Ana Carolina Lopes Oliveira

TREATMENT OF LIQUID PHARMACEUTICAL INDUSTRY EFFLUENTS BY FENTON'S PROCESSES

Master dissertation in Industrial Pharmaceutical Chemistry, supervised by Professor Doctor Jorge António Ribeiro Salvador and Professor Doctor Rosa M. Quinta-Ferreira and submitted to the Faculty of Pharmacy, University of Coimbra

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TREATMENT OF LIQUID PHARMACEUTICAL INDUSTRY EFFLUENTS BY FENTON'S PROCESSES

Dissertation by

ANA CAROLINA LOPES OLIVEIRA

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“The illiterates of XXI century will not be those who can’t read and write, but those who can’t learn, forget what they have learned and learn again.”

Alvin Toffler

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RESUMO:

O crescente desenvolvimento industrial levou a uma crescente produção de poluentes que ameaçam gravemente o ecossistema. Em particular, a indústria farmacêutica produz águas residuais com compostos de elevada complexidade e potencialmente perigosos quando lançados diretamente para os cursos de água provocando toxicidade aquática, desenvolvimento e resistência de bactérias patogénicas e genotoxicidade. Portanto, a eliminação de resíduos farmacêuticos nos efluentes deve ser encarada como um passo essencial no circuito do medicamento (produção). Deste modo, é necessário desenvolver tecnologias eficazes para o seu tratamento e/ou recuperação tendo em conta as normas ambientais atuais. Os processos biológicos convencionais são de difícil aplicação dada a forte toxicidade e baixa biodegradabilidade das espécies químicas que tipicamente caracterizam estes efluentes. Assim, esta dissertação teve como objetivo de estudo avaliar a eficiência de remoção de fármacos através de processos de oxidação avançada (POAs). Utilizando do Processo de Fenton Heterogéneo efetuou-se o estudo cinético da remoção de matéria orgânica presente num efluente farmacêutico real usando catalisadores óxidos mássicos nos quais o ferro é suportado, com resultados apreciáveis na oxidação catalítica por Peróxido de Hidrogénio. Este processo permite a eliminação do problema associado à separação de lamas de ferro do processo de Fenton Homogéneo. Deste modo realizou-se o “screening” de quatro catalisadores, comerciais e preparados no laboratório, N-150, Fe-Ce-O 70/30, Rocha Vulcânica Vermelha, e ZVI (ferro de valência zero) concluindo-se que o Fe-Ce-O 70/30 é o catalisador que proporciona melhores resultados experimentais no “Dark-Fenton”, obtendo-se 34%; 59% e 66% para a remoção de TPh, COD e TOC respetivamente. Estudou-se também a influência do pH e verificou-se que este parâmetro afeta a eficiência da degradação da matéria orgânica, considerando como ótimo o pH 3. Foram realizados ensaios de Foto-Fenton, onde o catalisador Rocha Vulcânica Vermelha obteve melhores resultados, 49%; 80% e 40% para a remoção de TPh, COD e TOC respetivamente. Além disso, verificou-se uma diminuição significativa na lixiviação de metal ativo com a utilização de radiação UV. Foram ainda realizados testes de biodegradabilidade que demonstraram a eficiência deste sistema catalítico na obtenção de um efluente passível de ser posteriormente depurado eficientemente por processos biológicos.

ABSTRACT:

The growing industrial development is leading to the production of contaminants that are seriously threatening the ecosystems. Especially pharmaceutical industry that produces residual waters containing high complexity compounds, which are potentially dangerous when sent directly to the waters courses, causing aquatic toxicity, development of resistance on pathogenic bacteria and genotoxicity. Therefore, the elimination of pharmaceutical residua in the effluents must be looked at as an essential step in medicine circuit (production). This way, it is necessary to develop effective technologies for their treatment and/or recovery considering the existing environmental regulations. The traditional biological processes are usually not efficient given the strong toxicity and low biodegradability of the chemical species that generally characterize these effluents. This way, this dissertation aimed to evaluate the drugs removal efficiency through Advanced Oxidation Processes (AOP).

Heterogeneous Fenton's Process was used to perform the kinetic study of the organic matter removal in an actual pharmaceutical effluent, by using mass oxide catalysts with iron over solid support, with interesting results in catalytic oxidation by Hydrogen Peroxide.

This process allows the problem's elimination associated to separation of iron sludge of Fenton Homogeneous' process. This way, the screening of four catalysts, commercial and laboratory prepared, was performed, involving N-150, Fe-Ce-O 70/30, Red Volcanic Rock, and ZVI (zero valent iron) being concluded that Fe-Ce-O 70/30 is the material that offers best experimental results in Dark-Fenton, getting 34%; 59% and 66% of TPh, COD and TOC's removal, respectively. It was also studied the pH influence and it came to notice that this parameter affects the organic matter degradation efficiency, considering pH 3 as optimal. Experiments of Photo-Fenton were also performed, where Red Volcanic Rock catalyst, had the best results, 49%; 80% and 40% concerning TPh, COD and TOC removal, respectively. Moreover, there was a significant reduction in the active metal leaching with the use of UV radiation.

Tests of biodegradability were made that showed the efficiency of this catalytic system in getting an effluent able of a posterior efficient purification by biological processes.

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1 INTRODUCTION:

This dissertation’s first chapter refers environmental problems related with liquid effluents and the most common treatment technologies with special focus on wastewaters originated in the pharmaceutical industry. In this context, the advanced oxidation processes (AOPs) are described as viable alternative in prejudice of classical biological sludge systems, with special attention to Fenton and Photo-Fenton systems. Finally, the aims and thesis’ structure are presented.

1.1 ENVIRONMENTAL PROBLEM

Despite the fact that pharmaceutical compounds concentration in the hydric system is only of a few traces, its continuous introduction may, in long term, become a potential risk to aquatic organisms and Man. This way, the concern regarding the presence of these toxic substances in environment has been increasing since early 90’s, as well as the need to analyze the inherent risks [71].

Except for antibiotics, most pharmaceutical compounds are chemical substances made by Man, and are therefore not found in Nature. Hence, if its presence is detected in the environment, it can only come from human or veterinarian usage. The main sources for human usage pharmaceutical compounds, in the hydric system are: its excretion after usage, the inappropriate destruction of non – used drugs and, to a smaller scale, the wastes and spilling during its production [71].

The drugs that are not removed in the wastewater treatment plants (WWTP) end up being unloaded along with the treated effluents, this way polluting rivers, firths, lakes and also, although rarely, subterraneous water and drinking water. Since these compounds are bio-refractory they are not destroyed in the WWTP, but can be partially transferred to the mud which is generally applied in agriculture, with the risk of contamination of the soil, and maybe leaching to surface water as well as getting infiltrated, endangering underground water quality [37].

Environmental concern is not necessarily related with the high volume of production of a certain drug compound, but its remaining in the ecosystems and its critical biological activity, resulting on high toxicity and potential to create effects on key biological processes, such as reproduction. According to FILHO (2007), beyond drugs remaining in environment, other problem comes from the fact that these have been produced to unchain specific physiologic effects. Although some pharmaceuticals concentrations are low, their combination can have strong effects due to the mechanism of synergetic action [40].

A large amount of drugs from different types (lipid regulators, antipyretics, analgesics, antibiotics, antidepressants, oral contraceptives, chemotherapeutic agents and others) are widely consumed all over the world [100].

A pharmaceutical industry that includes different types of production processes, such as fermentation, chemical synthesis, extraction and formulation, usually creates a highly resistant and variable effluent (in concentration of organic matter and in volume) considering the production process that was used and the season of the year which difficult the applicability of the traditional biological systems. This way, it is necessary a former chemical treatment, particularly for effluents coming from antibiotics' production, which contain high bio-inhibiter compounds concentrations reducing the direct use of classical biological purification technologies [11].

Drugs and metabolites destiny and behaviour in the aquatic environment have not yet been deeply explored. The reduced volatility of the compounds states that its distribution in the surroundings is done, mainly, by water dispersion or through the food chain [93].

There are a large number of original articles and comments from different authors concerning the occurrence and quantity of pharmaceutical compounds marked in hydric systems. According to FENT *et al*. (2006), about 80 to 100 drugs and their metabolites are found on both effluents and superficial water. These compounds are mainly detected on nanograms and micrograms scale per liter (ng-µg/L). However, this can be sufficient to induce toxic effects [37].

1.2 MOST COMMON TECHNOLOGIES FOR EFFLUENTS TREATMENT

A rising subject in environmental and engineer science is the development of processes, which promote the definite removal of drugs from industrial wastewaters, before ecosystems contamination. Since common water and effluents treatment are unable to destroy definitely persevering compounds, it is necessary to introduce additional advanced treatment technologies [5], [6], [50], [69], [76], [128].

Figure 1.1 shows the different treatment industrial effluent treatment.

Definitely, treatments based on biological processes are most commonly used, since they allow handling large masses of effluents transforming the toxic organic compounds into CO_2 and H_2O (or CH_4 and CO_2), with relatively low costs. The ability for certain microorganisms to degrade toxic organic substances is a well-documented fact [17].

Biological systems are based on the use of interest toxic compounds as substrate for organisms growth and maintenance. Depending on the electron's receiver nature, the bioprocesses may be divided into aerobia and anaerobia. While in the former, which lead to CO_2 and H_2O, the electron receiver is molecular oxygen in the latter, CO_2 and CH_4, are produced in the absence of

O_2. Some carbon forms, sulphur and nitrogen may participate as electron receivers (ex.NO_3^-,SO_4^{-2}, CO_2) [63], [127].

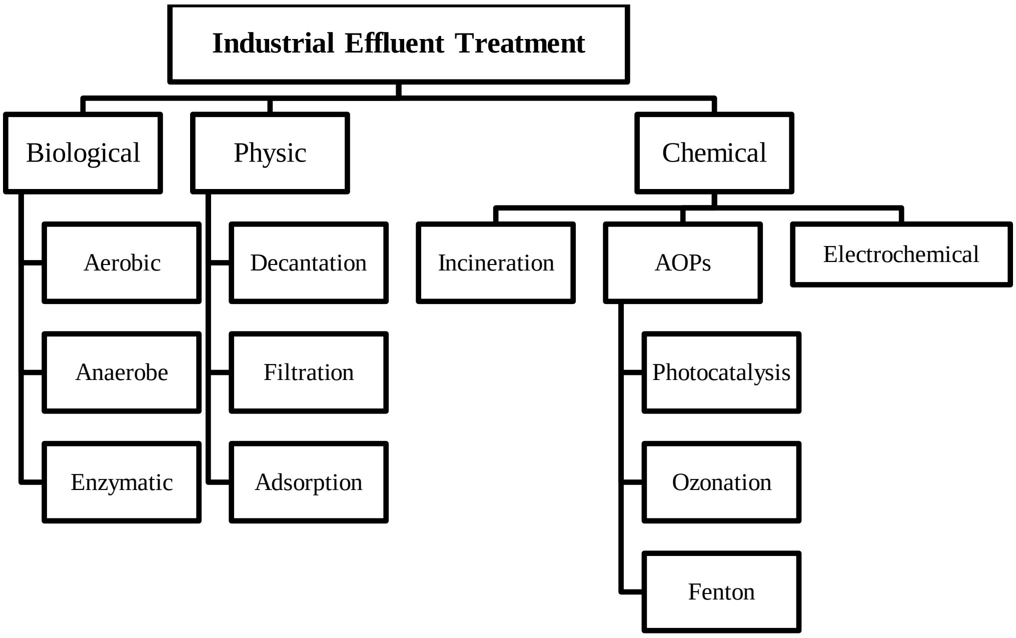

Figure 1.1 – **Organogram of types of effluent treatments.**

These methods are widely used in industrial effluents treatment. Meanwhile, these systems have some inconvenient issues such as: a) its implementation requires a large territory area, specially for aerobic technologies; b) the difficulty in controlling the microorganisms population, which requires a thorough maintenance of best pH conditions, temperature and nutrients since environment changes also produce changes in microorganisms' metabolism; c) there is the need for a fairly long time in order the effluents may reach the demanded patterns. Besides, small differences in compound structure or effluents composition are quite significant for a certain biological system to work properly. Due to this, microorganisms may not recognize some substances and subsequently will not degrade them, or yet, they may transform them into more toxic products [17].

In this context, the development of alternative techniques, with high efficiency in destroying recalcitrant pollutant at the lowest cost, has grown in last years [127].

There are two important elimination processes in industrial effluents treatment: adsorption on suspended solids and biodegradation. Adsorption depends of the drugs characteristics (hydrophobicity and electrostatic interactions), and that way drugs will or will not get associated to particles or microorganisms. Drugs with an acid character, such as some nonsteroidal antiinflammatory drugs (NSAIDs) (acetylsalicylic acid, ibuprofen, ketoprofen, naproxen, diclofenac, indomethacin), with a pKa that goes from 4.9 to 4.1, as well as chlofibric[1] acid and bezafibrate[2] (pKa 3.6), occur as ions in neutral pH. In those conditions, these compounds have a negative charge; therefore, they will be preferably in the effluents dissolved phase. For those species, sorption[3] does not seem to be relevant [18], [78]. However, drugs of a basic and amphoteric[4] character can be adsorbed in activated sludge in a significant way as, for example, antibiotics of fluoroquinolones' group [53].

In general, during the treatment, the micro pollutant biological decomposition, including drugs, increases with hydraulic retention time and with sludge's age. For example, diclofenac presents a significant biodegradability only when mud retaining time is superior to 8 days. As a counterpart, METCALFE et al. (2003) indicate that regardless hydraulic retaining time, compounds with a low index of biodegradability, such as carbamazepine, are only removed in very low quantities (usually less than 10%) [97].

Recalcitrant organic pollutants' removal, such as drugs, present in water and liquid effluents, can be obtained using advanced treatment technologies instead that are to be approached along this dissertation. Such treatment technologies can eliminate potentially dangerous compounds through mineralization or conversion into less harmful products to human health and aquatic environment [84].

1.3 ADVANCED OXIDATIVE PROCESSES

Chemical oxidation is a process that shows great potential in treating effluents comprising non-biodegradable toxic compounds. Conventional oxidative processes use oxygen, ozone, chlorite, sodium hypochlorite, chlorine dioxide, potassium permanganate and hydrogen peroxide, as oxidative agents [57] but there are a number of compounds resistant to such direct action. In these cases, the use of Advanced Oxidative Processes (APOs) becomes necessary. These systems generally involve the generation of hydroxyl radicals which present a quite elevated oxidative potential (2.06V) and are capable of reacting with almost every type of organic compounds. If the oxidative extension is enough, it can even reach a total mineralization into CO_2, H_2O and inorganic minerals [101].

