Under the Patronage of HRH Prince Faisal bin Bandar bin Abdulaziz
Governor of Riyadh Region

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Ministry of Environment Water & Agriculture

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saudi water forum SWF 2022
Water Sustainability.. A Responsibility for All

Treatment of Oil-Produced Water By Advanced Electrochemical Oxidation Process

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Outline

Introduction : Fresh Water Scarcity

The Produced Water : Challenges & Management

Study Objectives

Methodology

Results and Conclusion

Introduction

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- The global fresh water scarcity
- Saudi Arabia is one of the largest oil producers in the world but also suffers form the **scarcity of fresh water resources.**
- The **Saudi national water strategy** considers **treated wastewater** an integral part of water resource planning.
- The **strict discharge limits** forced industrial facilities to search for **best available technologies** to treat polluted water.

Oil & Gas Industry – An Economic Drive

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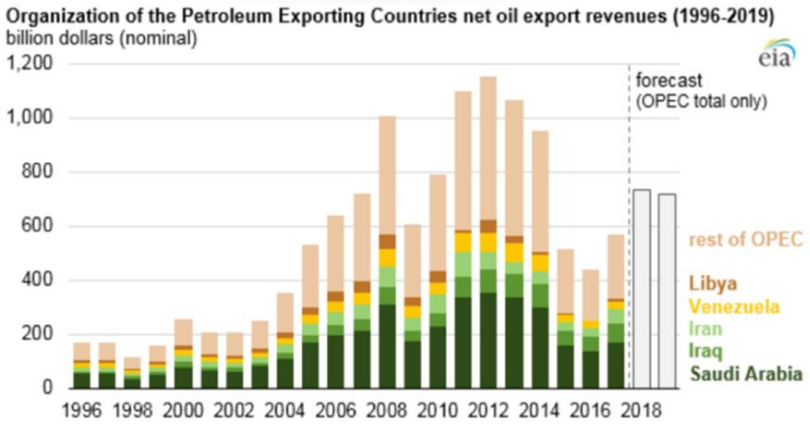
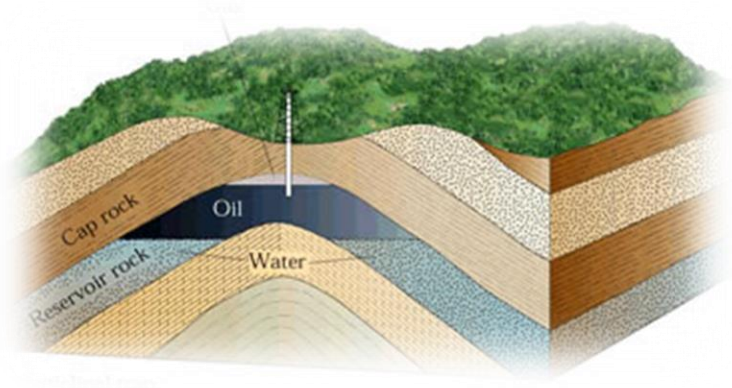
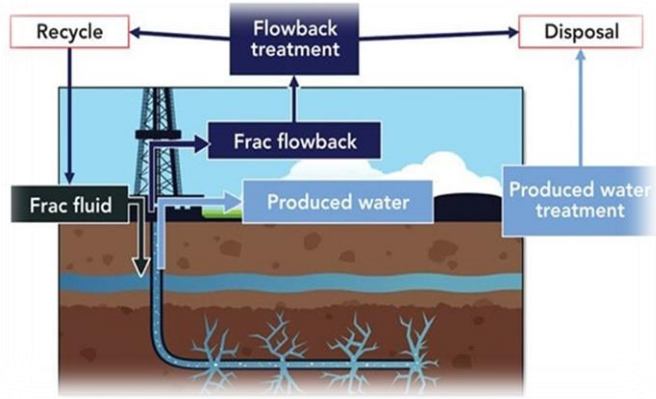


- Energy is essential to life and all living organisms
- Economic drive of many countries
- Oil, coal & gas fuels the world
- The petrochemical products are heavily used
- Crude oil is most traded commodity in international market

What is Produced Water (PW)?

- A term used in the oil industry to describe water that is produced as a byproduct during the extraction of oil and natural gas.
- It may include: natural water, formation water and injected water.
- May also generate from EOR activities designed to increase oil production such as hydraulic fracking and flooding operations.



