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Photolysis of In-Situ Electrogenerated Hydrogen Peroxide for the Degradation of Emerging Pollutants

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This study investigates the degradation of paracetamol, an emerging contaminant widely used as pain and fever reliever, by means of hydrogen peroxide either alone or in combination with UV-C photolysis.
In particular, we provide a comparison between the performance of both commercial and electrogenerated H_2O_2 whose production has been achieved by galvanostatic electrolysis in undivided reactor with a gas diffusion cathode.
The performance of the treatments has been assessed in terms of both pollutant decay and mineralization. The influence of the H_2O_2 to paracetamol molar ratio is discussed.
The results show that the electrogenerated hydrogen peroxide, when activated by UV-C irradiation, results in faster degradation and mineralization of paracetamol. However, under the conditions adopted, complete depletion of the total organic carbon (TOC) has never been attained.

1. Introduction

Civil, industrial and agricultural activities produce and release a broad range of chemicals. These compounds, although present at a low concentration may undergo accumulation becoming dangerous to the ecosystem. In particular, in recent years great attention has being focused on a group of contaminants collectively named 'emerging pollutants' (EPs). These are both synthetic and naturally occurring chemicals, rarely found in the environment, that range from pharmaceuticals to personal care products and exhibit persistence and recalcitrance to the traditional depuration methods. Paracetamol, known also as acetaminophen, is a drug widely used as analgesic and antipyretic. Several studies report the occurrence of paracetamol in aquatic environment so that there is growing concern over possible health effects.
Several treatment methods have been so far tested. Many of them report the achievement of complete removal of paracetamol but only partial depletion of the total organic carbon (TOC) thus suggesting the formation of persistent by-products. In particular, adsorption (Saucier et al., 2017), microbial degradation (Wu et al., 2012), the use of ozone (Neamtu et al., 2013) and hydrogen peroxide (Andreozzi et al., 2003) alone and combined also with UV irradiation, TiO_2 photocatalysis (Xiong et Hu, 2017) and both conventional (Le et al., 2016) and modified Electro-fenton systems (Sirès at al., 2006) have all been discussed.
In particular, while the oxidation treatment based on the photo-decomposition of oxidants has extensively been used, only recently the combined use of UV radiation and electrochemically produced hydrogen peroxide has been proposed (Frangos et al., 2016).
The hydrogen peroxide electrogeneration is commonly performed on carbon–based cathodes via reduction of molecular oxygen, according to the global reaction:

$$O_2 + H_3O^+ + 2e^- \rightarrow H_2O_2 + 2H_2O \quad (1)$$

Enhanced production has been achieved by replacing the classical graphite with a gas diffusion electrode (GDE) whose better performance (Da Pozzo et al., 2005a) has been ascribed to its increased reactive area and porosity, that contribute to improve oxygen solubility and reagent diffusion. Others cathodes made of reticulated vitreous carbon or carbon felt can be successfully used (Petrucci et al, 2016) but their efficiencies remain lower that that presented by GDE electrodes.

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The advantage of the electrochemical approach is primarily to produce hydrogen peroxide directly in-situ thus avoiding the hazard that the handling of concentrated solutions of this oxidant implies. The matrix effect has to be carefully considered since it can reduce the hydrogen peroxide persistence (Petrucci et al., 2012).
The main purpose of this study was to evaluate whether the use of electrogenerated hydrogen peroxide activated by UV-C irradiation, improves the degradation of paracetamol, in comparison with that commercially available.

2. Experimental

2.1 Materials

Reagents, from Carlo Erba and Sigma Aldrich, were used as received without further purification.
Unless differently specified, sample solutions were prepared by dissolving in distilled water 50 mg L^{-1} of paracetamol ($C_8H_9N_3NO_2$, MW 151.17 g mol^{-1}) and 0.05 M Na_2SO_4.
The initial TOC value was about 32 mg L^{-1}.