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[1] is biological active chlofibrate's metabolite (from fibric acid used in hyperlipoproteinemia type III and hypertriglyceridemia severe treatment)

[2] Bezafibrate is a cholesterol reducer; triglyceride reducer; (from **f**ibric acid; fibrate).

[3] Absorption and adsorption happen simultaneously.

[4] Amphoteric, according to Bronsted-Lowry acid – base theory, is the substance that has the ability to behave as an acid or as a base, depending on other reagent's presence.

These are non-selective processes for they degrade innumerous compounds regardless of the presence of others. Hydroxyl radicals can be produced by reactions with strong oxidant, as previously quoted and now described, ozone (O_3) and hydrogen peroxide (H_2O_2); semiconductors, such as titanium dioxide (TiO_2) and zinc oxide (ZnO); and ultraviolet radiation (UV) [87]. Processes that present solid catalysts are called heterogeneous, while others are referred as homogenous. The main AOPs systems are presented on Figure 1.2.

AOPs present some advantages that go through polluter's mineralization and not only through phase's transfer; they are used on effluent hard removing compounds (refractive compounds to other treatments), and transform those cumbersome species into biodegradable moieties; they can be used associated to other processes (pre and post treatment); have a strong oxidative capability, with high reaction kinetics; if enough harsh conditions are used, they mineralize contaminants and do not form sub products; usually they improve the organoleptic qualities of the treated water; in many cases, they use less energy (when compared with other treatments), leading to minor costs; and allow the treatment in situ [7], [8], [9], [69].

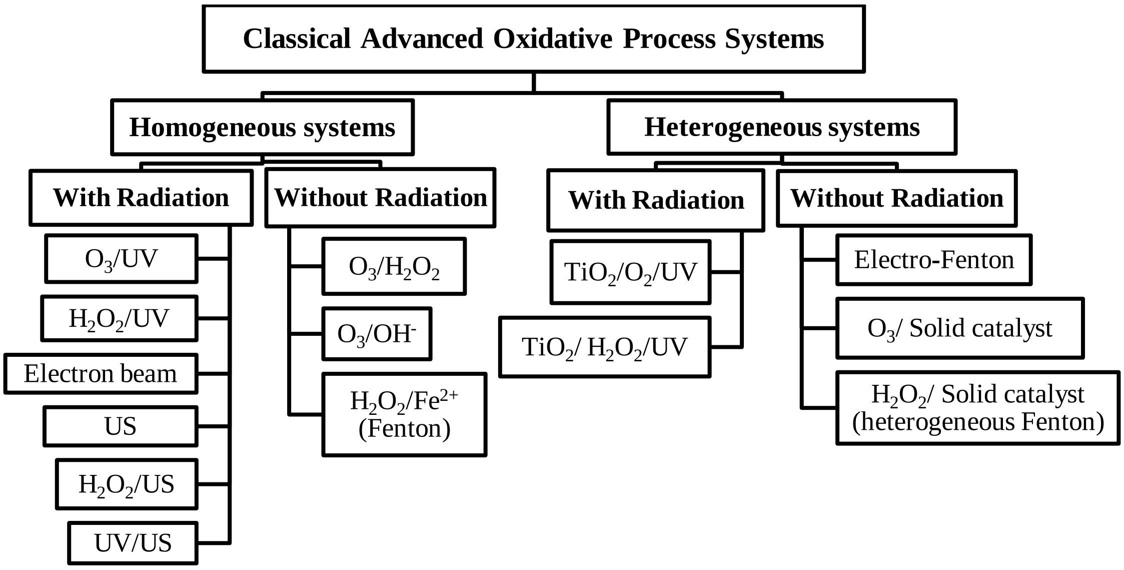

Figure 1.2 – Organogram of Classical Advanced Oxidative Process Systems. (Source: HUANG *et al.*, 1993).

One has to add that main benefits of advanced oxidative processes are related to the possibility of carrying out polluters' degradation in low concentrations, and the easiness in combining with other processes such as biological and activated charcoal adsorption, adding to the fact that these processes are conducted at ambient pressure and temperature [7], [8], [9], [69].

Hydrogen peroxide is one of the most versatile oxidant, surpassing chloride, chloride dioxide and potassium permanganate. When used along with catalytic agents (iron compounds, UV light, semiconductors, etc.) it can be converted into hydroxyl radicals (•OH) whose reactivity is only lower to that of fluorine [7], [8], [9], [69].

Table 1.1 shows the oxidation potential of most important oxidative agents.

Table 1.1 – Main oxidant agents' oxidation potential (Source: MARTINEZ, *et al.*, 2001.)

OXIDATIVE AGENT	OXIDATIVE POTENTIAL (EV)
Fluoride	3.00
Hydroxyl radical (•OH)	2.80
Ozone	2.10
Hydrogen peroxide	1.80
Potassium permanganate	1.70
Carbone chloride	1.50
Chlorine	1.40

The advanced oxidative processes (AOPs) are based on hydroxyl (•OH) free radical formation, highly reactive, with a superior oxidation potential than ozone and slightly inferior to fluorine. These species are non-selective, acting as an intermediate oxidant agent with a semi-lifetime that rounds milliseconds. Due to its high reduction standard potential (Equation 1), it is capable of oxidizing a large variety of organic compounds to carbon dioxide, water and inorganic ions that come from heteroatoms [72], [102].

$$^{\bullet}OH + e^{-} + H^{+} \rightarrow H_{2}O \qquad E^{0} = 2,730V \qquad \text{Equation 1}$$

Hydroxyl radicals are strong oxidatives, that react with most of the organic contaminants, with a controlled diffusion limit. The most common mechanism for oxidation through hydroxyl radicals is by electrophilic addition at unsaturated compounds or aromatics, while hydrogen separation usually occurs with saturated compounds [136].

Hydrogen peroxide is used to form hydroxyl radicals; meanwhile, it is necessary to add activators, such as iron minerals, ozone and/or ultraviolet light, in order to enhance that production. The free radicals (HO•) formed attack the organic compounds and may lead to their fully oxidation, producing CO_2 and H_2O. Nevertheless, in some situation, a partial oxidation can be the main route usually reaching more biodegradable by-products [83].

Fenton's reaction (H_2O_2+Fe^{2+}) is among the most promising advanced methods for effluents improvement degradation. This process will be discussed in the following section [90].

1.3.1 H_2O_2 / FE^{2+} (FENTON)

In 1876, H.J.H. Fenton watched for the first time highly oxidative properties of a hydrogen peroxide and Fe^{2+} ions solution [38]. Many organic molecules could be easily oxidized by using this reagent without the use of high pressure or temperatures and complex equipment's were not needed. Fenton's reaction is defined nowadays as a "hydroxyl radicals catalytic generation from chain reaction between iron ion (Fe^{2+}) and hydrogen peroxide (H_2O_2), in an acid environment, creating CO_2, H_2O and inorganic minerals as final result" [31], [36], [41], [51].

According to FLOTRON et al. (2005), Fenton's reagent can be used in treating aromatic hydrocarbons, meaning low biodegradability polluters. Its application is well accepted because involves a low cost and simple operation with advanced oxidative potential, hydroxyl radicals formation in aqua solution [42].

NOGUEIRA et al. (2007) refer that hydroxyl radicals are formed in reactions that result from the combination of metallic ions or semiconductors with oxidants such as ozone and hydrogen peroxide with or without ultraviolet (UV) or visible (Vis) radiation. With Fenton's reaction, Equation 2, one can observe that hydroxyl radical is produced throughout H_2O_2 decomposition catalyzed by ferrous ions; these moieties are the oxidative specie involved in this process, able to react with several types of organic compounds in a spontaneous reaction that occurs in the dark [102].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad Equation\ 2$$

The formed hydroxyl radicals can oxidize Fe (II) ion leading to Fe (III) Equation 3:

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \qquad Equation\ 3$$

Protons are added so that there is water formation, Equation 4:

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow Fe^{3+} + 2H_2O \qquad Equation\ 4$$

This equation shows that Fenton's reaction depends on solution's pH. Only under acid conditions does HO• becomes the predominant reactive oxidant [25], [39].

The ferrous ions that are formed can further dissociate H_2O_2, always depending on pH, as can be seen in Equations 5 to 9, also leading to iron ions and other radicals:

$$Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^+ \qquad Equation\ 5$$

$$FeOOH^{2+} \rightarrow Fe^{2+} + OH_2^{\bullet} \qquad \textit{Equation } 6$$

$$Fe^{2+} + OH_2^{\bullet} \rightarrow Fe^{3+} + OH_2^{-} \qquad \textit{Equation } 7$$

$$Fe^{3+} + OH_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+} \qquad \textit{Equation } 8$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad \textit{Equation } 9$$

As one can see in reaction 9, hydrogen peroxide can also act as a scavenger of hydroxyl radical, forming peroxyl radical ($HO_2^{\bullet}$), that has a smaller oxidation potential (1.42V) than the hydroxyl radical ($^{\bullet}OH$) (2.730V), harming the efficiency of the degrading process. That occurs when there is an excess of hydrogen peroxide, since in this case Fe^{2+} concentration is low when compared to Fe^{3+}. In fact the reaction between Fe^{3+} and H_2O_2 (Equation 5) is slower than the decomposition of hydrogen peroxide in presence of Fe^{2+} (Equation 3). The negative effect of H_2O_2 excess in degrading organic compounds demands an extra attention when defining its proper concentration [39], [102].

According to AGUIAR et al. (2007), hydroxyl radical high reactivity leads to rapid and unspecified reactions with different substrates. If Fe^{3+} is used instead of Fe^{2+} and hydrogen peroxide in excess, other minor oxidative potential radicals are also formed, such as peroxyl radical ($HO_2^{\bullet}$) and the superoxide anion ($O_2^{\bullet}$). The hydroxyl radical can act as an electrophile or a nucleophile, attacking organic molecules by hydrogen exit or connecting into multiple bounds and aromatic rings (hydroxylation), even in replaced positions, leading to reactions such as demethoxylation, dehalogenation, dealkylation, denitration, deamination and decarboxylation [1].

Despite the higher reaction velocity between Fe^{2+} and hydrogen peroxide, the use of Fe^{3+} is more convenient because, in this state of oxidation, iron is more abundant, which leads to costs reduction. H_2O_2 decomposed by Fe^{3+} creates reduced Fe^{2+}, according to Equations 10 and 11, that also react with H_2O_2 [89], [91].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \qquad \textit{Equation } 10$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+} \qquad \textit{Equation } 11$$

Since both Fe^{2+} and Fe^{3+} ions are coagulants[5], Fenton's reagent can have both functions oxidization and coagulation in the treatment processes. One of the benefits in using Fenton's

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[5] Coagulants are all products, natural or chemical, used to condense liquids, separating their solid phase.

reagent is the fact that there is no unwanted halogenated compounds formation during the oxidation process [72].

The use of iron minerals to catalyst decomposition of hydrogen peroxide is a low cost solution compared to other advanced oxidation processes, since it uses a residue from steel production industries (ferrous sulphate) [27].

An important advantage is that Fenton's reagent is easy to apply on effluents treatment, since the reaction occurs at ambient temperature and pressure, involves safe and easy to handle reactants, not requiring special equipment and can be implemented with a great variety of compounds. Besides, iron is the fourth most abundant element on earth's surface [89], [91].

It has been said above that hydroxyl radicals are the species that begin organic compounds oxidation in Fenton's reaction. However, some studies have suggested other oxidizing species, such as high valence iron intermediates, like FeO^{3+} and ferrite ion FeO^{2+} (it has colour and presents itself as a viable alternative to treatment of several effluents) [89], [91].

Fenton's reaction can be used as the only effluents' treatment in a specific case or it can be integrated into an overall purifying system (pre or post). There are several facts that have influence into the degradation rate, such as contaminant's chemical structure, pH, iron and hydrogen peroxide concentration and organic charge [102]. Oxidation efficiency depends on the environment reaction conditions, and it is very important to study factors such as: reagents dosage, ratio between oxidant and catalyst load, catalyst type, time of reaction, environment's pH and temperature [15].

Fenton's system may have different treatment functions, depending on H_2O_2/Fe^{2+} ratios. When the Fe^{2+} amount surpasses that of hydrogen peroxide, the system tends to have a chemical coagulation effect. With an inverted H_2O_2/Fe^{2+}, chemical oxidation effect is stronger [72], [101].

The dosage level among reagents to be properly used is different according to the type of affluent. Classical margin to H_2O_2/Fe^{2+} relation is 5:1 up to 25:1 in mass [15], [73]. Reaction velocity increases with temperature rising. Nevertheless, when temperature rises above 40-50ºC, H_2O_2 usage efficiency decreases due to high dissociation in H_2O and $O_{2.}$ Most reactions with Fenton's process occur at temperatures between 20 and 40ºC [2]. Reaction time depends on variables such as temperature and reactants' dosage. The oxidation treatment end is governed by the relation between hydrogen peroxide and substrate (organic compound), and the rate of oxidation is determined by the initial iron concentration and by temperature [15], [73].

The main limitation/ disadvantage of the Fenton's process is the narrow pH gap in which degradation efficiency is maximum (3 to 4). However, this can be solved by adding organic iron complexes that stabilize iron in a wider pH interval [102]. The reaction's pH is more important since some factors depend on it. One of them is the used reagents' stability, hydrogen peroxide and ferrous ions are more stable in acid pH [80]. At alkaline conditions, hydrogen peroxide decomposes into H_2O and O_2 which reduces its oxidation's potential. Hydroxyl radicals' oxidation decreases too with pH's increase. Some authors have proved that to near 3 pH, radical •OH is the most active specie in degrading organic compounds. Optimum pH gap for reaction is between 3 and 4 [2].

It is convenient to mention that, although Fenton's reagent is very efficient in some cases, its usage leads to an additional step, which is the destruction of the formed iron minerals. This way, usually, a strong base is added that leads to iron precipitation for further removal [89], [91].

1.3.2 H_2O_2 / FE^{2+}/ UV (PHOTO-FENTON)

The process that combines hydrogen peroxide with ultraviolet radiation is more productive than the use of each of them separately. That happens due to high hydroxyl radicals' production, extremely oxidative. According to HUANG et al (1993) and LEGRINI et al (1993), most common accepted mechanism for photolysis of H_2O_2 with UV is molecule break into hydroxyl radicals with an income of two •OH for each H_2O_2 molecule (Equation 12). However, it must be taken under consideration that there is also the possibility of these radicals' recombination, transforming into H_2O_2 again (Equation 13) [68], [86].

$$H_2O_2 \rightarrow 2^{\bullet}OH \qquad \textit{Equation } 12$$

$$2^{\bullet}OH \rightarrow H_2O_2 \qquad \textit{Equation } 13$$

There are some available articles quoting the exclusive usage of UV/ H_2O_2 oxidation process for organic compounds degradation, such as methyl terc – butyl ether (MTBE) and dyes or as a pre treatment to increase surfactants[6] biodegradability [70].

