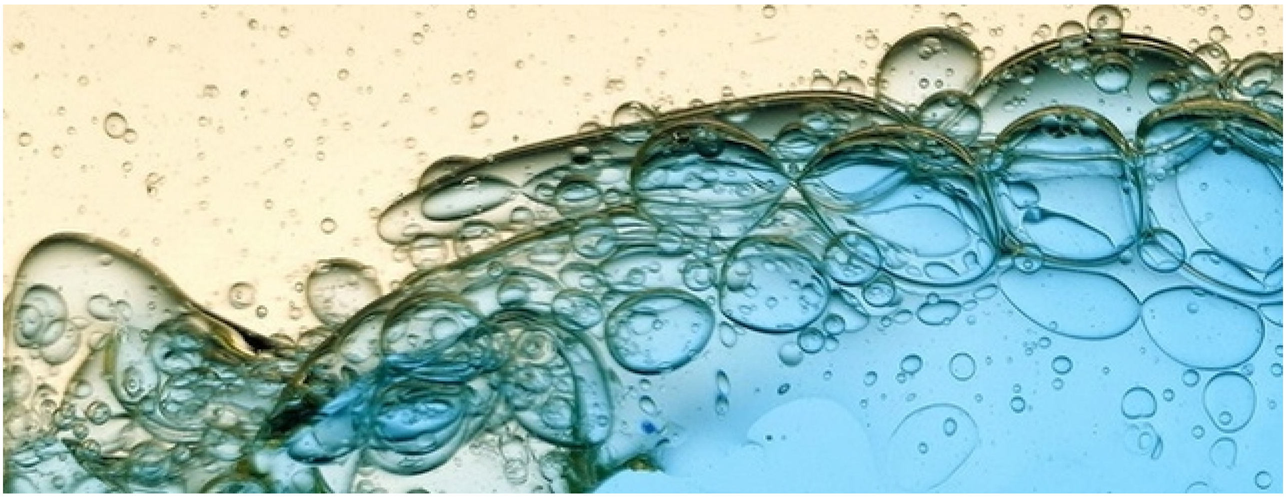

Pilot scale study of pharmaceutical wastewater treatment with Electro-Fenton Technology

Electro-Peroxi-Coagulation Pilot Project

Ana Marilia da Trindade Barata

Thesis to obtain the Master of Science Degree in

Chemical Engineering

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Abstract

All industries Wastewater (WW) discharges are regulated by environmental licenses accordingly to its downstream treatment. Currently, the concentration of Active Pharmaceutical Ingredient (API) is not yet amongst the established Emission Limit Value (ELV) - the need for a treatment that can ensure API degradation is rising rapidly, motivated by studies of prolonged exposition to API.

Pharmaceutical industries are investing in top of the range equipment for Wastewater Treatment Plant (WWTP) capable of guaranteeing compliance to both environmental and eventual API discharge limits.

In line with the emerging changes regarding pharmaceutical plants, a pharmaceutical industry proposed a project to explore the potential of electrochemical technology as a pre-treatment of its WW before discharging to municipal WWTP. The current treatment is based on solvent separation with a stream stripping column. The acceptance criteria for the technology validation was established.

With consideration to typical pharmaceutical WW characteristics - high variability organic load, Electro-Peroxi-Coagulation (EPC) was chosen as the adequate technology to evaluate. EPC is an Advanced Oxidation (AO) promoted by the addition of chemicals and electrical current to decompose complex effluents.

This master's thesis dissertation is the result of the application of EPC technology in pharmaceutical WW and subsequent data processing. WWTP was simulated in a pilot plant with several electrochemical and separation equipment available to lay out in the desired sequence. Grabs were collected through the treatment in every trial and analyzed accordingly to a detailed analysis plan. Data evaluation was oriented to EPC reaction characterization: kinetics, optimal setup and reactor design.

Keywords

WW – Waste Water; WWTP – Waste Water Treatment Plant; API – Active Pharmaceutical Ingredient; EPC – Electro Peroxi Coagulation; AO – Advanced Oxidation

Resumo

A descarga de Águas Residuais (AR) está regulada numa licença ambiental adequada ao tratamento a montante. Mo conjunto dos parâmetros regulados ainda não existe Valor Limite de Emissão (VLE) para Princípio Activo Farmacêutivo (API); surge a necessidade de criar um sistema de degradação de API capaz de acomodar os VLE no futuro.

As indústrias farmacêuticas estão a investir em equipamento topo de gama para as suas estações de tratamento de águas residuais industriais (ETARI), de modo a acompanhar a tendência e garantir futura conformidade para com os VLE e eventuais limites de API.

Uma empresa farmacêutica propôs um projecto para explorar o potencial da tecnologia electroquímica como pré-tratamento das suas AR. O actual tratamento baseia-se na separação de solventes com uma coluna de stripping com vapor directo.

Considerando as características típicas de AR farmacêutica – alta carga e variabilidade, escolheu-se avaliar a tecnologia Electro-Peroxi-Coagulação (EPC), uma Oxidação Avançada (OA) promovida pela adição de peróxido de hidrogénio e corrente eléctrica para decomposição de efluentes complexos.

Esta dissertação de mestrado é o resultado da aplicação da tecnologia EPC a AR farmacêutica e subsequente tratamento de resultados. A ETARI foi simulada numa planta piloto com equipamentos electroquímicos e de separação disponíveis para criar a sequência de tratamento desejada. Amostras foram recolhidas ao longo do processo de tratamento em todos os testes e analisadas de acordo com um plano detalhado de testes. O tratamento de resultados foi orientado para a caracterização do reactor EPC (cinética, condições operatórias óptimas e dimensionamento) e sua integração numa ETARI.

Palavras Chave

AR – Águas Residuais; ETAR - Estação de Tratamento de Águas Residuais; API - Active Pharmaceutical Ingredient; EPC – Electro Peroxi Coagulation; OA - Oxidação Avançada

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Acronyms

API	Active Pharmaceutical Ingredient
AO	Advanced Oxidation
AOP	Advanced Oxidation Processes
AOX	Adsorbable Organic Halides
BOD	Biological Oxygen Demand
BOD5	5 day biochemical oxygen demand
BOD20	20 day biochemical oxygen demand
CAF	Carbon Activated Filter
CIP	Cleaning-in-Place
COD	Chemical Oxygen Demand
COL	Change-of-Line
DAF	Dissolved Air Flotation
DO	Dissolved Oxygen
DOUR	Dissolved Oxygen Uptake Rate
EC	Electro Coagulation
EF	Electro Fenton
EPC	Electro-Peroxi-Coagulation
EO	Electro Oxidation
FOG	Fats, Oils and Greases

HAT	Hydrogen Atom Transfer
IBC	Intermediate Bulk Container
IC	Inorganic Carbon
MBBR	Moving Bed Biologic Reactor
PLC	Program Logic Controller
RO	Reverse Osmosis
SDS	Safety Data Sheet
TC	Total Carbon
TOC	Total Organic Carbon
TSS	Total Suspended Solids
TU	Toxic Units
UF	Ultrafiltration
UV	Ultra-Violet Radiation
VOC	Volatile Organic Carbon
VSS	Volatile Suspended Solids
WGK	TO BE DEFINED
WWTP	Wastewater Treatment Plant
WW	Wastewater

1

Introduction

1.1 Scope

Wastewater treatment is vital as the amount of fresh water available is scarce and continuously decreasing due to abusive human consumption. In several regions of the world, the economic and social growth of underdeveloped countries is being limited by the scarcity of safe water. Overall the world population growth alongside with the industrial growth is greatly impacting the natural water courses and sustainable measures must be implemented. [9]

At a population level, sustainability should be promoted as a mindset conversion. The behavioral changes are difficult to measure and it's the responsibility of governments to implement strategies and to educate towards water saving and reutilization.

Industries and agriculture are also highly accountable for their water consumption (in refrigeration circuits, steam production systems and irrigation) as well as for the treatment and discharge of its wastewater. Organic and inorganic compounds generated through or added to industrial and agricultural processes, often exit such processes in their wastewater, eventually making them toxic to several aquatic ecosystems or the underground aquifers that may be entered.

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. [10]

Metals, halogens and nitrogenous compounds are conventional contaminants, but other not yet regulated contaminants may be more harmful to the environment and life. At the present day, active pharmaceutical ingredients 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. Sources and pathways of emerging contaminants into the environment depend on how they are used and how the products containing them are disposed of (figure 1.1).

Most of these compounds are present in the WW sent to WWTP, not adapted for treatment of emerging contaminants. The removal of micropollutants such as APIs in WWTP is mostly based on stripping, sorption, and biological degradation, which are fallible degradation processes for API molecules, the focus of this thesis.

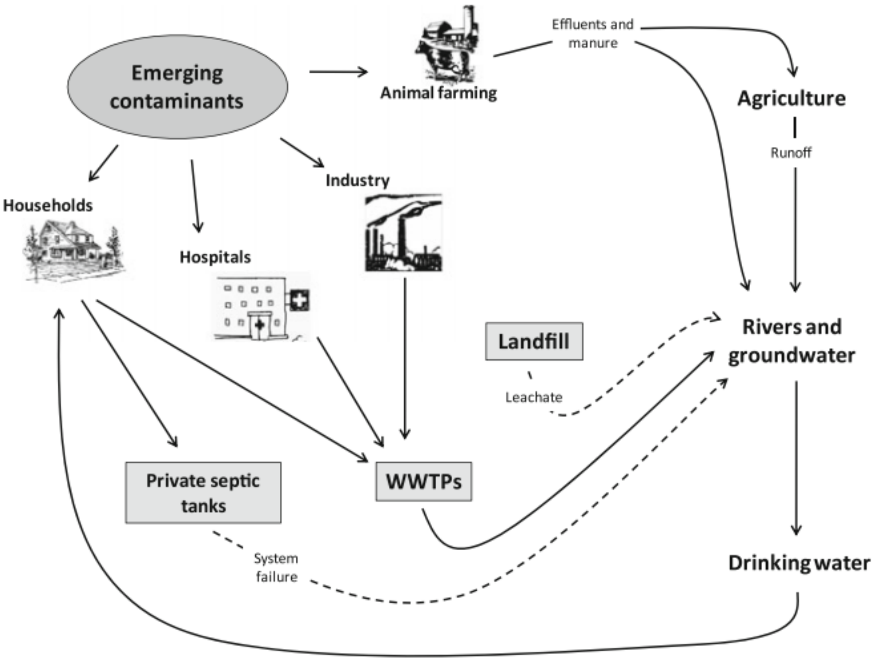


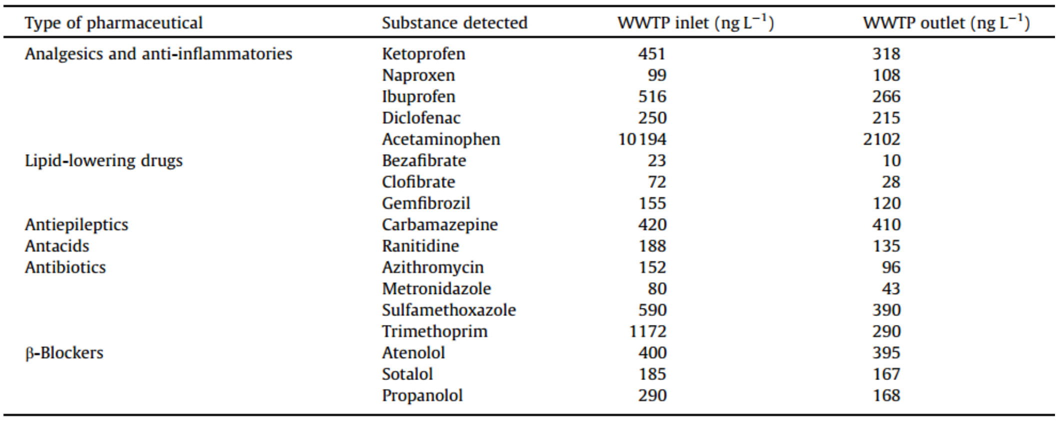
Figure 1.1: Potential sources and pathways of emerging compounds into the environment. [3]

Stripping separation is applied to contaminants with low boiling points and as most of emerging compounds are characterized by low volatility, stripping cannot be considered a robust treatment option. Sorption of API molecules on primary and secondary sludges of a conventional WWTP is a more efficient treatment. It occurs as absorption in the lipid fraction of the sludge (primary sludge), and adsorption onto the secondary sludge through electrostatic interactions between positively charged compounds and negatively charged microorganisms surfaces. However it's important to keep in mind that both this processes are result only in transfer of the compound between phases, and API molecules should be decomposed to guarantee that they do not enter the environment. [11] [3]

Lastly on API, biological digestion does not guarantee decomposition nor an efficient removal. API molecules are a large class and the types more commonly found in water are those described in figure 1.1. The table on figure 1.1 is an example of many the studies made on several countries around the world on the presence of API on surface or groundwater. Through it is possible to comprehend the unreliability of an WWTP on treating wastewater containing API. The removal of API in conventional WWTP can be efficient as well as inefficient and such studies confirmed that it is not possible to deduct API removal effectiveness by type of pharmaceutical. [12] [13] [14] [15] [16]

Besides not being degraded, the presence of API molecules may put at risk the overall efficiency of WWTP. API are, therefore, chemicals which are resistant to degradation, persistent in aqueous media, and have the ability to negatively impact water organisms and even the bacterial populations in WWTP.

Table 1.1: Concentrations of pharmaceuticals detected in wastewaters of various WWTPs before and after treatment. [8]



Type of pharmaceutical	Substance detected	WWTP inlet (ng L^{-1})	WWTP outlet (ng L^{-1})
Analgesics and anti-inflammatories	Ketoprofen	451	318
	Naproxen	99	108
	Ibuprofen	516	266
	Diclofenac	250	215
	Acetaminophen	10194	2102
Lipid-lowering drugs	Bezafibrate	23	10
	Clofibrate	72	28
	Gemfibrozil	155	120
Antiepileptics	Carbamazepine	420	410
Antacids	Ranitidine	188	135
Antibiotics	Azithromycin	152	96
	Metronidazole	80	43
	Sulfamethoxazole	590	390
	Trimethoprim	1172	290
β-Blockers	Atenolol	400	395
	Sotalol	185	167
	Propanolol	290	168

One major issue related to environmental impacts is the difficulty to prove the efficiency of the preventive measures and to turn such preventive measures into worthy investment strategies. As the impacts of water pollution are long term and affect first and foremost the weakest economies, for a long time large industries tended to overlook their pollution trails. However, these tendencies have been inverted as result of massive investment from governmental authorities to promote sustainability and environmental awareness. In the industry context, a process diagram is the schematics of the steps necessary to transform an inlet stream of raw materials into an outlet stream of products. Since waste is not a product outlet stream, design engineers often dismiss the importance of waste treatment and its conversion into products adequate to re-enter nature. The waste treatment process is as important as the production process but at the present day the economic framework of industrial sites is not able to support the investment on the necessary equipment. When a production site does not have the ability to treat its waste, the latter is forwarded to adequate treatment by external contractors.

Waste treatment focus is in the degradation of the pollution but as in any chemical engineering process it is also focused on energetic appreciation. If its solvent load is high, liquid waste can be incinerated to for energy recovery. When the water content is high, liquid waste can then be called wastewater - WW - and is treated to remove organic load and other pollutants from the water and enable it to re-enter the natural water resources.

Wastewater treatment steps can be divided in two categories, namely, physical and chemical treatment in primary and tertiary stages (for the separation of unsolubles and micropollutant removal, respectively). While physical and chemical treatments can be adjusted to WW composition, conventional biological treatments are much less flexible in terms of WW composition admission.

From the process diagram schematics in figure 1.2, it is possible to understand that the WW management is as complex as any industrial production line, with the difference being that the raw materials in this process are much less predictable. Industrial sites direct their WW to sewage network, and further to a downstream complex Wastewater Treatment Plant - WWTP. Frequently this WWTP is managed by a municipal authority and is designed with the capacity to receive industrial WW alongside with domestic WW.As in these conventional WWTP the secondary treatment is biological, the accepted pollution parameter ranges are well defined to avoid toxic shocks. Municipal authorities fix limit values for every parameter relevant for the treatment design. Environmental licenses are established taking those limits into account and every entity discharging to into municipal sewers must comply with such limits.

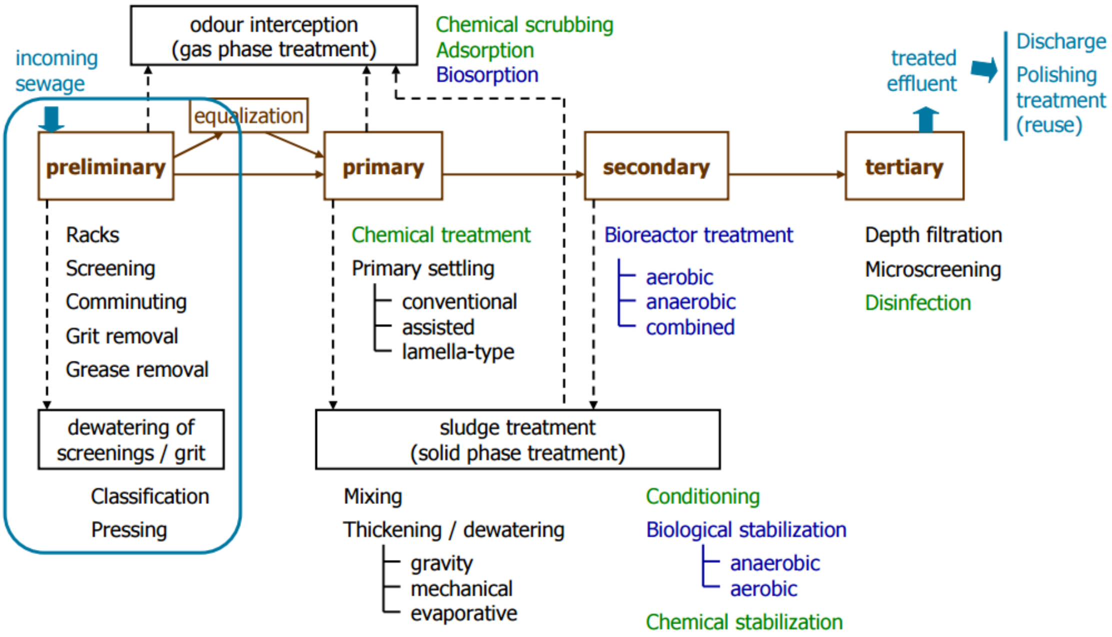


Figure 1.2: Conventional WWTP schematics. [4]

Conventional pre-treatment on industrial sites are based on compound separation with resource to distillation of solvents and filtrations of suspended particles, prior to downstream treatment in external WWTP. More complex treatment oriented to decompose WW is applied in sites where water reutilization is a possibility or a priority.

New wastewater treatment technologies are emerging and with it the possibility to apply at industrial sites operations able to treat WW and guarantee a consistent effluent quality regardless of its initial composition. This possibility is advantageous both to industries that discharge the treated WW to downstream systems, and to industries who re-utilize water.

At the forefront of emerging technologies in industrial wastewater treatment are the electrochemical technologies. These are based on organic compound precipitation or degradation making use of electrochemical phenomena promoted by the addition of chemicals and the application of an electric current. These processes are mainly used to achieve the downgrade of the organic complexity of the WW, rendering it adequate for to downstream biological treatment in existent WWTP.

1.2 The Challenge

An industrial site – a pharmaceutical multipurpose factory – was not able to attain 100 % compliance of its environmental license due to the high variability of its WW and the unreliability of its pre-treatment. As the production of API is entirely carried out in batch operation, the composition of the WW at this pharmaceutical site is essentially unpredictable and any pre-treatment designed to ensure compliance should accept such variability without compromising compliance demands. Moved by the need to improve the effectiveness and capacity of the site's industrial WW a study on the effectiveness and robustness of an EPC treatment unit was conducted. The results and conclusions of this study will be presented in this thesis.

Presently, the site's liquid waste management system relies on a thermal oxidation unit for the incineration of high solvent load and potent product stream's, with steam production, and a steam stripping system for solvent recovery from other aqueous streams, discharging into a municipal sewer with a biological based downstream WWTP, figure1.3. The site produces daily an average of 240 m^3 wastewater (WW), treated in the steam stripping column. The stripped aqueous phase is equalized with the condensate phase from the thermal oxidizer off-gases cleaning circuit and sent the municipal WWTP. The pre-treatment objective is therefore to remove most of the pollutant loads and to discharge a wastewater complying with the quality limits for all parameters established in the site's environmental license.

The thermal oxidizing unit, figure 1.4, works in deep feed mode from retention tanks collecting immiscible, miscible and aqueous effluents. The heat generated is used to produce vapor to be used in the

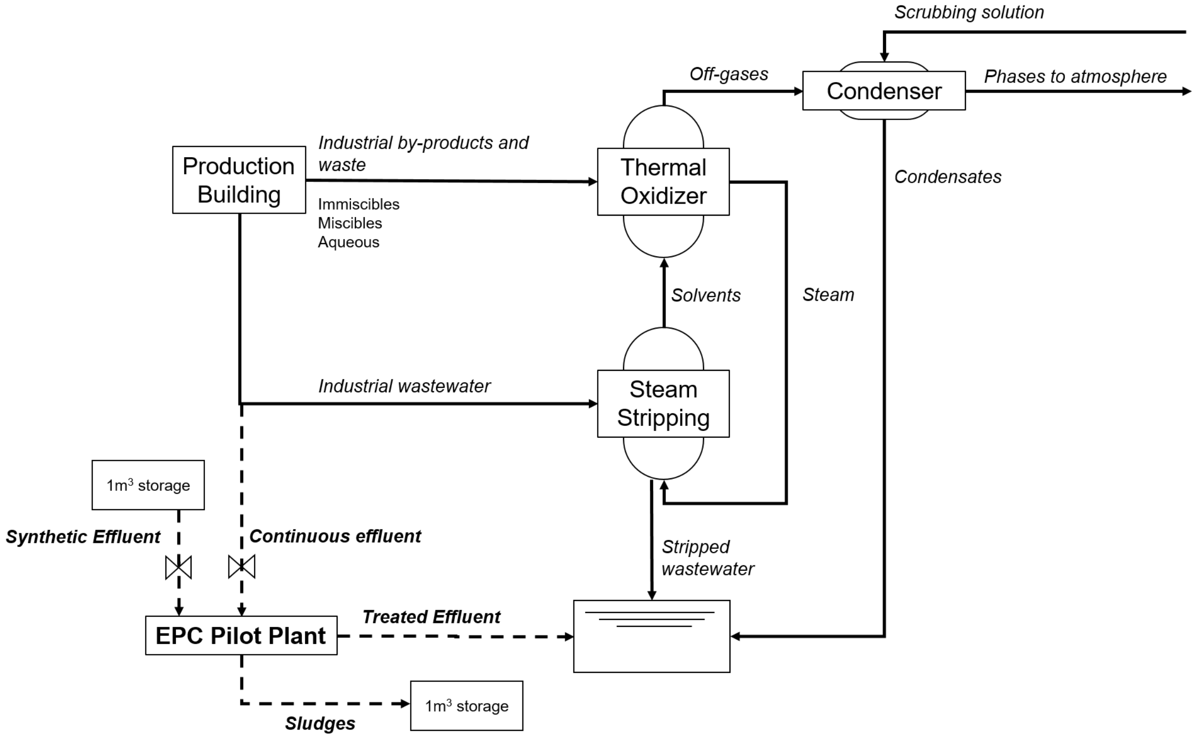


Figure 1.3: The present pre-treatment schematics diagram with the Pilot Plant feeding system.

steam stripping unit and operations carried out in production buildings. Combustion is conducted at 1100-1300^0C to minimize the formation of dioxins and furans, and a rigorous control of the temperature in the off-gas condenser is ensured to avoid the formation of such hazardous compounds.

All the gaseous emissions exiting the condenser are in compliance with the environmental license parameter values monitored by an accredited external entity on a regular basis. Whenever needed, corrective actions are taken to ensure that the unit operates in compliance with the legal limits for gaseous emissions.

This step can be considered efficient as a waste management strategy, since it guarantees the thermal decomposition of waste products and is integrated in an energy recovery strategy. However the capacity of this equipment is not sufficient to cover neither the incineration needs of the site (in 2016, 900 ton of waste fit for burning was sent to external treatment) nor its steam needs (the steam consumption requires the utilities central to use additional boilers). Meanwhile, also in 2006, 2200 ton of aqueous waste water was processed in the thermal oxidizer, due to the lack of an appropriate alternative to low solvent content streams.

The other equipment main unit integrated in the liquid effluent treatment strategy is a steam stripping column that strips the solvents from aqueous streams, figure 1.5. Solvents are removed due to their low boiling point, vaporizing in direct contact with steam introduced at the bottom of the stripping column.

The steam contacts the aqueous effluent in counter-current flow and solvents with a normal boiling point under 100 ^0C are removed from the wastewater. The steam is provided by the thermal oxidizer and the stripping unit accounts for 60% of its daily steam production. The stripped solvents are fed to the thermal oxidizer to be incinerated, occupying approximately 20% of its capacity on a daily basis. The treated wastewater carries organic and inorganic loads which are appropriate for downstream treatment at the municipal WWTP.The quality of this discharged wastewater is monitored internally (daily) and by an accredited external lab on a regular basis. All the industrial wastewater collected from building drains is equalized in an equalization tank (140 m^3)before being fed to the stripping unit.The effluent from the latter is combined with the condensates from the off-gases line of the thermal oxidizer and equalized before, discharging to the municipal sewer in another equalization tank (45 m^3).

Figure 1.4: The thermo-oxidizer.

Figure 1.5: Steam Sptripping column.

The drivers of the project reported in this thesis were full environmental compliance and innovation. Thus, the EPC system was evaluated for possible implementation during the revamping of the waste management system at the industrial site.

The site's expansion regarding production capacity is ongoing and will imply the need for an upgrade on the waste management system, since the new and improved system must be designed to cope with an increase on the WW volume and variability.

