Electro-Fenton process. Influence of the electrode materials

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Outline

- Fenton process

- Electro-Fenton Process

- Applications

- Impact of electrode materials:

  Anodes and Cathodes

- Conclusion

Wastewater treatment process

Toxic and persistent organic pollutants (POPs) are removed BUT not eliminated by conventional processes:

- **Microbiological**
- **Physical (decantation, filtration, adsorption)**
- **Physicochemical (coagulation, flocculation)**
- **Chemical (chemical oxidation)**

Only the use of very strong oxidizing agents permits the degradation of POPs

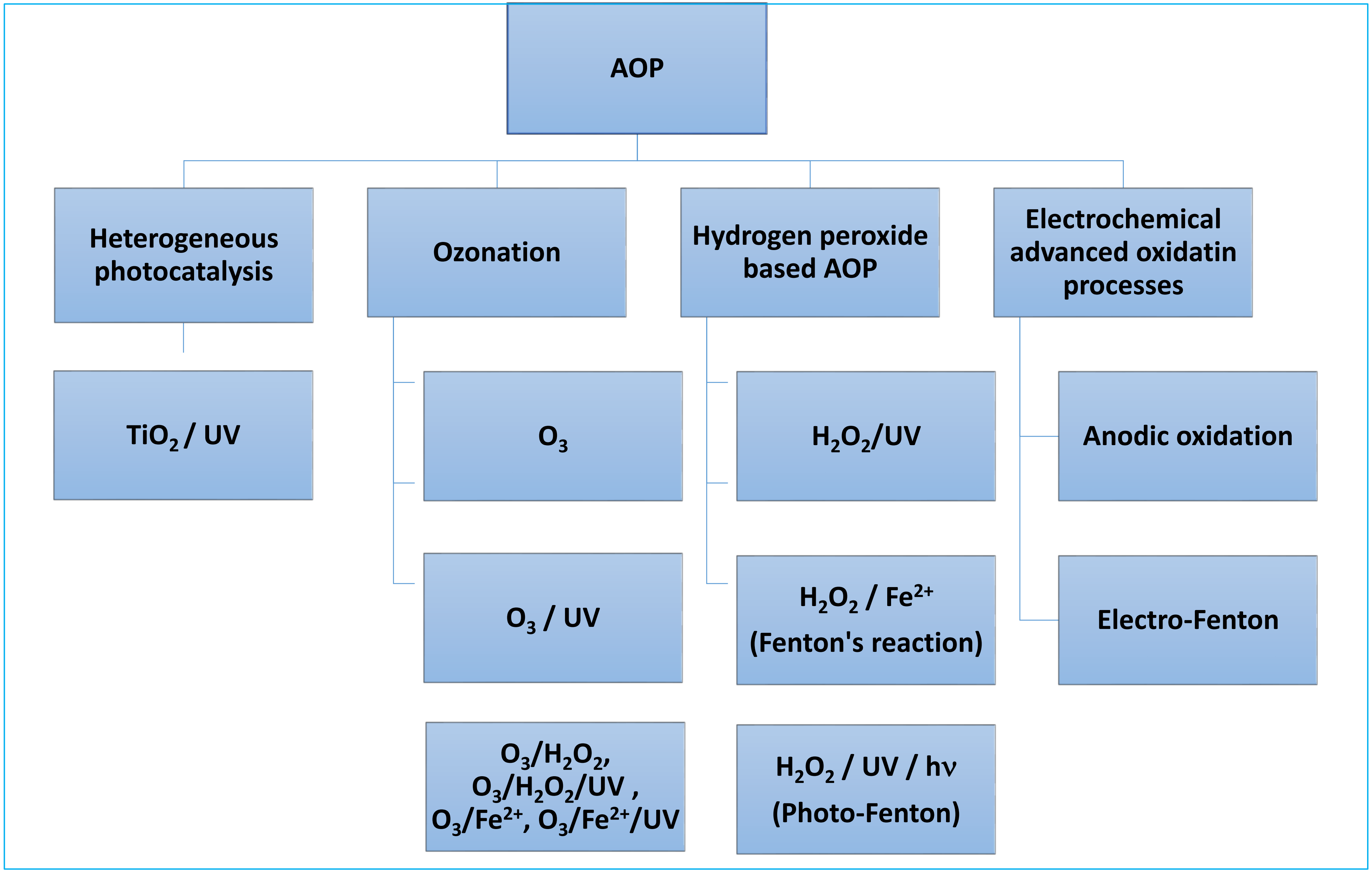

AOP
Heterogeneous photocatalysis
Ozonation
Hydrogen peroxide based AOP
Electrochemical advanced oxidatin processes
TiO_2 / UV
O_3
O_3 / UV
O_3/H_2O_2, $O_3/H_2O_2/UV$, O_3/Fe^{2+}, $O_3/Fe^{2+}/UV$
H_2O_2/UV
H_2O_2 / Fe^{2+}
(Fenton's reaction)
H_2O_2 / UV / hν
(Photo-Fenton)
Anodic oxidation
Electro-Fenton

Table . Standard Reduction Potentials in Aqueous Medium of the Most Commonly Reported Oxidizing Agents for the Destruction of Organic Pollutants

oxidant	reduction reaction	$E°/V$ vs SHE
fluorine	$F_{2(g)} + 2H^+ + 2e^- \rightarrow 2HF$	3.05
hydroxyl radical	$^{\bullet}OH + H^+ + e^- \rightarrow H_2O$	2.80
sulfate radical anion	$SO_4^{-\bullet} + e^- \rightarrow SO_4^{2-}$	2.60
ozone	$O_{3(g)} + 2H^+ + 2e^- \rightarrow O_{2(g)} + H_2O$	2.075
peroxodisulfate ion	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	2.01
hydrogen peroxide	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.763
hydroperoxyl ion (I)	$HO_2^{\bullet} + 3H^+ + 3e^- \rightarrow 2H_2O$	1.65
hydroperoxyl ion (II)	$HO_2^{\bullet} + H^+ + e^- \rightarrow H_2O_2$	1.44
chlorine	$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-$	1.358
oxygen	$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229

Bard, A. J.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solutions*; Marcel Dekker Inc.: New York, 1985

Sharma, V. K. *AdV. EnViron. Res.* **2002**, *6*, 143.

Fenton process

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$$ k = 63 L mol^{-1} s^{-1}

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O$$

Reactions of hydroxyl radicals

Abstraction

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O$$ $k = 10^7\text{-}10^9$ dm^3 mol^{-1} s^{-1}

Addition

$$ArH + {}^{\bullet}OH \rightarrow ArHOH^{\bullet}$$ $k = 10^8\text{-}10^{10}$ dm^3 mol^{-1} s^{-1}

$$ArHOH^{\bullet} + O_2 \rightarrow ArOH + HO_2^{\bullet}$$

Electron transfer

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-$$

$$RH + {}^{\bullet}OH \rightarrow RH^{\bullet+} + OH^-$$

Ipso attack

$$CCl_4 + {}^{\bullet}OH \rightarrow CCl_4({}^{\bullet}OH)$$

$$CCl_4({}^{\bullet}OH) \rightarrow CCl_3OH + Cl^{\bullet}$$

Fenton, H. J. H. *J. Chem. Soc.* **1894**, *65*, 899.
Brillas, E.; Sires, N.; Oturan, M.A., Chem. Rev. **2009**, 109,6570-6631.
Mousset, E.; Oturan, N.; Oturan, M.A., App Cat. B: Env. **2018**, 226,135–146

Regeneration of iron catalyst

Fenton-like reaction

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$ $k = 2x10^{-3}\ dm^3\ mol^{-1}\ s^{-1}$

$Fe^{3} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+$

$Fe^{3+} + R^{\bullet} \rightarrow Fe^{2+} + R^+$

$Fe^{3+} + O_2^{\bullet -} \rightarrow Fe^{2+} + O_2$

Parasitic reactions

$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-$ $k = 3.2x10^{8}\ dm^3 mol^{-1} s^{-1}$

$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet}$ $k = 2.7x10^{7}\ dm^3\ mol^{-1}\ s^{-1}$

$R^{\bullet} + Fe^{2+} + H^+ \rightarrow RH + Fe^{3+}$

$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2$ $k = 7.1x10^{9}\ L\ mol^{-1}\ s^{-1}$

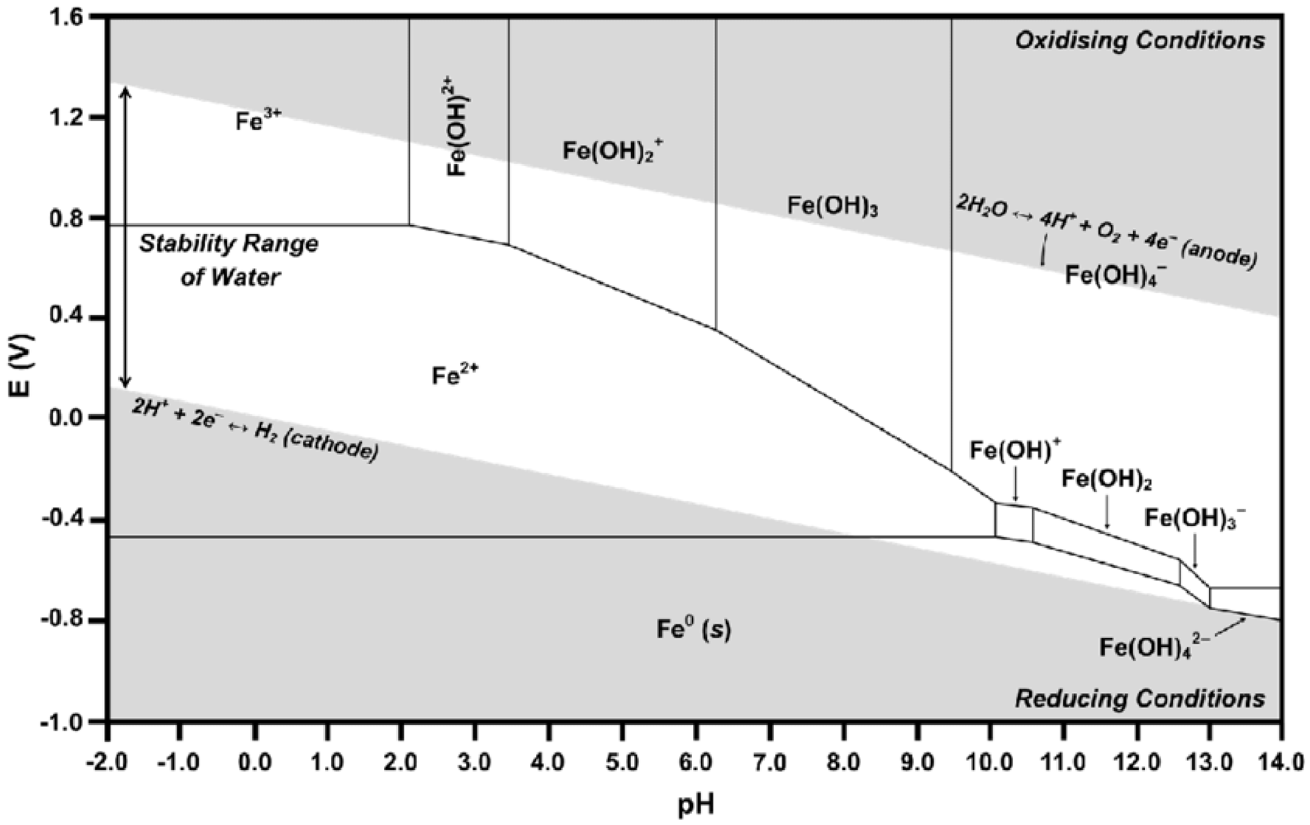
${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$ $k = 6.0x10^{9}\ L\ mol^{-1}\ s^{-1}$

Brillas, E.; Sires, N.; Oturan, M.A., Chem. Rev. **2009**, 109,6570-6631.

Operation mode for the Fenton process

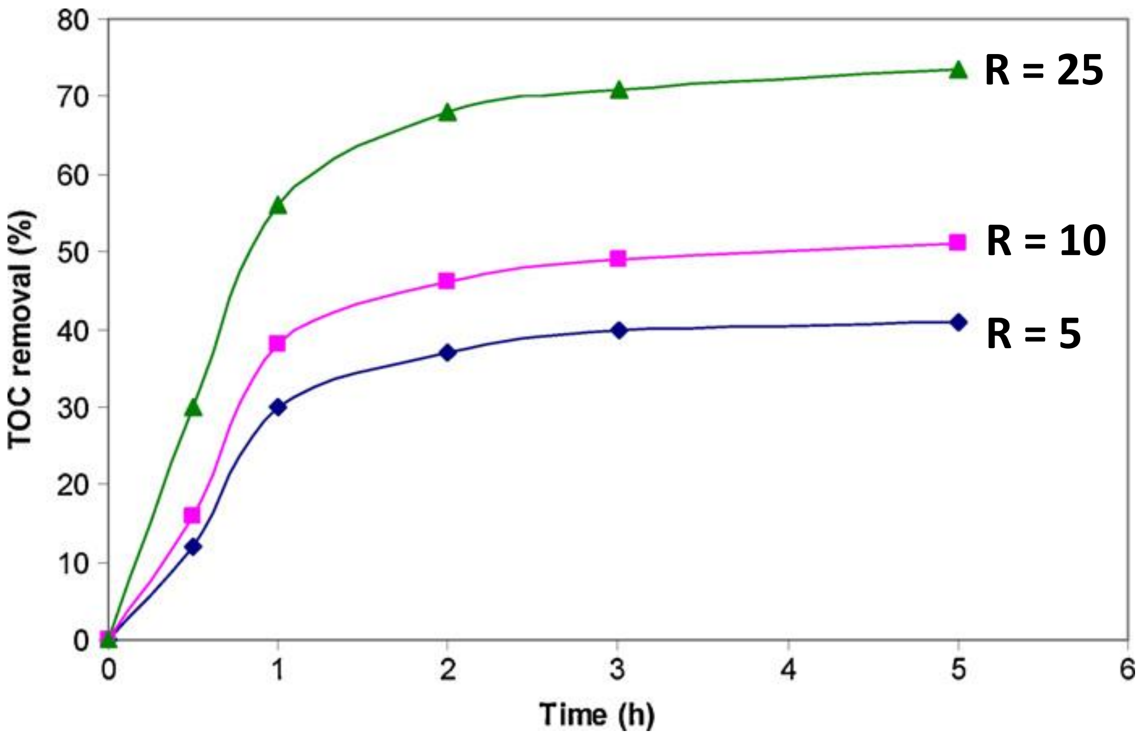
The procedure requires:

- **adjusting the wastewater to pH 3-4;**
- **adding the iron catalyst (as a solution of $FeSO_4$);**
- **adding slowly the H_2O_2. If the pH is too high, the iron precipitates as $Fe(OH)_3$ and catalytically decomposes the H_2O_2 to oxygen**



Pourbaix diagramme for Iron

Impact of $[H_2O_2]/[Fe^{2+}]$ ratio in the Fenton process



$[Fe^{2+}]$ = 0.2 mM

$[Fe^{2+}]$ = 0.5 mM

$[Fe^{2+}]$ = 1 mM

$[H_2O_2]$ = 5 mM

TOC removal as function of time during chemical degradation of diuron aqueous solution

[Diuron] = 0.17 mM

M.A. Oturan, F. I. Podvorica, N. Oturan, M. C. Edelahi, K. El Kacemi, *Chemical Engineering Journal*, **2011**, *171*, 127.

Fenton process

Advantages:

- **Simple and easy operation.**
- **No energy consumption.**

Disadvantages :

- **Relatively high cost and risks related to the transport and storage of H_2O_2.**
- **High amounts of chemicals to acidify the effluents at favourable pH for the Fenton reaction and neutralise the effluent after the treatment.**
- **High iron sludge quantities at the end of treatment.**
- **The complete mineralisation is not attained because of the formation of some iron (III) complexes with carboxylic acids that cannot be destroyed by bulk hydroxyl radicals.**

Electrochemical advanced oxidation processes (EAOPs)

The main reagent in EAOPs is electrical current and these technologies do not use harmful chemicals to produce strong oxidants.

