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

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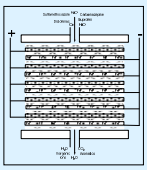
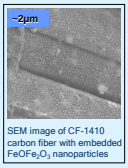
Scope



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.

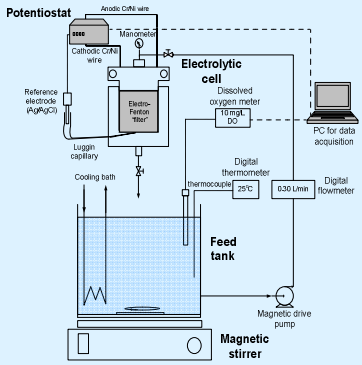


SEM image of CF-1410 carbon fiber with embedded $FeOFe_2O_3$ nanoparticles

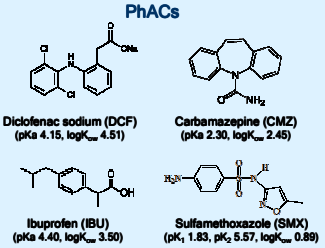
Development of specific conductive **electrodes** with embedded **catalytic ferric ions and/or iron nanoparticles** (nFe) for the efficient production of the highly active hydroxyl radicals (•OH).

Experimental Equipment - Procedures

Experimental setup



PhACs



Diclofenac sodium (DCF) (pKa 4.15, $logK_{ow}$ 4.51)

Carbamazepine (CMZ) (pKa 2.30, $logK_{ow}$ 2.45)

Ibuprofen (IBU) (pKa 4.40, $logK_{ow}$ 3.50)

Sulfamethoxazole (SMX) (pK_1 1.83, pK_2 5.57, $logK_{ow}$ 0.89)

Analysis

PhACs: SPE/HPLC/UV

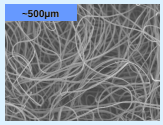
Degradation intermediates: GC/MS

TOC: TOC analyzer - preliminary filtration of samples through 0.45 μm PTFE membranes

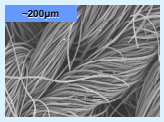
H_2O_2: Spectrophotometrically (351nm) by the iodide method

Fe: Inductively Coupled Plasma-ICP

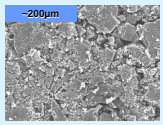
Electrode materials



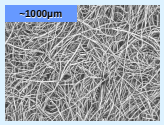
Carbon fiber (CF-1410)
S_{BET}: 1410m^2/gr



Carbon fiber (CF-1371)
S_{BET}: 1371m^2/gr



Coconut Carbon Block (CCB-470)
S_{BET}: 470m^2/gr
[Pentair CCBC-10]

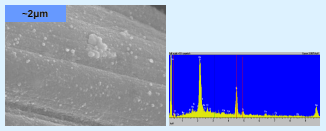


Carbon fiber (CFm-1005)
S_{BET}: 1005m^2/gr
[MAST Carbon International Ltd]

Synthesis of cathodic Fe/C electrodes

Dispersion/impregnation of catalytic iron using as Fe source:
- $Fe(NO_3)_3 9H_2O$
- $FeCl_3$; $FeCl_3 6H_2O$
- $FeOFe_2O_3$ nanoparticles

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



SEM / EDS X-ray analysis of CFm-1005 embedded $FeOFe_2O_3$ nanoparticles

Characterization

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

Results

Hydrogen peroxide electrogeneration by different electrode materials

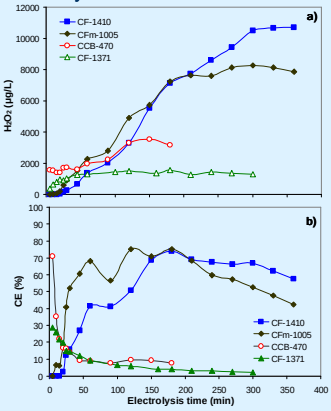


Fig. a) H_2O_2 concentration and b) current efficiency as a function of electrolysis time, at optimum cathodic potentials, for the four different carbon materials: CF-1371 and CF-1410 at 1.3V/Ag/AgCl, CFm-1005 at 1.0V/Ag/AgCl, CCB-470 at 0.5V/Ag/AgCl. Solutions of 0.05M Na_2SO_4, pH 3, recirculation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

Hydrogen peroxide electrogeneration as a function of solution pH

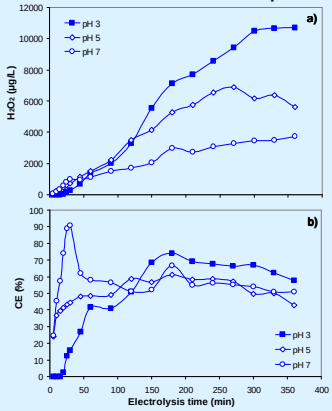


Fig. Effect of solution pH on a) H_2O_2 electrogeneration and b) current efficiency as a function of electrolysis time. Electrolysis of 0.05M Na_2SO_4 solutions at a constant potential 1.3 V/Ag/AgCl, using CF-1410 electrodes. Recirculation liquid flow 300 mL/min, temperature 25 °C.

Hydrogen peroxide electrogeneration as a function of ionic strength

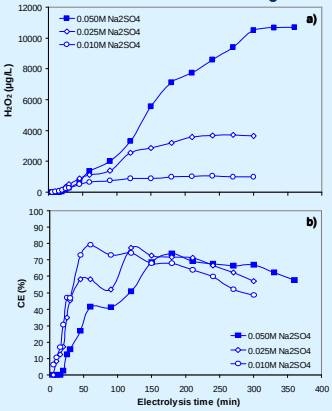


Fig. Effect of solution ionic strength (different Na_2SO_4 concentrations) on a) H_2O_2 electrogeneration and b) current efficiency as a function of electrolysis time. Electrolysis at pH 3 and constant potential 1.3 V/Ag/AgCl, using CF-1410 electrodes. Recirculation liquid flow 300 mL/min, temperature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

Removal/Degradation of PhACs by the EF "filter"

Table. Effect of iron source and Fe/C content on DCF removal

	Adsorption stage		Electrolysis stage		
Electrodes	$m_{DCF,o}$ (g)	$m_{ads,\ DCF}$ ($g/g_{CF-1410}$)	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% ($FeCl_3 6H_2O$)	0,073	0,064	1155,0	73,0	32,2
Anode: CF-1410 Cathode: CF-1410, Fe/C 30% ($FeCl_3 6H_2O$)	**0,065**	**0,055**	**3574,0**	**82,4**	**54,2**
Anode: CF-1410 Cathode: CF-1410, Fe/C 30% ($FeOFe_2O_3$)	0,101	0,010	6460,6	62,7	35,9

Table. Results of of PhACs removal by the EF "filter" (anode: CF_m-1005, cathode: CFm-1005 + CF_m-Fe 30% Fe/C, physical pH, 0.05M Na_2SO_4, recirculation liquid flow 50 mL/min, temperature 25 °C).

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

*Recirculation 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.

Acknowledgements

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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.

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