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

Chedly Tizaoui, PhD, FIChemE, CEng
Director of Chemical and Environmental Engineering Portfolio
College of Engineering, Swansea University
United Kingdom
Email: c.tizaoui@swansea.ac.uk
Ozone
UV
Membrane Adsorption
Coagulation/floc
Filtration
CNTs and graphene
Plasma
Photocatalysis
H2O2

Water and wastewater treatment

Research Interests
Fundamental
Ozone
UV
Plasma
H2O2
Membrane
CNTs and graphene
Coagulation/floc
Photocatalysis
Adsorption
Filtration

Applied

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

Modelling of ozone mass transfer in static mixers
Advanced Oxidation Processes for the Removal of Endocrine Disrupting Chemicals and Enhanced Water Treatment

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

- Biodegrade (e.g. aspirin)
- Partial biodegradation (e.g. penicillins)
- Persist (e.g. clofibrate, triclosan, triclocarban)

Conventional WWTPs are not designed to eliminate micropollutants.

Further treatment

Problems for drinking water industry

Threats to wildlife and aquatic system

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Endocrine Disrupting Chemicals/Compounds


REVIEWS

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 4TF

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

Examples of EDCs

![Estrone](image1.png)  ![Testosterone](image2.png)  ![Carbamazepine](image3.png)  ![Bisphenol A](image4.png)  ![Nonylphenol](image5.png)
Removal Techniques

• 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.

<table>
<thead>
<tr>
<th>Estrogen</th>
<th>Oxidant</th>
<th>K (M⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>O³ O³ O³ O³ OH</td>
<td>6.2×10³ (pH 4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.4×10⁵ (pH 7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.1×10⁷ (pH 8.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5×10⁹ (pH 10.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.6×10¹⁰</td>
</tr>
<tr>
<td>E2</td>
<td>°OH</td>
<td>1.41×10¹⁰ (pH 6.8)</td>
</tr>
<tr>
<td>EE2</td>
<td>O³ O³ OH</td>
<td>7×10⁹ (pH 6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.08×10¹⁰ (pH 6.8)</td>
</tr>
</tbody>
</table>

Second-order rate constants for the ozonation of estrogens.
Ozone is a Powerful Oxidising agent
\[ \text{O}_3 + 2\text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow \text{O}_2 + 3\text{H}_2\text{O} \quad E^0 = 2.07 \text{ V} \]

<table>
<thead>
<tr>
<th>Species</th>
<th>Oxidation Potential eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl radical, •OH</td>
<td>2.80</td>
</tr>
<tr>
<td><strong>Ozone, O_3</strong></td>
<td>2.07</td>
</tr>
<tr>
<td>Hydrogen peroxide, ( \text{H}_2\text{O}_2 )</td>
<td>1.77</td>
</tr>
<tr>
<td>Perhydroxyl radical, •OOH</td>
<td>1.70</td>
</tr>
<tr>
<td>Chlorine dioxide, ( \text{ClO}_2 )</td>
<td>1.50</td>
</tr>
<tr>
<td>Hypochlorous acid, ( \text{HOCl} )</td>
<td>1.49</td>
</tr>
<tr>
<td>Chlorine, ( \text{Cl}_2 )</td>
<td>1.36</td>
</tr>
<tr>
<td>Oxygen, ( \text{O}_2 )</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Theor: 1.65 kWh/kg, Prac. ~10 kWh/kg O_3
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)
- Mol formula: $C_{18}H_{24}O_2$
- Molecular weight: 272.39 g/mol
- Produced by all mammals
- Binds easily with human receptor

#### 17α-ethinylestradiol (EE2)
- Mol formula: $C_{20}H_{24}O_2$
- Molecular weight: 296.403 g/mol
- Synthetic
- Main ingredient of contraceptive pills

#### Estrone (E1)
- Mol formula: $C_{18}H_{22}O_2$
- Molecular weight: 270.366 g/mol
- Secreted by the ovary
- Product resulting from oxidation of E2
The Process

OZONE

OZONE DISSOLVED IN SOLVENT

SOLVENT

SOLVENT / WATER CONTACT

POLLUTED WATER

POLLUTANT OXIDATION

SOLVENT / WATER SEPARATION

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

is a challenge!

Sample Collection → SPE → HPLC-MS-MS analysis
The analytical method

Solid phase extraction recoveries

<table>
<thead>
<tr>
<th>EDC</th>
<th>E1</th>
<th>E2</th>
<th>EE2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovery (%)</td>
<td>79.1</td>
<td>81.2</td>
<td>77.6</td>
</tr>
</tbody>
</table>

LC/MS/MS

<table>
<thead>
<tr>
<th>Estrogen</th>
<th>Ions (m/z)</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E2</td>
<td>271 / 143</td>
<td>3.17</td>
</tr>
<tr>
<td>EE2</td>
<td>295 / 143</td>
<td>3.51</td>
</tr>
<tr>
<td>DE1</td>
<td>273 / 147</td>
<td>3.82</td>
</tr>
<tr>
<td>E1</td>
<td>269 / 143</td>
<td>3.85</td>
</tr>
</tbody>
</table>
Extraction of EDCs to the solvent