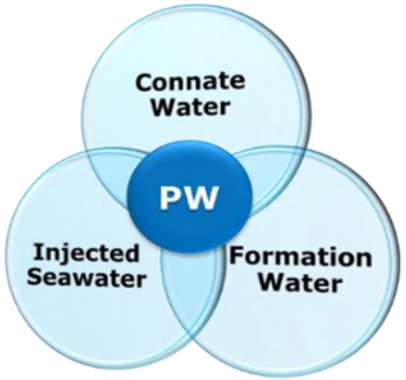


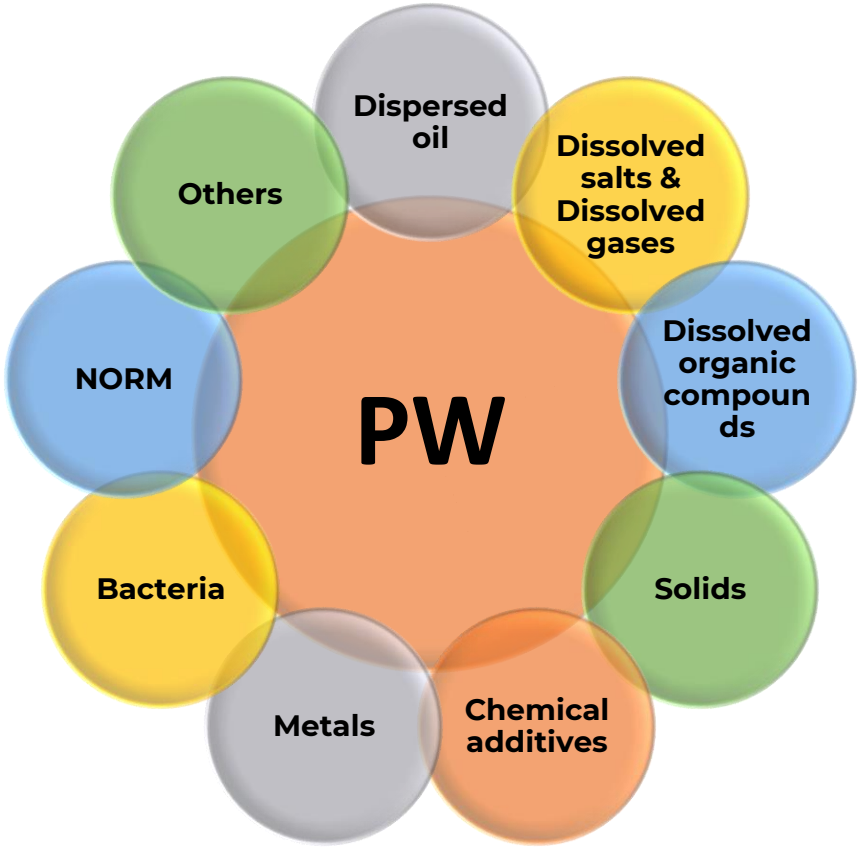
The Produced Water Dilemma

- The issues of concern related to PW management include:
  - The huge quantity of water used (**1 bbl.** of oil, **4 - 10 bbl**. of water)
  - More than **70 billion bbl** of **PW** is generated **per year** in the petroleum industry worldwide
  - The **contamination** of freshwater resources
  - The **consequences** of its management strategies
- PW contains high levels of **chemicals** that cause harm to the environment **if improbably disposed of**.
- Phenols, BTEX, solvents and metals are common water **pollutants** that are health hazards.
- Treating PW to the degree of **recycle & reuse** for beneficial use is quite **challenging**.

Produced Water Characteristics

- The chemical and physical characteristics of PW vary considerably depending on the source
- Characteristics also vary from well to well.
- PW is a highly saline, chemically complex and contains the characteristics of the formation.





Characteristics of PW

Parameter	Abdalla et al., 2011[b]	Rosenblum et al., 2017[c]
Total alkalinity (mg/L)	138	475
Hardness (as $CaCO_3$) (mg/L)	17,700	-
Total Suspended Solids (TSS) (mg/L)	99	172
Total Dissolved Solids (TDS) (mg/L)	67,300	18,756
Turbidity (NTU)	80	223
Chloride (mg/L)	41,850	11,650
Bromide (mg/L)	445	168.5
Conductivity (mS/cm)	16,750	-
Total Kjeldahl nitrogen (mg/L)	86.1	-
Ammonia nitrogen (mg/L)	71.2	-
Biochemical Oxygen Demand (BOD_5) (mg/L)	144	-
Chemical Oxygen Demand (COD) (mg/L)	4,870	2,543
Total Organic Carbon (TOC) (mg/L)	62.8	-
Dissolved Organic Carbon (DOC) (mg/L)	114	-
pH	-	6.80

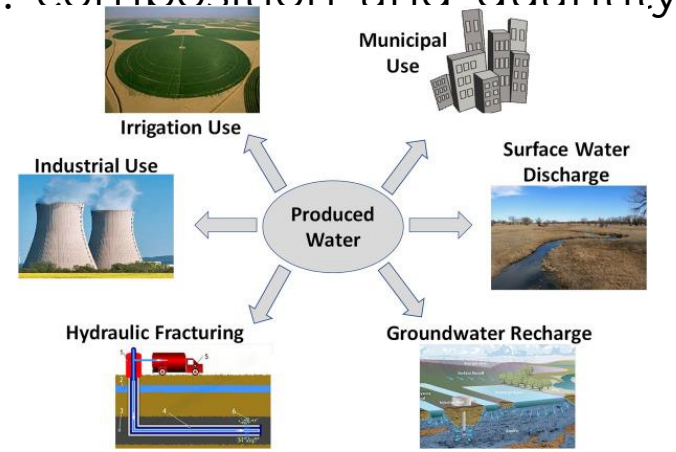
Parameter	Value
pH	8.0
Conductivity (mS/cm)	13,288
TDS (mg/L)	8,637
Total Alkalinity (mg/l as CaCo3)	122
Turbidity (NTU)	157
Total Hardness (mg/L as CaCO3)	1,450
Sodium (mg/L)	1315.8
Potassium (mg/L)	37.1
Magnesium (mg/L)	103.7
Calcium (mg/L)	410.5
Chloride (mg/L)	3728
Bromide (mg/L)	26.8
TOC (mg/L)	148.4
Benzene(mg/L)	762.1
Toluene (mg/L)	394.3
Ethylbenzene (mg/L)	20.4
m&p-Xylene (mg/L)	98.6
o-Xylene (mg/L)	973.9

Management of Produced Water

- PW management is one of the **largest challenges** facing the oil & gas industry all over the world.
- Needs **economical** and **environmental** friendly methods of treatment for the sake of recycling/reuse
- The strategies applied to management options can be of a **3-tiered water hierarchy** : Minimization >>>>Disposal>>>>Treatment for Reuse/recycle
- The methodology of handling produced water depends on: composition and quantity of PW, location and resources (

our options?

