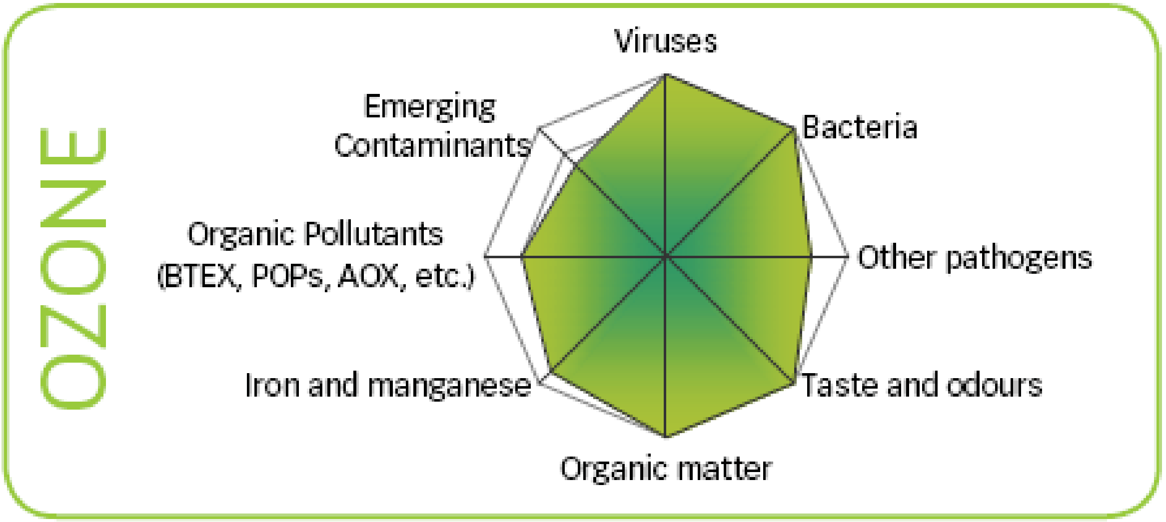
# AOPs for Water and Wastewater Treatment

**Applicability**



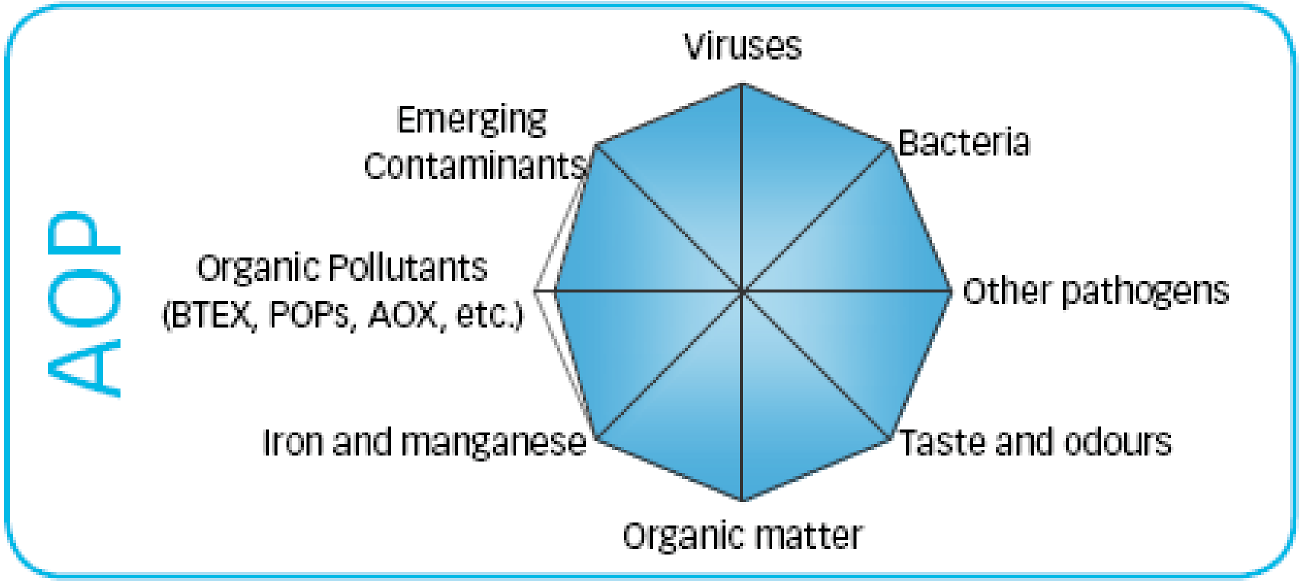
# AOPs for Water and Wastewater Treatment

## Applicability



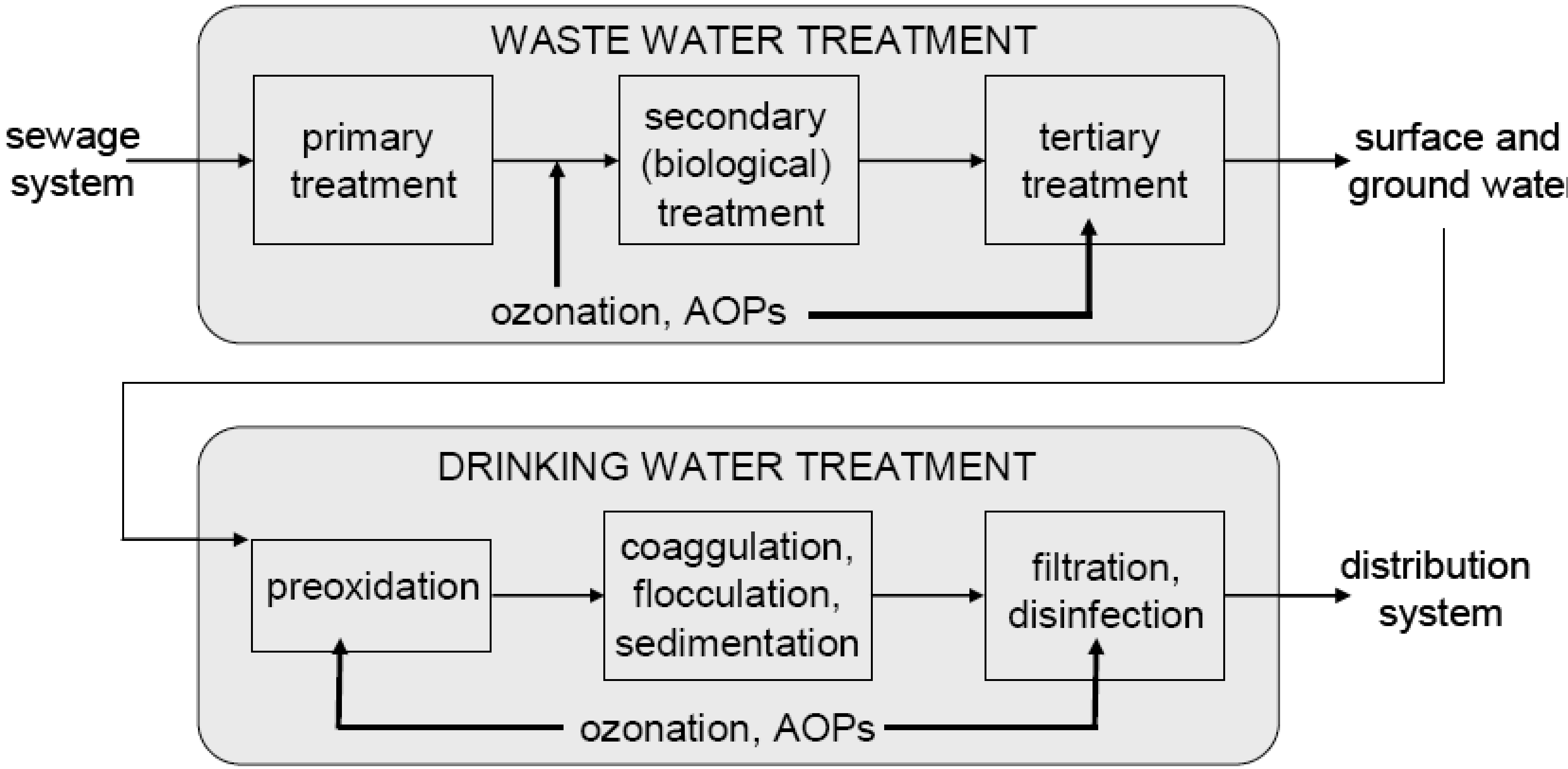
# AOPs for Water and Wastewater Treatment

