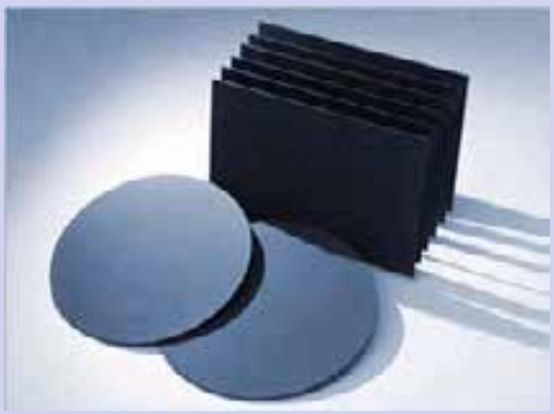
Advances in Diamond Electrochemistry: Applications in Industrial Wastewater Treatment

Water Arabia 2015



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Outline

- ✓ Introduction
- ✓ Electrochemical AOP for wastewater treatment
- ✓ The boron doped diamond (BDD) thin film electrodes
- ✓ Applications of BDD in industrial wastewater treatment
- ✓ Challenges and Prospects

Introduction

- 21th Century has witnessed record increase in global urbanization and industrialization which let to dramatic increase in industrial wastewater production

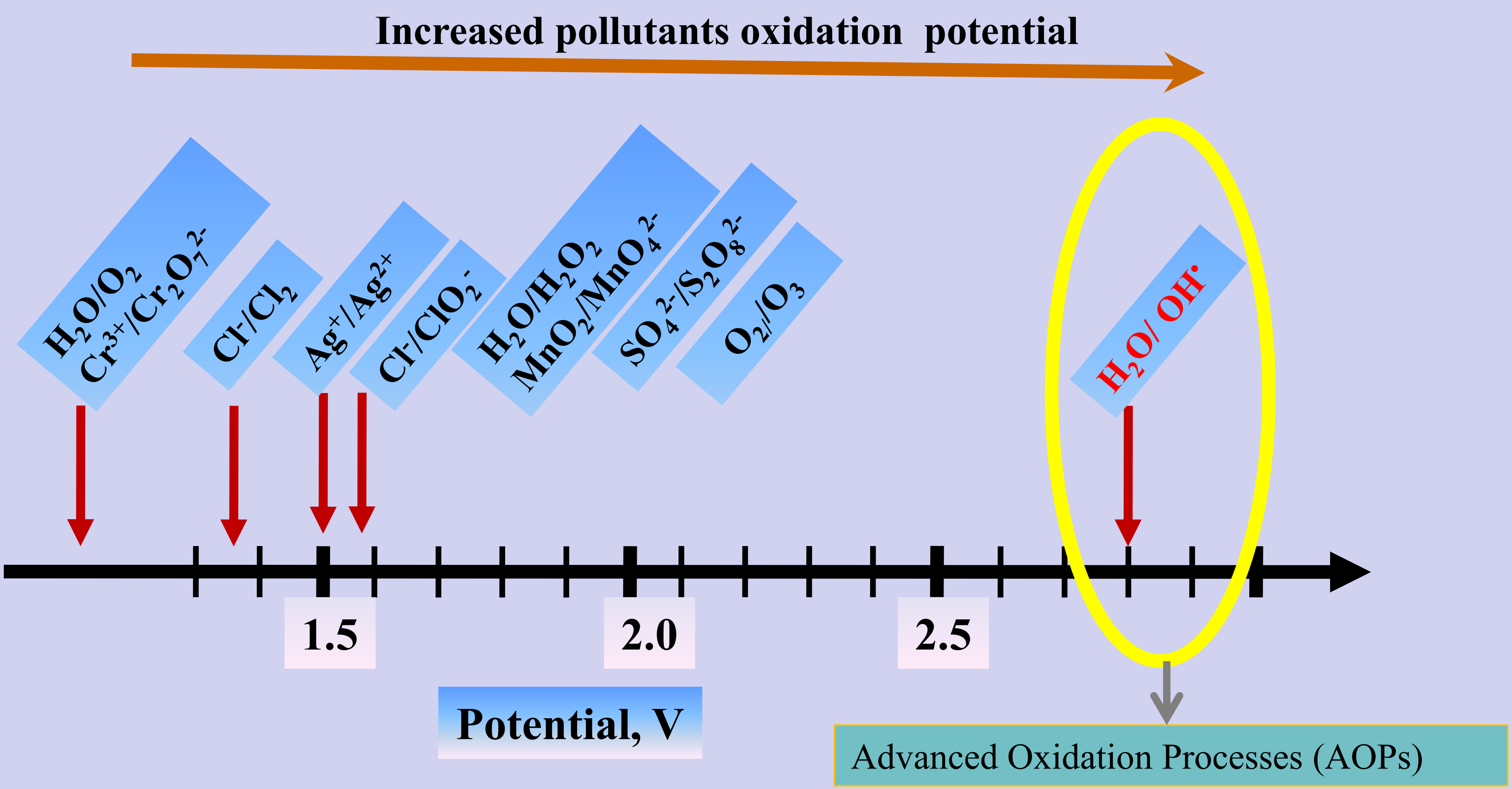
- Improper discharge of wastewater containing toxic substances is detrimental to the ecosystem and sustainable development

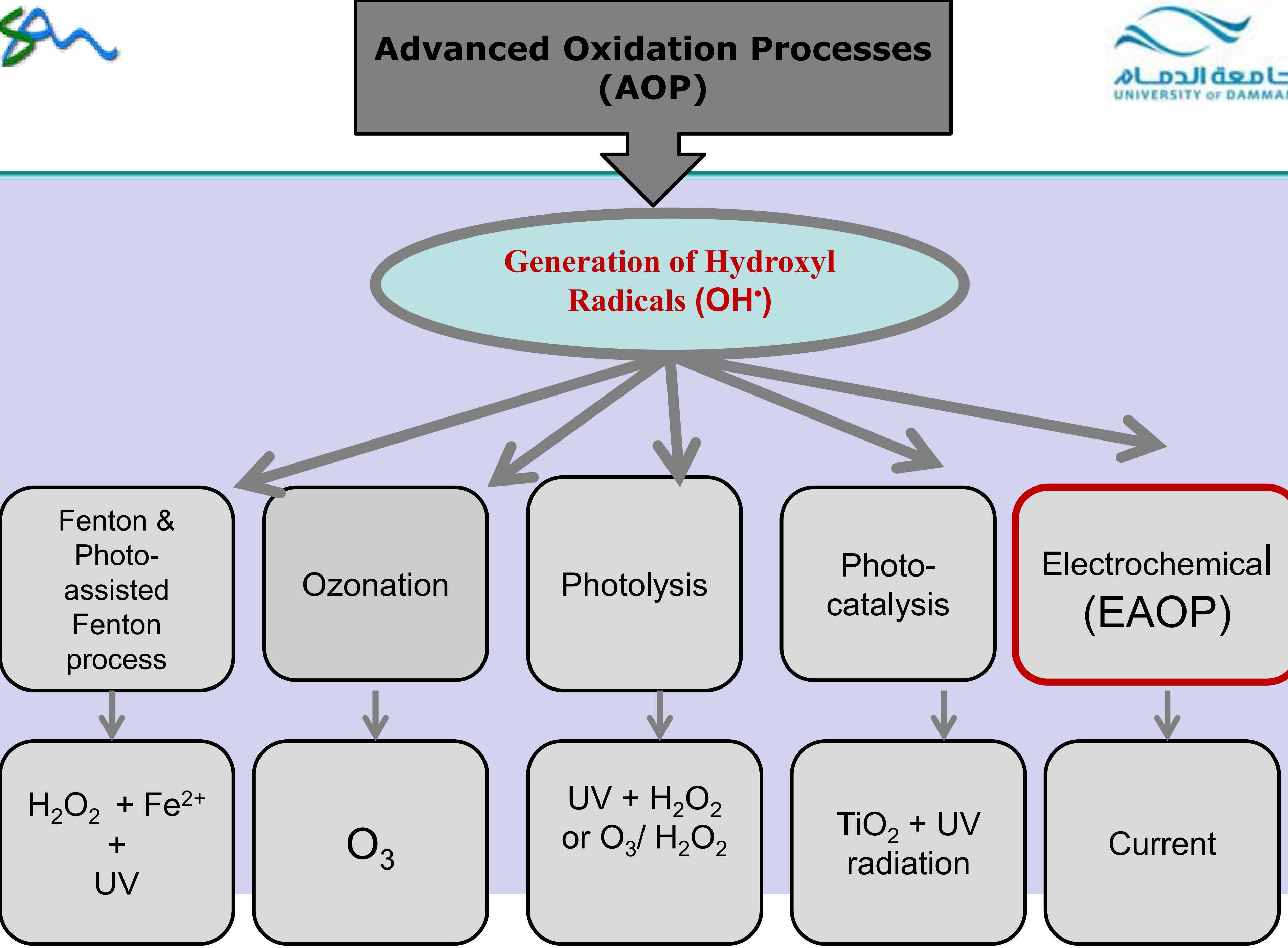
- Increased demand for water conservation and compliance with stricter environmental regulations have raised the awareness and the need for cost-effective wastewater treatment schemes

Wastewater Treatment Technologies

- ✓ Emergence of several of biological, physical and chemical treatment technologies
- ✓ Biological technologies are more preferable due to their low cost and cheaper materials requirements
- ✓ Due to bio-refractory nature of some pollutants a number of innovative technologies emerged to supplement or replace conventional biological technologic
- ✓ Chemical oxidation techniques became amongst most attractive techniques for effective decontamination of industrial wastewater

Chemical Oxidation Techniques




Advanced Oxidation Processes (AOP)
Generation of Hydroxyl Radicals (OH•)
Fenton & Photo-assisted Fenton process
Ozonation
Photolysis
Photo-catalysis
Electrochemical (EAOP)
H_2O_2 + Fe^{2+} + UV
O_3
UV + H_2O_2 or O_3/ H_2O_2
TiO_2 + UV radiation
Current

Merits of EAOP

✓**High efficiency with proper choice of anode material and cell design**

✓Environmental compatibility: the main reagent used is electron

✓May require no additional of chemical reagents

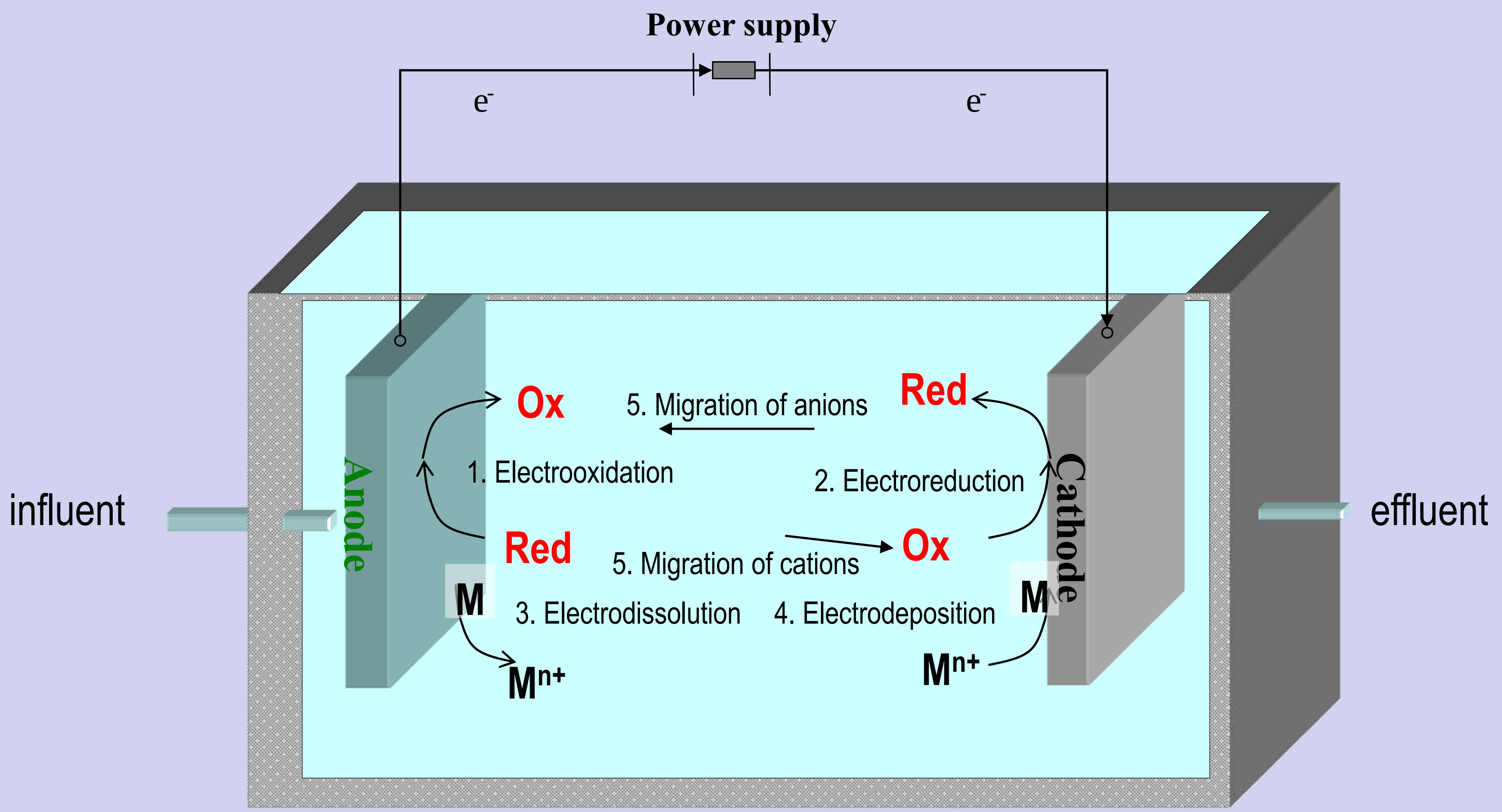
✓Operation at room temperature and atmospheric pressure

