

Studies on the treatment of urban landfill leachates by Fenton-like processes with zero-valent iron

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RESUMO

A deposição de resíduos sólidos urbanos em aterro dá origem a vários impactos negativos, de entre os quais se destaca a produção de lixiviados, que têm associada uma carga poluente muito elevada. Esta dissertação surge no âmbito do tratamento de lixiviados de aterro, tendo como objectivo principal a proposta de um novo processo de tratamento que possa ser aplicado à escala industrial e que garanta o cumprimento dos limites de descarga do efluente para o colector municipal local.

Os métodos de tratamento seleccionados para o tratamento do lixiviado tiveram por base a utilização de ferro de valência zero (ZVI), o processo de Fenton-like ($\text{Fe}^{3+} + \text{H}_2\text{O}_2$) e o processo de Fenton-like com ZVI. Este último tratamento foi estudado, numa primeira fase com ferro finamente dividido e, seguidamente, com limalhas de ferro. Estes tratamentos foram aplicados a lixiviados recolhidos em três fases distintas do processo de tratamento: antes do tratamento (E_{Raw}), após o tratamento biológico ($E_{\text{Post-Bio}}$) e à saída da estação de tratamento (E_{Treat}).

Os resultados experimentais a dois dos três lixiviados testados (E_{Raw} e E_{Treat}) revelam que as condições óptimas são: gama de pH entre 2 e 4, 13.40 g $\text{H}_2\text{O}_2/\text{L}$, 62.5 g Fe^0/L (E_{Raw}) e 25 g Fe^0/L (E_{Treat}), em 60 min. As limalhas de ferro foram testadas nas condições óptimas, obtendo uma remoção de CQO de 38 % em 5 min (E_{Treat}). Contudo, para o $E_{\text{Post-Bio}}$, após os 7 min ocorreu uma remoção de 49 % de CQO, o que permitiu cumprir o limite legal para descarga num colector municipal local. A biodegradabilidade (CBO_5/CQO) foi melhorada de 0.01 para 0.11, no caso do E_{Treat} , e de 0.04 para 0.27, no caso do $E_{\text{Post-Bio}}$, em 30 min. O reuso das limalhas de ferro foi realizado em 10 testes cíclicos, de 1 h cada, onde houve uma remoção de CQO máxima de 65.3 % no segundo reuso. É importante salientar que as limalhas de ferro continuaram a apresentar eficiências elevadas, após este máximo.

Deste modo, pode destacar-se como principal conclusão que o tratamento de lixiviados através do processo de Fenton-like com limalhas de ferro, traz benefícios ambientais e económicos, devido ao uso de um potencial subproduto industrial, que pode ser adquirido a baixo custo. Os resultados mostram que este processo parece ser mais adequado para ser integrado no actual processo industrial depois do reactor biológico e antes da descarga do lixiviado tratado para o colector municipal local, substituindo o tratamento físico-químico utilizado na estação de tratamento de águas lixiviantes do aterro estudado.

ABSTRACT

Urban solid waste disposal in landfills originates several negative impacts, among them stands out leachates generation, which have associated a high pollutant load. This thesis appears in the scope of landfill leachate's treatment and the principal objective is to propose a new treatment process that can be applied at industrial scale and to ensure compliance with the effluent discharge limits for the local municipal sewage.

The selected treatment methods for the treatment of the leachate were based on the use of zero-valent iron (ZVI), the Fenton-like process ($\text{Fe}^{3+} + \text{H}_2\text{O}_2$) and Fenton-like process with ZVI. This last treatment was studied in a first phase with iron powder and then with iron shavings. These treatments were applied to leachate collected in three distinct phases of the treatment process: before treatment (E_{Raw}), after the biological treatment ($E_{\text{Post-Bio}}$) and at the exit of the treatment plant (E_{Treat}).

The experimental results on two of three tested leachates (E_{Raw} and E_{Treat}) show that the optimal conditions are: a pH range between 2 and 4, 13.40 g $\text{H}_2\text{O}_2/\text{L}$, 62.5 g Fe^0/L (E_{Raw}) and 25 g Fe^0/L (E_{Treat}), in 60 min. Iron shavings were tested in these optimal conditions, achieving a COD removal of 38 % in 5 min (E_{Treat}). However, for the $E_{\text{Post-Bio}}$ after 7 min with 49 % removal of COD was attained meeting the legal limit for discharge to the local municipal sewage. The biodegradability (BOD_5/COD) was improved from 0.01 to 0.11, in the case of E_{Treat} , and 0.04 to 0.27, in the case of $E_{\text{Post-Bio}}$ in 30 min. The reuse of iron shavings was conducted in 10 test cycles of 1 h each, where there was a maximum COD removal of 65.3 % in the second reuse. It is noteworthy that iron shavings continued to show high efficiencies after this maximum.