**Applicability**



# AOPs for Water and Wastewater Treatment

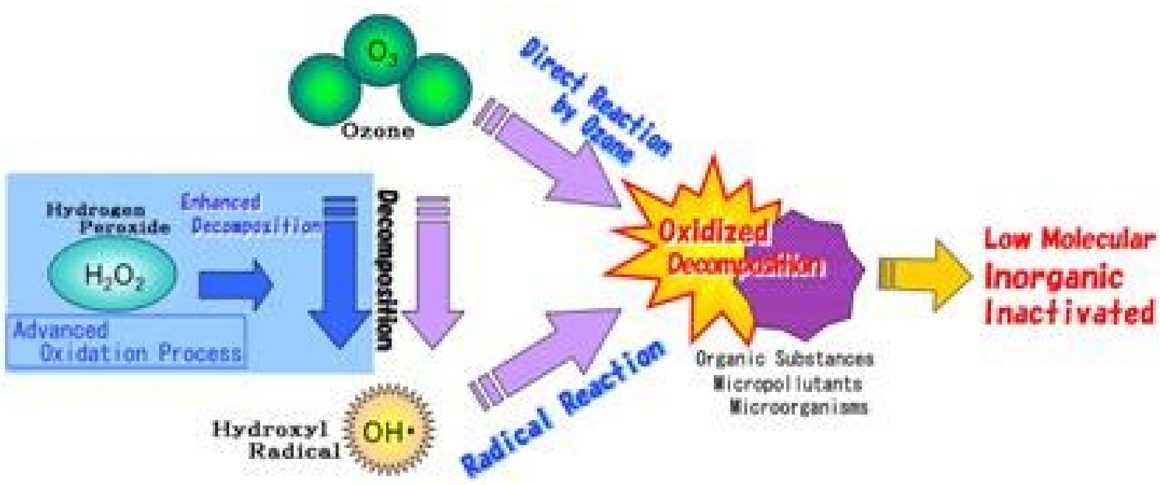
**Applicability**



# AOPs for Water and Wastewater Treatment

## Ozone, Hydrogen peroxide

Ozone can react with organic compounds **directly** or **indirectly** (through decomposition and formation of hydroxyl radicals).



# AOPs for Water and Wastewater Treatment

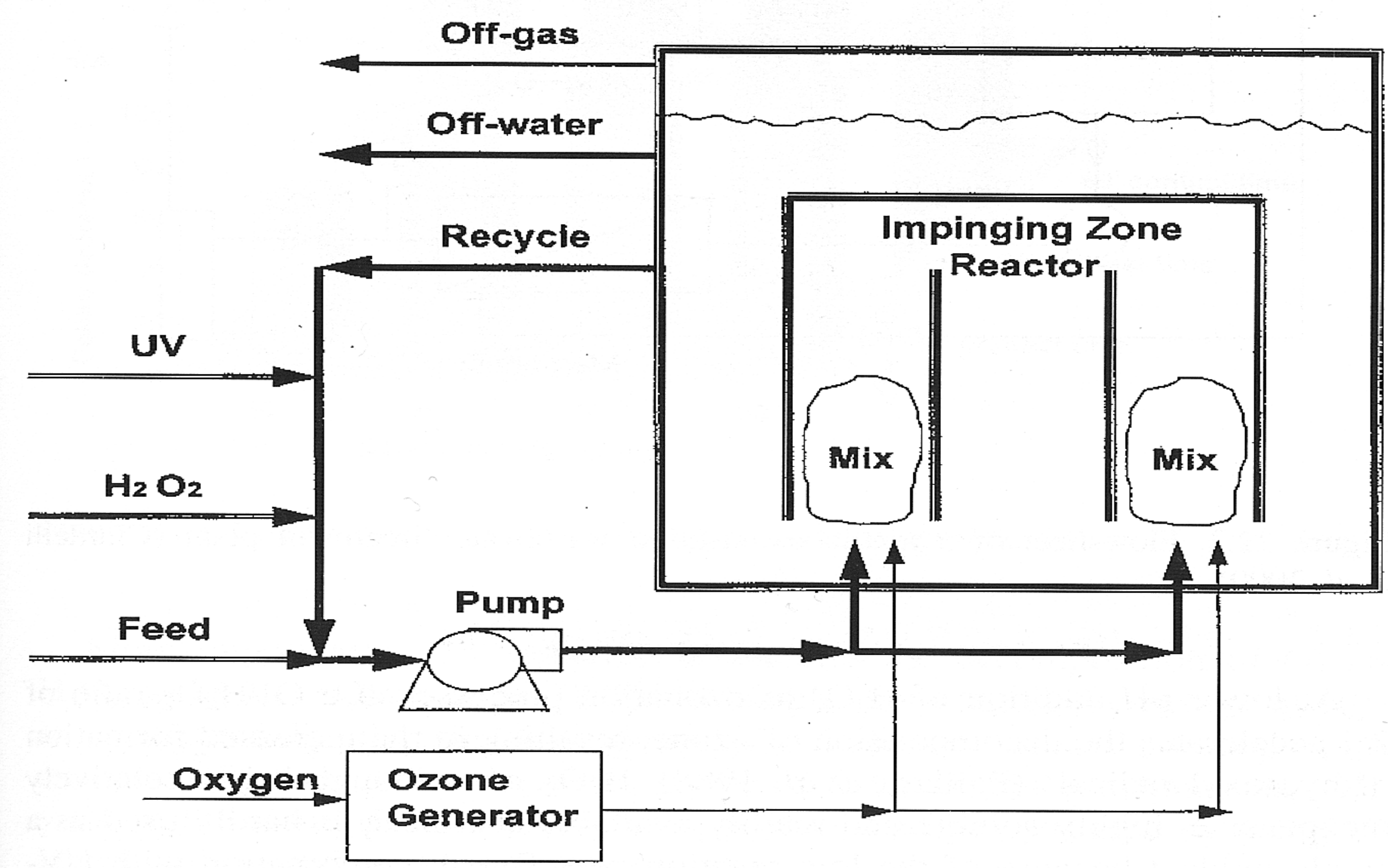
## Ozone, Hydrogen peroxide

- **Ozone lifetime** in an industrial wastewater can vary from **1 min to 30 min**, depending on the type of pollutant, ozone-pollutant reactivity and pH
- When pH raises, ozone decomposition rate in water increases. For example, at pH=10, ozone lifetime can be **lower than 1 min**

