Advanced Oxidation Processes for the Removal of Endocrine Disrupting Chemicals and Enhanced Water Treatment

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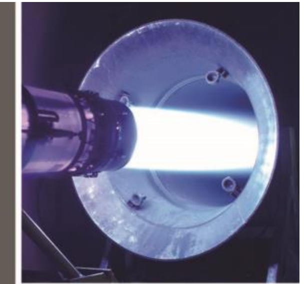

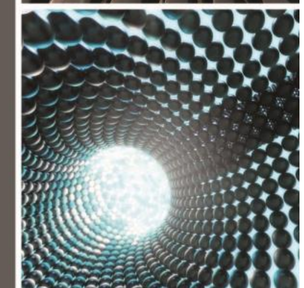

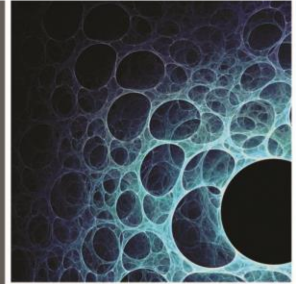

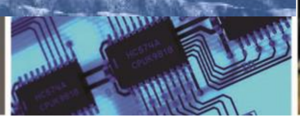

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Research Interests

Fundamental ⟷ **Applied**

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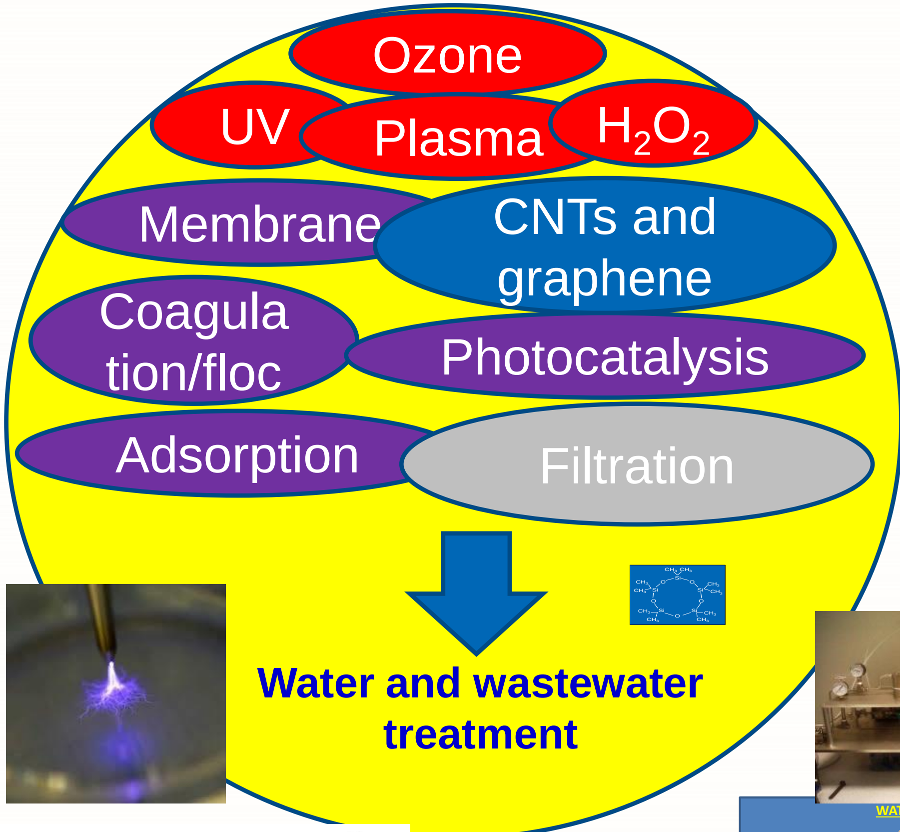
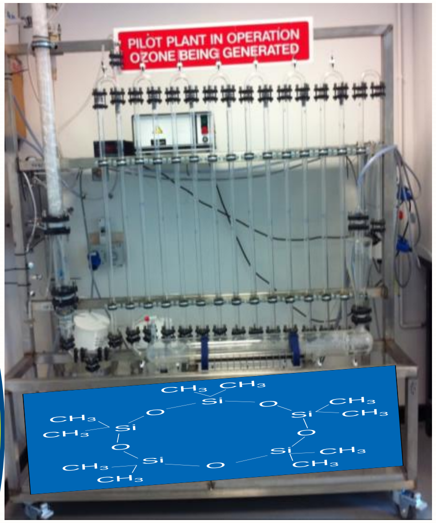
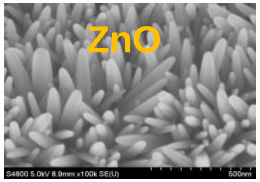
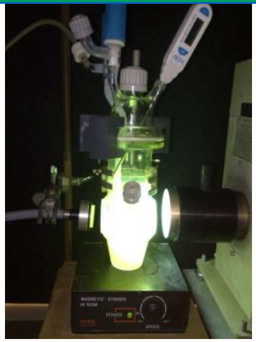
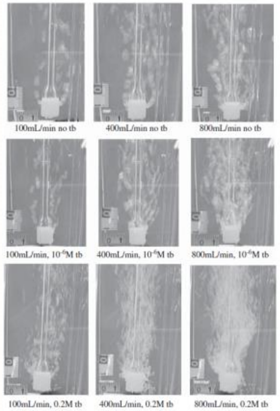
Novel waste/water treatment technologies; oxidation, separation processes; reaction engineering



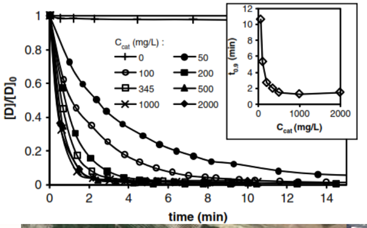


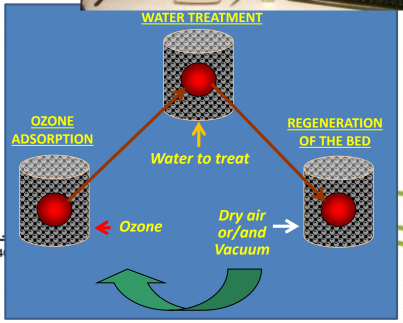


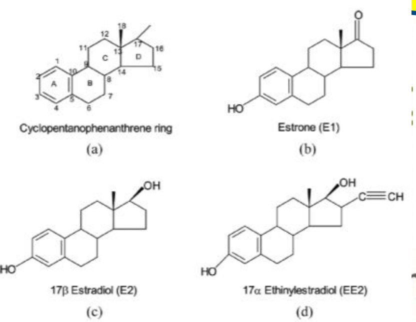


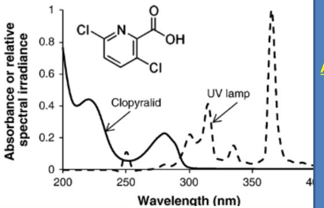


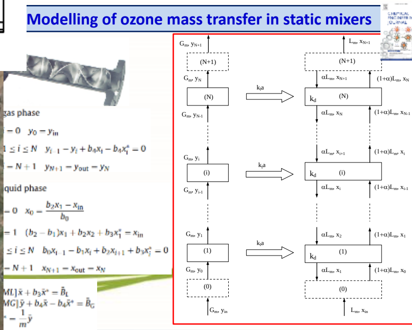
$$r_D = \frac{k_1k_2K[L-Mn^{3+}][H_2O_2]}{k_2[D][H^+]+k_4[H_2O_2][H^+]+\frac{k_1k_6K}{k_-}[L-Mn^{3+}]}[D]$$