Within these results, the main conclusion is that the treatment of leachate by Fenton-like process with iron shavings brings environmental and economic benefits due to the potential use of an industrial by-product, which can be acquired at low cost. It was shown that this system seems more appropriate to be integrated into the existing process after the biological reactor and prior to discharge the treated leachate to the local municipal sewage, replacing the physico-chemical used in the landfill leachate treatment plant studied.

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ACRONYMS

AOP – advanced oxidation processes

APA – Agência Portuguesa do Ambiente

BOD – biochemical oxygen demand

BOD₅ – biochemical oxygen demand in 5 days

BOD₅/COD – biodegradability ratio

COD – chemical oxygen demand

CMP – 4-chloro-3-methyl phenol

DDT – dichlorodiphenyltrichloroethane

DEQ-FCTUC – Departamento de Engenharia Química da Faculdade de Ciências e Tecnologia da Universidade de Coimbra

EDTA – ethylenediaminetetraacetic acid

E_{Raw} – raw effluent

E_{Raw} (1) – raw effluent collected at 4th April of 2011

E_{Raw} (2) – raw effluent collected at 2nd May of 2011

E_{Treat} – treated effluent

E_{Treat} (1) – treated effluent collected at 4th April of 2011

E_{Treat} (2) - treated effluent collected at 2nd May of 2011

E_{Treat} (2nd) - repetition of E_{Treat} (1) assay to guarantee the reproducibility of the results

E_{Post-Bio} – post-biological treated effluent

LLD – legal limit of discharge

L/S – liquid/solid ratio

MAOTDR – Ministério do Ambiente, Ordenamento do Território e Desenvolvimento Regional

MSW – municipal solid waste

n.d. – not determined

nZVI – nano zero-valent iron

ORP – oxidation reduction potential

ORU – organic recovery units

PERSU I – Plano Estratégico de Resíduos Sólidos Urbanos I

PERSU II – Plano Estratégico de Resíduos Sólidos Urbanos II

PNGR – Plano Nacional de Gestão de Resíduos

RB5 – Reactive Black 5

RDX - hexahydro-1,3,5-trinitro-1,3,5-triazine

S_{BET} - Brunauer-Emmett-Teller surface area

TPh – total phenolic compound

TDS – total dissolved solids

TSS – total suspended solids

TOC – total organic carbon

TNT – trinitrotoluene

T1 – addition of Fe⁰

T2 – addition of H₂O₂

T3 – addition of Fe⁰ and H₂O₂

UV – ultraviolet

VFA – volatile fatty acids

ZVI – zero-valent iron

1. INTRODUCTION

The present chapter allows to understand the scope of the present thesis by giving an overview about the environmental problems related with the landfill leachates and the possible treatment technologies available. Moreover, the thesis motivation and objectives are expressed below. Finally, the thesis structure is also indicated.

1.1. MOTIVATION AND SCOPE OF THE THESIS

The increase of the population needs are causing shortages of resources, as well as a high rate of waste generation. One of the most concerning issues is the strong industrial development essential to address mankind necessities, which is causing an excessive consumption of natural resources. Beyond that, the high amount of pollutants produced in the industrial processes lead to environmental damages if directly discharged towards soil, water and air.

Environmental protection has been growing over the past years due to the increase on the ecological awareness, leading to stricter policies establishing that economical growth must consider the resources sustainability.

The depletion of fresh water is a problematic issue putting in risk every forms of life in our planet. Thus, it is essential to preserve water resources and protect them from contaminations, besides promoting the application of technologies to treat and reuse water.

This thesis arises in the scope of treating and reducing effluents with low-cost methodologies focusing on landfill leachates treatment.

The conventional biological techniques tend to be inefficient in this ambit due to the high load and variable composition of these effluents. Besides, depending on the landfill's age, leachates main present low biodegradability (Renou *et al.*, 2008). The application of advanced oxidation processes (AOPs) arises as an interesting alternative whenever bio-remediation is not suitable. Among them, Fenton's process, based on the oxidant power of hydrogen peroxide catalysed by iron salts, is interesting since operates at ambient conditions of pressure and temperature. However, classic Fenton's system requires high amounts of dissolved iron salts (FeSO_4 is the most common) which are not easily reused after the treatment constituting

one of the major drawbacks of this depuration technology (Neyens and Baeyens, 2003; Eckenfelder, 2000). The use of iron shavings as catalyst, which are a waste of iron industry, can reduce the costs of the treatment process besides given a use to an industrial waste.

In this context, the present research aims to study the application of zero-valent iron (ZVI) as catalyst in Fenton's process for the depuration of landfill leachates. More specifically the main goals of this thesis are:

- propose a new treatment, the Fenton-like process with ZVI, to treat municipal landfill leachates with an environmental and economical feasibility;
- improve the leachates biodegradability;
- ensure that the legal limits of discharge of effluents are fulfilled;
- see if there are future prospects of implementing this treatment at a industrial scale.

1.2. THESIS STRUCTURE

This thesis is divided in 6 chapters. The first chapter consists in an introductory note about the motivation and scope of this study.