If the EPC technology proves to be effective as a conversion treatment able to degrade multiple organic pollutants and API molecules, the treated WW may be fit for discharge into the municipal WWTP in full compliance.

Furthermore, it is expected that the conversion of the organic load will render the WW components less toxic and more biodegradable, therefore more appropriate for a biological treatment which is presently performed at the municipal WWTP. As a biological treatment can complete the removal of the organic pollutants, it could be a good investment within the site's water management system, the clean water being utilized for the industrial refrigeration circuits. In any case, the effectiveness of the EPC treatment is critical.

The legitimacy of the investment in an EPC unit will depend on the economic analysis of its returns. To estimate soft gains and the payback period it is necessary to estimate the production capacity and the WW organic contamination levels in the future WW according to the company's expansion plan. Estimates will be presented for a doubling of both the capacity and the contamination level.

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.

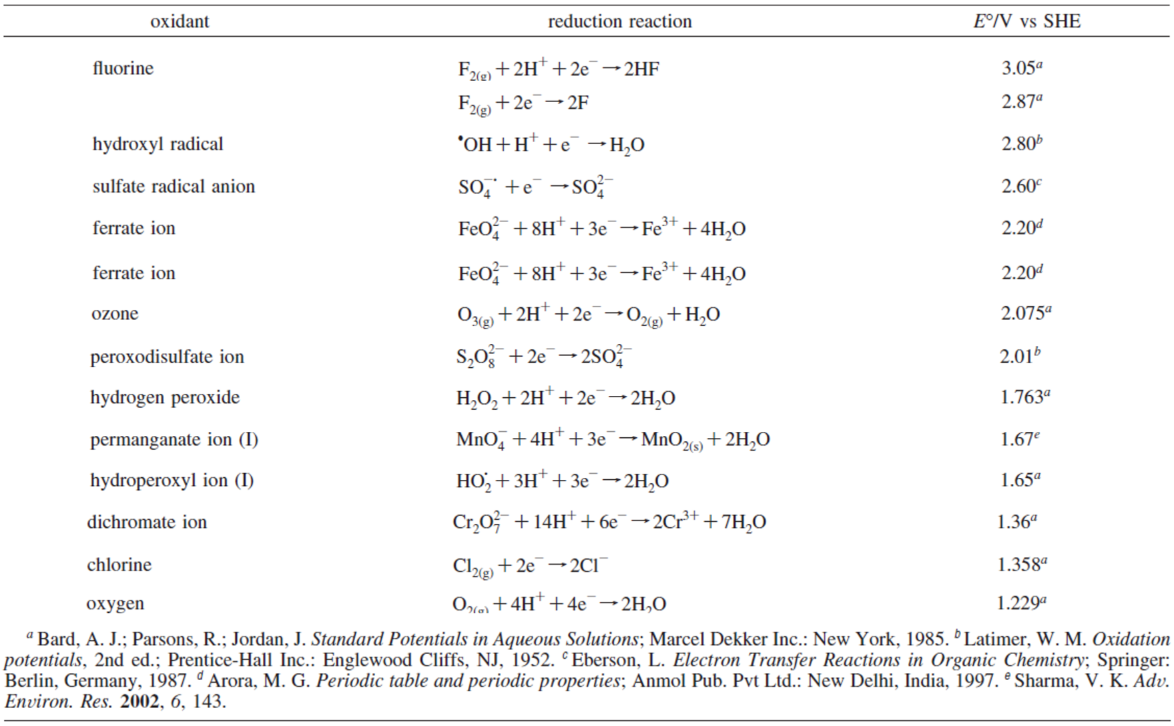
2

Scientific Background

2.1 Advanced Oxidation Processes (AOPs)

2.1.1 Redox reactions

The transfer of electrons from an electron donor species to an electron acceptor species is defined, in what regards the former, as oxidation, and, in what regards the latter, as reduction. This transfer occurs due to higher electronic affinity on the part of the acceptor species. The oxidation (loss of an electron) and reduction (acceptance of an electron) can imply several chemical transformations on the pair of species, and if the transfer results in an odd number of valence electrons a radical will be formed. Radicals are highly unstable species due to this electronic unevenness and are consequently very reactive. Whenever a radical is formed by oxidation, a subsequent oxidation-reduction reaction usually occurs between the radical and another species to form more stable products, in thermodynamic terms. The reactivity of an oxidative species, including the radicals, can be measured by its oxidation potential (Figure 1), and from the listing of such values it is possible to determine whether a species will be an adequate oxidant for a given oxidation reaction.



oxidant	reduction reaction	$E°$/V vs SHE
fluorine	$F_{2(g)} + 2H^+ + 2e^- \rightarrow 2HF$	3.05[a]
	$F_{2(g)} + 2e^- \rightarrow 2F$	2.87[a]
hydroxyl radical	${}^\bullet OH + H^+ + e^- \rightarrow H_2O$	2.80[b]
sulfate radical anion	$SO_4^{-\bullet} + e^- \rightarrow SO_4^{2-}$	2.60[c]
ferrate ion	$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O$	2.20[d]
ferrate ion	$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O$	2.20[d]
ozone	$O_{3(g)} + 2H^+ + 2e^- \rightarrow O_{2(g)} + H_2O$	2.075[a]
peroxodisulfate ion	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	2.01[b]
hydrogen peroxide	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.763[a]
permanganate ion (I)	$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_{2(s)} + 2H_2O$	1.67[e]
hydroperoxyl ion (I)	$HO_2^\bullet + 3H^+ + 3e^- \rightarrow 2H_2O$	1.65[a]
dichromate ion	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.36[a]
chlorine	$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-$	1.358[a]
oxygen	$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229[a]

[a] Bard, A. J.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solutions*; Marcel Dekker Inc.: New York, 1985. [b] Latimer, W. M. *Oxidation potentials*, 2nd ed.; Prentice-Hall Inc.: Englewood Cliffs, NJ, 1952. [c] Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer: Berlin, Germany, 1987. [d] Arora, M. G. *Periodic table and periodic properties*; Anmol Pub. Pvt Ltd.: New Delhi, India, 1997. [e] Sharma, V. K. *Adv. Environ. Res.* **2002**, *6*, 143.

Figure 2.1: List of oxidation potentials (Eº) of common chemical species (with respect to the standard hydrogen electrode – SHE), with respective reduction reactions. [5]

2.1.2 The Hydroxyl Radical in Advanced Oxidation

In wastewater treatment, conventional oxidation techniques, such as biological oxidation, can be limited by slow kinetics, by oxidation resistance of refractory pollutants in aqueous medium, or because the oxidation products are more hazardous than the original pollutants. (Advanced Oxidation Processes (AOP)s) are thus an upgrade from conventional oxidation in the sense that they can overcome such problems. However, to a higher degree than that of alternative treatment processes, AOPs are not completely understood in their scientific basis and therefore need to be further studied through projects such as that reported in the present thesis.

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”. [17] 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 (${}^\bullet OH$) 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. [18]

Once the hydroxyl radical is made available, the degradation of organics can occur by dehydrogenation (Hydrogen Atom Transfer (HAT), eq. 2.1) producing organic radicals that will undergo further reactions to generate simpler organic forms, water, carbon dioxide and inorganic salts.

$$HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \tag{2.1}$$

Another path for organics degradation is hydroxylation (addition of a hydroxyl to an unsaturated bond) in compounds with chemicals π bonds, which also results in organic radicals that degrade further into water, carbon dioxide and organic salts. An example is shown in figure 2.2.

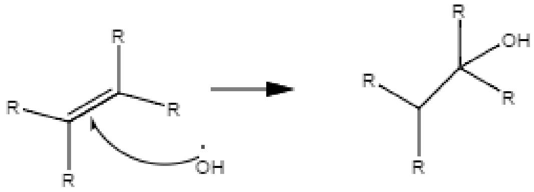


Figure 2.2: Radical attack in the hydroxylation mechanism.

If neither HAT nor electrophilic addition are favoured by the reactants, electronic transfer may also occur (eq. 2.2).

$$^{\bullet}OH + RX \rightarrow OH^{-} +^{\bullet} RX^{+} \tag{2.2}$$

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.

One common type of intermediate product generated in AOP are carboxylic acids, formed by a chain reaction that can be generalized as in Figure 2.3. The chemical degradation of methanol is an example of this chain reaction, schematized in Figure 2.4.

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 (Figure 2.5).

The originated hydroxyl radicals will interact very rapidly with organic compounds. In Figure 6 a comparison is shown between the reaction rates of ozonation and oxidation with hydroxyl radical, evidencing the high rate of AOPs in relation to other oxidation processes.

$$RH + {}^{\cdot}OH \longrightarrow H_2O + {}^{\cdot}R$$
$$2\,{}^{\cdot}OH \longrightarrow H_2O_2$$
$${}^{\cdot}R + H_2O_2 \longrightarrow ROH + {}^{\cdot}OH$$
$${}^{\cdot}R + O_2 \longrightarrow ROO^{\cdot}$$
$$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$$

Figure 2.3: Radical chain reaction initiated by the abstraction of a hydrogen atom. [6]

$$CH_3OH + {}^{\bullet}OH \rightarrow {}^{\bullet}CH_2OH \xrightarrow{{}^{\bullet}OH/O_2} H_2C{=}O \xrightarrow{{}^{\bullet}OH/O_2} O{=}CHOH \xrightarrow{{}^{\bullet}OH/O_2} CO_2 + H_2O$$

Figure 2.4: Example of a radical chain reaction initiated by the abstraction of a hydrogen atom. [6]

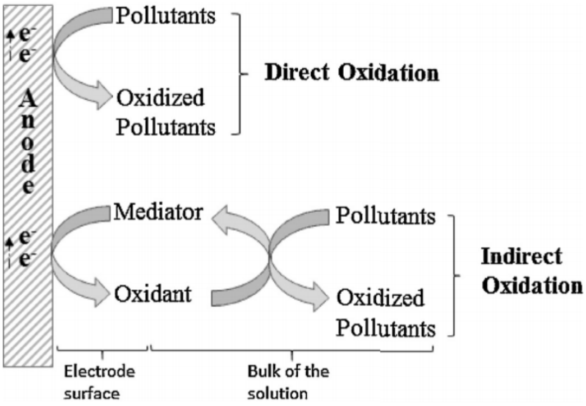


Figure 2.5: Schematic depiction of the direct and indirect (mediated) mechanisms in electrochemical oxidation. [2]

Compound	O_3	${}^{\cdot}OH$
Chlorinated alkenes	10^3–10^4	10^9–10^{11}
Phenols	10^3	10^9–10^{10}
N-containing organics	10–10^2	10^8–10^{10}
Aromatics	1–10^2	10^8–10^{10}
Ketones	1	10^9–10^{10}
Alcohols	10^{-2}–1	10^8–10^9

Figure 2.6: Reaction rate constants (k, [M–1 s–1]) of ozone vs. hydroxyl radical. [7]

In electrochemical AOP, anodic oxidation produces hydroxyl radicals by water oxidation on a high O_2-overvoltage anode (eq.2.3), favouring the generation of ${}^{\bullet}OH$ adsorbed at its surface.

$$H_2O \rightarrow OH^{\bullet}_{ads} + H^+ + e^- \tag{2.3}$$

In electro-Fenton processes, H_2O_2 is electrogenerated at the cathode and reacts with Fe^{2+} leading to the formation of the hydroxyl radicals (eq. 2.12).

2.2 Fenton's Reaction

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 (eq. 2.4 to 2.5):

$$H_2O_2(l) + Fe^{2+}(aq) \rightarrow HO^{\bullet}(aq) + OH^{-}(aq) + Fe^{3+}(aq) \tag{2.4}$$

$$H_2O_2(l) + Fe^{3+}(aq) \rightarrow HO_2^{\bullet}(aq) + H^{(}aq) + Fe^{2+}(aq) \tag{2.5}$$

In situ O_2H^+ ions generation

$$H_2O_2(aq) + HO^{\bullet}(aq) \rightarrow HO_2^{\bullet}(aq) + H_2O(l) \tag{2.6}$$

Hydroperoxyl radical generation

$$Fe^{2+}(aq) + HO^{\bullet}(aq) \rightarrow Fe^{3+}(aq) + OH^{-}(aq) \tag{2.7}$$

$$Fe^{3+}(aq) + HO_2^{\bullet}(aq) \rightarrow Fe^{2+}(aq) + O_2H^{+}(aq) \tag{2.8}$$

$$Fe^{2+}(aq) + HO_2^{\bullet}(aq) + H^{+}(aq) \rightarrow Fe^{3+}(aq) + O_2H^{+}(aq) + H_2O_2(l) \tag{2.9}$$

$$2HO_2^{\bullet}(aq) + H^{+}(aq) \rightarrow H_2O_2(l) + O_2(g) \tag{2.10}$$

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.

2.3 Electro-Fenton Processes [1] [2]

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*. Electro-Fenton 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 eq.2.11, as schematized in Figure 2.7. Iron ions (Fe^{2+} or Fe^{3+}) are added to the solution increasing the oxidation power of the generated H_2O_2. The Fe^{3+}/Fe^{2+} system provides the basis for the metal-catalysed oxidation, namely, H_2O_2 oxidizes Fe^{2+} (eq.2.12) generating the hydroxyl radical and Fe^{3+} (eq.2.13)

$$O_2(g) + 2H^+2e^- \rightarrow H_2O_2 \tag{2.11}$$

$$H_2O_2 + Fe^{2+} \rightarrow HO^\bullet + OH^- + Fe^{3+} \tag{2.12}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{2.13}$$

The electrochemical cell can either be a three-cathode divided cell (where the aqueous solution is maintained under oxygen saturation with the introduction of compressed air) or a two-electrode undivided cell (the generation of H_2O_2 can be controlled by a carbon-felt cathode, for example).

Different configurations can be designed in an EF process: external addition of ferrous ions with electro generation of H2O2 and Fe^{3+} at the cathode (eq.2.12); external supply of H2O2 with electro generation of Fe^{2+} from a sacrificial anode via reduction of ferric ions (eq.2.13); or use of both sacrificial anode and cathode to generate H_2O_2 and Fe^{2+}.

2.4 Electro-Peroxi-Coagulation [1] [2]

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 (eq.2.14), which is further oxidized to Fe^{3+} through Fenton's reaction (eq.2.12) 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.

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{2.14}$$

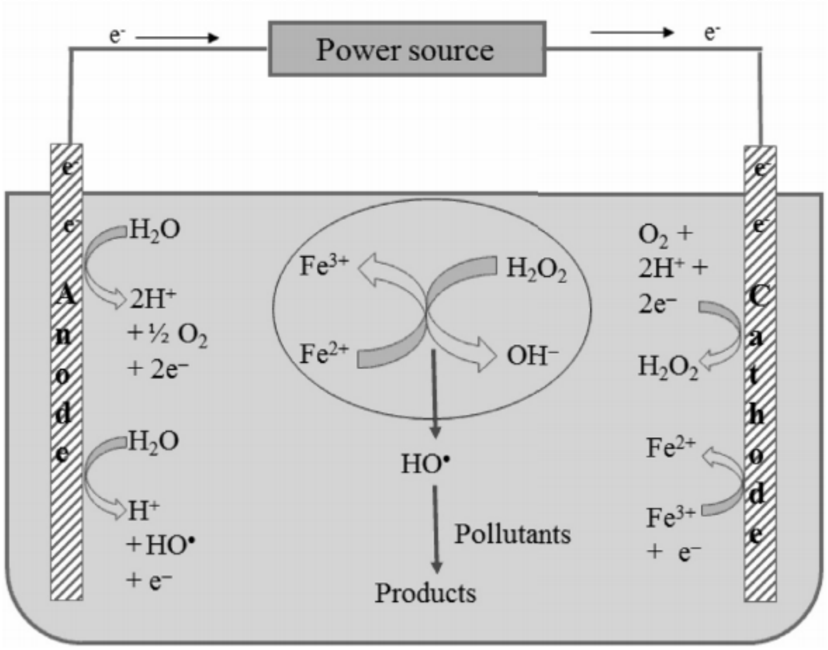


Figure 2.7: Schematic diagram of an EF cell showing the main reactions involved in an EF process using a carbonaceous material cathode. [2]

The performance of EPC as a treatment step in pharmaceutical wastewater treatment is being assessed, and therefore some operational aspects must be addressed in detail, namely:

1. Reagent dosage: H_2O_2 dosage, Fe dosage, dosing method;
2. Operational setup: reaction pH, applied electrical current, electrode configuration;

2.4.1 Reagent Dosage

2.4.1.A H_2O_2 Dosage

Several authors have studied the optimal Fenton's reagents concentrations and their impact on reactor performance in several types of WW treatment. 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. apparently, there is a range of H_2O_2:COD ratio values for which the reaction performance is directly proportional to the ratio value, specifically, to higher H_2O_2 doses correspond increased COD removals. Above a certain ratio value, the effectiveness of higher H_2O_2 dosages decreases.

The main source of hydroxyl radicals in the process is in fact hydrogen peroxide. In low peroxide concentration environments, Fenton's reaction (eq.2.4) does not generate enough hydroxyl radicals to reach the desired COD removal levels. In higher concentration environments, the hydroxyl radicals can be scavenged (eq. 2.7 and 2.15) and sludge separation through gravity sedimentation can be impaired due to

O_2 off-gassing (with the possibility of sludge flotation occurring). As the radical attacks to the organic molecules are non-selective, the higher concentration of hydroxyl radicals can also imply higher chances of hydroxyl radical recombination (eq.2.16), or difficulties with the further oxidation of the intermediate short chain organic acids.

Hydrogen Peroxide Regeneration:

$$HO_2^\bullet(aq) + HO^\bullet \rightarrow H_2O(l) + O_2(g) \tag{2.15}$$

$$2HO^\bullet \rightarrow H_2O_2(l) \tag{2.16}$$

2.4.1.B Fe^{2+} Dosage

As in the other Fenton's reagent applications, the dosage of Fe^{2+} is tailored to the organic load measured by COD, expressed also as a ratio between [Fe^{2+}] and COD. The correlation between Fe^{2+}: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 eq.2.8 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.

Some authors defend the need to also control the [H_2O_2]/[Fe^{2+}] ratio to decrease the hydroxyl consumption by either species, though the optimal ratio is yet of little consensus. Low ratio values lead to a faster disappearance of both ferrous ions and hydroxyl radicals (eq. 2.8), while higher ratio values enhance the production of the hydroperoxyl radical (eq.2.7), a weaker oxidizer in comparison to the hydroxyl radical.

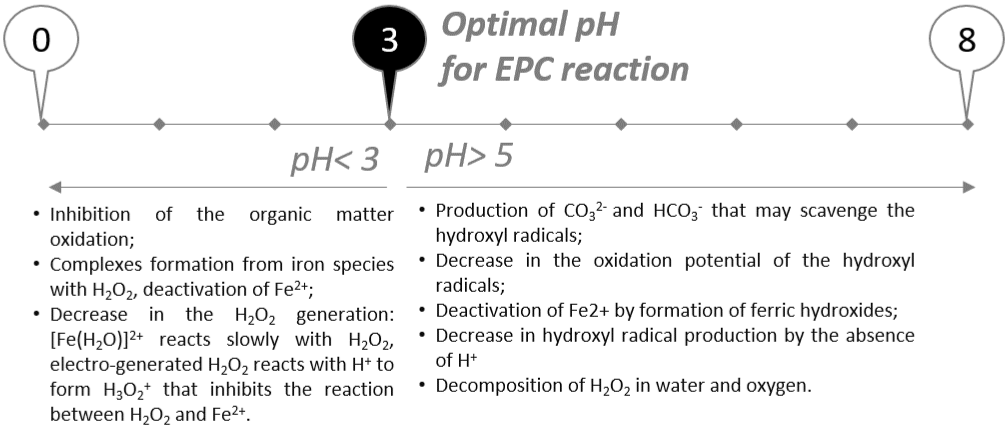
2.4.1.C Dosing Method

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 H2O2 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.

2.4.2 Operational Setup

2.4.2.A Optimal pH for the reaction

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 inhibitive effects promoted by lower or higher pH values are presented in Figure 2.8.



- Inhibition of the organic matter oxidation;
- Complexes formation from iron species with H_2O_2, deactivation of Fe^{2+};
- Decrease in the H_2O_2 generation: $[Fe(H_2O)]^{2+}$ reacts slowly with H_2O_2, electro-generated H_2O_2 reacts with H^+ to form $H_3O_2^+$ that inhibits the reaction between H_2O_2 and Fe^{2+}.

- Production of CO_3^{2-} and HCO_3^- that may scavenge the hydroxyl radicals;
- Decrease in the oxidation potential of the hydroxyl radicals;
- Deactivation of Fe2+ by formation of ferric hydroxides;
- Decrease in hydroxyl radical production by the absence of H^+
- Decomposition of H_2O_2 in water and oxygen.

Figure 2.8: Schematics and listing of the pH effects on the EPC reaction.

2.4.2.B Applied current density

Theoretically, an increase in the applied electric current density should increase the electro-generation of Fe^{3+} species from Fe^{2+} and promote more efficient Fenton's reactions. But, as in many aspects of the Fenton's reactional system, the experimental data do not support this theory and rather point towards the fact that under high current density competitive reactions take place (eq. 2.17 and 2.18), which may inhibit the generation of hydroxyl radicals and Fe^{2+} ions.

Anode: oxygen discharge

$$2H_2O_2(l) \rightarrow 4H^+(aq) + 2O_2(g) + 4e^- \tag{2.17}$$

Cathode: hydrogen generation

$$2H^+(aq) + 2e^- \rightarrow 2H_2(g) \tag{2.18}$$

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

As the EPC system is a relatively new approach in EF processes, the published literature does not provide consensual indications on the optimal density to be applied, and guiding values cannot be readily established from studies of the EPC application to different industrial areas.

2.4.2.C Electrode configuration

Fenton's reagent Fe^{2+} is continuously regenerated at the cathode via the conversion of ferric ions. The distance between electrodes can compromise Fenton's chain reactions, namely, if the electrodes are too close together Fe^{2+} may be oxidized to Fe^{3+} at the anode and even decrease the ohmic gradient through the electrolyte (which leads to a higher energy consumption). This distance can also impair the mass transfer of ferric ions to the cathode surface, in case it is too large.

3

Project Planning

The testing of the EPC process was carried out in a Pilot Plant, operated by a specialized operator. All the operations were monitored *in situ* and grab samples were taken every test according to the experimental plan described subsequently.

The objective of the pilot unit tests was to validate the EPC technology as a WW treatment stage, therefore a complex and thorough trials and analysis plan was implemented to ensure that all the possible demand situations were tested together with the evaluation of API removal. The trials began on the 7^{th} of November 2016 and ended on the 23^{rd} of January 2017. This two month pilot project coincided with the production site's shutdown and the trials were suspended for two weeks, during this period.

In every test trial, grab samples were collected at different stages of the treatment to evaluate stream composition through analysis at the factory's internal lab. Twice every week, grab samples were collected at the pilot unit's inlet and outlet during selected tests, to analyze for a broader spectrum of parameters. A TOC analyzer was setup on-line to continuously monitor effluent quality and establish a TOC baseline for future operation. All the operational parameters and the trial setup were registered in a trial test log sheet during the tests by the pilot operator.

3.1 General Plan

The overall schedule of the present project is presented in figure 3.1. Details on each stage are given subsequently.

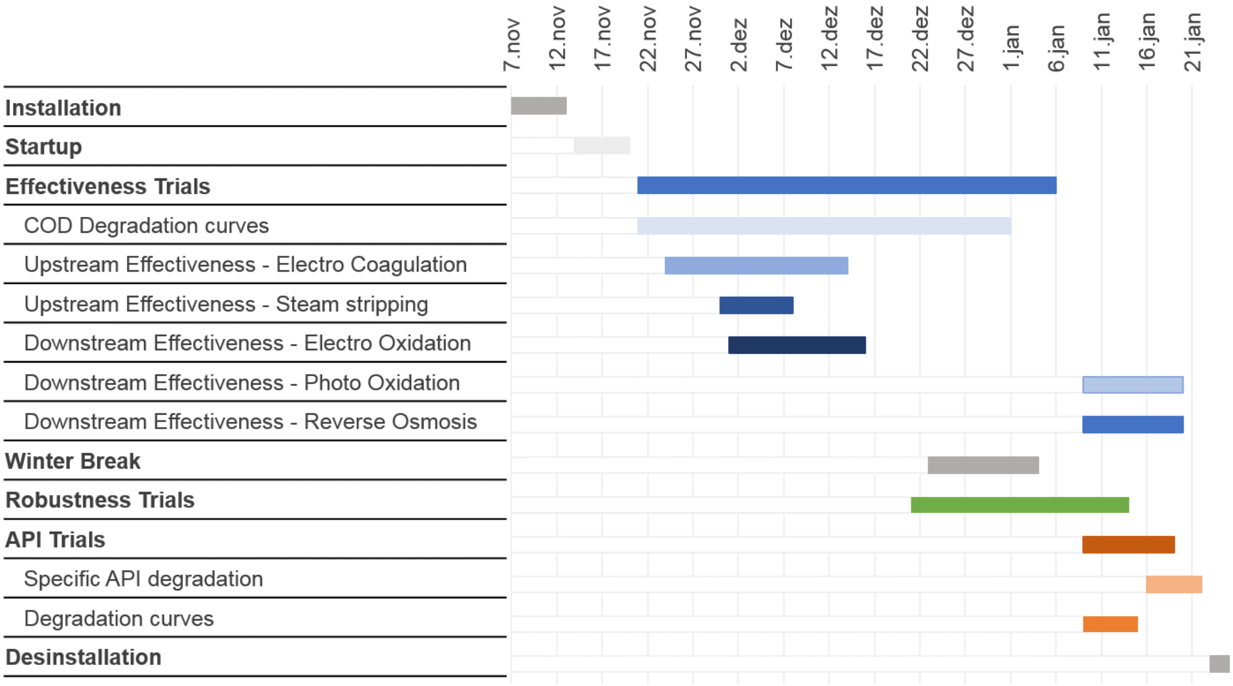


Figure 3.1: EPC Pilot Project Program.