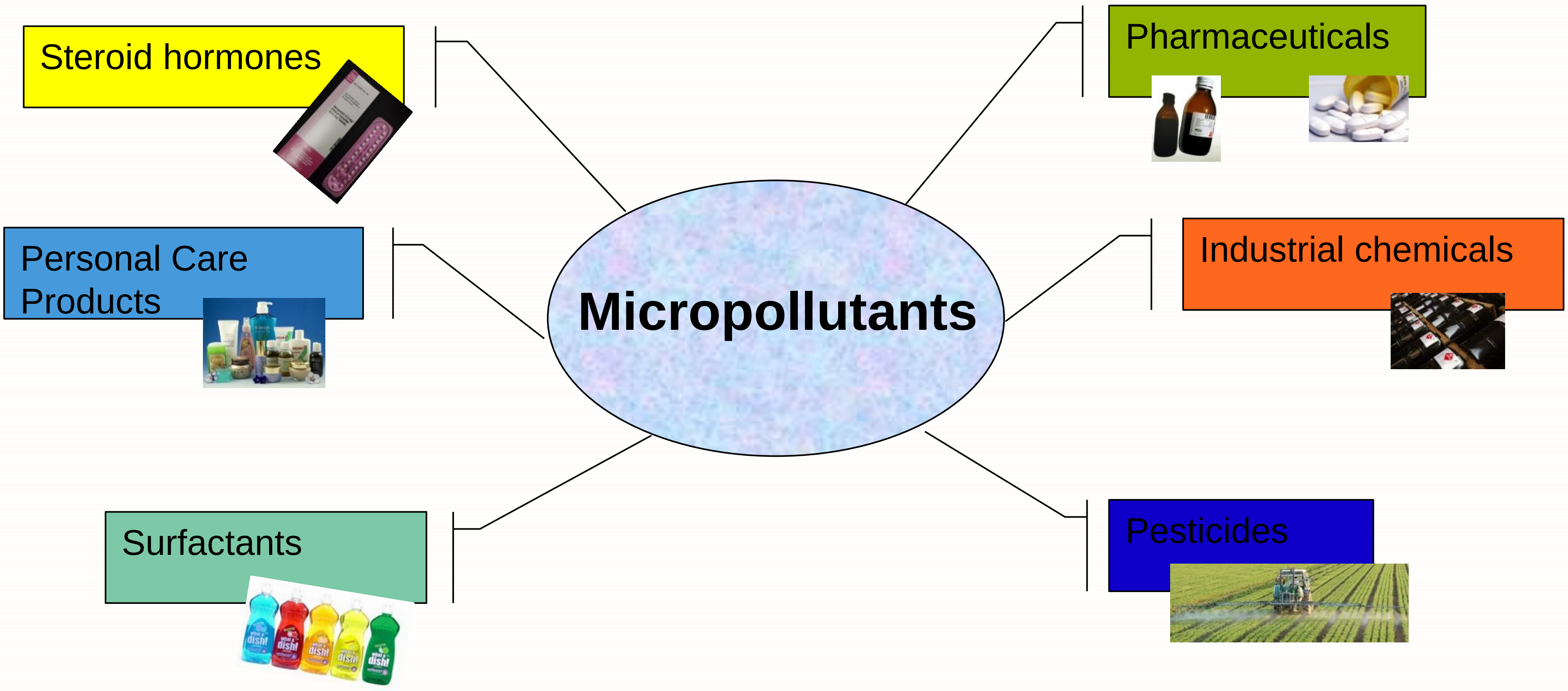




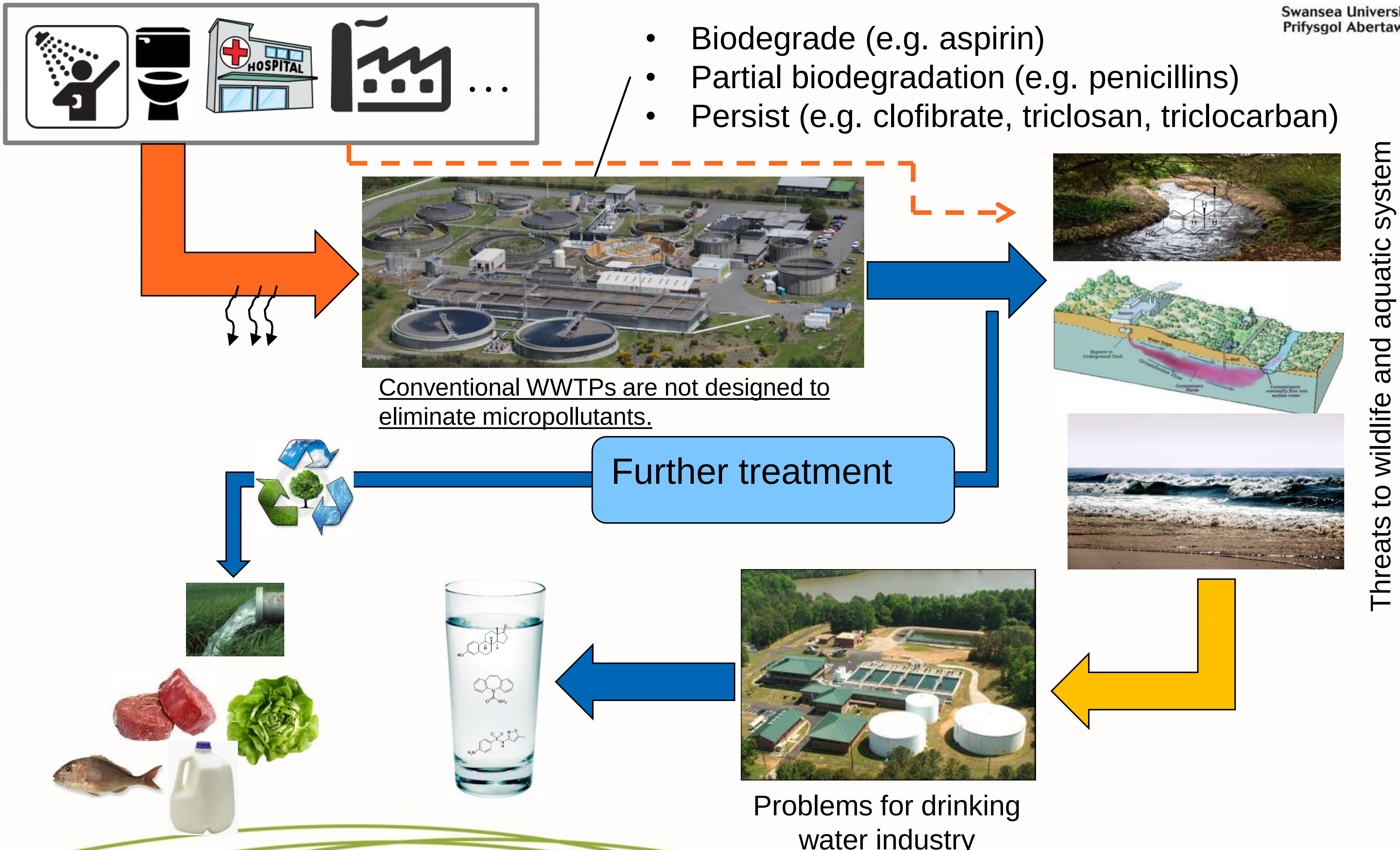
Content

- Introduction
- Results of studies on:
  - Removal of E1, E2, and EE2 using the Liquid/Liquid-Ozone system
  - Removal of the antimicrobial triclocarban
  - Removal of the herbicide clopyralid
  - Heterogeneous Nanocatalytic Ozonation
  - Hybrid ozone/membrane
- Conclusions

Micropollutants (MPs) /Trace Organic compounds (TOrCs)



Micropollutants in the environment



Levin et al. **1951.** "Estrogenic, androgenic and gonadotrophic activity in wheat germ oil", *Endocrinology* 49(3): 289-301

Fisher et al. **1952**. "Estrogenic action of some DDT analogues", *Proc. Soc. Exptl. Biol. Med.* 81(2): 439-441

Tabak, H.H., and R.L. Bunch. **1970**. *steroid hormones as water pollutants*. Developments in Industrial Microbiology

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J. Pharm. Pharmacol. 1985, 37: 1–12

REVIEW

The fate of pharmaceutical chemicals in the environment

MERVYN L. RICHARDSON AND JUDITH M. BOWRON

Thames Water Authority, New River Head, Rosebery Avenue, London EC1R 4TP

Increased demands for potable water, especially where supplies are drawn fro rivers has necessitated a greater degree of water re-use. As water undertakings h to maintain the wholesome quality of potable water supplies, increasing conce expressed over the presence of organic micro-contaminants (contaminants μg litre^{-1} concentrations). This study outlines some of the problems encou assessing the risk from pharmaceutical chemicals which might enter the water domestic and industrial sources. Analytical chemistry was of value for only a few compounds studied. However, much useful information was derived from t metabolic routes of the drugs and is collated in Appendix I. Biodegradation s other ecotoxicity/environmental toxicology data may be required to a greater ex future. Particular consideration is given to vulnerable sections of the populatio

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ESTROGENIC ACTIVITY IN FIVE MEASUREMENT OF VITEI

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†Ministry of Agriculture, Fisheries, and F Remembrance Avenue,

‡Department of Biology and Biochemis

(Received 14 M

Abstract—It was recently demonstrated that most, if r are estrogenic to fish. As many STWs discharge into effluent enters might also be estrogenic. To assess this at various distances downstream of the effluent entry into five rivers in England were studied. In four cases, very marked and rapid increases in their plasma vitello of these four cases, none of the downstream sites were e did respond by synthesizing appreciable amounts of situation in the fourth river was quite different; not on in the mg/ml range was attained), but so were all the where the effluent entered. This particular river recei concentrations of alkylphenolic chemicals than any of account for the estrogenic activity of this river. The fi This discharge comes from a very small STW, which why the effluent (and hence the river) was not estroge

Keywords—Estrogen Sewage *Oncorhynchus*

Environ. Sci. Technol. 1998, *32*, 2498–2506

Widespread Sexual Disruption in Wild Fish

SUSAN JOBLING,*,† MONIQUE NOLAN,‡ CHARLES R. TYLER,† GEOFF BRIGHTY,§ AND JOHN P. SUMPTER†

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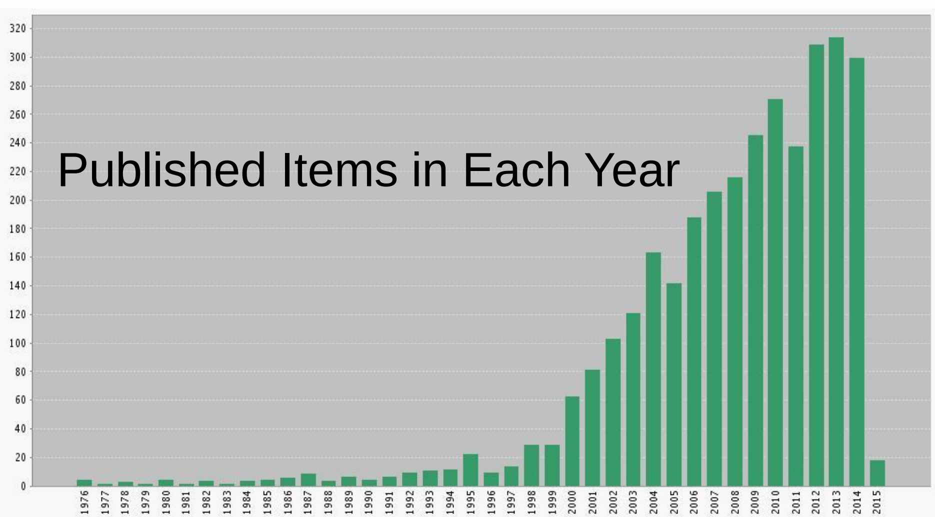
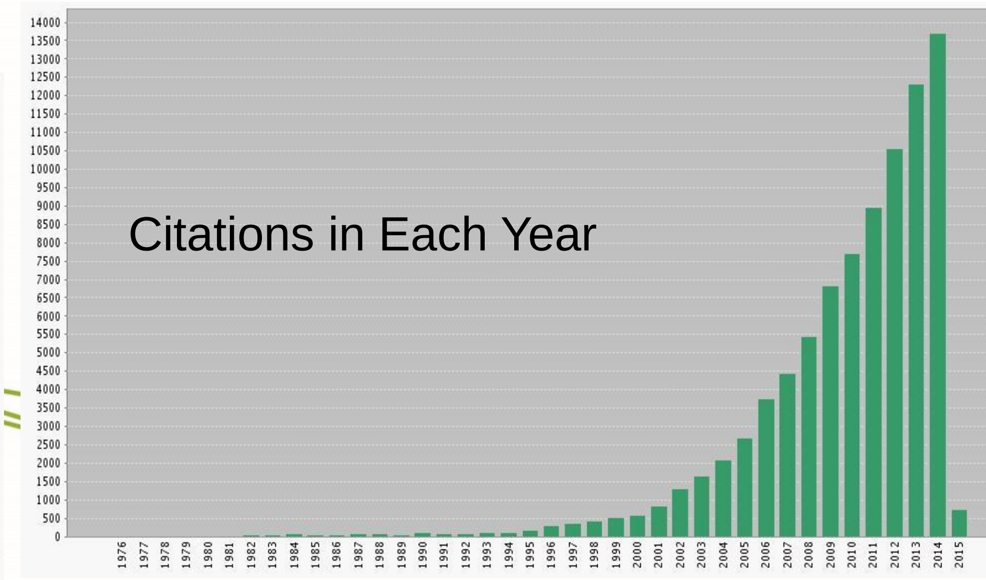
A number of chemicals present in the environment have been shown to mimic or antagonize the actions of steroid hormones, an issue often described as "endocrine disruption/modulation". There is very little evidence, however, to support the hypothesis that exposure to endocrine-disrupting chemicals is a global environmental health problem. In this paper, we demonstrate a high incidence of intersexuality in wild populations of riverine

mented, but geographically limited, p (8–14). Most of the chemicals that many orders of magnitude less potent counterparts, and it therefore seems exposure will cause significant healt standing this, it is entirely possible tha of endocrine-modulating substances present in the environment, may cau even synergistic effects. Furtherm unknown chemicals that may be m known to date or whose actions d toxicological dose–response curve (The critical issue is whether suffi endocrine-modulating substances e vironment to exert adverse reproduc and/or humans. It is primarily this qu the basis of the international conce environmental impact of endocrine-m While this debate has been the subjec meetings and has received much pu support the hypothesis that endoc stances are a significant human and problem is lacking (for a recent review this conclusion seems to be due to t studies on this subject and not to support of the converse hypothesis.

Rivers and estuaries throughout th

Endocrine Disrupting Chemicals/Compounds





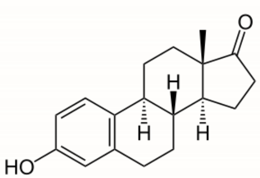
Effects of MPs and EDCs

- Feminisation of male fish via exposure to hormones (e.g. E1, E2, EE2).
- Effect on many other species (e.g. diclofenac on vultures).
- EDCs ➔ learning disabilities, severe attention deficit disorder, breast cancer, prostate cancer, thyroid and other cancers.
- Feminising of males or masculinising effects on females.
- Damage to a developing fetus.
- Link between phthalate concentration and genital abnormalities in newborn males.
- Reproductive organ malformations in birds, mammals and alligators (Florida, USA).
- Bacterial resistance caused by exposure of bacteria to pharmaceuticals
- Antimicrobial resistance ➔ antibiotics fail to treat a number of infections

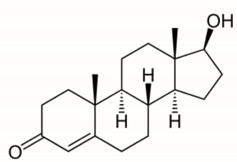
Examples of EDCs

Several thousand natural and synthetic chemicals have been identified as EDCs including (the list continues to grow):

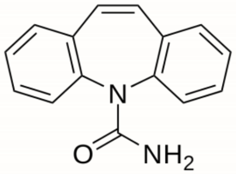
- Natural and synthetic estrogens, androgens (estrone, ethinyl estradiol, testosterone)
- Certain pharmaceuticals (β-blockers, carbamazepine etc.)
- Surfactants (e.g. nonylphenol and its ethoxylates)
- Pesticides, herbicides and fungicides (e.g. DDT, Dieldrin)
- Polyaromatic compounds (e.g. PAHs, PCBs, brominated flame retardants)
- Organic oxygen compounds (e.g. phthalates, bisphenol A)
- Many other industrial chemicals



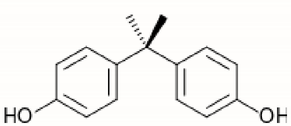
Estrone



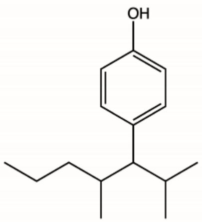
Testosterone



Carbamazepine



Bisphenol A



Nonylphenol

Removal Techniques

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- Data for UK rivers and streams has shown that median concentrations of pharmaceuticals are almost always ≤100 ng/L
- Only a few are oxidised by chlorine or chlorine dioxide
- Most non-polar organic compounds are removed by activated carbon
- Ozone/GAC effective for almost all pharmaceuticals
- Ozonation and advanced oxidation processes effective
- Photolysis reactions and photocatalytic processes.

