KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
College of Petroleum
Engineering & Geosciences

Removal of BTEX & Phenols from Highly Saline Water Using an Advanced Electrochemical Unit

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مؤتمر و معرض
المياه
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١١، ١٢، ١٣ فبراير ٢٠٢٠
الخبر، المملكة العربية السعودية

Innovative Water & Wastewater Technologies in the Fourth Industrial Revolution (IR 4.0)

التقنيات المبتكرة لتحلية المياه ومعالجة مياه الصرف الصحي في إطار الثورة الصناعية الرابعة (IR 4.0)

Outline

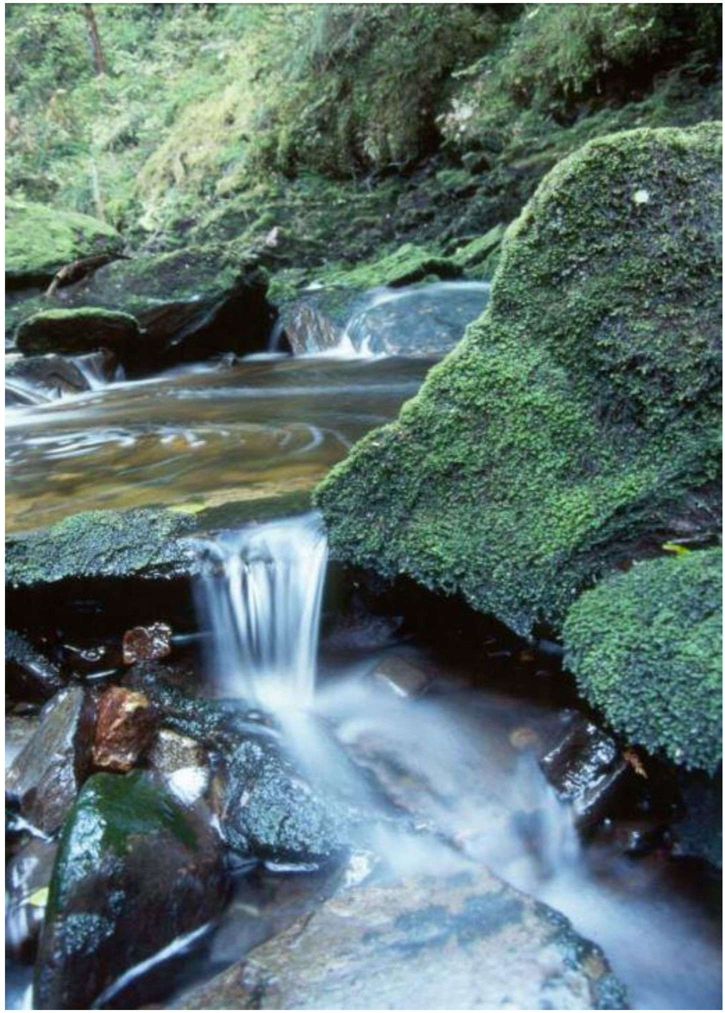
- Introduction
- The Problem Statement (Produced Water)
- Research Objectives
- Methodology
- Results and Discussions
  - Removal of Phenols
  - Removal of BTEX
- Concluding Remarks

Environmental Challenges

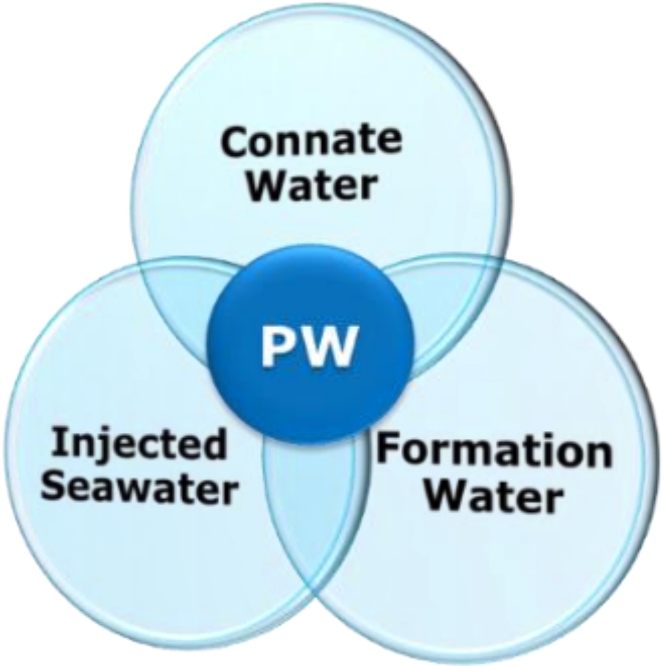
- Overpopulation and Environmental Health
- Poverty & Social Aspects
- Resources Utilization and Conservation
- Environmental Pollution
- Waste Management
- Ecology and Biodiversity
- Desertification, Deforestation….etc.

Human Use of Resources - Water

- Access to clean water is essential to life (a human right).
- More than **780 million** people do not have access to potable water
- Additional **2.8 billion** people live in water-scarce environments.
- Freshwater is **unsustainably managed** by wasting it, polluting it, and charging too little for it.
- Population, urbanization, economic development and even climate change cause water scarcity. In 2080, expected rise in global temperature by **3-4°C** could add **1.8 billion people** in areas of high water-stress.



Produced Water (PW)

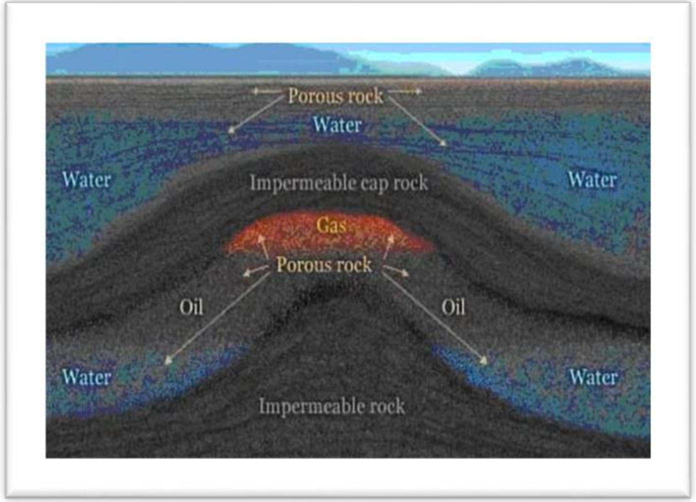

Connate Water

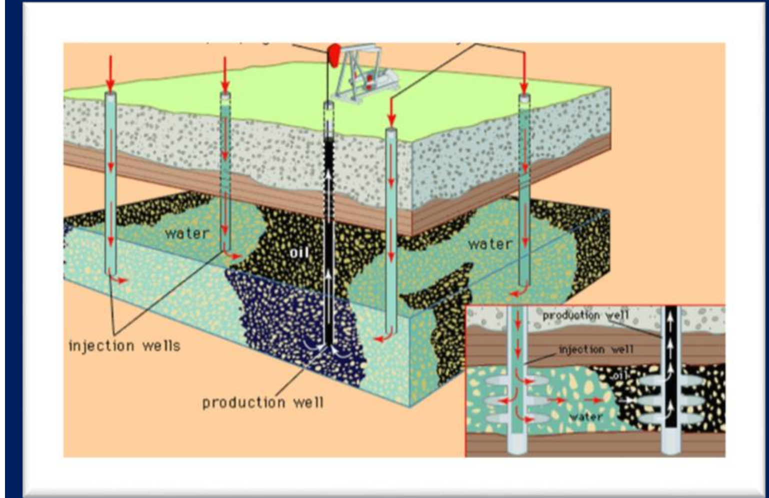
PW

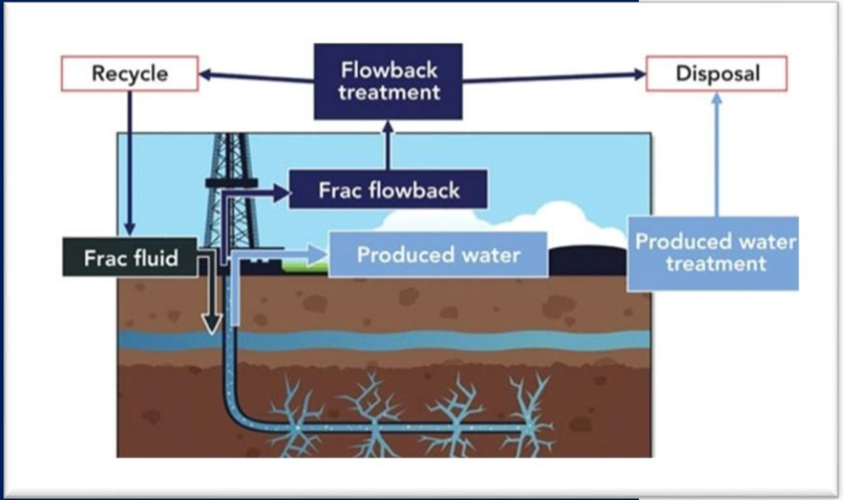
Injected Seawater

Formation Water

- PW is the water found in the same formations as oil and gas brought to the surface with the hydrocarbons.
- It includes natural connate water, formation water and injected water.
- May also generate from activities designed to increase oil production (EOR) from the formations such as
  - water flooding
  - hydraulic fracking (fracking fluid and flowback)
  - steam flooding operations

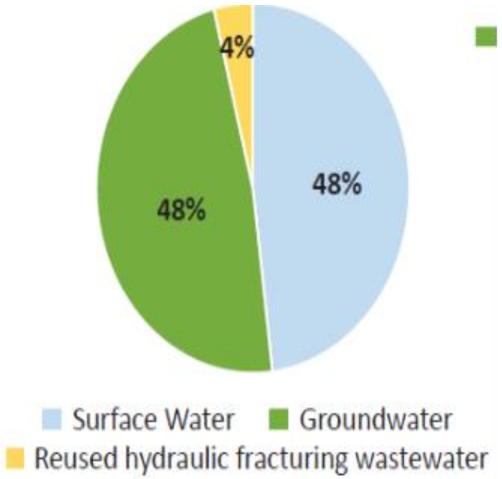


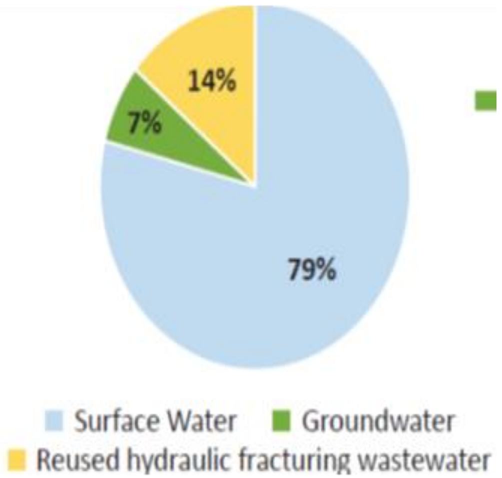




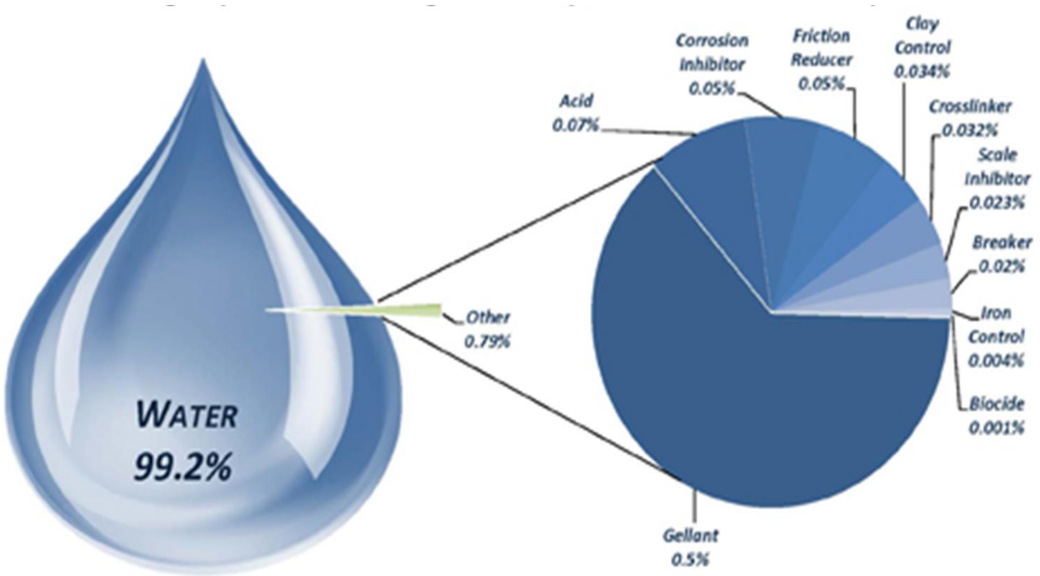
PW Waste Stream

- PW is the **largest** waste stream from the oil and gas industry
- For every **1 bbl.** of crude oil, **4 - 10 bbl**. of water are produced
- Water use ranges from **280 thousands** to **23 million L** per well.
- In 2012, **21.2 billion bbl**. of PW were generated in the **USA alone**.
- Globally, > **300 million bbl./day** and **70 billion bbl. of PW/year** .
- In some countries, there is ***heavy reliance*** on **fresh water** from ground water and surface water sources in oil and gas operations