Organic compounds' oxidation under UV radiation in the presence of ferrous ions in an acid environment was tested in the 50's, when it was discussed the hypothesis that an electronic transfer initiated by radiation resulted in •OH creation, responsible for oxidation reactions. The formation of •OH from Fe (III) species' photolysis was also observed in oxidation processes of atmospheric water and in aquatic environment, considered responsible for hydrocarbon's oxidation. In an aqua solution, ferrous ions exist as aqua – complexes, for example $[Fe(H_2O)_6]^{3+}$. With pH increase, hydrolysis takes place creating hydroxyl species, whose proportion depends of pH. First hydrolysis balance is represented in Equation 14. Ultra violet irradiation increases contaminant's degradation quantity, mainly because it stimulates Fe^{3+} to Fe^{2+} reduction [10]. This process is called Photo-Fenton and it is demonstrated in Equation 15:

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[6] Compounds that diminish liquid's surface tension and interfacial tension between two liquids, or between a liquid and a solid. Surfactants can act as detergents, moistening, emulsifiers and dispersants.

$$Fe^{3+} + H_2O \xrightarrow{luz} Fe\ \ OH\ ^{2+} + H^{+} \qquad \textit{Equation } 14$$

$$Fe^{3+} + H_2O \xrightarrow{luz} Fe^{2+} + {}^{\bullet}OH + H^{+} \qquad \textit{Equation } 15$$

According to BACARDIT et al. (2007), the presence of inorganic ions, such as chlorite or sulphate, can reduce the oxidation process efficiency based on hydroxyl radical [10]. These anions can “lock” hydroxyl radical, producing less reactive anionic radicals, which may react with hydrogen peroxide. Chloride’s interaction in Fenton’s mechanism can be from Fe^{2+} to Fe^{3+} with Cl^{-} complexation, according to Equation 16 to 19, or hydroxyl radical’s “capture” (Equation 20), which can lead to $Cl^{\bullet}$ radicals production, less reactive than hydroxyl radical[10]:

$$Fe^{2+} + Cl^{-} \leftrightarrow FeCl^{+} \qquad \textit{Equation } 16$$

$$FeCl^{+} + Cl^{-} \leftrightarrow FeCl_2^{0} \qquad \textit{Equation } 17$$

$$Fe^{3+} + Cl^{-} \leftrightarrow FeCl^{2+} \qquad \textit{Equation } 18$$

$$Fe^{3+} + 2Cl^{-} \leftrightarrow FeCl_2^{+} \qquad \textit{Equation } 19$$

In presence of Cl^{-}radical •OH is captured [10]·

$$Cl^{-} + {}^{\bullet}OH \rightarrow\ ClOH\ ^{\bullet -} \qquad \textit{Equation } 20$$

When studying chloride anions (Cl^{-}) effect in Photo-Fenton’s process, MACHULEK et al., (2007) concluded that keeping pH close to 3 during reaction made the process suffer no changes. However, with different pH from 3 negative effect of Cl^{-} ions increased reducing Fenton’s process efficiency [90].

Fe^{2+} originated during radiation reacts with, hydrogen peroxide, according to Fenton’s reaction (Equation 21). Here, reaction is catalytic and a cycle is established at which Fe^{2+} is regenerated. The use of $Fe^{2+/3+}$ in hydrogen peroxide’s presence under radiation is then referred as Photo-Fenton’s reaction [90].

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \qquad \textit{Equation } 21$$

Fenton and Photo-Fenton processes are catalyzed by Fe^{2+}/Fe^{3+} ions, and if we consider that these ions are hydrolyzed and form insoluble hydroxides, environment's pH has a very important role in involved reactions, which affects organic compounds' degradation velocity. pH's limited gap is due to Fe (III) precipitation when pH is above 3, besides hydrogen peroxide is less stable for higher pH drastically reducing H_2O_2 interaction and, subsequently, •OH production. Below pH equal to 2.5 degradation velocity decreases since H^+ high concentrations in solution lead to hydroxyl radicals consumption according to Equation 22 [90].

$$^{\bullet}OH + H^{+} + e^{-} \rightarrow H_2O \qquad \textit{Equation } 22$$

Using Fenton or Photo-Fenton's heterogeneous process with immobilized iron in membranes or other supports presents its advantages, such as iron reuse, avoiding iron removal procedures, since iron's limit within an effluent is approximately $15mg.L^{-1}$ [90].

Whenever hydrogen peroxide is used, alone or combined with UV or iron minerals, it must be used in a proper amount in order not to create residua (unnecessary expense). It is important to quote that hydrogen peroxide can interfere with some analyses, as in Chemical Oxygen Demand (COD) [90].

1.4 OBJECTIVES OF THE THESIS:

This work's main objective is to evaluate solid catalysts' efficiency in order to purify liquid effluents in pharmaceutical industry through Fenton and Photo-Fenton heterogeneous' processes.

Specific objectives:

Catalysts preparation and selected catalyst's characterization;

Degradation study of a real wastewater containing several pharmaceutical origins (unknown) through hydrogen peroxide catalytic oxidation in a batch reactor;

Process's treatment analysis through pH variation and different catalysts, presence and absence of light in the removal of Total Phenol Content's (TPh), Chemical Oxygen demand (COD) and Total Organic Carbon (TOC) depletion;

Discussion about the possibility of integrating this process with biological methods of treatment through the analysis of the effluents biodegradability.

1.5 THESIS' STRUCTURE

In order to contextualize this thesis, this first chapter focuses on environmental problems related to pharmaceutical effluents, being discussed the reasons why their treatment is so important and why to choose advanced oxidative processes (Fenton and Photo-Fenton).

Chapter 2 presents a global sight of what is written in scientific literature, state of art, about some drugs (therapeutic class), and average concentrations they occur at several matrixes (sewer, surface water, effluents) in different countries. It also overviews the application of advanced oxidative processes on the degradation of some of those drugs.

Chapter 3 describes the methodologies involved in the study. Experimental equipment description, procedure and analysis methods to infer the process efficiency such as TOC, COD, TPh and BOD_5 removal. Catalyst characterization and the actinometrical procedure used in Photo-Fenton are also described in this chapter.

Chapter 4 discusses the results obtained through the oxidation study. More specifically it shows the raw effluent's characterization and catalysts screening, as well as the analysis of the pH influence in the Fenton process.

Main conclusions from the work and suggestions for forthcoming investigation are described in chapter 5.

2 STATE OF THE ART:

This chapter describes what is found in scientific literature about some drugs (therapeutic class), and their occurrence in several matrixes (sewer, surface water, effluents) in different countries. It also shows advanced oxidative processes applied to some drugs degradation.

Demographic growth and industrial expansion brought contamination scenarios of soil and hydric resources all over the world. That is leading to environment deterioration and to the need to revert or minimize that process [45].

In the 70's, the presence of drugs in aqua environment became known. Since then, there have been made several studies which reveal the presence of drugs' residua in liquid effluents in several parts of the world. Water contamination by drugs is worth special attention since the risks to human health and aqua environment are not completely identified. First studies about the presence of drugs in environment were made by GARRISON and assistants [45] and HIGNITE AND AZARNOFF [64]. They detected the presence of clofibric acid, clofibrate, etofibrate in $\mu g\ L^{-1}$ concentrations, at a Water Residua Treatment Station (WRTS) in the United States.

The main way for drugs residua to enter the environment is through domestic sewer draining, treated or not, in watercourses. However, pharmaceutical industry effluents, rural effluents and the inadequate dumping of out of date drugs must also be taken under consideration [16], [58], [60].

Most drugs that arrive to WRTS come from human or veterinarian metabolic excretion. These residua follow with rough sewer to WRTS where they are, in most cases, submitted to traditional treatment processes. Nevertheless, these processes are mainly based on contaminants biological degradation, and are not efficient on completely removing these cumbersome compounds due to their biocide action and complex chemical structures that cannot be easily bio-degraded, as has been proved by several studies that show the presence of this type of contaminant in WRTS effluents [8], [14], [19], [22], [24], [46], [64] [88], [126], [129].

Different class drugs, such as antibiotics, hormones, lipid-lowering, anti-inflammatory, analgesic, among others, are frequently detected on domestic sewers, surface and underwater in concentrations around $ng.L^{-1}$ to μgL^{-1} in several parts of the world (Table 2.1).

Table 2.1 – **Drugs concentration's average in aqua environment.**

DRUG (therapeutic class)	CONCENTRATION (µg L-1)	MATRIX	REFERENCE
Amoxicillin (antibiotic)	0.013	Rough sewer/Italy	Castiglioni et al., 2009
Atenolol (β-blocker)	0.49	Rough sewer / Italy	Castiglioni et al., 2009
	0.28	WRTS effluent/Italy	Castiglioni et al., 2009
	0.050	Surface water/ Italy	Calamari et al., 2003
	0.30	Rough sewer /Sweden	Bendz et al., 2005
	0.16	WRTS effluent / Sweden	Bendz et al., 2005
Bezafibrate (lipid-lowering)	0.54	WRTS effluent /France	Andreozzi et al., 2003
	0.30	WRTS effluent Italy /	Andreozzi et al., 2003
	0.070	WRTS effluent /Canada	Gagné et al., 2006
	0.42	Rough sewer /Finland	Lindqvist et al., 2005
	1.2	Rough sewer /Brazil	Stumpf et al., 1999
	0.18	Surface water / Brazil	Stumpf et al., 1999
	2.2	WRTS effluent / Germany	Ternes, 1998
	0.35	Surface water / Germany	Ternes. 1998
Carbamazepine (anticonvulsant)	1.7	Rough sewer / Sweden	Bendz et al., 2005
	1.2	WRTS effluent / Sweden	Bendz et al., 2005
	1.0	WRTS effluent / France	Andreozzi et al., 2003
	1.0	WRTS effluent Greece	Andreozzi et al., 2003
	0.38	WRTS effluent / Italy	Andreozzi et al., 2003
	0.085	WRTS effluent /Canada	Gagné et al., 2006
	2.1	WRTS effluent / Germany	Ternes. 1998
	0.25	Surface water / Germany	Ternes. 1998
	0.50	Rough sewer /Spain	Santos et al., 2005
	0.48	WRTS effluent /Spain	Santos et al., 2005
Tetracycline (antibiotic)	0.010	Surface water / Italy	Calamari et al., 2003
	0.11	Surface water /USA	Kolpin et al., 2002

DRUG (therapeutic class)	**CONCENTRATION** (µg L-1)	**MATRIX**	**REFERENCE**
KETOPROFEN (ANTI-INFLAMMATORY)	0.94	Rough sewer / Sweden	Bendz et al., 2005
	0.33	WRTS effluent / Sweden	Bendz et al., 2005
	0.81	WRTS effluent /France	Andreozzi et al., 2003
	2.0	Rough sewer /Finland	Lindqvist et al., 2005
	0.15	Rough sewer /Brazil	Stumpf et al., 1999
	0.22	Surface water / Brazil	Stumpf et al., 1999
	0.20	WRTS effluent /Germany	Ternes. 1998
	1.1	Rough sewer /Spain	Santos et al., 2005
	0.98	WRTS effluent /Spain	Santos et al., 2005
CIPROFLOXACIN (ANTIBIOTIC)	0.26	Rough sewer /Italy	Castiglioni et al., 2009
	0.097	WRTS effluent / Italy	Castiglioni et al., 2009
	0.060	WRTS effluent /France	Andreozzi et al., 2003
	0.070	WRTS effluent /Greece	Andreozzi et al., 2003
	0.030	WRTS effluent / Sweden	Andreozzi et al., 2003
	0.37	WRTS effluent /Switzerland	Golet et al., 2001
	0.020	Surface water /USA	Kolpin et al., 2002
DICLOFENAC (ANTI-INFLAMMATORY)	0.16	Rough sewer / Sweden	Bendz et al., 2005
	0.12	WRTS effluent / Sweden	Bendz et al., 2005
	0.33	WRTS effluent / France	Andreozzi et al., 2003
	0.84	WRTS effluent /Greece	Andreozzi et al., 2003
	2.47	WRTS effluent / Italy	Andreozzi et al., 2003
	0.35	Rough sewer /Finland	Lindqvist et al., 2005
	0.40	Rough sewer /Brazil	Stumpf et al., 1999
	0.020	Surface water /Brazil	Stumpf et al., 1999
	0.81	WRTS effluent / Germany	Ternes. 1998
	0.15	Surface water / Germany	Ternes. 1998
	2.9	Rough sewer /Brazil	Ghisele. 2006
	1.8	WRTS effluent /Brazil	Ghisele. 2006
	4.0	Surface water /Brazil	Ghisele. 2006
17 A-ETHINYL ESTRADIOL (CONTRACEPTIVE HORMONE)	0.073	Surface water /USA	Kolpin et al., 2002
	0.001	WRTS effluent / Germany	Ternes et al., 1999
	0.009	WRTS effluent /Canada	Ternes et al., 1999
	0.005	Rough sewer /Brazil	Ternes et al., 1999
	5.8	Rough sewer /Brazil	Ghisele, 2006
	5.0	WRTS effluent /Brazil	Ghisele, 2006

DRUG (therapeutic class)	**CONCENTRATION** (µg L-1)	**MATRIX**	**REFERENCE**
GENFIBROZIL (LIPID-LOWERING)	0.71	Rough sewer / Sweden	Bendz et al., 2005
	0.18	WRTS effluent/ Sweden	Bendz et al., 2005
	0.70	WRTS effluent /France	Andreozzi et al., 2003
	0.71	WRTS effluent /Greece	Andreozzi et al., 2003
	2.14	WRTS effluent / Italy	Andreozzi et al., 2003
	0.071	WRTS effluent Canada	Gagné et al., 2006
	0.40	Rough sewer /Brazil	Stumpf et al., 1999
	0.048	Surface water /USA	Kolpin et al., 2002
IBUPROFENO (ANTI-INFLAMMATORY)	3.6	Rough sewer / Sweden	Bendz et al., 2005
	0.15	WRTS effluent / Sweden	Bendz et al., 2005
	0.92	WRTS effluent / France	Andreozzi et al., 2003
	0.050	WRTS effluent /Greece	Andreozzi et al., 2003
	0.070	WRTS effluent / Italy	Andreozzi et al., 2003
	0.79	WRTS effluent /Canada	Gagné et al., 2006
	13.1	Rough sewer /Finland	Lindqvist et al., 2005
	0.60	Rough sewer /Brazil	Stumpf et al., 1999
	0.19	Surface water /Brazil	Stumpf et al., 1999
	0.37	WRTS effluent / Germany	Ternes et al., 1999
	0.070	Surface water / Germany	Ternes et al., 1999
	0.20	Surface water /USA	Kolpin et al., 2002
	54.2	Rough sewer /Brazil	Ghisele. 2006
	48.4	WRTS effluent /Brazil	Ghisele. 2006
	3.7	Rough sewer /Spain	Carbala et al., 2004
	1.3	WRTS effluent /Spain	Carbala et al., 2004
PROPRANOLOL (B-BLOCKER)	0.050	Rough sewer / Sweden	Bendz et al., 2005
	0.030	WRTS effluent / Sweden	Bendz et al., 2005
	0.030	WRTS effluent /France	Andreozzi et al., 2003
	0.010	WRTS effluent /Greece	Andreozzi et al., 2003
	0.040	WRTS effluent / Italy	Andreozzi et al., 2003
	0.17	WRTS effluent / Germany	Ternes et al., 1999
	0.010	Surface water / Germany	Ternes et al., 1999
NAPROXEN (ANTI-INFLAMMATORY)	3.7	Rough sewer / Sweden	Bendz et al., 2005
	0.25	WRTS effluent / Sweden	Bendz et al., 2005
	1.1	WRTS effluent /France	Andreozzi et al., 2003
	2.0	WRTS effluent / Italy	Andreozzi et al., 2003

