Industrial Wastewater Treatment using Advanced Oxidation Processes

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Industrial Wastewaters with non-biodegradable Pollutants

- Textile Dyeing
- Pulp and Paper
- Pesticides
- Pharmaceuticals
- Distillery
- Dyes and Dye intermediates
- Tannery
- Phenol and Phenolic Compounds

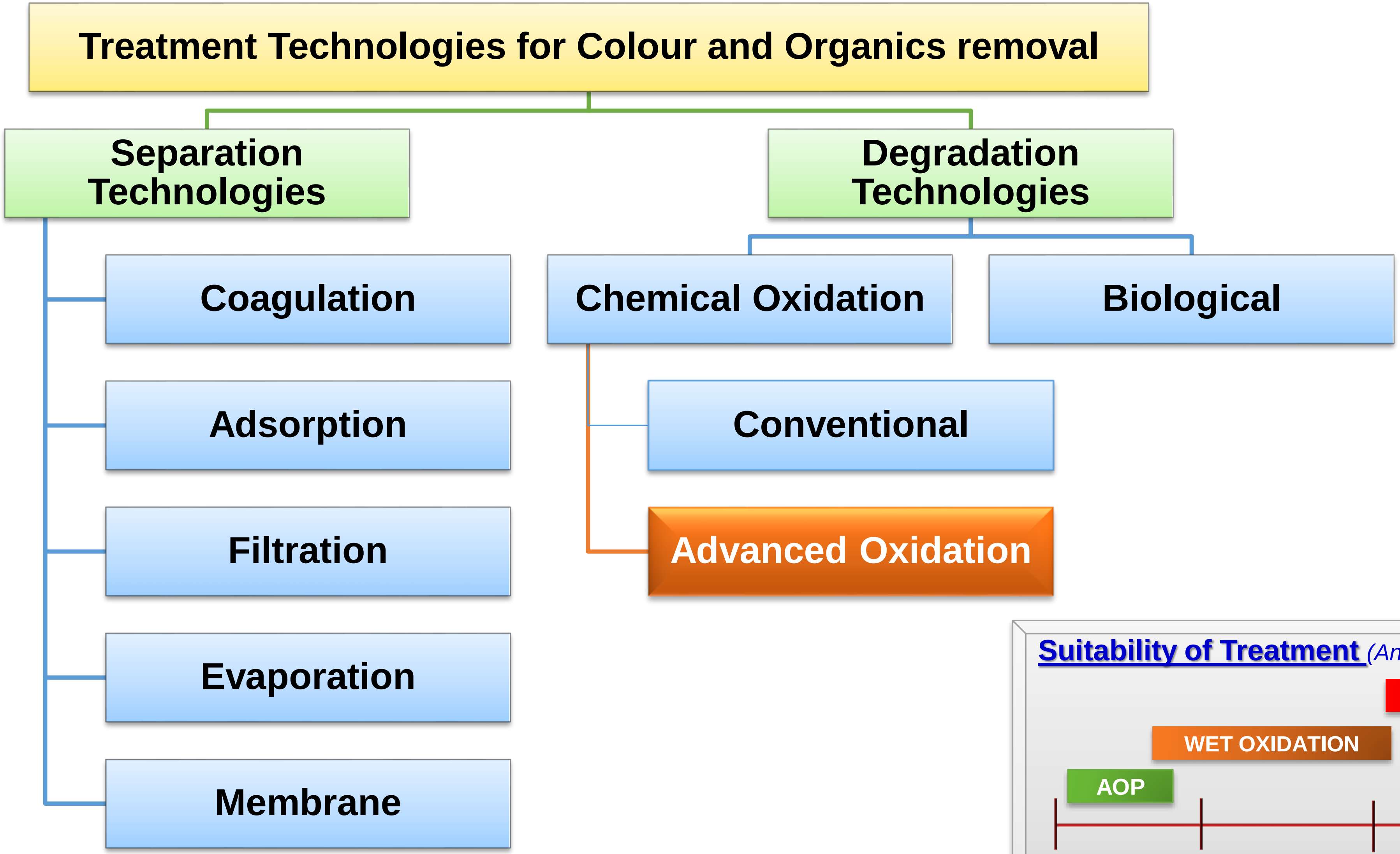
Industrial Wastewater Characteristics

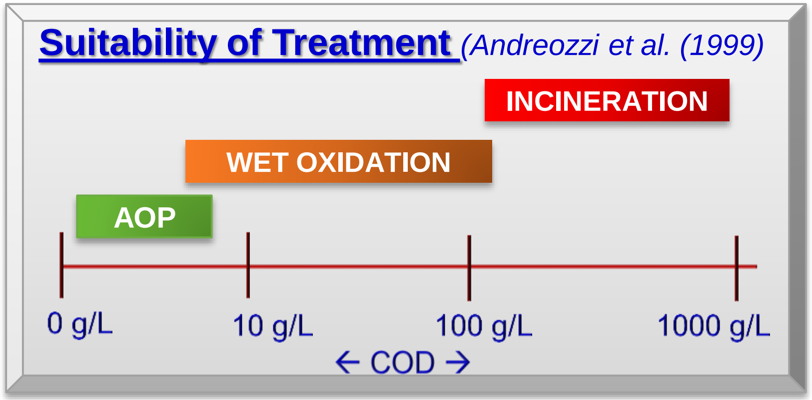
Parameters	Textile Dyeing	Distillery	Pharmaceutical	Pesticide	Paper		CPCB Industry Specific Standards (for discharging into water bodies)
					Pulp & Paper (includes Black Liquor)	Waste Paper Recycling	
pH	8 – 9	4	3.9 – 9.2	8.98 – 12.95	10 – 11.6	6.8 – 6.9	6.0 – 8.5
TDS (mg/L)	6280 – 7360	38200	675 – 9320	12000 – 13000	3000 - 50000	1200 – 3600	-
TSS (mg/L)	108 – 288	4200	200 – 1800	250 – 300	100 – 10000	200 - 956	100
COD (mg/L)	650 – 2500	57164	375 – 32500	6000 – 7000	10000 – 150000	1100 – 2500	250
BOD (mg/L)	228 – 345	32300	200 – 6000	184 – 685	350 – 15000	180 – 350	30

(Source: Farid Ansari et al. (2012); Chandrakanth et al. (2014); Bhausaheb et al. (2014); www.cpcb.nic.in)

- Effluents are highly coloured due to the presence of dyes, pigments, fermented products, lignin and other such compounds

Treatment Technologies





Advanced Oxidation Process

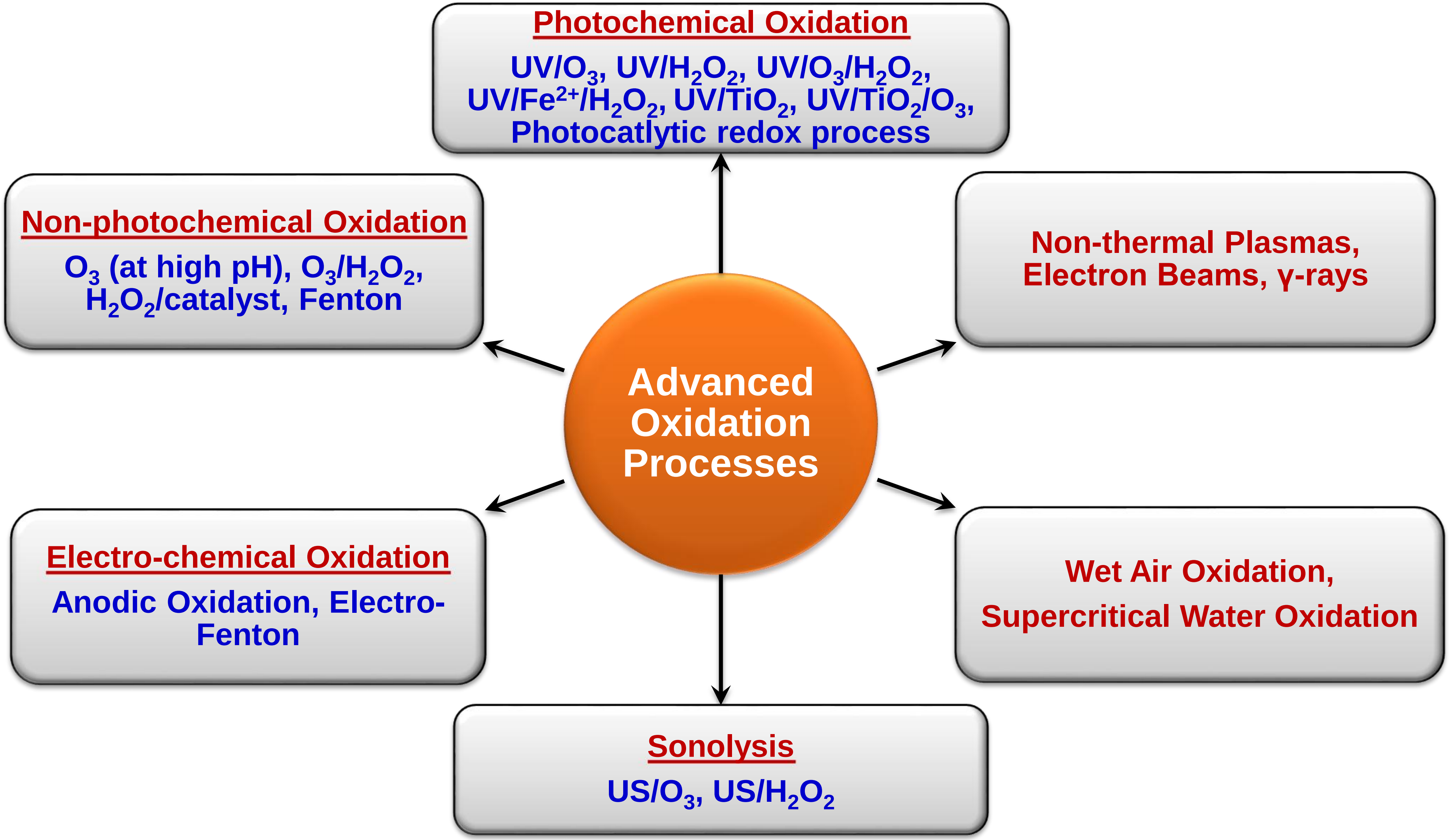
Definition by Glaze *et al.* (1987)

Near ambient temperature and pressure water treatment processes which involve the generation of highly reactive **hydroxyl radical** (HO°)