# AOPs for Water and Wastewater Treatment

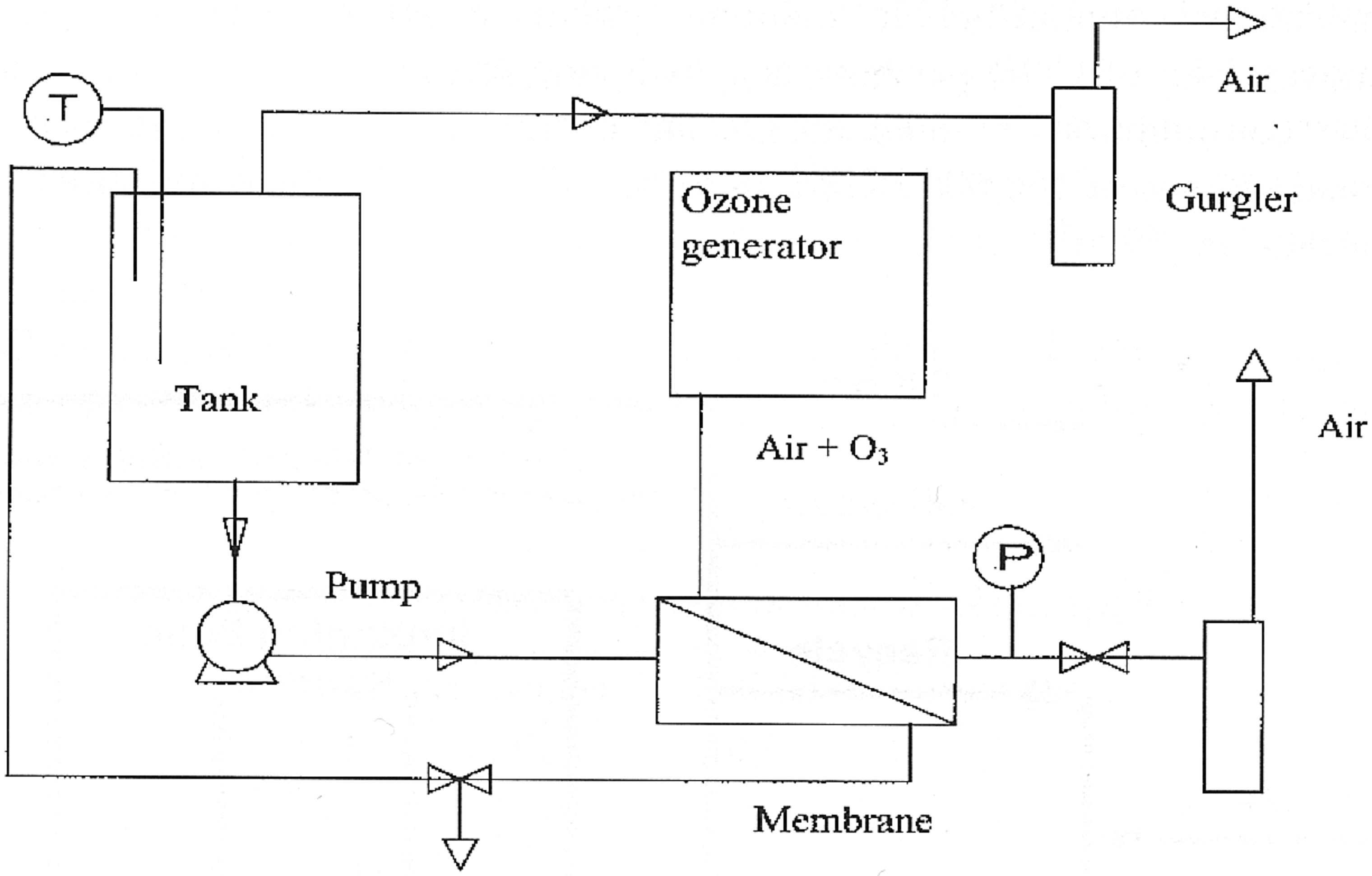
**Ozone, Hydrogen peroxide**

**CHEMOX Process**



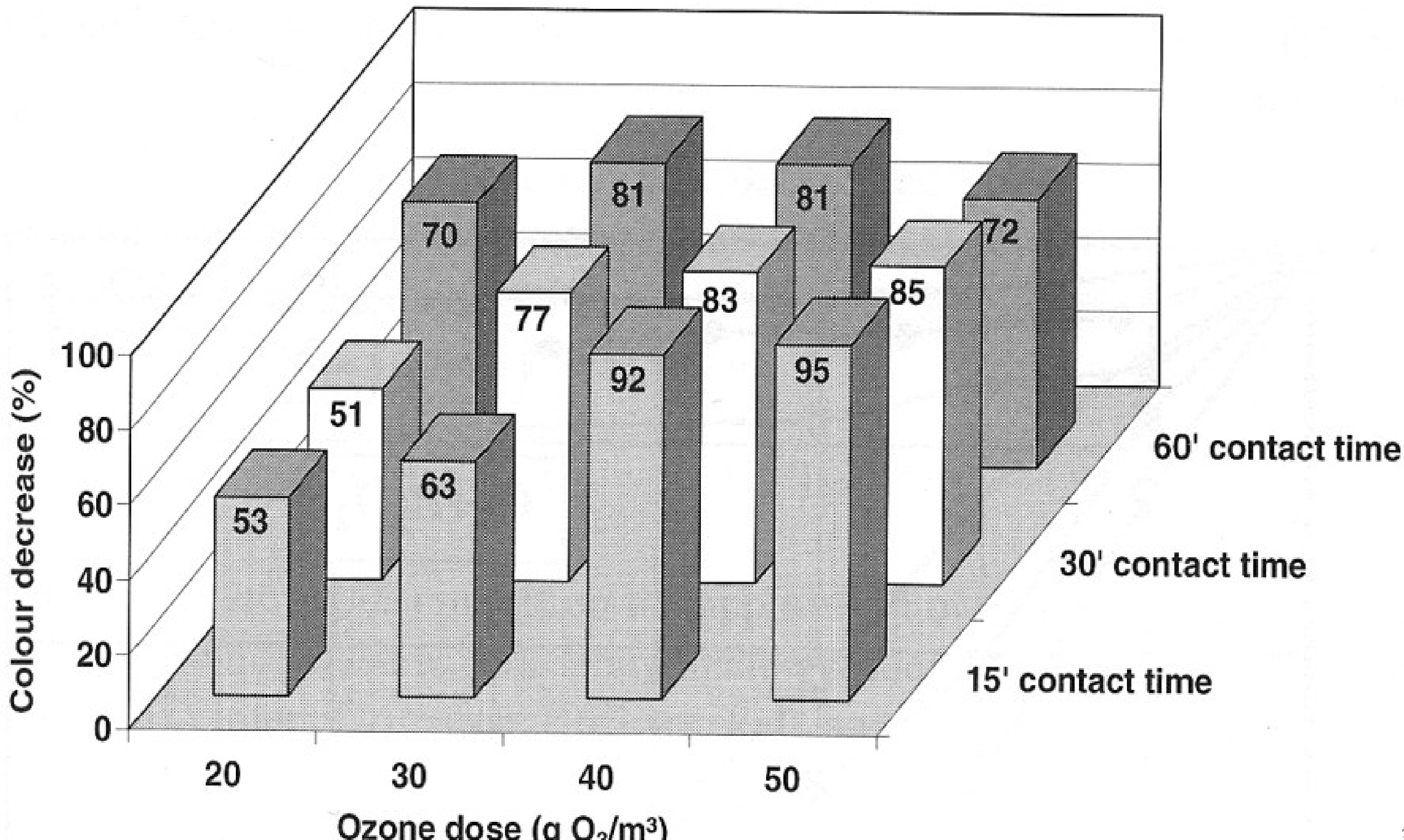
# AOPs for Water and Wastewater Treatment