DRUG (therapeutic class)	**CONCENTRATION (µg L-1)**	**MATRIX**	**REFERENCE**
NAPROXEN (ANTI-INFLAMMATORY) CONTINUATION	0.27	WRTS effluent /Canada	Gagné et al., 2006
	4.9	Rough sewer /Finland	Lindqvist et al., 2005
	0.60	Rough sewer /Brazil	Stumpf et al., 1999
	0.020	Surface water /Brazil	Stumpf et al., 1999
	0.30	WTRS effluent / Germany	Ternes et al., 1999
	0.070	Surface water / Germany	Ternes et al., 1999
	4.7	Rough sewer /Spain	Santos et al., 2005
	1.5	WRTS effluent /Spain	Santos et al., 2005
SULFAMETHOXAZOLE (ANTIBIOTIC)	0.080	WRTS effluent / France	Andreozzi et al., 2003
	0.090	WRTS effluent /Greece	Andreozzi et al., 2003
	0.010	WRTS effluent / Italy	Andreozzi et al., 2003
	0.020	WRTS effluent /Sweden	Andreozzi et al., 2003
	0.049	WRTS effluent /Canada	Gagné et al., 2006
	0.58	Rough sewer /Spain	Carbala et al., 2004
	0.25	WRTS effluent /Spain	Carbala et al., 2004
	0.40	WRTS effluent / Germany	Hirsch et al., 1999
	0.41	Underwater/ Germany	Sacher et al., 2001
	0.05	Surface water /USA	Stackelberg et al 2004
TRIMETHOPRIM (ANTIBIOTIC)	0.080	Rough sewer/ Sweden	Bendz et al., 2005
	0.040	WRTS effluent/ Sweden	Bendz et al., 2005
	0.030	WRTS effluent /France	Andreozzi et al., 2003
	0.080	WRTS effluent /Greece	Andreozzi et al., 2003
	0.070	WRTS effluent / Italy	Andreozzi et al., 2003
	0.065	WRTS effluent /Canada	Gagné et al., 2006
	0.15	Surface water /USA	Kolpin et al., 2002
	0.32	WRTS effluent /Germany	Hirsch et al., 1999

Studies show that drugs concentration levels found in aqua environments are related to population consumption pattern, by removal tax in WRTS, by the kind of effluent that ports at WRTS and by season’s hip [25], [27].

Drugs used in therapeutics, after working in the organism, can be excreted as metabolites, hydrolyzed or in its original form. They can also be conjugated with polar molecules such as glucuronides. However, these conjunctions are easily cleaved by applying pharmacologically active substances into domestic sewers [37], [59].

Once in environment, drugs' destiny depends on their structural characteristics and chemical – physical properties, such as photo sensibility, biodegradability and lipophilicity.

LAM and MABURY (2005) studied the following drugs photo degradation**:** lipid-lowering, carbamazepine (anticonvulsant), levofloxacin and sulfamethoxazole (antibiotics**)** and proposed that photo transformation reactions are an important factor in limiting these drugs persistence in surface water, either by direct or indirect photolysis by reacting with reactive species (hydroxyl radicals, for example) [81].

Some drugs, such as acetylsalicylic acid and caffeine are biodegradable and, therefore, removed from WRTS with efficiency, reaching removal percentages of 99, 9% [59], [116]. Penicillin is also hard to find in environment, due to their β-lactam ring chemical instability, which makes it susceptible to hydrolysis and biodegradation by microorganisms that have a β-lactamase enzyme [64].

Synthetic estrogens and tetracycline (antibiotic) tend to be adsorbed to WRTS slime and / or sediments, due to their high lipophilicity and the formation of sediment with calcium [60], [64], [62].

Biological processes are most frequently used because they allow large volumes treatment, can reach high organic matter removal and they cost relatively low. However, some compounds are recalcitrant and can even be toxic to microorganisms. Studies on drugs biodegradability have shown removal taxes around 50% in activated slime traditional systems [29], [111].

Phase transfer of the contaminant characterizes physical processes (decantation, filtration, and adsorption), without the compound being really eliminated. On other hand, they are usually very efficient, and can be useful as pre or post treatment [44].

Chemical processes are based on contaminant' oxidants by reaction with strong oxidants, such as hydrogen peroxide (H_2O_2), chlorite (Cl_2), chlorine dioxide (ClO_2) and permanganate (MnO_4^-).In most cases, however, using this kind of treatment does not promote total mineralization of pollutants to CO_2, and there is formation of great variety of degradation sub products, usually organic acids (oxalic acid, formic and acetic acid). In case of Cl_2, there is formation of organochlorine compounds, which can be more toxic than former contaminants, making it inconvenient for a proper treatment [133].

Drugs removal efficiency in WRTS depends on the chemical and physical properties of each compound. Different studies show that these compounds' elimination is usually incomplete with an unsteady removal percentage. For example, anticonvulsant carbamazepine has a 7% removal, while acetylsalicylic acid (analgesic) reached 99% in WRTS in Germany [128]. This fluctuation in removal percentage was also observed in WRTS in Finland, where diclofenac got a 26% removal and ibuprofen 92% [88].

The presence of drugs in WRTS effluents is the reflex of the removal methods' low efficiency through traditional treatment processes, which claims for the research for more effective methods, able to promote contaminants mineralization or, at least, its transformation into products that do not represent hostile effects to the environment.

Drugs amoxicillin, bezafibrate, paracetamol [132] and tetracycline's [13] degradation were studied in WRTS effluents using the Photo-Fenton's process under solar radiation. There was over 95% degradation for all drugs in 5 minutes, highlighting the importance of this process to drugs degradation in this matrix.

The use of UV radiation lamps was also efficient to pharmaceuticals degradation, such as Diclofenac [114], metronidazole [122] and sulfamethoxazole [54], showing Photo-Fenton's versatility in different sources of radiation use.

Beside works quoted in literature, several others approach drugs' degradation by Advanced Oxidation Process (AOPs). Table 2.2 presents a compilation of some of these works.

Table 2.2 – **Advanced Oxidative Processes applied to drugs' degradation**

DRUG	**AOP**	**REFERENCE**
AMOXICILLIN	O_3	Andreozzi et al., 2005
	Fe^{3+}, FeOx/ H_2O_2/ UV, solar	Trovó et al., 2008
BEZAFIBRATE	O_3	Dantas et al., 2007
	O_3, O_3/ H_2O_2	Huber et al., 2003
	TiO_2/ UV	Lambropoulou et al., 2006
	Fe^{3+}, FeOx/ H_2O_2/ UV, solar	Trovó et al., 2008
CARBAMAZEPINE	O_3, O_3/ UV, H_2O_2/ UV	Gerbhardt et al., 2007
	O_3/ H_2O_2	Huber et al., 2003
	H_2O_2/ UV	Vogna et al., 2004
DIAZEPAM	O_3, O_3/ UV, H_2O_2/ UV	Gerbhardt et al., 2007
	O_3/ H_2O_2	Huber et al., 2003
DIPYRONE	Fe^{2+}/ H_2O_2/solar	Pérez-Estrada et al., 2006
	TiO_2/solar	
DICLOFENAC	TiO_2/ UV	Calza et al., 2006
	Fe^{2+}/ H_2O_2/solar	Pérez-Estrada et al., 2005
	Fe^{3+}/ H_2O_2/UV	Ravina et al., 2002
	Fe^{2+}/ H_2O_2	Packer et al., 2003
	O_3, O_3/ UV, H_2O_2/ UV	Gerbhardt et al., 2007
	O_3, O_3/ H_2O_2	Zwiener et al., 2000
	H_2O_2/ UV	Vogna et al., 2004

Table 2.2 – **Advanced Oxidative Processes applied to drugs' degradation (continuation)**

DRUG	**AOP**	**REFERENCE**
17 A-ETHINYL ESTRADIOL	TiO_2/UV	Coleman et al., 2004
	O_3/ H_2O_2	Huber et al., 2003
IBUPROFEN	O_3/ H_2O_2	Zwiener et al., 2000; Huber et al., 2003
	Fe^{2+}/ H_2O_2	Packer et al., 2003
IOPROMIDA	O_3	Huber et al., 2005
	O_3/ H_2O_2, O_3/ UV	Ternes et al., 2003
METRONIDAZOLE	H_2O_2/ UV	Shemer et al., 2006
	Fe^{2+}/ H_2O_2	
	Fe^{2+}/ H_2O_2/ UV	
NAPROXEN	O_3	Huber et al., 2005
	H_2O_2/ UV	Pereira et al., 2007
	Fe^{2+}/ H_2O_2	Packer et al., 2003
PARACETAMOL	O_3, H_2O_2/ UV	Andreozzi et al., 2003
	Fe^{3+}, FeOx/ H_2O_2/ UV, solar	Trovó et al., 2008
RANITIDINE	TiO_2/ UV	Addamo et al., 2005
	Fe^{2+}/ H_2O_2	Abellán et al., 2007
SULFAMETHAZINE	TiO_2/ UV ZnO/ UV	Kaniou et al., 2005
SULFAMETHOXAZOLE	TiO_2/ UV	Abellán et al., 2007
	Fe^{2+}/ H_2O_2/ UV	González et al., 2007
	O_3	Ternes et al 2003
	O_3/ H_2O_2	Huber et al., 2003
TETRACYCLINE	H_2O_2/UV	Kim et al., 2009
	TiO_2/ UV	Reyes et al., 2006 Addamo et al., 2005
	Fe^{3+}, FeOx/ H_2O_2/ UV, solar	Bautitz et al., 2007

Under an operational point of view, AOPs can be applied to drugs residua degradation in WRTS exit as well as in final water treatment process steps.

Drugs degradation through AOPs, as well as direct photolysis (which depends of each compound absorbency), involves several different stages and several reactions that result in different sub products, which can be more or less toxic when compared to the original drug. These intermediates can, or not, maintain functional activity of the original compound.

Since several intermediates can be formed during treatment, it is important to identify a degradation route as well as to evaluate their toxicity and destiny in the environment. One of the parameters that allow evaluating intermediates' toxicity is biodegradability, which is given by the ratio between biochemical oxygen demand after 5 days and chemical oxygen demand (BOD_5/COD).

Intermediates' toxicity and biodegradability of sulfamethoxazole [54] ($200mg.L^{-1}$) antibiotic were determined after photo-Fenton's process appliance. The BOD_5/COD results showed that by increasing the H_2O_2 dose from 50 to $550mg.L^{-1}$ during treatment, there was an increase in biodegradability. Another relevant data was that for the smallest dose H_2O_2 ($50mg.L^{-1}$) there was an increase in solution's toxicity, which indicates that under such condition more toxic intermediates were formed than the original drug.

In sulfonamide's degradation, sulfadiazine, sulfamerazine**,** sulfadimethoxine sulfathiazole, by heterogeneous photocatalysis, it was seen that all these molecules follow the same degradation mechanism ,that is, hydroxyl radical's attack to aromatic ring with one or two hydroxisulfonamides formation, or S-N bound break and subsequent sulphate ions release [20].

In synthetic estrogen diethylstilbestrol (DES) degradation's, the complex Fe (III)-oxalate presence under radiation was evaluated. Three main intermediates were formed, being that an OH group to the aromatic ring created one of them. Later, degradation followed two different reaction mechanisms, which resulted in DES-4-semiquinone and DES-o-quinone formation [138].

Heterogeneous photocatalysis and photo-Fenton's process under solar radiation were applied to stable 4-Methylaminoantipyrin intermediate degradation formed during dipyrone analgesic hydrolysis [107]. After treatment by heterogeneous photocatalysis 12 degradation products were identified, formed from aromatic ring hydroxylation and pyrazole ring's opening. No intermediate was detected in the Photo-Fenton's process and it presented a 5 times larger efficiency than heterogeneous photocatalysis.

Different advanced oxidative processes (ozonation, H_2O_2/UV, etc) were applied to several drugs mixture (carbamazepine, acid clofibric, diclofenac, sulfamethoxazole, ofloxacin and propranolol) and after a short exposure time to these processes (3-5 min), solution containing with created metabolites presented less toxicity when compared to the original solution [5].

As a counterpart, when evaluating antiepileptic carbamazepine degradation after the process H_2O_2/UV appliance, a series of acridines was obtained as intermediates [134]. Acridines present mutagenic and carcinogenic activity and the possibility of its formation, even residual, can make the process' application not viable.

Based in the presented results, treatment processes improvement is imperious to assure total mineralization of target compounds, this way reducing toxic intermediates formation.

CONCLUSIONS:

To summarize, different therapeutics class drugs, used both in human and veterinarian medicine, are excreted in its original form or as metabolites. These residua can contaminate aquatic environment if they are not natural biodegraded or efficiently removed in treatment stations. Advanced Oxidation Processes (AOPs) are viable alternative when the contaminated matrix has a low organic concentration (hundreds of $mg.L^{-1}$) and pollutants are not biodegradable. Besides, they are adequate when classical treatment is not possible or not even appropriate. Treatment's efficiency depends on the matrix, contaminants, purpose of the treatment, volume to be treated, as well as other factors.

These substances continuous hauling to environment characterizes them as pseudo persistent, which may result in severe effects in aquatic environment and even to human health.

Different advanced oxidative processes applied to different therapeutics class drugs' degradation have been described. Despite these molecules complexity, low concentrations found allow these methodologies to be used, which reach high degradation efficiency, as some works have demonstrated.

3 EXPERIMENTAL METHODOLOGY:

This chapter refers to the preparation techniques and solid catalysts' characterization, oxidation tests procedures and analytical methods used to evaluate catalytic process.