The second chapter is directed to the management and treatment of urban landfill leachates, which includes an overview about the legal state of municipal solid wastes (MSW) in Portugal, the problematic of leachates and its environmental impacts, common treatment techniques, description of Fenton-like processes with ZVI and, finally, an overview of the landfill leachate treatment plant under analysis.

The third part contains a literature survey on Fenton-like ZVI methods, which will be the focus of the present research.

The forth part is related with the experimental methodologies used in the work encompassing the sampling of effluents, oxidation procedures applied and the analytical techniques.

The fifth chapter is divided in four sections. It starts with a characterisation of the effluents collected at the landfill, followed by the analysis of the preliminary tests performed that allowed to choose the best methodology of treatment to implement. After that, the laboratorial study focuses at the Fenton-like processes with ZVI, by testing the effect of several parameters, such as pH, concentration of H₂O₂, concentration of Fe⁰ and residence time. The

application of iron shavings coming from iron industry closes the results and discussion chapter.

Finally, the last chapter, summarizes the conclusions and the suggestions for future work to improve the study approached by this thesis.

2. MANAGEMENT AND TREATMENT OF URBAN LANDFILL LEACHATES: AN OVERVIEW

This chapter aims to do an overview of management and treatment of leachates. Chapter 2 is divided into 5 sections: firstly, the situation of MSW management in Portugal is established, followed by the problematic of landfill leachates, which include the generation of leachates, its constitution and composition, their environmental impacts and management. The third section talks about the common techniques of treatment, biological and physico-chemical, of leachates and, in fourth section, the Fenton-like processes with ZVI are described. Finally, the last section, explores the landfill leachate treatment plant under analysis.

2.1. MUNICIPAL SOLID WASTE MANAGEMENT IN PORTUGAL

A few years ago, the deposition in dumps was very frequent in Portugal and in 1995, there were 300 sites at open sky. However, the contamination of soil and water, the air quality degradation and the associated risks to the human health related with this procedure jeopardize environmental sustainability (Levy and Cabeças, 2006). Thus, in order to protect the environment, it became urgent to consider new methodologies to the waste management. In this context, more strict policies for waste management were proposed. The first strategic plan of solid wastes, known as PERSU I, arose in 1997 by the 75/442/CEE European Directive (15th of July). The new European Union waste management plans allowed Portugal to define a waste management hierarchy which sets that prevention measures, as waste reduction at the source, should be firstly considered; afterwards, the possibility of reuse, recycling or recovery of the materials should be analyzed while the disposal into landfills ought to be the last option whenever the former ones fail. PERSU I was in force until 2006 and its main objectives were the closure of dumps, the construction of infrastructure to the MSW management, reinforcing, this way the selective waste collection and establishing recycling targets for 2000 and 2005 (APA, 2011a).

In 2007, PESU II substituted PERSU I and it will be operational until 2016. Its principal goals are a review of the PERSU I objectives encompassing the commitment to reduce the greenhouse effect, the reduction of the amount of waste disposed in landfills, the

implementation of recovery techniques, besides the optimization and maximization of recycling with the final aim of reducing the number of landfills in Portugal. PERSU II comprise stricter objectives imposing, for example, that biodegradable wastes should be directed to organic recovery units (ORU) involving anaerobic digestion, composting, mechanical or biological treatments instead of its direct disposal into a landfill (MAOTDR, 2007).

According to data of 2009, Portugal is not reducing the total amount of wastes with roughly 1.4 kg/inhabitant.day produced (APA, 2010). Thus, according to the Relatório de Acompanhamento 2009 of PERSU II from Agência Portuguesa do Ambiente (APA), Portugal is generating higher loads of waste than the established limits imposed by PERSU II. As an example, the goal of production of urban wastes in 2009 should be 5.043.000 tonnes but in that year 5.403.000 tonnes were produced (APA, 2011b). Moreover, in 2008 and 2009, 65.5 % and 62 % of the urban wastes were dumped in sanitary landfills, respectively. These values reflect the low rate of recycling and recover of wastes in Portugal (APA, 2010).

One of the major issues regarding landfilling is related with the disposal of biodegradable wastes due to their contribution to the formation of leachates. In this context, PERSU II has as objective the decreasing on the amount of this kind of waste directed to landfills. This would greatly reduce the production of leachates and decrease their organic load. However, in Mainland Portugal, the goals of PERSU II to 2008 and 2009 for bio-wastes dumping in landfills were not accomplished (APA, 2011b).