## Ozonation process in a textile industry wastewater treatment plant



# AOPs for Water and Wastewater Treatment

## Colour reduction versus contact time



# AOPs for Water and Wastewater Treatment

**Ozone, Hydrogen peroxide UV radiation**

**UV radiation** can lead to complete oxidation reactions:

- By Photolysis
- Because compounds absorb energy due to UV radiation

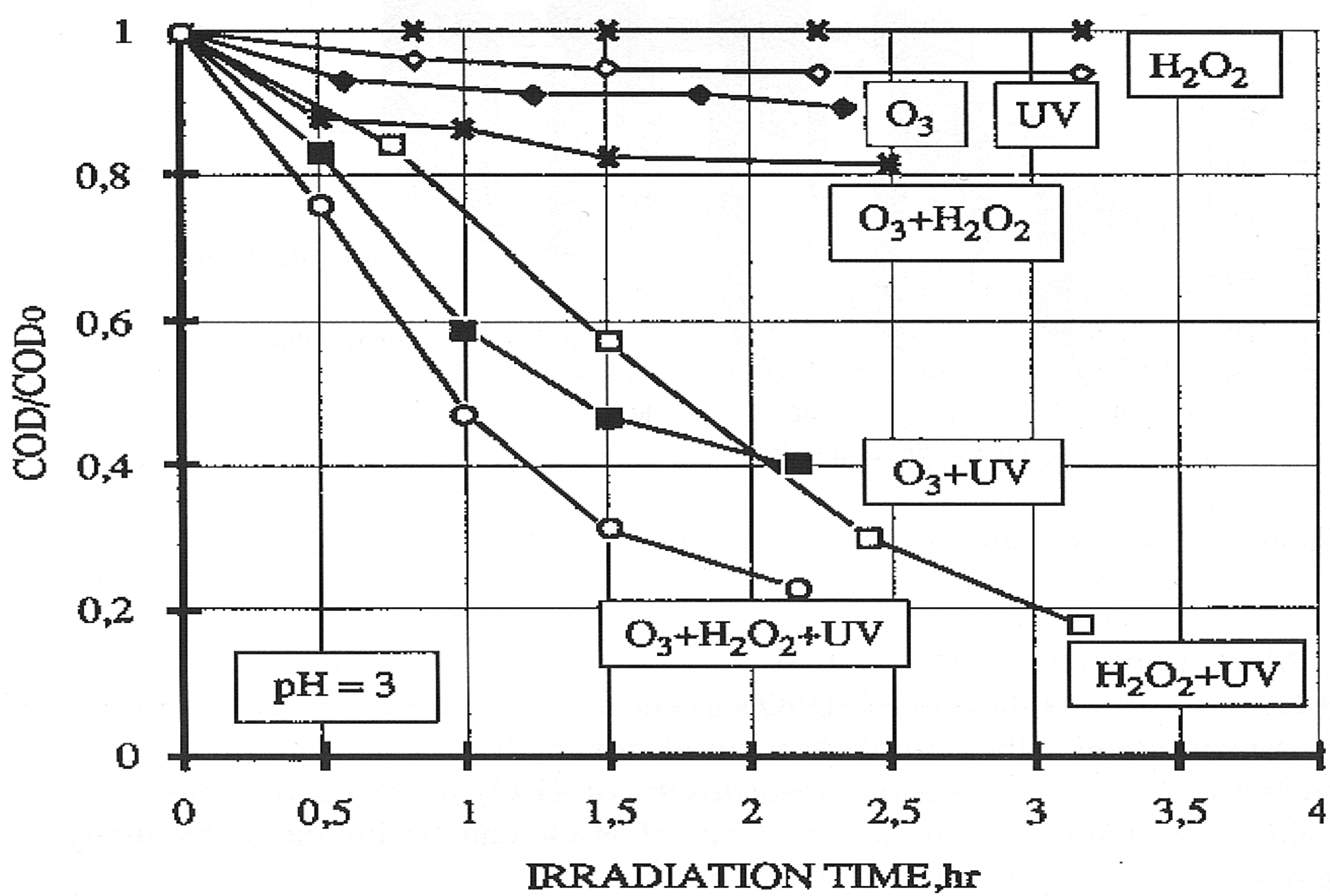
↓

Become more reactive

↓

React more effectively
with ozone or $H_2O_2$

# AOPs for Water and Wastewater Treatment



# AOPs for Water and Wastewater Treatment

## Fenton and Photo-Fenton

Fenton:

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

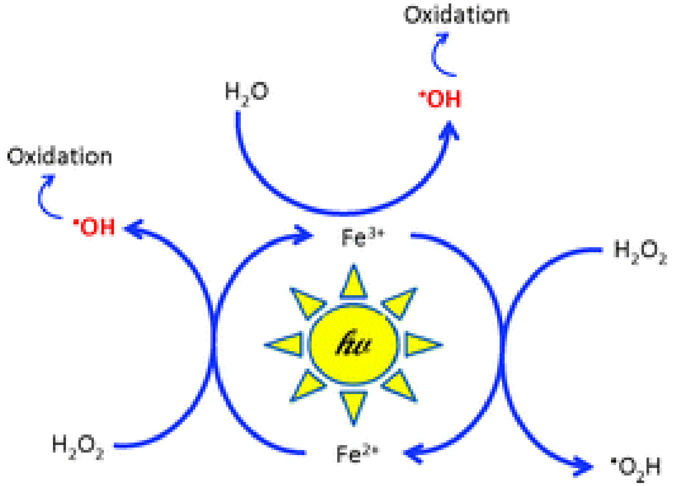



Photo-Fenton:

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

$$Fe^{3+} + H_2O + h\nu_{(\lambda=254\ nm)} \rightarrow Fe^{2+} + H^+ + {}^{\bullet}OH$$