Estrogen	Oxidant	K ($M^{-1}s^{-1}$)
E1	O_3 O_3 O_3 O_3 ^{o}OH	6.2×10^{3} (pH 4) 9.4×10^{5} (pH 7) 2.1×10^{7} (pH 8.5) 5×10^{9} (pH 10.5) 2.6×10^{10}
E2	^{o}OH	1.41×10^{10} (pH 6.8)
EE2	O_3 ^{o}OH	7×10^{9} (pH 6) 1.08×10^{10} (pH 6.8)

Second-order rate constants for the ozonation of estrogens

Ozone and AOPs

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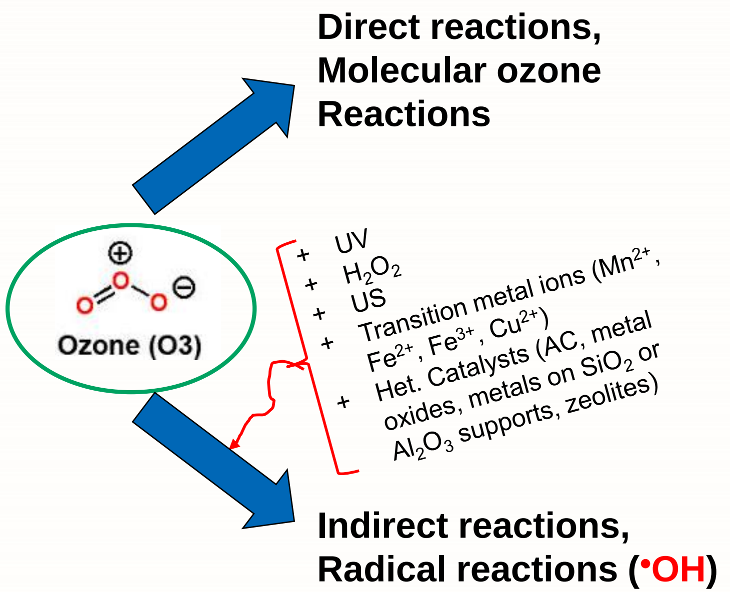
$$3\,O_2 \rightleftarrows 2\,O_3 \qquad \Delta H_f^o \text{ at 1 atm} = +284.5\ \text{kJ.mol}^{-1}$$

Theor: 1.65 kWh/kg, Prac. ~10kWh/kg O_3

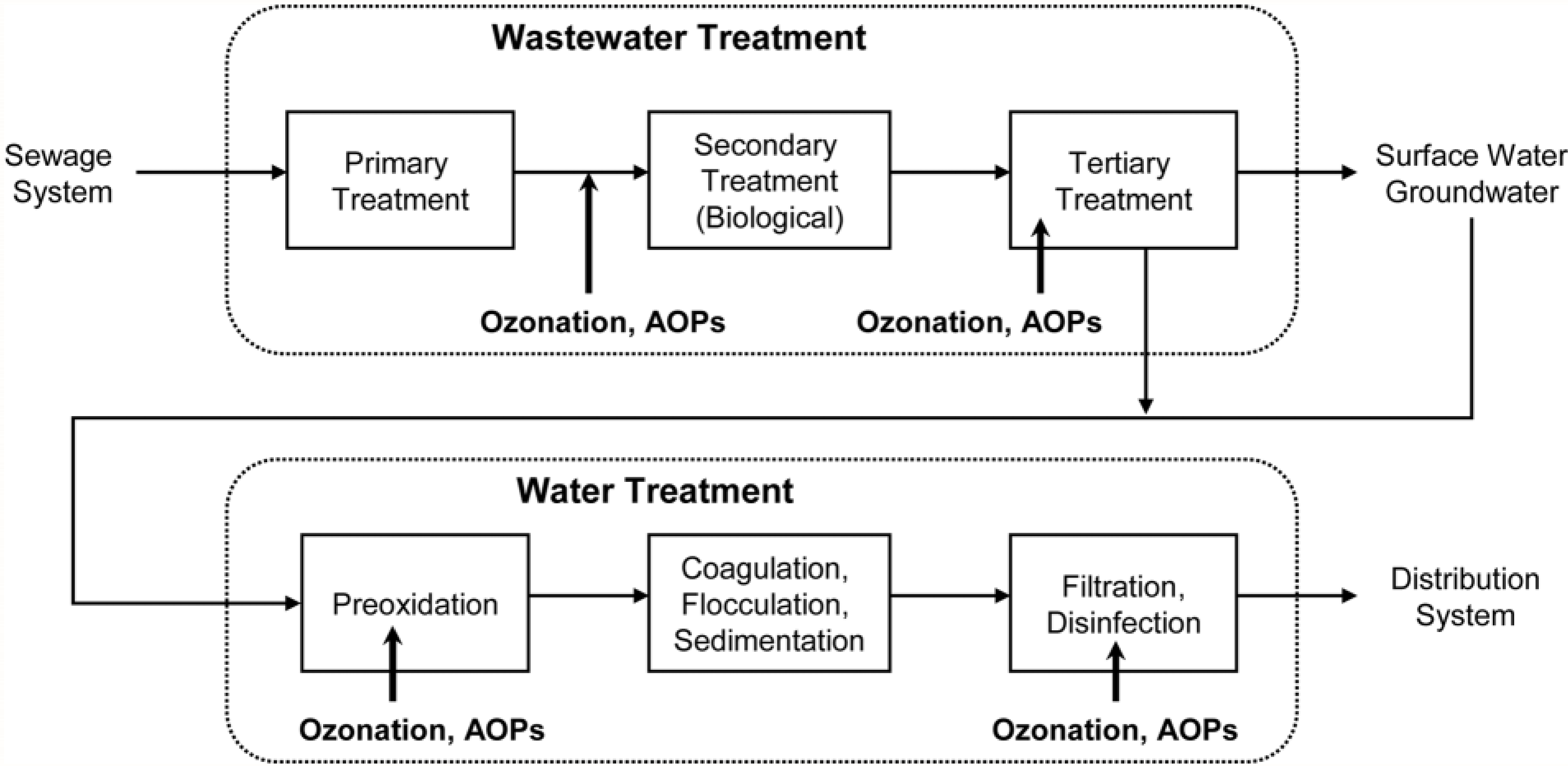
- Ozone is a Powerful Oxidising agent

$$O_3 + 2H_3O^+ + 2e^- \rightarrow O_2 + 3H_2O \qquad E^0 = 2.07\ \text{V}$$

Species	Oxidation Potential eV
Hydroxyl radical, $^{\bullet}OH$	2.80
Ozone, O_3	2.07
Hydrogen peroxide, H_2O_2	1.77
Perhydroxyl radical, $^{\bullet}OOH$	1.70
Chlorine dioxide, ClO_2	1.50
Hypochlorous acid, HOCl	1.49
Chlorine, Cl_2	1.36
Oxygen, O_2	0.40



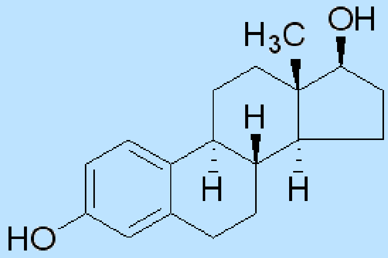
Possible points to apply ozonation and AOPs



(Ikehata et al., 2006)

Removal of E1, E2, and EE2 using the Liquid/Liquid-Ozone system

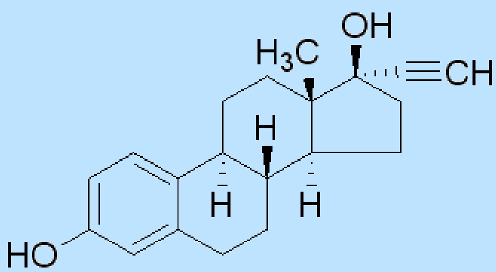
Estrogens of interest



17β-estradiol (E2)

$C_{18}H_{24}O_2$ M=272.39 g/mol

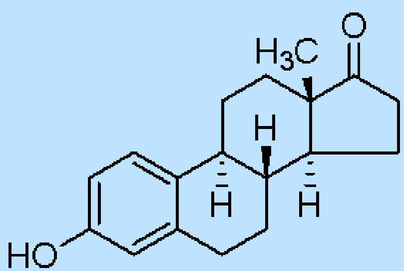
- Produced by all mammals
- Binds easily with human receptor



17α-ethinylestradiol (EE2)

$C_{20}H_{24}O_2$ M=296.403 g/mol

- Synthetic
- Main ingredient of contraceptive pills

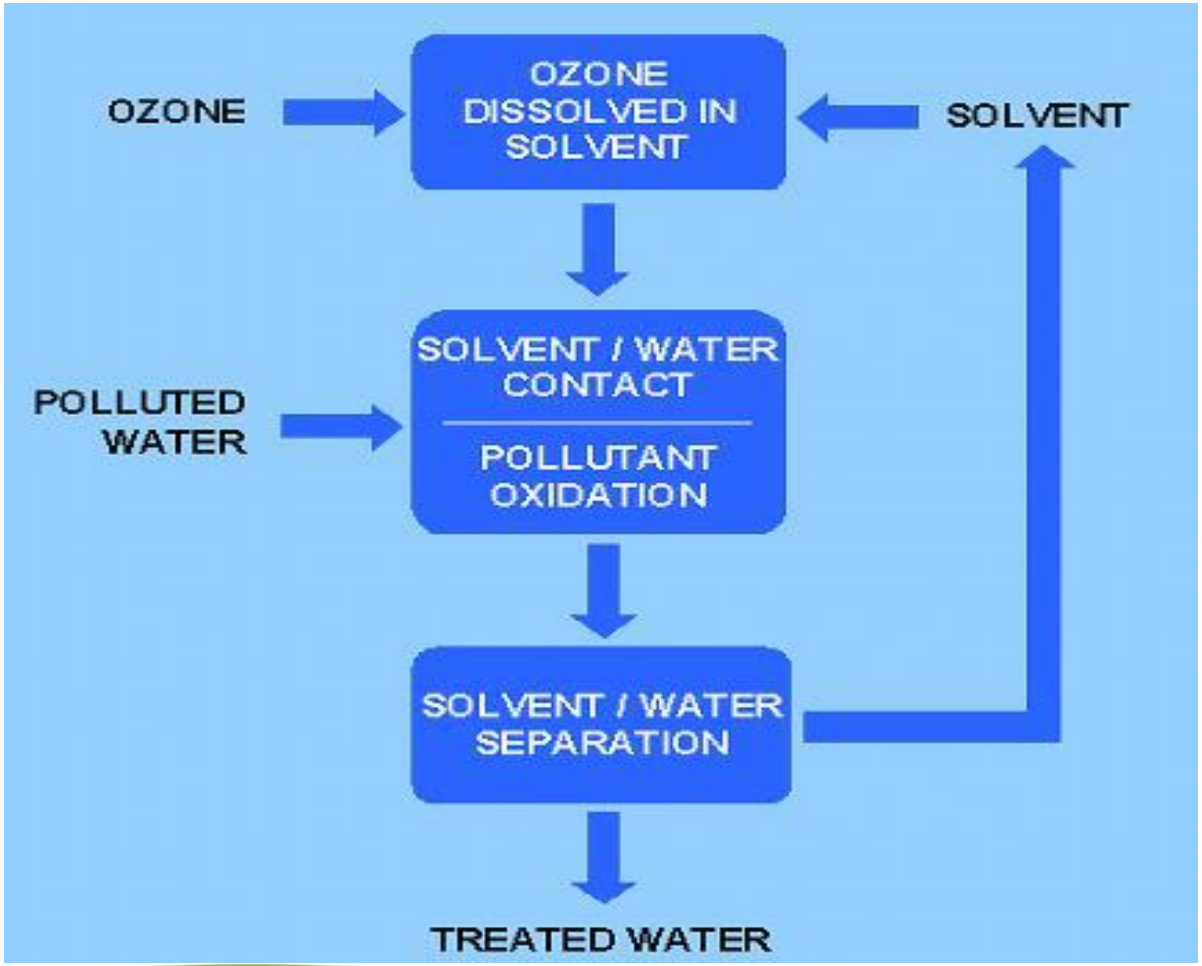


Estrone (E1)

$C_{18}H_{22}O_2$ M=270.366 g/mol

- Secreted by the ovary
- Product resulting from oxidation of E2

The Process


OZONE
OZONE DISSOLVED IN SOLVENT
SOLVENT
POLLUTED WATER
SOLVENT / WATER CONTACT
POLLUTANT OXIDATION
SOLVENT / WATER SEPARATION
TREATED WATER

Marley STW, Yorkshire, UK

Sampling point

☞Sample preservation (15 mL of a solution containing hydrochloric acid (30%) and copper nitrate (0.25 g/L) added to 5L sample).

