Solar foto-electroFenton process for the removal of carbamazepine in real grey water from a Euro-Mediterranean touristic resort

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INTRODUCTION

Fenton process is an Advanced Oxidation Process (AOP) based on the generation of hydroxyl radical (·OH, E^o_{NHE} (·OH/H_2O) = 2.80 V vs NHE), highly oxidant agent able to mineralize organic matter in water [1] under acidic media.

$$Fe^{2+}_{(aq)} + H_2O_{2\,(aq)} \rightarrow Fe^{3+}_{(aq)} + OH^-_{(aq)} + \cdot OH_{(aq)}$$

In **electroFenton type process**, **H_2O_2 reagent** can be **electrogenerated in situ** in an Advanced Electrochemical Process thorough a gas diffusion electrode [1]. The process efficiency can be enhanced by near-UV to visible light assistance (up to around 550 nm [2], and **could be then driven under solar irradiation** significantly reducing the economic and environmental burden.

In the last years, these processes have been oriented to the **removal of micropollutants** in water. In the present work, which has been developed under the **European demEAUmed project**, the solar assisted foto-electroFenton process has been applied for the **removal of carbamazepine** (CBZ), a common pharmaceutical product detected in some **grey waters** coming from the daily activity of a representative **Euro-Mediterranean resort**.

METHODS

The electroFenton electrochemical cell was designed and constructed in LEITAT facilities. It consisted on a 37 ml PTFE mono-compartimental water chamber with 37 cm^2 Bored Doped Diamond supported on Niobium anode and 37 cm^2 Gas Diffusion Cathode (GDC) with carbon catalyst membrane to **electrogenerate H_2O_2**.

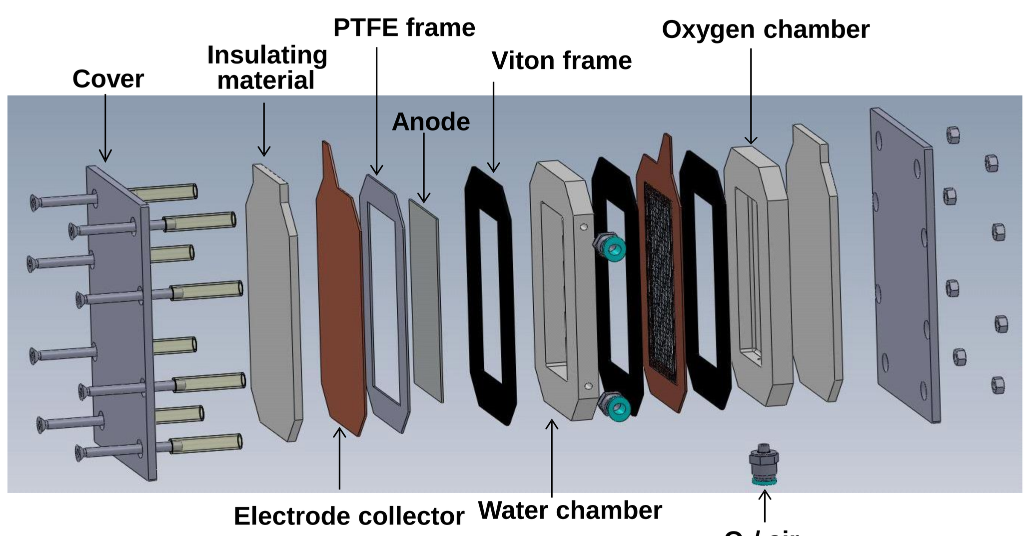
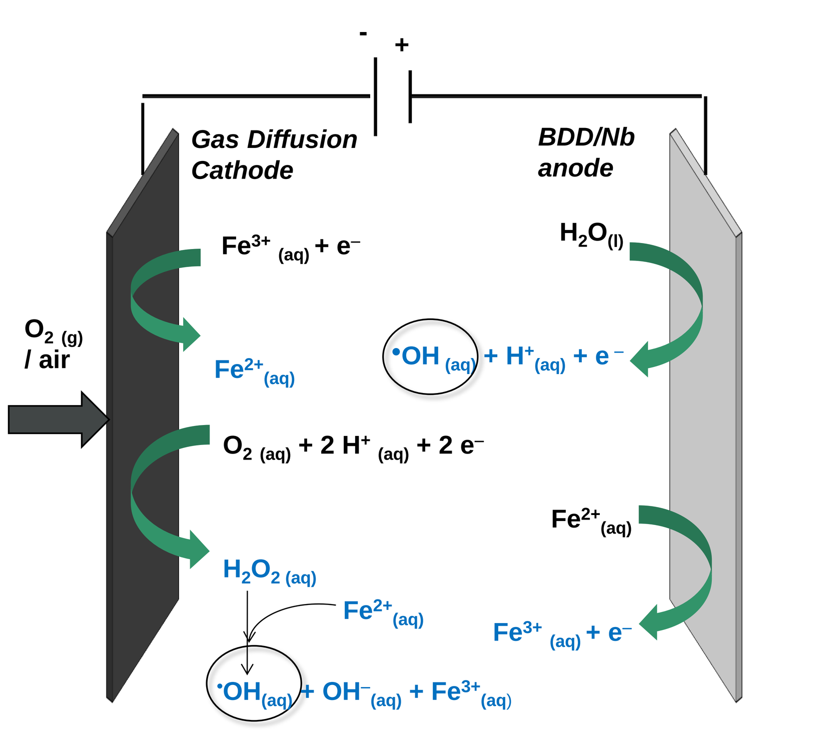