# AOPs for Water and Wastewater Treatment

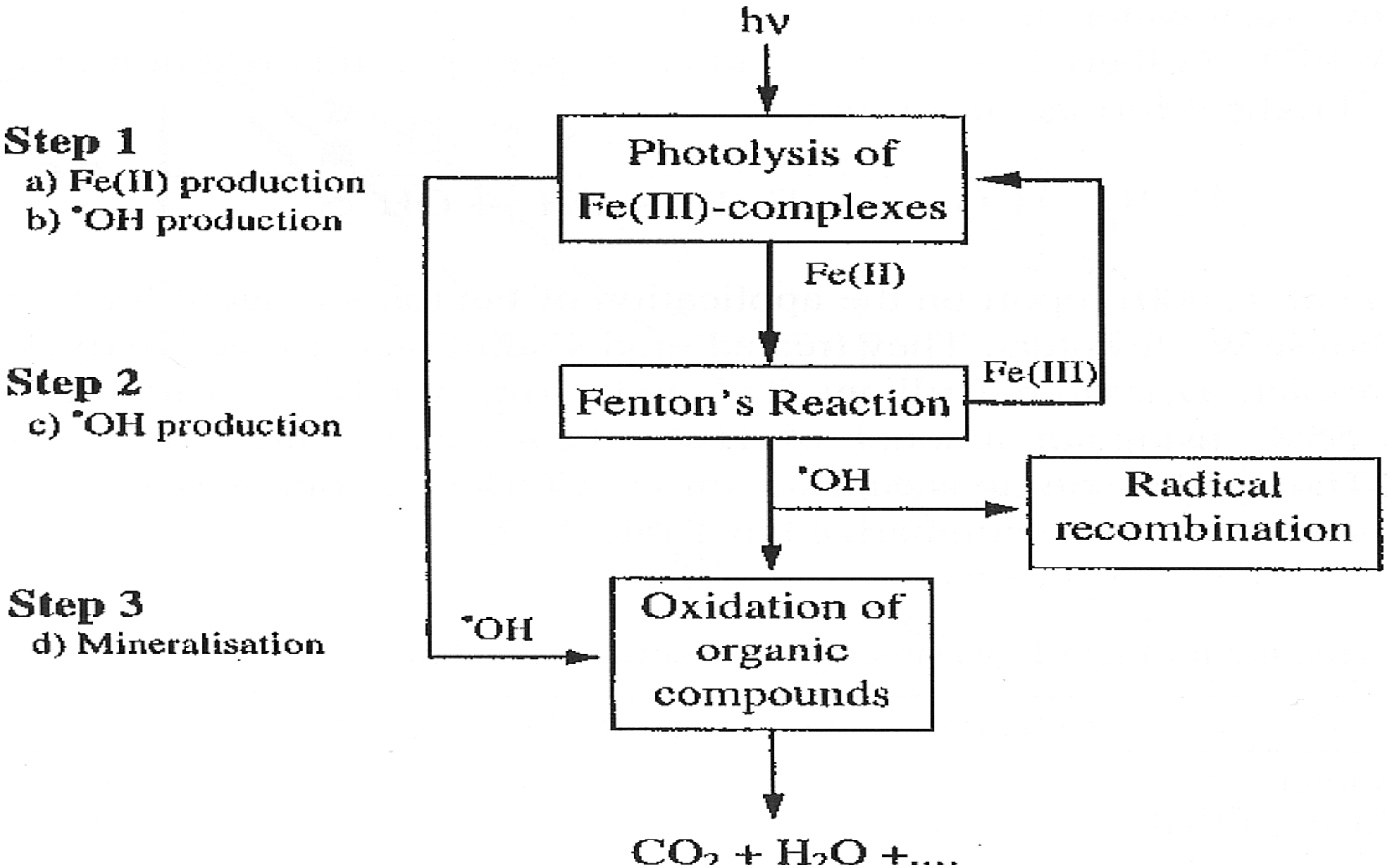
## Fenton

### Textile wastewater treatment by Fenton

| Pigment | COD removal | Colour removal |
|---|---|---|
| Drimaren Violet | 80% | > 99% |
| Drimaren Brilliant Red | 77% | 88% |
| Drimaren Black | 92% | > 99% |

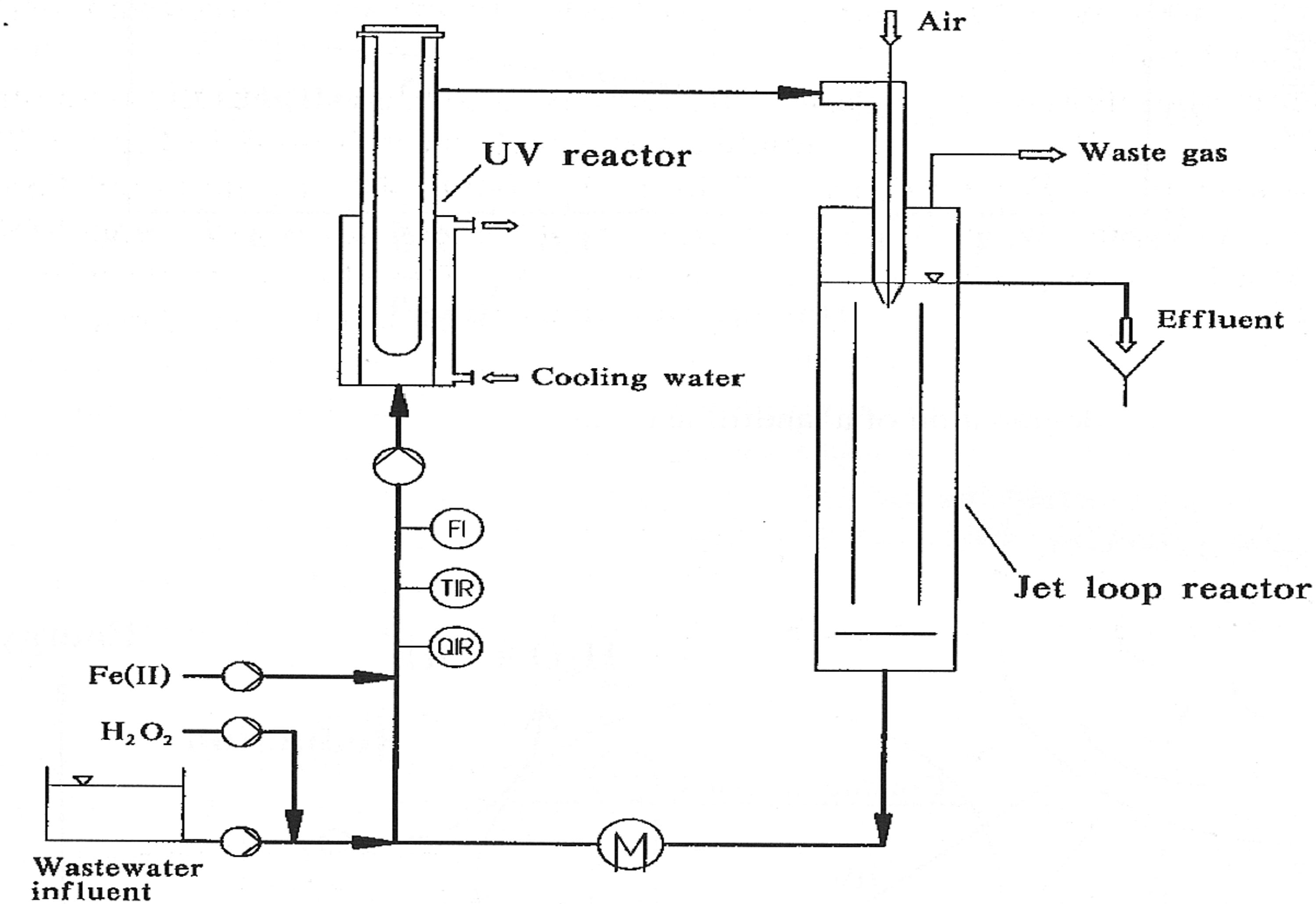
# AOPs for Water and Wastewater Treatment

