Pilot scale study of pharmaceutical wastewater treatment with Electro-Phenton Technology

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Abstract

This work was developed in a pharmaceutical industry, simulating an industrial Wastewater Treatment Plant (WWTP) in a pilot plant testing in situ pharmaceutical wastewater. Project drivers were the installation of a new top-of-the-range WWTP on site that was reliable for API degradation and full compliance to the environmental license. Treatment setup varied along the project to better assess the best configuration and operational parameters for future operation.

The future WWTP primary degradation stage should be based on Electro-Peroxi-Coagulation technology (EPC), an Advanced Oxidation Process (AOP) included in the Best Available Techniques (BATs) for pharmaceutical wastewater treatment. EPC technology promotes the chemical degradation of double bounded and branched chain organics through oxidation with the addition of hydrogen peroxide and ferric ions dosed by iron electrodes at an electrochemical reactor. EPC Reactor performance was assessed with focus on some critical parameters (Chlorides, Adsorbable Organic Halides (AOX), Dichloromethane (DCM), Chemical Oxygen Demand (COD) and Metals) as well as on wastewater biodegradability and API degradation.

In a total of 80 trial tests, the EPC reactor degraded 72.33 % of the initial organic matter with 70 to 90% of the overall degradation occurring in the first 30minutes of reaction. Environmental parameter assessment concluded that the EPC technology treats efficiently the pharmaceutical wastewater (with compound degradation from 50 to 60% removal of chlorides and ammonia and 80 to 99% removal of the remaining profiled compounds). Wastewater toxicity and respiratory inhibition to the aquatic environmental decreased 95% and biodegradability increased in 89%. API degradation was for all the profiled API above 90%.

Overall, this project validated the EPC technology as suited to be installed in the pharmaceutical site as a reliable and robust treatment. Future WWTP will also include a biologic reactor downstream the EPC reactor to upgrade de treatment performance. Economic analysis concluded that this high value investment will have a payback bellow three years for an WWTP suited to a site expansion that should double present capacity and wastewater complexity.

Keywords: Electro-Peroxi-Coagulation, Advanced Oxidation, Pharmaceutical Wastewater, Hydrogen Peroxide, Active Pharmaceutical Ingredient

1. Scope and Objectives

1.1. Pharmaceutical Wastewater

Water contaminants not treated or not contained can impact the water courses (on surface and underground waters) and contaminate the soils affecting living creatures and endangering the supply of safe water as a human resource. At the present day, API are considered as emerging contaminants. Emerging contaminants are defined as compounds that are still unregulated or in process of regulation and that can be a threat to environmental ecosystems and human health. Despite the absence of regulatory limits for the API content in pharmaceutical wastewater entering the hydric environment and the sewers, predicted non effect concentrations (PNEC) are listed as results of several studies on the hazard APIs pose to aquatic ecosystems. These PNECs are being used by pharmaceutical industries as guidelines to the optimal API degradation and the goals for API content in their wastewater. [2] [3]

As API molecules are synthetized to resist bacterial degradation, one issue regarding API accumulation in nature is the unsuitability of conventional WWTP for treatment of pharmaceutical wastewater collected in the municipal sewers.

Conventional WWTPs are biologic based and the toxicity associated with API content can be harmful to the treatment performance. [8] [5]

One technology that has been proved to degrade efficiently double bound and long ramified organic compounds, are AOPs. Advanced Oxidation is based in Fenton Chemistry. From the several processes derived from it, Photo-Oxidation as been successfully validated in the treatment of pharmaceutical wastewater with API degradation validated. Electro-Peroxi-Coagulation uses the same principles with expected operational costs and high efficiency in organics degradation.

In this project, pharmaceutical wastewater was treated with EPC technology. The project was funded by a pharmaceutical industry and the trials occurred at the site in a pilot plant with a continuous feed of the wastewater generated *in situ*.

1.2. The Challenge

At the pharmaceutical industry site, the present treatment configuration is based on the steam stripping of the wastewater as a pre-treatment before discharge to the municipal sewer and thermal-oxidation of high solvent waste for steam generation.

The steam stripping column uses direct steam to strip the solvents with a lower boiling point that the water. The steam used in this column if produced at the thermo-oxidizer, 60% of the steam produced is directed to the steam stripping column.

The direction of effluents to either the steam stripping or to thermal-oxidation is made according to the streams organics content, aqueous streams are equalized and then introduced in the stripping column, high solvent streams are directed to the thermal-oxidizer. This configuration is not yet optimal, waste management wise or costs wise. The pollutants are purely separated instead of degraded. Due to the high daily volume of wastewater, several tons of waste is shipped to external treatment.

With the possibility of expanding the production capacity and the probability of increasing the site's WWTP, the present WWTP will be revamped and the addition of an EPC reactor was considered as a possibility due to its ability to degrade organics instead of separating them.

The challenge presented was to compose a robust and efficient WWTP that guaranteed environmental compliance, API degradation and reasonable investment and operational costs.

At present the site produces 240 m^3/day of with an average COD value of 10135 mg O$_2$/L. Future installation will be design for an average of 500 m^3/day of wastewater and a discharge in compli-ance with the emission value, 1500 mg O$_2$/L.