3.1 CATALYST PREPARATION AND CHARACTERIZATION

Four distinctive catalysts were used in this work. One of them, the only commercial one, *Envicat® N-150* (Fe2O3-MnO*x*) was kindly provided by Süd-Chemie AG, Munich, Germany. Laboratory prepared catalyst was Fe-Ce-O (70/30), synthesized by co precipitation, through an aqua solution of precursor minerals, namely metallic nitrates, such as iron nitrate (Riedel-de-Häen) and cerium nitrate (Riedel-de-Häen). Its synthesis was performed with molar proportion defined in order not to surpass 15 g of minerals per 100 mL of water, and precipitated by adding 200 mL of NaOH solution at 3M (from NaOH with 98% of purity). Final precipitate was filtered and washed with 2.5 L of water, dried at 105 ºC, crushed and calcined at 300 ºC [124]. Commercially available red volcanic rock (abundant in nature) was also used as catalyst and its chemical composition, determined in our laboratory, is as follows: 6.31% of Fe; 0.03% of Cu; 0.02% of Zn; 0.44% of K; 1.54% of Na; 0.06% of Cr; 0.07% of Mn, 8.32% of Ca and 2.31% of Mg. ZVI particles, iron catalyst with zero valent state (low commercial value), were chemically composed by nearly 100% of Fe with some residual elements (Cu, Zn, K, Na, Cr, Mn, Ca and Mg) and it was supplied by a metallurgical industry in the area.

Selected catalysts were characterized before (fresh catalyst) and after (used catalyst) they were applied in the oxidation process.

3.2 COAGULATION PROCEDURE

Coagulation/flocculation procedure has in goal colloidal substances removal, that is, solid material in suspension and/ or dissolved. That operation is usually considered as pre treatment.

RITCHER & NETTO (2003) and CARDOSO (2007) say that coagulation is the process by which a coagulant agent added to water reduces forces that tend to keep solids in suspension separated forming larger particles that can sediment [23], [117].

Coagulation cancels repulsion forces between colloidal substances through connection and adsorption mechanisms in colloidal particle surface by adding chemical agents, called electrolytes. According to DI BERNADO & DANTAS (2005), in order for coagulation process to be efficient, it must be made through intense agitation (quick mixture) so that interactions between coagulant and water (effluent) can occur. Formation velocity for these flocks depends, in thermo agitation beginning (Brownian movement) and, by reaching around 0.1 mm size. Of course that mechanical agitation must be at a moderate level (slow mixture) for otherwise; it may cause already formed flocks' degradation, which will make their removal more difficult [33].

The coagulant that used in this work was p19, an acid coagulant (provided by Adventech), in 1:10 (10mL of p19 diluted into 100mL of water) proportion.

Coagulation trials were performed in a Jar-Test equipment with 600mL reactors, under constant agitation at 300rpm, for 5 minutes and, then agitation was reduced to 30rpm for 30 minutes.

Initially, 200mL of effluent and 7mL of coagulant were placed in 5 reactors. In one of them effluent's pH was kept (5.4) and for others pH was adjusted to values of 3; 5; 7 and 9 with H_2SO_4 or with NaOH. COD was evaluated.

After COD evaluation for the different pH conditions, procedure was repeated, keeping the pH value with a lower COD and placing different coagulant quantities 2mL; 3,5mL; 7mL; 10mL and 14mL. COD was evaluated again.

3.3 OXIDATION PROCEDURE

3.3.1 DARK FENTON´S TREATMENT

Heterogeneous Fenton experiment were made in batch 600 mL reactors, under constant 300rpm agitation, during a maximum of 120 minutes period. Initially, 200mL of real effluent was added and pH was adjusted with H_2SO_4 or NaOH. Later, previously defined catalyst quantity was added as the select iron source, and by last hydrogen peroxide, at 50%, was introduced in the desired concentration marking the beginning of the reaction. Samples were taken during time, at 0, 15, 30, 45, 60, 75, 90, 105 and 120 minutes. Each sample was filtered through a 0.45 μm filter and a certain volume of NaOH was added (In first experiments 1,5mL of $NaHSO_3$ were added to guarantee reaction's terminus) to end the reaction, in order to eliminate residual hydrogen peroxide that interferes with some analytical determinations. Later, samples were acidized for the analysis mentioned next. Along experiments, the following parameters were evaluated: Total Phenolic Content (TPh), Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC). Biological tests involving Biochemical Oxygen Demand (BOD_5), were made to previously selected samples. As many tests as necessary were made, in order to obtain agreeing values [96].

It should be noticed that some runs were performed under orbital agitation (Heidolph Reax 20) under constant 16rpm agitation, in 50mL reactors.

3.3.2 PHOTO FENTON´S TREATMENT

The Photo-Fenton’s installing process consisted of a magnetically agitated photo reactor (3L glass reactor), with a 9W black light (Phillips), axially placed inside a glass tube in the reactor. Glass tube with double wall was used to cool the lamp; the temperature was kept at 25 º C, through a thermo static bath. Preferred used lamp produces wave – length between 350-400nm. Equipment was covered with aluminum foil to avoid radiation leaks and to avoid external influences [105].

Heterogeneous Photo-Fenton’s experiments were made under constant agitation, during a maximum time of 120 minutes. First, 300 mL of real effluent were added and pH was adjusted, with H_2SO_4 or NaOH, to the given value. Hydrogen peroxide, at 50%, in desired concentration, was placed 30 minutes later (zero sample), and reaction began. Samples were taken through time, at 0, 30, 60, and 120 minutes. Each sample was filtered through a 0.45 μm filter and a certain volume of NaOH was added to end reaction, in order to eliminate residual hydroxide peroxide that interferes with some analyses. Later, the sample was acidized to perform further [96]. Along these experiments, the following parameters were evaluated: Total Phenol Content (TPh), Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC). Again, tests were repeated until agreeing values were obtained.

3.4 ANALYTICAL TECHNIQUES

3.4.1 COD - Chemical Oxygen Demand

Chemical Oxygen Demand (mg O_2 L^{-1}) is defined as the amount of oxygen used to chemically oxidize all the organic matter, and it is commonly used as an indirect measure for organic constituents in water. Residual COD was analyzed through *Closed Reflux Colorimetric Standard Method 5220D* [56], which involves a sample’s digestion in an acid environment for two hours in presence of dichromate de potassium dichromate (K2Cr2O7), a strong oxidative agent, and mercury sulphate as catalyst. During reaction, the organic compounds are oxidized and the orange colored dichromate ($Cr2O7^-$) is reduced to a green colored chromate (Cr^{3+}), which is colorimetrically detected. Reaction between chromate absorbance and COD is given by the device internal calibration, periodically verified, with a standard solution of potassium hidrogenophthalate.

The thermo reactor *WTW CR3000* was used as digester and the photometer *WTW MPM3000* was used to detect dichromate excess, with a double performance for each sample.

3.4.2 TPh - Total Phenol Content

Total Phenol Content **(**TPh) was colorimetrically analyzed through Foulin-Ciocalteau method [43]. 20 µL of the sample were introduced in a 2mL cuvette later diluted with 1.58mL distilled water. Next, 100 µL Foulin-Ciocalteau's reagent was added and after 3 to 6 minutes, 300µL of a Sodium Carbonate (Na_2CO_3) saturated solution. Cuvettes were placed in light's absence for 2 hours, and absorbance measured at 765nm through a *T60 PG Instruments* Spectrophotometer, against a blank that contained distilled water instead of a sample. Concentration's value is expressed in mg.L^{-1} equivalent to gallic acid, corresponding to a calibration curve, previously performed with different concentrations of this compound [94].

3.4.3 TOC - Total Organic Carbon

Total Organic Carbon is indirectly obtained from Total Carbon (TC) and Inorganic Carbon (IC) difference; first TC is measured, and then IC is determined. Samples were introduced by automatic injection in a suction tube, through an *auto-sampler Shimadzu ASI-5000A* which improves analyses' efficiency. Their measure was made with a *Shimadzu 5000 TOC Analyser* that works through the combustion/Infrared Analyses Method gas non-disperser (NDIR). This device uses ultra pure air (<1 mg $L^{-1}$of hydrocarbons), that in presence of a catalyst (platinum supported in alumina), oxidizes Total Carbon to CO_2 inside the reactor, being the carbon dioxide detected in NDIR. The resultant signal is electronically analyzed, and the area of its peak calculated that, in turn is proportional to Total Carbon concentration, corresponding to the value of a calibration curve which is obtained through several solutions, prepared with a standard solution with 2.125g Potassium hidrogenophthalate per distilled water liter. IC (Inorganic Carbon) is determined after the samples' injection in the IC reactor, where gas passes through an acid solution. IC contained is decomposed into CO_2 also detected in NDIR. The calculated peak area corresponds to the value of the calibration curve obtained by a standard solution with 3.500g of Sodium Hidrogenocarbonate 4.410g and of Sodium Carbonate per distilled water liter [125].

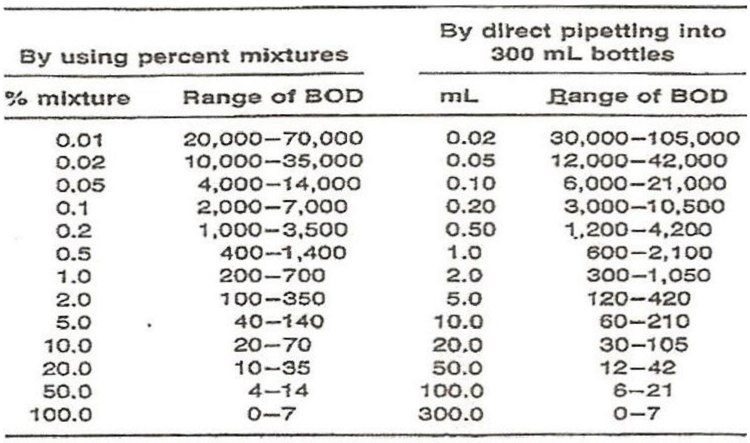
3.4.4 BOD_5 – Biochemical Oxygen Demand

Biochemical Oxygen Demand (mg O_2 L^{-1}) corresponds to the amount of oxygen used in organic matter degradation by biological processes action, at a medium temperature of 20ºC for 5 days and with adjusted pH between 6.5 and 8.5. BOD_5 was calculated by the difference of oxygen amount between the moment of preparation and after the incubation period. First, a mineralized solution was prepared (with a solution of hexahidrated ferric chloride, heptahydrate sulphate magnesium and Calcium chloride anhydrous), that was pumped with air in order to saturate it with oxygen. After that period, inoculum was prepared with organisms from earth and garden according to Standard Methods [56]. At each 300mL (V) erlenmeyer 300µL inoculums was placed, mineralized solution was added, a certain sample value (Vs), that depends of its COD value, and dissolved oxygen was measured (ODi) with the help of a *WTW Inolab 740*. Erlenmeyer's volume was made up and was closed to be isolated and without any air bubbles inside, with each rehearsal being performed in double. At incubation's end period (5 days) dissolved oxygen was measured again (ODf) and considering dilution made CBO_5 was calculated through equation 23. This procedure was also performed with a flask without sample (B), to take O2 used by inoculums endogenous' respiration value under consideration.

$$CBO_5 = \frac{(OD_I - OD_f) - (OD_I - OD_f)_B}{\frac{V_S}{V}} \qquad \text{Equation 23}$$

The range of BOD and the correlated volume needed are shown in Table 3.1

Table 3.1 – The amount of effluent sample to be used in the BOD_5 experimental procedure. (Adapted from Metcalf and Eddy, 2003)



By using percent mixtures		By direct pipetting into 300 mL bottles	
% mixture	Range of BOD	mL	Range of BOD
0.01	20,000–70,000	0.02	30,000–105,000
0.02	10,000–35,000	0.05	12,000–42,000
0.05	4,000–14,000	0.10	6,000–21,000
0.1	2,000–7,000	0.20	3,000–10,500
0.2	1,000–3,500	0.50	1,200–4,200
0.5	400–1,400	1.0	600–2,100
1.0	200–700	2.0	300–1,050
2.0	100–350	5.0	120–420
5.0	40–140	10.0	60–210
10.0	20–70	20.0	30–105
20.0	10–35	50.0	12–42
50.0	4–14	100.0	6–21
100.0	0–7	300.0	0–7

3.4.5 pH

pH was determined by the potentiometric method, using a pH measurer (*Crison micropH2000*), previously calibrated with buffer solutions of pH 4.0 and 7.0.

3.4.6 Residual hydrogen peroxide

Processes' efficiency was also evaluated by residual hydrogen concentration. Residual H_2O_2 analyses were performed through a colorimetric method, Peroxide Test Strip of Precision Laboratories, which presented a 1; 3; 10; 50 and 100ppm scale.

3.4.7 Effluent's biodegradability

In order to define or control an effluent's treatment process it is important to evaluate effluent's biodegradability connecting BOD_5 with COD, whose ratio may give an effluent's biodegradability reference:

$$\frac{BOD_5}{COD} = \text{biodegradability}$$

If biodegradability tends to 0 it is an effluent biologically hard to treat. If, by contrary, the value tends to 1 it is an effluent with some availability for biological treatment [35].

3.4.8 Actinometry

Actinometry is a classical method to determine radiation source's intensity. The main substance used is salt from Parker's actinometre, $K^3(Fe(C_2O_4)_3).3H_2O$ (tris (oxalate) ferrate (III), tri hydrate), a light green solid. Another substance commonly used is potassium ferrioxalate, since it is easy to handle with and sensible to a wide variety of wavelengths (254 to 500 nm). These crystals are prepared by mixing 500mL of 1.5M ferric chlorite (Riedel-de Haen) with 1.5L of potassium oxalate solution 1.5M (Panreac), at 60ºC. The resulting mixture is then cooled with an ice bath at 0ºC. This temperature is kept until salt's crystallization is complete. Next, final product is filtered through a disposable 0.45μm filter, washed with a small amount of cold water and a small cold methanol volume to remove excess of water. After that, the product is left in a desiccator to dry, kept in the dark to be protected from light. Finally, the obtained crystals are stored in a plastic flask covered with aluminum leaf to stop light from entering [99], [119], [120].

Next, 0.006 M solution is prepared through 2.947g of crystals dissolution in 100mL of H_2SO_4 (1N) (Panreac) and dissolved in distilled water until it makes 1L. This solution is then irradiated in the photo reactor under efficient agitation, for 3minutes. Then, 2.0 mL of irradiated solution is placed in a 10mL volumetric balloon, containing a 1.0mL mixture of 0.12% of 1.10-fenantrolina (Panreac) and 2.5mL of sodium acetate tampon solution (tampon solution: 600mL of 1.0M of sodium acetate solution (Riedel-de Haën), 360ml of 0.5M of H_2SO_4, diluted in a 1L balloon with distilled water), that is diluted with distilled water until it makes the necessary volume. The blank is prepared the same way; the only difference is that this one is not irradiated. Both solutions are kept in the dark (for about one hour) until color development reaches its full. Both samples' absorbance difference is measured at 510nm in a spectrophotometer [119], [120].