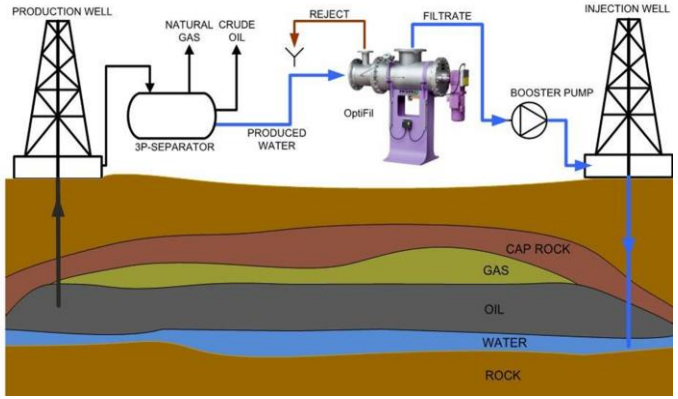
- **Minimization** by mechanical methods
- **Re-injection** for EOR processes
- **Evaporation** (ponds)
- **Disposal** : On-shore or off-shore
- **Treatment** for beneficial reuse in oil & gas



Disposal of Produced Water

Evaporation Ponds

- ✓ Hydrocarbons lighter than water will float to the surface.
- ✓ VOCs evaporate and contribute to air pollution.
- ✓ Other hydrocarbons get **oxidized** and **hydrated** and sink to the bottom.
- ✓ Becomes food for **anaerobic** bacteria such as SRB's that produce **H2S** and **CO2**.



Re-Injection

- ✓ Does not always meet the quality required.
- ✓ May generate seismic disturbances.
- ✓ May contaminate the subsurface aquifers.

Onsite Produced Water Treatment...

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Constructed Wetland

- Interactions between water, plants, microorganisms, filter media and oxygen.
- The Bauer-Nimr Water Treatment Plant (NWTP) is the world's largest engineered constructed wetland, located in Oman for PDO Co.
- It can treat more than 115,000m^3/day of produced water.

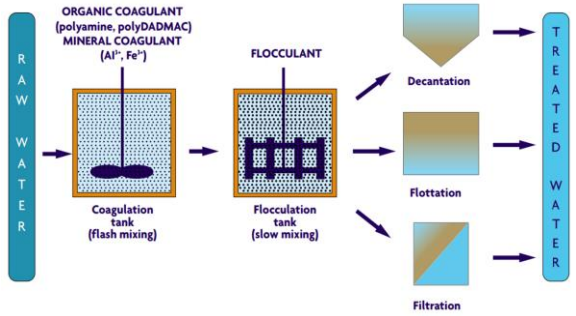
Treatment of Produced Water

TSS, oil and grease	Scaling ions	Dissolved organics	Bacteria, fungi, algae	TDS
• Screening • Settling/Sedimentation ponds • Coagulation/ Flocculation • Filtration • Biological Aerated Filters (BAF) • Hydrocyclones • Dissolved Gas Flotation (DGF) • Dissolved Air Flotation (DAF) • Microfiltration (MF) • Ultrafiltration (UF)	• Aeration • Settling • Filtration • Lime Softening • Ion exchange (IEX) • Nanofiltration (NF)	• Adsorption (activated carbon, resins, zeolite, etc.) • Biological Aerated Filters (BAF) • Ozonation • Fenton oxidation • Electrochemical treatment (electro-coagulation, electro-Fenton) • Photocatalytic oxidation • Biodegradation • Nanofiltration (NF) • Reverse Osmosis (RO)	• Ozonation • Ultraviolet irradiation (UV) • Chlorine dioxide • Chloramines	• **Non-thermal** • Reverse Osmosis • Ion exchange (IEX) • Electrodialysis (ED)* • Forward Osmosis (FO)* • Capacitive deionization (CDI)* • Advanced adsorption* • **Thermal** • Multi-effect distillation (MED) • Vapor compression distillation (VCD) • Multistage flash distillation (MSF) • Crystallization • Evaporation
Performance parameters TSS, Turbidity, Oil and grease, TOC, COD, BOD	**Performance parameters** Hardness, Specific ions (nitrates, sulphates), Specific metals (Ba, Fe, Sr)	**Performance parameters** DOC, TOC, COD, VOC, Specific organics (BTEX, phenol, benzene, toluene, xylene), Chemical additives (Table A2)	**Performance parameters** Bacteria, viruses, fungi microorganisms, algae	**Performance parameters** Conductivity, specific ions (Cl^-, Na^+, Br^-, K^+, I^-, NH_4^+)

End uses	Water quality required
Reuse for hydraulic fracturing	Moderate TDS Low SS Low Ca, Mg, Fe, sulfate (scale formers)
Deep well disposal	Low Ca, Mg, Fe, sulfate (scale formers) Low SS
Discharge to surface water (e.g. in, US)	< 500mg/L TDS < 250 mg/L chloride < 250 mg/L sulfates < 10mg/L total barium < 10mg/L total strontium
Crop irrigation	Low salinity (TDS) Low sodium adsorption ratio (SAR <6) Low toxicity
Wildlife and livestock consumption	Moderate TDS (<5,000 mg/L) pH 6.5–8 SAR 5–8
Aquaculture and hydroponic vegetable culture	Moderate TDS Low metals
Dust control on roads and in mining	Low SS Low in specific constituents like metals
Vehicle and equipment washing	Low SS Moderate TDS
Power-generation cooling	Low SS Moderate TDS Low Ca, Mg, Fe, sulfate (scale formers)
Indirect potable reuse through aquifer recharge	Low DBP potential; Adequate mineral content Legislative drinking water criteria (e.g. SDWA)

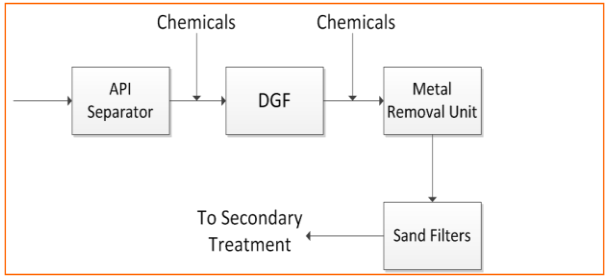
Produced Water Treatment

Typical PW treatment technologies are classified as primary, secondary and tertiary processes.