1.3. Objectives

In the described contexts, the main objectives of the work reported in this thesis were:

• To evaluate the effectiveness of the EPC system as a pre-treatment for pharmaceutical wastewater presenting a high variability in its composition;

• To evaluate the effectiveness of the EPC system as a destruction treatment for API molecules present amongst other organic and inorganic pollutants in the pharmaceutical wastewater;

• To evaluate upstream and downstream operations to complement the EPC technology to be installed in a pharmaceutical multipurpose factory.

2. Scientific Background
### 2.1. Advanced Oxidation Processes

AOPs were first defined in 1987 by Glaze as "near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification".[6]

The main advantage of AOPs when compared to other wastewater treatment chemical technologies is the fact that the pollutants removal in made through degradation instead of separation. However, studies reveal that the type of AOP to be selected can vary with the water matrix, and in this optic, AOPs are yet to be fully understood. [7]

AOP technologies can be broadly divided into the following groups: (1) Vacuum UV (VUV) photolysis, (2) UV/oxidation processes, (3) Photo-Fenton process, and (4) sensitized APO processes. [1]

The theoretical basis of AOPs is the use of extremely strong oxidizing agents generated *in situ* within the reaction medium. The most frequently used is the hydroxyl radical (•OH) which is one of the strongest oxidants. The radicals can destroy most of the organic and organometallic compounds present in the aqueous medium through mineralization, i.e., converting them first into simpler, linear chain organics and finally into CO$_2$, water and inorganic ions. The oxidation is mostly non-selective and quick due to the high reactivity of the hydroxyl radicals.

Once the hydroxyl radical is made available, the degradation of organics can occur by dehydrogenation (Hydrogen Atom Transfer (HAT), equation 1), hydroxylation (addition of an hydroxyl to an unsaturated bound or by electronic transfer (equation 2).

$$HO^\bullet + RH \rightarrow R^\bullet + H_2O \qquad (1)$$

$$^\bullet OH + RX \rightarrow OH^- +^\bullet RX^+ \qquad (2)$$
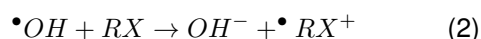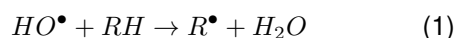
The type of radical reaction that will occur depends on several factors that must be well explored
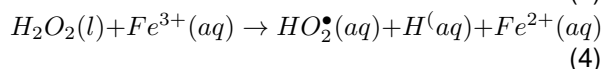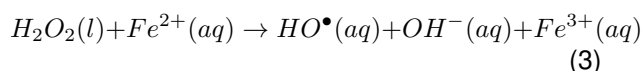
and defined during AOP studies, namely, the concentration and recalcitrance level of pollutants can highly influence process performance.

Electrochemical methods are effective for the production of hydroxyl radicals, either by direct production (anodic oxidation) or indirect generation through a mediator such as Fe^{2+} in a Fenton's reaction Environment. Anodic oxidation produces hydroxyl radicals by water oxidation on a high O_2 - overvoltage anode, favouring the generation of $^\bullet OH$ adsorbed at its surface. In electro-Fenton processes, H_2O_2 is electro-generated at the cathode and reacts with Fe^{2+} leading to the formation of the hydroxyl radicals (equation 6).

2.2. Electro-Peroxi-Coagulation Technology
2.2.1 Fenton Environment

In 1984, Fenton observed that, in the presence of H_2O_2 and Fe^{2+}, hydroxyl radicals are produced through electron transfer. In the absence of organic compounds, the classical Fenton's free radical mechanism involves the following reactions (equations 3 and 4):

$$H_2O_2(l) + Fe^{2+}(aq) \rightarrow HO^\bullet(aq) + OH^-(aq) + Fe^{3+}(aq) \tag{3}$$

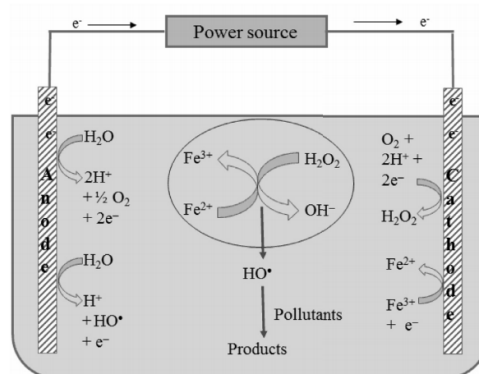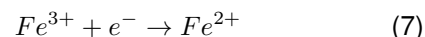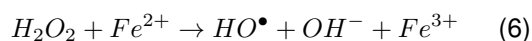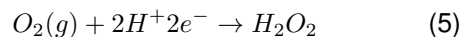$$H_2O_2(l) + Fe^{3+}(aq) \rightarrow HO_2^\bullet(aq) + H^(aq) + Fe^{2+}(aq) \tag{4}$$

The first Fenton's reaction applications in AOP involved the addition of Fenton's reagent (H_2O_2 and Fe(II) salts) originating iron sludge from the precipitation of iron oxyhydroxides. From this initial approach several adaptations and techniques were developed and adapted to a wide range of water treatment situations.