Through this actinometrical method of potassium ferrioxalate one can know radiation's flux intensity, where Fe^{3+} is photo chemically transformed into Fe^{2+} according to the equation 24:

$$2Fe^{3+} + C_2O_4^{2-} \longrightarrow 2Fe^{2+} + 2CO_2 \qquad \textit{Equation } 24$$

(The amount of produced Fe^{2+} is measured due to its with 1.10fenantrolina at 510nm.) [26].

Using the obtained absorbance, light intensity is calculated through the equation:

$$I = \frac{\Delta A.V_2.V_3}{\varepsilon.\Phi.d.t.V_1}$$

Where:

$I =$ light intensity (Einstein/min);

$\Delta A =$ the optical difference in absorbance (λ=510nm) between the irradiated solution and that taken in the dark;

$d =$ Width cell used to measure the absorbance (A);

$\varepsilon =$ is that of the complex $Fe(phen)_3^{2+}$ to 510nm ($\approx 1{,}11 \times 10^4 \, L/mol.cm$);

$\Phi =$ is the quantum yield of ferrous ion prodution at the irradiation wavelength;

$V_1 =$ is the aliquot of the irradiated solution taken for the determination of the ferrous ions;

$V_2 =$ is the irradiated volume (mL);

$V_3 =$ is the final volume after complrxation with phenanthroline (mL);

$t =$ the irradiation time (min).

3.4.9 Iron Leaching Measurement

Aiming to get iron leaching on long terms data, an experimental run was performed with the same characteristics of the others without stopping the reaction. Iron concentration in the liquid was determined by atomic absorption using a Perkin-Elmer 3300 spectrometer.

3.4.10 Suspended Solids

Before beginning experiments, porcelain capsules were washed and 45 ηm filters were humidified with distilled water. Later they were placed in the glasshouse at, approximately, 105º C in order to volatize volatile constituents present in both capsules and filter papers. Filter papers and porcelain capsules were weighted.

Afterwards, 50mL of effluent was filtrated at low pressure using the mentioned former paper filter. From the filtrate, 20mL were placed in a porcelain capsule. Paper filter was placed at 105ºC in glasshouse and the porcelain capsule in muffle at 600ºC for 1h-2h. After this, they were left in the dessicateur to cool and they were weighted again.

a) Total Solids (TS)

Inside of a crucible previously dried, a known volume of sample was taken to glasshouse at 105ºC until constant weight. Total solids are those that remain as residue after that procedure. With mass values from the crucible (with and without dried solids), TS may be calculated this way:

$$TS = M_1 - M_2$$

Equation 25 – Total Solids calculation. Where *M_1* is mass before evaporation and *M2* is mass after evaporation.

b) Total Fix Solids (TFS)

Total fixed solids are the portion remaining in the recipient even after calcination (made in a muffle, at 600ºC for two hours). With crucible's mass values before and after that stage, TFS can be calculated as follows:

$$TFS = M_2 - M_3$$

Equation 26 – Total fixed solids calculation. Where *M_2* is mass before calcinations and *M_3* is mass after calcinations.

c) Total Volatile Solids (TVS)

Total volatile solids constitute the part of total solids that volatize during calcination. TVS value is obtained through difference between total solids and total fix solids (TFS), as shown in equation below:

$$TVS = TS - TFS$$

Equation 27 – Total volatile solids' calculation.

d) Total Suspended Solids (TSS)

Suspended solids are those with diameter higher than 0.45µm. They correspond to the remaining residue over filter paper with pores diameter equal to 0.45µm after a known volume sample is filtered. With masses values from paper filters (dried in glasshouse at 105ºC for one hour) before and after containing the filtrate residua, TSS can be calculated this way:

$$TSS = P_1 - P_2$$

Equation 28 – Total suspended solids calculation. Where P_1 is mass from washed and dried paper filter before it contains the solids and P_2 is mass from dried paper filter after it contains the solids.

e) Fix Suspended Solids (FSS)

Fix suspended solids are the portion of total suspended solids that remain as residua in a crucible after calcination (600ºC for two hours). Through crucible's masses difference before and after calcination, fix suspended solids mass can be calculated through the equation below:

$$FSS = P_2 - P_3$$

Equation 29 – Fix suspended solids calculation. Where P_2 is dried crucible's mass before calcinations and P_3 is crucible's mass after calcinations.

f) Volatile Suspended Solids (VSS)

Volatile suspended solids are the filtered part of residua that volatizes during calcination (600ºC for two hours). Volatile suspended solids mass can be calculated through the following difference:

$$VSS = TSS - FSS$$

Equation 30 – Volatile suspended solid' calculation.

g) Total Dissolved Solids (TDS)

$$TDS = TS - TSS$$

Equation 31 – Total dissolved solids' calculation.

h) Fix Dissolved Solids (FDS)

$$FDS = TFS - FSS$$

Equation 32 – Fix dissolved solids' calculation.

i) Volatile Dissolved Solids (VDS)

$$VDS = TVS - VSS$$

Equation 33 – Volatile dissolved solids' calculation.

4 RESULTS AND DISCUSSION:

In this chapter, the industrial effluent is characterized and all the results are presented and discussed.

4.1 EFFLUENT'S CHARACTERIZATION

The real effluent in study was collected from a pharmaceutical industry and its composition is unknown. The plant synthesizes and produces active substances and develops formulas of several therapeutic classes.

Effluent's chemical characteristics are summed in the table 4.1.1, as well as the standard deviations associated to each analyses technique.

Table 4.1 – Chemical characteristics of the real liquid effluent in study with the corresponding experimental deviation presented in parenthesis

Characteristics	Values
COD (mg O_2 L^{-1})	9520 (± 10)
BOD_5 (mg O_2 L^{-1})	4710 (± 20)
BOD_5/COD	0.4
TOC (ppm)	5134 (± 10)
TPh (mg GA L^{-1})	211 (± 20)
pH	5.4

Liquid effluent treatments based on advanced oxidation process have as main goal to obtain an effluent that corresponds to discharge legal limits in the environment. When this is not possible or economically not viable, the targets become reducing its toxicity and increase its biodegradability. According to present environmental laws, an effluent must not have COD and BOD_5 values above 150mg O_2 L^{-1} and 40mg O_2 L^{-1}, respectively, to be released into surroundings.

The studied effluent presents a high organic charge, with COD of 9520 mg O2 L^{-1}, BOD_5 of 4710 mg O2 L^{-1} and TOC of 5134ppm (Table 4.1.1). Even if biodegradability is not so low (BOD_5/COD) = 0.4, as an effluent is considered to be completely biodegradable when this ratio is superior to 0.4 [35] it is known that it can not be directly subjected to biological treatment, sustaining the need to proceed to an oxidative chemical process. In fact, its cumbersome composition comprising highly toxic substances such as phenolic compounds (211 mg GA L^{-1}) which are known for being refractory and toxic to microorganisms, is continuously changing throughout time due to variations on the drugs being produced.

For effluents' directly release into the natural water courses, Decretory-Law nº 236/98 establishes limited emission values. The most commonly quoted and analyzed parameters are summed in the table 4.2.

Table.4.2 – Emission limit values (ELV) in residual water release

Parameters	**Results expression**	**ELV**
pH	Sorensen' Scale	6,0-9,0
Temperature	ºC	3ºC increase
BOD$_5$	mg O_2 L^{-1}	40
COD	mg O_2 L^{-1}	150
TSS	mg L^{-1}	60
Color	-	Not detectable in dilution 1:20
Odor	-	Not visible in dilution 1:20

4.2 PRELIMINARY EXPERIMENTS

4.2.1 Coagulation

The raw effluent presents brownish color, intense odor and suspended solids. This way, before the experimental procedure related to the study of the Heterogeneous Fenton's process behavior, coagulation tests and posterior suspended solids analyses were made.

In figure 4.1 it is possible to see a significant reduction of COD and TOC by placing 7mL (1g mL^{-1}) of coagulant p19 and pH 3.

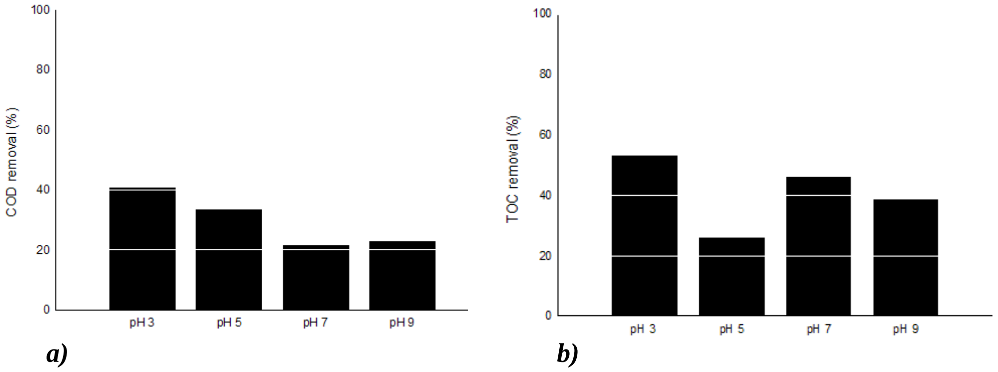
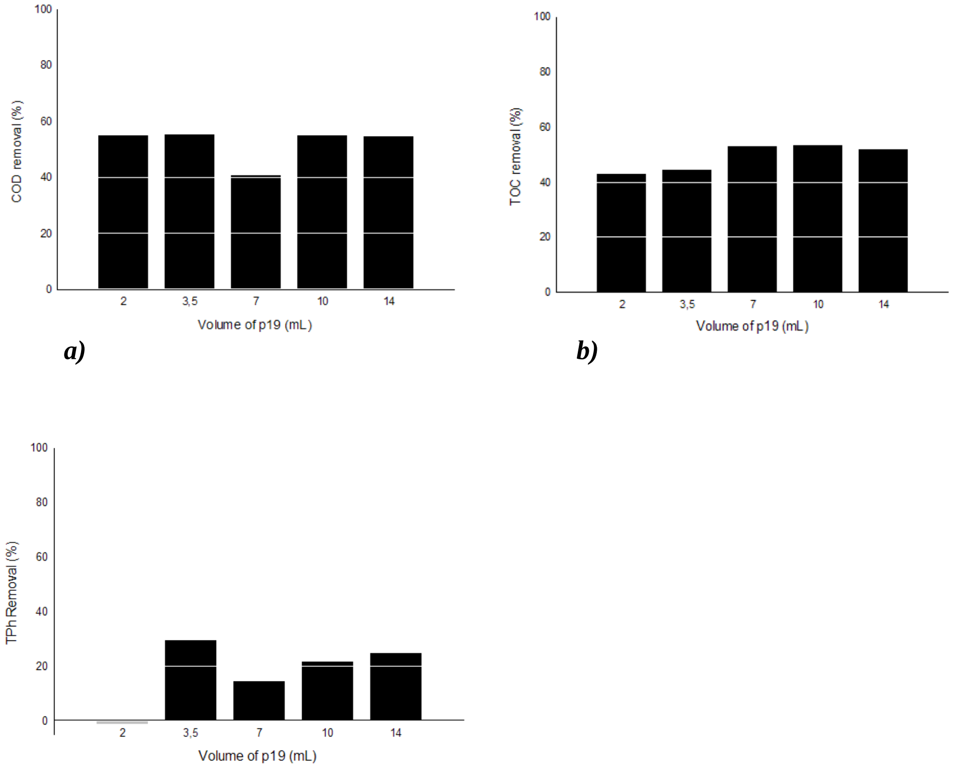


Figure 4.1 – Effect of the different pH on COD (a) and TOC (b) degradation by placing 7mL of coagulant p19.

It was seen that pH has influence over coagulation's process. At pH 3, not only does one get better results but also, it will not be necessary to make future pH corrections in order to proceed with the Fenton's process, since process' optimum pH is 3.

After this, it was observed that by adding lower (2mL; 3.5) and higher (10mL; 14mL) quantities of coagulant at pH3 COD removal percentage increased (figure 4.1.2). However, the obtained results show that the TOC removal was not favored by lowering the p19 amount while a slight increase was reached when adding 10mL. In what regards TPh values, bigger reductions were detected, with the exception of 2mL that led to a removal percentage near zero, which reveals that the quantity of coagulant used was not enough to remove phenol content.



a) *b)*

c)

Figure 4.2 – **Effect of the different concentration of p19 on COD (a) , TOC (b) and TPh (c) degradation by placing pH 3.**

As for effluent's BOD_5, a significant decrease was observed, given that this parameter went from 4710 mg O_2 L^{-1} to 2441 mg O_2 L^{-1}.

4.2.2 Suspended solids

From a chemical point of view, solids are classified as volatiles and fix. Volatile solids are those that volatize at temperatures below 600ºC, either organic substances or mineral salts.

Fix solids are those that remain after water's complete evaporation, usually salts. Dissolved solids excess in the effluent can cause corrosion problems. As for suspended solids, they make water muddy creating aesthetic problems and harming photosynthetic activity.

Through the figure 4.3 it is possible to check a further reduction in the amount of solids present in the effluent coagulated with 3.5mL of p19 and pH 3. The excess coagulant (10mL and 14mL) discloses increased TSS because for large concentrations of coagulant restabilization occurs, i.e., colloids become positively charged by excess coagulant.

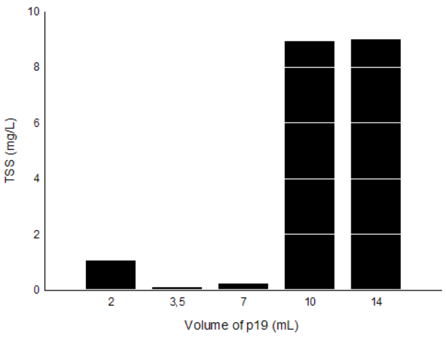


Figure 4.3 – **Effect of the different concentration of p19 on TSS by placing pH 3.**

4.3 CATALYSTS SCREENING

The effluent used for all experimental tests (except those marked) was coagulated effluent (with 3.5mL of p19 and pH 3).