3.2 Trial Test Plan

The timetable and main features of the trials performed at the EPC pilot plant are listen in figure 3.2. Details on the employed conditions are given in subsection 3.3.1.

Effectiveness trials

Simulation of an Industrial WWTP in a Pilot Plant
- Assessment on organics degradation through treatment in EPC reactor for continuous effluent
- COD degradation curves through treatment for continuous effluent
- Complementary technologies evaluation: Electro coagulation, Steam stripping, Electro oxidation, Reverse osmosis, Photo-oxidation (bench scale).

Robustness trials

Simulation of the following scenarios

Integration of segregated streams in equalization
- Condensate phase from the thermo-oxidizer treatment
- High Solvent load aqueous effluent
- Condensed Utilities effluent
- COL (Change of Line) effluent – with the presence of detergent and API

Stress situation treatment with synthetic effluent.
- Glycol leak
- Heptane leak
- DCM leak

API degradation trials

Simulation of an Industrial WWTP in a Pilot Plant
- Specific API degradation through treatment with synthetic effluent.
- Degradation curves of general API through treatment with continuous effluent.

Figure 3.2: Trials tests plan for the EPC Pilot Project.

3.3 Operational Plan

Due to confidentiality protocols, the pilot unit P&I diagram and operation manuals are not public an will not be presented. Bellow is presented a schematics of the equipment available and the treatment possibilities, figure 3.3. All the descriptions in the present chapter provide the generic technical information of the unit and the equipment operated during the lease period of the pilot plant.

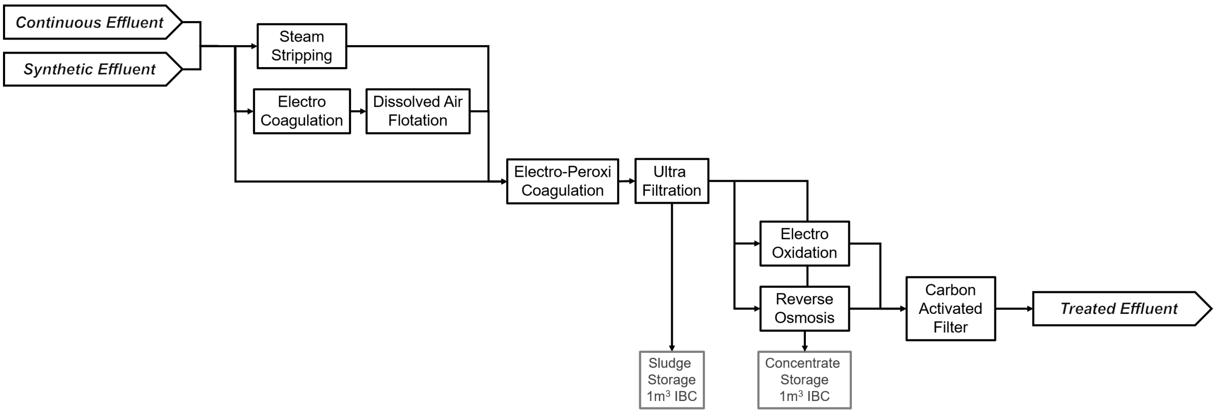


Figure 3.3: EPC Pilot Plant: Wastewater treatment possibilities.

3.3.1 Pilot Plant

The mechanical and electrical connections were made to ensu re a multi-sequence plant able to treat the wastewater of every test trial according to its needs.During the project the pilot plant was secured in two leveled structures placed in a concrete area with conditions to support 18 tons and 12 tons - figure 3.4. The two 40 ft containers were leveled with a distance of 1,5 m between them with the hydraulic connections facing each other in each container. The hydraulic and electrical connections were made by flexible hoses.

The pilot plant inlet feed and outlet discharge connections were made by flexible hoses: the provision of continuous effluent was made with pressure and flow to reach the admission tank at the pilot unit. Inlet feed had two points to the main supply of the pilot plant: 1^{st}) continuous effluent connection from the site's untreated effluent tank with an isolation valve and 2^{nd}) raw connection from an IBC [1] with an isolation valve. The inlet feed was selected accordingly to the test trial plan.Outlet discharge was made to the site's final effluent tank – discharging to the municipal WWTP. The sludge generated in the overall process was collected in an IBC to be treated afterwards - figure 3.5.

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[1] IBC stands for Intermediate Bulk Containers. This plastic $1m^3$ containers were used for liquid temporary storage and temporary auxiliary tanking.

Figure 3.4: Picture of the pilot plant used in the project and stationed at the pharmaceutical site.

Figure 3.5: Picture of the IBC station.

3.3.2 Treatment Setup

Operational control was made by a specialized operator and was thoroughly recorded in the trial test logbooks, the information was collected through visual inspection and in the plant PLC - figure 3.6. With consideration to the test trial program several setups were composed - the purpose of this range of treatment sequences was to guarantee that the final setup to be implemented was the correct and adjusted. The opening and closure of vales was automatic and actuated through the PLC. Equipment parameters were also set in the PLC. The setup of the treatment was determined by the manual opening and closure of isolation valves, determining the desired treatment sequence.Treatment sequences tested are presented in figure 3.7.

Figure 3.6: The pilot plant control interface - PLC.

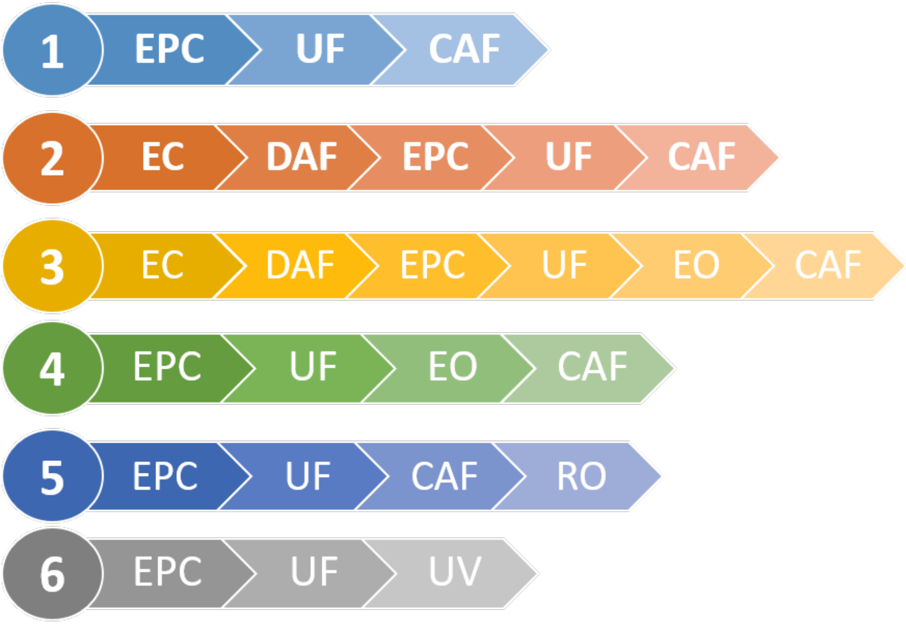


Figure 3.7: Treatment sequence possibilities.

Setup selection relied on the effluent characteristics: turbidity and organics/chlorides load; the selection was made following the steps described on the fluxogram on figure 3.8.

Collection logistics of effluent storage prevented the possibility of including an EC stage in Intermediate Bulk Container (IBC) feed test trials - the Dissolved Air Flotation (DAF) tank capacity was 2 m^3 and the introduction of two separate IBCs difficult the certainty of effluent mixture through the trial and effluent representativeness from the samples. Therefore the visual inspection was not applied on IBC feed test trials. On the continuous feed test trials this issue did not present as the fill of the reception tanks was very quick and the mix on the tanks prevented the uneven effluent mixture through the treatment.

EPC stage is common to every test trial and the distribution of equal tests for every COD:H_2O_2:Fe rations considered is independent of the setup; the collection of samples at the inlet and outlet of every step of treatment enables the separation of data to review the performances of each stage. This method of selecting the treatment setup guaranteed that the wastewater was treated according to its need while still guaranteeing the representativeness of data in each setup.

It's important to state that the data was processed during the project to enable adjusts on the trial planning and still test every possibility available. During some of the Robustness and Refinement trials, a RO set was installed mid project to evaluate the need for a re-concentration of the effluent to elevate the overall process efficiency; some bench trials of Photo-Oxidation with UV light were performed as well to evaluate the validity of an extra Advanced Oxidation (AO) stage with the residual H_2O_2 from the EPC stage.

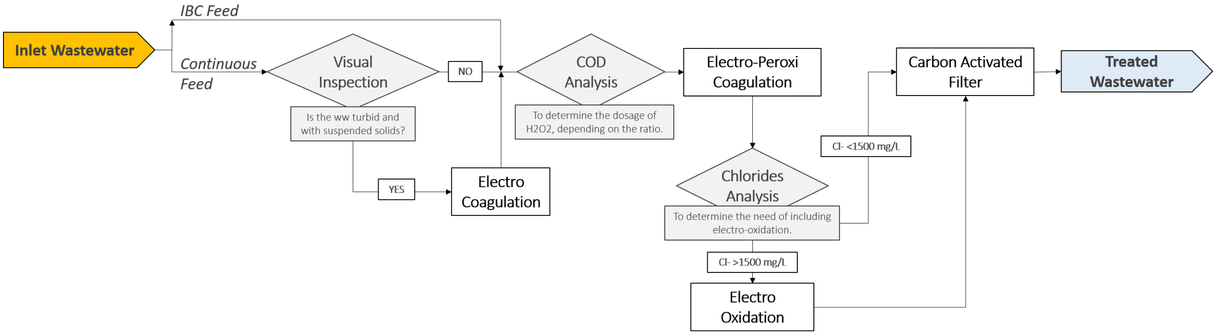


Figure 3.8: Setup Fluxogram.

3.3.3 Equipment

This pilot plant was designed to be multi-stage and multi-purpose; the unit is composed of several types of equipment adapted to treat the critical parameters in wastewater, from halogens to oils and greases the pilot had a specif equipment focused on the removal of each type of pollutant. As the critical issues identified in the pharmaceutical wastewater are metals, solvents and API, not all the available equipment was connected to the hoses circuits. All the used equipment in the test trials is listed and thoroughly described for a better understanding of the operation. Pictures of the equipment placed in the unit are presented as well.

Table 3.1: Electro Coagulation Reactor technical information.

Equipment Type	Reactor
Equipment Name	Electro Coagulation Reactor
Equipment ID	EC
Description	Electrochemical reactor with aluminum plates and passage of electric current promoting electric charge inversion and polar bindings between solid particles. Working in recirculation.
Function	To clarify turbid effluent by solids precipitation.
Chemicals	*Hydrochloric Acid* To clean the reactor in recirculation
Complementary Equipment	*Tank/Pumps* - To assist in recirculation; *Dissolved Air Float* - To promote physical separation of the coagulated particles.

Figure 3.9: Electro Coagulation Reactor picture.

Table 3.2: Dissolved Air Float technical information.

Equipment Type	Separator
Equipment Name	Dissolved Air Float
Equipment ID	DAF
Description	Large long vessel open to air with compressed air flow from bottom to top that promotes the ascension of fine particles to the air/liquid surface – to be scrapped. Clear effluent outlet in the middle of the height.
Function	To separate flocs and solid particles from the effluent by precipitation and ascention.
Chemicals	*Floculant*- To promote separation of particles to deposit at the bottom and liquid/air surface.
Complementary Equipment	None.

Figure 3.10: Dissolved Air Float picture.

Table 3.3: Electro Peroxi Coagulation Reactor technical information.

Equipment Type	Reactor
Equipment Name	Electro Peroxi Coagulation Reactor
Equipment ID	EPC
Description	Electrochemical reactor with iron plates and passage of electric current. Working in recirculation.
Function	To decompose the organic compounds.
Chemicals	*Hydrogen Peroxide* - Added to promote Fenton environment dose dependent of the inlet COD load. *Hydrochloric Acid* - To clean the reactor in recirculation.
Complementary Equipment	*Tank/Pumps* To assist in recirculation. *Ultrafiltration* To promote physical separation of the decomposed compounds.

Figure 3.11: Electro Peroxi Coagulation Reactor picture.

Table 3.4: Ultrafiltration membranes module technical information.

Equipment Type	Separator
Equipment Name	Ultrafiltration membranes module.
Equipment ID	UF
Description	Circular membrane modules that act as selective filter, with pores 10-100 nm. Tangential effluent flow and central outlet of rejection sludge. Working in recirculation to promote high water content sludge.
Function	To separate the decomposed organic compounds.
Chemicals	*Sodium Hypochlorite* - To release organic substances retained in the pores. *Citric acid* - To release inorganic substances retained in the pores.
Complementary Equipment	*Tank/Pumps* To assist in recirculation

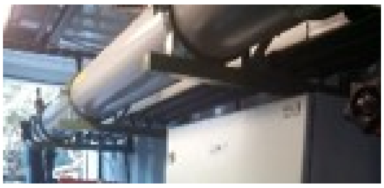


Figure 3.12: Ultrafilration membranes module picture.

Table 3.5: Electro Oxidation reactor technical information.

Equipment Type	Reactor
Equipment Name	Electro Oxidation reactor.
Equipment ID	EO
Description	Electrochemical reactor with titanium plates and passage of electric current, working in recirculation.
Function	To oxidize the halogen compounds.
Chemicals	*Hydrochloric Acid*- To clean the reactor in recirculation.
Complementary Equipment	*Tank/Pumps* To assist in recirculation.

Figure 3.13: Electro Oxidation reactor picture.

Table 3.6: Reverse Osmosis membranes module technical information.

Equipment Type	Separator
Equipment Name	Reverse Osmosis membranes module.
Equipment ID	RO
Description	Circular membrane modules that act as selective filter, with 0,001μm pores. Tangential effluent flow and central outlet of rejection sludge. Working in recirculation to promote medium water content sludge.
Function	To separate salts and ions.
Chemicals	*Sodium Hypochlorite* To release organic substances retained in the pores.
Complementary Equipment	*Tank/Pumps* To assist in recirculation.

Figure 3.14: Reverse Osmosis module picture.

Table 3.7: Carbon Activated Filter technical information.

Equipment Type	Filter
Equipment Name	Carbon Activated Filter.
Equipment ID	CAF
Description	Vertical bed of packed activated charcoal multi size particles with porosity and polarity adequate to retain pollutants – organic and inorganic.
Function	To retain and neutralize the halogen compounds and remain organic compounds.
Chemicals	*Sodium Hypochlorite* To release organic substances retained in the pores and flow channels.
Complementary Equipment	None

Figure 3.15: Carbon Activated Filter picture.

3.4 Sampling Plan

Figure 3.16 presents a scheme of the EPC Pilot Plant, indicating the locations of the collected grab samples and respective identifications.

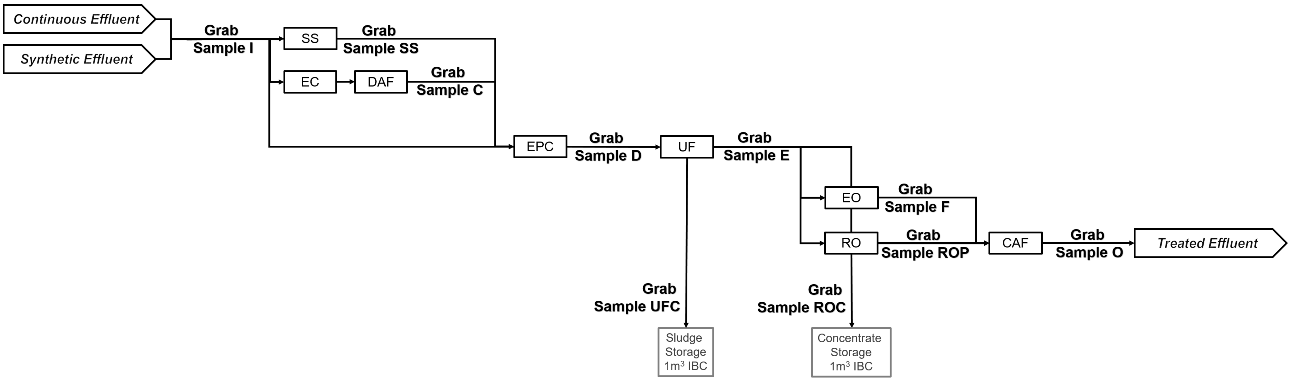


Figure 3.16: EPC pilot plant rig sequence and the options of grab sample possible depending on the stage of the treatment.

3.5 Analytical Plan

3.5.1 General aspects

The analytical plan was designed to ensure that a maximum of data was collected and the operation of the pilot plant was the most efficient possible in the limited available time. The operation details were given in section 3.3.

Several analyses were done in external laboratories to detail the quality of the untreated (inlet samples) and treated (outlet samples) wastewater from selected test trials. The parameters listings and analytical methods are presented in subsection 3.5.4 and subsection 3.5.5.

Daily analyses were done in the internal laboratory, taking into account the startup timing for each treatment test at the pilot plant and the residence time in each treatment stage. The daily analysis planning was critical to avoid interruptions and delays between stages and test trials. Online TOC measurements were collected to monitor the site's pre-treatment inlet stream and establish a baseline for future operation. Selected grab samples were analyzed for TOC as well.

A scheme of the analytical plan is presented in figure 3.17 identifying the purpose of each analysis , namely compliance validation, effluent toxicity verification and API degradation evaluation.

Continuous Monitoring - Compliance

Effluent Location: Treatment Inlet (Grab Sample I)
Sampling: Online
Parameter: TOC

Trial Test Internal Analysis - Compliance

Effluent Location: Treatment Inlet (Grab Sample I), Equipment Outlet (Grab Samples SS, C, D, E, F, ROP, ROC, UFC) and Treatment Outlet (Grab Sample O)
Sampling: Grab Sample
Parameter: TOC, CQO, Chlorides, pH, Condutivity, Hydrogen Peroxide
Frequency: Every sample collected from the Pilot Plant

Trial Test External Analysis - Compliance

Effluent Location: Treatment inlet (Grab Sample I) and outlet (Grab Sample O)
Sampling: Grab Sample
Parameter: External Analysis parameter listing in Section 3.5.4.
Frequency: a total of 8 test trials during effectiveness trials

Trial Test External Analysis – API Trials

Effluent Location: Treatment inlet (Grab Sample I), EPC outlet (Grab Sample D) and treatment outlet (Grab Sample O)
Sampling: Grab Sample
Parameter: API detection and quantification.
Frequency: a total of 29 samples from 9 test trials.

Trial Test Internal Analysis – WWTP Toxicity

Effluent Location: Treatment Inlet (Grab Sample I) and outlet (Grab Sample O)
Sampling: Grab Sample
Parameter: DOUR
Frequency: Every sample collected from the Pilot Plant

Figure 3.17: Schematics of the analytical planning.

3.5.2 Internal Analysis - Environmental License Compliance

3.5.2.A Rationals and sequencing of analyses

As some data reports of the analysis performed externally were delivered several days after the respective test trial, there was the need to gather information at a faster pace to continuously evaluate the efficiency of each test trial and adjust operations throughout the project duration.

Chemical Oxygen Demand measures the oxygen required to oxidize soluble and particulate organic matter in wastewater, thus a high COD load indirects the presence of an high concentration of organic matter. COD measurement is a quick analytical method and standard parameter in environmental studies, so COD analysis were done multiple times a day.

TOC is another analytical method used to measure concentration of organic matter in wastewater; some of the COD tests were required to determine the reagent dosage in the EPC reactor. In real operation, this measure can be replaced by a TOC analysis as the chemical oxidation in TOC analyzers is more similar to the oxidation to occur in the EPC reactor. Therefore a TOC analyzer was installed to monitor the equalized effluent at the inlet of the pre-treatment stage, namely the steam stripping inlet stream that was the continuous effluent feed to the pilot plant. The analyzer had the possibility to perform print measurements on grab samples, and in some of these samples TOC was also measured.

Other operational parameters were monitored along every test trial, either using probes (pH and conductivity probes present in the pilot plant unit and connected to its control system) or quantitative strips (chlorides and hydrogen peroxide strips were used to evaluate the interference in COD and TOC analytical tests).

The analytical protocol applied to every sample processed in the internal lab schematics are presented in figure 3.18.

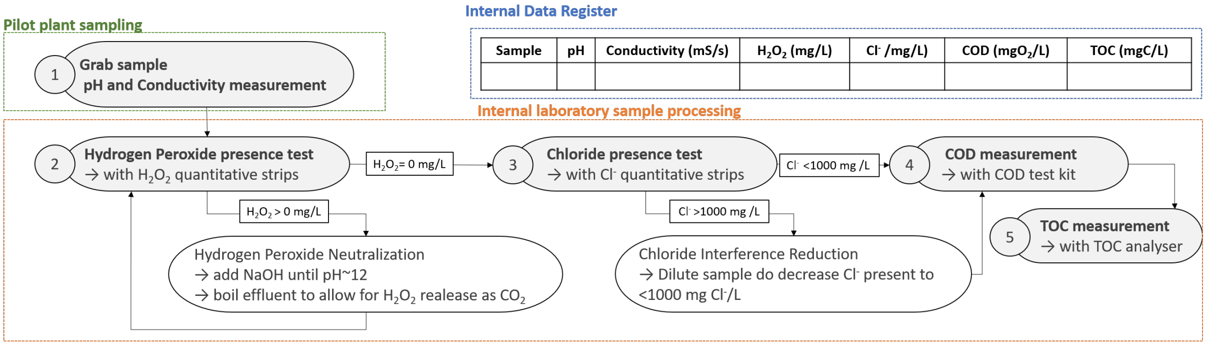


Figure 3.18: Processing protocol applied to the samples for internal analysis.

3.5.2.B Parameter Listing and Analytical Methods

Table 3.8 lists the parameter and the method references for the internal analyses.

Table 3.8: 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)

For Chemical Oxygen Demand analysis, the water sample is oxidized with a hot sulfuric solution of potassium dichromate, with silver sulfate as the catalyst. Chloride is masked with mercury sulfate, nevertheless its important to guarantee that the chloride concentration is bellow the established interference limits . Reaction temperature is maintained through the reaction time by a thermo reactor - the Spectroquant® thermoreactor TR 420 from Merck. The concentration of green Cr^{3+} ions oxidized is then determined photometrically, with the use of a spectrophotometer - the *Spectroquant® NOVA 30 A* from *Merck*.

The TOC analyzer installed during this project used a measurement technique based on supercritical water oxidation. Water is brought to a supercritical state by heating the sample inside a sealed reactor module to 375 ^0C and raising the pressure to 22$\times 10^3 kPa$. This allows the analyzer to achieve efficient oxidation regardless of the type of organic compounds and impurities present in the water. This process also avoids oxidation byproducts and sample contamination between each analytical run, eliminating frequent maintenance and of replacement expensive parts. The used equipment was *Sievers InnovOx On-Line Total Organic Carbon (TOC) Analyzer by GE Analytical Instruments*. The TOC measurement setup was applied to guarantee the minimum error and measured the Inorganic Carbon (IC) and Total Carbon (TC) contents in the sample to determine the TOC=TC-IC.

The chloride test is a rapid exploratory test for chloride compounds presence detection and quantification. Chloride ions react with silver ions, decolorizing red-brown silver chromate. The chloride concentration is measured semiquantitatively by visual comparison of the reaction zones of the test strip with the color rows of a color scale, figure 3.9. The test kit consists of a plastic strip with attached sealed test paper, the test paper is immersed in the sample and the color is compared with fields of equal size on the color scale provided. The used strips are indicative for the range of 500 - 3000 mg Cl^-/L.

The presence and approximate concentration of H_2O_2 in a sample can be determined with a semi-quantitative method, namely a colorimetry method. The enzyme peroxidase transfers oxygen from peroxide to an organic redox indicator, producing a blue oxidation product. The peroxide concentration is measured semiquantitatively by visual comparison of the reaction zone of the test strip with the fields of a color scale. The used strips are indicative for the range of 1 - 100 mgH_2O_2/L. The schematics of the test protocol is described in figure 3.10.

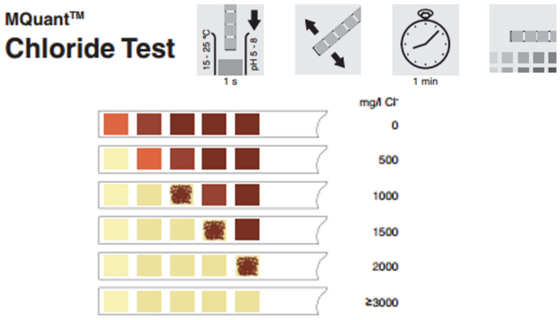


Table 3.9: Cl^- colorimetric method tests protocol schematics.

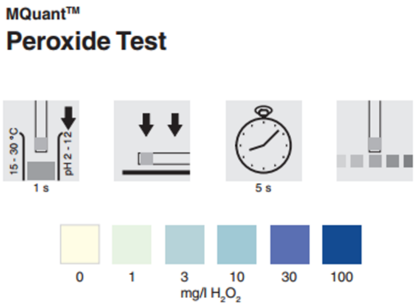


Table 3.10: H_2O_2 colorimetric method test protocol schematics.

3.5.3 Internal Analysis - WWTP Toxicity Assessment

The measurement of Dissolved Oxygen Uptake Rate (DOUR) is often used to monitor the health of an aerobic biological system. A Dissolved Oxygen (DO) meter reads oxygen concentration changer in an initially saturated sample over a set period of time. The changes in dissolved oxygen are primarily due to the use of oxygen by microbes in the sample. The measurement of the rate at which oxygen is used (in mg O_2/(L.hour)), is a useful tool to evaluate the biodegradability of the wastewater before and after treatment and to assess the treatment ability to decrease the wastewater's toxicity to wards microbial populations in a biological reactor. The toxicity increase/decrease assessment is made by comparison of the DOUR measured in a biomass suspension in nutrient medium before and after addition of the sample. Biomass collected from the municipal WWTP reactor was used after proper aeration. The method reference is given in 3.11.