EAOPs include heterogeneous processes like :

anodic oxidation where the pollutant is oxidized on the electrode surface or $^{\bullet}OH$ are generated there

and homogeneous processes like:

Electro-Fenton in which the $^{\bullet}OH$ are produced in solution

Anodic oxidation

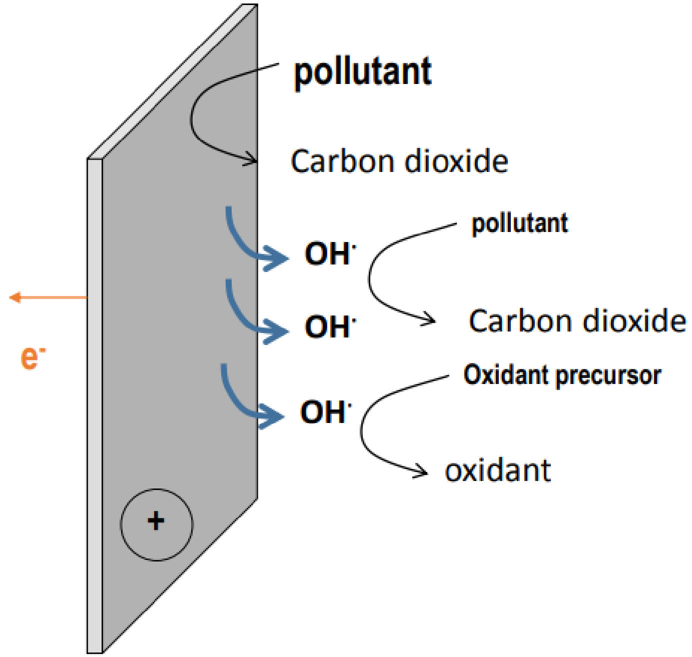


Table Potential for O_2 evolution at various anodes materials used in AO

Anode material	Potential for O_2 evolution (V/SHE)
RuO_2	1.4–1.7
IrO_2	1.5–1.8
Pt	1.6–1.9
Graphite	1.7
Ebonex® (Ti_4O_7)	1.7–1.8
PbO_2	1.8–2.0
SnO_2	1.9–2.2
BDD	2.2–2.6

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

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

$$2M(^{\bullet}OH) \rightarrow 2M + H_2O_2$$

$$3H_2O \rightarrow O_3 + 6H^+ + 6e^-$$

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+$$

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$$

Brillas et al. Applied Catalysis B: Environmental 202 (2017) 217–261

Electro-Fenton process

Fenton process

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O$$

Organic pollutant degradation until

Electrochemical generation of Fe^{2+} and H_2O_2 CO_2 Cold incineration

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

$$Fe(OH)^{2+} + e^- \rightarrow Fe^{2+} + OH^-$$

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$$

E. Brillas, I. Sires, M.A. Oturan, Chem. Rev. 109 (2009) 6570–6631.

M.A. Rodrigo, N. Oturan, M.A. Oturan, Chem. Rev. 114 (2014) 8720–8745.

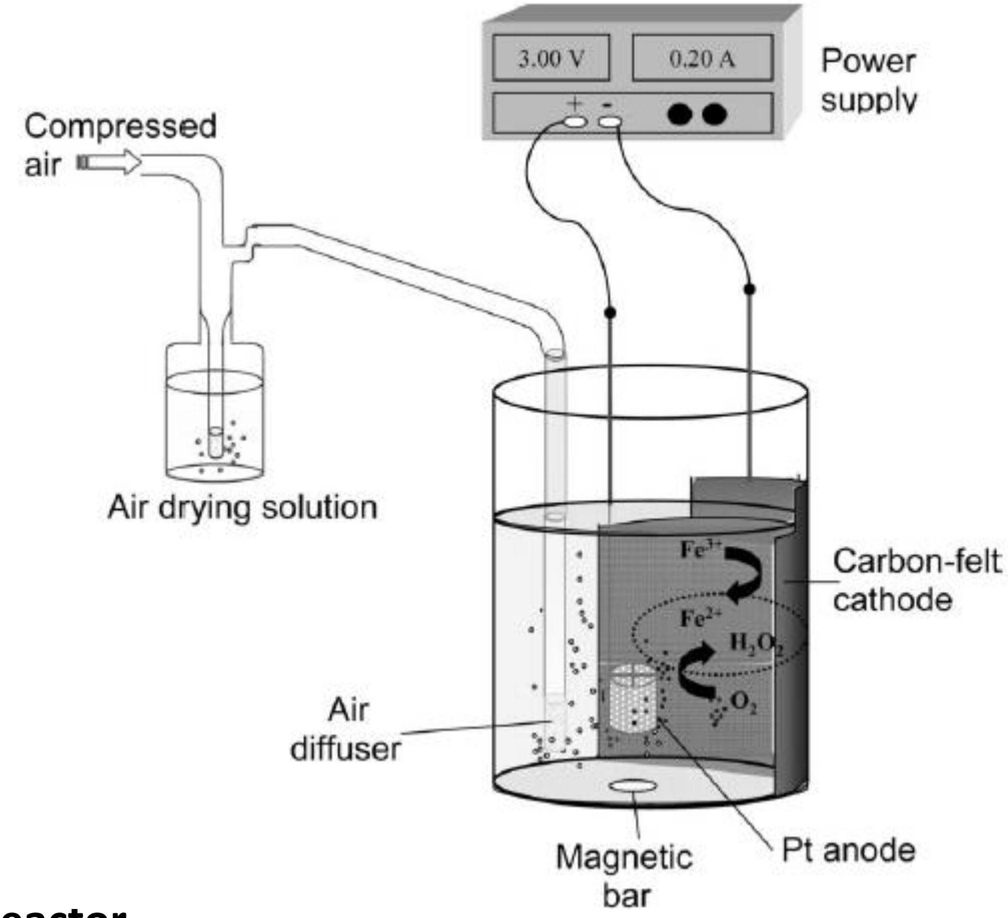
E. Brillas, J.C. Calpe, J. Casado, Water Res. 34 (2000) 2253–2262.

I. Sires, Brilas, M.A. Oturan, M. Rodrigo, M. Panizza, Env. Sci. And Pollution Res. 21 (2014), 8336-8367

Oturan et al. , Chemosphere 197 (2018) 210e227

Electro-Fenton process

Electrocatalytic production of $^{\bullet}OH$ radicals



EC reactor
Compressed air/O2

Cathodes with high overvoltage for HER
Low activity for H2O2 decomposition

Gaz Diffusion Electrode

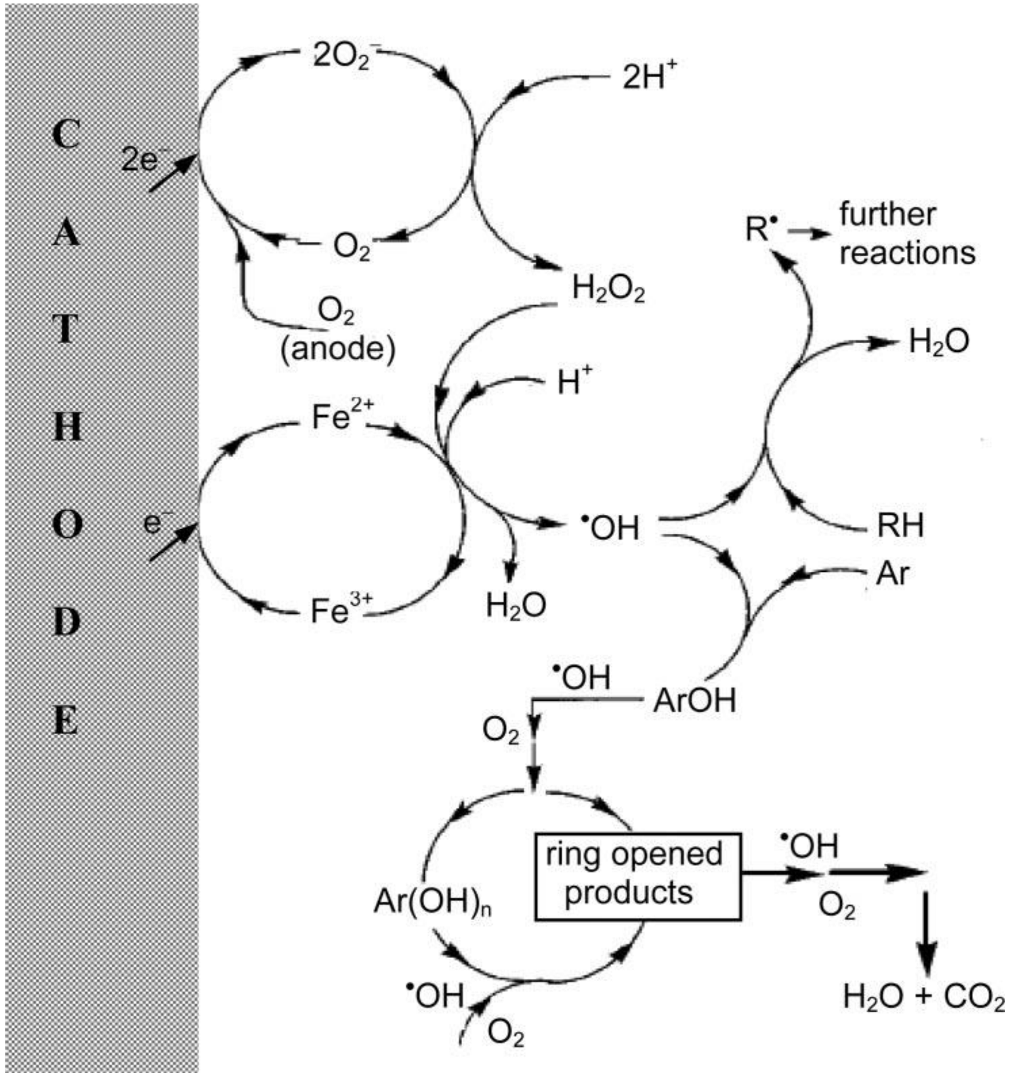
Carbon-PTFE air-diffusion cathode

Carbon felt
Carbon fibers
CNT
Metals (Ni, SS)

Oturan et al., J. of Electroanal. Chem. 2001, 507, 96

Electro-Fenton process

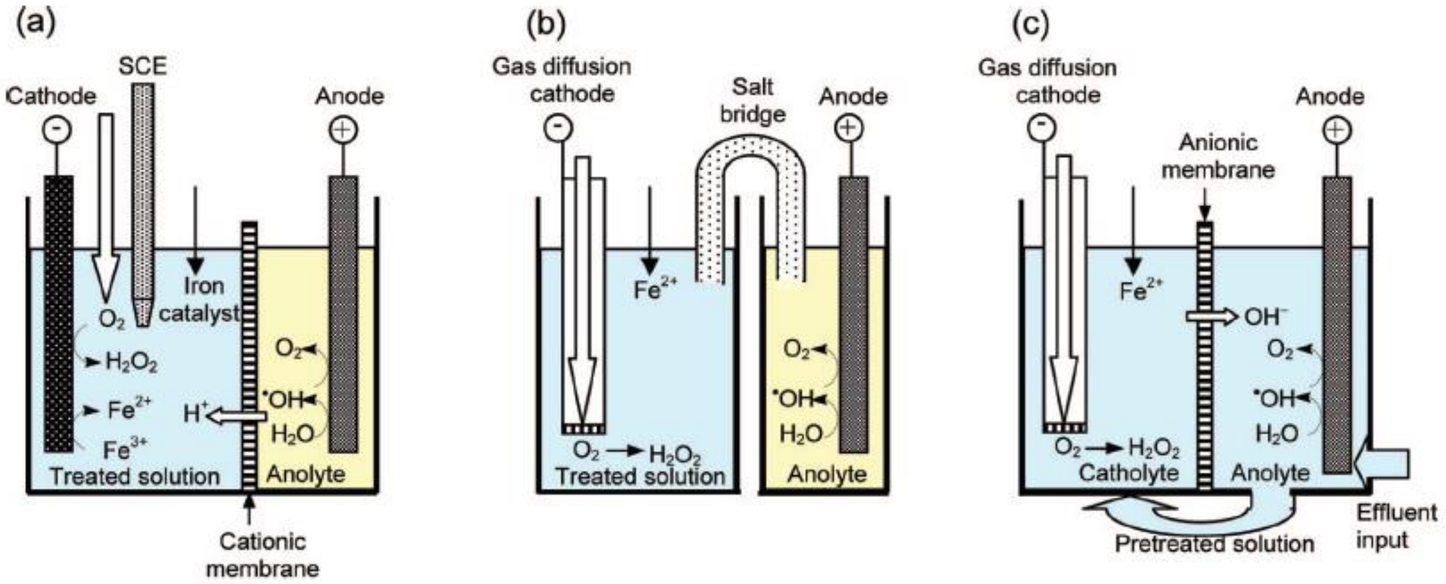
Degradation vs mineralization of POPs



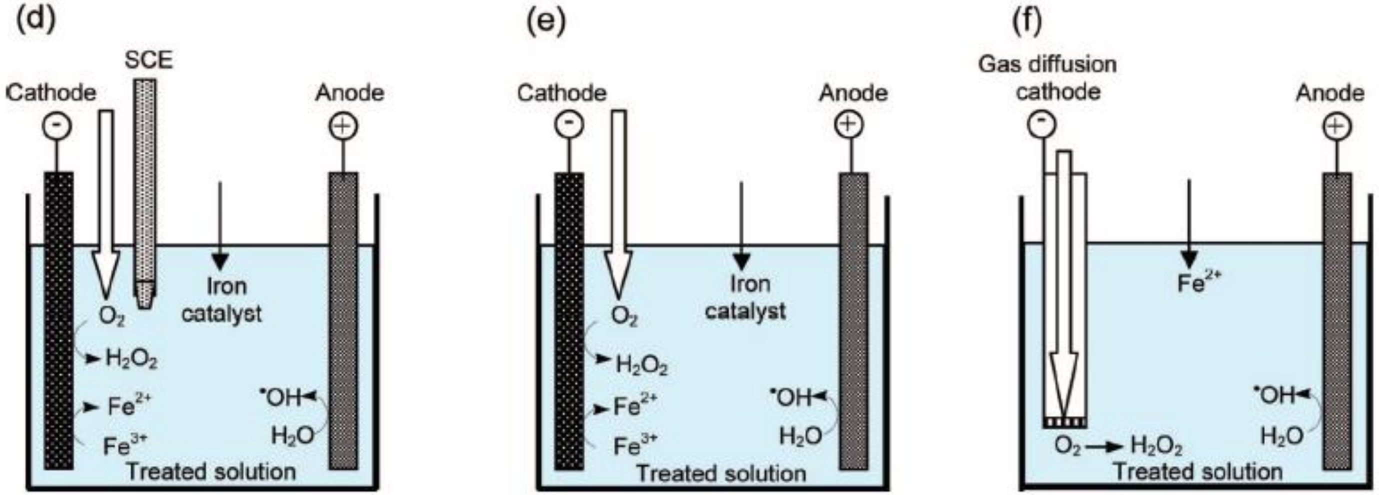
Mineralization is the conversion of organic pollutant to carbon dioxide, water and other inorganic minerals by oxidation of its molecule until the ultimate oxidation degree

E. Brillas, I. Sires, M.A. Oturan Chem. Rev. 2009, 109, 6570–6636

Different kinds of electrochemical cells used in Electro-Fenton treatments of organics from wastewaters