Produced Water Characteristics



Average hydraulic fracturing fluid composition for US shale

- Chemical and physical characteristics of PW **vary** considerably from well to well.
- Produced water is usually **highly saline** (> 250,000 ppm), **chemically complex** and contains the characteristics of the formation from which it was produced.
- Typical produced water may consists of :

- Dispersed oil
- Dissolved salts
- **Dissolved organic compounds: PAHs, BTEX, phenols, VOCs, organic acids…etc.**
- Dissolved gases

- Solids
- Chemical additives
- Metals
- Bacteria
- NORMs
- Others

Contents of flowback/produced water

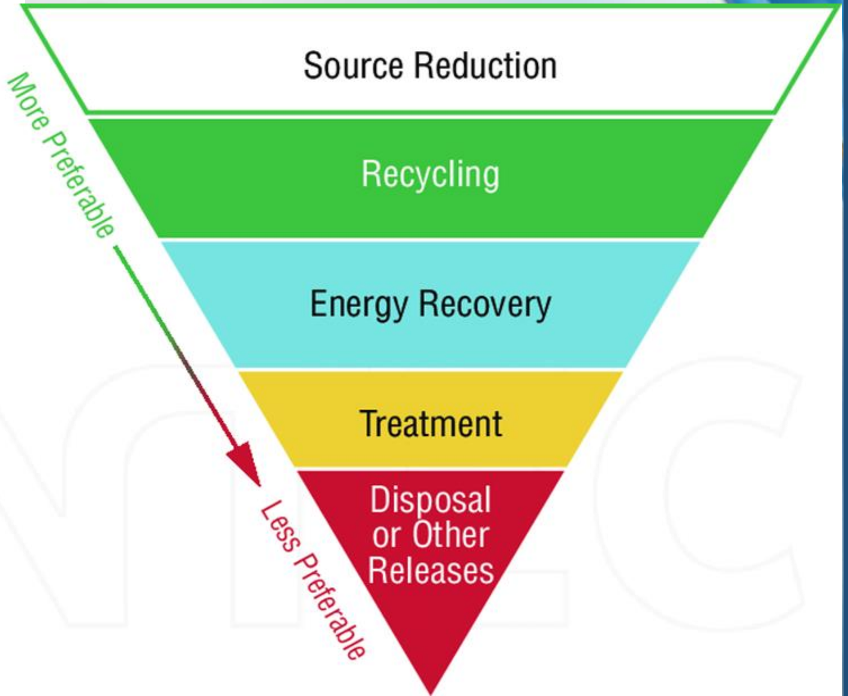
Parameter	Abdalla et al., 2011	Rosenblum et al., 2017
Total alkalinity (mg/L)	138	475
Hardness (as $CaCO_3$) (mg/L)	17,700	-
Total Suspended Solids (TSS) (mg/L)	99	172
Total Dissolved Solids (TDS) (mg/L)	67,300	18,756
Turbidity (NTU)	80	223
Chloride (mg/L)	41,850	11,650
Bromide (mg/L)	445	168.5
Specific conductance (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

- TSS may be in hundreds of ppm
- TDS range from 8,000 to 200,000 ppm
- TOC can be up to 2000 ppm
- COD may reach 20,000 ppm in the flowback water
- Iron (Fe) can reach a max. of 500 ppm
- Heavy metals are also present in PW in varying levels
- High organic contents of hydrocarbons (phenols, BTEX, PAHs…etc.)

Abdalla, C.W. et al (2011) Marcellus shale wastewater issues in Pennsylvania–current and emerging treatment and disposal technologies, Penn State Water Resources Extension, The Pennsylvania State University

Rosenblum, J., et al (2017) Science of the Total Environment 596–597, 369–377.

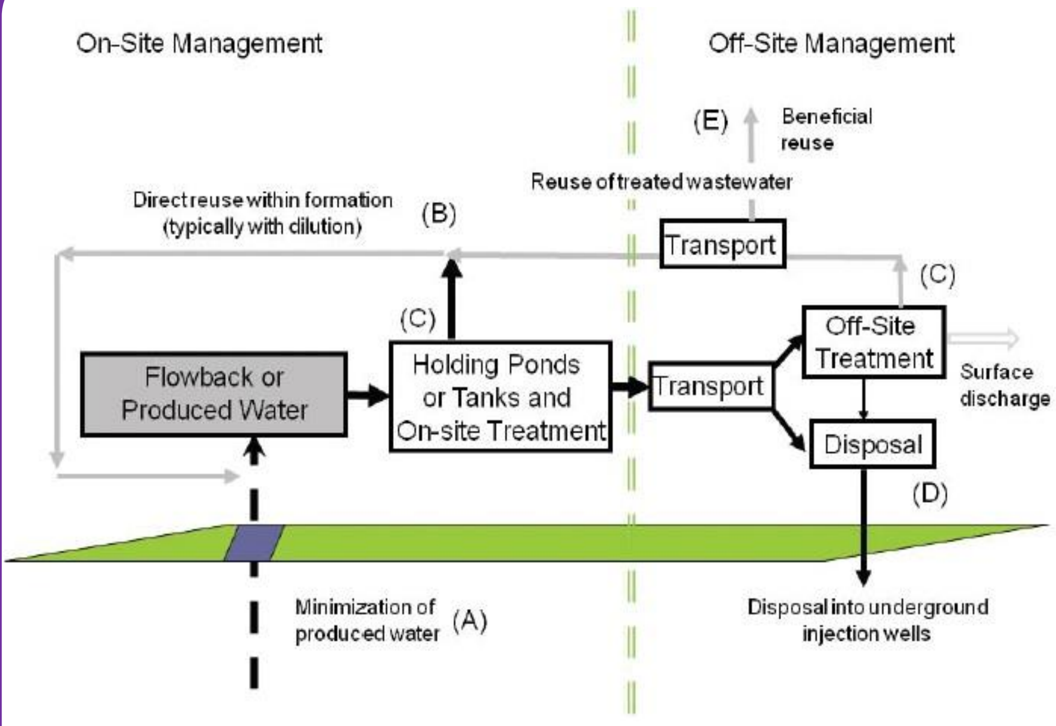
Management of Produced Water



Source Reduction
Recycling
Energy Recovery
Treatment
Disposal or Other Releases
More Preferable
Less Preferable

- One of the largest challenges facing the oil & gas industry
- Needs economical and environmental friendly methods of treatment for the sake of recycling/reuse for *beneficial use*.
- The methodology of handling PW depends on:
  - The composition and quantity of PW
  - Location
  - The availability of resources (cost…etc.)
- The strategies applied to management options can be of a 3-tiered water hierarchy :
  - Minimization
  - Reuse/recycle, and
  - Disposal

Management of The Produced Water…



What are our options?

Minimization

- Reduce water use via mechanical methods

Reuse/Recycle

- Treatment for beneficial reuse in the O&G
- Re-injection for EOR processes
- Treatment for beneficial recycle (irrigation, livestock consumption, industrial cooling…etc.)

Disposal

- Onshore-Offshore Disposal
- Evaporation (ponds)
- Deep well Injection (Class II)

Disposal of Produced Water

Evaporation Ponds

Evaporation ponds cause a series of problems :

- Hydrocarbons lighter than water will **float to the surface.**
- **VOCs** evaporate and contribute to **air pollution**.
- Other hydrocarbons get oxidized and hydrated and become heavier than water and **sink to the bottom** of the pond.
- At the bottom of the pond this material becomes food for anaerobic bacteria such as SRB's that **produce H_2S and CO_2**.

Produced Water Treatment

Multiple processes are needed for the treatment for PW aiming to:

- **De-oiling** – removal of free and dispersed oil, grease, etc.
- **Soluble organics removal** – removal of dissolved organics
- **Suspended solids removal** – removal of sand, clay, etc.
- **Dissolved gas removal** – removal of CO_2, H_2S, etc.
- **Desalination or demineralization** – removal of salts, etc.
- **Softening** – removal of excess water hardness
- **Miscellaneous** –NORM removal
- **Disinfection** – removal of bacteria, etc.

Treatment Methods of Produced Water

TSS, oil and grease

- Screening
- Settling/Sedimentation ponds
- Coagulation/ Flocculation
- Filtration
- Biological Aerated Filters (BAF)
- Hydrocyclones
- Dissolved Gas Flotation (DGF)
- Dissolved Air Flotation (DAF)
- Microfiltration (MF)
- Ultrafiltration (UF)

Performance parameters

TSS, Turbidity, Oil and grease, TOC, COD, BOD

Scaling ions

- Aeration
- Settling
- Filtration
- Lime Softening
- Ion exchange (IEX)
- Nanofiltration (NF)

Performance parameters

Hardness, Specific ions (nitrates, sulphates), Specific metals (Ba, Fe, Sr)

Dissolved organics

- 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)

Performance parameters

DOC, TOC, COD, VOC, Specific organics (BTEX, phenol, benzene, toluene, xylene), Chemical additives (Table A2)

Bacteria, fungi, algae

- Ozonation
- Ultraviolet irradiation (UV)
- Chlorine dioxide
- Chloramines

Performance parameters

Bacteria, viruses, fungi microorganisms, algae

TDS

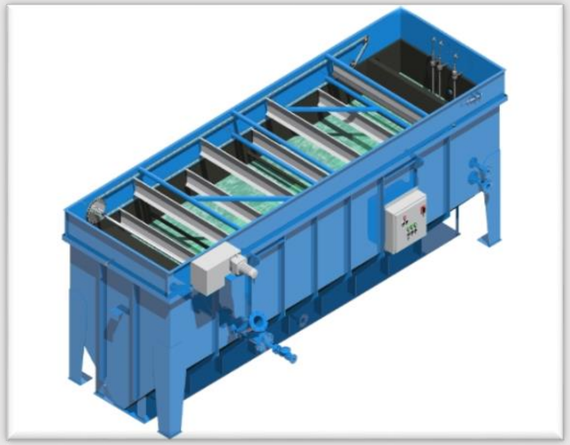
- **Non-thermal**
- Reverse Osmosis
- Ion exchange (IEX)
- Electrodialysis (ED)*
- Forward Osmosis (FO)*
- Capacitive deionization (CDI)*
- Advanced adsorption*
- **Thermal**
- Multi-effect distillation (MED)
- Vapor compression distillation (VCD)
- Multistage flash distillation (MSF)
- Crystallization
- Evaporation

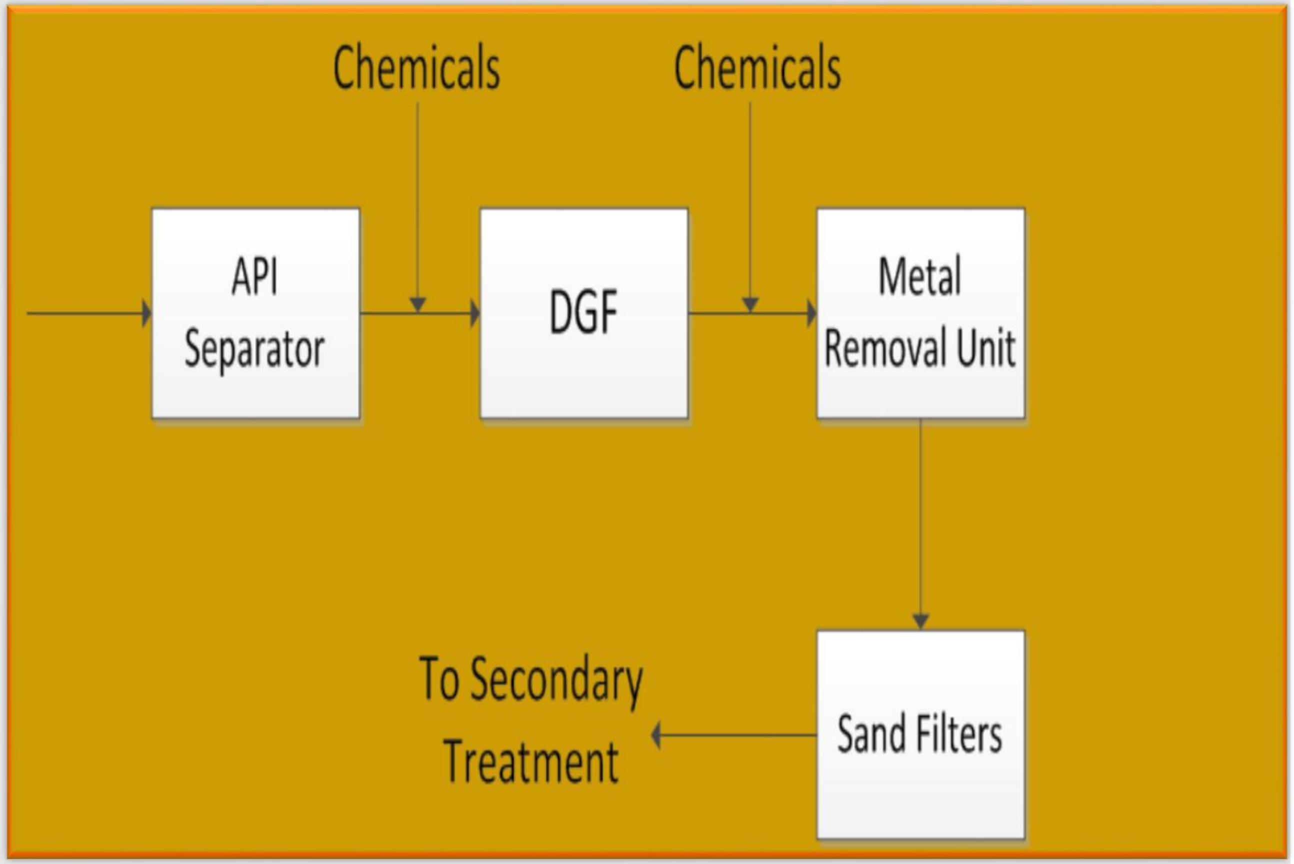
Performance parameters

Conductivity, specific ions (Cl^-, Na^+, Br^-, K^+, I^-, NH_4^+)

