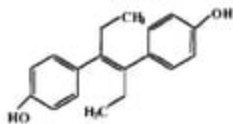


## Introduction

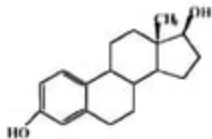
- ▶ Endocrine system is a system which includes variety of glands, producing hormones which regulates the growth, development, reproduction, and behaviour.
- ▶ Chemicals with the potential to elicit negative effects on the endocrine system of humans and wildlife are termed as Endocrine Disrupting Chemicals (EDC).
- ▶ An exogenous agent that interferes with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behaviour. (USEPA)

## Classification

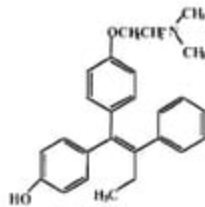
- ▶ Natural and synthetic estrogen or steroids. - Estradiol, testosterone, ethynylestradiol, etc.
- ▶ Pharmaceuticals. - Acetaminophen, diclofenac(pain-killer), etc.
- ▶ Personal care products (PPCPS) - Caffeine, oxybenzone (sunscreen), etc.
- ▶ Industrial chemicals. - Bisphenol A, Phthalate, Nonylphenol, etc.
- ▶ Pesticides. - Atrazine, DDT, etc.
- ▶ Combustion by-products. - Dioxin, etc.



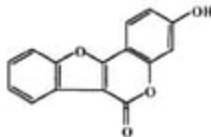
Diethylstilbestrol



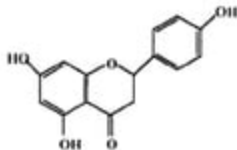
Estradiol



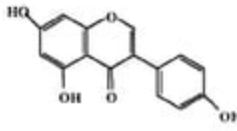
4-Hydroxy-Tamoxifen



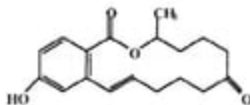
Coumestrol



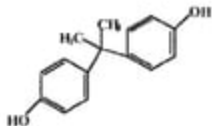
Naringenin



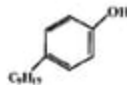
Genistein



Zearalenone



Bisphenol A



4-Nonylphenol

## Exposure

- ▶ Major exposure pathways for humans to many EDCs are through inhalation of air and particles, consumption of contaminated food and drinking water, and through direct dermal contact.
- ▶ Human exposure to these chemicals in the environment is a critical concern with unknown long-term impacts.
- ▶ Consumer goods are another potential source of exposure to endocrine disruptors.
- ▶ The toxic effects of EDCs have resulted in the restriction of their use in countries where evidence of extensive exposure is ample.

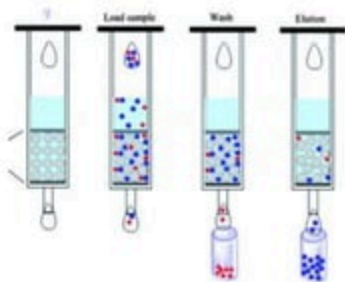
## Effects

- ▶ Any system in the body controlled by hormones can be derailed by hormone disruptors.
- ▶ EDCs have been attributed as a cause of following problems:
  - Deformations of the body (including limbs).
  - Breast cancer.
  - Prostate cancer.
  - Thyroid and other cancers.
  - Reproductive disturbance.
  - Cognitive and brain development problems
  - Development of learning disabilities.

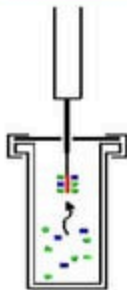
## Analysis

- ▶ EDCs at trace concentration levels and with extremely diverse groups, make the detection and analysis procedures quite challenging.
- ▶ Currently, the most prevailing methodological approach designed to analyse EDCs incorporates a mass-based analysis process.
- ▶ Mass-based methods employing mass spectrometry (MS) show relatively low detection limits as compared to other methods.
- ▶ Various combinations of instruments and detectors can be applied to obtain improved analytical results, such as GC/MS, HPLC/MS, LC/UV, and GC/tandam mass spectrometer, etc.