Divided cells

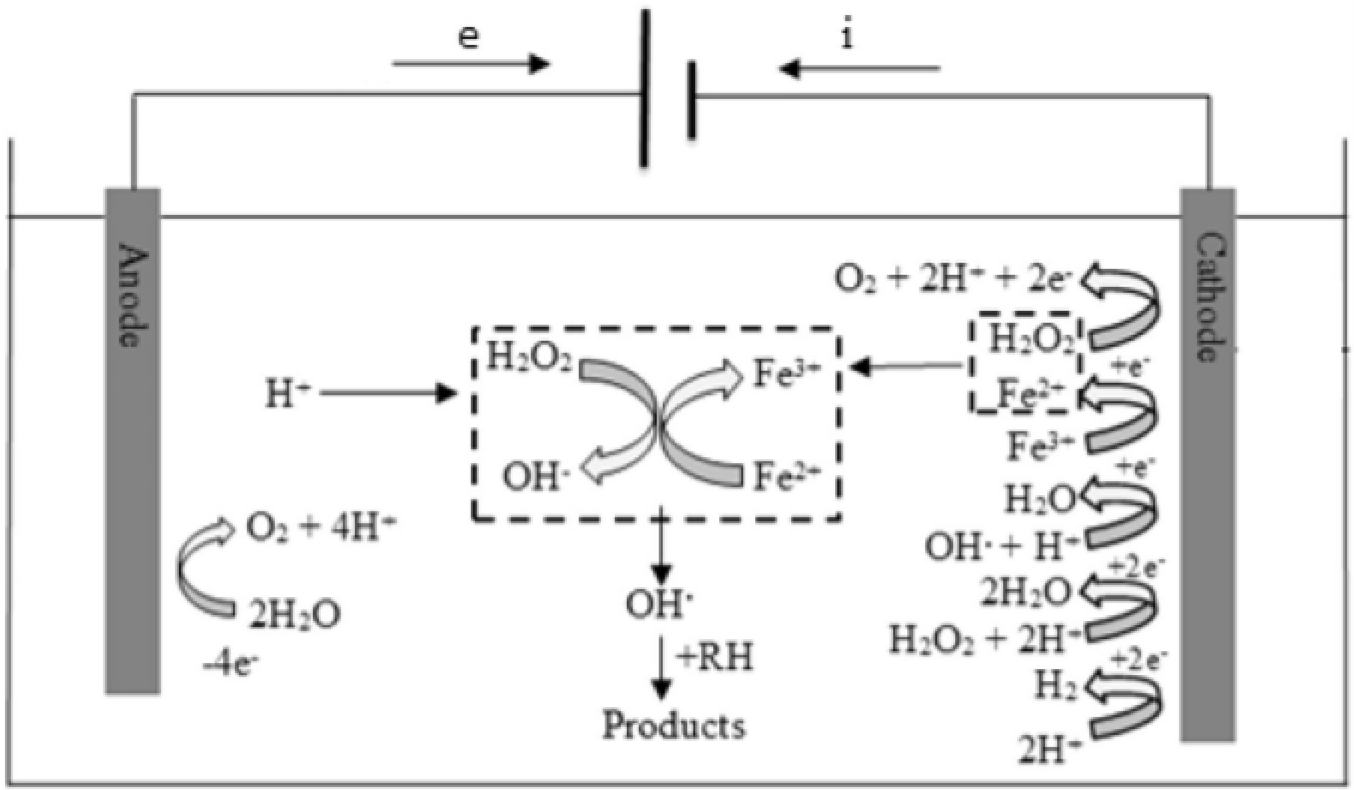


Undivided cells

E. Brillas, I. Sires, M.A. Oturan Chem. Rev. 2009, 109, 6570–6636

Electro-Fenton process

Side reactions



Main side reactions

- Hydrogen Evolution Reaction
- Hydrogen peroxide reduction into water

Cathodes with high HER

H2O2 is oxidized on the Anode

H2O2 decomposition if T is increased

Parameters that influence Electro-Fenton process

Solution pH, catalyst concentration, oxygen or air feed rate, applied current, electrode material and temperature

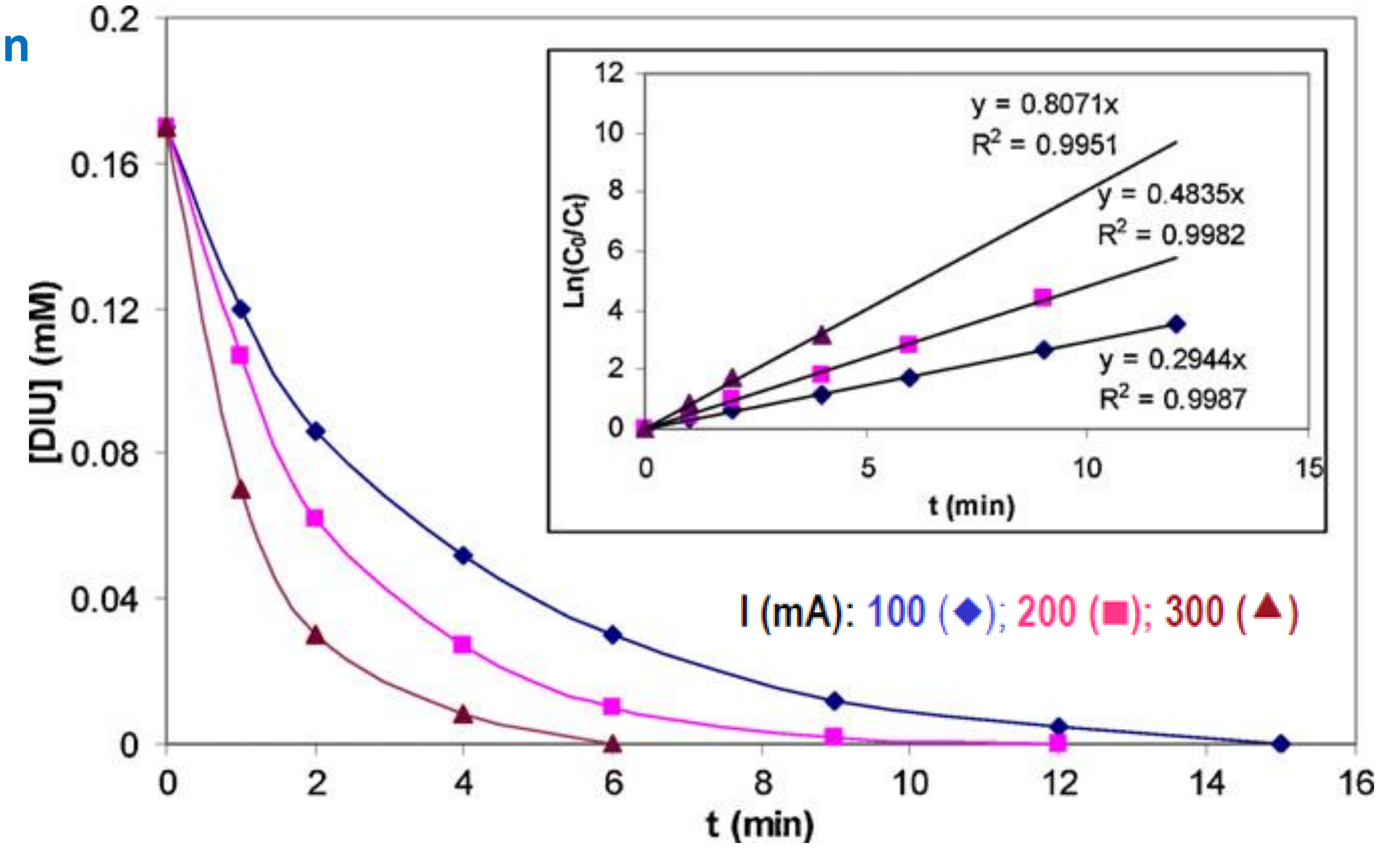
Effect of current intensity

Degradation kinetics of Diuron - Chlorophenylurea herbicide

[Diuron] = 0.17 mM
pH = 3

$[Fe^{2+}]$ = 0.2 mM

Cathode: GF



M.A. Oturan, F. I. Podvorica, N. Oturan, M. C. Edelahi, K. El Kacemi, *Chemical Engineering Journal*, **2011**, *171*, 127.

Electro-Fenton process

Follow up of degradation/mineralization

HPLC-MS: Concentration decay of POPs and aromatic intermediaries

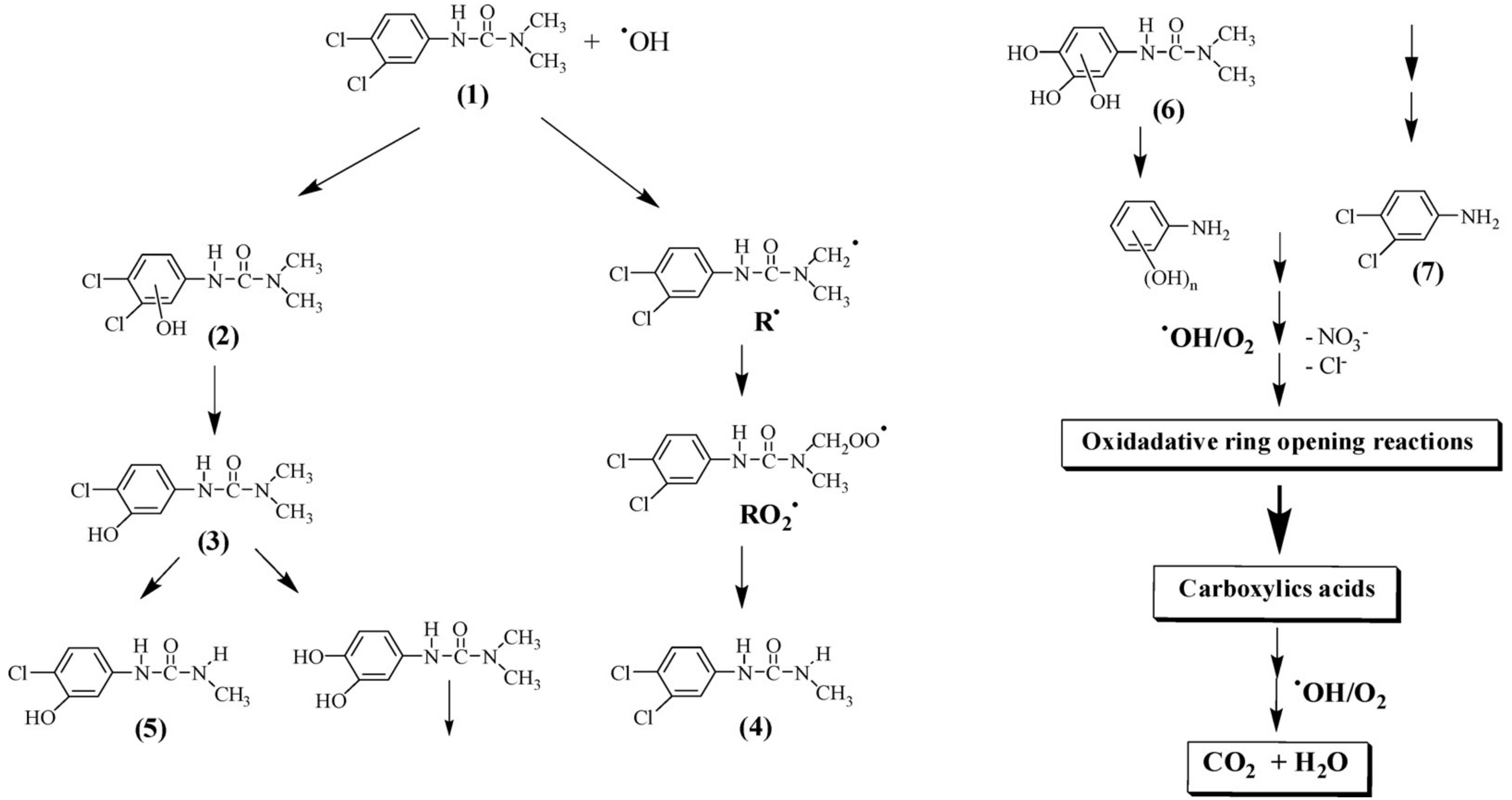
Ion exclusion chromatography: Carboxylic acid evolution

Ionic chromatography: Liberated mineral ions or heteroatoms

TOC/COD: Mineralization efficiency

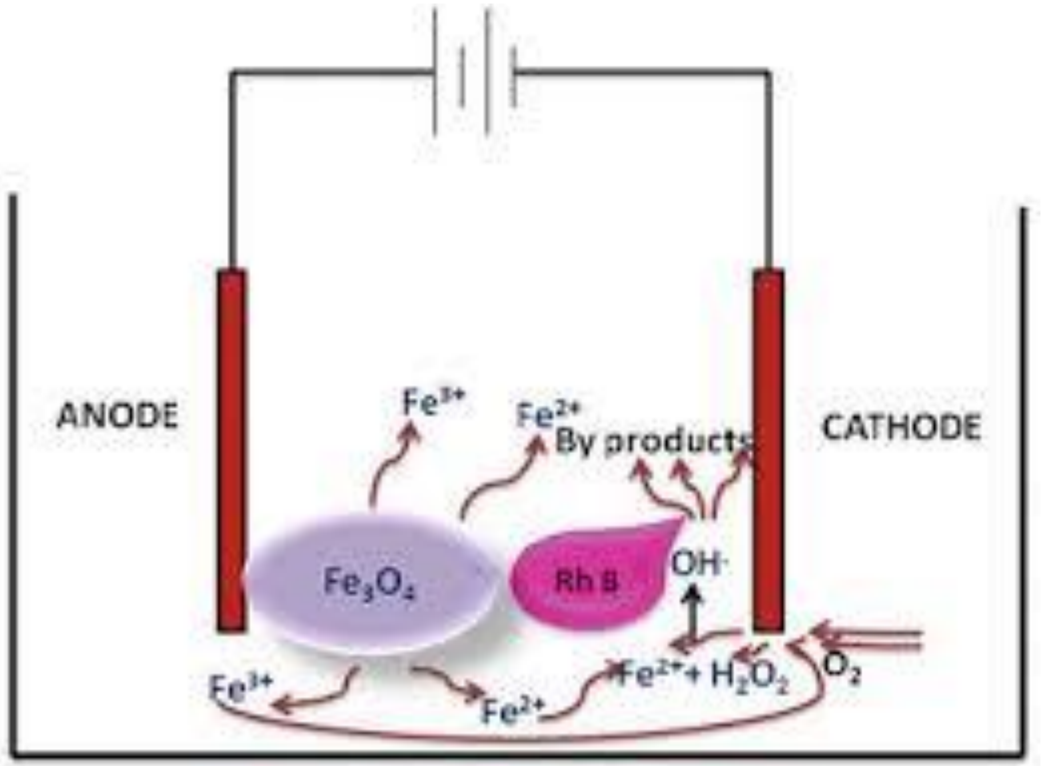
Microtox: Toxicity of pollutants and their intermediate products

Diuron degradation-mineralization mechanism



M.A. Oturan, F. I. Podvorica, N. Oturan, M. C. Edelahi, K. El Kacemi, *Chemical Engineering Journal*, **2011**, *171*, 127.

Heterogeneous Fenton

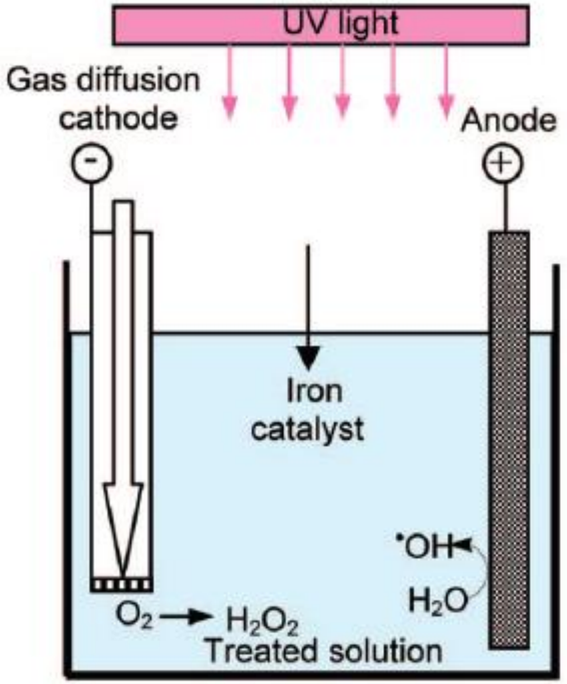


One can treat real industrial effluents/wastewater, which usually have different pH depending on the origin

Avoid the use Fe ions in the solution

Oturan et al. Chemical Engineering Journal 350 (2018) 844–855

Photo Electro-Fenton and Solar Photo Electro-Fenton



$$[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH$$

The quantum yield for this reaction was found to be 0.14-0.19 at 313 nm

$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^{\bullet}$$

Fe and carboxylic acid complexes useful for the regeneration of Fe^{2+}

$$2\,Fe(C_2O_4)_n^{(3-2n)} + h\nu \rightarrow 2\,Fe^{2+} + (2n-1)C_2O_4^{2-} + 2\,CO_2$$

$$H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH$$

$$H_2O_2 + h\nu \rightarrow H^{\bullet} + HO_2^{\bullet}$$

S. Garcia-Segura, L.C. Almeida, N. Bocchi, E. Brillas, J. Hazard. Mater. 194(2011) 109–118.

Table 3

Degradation of several pollutants by EF-based technologies.