Produced Water Treatment For Beneficial Use

Water 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 toxicity (free of organic and trace metals) Low sodium adsorption ratio (SAR <6)
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 and Low in specific constituents like metals
Vehicle and equipment washing	Low SS and Moderate TDS
Power-generation cooling	Low SS, Moderate TDS, Low Ca, Mg, Fe, sulfate (scale formers)
Fire control	Low SS, Low organics
Indirect potable reuse through aquifer recharge	Legislative drinking water criteria (e.g. Safe Drinking Act in US)





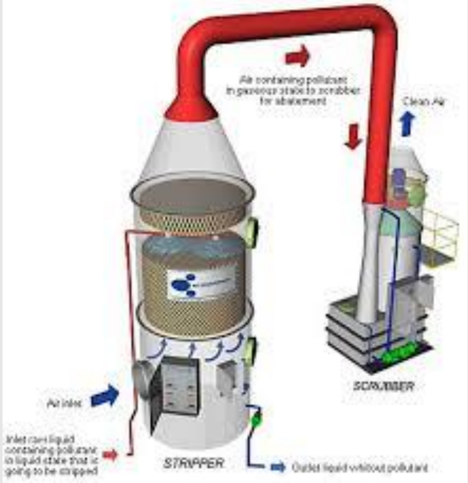
Produced Water Treatment

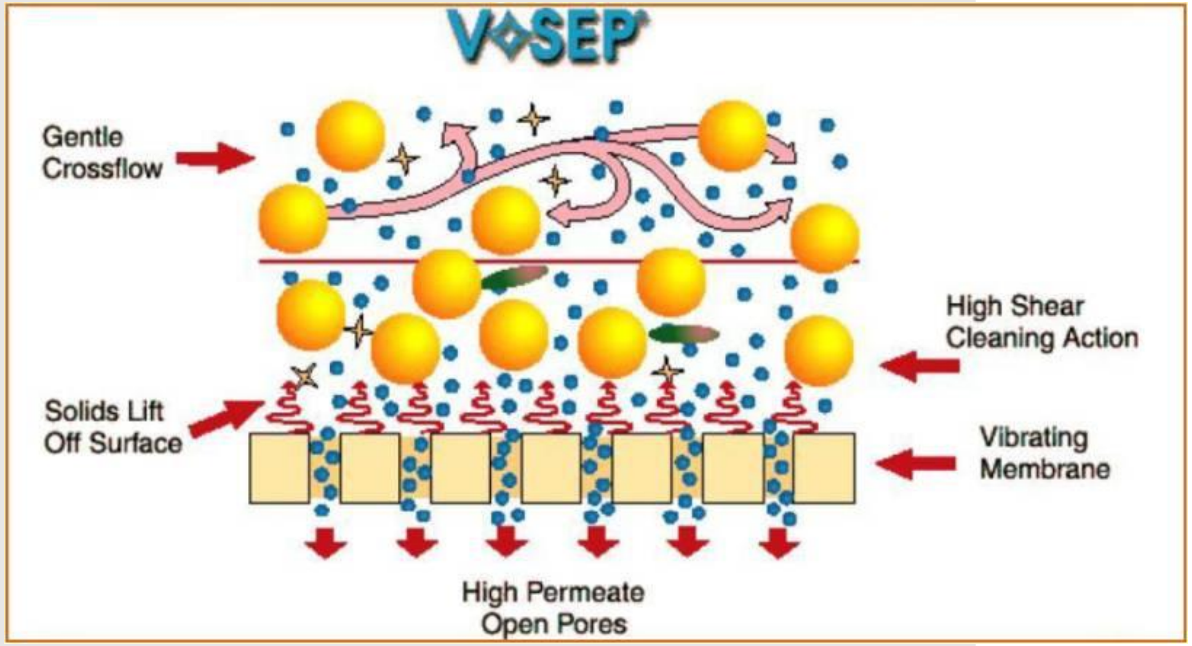
Typical PW treatment technologies are classified as primary, secondary and tertiary processes.

1. Primary Treatments:

- Mainly used to remove ***suspended hydrocarbons*** components and ***solids***.
- API separator, DAF for ***Oil removal***
- Coagulation/Flocculation for ***Metal removal***
- Filtration for **solids removal**

Produced Water Treatment..





2. Secondary Treatments:

These techniques include :

- Adsorption (i.e. GAC)
- Biodegradation
- Gas/Air stripping
- Membrane separation

For the removal of :

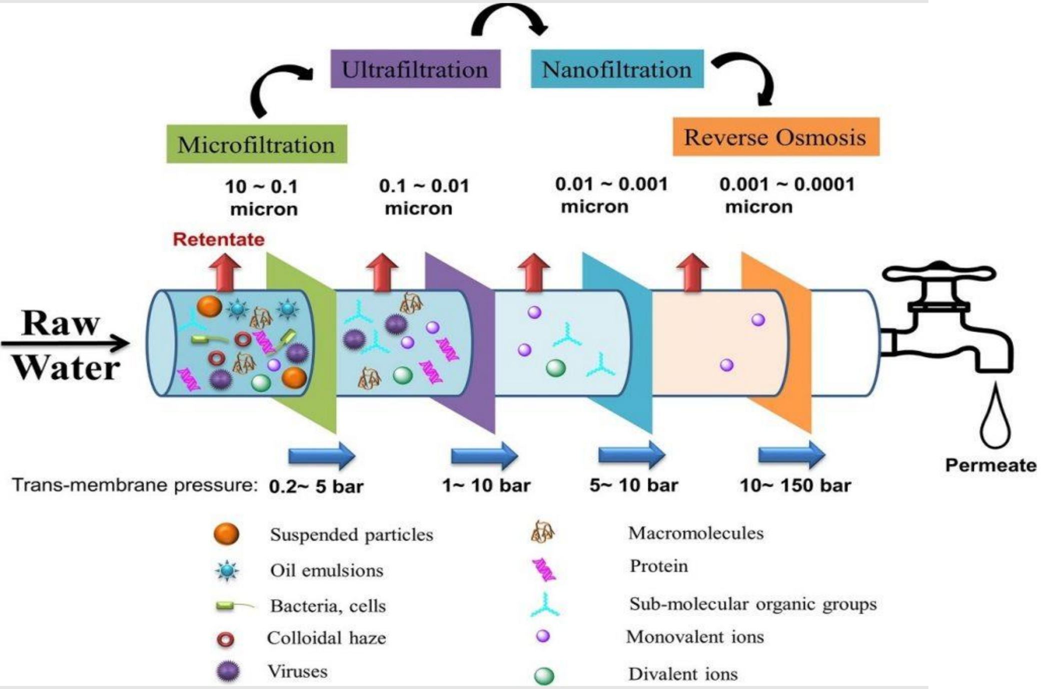
- organic compounds and organic acids
- suspended solids and oil
- dissolved aromatic hydrocarbons (phenols and BTEX)

Produced Water Treatment..

3. Tertiary Treatments:

- Focused on the salts removal from treated PW coming from secondary processes
- RO membranes to reduce the levels of **salts, hardness** (Mg, Ca ions) and **nutrients**
- May provide the necessary attributes for the reuse of water for industrial and agricultural purposes

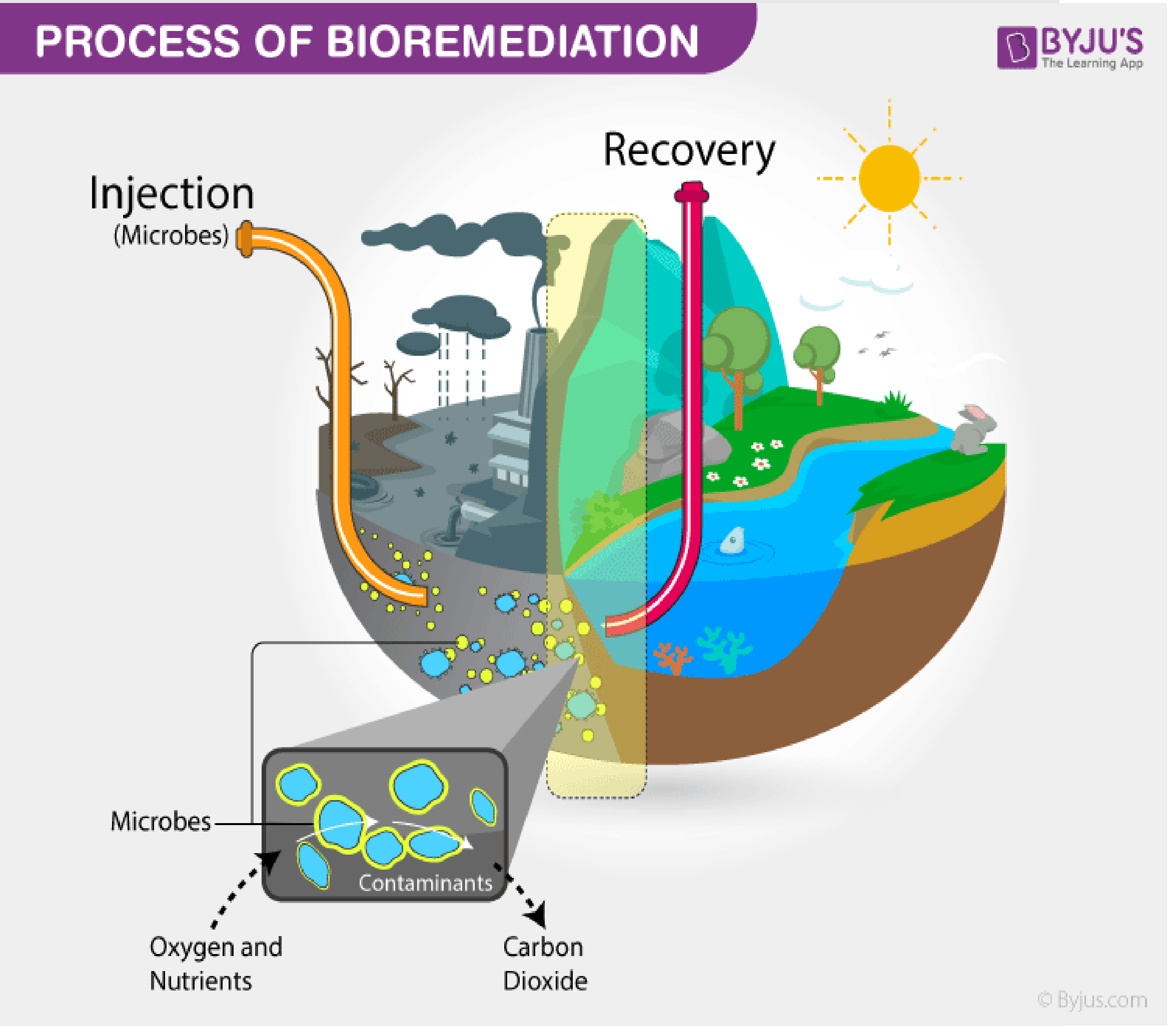
Produced Water Treatment..



Membrane filtration

- Classified based on the size of the particles they are able to reject in process:
  - Microfiltration (MF)
  - Ultra-filtration (UF)
  - Nano-filtration (NF)
  - Reverse osmosis (RO)
  - Ceramic membranes
  - Synthetic Membranes
- Offer several advantages such as compact module, lower energy consumption, environmental friendliness and high quality product independently on fluctuations in feed quality
- Issues include high cost, fouling and residue.