2.2.2 Electro-Fenton (EF)

One of the technologies derived from Fenton's reaction has been named Electro Fenton (EF). This is a method based on the oxidation of the organic compounds via an indirect electrochemical oxidation through hydroxyl radicals, with the possibility of generating H_2O_2 and Fe^{2+} in situ.

EF is an electrochemical technique with a higher oxidation power than the simpler anodic oxidation. Oxidation occurs through the continuous supply of the contaminated wastewater and a hydrogen peroxide solution at an acidic pH to an electrochemical cell with O_2-diffusion cathodes, where the two-electron reduction of oxygen takes place according to equation 5, as schematized in Figure 1. Iron ions (Fe^{2+} or Fe^{3+}) are added to the solution increasing the oxidation power of t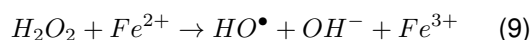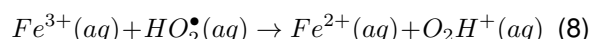he generated H2O2. The Fe^{3+}/Fe^{2+} system provides the basis for the metal-catalysed oxidation, namely, H_2O_2 oxidizes Fe^{2+} (equation 6) generating the hydroxyl radical and Fe^{3+}, equation 7.

$$O_2(g) + 2H^+ 2e^- \rightarrow H_2O_2 \tag{5}$$

$$H_2O_2 + Fe^{2+} \rightarrow HO^\bullet + OH^- + Fe^{3+} \tag{6}$$

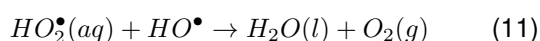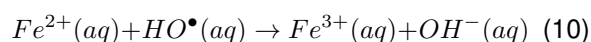$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{7}$$

Figure 1: Schematic diagram of an EF cell showing the main reactions involved in an EF process using a carbonaceous material cathode. [4]

2.2.3 Electro-Peroxi-Coagulation (EPC)

The Electro-Peroxi-Coagulation (EPC) process is based on the use of a sacrificial iron anode that continuously injects Fe^{2+} to the reaction solution (equaltion 8), which is further oxidized to Fe^{3+} through Fenton's reaction (equation 9) generating the hydroxyl radical. With this electrochemical technique, organic pollutants are removed both by oxidation and by coagulation with the Fe(OH)$_3$ that precipitates from the excess of Fe^{3+} obtained from Fenton's reaction.

$$Fe^{3+}(aq) + HO_2^\bullet(aq) \rightarrow Fe^{2+}(aq) + O_2 H^+(aq) \tag{8}$$

$$H_2O_2 + Fe^{2+} \rightarrow HO^\bullet + OH^- + Fe^{3+} \tag{9}$$

Dosage is made with consideration to the WW organic load and parameterized by COD measurements, through a given value of the ratio between [H_2O_2] and COD. higher concentration environments, the hydroxyl radicals can be scavenged (equations 10 and 11) and sludge separation through gravity sedimentation can be impaired due to O_2 off-gassing (with the possibility of sludge flotation occurring).

$$Fe^{2+}(aq) + HO^\bullet(aq) \rightarrow Fe^{3+}(aq) + OH^-(aq) \tag{10}$$

$$HO_2^\bullet(aq) + HO^\bullet \rightarrow H_2O(l) + O_2(g) \tag{11}$$

The correlation between Fe2+:COD ratios and COD removal effectiveness seems to follow the

pattern identified for H_2O_2, namely, a higher Fe^{2+} concentration generally implies higher COD removal, but beyond certain values this effect decreases.

Again, the higher concentration of the added reagent can result in scavenging of the hydroxyl radicals, the ferrous ions promoting competitive reactions with the latter, which will be consumed as in equation 12 compromising the generation of H_2O_2. In particular, the deposition of $Fe(OH)_3$ on the cathode can decrease the active sites for the production of H_2O_2.

$$Fe^{3+}(aq) + HO_2^{\bullet}(aq) \rightarrow Fe^{2+}(aq) + O_2H^+(aq)$$
(12)
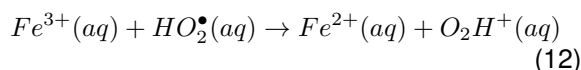
The hydrogen peroxide feeding method also affects markedly the effectiveness of the COD removal as it impacts on the $[H_2O_2]/[Fe^{2+}]$ ratio. Reported studies showed that the step-feed of the H_2O_2 solution reduced the probability of hydroxyl radical scavenging and achieved higher COD removal levels, while the single step dosage of H_2O_2 resulted in a rapid and efficient generation of radicals but increased the possibility of parasite reactions of the hydroxyl radical with hydrogen peroxide.

The value of pH interferes in the speciation of Fe ions in solution and in H_2O_2 decomposition. Several studies tested pH ranges between 2 and 8 in EPC processes, but most concluded that the optimal pH for the EPC reaction is around 3.

The optimal current density should be determined experimentally, through a trial period of with increased and decreased current density values, as a better approach for each individual installation.

3. Materials and Methods
3.1. Operational Plan

The EPC Pilot Plant was a lease for a 2 month period, therefore the trial tests and analytical tests plans were made to maximize the data collected and the treatment setup variations.