✓The efficiency can be easily increased by promoting indirect processes

✓Easy operation amenability to automation

✓Pollutants can be completely destroyed: no by-product or residue production

EAOP for wastewater Treatment



Challenges to Wastewater Treatment Using EAOP

✓The difficulty in selecting suitable electrode material:

- Low activity toward secondary reactions(e.g., oxygen evolution)
- High activity toward pollutants oxidation
- Low cost-to-lifetime ratio

✓Selection of most appropriate/optimal cell design and operating conditions

- Simple and durable mechanical design
- Homogenous current distribution
- Enhanced mass transfer

✓Other substances presence in the wastewater

✓ Accumulation of intermediate byproducts

Typical Anodic Materials for Wastewater Decontamination

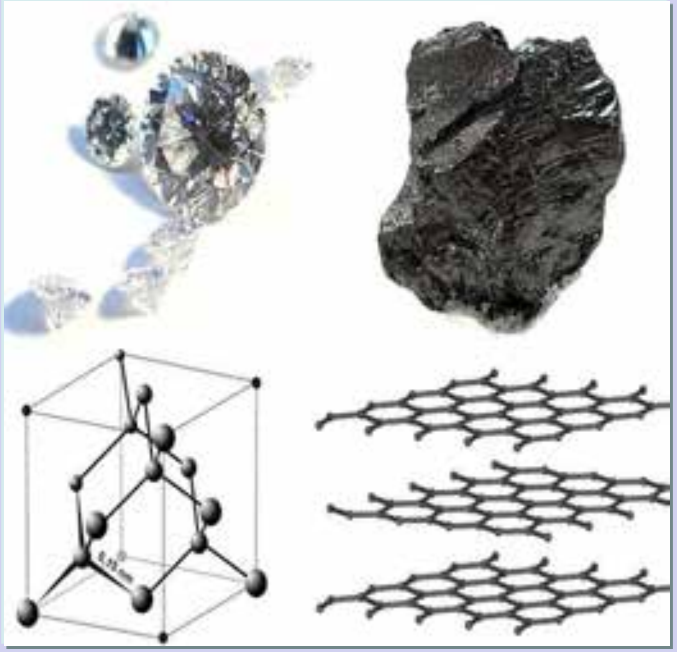
Electrode Type	Example Electrode	Merits	Notable Demerits
Carbon based	Graphite	✓Cheap ✓Availability	✓Accumulation of stable intermediates ✓Low over-potential ✓Low current efficiency
	Glassy carbon	✓Cheap	✓Loss of activity due to surface fouling ✓Low over-potential ✓Low current efficiency
Metal	Stainless steal	✓Cheap ✓Electro-coagulation	✓Low overpotential ✓Short life ✓Residue generation ✓Low current efficiency
Noble Metals	Platinum, gold, rhodium, and palladium	✓Improved efficiency	✓Loss of activity due to surface fouling ✓Accumulation of stable intermediates ✓Low over-potential ✓Low current efficiency ✓Expensive

Anodic Materials for Wastewater Treatment

Electrode Type	Example	Merits	Demerits
Metal Oxide	SnO_2	✓ Improved overpotential	✓Limited service life ✓Release of toxic ions ✓Low current efficiency
	PbO_2	✓Improved overpotential	✓Release of toxic ions
	RuO_2	✓Improved overpotential	✓Accumulation of stable intermediates ✓Low efficiency
	IrO_2	✓Improved overpotential	✓Selective oxidation ✓Accumulation of stable intermediates
DSA-Type	Ti/SnO_2	✓High overpotential ✓Improved current efficiency	✓Limited service life

The Natural Diamond

- ✓ Carbon based material
- ✓ Precious material occurring as natural mineral deposit
- ✓ A transparent crystal of tetrahedrally bonded carbon atoms that formed a face centered lattice structure
- ✓ The strongest known material
- ✓ Highest thermal conductivity
- ✓ An excellent electrical insulator with high resistivity



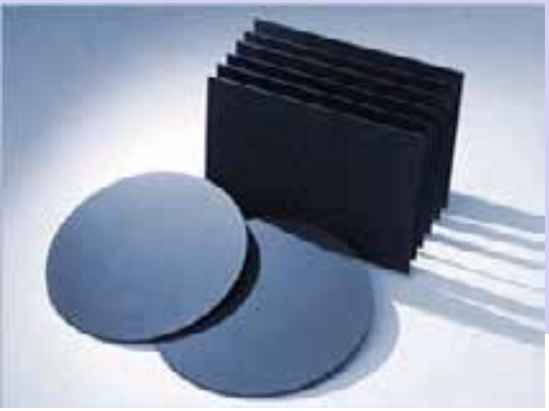
Synthetic Thin-film Diamond Surfaces

- The large band gap of un-doped diamond makes it electrically insulating and unsuitable electrode material
- Advances in electrochemistry let to invention of synthetic diamond film conductive
- Diamond films surfaces are rendered conductive by doping with boron, nitrogen, sulfur and phosphorous
- Majority of diamond electrodes currently in use are doped with boron
- Boron has low charge carrier activation energy compared to other dopants
- Boron doping leads to a p-type semiconductor while others form n-type semi-conductor

Synthetic Thin-film Diamond Surfaces

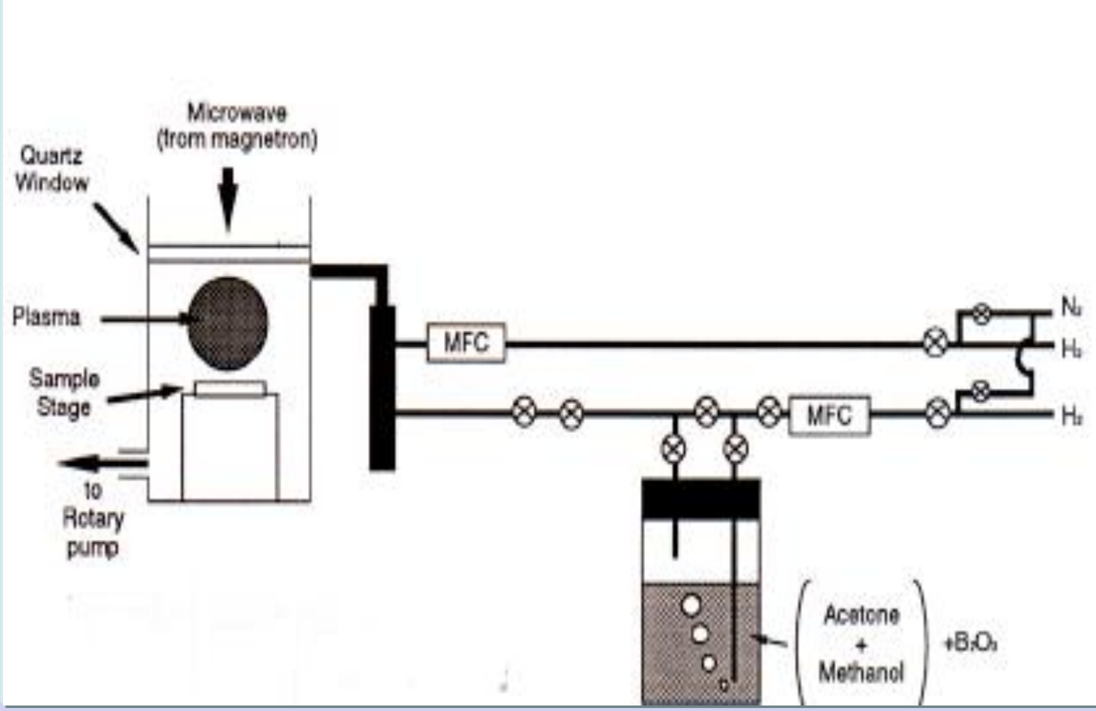
Two major methods for artificially depositing or growing thin diamond films on based materials are

Method	Pressure	Substrate temperature
High Pressure High Temperature (HPHT)	50-100 kbar	1500-2000^{o}C
Hot Filament Chemical Vapor Deposition (HFCVD)	< 27x10^{-5} kbar	750-850^{o}C

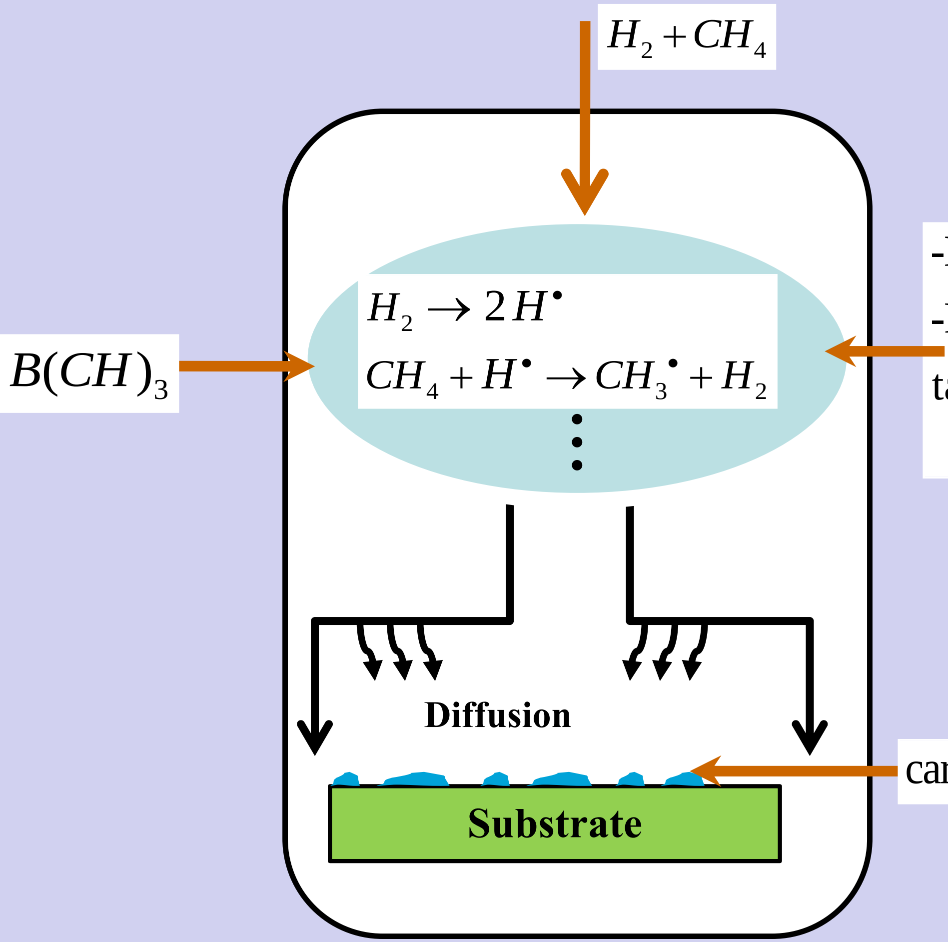


BDD Electrodes using HFCVD

- Methane (0.5% - 3% CH_4 in H_2) or acetone/methane mixture as carbon source
- Diborane or trimethyl borane used to introduce boron into the diamond material during film growth a boron containing substance is added to the deposition gas mixture
- Hydrogen as the carrier gas