EDCs Analysis

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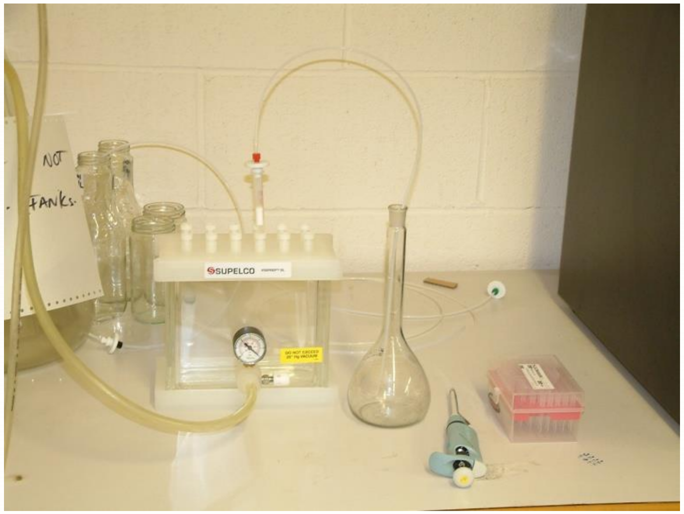
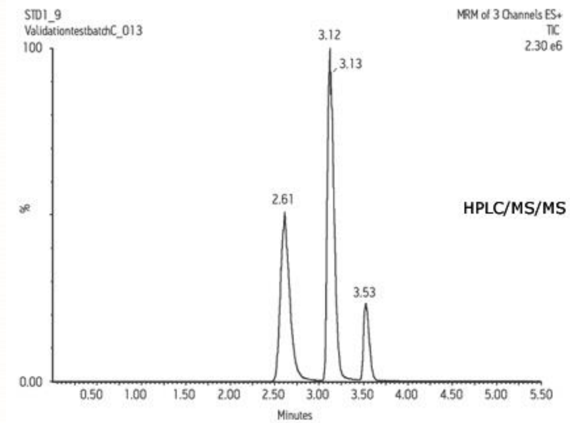
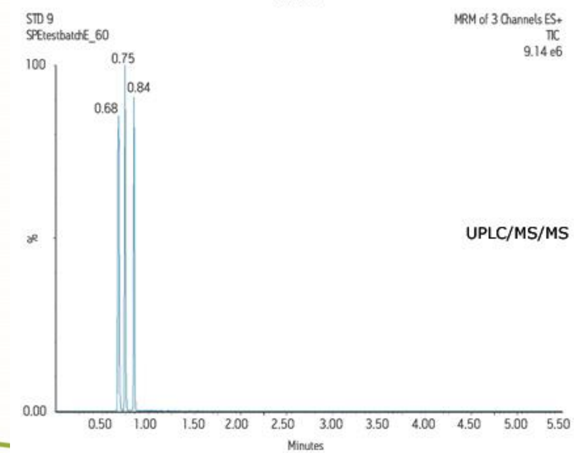
is a challenge!

Sample Collection → SPE → HPLC-MS-MS analysis







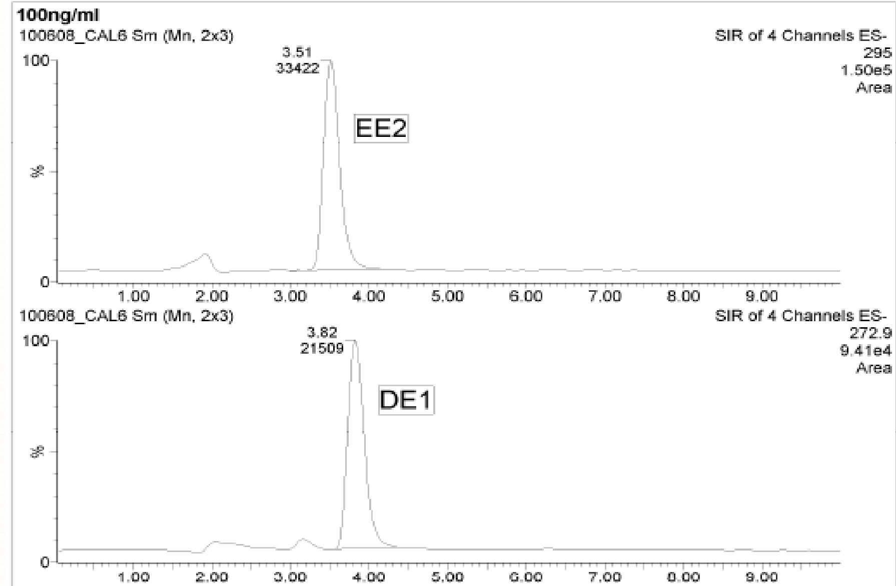
The analytical method

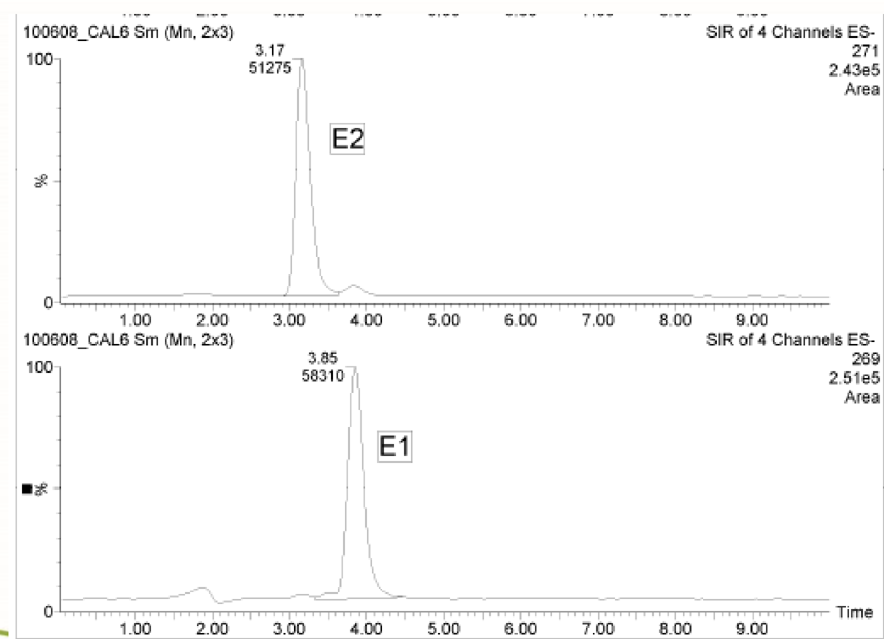
Solid phase extraction recoveries

EDC	E1	E2	EE2
Recovery (%)	79.1	81.2	77.6

LC/MS/MS

Estrogen	*Ions (m/z)*	Retention time (min)
E2	271 / 143	3.17
EE2	295 / 143	3.51
DE1	273 / 147	3.82
E1	269 / 143	3.85





Extraction of EDCs to the solvent

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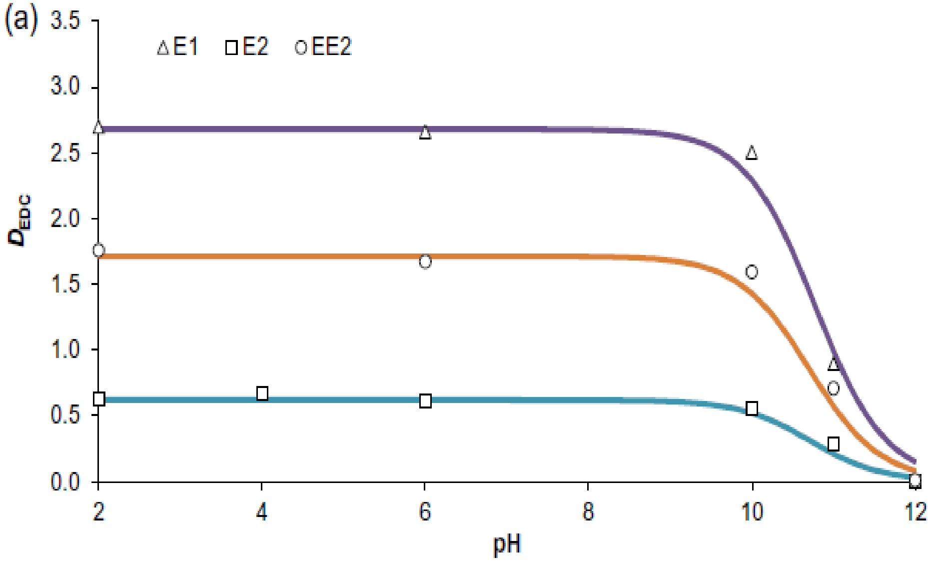
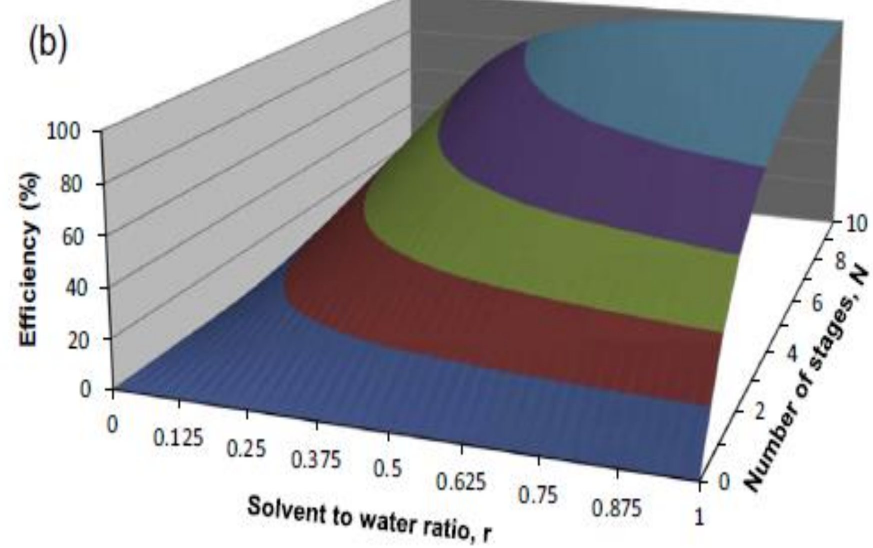
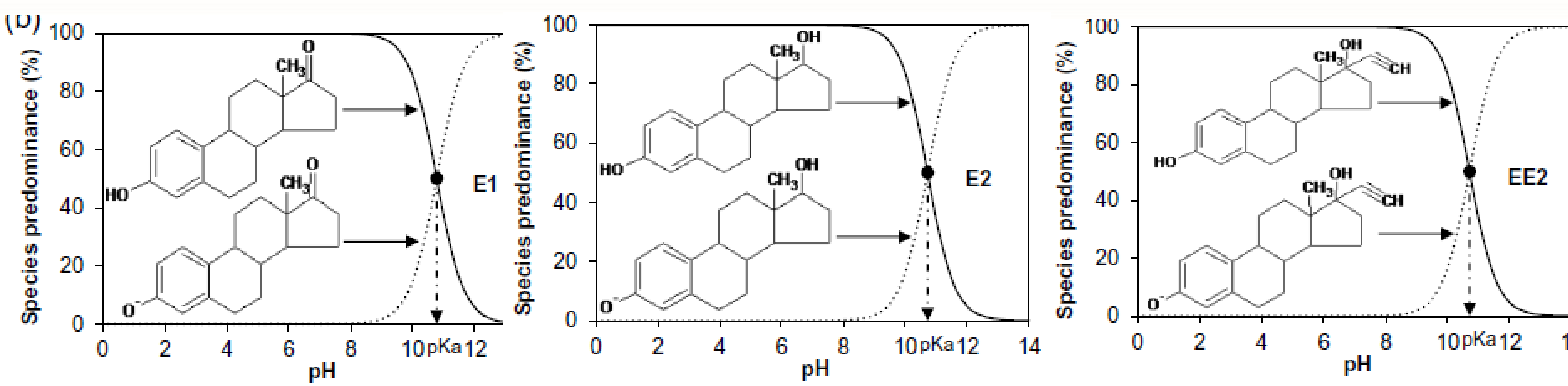
Distribution coefficients