Produced Water Treatment…



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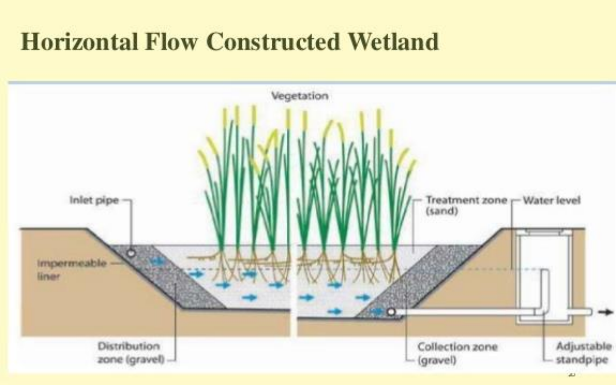
Bioremediation

- Select microbial consortiums able to use hydrocarbons as food
- In the presence of oxygen they convert hydrocarbons into carbon dioxide and water
- During bioremediation, microorganisms metabolize hazardous substances found in produced water into carbon dioxide and water
- Issues include:
    - Microbes require a proper pH, temperature, trace elements, and nutrient sources
    - Time consuming (treatment extends for years)
    - Not effective for very saline PW



Produced Water Treatment…

Constructed Wetland

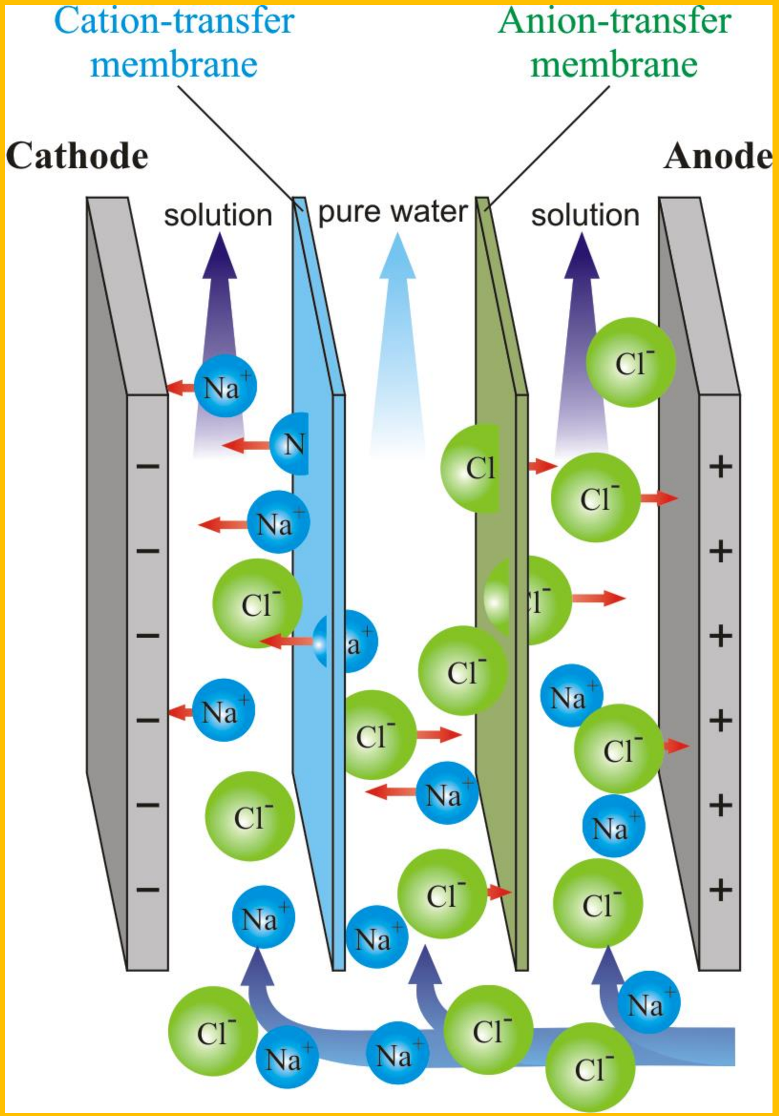
Achieved by interactions between water, plants, microorganisms, filter media and oxygen.

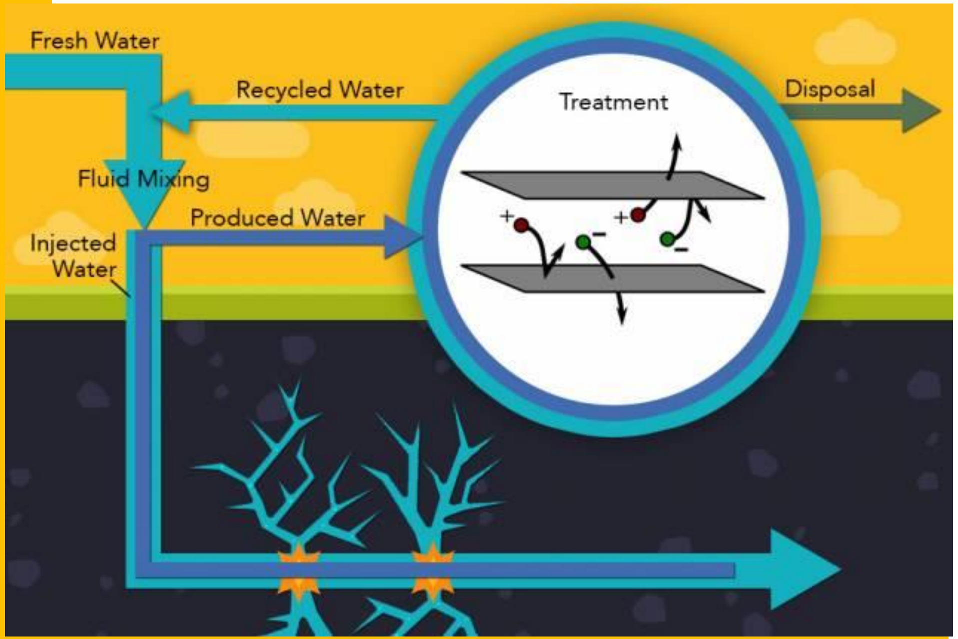
- The Bauer-Nimr Water Treatment Plant (NWTP) is the world's largest engineered constructed wetland, located in Oman for Petroleum Development-Oman Co.
- It can treat more than 115,000m^3/day produced water.

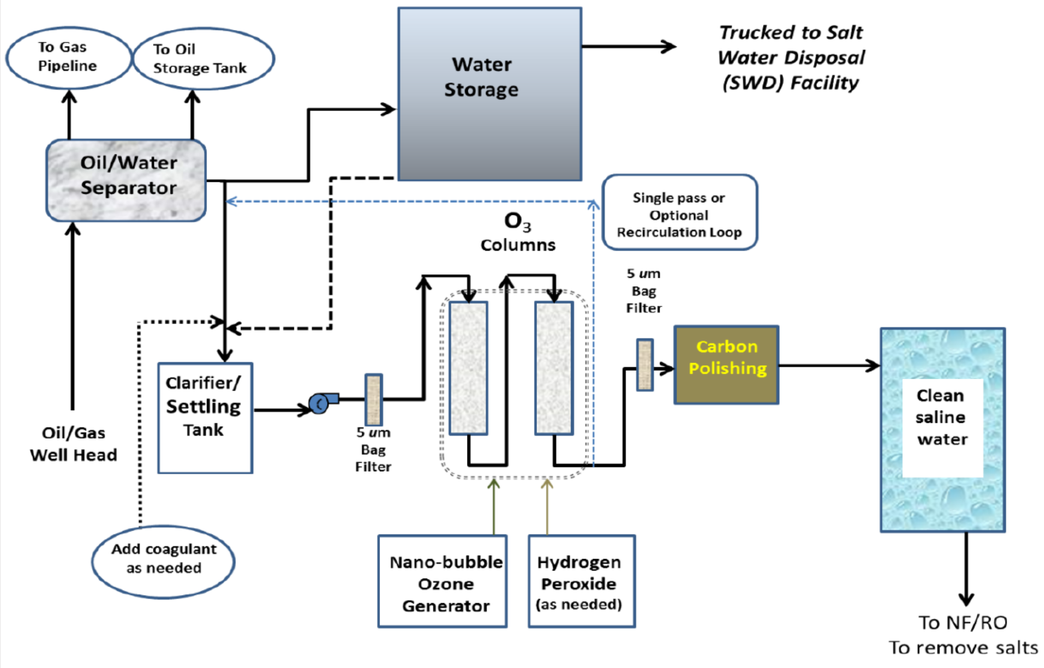
Produced Water Treatment…

Electrodialysis

- Researchers at **MIT** and **KFUPM** have found that **Electrodialysis** is an economical solution for removing the salt from PW
- Salts in produced water can be effectively removed through succession of stages of electrodialysis





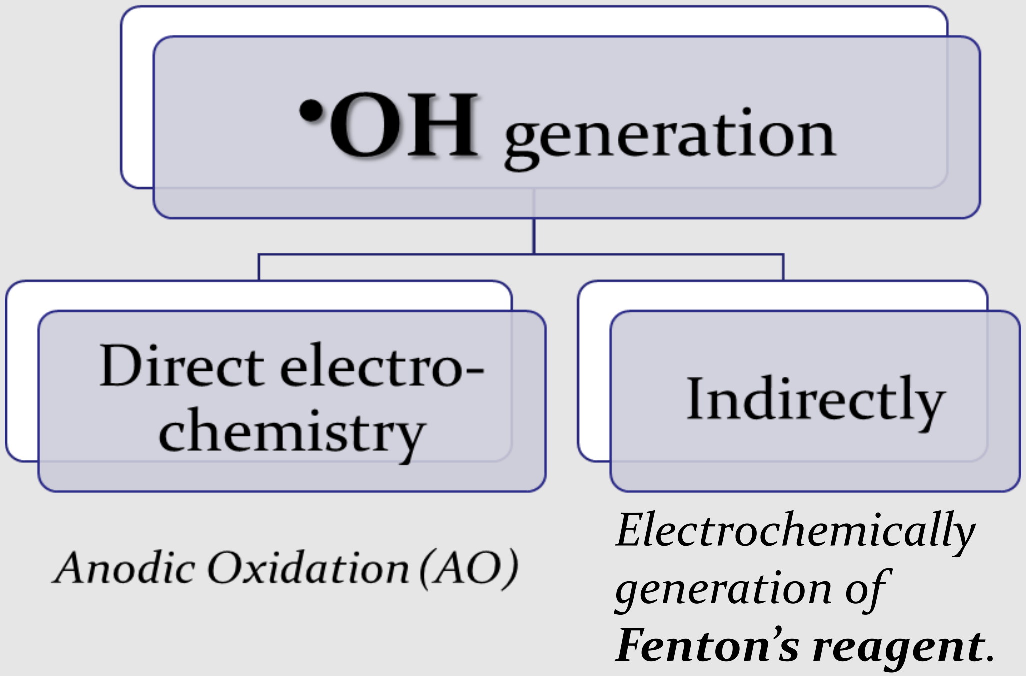


Produced Water Treatment…

Advanced Oxidation

- A technology that includes a combination of nano-bubbles ozone coupled with hydrogen peroxide (H_2O_2) advanced oxidation and chemical precipitation
- Peroxone ($O_3 + H_2O_2$) produce highly reactive hydroxyl radicals ($^{\bullet}OH$) capable of degrading contaminants
- Issues include ozone generation, cost and safety

Produced Water Treatment…



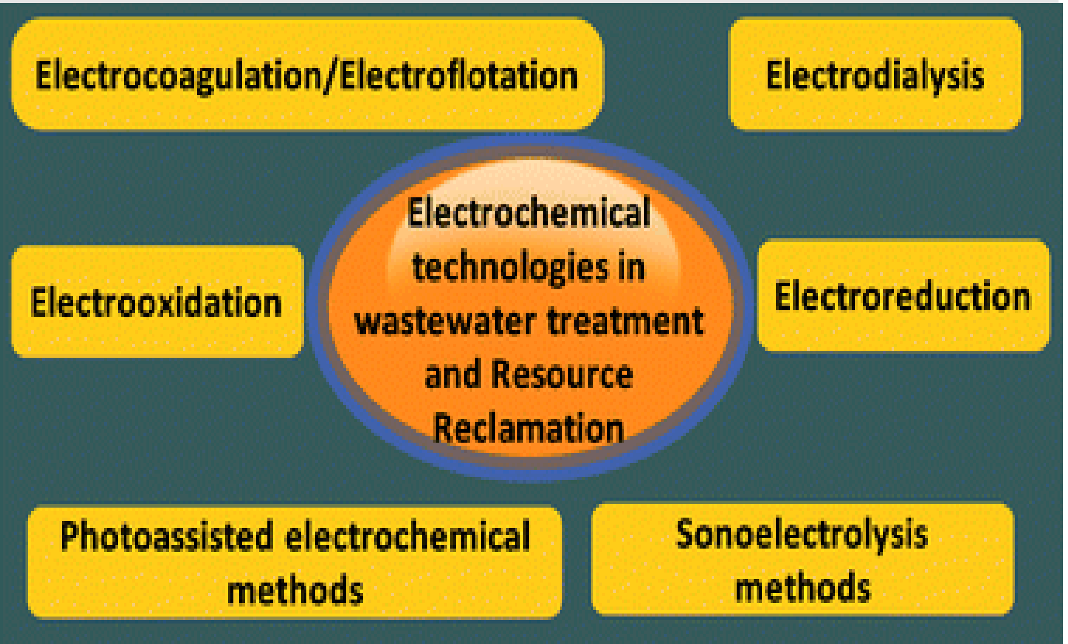
$^\bullet$OH generation

Direct electro-chemistry

Anodic Oxidation (AO)

Indirectly

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



Electrochemical treatment

- Based upon the **complete degradation of contaminants** in water via electro-generated oxidants (H_2O_2 and O_3) and strong oxidants such as hydroxyl radicals ($^\bullet$OH)
- Can be of different types :
  - Electrooxidation / Electroreduction
  - Electrodialysis
  - Electrocoagulation/Electroflotation
  - Photo-assisted electrochemical
  - Fenton-based electrochemical