BDD Electrodes using HFCVD

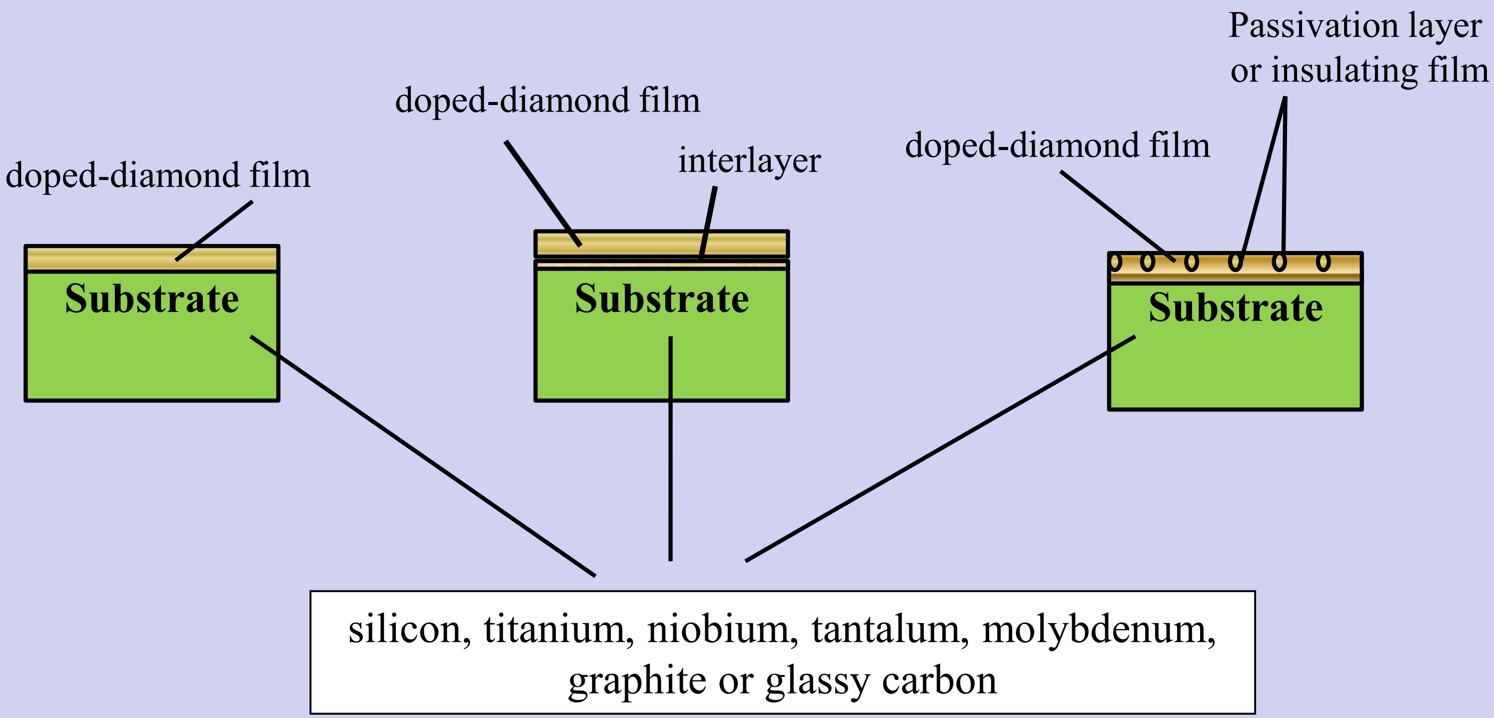


-High-temperature plasma generated using microwaves

-Radicals produced on the surface of a heated tungsten, tantal or rhenium wire

carbon atoms deposit/grown to form thin-film diamond crystals

BDD Electrodes using HFCVD



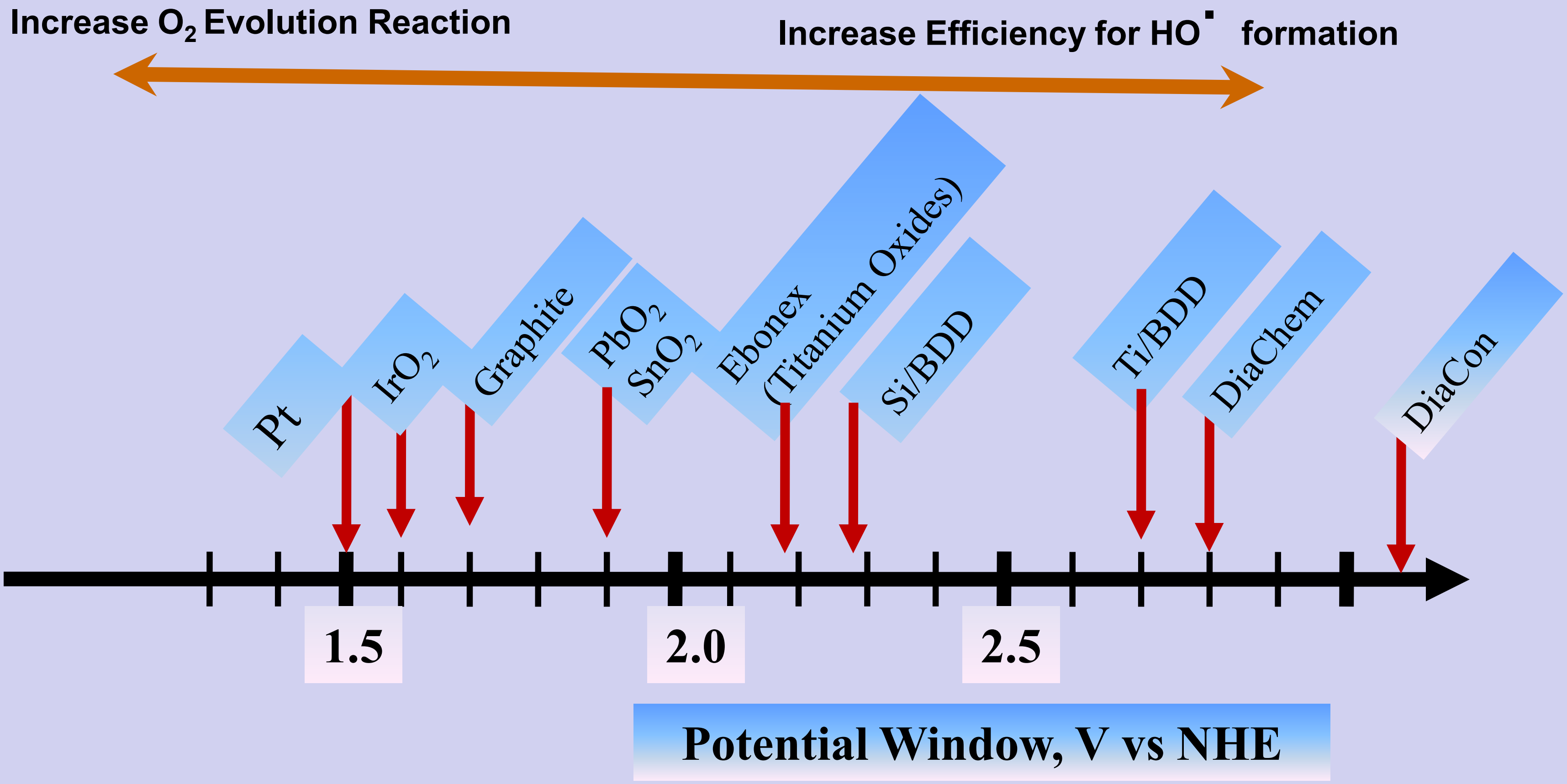
✓Wide range of boron doping levels: Semiconductors

✓Heavily doped films: Metallic conductivity

Oxygen Evolution for Different Anodes

$$M(^{\bullet}OH) \rightarrow M + \frac{1}{2}O_2 + H^+ + e$$

$$M(^{\bullet}OH) + R \rightarrow M + mCO_2 + H_2O + H^+ + e^-$$



Characteristics of BDD Electrodes

- ✓ High electric conductivity
- ✓ High potential window for $OH^{\bullet}$ production with higher current efficiency (low oxygen evolution)
- ✓ Chemically inert, mechanically robust and very high stability to corrosion in aggressive environment
- ✓ Operating conditions ,pH ~ 14, temperatures ~ 500°C and current density ~ $500 mAcm^{-2}$
- ✓ Non-Porous with low adsorption phenomena and high fouling resistance
- ✓ Stable as anode and cathode
- ✓ Complete mineralization of organic and inorganic impurities in water and wastewater
- ✓ Low ratio Cost/lifetime
- ✓ Morphology: varying shapes and sizes

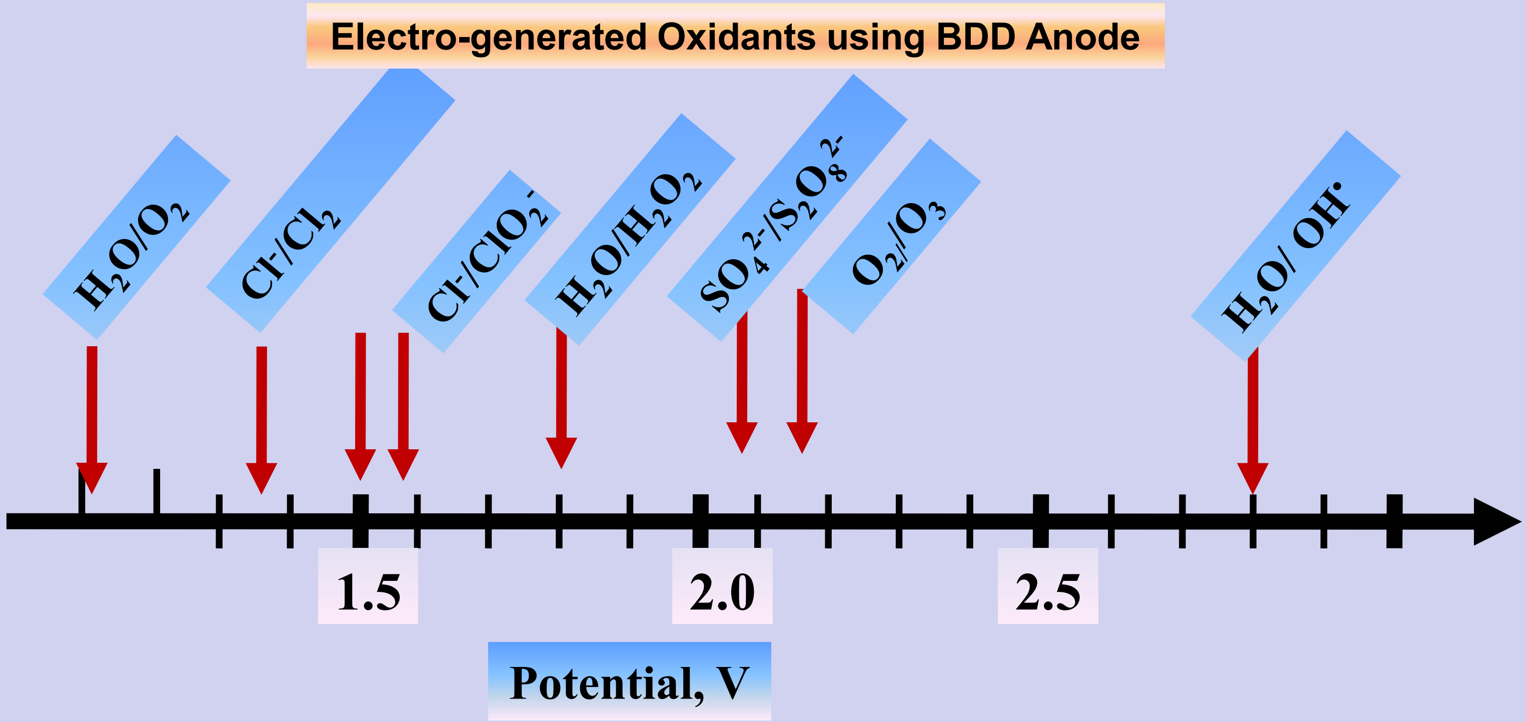
Applications of BDD Elecrodes

- ✓ Degradation of toxic and biologically refractory organic compounds
- ✓ Treatment of actual industrial wastewater at bench and pilot scale
- ✓ Efficient water and wastewater disinfection
- ✓ Production of strong oxidants in-situ
- ✓ Electro-analysis of chemical compound
- ✓ Electro-synthesis of chemical compound
- ✓ Galvanic applications such as lead free chroming or recycling processes