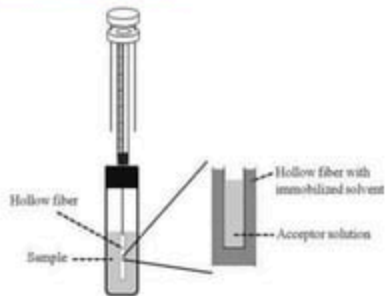
## Extraction methods



Solid phase extraction  
(SPE)

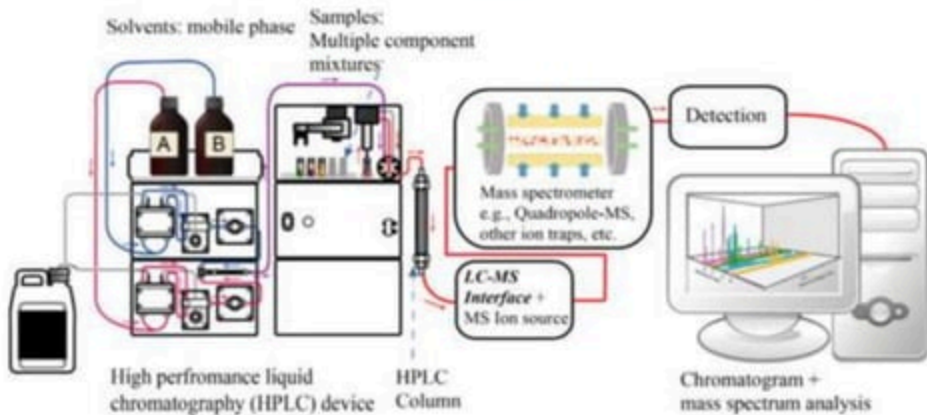


Solid phase micro-extraction  
(SPME)



Liquid phase micro-extraction  
(LPME)

# Ultra-high-Performance Liquid Chromatography-Tandem Mass spectrometry



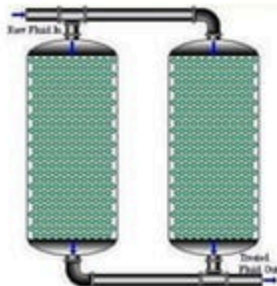


## Treatment

- ▶ Activated carbon.
- ▶ Sub-micron sized resin particles.
- ▶ Ozonation and Advanced oxidation process.
- ▶ Membrane fouling during UF process.
- ▶ Hybrid constructed wetland.
- ▶ Photodegradation.

## Activated carbon

- ▶ AC's ability to adsorb a large number of chemical substances and to be regenerated has made the process one of the most effective and economically feasible processes.
- ▶ Applied mainly in two forms; a powdered (PAC) and a granular one (GAC) in packed bed filters.
- ▶ Various carbons with different base materials such as coal, coconut, and wood can be used.
- ▶ GAC adsorption was effective in removal of EDCs with high  $K_{ow}$  value.

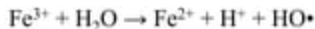
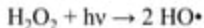


## Activated carbon

- ▶ GAC adsorption was effective in removing EDCs at the empty bed contact time (EBCT) of 15 min.
- ▶ Nonylphenol and BPA were effectively adsorbed onto all carbons.
- ▶ Since the microbes residing at the used carbons already accustomed to amitrol, the used carbons removed amitrol better than the virgin carbon.
- ▶ BPA removal 40% for coconut based carbon, Nonylphenol removal 76% for coal based carbon.
- ▶ Not recommended for Amitrol as 9-87% passed through GAC column.

## Ozonation and Advanced Oxidation Process.

- ▶ This is a group of chemical-oxidative processes called advanced oxidation processes (AOP), characterized by the generation of hydroxyl ions.
- ▶ The hydroxyl radical is a strong oxidant.