Produced Water Treatment

Electrochemical

The Research Team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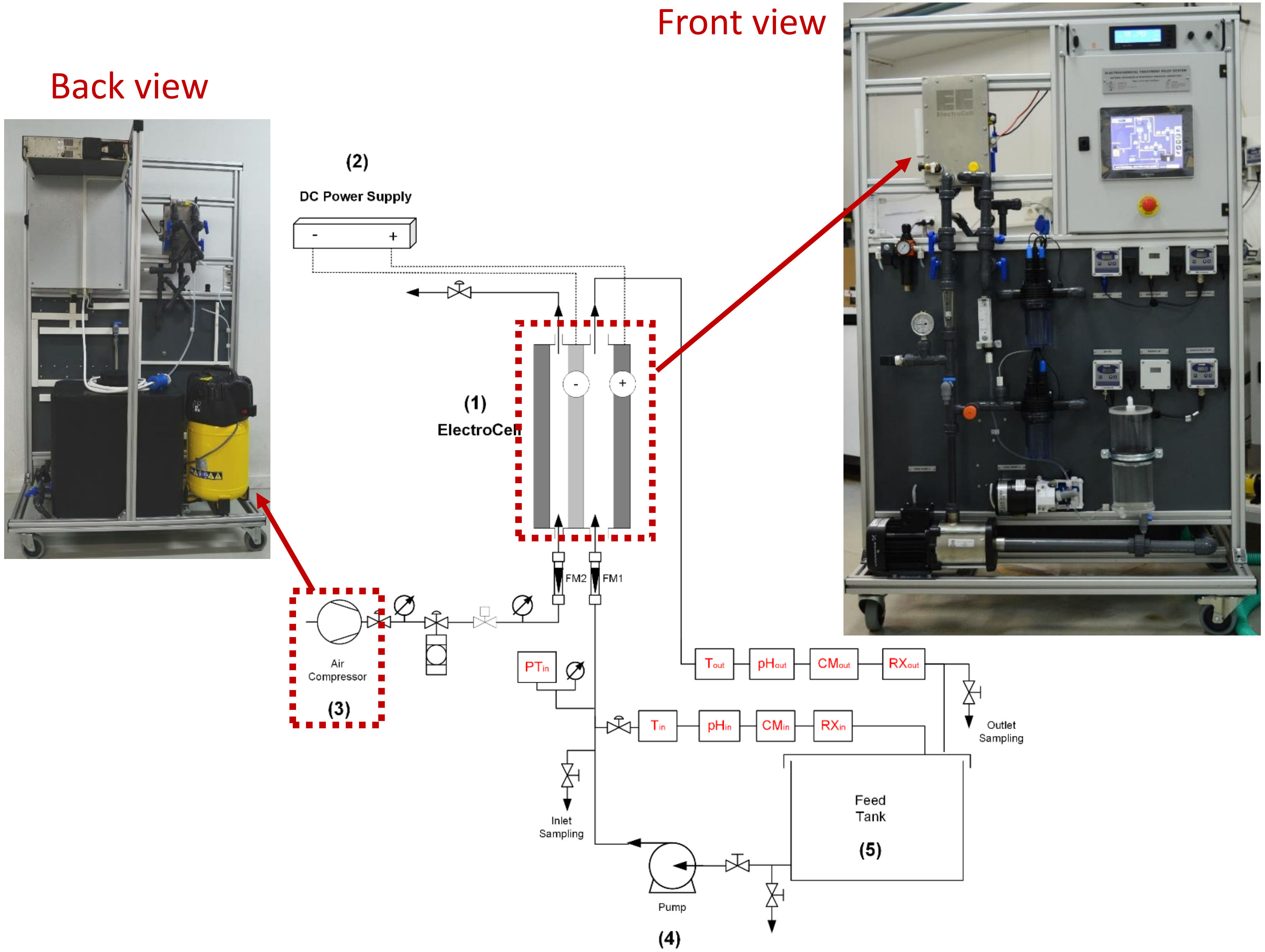
Research Objectives

1. To investigate the performance of a custom-made laboratory scale electrochemical oxidation unit using phenol and BTEX as model compounds
2. To investigate the potential of phenol/BTEX degradation/mineralization in brine by means of Anodic Oxidation (AO) alone or coupled with cathodic Electro-based Fenton (EF) oxidation
3. To determine the optimum treatment parameters such as current density (mA/cm^2), air flow rate (NL/min), Fe(II) dosage (mM), water conductivity (mS/cm), pH, residence time (min), etc.
4. To identify the degradation intermediates and by-products
5. To calculate the cost associated with the EC treatment at the optimum conditions

The Pilot EC Unit

A pilot scale EC unit:

- batch recirculation mode
- undivided plate-and-frame EC cell
- boron doped diamond (BDD) anode and carbon-PTFE (GDE) cathode
- pH, conductivity, temperature and redox potential are monitored and recorded
- untreated and treated brine spiked with **phenols** and **BTEX** was assessed under various treatment conditions
- degradation by-products were monitored

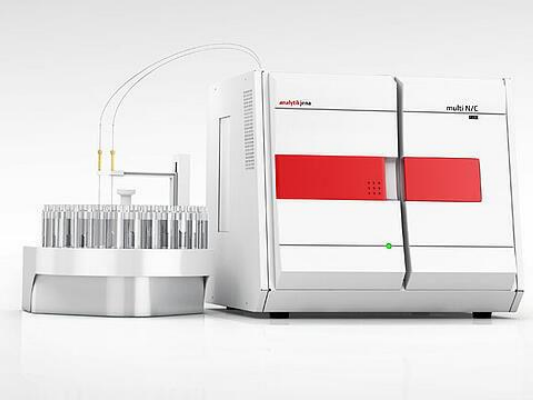


Schematic diagram of the Electrochemical Treatment System pilot plant equipped with (1) a plate-and-frame electrochemical cell, (2) a DC power supply, (3) a compressed air system, (4) an horizontal multistage pump, (5) a feed tank and several sensors located at the inlet and the outlet of the cell, measuring different operating variables. (b) Front view of the pilot unit.

Phenol/BTEX Degradation Tests

- Phenol Initial Concentration: 50 mg/L
- BTEX Initial Concentration: 0.5-2.5 mg/L
- Water Matrix: Distilled water, Brackish water (GW), Synthetic saline water(water + NaCl), Seawater and RO reject water.
- Conductivity : ~ 2000 to 70,000 µS/cm
- pH : 3 - 10
- Fe(II): 0.5 – 2 mM (28-112 mg/L)
- Current density (*j*) : 0 – 60 (mA/cm^2 or 2-6 Amp)
- Air Flowrate : 0 - 5 (NL/min)
- Water Circulation Rate : 0.2 - 0.4 (m^3/h)
- Phenol and BTEX Concentrations: measured by Thermo GC/MS
- TOC by Analytik Jena Multi N/C 3100 TOC Analyzer

Thermo Fisher ISQ Series Single Quadrupole GC-MS Systems



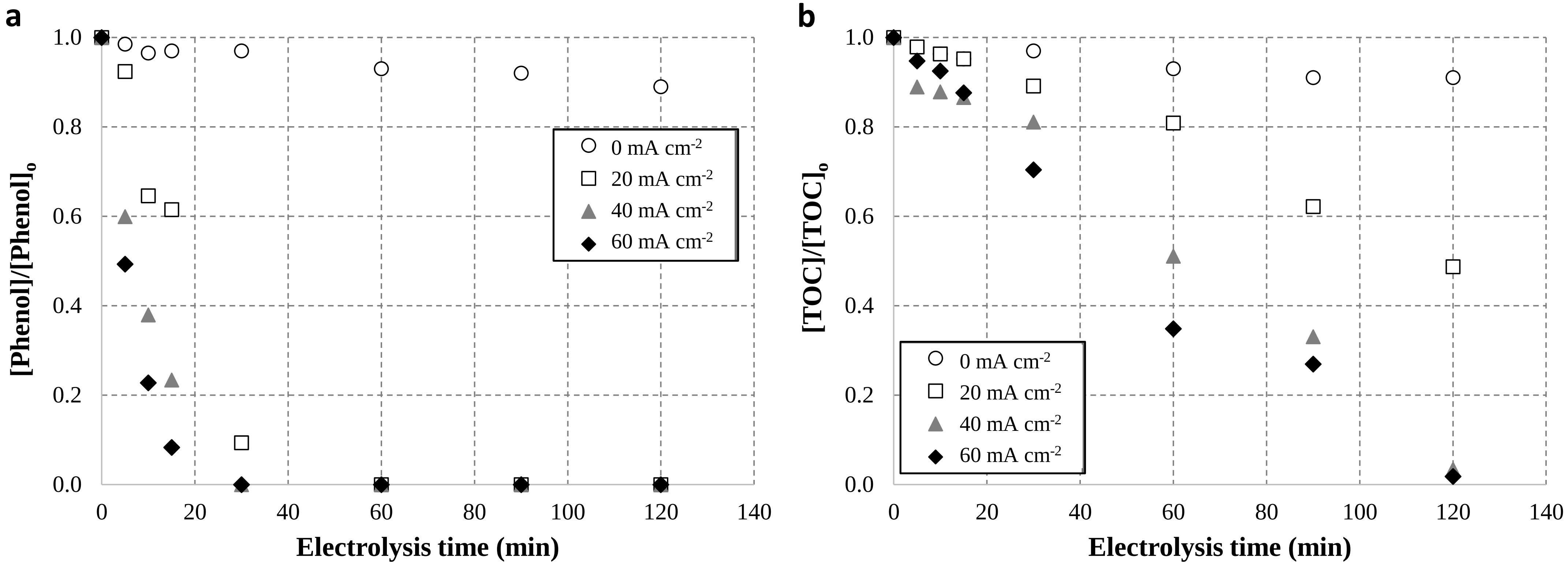
N/C 3100 pharma Analytik Jena TOC analyzer

Water quality parameters of feed water types used in the experiments

Parameter	**Unit**	**Distilled water**	**Brackish water**	**Seawater**
Conductivity	µS/cm	2.2	5706.5	63925.0
pH	-	6.1	6.9	8.2
TOC	mg/L	n.d	0.0	0.3
Inorg. Carbon	mg/L	n.d	62.0	0.0
Na^+	mg/L	n.d	467.8	8860.0
K^+	mg/L	n.d	20.1	306.4
Mg^{2+}	mg/L	0.5	104.5	1657.3
Ca^{2+}	mg/L	n.d	297.1	769.9
Li^+	mg/L	n.d	0.5	n.d
NH^{4+}	mg/L	n.d	n.d	n.d
F^-	mg/L	n.d	1.8	6.9
Cl^-	mg/L	0.1	1387.7	23121.5
SO_4^{2-}	mg/L	0.3	661.5	3550.5
Br^-	mg/L	n.d	8.7	108.4
NO_3^-	mg/L	n.d	9.2	32.5
HPO_4^{2-}	mg/L	n.d	n.d	n.d
NO_2^-	mg/L	n.d	n.d	n.d

Phenol Removal

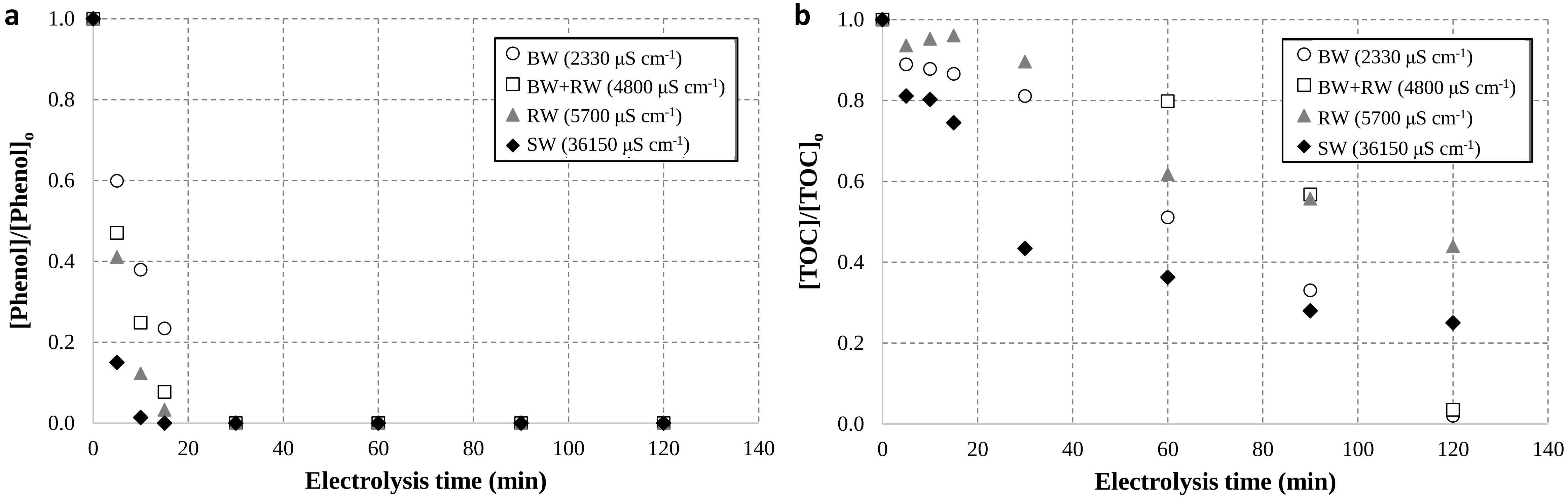
Effect of current density



- The higher the current density the faster the degradation.