2.2 Experimental setup and procedure

Tests of degradation with UV was conducted using a 100-mL cylindrical quartz reactor. A 8 W low-pressure mercury lamp with a maximum emission at 254 nm (Spectroline ENF-260C/FE, Spectronics Corp., USA) was used as UV source. The radiation intensity, measured with AccuMax XR-1000 Spectronics Corp, was about 1,100 μW cm^{-2}.
Electrolyses were performed under galvanostatic conditions using a potentiostat AMEL 2051.
The membrane-free cell was thermostated and stirred with a magnetic bar. The cathode was a gas diffusion electrode (GDE), coated on the upper side with hydrophobic Shawinigan acetylene black carbon (SAB) while the side towards the solution was coated with hydrophilic Vulcan XC-72 carbon, provided by Industrie De Nora (Milan, Italy). The electrode, described in detail in previous work (Petrucci et al, 2009), had a geometric area of about 5 cm^2 and was fed with oxygen (100 mL/min). A commercial Platinum wire was used as the anode (supplied by Amel mod. 805/SPG/12J). The experiments were conducted at a current density of 100 A m^{-2}, at ambient temperature.
To obtain large amounts for ex-situ experiments, hydrogen peroxide was electrogenerated in a divided reactor separated by a cation exchange membrane (Nafion® 324).

2.3 Analyses

The pH was measured using a Crison GLP 421 pH meter, conductivity using a HD9213-R1Delta Ohm meter.
Hydrogen peroxide concentrations were determined reflectometrically by means of Merck analytical tests based on a peroxidase catalyzed reaction.
Paracetamol decay was measured by monitoring the absorbance decrease of the peak at 243 nm with a double-beam UV/Vis spectrophotometer (UV-2700, Shimadzu Co., Kyoto, Japan) with quartz cells of 1-cm path length.
The mineralization of the molecule, that is the conversion to CO_2 and H_2O, was monitored by measure of TOC concentration (Shimadzu TOC-L CSH/CSN analyzer).
The removal efficiencies of paracetamol and TOC were calculated using the following Eq(2), where x_0 and x_t represent the initial and remaining value of the x variable at a given time:

$$R(\%) = \frac{(x_0 - x_t)}{x_0} * 100 \quad (2)$$

3. Results and discussions

Preliminary tests were conducted by treating solutions containing 50 mg L^{-1} paracetamol and 0.05 M sulfate with commercial hydrogen peroxide and UV either alone or combined. The treatments were extended for at least three hours. Figure 1 indicates that hydrogen peroxide or UV alone were not able to degrade paracetamol under the adopted operative condition. In particular, no removal was observed when 350 mg L^{-1} of hydrogen peroxide was added to solution, while only a slight decrease in paracetamol concentration was verified in UV irradiation test. In this case, also a barely visible change in the colour of solution was observed as confirmed by the appearance of a spectrophotometric peak at a wavelength of 377 nm with increasing absorbance (data here not reported). Conversely, combined treatment with the same amount of hydrogen peroxide, resulted in the removal of 28 mg L^{-1} of paracetamol (about 56%) thus confirming that coupling UV with H_2O_2 was a feasible treatment for the oxidation of this compound in aqueous solution via hydroxyl radical produced by the photolysis of the hydrogen peroxide.

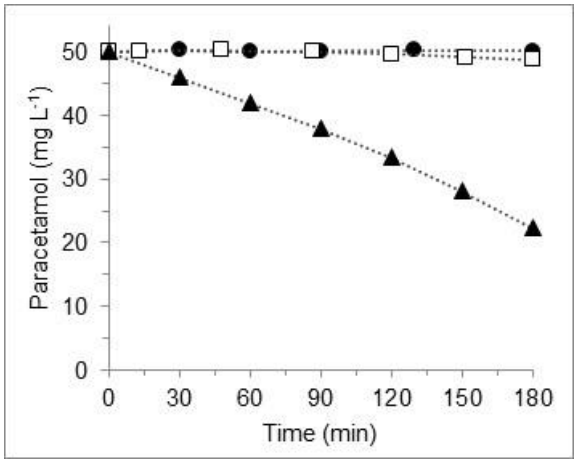

Figure 1: Removal of 50 mg L^{-1} Paracetamol by using 350 mg L^{-1} H_2O_2 (●), UV irradiation (□) and combined UV/H_2O_2 (▲) treatments.