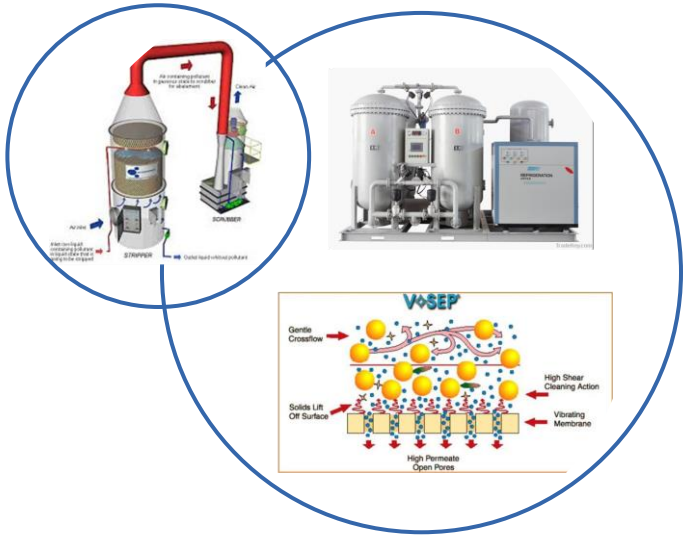
Primary Treatments

- To remove **suspended hydrocarbons** components and **solids**.
- **Includes** : API separator, Dissolved Gas/Air Flotation (DGF) for **De-oiling**
- **Metal removal** unit (Coagulation/Flocculation Process)
- **Filtration** (i.e. sand filters) fo

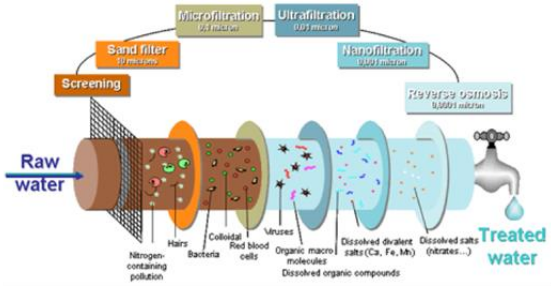


Produced Water Treatment…

Secondary Treatments



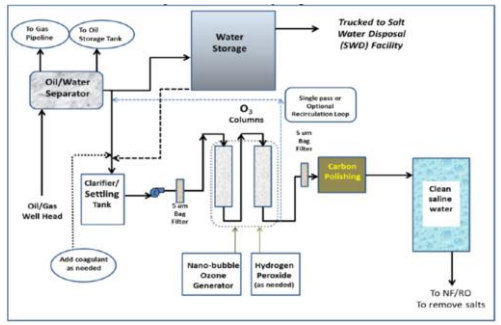
- These techniques include:
  - Adsorption (i.e. GAC)
  - Bio-treatment
  - Gas/Air stripping and
  - Membrane separation.
- Used for the removal of organic compounds and organic acids, suspended solids and oil and dissolved aromatic hydrocarbons.



Produced Water Treatment…

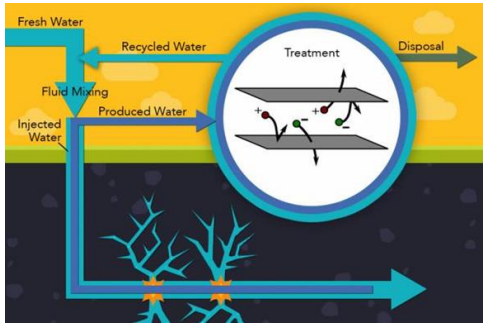
Tertiary Treatments: Focused on the salts removal

- Tertiary treatment may provide the necessary attributes required by the law for the reuse of water for industrial and agricultural purposes. It may include:



- **RO membranes** to reduce the levels of salts, **hardness** and **nutrients** (N and P)

- **Advanced Oxidation**: A technology that includes a combination of ozone nano-bubbles coupled with hydrogen peroxide to generate super oxidants (hydroxyl radicals) that degrade dissolved organic pollutants.



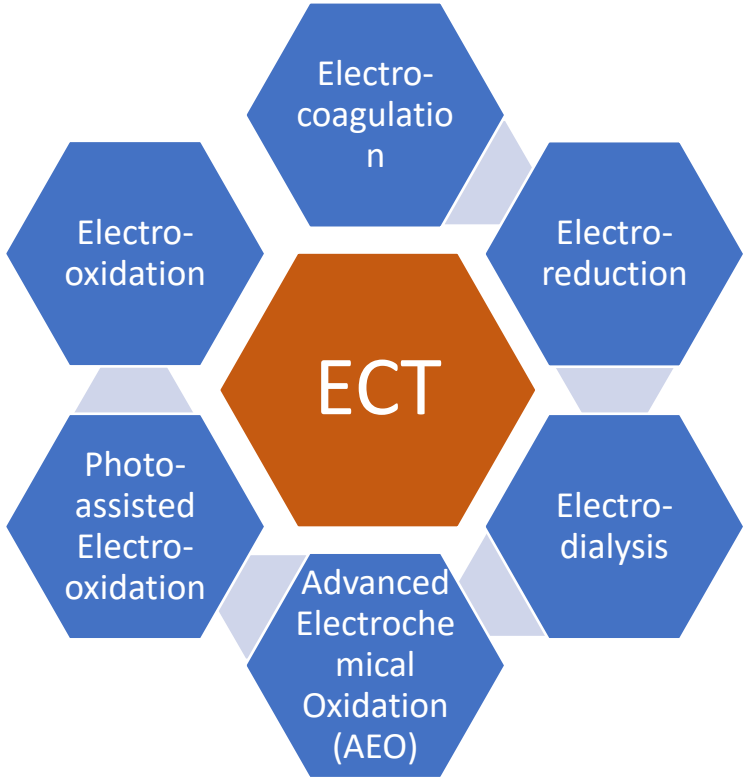
- **Electro-dialysis**: Researchers at MIT and KFUPM have found that Electrodialysis is an economical solution for removing the salt from PW

Electrochemical Technologies

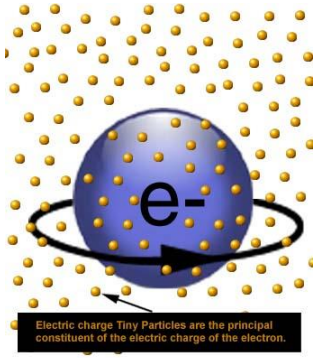
- Electrochemical technologies have the ability to simultaneously **treat** contaminants via in situ production of chemicals (i.e. H_2O_2) at the electrode surfaces with low power / energy demands.