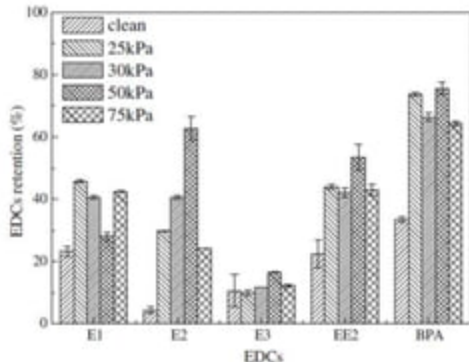
- ▶ Ozonation is the dark oxidation method most used in the removal of new emergent pollutants.
- ▶ Removals higher than 90% can be achieved for several compounds, such as, pesticides, anti-inflammatories, antiepileptics, antibiotics and natural and synthetic estrogens by using ozone dose from 0.1 – 30 mg/L.

## Ozonation and Advanced Oxidation Process.

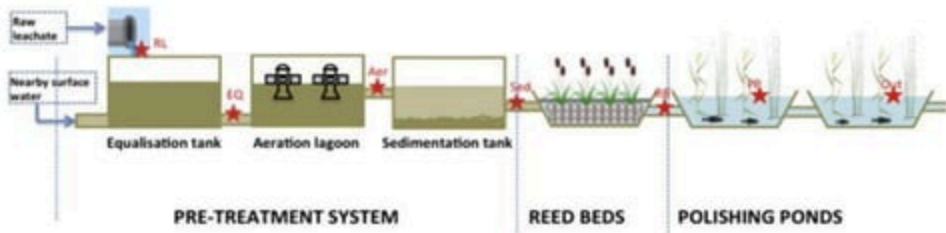
- ▶ UV/H<sub>2</sub>O<sub>2</sub> and titanium dioxide photocatalysis are the light oxidation processes most used to destroy EDCs and PPCPs.
- ▶ Removals higher than 98% were obtained by using TiO<sub>2</sub> photocatalysis, estrogens (17 $\beta$ -estradiol, estrone and 17 $\alpha$ - ethinylestradiol), bisphenols and antiepileptics.
- ▶ In order to achieve high removals, large irradiation times were required compared with dark ozonation processes.
- ▶ The range of H<sub>2</sub>O<sub>2</sub> concentrations used went from 0.1 to 1 mol/L.

## Membrane fouling during UF process.

- ▶ EDC elimination by fouled membrane was better than clean membrane.
- ▶ Clean membrane had only 5%–34% removal rate of EDCs, while fouled membrane had 10%–76% removal rate of EDCs.
- ▶ Cake layers formed under different pressures had different abilities on retaining different EDCs.
- ▶ With increase in pressure, fouling potential of feed dropped. However, cake resistance and average specific resistance both increased with pressure rising.



## Hybrid Constructed Wetland



Schematic diagram of hybrid constructed wetland (Singapore)

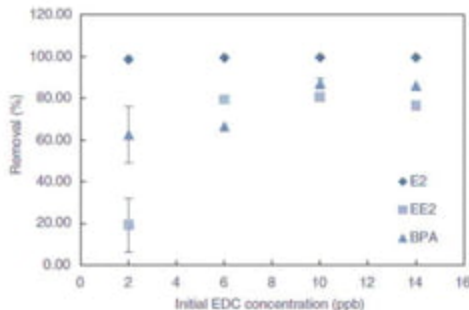
## Hybrid Constructed Wetland

- ▶ The overall removal of EDCs in the hybrid CW system were greater than 77.2%.
- ▶ Several compounds, such as BPA (bisphenol A), CA (clofibric acid), and SMZ (Sulfamethazine), exhibited excellent removal efficiencies (>99.9%).
- ▶ The open-air aerobic lagoons were found to be effective in the elimination of most EDCs.
- ▶ The reed beds also allowed for the effective removal of the majority of PPCPs and EDCs, especially ACT (Acetaminophen), GFZ (Gemfibrozil), DEET (N, N-diethyl-m-toluamide), CF (Caffeine), DCF (diclofenac), and CA.