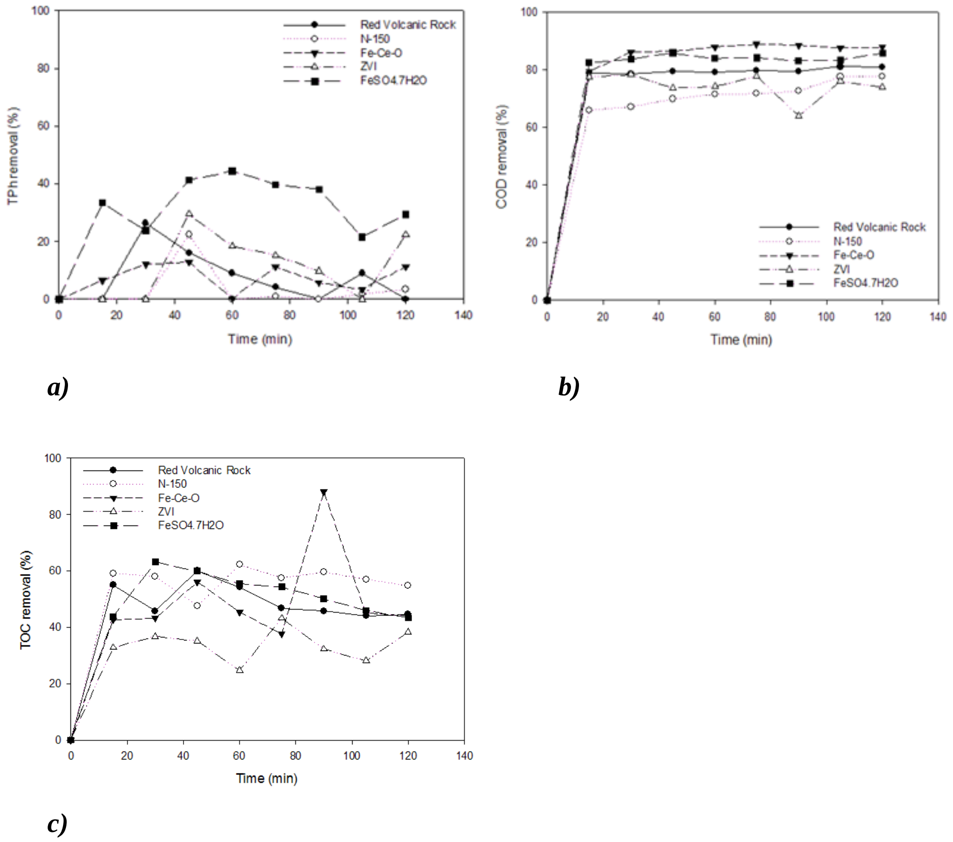
Effluent's chemical characteristics are summed in the table 4.3, as well as the standard deviations associated to each analyses technique.

Table 4.3 – **Chemical characteristics of the coagulated liquid effluent with analytical deviations in parenthesis**

Characteristics	Values
COD (mg O_2 L^{-1})	4270 (± 10)
BOD_5 (mg O_2 L^{-1})	2441 (± 20)
BOD_5/COD	0.57
TOC (ppm)	2855 (± 10)
TPh (mg GA L^{-1})	149 (± 20)
pH	3

4.3.1 Dark Fenton´s Treatment

The catalyst screening was made through a series of tests with different solids, analyzing their abilities for the reaction's proposed system, in order to select the most active catalyst, so that the process' efficiency can be improved. Four catalysts were used, namely, N-150 (Fe_2O_3-MnO*x*), Fe-Ce-O (70/30), Red volcanic rock and ZVI, having been studied their effect in TPh, COD and TOC removal and biodegradability as well. Experimental performance was equal in all cases, with pH values between 3.6 and 3.2, catalyst concentration of 1.0 g L^{-1}, environment temperature and hydrogen peroxide volume of 2,50mL (5g.L^{-1}) (stoichiometric quantity, 1:5) [11,40] with mechanical agitation. Figure 4.4 represents Total Phenol Content (TPh), COD and TOC removal along the reaction period, in presence of those catalysts for the raw effluent without being submitted to the pre-coagulation process. An experiment was also performed with FeSO4.7H2O to compare heterogeneous and homogeneous Fenton's oxidation.



a)

b)

c)

Figure 4.4 – Effect of different catalysts at pH 3 under mechanical stirring in Dark-Fenton. (catalyst concentration of 1.00g L^{-1}, room temperature and hydrogen peroxide volume of 2.50mL) on TPh (a), COD (b) and TOC (c).

Through these data, it is seen that there was inconsistency in the obtained results reflected on the irregular profiles along time. That can be explained by the impossibility to maintain the solid catalysts with the same uniform concentration in solution under homogeneous agitation since with mechanical stirring that was used in the experiment system the presence of catalyst's deposit in the reactor could be observed. Besides, effluent's coagulation had not yet been made, which shows that the presence of dissolved solids makes phenol compounds and organic matter measurement impracticable.

It is also important to note that, in these first experiments, the method for that was used for the reaction terminus was the addition of 1.5mL of $NaHSO_3$, to consume all hydrogen peroxide still present, according to equation 4.3:

$$H_2O_2 + SO_3^- \longrightarrow H_2O + SO_4^- \qquad \textit{Equation } 34$$

However, it was discovered that this reagent also interfered with the COD determination and for that reason all the runs had, as method for ending the reaction, a pH increase for values near pH=10. Besides, since no homogeneity was possible to be attained with mechanical stirring, all the following experiments were then performed in an orbital agitator. In fact, with these changes in the operation mode, those irregularities in the values measured along treatment were eliminated, as can be observed in the results shown below. Moreover, the quite different range levels detected now indicate that the previous procedure was inappropriate.

In figure 4.5 it is possible to see the total phenol content removal given by the oxidation reaction performed for the different catalysts under the new operating characteristics.

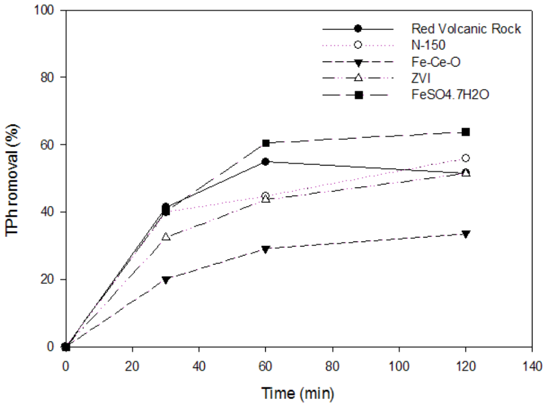


Figure 4.5 – **Effect of different catalysts at pH 3 with orbital agitator in Dark-Fenton (catalyst concentration of 1.00g L^{-1}, room temperature and hydrogen peroxide volume of 0,33mL) on TPh degradation profiles.**

It can be observed that all catalytic systems had satisfactory results, in what concerns TPh, with removals above 50% (except for Fe-Ce-O) under high initial velocities. The laboratory made catalyst, Fe-Ce-O, is the one presenting lower efficiency, with phenolic decrease removal around 34%. Among other catalysts, there are similar degradation profiles for the reaction's first 30 minutes. After 120 minutes, it was achieved 56% degradation with the commercial catalyst, N-150, and 52% on those of low commercial value, red volcanic rock (RVR) and ZVI In what regards the red volcanic rock, after 30 minutes of reaction no further TPh abatement is observed maintaining itself practically unaltered, most likely due to refractive phenol compounds formed during the oxidation process. In this case, the heterogeneous Fenton's process, with any of those catalysts, was much below expectation when compared with the homogeneous process, since when $FeSO_4.7H_2O$ was used 64% of the phenolic compounds were removed after 120 minutes.

Figure 4.6 presents Chemical Oxygen Demand removal through time for the different catalytic systems.

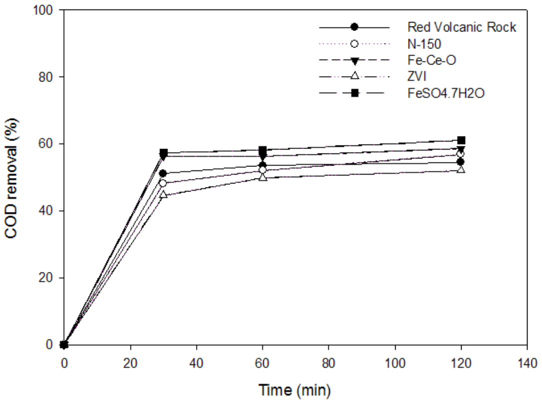


Figure 4.6 – **Effect of different catalysts at pH 3 under orbital agitator in Dark-Fenton. (catalyst concentration of 1.00g L^{-1}, room temperature and hydrogen peroxide volume of 0,33mL) on COD degradation profiles.**

Each one of the catalysts presents similar evolution until 30 minutes, with removals in the range 50-60% removal, which are nearly maintained until 120 minutes. Fe-Ce-O presents 59% of COD degradation at the reaction's end, while the red volcanic rock catalyst reaches little more than 50% of Chemical Oxygen Demand abatement. Even though the heterogeneous systems reached similar results to those of the homogeneous operation, in this case the efficiency was slightly higher with 61% final depuration.

TOC removal allows evaluating the mineralization degree obtained by the oxidation process of the involved compounds. Figure 4.7 shows the TOC degradation profiles for all the systems under study.

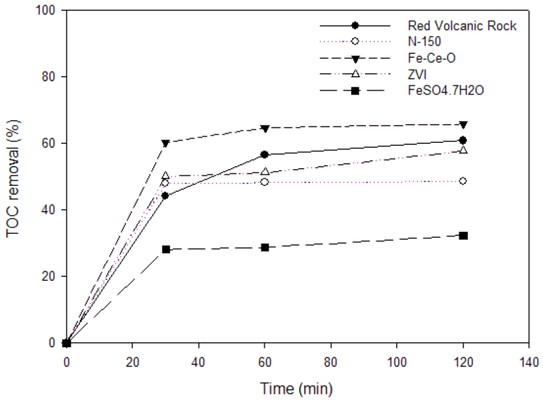


Figure 4.7 – **Effect of different catalysts at pH 3 under orbital agitator in Dark-Fenton. (catalyst concentration of 1.00g L^{-1}, room temperature and hydrogen peroxide volume of 0,33mL) on TOC degradation profiles.**

These results point out that most catalysts have a higher TOC than COD removal (figure 4.6). In the volcanic rock's (RVR) case it was verified 54% COD and 61% TOC removal, for Fe-Ce-O 59% COD and 66% TOC, whereas the ZVI catalyst system had degradations around 52% for COD and 58% for TOC. It is important to distinguish, while studying treatment processes, the total oxidation reactions from the partial oxidation reactions, to infer on the used catalysts selectivity. According to MANTZAVINOS *et al.* (2000) [92], it is possible to determine the COD removed quantity and COD degradation efficiency by partial oxidation (equations (35) and (36)).

$$COD_{parcial} = COD_0 \times \left(\frac{TOC}{TOC_0} \right) - COD \qquad \text{Equation 35}$$

$$X = \frac{COD_{partial}}{COD_0 - COD} \qquad \text{Equation 36}$$

If X is near 0, treatment selection is for total mineralization, while if X is near 1, oxidation tends to be partial [92].

According to the obtained results for the studied catalysts an X value near 0 (0.1) is always verified, meaning that catalysts selectivity aims to total mineralization with CO_2 and H_2O formation.

For the environment parameters in analyses, it is verified that Fe-Ce-O and red volcanic rock catalytic systems are those presenting better results. In fact, in the field of oxidative processes, cerium based catalysts are promising due to their oxygen in cerium oxide storage ability. This way, when Ce is among other elements, it provides or takes oxygen to those elements according to need, allowing a better electronic balance and this way favoring oxidative reactions [131].

Table 4.4 presents final COD and BOD_5 values, which according legislation may not exceed 40 and 150 mg O_2 L-1 if the wastewater is to be directly discharged in surroundings. As can be seen, the effluent after this chemical treatment is still not under legal limits for release. This way, biodegradability (BOD_5/COD) at the end of the Fenton's treatment was evaluated in order to determine posterior biological treatment applicability to further purify the effluent. It was then seen that the less efficient catalyst in the organic removal and with lower BOD_5/COD ratio with a 0.54 value was N-150, meaning the effluent is more biodegradable while all other catalysts increased BOD_5/COD ratio compared to 0.57 of initial coagulate effluent and were close to reaching biodegradability. Homogeneous system had lower value discrepancy when compared to heterogeneous.

Table 4.4 – BOD, COD and Biodegradability quantification of the residual water

Catalyst	BOD_5 (mg O2 L^{-1})	COD (mg O2 L^{-1})	Biodegradability
Red Volcanic Rock	1253	1945	0,64
N-150	1010	1840	0,54
Fe-Ce-O 70/30	1115	1770	0,62
ZVI	1889	2050	0,58
$FeSO_4.7H_2O$	1113	1665	0,67

In order to evaluate catalyst stability the amount of iron leached (mg Fe L^{-1}) was quantified at the end of oxidation process and is shown in figure 4.8.

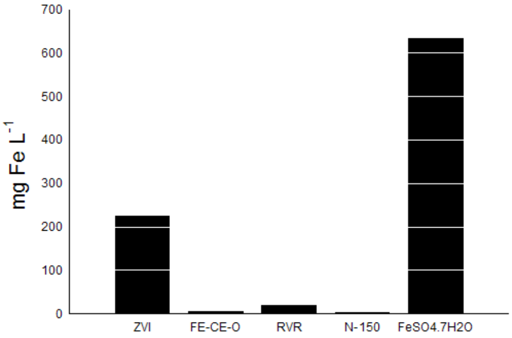


Figure 4.8 – Amount of iron leached after 120 minutes of Dark-Fenton Process for different catalysts.

The lower iron leached value is attained by the commercial catalyst N-150, 2.90 mg Fe L^{-1}. However, Fe-Ce-O and volcanic rock (RVR) also presented low values, 6.0 and 18.6 respectively, when compared to ZVI with 224 mg Fe L^{-1} and with the more drastically higher result for the homogeneous process with 634 mg Fe L^{-1} (the legal limit for discharge of wastewater is 2 mg Fe L-1, Decretory-Law nº236/98).

In the following study we only pursued with the laboratorial Fe-Ce-O catalyst as well as with the low cost solids, red volcanic rock and ZVI, since the commercial catalyst N-150 may be more expensive without revealing, in general, better performance. Indeed it presented lower biodegradability results and was very close to other catalysts in TOC, COD and TPh depuration levels.