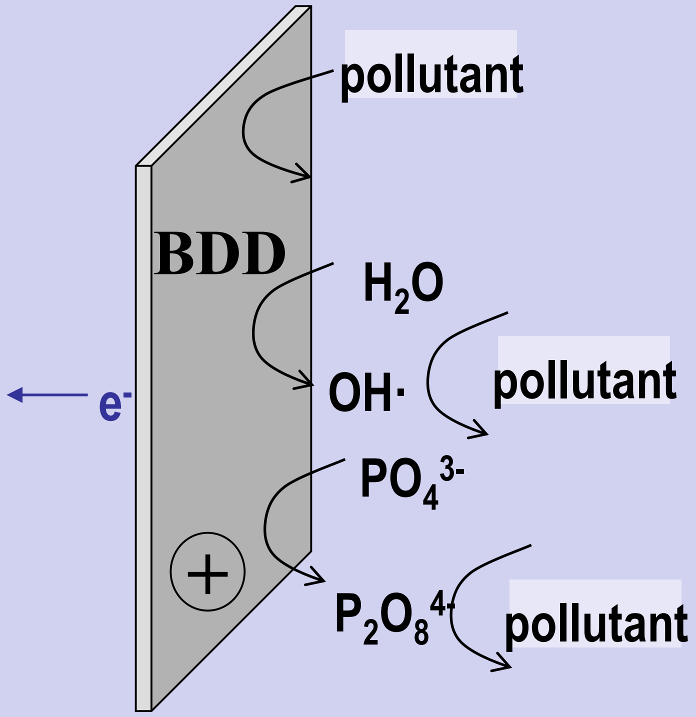
EAOP for Wastewater Decontamination Using BDD Anode

✓High production of OH• radicals electrochemically in an anodic reaction in the wastewater to be treated

✓Other oxidants can be produced from appropriate ions in the wastewater or added electrolyte(s)



Techniques for Wastewater Treatment using BDD Anode

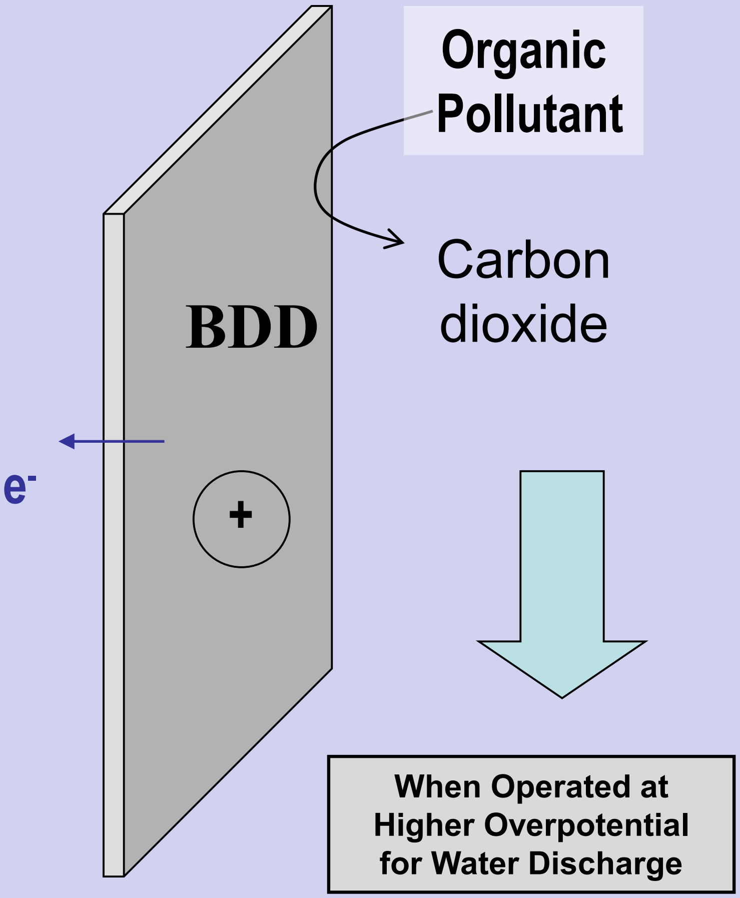


1. **Direct electrolysis**
   Oxidation of the pollutant on the electrode surface

2. **Advanced oxidation processes**
   Generation of large amount of OH·

3. **Chemical oxidation**
   Several in-situ oxidants formed from the salts contained in solution

BDD: High Efficiency Electrodes

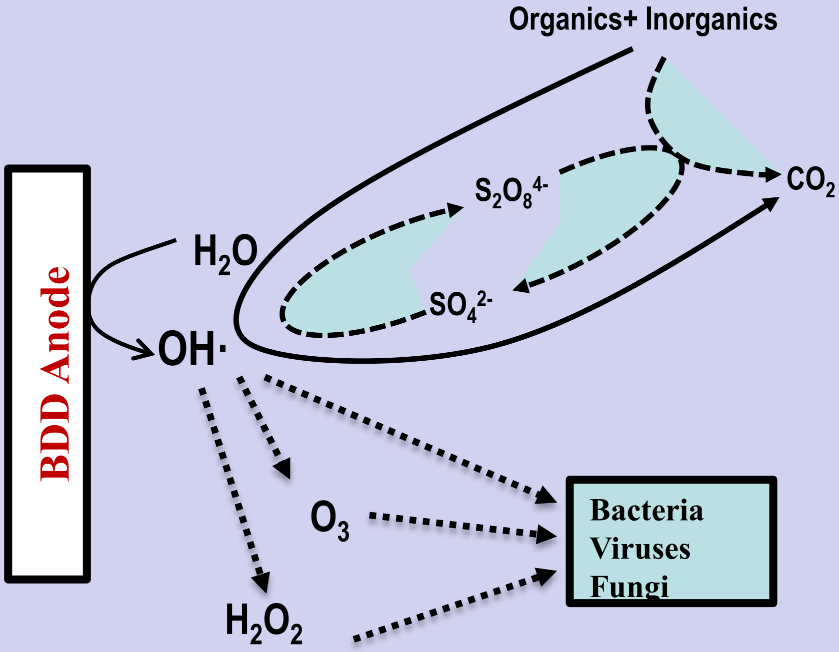


HARD OXIDATION CONDITIONS

- Few or no intermediates are formed
- Large conversion to carbon dioxide
- Large current efficiencies only limited by mass transfer
- Large amount of OH· generation
- Low side reactions
- Formed polymer on surface can be destroyed to restore surface activity

EAOP using BDD Anode Potentials

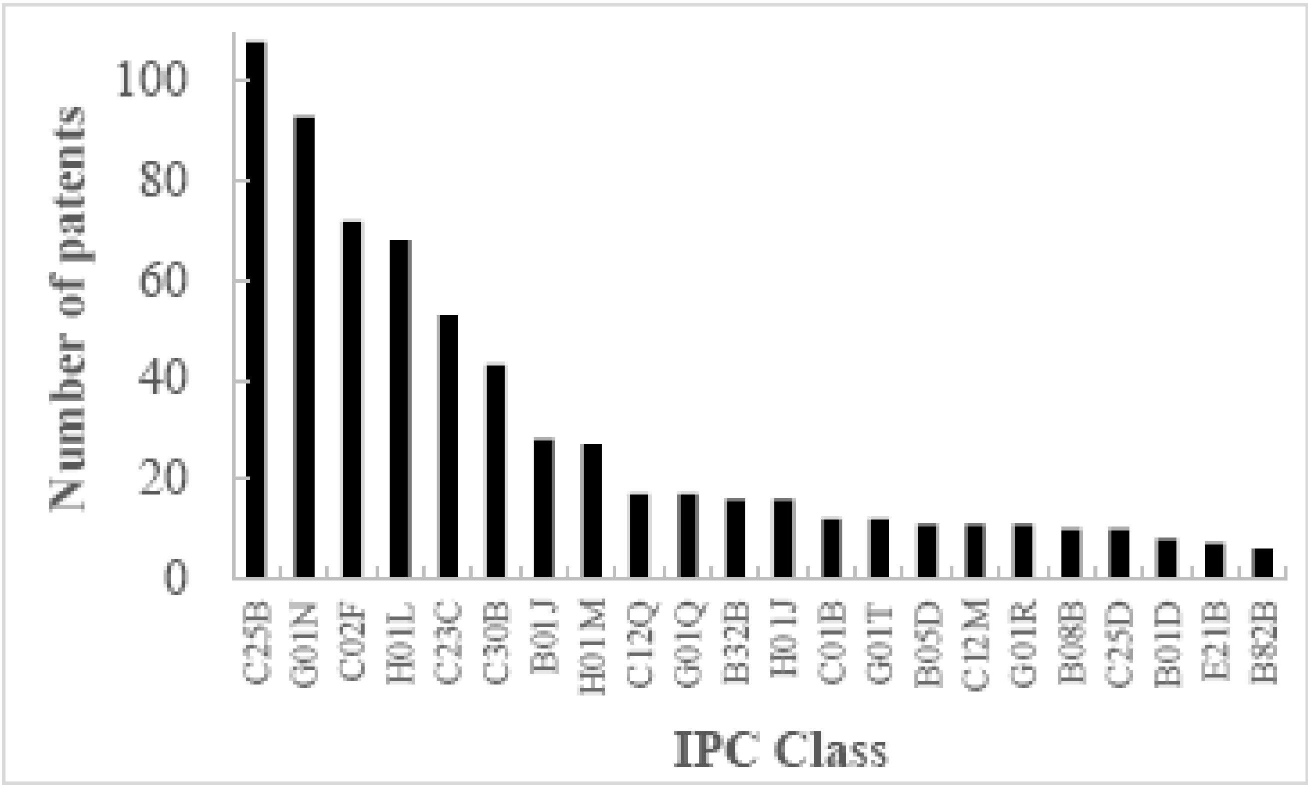
- Successful TOC / COD – removals were demonstrated from industrial watewater
- Halogenated Organics
- Heavy metals reduction- e.g Cr(IV)
- Phosphorous Organics
- Phenolic compounds
- Color-dyes
- Aniline
- Bacteria, viruses and fungi-Disinfection
- EDTA



Some applicants list of patents related to wastewater treatments by electro-oxidation with BDD