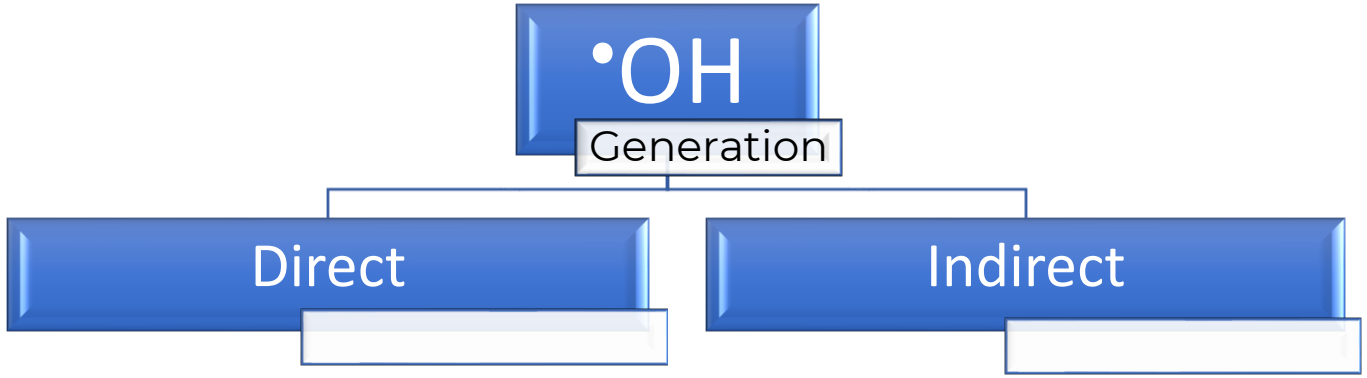
- Several types of electrochemical water treatment technologies

- Electrochemical advanced oxidation processes (EAOPs): Based on the generation of **hydroxyl radicals (OH*).**



Electrochemical Advanced Oxidation Processes (EAOPs)





Anodic Oxidation (AO)

Electrochemically generation of **Fenton's reagent**.

Applications in a variety of media (gas, liquid, solid) and volumes :


drinking water


groundwater remediation


industrial process wastewater


high purity water


ballast water


odor control

Study Objectives

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1 To investigate the performance of a pilot-scale electrochemical oxidation unit using BTEX and Phenols as model compounds.

2 To identify the optimum treatment parameters such as:

a) Current density (mA/cm^2)
b) Air flow rate (NL/min),
c) Fe(II) dosage (mM),
d) Water salinity (mS/cm),
e) Residence time (min), etc.

3 To test the optimum treatment conditions on a real PW sample

Experimental | The EC Unit

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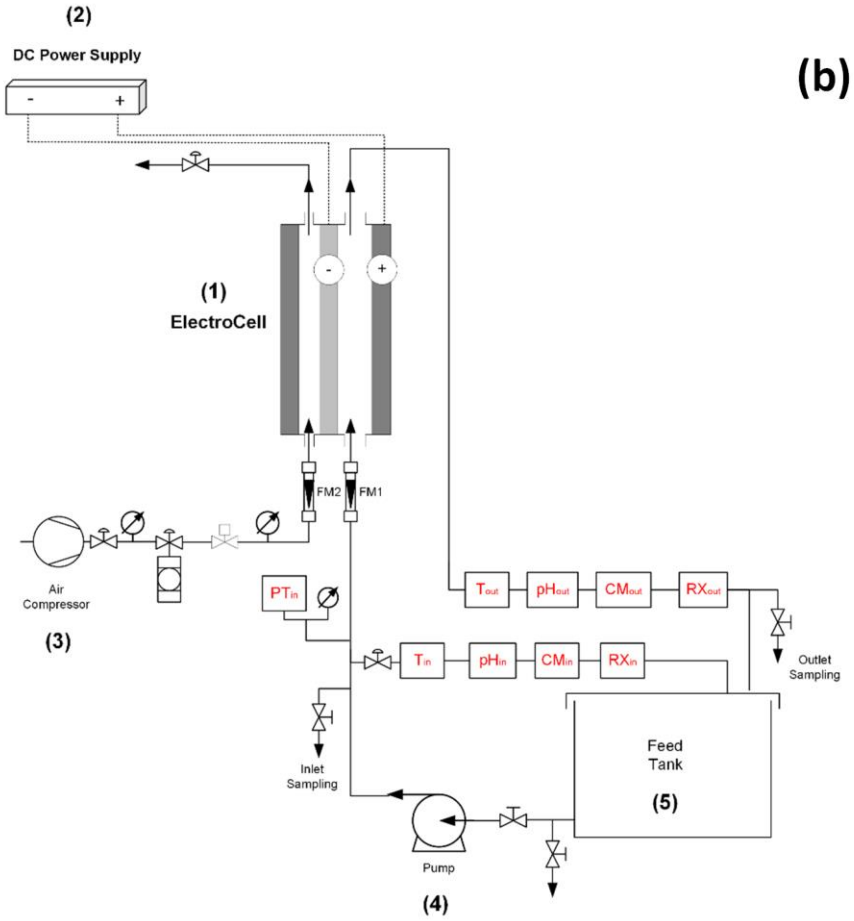
- A pilot scale unit in batch recirculation mode, with an undivided plate-and-frame cell equipped with a **boron doped diamond (BDD)** anode and **a carbon-PTFE** (gas diffusion electrode, GDE) cathode

- Parameters such as pH, conductivity, temperature and redox potential were monitored and recorded.

- Untreated and treated brine samples were tested for BTEX, by-products and TOC levels using GC/MS and TOC analyzer.

- Spiked Seawater samples with BTEX and Phenols and treated by EC Unit.