The complete operating manual of the pilot unit as well as the P&I diagram, are not public due to confidentiality.

The Pilot Plant consisted in two containers with several equipment inside and adjustable connexions between equipment.

With several equipment available at the Pilot Plant, several setups were composed to combine separation and degradation technologies prior and posteriorly to the EPC step.

The upstream technologies experimented were Steam Stripping and Electro Coagulation, the downstream technologies experimented were Photo-Oxidation, Electro Oxidation and Reverse Osmosis (with retreatment of the concentrate in a

second EPC batch reaction). The flow possibilities for treatment at the Pilot Plant are schematized in Figure 2.

All the equipment listed above operated in recir-
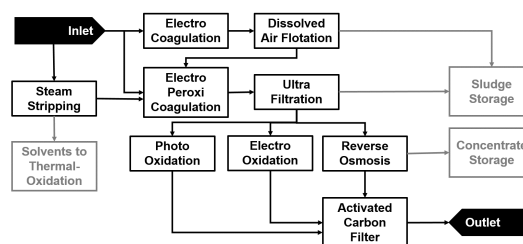
Figure 2: Schematic diagram the available equipment inside the EPC Pilot Plant and the sequence possibilities.

culation in 1m3 open tanks to prevent explosive atmosphere formation, therefore the Pilot Plant batch capacity was $1m^3$.

Water was admitted in $1m^3$ tanks to proceed to automatic pH correction according to the step that followed. Chemical dosage was also automatic. Temperature probes indicated the temperature inside the tanks and the Pilot Plant control system actuated in the dosing to prevent high temperatures – studies and manufacturer's experience indicated that above 50ºC the reaction could rapidly get out of the operator control.

As the tanks were open and due to the presence of organic solvents with high volatility, ventilation was ensured to prevent explosive atmosphere formation, with the permanent opening of the containers doors during operation. The plant also had LEL indicators and above a certain point of LEL, the Plant's electricity was shut down as a safety measure.

Operational parameters: current density, dosing method (on/off dosing pump), hydrogen peroxide volume to add and reaction time; were computed by the manufacturer's simulator that adapts the batch reaction to the wastewater according to its COD value.

The Pilot Plant had two feeding options: continuous effluent (fresh wastewater from the site's wastewater equalization tank) and simulated effluent (synthetic wastewater prepared from collected fresh wastewater with addition of specific compounds – APIs, solvents, liquid wastes).

3.2. Analytical Plan

Samples were collected according to a sampling plan regarding frequency and sampling position in the treatment.

Each trial test was grab sampled at the end of every step and samples were tested in an internal laboratory for: conductivity, pH, COD, TOC Chlorides and hydrogen peroxide concentration.

For specific trials, wastewater was collected at the

inlet and outlet of the Pilot Plant and analysed for several environmental parameters as well as for API content.

For specific trials, wastewater was collected at the inlet and outlet of the Pilot Plant and tested for respiratory inhibition by dissolved oxygen measurements in a biomass suspension in nutrient medium before and after addition of the sample.

The analytical tests performed internally, methods are listed in Table 1, and externally in Tables and 2 3.

Table 1: Internal analysis parameters and respective analytical method

Parameter	Analysis Method
Chemical Oxygen Demand	Merck Spectroquant® COD cell test (300-3500 mg O_2/L)
Total Organic Carbon	G&E Waters® Innovox TOC Analyzer (0-5000 mg O_2/L)
Hydrogen Peroxide Concentration	Merckoquant® Peroxide test strips (1 to 100 mg H_2O_2/L)
Chlorides Concentration	Merckoquant® Chloride test strips (500 to 3000 mg Cl^-/L)
Dissolved Oxygen Uptake Rate	HachLange® HQ40d Portable Multi-Parameter Meter with DO (0.01 - 20 mgO_2/L)

Table 2: External analysis API detection methods and respective quantification limits.

API	Analysis Method	Quantification Limit
Betamethasone Acetate	HPLC	2 microg/L
Betamethasone Phosphate	HPLC	15 microg/L
Fluticasone Propionate	HPLC	2 microg/L
Lisacline	UPLC	2 microg/L
Mynocline	UPLC	2 microg/L

Table 3: External analysis parameters for effluent and respective analytical method