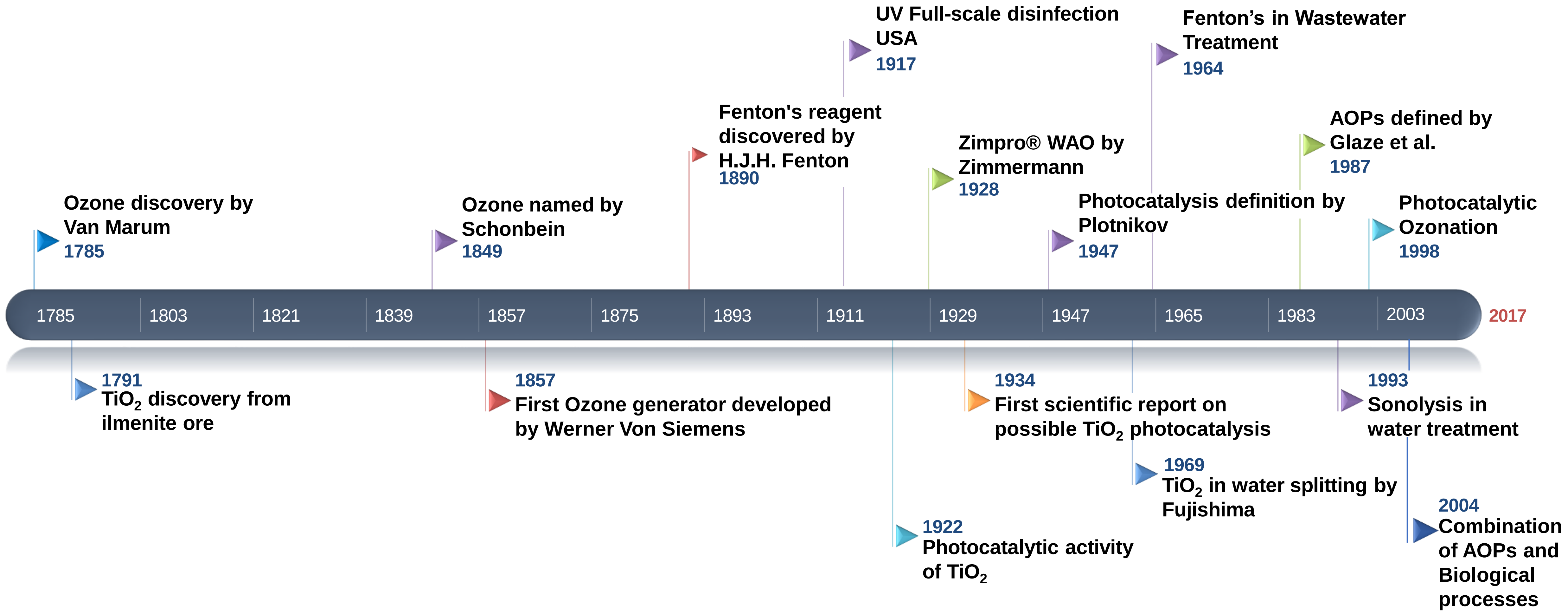
Hydroxyl radical:

- Powerful, non-selective chemical oxidant
- Reacts with most organic compounds

Advanced Oxidation Processes

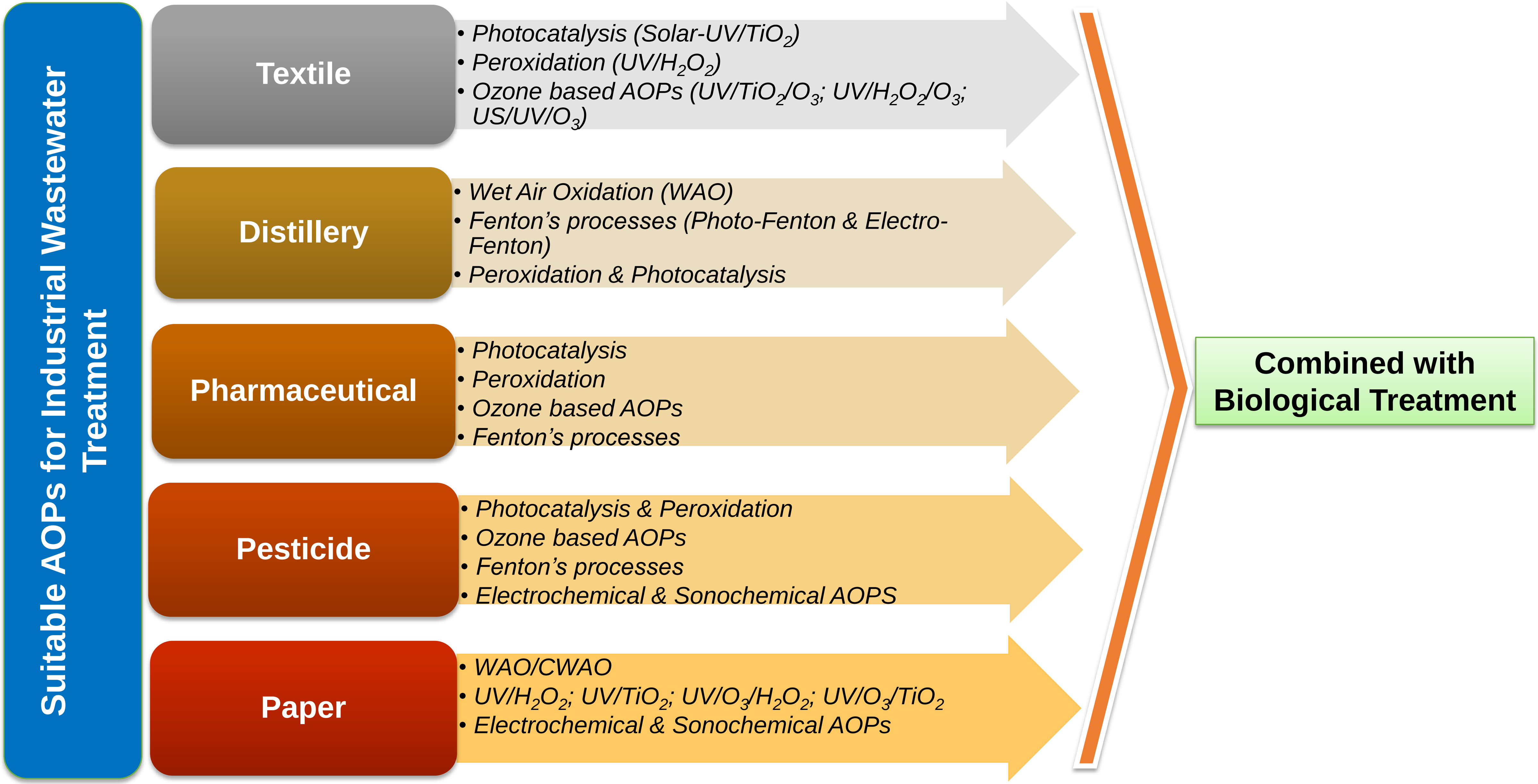


Timeline

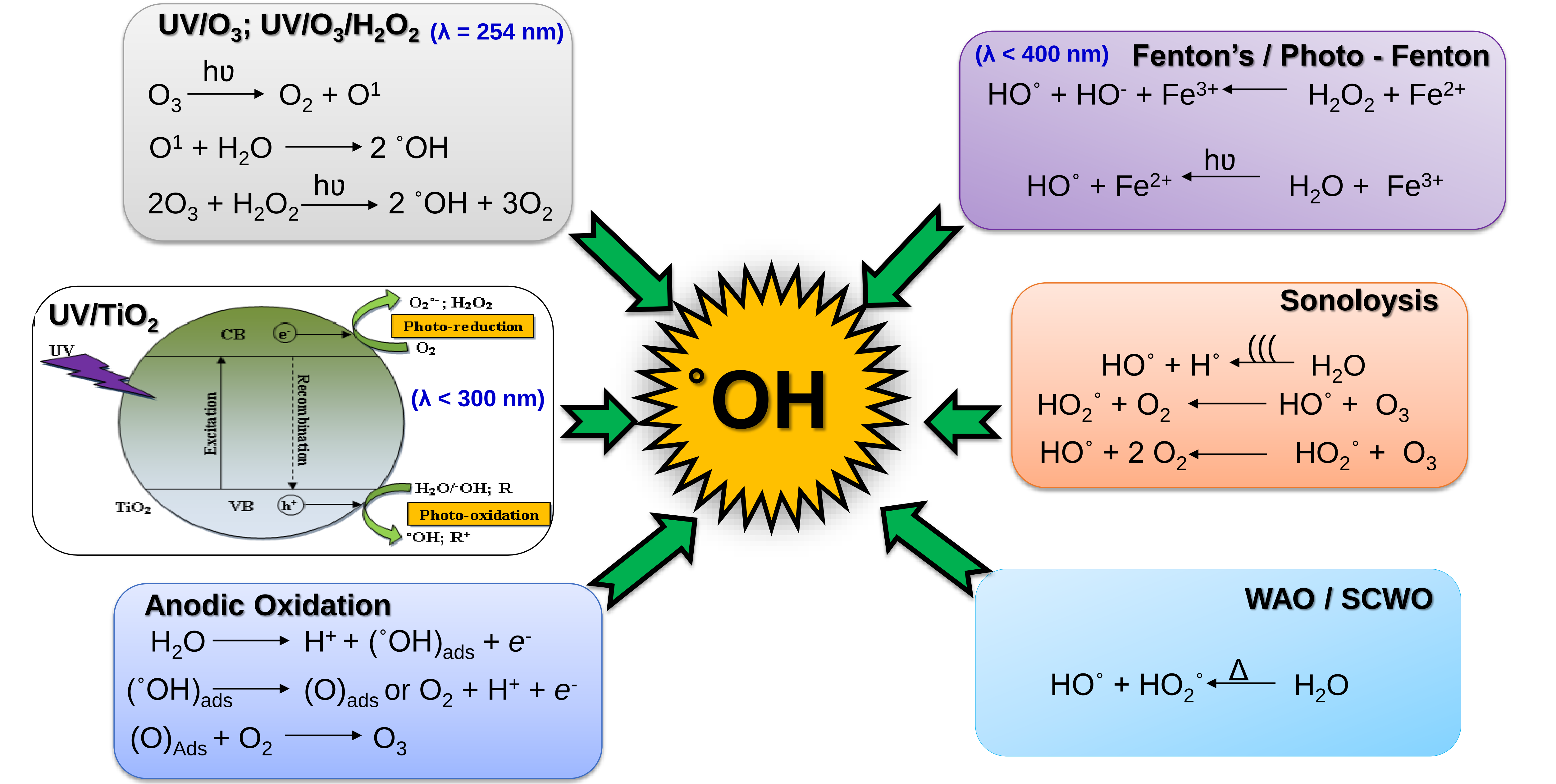


(Source: Thomas Oppenlander (2003); Wikipedia)