Figure 1. Electrochemical cell detail.

10 mg/l Fe was directly added into the system to produce electro-Fenton reaction. The system was connected to a **CPC system** [4] that promoted solar photo-Fenton reactions with an average irradiation value of **35 W/m²**.



$$Fe^{3+}_{(aq)} + H_2O_{(l)} \longrightarrow [FeOH]^{2+}_{(aq)} + H^+_{(aq)}$$
$$[FeOH]^{2+}_{(aq)} \longrightarrow {}^{\bullet}OH_{(aq)} + Fe^{2+}_{(aq)}$$
$h\upsilon$ (λ = 290-400 nm)

Figure 2. Solar photo-electroFenton mechanism.

The **real grey water** was obtained from a representative Euro-Mediterranean resort (Samba Hotel) placed in Lloret de Mar (Catalonia, Spain).

The treated sample volume was **2.5 litters** adjusted to **pH 3** and controlled at **25 ºC**. Samples were taken after **15, 30 and 60 minutes**.

Table 1. Real grey water effluent characterization.

Parameter	Value	Units	Methodology
Carbamazepine	11	µg/L	HPLC-MS-MS
10,11-epoxycarbamazepine*	<LD	µg/L	HPLC-MS-MS
pH	8.0	-	Potenciometry
CE	0.62	mS/cm	Conductimetry
COD	135	mg O_2/L	ISO/CD 20236
TC	86	mg/L	
IC	40	mg/L	
DOC	46	mg/L	ISO 15705:2002

* Potential carbamazepine degradation byproduct

All experimental trials were performed with the main objective of achieving **100% carbamazepine reduction** with **less than 10 kWh/m³** energy consumption.

RESULTS AND DISCUSSION

First 1-3 experimental trials were used to optimize recirculation flow-rate and the use of either oxygen or synthetic air as GDC gas. Best results were obtained with **lower recirculation flow rate** (61% COD removal vs 16% at 60 min, with 100% carbamazepine reduction in both cases). On the other, hand, since it was obtained the same 100% carbamazepine removal and 57% COD removal at 60 min when **using synthetic air in the GDC**, the last was subsequently used because of economic reasons.

Table 2. Operational conditions of solar electro-Fenton treatment.

Trial	Recirculation flow rate (l/h)	Current density (mA/cm²)	Applied charge (Ah/l)	GDC gas	Gas flow rate (l/min)*	Electrogenerated H_2O_2 after 60 min
1	**55**	70	1.01	O_2	0.3	355
2	**35**	70	1.01	**O_2**	0.3	505
3	35	70	1.01	**air**	1.5	358
4	35	**50**	0.72	air	1.5	246
5	35	**12**	0.18	air	1.5	83

* Air flowrate was increased to maintain similar oxygen level

Subsequently, when optimizing current density (trials 3-5), **all tested conditions reached maximum carbamazepine degradation**. No 10,11-epoxycarbamazepine by-product was obtained at any reaction time.