Further experiments on combined treatment were conducted with the aim of evaluating the effect of different [H_20_2]/[Paracetamol]molar ratio. In a first series of tests at fixed paracetamol concentration (50 mg L^{-1}) we varied the amount of hydrogen peroxide to obtain a molar ratio of 13, 31 and 44 corresponding to 150, 350 and 500 mg L^{-1} H_2O_2, respectively. As can be observed in Figure 2a, the combined UV/H_2O_2 process was enhanced by increasing hydrogen peroxide concentration even if total removal of paracetamol was not achieved in the adopted treatment time. In particular, after 3 hours 31%, 55% and 83% removal was observed with increasing [H_20_2]/[Paracetamol] molar ratio, in the range investigated. By fitting the experimental data, a linear correlation between time and concentration was always found. Additionally, the slope values were also linearly dependent on the molar ratio.

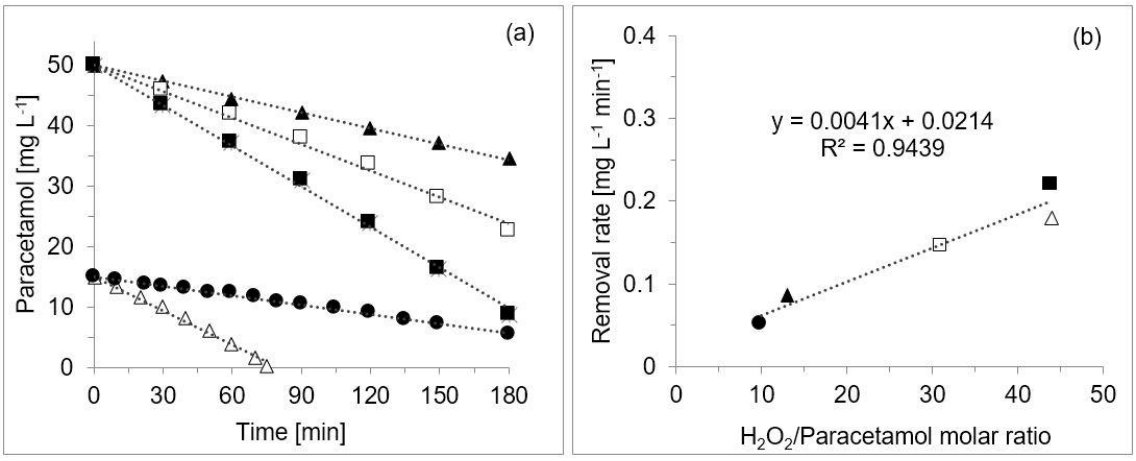

Figure 2: Effect of reactants concentration in UV/H_2O_2 treatment of paracetamol (a) and correlation between removal rates and [H_2O_2]/[Paracetamol] molar ratio (b). Conditions: 150 mg L^{-1} (▲), 350 mg L^{-1} (□), 500 mg L^{-1} (■) H_2O_2 with 50 mg L^{-1} Paracetamol; 35 mg L^{-1} (●), 150 mg L-1 (Δ) H_2O_2 with 15 mg L^{-1} Paracetamol.

The observed behaviour, suggesting a possible pseudo zero-order kinetics, differed to what was found in previous study (Feng et al., 2015) that indicated a pseudo first-order reaction for the total degradation of paracetamol at very low concentration with [H_2O_2]/[Paracetamol] ranging from 2.5 to 10. In order to verify that the removal trend maintained the linear correlation with treatment time until complete degradation, we conducted tests at lower concentration of paracetamol (15 mg L^{-1}). The results illustrated in Figure 2a indicate that three hours of treatment were not sufficient to completely remove paracetamol when a [H_2O_2]/[Paracetamol] molar ratio equal to 10 was adopted. Total degradation of paracetamol in about 75 minutes was reached using a higher concentration of hydrogen peroxide (150 mg L^{-1}) with a molar ratio equal

