

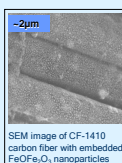
Efficient Electro-Fenton Degradation of Pharmaceutically Active Compounds in a Novel Electrochemical Flow-Through Device

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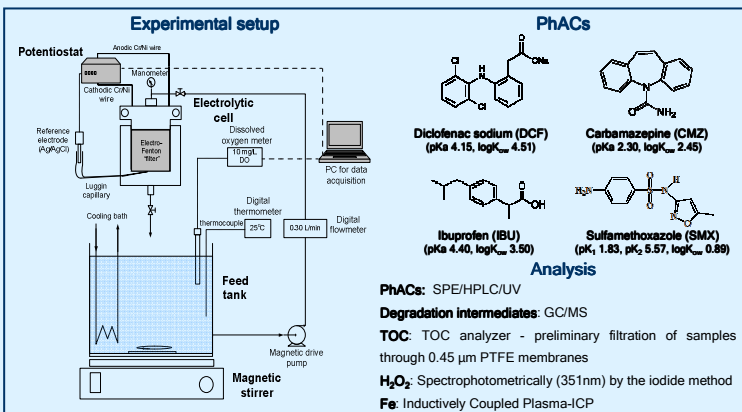
Scope

Development of a novel electrochemical flow-through device for the purification of contaminated aqueous media from toxic organic micropollutants (e.g. pharmaceutically active compounds - PhACs) through Fenton reactions.



Development of specific conductive electrodes with embedded catalytic ferric ions and/or iron nanoparticles (nFe) for the efficient production of the highly active hydroxyl radicals ($\cdot\text{OH}$).

Experimental Equipment - Procedures



Electrode materials

- Carbon fiber (CF-1410) S_{BET} : 1410 m^2/gr
- Carbon fiber (CF-1371) S_{BET} : 1371 m^2/gr
- Coconut Carbon Block (CCB-470) S_{BET} : 470 m^2/gr [Pentair CCBC-10]
- Carbon fiber (CFm-1005) S_{BET} : 1005 m^2/gr [MAST Carbon International Ltd]

Synthesis of cathodic Fe/C electrodes

Dispersion/impregnation of catalytic iron using as Fe source:

- $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
- $\text{FeCl}_3 \cdot \text{FeCl}_2 \cdot 6\text{H}_2\text{O}$
- FeOFe_2O_3 nanoparticles

for different Fe/C ratios (10, 30, 50, 70% w/w)

Characterization

- N_2 adsorption/desorption
- SEM
- porosimetry
- pH_{zpc}
- XRD
- Conductivity

Results

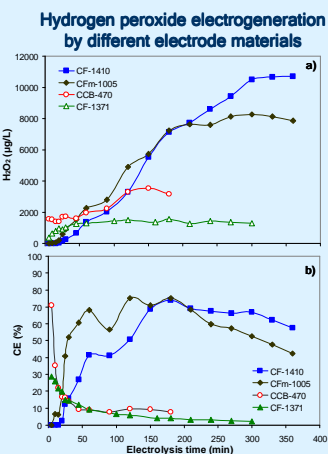


Fig. a) H_2O_2 concentration and b) current efficiency as a function of electrolysis time, at optimum cathodic potentials, for the four different carbon materials: CF-1371 and CF-1410 at 1.3V/Ag/AgCl, CFm-1005 at 1.0V/Ag/AgCl, CCB-470 at 0.5V/Ag/AgCl. Solutions of 0.05M Na_2SO_4 , pH 3, recirculation liquid flow 300 mL/min, temperature 25 $^\circ\text{C}$, anodic and cathodic electrodes of the same material.

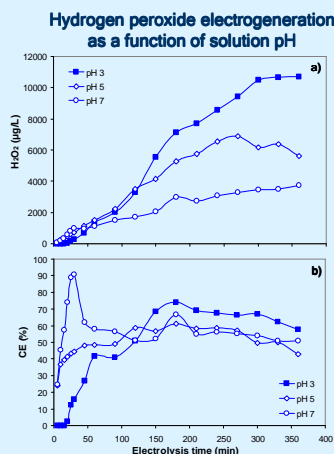


Fig. b) Effect of solution pH on a) H_2O_2 electrogeneration and b) current efficiency as a function of electrolysis time. Electrolysis of 0.05M Na_2SO_4 solutions at a constant potential 1.3 V/Ag/AgCl, using CF-1410 electrodes. Recirculation liquid flow 300 mL/min, temperature 25 $^\circ\text{C}$.