(a)


(2)
DC Power Supply
- +
(1)
ElectroCell
FM2
FM1
Air
Compressor
(3)
PTin
Tout
pHout
CMout
RXout
Tin
pHin
CMin
RXin
Outlet
Sampling
Inlet
Sampling
Feed
Tank
(5)
Pump
(4)

(b)

(c)

Main Results | Seawater Characteristics

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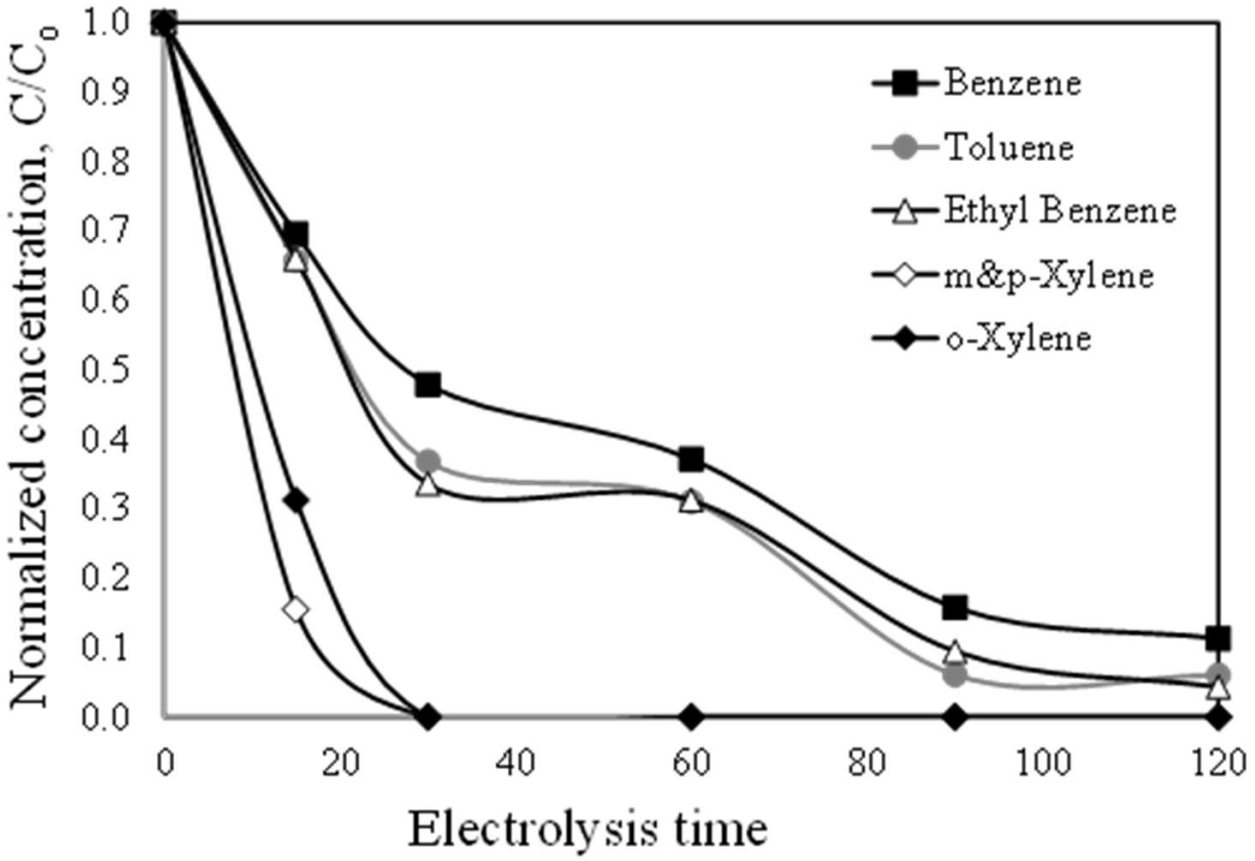
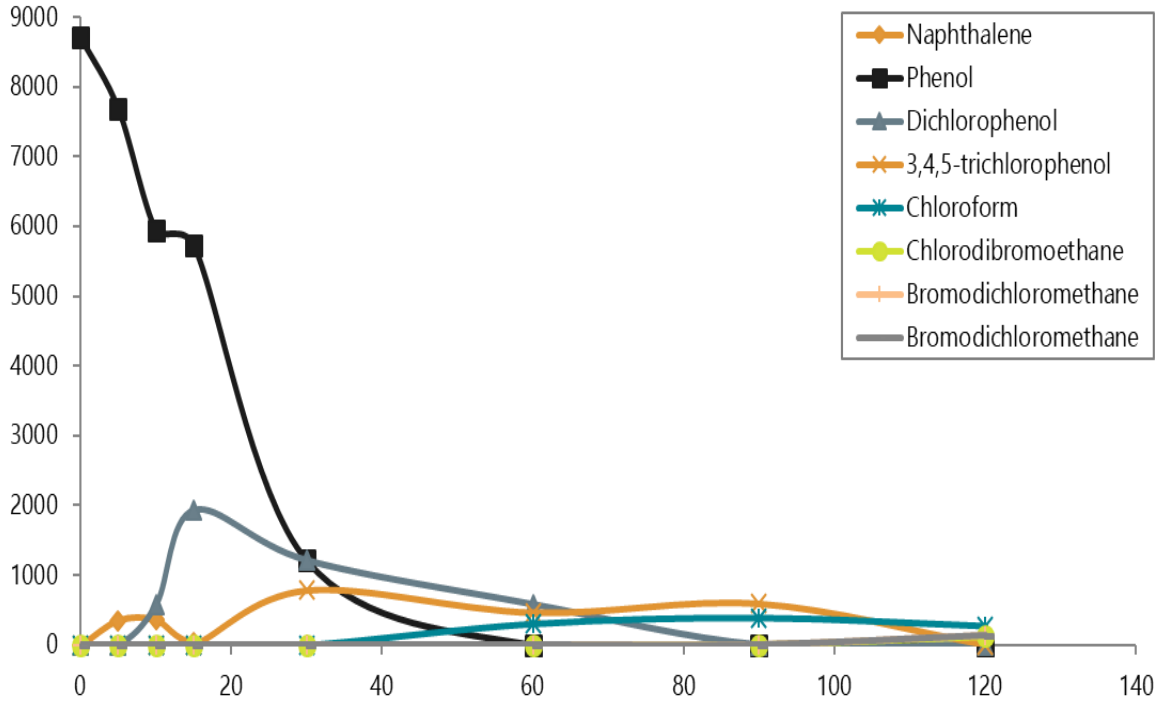
Water quality parameters of seawater used in the experiments