E2 removal





Rates: LLO vs LGO

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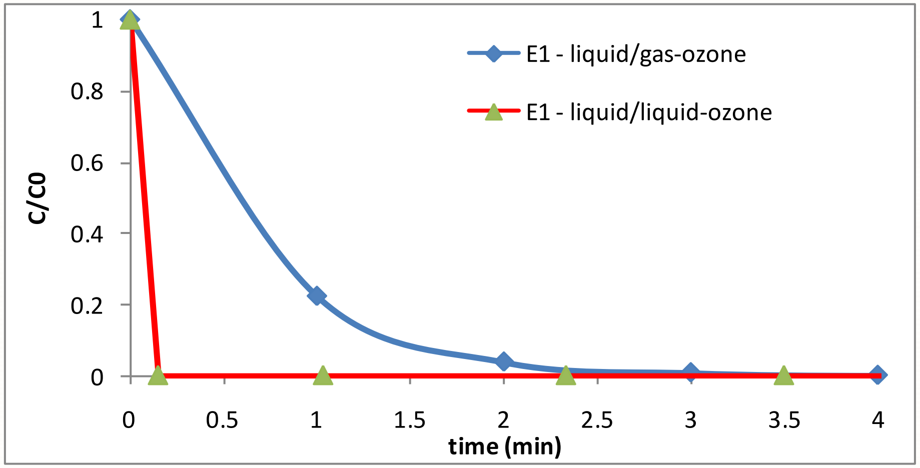
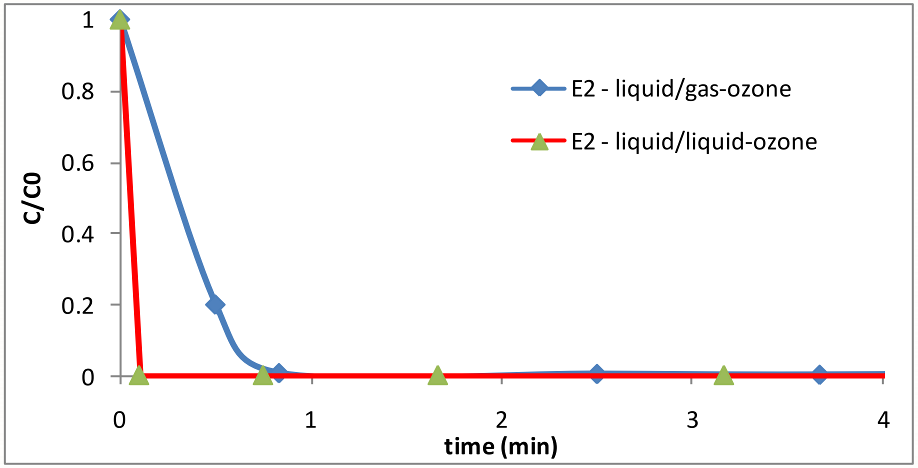
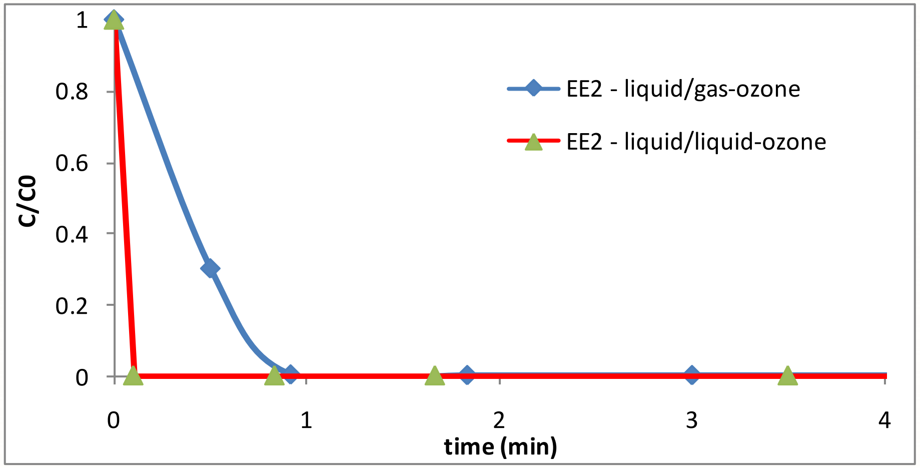
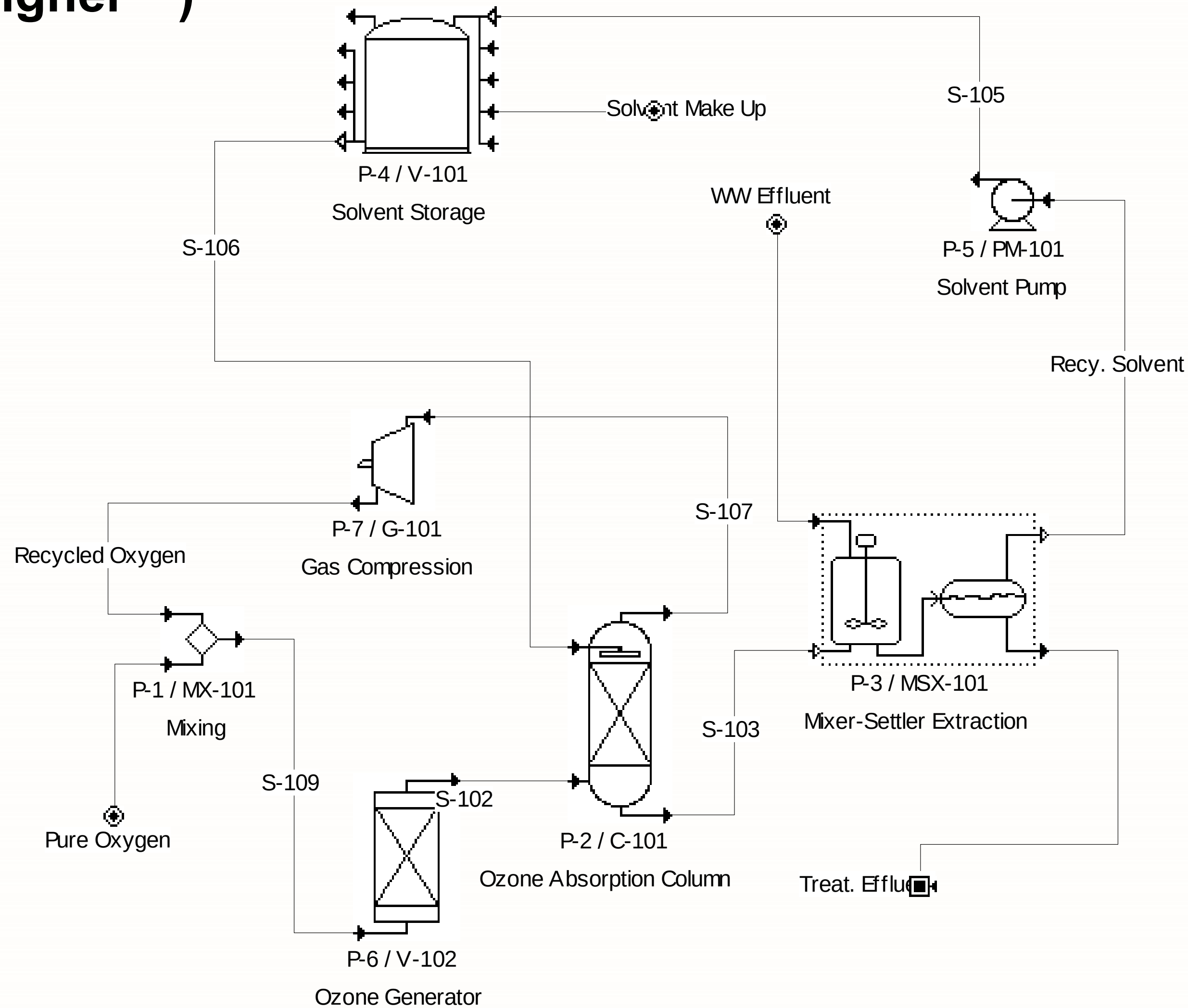






Process calculation and estimation of basic operational costs (Super Pro Designer™)



PROCESS CALCULATION AND ESTIMATION OF BASIC OPERATIONAL COSTS

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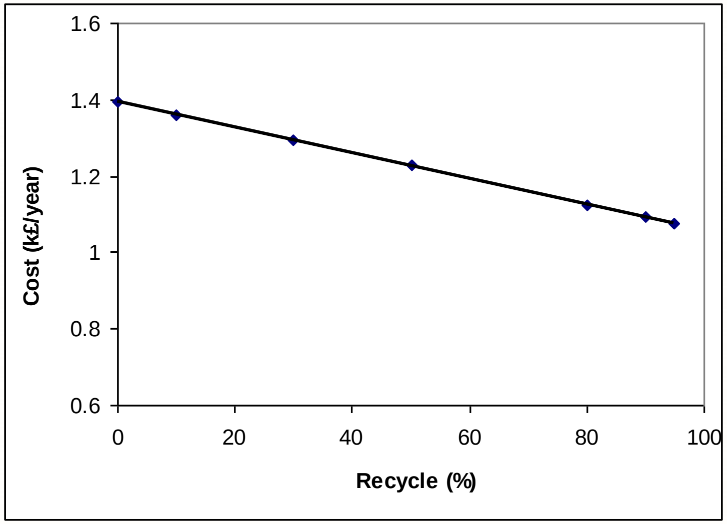
Input

Parameter	Value
Effluent flow rate (L/s) (highest at Marley)	400
Effluent flow rate (MLD)	34.6
E1 (ng/L)	100
E2 (ng/L)	100
EE2 (ng/L)	100
Ozone gas concentration (g/m3) NTP	100
Solvent ozone transfer efficiency (%)	95
Ozone transfer efficiency to water (%)	90
Ozone dose (mg/L)	1
Percentage solvent/water (%)	1
Solvent+ozone/water contact time (min)	1
Ozone production specific energy consumption (kWh/kg)	10
Cost unit power (£/kg)	0.1
Cost unit oxygen (£/kg)	0.1
Cost unit solvent (£/L)	7
Solvent replacement frequency/year	0.5
Contingency solvent volume ratio	0.2

Output

Parameter	Value	Value
Oxygen recycle (%) (var)	**0**	**80**
Volume of LLO contactor (m^3)	24.2	24.2
Total cost (£/ML)	**0.111**	**0.089**

(NDP (O_3 only) ➔ cost of ~£4/ML



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Removal of estrone (E1), 17β-estradiol (E2), and 17α-ethinylestradiol (EE2) from wastewater by liquid–liquid extraction

CrossMark

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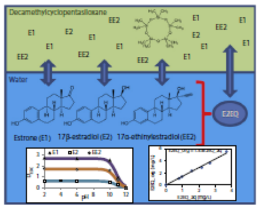
[b] Centre for Water Advanced Technologies and Environmental Research, College of Engineering, Swansea University, SA2 8PP, UK

HIGHLIGHTS

- Huge concerns about occurrence of endocrine disrupting chemicals (EDCs) in water.
- EDCs have tendency to distribute to organic solvents.
- Decamethylcyclopentasiloxane was effective to extract E1, E2 and EE2.
- The distribution coefficients were not affected by pH up to pH 9.5.
- Liquid–liquid extraction was effective to remove estrogenic potency from water.

GRAPHICAL ABSTRACT



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DOI: 10.1080/01919512.2013.836956

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A Modified Indigo Method for the Determination of Ozone in Nonaqueous Solvents

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The indigo method for the analysis of aqueous ozone was modified to allow analysis of dissolved ozone in nonaqueous liquid phases. The method was tested using the solvent

hurdles which must be overcome if the use of ozone in water treatment is going to continue to grow (Gottschalk et al. 2010). Traditionally, it has been difficult to expose contaminants of

Ben Fredj, S., J. Nobbs, C. Tizaoui, and L. Monser. 2015. "Removal of estrone (E1), 17β-estradiol (E2), and 17α-ethinylestradiol (EE2) from wastewater by liquid–liquid extraction", *Chemical Engineering Journal* 262 pp:417-426.