Pollutant/Effluent	Electrodes	Remarks	Removal efficiency
PC			
Chlorinated herbicides	SS anode/RVC cathode	200 mL of alachlor (175 mg L^{-1} COD), atrazine (68 mg L^{-1} COD) or chlorbromuron (47 mg L^{-1} COD) in 0.05 M Na_2SO_4, pH = 2.0, E_{cell} = 2.5 V, 75 min.	93%–96% COD
Textile wastewater	Fe anode/graphite felt cathode	300 mL of wastewater (1310 mg L^{-1} COD, pH = 6.5), cylindrical reactor, air flow rate = 2 L min^{-1}, I = 200 mA, 120 min.	59% color 71% COD
PEF			
Naproxen	GDE cathode (20 cm^2 area) /Anodes: BDD, Pt, IrO_2 and RuO_2 (20 cm^2)	2.5 L of 40 mg L^{-1} drug solution in 0.05 M $NaClO_4$, pH = 3.0, flow cell, 0.50 mM Fe^{2+}, 160 W UVA, j = 50 mA cm^{-2}, 120 min.	TOC removal: 83% BDD; 80% Pt; 78% IrO_2; 76% RuO_2
Methylparaben	GDE cathode (3 cm^2 area)/Anodes tested: BDD, Pt, IrO_2 and RuO_2 (3 cm^2)	100 mL of 158 mg L^{-1} in 0.025 M Na_2SO_4 + 0.035 M NaCl, pH = 3.0, stirred tank reactor, 0.50 mM Fe^{2+}, 6 W UVA, j = 66.7 mA cm^{-2}, 360 min.	TOC removal: 89% BDD; 43% Pt; 1.9% IrO_2; 43% RuO_2
SPEF			
Dyes mixture	BDD/GDE cathode	2.5 L of 100 mg L^{-1} DOC of food dyes, 0.05 M and 0.50 mM Fe^{2+} at pH 3.0 using the flow plant at j = 100 mA cm^{-2}, 35 °C and liquid flow rate of 200 L h^{-1}, 300 min.	96%–97% DOC 85% DOC
Triclosan	Ti/Pt anode/graphite-felt cathode (64 cm^2 area)	10 L of 0.225 mM drug in 0.05 M Na_2SO_4, pH = 3.0, FM01-LC reactor coupled to solar CPC photoreactor, 0.50 mM Fe^{2+}, liquid flow rate = 180 L h^{-1}, E_{cat} = -0.35 V/SHE, 300 min.	78% TOC
Heterogeneous-EF			
Winery wastewater	BDD/Ni-foam	undivided cylindrical glass reactor; 150 mL solution in 0.01 M Na_2SO_4; 15 V constant voltage; 1 L min^{-1} air flow; 8.7, 14.25 and 3 g of Fe-AB, Mn-AB and Fe-AC.	COD removal: 56% Fe-AB, 54% Mn-AB, 82% Fe-AC
	Catalyts (Mn-AB, Fe-AB, and Fe-AC)		
Imidapricloprid and chlorpyrifos	BDD/graphite	undivided reactor of 150 mL; 5 V voltage; air flow rate of 1 L min^{-1}; 50 – 700 mg L^{-1} Fe-Y zeolite; pH 3 during 120 min; reusability enhanced embedding the Fe-Y zeolite.	98% TOC
	Catalyst (Fe-Y zeolite/ Alginate)		

AB = alginate beads, AC = activated carbon, SS = stainless steel, RVC = reticulated vitreous carbon, UVA = long-wavelength ultraviolet, COD = chemical demand, TOC = total organic carbon, DOC = dissolved organic carbon and CPC = compound parabolic concentrator.

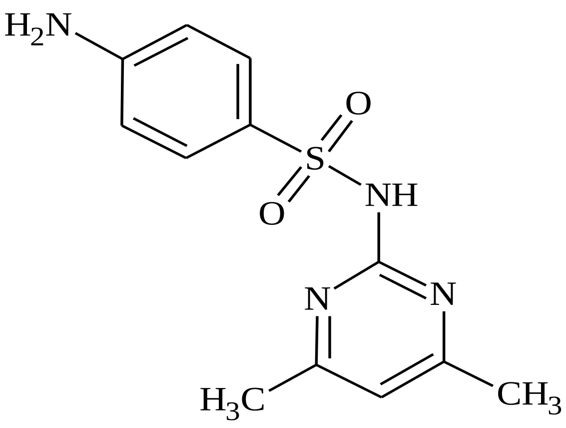
Carlos et al. 2018

Effect of electrode material on the EF and AO:

Impact of anodes: Pt, DSA, BDD, GF

Cell Operation conditions: galvanostatic

Cathode: GF



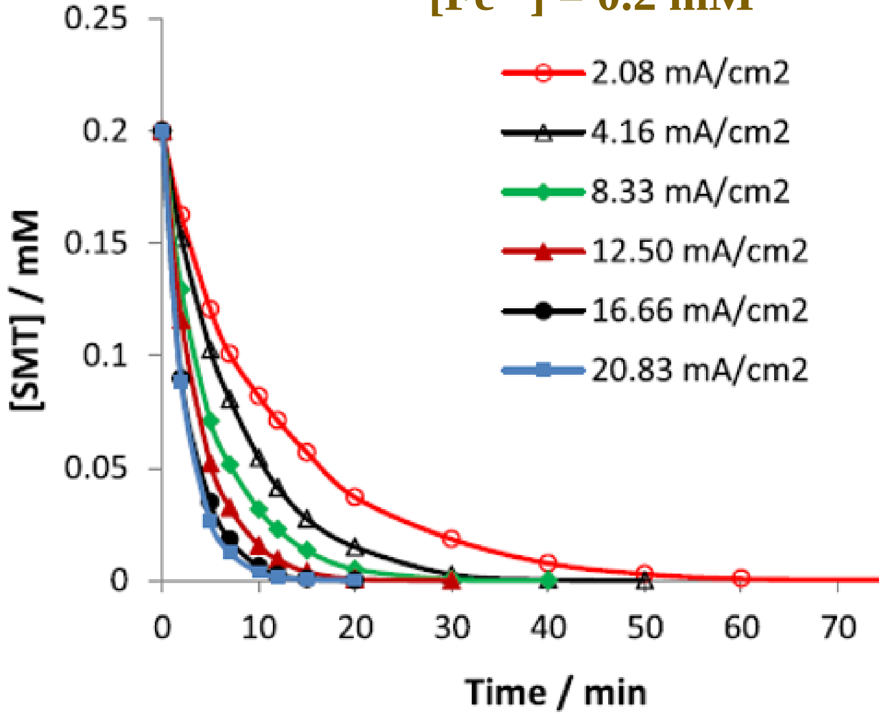
[SMT] = 0.2 mM
pH = 3
[Na_2SO_4] = 50 mM
Vs = 300 mL

The sulfamethazine (SMT), one of the most commonly used antibiotics from the ‘sulphonamides’ family, was selected as model pollutant because of its occurrence in natural water stream

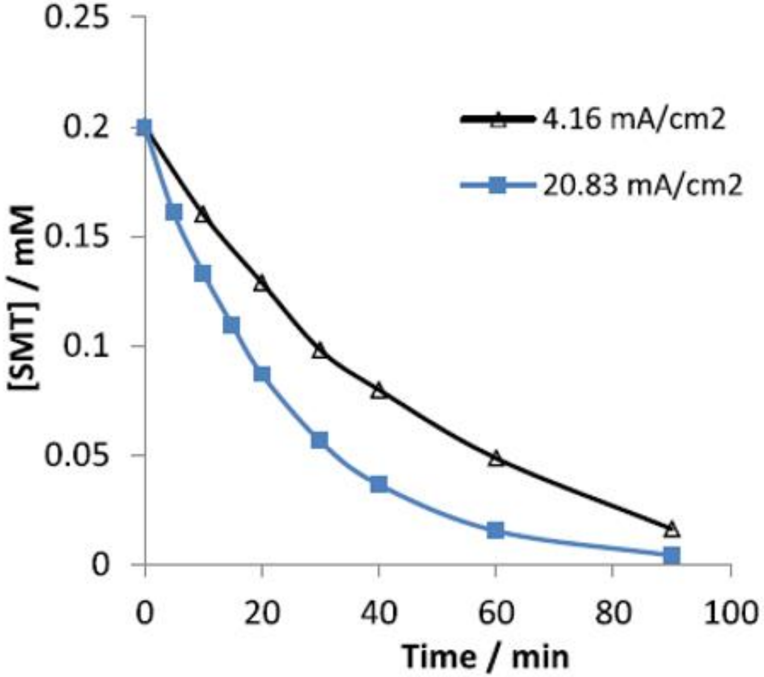
F. Sopaj, N. Oturan, J. Pinson, F. Podvorica, M. A. Oturan. *Appl. Cat. B: Env.*, **2016,** *199*, 331-341.

Effect of anode material on the efficiency of EF process for the oxidation of SMT

$[Fe^{2+}] = 0.2$ mM



a) electro-Fenton:



b) anodic oxidation

Anode of Pt

Cathode: GF

$[SMT] = 0.2$ mM
pH = 3
$[Na_2SO_4] = 50$ mM
Vs = 300 mL

Side reactions

High density currents:

$$2H^+ + 2e^- \rightarrow H_2$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

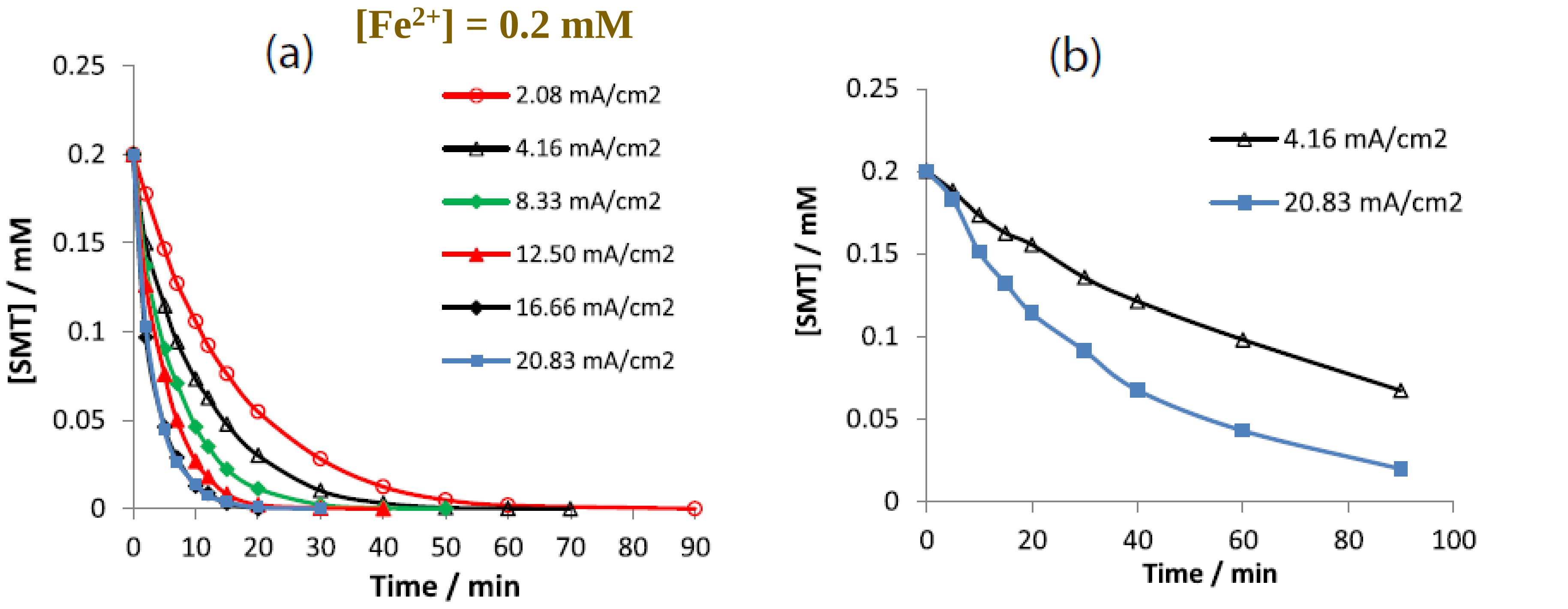
$$2Pt(^{\bullet}OH) \rightarrow 2Pt + O_2 + 2H^+ + 2e^-$$

Oxidation by homogeneous $^{\bullet}OH$ > efficient than heterogeneous $^{\bullet}OH$

Comninellis et al. . *J. Electrochem. Soc.* **2000**, *147*, 2614.

Effect of anode material on the efficiency of EF process for the oxidation of SMT

Anode of DSA ($Ti/RuO_2/IrO_2$)



a) electro-Fenton **b) anodic oxidation**

Cathode: GF

[SMT] = 0.2 mM
pH = 3
[Na_2SO_4] = 50 mM
Vs = 300 mL

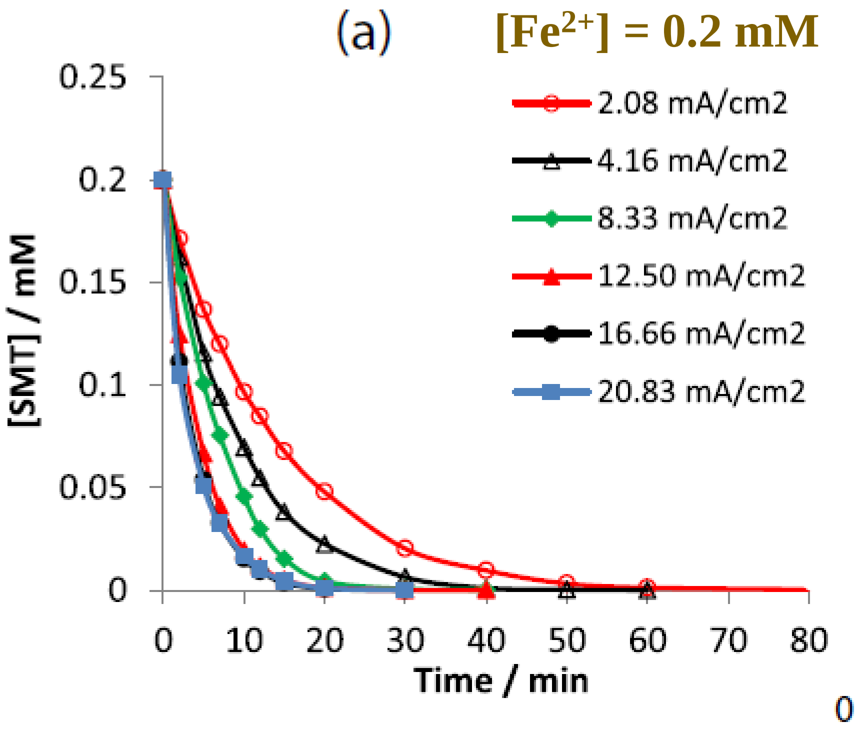
DSA(•OH) are more strongly adsorbed on the anode surface than Pt(•OH) and consequently less available for oxidation of SMT

Oxidation by homogeneous •OH > efficient than heterogeneous •OH

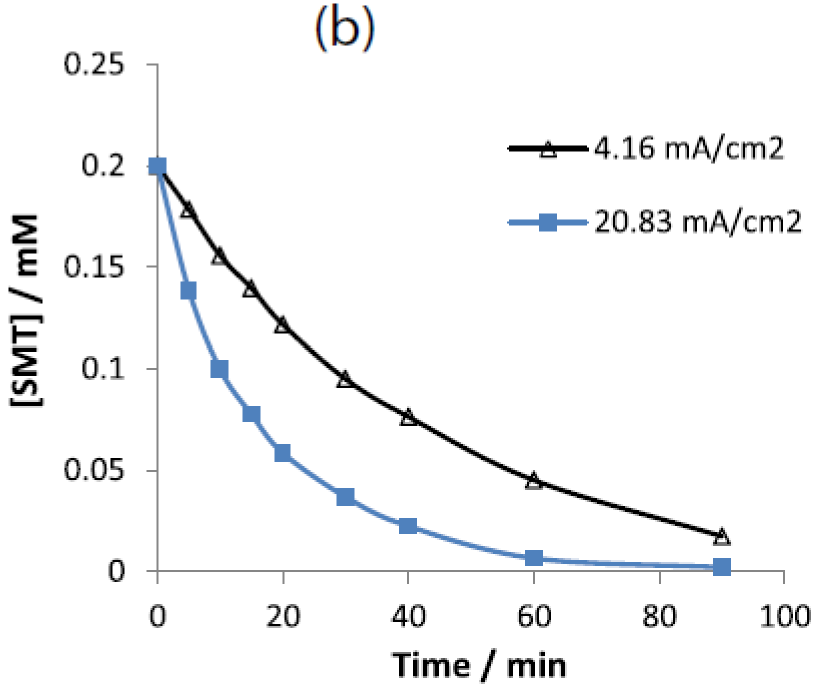
Effect of anode material on the efficiency of EF process for the oxidation of SMT