With these results, Portugal needs to improve and invest in new measures to successfully fulfil the PERSU II. The Decreto-Lei n.º 73/2011, de 17 de Junho is the third change of Decreto-Lei n.º 178/2006, de 5 de Setembro and transposes the Directiva n.º 2008/98/CEE do Parlamento Europeu e do Conselho, de 19 de Novembro de 2008, has measures to improve the situation. In general terms, this law aims to:

- strengthening the prevention of waste production and encouraging materials reuse and recycling;
- encourages the selective collection, especially in what regards bio-wastes;
- approval of prevention programs with goals to be met by 2020, for reuse, recycling and other forms of waste material recovery;

- definition of requirements so that substances or objects resulting from a production process can be considered sub-products and not waste;
- delineate criteria to withdraw the category of waste for certain materials;
- introducing the mechanism of extended producer responsibility, taking into account the life cycle of products and materials and not only the end-of-life.

This new approach for MSW management in Portugal starts this year (2011) and will be applied until 2020, comprising a national wastes management plan, the PNGR, which sets the consistency of the specific plans for waste management and the formation of integrated facilities for recovery and elimination of all types of waste, taking into account the best technologies at economically sustainable costs (APA, 2011c).

2.2. THE PROBLEMATIC OF LANDFILL LEACHATES

Leachates are liquids produced due to the percolation of rainwater through the landfill soil, the waste moisture content and the biochemical decomposition of the waste. This effluent generally presents a dark colour, an unpleasant odour and its percolation through the landfill drags many contaminants from the waste decomposition (Levy and Cabeças, 2006; Tchobanoglous *et al.*, 1993).

2.2.1. GENERATION OF LEACHATES

A sanitary landfill is like a biochemical reactor, with the MSW and the rainwater as the main inputs, and the landfill gas and leachates as the outputs. The landfill gas and leachates are generated over the time as products of the biochemical degradation of MSW (Tchobanoglous and Kreith, 2002). The leachate's stabilization occurs after 5 stages and its constitution varies over each one. Fig. 2.1 represents the five phases of gas and leachates production at a sanitary landfill.

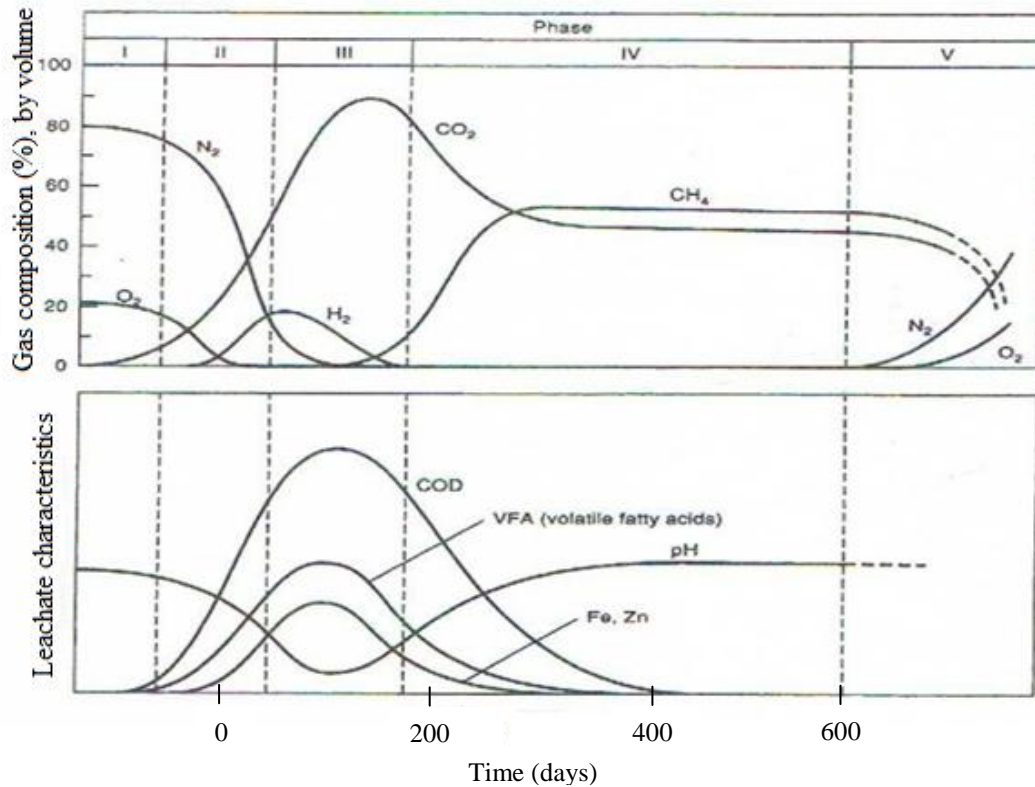


Fig. 2.1 - Phases of gas and leachates production at a sanitary landfill (Adapted from Tchobanoglous and Kreith, 2002; Adapted from Miller and Townsend, 1991).

The duration of each phase is very variable. It depends on the organic matter distribution in the landfill, the waste moisture content and the degree of initial compactation, among others factors. Each one of the 5 stages is described below (Tchobanoglous and Kreith, 2002):

Phase I – Initial Adjustment: The organic fraction of waste dumped at the landfill starts to decompose due to the bacterial action. These microorganisms are aerobic and oxygen (O_2) is supplied from the air retained beneath the landfill soil cover.