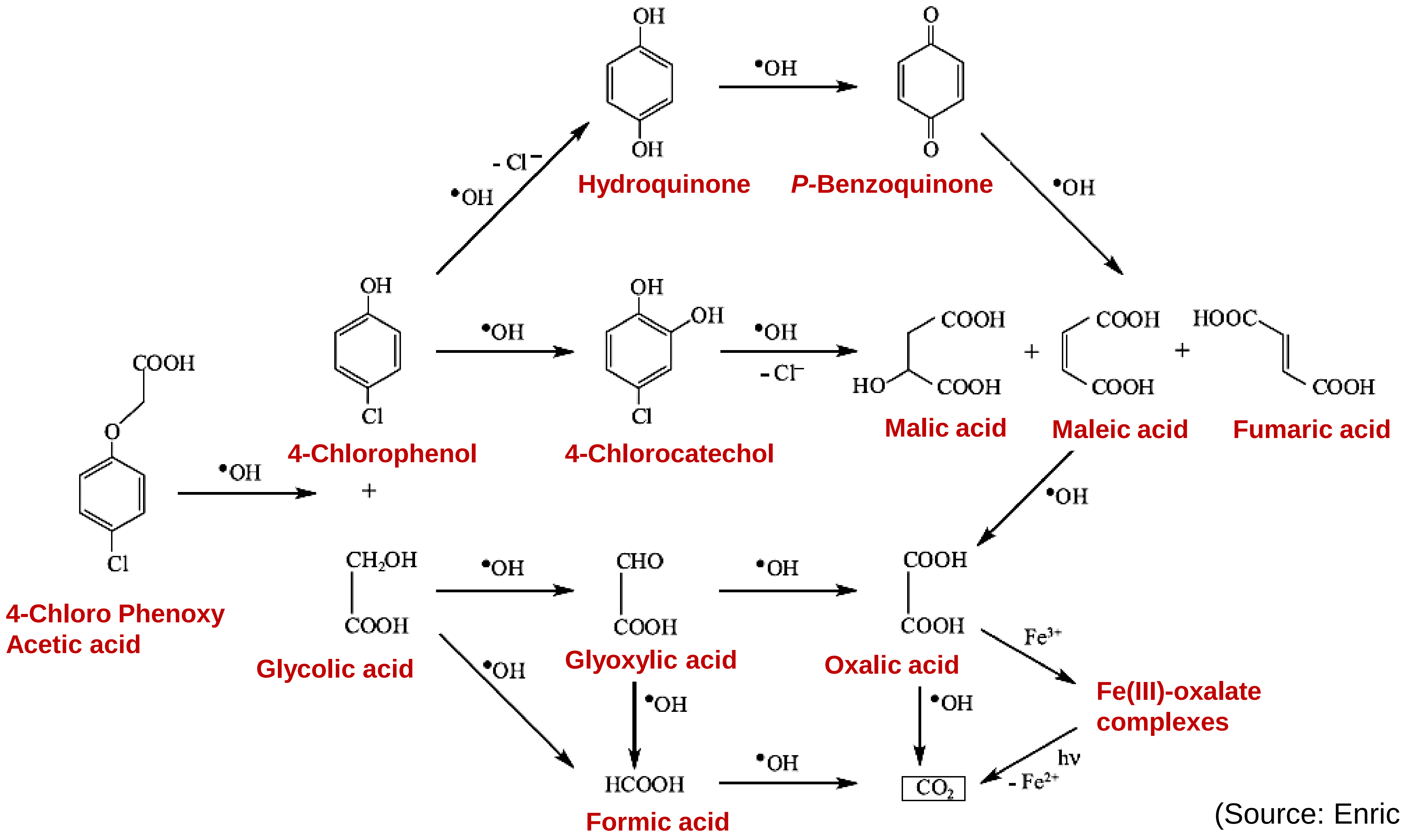
Advanced Oxidation Processes



Advanced Oxidation Process



Degradation Pathway

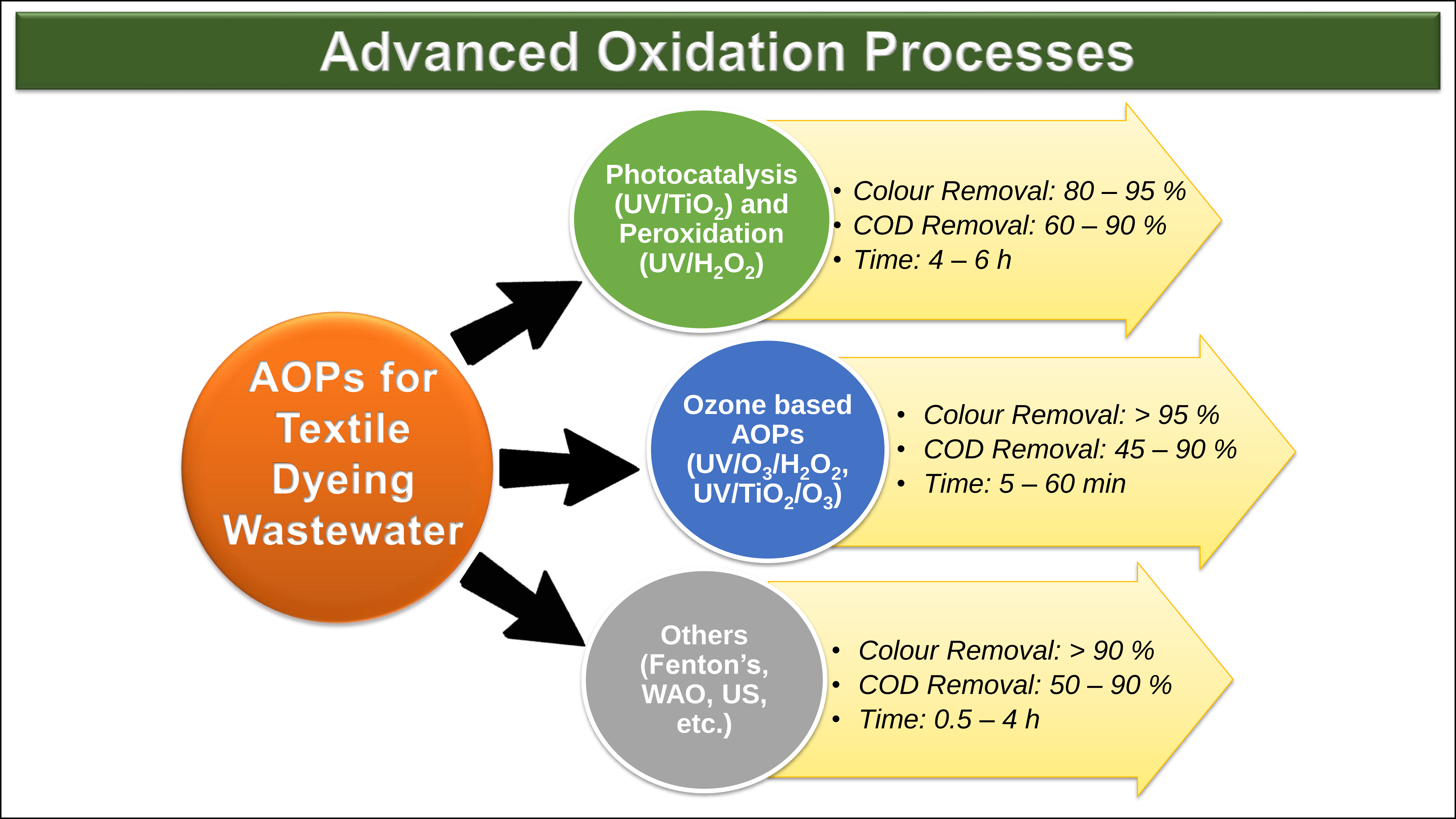


(Source: Enric Brillas (2013))