Anode of BDD

$$BDD(HO^{\bullet}) + R \rightarrow BDD + ROH^{\bullet} \text{ (or } R^{\bullet} + H_2O)$$



a) Electro-Fenton



b) anodic oxidation

Cathode: GF

[SMT] = 0.2 mM
pH = 3
[Na2SO4] = 50 mM
Vs = 300 mL

Side reactions

Higher density currents:

$$2H^+ + 2e^- \rightarrow H_2$$

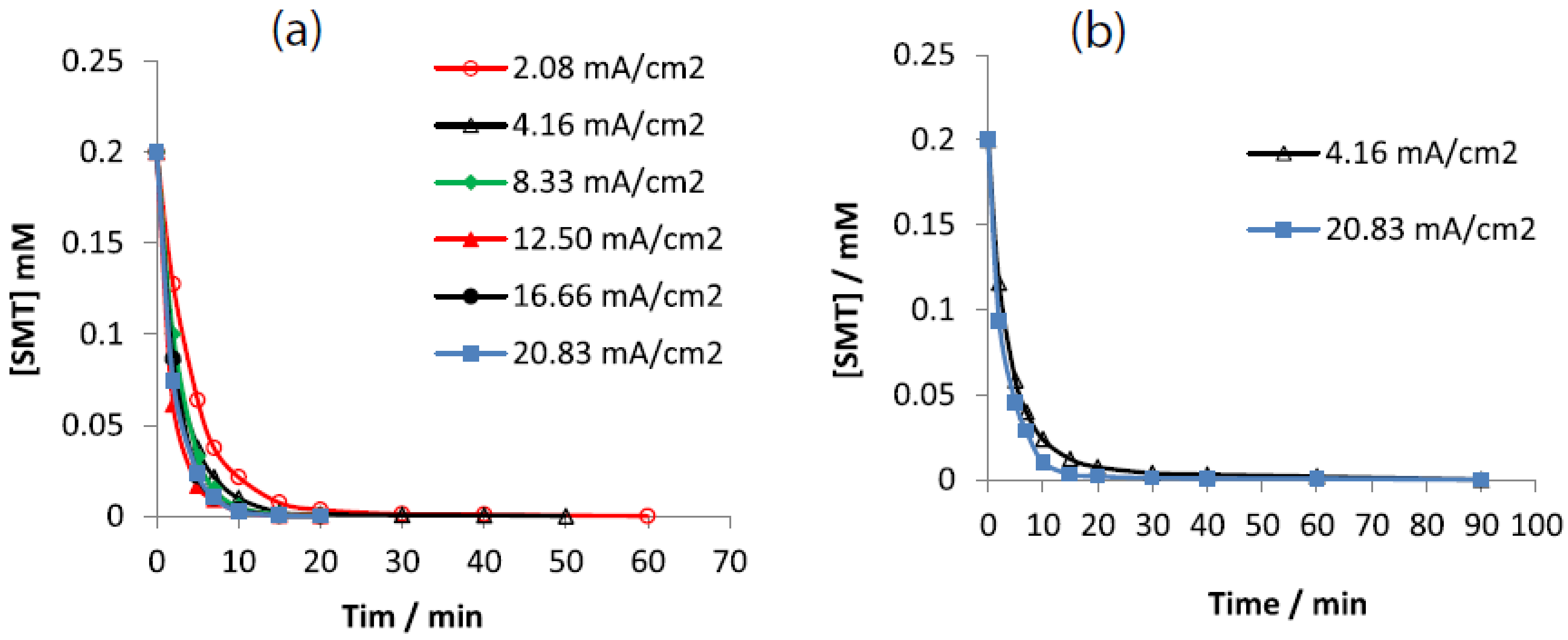
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

$$2BDD(^{\bullet}OH) \rightarrow 2BDD + H_2O_2$$

Oxidation by homogeneous $^{\bullet}OH$ > efficient than heterogeneous $^{\bullet}OH$

Effect of anode material on the efficiency of EF process for the oxidation of SMT



a) Electro-Fenton

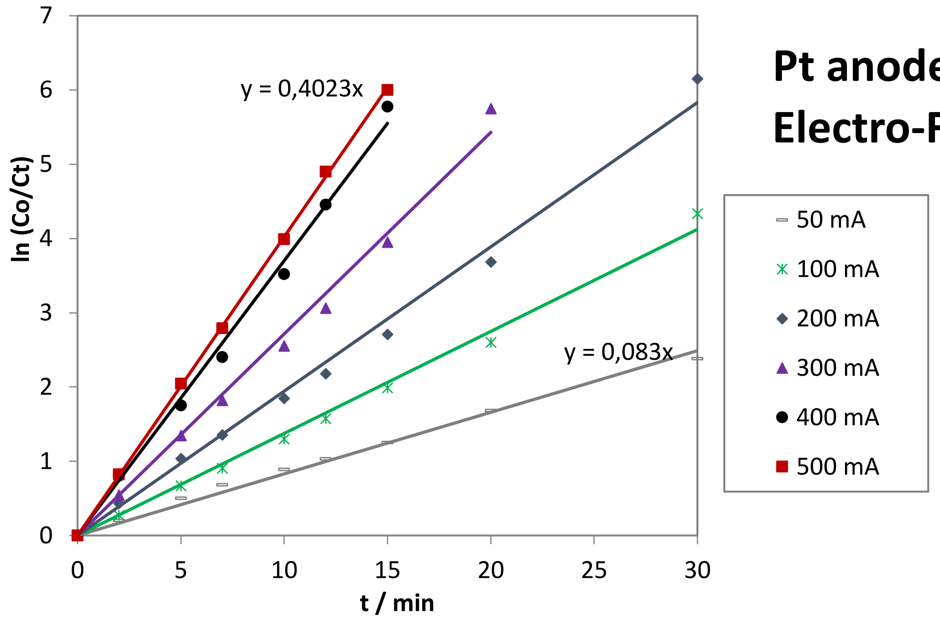
b) anodic oxidation

Anode of GF

Cathode: GF

[SMT] = 0.2 mM
pH = 3
$[Na_2SO_4]$ = 50 mM
Vs = 300 mL

Calculation of apparent rate constants for oxidation of SMT with $^{\bullet}OH$



Pt anode

Electro-Fenton

$$ln\frac{[SMT]_0}{[SMT]_t} = k_{app} \cdot t$$

Optimal current density 12.50 and 16.66 mA/cm2 for EF

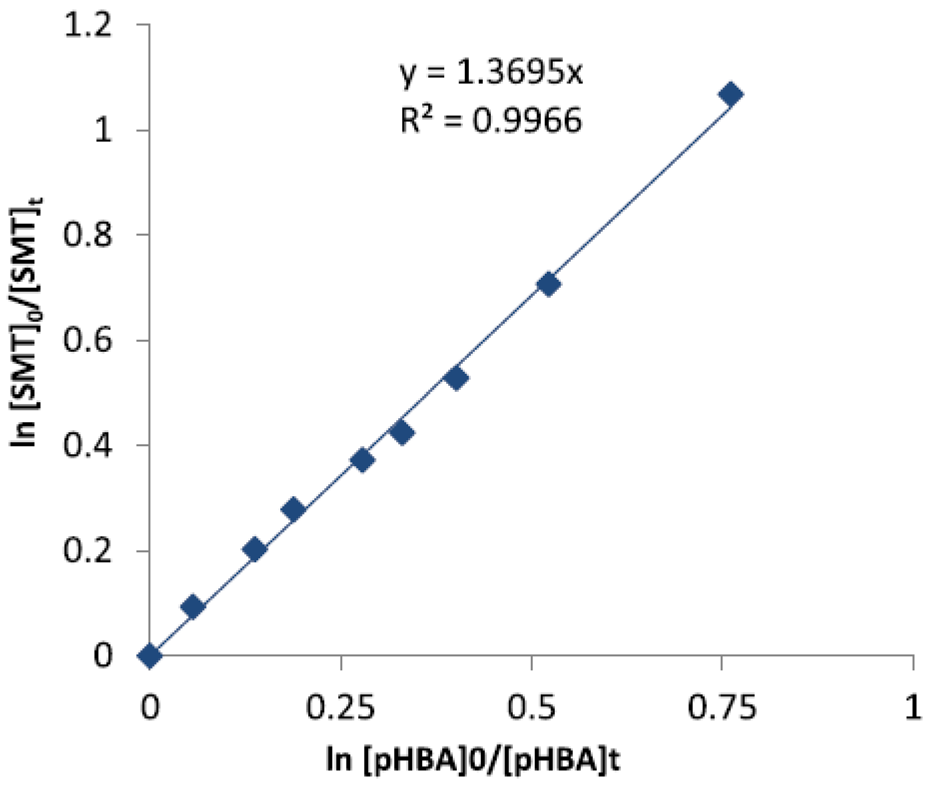
Table 1
Apparent rate constants (k_{app} in min^{-1}) as a function of the anode material and the current density for electro-Fenton process with graphite felt cathode.

Anode	k_{app} (min^{-1})			
I ($mA\,cm^{-2}$)	Pt	DSA	BDD	GF
2.08	0.08	0.06	0.07	0.22
4.16	0.15	0.09	0.12	0.31
8.32	0.19	0.14	0.18	0.37
12.50	0.27	0.20	0.24	0.44
16.66	0.37	0.27	0.27	0.43
20.83	0.40	0.27	0.25	0.43

Table 2
Apparent rate constants as a function of the anode material and the current density for the anodic oxidation process. The cathode is graphite felt.

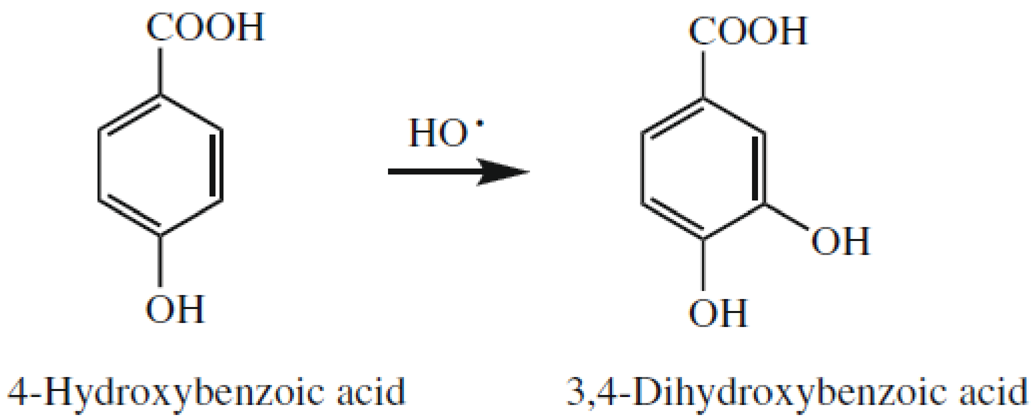
Cell	Pt	DSA	BDD	C F
I (mA)		k_{app} (min^{-1})		
100	0.02	0.01	0.02	0.22
500	0.04	0.02	0.06	0.29

Calculation of absolute rate constant for oxidation of SMT with $^{\bullet}OH$



Pt/Carbon felt, V_s = 300 mL, $[Fe^{2+}]$ = 0.2 mM,

$[Na_2SO_4]$ = 50 mM, I = 50 mA, pH = 3.



$$-\frac{d[SMT]}{dt} = k_{SMT}[SMT]\,[HO^{\bullet}]$$

$$-\frac{d[pHBA]}{dt} = k_{SMT}[pHBA]\,[HO^{\bullet}]$$

$$ln\frac{[SMT]_0}{[SMT]_t} = \frac{k_{SMT}}{k_{pHBA}}\;ln\frac{[pHBA]_0}{[pHBA]_t}$$

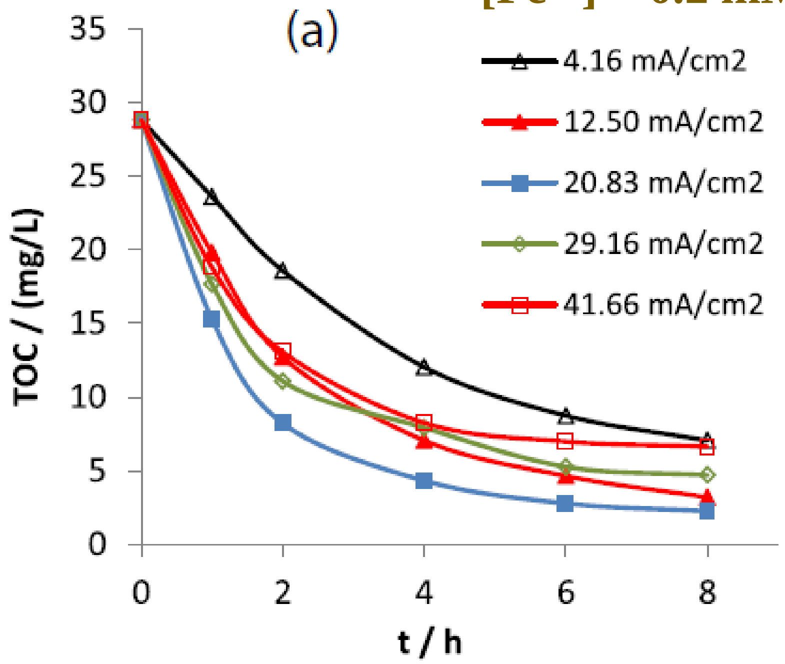
$\boldsymbol{k_{SMT}}$**= 2.9x10^8 $M^{-1}s^{-1}$**

$\boldsymbol{k_{pHBA}}$ **= 2.19 x 10^9 M^{-1} s^{-1}**

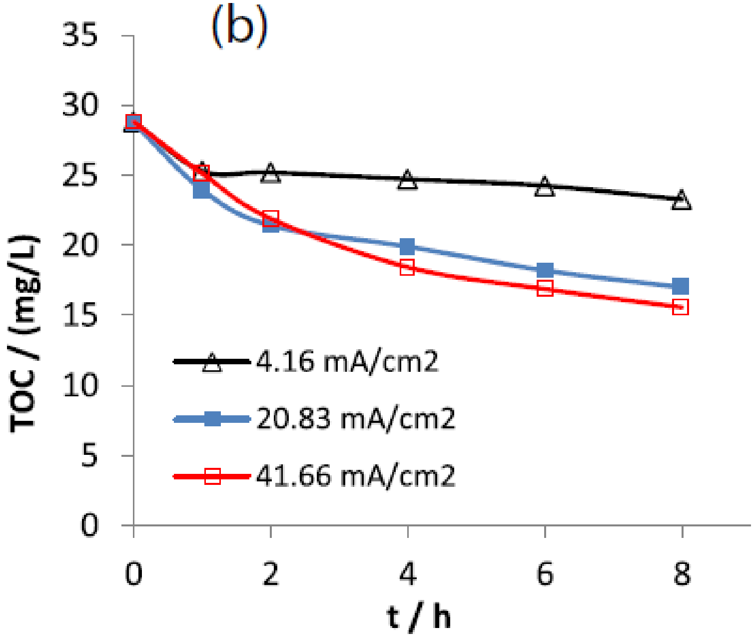
Effect of anode material on the efficiency of EF process for the degradation/mineralization of SMT

Overall reaction $C_{12}H_{14}N_4O_2S + 38H_2O \rightarrow 12CO_2 + 4NO_3^- + SO_4^{2-} + 90H^+ + 84e^-$

$[Fe^{2+}] = 0.2$ mM



a) Electro-Fenton



b) anodic oxidation

Anode of Pt

Cathode: GF

[SMT] = 0.2 mM
pH = 3
[Na2SO4] = 50 mM
Vs = 300 mL

Side reactions

$2H^+ + 2e^- \rightarrow H_2$

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

$2Pt(^{\bullet}OH) \rightarrow 2Pt + O_2 + 2H^+ + 2e^-$

Competition reactions

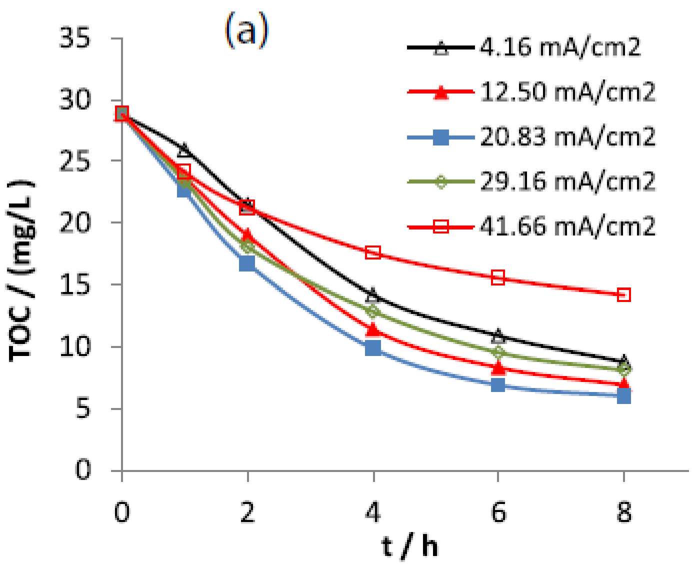
$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-$ $k = 3.2\times10^8\ M^{-1}s^{-1}$