Phase II – Transition Phase: The air trapped at the phase I is depleted and aerobic decomposition is no longer possible. Thus, anaerobic microorganisms are now able to convert the organic matter. Nitrate (NO_3^-) and sulphate (SO_4^{2-}) conversion into nitrogen gas (N_2) and hydrogen sulphide (H_2S) is possible, at this stage, due to the absence of O_2 . The MSW field capacity is exceeded and leachates are formed. Due to the organic acids production and the elevated concentration of carbon dioxide (CO_2), pH starts to decrease.

Phase III – Acid Phase: The previous microbial activity is accelerated with the production of organic acids. Enzymes transform the high molecular weight compounds into simpler compounds (hydrolysis) which will be the substrate for the microorganisms. Those substances are transformed by microorganisms into intermediary compounds such as acetic acid (CH_3COOH) and other acids (acidogenesis). CO_2 is the principal gas produced while H_2 is generated in smaller quantities. This will promote pH decrease to 5, which will enhance heavy metals and other inorganic compounds solubilization. Moreover, the organic acids dissolution increases the leachates chemical oxygen demand (COD) and biochemical oxygen demand in 5 days (BOD_5) content.

Phase IV – Methane Fermentation Phase: Methanogenic bacteria, which are strictly anaerobic, transform the CH_3COOH and H_2 formed at Phase III, into CH_4 and CO_2 gases (known as biogas). This will increase the pH to 6.8 – 8 leading to lower heavy metals solubilisation. Moreover, the leachates COD and BOD_5 decrease.

Phase V – Maturation Phase: This phase occurs after the conversion of the readily biodegradable organic compounds into CH_4 and CO_2 . Some organic matter that was previously unavailable can now be degraded. The rate of landfill gas production lowers due to the decrease of the amount of available nutrients. The leachates produced at this stage present low biodegradability due to the high content on fulvic and humic acids.

2.2.2. LEACHATES CONSTITUTION AND COMPOSITION

Leachates contain large amounts of organic matter, both biodegradable and refractory, and generally encompass humic constituents, heavy metals, ammonia-nitrogen compounds, inorganic salts and chlorinated organic substances (Renou *et al.*, 2008). Its composition is variable and depends on many factors, like those indicated in Table 2.1.

Table 2.1 - Factors and parameters affecting the leachates composition (Adapted from Levy and Cabeças, 2006).

Factors	Parameters
Nature of solid waste at landfills	Organic fraction of waste
	Biodegradability
	MSW solubility
	MSW dimension
Landfill exploration	Temperature
	pH
	Moisture content
	Landfill age
Characteristics of water sources outside the landfill	Nature of the cover material
	Precipitation

Table 2.2 shows the typical characteristics found in leachates and their typical dependence with the landfill's age.

Table 2.2 - Landfill parameters (mg/L), according to the landfill age (Tchobanoglous and Kreith, 2002).

Parameters(mg/L)	New landfill (less than 2 years)		Mature landfill (greater than 10 years)
	Range	Typical	
BOD ₅	2000 – 30000	10000	100 – 200
TOC	1500 – 20000	6000	80 – 160
COD	3000 – 60000	18000	100 – 500
TSS	200 – 2000	500	100 – 400
Organic nitrogen	10 – 800	200	80 – 120
Ammonia nitrogen	10 – 800	200	20 – 40
Nitrate	5 – 40	25	5 – 10
Total phosphorus	5 – 100	30	5 – 10
Ortho phosphorus	4 – 80	20	4 – 8
Alkalinity as CaCO ₃	1000 – 10000	3000	200 – 1000
pH	4.5 - 7.5	6	6.6 - 7.5
Total hardness as CaCO ₃	300 – 10000	3500	200 – 500
Calcium	200 – 3000	1000	100 – 400
Magnesium	50 – 1500	250	50 – 200
Potassium	200 – 1000	300	50 – 400
Sodium	200 – 2500	500	100 – 200
Chloride	200 – 3000	500	100 – 400
Sulfate	50 – 1000	300	20 – 50
Total iron	60 – 1200	60	20 – 200

The most important parameters according to Renou *et al.* (2008) are BOD₅, COD, the BOD₅/COD ratio, pH, TSS (total suspended solids) and ammonia nitrogen. The age of the landfill has an important role on the leachate composition due to the degree of waste stabilization. COD and BOD₅ correspond to an estimate of the amount of organic matter and the quantity of the biodegradable compounds present in the leachate, respectively. TSS values are associated with the suspended matter present in leachates.

The BOD₅/COD ratio represents the leachate biodegradability and this parameter is very variable with the landfill's age. An effluent is typically considered to be very biodegradable when presents ratios above 0.4 (Esplugas *et al.*, 2004). In accordance with Renou *et al.* (2008), the biodegradability decreases with the age of the landfills: for recent landfills (age < 5 years), leachates with BOD₅/COD ratios superior to 0.3 are found, while values between the range of 0.1 – 0.3 are generally determined for intermediate age (5 - 10 years). Biodegradability decreases to 0.1 for old landfills (age > 10 years) due to the existence of humic and fulvic acids, that are released from solid wastes.