## Photo-Fenton process



# AOPs for Water and Wastewater Treatment

Lay-out of a Photo-Fenton process for wastewater treatment



# AOPs for Water and Wastewater Treatment

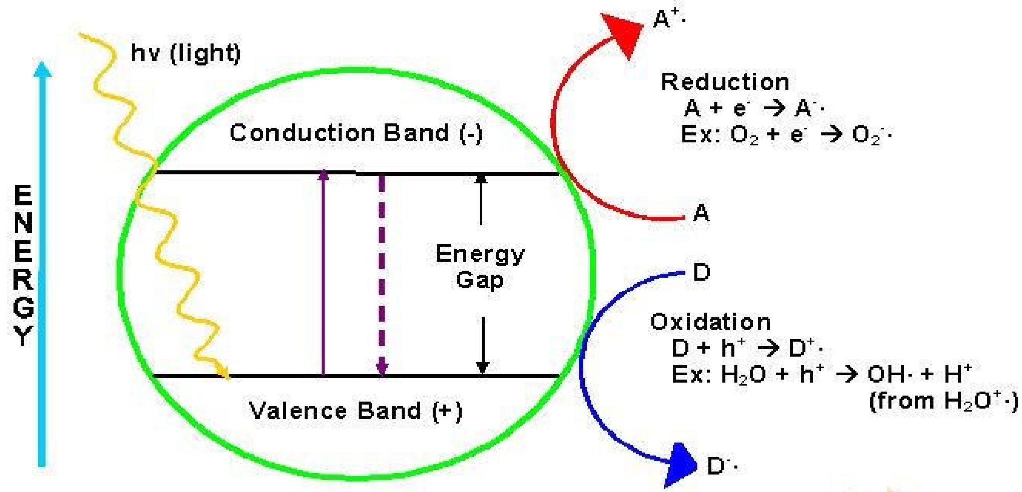
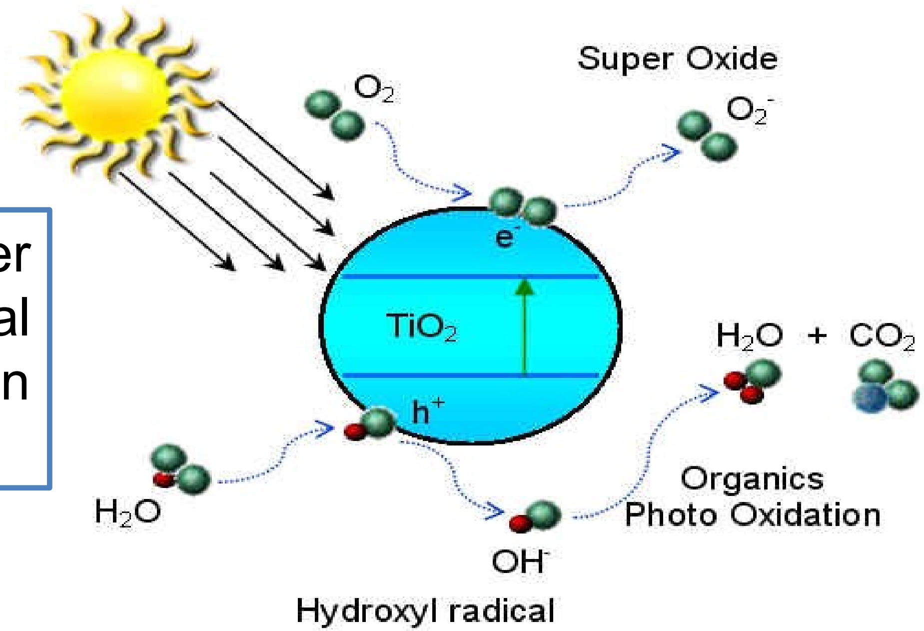



**Photo-catalysis**

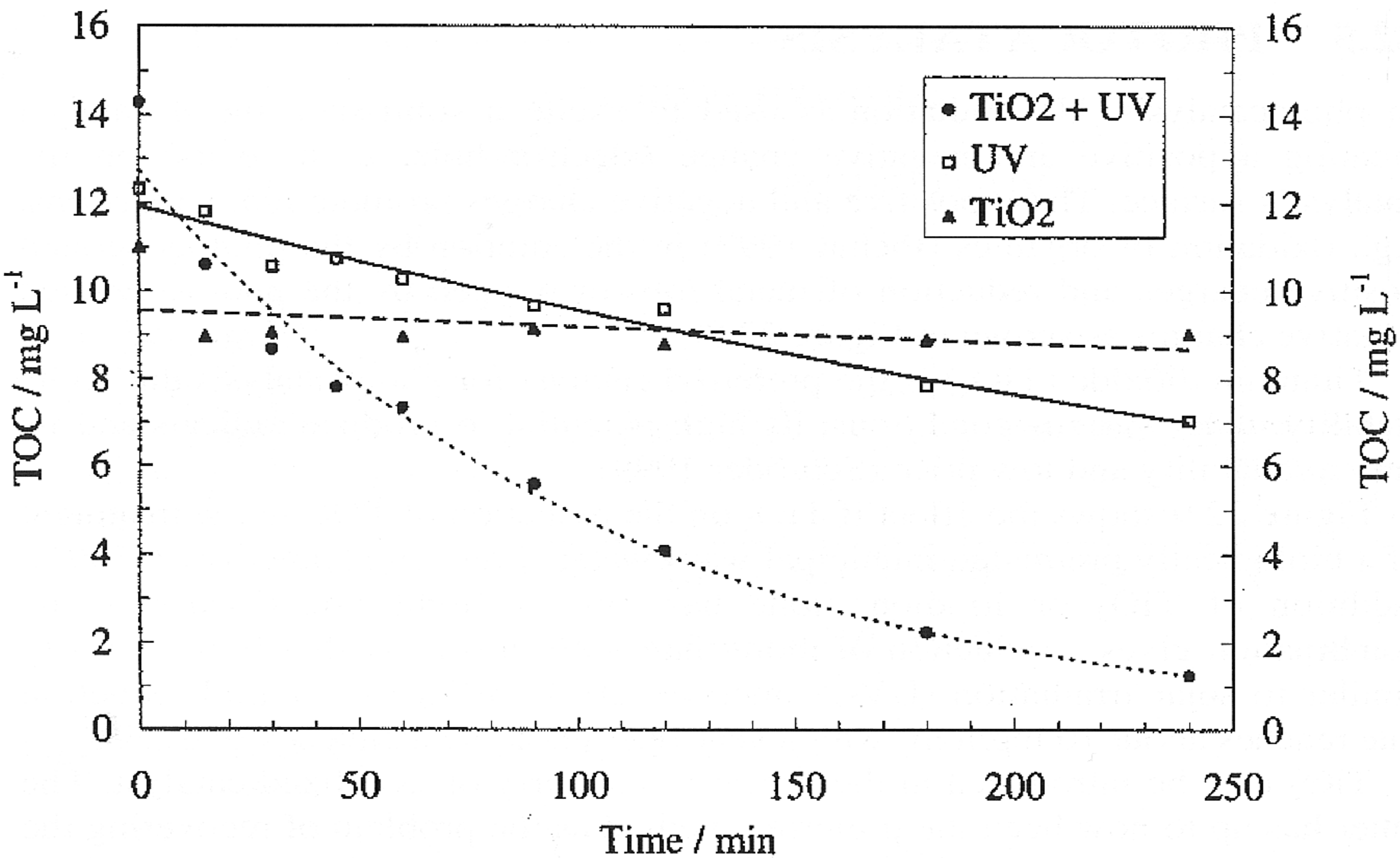
$TiO_2$ is a recommended catalyser because it s stable, high potential for hydroxyl radicals production and low cost.