$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O$ $k = 10^7\text{-}10^9\ M^{-1}s^{-1}$

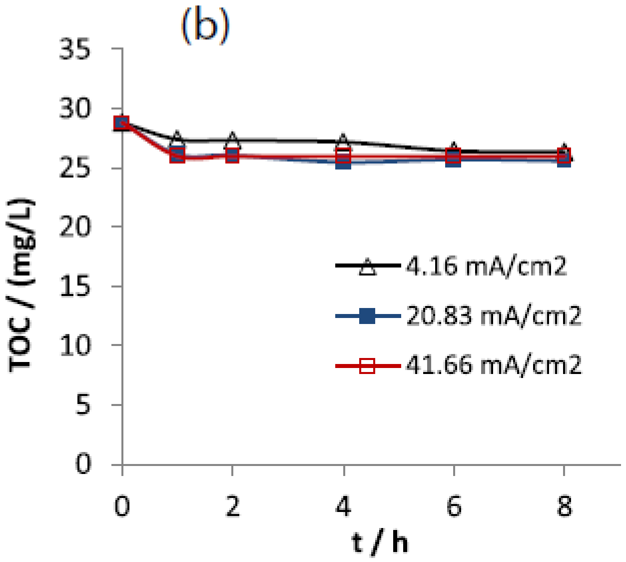
Effect of anode material on the efficiency of EF process for the degradation/mineralization of SMT

DSA anode

$[Fe^{2+}]$ = 0.2 mM



a) Electro-Fenton



b) anodic oxidation

Cathode: GF

[SMT] = 0.2 mM
pH = 3
$[Na_2SO_4]$ = 50 mM
Vs = 300 mL

Very low efficiency

$$M + H_2O \rightarrow MO_x(OH) + H^+ + e^-$$

$$MO_x(OH) \rightarrow MO_{x+1} + H^+ + e^-$$

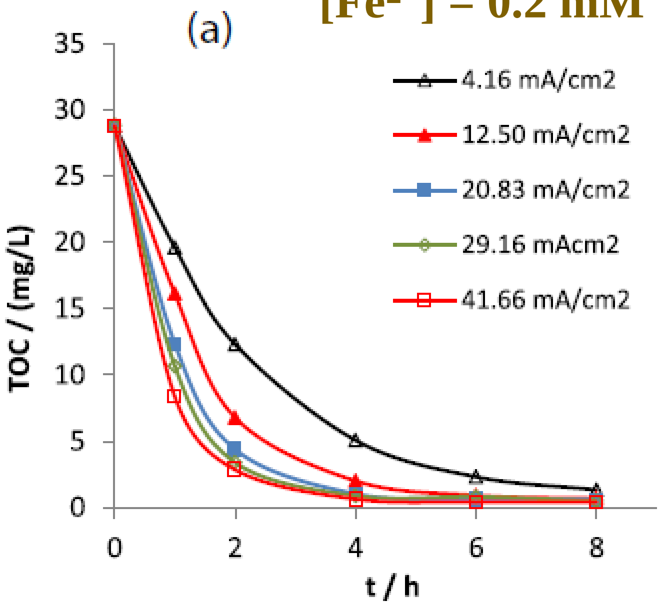
$$MO_{x+1} \rightarrow MO_x + \frac{1}{2} O_{2(g)}$$

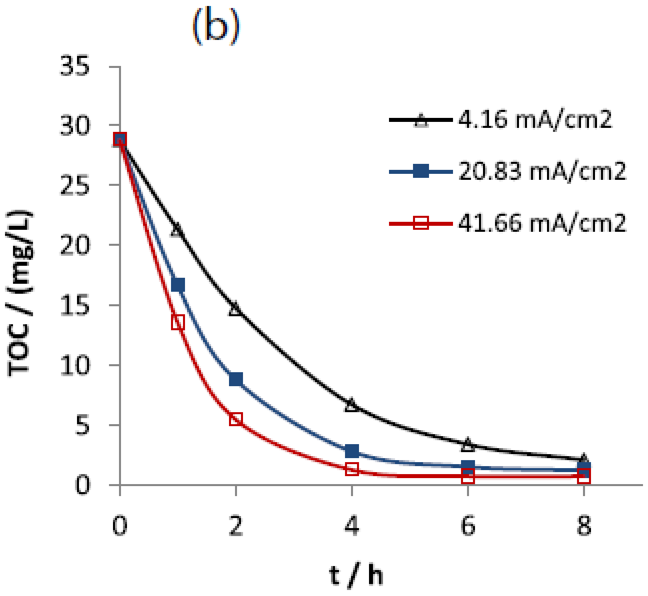
The OER is the prevailing process leading to low degradation efficiencies and loss of electrical energy.

Effect of anode material on the efficiency of EF process for the degradation/mineralization of SMT

BDD anode

$[Fe^{2+}] = 0.2$ mM





Cathode: GF

[SMT] = 0.2 mM
pH = 3
$[Na_2SO_4]$ = 50 mM
Vs = 300 mL

Very efficient electrode

$$BDD + H_2O \rightarrow BDD(HO^\bullet) + H^+ + e^-$$

$$BDD(HO^\bullet) + R \rightarrow BDD + ROH^\bullet \text{ (or } R^\bullet + H_2O)$$

$$2BDD(^\bullet OH) \rightarrow 2BDD + H_2O_2$$

$$BDD(HO^\bullet) \rightarrow BDD + \tfrac{1}{2} O_2 + H^+ + e^-$$

Soft oxidants

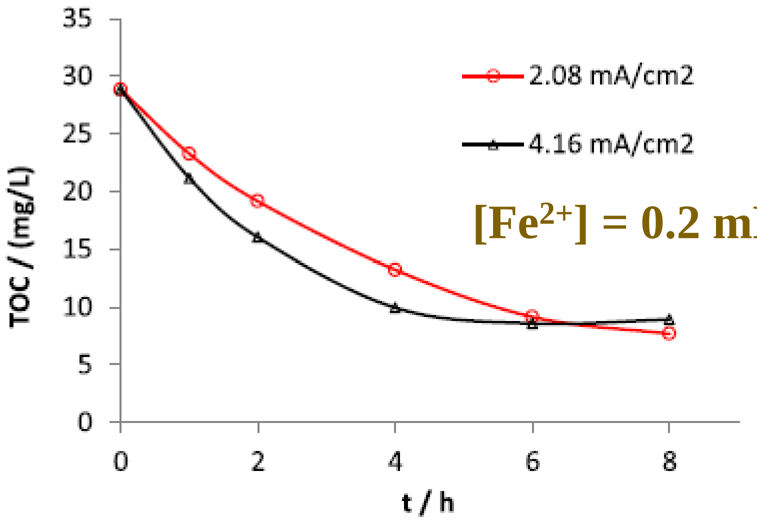
$$^\bullet OH + Cl^- \rightarrow ClO^- + H^+ + e^-$$

$$O_2 + 2\,^\bullet OH \rightarrow O_3 + H_2O$$

$$^\bullet OH + HSO_4^- \rightarrow SO_4^{-\bullet} + H_2O$$

$$SO_4^{-\bullet} + SO_4^{-\bullet} \rightarrow S_2O_8^{2-}$$

TOC removal



$[Fe^{2+}]$ = 0.2 mM

Cathode/Anode: GF

[SMT] = 0.2 mM
pH = 3
$[Na_2SO_4]$ = 50 mM
Vs = 300 mL

Table. 3
TOC removal percentages during electro-Fenton treatment of 0.2 mM SMT solution as function of the anode material and the current density at treatment times of 2 and 6 h.

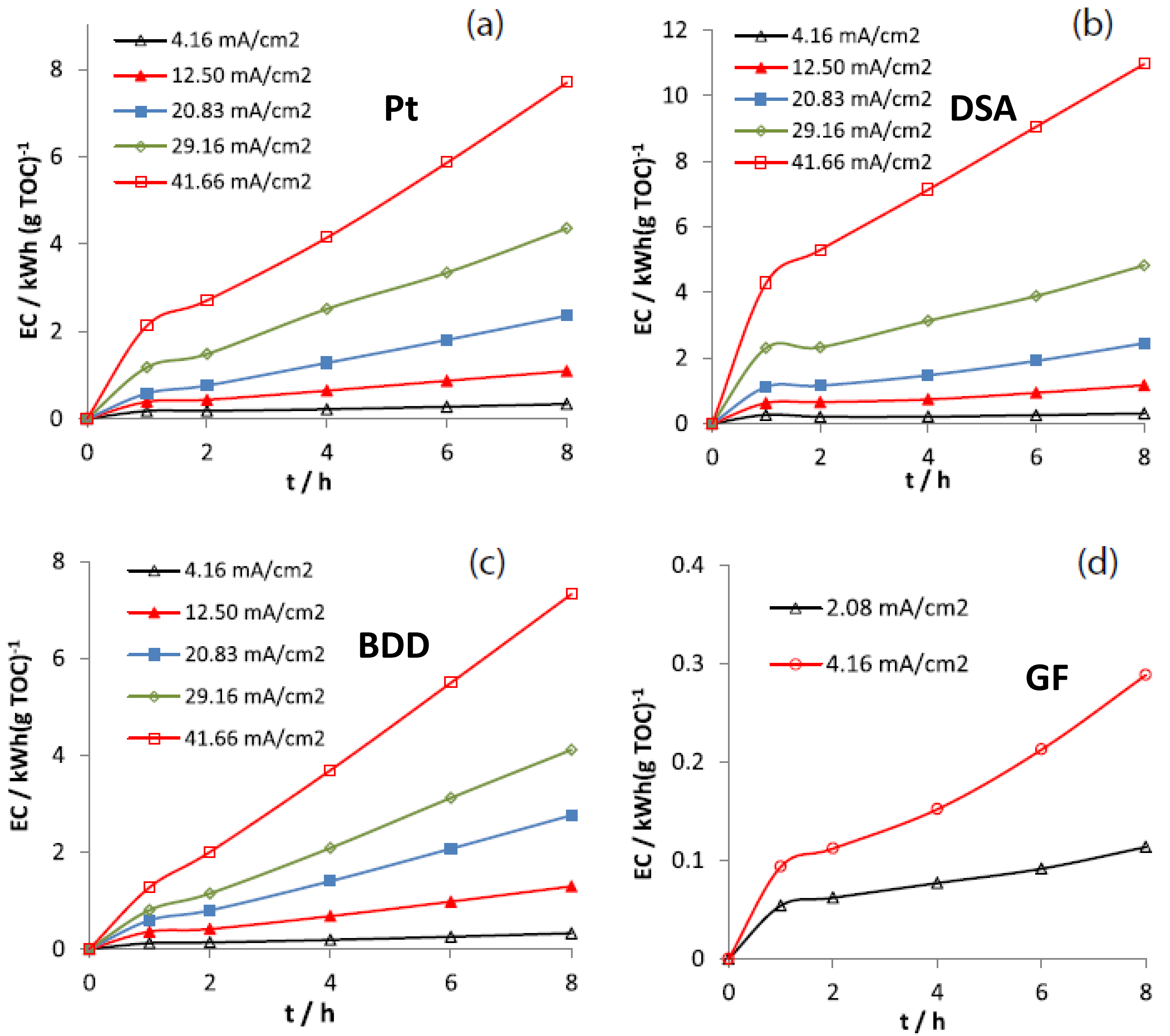
Anode	TOC removal (%) at 2/6 h			
I (mA cm^{-2})	Pt	DSA	BDD	GF
2.08				33.6/68.2
4.16	35.5/69.6	25.5/62.2	57.2/91.9	44.4/70.2
12.50	55.9/83.9	34.1/71.1	76.4/96.8	
20.83	41.5/90.3	41.9/76.1	84.7/96.9	
29.16	61.4/81.7	34.8/75.2	88.2/97.4	
41.66	54.7/75.8	26.3/46.1	90.1/98.5	

Table 4
TOC removal percentages during the anodic oxidation of 0.2 mM SMT solution as a function of anode material and current density.

Anode	TOC removal (%) at 2/6 h			
I (mA cm^{-2})	Pt	DSA	BDD	GF[1]
4.16	12.5/15.8	5.2/8.3	48.7/88.1	–
20.83	25.7/36.8	9.6/10.8	69.4/94.6	–
41.66	24.0/41.4	9.8/9.8	80.9/97.	–

[1] TOC could not be correctly measured because of carbon released from the cathode during long time electrolysis.

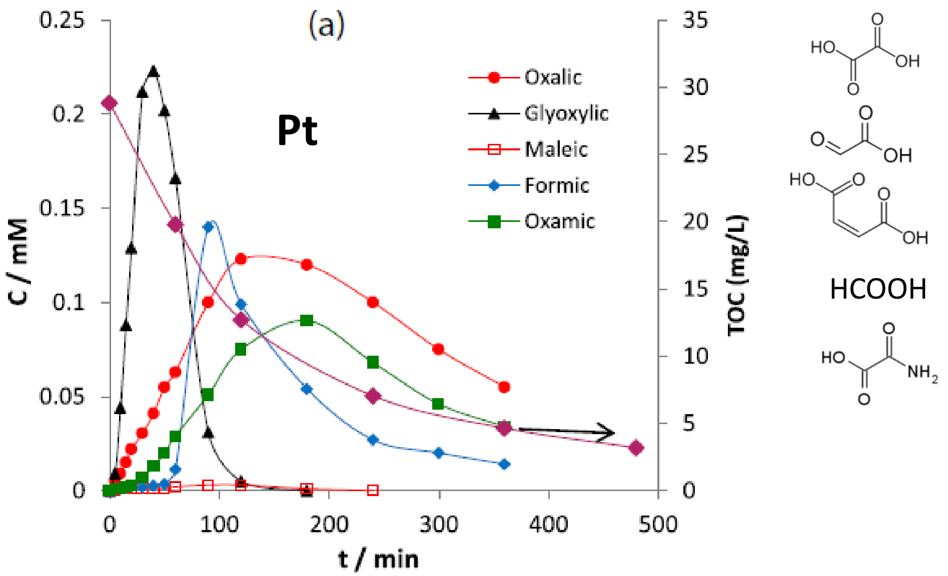
Energy consumption for the mineralization of SMT

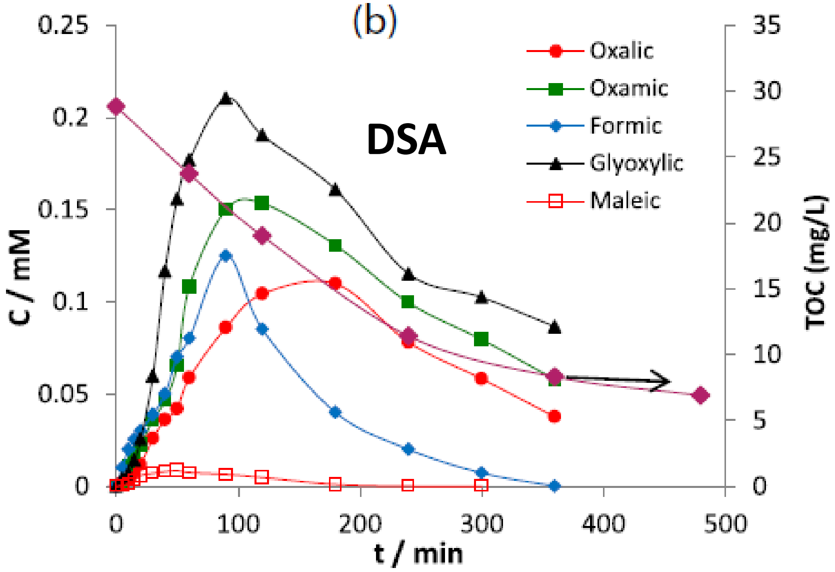


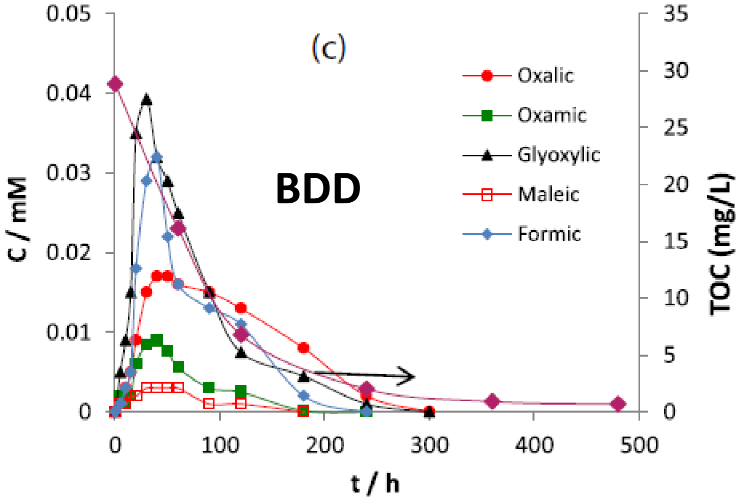
$$\text{EC (kWh (g TOC)}^{-1} = \frac{E_{cell}\ I\ t}{(\Delta(\text{COD})_t\ V_s}$$

E_{cell} is the average cell voltage (V), I is the applied current (A), t is the electrolysis time (h), V_s is the solution volume (L) and $(\Delta TOC)_t$ is the TOC decay (g of C per L^{-1}) at time t.