Parameter	Analysis Method
pH	MI LAQ 150.03
Condutivity	MI-LAQ-104-02
COD	ISO 6060:1989
BOD5	MI LAQ 167.02
BOD20	MI LAQ 167.02
AOX	CSN EN ISO 9562
TSS	MI LAQ 166.02
VSS	SMEWW-2540-G- 21st edition
TKN	SMEWW 4500-B – 21st edition
NH3	MI LAQ 164.01
NO2	NP EN 26777:1996
NO3	MI LAQ 211.01
Cl	SMEWW 4500-D-21st edition
S	CZ SOP D06 07 15.A (CSN 830520-16, CSN 83053 -part 31)SM4500-S2-D
Detergents	CZ SOP D06 07 031 (CSN EN 903)
FOG	CZ SOP D06 02 059 (based on CSN 75 7506)
Total Hydrocarbon	CZ SOP D06 02 057 (based on CSN 75 7505, CSN 830540-4)
Phenols	CZ SOP D06 07 030 (CSN ISO 6439)
Total Heavy Metals	
. As	MI LAQ 163.04
. Cd	MI LAQ 163.04
. CN	CZ SOP D06 02 089.A (CSN 757415, CSN EN ISO 14403-2)/CZ SOP D06 07 010 (CSN 75 7415)
. Cr	CZ SOP D06 02 J06
. Cu	MI LAQ 163.04
. Fe	MI LAQ 147.01
. Hg	EPA 245.7:2005
. Pb	MI LAQ 163.04
. Zn	MI LAQ 163.04
VOC	CZ SOP D06 03 155 except chapter 9.2 (US EPA 624, US EPA 8260,EN ISO10301, MADEP 2004, rev.1.1)
Solvents	DIN 38407-F9-1/ DIN EN ISO 10301-F4
MEK	HS-GC-MS
MEG	Housemethod PI- MA-M 3-77
THF	HS-GC-MS
Daphnia Magna	CZ SOP D06 03 178 (ISO 18857-2)

SMEWW stands for Standard Methods for Examination of Water and Waste Water, which is a publication of the American Public Health Association.

ISO stands for International Organization for Standardization.

4. Results & discussion
4.1. Pharmaceutical Wastewater Characterization

The average WW levels and regulatory limits for the critical environmental parameters were identified after a thorough processing of the data regarding the analytical tests performed on samples of the continuous effluent. These values are summarized in Table 4, together with the established acceptance criteria for the performance of the EPC treatment technology when applied to this site's wastewater.

Table 4: EPC Reactor Acceptance Criteria for pollutant removal based on the regulatory limits.

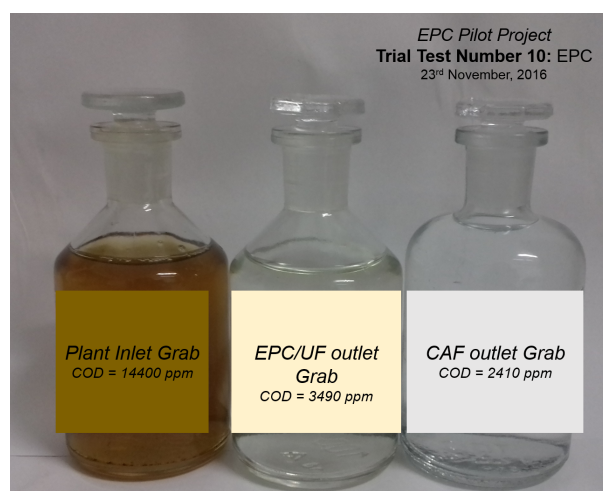| Parameter	Inlet wastewater average values	Regulatory limit values	Minimum removal yields (%)
COD (mg O_2/L)	10134.8	1500.0	85.2
BOD5 (mg O_2/L)	3335.7	1000.0	70.0
TOC (mg C/L)	3010.4	500.0	83.4
AOX (mg/L)	496.5	8.5	98.2
VOC: DCM (mg/L)	574.4	0	100.0
Ammonia (mg NH_4/L)	151.3	100.0	51.3
Chlorides (mg Cl/L)	3129	1500	52.1
Iron (mg Fe/L)	8.5	2.5	70.6
Zinc (mg Zn/L)	0.713	0.500	29.9
Solvents (mg/L)	From 4 to 1260	0	100.0

4.2. EPC Reactor Performance

To assess EPC Reactor performance, results includes data from trials using the industrial wastewater continuously gathered at the tank feeding the steam stripping column. Data from synthetic effluent will be referenced at the API Degradation assessment and Robustness Assessment.

Grab samples were collected at the entrance of the EPC and at the outlet of the UF in every trial. In principle, all the organics removal occurred at the EPC reactor and the resulting sludge was separated from the treated wastewater at the ultrafiltration unit.

4.2.1 Effluent Coloration

As a rapid approach, contaminated water can be visually analyzed for turbidity and coloration. Treated water is transparent and colorless while contaminated water has a characteristic amber/green coloration and is turbid. Although these features of the effluent are no guarantee of its non-contaminated nature, experience with the site's WW makes it possible to associate more heavily loaded effluents with darker shades and less contaminated effluents with lighter shades. In Figure 3 is possible to identify a decrease in the colouring of the effluent through treatment.


EPC Pilot Project
Trial Test Number 10: EPC
23rd November, 2016

Plant Inlet Grab
COD = 14400 ppm

EPC/UF outlet Grab
COD = 3490 ppm

CAF outlet Grab
COD = 2410 ppm

Figure 3: Pictures of the inlet, EPC outlet (after ultrafiltration) and CAF outlet grab samples for trial test number 10 carried out on 23rd November 2016 at the EPC Pilot Plant.

4.2.2 COD Removal

The operational parameters varied from trial to trial, and only through the review of individual results from reagent ratio can allow the assessment of the possibility of optimizing reactor performance.