Table 3.11: Internal analysis for toxicity and respective analytical method

Parameter	**Analysis Method**
Dissolved Oxygen Uptake Rate	HachLange® HQ40d Portable Multi-Parameter Meter with DO (0.01 - 20 mgO_2/L)

3.5.4 External Analysis - Environmental License Compliance

The parameters analysed by external laboratories on wastewater and sludge sampled from the EPC Pilot trials are listed in table 3.12 and table 3.13.

Table 3.12: External Analysis Parameter Listing - Effluents.

Effluent Analysis Parameters and
pH
Condutivity
COD – Chemical Oxygen Demand
BOD_5 – Biological Oxygen Demand at 5 days
BOD_{20} – Biological Oxygen Demand at 20 days
AOX - Adsorvable Organic Halides
TSS – Total Suspended Solids
VSS – Volatile Suspended Solids
TKN – Total Kjeldahl Nitrogen
NH_3 – Ammonia
NO_2 – Nitrites
NO_3 – Nitrates
Cl – Chlorides
S – Sulfides
Detergents
FOG – Oils and Grease
Total Hydrocarbon
Phenols
Total Heavy Metals
. As- Total Arsenium
. Cd – Total Cadmium
. CN – Cyanides
. Cr – Total Cromium
. Cu – Total Copper
. Fe – Total Iron
. Hg – Total Mercury
. Pb – Total Lead
. Zn – Total Zinc
VOCs - Volatile Organic Solvents
Solvents
. Acetone
. Dimethylformamide
. Ethanol
. Ethyl Acetate
. Hexane
. Isopropyl Alchohol
. Methanol
. Methyl ethyl ketone
. Monoethylene Glycol
. Tetrahydrofuran
Ecotoxicity test
. *Daphnia Magna*

Table 3.13: External Analysis Parameter Listing - Sludge samples.

Sludge Analysis Parameters
W% - Humidity
O.M. - Organic Matter
Total Heavy Metals
. As- Total Arsenium
. Cd – Total Cadmium
. CN – Cyanides
. Cr – Total Cromium
. Cu – Total Copper
. Fe – Total Iron
. Hg – Total Mercury
. Pb – Total Lead
. Zn – Total Zinc
Solvents
. Acetone
. Dimethylformamide
. Ethanol
. Ethyl Acetate
. Hexane
. Isopropyl Alchohol
. Methanol
. Methyl ethyl ketone
. Monoethylene Glycol
. Tetrahydrofuran

Table 3.14: 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
Methyl ethyl ketone	HS-GC-MS
Monoethylene Glycol	Housemethod PI- MA-M 3-77
Tetrahydrofuran	HS-GC-MS
Ecotoxicity test	
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.

3.5.5 External Analysis - API Degradation Studies

The list of API analyzed in external laboratories in given in table 3.15, their chemical structures are shown in figures 3.19, 3.20, 3.21, 3.22 and 3.23.

Table 3.15: 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

MIN Minocycline Hydrochloride

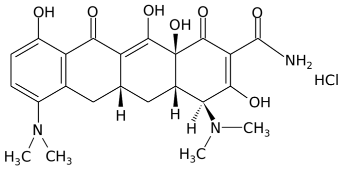


Figure 3.19: Chemical structure of minocycline hydrochloride.

FLU Fluticasone Propionate

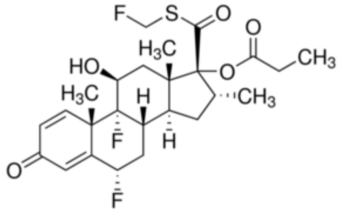


Figure 3.20: Chemical structure of fluticasone proprionate.

BPH Betamethasone Phosphate

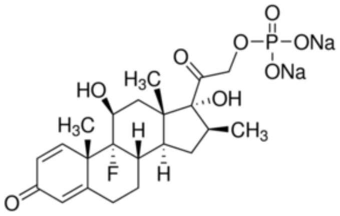


Figure 3.21: Chemical structure of betamethasone phosphate.

BAC Betamethasone Acetate

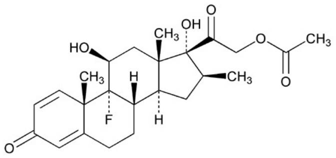


Figure 3.22: Chemical structure of betamethasone acetate.

IOH Iohexol

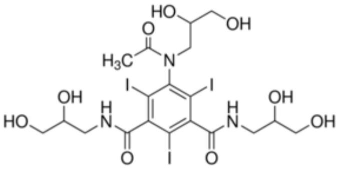


Figure 3.23: Chemical structure of iohexol.

4

Results

4.1 Pharmaceutical wastewater characterization

4.1.1 Main Environmental Parameters

4.1.1.A Organic load

To better understand and establish the treatment objectives in terms of critical compounds present in pharmaceutical wastewater it was necessary to characterize the WW with typical ranges and removal goals for the compounds typically present at the site. All the values presented below were computed from data regarding the inlet of continuous trials and the history of the site's WW analyses.

The less specific parameters presented in this characterization are the oxidation related parameters: Chemical Oxygen Demand (COD), 5-day Biological Oxygen Demand (BOD5), and Total Organic Carbon (TOC). Oxidation related parameters will reflect the amount of oxidizable substances present in the WW and from that it is possible to infer values for the organic load and the reagent dosage in an EPC reaction. A TOC baseline was constructed from the data collected with an on-line TOC analyzer monitoring the WW before the existent pre-treatment at the site, namely, the steam stripping column. The data was collected within the two months of the project with gaps regarding technical issues and interruptions to collect and analyze grab samples. The graph with the time distribution of TOC values is presented in Figure 4.1 and the statistic of the referred parameters are presented in Table 4.1.

Previous studies on general WW compositions point to an empirical value of the COD:TOC ratio close to 3, however this correlation has not been set for pharmaceutical WW and may be established for each specific site, with access to a database to further validate it. In this project, some of the inlet and intermediate stage samples were tested for both COD and TOC to evaluate the validity of this ratio. Even though the data were not representative enough to establish a trustworthy ratio, the values' dispersion indicates that an online TOC analyser can be a good and faster option for the diagnoses of organic load at the entrance of the treatment. This is needed to make a quick and reliable determination of the dosage of Fenton's reagents, Fe and H_2O_2.

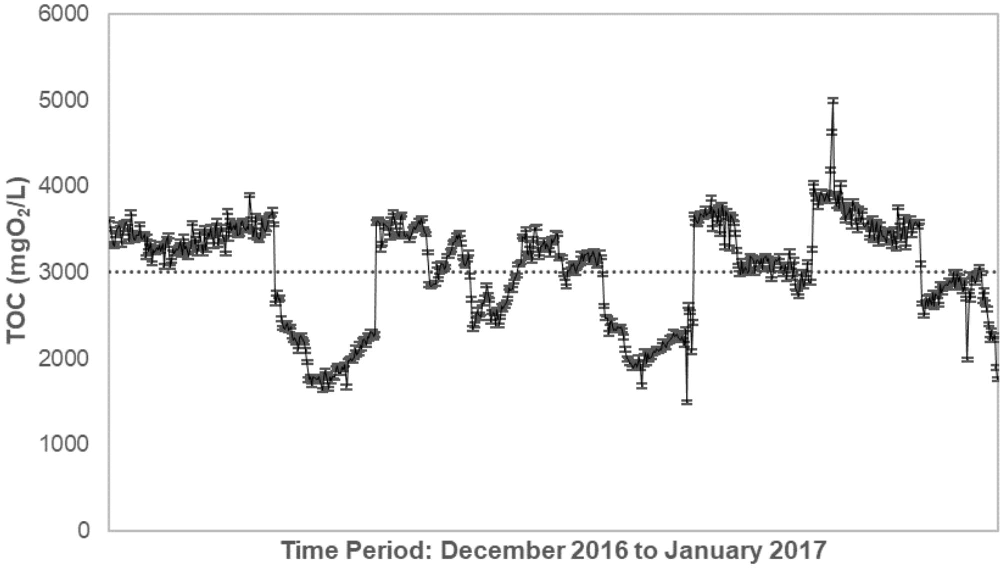
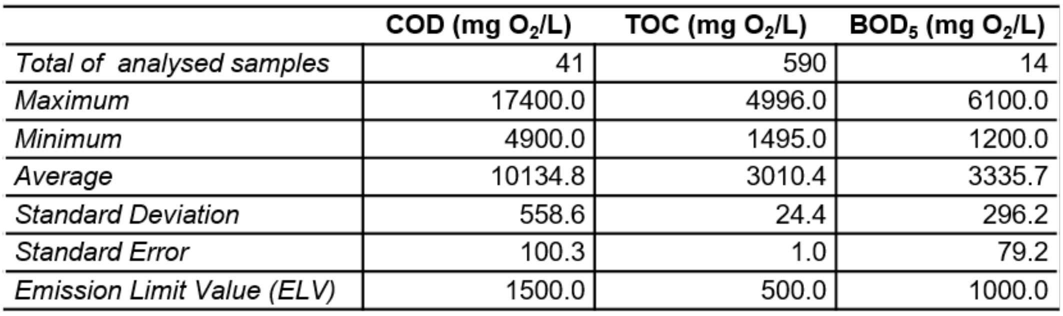


Figure 4.1: TOC baseline for the pharmaceutical wastewater at the inlet of the treatment .

Table 4.1: Basic statistics for the COD and BOD5 values at the inlet of the WW treatment.



	COD (mg O_2/L)	TOC (mg O_2/L)	BOD$_5$ (mg O_2/L)
Total of analysed samples	41	590	14
Maximum	17400.0	4996.0	6100.0
Minimum	4900.0	1495.0	1200.0
Average	10134.8	3010.4	3335.7
Standard Deviation	558.6	24.4	296.2
Standard Error	100.3	1.0	79.2
Emission Limit Value (ELV)	1500.0	500.0	1000.0

From Table 4.1, it is possible to verify that the COD:TOC ratio values are around 3 in the maximum, minimum and average levels. The expected average for COD at the inlet of the treatment is 10100 mgO_2/L with high peaks up to 17400 mgO_2/L and low extremes of 4900 mgO_2/L. In terms of COD, the site's history mirrors the production expansion occurring during the last years (Table 4.2 and Figure 4.2). Therefore, for economic analysis and future treatment design proposal inclided in this report, the WW average load will be considered as the double of the present value, to account for the site's expansion.

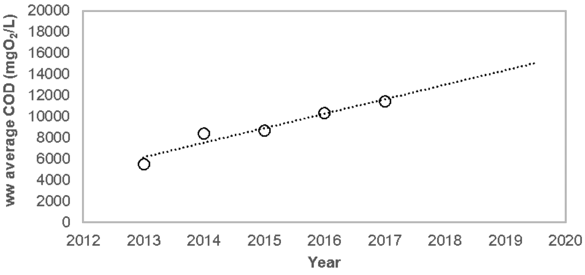


Figure 4.2: Site's WW average COD through the years; period from 2013 to 2017 (provisional value). Linear projection to 2018 and 2019.

Table 4.2: Site's WW average COD through the years; period from 2013 to 2017.

Year	***2013***	***2014***	***2015***	***2016***	***2017*** *(provisional)*	***2019*** *(projection)*
Inlet Average (mg O_2/L)	5548	8469	8688	10355	11454	16000

4.1.1.B Solvents

One of the contributors for the chemical oxygen demand are solvents, and a small amount of solvent in WW can result in a big increment of COD.

In pharmaceutical industries, solvents are present in many stages of the API process production, from reaction to product refinement. From the solvent profiles determined on the inlet streams at the EPC treatment, it is possible to understand the nature of the solvents that may be present in the WW at the entrance of the treatment. On average, the WW at the inlet of the EPC stage carried approximately 0,5% (vol/vol) of solvent, distributed as represented in Figure 4.3. In Table 4.4 basic statistics on the analyses for the site's most used solvents are presented.

Regarding organic solvents, when assessing the adaptability of the WW to a biological downstream treatment it is convenient to check their classification in the WGK. WGK is a water hazard classification system with classes 1 to 3, from low to severe hazard to water. The value is often included in Safety Data Sheet (SDS), each chemical being classified according to its impact on water and its ecosystems.

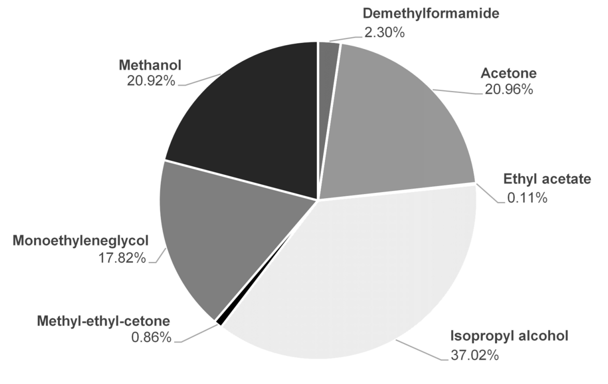


Figure 4.3: Distribution of solvent concentrations in the WW at the treatment inlet

Table 4.3: Solvents WGK classification.

Component	WGK Class
Acetone	1
Dichloromethane	2
Dimethylformamide	1
Ethyl Acetate	1
Ethylene glycol	1
Isopropyl alcohol	1
Methanol	1
Methyl Ethyl Ketone	1
Ethanol	1

Table 4.4: Basic statistics for solvent concentration values at the inlet of the WW treatment.

Solvent Concentration (mg/L)	Dimethyl formamide	Acetone	Ethyl Acetate	Isopropyl Alcohol	Methyl-Ethyl-Cetone	Monoethylene Glycol	Methanol
Total of analysed samples	15	15	15	15	15	15	15
Maximum	250.00	1500.00	34.00	2000.00	220.00	3400.00	2200.00
Minimum	25.00	98.00	0.22	150.00	0.50	2.10	130.00
Average	93.64	714.53	4.41	1254.00	29.90	852.14	714.00
Standard Deviation	18.62	112.75	2.25	138.17	16.55	205.56	148.47
Standard Error	4.98	29.71	0.60	35.68	4.41	53.08	38.33

WGK computes the substance's hazard data for both human health and the environment. To determine if the need for a solvent's degradation in the pre-treatment is critical, a compilation of their WGK was done (Table 4.3)[1]. Considering that all solvents are hazardous to the water environment, even if the hazard level is low, the need for the degradation of the present solvents was identified.

4.1.1.C Chlorides, AOX and VOC

Chlorides are essential for water ecosystems, however in high levels chloride can have negative effects on such ecosystems. Chloride may impact freshwater organisms and plants by altering reproduction rates, increasing species mortality, and changing the characteristics of the entire local ecosystem.

The value of Adsorbable Organic Halogen (AOX) measures the concentration of chlorine, iodine and bromine bound to carbon. These organo-halide compounds may be toxic or not. Dioxins, for instance,

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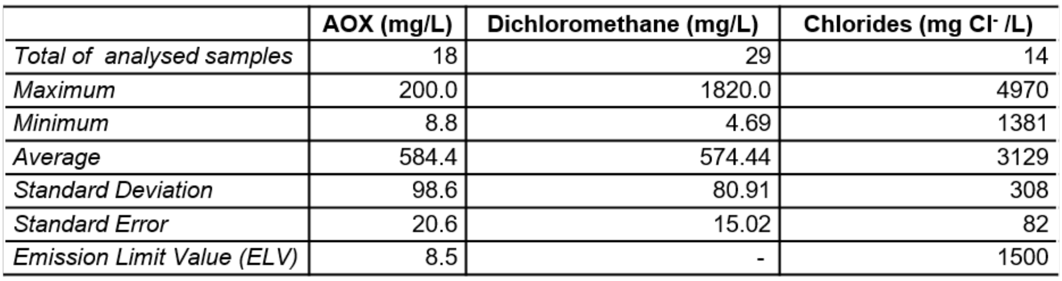
[1] Values indicated in the respective MSDS.

and other chlorinated aromatics can be very toxic. Some AOXs are further reported to be mutagenic or carcinogenic. Most AOXs are persistent organic pollutants and are of concern due to their resistance to decomposition in the environment and consequent availability for bio-accumulation.

The release of volatile organic carbon (VOC) compounds into the air during WW treatment is an environmental concern due to the adverse health effects that may result. Most studies focus of the most hazardous VOCs, namely, aromatic (benzene, toluene, and xylenes) and chlorinated (dichloromethane, chloroform, carbon tetrachloride, trichloroethylene, and tetrachloroethylene). The site's solvent portfolio includes some VOCs, and VOC concentration measurements lead to a concern with the dichloromethane content in WW, included in Table 4.5. However, the measurements also reflected that rest of the profiled VOCs are below quantification limits and therefore do not represent a concern for this project.

Table 4.5: Basic statistics for the levels of AOX, dichloromethane (the site's predominant VOC) and chlorides at the inlet of the WW treatment.



	AOX (mg/L)	**Dichloromethane (mg/L)**	**Chlorides (mg Cl$^-$ /L)**
Total of analysed samples	18	29	14
Maximum	200.0	1820.0	4970
Minimum	8.8	4.69	1381
Average	584.4	574.44	3129
Standard Deviation	98.6	80.91	308
Standard Error	20.6	15.02	82
Emission Limit Value (ELV)	8.5	-	1500

4.1.1.D Heavy Metals

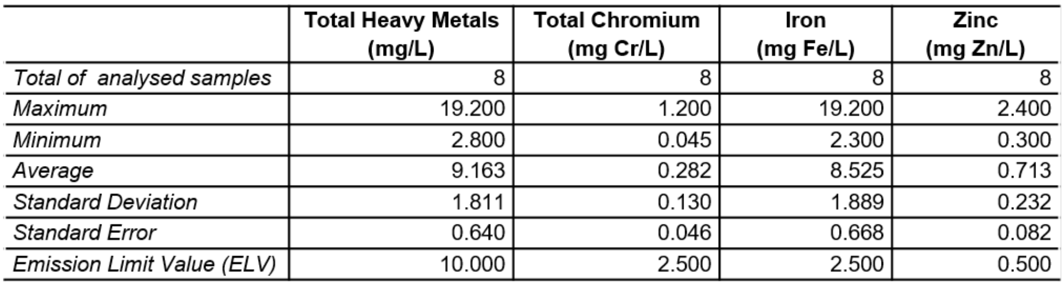
A general concern common to many industrial WW types is the load of heavy metals. Due to their high toxicity, some heavy metals have inhibitory effects on biological treatment processes and can impact greatly on the environment and health. On average, the total heavy metals load present in the site's WW is below regulatory limits, but considering the discriminated metal levels for this industrial plant, iron and zinc were identified as problematic for being well above their emission limits (Table 4.6).

This does not pose a problem for the WW treatment, as dissolved iron will serve as Fenton's reagent and be further precipitated alongside with the ferric ions provided by the iron plates in the EPC reactor. However a careful analysis of the iron content of the EPC sludge is advised in a later stage of this project.

4.1.1.E Nitrogen Compounds

The amount of nitrogen present in WW must be controlled due to impacts on aquatic life in the receiving waters and to avoid eutrophication. Based on predicted no-effect concentrations for nitrogen compounds

Table 4.6: Basic statistics for the levels of heavy metals at the inlet of the WW treatment.

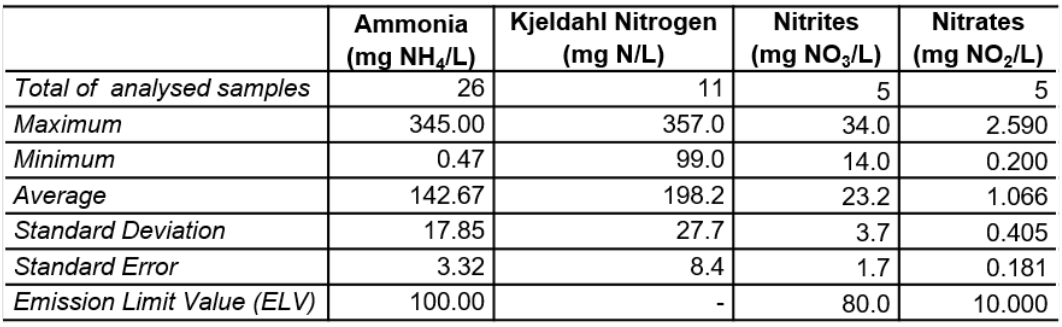


	Total Heavy Metals (mg/L)	Total Chromium (mg Cr/L)	Iron (mg Fe/L)	Zinc (mg Zn/L)
Total of analysed samples	8	8	8	8
Maximum	19.200	1.200	19.200	2.400
Minimum	2.800	0.045	2.300	0.300
Average	9.163	0.282	8.525	0.713
Standard Deviation	1.811	0.130	1.889	0.232
Standard Error	0.640	0.046	0.668	0.082
Emission Limit Value (ELV)	10.000	2.500	2.500	0.500

in natural waters, emission limit values are established taking into account the performance of conventional WWTPs regarding their elimination.

In Table 4.7, statistics for nitrogen compound levels in the industrial WW are presented. As the average values for ammonia are above the regulatory limits, it is important to evaluate the need to add an upstream or downstream stage to the EPC process, in order to reduce this content.

Table 4.7: Basic statistics for the levels of nitrogen compounds at the inlet of the WW treatment.



	Ammonia (mg NH_4/L)	Kjeldahl Nitrogen (mg N/L)	Nitrites (mg NO_3/L)	Nitrates (mg NO_2/L)
Total of analysed samples	26	11	5	5
Maximum	345.00	357.0	34.0	2.590
Minimum	0.47	99.0	14.0	0.200
Average	142.67	198.2	23.2	1.066
Standard Deviation	17.85	27.7	3.7	0.405
Standard Error	3.32	8.4	1.7	0.181
Emission Limit Value (ELV)	100.00	-	80.0	10.000

4.1.1.F Detergents, Solids and Fats, Oils and Greases

Lastly, the presence of surfactants and fatty organic material in the WW can have a strong impact any treatment due to the high resistance of these pollutants to degradation. Suspended solids are also monitored together with these parameters, due to their tendency to settle out and to cause clogging problems. A WWTP is designed to remove these parameters through mostly physical separation stages, and their performance limits are established depending on the capacity of the downstream treatment units. As can be seen from the values in Table 4.8, none of these parameters are identified as critical and thus they will not be considered when assessing the EPC reactor performance and adaptability to the site's needs.

Table 4.8: Basic statistics for the levels of detergents, fats, oils and greases (FOG), total suspended solids (TSS) and volatile suspended solids (VSS) at the inlet of the WW treatment.

	Detergents (mg/L)	**FOG (mg/L)**	**TSS (mg/L)**	**VSS (mg/L)**
Total of analysed samples	5	5	12	5
Maximum	3.070	128.0	871	138
Minimum	0.456	28.1	76	42
Average	1.181	53.7	234	79
Standard Deviation	0.430	16.9	69	14
Standard Error	0.192	7.6	20	6
Emission Limit Value (ELV)	60.000	128.0	1000	-

4.1.2 Wastewater Characterization and Treatment Acceptance Criteria

The average WW levels and regulatory limits for the critical environmental parameters identified in subsection 4.1.1. are summarized in Table 4.9 , together with the established acceptance criteria for the performance of the EPC treatment technology when applied to this site's wastewater.

Table 4.9: 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)	574.44	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

4.2.1 Visual Inspection

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. Turbidity can also be identified through visual inspection and this is an easy method for assessing the need for a physical separation stage to remove suspended solids.

In this project, visual inspection was part of the initial analysis routine applied to the wastewater collected at the admission tank to the EPC. This wastewater was equalized and sampled to test for pH, COD and visual assessment of turbidity. Turbidity inspection was done to validate the need of including an Electro-Coagulation stage in the treatment setup. This stage will be further reviewed in subsubsection 4.2.3.B.

In the following figures some representative pictures of grab samples taken in different treatment setups (trials) are shown. In each, the grab point identification is given alongside the measured organic load (Figure 4.4, Figure 4.5, Figure 4.6, Figure 4.7, Figure 4.8 and Figure 4.9). Comments are given beside each picture.

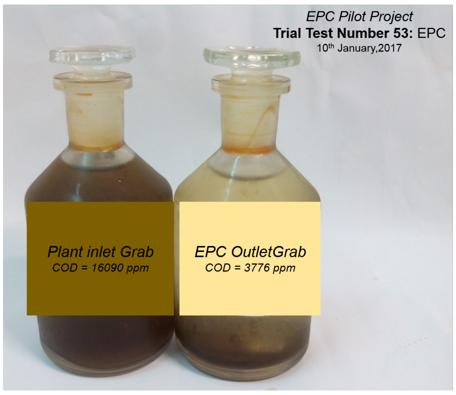


Figure 4.4: Pictures of the inlet and EPC outlet (no ultrafiltration) grab samples for trial test number 53, carried out on 10^{th} January 2017 at the EPC Pilot Plant.

Trial 53: The measured 76% reduction of COD, meaning the degradation of organic compounds, is visually noted as a decrease in coloration. In this trial the EPC reaction seems to have been completed due to the absence of an orange coloration typical of ferrous ions in solution. Some precipitated oxides (darker) are also identifiable.

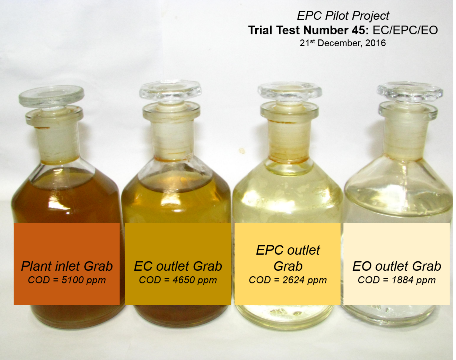


Figure 4.5: Pictures of the inlet, EC outlet, EPC outlet (after ultrafiltration) and EO outlet grab samples for trial test number 45 carried out on 21st December 2017 at the EPC Pilot Plant.

Trial 45: An overall 63% reduction of COD is visually noted as a gradual decrease in coloration. The Electro Coagulation (EC) stage did not result an accentuated COD reduction, but did reduce the initial coloration. The Electro Oxidation (EO) stage converted the halogenated and nitrogenous compounds (see subsubsection 4.2.4.D) refining the overall COD removal and visually further reducing the coloration of the already clear water.