Determination and evolution of carboxylic acids during electro-Fenton treatment of SMT



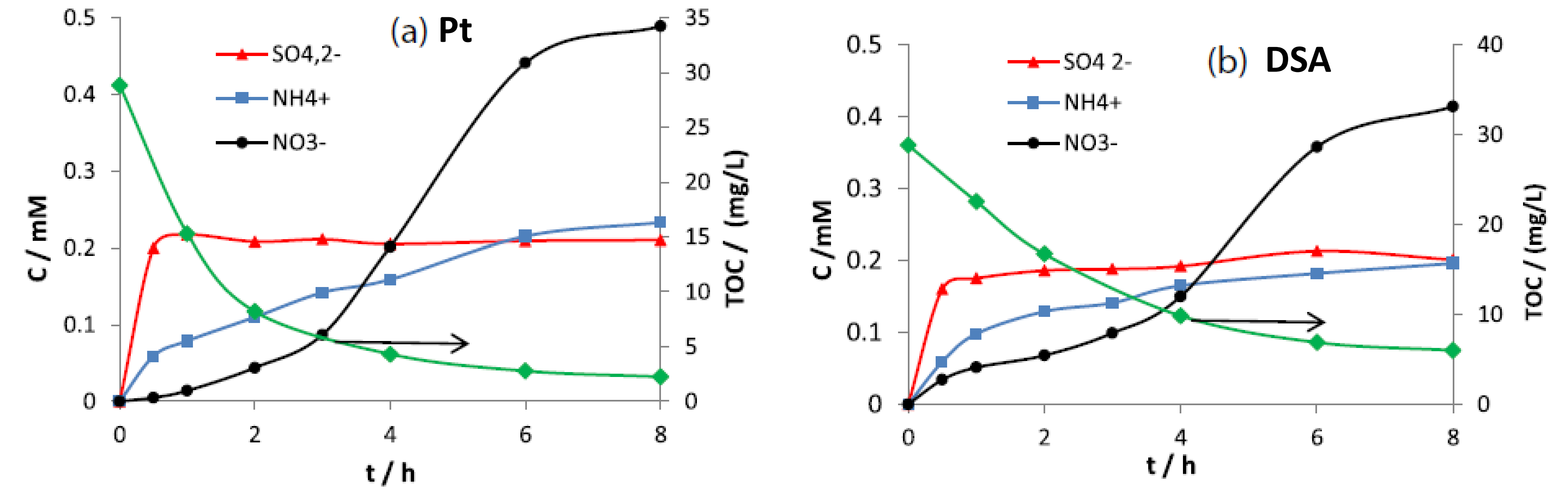




Cathode: GF

[SMT] = 0.2 mM
I **= 12.50 mA/cm2**
pH = 3
[Na_2SO_4] = 50 mM
Vs = 300 mL

Evolution of inorganic ions during the mineralization of SMT



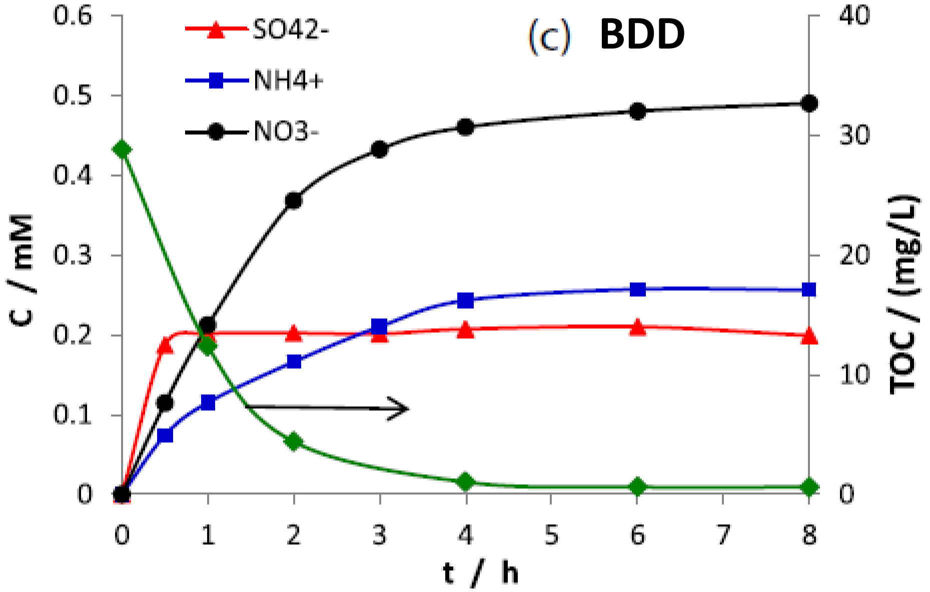
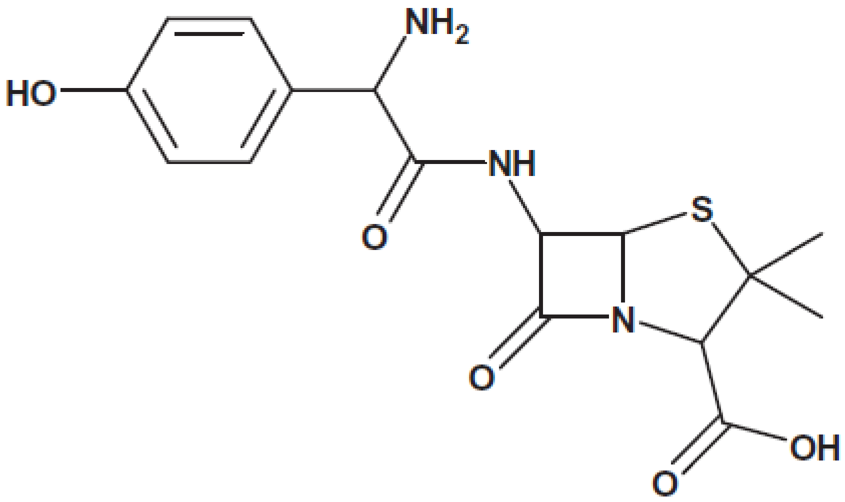


Fig. 12. Time course of inorganic ions formed during electro-Fenton treatment of SMT with electrolytic cells: (a) Pt/GF, (b) DSA/GF and (c) BDD/GF. For NO_3^-: V_s = 300 mL, $[SMT]_0$ = 0.2 mM, $[Fe^{2+}]$ = 0.2 mM, $[Na_2SO_4]$ = 50 mM, I = 20.83 mA cm^{-2}, pH = 3. For NH_4^+: V_s = 300 mL, [SMT] = 0.2 mM, $[Fe^{2+}]$ = 0.2 mM, $[K_2SO_4]$ = 50 mM, I = 20.83 mA cm^{-2}, pH = 3. For SO_4^{2-}: V_s = 300 mL, [SMT] = 0.2 mM, $[Fe^{2+}]$ = 0.2 mM, [NaCl] = 50 mM, I = 20.83 mA cm^{-2}, pH = 3. The green curve (–♦–) represents the evolution of solution TOC during treatment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

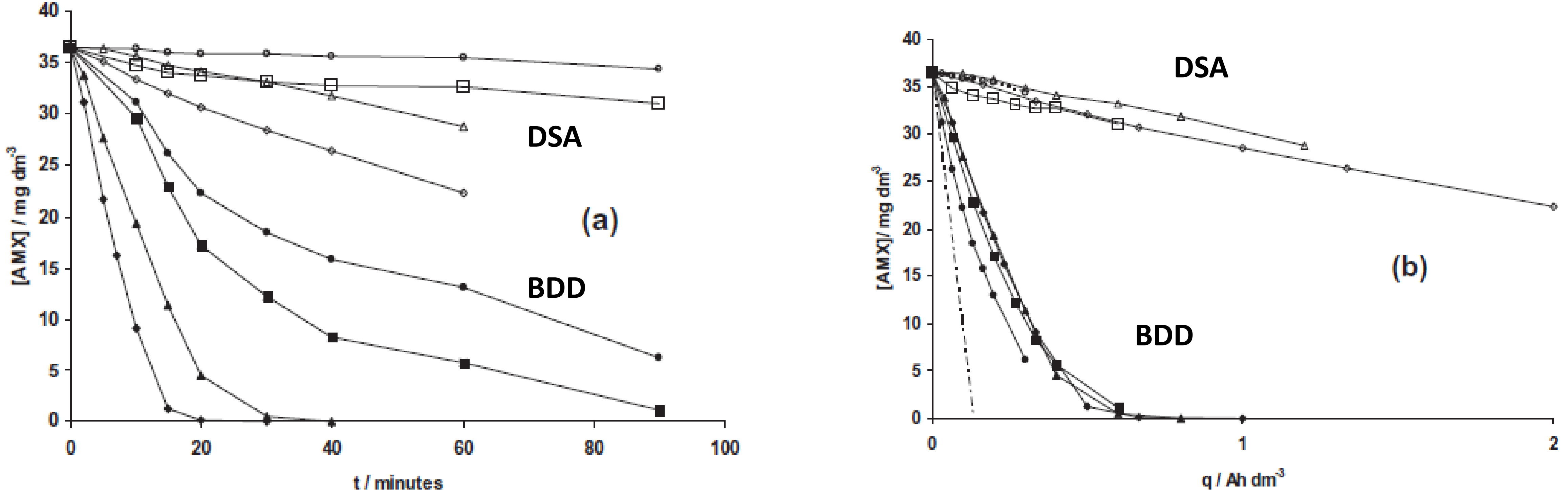
Impact of anode materials on the electrochemical oxidation and degradation of amoxicillin AMX



Tested anodes:
Pt, DSA, DBB, PbO2, GF, carbon fiber

F. Sopaj, M. A. Rodrigo, N. Oturan, **F. I. Podvorica**, J. Pinson, M. A. Oturan. *Chem. Eng. Journal*, **2015**, *262*, 286-294.

Effect of current density (mA/cm2) on the oxidation of AMX for DSA and BDD anodes



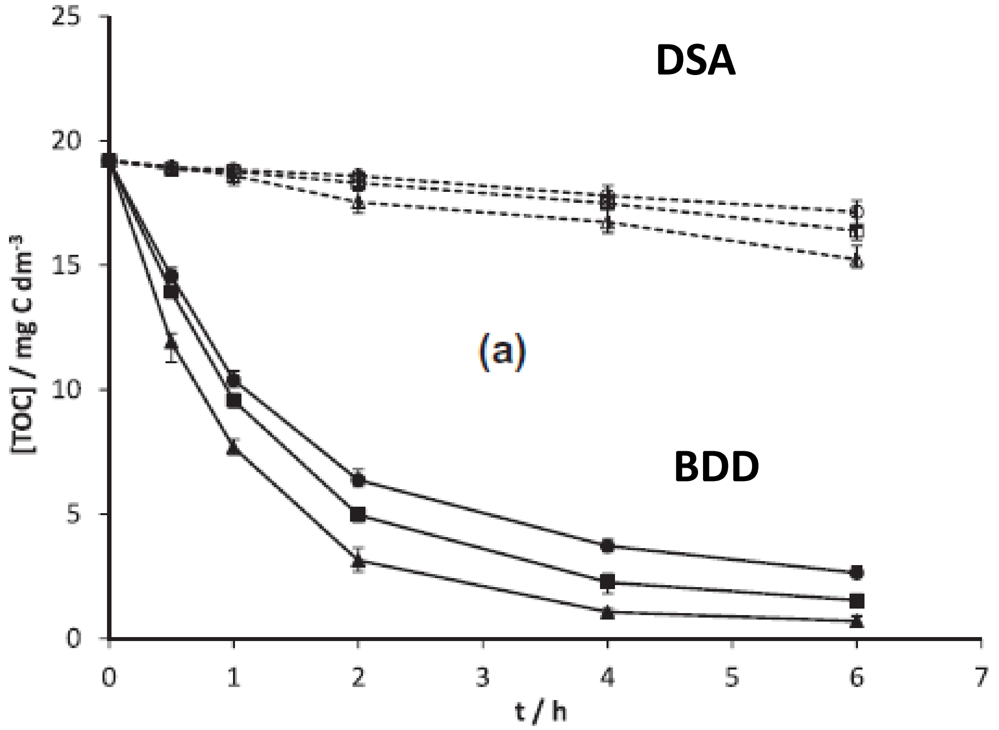
[AMX] = 0.1 mM
pH = 5.3
[Na_2SO_4] = 50 mM
Vs = 300 mL

BDD (●: 2.08; ■: 4.60; ▲: 12.50; and ♦: 20.83 mA cm^{-2})
DSA (○: 2.08; □: 4.60; Δ: 12.50; and ◇: 20.83 mA cm^{-2})

F. Sopaj, M. A. Rodrigo, N. Oturan, **F. I. Podvorica**, J. Pinson, M. A. Oturan. *Chem. Eng. Journal*, **2015**, *262*, 286-294.

Effect of current density on the mineralization of AMX

$$C_{16}H_{19}N_3O_5S + 40\ H_2O \rightarrow 16\ CO_2 + 3NO_3^- + SO_4^{2-} + 99\ H^+ + 94\ e^-$$