to 44. However, in both cases the linear correlation of data was again observed. Moreover, the removal rates seemed to be affected only by the [H_2O_2]/[Paracetamol] as confirmed by the similar slope of curves referring to tests conducted using different paracetamol and hydrogen peroxide concentrations but with similar molar ratio. Data in figure 2b show an almost linear dependence of removal rates with molar ratio.
Before evaluating the efficiency of the UV/H_2O_2 treatment with in-situ electrogenerated hydrogen peroxide, a comparison between the reactivity of the commercial H_2O_2 35% solution, used in preliminary tests, with the H_2O_2 produced via electrochemical reduction of oxygen, but then used ex-situ, was needed. In fact, we wanted to exclude that photolysis of H_2O_2 could be affected by the stabilizing agents plausibly presents in the commercial product.
Electrochemical generation of H_2O_2 was then performed in a divided cell using a 0.05 M Na_2SO_4 solution as catholyte. Several electrolyses were conducted and stopped at different time to achieve different concentration of hydrogen peroxide. In particular, we obtained about 85, 150, and 370 mg L^{-1} H_2O_2. After dissolving 50 mg L^{-1} of paracetamol, corresponding to [H_2O_2]/[Paracetamol] equal to 7.5, 13 and 33, UV irradiation was applied and the degradation was monitored for three hours. The linear trend of paracetamol concentration decay was confirmed in test with combined UV and ex-situ electrogenerated H_2O_2. Moreover, the removal rates showed almost the same linear correlation with molar ratio previously found in tests conducted using commercial H_2O_2 (Figure 3), thus proving that commercial and electrogenerated H_2O_2 equally behaved in the photolysis reaction.

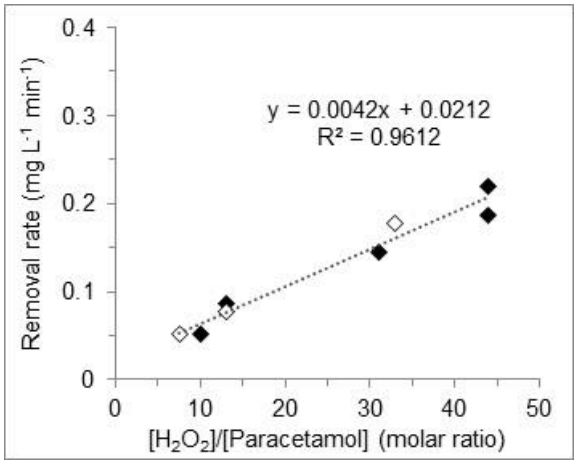

Figure 3: Correlation between removal rates and [H_2O_2]/[Paracetamol] in test conducted with commercial H_2O_2 (full symbol) and ex-situ electrogenerated H_2O_2 (empty symbol).

As the degradation of paracetamol via photolysis of in-situ electrogenerated hydrogen peroxide was performed in a membrane-free reactor, the H_2O_2 production efficiency in an undivided cell was verified with the aim of evaluating the accumulation tendency and the persistence in water solution (Figure 4). According to previous results (Da Pozzo et al., 2008) we confirmed that in an undivided reactor several reactions simultaneously occur thus limiting H_2O_2 accumulation. An average faradaic efficiency of only 20% was observed. Agladze et al. (2007) indicate as parasite reactions H_2O_2 anodic oxidation to oxygen evolution, cathodic reduction to water, chemical reaction with species either anodically or cathodically produced ($O_2^{\bullet-}$, $^{\bullet}OH$, $O_2H^{\bullet}$). On the contrary in a divided cell higher efficiency was verified as expected due to the exclusion of anodic reactions.
Finally, the removal of 50 mg L^{-1} of paracetamol via photolysis of in-situ electrogenerated hydrogen peroxide is shown in Figure 5. Complete degradation was obtained after a 4-hour treatment with a trend of concentration decay significantly different to what previously found. In particular, no removal was observed at the beginning of the process probably because of the initial low concentration of the hydrogen peroxide. After 60 minutes the concentration of paracetamol linearly decreased with a constant rate even higher than that found in test conducted using 500 mg L^{-1} H_2O_2, although similar amount of hydrogen peroxide could not to be reached via electrochemical production in the undivided reactor. This behaviour can be attributed to the cathodic co-production of other oxidizing species (Da Pozzo et al., 2005b) supporting the hydroxyl radicals generated by means of H_2O_2 photolysis. In particular, the oxygen reduction to hydrogen peroxide is a complex process that implies the formation of numerous radical species such as superoxide radicals $O_2^{\bullet-}$ and hydroperoxide radicals $HOO^{\bullet}$ (Da Pozzo et al., 2005a).