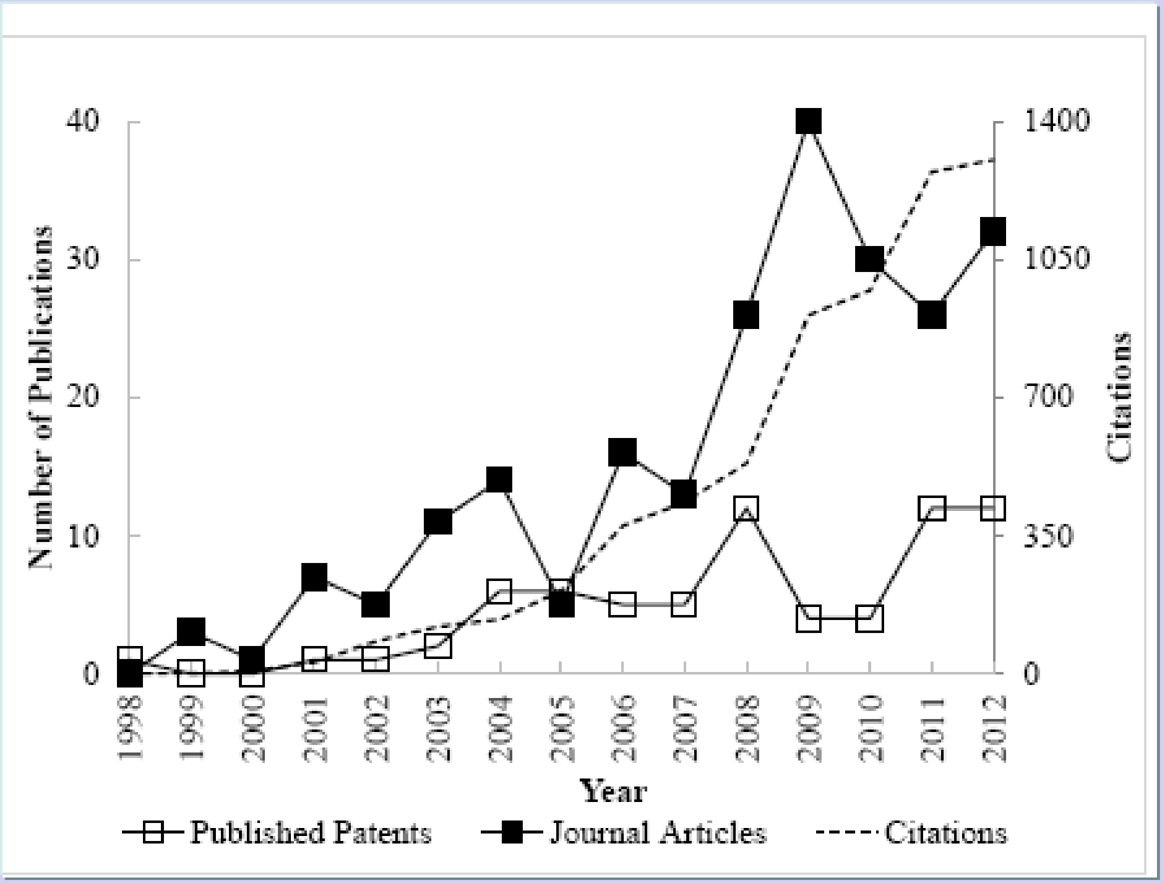
Applicant	Number of granted patents or applications *	Country of origin
Permelec Electrode LTD	4	Japan
Pro Aqua Diamantelektroden Produktion	4	Austria
Sumitomo Electric Hardmetal COR.	3	Japan
Watkins Manufacturing Corporation	3	EE.UU
Element Six LTD	3	Luxemburg
Industrie De Nora S.p.A.	2	Italy
Michigan State University & USA Energy Depart.	2	EE.UU
Kurita Water Industries LTD	2	Japan
Schwartzel, David, T.; Fraim, Michael, L.	2	EE.UU
A-Zone Technologies LTD	1	U.K
Battelle Energy Alliance, LLC	1	EE.UU
Deshmukh, Prasanna	1	India
Dow Global Technologies INC	1	EE.UU
Fuji Photo Film Co LTD	1	Japan
Kabushiki Kaisha Kobe Seiko Sho	1	Japan
Linxross INC	1	Japan

Patents Applications by IPC (1998-2012) Industrial Wastewater Treatment using BDD



No. of Patents Applications by 4-digit International Patent Classifications (IPC) [Juan et al. 2014]

Trends Industrial Wastewater Treatment using BDD (1998-2012)



Trends in published patents, articles and citations related to treatment of Wastewater using BDD [Juan et al. 2014]

Applications of BDD in real industrial WW treatment

Industry	Wastewater characteristics	Treatment efficiency	Ref.
Automotive	3200mg/ l COD	CE= 65% Residual COD 400mg/L	(Troster et al., 2002
Automotive	A condensate from a cooling lubricant cycle in motor fabrication initial COD 2500 mg/l	CE > 90%; COD >500 mg/l	(Troster et al., 2002)
Paper and pulp	pH 6.6, conductivity 2.9 mS/cm, chloride concentration 528 mg/l and COD 4023 mg O_2/l.	COD 100%	(Alexander et al., 2003)
Motor	pH 5.19; conductivity, 3.74. COD=3200mg/L;hardness 5.2 dH, chloride; 135mg/L	COD < 20 mg O2/l CE 85% for COD >500 mg/l CE 50% for for COD < 500 mg/l	(Alexander et al., 2003)
Motor industry	pH 6.62; conductivity, 5.67. COD=1496mg/L;hardness less than 1 dH, chloride; 43mg/L	Residual COD 20 mg O_2/l 26	(Alexander et al., 2003)
Fenton-treated refractory olive oil mill	COD of nearly 700mg/L The conductivity= 2.5mScm−1. pH 7.13	TOC and COD decrease with time down almost to zero	(Cañizares et al., 2006)
136 factories from industrial park	Biological & electrocogulation pretreated COD=250 mg/l; Color= 200 Pt-Co units; TOC= 557 mg/L	TOC 42.4%; Color 100% COD 98%; SEC 0.112 kWh	(García-García et al.)
Industrial WWT plant raw sludge	pH 3.01; Total solids, % 1.24; COD 12,200mg/L; sCOD 2120, mg L^{-1}	COD 27% sCOD 56%	(Barrios et al.) 2014
Olive-oil mills	3000 mg dm_3 of COD and 840 mg dm_3 of TOC. Its conductivity is 2.29 mS cm_1 and the pH is around 6.	Complete mineralization with high current efficiencies	(Cañizares et al., 2007)
Mustard tuber factory	pH 6.50 Conductivity (mS cm−1) 26.4 COD (mg L−1) 3,250 TOC (mg L−1) 980 NHþ4 -N (mg L−1) 215	ammonium was completely removed, and 80.4% of COD was electrodegraded, with specific energy consumption of 45.8 kWh m−3.	(Sheng et al., 2014)
Metal Plating plant	chromate-bearing industrial wastewater Cr(VI) mg L-1; pH 3.7 Electrical Conductivity (mScm1) 25.6	complete reduction of 180 mg Cr(VI)/L in 25 min, with 40% less sludge produced	(Velazquez-Peña et al., 2013)

Applications of BDD in real industrial WW treatment

cork-Processing	COD 2000mg?L TPh 142mg/L; pH 6.5-7; conductivity 0.7-0.77 mS/cm	after 8 h, reductions greater than 90% were achieved for COD, dissolved organic carbon, total phenols and colour	(Fernandes et al., 2014)
dairy industry	cheese whey diluted with domestic sewage; pH 5–5.5; COD 75–100 g/L; BOD5 23–28 g/L; DOC 8–10 g/L; NH4-N 40–50 mg/L	COD removal was 97 and 89 % after 2 h	(Katsoni et al., 2014)
Petrochemical industry	oil is separated from Initial COD 2,746mg L^{-1}; 63.88 µS cm−1;pH 7.9	76.2- 98.7 % of COD removal	(Vieira dos Santos et al., 2014)
Petrochemical industry	Pretreated produced water initial COD 1,588 mg L−1; pH7.5 ;Conductivity =4.64 µS cm−1; 2.7 mg L^{-1} phenol and 15 mg L^{-1} oils and grease	50.3- 59.1 % of COD removal	(Rocha et al., 2012)
Petrochemical	Produced water (fresh, brine and saline) COD 250-11,541mg/L TOC 458-15,015 mg/L Conductivity 0.61-143.9 mS cm_1 pH 6.87-7.03 salinity 78.8 -43170mg/L	2 hours Fresh PW: COD 100% TOC 40-90% 4 hours Brine PW: COD 100% TOC 92-99% Saline PW after 8hours COD 44% ; TOC < 37%	(da Silva et al., 2013)
Petroleum refinery	Phenol concentration 192.9 mg/L COD of 590 mg/L. Electrical conductivity 15.63 mS/cm.	96.04% COD removal 99.53% Phenol removal	(Yavuz et al., 2010)
Steel plant	COD mg/L 120–190 TOC mg/L 25–36 Conductivity µs/cm 22300 TDS mg/L 14745	COD 100% in 1.5 hour at 25 mA/cm2	(Zhou et al., 2011)

Commercial BDD Electrode Cell for Wastewaters Treatment

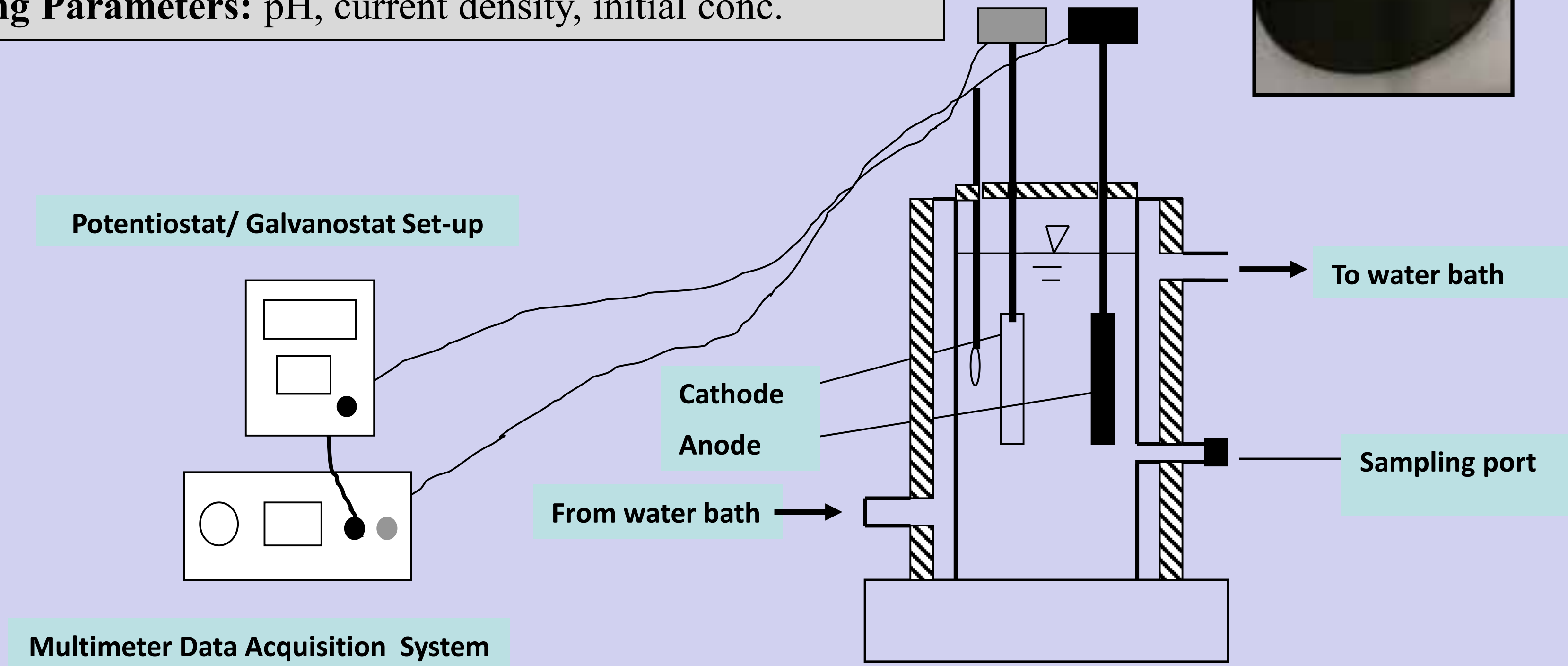
- ✓ Batch recycling reactor
- ✓ Tank Capacity 250-1000L

Large Industrial Cooling Water Disinfection (Rychen et al 2010)

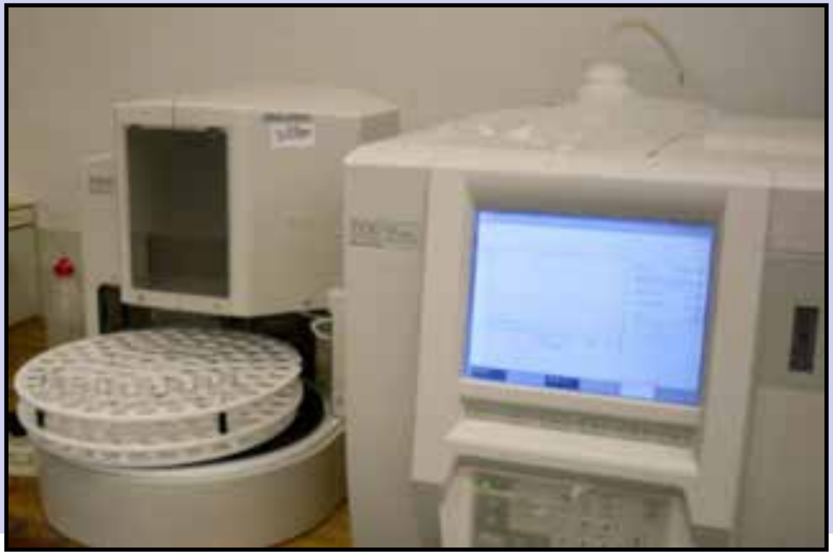
- ✓ 7.5 m3/h; Continuous operational run 2-3 years with good feedback from costumers
- ✓ Cost-effectiveness

Treatment of Phenolic Wastewater Treatment

Anode: Ni/BDD Electrode 10 cm diameter
Cathode: Graphite 10 cm diameter
Reactor: 2 liters capacity, batch
Wastewater constituents: Phenol, NH_4^+, S^{2-}, CN^-
Operating Parameters: pH, current density, initial conc.