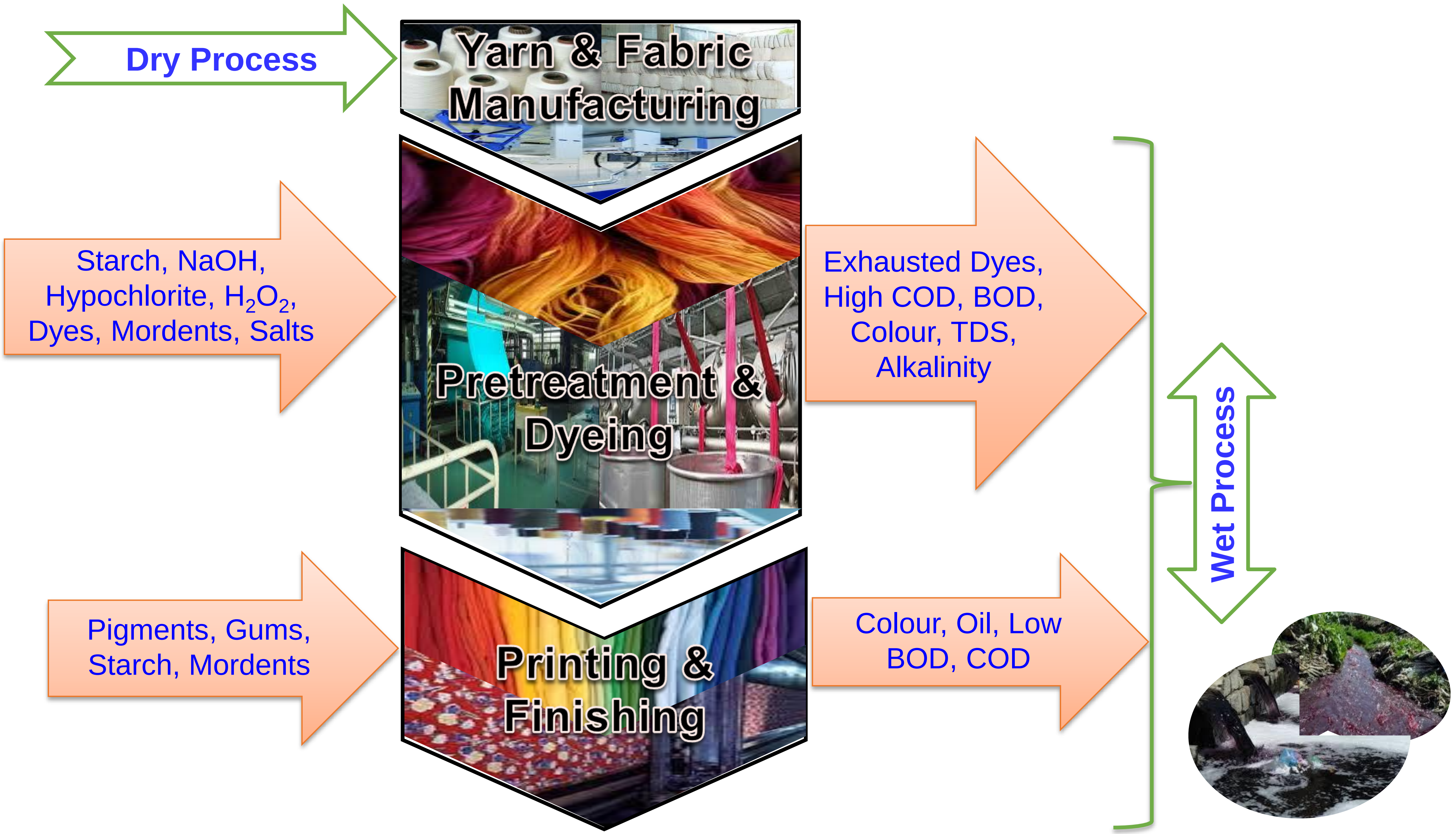
Our Research

Advanced Oxidation Process

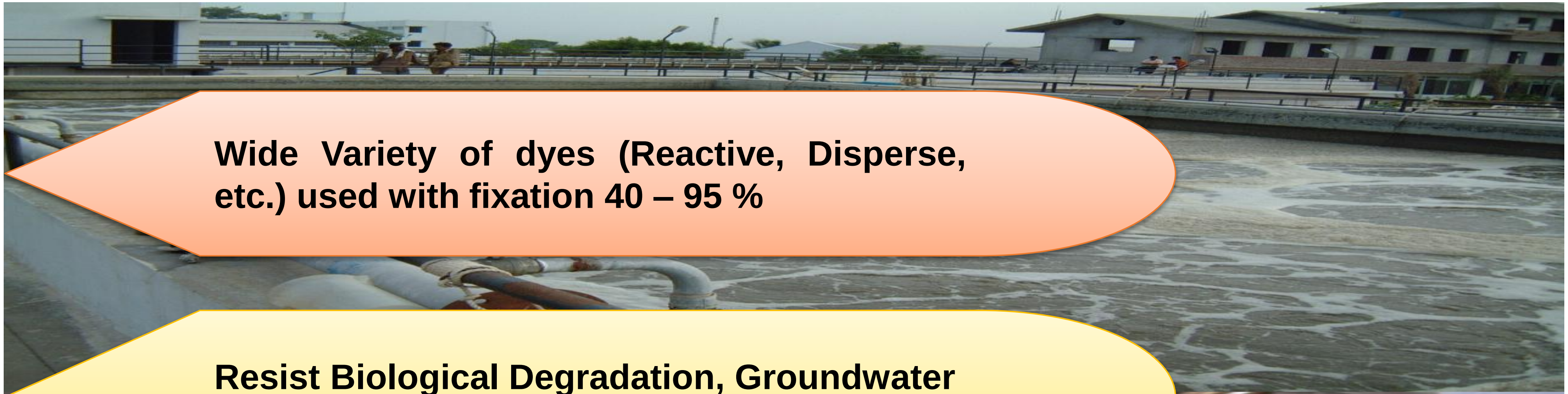
AOP in combination with Biological Treatment

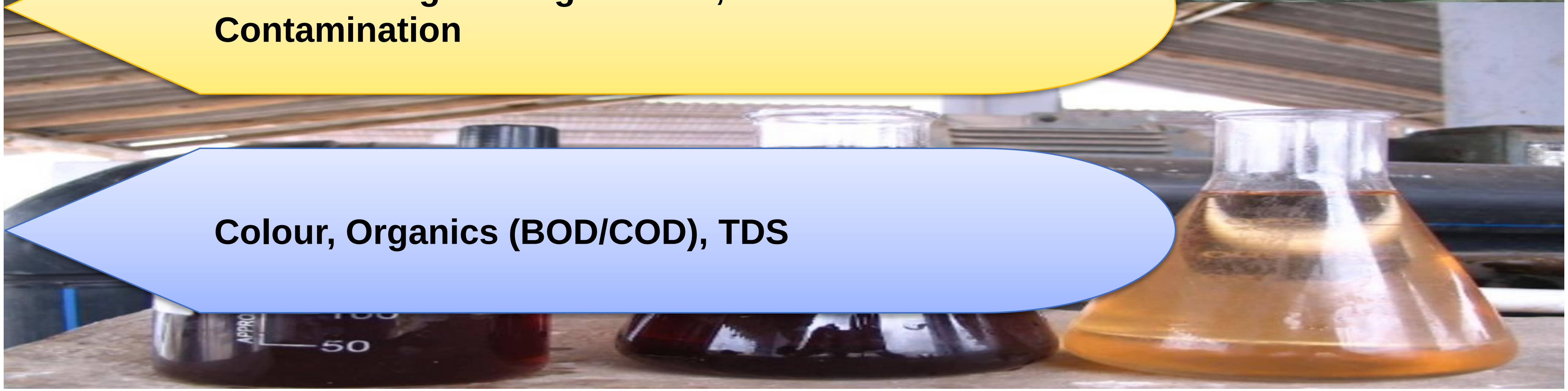

Advanced Oxidation Processes
AOPs for Textile Dyeing Wastewater
Photocatalysis (UV/TiO_2) and Peroxidation (UV/H_2O_2)
• Colour Removal: 80 – 95 %
• COD Removal: 60 – 90 %
• Time: 4 – 6 h
Ozone based AOPs ($UV/O_3/H_2O_2$, $UV/TiO_2/O_3$)
• Colour Removal: > 95 %
• COD Removal: 45 – 90 %
• Time: 5 – 60 min
Others (Fenton's, WAO, US, etc.)
• Colour Removal: > 90 %
• COD Removal: 50 – 90 %
• Time: 0.5 – 4 h

Textile Processes



Causes and Concern



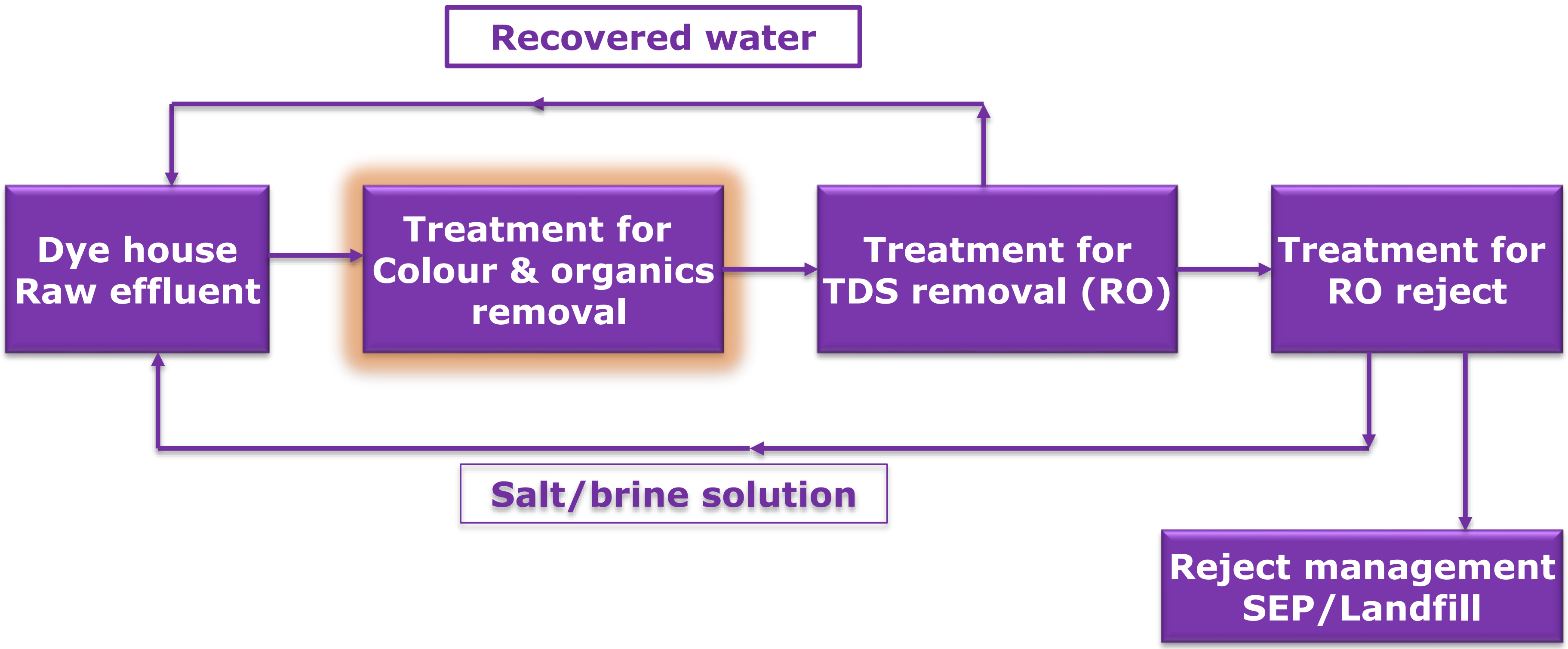


Wide Variety of dyes (Reactive, Disperse, etc.) used with fixation 40 – 95 %

Resist Biological Degradation, Groundwater Contamination

Colour, Organics (BOD/COD), TDS

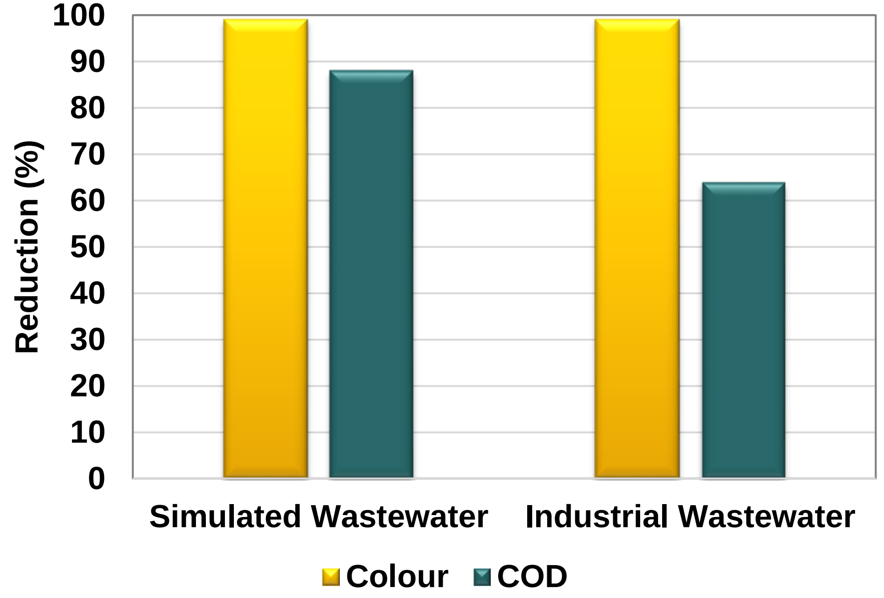
Treatment Scheme for Zero Liquid Discharge System



Textile Wastewater Treatment

Experimental Setup - UV/TiO_2/O_3

Dye Degradation



EXPERIMENTAL CONDITIONS:

Volume = 15 L

Simulated COD = 340 mg/L

Industrial COD = 1380 mg/L

Catalyst dose = 100 mg/L ; 5 mg/cm^2

O_3 dose = 8.88 g/h

Contact time = 30 min

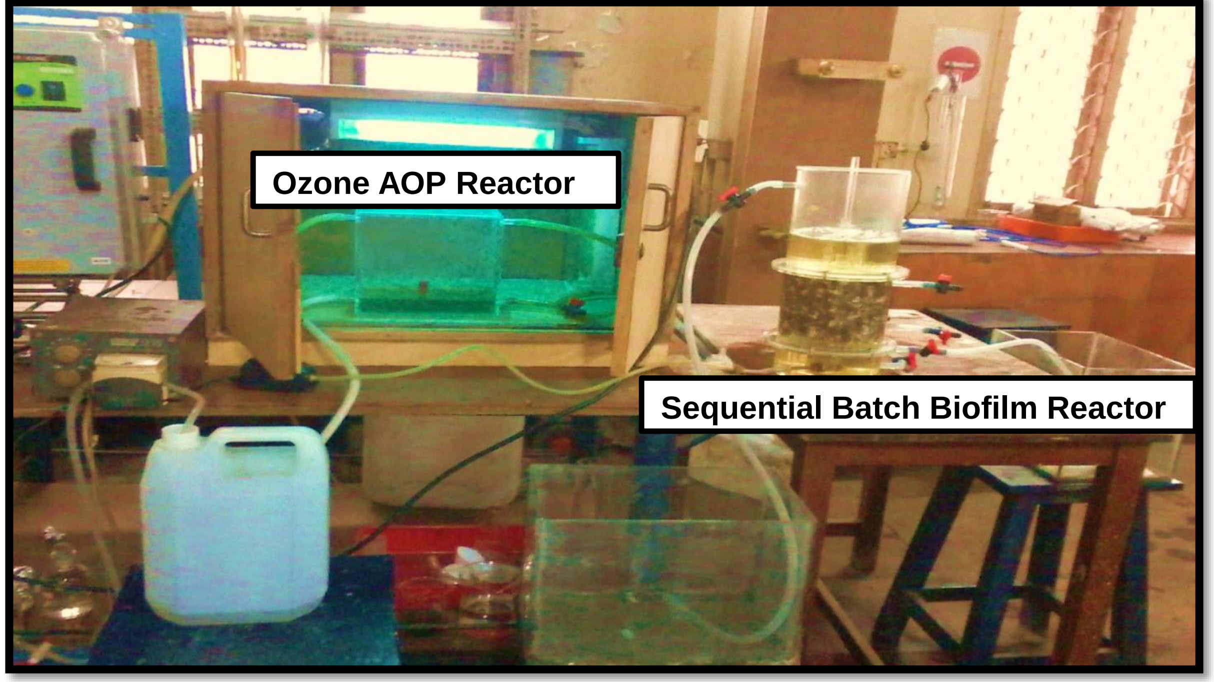
S. No	Treatment Technology for Textile Dyeing Wastewater	Removal (%)		Operational Cost/KL (Rs)
		Colour	COD	
1	Ozone Treatment	90	20 – 30	25.00
2	Photocatalytic-ozonation Treatment	90-95	40 – 60	34.00

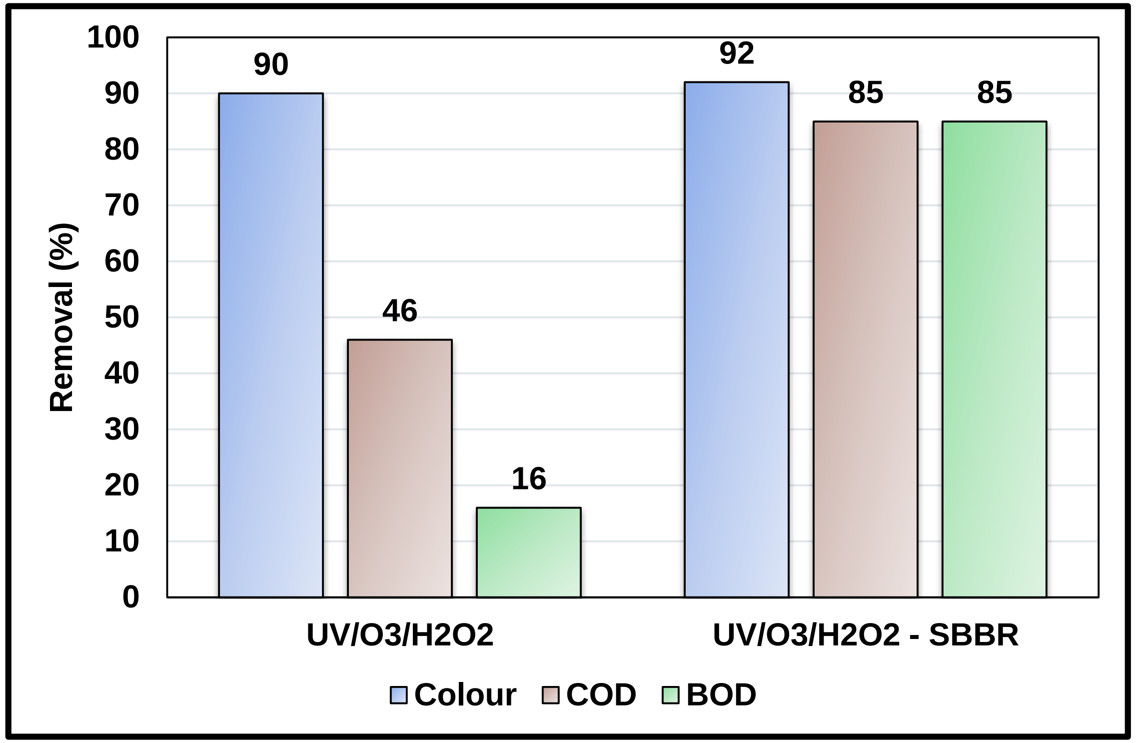
References:

- **Rajendiran & Kanmani, *Mat. Focus.* (2015)**
- **Rajendiran, Shriram & Kanmani, *Int. Adv. Res. J. Sci. Engg. Tech.* (2016)**

Textile Dyeing Wastewater Treatment

Experimental Setup - $UV/O_3/H_2O_2$ - SBBR





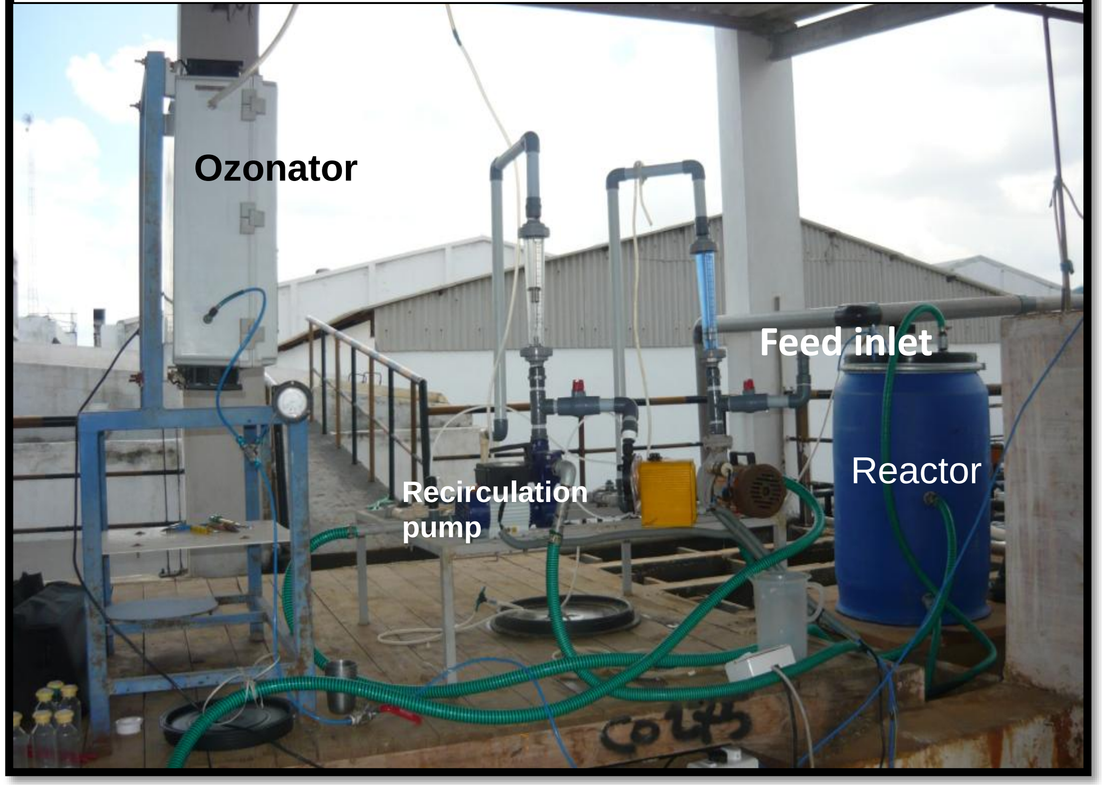
EXPERIMENTAL CONDITIONS:

Volume = 5 L
COD = 800 - 980 mg/L
BOD_3= 220 – 285 mg/L
O_3 dose = 150 mg/L
H_2O_2 dose = 150 mg/L
Contact time: AOP = 2 h; SBBR = 6 h

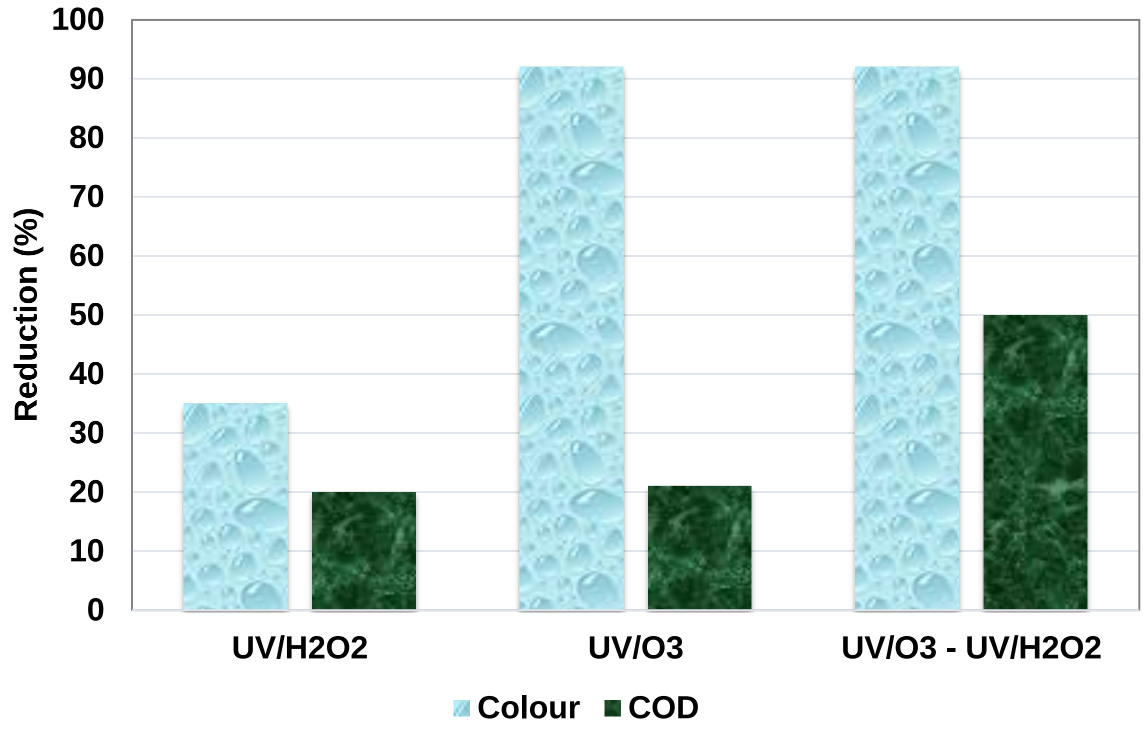
(Reference: Aruna & Kanmani (2015))