Distribution coefficients

E2 removal

Efficiency (%) vs. Solvent to water ratio, $r$

Species predominance (%) vs. pH

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Rates: LLO vs LGO

- E1 - liquid/gas-ozone
- E1 - liquid/liquid-ozone

- E2 - liquid/gas-ozone
- E2 - liquid/liquid-ozone

- EE2 - liquid/gas-ozone
- EE2 - liquid/liquid-ozone
Process calculation and estimation of basic operational costs (Super Pro Designer™)
PROCESS CALCULATION AND ESTIMATION OF BASIC OPERATIONAL COSTS

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen recycle (%) (var)</td>
<td>0</td>
</tr>
<tr>
<td>Volume of LLO contactor (m³)</td>
<td>24.2</td>
</tr>
<tr>
<td>Total cost (£/ML)</td>
<td>0.111</td>
</tr>
</tbody>
</table>

(NDP (O₃ only) ➔ cost of ~£4/ML)

![Graph showing cost vs. recycle percentage]

Cost (£/year) vs. Recycle (%) graph


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Removal of the antimicrobial triclocarban
Removal of the antimicrobial triclocarban
Removal of the antimicrobial triclocarban with ozone

\[ O_3 + bTCC \rightarrow \text{products} \quad b=1 \]

\[ \frac{1}{b} \frac{dC_B}{dt} = N_{O_3} = aC_{O_3}^* \sqrt{D_{O_3}k_2C_B} \quad \text{for} \quad 5H_a < E_i \]

\[ N_{O_3} = k_L aC_{O_3}^* H_a \quad \text{for} \quad 5H_a < E_i \]

\[ H_a = \frac{\sqrt{D_{O_3}k_2C_B}}{k_L} \]

\[ E_i = 1 + \frac{C_B D_B}{bC_{O_3}^* D_{O_3}} \]

\[ C_{B_0}^{0.5} - C_B^{0.5} = baC_{O_3}^* \frac{\sqrt{k_2D_{O_3}}}{2} t \]

Degradation of the antimicrobial triclocarban (TCC) with ozone

Removal of the herbicide clopyralid
\[ TiO_2 + hv \rightarrow h^+ + e^- \]
\[ h^+ + H_2O_{ads} \rightarrow \cdot OH + H^+ \]
\[ h^+ + OH^-_{ads} \rightarrow \cdot OH \]
\[ e^- + O_2(ad) \rightarrow \cdot O^2^- \]
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
Kinetics Model

Homogeneous reactions:

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

$$R + \cdot OH \xrightarrow{k_{OH-homo}} \text{products} \quad - \frac{d[R]}{dt} = k_{OH-homo}[\cdot OH][R]$$

Heterogeneous reactions

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

$$S - R + \cdot OH \xrightarrow{k_{OH-het}} \text{products} \quad - \frac{d\{S - R\}}{dt} = k_{OH-het}\{S - R\}\{\cdot OH\}$$

$$\frac{d[R]_{overall}}{dt} = \left( -k_{O_3-homo}[O_3] - k_{OH-homo}[\cdot OH] - k_{Ads}\{S - act\}\left( 1 - \frac{k_{Des}\{H^+\}}{k_{Des}\{H^+\} + (k_{O_3-het}\alpha_{O_3} + k_{OH-het}\alpha_{OH})[O_3]} \right) \right)[R]$$

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

Comparison between CNT and activated carbon

Figure 10: Comparison between CNT and AC as catalysts in heterogeneous catalytic ozonation (ozone concentration= 2 g/m³, C₀= 20 mg/L, pH=3, CNT dose = 10 mg/L, AC dose = 10 mg/L)
Hybrid ozone/membrane
Contact Angle

- CNTs-O
- CNTs-P

Zeta Potential

- Pure Membrane
- 0.3% mass CNTs-P
- 0.3% mass CNTs-O

Porosity

- CNTs-P
- CNTs-O

Mean Pore Size

- CNTs-O/PVDF membrane
- CNTs-P/PVDF membrane

Oxygen content

- CNTs-P/PVDF membrane
- CNTs-O/PVDF membrane

Membrane surface functional groups

- 0% CNTs
- 0.05% CNTs-O
- 0.1% CNTs-O
- 0.2% CNTs-O
- 0.3% CNTs-O
- 0.4% CNTs-O

- 0% CNTs-P
- 0.05% CNTs-P
- 0.1% CNTs-P
- 0.2% CNTs-P
- 0.3% CNTs-P
- 0.4% CNTs-P

Surface Roughness

- CNTs-P/PVDF membrane
- CNTs-O/PVDF membrane

Active skin layer have

- 10 – 50 nm pore diameter
- Thickness about 1.3 – 1.7µm

Membrane Thickness: 100±10µm

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Hybrid Ozone/Membrane Performance

Membrane flux

- PVDF Membrane*
- CNTs-P/PVDF membrane*
- CNTs-O/PVDF membrane*
- PVDF membrane**
- CNTs-P/PVDF membrane**
- CNTs-O/PVDF membrane**

Membrane rejection

- PVDF membrane*
- CNTs-P/PVDF membrane*
- CNTs-O/PVDF membrane*
- PVDF membrane**
- CNTs-P/PVDF membrane**
- CNTs-O/PVDF membrane**

*: no ozone; **: with ozone
Ozone in food security

A, B, C, D : 0, 2, 7, 21 g/m³
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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Institut National de Recherche Scientifique et Technique, Tunisia
OZONE PLANTS