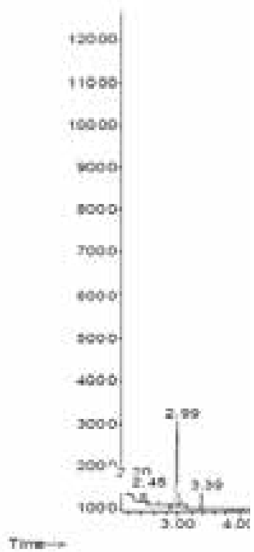


Phenol, Oxidation Byproducts,TOC and COD Analyses



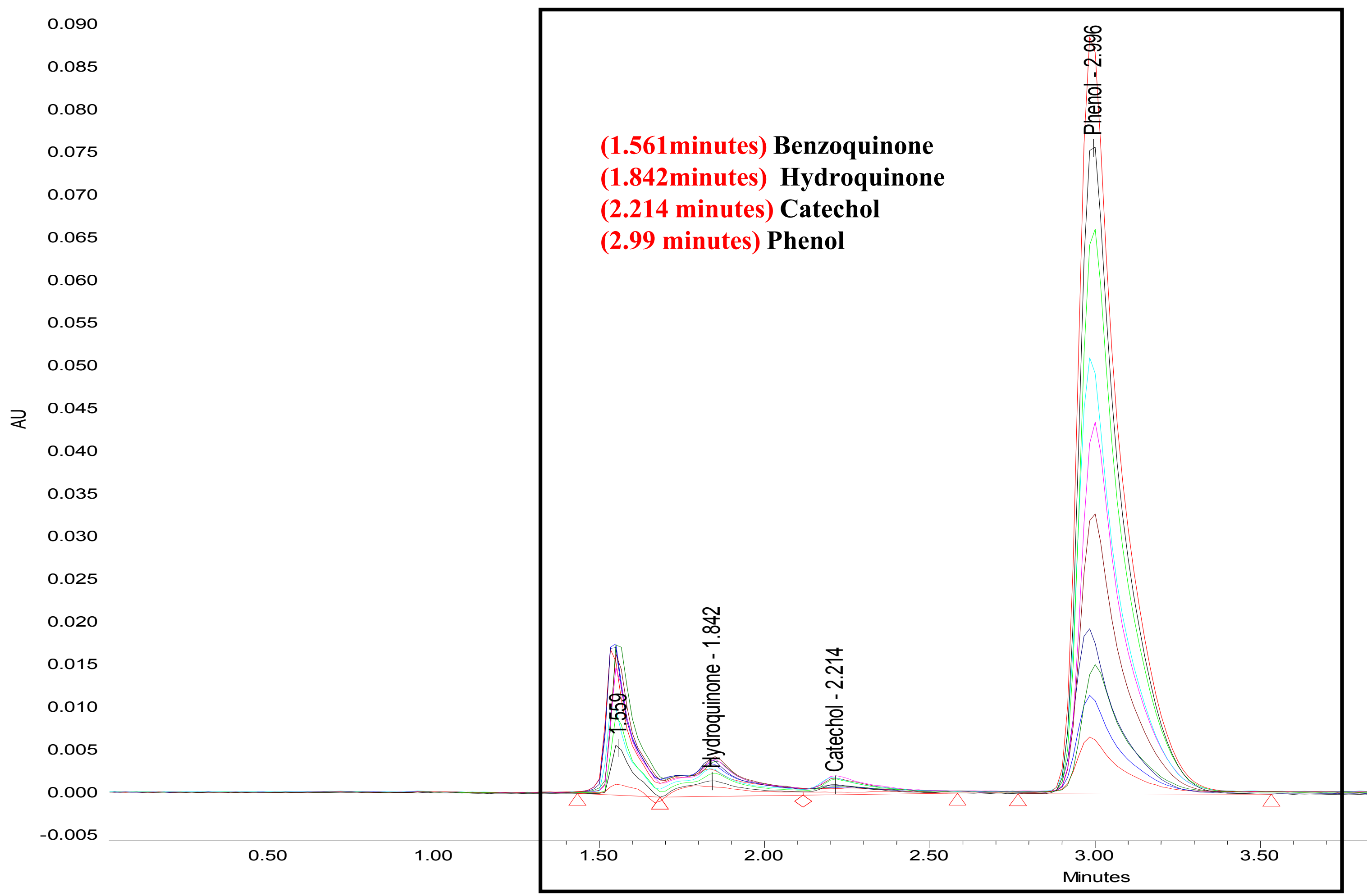
Zero Sludge Production

Quantitative and Qualitative Analyses

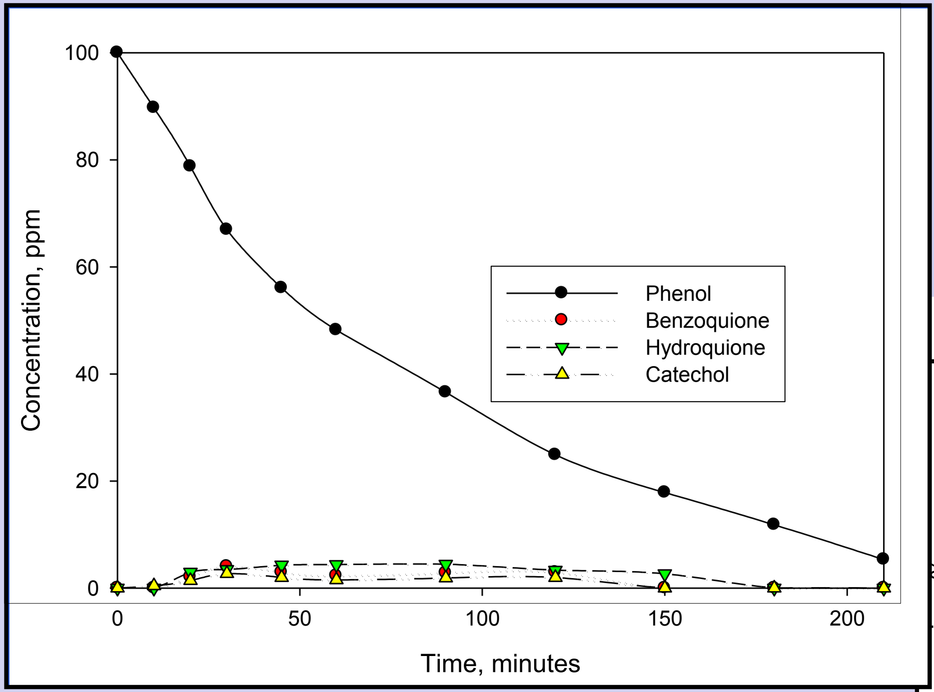


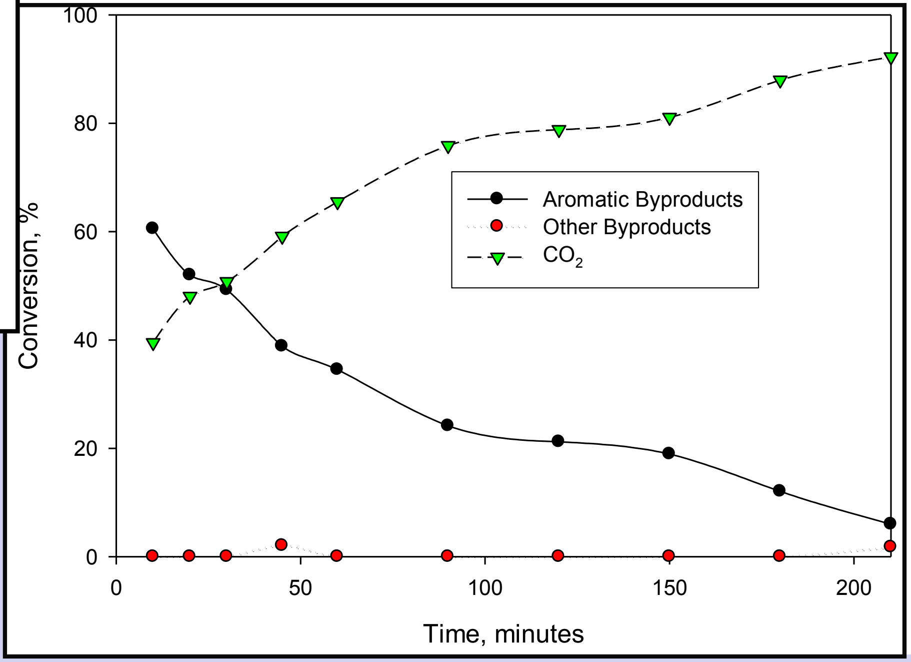
GC-MS Chromatogr

- (2.45 minutes) (1) Propanoic acid, 2-
- (2.58 minutes) (1) Dimethylamine (C2H
  (4) Carbonic acid dimethyl ester (C3H6O
- (3.39 minutes) (1) Cyclohexanethiol (C
- (5.37 minutes) Phenol
- (10.76 minutes) p-Benzoquinone