Phenol Removal

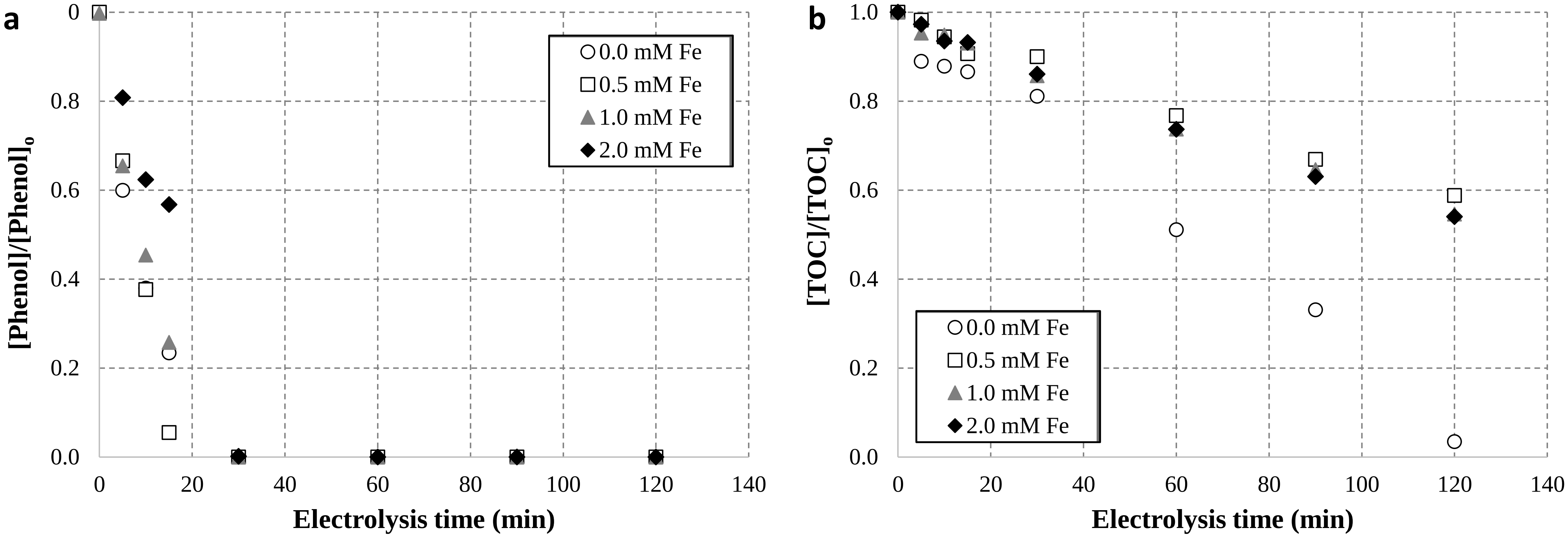
Effect of the water matrix (chloride content)



- ☐ Increasing the salinity tends to significantly enhance phenol removal and the respective degree of mineralization.
- ☐ highly reactive chlorine species electrogenerated in the cell can effectively strengthen the oxidation of the dissolved phenol in the bulk.

Phenol Removal

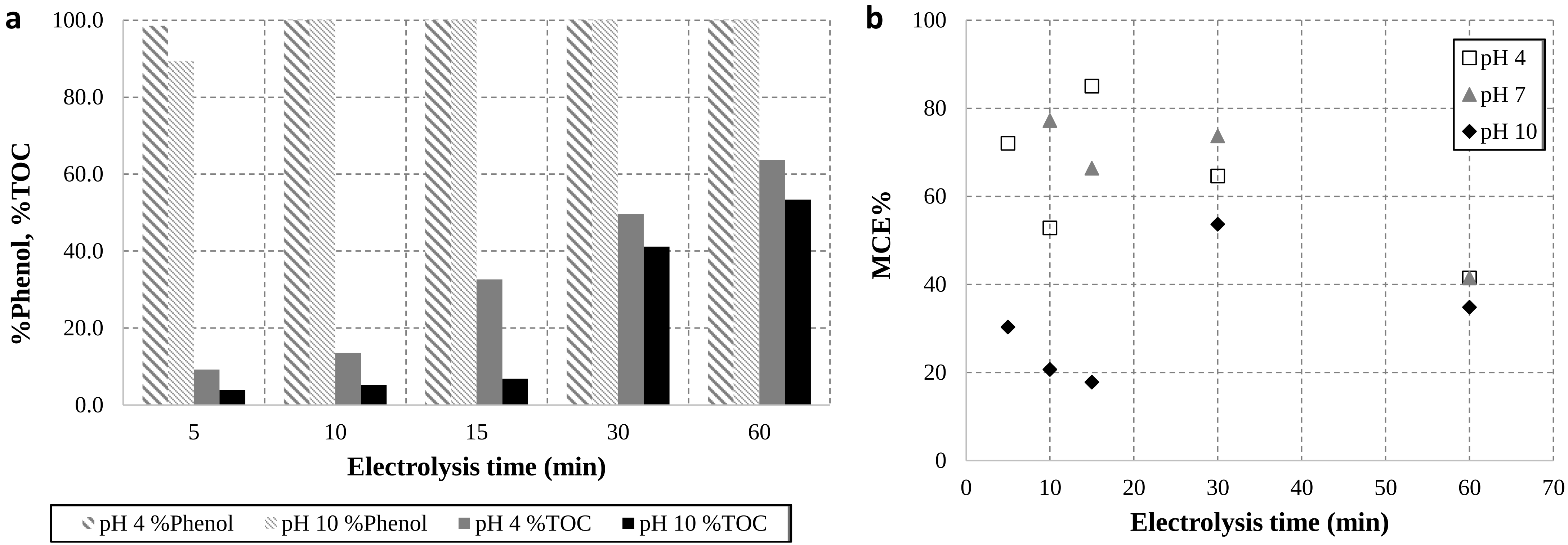
Effect of Fe(II) concentration –Electro-Fenton investigation



- ❑ The addition of ferrous ions did not enhance the degradation and the mineralization rate of phenol (i.e. **negligible Fenton reactions due to scavenging effect of chloride ions**)

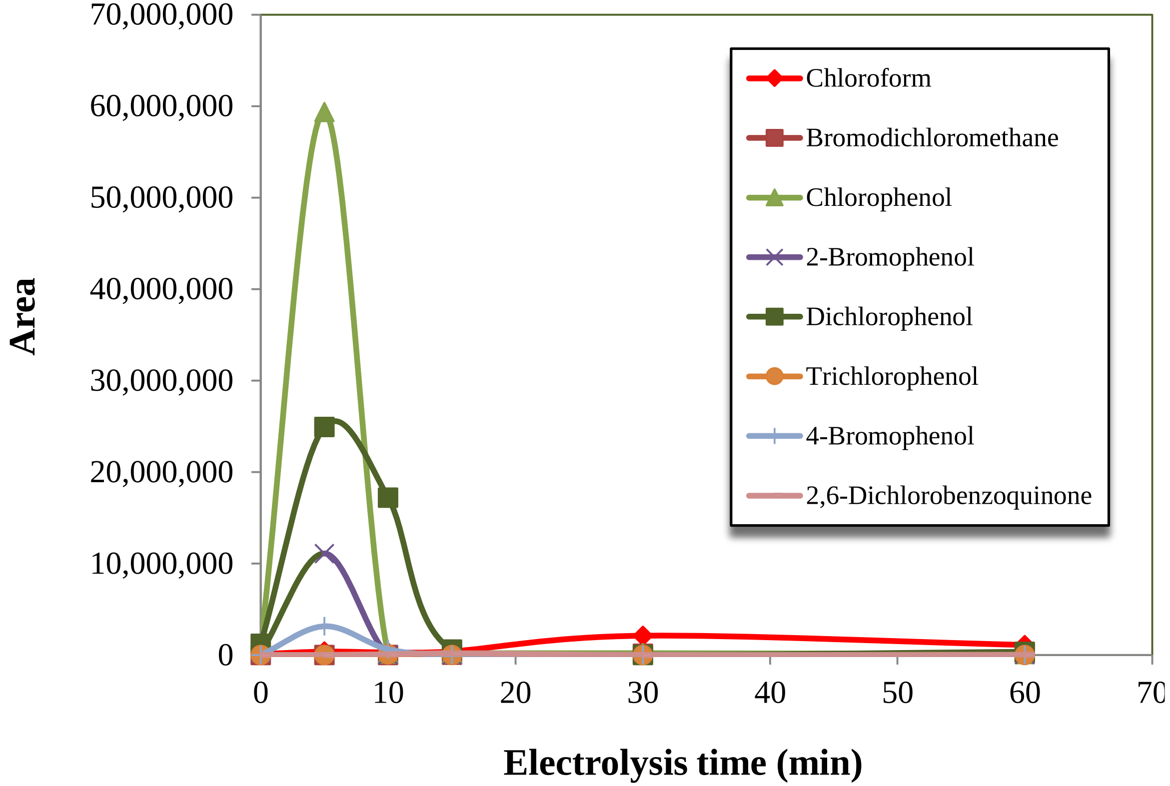
Phenol Removal

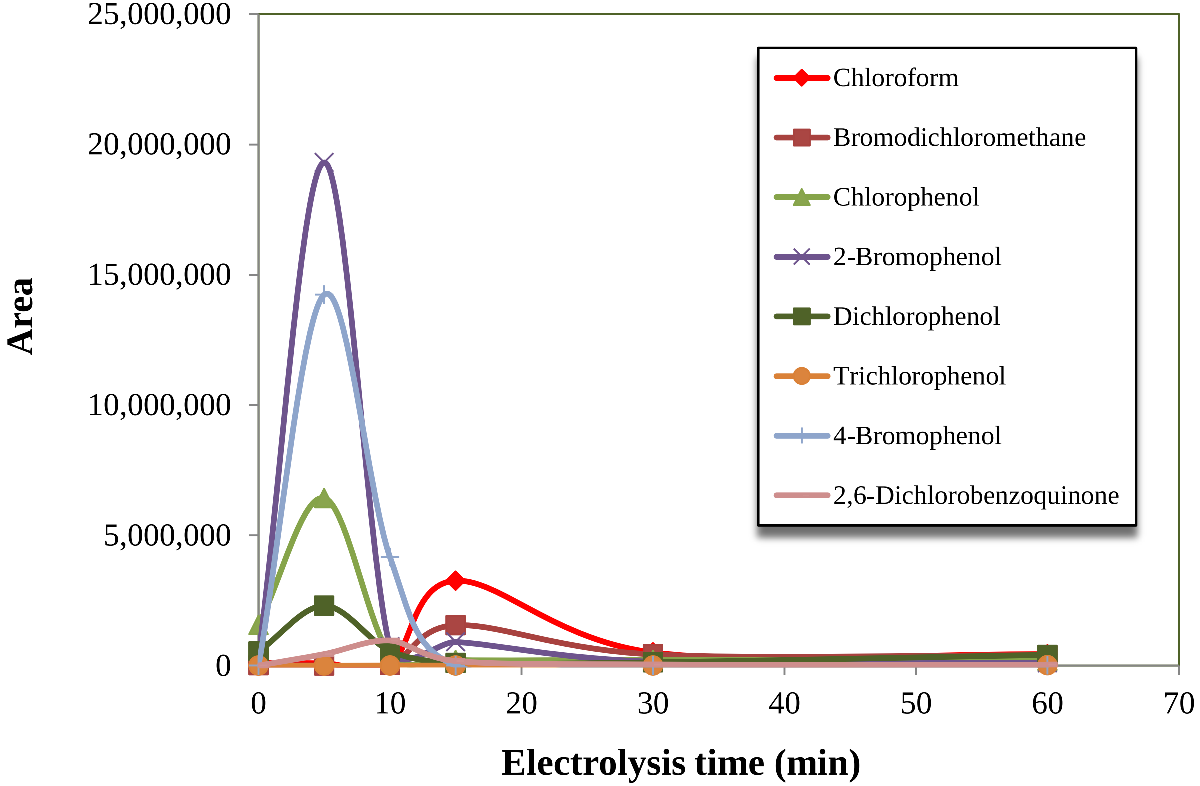
Effect of pH



- Phenol and TOC removal were enhanced in the acidic SW due to the higher evolution of Cl_2 in acidic conditions

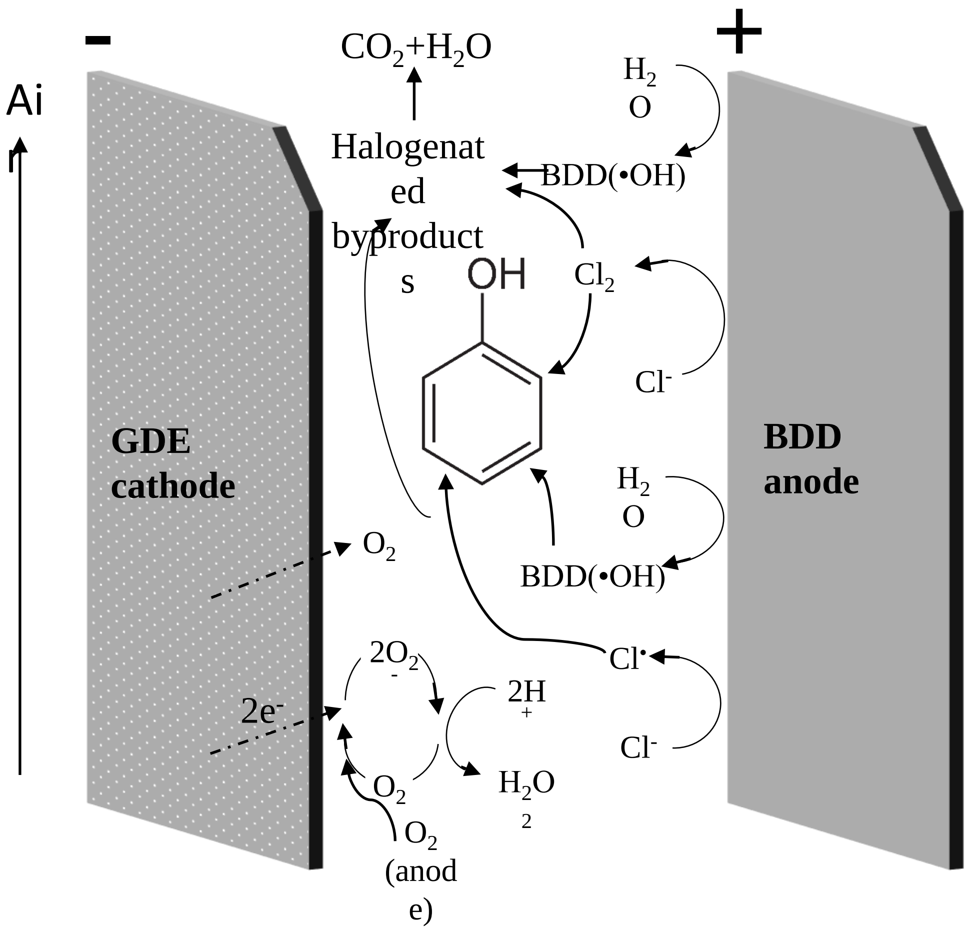
Formation of phenol degradation byproducts





- ❑ Two major THMs (chloroform, bromodichloromethane) and six chlorinated and/or brominated phenolic intermediates developed during the oxidation of phenol, at different extent and electrolysis times.
- ❑ In all matrices **all phenol degradation byproducts were eliminated after 60 min of treatment**.