Pilot-Scale Textile Wastewater Treatment

Experimental Setup - UV/O_3/H_2O_2



Textile Dyeing Wastewater Degradation



EXPERIMENTAL CONDITIONS:

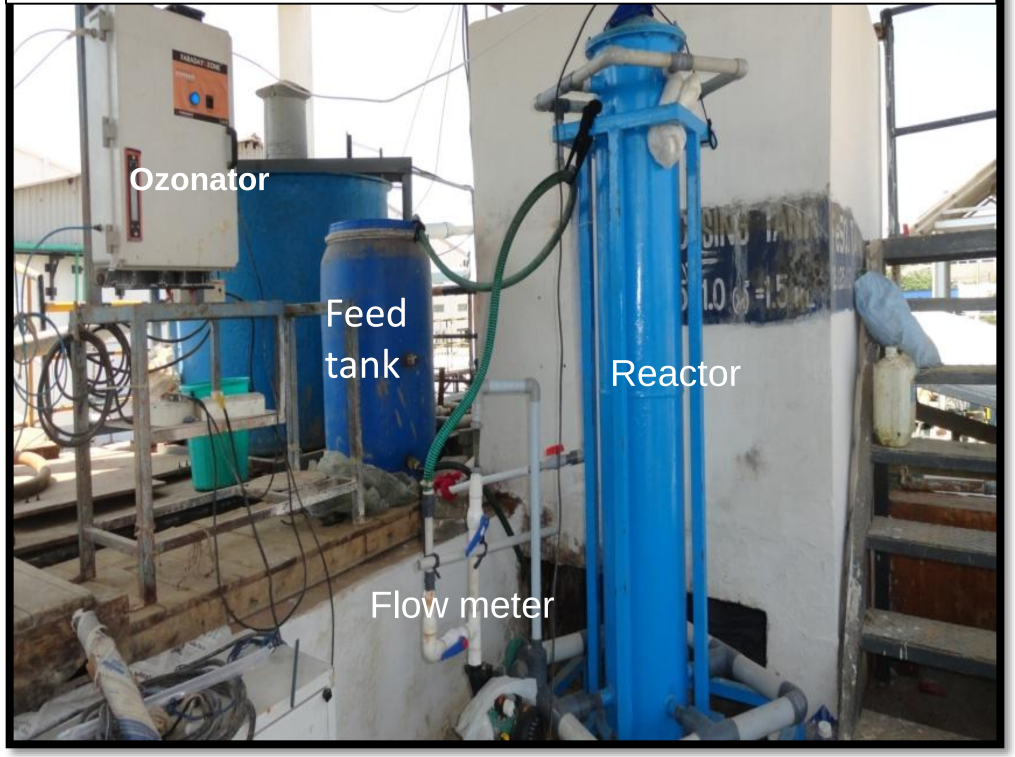
Volume = 200 L
pH = 10.5
COD = 600 – 1060 mg/L
H_2O_2 dose = 0.5 g/L
O_3 dose = 10 g/h
Contact time = 60 min

S. No	Treatment Technology for Textile Dyeing Wastewater	Removal (%)		Operational Cost/KL (Rs)
		Colour	COD	
1	Ozone Treatment	90	20 – 30	25.00
2	UV/O_3-UV/H_2O_2 in sequence	> 90	35 - 50	47.00

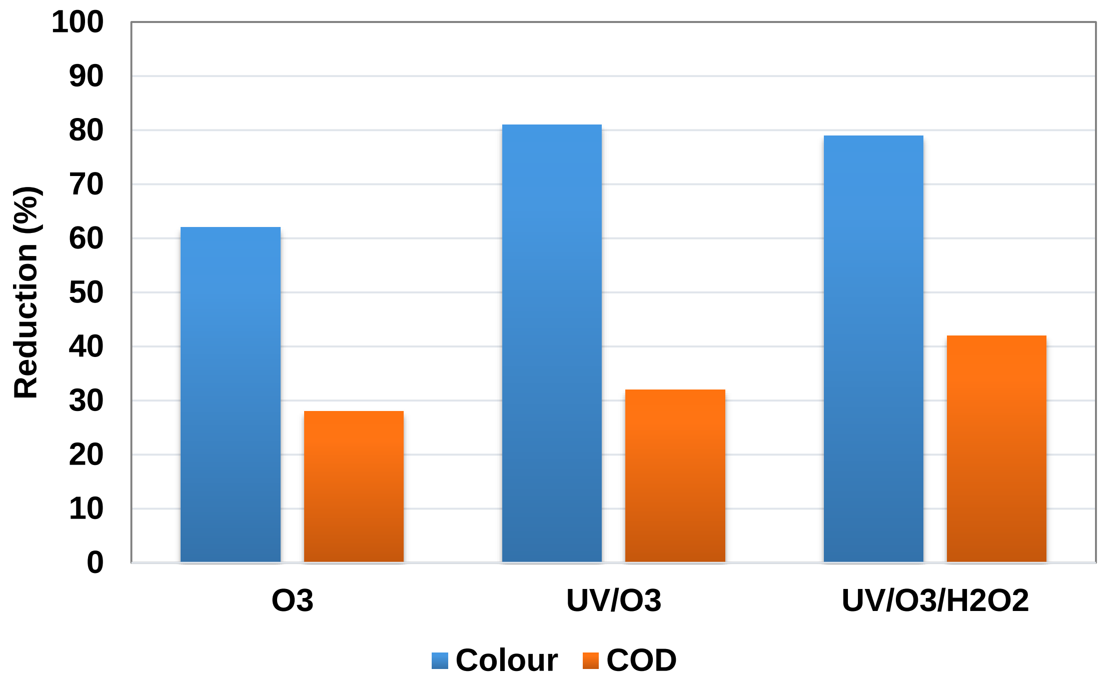
(Reference: Shriram & Kanmani, *Indian J. Env. Prot.* (2016))

Pilot-Scale Textile Wastewater Treatment

Experimental Setup - UV/O_3/H_2O_2



Textile Wastewater Degradation



EXPERIMENTAL CONDITIONS:

Volume = 200 L

pH = 9.5

COD = 950 mg/L

H_2O_2 dose = 0.2 g/L

O_3 dose = 10 g/h

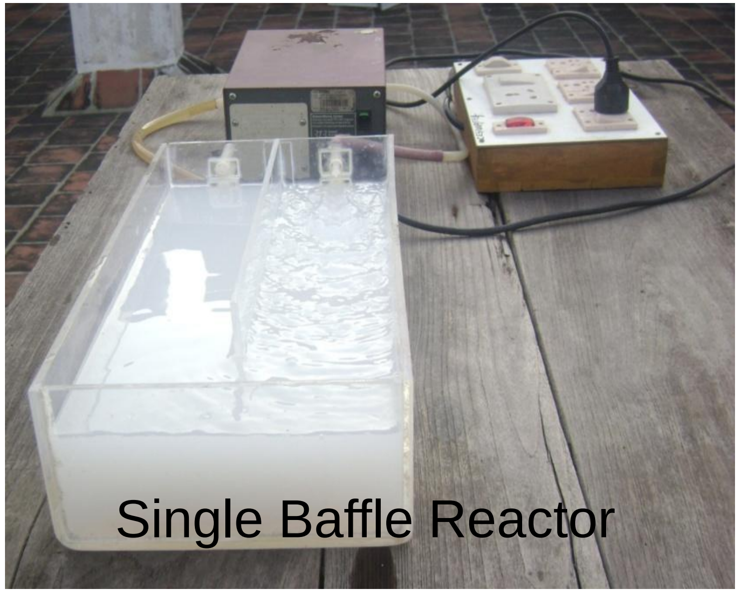
Contact time = 60 min

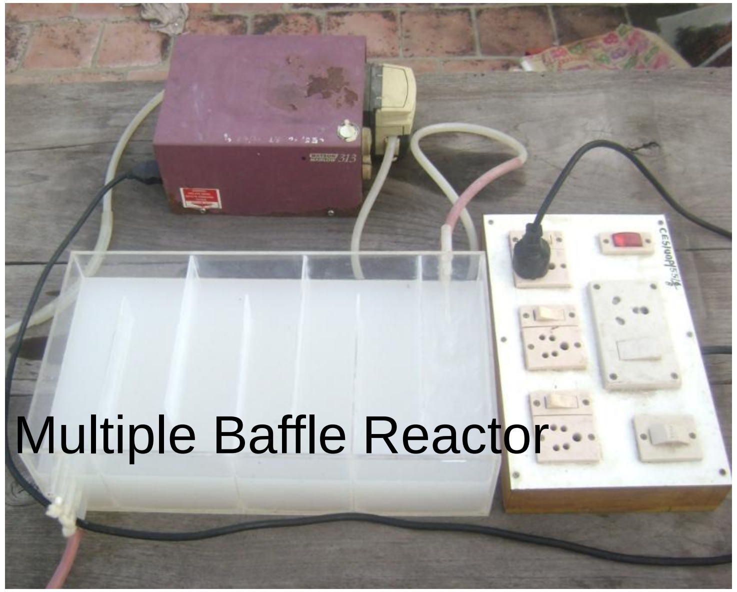
(Reference: Sathya & Kanmani, *Poll. Res.* (2014))

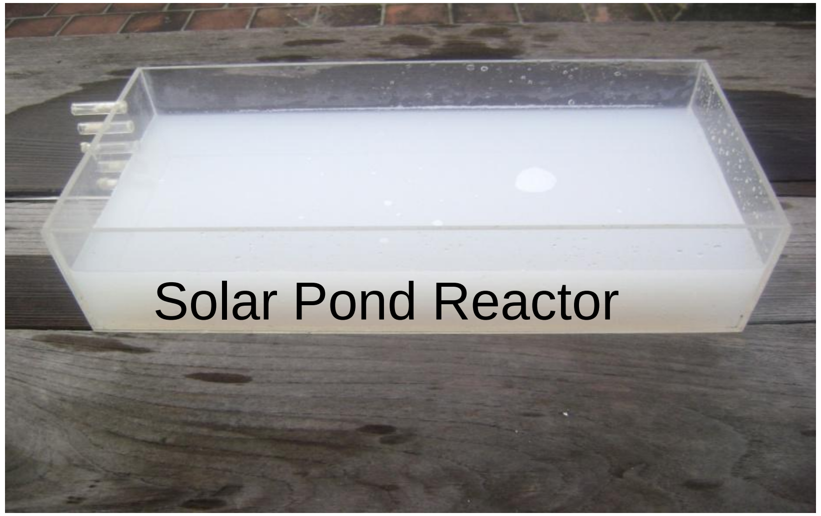
AOPs in Pilot-scale for Textile Wastewater Treatment