Assessment of Phenol Mineralization





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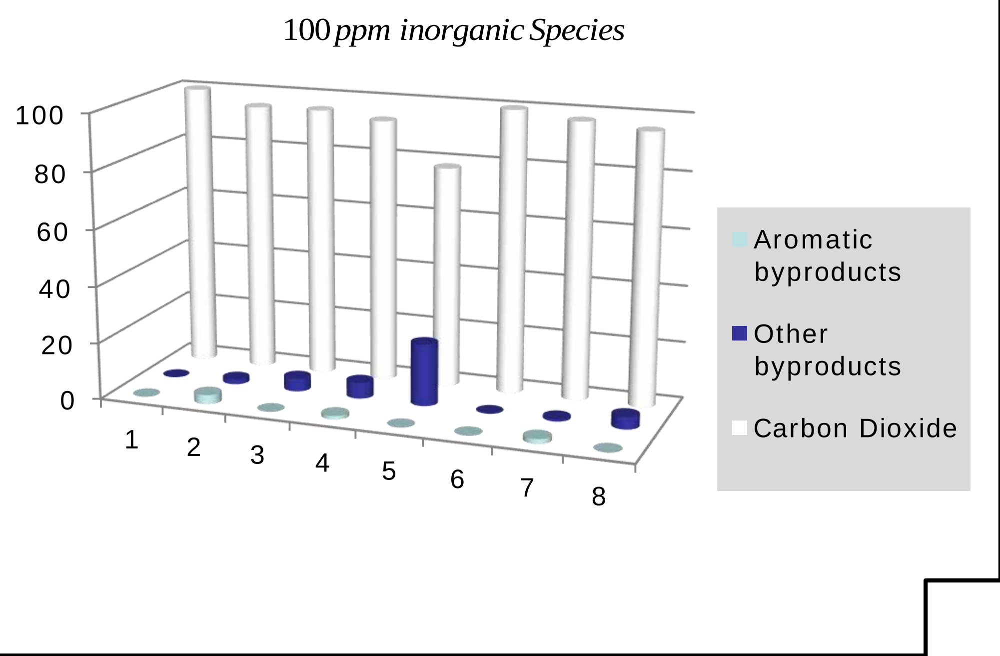
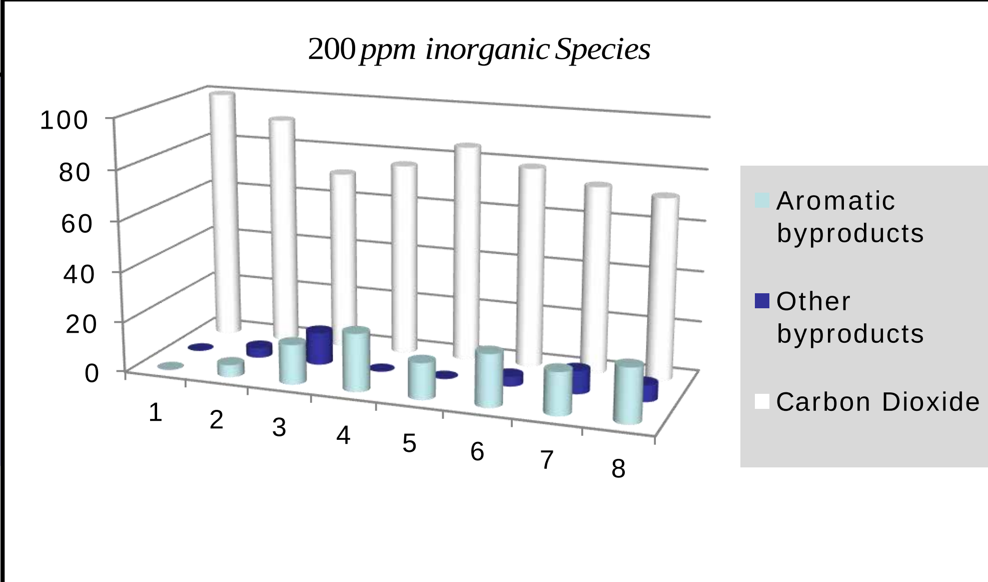
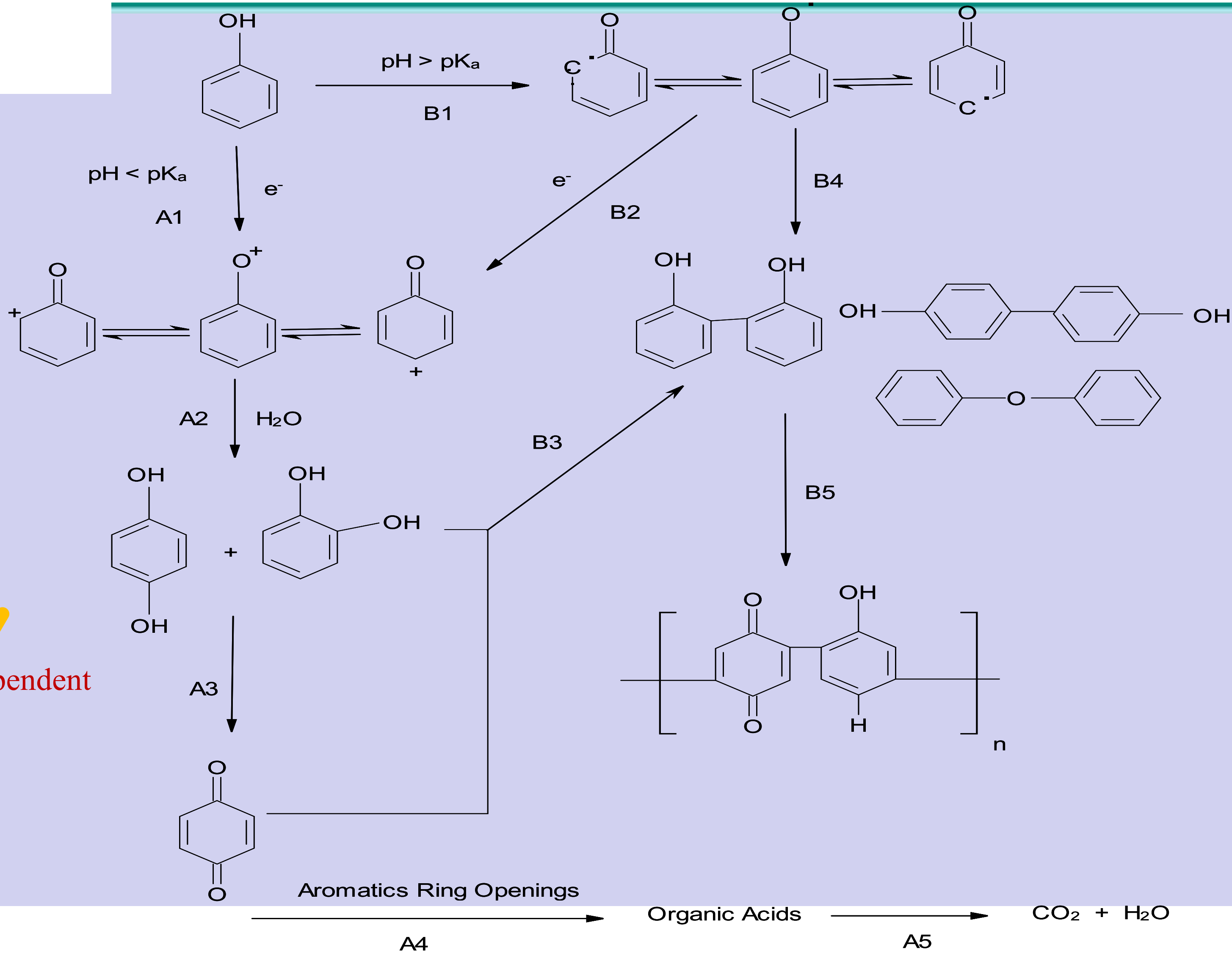


1. Phenol,
2. Phenol, NH_4^+
3. Phenol, CN^-
4. Phenol , S^{2-}
5. Phenol, NH_4^+, S^{2-}
6. Phenol, NH_4^+,CN^-
7. Phenol, CN^-, S^{2-}
8. Phenol, NH_4^+, S^{2-}, CN^-



Pathways for Phenol Mineralization

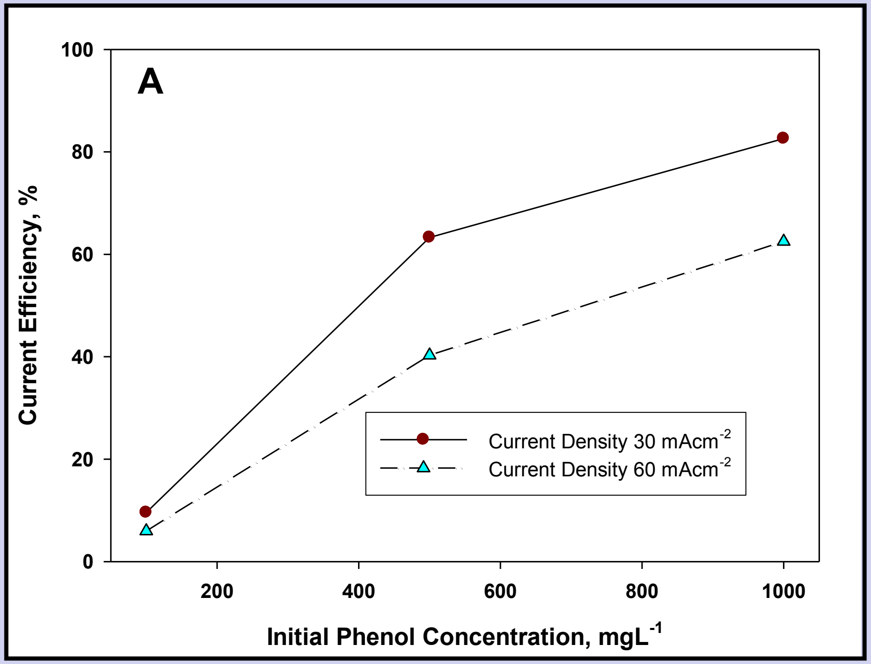
High pH; concentration dependent

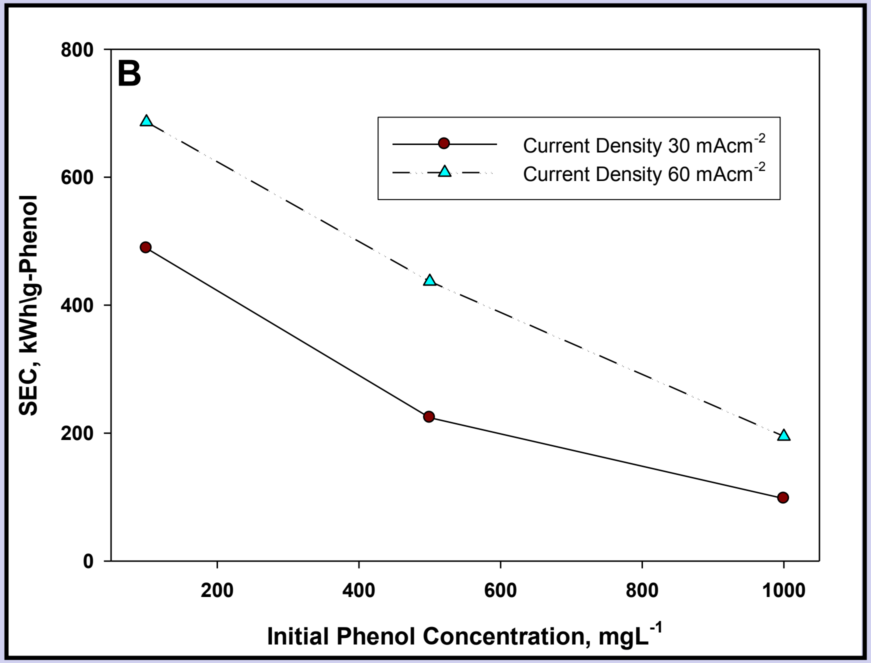


✓Low pH

✓Not concentration dependent

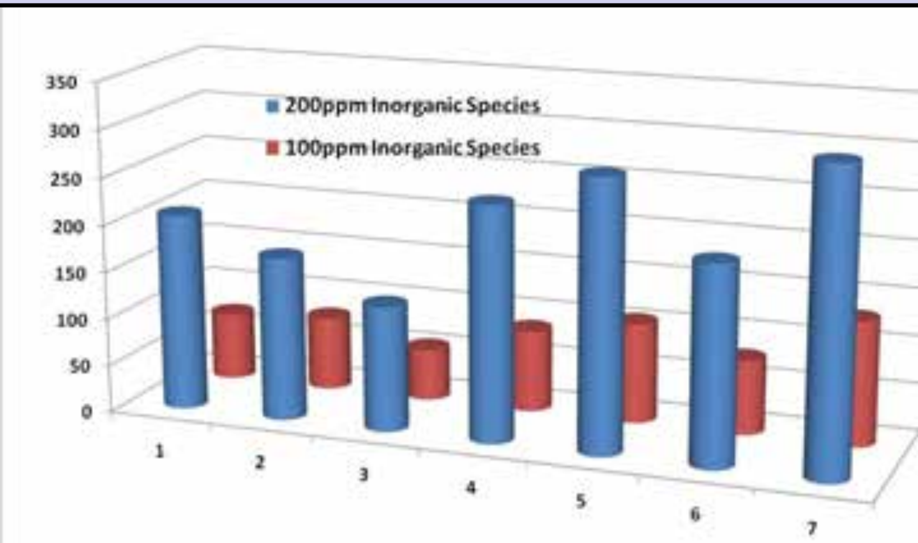
Mass Transfer Effect: Current and Energy Efficiencies