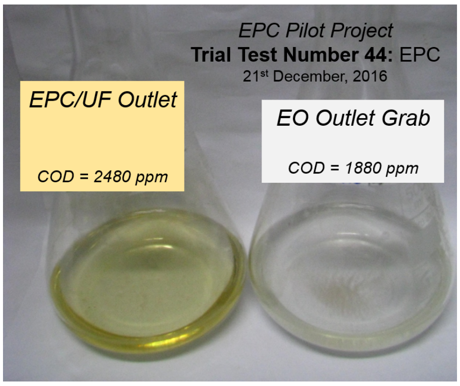


Figure 4.6: Pictures of the EPC outlet (after ultrafiltration) and EO outlet grab samples for trial test number 44 carried out on 21st December 2016 at the EPC Pilot Plant.

Trial 44: A visual comparison between the wastewater before and after the Electro Oxidation (EO) step allows the verification that although the operation is not specific for organic load degradation, the EO reaction eliminates contaminants. Visually, it corresponds to a change from a yellow coloring to virtual colorlessness.

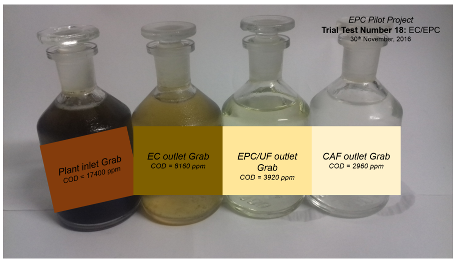


Figure 4.7: Pictures of the inlet, EC outlet, EPC outlet (after ultrafiltration) and CAF outlet grab samples for trial test number 18 on 30th November 2016 carried out at the EPC Pilot Plant.

Trial 18: From the visual inspection of the inlet and EC outlet samples it is possible to observe that in some of the collected samples, Electro Coagulation (EC) was able to remove contaminants through physical separation. In trial 18, from an overall 83% removal of organic compounds, EC removed 64%.

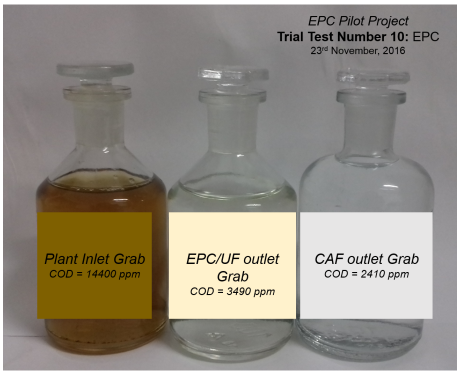


Figure 4.8: Pictures of the inlet, EPC outlet (after ultrafiltration) and CAF outlet grab samples for trial test number 10 carried out on 23rd November 2016 at the EPC Pilot Plant.

Trial 10: The introduction of an Activated Carbon Filter (CAF) at the end of the treatment line was a safety measure to guarantee the neutralization of residual hydrogen peroxide. This stage was also able to retain undegraded dissolved contaminants, visually turning a slightly colored water into colorless.

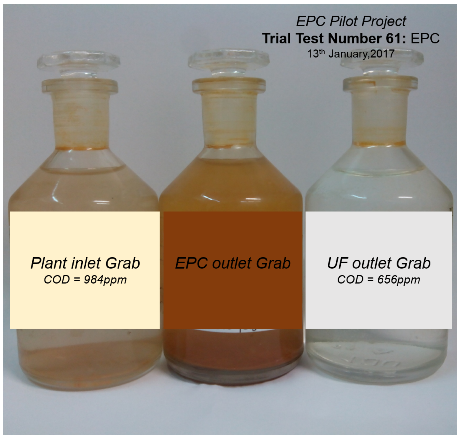


Figure 4.9: Pictures of the inlet, EPC outlet (no ultrafiltration) and UF outlet grab samples for trial test number 61 carried out on 13th January 2017 at the EPC Pilot Plant.

Trial 61: Ultrafiltration (UF), applied after the EPC treatment, is a separation stage designed to retain the precipitated oxides formed during the reaction as well as ferric ions that did not react. In trial 61, the inlet organic load was low and although some organics degradation occurred, at the outlet of the EPC stage the reagents were still present as can be seen from visual inspection of the sample's color and turbidity. After UF the water is clear and colorless, indicating that the UF membranes retained the ferric ions.

4.2.2 EPC Reactor Performance on Organics Degradation

In environmental studies, wastewater treatment performance is assessed in two phases, namely, by a general overview based on analyses to the organic content indicator (COD), and subsequently through a more detailed examination of other critical parameters.

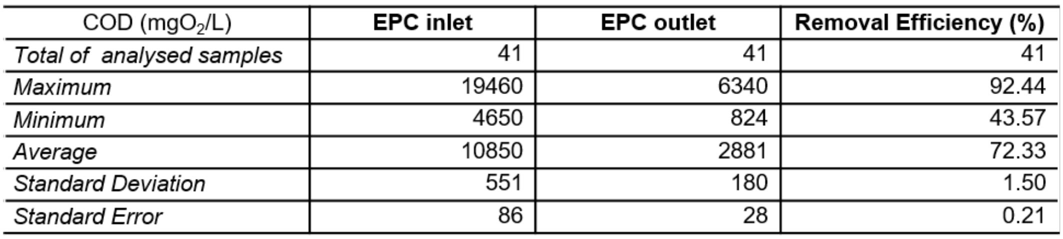
Although the overall COD load can be contributed to by several types of pollutants and that these pollutants have high variability in pharmaceutical wastewater, the primary COD analysis is essential when reviewing the feasibility of the EPC technology. The EPC rationale is to achieve the non-selective degradation of organic compounds through oxidation. Its performance will thus firstly be reviewed on the basis of the overall wastewater load and secondly on its robustness regarding the degradation of other critical parameters.

4.2.2.A Reactor Efficiency Range

This section of treatment results includes data from trials using the industrial wastewater continuously gathered at the tank feeding the steam stripping column. 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. Regardless of the operational conditions applied in the treatment runs (i.e., reagent ratios), the COD profile for the inlet stream seems to be very roughly mirrored in the COD removal efficiency. In such primary analysis, oxidation appears to be more effective on more contaminated wastewater. The inlet COD range is thus attenuated at the EPC, namely, although the outlet stream COD profile reflects the inlet peaks, its range is narrower than the that of the inlet (Figure 4.10 and Table 4.10).

Considering only the EPC, this technology removed on average 72.33 % of the organic load present at the entrance of the treatment. 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 (see subsubsection 4.2.2.B.).

Table 4.10: EPC reactor performance: basic statistics on COD removal efficiency data from the trials with continuously collected pharmaceutical wastewater.



COD (mgO$_2$/L)	**EPC inlet**	**EPC outlet**	**Removal Efficiency (%)**
Total of analysed samples	41	41	41
Maximum	19460	6340	92.44
Minimum	4650	824	43.57
Average	10850	2881	72.33
Standard Deviation	551	180	1.50
Standard Error	86	28	0.21

From Figure 4.11, it is possible to further argue that there is a range of inlet COD values resulting

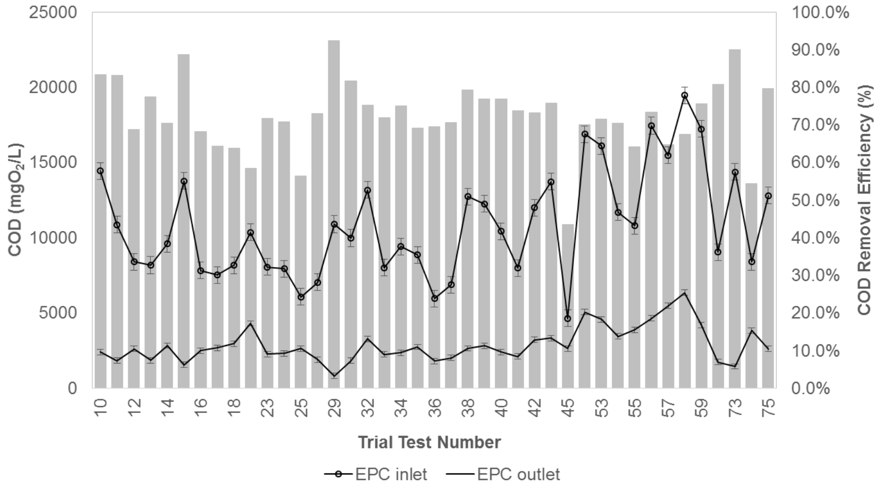


Figure 4.10: COD values for the continuously collected pharmaceutical wastewater at the inlet and outlet of the EPC with correspondent COD removal efficiency levels (grey bars).

in higher degradation efficiencies, given that the operational condition ranges were evenly distributed along the whole range of inlet COD. It can be noted that 75% of the trials had a range of inlet COD between 7000 and 16000 mgO_2/L and gave an average COD removal of 75.0%. On the lower 12.5% range of the inlet COD distribution, between 0 and 7000 mgO_2/L, the COD removal was on average 62.6% while on the upper 12.5% range, between 16000 and 20000 mgO_2/L, the average removal was 71.6%.

A possible explanation for this could be that in the lowest and highest contamination environments, the reagents are more involved in secondary reactions due to unavailability or excess of organics. This explanation is in line with the question of the H_2O_2 dosage increasing with the COD load. Specifically, in low reagent dosage ranges, not enough hydroxyl radicals are formed and the organics concentration is also not high enough to ensure and efficient reaction between radicals and organics. For higher COD levels, as the reagent is also in higher concentration, the chance of side reactions between the radicals and the latter is higher.

This analysis points to the probability of optimal conditions needing to be established for different ranges of COD, a rationale to be further explored in subsequent projects.

4.2.2.B Effect of reactor operational parameters on treatment efficiency

To evaluate the time course of COD degradation, grab samples were collected at the recirculation tank for COD analysis and the result were plotted against treatment times. Organic matter degradation kinetics tends to be faster for more concentration effluents, with a large COD drop in the first 30 minutes of reaction and a lower degradation rate for the remaining reaction time (Figure 4.12).

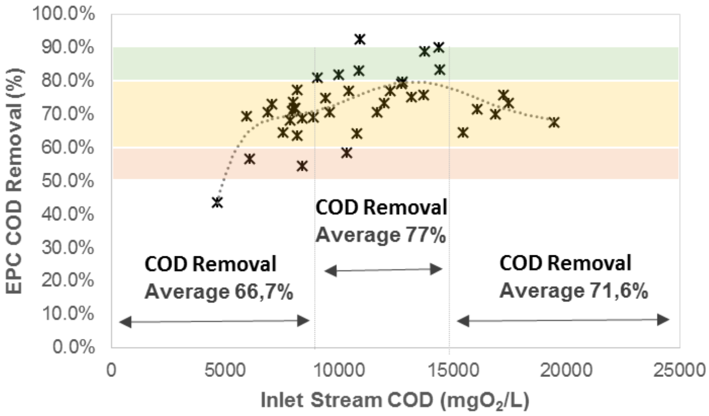


Figure 4.11: COD removal efficiency values of Figure 10 plotted against the inlet stream COD levels.

Overall, the reactions were planned for two-hour periods, with multi-step addition of hydrogen peroxide to better control the radical attack process. The reaction time was set taking into consideration the recirculation mode of operation and the maximum space available at the pharmaceutical site which was only enough to install three tanks with a volume equivalent to 2 h of retention time. Hydrogen peroxide was dosed as a 49.5% solution in water as a safety measure and all the reagent ratios were calculated in relation to this feed.

One issue which is identifiable in Figure 4.12 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. In some grab samples, the sampled volume may have not been recirculated long enough after reagent dosage and the dosed hydrogen peroxide had not had time to react with the ferric ions dosed at the reactor chamber. This issue also suggests that the pilot plant recirculation tanks could have been insufficiently mixed and the organics degradation was not uniform. At the design phase, it is thus important that efficient mixture is ensured.

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. Above approximately 45º C, the electro-fenton process efficiency trend becomes unfavourable and some of the solvents may evaporate and form an explosive atmosphere.

The planning of the trial test operational parameter variations was made taking into account the need to obtain representative results and the limited lease time of the pilot plant. As a result, to achieve the testing of a maximum of ratio combinations without compromising the possibility of drawing reliable conclusions, a minimum of three replicate trial tests were made with each selected combination of reagent

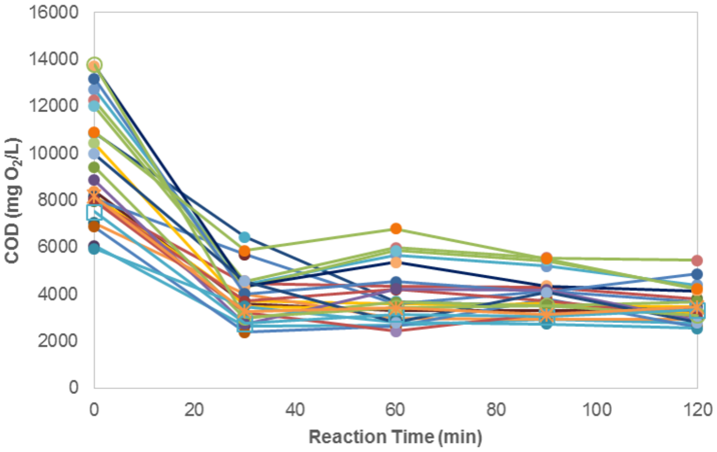


Figure 4.12: Time course of COD degradation in all the effectiveness trial tests.

ratios, as suggested by the reactor's manufacturer.

It is important to bear in mind that, to ensure result reproducibility and representativeness at the pilot plant, equalized inlet wastewater would have to be preserved, to guarantee a set of trial tests with the same inlet wastewater composition. In a large pharmaceutical site, this is impossible to manage. To avoid organics degradation, large refrigeration and storage capacities would be required for the wastewater, and this was just not feasible.

In Figure 4.13, the COD degradation efficiency is plotted against the applied COD/H_2O_2 ratio for each of the COD/Fe ratio values. These ratio values were suggested by the EPC pilot manufacturer, since the technical team's knowledge was critical for the success of this project.

In the wastewater characterization section (subsection 4.1.2), the treatment acceptance criteria established a minimal COD degradation yield of 85.2% in the overall treatment . In the graphs of Figure 4.13 this value is highlighted in green with an acceptable range of ± 5%, considering a small margin for the possibility of adding a complementary downstream stage to upgrade the treatment. 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. 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.

Table 4.11 presents the summary of the organics degradation efficiencies, expressed in COD removal in percentage and in mass of removed COD. A 70-90% range of the overall degradation occurs in the first 30 minutes of reaction.

A more thorough study on the optimal doses and dosing method is advised when applying EPC as a treatment stage during wastewater treatment. In Table 4.11, 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

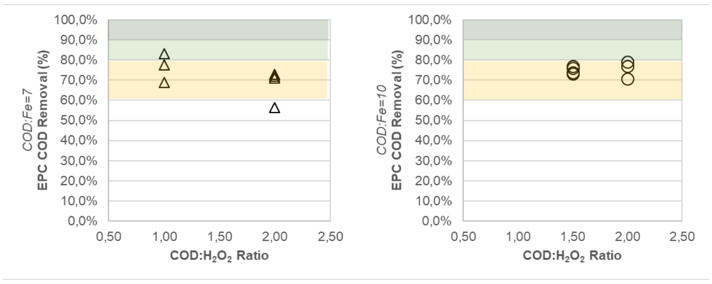


Figure 4.13: COD removal efficiency values plotted against the COD/H2O2 ratio for several COD/Fe ratios (indicated on the left axes), for the effectiveness trial tests. The green range represents the minimal treatment acceptance criteria for COD.

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.

This project lacked flexibility regarding time due to the pilot rental period. However, after installation, in the startup period, a similar and more extended trial plan should be carried out with process optimization as a goal. This project's goal was mainly a proof of concept. The hypothesis of applying this EPC technology with a lower residence time and a complementary treatment step to ensure the desired organics removal levels will be later analyzed in the Economic Analysis section (section 5.5).

Table 4.11: COD removal efficiency values (in percentage and 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.

COD:Fe Ratio	**7**		**10**		**15**		
COD:H_2O_2 Ratio	1	2	1,5	2	1	1,5	2
Rem @30' (% COD)	50.9%	43.2%	64.8%	64.5%	65.5%	60.5%	50.2%
Rem @30' (kg COD)	4.6	3.1	7.2	6.8	6.3	5.7	5.2
Rem @120' (% COD)	69.9%	70.6%	85.7%	81.6%	70.3%	80.0%	89.1%
Rem @120' (kg COD)	6.5	5.2	9.5	8.7	6.8	7.4	9.3

4.2.3 Complementary treatments

4.2.3.A Steam Stripping

From the site's database on wastewater quality monitoring, after optimization the steam stripping column is operating daily with an average removal of 75% for the solvent load. It is however important to stress that this technology transfers contamination to a gaseous phase without degradation. These solvents are not reused in process due to the necessity of grade AA solvents in pharmaceutical production. Presently the removed solvents are incinerated, which is an efficient energetic integration measure.

In the present project, one of the set objectives was to assess whether the stripping column could be used as a pretreatment in order to increase the EPC treatment's efficiency. Therefore, stripped wastewater was collected at the outlet of the column and treated in the EPC reactor. The rationale of this setup was to assess if the absence of solvents could be favorable for the EPC reaction.

The EPC reactor was operated with the COD/Fe/H_2O_2 ratios of 15/1/15 and 15/1/30 and with a reaction time of 2 h. For an inlet stream COD range of 3637 mgO_2/L, the outlet stream COD range was 1399 mgO_2/L. Although the final wastewater reaches a lower COD value than that attained with an EPC step alone, the EPC reactor efficiency did not show an improvement (Table 4.12 and Figure 4.14).

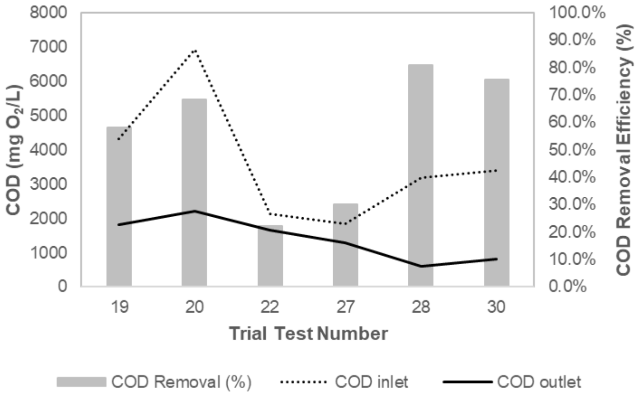


Figure 4.14: COD values at the inlet and outlet of theEPC reactor in the effectiveness trial tests with pharmaceutical wastewater pre-treated through steam stripping, with correspondent COD removal efficiency values.

4.2.3.B Electro Coagulation

In the EPC pilot plant arrangement, the Electro Coagulation (EC) module promotes charge neutralization at the suspended solids particles' surface allowing this suspended matter to form agglomerates which are separated in a subsequent step. In the pilot plant a Dissolved Air Flotation (DAF) step is used. The process principles are schematized in Figure 4.15. The EC reactor noes not require the addition of any

Table 4.12: EPC reactor performance with pharmaceutical wastewater pre-treated through steam stripping: Basic statistics on COD removal efficiency values.

COD (mgO_2/L)	**EPC inlet**	**EPC outlet**	**Removal Efficiency (%)**
Total of analysed samples	6	6	6
Maximum	6940	2200	80.8
Minimum	1840	616	22.2
Average	3637	1399	55.8
Standard Deviation	690	226	22.3
Standard Error	1690	553	54.6

chemicals, which is an advantage in comparison to conventional coagulation processes. Aluminum ions which neutralize the surface charge of the particles are displaced from aluminum plates in the reactor through the flow of an electric current. [19] [20]

Electro Coagulation is therefore a separation operation that should be applied to turbid wastewater,

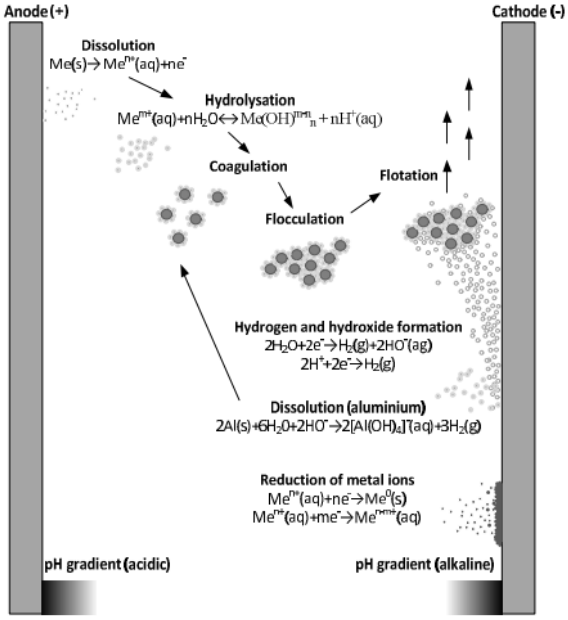


Figure 4.15: Schematics of the Electro Coagulation operation carried out at the EPC pilot plant.

with a high content of suspended solids. At the EPC Pilot, the EC reaction was applied to the pharmaceutical wastewater in recirculation mode, and was followed by a DAF stage. The clarified wastewater was afterwards treated in the EPC reactor for the degradation of organic load. The EC process acts on the suspended solids and thus the decrease in COD is associated with the degree of wastewater clarification. The average COD average efficiency in this step was 15.7 % (Table 4.13). From the results in Figure 4.16, it can be seen that the organic load removal is not easy to predict.

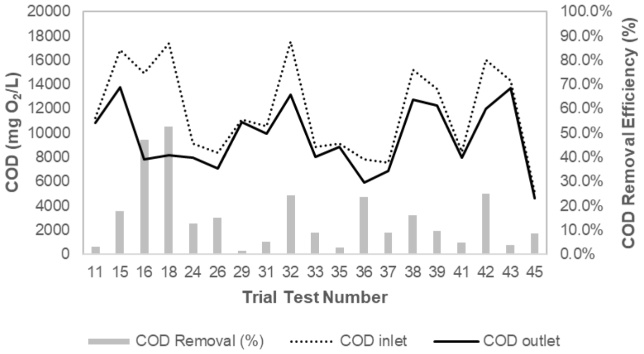


Figure 4.16: COD values at the inlet and outlet of the EC reactor in the effectiveness trial tests with pharmaceutical wastewater, with the correspondent COD removal efficiency values.

Table 4.13: EC reactor performance in treating pharmaceutical wastewater: Basic statistics on COD removal efficiency values.

COD (mgO$_2$/L)	**EC inlet**	**EC outlet**	**Removal Efficiency (%)**
Total of analysed samples	19	19	19
Maximum	17500	13780	53.1
Minimum	5100	4650	1.7
Average	11741	9616	15.7
Standard Deviation	197	142	0.7
Standard Error	858	620	3.2

4.2.3.C Electro Oxidation

The pilot plant used in this project included an Electro Oxidation (EO) reactor with titanium plates and a polarity inversion system. Electro Oxidation with titanium plates is an electrochemical technique mainly used to remove dissolved halogenated pollutants from wastewater. The halogenated compounds are indirectly oxidized by oxidants generated in situ by anodic oxidation, such as H_2O_2, O_3, HClO, and HBrO. The oxidants generated at the anode can also be used to remove nitrogen compounds through oxidation to N_2. The oxidizing agents involved can be chlorine/hypochlorite, hydrogen peroxide, and metal ion mediators. Chloride present in the WW can be easily converted to chlorine/hypochlorite by anodic oxidation. [20]

The evaluation of the adequacy of an EO reactor as a post-treatment of the EPC process for the pharmaceutical WW was done by adding the EO reaction step after the EPC treatment in some of the test trials. The aim was to assess whether chloride and nitrogen compounds could be minimized or eliminated though final EO. The formed hypochlorite also acts as a disinfection agent. The nitrogen released to the air does not represent an explosion hazard. [21]

However when the residual COD level in the WW is high nitrogen removal is inhibited, since the organic contaminants can undergo direct oxidation and thus introduce a competing mechanism. Kinetics tests demonstrated that ammonium was removed first when the indirect oxidation mechanism was available but COD was preferentially removed when direct oxidation was prevalent. Therefore, for an effective removal of nitrogen organic carbon should be removed in advance in order to minimize energy consumption in the electrochemical oxidation step.

On average in the performed tests, the EO reactor removed 32.6 % of COD (Table 4.14). This removal percentage was higher than the average value obtained in the last 1.5 h of the 2-h EPC reaction. From the results in Figure 4.17, its can be seen that the organics removal efficiency trends do not seem to be related to inlet COD values but may be related with the inlet concentrations of halogenated and nitrogen compounds.

Depending on the treatment objectives regarding the removal of COD, Cl and ammonia, investment and operational costs associated to a reactor with titanium plates may or may not be justifiable. To better support future decisions, an assessment on the removal of EO target compounds will be presented subsequently subsection 4.2.4).