S. No.	Treatment System	Pollutant	Efficiency	Reference
1	Ozonation/UV O_3: 0.26 – 20 g/h Volume: 18 and 100 L	Raw textile wastewater, Azo dyes, Malachite green, Procion Red MX-5B	Colour Removal: 67 – 99 % COD Removal: 25 %	Cleder Somensi et al. (2010); Hung – Yee Shu et al., (1995)
2	UV/H_2O_2; H_2O_2: 3.7 mM Volume: 100 L	Reactive red 174, Reactive yellow 145	Colour Removal: 100 %	Hung-Yee & Ming-Chin (2005)
3	UV/TiO_2/H_2O_2; UV/Fe^{2+}/H_2O_2 CPC: 100 L	Textile wastewater	98 % decolourisation and 89 % mineralization	Vitor et al. (2011)
4	Dyeing wastewater treatment plant: 100 MLD biological (pure-oxygen activated sludge) treatment followed by Fenton's	Textile dye wastewater	63 % sCOD and 73 % Colour reductions	Wookeun et al. (2015)

Phenol Degradation



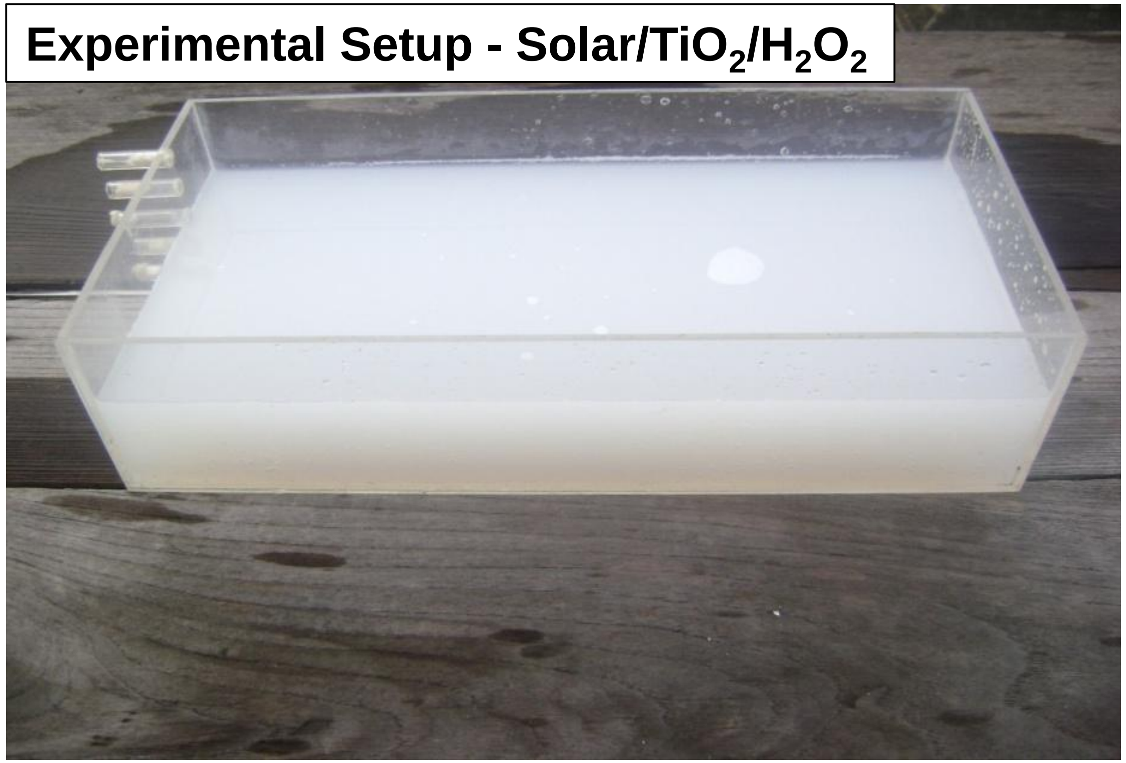


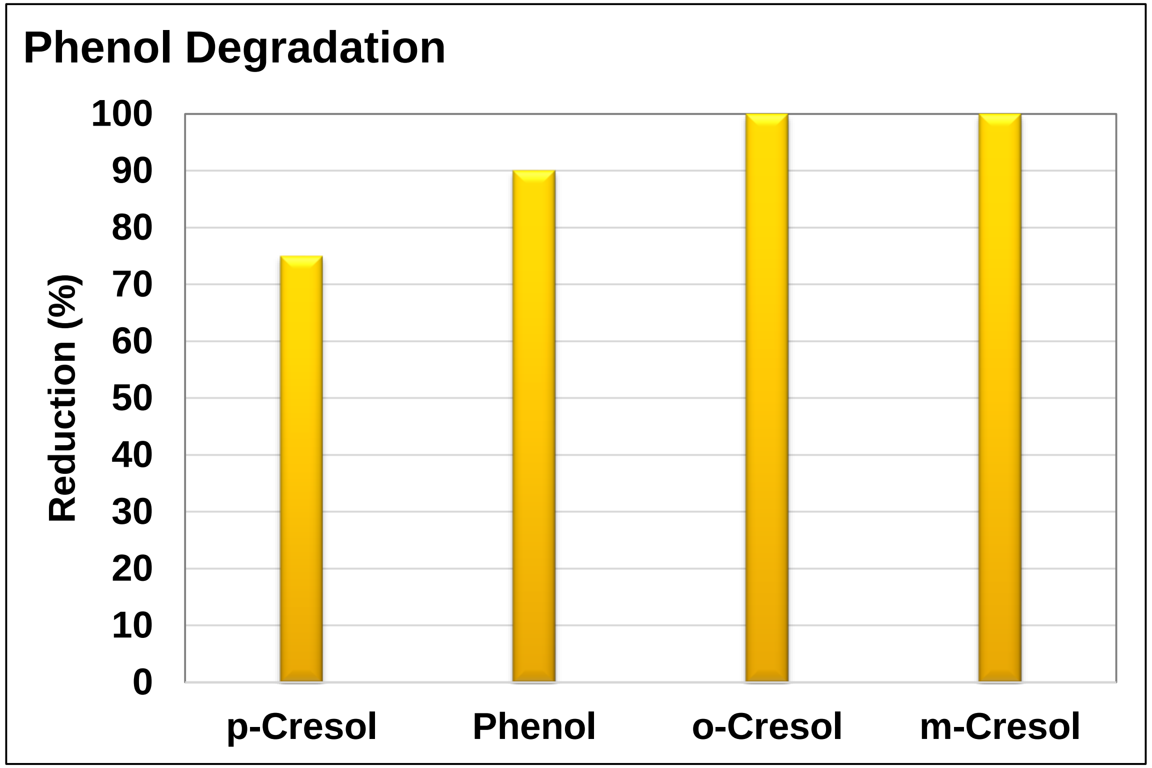


(Reference: Adish Kumar & Kanmani, (2009))

Phenol Degradation

Experimental Setup - Solar/TiO_2/H_2O_2





EXPERIMENTAL CONDITIONS:

Volume = 1.5 L
Conc. = 100 mg/L (λ_{max} = 279 nm)
pH = 7
TiO_2 = 0.25 g/L
H_2O_2 dosage = 0.3 g/L
Contact time = 4 h

(Reference: Adish Kumar & Kanmani, *Int. J. Env. and Waste Mgmt.* (2012))

Phenol Degradation

COMPARSION OF INDIVIDUAL PROCESS (Vs) COUPLED PROCESS

Phenol (mg/L)	Solar photocatalytic process		Biological process		Coupled processes	
	Phenol removal (%)	Treatment time (h)	Phenol removal (%)	Treatment time (h)	Phenol removal (%)	Treatment time (h)
100	97	5	100	5	99	3
200	70	5	99	5	97	3
300	54	5	95	5	98	5
400	47	5	79	5	96	5
500	45	5	68	5	96	7

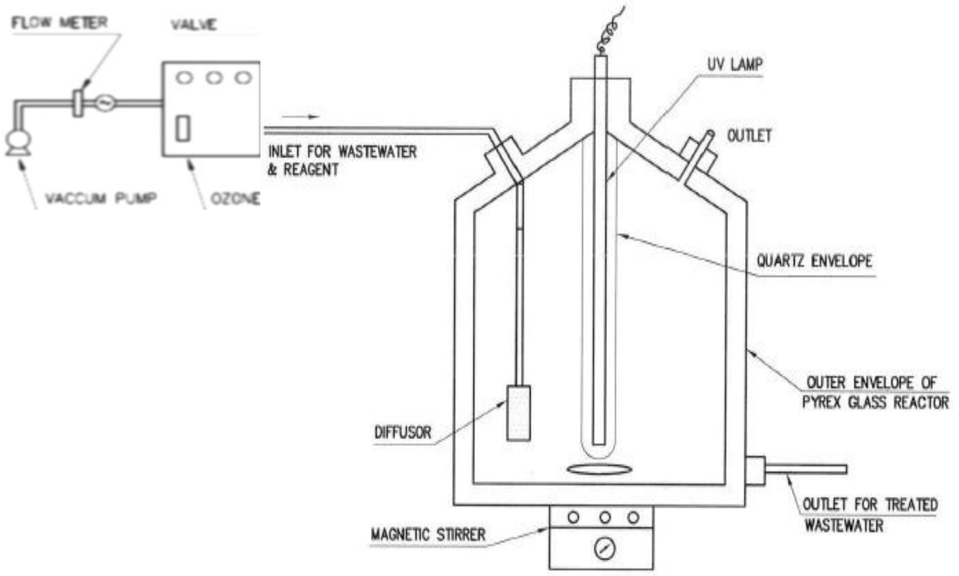
EXPERIMENTAL CONDITIONS:
Photocatalysis:
Volume = 5 L
pH = 7
TiO_2 = 0.25 g/L
H_2O_2 dosage = 0.3 g/L

EXPERIMENTAL CONDITIONS:
Sequential Batch Reactor:
Volume = 5 L
pH = 7
MLSS = 4100 mg/L