2.2.3. ENVIRONMENTAL IMPACTS AND LEACHATES MANAGEMENT IN THE SANITARY LANDFILL

Leachates generation are one of the greatest environmental issues related with sanitary landfills. The production of this effluent is inevitable, but could be minimized by decreasing the amount of biological waste dumped at the landfill and increasing the compacting rate of wastes. It is necessary to avoid the contact of landfill leachates with soil, groundwater and surface water (Matejczyk *et al.*, 2010). This polluted effluent constitutes a risk to the quality of groundwater and, consequently, to the human health. It is necessary, in this way, to have a special care in captation, treatment and monitoring of leachates to avoid contamination of the soils and, consequently, groundwater contamination (Faria, 2002). Table n.º 1 from the appendix III of Decreto-Lei n.º 183/2009, de 10 de Agosto, presents the legal frequency for the measurements of leachate's parameters.

Landfills should have impermeable systems to avoid soil contamination, which are placed between the soil and the wastes layer, allowing to restrict the wastes, leachates and landfill gas, preventing them to pass to the exterior (Levy and Cabeças, 2006). Leachates are collected

from landfill with a system of collection pipes. After the captation, leachates are usually drained to basins in order to regulate and homogenize the flow (Tchobanoglous and Kreith, 2002).

2.3. COMMON TECHNIQUES OF TREATMENT

Leachates are aqueous solutions with organic and inorganic matter. While some organic matter can be treated biologically, inorganic matter is more easily removed by physico-chemical processes. Thus, in landfill leachate treatment plants, in general, the leachate depuration combines these two types of technologies (Faria, 2002).

The selection of the treatment greatly depends upon the leachates characteristics.

2.3.1. BIOLOGICAL TREATMENTS

Biological treatments are the mostly often applied due to their low operating costs and high efficiency. These processes degrade organic and nitrogenous compounds, reducing COD and BOD. Generally, these systems can be aerobic, where organic compounds are decomposed into CO₂ and sludge, or anaerobic, with the production of biogas (a mixture of CO₂ and CH₄) (Renou *et al.*, 2008). Table 2.3 summarizes the most common biological treatments available.

Table 2.3 - Common biological treatments (Faria, 2002; IRAR, 2008; Renou *et al.*, 2008).

Aerobic treatment	Activated sludge processes*	Inadequate for landfill leachate treatment, according to Lin <i>et al.</i> (2000) due to the long aeration time required which implies high energy consumption. Moreover, excessive sludge production occurs. Requires a separate clarifier. Advantages of this process are the high reduction of organic carbon, removal of nutrients and ammonia.
	Sequencing batch reactor*	Ideal for nitrification-desnitrification processes. COD removal of 75 % and 99 % of NH ₄ ⁺ - N removal with a 20 – 40 days residence time (Lo, 1996). Only appropriate to low rate flows. No need of separate clarifier.
	Lagooning*	Efficient to remove pathogens, organic and inorganic matter, with low operational and maintenance costs. Presents efficiencies of COD removal within the range of 55 – 64 %. The temperature of lagooning is a limitation factor because affects bacterial activity. Require high residence time.
	Trickling filters and fluidized bed reactor**	Appealing option for nitrification because of the filters low-cost. High risk of biomass obstruction. Low sensitivity to toxic compounds (Levy and Cabeças, 2006; Loukidou <i>et al.</i> , 2001).

Table 2.3 - Common biological treatments (Faria, 2002; IRAR, 2008; Renou *et al.*, 2008) (continuation).

Anaerobic treatment	Digester*	Compared with aerobic processes, anaerobic treatments save energy, present low reaction rates and low production of solids. Some experimental tests reached 96 % and 53 % of BOD and COD removal, respectively (Bull <i>et al.</i> , 1983).
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* suspended-growth biomass process; **attached-growth biomass process.

In attached processes, beyond what was already mentioned in trickling filters and fluidized bed reactor, there are no loss of biomass, nitrification is less affected by low temperatures and less energy is consumed (Renou *et al.*, 2008; IRAR, 2008).

2.3.2. PHYSICO-CHEMICAL TREATMENTS

The physico-chemical treatment completes the biological treatment. It can be located before the biological treatment, to reduce the organic matter of the raw effluent, or after to improve the quality of the final stream. Biological treatment coupled with the physico-chemical is a good treatment system when the legal limits of discharge to a municipal sewage cannot be fulfilled. Using this system allows to reduce the organic load of leachates before sent them to a wastewater treatment plant (Levy and Cabeças, 2006). Only with old landfill leachates, the physico-chemical treatment could be, by itself, able to fulfil the legal requirements (Faria, 2002). Table 2.4 resumes the most common physico-chemical processes.