# AOPs for Water and Wastewater Treatment

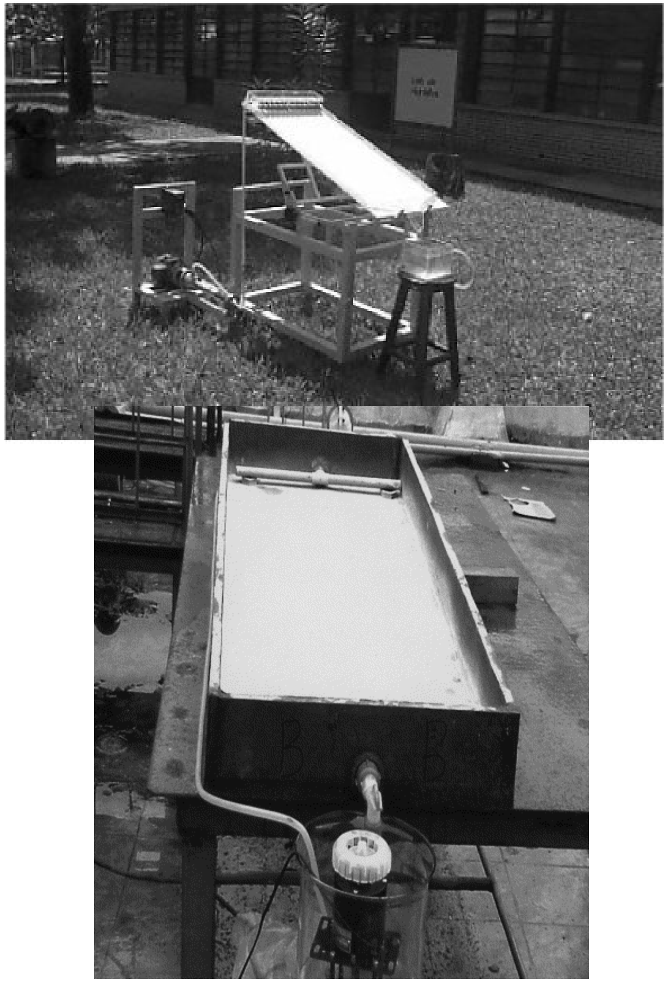
## Photo-catalysis

**Example of domestic wastewater treatment**



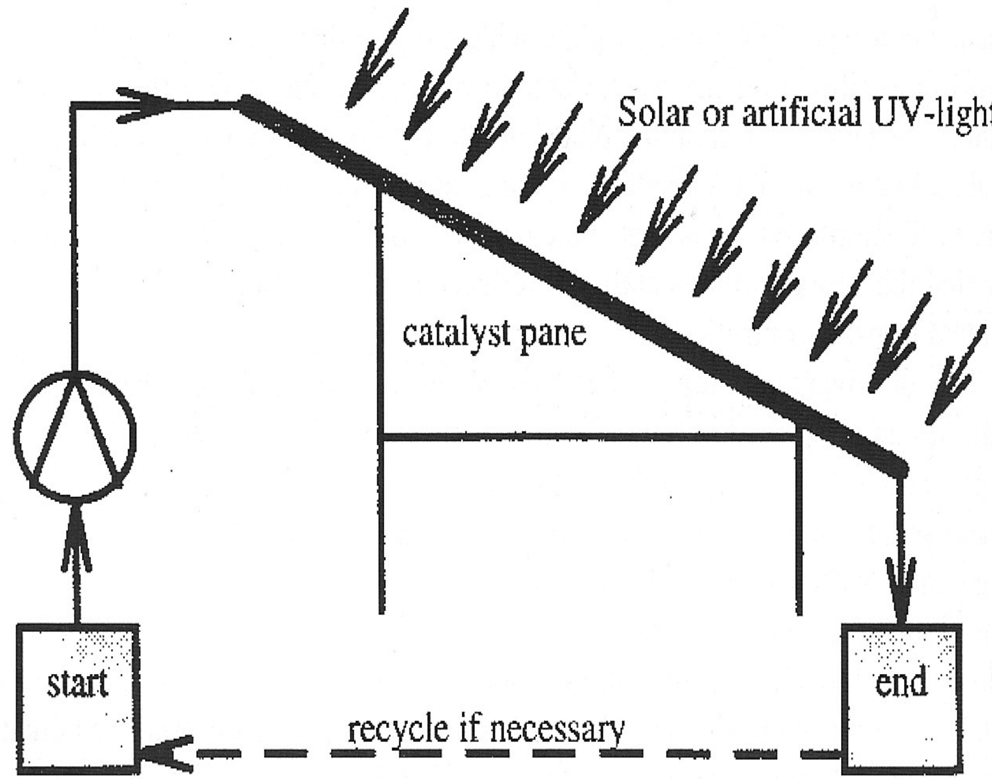
# AOPs for Water and Wastewater Treatment

## Photo-catalysis



$TiO_2$ TFFBR. Size: 144 cm×52 cm×10 cm; solution flow rate: 750 ml min$^{-1}$; batch size: 5 l.

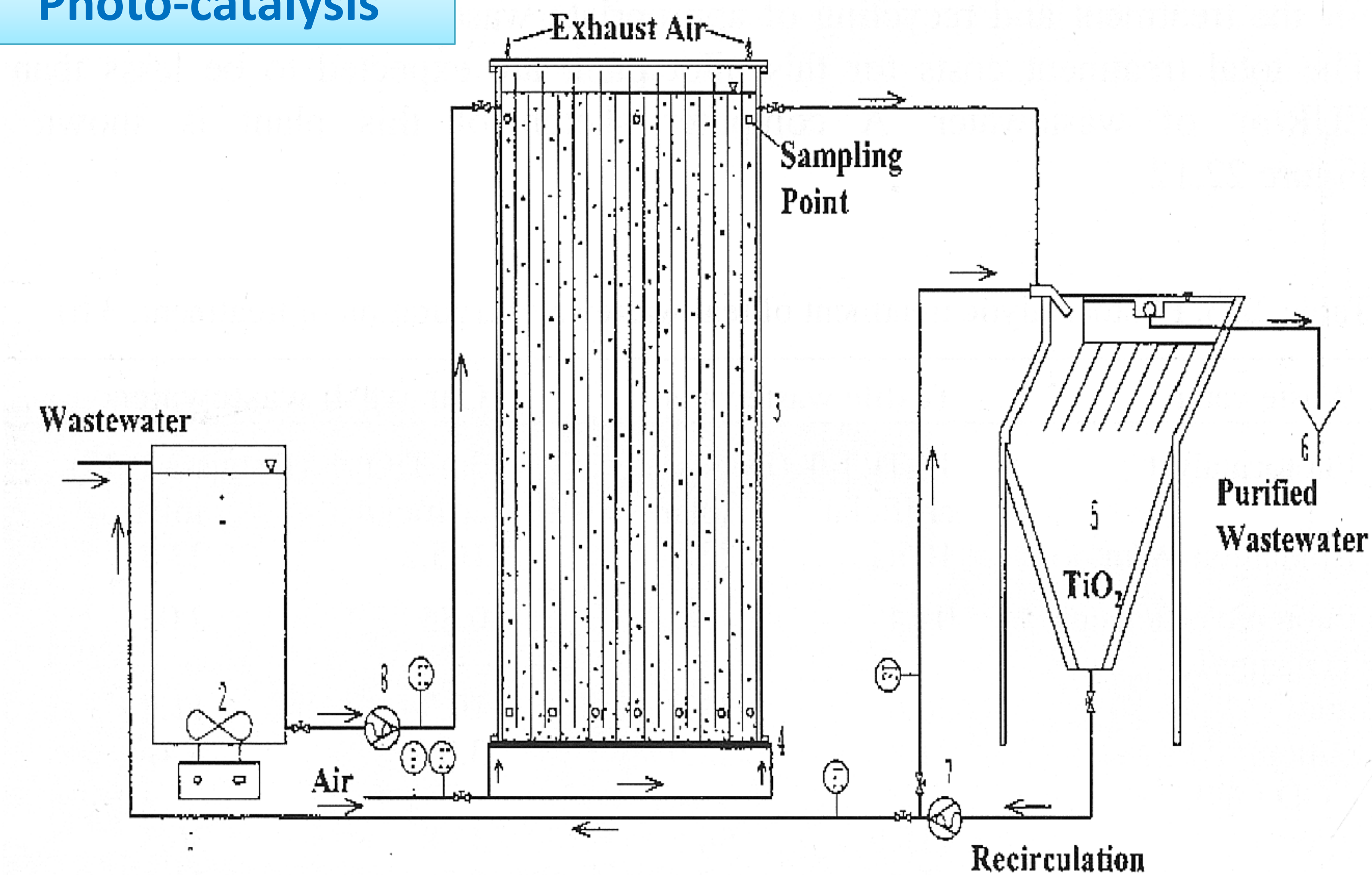
## TFFBR
## (Thin Film Fixed Bed Reactor)