During the effectiveness trial tests, the combinations of reagent ratios that resulted in higher and more consistent COD removal were COD/Fe/H_2O_2=15/1/15 and COD/Fe/H_2O_2=15/1/30, Figure 4. When analyzing in more detail the trials that registered similar COD removal efficiencies for the same applied ratios, it was possible to conclude that the optimal ratio combinations seem to be different for different ranges of inlet COD.
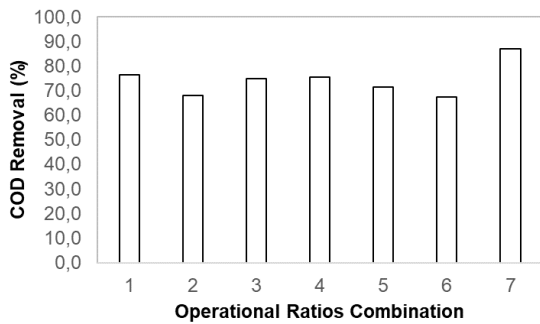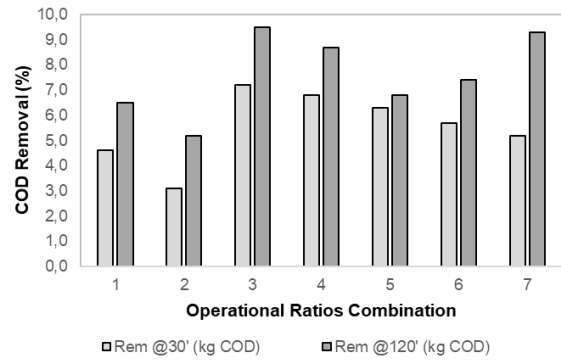
[H2O2]:COD	[H2O2]:Fe	Combination
1	7	1
2	7	2
1.5	10	3
2	10	4
1	15	5
1.5	15	6
2	15	7

Figure 4: COD removal efficiency values plotted against the COD/H_2O_2/Fe ratios.

A more thorough study on the optimal doses and dosing method is advised when applying EPC as a treatment stage during wastewater treatment. In Figure 5, percentage removal values indicate that the best ratios are COD/Fe/H_2O_2=15/1/30, while organics mass removal values suggest that the ratios COD/Fe/H_2O_2=10/1/15 may be better suited. This difference is due to the varying organics load in the inlet wastewater and again reinforces the need for complementary studies.

Overall, the reactions were planned for two-hour periods, with multi-step addition of hydrogen peroxide to better control the radical attack process. One issue which is identifiable in Figure 5 is that in some curves sequential points show apparently erratic COD level behavior. This suggests difficulties in collecting properly mixed, representative effluent samples throughout the treatment.

[H2O2]:COD	[H2O2]:Fe	Combination
1	7	1
2	7	2
1.5	10	3
2	10	4
1	15	5
1.5	15	6
2	15	7

Figure 5: COD removal efficiency values (in kg of COD removed) for the tested COD/Fe and COD/H_2O_2 ratios, obtained at 30 minutes and at 120 minutes of reaction, in the effectiveness trial tests.

At the end of the effectiveness trial tests, given that organics degradation seemed to follow an exponential decay curve, the decision to shorten residence time at the reactor was made. Assessing the adequate reagent dosage was necessary to ensure that the multi-step addition was occurring and avoid scavenging of the hydroxyl radicals (possible when H_2O_2 is dosed in a single step) as well as the raising temperature as a result of uncontrolled reactions.
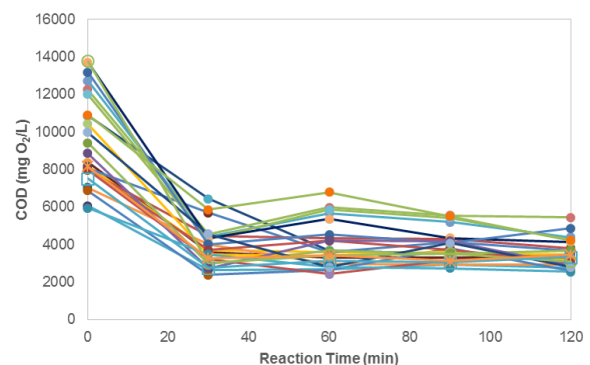
Figure 6: Time course of COD degradation in all the effectiveness trial tests.

4.2.3 Complementary Equipment

To improve the overall treatment performance, several equipment was introduced in the treatment setup an their performance was also assessed in terms of COD removal. The summary of the conclusions regarding the complementary equipment are presented in Tables 5 and 6.

Table 5: COD removal efficiency values (% of COD removed) for the complementary equipment in the EPC Pilot Plant, that can upgrade the overall efficiency.

Treatment	COD Removal (%)	Objective
Steam Stripping	75.0	To strip the wastewater of solvents prior to EPC reaction.
Electro Coagulation	15.7	To remove suspended solids prior to EPC reaction.
Electro Oxidation	32.6	To remove the nitrogen and halogen compounds post EPC reaction.
Photo Oxidation	55,3	To further degrade organics post EPC reaction.
Reverse Osmosis	65.5	To separate salts and undegraded organics post EPC reaction.

Table 6: Complementary Equipments Influence on the treatment assessment.