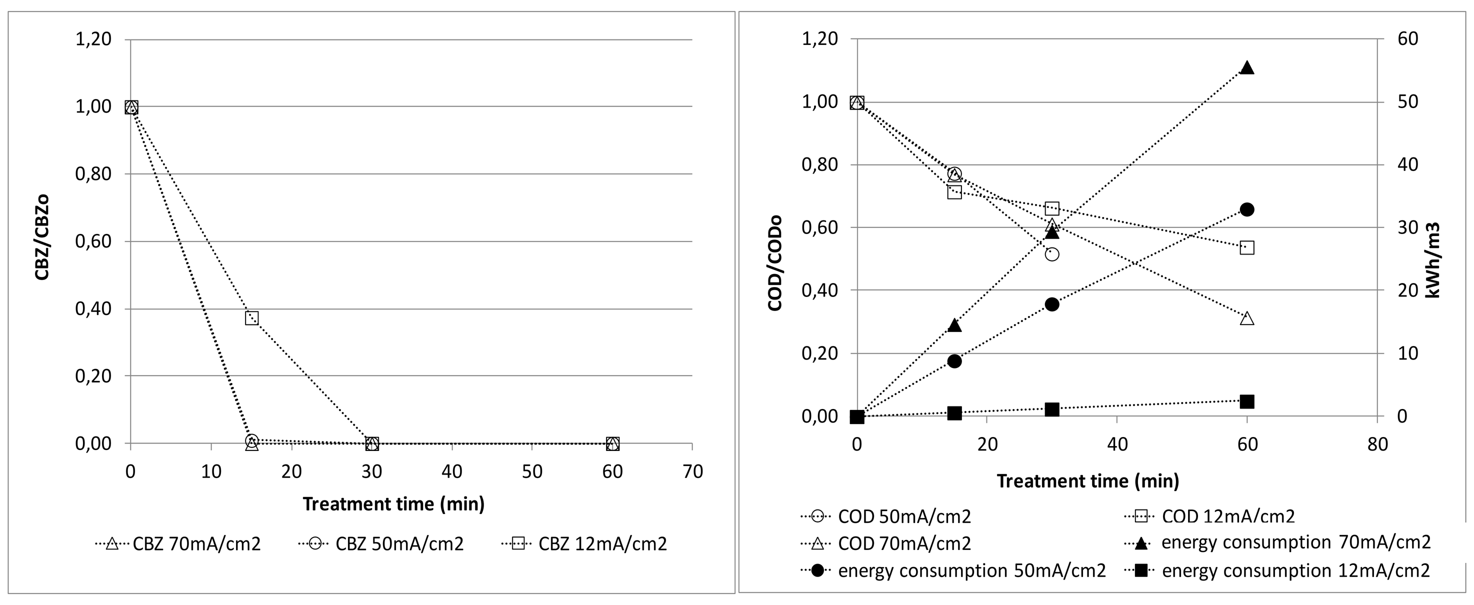


Figure 3. Carbamazepine evolution (a), COD evolution and energy consumption (b) when optimizing current density. pH 3, 10 mg/l Fe. Air GDC. 35 l/h recirculation flow rate.

Best conditions were obtained at **50 mA/cm²** current density after **15 minutes** of solar foto-electroFenton treatment, with 100% carbamazepine and 23% of COD removal, with **only 8.9 kWh/m³** energy consumption.

CONCLUSIONS

Obtained results show the **potential of solar foto-eletroFenton technology** for the efficient removal of organic matter and micropollutants, specifically carbamazepine, present in grey water from a representative existing resort in the Euro-Mediterranean area.

100 % carbamazepine removal and absence of 10,11-epoxycarbamazepine by-product indicated deep degradation and mineralization of micropollutants in studied real grey water, with only 8.9 kWh/m³ energy consumption under optimum conditions.

[1] Fenton H.J.H., (1894), *Journal of the Chemical Society*, **65**, 899-910.
[2] Brillas E. (2014), Electro-Fenton, UVA Photoelectro-Fenton and Solar Photoelectro-Fenton Treatments of Organics in Waters Using a Boron-Doped Diamond Anode: A Review. *J. Mex. Chem. Soc*, **58** no.3.
[3] Pignatelo J., Liu D., Huston P. (1999), Evidence for an additional oxidant in the photoassisted Fenton reaction. *Environ. Sci. Technol.*, **33**, 1832-1839.
[4] Blanco J., Malato S., Fernández P., Vidal A., Morales A., Trincado P., Oliveira J.C., Minero C., Musci M., Casalle C., Brunote M., Tratzky S., Dischinger N., Funken K.-H., Sattler C., Vincent M., Collares-Pereira M., Mendes J.F., Rangel C.M. (2000), Compound parabolic concentrator technology development to commercial solar detoxification applications. *Sol. Energy*, **67**, 317-330.

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