The second curve in the figure shows the influence of the cathode lifetime on paracetamol removal. The test was conducted using an aged cathode, thus suffering loss in efficiency of hydrogen peroxide electrogeneration. The lower degradation of paracetamol observed in this case confirmed the relevance of the amount of H_2O_2 available in solution.

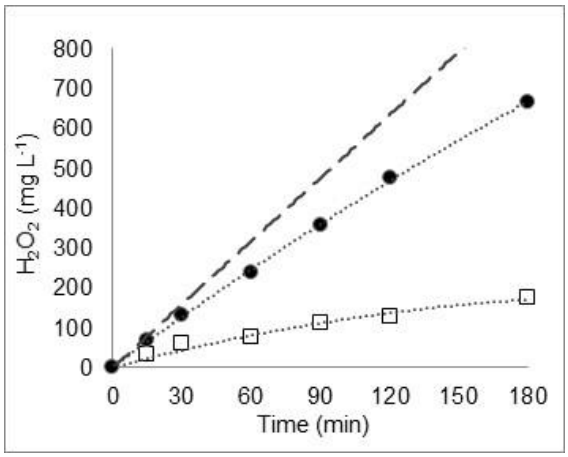

Figure 4: Electrogeneration of the hydrogen peroxide in divided (●) and undivided (□) cell using a PTFE Gas Diffusion Electrode compared with theoretical production (dotted line). Conditions: 0.05 M Na_2SO_4, volume 100 mL, current density 100 A m^{-2}.

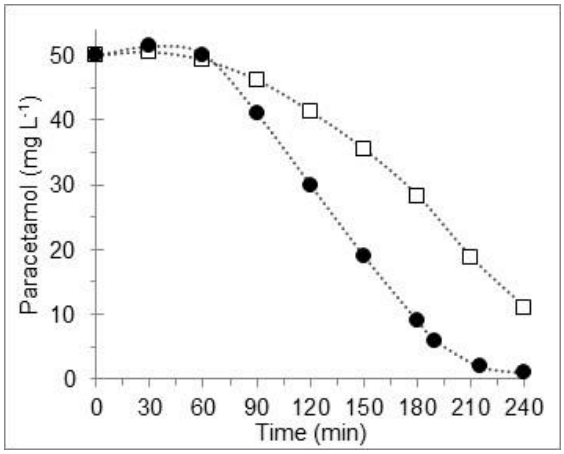

Figure 5: Removal of Paracetamol during UV/H2O2 treatment with in situ electrogenerated hydrogen peroxide. Condition: 50 mg L^{-1} Paracetamol, 0.05 M Na_2SO_4, volume 100 mL, current density 100 A m^{-2}, new cathode (●), aged cathode (□).

Table 1: Summary of performances of different UV/H_2O_2 treatments of paracetamol solutions.

Paracetamol [mg L^{-1}]	H_2O_2 [mg L^{-1}]	[H_2O_2]/[Paracetamol] molar ratio	H_2O_2 source	Operative time [min]	Paracetamol removal rate (%)	TOC removal rate (%)
50	500	44	Commercial	180	83	22
50	350	31	Commercial	180	55	10
50	150	13	Commercial	180	31	< 5
15	150	44	Commercial	75	100	44
15	35	10	Commercial	180	65	14
50	370	33	Ex-situ electrogen.	180	59	9
50	150	13	Ex-situ electrogen.	180	32	< 5
50	85	7.5	Ex-situ electrogen.	180	17	< 5
50	-	-	In-situ electrogen.	240	100	45

Finally, performances of different UV/H_2O_2 treatment in terms of paracetamol degradation and Total Organic Carbon (TOC) removal are reported in Table 1. Generally, low TOC removals were achieved in all tests and only at the lowest paracetamol concentration and highest [H_2O_2]/[Paracetamol] molar ratio, significant mineralization was observed. Treatment with in-situ electrogenerated hydrogen peroxide showed the best results even if TOC removal was lower than 50% due to the formation of hardly oxidizable by-products.

4. Conclusions

Hydrogen peroxide activation by UV photolysis has been tested to remove paracetamol from aqueous solutions. Safety issues concerning manipulation and transport of hydrogen peroxide can be overcome by providing a system for the in-situ production of this chemical.