Table 2.4 - Common biological treatments (Faria, 2002; IRAR, 2008; Renou *et al.*, 2008).

Adsorption	This methodology has been used in leachates after the biological treatment. Non-biodegradable organic compounds and color may be reduced in a satisfactory way. According to Rodriguez <i>et al.</i> (2004), COD removal reaches 85 %.
Coagulation-flocculation	Successfully used as a pre-treatment at old landfill leachates. This process decreases the leachate's pH. However, generally lead to high sludge production, low efficiency on removal of ammonia compounds. Moreover, it is required the introduction of high concentrations of aluminum or iron in the liquid phase to act as coagulant.
Chemical precipitation	Removal of metals and the produced sludge has to be placed at hazardous landfills.
Chemical oxidation	Appropriate to treat leachates due to its refractory compounds. Use advanced oxidation processes (AOP), improving the effluent biodegradability and reach mineralization. Could have high costs due to energy consumed, UV lamps, high oxidant doses, among others, depending on the type of treatment.

Table 2.4 - Common biological treatments (Faria, 2002; IRAR, 2008; Renou *et al.*, 2008) (continuation).

Membrane processes (new treatments)	Ultrafiltration	Efficient to remove high molecular weight compounds and ammonium nitrogene (NH ₄ ⁺ -N). According to Yangin <i>et al.</i> (2002), 66 % of ammonia removal, at pH = 9.3 can be achieved.
	Reverse osmosis	It is the most efficient methodology to treat leachates. This treatment removes 98 and 99 % of COD and metals, respectively (Linde <i>et al.</i> , 1995). The membrane fouling, the production of large volume of concentrate and expensive costs are the limitations of membrane processes.

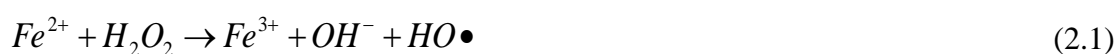
2.4. FENTON-LIKE PROCESSES WITH ZERO-VALENT IRON

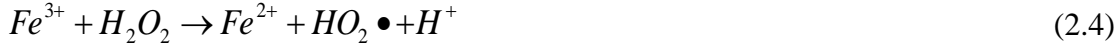
Due to the high load of organic matter present in leachates, already mentioned at section 2.2, besides the low biodegradability of some effluents, it is necessary to use physico-chemical treatment techniques able to degrade bio-refractory organic compounds.

The AOPs consist in technologies able of produce hydroxyl radicals (HO·), which are highly reactive and quickly degrade organic matter (Ozdemir *et al.*, 2010). HO· radicals may mineralize organic matter into CO₂ and H₂O or partially oxidize it into smaller by-products generally more amenable to be bio-processed. Thus, AOPs can be applied to improve leachates biodegradability enabling the application of a subsequent biological treatment (Kurniawan *et al.*, 2006).

Fenton oxidation is one of the AOPs extensively applied to several wastewaters. It consists in producing HO· radicals by the addition of a strong oxidant, the hydrogen peroxide (H₂O₂), in the presence of a iron catalyst, at a acid pH, between 2 and 4 (Neyens and Baeyens, 2002; Ahmadi *et al.*, 2005).

This methodology is carried out in four steps, involving the pH adjustment to an acid range, oxidation, neutralization and coagulation. The following equations describe Fenton's reaction with the production of HO· radicals, Eq. (2.1), and the degradation of organic compounds, Eq. (2.2), represented as R· (Ozdemir *et al.*, 2010; Neyens and Baeyens, 2002):





The Fe^{3+} produced in Eq. (2.3) can be now reduced by the H_2O_2 in the solution and this process is called Fenton-like, which is slower than the Fenton process due the formation of less reactive radicals, the hydroperoxyl radicals ($HO_2\cdot$) Eq. (2.4) (Kallel *et al.*, 2009b). A cycle of iron redox (Fe^{2+}/Fe^{3+}) is formed, Eqs. (2.5) to (2.6).



In Fenton-like processes, excessive amounts of iron salts and H_2O_2 may inhibit the production of $HO\cdot$ radicals. Consequently, the oxidation of organic matter is jeopardized. This happens due to the production of $HO_2\cdot$. This effect is called as radical scavenging and can be seen at Eqs. (2.7) and (2.8) for excessive concentration of iron salts and H_2O_2 , respectively (Martins, 2010; Kallel *et al.*, 2009a).



Fenton-like processes are attractive treatments since occur at room temperature, iron is a non toxic element and H_2O_2 is environmentally safe. The disadvantages are the production of sludge due to ferric hydroxide precipitation, which is caused by the neutralization of the reactor content, the expensive costs of the sludge disposal and the costs associated with the pH adjustment (Andreozzi *et al.*, 1999; Cao *et al.*, 2009).

Zero-valent iron (Fe^0 or ZVI) can be used as a catalyst in Fenton-like processes. Acid conditions are need to the corrosion of metal iron originating Fe^{2+} and H_2 Eq. (2.9) (Ozdemir *et al.*, 2010).