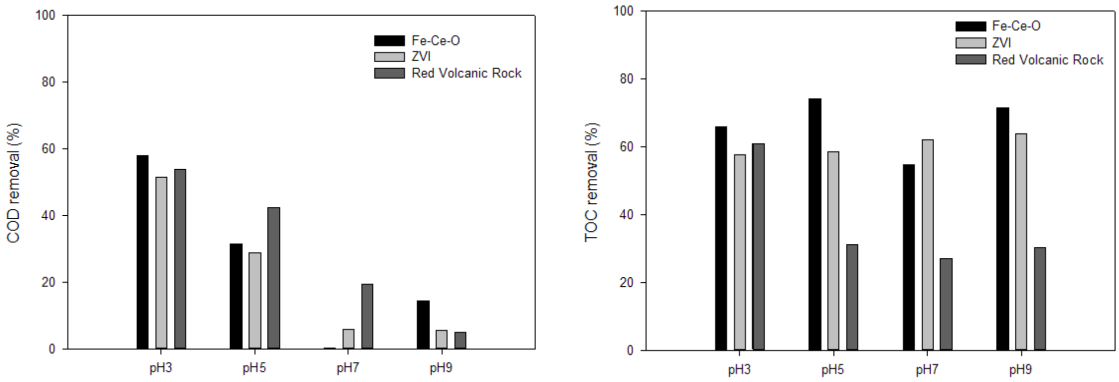
4.3.1.1 pH's influence on the process performance

Since Fenton's processes are catalyzed by Fe^{2+}/Fe^{3+} ions and considering that these ions are hydrolyzed forming insoluble hydroxides, environment's pH has a strong role in organic compounds degradation velocity, since iron ions precipitate when pH is higher than 6 [95], [109]. At pH 3 Fe^{3+} dominant species in aqua solution are $FeOH^{3+}$ [12]. Below optimum pH for reaction's success, active species' concentration is low and for high pH Fe^{3+}/Fe^{2+} ions precipitate as hydroxides [55].

In order to evaluate the influence of pH's liquid mixture during the treatment process, values (in range 3-9) of pH 3, 5, 7 and 9 were taken under consideration. pH 3 was chosen because it is indicated for Fenton's reaction; pH 5, on other turn, was selected because it is close to effluent's pH; pH 7 is ideal for discarding the effluent in environment; lastly, pH 9 to verify if there is still reaction to a high pH, since to end reaction pH was settled near 10.

It is known that with neutral to alkaline pH there is fast H_2O_2 decomposition with molecular oxygen production without corresponding hydroxyl radicals formation, prejudicing the desirable degradation process [112], since molecular oxygen is not capable of an efficient organic compounds oxidation at environment's pressure and temperature. Another important parameter is active species' leaching, demanding the need to quantify iron in solution after the process in order to evaluate catalyst stability and reuse. Several references show that leaching increases as pH decays [112], [28]. This way it is also essential to estimate the amount of iron in the liquid after experimental performance because iron has to be lower than 2 mg L^{-1}, the legal limit, so that the effluent can be released into natural courses.

Figure 4.9 presents COD and TOC removal efficiency to different used pH, intending for the select a pH value that has better global catalyst system efficiency, and that provides better removal rates and higher catalyst stability. For pH 7, it is verified that the COD removal percentage is low, even null in the Fe-Ce-O case. That can be explained through H_2O_2 fast decomposition, into molecular oxygen without formation of hydroxyl radicals. At pH9 oxidation is not significant, and that was expected since iron ions begin to precipitate forming hydroxides.



a) *b)*

Figure 4.9 – **COD *(a)* and TOC *(b)* removal to different used pH at 120 minutes in Dark-Fenton. (Fixed pH during the experimental test. Pressure and Room temperature).**

However, TOC results show that there is significant mineralization (above 50%) to all pH range for ZVI and Fe-Ce-O. For the red volcanic rock (RVR), there is clearly a remarkable difference between reaction under pH 3 and higher values with TOC depletion being favored at pH 3. It is known that removed carbon can be due to adsorption or oxidation. In order to identify which are the paths involved the used catalysts were analyzed after treatment and the results point out that there is larger adsorption under pH 9 in Fe-Ce-O, around 16.5mg L^{-1}, while under pH 3,5 and 7 was 0.3mg.L^{-1}, 0.4mg.L^{-1} and 1.4mg.L^{-1}, respectively. ZVI also had high adsorption, with the lower one at pH 3, around 0.4mg.L^{-1}, whereas in the cases of pH 5, 7 and 9 had 13.7mg.L^{-1}, 15.4mg.L^{-1} and 13.2mg.L^{-1} of carbon, respectively. The red volcanic rock presented lower carbon concentration, around 1mg L^{-1} for pHs 5, 7 and 9.

These result lead to the conclusion that the possibility of using equal to 5 or above may be excluded once the process' stability and adequate results obtaining is affected with subsequent lower degradation [113]. In order to determine pH's impact in the catalyst stability, the leached iron was quantified (mg L^{-1}) after the oxidation's process performed to different pH values, as presented in figure 4.10.

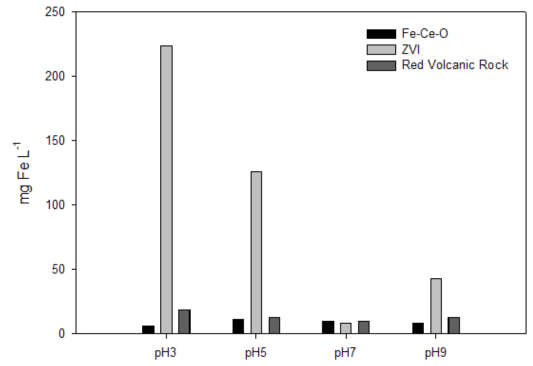


Figure 4.10 – **Amount of iron leached after 120 minutes of Heterogeneous Fenton Process for different pHs.**

As seen, the Fe quantity in solution after 120 minutes reaction with ZVI is very high, and that is also observed at naked eye, showing a clear pH influence in the solid catalyst stability.

Therefore, in order to ensure a stable solid, it is considered that the Fe-Ce-O and Red volcanic rock catalysts are more adequate for this treatment.

4.3.2 Photo-Fenton´s Treatment

To proceed with the heterogeneous Fenton's process with UV radiation, the catalysts ZVI, Fe-Ce-O and Red volcanic rock were used.

Light intensity in the process was 0,366 Einstein/min [86].

Total Phenolic Content removal for the different catalysts can be seen in figure 4.11.

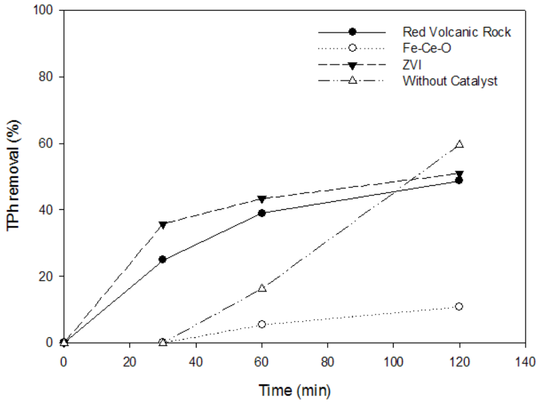
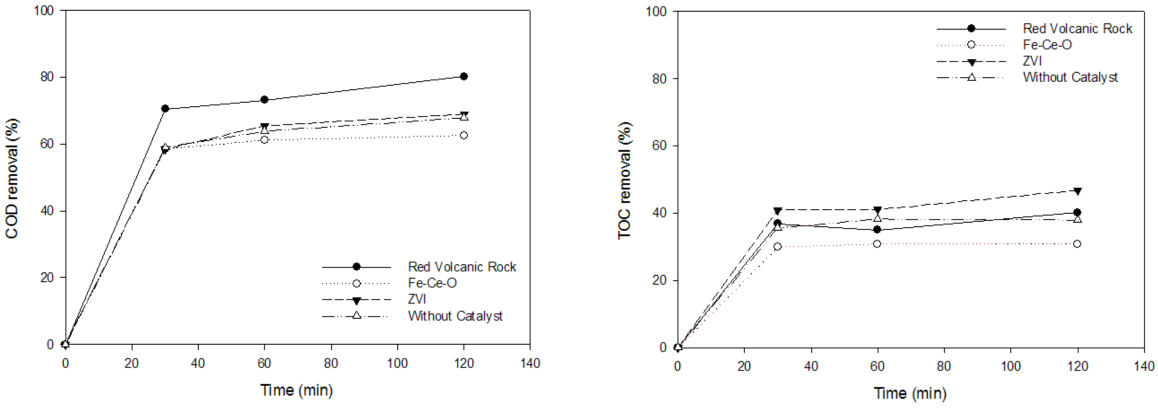


Figure 4.11 – **TPh removal along photo-Fenton´s process operating time. (Fixed pH during the experimental test. Pressure and Room temperature.)**

The red volcanic rock and ZVI present similar behavior, while Fe-Ce-O reveals only 11% removal, below the expected values, since one could presume to benefit from ultra violet light instead of an activity reduction (when compared to Dark-Fenton, 34%).

Those solid catalysts (volcanic rock and ZVI) could reach a TPh final degradation around 51% presenting a higher reactive velocity along time when compared to the process carried out without a catalyst, which, however, allowed a higher depuration at the end of the treatment.

Figure 4.12 presents COD and TOC removal profiles.



a)

b)

Figure 4.12 – **COD *(a)* and TOC *(b)* removal along photo-Fenton´s process operating time. (Fixed pH during the experimental test. Pressure and Room temperature)**

For Chemical Oxygen Demand removal, the most efficient catalyst was the red volcanic rock, reaching 70% after 30 min and a final efficiency of 80%. All catalysts have high reactive velocity during the first 30 minutes. Fe-Ce-O 70/30 presents again similar reaction profiles and inferior oxidation, around 63%, showing lower selectivity for this environmental parameter's removal.

In what regards Total Organic Carbon degradation all catalysts have a high reaction rate in the first 30 minutes. However, ZVI presents a better removal percentage, 47%, being, therefore, the most efficient catalytic system for TOC removal. The other catalysts showed lower activity.

The most commonly accepted mechanism for photolysis with UV/H_2O_2 is the breakdown of the molecule leading to two hydroxyl radical •OH according to equation 12. However, it should be noted that there is also the possibility of recombination of these radicals, producing H_2O_2 again (equation 13). And if there is excess of H_2O_2, it can possibly act as radical scavenger and subsequently promote a low yield because the oxidation of organic matter will be slower. In literature, there are tests described using less UV light intensity, which supports this assertion.

Since the obtained results were beyond expectations, no biodegradability tests were performed.

To evaluate catalyst stability, the leached iron was quantified (mg Fe L^{-1}) at the end of the oxidation process and it was verified that Fe-Ce-O presents a better result, 2.40 mg Fe L^{-1}, figure 4.13. An interesting aspect is that all of them had a decrease of dissolved iron in solution quantity (for ZVI 16.0 mg Fe L^{-1} and volcanic rock (RVR) 11.9 mg Fe L^{-}1), when compared to Dark-Fenton.

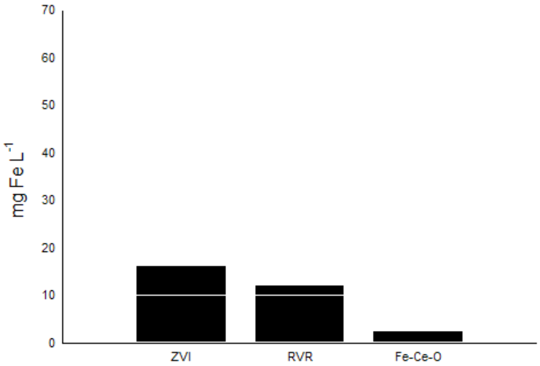


Figure 4.13 – Amount of iron leached after 120 minutes of Photo-Fenton Process for different catalysts.

Effluent's color may influence the treatment process's efficiency, once the presence of suspended material, colloidal or solution, and other substances absorb light's radiation, blocking effluent's penetration and reducing oxidatives' action.

5 CONCLUSIONS AND FUTURE WORK SUGGESTION:

In this part of the thesis, a general overview of the main results is presented, along with the most relevant conclusions. Suggestions for future work are also bring forward.

5.1 CONCLUSIONS:

This work was done into several steps, and it aimed to determine best operational conditions for an actual pharmaceutical effluent's degradation, whose characteristics and constitution were unknown, through Fenton's process. Different massic catalysts were tested, namely, the commercial N-150 (Fe2O3-MnO*x*), the laboratory made Fe-Ce-O 70/30, and low cost volcanic rock (nature) and ZVI (metallurgic industry) solids. In order to take advantage from Fenton's and to minimize solid residue formation, ultraviolet radiation was studied as adjuvant in hydroxyl radicals' formation.

The obtained results award the Fe-Ce-O 70/30 system as most efficient in Dark Fenton and Red Volcanic Rock in Photo-Fenton. Fe-Ce-O 70/30 in Dark-Fenton, had a TPh 34% degradation and removals around 59% and 66% for COD and TOC respectively, after 120 minutes of reaction, presenting selectivity towards total mineralization. Due to its high storage capacity for oxygen in cerium oxide, Fe-Ce-O 70/30 allows a better electronic equilibrium and, therefore favors oxidative reactions. Besides, it is a stable catalyst, since among all it was the one presenting lower leached iron quantity. Red Volcanic Rock in Photo-Fenton led to 49% of TPh decrease and removals around 80% for COD and 40% for TOC after 120 minutes of reaction.

In what concerns the effect of pH, if, in one hand, reaction efficiency increases with pH reduction, iron leaching also increases originating activity and catalyst stability reduction. Moreover, under higher pH there is fast H_2O_2 decomposition, without corresponding hydroxyl radicals formation harming the desired degradation process.

In what respects to biodegradability, it was possible to achieve acceptable results.

An important aspect is that the experimental coagulation pre-treatment was able to remove large amounts of suspended solids and achieve better results in the Fenton process.

Finally, this work points out the catalyst Fe-Ce-O 70/30 and the Red Volcanic Rock as promising in the catalytic oxidation through Heterogeneous Fenton and Photo-Fenton, respectively, in the effluent's degradation. This shows capabilities for implementing these technologies as residual water treatment, so that it can be possible to include in posterior biological systems.

5.2 FUTURE WORK SUGGESTION:

While preparing this dissertation, it was verified that there is lack of information concerning hydric environment and human health possible effects in presence of persistent drugs in the environment. Therefore, information about formed degradation products' identity and sample's toxicity after treatment are fundamental information in order to ensure Fenton's process appliance' safety and effectiveness in treating effluents with drugs' residua. This way, biodegradability and toxicity experiments and, mostly, identification of effluent's active constituents before and after treatment, are extremely important.

Based on the obtained promising results and considering the industrial interest for this liquid effluents' treatment method, it would be important to adjust the process intervenient variable, such as, catalyst concentration, hydrogen peroxide concentration and reaction time in order to attempt to achieve better results. Besides, using UV radiation during the process has proven to involve a capital gain in reducing catalyst' leaching. This way, it would be very important to deepen the analysis of this process, as one of the stronger Fenton's inconvenient is iron's high leaching at optimum pH (pH3).

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