Significant results were observed only in combination with UV irradiation due to the production of hydroxyl radicals. Under the conditions adopted, we achieved complete removal of paracetamol but only partial mineralization, thus suggesting the formation of persistent organic by-products during the treatment.

The superior effect of the electrogenerated hydrogen peroxide can be presumably attributed to the concomitant production of different radical species that contribute to the molecule degradation.

Reference

Agladze G.R., Tsurtsumia G.S., Jung B.-I., Kim J.S., Gorelishvili G., 2007, Comparative Study of Hydrogen Peroxide Electro-Generation on Gas-Diffusion Electrodes in Undivided and Membrane Cells. J. Appl. Electrochem., 37, 375–383.

Andreozzi R., Caprio V., Marotta R., Vogna D., 2003, Paracetamol oxidation from aqueous solutions by means of ozonation and H2O2/UV system, Water Res., 37, 993-1004.

Da Pozzo A., Di Palma L., Merli C., Petrucci E., 2005a, An Experimental Comparison of a Graphite Electrode and a Gas Diffusion Electrode for the Cathodic Production of Hydrogen Peroxide. J. Appl. Electrochem., 35, 413-419.

Da Pozzo A., Ferrantelli P., Merli C., Petrucci E.,, 2005b Oxidation efficiency in the electro-Fenton process, J. Appl. Electrochem. 35, 391-398.

Da Pozzo A., Petrucci E., Merli C., 2008, Electrogeneration of Hydrogen Peroxide in Seawater and Application to Disinfection. J. Appl. Electrochem., 38, 997-1003.

Frangos P., Shen W., Wang H., Li X., Yu G., Deng S., Huang J., Wang B., Wang Y., 2016, Improvement of the degradation of pesticide deethylatrazine by combining UV photolysis with electrochemical generation of hydrogen peroxide, Chem. Eng. J., 291, 215-224.

Neamţu M., Bobu M., Kettrup A., Siminiceanu I., 2013, Ozone photolysis of paracetamol in aqueous solution, J. Environ. Sci. Health A Tox. Hazard Subst Environ Eng, 48, 1264-1271.

Petrucci E., Montanaro D., Le Donne S., 2009, Effect of Carbon Material on the Performance of a Gas Diffusion Electrode in Electro-Fenton Process. J. Environ. Eng. Manage. 19(5), 299-305.

Petrucci E., Montanaro D., Di Palma L., 2012, A feasibility study of hydrogen peroxide electrogeneration in seawater for environmental remediation, Chemical Engineering Transactions 28, 91-96. DOI: 10.3303/CET1228016.

Petrucci E., Da Pozzo A., Di Palma L., 2016, On the ability to electrogenerate hydrogen peroxide and to regenerate ferrous ions of three selected carbon-based cathodes for electro-Fenton processes, Chem. Eng. J., 283, 750-758.

Saucier C., Karthickeyan P., Ranjithkumar V., Lima E.C., Dos Reis G.S., de Brum I.A.S., 2017, Efficient removal of amoxicillin and paracetamol from aqueous solutions using magnetic activated carbon (2017) Environ.Sci. Poll. Res., 1-15. Article in Press.

Sirés I., Garrido J.A., Rodríguez R.M., Cabot P.L., Centellas F., Arias C., Brillas E., 2006, Electrochemical degradation of paracetamol from water by catalytic action of Fe2+, Cu2+, and UVA light on electrogenerated hydrogen peroxide, J. Electrochem. Soc., 153, D1-D9.

Wu S., Zhang L., Chen J., 2012, Paracetamol in the environment and its degradation by microorganisms, Appl. Microbiol.Biotechnol.,96, 875-884.

Xiong P., Hu J., 2017, Decomposition of acetaminophen (Ace) using TiO2/UVA/LED system, Catal. Today, 282, pp. 48-56.

Yamamoto H., Nakamura Y., Moriguch, S., Nakamura Y., Honda Y., Tamura I., Hirata Y., Hayashi A., Sekizawa J., 2009, Persistence and partitioning of eight selected pharmaceuticals in the aquatic environment: Laboratory photolysis, biodegradation, and sorption experiments, Water Res., 43, 351-362.