Removal mechanism



- ❑ Oxidation owing to the high oxidation power of the heterogeneously formed hydroxyl radicals (BDD($^{\bullet}$OH)) on the BDD anode:

$$BDD + H_2O \rightarrow BDD(^{\bullet}OH) + H^+ + e^-$$

- ❑ Oxidation by other oxidants formed homogeneously in the bulk electrolyte:

$$3H_2O \rightarrow \mathbf{O_3(g)} + 6H^+ + 6e^-$$
$$2Cl^- \rightarrow \mathbf{Cl_2}$$
$$2SO_4^{2-} \rightarrow \mathbf{S_2O_8^{2-}} + 2e^-$$
$$2HSO_4^- \rightarrow \mathbf{S_2O_8^{2-}} + 2H^+ + 2e^-$$

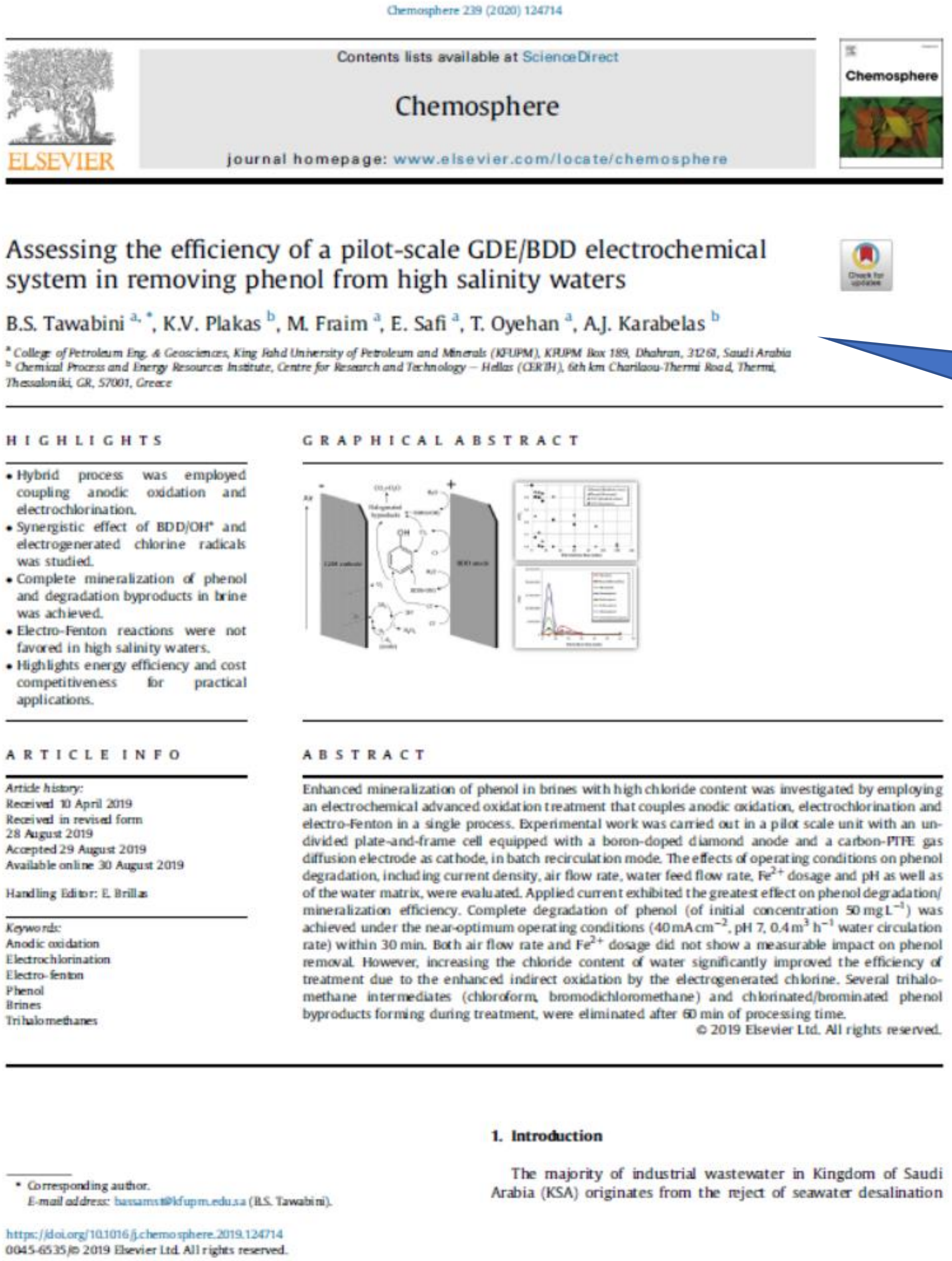
Cost Calculation For Phenol Removal

Exp. No	Water matrix	Conductivity (μS cm^{-1})	E_{cell} (V)	I (A)	ΔTOC (g L^{-1})	EC (kWh gTOC^{-1})	CE (USD m^{-3})
#1	BW	2480	0.00	0	0.0035	-	-
#2	BW	2480	17.63	2	9.58	0.74	0.34
#3	BW	2330	31.55	4	24.46	1.03	1.21
#4	BW	2580	33.87	6	32.59	1.25	1.95
#5	BW	2650	53.90	4	13.16	3.28	2.07
#6	BW	2050	56.62	4	8.91	5.09	2.17
#7	BW	2820	26.82	4	11.64	1.84	1.03
#8	BW	2820	21.30	4	13.15	1.30	0.82
#9	BW	2850	18.40	4	13.17	1.12	0.71
#10	BW	4500	25.10	4	19.20	1.05	0.96
#11	BW	2380	39.42	4	31.85	0.99	1.51
#12	BW	2400	39.13	4	37.28	0.84	1.50
#13	BW+50 g L^{-1} NaCl	39350	7.08	4	29.28	0.19	0.27
#14	BW+100 g L^{-1} NaCl	71580	9.37	4	29.31	0.26	0.36
#15	DW+10 g L^{-1} Na_2SO_4 [b]	6530	24.10	4	12.38	1.56	0.93
#16	BW+50 g L^{-1} NaCl	39600	5.97	4	14.00	0.34	0.23
#17	BW+100 g L^{-1} NaCl	70550	5.70	4	15.00	0.30	0.22
#18	BW	2650	26.33	4	9.35	2.25	1.01
#19	BW	2630	30.57	4	9.82	2.49	1.17
#20	BW	2820	25.40	4	9.50	2.14	0.98
#21	BW+RW (1:1)	4800	22.85	4	10.08	1.81	0.88
#22	RW	5700	21.37	4	19.13	0.89	0.82
#23	SW	36150	6.43	4	31.86	0.16	0.25
#24	SW	34320	8.47	4	31.80	0.21	0.33
#25	SW	33020	7.95	4	26.70	0.24	0.31

[a] Calculations for 1 hour of electrolysis. [b] Reference experiment with distilled water (DW, conductivity < 20 μS cm^{-1}).

Comparison with Other Studies

Treatment technology	Wastewater type	Initial [Phenol] (mg L^{-1})	Max% treatment efficiency	Cost (USD m^{-3})	Reference
Membrane separation (Reverse Osmosis-RO)	Olive mill wastewater	0.4	100%	1.77	Ochando-Pulido et al., 2013
Solar photo-Fenton (SPF)	Synthetic phenol solution	100	100%	2.87	Gar Alalm et al., 2017
Enzyme catalyzed treatment	Foundry wastewater	357	98%	49.70	Cooper et al., 1996
Ozonation	Synthetic phenol solution	100	100%	5.31	Canton et al., 2003
Fenton Oxidation	Synthetic phenol solution	100	100%	1.92	Krichevskaya et al., 2011
Integrated Ultrasonic + UV/O_3	Wastewater	235	-	23.51	Mahamuni and Adewuyi, 2010
Adsorption (Low cost rice husk ash)	Synthetic phenol solution	100	96%	3.48	Mahvi et al., 2004, Ahmaruzzaman, 2008
Electrochemical Treatment	Synthetic phenol solution	50	100%	0.2-2.0	Tawabini et al., 2019



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Assessing the efficiency of a pilot-scale GDE/BDD electrochemical system in removing phenol from high salinity waters

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HIGHLIGHTS

- Hybrid process was employed coupling anodic oxidation and electrochlorination.
- Synergistic effect of BDD/OH* and electrogenerated chlorine radicals was studied.
- Complete mineralization of phenol and degradation byproducts in brine was achieved.
- Electro-Fenton reactions were not favored in high salinity waters.
- Highlights energy efficiency and cost competitiveness for practical applications.

GRAPHICAL ABSTRACT

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ABSTRACT

Enhanced mineralization of phenol in brines with high chloride content was investigated by employing an electrochemical advanced oxidation treatment that couples anodic oxidation, electrochlorination and electro-Fenton in a single process. Experimental work was carried out in a pilot scale unit with an undivided plate-and-frame cell equipped with a boron-doped diamond anode and a carbon-PTFE gas diffusion electrode as cathode, in batch recirculation mode. The effects of operating conditions on phenol degradation, including current density, air flow rate, water feed flow rate, Fe^{2+} dosage and pH as well as of the water matrix, were evaluated. Applied current exhibited the greatest effect on phenol degradation/mineralization efficiency. Complete degradation of phenol (of initial concentration 50 mg L^{-1}) was achieved under the near-optimum operating conditions (40 mA cm^{-2}, pH 7, 0.4 m^3 h^{-1} water circulation rate) within 30 min. Both air flow rate and Fe^{2+} dosage did not show a measurable impact on phenol removal. However, increasing the chloride content of water significantly improved the efficiency of treatment due to the enhanced indirect oxidation by the electrogenerated chlorine. Several trihalomethane intermediates (chloroform, bromodichloromethane) and chlorinated/brominated phenol byproducts forming during treatment, were eliminated after 60 min of processing time.

1. Introduction

The majority of industrial wastewater in Kingdom of Saudi Arabia (KSA) originates from the reject of seawater desalination

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For more information please refer to our recent publication **Chemosphere 239 (2020) 124714**

BTEX Removal

DESIGN OF EXPERIMENTS (by Response Surface Methodology, Face Centered Composite design)

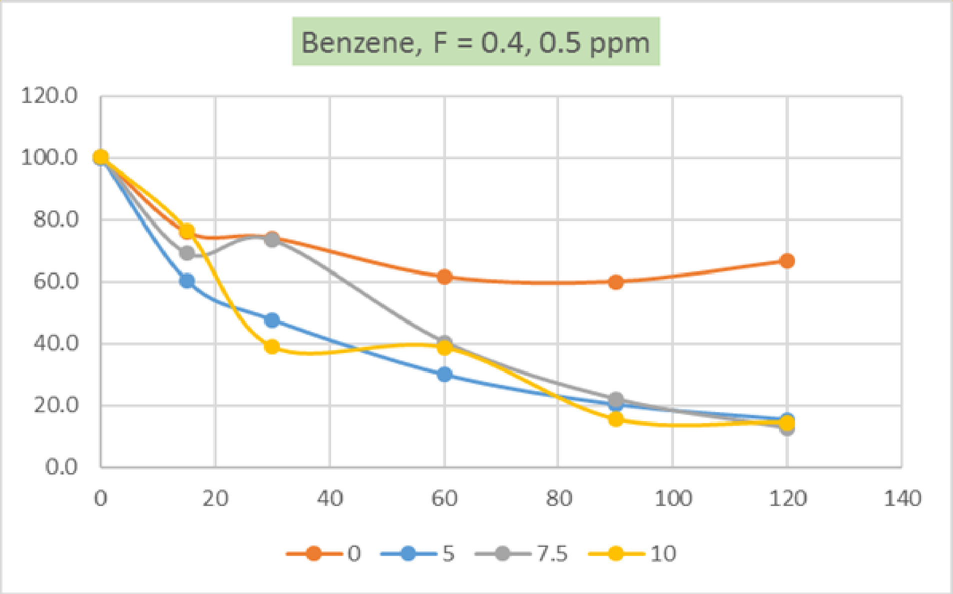
File Version	11.1.2.0		
Study Type	Response Surface	**Subtype**	Randomized
Design Type	Central Composite	**Runs**	17
Design Model	Quadratic	**Blocks**	No Blocks
Build Time (ms)	1.0000		