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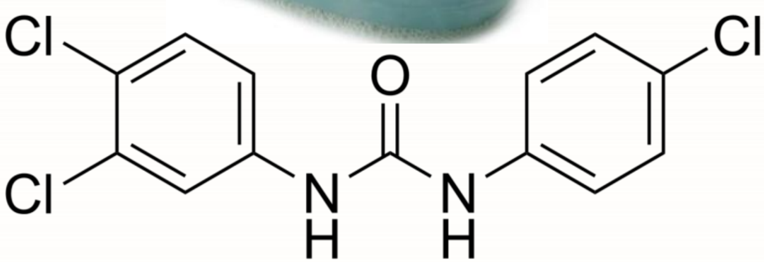
Nobbs, J., and C. Tizaoui. 2014. "A Modified Indigo Method for the Determination of Ozone in Nonaqueous Solvents", *Ozone: Science & Engineering* 36(1): 110-120

Removal of the antimicrobial triclocarban

Removal of the antimicrobial triclocarban

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Triclocarban Enhances Testosterone Action: A New Type of Endocrine Disruptor?

Jiangang Chen, Ki Chang Ahn, Nancy A. Gee, Mohamed I. Ahmed, Antoni J. Duleba, Ling Zhao, Shirley J. Gee, Bruce D. Hammock, and Bill L. Lasley

Center for Health and the Environment (J.C., N.A.G., B.L.L.), Department of Entomology (K.C.A., S.J.G., B.D.H.), California National Primate Research Center (N.A.G., B.L.L.), Division of Reproductive Endocrinology and Infertility, University of California, Davis, Medical Center (A.J.D.), Department of Nutrition (L.Z.), Cancer Research Center (B.D.H.), University of California, Davis, California 95616; and Department of Obstetrics and Gynecology (M.I.A., A.J.D.), Yale University School of Medicine, New Haven, Connecticut 06510

Many xenobiotics h… in a wide range of … usually between sı… ceptor signaling sy… 3,4,4′-trichlorocarb… care products that … uated and found t… disrupting substan… ated bioassay was … urea compounds wi… no endocrine activ…

Removal of the antimicrobial triclocarban with ozone

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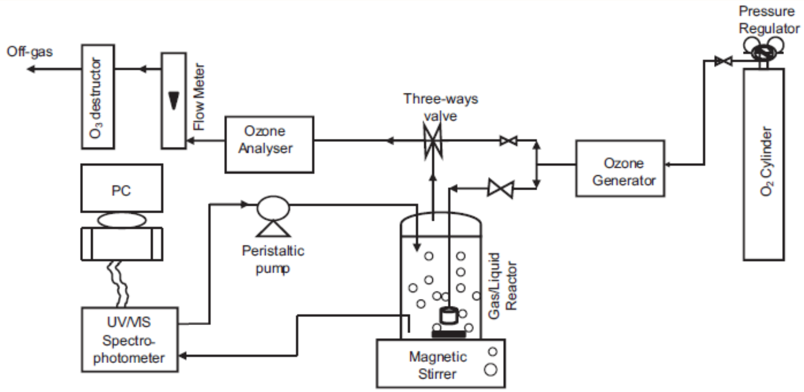


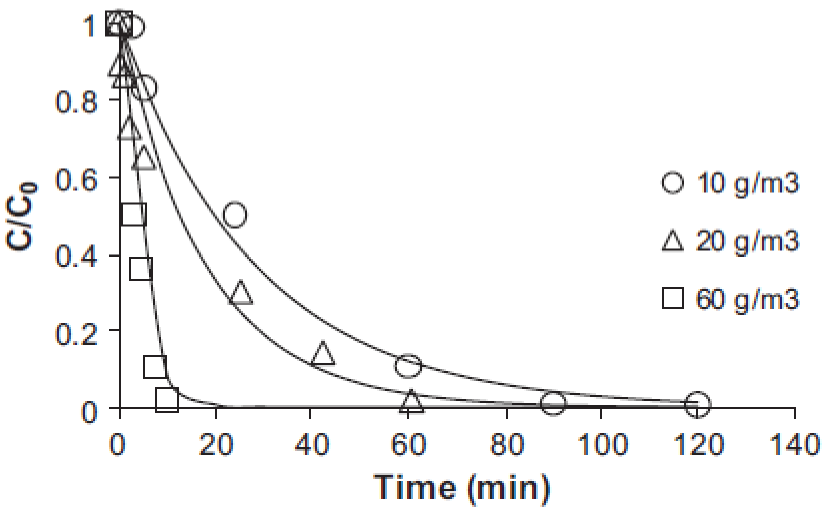
$$O_3 + bTCC \rightarrow products \quad b=1$$

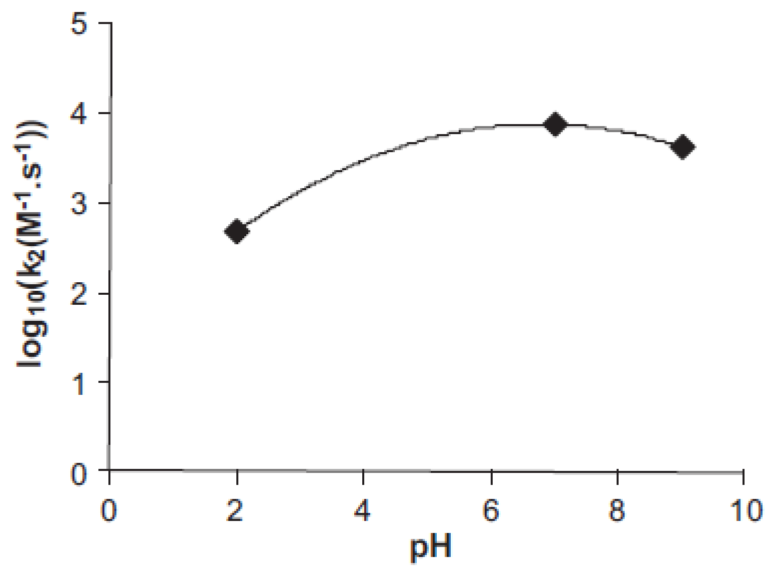
$$r_B = -\frac{1}{b}\frac{dC_B}{dt} = N_{O_3} = aC^*_{O_3}\sqrt{D_{O_3}k_2C_B} \text{ for } \quad 5H_a < E_i$$

$$N_{O_3} = k_L aC^*_{O_3}H_a \quad \text{for} \quad 5H_a < E_i$$

$$H_a = \frac{\sqrt{D_{O_3}k_2C_B}}{k_L} \qquad E_i = 1 + \frac{C_B D_B}{bC^*_{O_3}D_{O_3}}$$

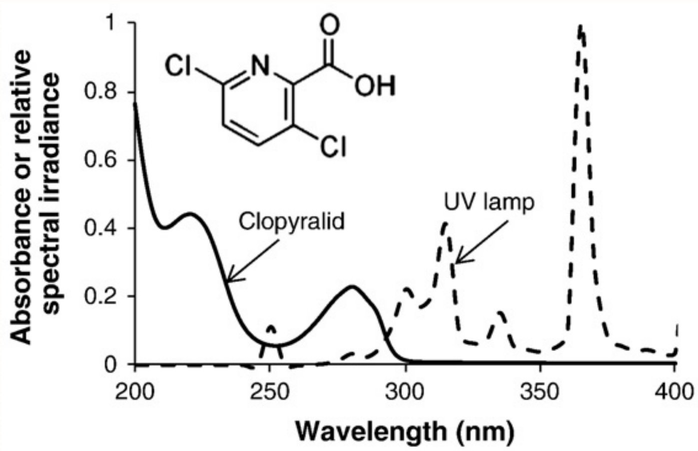
$$C_{B_0}{}^{0.5} - C_B{}^{0.5} = baC^*_{O_3}\frac{\sqrt{k_2 D_{O_3}}}{2}t$$



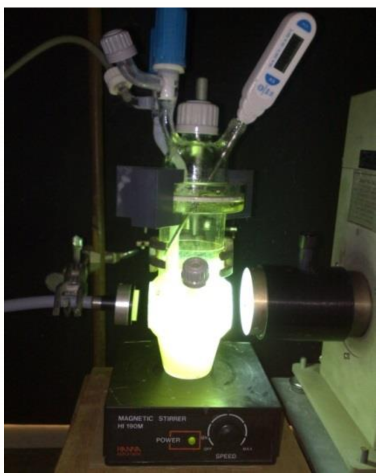


Tizaoui et al. 2011. "Degradation of the antimicrobial triclocarban (TCC) with ozone", *Chem. Eng. Proc* 50(7): 637-643

Removal of the herbicide clopyralid



UV/TiO$_2$

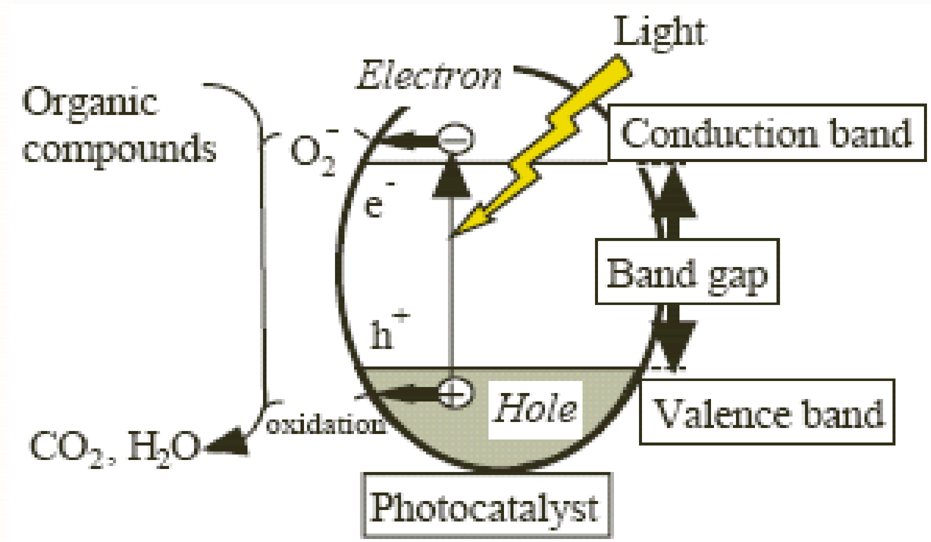


$$TiO_2 + hv \rightarrow h^+ + e^-$$

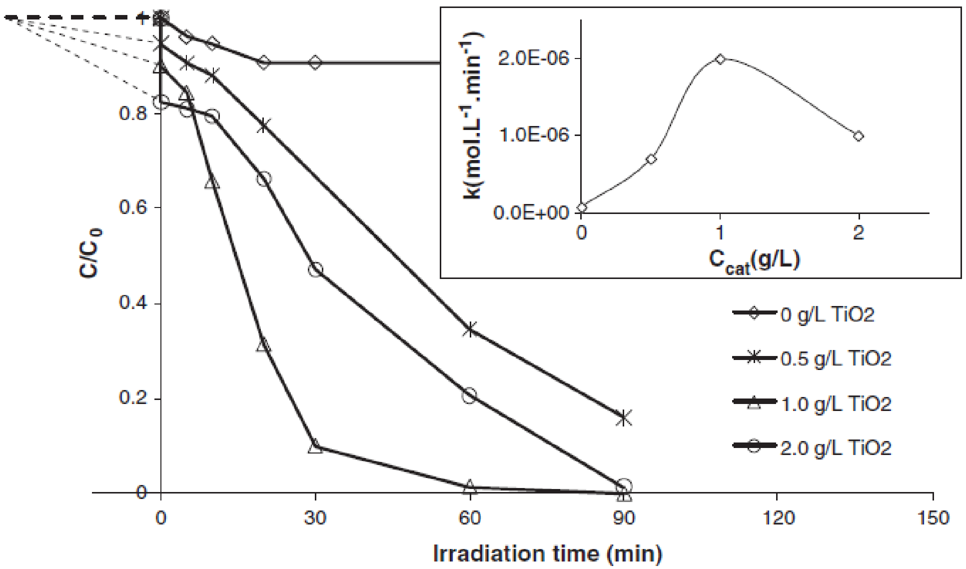
$$h^+ + H_2O_{ads} \rightarrow {}^{\cdot}OH + H^+$$

$$h^+ + OH^-{}_{ads} \rightarrow {}^{\cdot}OH$$

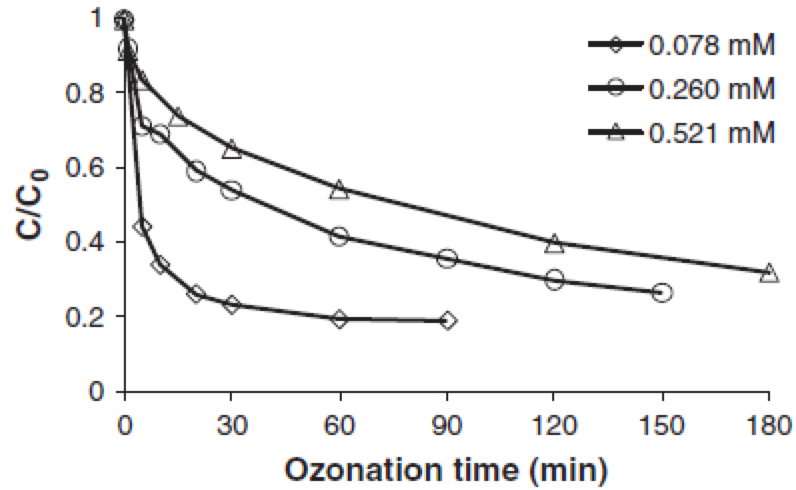
$$e^- + O_{2(ads)} \rightarrow {}^{\cdot}O^-{}_2$$