Complementary Treatment	Assessment
Steam Stripping	EPC Reactor decreased in the trial tests with wastewater pre treated in the Stream Stripping column.
Electro Coagulation	The suspended solids content in the site's wastewater was not high enough to justify EC as a pre treatment.
Electro Oxidation	Although the chlorides removal improved with the introduction of an electro oxidation, the objective removal was obtained in the trial tests without electro oxidation.
Photo Oxidation	COD removal at the photo oxidation is 56% and did not required the addition of hydrogen peroxide, using residual from the EPC reaction.
Reverse Osmosis	COD removal improved greatly with the introduction of the RO membranes module, the treated wastewater toxicity increased and the biodegradability decreased.

4.2.4 EPC Reactor Robustness

The trials plan included the designated Robustness Tests, namely, trials on synthetic wastewaters simulating likely future changes in the site's wastewater composition or stress situations that mimic nearmiss situations on the site's history.

● Integration of segregated streams

At present, the liquid waste is segregated to best fit the site's WWTP. Considering the installation of an EPC unit on site, some of the presently segregated stream can be integrated in the WWTP equalization.

The simulation of the integration in the treatment of streams with an expected low organic load consisted in treating 1 m^3 of these effluents at the EPC Pilot Plant, characterizing them and evaluating the treatment performance, as these effluents will just dilute the pharmaceutical wastewater.To simulate the integration of presently segregated streams effluents, these effluents were added to the pharmaceutical wastewater in ratios according to future expectations, considering the expected daily flow rates and equalization volumes existent at the site's industrial WWTP. The effluents treated were 1) Condensate phase from the thermo-oxidizer's off-gas treatment, 2) Utilities condensates and 3) COL (Change of Line) effluent. In these trials, effluent biodegradability increased and the toxixity decreased.

● Simulation of a solvent leaks

Stress situations were simulated with addition of key solvents to the pharmaceutical wastewater, with the ratio mimicking the site's incidents history, specifically, when solvent leaks occurred.

The site's incidents history with respect to solvent leaks was used to simulate the addition of a leak to the pharmaceutical wastewater fed to the EPC. Regardless of the high load of solvents, the EPC performance was within expected ranges (Table 7).

Table 7: EPC treatment of simulated solvent leaks together with the pharmaceutical wastewater: summary of COD removal efficiency results.

Solvent added	EPC step COD Removal (%)
Dichloromethane	89.1%
Monoethylene glycol	83.2 %
Heptane	83.3 %

4.3. API Degradation

Due to confidentiality issues, the quantification of specific API in the wastewaters from the EPC test trials will not be presented, but Figure 7 shows the average API removal levels including the main APIs tested.

These averages were computed from API removal results in tests for the treatment of synthetic effluents, namely pharmaceutical wastewater supplemented with specific amounts of API to detect their presence and degradation, and in tests carried out with unsupplemented pharmaceutical wastewater. In all the tests, the API removal levels were over 97% and the degradation time curves presented the same behavior identified for COD, with 90% of the API being degraded in the first 30 minutes of the EPC reaction.
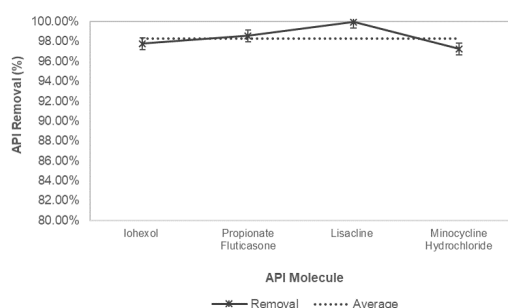
Figure 7: Average removal for selected APIs, in trials performed at the EPC Pilot Plant using pharmaceutical wastewater with or without supplementation with the same APIs.

4.4. Treatment Environmental Performance

The biodegradability and toxicity assessment was made considering the discharge of the pre-treated pharmaceutical wastewater into a downstream municipal WWTP or the alternative of introducing a biological step in the industrial WWTP to complete the wastewater treatment. In either cases there is still a final discharge into a natural water course and effluent toxicity to aquatic environments was assessed.

Toxicity tests can measure the impact of a sample on aquatic fauna and in this project the toxicity tests were done by measuring the acute toxicity of the treated effluent towards Daphnia magna. Another used measure of the effluent toxicity was the respiratory inhibition on an aerobic microbial population, determined through measurements of the dissolved oxygen uptake rate with a dissolved oxygen probe.

The recommended emission limit is 2 toxicity units (TU), and as can be seen in Figure 8, the EPC trials resulted in an effluent of low toxicity. With and average toxicity of 1.25 Toxic Units (TU) at the outlet, treatment at the EPC provided on average a

95.8 % decrease in relation to the inlet wastewater toxicity.
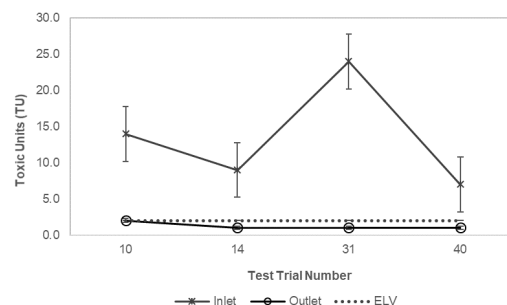
Figure 8: Inlet and outlet eco-toxicity levels, measured in toxicity units (TU) towards *Daphnia magna*, for some of the effectiveness trials performed at the EPC Pilot Plant.