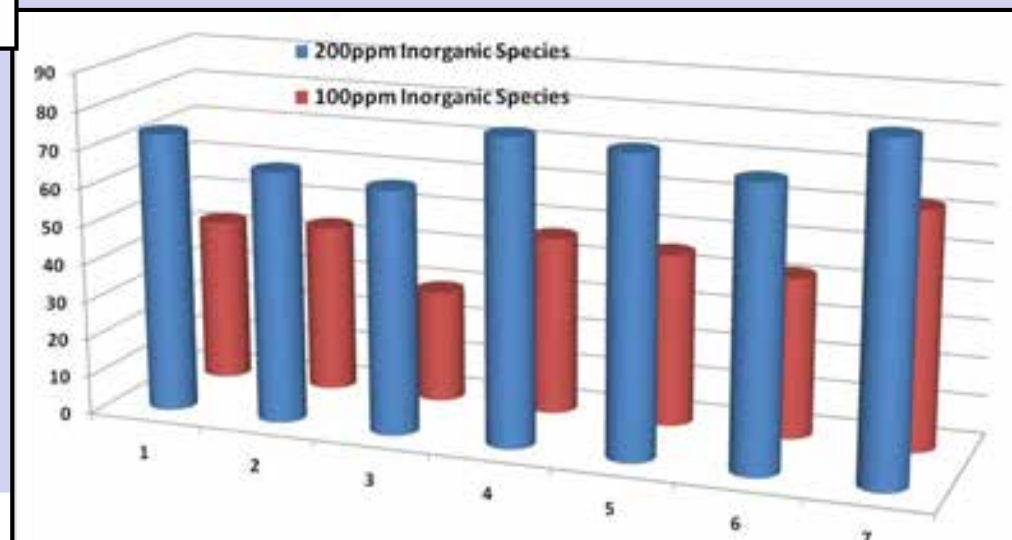
Mass Transfer Effect:
Current and Energy Efficiencies

% Increase in Average Current Efficiency

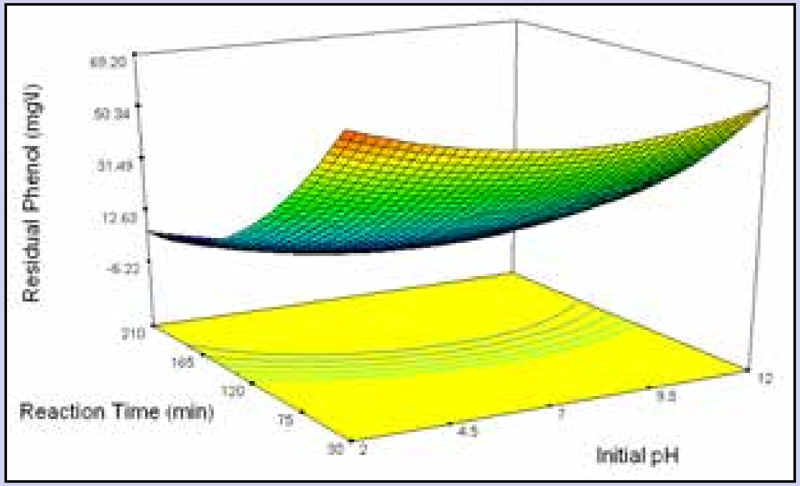


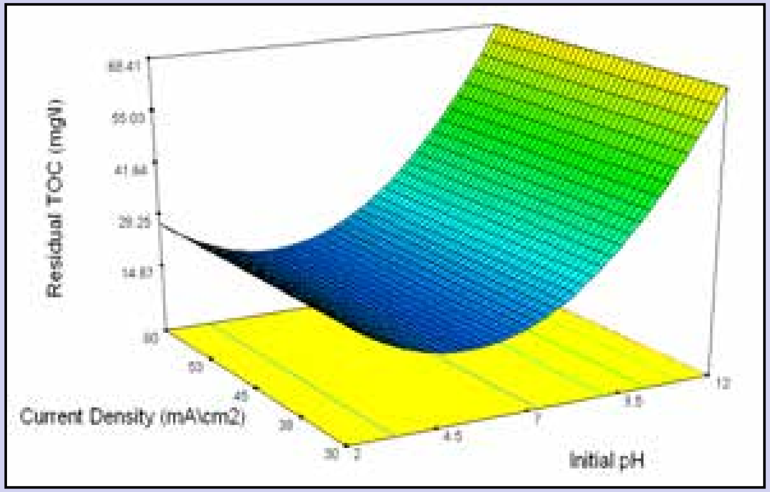
1. Phenol-NH_4^+
2. Phenol-CN^-
3. Phenol -S^{2-}
4. Phenol-NH_4^+-S^{2-}
5. Phenol-NH_4^+-CN^-
6. Phenol-CN^--S^{2-}
7. Phenol-NH_4^+-S^{2-}-CN^-

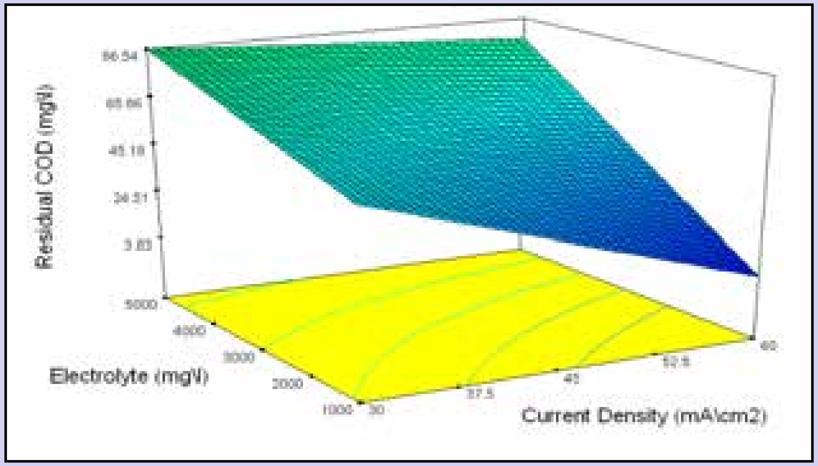
% Decrease in COD Removal Specific Energy Consumption

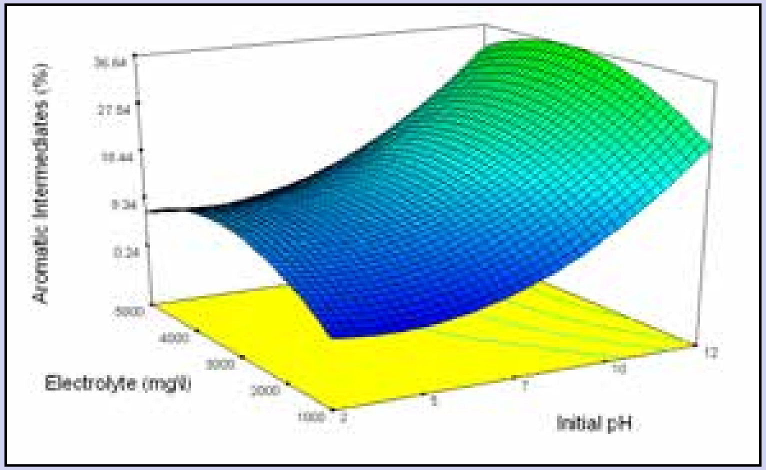


Treatment Optimization using RSM

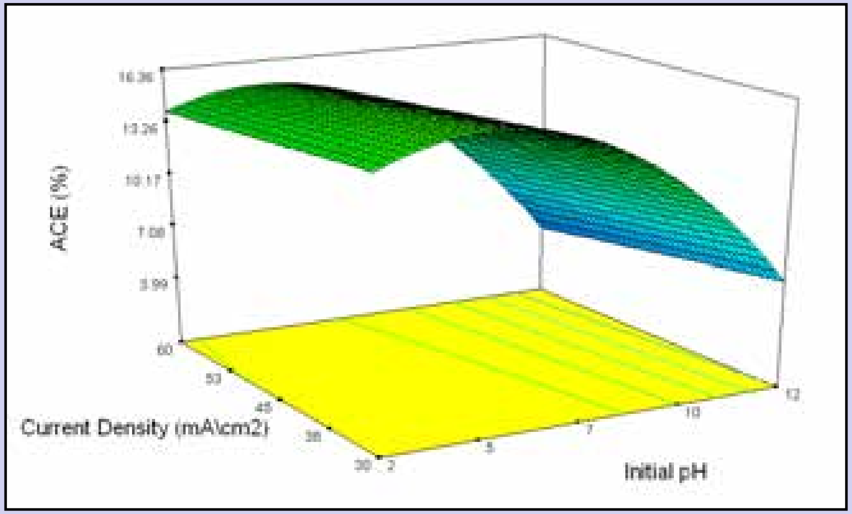


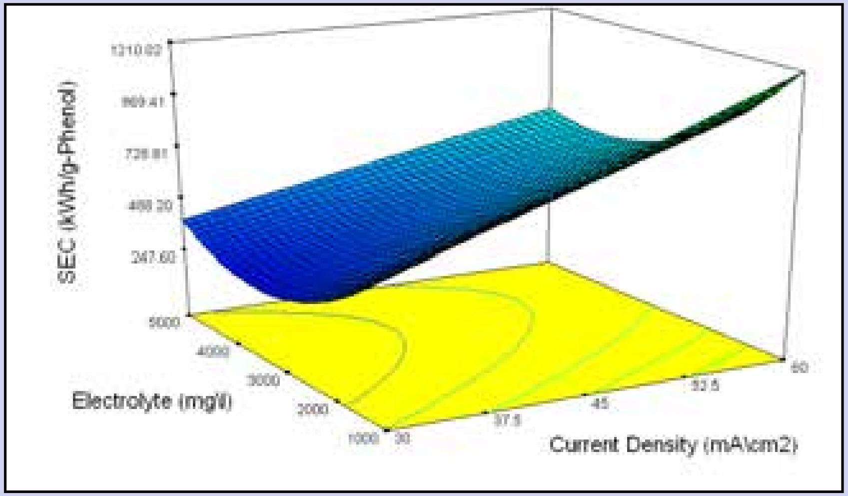


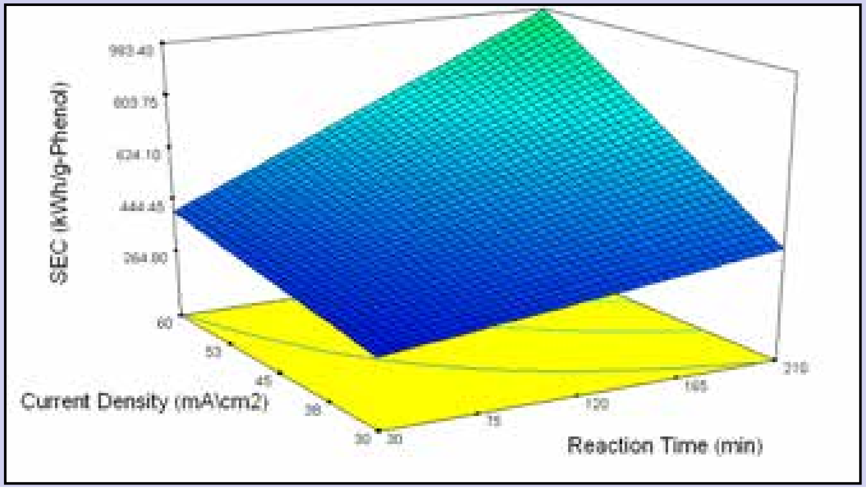




Treatment Optimization using RSM







Inorganic Species Removal Efficiencies

Mixed Components	Cyanide		Sulfide		Ammonium	
	Initial Concentration, ppm					
	100	200	100	200	100	200
Phenol-NH_4^+					1.00	1.00
Phenol-CN^-	0.8858	0.9999				
Phenol -S^{2-}			0.9990	1.00		
Phenol-NH_4^+-S^{2-}			0.9994	1.00	1.00	1.00
Phenol-NH_4^+-CN^-	0.9335	0.9999			1.00	1.00
Phenol-CN^--S^{2-}	0.8346	0.9997	1.0000	1.00		
Phenol-NH_4-S^{2-}-CN^-	0.8421	0.9758	0.9997	1.00	1.00	1.00

Challenges and Prospects

- ✓ BDD electrode, an excellent anodic material for EAOP treatment of industrial wastewater
- ✓ Lower efficiencies are attributed to diluted industrial wastewater
- ✓ Cost prohibiting challenges applications of BDD for large scale industrial WWT
- ✓ Bottle-neck: Reactor configuration design and process optimization are imperative in ensuring optimal and effective decontamination
- ✓ A promising technology: Recent advances in BDD production technology/reactor design and recorded cost-effectiveness

Thank you for your Attention