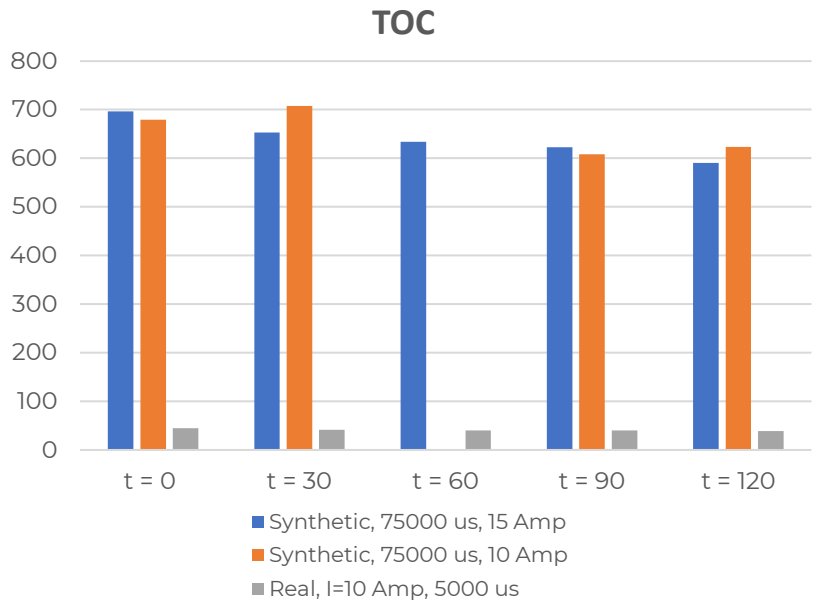
Parameter	Unit	Value	Parameter	Unit	Value
Conductivity	mS/cm	44.8 ± 3.2	TOC	mg/L	0.3 ± 0.05
pH	-	9.4 ± 0.6	Inog. Carbon	mg/L	0.0
Cations					
Na^+	mg/L	8860.0	Ca^{2+}	mg/L	769.9
K^+	mg/L	306.4	Li^+	mg/L	*n.d*
Mg^{2+}	mg/L	1657.3	NH_4^+	mg/L	*n.d*
Anions					
F^-	mg/L	6.9	NO_3^-	mg/L	32.5
Cl^-	mg/L	23121.5	HPO_4^{2-}	mg/L	*n.d*
SO_4^{2-}	mg/L	3550.5	NO_2^-	mg/L	*n.d*
Br^-	mg/L	108.4			

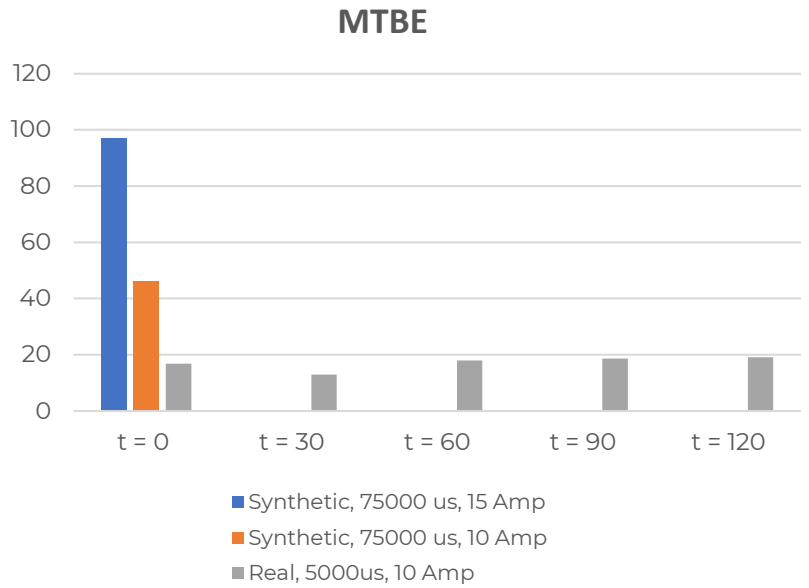
**n.d:* not detected.