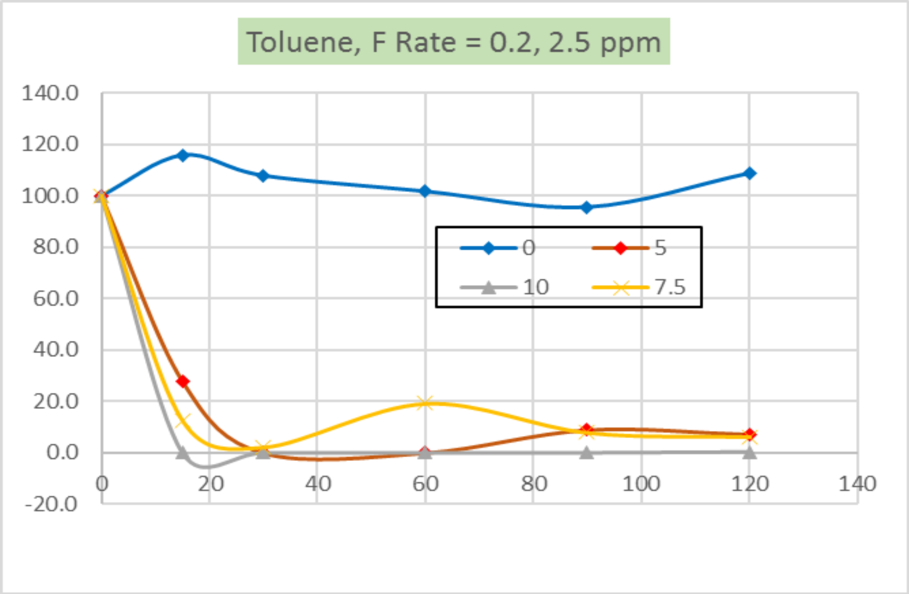
Factor	Name	Units	Type	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	**Current density**	**mA/cm^2**	Numeric	**50.00**	**100.00**	-1 ↔ 50.00	+1 ↔ 100.00	75.00	19.76
B	**Feed flow rate**	**m^3/h**	Numeric	**0.2**	**0.4**	-1 ↔ 0.2	+1 ↔ 0.4	0.3	0.0791
C	**BTEX concentration**	**mg/L**	Numeric	**0.5**	**2.5**	-1 ↔ 0.5	+1 ↔ 2.5	1.5	0.7906

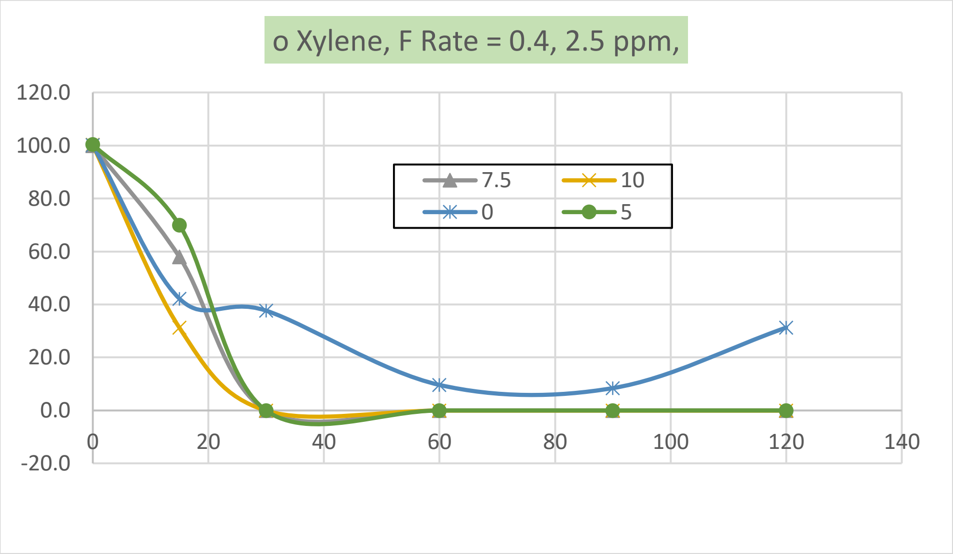
Response	Name	Units	Analysis	Min	Max	Mean	Std. Dev.	Ratio	Transform	Model
R1	Benzene	%	Polynomial	14.8	80.0	38.91	16.81	5.41	None	Reduced Quadratic
R2	Toluene	%	Polynomial	39.4	100.0	83.61	22.39	2.54	None	Quartic
R3	Ethyl Benzene	%	Polynomial	66.6	100.0	93.01	10.39	1.50	None	Cubic
R4	m&p-Xylene	%	Polynomial	89.9	100.0	98.62	2.88	1.11	None	Mean
R5	o-Xylene	%	Polynomial	43.9	100.0	95.54	13.87	2.28	None	Mean

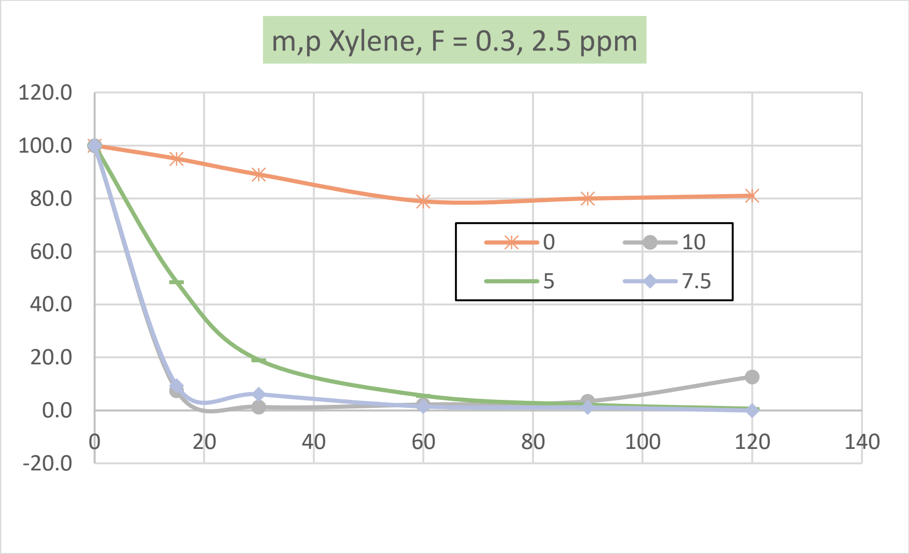
BTEX Removal

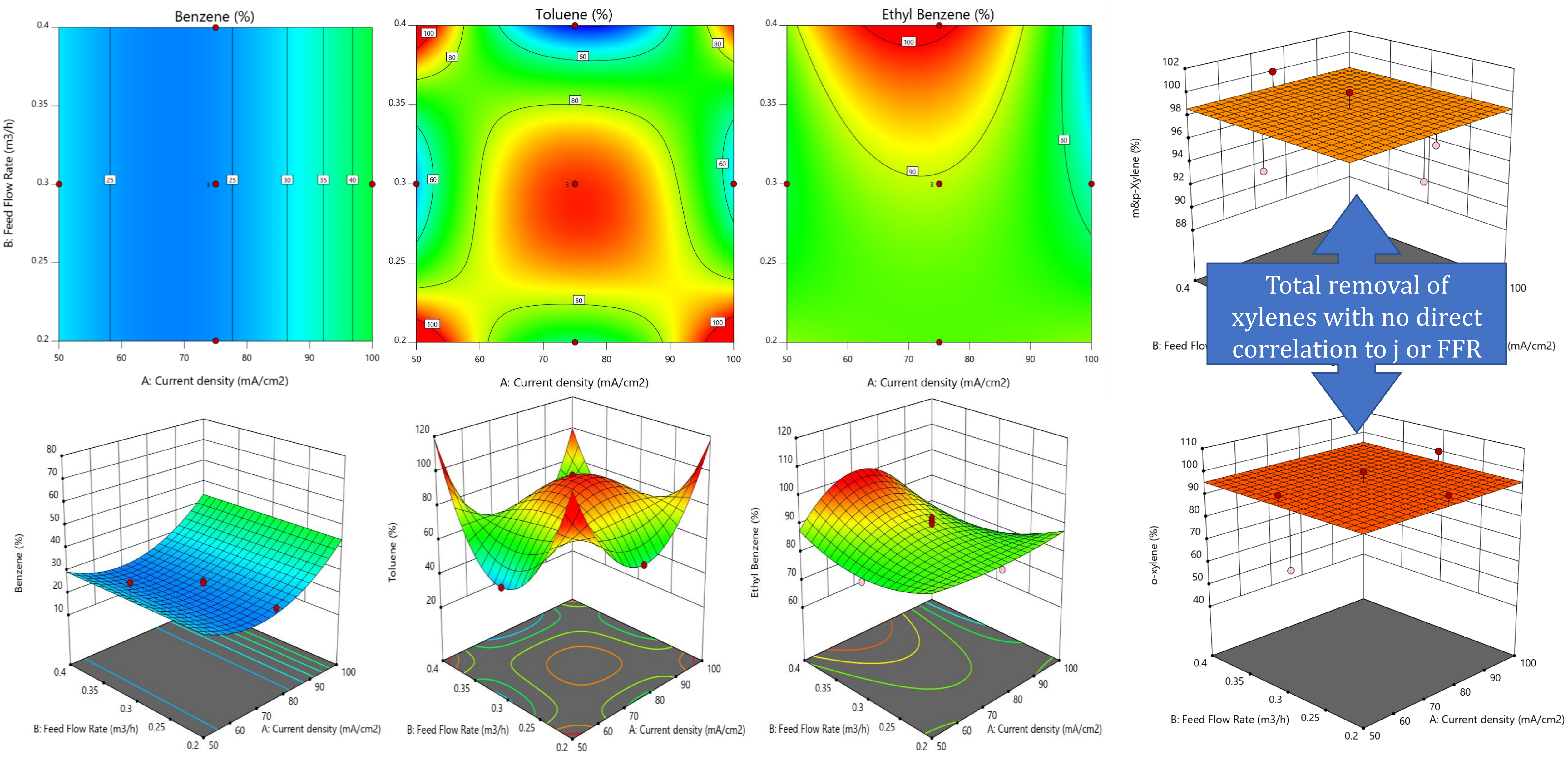
BTEX compounds removal as function of current (0-10 A)


Benzene, F = 0.4, 0.5 ppm


Toluene, F Rate = 0.2, 2.5 ppm


o Xylene, F Rate = 0.4, 2.5 ppm,


m,p Xylene, F = 0.3, 2.5 ppm



Total removal of xylenes with no direct correlation to j or FFR

a) Contour plots and b) 3D surface plots for the five BTEX molecules as function of the electric current (A) and feed flow rate (B). Experimental data correspond to 30 min of batch operation at [BTEX]=1.5 mg/L

BTEX Removal…

Summary of main experimental conditions and results (for electrolysis time 30 min)

Run	A: j (mA/cm²)	B: FFR (m³/h)	C: [BTEX] (mg/L)	%Benzene Removal	%Toluene Removal	%Ethyl Benzene Removal	%m&p-Xylene Removal	%o-Xylene Removal
1	100	0.4	0.5	61.2	100	100	100	100
2	75	0.3	1.5	22.9	97.9	90.3	100	100
3	50	0.4	2.5	38.3	100	100	100	96.3
4	100	0.2	2.5	34	100	100	99.9	100
5	75	0.3	1.5	25.3	98.1	92.4	100	100
6	50	0.2	0.5	40.6	99.8	100	99.9	84
7	75	0.3	2.5	24.6	58.5	100	93.8	100
8	50	0.3	1.5	37.4	50.8	80.4	95.6	100
9	75	0.3	0.5	55	99.9	100	100	100
10	75	0.4	1.5	14.8	39.4	100	100	43.9
11	50	0.4	0.5	52.5	99.9	100	99.9	100
12	100	0.3	1.5	42.4	54.6	75.7	89.9	100
13	100	0.4	2.5	52.1	63.2	66.6	100	100
14	50	0.2	2.5	29.3	100	100	100	100
15	100	0.2	0.5	80	99.1	100	99.8	100
16	75	0.3	1.5	24.6	96.8	91.1	100	100
17	75	0.2	1.5	26.5	63.4	84.6	97.7	100

Summary and Conclusion

- The performance of a novel process scheme, employing an electrochemical advanced oxidation treatment that couples anodic oxidation (AO), electro-Fenton (EF) and electrochlorination (ECL) has been investigated for degradation of phenol and BTEX present in high salinity waters.
- Contrary to expectations, EF reactions are not favored in high salinity waters as evidenced by the reduced phenol/BTEX mineralization efficiencies in the presence of ferrous iron.
- Feeding air to the cathodic electrode (GDE) reduced the degradation and overall process performance.
- The electrochemical treatment of strongly saline waters and of elevated chloride content resulted in an increased phenol and BTEX degradation/mineralization.
- Major phenol degradation by-products, identified during water treatment, including dichlorophenol, trichlorophenol, napthalene, THMs, were totally degraded under the highly oxidative conditions prevailing in the cell.
- Estimated energy consumption and cost of treatment of the investigated novel process, contrasted to those of other relevant technologies are encouraging.
- Currently, the research team is investigating the by-products of BTEX degradation by ECL.

Thank you