Removal of clopyralid with O_3 and UV/TiO_2

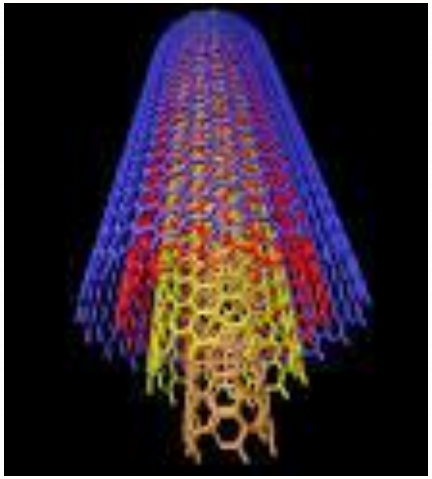


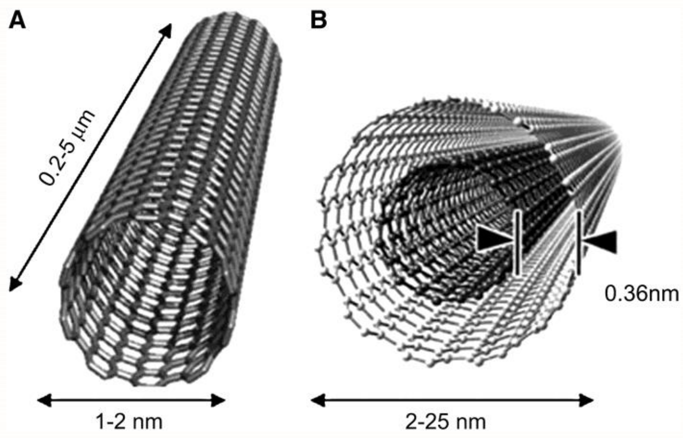
Removal of clopyralid with UV/TiO_2 (C_0=0.078 mM, Power=160 W, pH=5). Inset: changes of the pseudo-zero-order rate constant vs. catalyst concentration

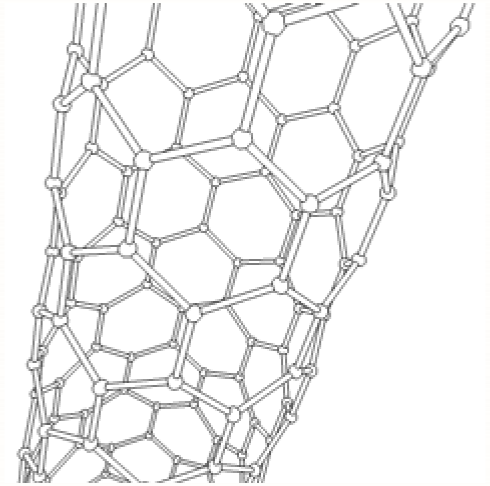


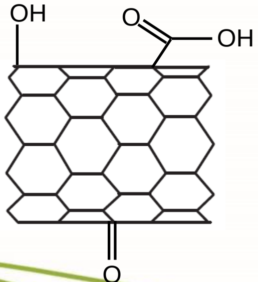
Removal of clopyralid with ozone (gas flow rate=200 mL/min, ozone gas concentration=60 g/m^3 NTP, pH=5.6, different initial clopyralid concentrations).

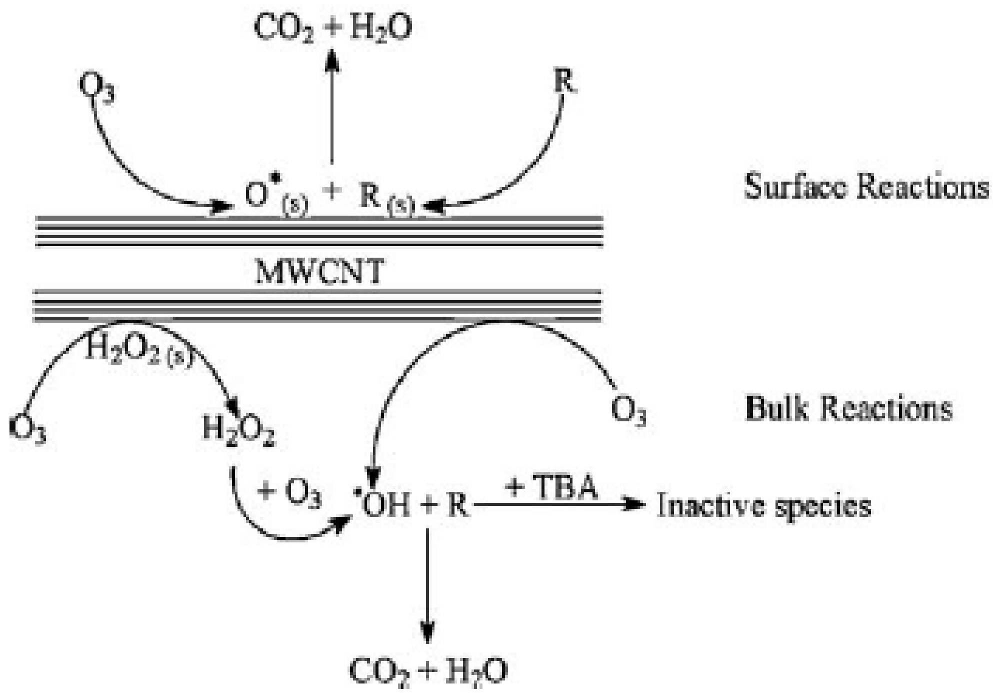
Heterogeneous Nanocatalytic Ozonation











Z.-Q. Liu, J. Ma, Y.-H. Cui, B.-P. Zhang, Mechanism of catalytic ozonation of oxalic acid in the presence of MWCNT. Applied Catalysis B: Environmental 92 (2009) 301–306.

Kinetics Model

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Homogeneous reactions:

$$R + O_3 \xrightarrow{k_{O3}-\text{homo}} products \qquad -\frac{d[R]}{dt} = k_{\text{O3-homo}}[O_3][R]$$

$$R + {}^{\bullet}OH \xrightarrow{k_{OH}-\text{homo}} products \qquad -\frac{d[R]}{dt} = k_{\text{OH-homo}}[{}^{\bullet}OH][R]$$

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www.deswater.com
doi: 10.1080/19443994.2013.766646
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Heterogeneous catalytic ozonation of diethyl phthalate

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Email: c.tizaoui@swansea.ac.uk

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Heterogeneous reactions

$$S - R + O_3 \xrightarrow{k_{O3-het}} products \qquad -\frac{d\{S-R\}}{dt} = k_{\text{O3-het}}\{S-R\}\{O_3\}$$

$$S - R + {}^{\bullet}OH \xrightarrow{k_{OH-het}} products \qquad -\frac{d\{S-R\}}{dt} = k_{\text{OH-het}}\{S-R\}\{{}^{\bullet}OH\}$$

$$\boxed{\frac{d[R]_{overall}}{dt} = \left(\begin{array}{l} -k_{\text{O3-homo}}[O_3] - k_{\text{OH-homo}}[{}^{\bullet}OH] - \\ k_{\text{Ads}}\{S-act\}\left(1 - \dfrac{k_{Des}\{H^+\}}{k_{Des}\{H^+\} + (k_{\text{O3-het}}\alpha_{O3} + k_{\text{OH-het}}\alpha_{OH})[O_3]}\right) \end{array} \right)[R]}$$

$$\boxed{\frac{d[DEP]_{overall}}{dt} = -k_{overall}[DEP]}$$

Mansouri, L., H. Mohammed, C. Tizaoui, and L. Bousselmi. 2013. "Heterogeneous catalytic ozonation of diethyl phthalate", Desalination and Water Treatment 51 pp:6698-6710

Comparison between CNT and activated carbon

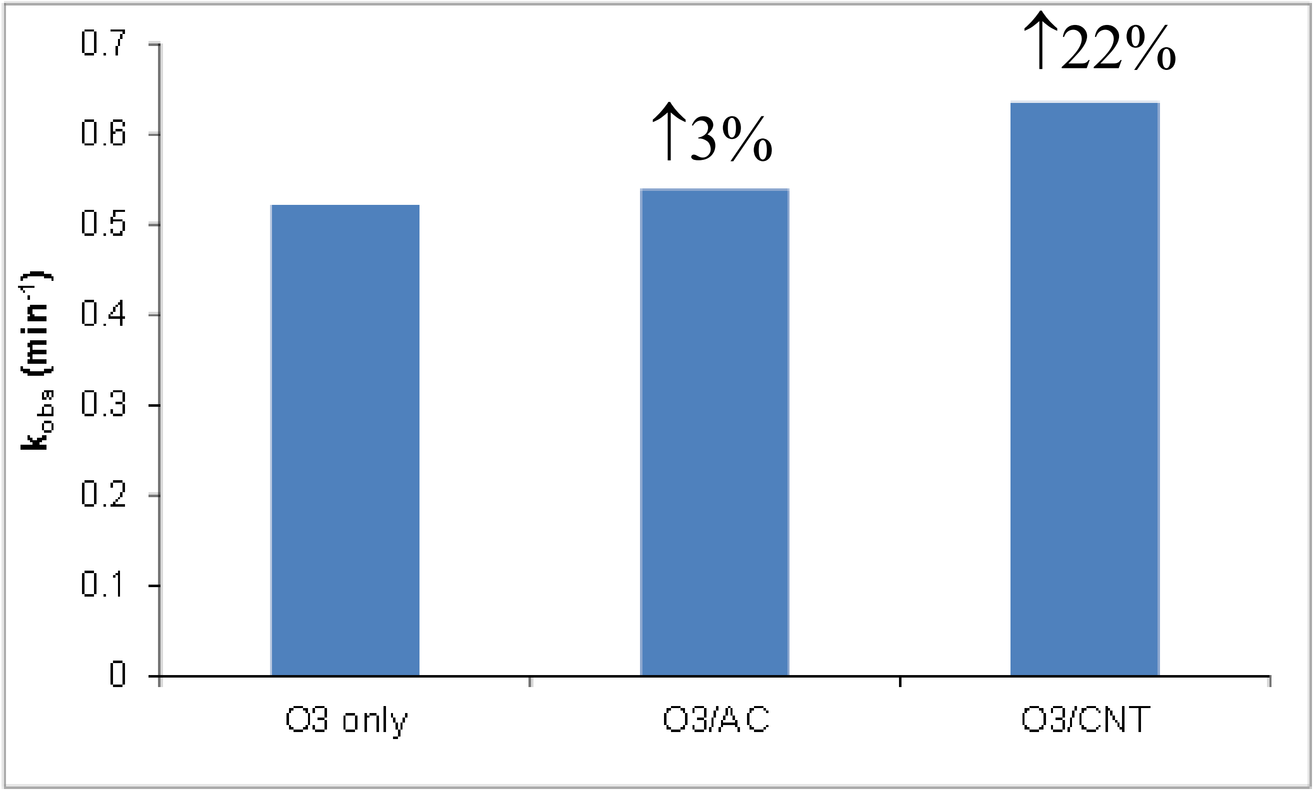
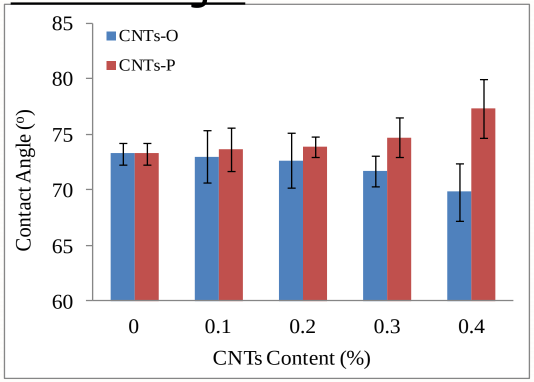
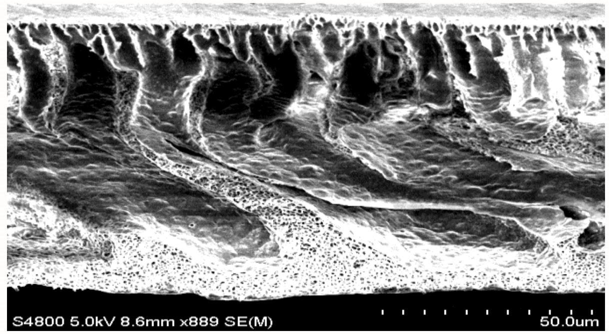