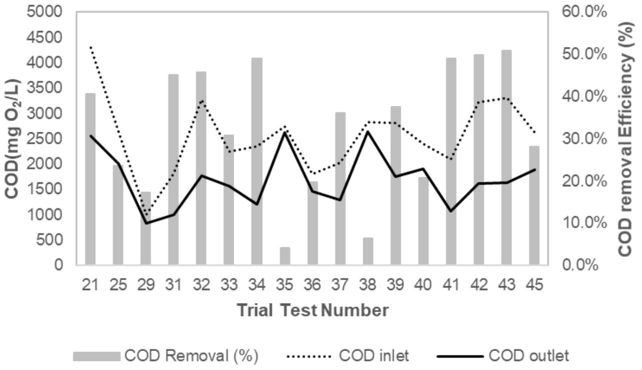
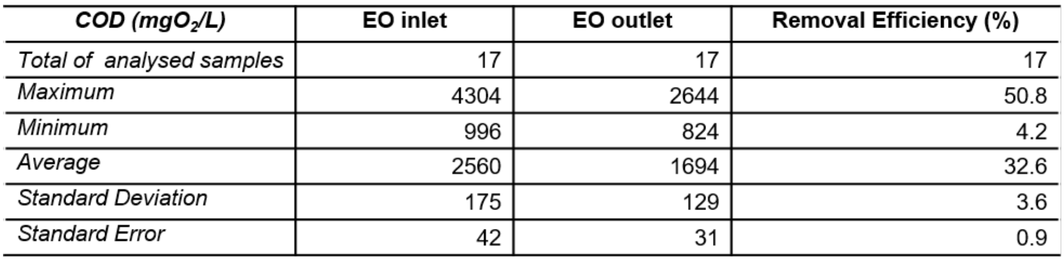


Figure 4.17: COD values at the inlet and outlet of the EO reactor in the effectiveness trial tests with pharmaceutical wastewater previously treated by EPC, with the correspondent COD removal efficiency values.

Table 4.14: EO reactor performance in treating pharmaceutical wastewater previously treated by EPC: Basic statistics on COD removal efficiency values.



COD (mgO$_2$/L)	EO inlet	EO outlet	Removal Efficiency (%)
Total of analysed samples	17	17	17
Maximum	4304	2644	50.8
Minimum	996	824	4.2
Average	2560	1694	32.6
Standard Deviation	175	129	3.6
Standard Error	42	31	0.9

4.2.3.D Photo Oxidation

Advanced oxidation of organic pollutants may also be promoted by the combination of UV radiation and hydrogen peroxide, with the photolysis of the oxidant (photolysis of the HO-OH bond) leading to the formation of hydroxyl radicals. The latter is further enhanced by the dosing of ferric ions (Photo-Fenton process). Previous studies pointed to a high efficiency of this process in the degradation of organics in wastewaters with COD levels in the lower range. [22] Thus, the application of a Photo-Fenton step was assessed for the removal of organics in the COD range corresponding to the outlet of the EPC step (2000-4000 mgO_2/L).

A Photo-Fenton process was simulated in a bench scale reactor operating under UV light at 300 nm, in acid environment (pH=2,5-3), with addition of $FeCl_3$ and without addition of H_2O_2. The presence of residual hydrogen peroxide in the outlet stream of the EPC was confirmed using semi-quantitative H_2O_2 strips. The tested wastewater was collected at the outlet of the UF module of the EPC pilot. This setup simulated the introduction of a photo oxidation step after the EPC to further extend the advanced oxidation's efficiency by making use of the remaining Fenton's reagents, aided by UV radiation, at a lower COD range.

As the UV irradiation apparatus was only available for a limited period of time, a total of four tests were carried out on pharmaceutical wastewater samples after EPC treatment. Although the produced data do not allow for representative conclusions and are not enough for rational decision making, the results revealed a consistently low COD level at the outlet of the UV irradiation step regardless of variations in the inlet organic load (Figure 4.18). Outlet stream COD levels were in the range of 942 mgO_2/L (Table 4.15).

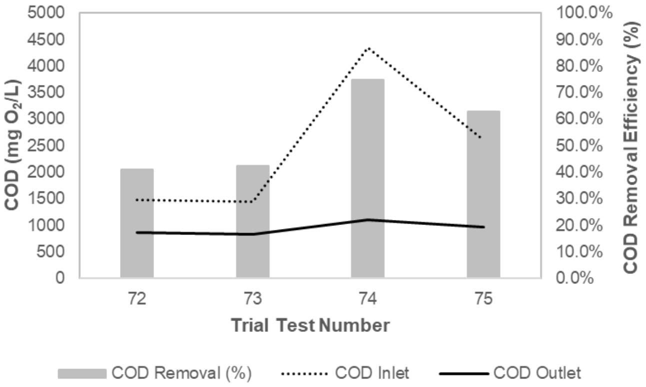


Figure 4.18: COD values at the inlet and outlet of the UV reactor in the effectiveness trial tests with pharmaceutical wastewater previously treated by EPC, with correspondent COD removal efficiency values.

Table 4.15: UV reactor performance in treating pharmaceutical wastewater previously treated by EPC: Basic statistics on COD removal efficiency values.

COD (mgO_2/L)	UV inlet	UV outlet	Removal Efficiency (%)
Total of analysed samples	4	4	4
Maximum	4352	1100	74.7
Minimum	1448	834	41.1
Average	2470	942	55.3
Standard Deviation	592	52	7.1
Standard Error	296	26	3.5

4.2.3.E Reverse Osmosis

Reverse osmosis (RO) is a pressure-driven separation process that does not involve phase changes or the addition of absorbents or solvents. Promoted by pressure gradients, the tangential-flow removal of organic and inorganic molecules occurs through size selection imposed by the pore size of a membrane (Figure 4.19). Membrane properties are essential for separation efficiency, and the chemical nature and physical structure of the membrane material determine its properties. Selecting an appropriate membrane determines the operation's efficiency. [23]

In the context of the present pharmaceutical wastewater treatment, introducing a reverse osmosis step at the end of the pilot plant treatment line adds an additional separation stage which focuses on the residual dissolved molecules and ions still present after the ultrafiltration step. Furthermore, as the first results of the project pointed to higher EPC efficiencies for higher inlet COD values, the introduction of a reverse osmosis step enables the use of EPC at high inlet stream concentrations and provides a sequential increase in the overall treatment efficiency.

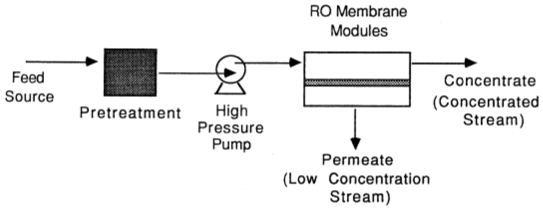


Figure 4.19: Schematics of the Reverse Osmosis operation.

A RO module with ceramic membranes was used in wastewater polishing trials with an operational ratio of 0.75 m^3 of permeate per m^3 of inlet wastewater. As the EPC recirculation tanks had a volume of 1 m^3, RO concentrate was equalized and further treated in the EPC reactor. In real operation, EPC would also operate in a semi-batch mode and, to avoid pollutant accumulation, the RO concentrate would also be treated in a dedicated EPC reaction step, rather than being equalized with fresh wastewater. The overall simulated setup is schematized in Figure 4.20.

The average COD level in the reverse osmosis permeate outlet was 1583 mgO_2/L, while the value for

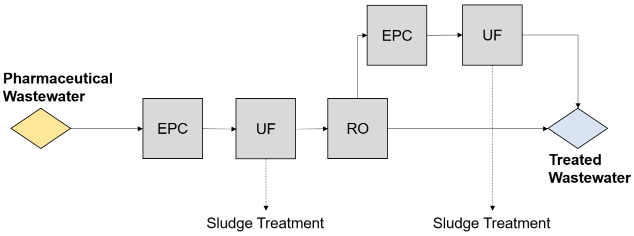


Figure 4.20: Schematics of the introduction of a RO operation in the treatment of pharmaceutical wastewater, with further EPC treatment of the RO concentrate.

the concentrate was 12422 mgO_2/L (Table 4.16 and Table 4.17). The quality of the permeate outlet was consistent, regardless of variations in the inlet organic load (Figure 4.21). The EPC reactor outlet COD level in the treatment of the RO concentrate was also consistent and the operation had a high efficiency (75%) (Figure 4.22).

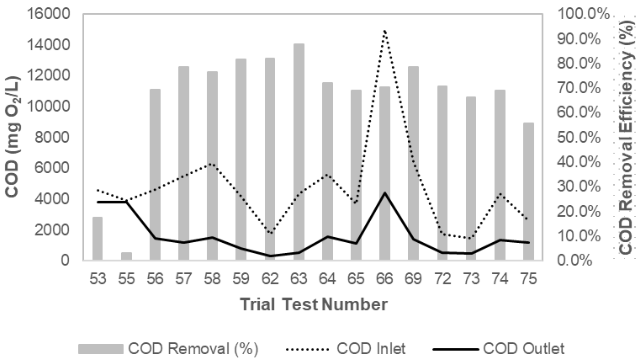


Figure 4.21: COD values at the inlet and outlet of the RO module in the effectiveness trial tests with pharmaceutical wastewater previously treated by EPC, with correspondent COD removal efficiency values.

Table 4.16: RO module performance in treating pharmaceutical wastewater previously treated by EPC: Basic statistics on COD removal efficiency values.

COD (mgO$_2$/L)	**RO inlet**	**RO outlet**	**Removal Efficiency (%)**
Total of analysed samples	16	16	16
Maximum	15024	4426	87.8
Minimum	1448	310	2.9
Average	4761	1583	65.5
Standard Deviation	761	308	5.6
Standard Error	190	77	1.4

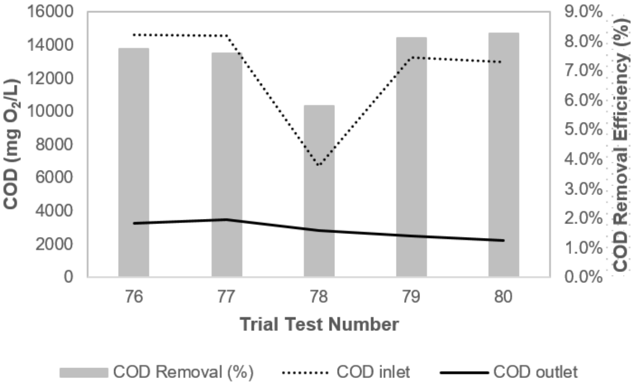
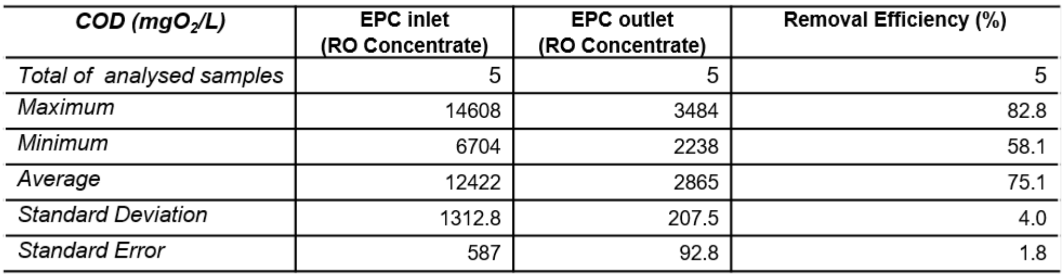


Figure 4.22: COD values at the inlet and outlet of the EPC module in the effectiveness trial tests with the RO concentrate from the polishing step of the pharmaceutical wastewater treatment, with correspondent COD removal efficiency values.

Table 4.17: EPC performance in treating the RO concentrate from the polishing step of the pharmaceutical wastewater treatment: Basic statistics on COD removal efficiency values.



COD (mgO_2/L)	EPC inlet (RO Concentrate)	EPC outlet (RO Concentrate)	Removal Efficiency (%)
Total of analysed samples	5	5	5
Maximum	14608	3484	82.8
Minimum	6704	2238	58.1
Average	12422	2865	75.1
Standard Deviation	1312.8	207.5	4.0
Standard Error	587	92.8	1.8

4.2.4 Treatment performance on the removal of specific components

4.2.4.A Solvents

Grab samples for the analysis of solvent contents were collected at the inlet and outlet of selected effectiveness trials regardless of the complementary steps included in the trial treatment setup. Regarding solvent removal, preliminary data processing revealed that the majority of the steps included in the trials, upstream and downstream of the EPC, had no significant influence.

The outlet streams solvent concentration profiles (Figure 4.23), were generally maintained within consistent ranges. In trial 54, the jump in the solvents concentration was due to an inadequate set of operational parameters applied in the reverse osmosis step. Specifically, the permeate/inlet volumetric ratio was higher than in subsequent trials 73, 74 and 75 and, with the membranes material being slightly permeable to solvents, the majority of residual solvents from the EPC step was transferred to the permeate instead of staying in the concentrate.

The solvents of concern in the present project can either be separated from the wastewater in the ultrafiltration and reverse osmosis steps, or degraded in the EPC process. Considering this, in the trials with

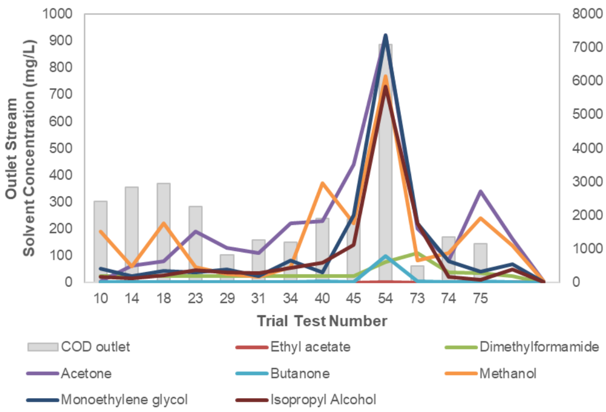


Figure 4.23: Concentration of the industrial site's specific solvents at the outlet of the effectiveness trials performed at the EPC Pilot Plant. Trial treatment setup identification: setup 1 - trials 10 and 14; setup 2 - trials 18 and 23; setup 3 - trials 29,31, 34,40 and 45; setup 5 - trials 54, 73, 74 and 75.

setups 1 to 4 the solvent removal is associated to the EPC reactor´s efficiency in solvent degradation. Thus, the solvent degradation efficiency results in Table 4.18 were computed excluding the trials with setup 5 that integrated a reverse osmosis step downstream of the EPC reactor.

Reviewing Table 4.18, the lowest average removal was observed for dimethylformamide. Highest removals were measured for alcohols, with degradation efficiency increasing with the increase of the alcohol molecule chain length. For the ketones, this relation seemed to be inversed. A possible explanation is that in alcohols, oxidation occurs at the extremity of the carbon chains while in ketones, oxidation occurs at the center of the chain and some stereochemical impediment may occur with longer chains.

Table 4.18: Average concentrations of solvents at the inlet and outlet of the effectiveness trials with pharmaceutical wastewater at the EPC Pilot Plant and correspondent removal efficiency values. Trials with setup 5 are not included.

Solvent	Inlet Average Concentration (mg/L)	Outlet Average Concentration (mg/L)	Average Removal (%)
Dimethylformamide	51.22 ± 1.07	25.000 ± 0.000	34.5 ± 1.1
Ethyl Acetate	5.92 ± 0.37	0.454 ± 0.005	74.7 ± 1.0
Methanol	887.79 ± 22.15	136.33 ± 4.17	78.9 ± 0.6
1.2-Ethanediol	983.33 ± 32.25	67.11 ± 2.47	90.8 ± 0.3
2 - Propanol	1213.33 ± 16.02	49.89 ± 1.33	95.6 ± 0.1
Acetone	813.33 ± 15.82	163.19 ± 4.46	76.2 ± 0.5
Methyl ethyl ketone	29.93 ± 2.49	1.05 ± 0.05	69.9 ± 1.4

4.2.4.B Heavy Metals

As identified in subsubsection 4.1.1.D, iron and zinc are heavy metals for which removal is critical. These metals have a discharge limit that is presently is a challenge for the site to comply with. In Table 4.19 the heavy metals for which a target removal efficiency was not imposed, due to their full compliance with discharge limits already at the inlet of the wastewater treatment. Figure 4.24 and Figure 4.25 present the results for iron and zinc removal at selected effectiveness trials with pharmaceutical wastewater at the EPC pilot plant.

Reviewing Figure 4.24 and Figure 4.25, the treated wastewater presents a consistent residual iron and zinc concentration regardless of variations in the metals load in the inlet pharmaceutical wastewater. Zinc concentration ranges were 8.53 mg Zn/L at the inlet of the treatment and 0.84 mg Zn/L at the outlet, average zinc removal efficiency being 97.9 % at the EPC reactor. Iron concentration ranges were 0.71 mg Zn/L at the inlet of the treatment and 0.10 mg Zn/L at the outlet, average iron removal being 86.1 % at the EPC reactor. Heavy metals are mainly removed from the wastewater in the EPC process through separation of the particle agglomerates formed by precipitation and coagulation of the oxidized metal species.

Table 4.19: Average concentration of non-critical heavy metals at the intlet of the EPC treatment and their correspondent emission limit values.

Metals (mg/L)	Arsenium	Cadmium	Chromium	Copper	Lead	Mercury	Nickel
Inlet Stream Average	0.01	0.1	0.28	0.3	0.3	0.01	0.3
Emission Limit Value	1	0.2	0.3	0.4	-	0.05	0.3

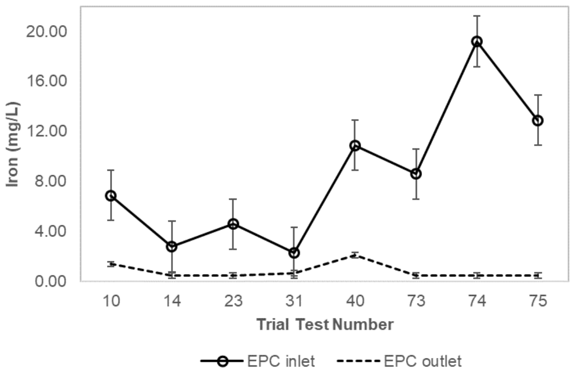


Figure 4.24: Iron removal: iron concentrations at the inlet and outlet of some of the effectiveness trials performed at the EPC Pilot Plant.

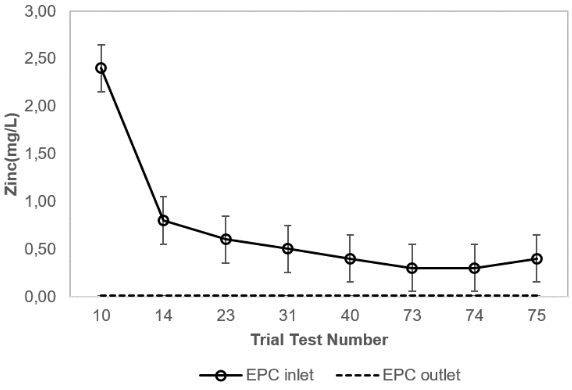


Figure 4.25: Zinc removal: zinc concentrations at the inlet and outlet of some of the effectiveness trials performed at the EPC Pilot Plant.

4.2.4.C Total Suspended Solids

The decision of introducing an Electro Coagulation (EC) step in the treatment setup was supported by the initial visual inspection of the wastewater. This inspection showed the presence of suspended particles that could be better separated in EC and DAF steps before the EPC reactor.

Trial Tests in which the setup lacked an EC step registered an average total suspended solids concentration of 16.0 mg TSS/L at the outlet of the treatment with a correspondent average TSS removal of 92.3 %. However, from Figure 4.26, it can be seen that the suspended solids removal is not higher in treatments with an EC step, when compared with removal values in trials for setups that did not include this step.

The removal of suspended solids in trials with an EC step was on average 92.0 %, indicating that the typical solids content in the site's wastewater is not high enough to justify the investment in an EC reactor to clarify the wastewater before the EPC reactor.

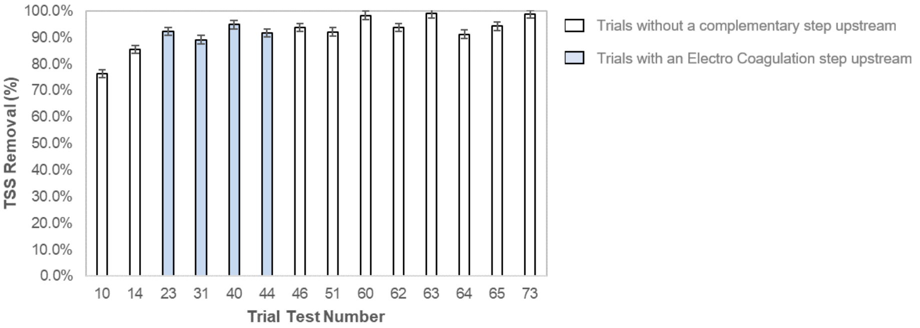


Figure 4.26: Total suspended solids removal levels for some of the effectiveness trials performed at the EPC Pilot Plant, with or without a complementary EC step upstream of the EPC stage.

4.2.4.D Halogenated and Nitrogen Compounds

The additional removal of halogenated and nitrogen compounds can be achieved through separation or oxidation in a downstream step, and the equipment tested for this at the EPC Pilot were an Electro Oxidation (EO) reactor and a Reverse Osmosis (RO) membrane module. In what concerns COD removal, the RO step provided a higher efficiency in comparison with the trials with an EO step. However, the focus of the tested equipment was to refine the treatment in what concerns other target components, and thus it is necessary to assess their impact on these.

Reviewing the results for halogenated compounds in the trials without downstream treatments (Table 4.20), average outlet concentrations revealed high removal performances (above 90% removal) for both dichloromethane and AOX.

Table 4.20: Summary of results for the removal of chlorides and halogenated compounds in the EPC trials without complementary treatments.

Halogenated Compounds	Chlorides (mg Cl^-/L)	Dichloromethane (mg DCM/L)	AOX (µg/L)
Average Outlet Concentration	1314.5 ± 88.5	10.3 ± 2.1	629.5 ± 163.1
Average Removal (%)	57.0 ± 5.7	99.8 ± 0.3	99.93 ± 0.01

Average removal for chlorides was higher in the trials with RO, 66.9 %, than in the trials with EO, 52.2 %. This unexpected low performance of the EO reactor on the removal of chlorides may be due to the variability of their concentration in the inlet pharmaceutical wastewater. Namely, trials 29 and 40 had a lower concentration at the inlet than the remaining trials, and their lower removal efficiency decreased the average value (Figure 4.27).

In contrast with chlorides, AOX and dichloromethane (DCM) removals maintained their high performances in trials with an EO step. On average, 98.9 % of the AOX and 99.7 % of the DCM present at the inlet of trials with an EO step were removed. These two components had lower removal performances in trials with a RO step. On average, 46.5 % of the AOX and 74.9 % of the DCM present at the inlet of trials with an RO step were removed. These trends can be identified in the graphs on Figure 4.28 and Figure 4.29.

The lower effectiveness of RO for AOX and DCM can be explained by the permeability of the membrane to these components. Chloride ions are species for which the reverse osmosis membranes are designed to be impermeable. However, dichloromethane is a solvent and most membranes are permeable to it.

The negative effect of COD on the removal of ammonia through EO, referred in subsubsection 4.2.3.C., can be identified in Figure 4.30.

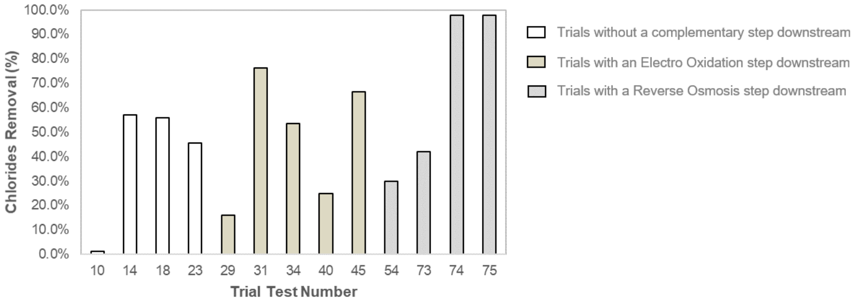


Figure 4.27: Chlorides removal levels for some of the effectiveness trials performed at the EPC Pilot Plant, with or without a complementary EO or RO step downstream of the EPC stage.

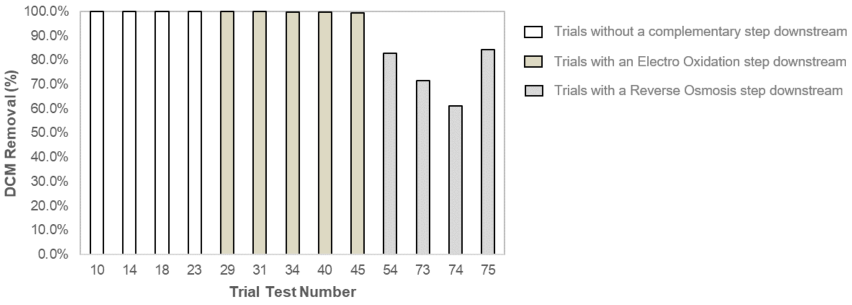


Figure 4.28: AOX removal levels for some of the effectiveness trials performed at the EPC Pilot Plant, with or without a complementary EO or RO step downstream of the EPC stage.

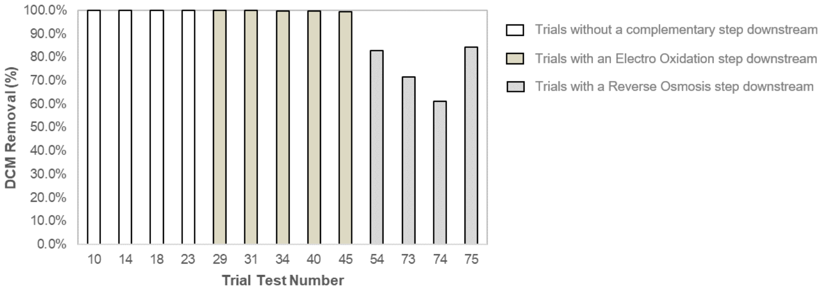


Figure 4.29: Dichloromethane removal levels for some of the effectiveness trials performed at the EPC Pilot Plant, with or without a complementary EO or RO step downstream of the EPC stage.

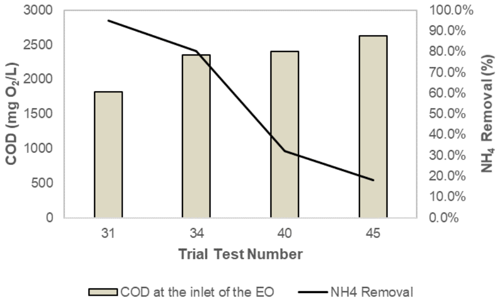


Figure 4.30: Ammonia removal levels for some of the effectiveness trials performed at the EPC Pilot Plant, with a complementary EO step downstream of the EPC stage. Ammonia removal performance in the EO reactor and COD levels at the inlet of this step.