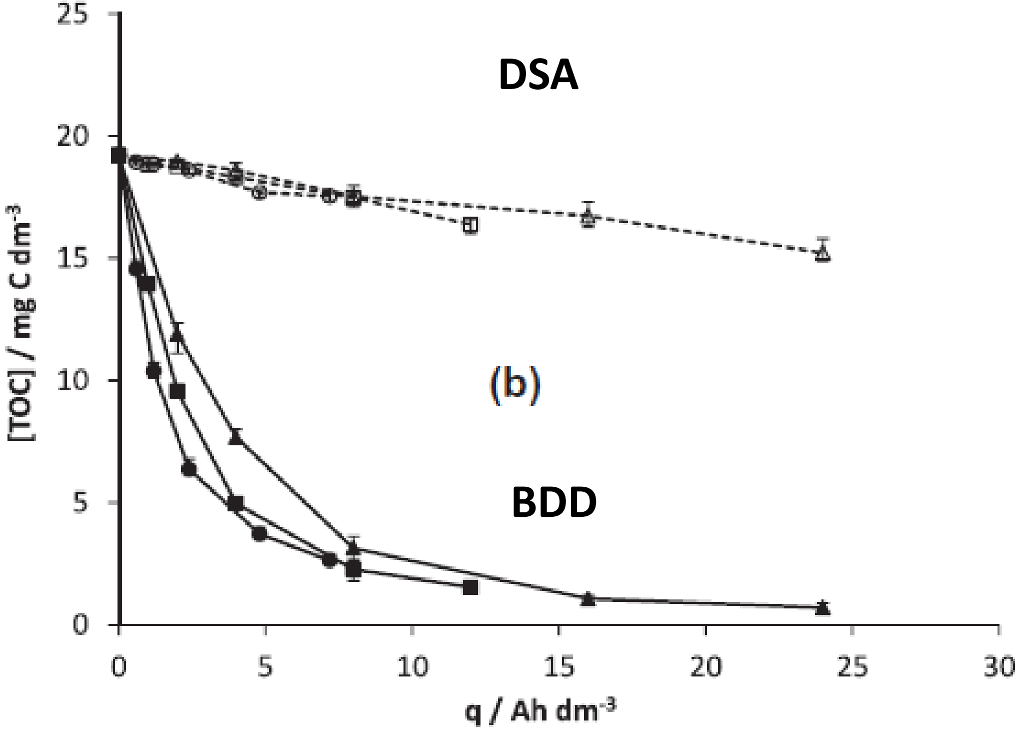
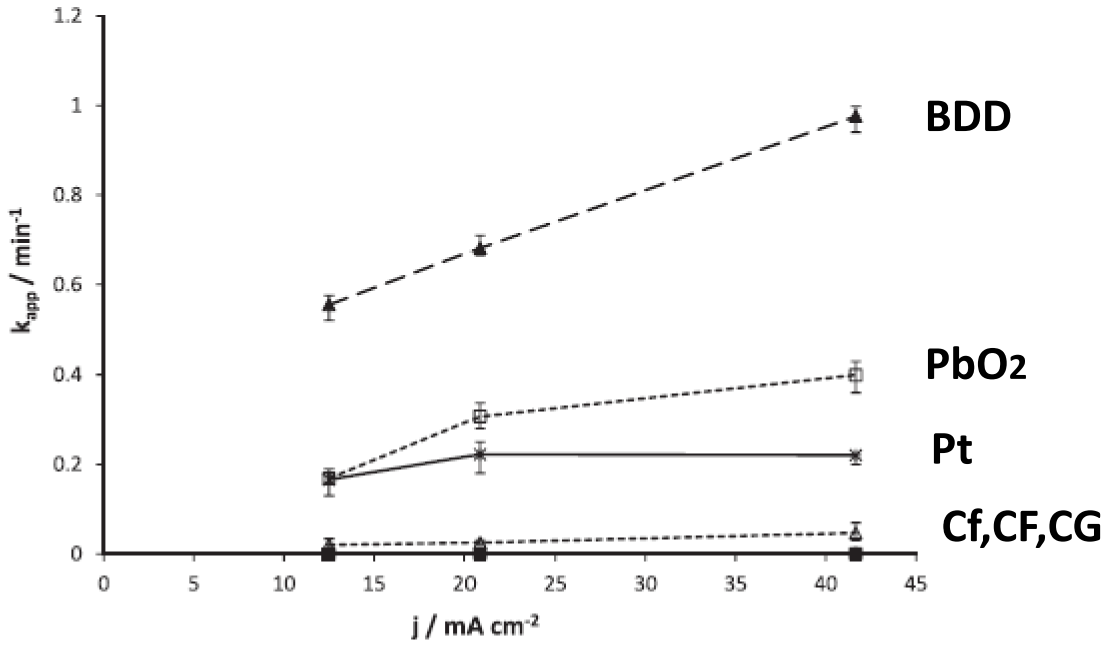
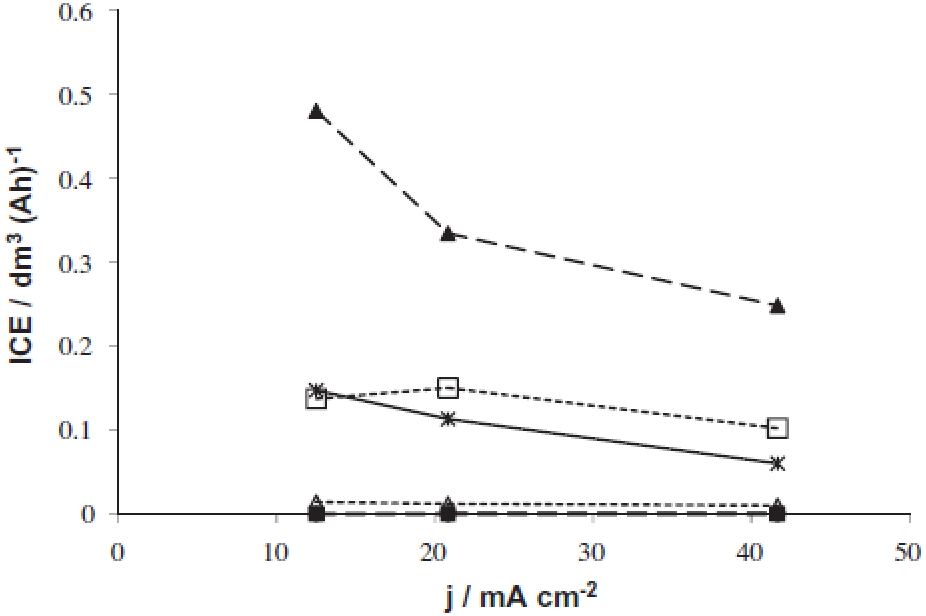


Fig. 3. Effect of current density on the mineralization of AMX with DSA (○: 12.50 mA cm^{-2}; □: 20.83 mA cm^{-2}; and Δ: 41.66 mA cm^{-2}) and BDD anodes (●: 12.50 mA cm^{-2}; ■: 20.83 mA cm^{-2}; and ▲: 41.66 mA cm^{-2}). (a) TOC changes vs. time and (b) TOC changes vs. electrical charge. Raw AMX solution: 0.1 mM AMX, 50 mM Na_2SO_4, pH 5.3. Room temperature.

Effect of the current density on the rate of mineralization of AMX with anodes





Current efficiency for mineralization

Performances of anodes

High efficient anodes

High overpotential for OER

- Efficient mineralization of pollutant
- EC reactions limited only by mass transfer of the pollutant
- Generation of power oxidant intermediates

BDD and PbO_2

Graphite cold incineration

Low efficient anodes

Low overpotention for OER

- Small conversion to CO_2
- Slow oxidation rates
- Small current efficiencies

Pt,DSA, CF

Effect of cathode material on the efficiency of Eelectro-Fenton process for the degradation/mineralization of SMT

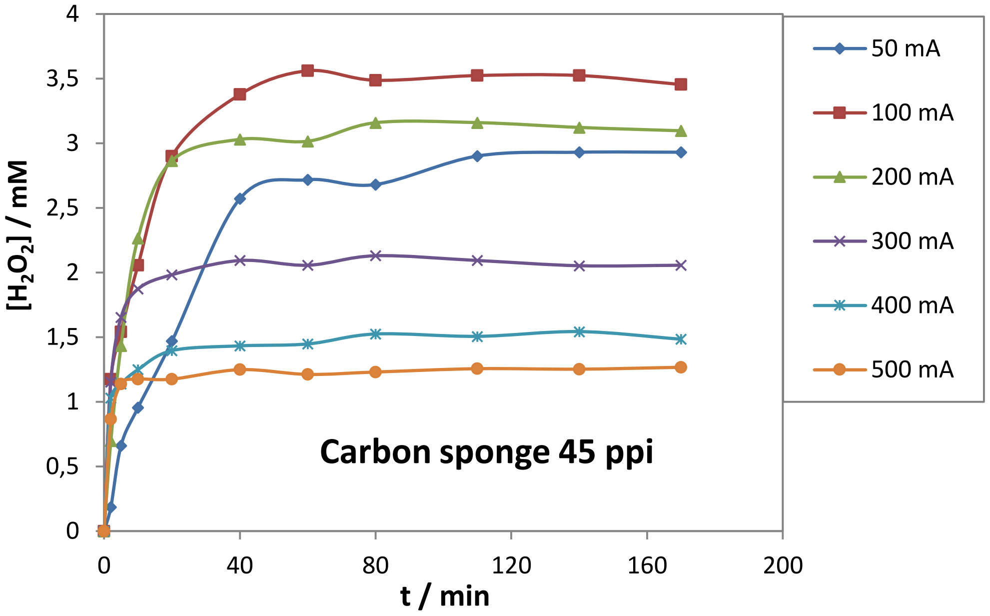
Used cathodes:

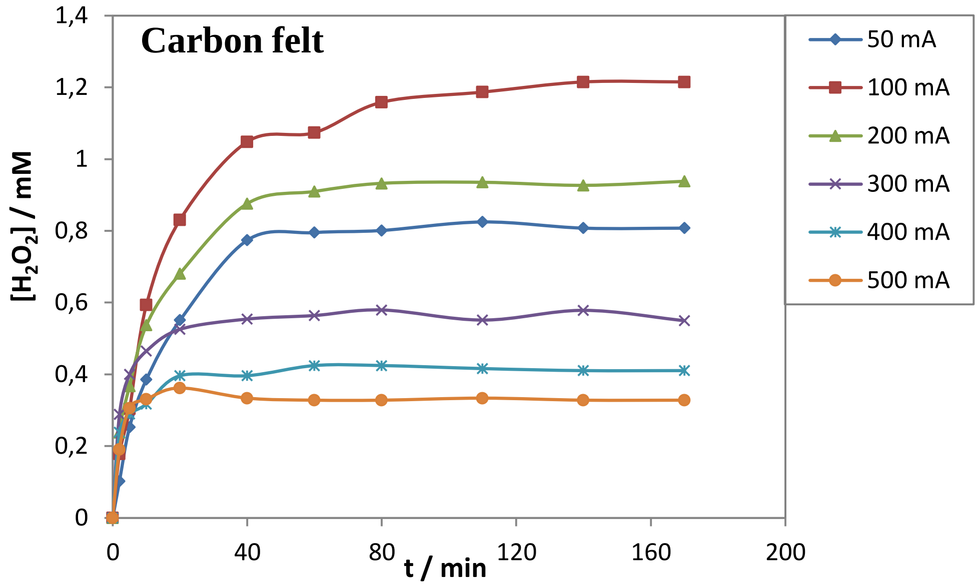
Carbon fiber
Carbon felt,
Carbon sponge of different porosities
Stainless steel

F. Sopaj, N. Oturan, J. Pinson, F. Podvorica, M. A. Oturan. *submitted*

Evolution of the concentration hydrogen peroxide in the cells

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$





Continuous compressed air bubbling.

V_s = 250 mL,

$[Na_2SO_4]$ = 50 mM,

pH = 3.

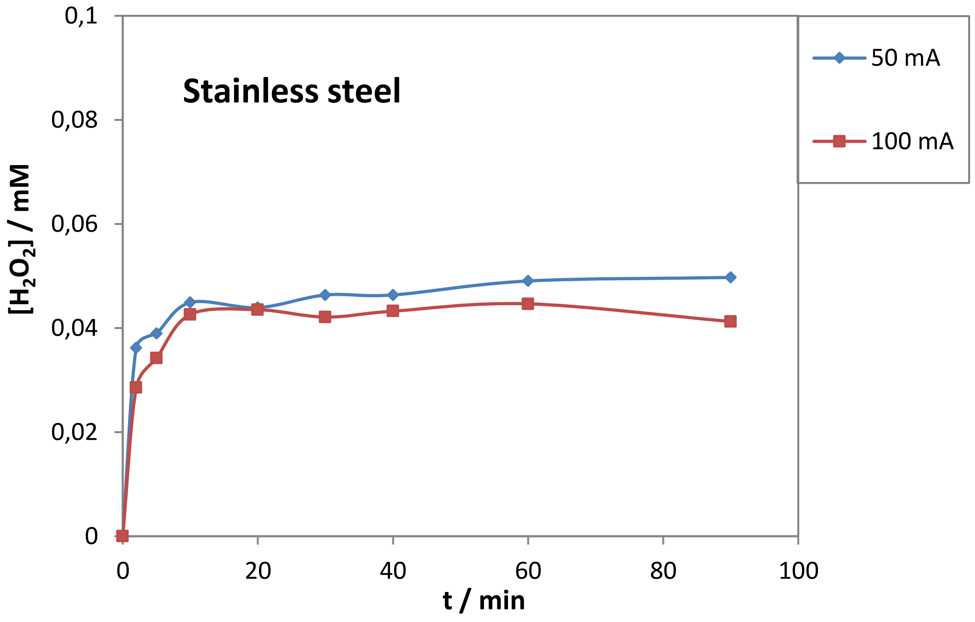
Parasitic reactions

$$2H^+ + 2e^- \rightarrow H_2$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

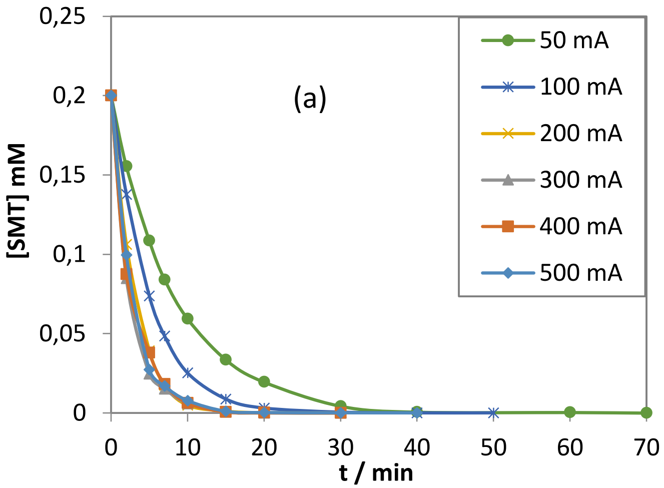
$$H_2O_2 \rightarrow HO_2^{\bullet} + H^+ + e^-$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O$$



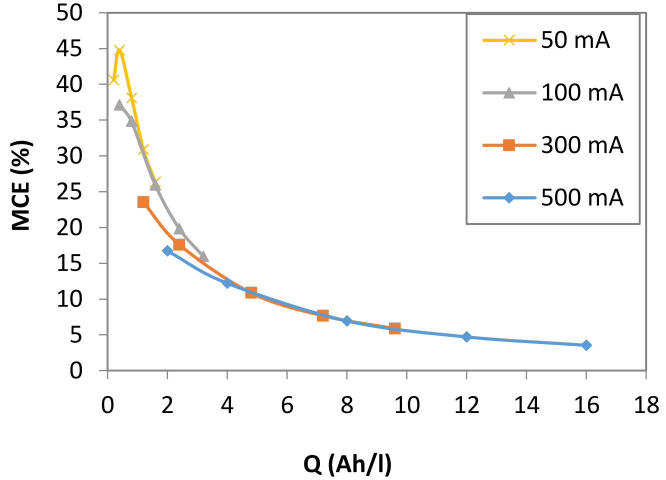
Best performance cell for EF: Carbon sponge 45ppi – BDD

Effect of current intensity

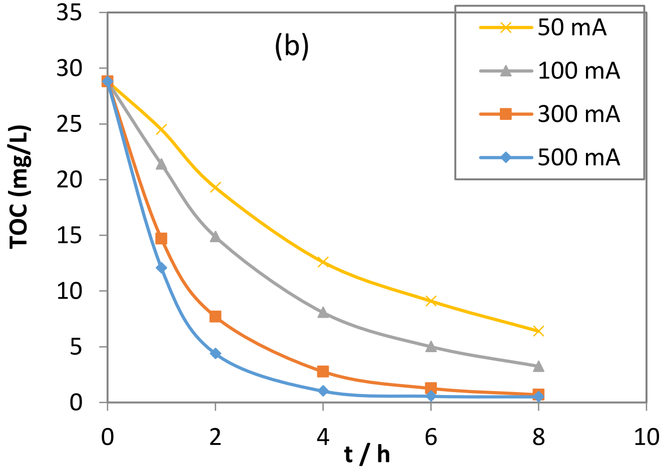


Oxidation of SMT

[SMT] = 0.2 mM,
$[Fe^{2+}]$ = 0.2 mM,
$[Na_2SO_4]$ = 50 mM,
pH = 3.
V_s = 250 mL,

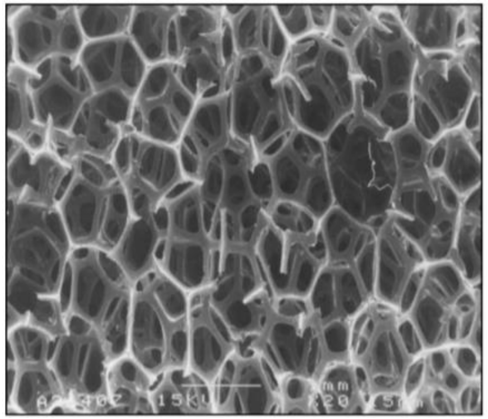


Mineralization current efficiency



Mineralization of SMT

Carbon sponge (open-pore honeycomb structure)



SEM micrograph of a 60 ppi (nominal pores per linear inch) reticulated vitreous carbon (RVC) sample

Friedrich et al. *J. Electroanal. Chem.* **2004**, *561*, 203.

CONCLUSION

Advantages

- **Electro-Fenton is a very efficient method for the degradation and full mineralization of POPs**
- **Easy to use and easy control of the degradation kinetics**
- **Nonuse of harmful of chemical reagents**
- **Total mineralization by optimizing the operating parameters: current density, solution pH, catalyst concentration**
- **Eco-friendly process: in situ generation of H_2O_2**
- **Anode and cathode materials plays a crucial role in the EAOPs**
- **Anodes with high over potential for OER allow to generate supplementary hydroxyl radical (M(•OH))**
- **Cathodes with high over potential for HER enhance the production of H_2O_2 and the regeneration of iron ions**

- **Drawbacks**
- **Release of inorganic ions during mineralization of POPs containing heteroatoms and the use of supporting electrolyte**
- **Use of acid solution for the control of pH**
- **High price of BDD electrode**
- **Formation of recalcitrant byproducts as intermediates**

- **Perspectives**

- **Use of hybrid AOPs**

- **Use of renewable energy sources together with electrochemical treatments**

- **Development of new materials with exciting properties must be widely explored (e.g. Ti_4O_7 anode)**

Acknowledgments

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Dr. F. Sopaj, University of Prishtina, Kosovo

Thank you very much for your attention