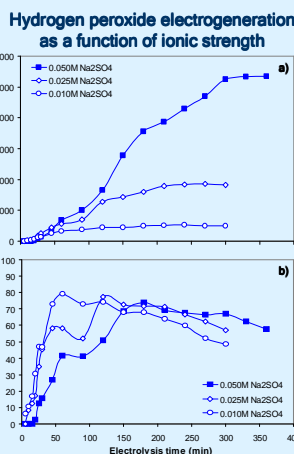


Fig. c) Effect of solution ionic strength (different Na_2SO_4 concentrations) on a) H_2O_2 electrogeneration and b) current efficiency as a function of electrolysis time. Electrolysis at pH 3 and constant potential 1.3 V/Ag/AgCl, using CF-1410 electrodes. Recirculation liquid flow 300 mL/min, temperature 25 $^\circ\text{C}$.

Removal/Degradation of PhACs by the EF "filter"

Electrodes	Adsorption stage		Electrolysis stage		
	$m_{\text{DCF},0}$ (g)	$m_{\text{DCF}}^{\text{max}}$ (g/9CF-1410)	Q (Coulomb)	% DCF	% TOC
Anode: CF-1410 Cathode: CF-1410, Fe/C 10% (FeCl ₃)	0.085	0.079	185.6	55.0	4.5
Anode: CF-1410 Cathode: CF-1410, Fe/C 30% (FeCl ₃)	0.100	0.089	417.2	63.0	26.8
Anode: CF-1410 Cathode: CF-1410, Fe/C 10% (FeCl ₃ ·9H ₂ O)	0.073	0.064	1155.0	73.0	32.2
Anode: CF-1410 Cathode: CF-1410, Fe/C 30% (FeCl₃·6H₂O)	0.065	0.055	3574.0	82.4	54.2
Anode: CF-1410 Cathode: CF-1410, Fe/C 30% (FeOFe ₂ O ₃)	0.101	0.010	6460.6	62.7	35.9

Table. Results of PhACs removal by the EF "filter" (anode: CF-1005, cathode: CFm-1005 + CF-1410, Fe 30% Fe/C, physical pH, 0.05M Na_2SO_4 , recirculation liquid flow 50 mL/min, temperature 25 $^\circ\text{C}$).

PhAC	Adsorption stage		Electrolysis stage	
	C_{initial} (mg/L)	$(\theta)_{\text{PhAC}}^{\text{CFm-1005}}$	%PhAC	%TOC
DCF	43	0.051	71.8	18.8
CMZ	19.6 (x2) ^a	0.025	68.0	20.1
IBU	48.4	0.061	73.6	67.0
SMX	39.6	0.057	87.1	34.9

^aRecirculation of feed solutions of the same initial concentration (considering carbamazepine water solubility).

Conclusions

- A significant electrogeneration of H_2O_2 can take place at low controlled electrode potential, regardless of the pH and/or the ionic strength of the feed water.
- The effective embedding/dispersion of catalytic iron on the cathodic electrode results in Fenton reactions that generate strong oxidizing species which are capable of degrading typical PhACs (diclofenac, carbamazepine, ibuprofen, sulfamethoxazole) frequently detected in source waters.
- Fe/C content of the cathodic electrode and the iron source used play a significant role on the efficiency of the "filter" to degrade the selected PhACs.
- Ongoing research on optimization of a continuously operated electro-Fenton "filter" by investigating system design and parameter modifications.

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Reference

Plakas, K.V., Karabelas, A.J., Sklari, S.D., Zaspalis, V.T. (2013) Toward the development of a novel electro-Fenton system for eliminating toxic organic substances from water. Part 1. In situ generation of hydrogen peroxide, Industrial and Engineering Chemistry Research 52 (39), 13948-13956.