## Sub-micron sized resin

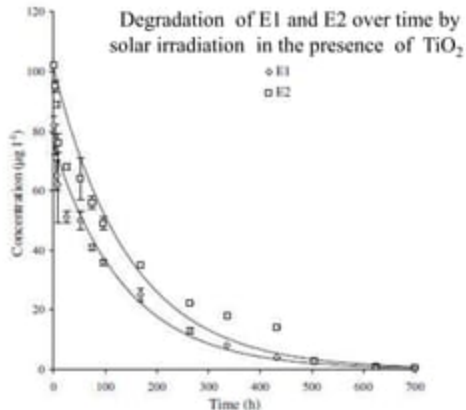
- ▶ For SMR, the mechanism for adsorption is non-specific.
- ▶ The high removal efficiency is also related to the SMR concentration used.
- ▶ Lower efficiencies are due to lower contact time.
- ▶ For 2–14 ppb of 17- $\beta$  estradiol (E2), 17- $\alpha$  ethinylestradiol (EE2), estrone (E1) and bisphenol A (BPA), the maximum percent removals achieved were 98%, 80%, and 87%, respectively.



Removal of E2, EE2, and BPA with SMR

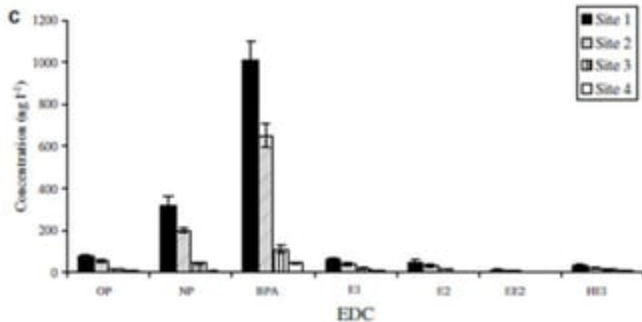
## Photodegradation (Sunlight)

- ▶ Solar irradiation for removing EDCs from water and wastewater is an environmentally friendly.
- ▶ No degradation of E1 and E2 occurs in the absence of either light or catalyst ( $\text{TiO}_2$ ), demonstrating the importance of the joint actions of the two.
- ▶ 50% of E1 and 55% of E2 degraded after 75 h of solar irradiation.
- ▶ The degradation rate is not dependent on the initial chemical concentration.



## Photodegradation (UV light)

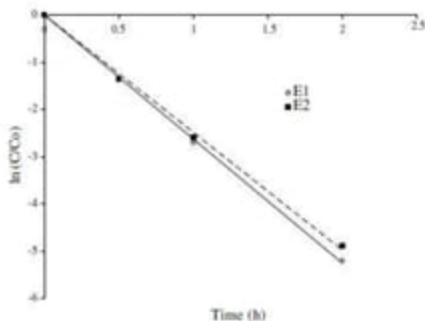
Compound	Removal (%)
4-tert-Octylphenol	90
4-Nonylphenol	83
Bisphenol A	93
Estrone	60
17 $\beta$ Estradiol	83
17 $\alpha$ -Ethinylestradiol	NA
16 $\alpha$ -Hydroxyestrone	81



Levels of selected EDCs in different sites from Horsham STP  
(Site 1: influent; site 2: post sedimentation tank;  
site 3: post biological filters; site 4: final effluent.)

## Photodegradation (UV light)

- ▶ In the absence of  $\text{TiO}_2$  or UV light, the changes in the concentrations of both E1 (Estrone) and E2 (Estradiol) were negligible.
- ▶ 98% of the initial E1 was decomposed under UV light within 16 min.
- ▶ Overall, Bisphenol A showed the highest removal efficiency (90–96%).
- ▶ UV photodegradation is far more efficient than solar irradiation.



## Summary

- ▶ Endocrine disruptors are chemicals that can interfere with endocrine (or hormone) systems at certain doses.
- ▶ As their concentrations are very less in terms of 'ng/L' or 'µg/L', they need to be determined by very sensitive measuring systems such as LC-MS.
- ▶ Various treatment methods Advanced Oxidation Process, Activated carbon method, Ozonation, Sub micron-sized resins, photodegradation, membrane, ultrafiltration, constructed wetlands, etc. gave high removal efficiencies for specific compounds.

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