Figure 10: Comparison between CNT and AC as catalysts in heterogeneous catalytic ozonation (ozone concentration= 2 g/m³, C_0= 20 mg/L, pH=3, CNT dose = 10 mg/L, AC dose = 10 mg/L)

Hybrid ozone/membrane

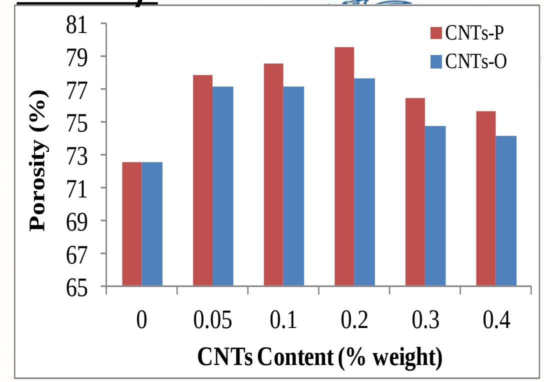
Contact Angle



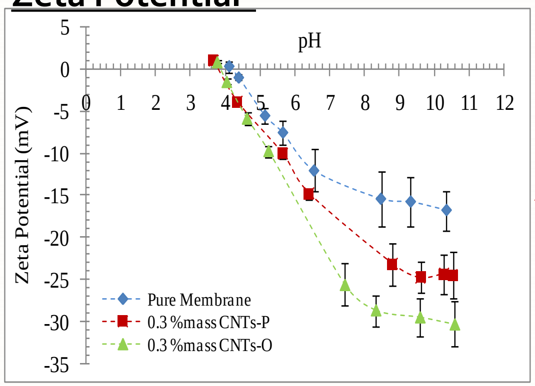


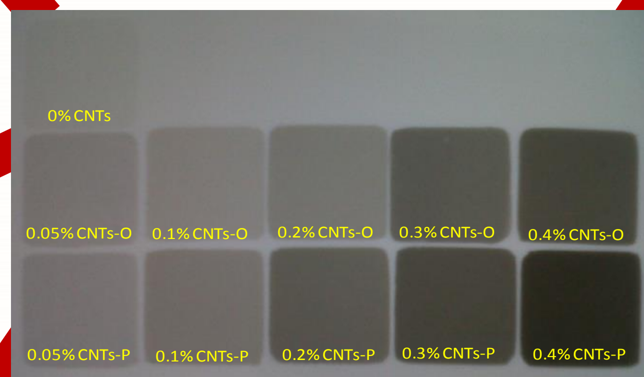
- Membrane Thickness: 100±10μm
- Active skin layer have
  - 10 – 50 nm pore diameter
  - Thickness about 1.3 – 1.7μm

Porosity

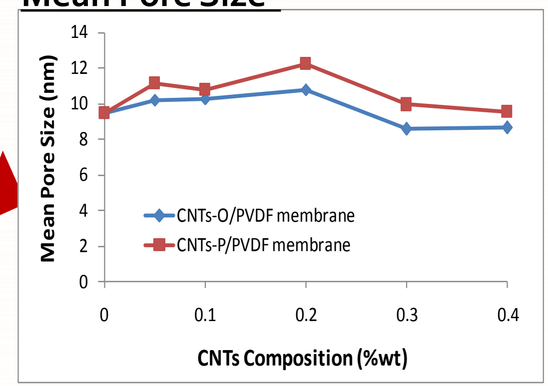


Zeta Potential

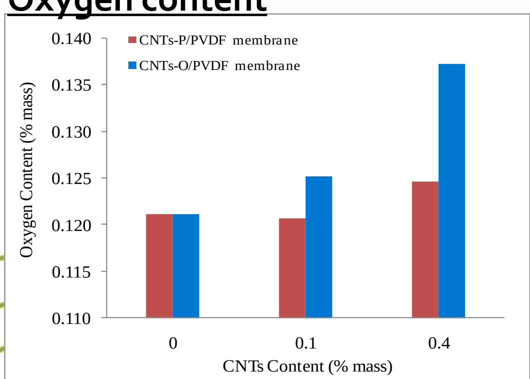




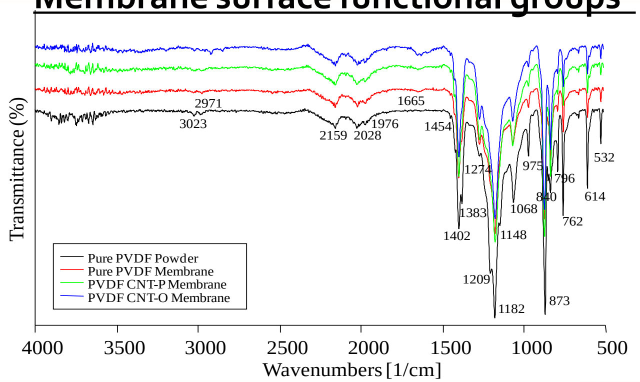
Mean Pore Size



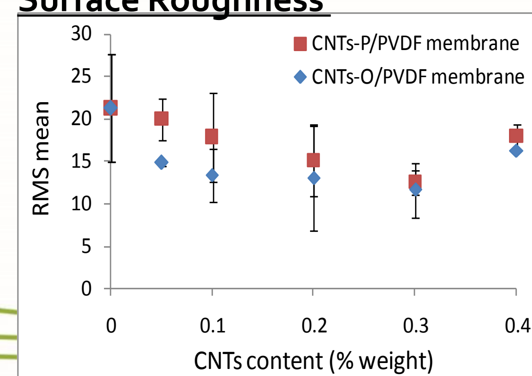
Oxygen content



Membrane surface functional groups



Surface Roughness



Hybrid Ozone/Membrane Performance

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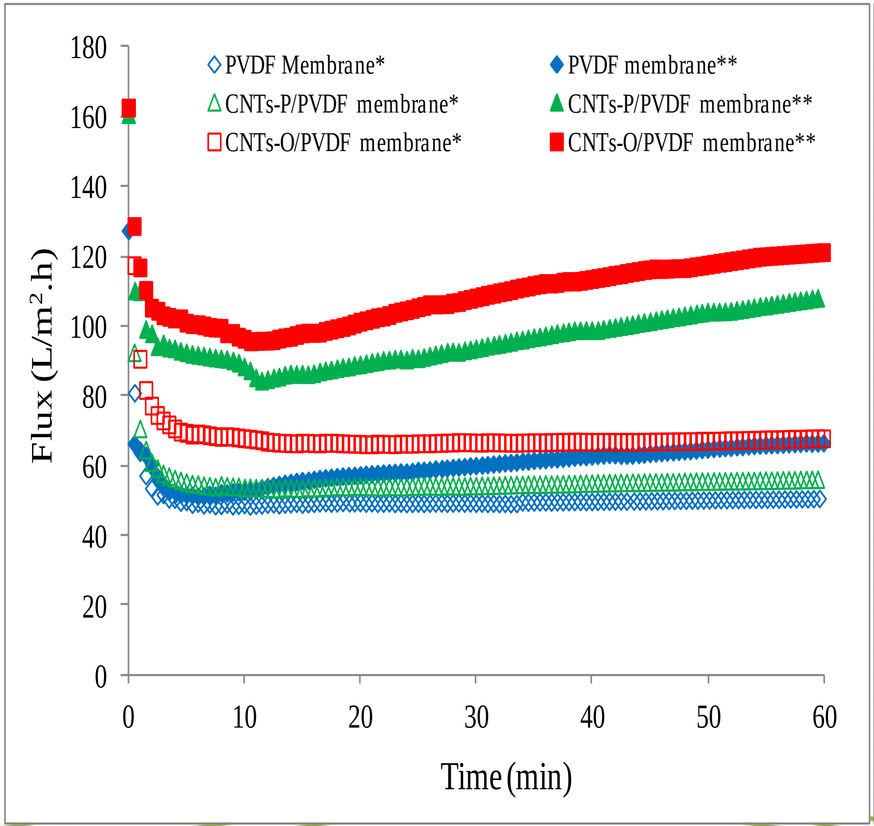
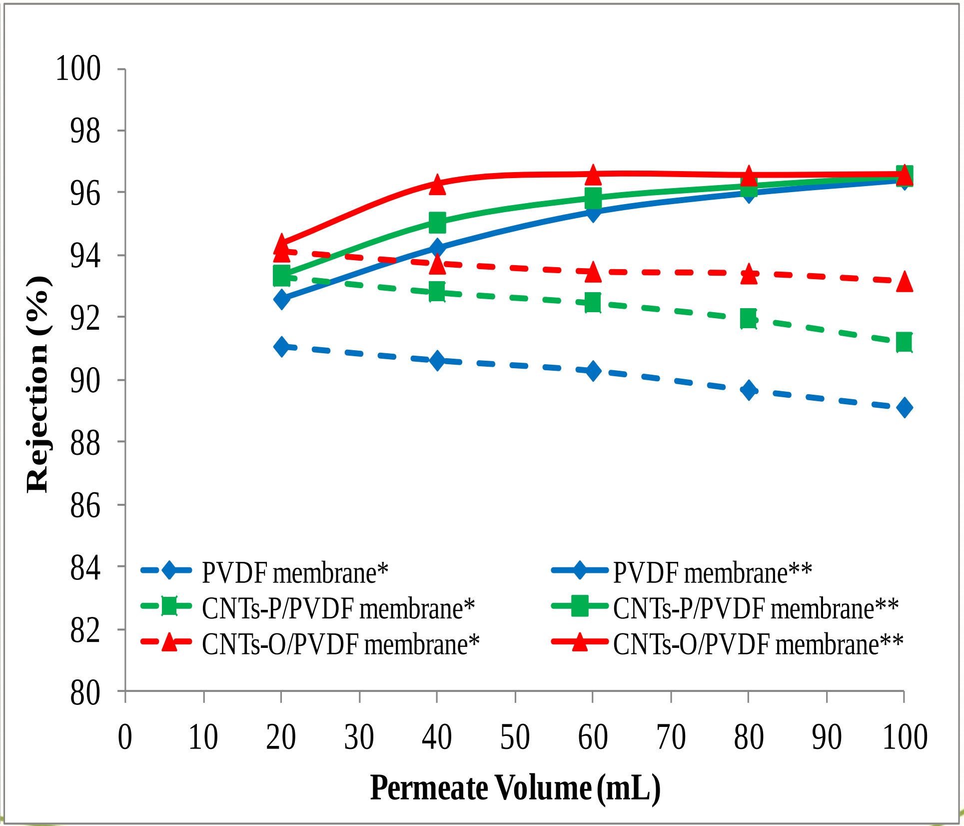
Membrane flux



Membrane rejection



*: no ozone; **: with ozone

Ozone in food security

Before Treatment After 7 days After 10 days After 14 days

A, B, C, D : 0, 2, 7, 21 g/m^3

Conclusions

• PPCPs, EDCs have serious effects on human health and the environment but still largely unnoticed
• Regulation is still lacking in this area though in recent years some regs started to emerge (e.g. Switzerland and EU “watch list”)
• Ozone-based AOPs have been found very effective to remove PPCPs, EDCs
• LLE/O_3 system was effective to extract/destroy EDCs
•The LLO system outperformed the conventional ozone gas system
•UV/TiO_2 is effective but there are issues with high UV cost and catalyst recovery/reuse
• Research in this area is needed:
  - Develop cost-effective treatment technologies
  - Potency of by-products
  - Understand the distribution, fate, effects of EDCs throughout the water cycle
  - Understand the health/env. effects of EDCs during water reuse (e.g. irrigation)

Energy/Water/Food nexus (quantity but also quality is important)

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Questions?

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OZONE PLANTS