# AOPs for Water and Wastewater Treatment

**Photo-catalysis**

## ACP (Aerated Cascaded Photoreactor)



# AOP Final remarks

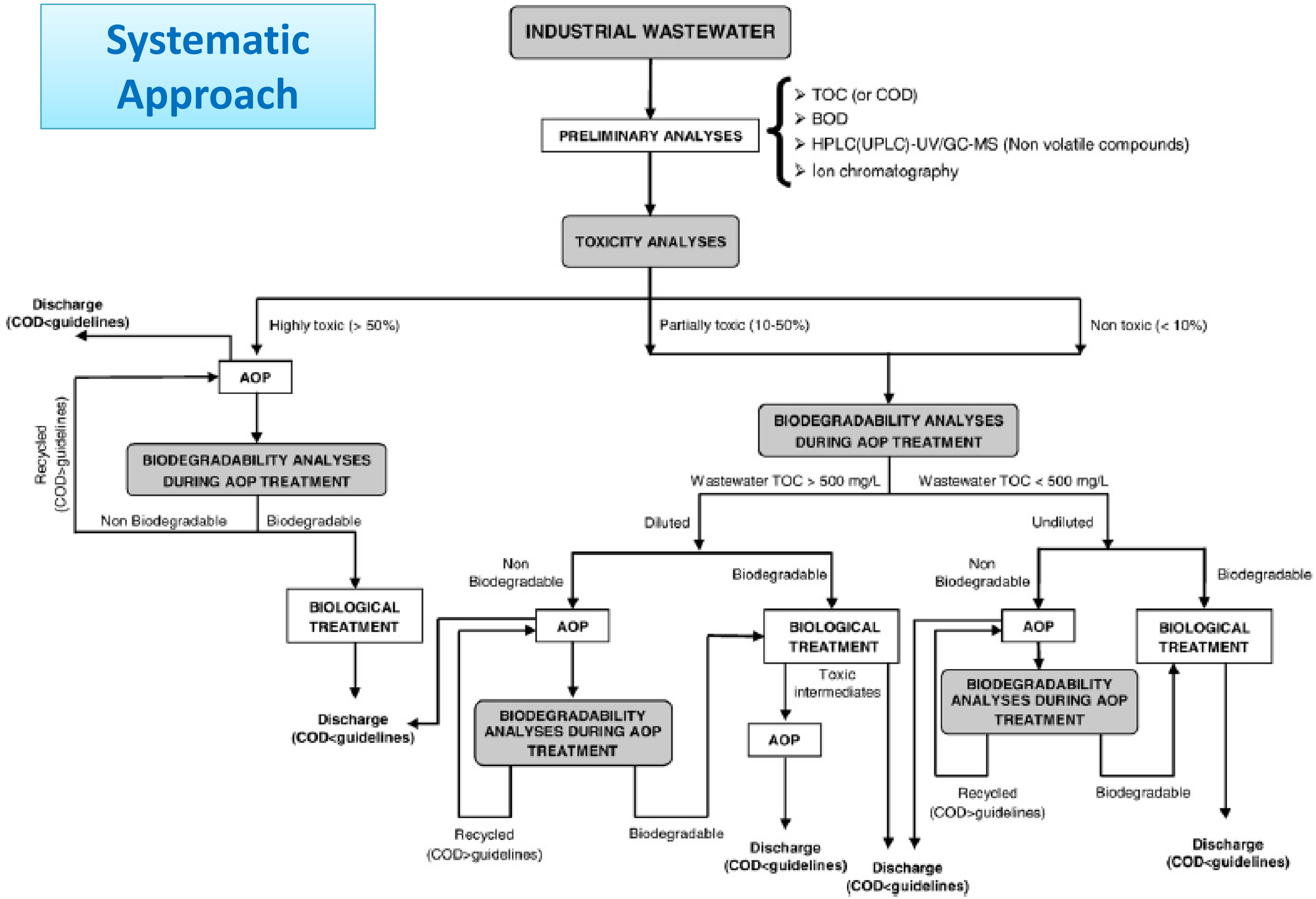
| Advanced oxidation technologies | Biological treatment technologies |
|---|---|
| Advantages | Advantages |
| 1. Complete oxidation possible | 1. Partial mineralization |
| 2. Can handle large recalcitrant molecules | 2. Eco-friendly |
| 3. Easy process operability | 3. Low capital and operating costs |
| 4. Ability to handle fluctuating flow rates and compositions | 4. True destruction of organics versus mere phase separation |
| 5. Absence of secondary wastes | 5. Simultaneous removal of reduced inorganic compounds, such as sulfides and ammonia, and total nitrogen removal possible through denitrification |
| 6. Inconvenient to produce undesired products more toxic than the initial ones | 6. Operational flexibility to handle a wide range of flows and wastewater characteristics |
| | 7. No use of chemicals |
| | 8. Requires less energy inputs |
| Disadvantages | Disadvantages |
| 1. Higher capital and operating costs | 1. Digestion rates are slow, in general days or weeks, requiring large storage tanks. |
| 2. Difficult to manage utilities in wastewater treatment plants | 2. Microorganisms must be fed constantly, or they will die off. If they die off, re-acclimating the microorganisms to the waste stream may take several days |
| 3. Radical scavenging which may lead to lowered degradation efficiency | 3. Changing from one organic removal compartment to another can greatly reduce or eliminate effective treatment. |
| 4. Simultaneous removal of inorganics not reported | |
| 5. Operational flexibility is not feasible | |
| 6. Often uses harsh chemicals | |
| 7. Energy input is higher | |

# AOPs for Water and Wastewater Treatment

## Final remarks

- AOPs can be used as pre-treatment or post-treatment
- AOPs can stand alone or combined, for example AOP/biological treatment
- A systematic approach (scheme in next slide) should be carried out before deciding treatment lay-out

# Systematic Approach



# Lesson’s Key Messages

- The presence of Pharmaceuticals/ EDCs are documented for a long time (>40 years)
- If we look hard enough, we will find contaminants
  - No treatment process is “perfect”
  - Contaminant reduction vs. pollution relocation
- AOPs are efficient for recalcitrant compounds removal
- AOPs can be used as pre-treatment or post-treatment