4.2.4.E Detergents

Industrial detergents contain surfactant molecules with anionic or cationic properties and their concentration in wastewater must be monitored due to their harmful effects on biological treatment units, among others. Although biological reactors in WWTP have the ability to degrade detergents, the environmental permits impose discharge limits to ensure that the WWTP performance stays within the design range.

As presented in section 4.1, the site's wastewater detergent content is presently comfortably under the discharge limit. However, as one of the possibilities that emerged from the revamping of the site's processes is the integration of segregated streams in the equalization system, the detergent removal capacity of the treatment system must be quantified before the integration of streams that can increase the typical detergent concentration can be accepted.

From Figure 4.31, a high removal trend was observed for the detergents in the EPC Test Trials. On average, 87.7 % of the detergents present at the inlet wastewater were removed.

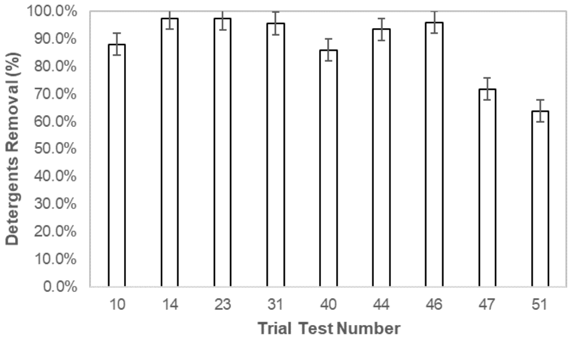


Figure 4.31: Detergents removal levels for some of the effectiveness trials performed at the EPC Pilot Plant.

4.2.5 Environmental Performance

Amongst the environmental parameters used to characterize industrial wastewater, toxicity parameters are an important group. Considering that the downstream treatment for the pharmaceutical wastewater in a municipal WWTP is biologically based and that the site's industrial WWTP is being revamped, with the complementary treatments to the EPC reactor still under evaluation and a biological step still being a hypothesis, the EPC treatment performance was also assessed regarding biodegradability toxicity. The parameters assayed were 5- and 20-day Biological Oxygen Demand (BOD5 and 20 day biochemical oxygen demand (BOD20)), Ecotoxicity to Daphnia magna and Respiratory Inhibition (DOUR, Dissolved Oxygen Uptake Rate).

4.2.5.A Biodegradability

Biological Oxygen Demand is the amount of oxygen consumed by aerobic organisms for the degradation of organic material present in wastewater. It is similar to COD in that it is a measure of the organics content. Biodegradability can be assessed by the ratio of Biological Oxygen Demand (BOD) to COD values measured in the wastewater, roughly quantifying the fraction of organics that can be degraded by biological oxidation in the total organics content.

The values for the BOD5/COD ratio measured in the pharmaceutical wastewater treated at the EPC Pilot Plant are presented in Figure 4.32. An effluent is considered biodegradable when the ratio of BOD5/COD is above 0.3, and readily biodegradable when it is above 0.5. The site's wastewater is moderately biodegradable and is converted into easily biodegradable after the treatment with the EPC technology. On average, treated wastewater presented ratio values in the range 0.548, corresponding to an average increase of 88.6 % in the wastewater biodegradability.

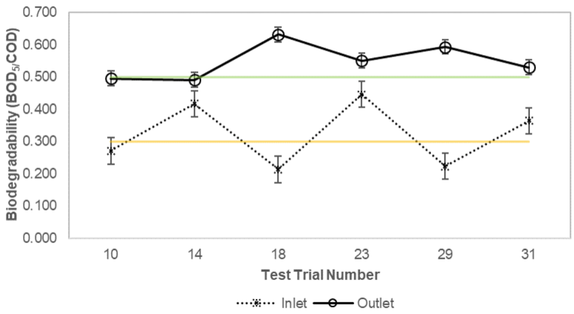


Figure 4.32: Inlet and outlet biodegradability levels, measured as the ratio of BOD5 to COD, for some of the effectiveness trials performed at the EPC Pilot Plant. The horizontal lines indicate the minimum (yellow) and ready (green) biodegradability levels.

4.2.5.B Ecotoxicity and Respiratory Inhibition

Even 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, there is still a final discharge into a natural water course and effluent toxicity to aquatic environments must be 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*. The recommended emission limit is 2 toxicity units (TU), and as can be seen in Figure 4.33, 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.

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. This method registers the amount of oxygen that was consumed during a specific period of time by both a control biomass sample and a test biomass sample exposed to the effluent. This method allows the quantification of the effect of the effluent on the respiration rate of the sample aerobic population.

Reviewing Figure 4.34, 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 4.33. 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 %.

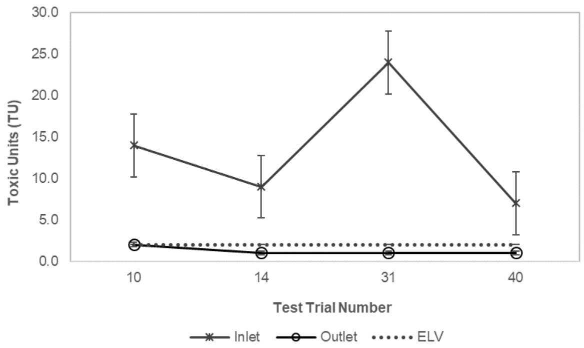


Figure 4.33: Inlet and outlet eco-toxicity levels, measured in toxicity units (TU) towards *Daphnia magna*, for some of the effectiveness trials performed at the EPC Pilot Plant.

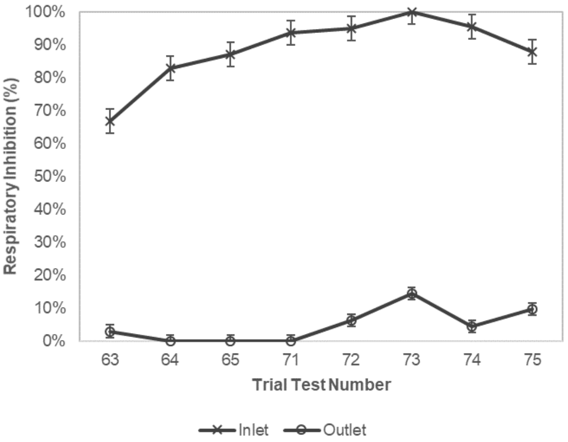


Figure 4.34: Inlet and outlet toxicity levels, measured as respiratory inhibition in an aerobic microbial population, for some of the effectiveness trials performed at the EPC Pilot Plant.

4.2.6 API Degradation Performance

Due to confidentiality issues, the quantification of specific API in the wastewaters from the EPC test trials will not be presented, but Figure 4.35 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.

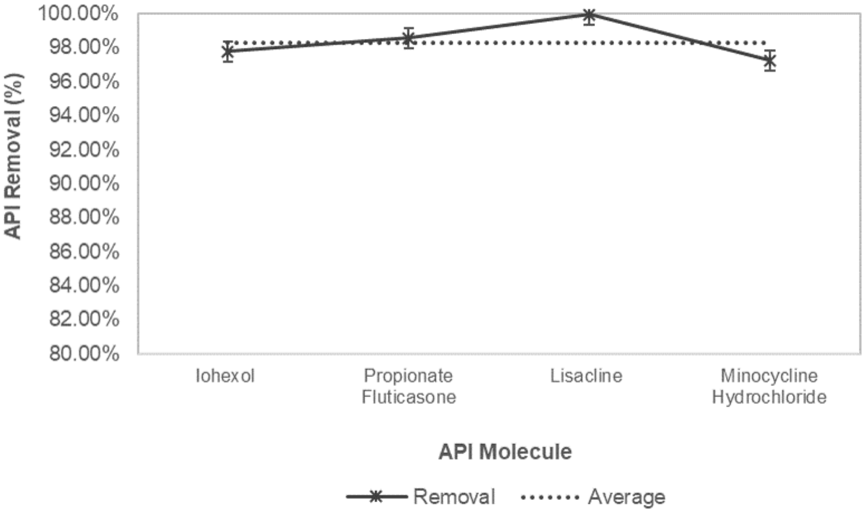


Figure 4.35: Average removal for selected APIs, in trials performed at the EPC Pilot Plant using pharmaceutical wastewater with or without supplementation with the same APIs.

4.2.7 Treatment Robustness

The trials plan included the designated Robustness Tests, namely, trials on synthetic wastewaters simulating likely future changes in the site's wastewater composition.
The simulation of the integration in the treatment of streams with an expected low organic load (condensate phase from the thermo-oxidizer's off gas treatment and utilities condensates) 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 high COD streams in the equalization and feed tank, namely, high solvent load aqueous effluents and change-of-line (COL) 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. Stress situations were also simulated with addition of key solvents to the pharmaceutical wastewater, with the ratio mimicking the site's incidents history, specifically, when solvent leaks occurred.

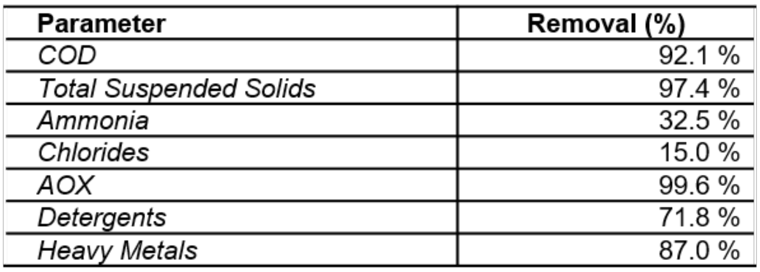
Robustness trial tests were thus fed with effluents prepared in separate IBCs, freshly for every trial, through the IBC feed slot.

4.2.7.A Integration of segregated streams

- **Condensate phase from the thermo-oxidizer's off-gas treatment**

This effluent was subjected to treatment at the EPC with setup 1. Pollutant removal measured through critical parameters is presented in Table 4.21, overall the treatment performance maintained the trends except in the removal of ammonia and chlorides – whose discrepancy from the trends is not significant due to their low content at the inlet of the trial (Ammonia at the inlet was 40 mg NH4/L and Chlorides at the inlet was 660 $mgCl^{-}/L$). The Biodegradability of the effluent increased in 91.6% after the treatment at the EPC Pilot Plant.

Table 4.21: EPC treatment of the condensate phase from the thermo-oxidizer's off-gas treatment: summary of removal efficiency results.



Parameter	Removal (%)
COD	92.1 %
Total Suspended Solids	97.4 %
Ammonia	32.5 %
Chlorides	15.0 %
AOX	99.6 %
Detergents	71.8 %
Heavy Metals	87.0 %

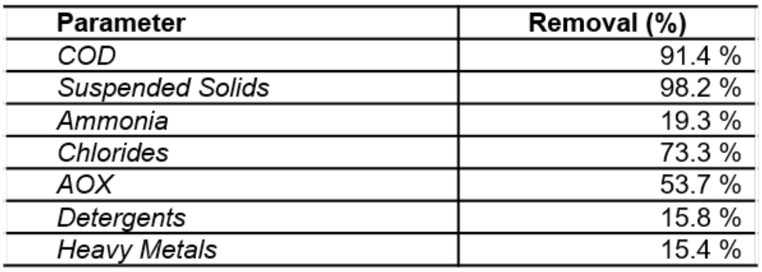
- **Utilities condensates**

This effluent was mainly composed by water, but as it includes the purged streams from the refrigeration water circuit, it could contain surface fouling components or traces of solvents from thermal fluid exchanges. The thermal equipment served by this circuit is multipurpose and fluid exchanges occur frequently, so some traces of thermal fluid other than water may end up on the refrigeration circuit. These fluids have high COD values due to their solvent content.

This effluent was subjected to treatment at the EPC with setup 4. Pollutant removal measured through critical parameters is presented in Table 4.22. Some components highly removed in other trials showed low removal efficiency due to their low content at the inlet of the trial, namely 5.0 mg AOX/L, 0.139 mg Detergents/L and 57 $mgNH_4/L$). Nevertheless, in this trial the treatment removed some of the highest loads registered during the entire project maintaining a high performance, specifically, 11680 $mgCl^{-}/L$ and 561 mg TSS/L.

The biodegradability of the effluent, measured as the BOD5/COD ratio, increased by 16.1% after the treatment at the EPC Pilot Plant, however this increase is relatively low since the biodegradability value at the inlet was already 0.6.

Table 4.22: EPC treatment of the utilities condensates: summary of removal efficiency results.



Parameter	Removal (%)
COD	91.4 %
Suspended Solids	98.2 %
Ammonia	19.3 %
Chlorides	73.3 %
AOX	53.7 %
Detergents	15.8 %
Heavy Metals	15.4 %

- **COL (Change of Line) effluent**

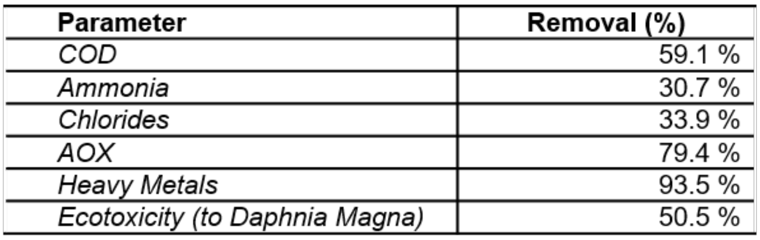
In a multipurpose industry, production lines are used for different processes and, to ensure product quality and process safety, strict cleaning protocols are applied at the end of each process. The cleaning of the equipment is done with detergent solutions and multiple water rinses, and the resulting effluents are collected due to the possibility of their containing, in addition to the cleaning agents, either API or residues of the process solvents. These effluents are designed as COLs. Presently, COLs are directed to incineration (first washes are incinerated due to the possible presence of potent API) or to external treatment (second washes will contain traces of solvents but high loads of detergents).

The integration of a first wash COL in the feed to the EPC was simulated by diluting it in the pharmaceutical effluent, at a volume ratio of 1:10. The resulting synthetic effluent was treated in the EPC Pilot Plant with setup 5.

The integration of a second wash COL in the feed to the EPC was simulated by diluting it in the pharmaceutical effluent, at a volume ratio of 1:4, and the resulting synthetic effluent was treated in the EPC Pilot Plant with setup 1.

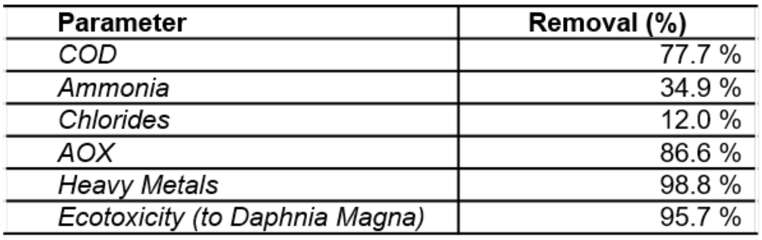
On average, the biodegradability of these effluents, measured as the BOD5/COD ratio, increased by 77.7%. Pollutant removal in these trials, measured through critical parameters, is presented in Table 4.23 and Table 4.24.

Table 4.23: EPC treatment of the first wash COL together with the pharmaceutical wastewater: summary of removal efficiency results.



Parameter	**Removal (%)**
COD	59.1 %
Ammonia	30.7 %
Chlorides	33.9 %
AOX	79.4 %
Heavy Metals	93.5 %
Ecotoxicity (to Daphnia Magna)	50.5 %

Table 4.24: EPC treatment of the second wash COL together with the pharmaceutical wastewater: summary of removal efficiency results.

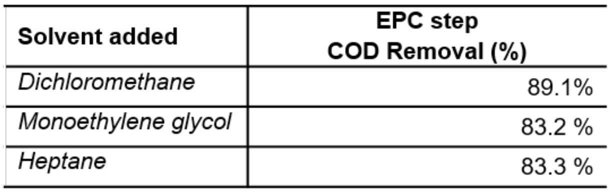


Parameter	**Removal (%)**
COD	77.7 %
Ammonia	34.9 %
Chlorides	12.0 %
AOX	86.6 %
Heavy Metals	98.8 %
Ecotoxicity (to Daphnia Magna)	95.7 %

4.2.7.B Simulation of a solvent leak

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. A volume of 5 L of one of 3 solvents was in turn added to 995 L of pharmaceutical wastewater in an IBC. These simulated effluents were then treated in the EPC Pilot Plant with the following setups: DCM with setup 3, monoethylene glycol with setup 4, and heptane with setup 1. Regardless of the high load of solvents, the EPC performance was within expected ranges (Table 4.25).

Table 4.25: 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 %

5

Implementation and Costs Analysis

5.1 Trials Results Review

In chapter 4 were presented the results and discussion of the EPC Pilot Plant test trials. A summary of conclusions is presented in Table 5.1. This table is presented to enlighten the overall performance of the EPC reactor and the need for complementary equipment to achieve better performances, and these aspects are reviewed for each individual environmental parameter.

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 will be considered in the implementation scenarios presented.

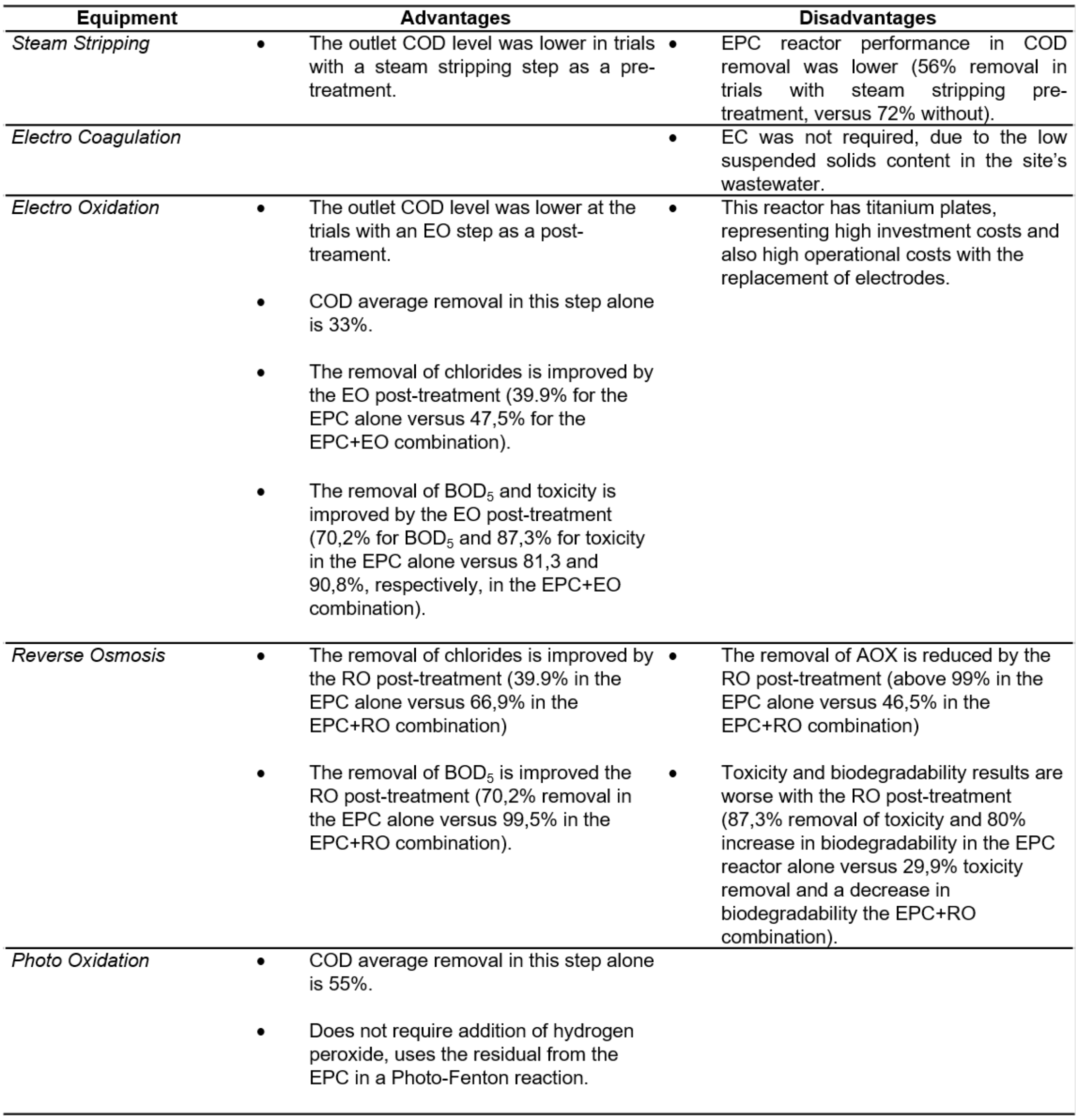
Table 5.1: Summary of EPC Project's preliminary results.

Parameter	Average removal range in the EPC reactor for pharmaceutical WW trials (%)	Performance objective achieved?	Impact of complementary equipment
Solvents (10 site-specific solvents measured)	75 to 95 DMF: 35% average removal	Yes	A post-treatment with activated carbon is suggested as an additional solvent retention measure.
Heavy Metals	86 to 98 %	Yes	-
Total Suspended Solids	90 to 95 %	Yes	EC is not necessary as a pre-treatment, due to the low suspended solids content at the inlet.
Chlorides	57 %	Yes	The introduction of a RO step after the EPC increases the removal of chlorides, but the target removal and residual concentration are achieved without that step.
AOX	> 99 %	Yes	The removal of both AOX and VOC is reduced by the introduction of a RO step. Studies on the best RO membrane material for the retention of AOX and VOC are required.
VOC (Dichloromethane)	> 99 %	Yes	
Ammonia	51 %	Yes	Introduction of an EO step did not improve NH_4 removal in comparison with the average value obtained without that step.
COD	72 %	No	The removal of both COD and TOC was improved by the use of post-treatment steps (after the EPC), either EO or RO.
TOC	73 %	No	
BOD_5	82 %	Yes	-
Biodegradability increase	89%	Yes	-
Toxicity reduction	95 %	There was no specific objective for these parameters	-
API	> 90%		-

5.2 Complementary Equipment Review

The introduction of complementary equipment in the WWTP setup was tested at the EPC Pilot by using different setups during the effectiveness trials. The impact s of this equipment in the performance parameters were analysed and presented in chapter 4. From those results, the advantages and disadvantages of each equipment are presented in Table 5.2, to aid in the design of the industrial WWTP.

Table 5.2: Complementary equipment to the EPC reactor results summary.



Equipment	Advantages	Disadvantages
Steam Stripping	• The outlet COD level was lower in trials with a steam stripping step as a pre-treatment.	• EPC reactor performance in COD removal was lower (56% removal in trials with steam stripping pre-treatment, versus 72% without).
Electro Coagulation		• EC was not required, due to the low suspended solids content in the site's wastewater.
Electro Oxidation	• The outlet COD level was lower at the trials with an EO step as a post-treament. • COD average removal in this step alone is 33%. • The removal of chlorides is improved by the EO post-treatment (39.9% for the EPC alone versus 47,5% for the EPC+EO combination). • The removal of BOD_5 and toxicity is improved by the EO post-treatment (70,2% for BOD_5 and 87,3% for toxicity in the EPC alone versus 81,3 and 90,8%, respectively, in the EPC+EO combination).	• This reactor has titanium plates, representing high investment costs and also high operational costs with the replacement of electrodes.
Reverse Osmosis	• The removal of chlorides is improved by the RO post-treatment (39.9% in the EPC alone versus 66,9% in the EPC+RO combination) • The removal of BOD_5 is improved the RO post-treatment (70,2% removal in the EPC alone versus 99,5% in the EPC+RO combination).	• The removal of AOX is reduced by the RO post-treatment (above 99% in the EPC alone versus 46,5% in the EPC+RO combination) • Toxicity and biodegradability results are worse with the RO post-treatment (87,3% removal of toxicity and 80% increase in biodegradability in the EPC reactor alone versus 29,9% toxicity removal and a decrease in biodegradability the EPC+RO combination).
Photo Oxidation	• COD average removal in this step alone is 55%. • Does not require addition of hydrogen peroxide, uses the residual from the EPC in a Photo-Fenton reaction.	

5.3 EPC Reactor Implementation

Given the results on COD removal kinetics (subsubsection 4.2.2.B), for the EPC reactor to guarantee the target COD removal (1500 mgO_2/L, discharge limit into the municipal sewer), the residence time would have to be extended further from the range tested during the trials (30 minutes to 2 hours). The average degradation results are shown in Figure 5.1. A rough extrapolation, taking also into account a projected average inlet COD of 15000 mgO_2/L, concluded that to achieve the target COD removal of 90%, residence time would have to be close to 6.5 h.

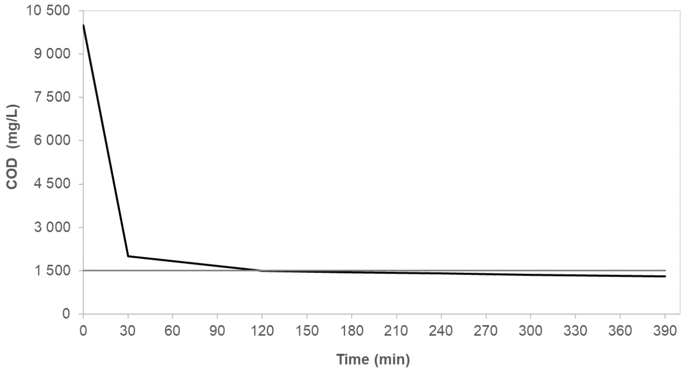


Figure 5.1: Average COD removal simulation: COD degradation curve with time.

Considering that the EPC reactor operates in a batch recirculation mode, and the base case requisites in Table 5.3, the EPC retention tank would need to retain 65 m^3 of wastewater, corresponding to a footprint that is unavailable at the industrial site. This limitation supported the decision of establishing an EPC reaction residence time of 1h with a maximum volume of 20 m^3 for the EPC recirculation tank.

The investment in a second treatment step to further degrade residual organic matter is therefore justified against the impossibility of installing the tank volume required to ensure a 90% removal of COD in a single EPC step.