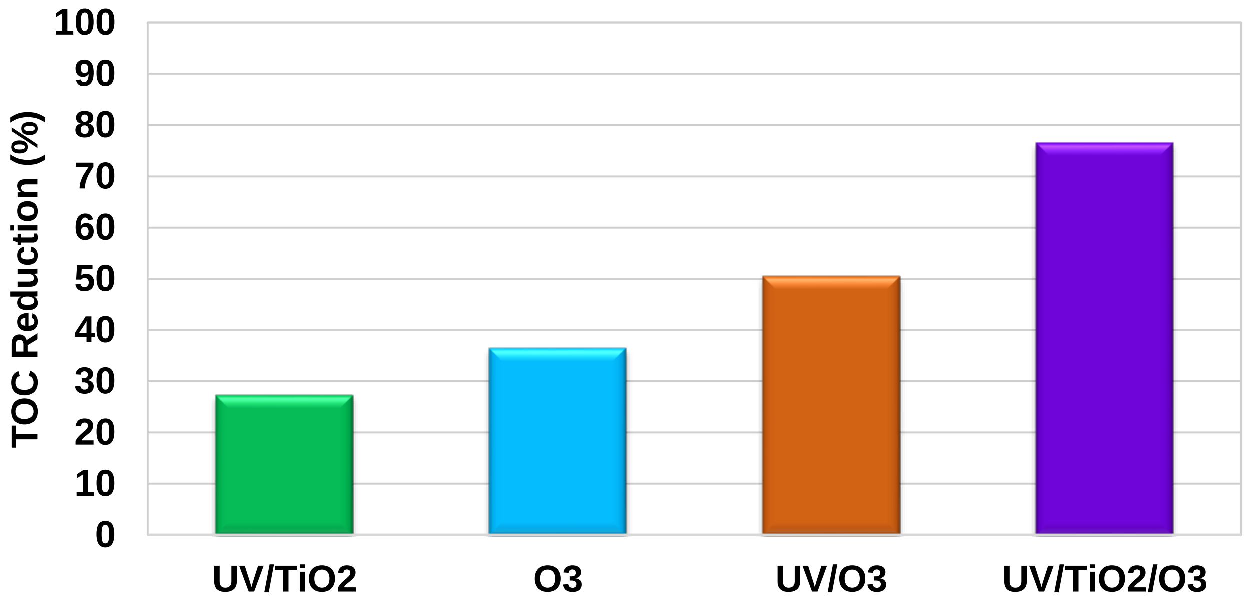
(Reference: Adish Kumar & Kanmani (2009))

Pesticide Degradation

Experimental Setup – Photocatalytic-Ozonation



Carbaryl Mineralization



EXPERIMENTAL CONDITIONS:

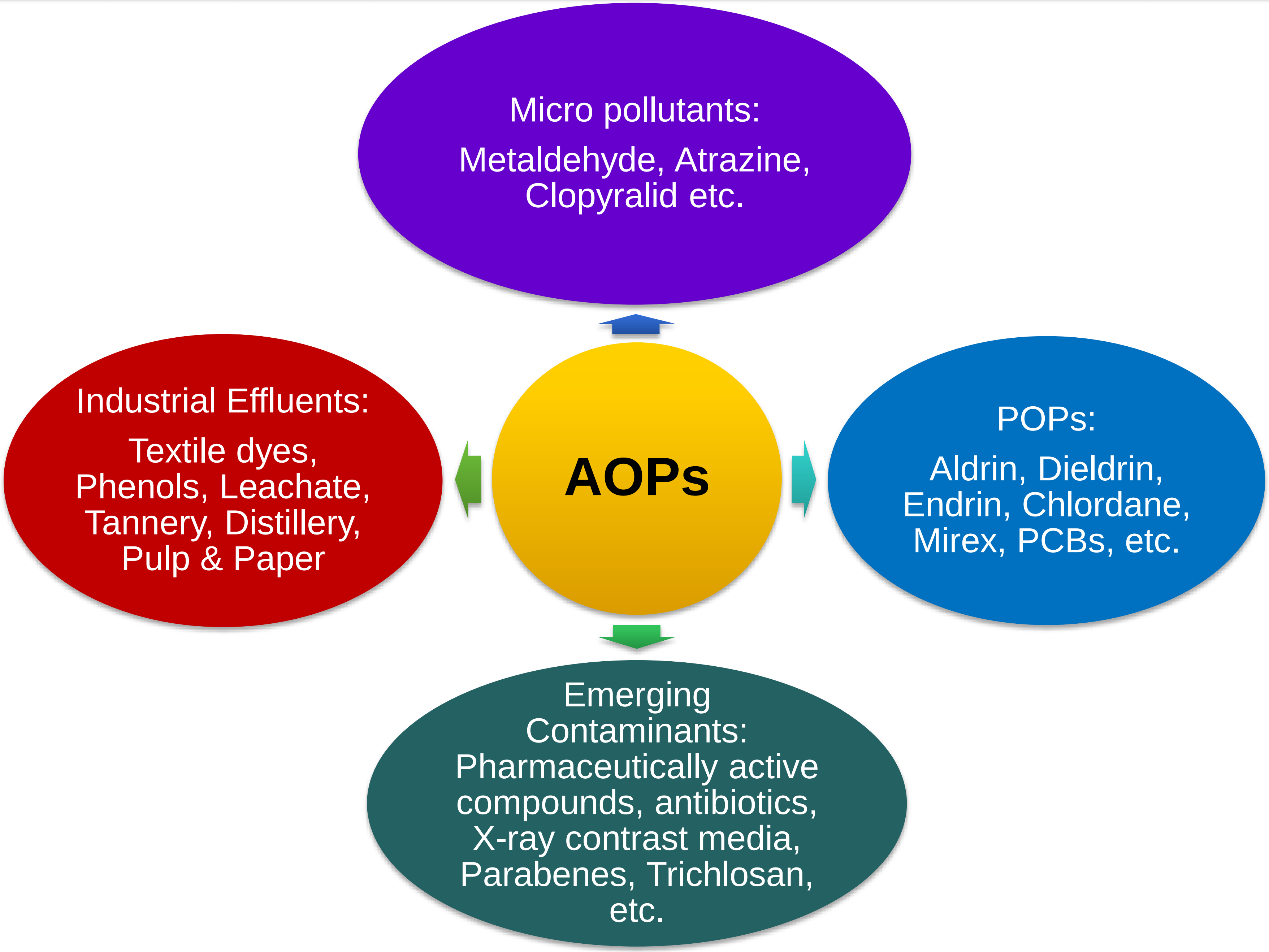
Volume = 500 mL
Carbaryl Conc. = 40 mg/L
pH = 6
TiO_2 = 1 g/L
O_3 dosage = 0.48 g/h
UVC = 125 W
Contact time = 180 min

(Reference: Rajeswari & Kanmani, *J. Adv. Oxid. Technol.* (2009)

Advanced Oxidation Treatment

S. No.	Process	Pollutant	COD Reduction	References
1	**O_3/UV and O_3/UV/H_2O_2**	Pharmaceutical, Chlorophenol	50 – 90 %	Ayla Arslan et al. (2014); Pieter Van Aken et al. (2015)
2	**Photocatalysis (TiO_2)**	Pesticide, Pharmaceutical	25 – 80 %	Abellan et al. (2009); Augustine & Malay (2013); Irene et al. (2014); Augustine & Anitha (2015); Mohamed et al. (2015b)
3	**(Solar) Photo-Fenton**	Pesticide, Pharmaceutical, Chlorophenol, MMA, Cosmetic	40 – 90 %	Vinita et al. (2010); Bautista et al (2014); Perla et al. (2014); Harjeet Kaur et al. (2014); Monsalvo et al. (2015); Mohamed et al. (2015a); Leandro et al. (2016)
4	**Electrocoagulation; Electro-Fenton; Electro-Peroxone**	Pharmaceutical, Pesticide, Paper-recycling watewater	80 – 96 %	Marcela Boroski et al. (2009); Adriana et al. (2012); Meral Turabik et al. (2014); Gholamreza & Mohammad (2014)
5	**US/TiO_2; US/Solar/TiO_2; US/H_2O_2; US/Fenton & US/Ozone**	Pharmaceutical, Pesticide, Chlorophenol	12 – 80 %	Vincenzo et al. (2009); Ning et al. (2009); Quesada-Penate et al. (2009); Gokce & Nilsun (2011); Stefanos et al. (2015); Chikang & Yiheng (2015); Pankaj & Parag (2015);
6	**O_3/Hydrocavitation; Hydrocavitation with Fenton**	4C2AP, Alachlor, Imidacloprid, Dichlorvos	70 - 80 % (TOC reduction)	Anand et al. (2008); Xikui and Yong (2009); Ravi & Parag (2012); Pankaj et al. (2014); Arati & Parag (2016); Sunita et al. (2016)
7	**Wet Air Oxidation**	Distillery wastewater (Raw & biomethanated)	60 – 75 %	Parmesh et al. (2008); Padoley et al. (2012); Malik et al. (2014); Negar Kazemi et al. (2015)

Advanced Oxidation Treatment



AOPs in Full-scale Water & Wastewater Treatment

- Major AOPs adopted are UV/H_2O_2, UV/O_3, $UV/O_3/H_2O_2$ (with and without catalyst) and Fentons
- Flow varies from 25 – 3000 m^3/h
- Full plant AOPs are installed in countries viz., **UK, USA, Canada, Netherland, Germany and Poland**
- Ozone and biological systems (ASP and SBR) are effective for municipal sewage
- Trojan^{UVSwift} (UV/H_2O_2) installed in North Holland for PWN water supply is the largest plant with 3000 m^3/h capacity running today



AOPs in Full-scale Water & Wastewater Treatment

S. No.	Particulars	Treatment System	Flow	Efficiency
1	Trojan Technologies @ PWN Water Supply company, North Holland, the Netherlands	Trojan UVSwift^{TM}ECT (UV/H_2O_2)	3000 m^3/h	80 % reduction in micropollutants concentration
2	Trojan Technologies @ Hall Water Treatment Works, Lincoln, United Kingdom	Trojan UVTorrent^{TM}ECT (UV/H_2O_2 with 96 low pressure UV lamps)	20 MLD	64 % removal of Metaldehyde, 92 % removal of Atrazine, 45 % removal of Clopyralid
3	Calgon Carbon @ Kelly Air force base, San Antonio, Texas	RAYOX (UV/H_2O_2)	200 gpm	Removal Efficiency: 88 % DCA; 67 % DCE; 97 % TCE & 99 % Vinyl chloride
4	Calgon Carbon for Dye wastewater from factory producing matches in Poland	Fentons process	50 m^3/d	91 – 96 % COD removal
5	Ozonia Technologies for pulp and paper bleaching effluents	Ozonia's IGSTM	• Ozone dose: 45 - 400 mg/L for 80 % color and 25 % COD abatement • Ozone dose: 100 mg/L for 40 % AOX, 50 % lipophilic wood extracts and 95 % resin acid abatement	

Summary

- AOPs can degrade almost all recalcitrant pollutants and emerging contaminants according to their suitability
- The running full-scale AOP systems prove their prowess in elimination of contaminants vis-à-vis water treatment
- As the ZLD scheme has become mandatory, AOPs can be adopted in IETPs/CETPs for enhancing the treatment efficiency
- Combination of AOPs can be adopted for complete degradation of organic compounds
- Significant cost reduction can be done by adopting AOP as pretreatment for improving the biodegradability of recalcitrant wastewater

Thank You