Reviewing Figure 10, it is possible to conclude that the treated effluent presents a decrease in respiratory inhibition upon treatment in the EPC pilot, which is coherent with the data on Figure 8. The treated wastewater was much less inhibitory to the biomass, with respiratory inhibition level of 5 %, that the inlet wastewater, corresponding to an average decrease in inhibition of 94.8 %.
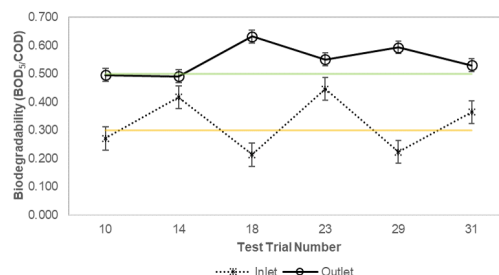
Figure 9: Inlet and outlet biodegradability levels, measured as the ratio of BOD5 to COD, for some of the effectiveness trials performed at the EPC Pilot Plant. The horizontal lines indicate the minimum (yellow) and ready (green) biodegradability levels.
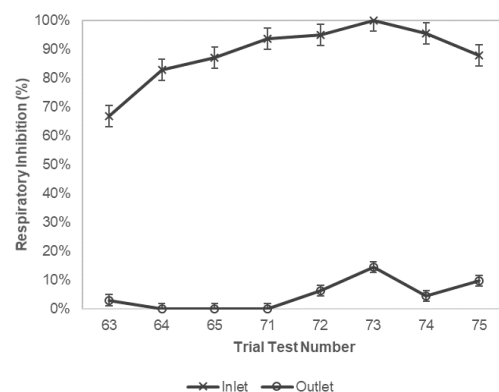
Figure 10: Inlet and outlet toxicity levels, measured as respiratory inhibition in an aerobic microbial population, for some of the effectiveness trials performed at the EPC Pilot Plant.

5. Economic Analysis and Conclusions

The effectiveness trials validated the EPC technology ability as an organics degradation technique fit to integrate the site's WWTP. The removal efficiencies for the relevant quality parameters achieved the objectives set in the technology acceptance criteria. Regarding COD and TOC, the performance objective was not achieved in the EPC alone although the presence of some degradation and separation technology promoted an overall higher removal. These issues were considered in the implementation scenarios explored.

In the robustness trials, the EPC technology's performance maintained the trends set in the effectiveness trials establishing the EPC reactor as a versatile treatment capable of buffering the stress situations and accept the alterations on the wastewater composition that may occur due to the site's expansion.

API Degradation studies and environmental performance assessment, revealed that the EPC reactor is capable of efficiently degrading API molecules and that the treated wastewater becomes more biodegradable and has a lower toxicity than at the entrance of the treatment.

Considering all this conclusions, a thorough economic analysis was made regarding treatment operational costs and installation investment.

With a treatment cost pf 1.93 euro/kg of COD removed, the revamped WWTP will operate in coordination with the wastewater segregation plan to treat it more efficiently and at an overall lower cost than those of the present operation.

In the designed WWTP - Figure 11, EPC reactor is complemented with a biological reactor, the 90% overall COD removal distribution is 70% COD at the EPC reactor and 20% at biological reactor.
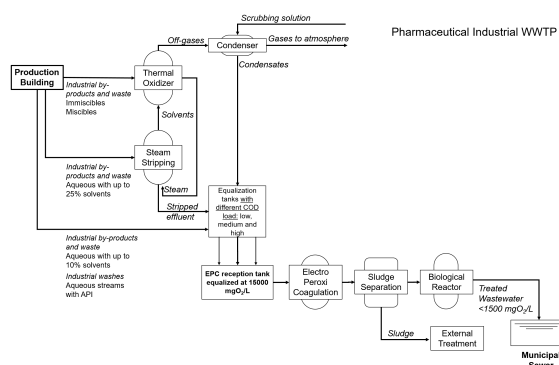
The evaluation of soft gains allowed the estimation of the payback period and validated the investment's feasibility. This analysis was done considering the actual waste management activities carried out in 2016 and the projected

management that would have been done in the new WWTP with the same streams and yearly flow rates.

The estimated soft gains for the year of 2016, when comparing the future treatment with the present treatment are 603,000 euros. This value considers a treatment capacity of 240 m^3/day and a wastewater with 10500 mg O_2=L of COD load. The future installation was designed for a higher feed flow rate and higher organics load, therefore it is not incorrect to consider that it will perform in compliance under the considered capacity and COD value. The expansion that motivated the WWTP revamping will be finished in five years and the estimated timeline for the new WWTP is to be operating in two years, therefore the payback period can consider the present wastewater composition and treatment capacity.

Considering an investment of 1,462,000 euros and soft gains of 603,000C, the future WWTP will have a payback time of two to three years. The design will be done to guarantee environmental compliance.

Figure 11: Industrial WWTP setup.

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