In line with that decision, all the EPC related costs and removal levels presented will be estimated for an EPC reaction time of 60 min with multistep, continuous dosage of hydrogen peroxide (to ensure the highest performance in the Electro-Fenton reaction), complemented with an initial 15-min recirculation period for iron dosage and a final 15-min recirculation period to complete the reaction.

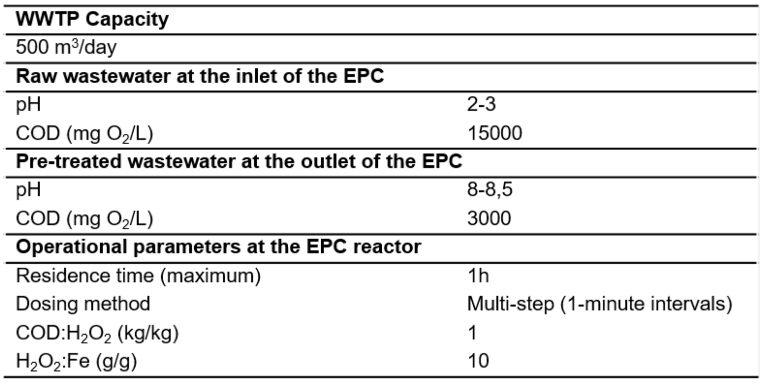
The installed, full-scale EPC systems often operate with several rectors working in parallel, with alternated Cleaning-in-Place (CIP) routines and pre- and post-adjustment of pH routines, to maintain the treated wastewater flow as consistent as possible. This arrangement also guarantees a sufficient retention volume in case of treatment failure in one of the units, without compromising the entire WWTP performance.

At the beginning of the present project, prior to operations start-up at the EPC Pilot Plant, the process safety engineering team carried out a Process Hazard Assessment (PHA) to ensure safety in operation. A focus issue in that exercise was the handling and supply of reagents. Considering the site's safety guidelines and the strong oxidant potential of hydrogen peroxide, this reagent was supplied in a 49,5% (w/w) aqueous solution. This choice will be also applied in future full-scale operations. All the added reagent ratios and cost estimates will thus consider H_2O_2 as a 49,5% solution. Another hydrogen peroxide related issue is compliance with the manufacturer's recommendation for the maximum amount of H_2O_2 (49,5% solution) added, namely, 20L/m^3 of wastewater.

The operational conditions at the Pilot Plant required to ensure 80% removal of the projected COD level at the inlet of the EPC, applying the previously chosen reagent ratios (Table 3), the volume of H_2O_2 (49,5%) would be 20,0 L per m^3 of wastewater , dosed continuously (intermittently) with a dosing pump in on/off mode. To dose the iron from the sacrificial plates, a continuous electric current amperage of 1043 A would be needed , comfortably below the manufacturer's recommended value of 2000 A as maximum current intensity in the reactor. The amperage, hydrogen peroxide volume and dose periods were obtained from the manufacturer's simulator, that computes the required operational conditions according to the operation's objectives.

In future, full-scale operation, these parameters can undergo alterations according to manufacturer's suggestions in order to minimize the number of EPC reactors in operation and to optimize the EPC system's performance. The basic requisites for the full-scale EPC reactor costs projections are presented in Table 5.3.

Table 5.3: Basic requisites for the implementation and cost projections: wastewater parameters and EPC process parameters.



WWTP Capacity	
500 m^3/day	
Raw wastewater at the inlet of the EPC	
pH	2-3
COD (mg O_2/L)	15000
Pre-treated wastewater at the outlet of the EPC	
pH	8-8,5
COD (mg O_2/L)	3000
Operational parameters at the EPC reactor	
Residence time (maximum)	1h
Dosing method	Multi-step (1-minute intervals)
COD:H_2O_2 (kg/kg)	1
H_2O_2:Fe (g/g)	10

The EPC reactor will operate in the setup arrangement shown in Figure 5.2, with the pH adjustments, recirculation and CIP alternating in the setup's parallel tanks. Operational control would rely on pH and COD probes inside the tanks (in case of COD, manual sampling and at line measurements would be an alternative) determining adjustments to the addition of chemicals and the decision between WW discharge to the separation step or further recirculation to achieve target treatment performance (Figure 5.3).

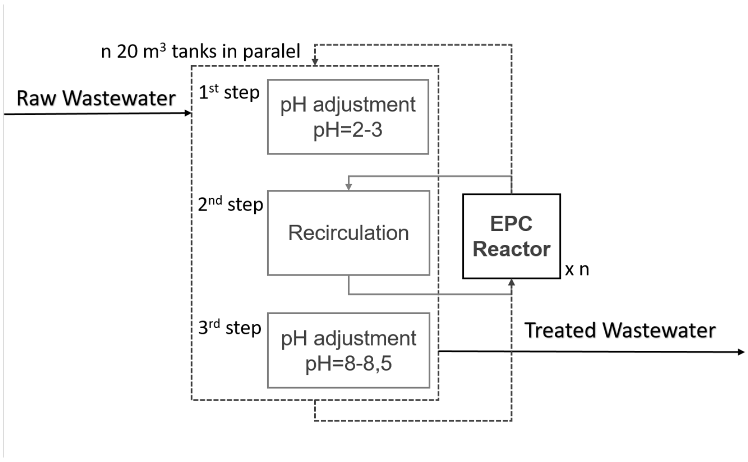


Figure 5.2: EPC system operation schematics for each of the *n* parallel lines.

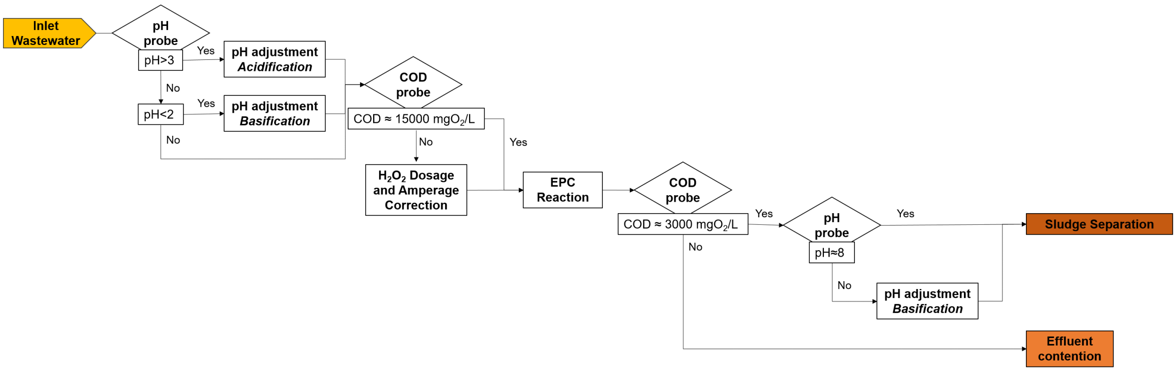


Figure 5.3: EPC control schematics: operational control and decision fluxogram.

5.4 Industrial WWTP setup

Considering the results presented in chapter 4 and after a thorough evaluation of the circumstances and needs of the site in terms of wastewater management, the two hypotheses for the treatment units and interactions to be included in the industrial WWTP are presented in Figure 5.4 and Figure 5.5.

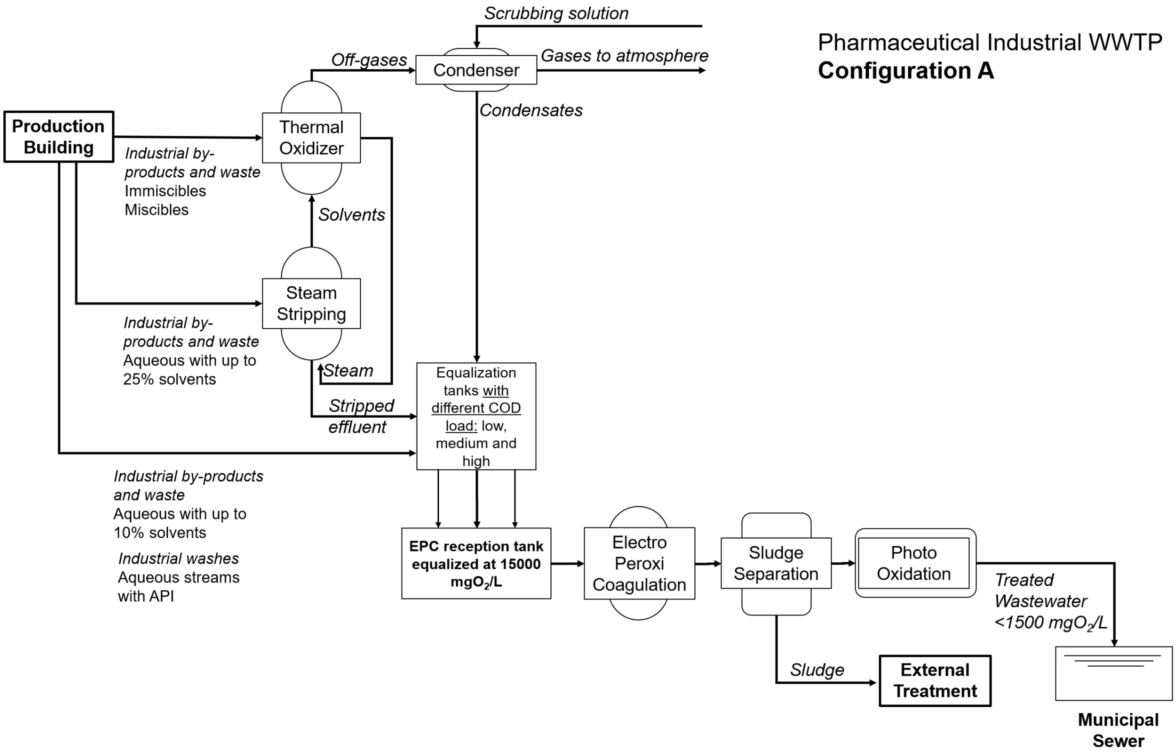


Figure 5.4: Industrial WWTP setup: Configuration A.

The suggested treatment configurations are in line with the site's environmental strategy. The present project was an integral part of the WWTP's revamping plan and activities, which also includes a wastewaster segregation project, intended to direct wastewaters to different buffer tanks according to their COD load. The aqueous streams will thus be directed to of three equalization tanks: a high COD tank (¡50000 mgO_2/L) receiving effluents from COLs and contained leaks, a medium COD tank (¡20000 mgO_2/L) receiving effluents with low solvent content, and a low COD tank (¡ 1000 mgO_2/L) receiving wastewaters from the industrial floor washes and equipment rinses. [24] [25] These tanks will feed a post-equalization tank to compose a wastewater with a medium COD load (15000 mgO_2/L) that will in turn feed the EPC reactor. The EPC-treated wastewater will be equalized before being directed either to a Photo-Oxidation post-treatment (configuration A) or a biological post-treatment (configuration B).

The full-scale WWTP would be designed for a daily capacity of 500 m^3 and an inlet wastewater with

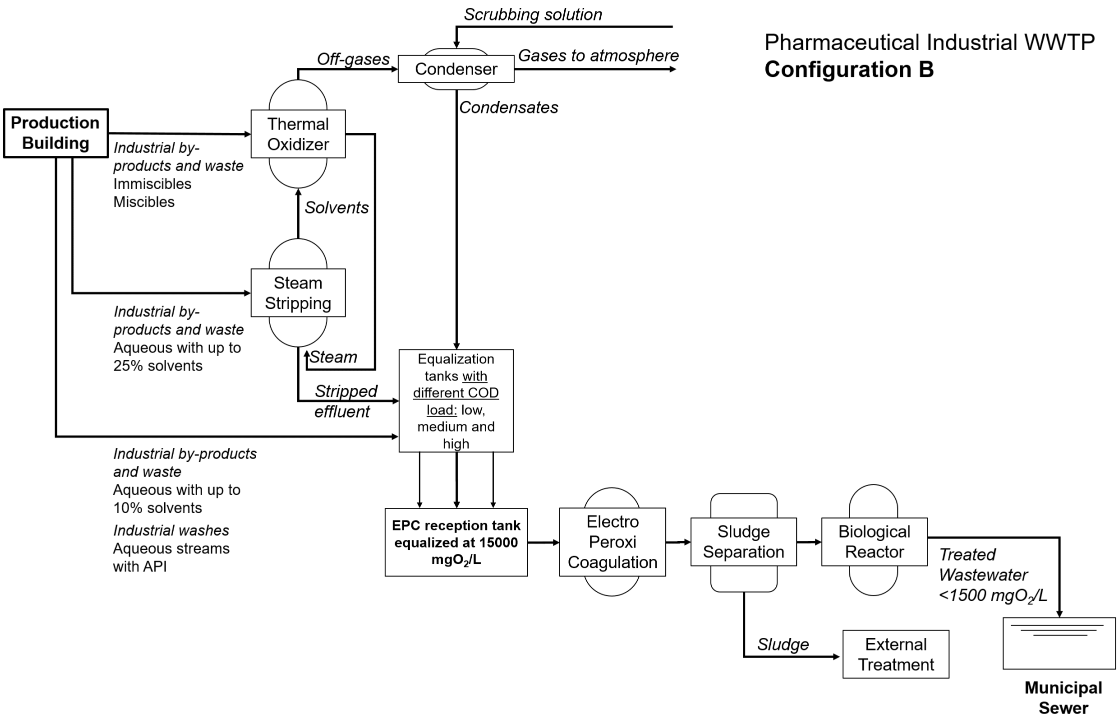


Figure 5.5: Industrial WWTP setup: Configuration B.

a COD load of 15000 mgO_2/L (Table 5.3). To guarantee a consistent admission of 20.8 m^3/h at the intlet of the WWTP, four EPC reactors with 10 m^3 recirculation tanks would be installed in parallel. The existence of four reactors facilitates the retention of poorly treated batches, pH correction and equalization routines, CIP routines and the possibility of reactor/tanks maintenance without compromising the overall discharge of the industrial WWTP. To further improve performance, an extended study towards establishing optimal operational parameter values is recommended during the start-up of the units and every time the pharmaceutical wastewater undergoes significant changes. The results obtained on the treated WW quality in what regards biological parameters validated the its suitability for further treatment in the municipal WWTP (with a biological reactor), but also validated the possibility of installing a biological reactor for post-treatment in the industrial WWTP. The installation of the latter would introduce the possibility of future water reutilization in the site, depending on adjustments to the EPC and biological reactor system's performance. For the present project, water reutilization will not be considered.

5.5 Economic Analysis

Operational and investment costs and were analysed to enable comparisons between complementary equipment and operation scenarios. Equipment costs were provided by the EPC manufacturer and obtained from several manufacturer catalogues.

The investment payback period was estimated considering the present overall liquid waste management system and the future treatment system. This method considers the wastewater volume processed in 2016 and compares the known real costs with the projected costs at each new section. From the estimated soft gains that the implemented WWTP provides in comparison to the current WWTP, the payback period was computed.

This analysis allowed for an economically reasoned decision on which WWTP arrangement to implement at the site.

5.5.1 Operational and Investment Costs

Operational costs were calculated for both configurations (Figure 5.4 and Figure 5.5).

In both configurations, the wastewater admitted to the EPC reactor is previously filtered to prevent excessive solids deposition in the recirculation tanks and fouling of the reactor and piping. The EPC technology manufacturer was consulted in what regarded the flow rate and current intensity nominal capacities, to validate the WWTP capacity distribution in the EPC system. A total of 4 reactors were accounted for in this analysis, with costs provided by the manufacturer.

Reactor maintenance operations consist essentially in the replacement of the iron plates. The recommended replacement frequency and costs were accounted for in the operational costs. Operational costs also considered the consumption of chemicals (hydrogen peroxide) according to the imposed COD mass removal rate at the EPC reactor and the associated electrical energy consumption.

In configuration A, EPC complemented with a Photo-Oxidation step, the 90% overall COD removal distribution is 80% COD at the EPC reactor and 10% at the UV/H_2O_2 reactor (Table 5.4). This configuration included the assumption that the UV/H_2O_2 reactor performs better in a low COD Fenton's environment and that the residual hydrogen peroxide left over from the EPC step was sufficient for the remaining 10% of COD degradation to occur. This required the addition of $FeCl_3$ to an H_2O_2:Fe2+ mass ratio of 4/1. The cost of this added ion chloride was accounted for as 10% of the total operational cost of the UV/H_2O_2 operation. Equipment investment costs and electrical energy consumption for the UV/H_2O_2 reactor was available from previous proposals and the costs were previously estimated in a project that tested a Photo-Oxidation Pilot Plant with the pharmaceutical wastewater.

In configuration B, EPC complemented with a biological reactor, the 90% overall COD removal distribution is 70% COD at the EPC reactor and 20% at biological reactor (Table 5.4). This configuration considers the installation of a Moving Bed Biologic Reactor (MBBR), operating with biomass pods and exhibiting a high resistance to the toxic shocks that may occur at this site due to the high variability and unpredictably of the pharmaceutical wastewater. The biological reactor design and cost estimations were performed by a member of this project's team and the equipment investment costs were obtained through consultation with the manufacturers. Reactor maintenance was accounted for in the running costs.

Table 5.4: Distribution of the overall COD/ mass removal (kg COD/m^3 of feed wastewater) between treatment steps in Configurations A and B.

	Configuration	
	A	**B**
EPC reactor	12000	10500
UV/H_2O_2 reactor	1500	-
Biological reactor	-	3000

Sludge separation and activated carbon units were also accounted for in the investment costs, provided by manufacturers. To separate the precipitate sludge from the treated wastewater after the EPC reaction, the considered hypotheses were ultra-filtration and dissolved air flotation. Both these operations involve sludge treatment costs that were included in the operational costs.

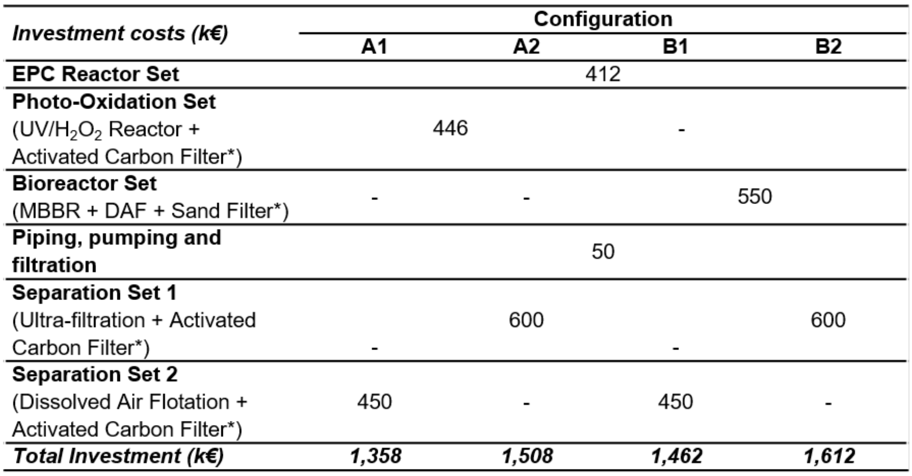
The summary of the operational and investment cost estimates associated with each configuration is presented in Table 5 and Table 6.

Table 5.5: Operational wastewater treatment costs for Configurations A and B (N. A. – not applicable).

Operational Unit and Parameter		**Cost in Configuration A**	**Cost in Configuration B**
EPC Reactor	**Electricity at the EPC**	0.003 €/kg COD removed	0.004 €/kg COD removed
	Chemicals at the EPC	0.736 €/kg COD removed	0.736 €/kg COD removed
	EPC maintenance	0.056 €/kg COD removed	0.049 €/kg COD removed
	Total	0.79 €/kg COD removed	0.80 €/kg COD removed
		9.47 €/m^3 treated WW	8.35 €/m^3 treated WW
UV/H_2O_2 Reactor	**Total (Chemicals + Electricity)**	1.83 €/kg COD removed	N.A.
		2.75 €/m^3 treated WW	
Biological Reactor	**Total**	N.A.	1.13 €/kg COD removed
			3.40 €/m^3 treated WW
Total Cost		2.62 €/kg COD removed	1.93 €/kg COD removed

Reviewing the operational and investment costs associated with each configuration, the winning configuration to be installed at the pharmaceutical site is option B. The revamped WWTP will operate in coordination with the wastewater segregation plan to treat it more efficiently and at an overall lower cost

Table 5.6: Investment costs for Configuration A and B with two sludge separation and polishing options (sets 1 and 2).



Investment costs (k€)	**Configuration**			
	A1	**A2**	**B1**	**B2**
EPC Reactor Set	412			
Photo-Oxidation Set (UV/H_2O_2 Reactor + Activated Carbon Filter*)	446		-	
Bioreactor Set (MBBR + DAF + Sand Filter*)	-	-	550	
Piping, pumping and filtration	50			
Separation Set 1 (Ultra-filtration + Activated Carbon Filter*)	-	600	-	600
Separation Set 2 (Dissolved Air Flotation + Activated Carbon Filter*)	450	-	450	-
Total Investment (k€)	***1,358***	***1,508***	***1,462***	***1,612***

than those of the present operation.

5.5.2 Soft Gains and Payback Period

The economic analysis carried out in subsection 5.5.1 made it possible to validate the best configuration for the new WWTP to be installed, which will keep up with the site's expansion plan and guarantee environmental compliance and the best practices in liquid waste management.

The evaluation of soft gains allows the estimation of the payback period and will validate 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.

One of the issues identified in section 1.2, in relation to improvement possibilities, was the shipping of streams with high solvent content to external incineration, due to the thermo-oxidizer already operating at full capacity, and the high proportion of the steam produced at the thermo-oxidizer being used at steam stripping column.

In line with the projected wastewater segregation plan, this analysis included the redirection of medium solvent streams ($<$25% vol/vol solvents) to be treated in the steam stripping column, with the streams now being shipped for external incineration being instead treated at the thermal oxidizer. The variation in the amount of steam produced at the utilities system (with natural gas boilers) was also accounted for.

The summary of waste management costs for 2016, according to the existing WWTP, are presented in Table 5.7. The summary of the projected costs for the waste management to be implemented, considering the 2016 waste streams, are presented in Table 5.8.

Table 5.7: Waste management costs summary for 2016 – Present WWTP.

Fiscal Year: 2016	**Capacity (m^3/year)**	**Cost (k€)**
,34 *Thermal-Oxidizing Treatment*	6652	1223,97
Steam Stripping	67805	579
Waste Shipped to external incineration	897	157,16
Total		**1957,47**

Table 5.8: Waste management costs summary for 2016 – Future WWTP.

Fiscal Year: 2016	**Capacity (m^3/year)**	**Cost (k€)**
Thermal-Oxidizing Treatment	2593	477,13
Steam Stripping	4956	42,12
Waste Shipped to external incineration	67805	835,25
Total		**1354,64**

The estimated soft gains for the year of 2016, when comparing the future treatment with the present treatment are 603,000€. This value considers a treatment capacity of 240 m^3/day and a wastewater with 10500 mgO_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 € and soft gains of 603,000€, the future WWTP will have a payback time of two to three years. This WWTP will operate according to the schematics of Figure 5.5, processing in the EPC reactor up to 500 m^3/day of wastewater with up to 15000 mgO_2/L of COD at 1.93€/kg COD removed. The design will be done to guarantee environmental compliance.

6

General Discussion and Conclusions

The challenge presented by the pharmaceutical industry that funded the EPC Pilot Project, was to validate the EPC technology as a suitable wastewater pollutant elimination technology and to pre-design an industrial WWTP capable of treating the site's wastewater to guarantee environmental compliance, regardless of the wastewater high variability, and at the same time guarantee the destruction of residual API.

After a total of 80 trials testing the site's real effluent, using all the possible treatment combinations the pilot's rig allowed, data was processed to assess the performance of the central EPC reactor, as well as to decide on the best use of complementary equipment. In addition to the basic trials, the EPC reactor was also used for API degradation trials and robustness trials to validate treatment robustness when faced with strong inlet wastewater load variations and to confirm the API degradation capacity.

Presently the site's WWTP performs a wastewater pre-treatment based on solvents separation by steam stripping with their subsequent destruction with energy recovery in a thermo-oxidizer. The latter also treats high solvent content liquid effluents. The wastewater presents an average COD of 10135 mgO_2/L with a discharge flow rate of 240 m^3/day. This project aimed to increase the treated COD load and flow rate (daily, 500 m^3 with a target degradation of 7500 kg of COD) when assessing the best treatment setup.

The wastewater's organic content was efficiently degraded, with an average degradation of 72 % of the COD load entering the EPC reactor and the remaining content being removed by solid-liquid separation, up to 97% overall removal. The effluent became about 89% more biodegradable after the treatment, going from moderately biodegradable to readily biodegradable. The effluent also became 95% less toxic either to aquatic environment indicator organisms or to aerobic microbial biomass. The removal efficiencies for the remaining relevant quality parameters achieved the objectives set in the technology acceptance criteria.

After the analysis of investment and operational costs and treatment scenario projections, the proposed revamping of the site's WWTP includes an EPC reactor as a primary treatment and a biological reactor as a secondary treatment, with the possibility of reclaimed water reutilization for the refrigeration water circuit. An equalization step to the different wastewater inputs must be included to guarantee a consistent effluent quality and flow rate at the inlet of the WWTP.

Considering the site's needs and treatment costs, other electrochemical equipment did not perform at the EPC level. The treatment is economically viable and impacts positively on the overall waste management strategy, as it frees some of the steam (presently reserved for the steam stripping column) to be used in the production buildings, and also frees some capacity on the thermo-oxidiser unit (as 20% of the capacity is currently occupied with the destruction of the gaseous outlet of the steam stripping column). Furthermore, the decrease in the steam requirements and the water saving derived from the possibility of water reutilization will translate in soft gains and a more sustainable operation at the pharmaceutical site.

Future steps at the site's wastewater management system will revamp the wastewater drainage system and implement segregation strategies that will allow the collection of wastewater in different buffer tanks according to its COD load and subsequent equalization prior to its feeding into the new WWTP.

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