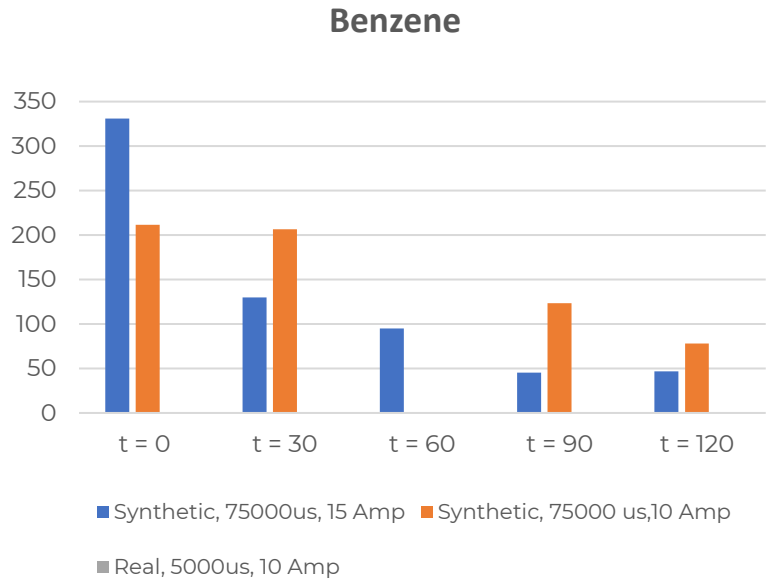




Main Results

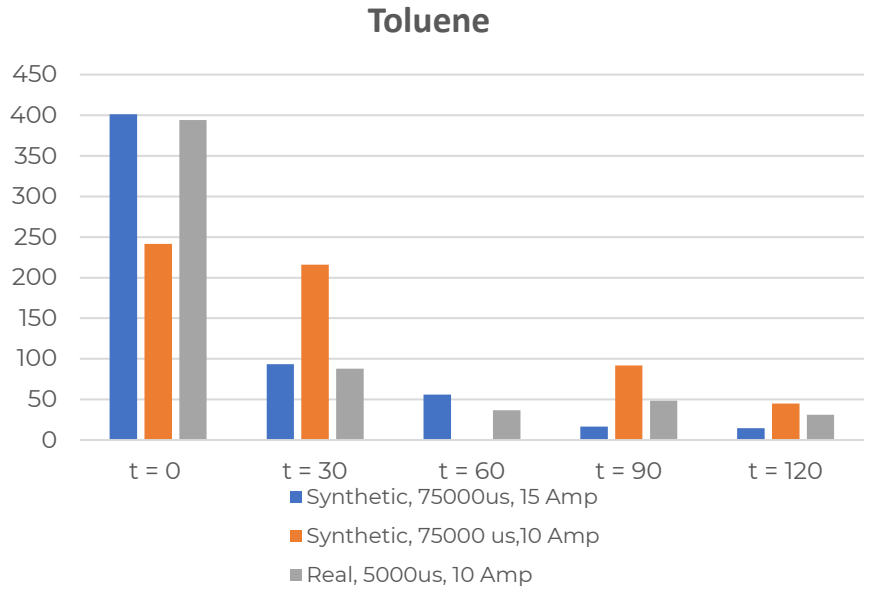


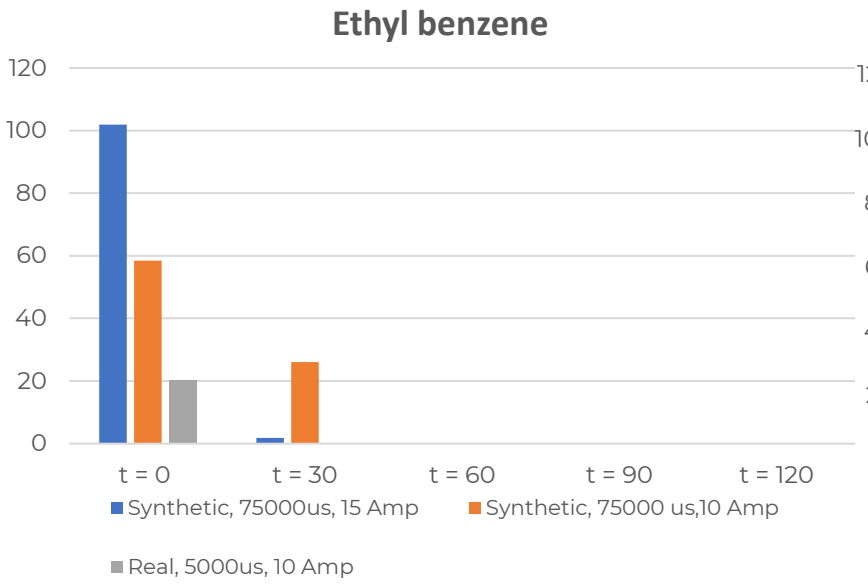


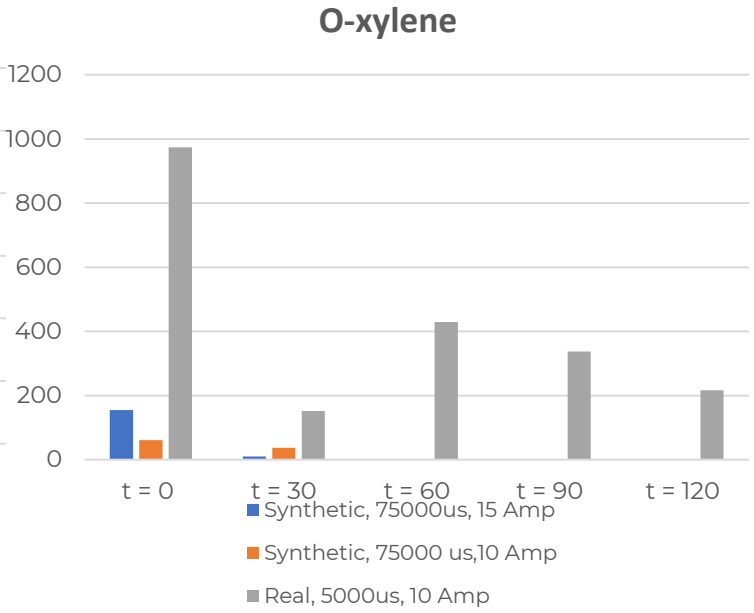


Testing Treatment Optimum Conditions of Synthetic and Real PW.

Main Results







Testing Treatment Optimum Conditions of Synthetic and Real PW.

Main Results

Results & Conclusion

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- High removal efficiency (>90%)of Phenols in less than 60 min, while Toluene was totally removed within 90 min. Benzene on the other hand was reduced by only 70-80% within 120 min.

- The results highlight the potential of the hybrid AO-ECL remediation technique for treating organics in brines, such as produced water.

- The degradation power of the system is attributed to the synergistic effect of heterogeneously formed hydroxyl radicals (BDD(• OH)) and the homogenous evolution of chlorine and/or generation of highly oxidizing chlorine radicals (Cl •), or ozone that have significantly improved the BTEX degradation process.

- Efficiency for selective removals of BTEX and phenols in spiked seawater, synthetic and PW were very high while overall reduction of TOC in the real PW was low.

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