Then, the dissolved iron reacts with H_2O_2 and the reaction occurs like the traditional Fenton's process Eq. (2.1). Eq. (2.10) shows a recycling of ferric iron at the surface of metal sheet.

The use of Fe^0 brings some advantages such as the fact of this solid iron decreasing the amount of iron ions at leachate, when compared with the traditional Fenton's where the catalyst ($\text{Fe}^{2+}/\text{Fe}^{3+}$) is totally dissolved in the liquid, which decreases the production of iron sludge. The Fenton-like ZVI process can be more cost-saving than the system involving iron salts since costless wastes from iron industries (such as iron shavings) can be used as catalyst (Ozdemir *et al.*, 2010; Kallel *et al.*, 2009a).

2.5. LANDFILL LEACHATE TREATMENT PLANT (UNDER ANALYSIS)

The leachates studied in this thesis were collected from a municipal sanitary landfill located in centre of Portugal. In this landfill, leachates are treated at the local leachate treatment plant, and then, they are routed to a municipal wastewater treatment plant, where the depuration is completed, before being released into the natural water courses. The leachate initial treatment must fulfil the emission limit values for the release of industrial wastewater, which are imposed for each municipality, before it is released at the municipal sewage.

Fig. 2.2 represents the flow-sheet of this specific landfill leachate treatment plant under analysis.

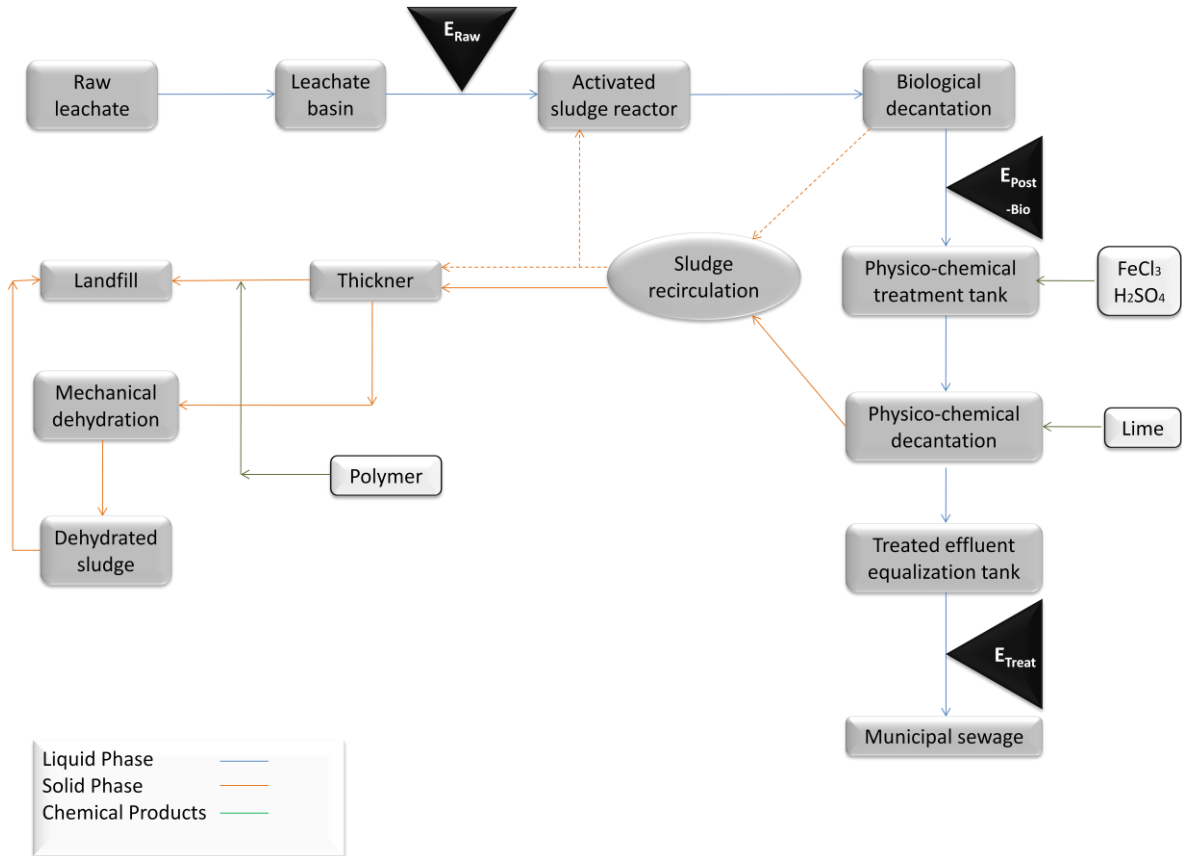


Fig. 2.2 - Flow-sheet of the landfill leachate treatment plant in the sanitary landfill under study.

As it can be seen, the leachate formed in the landfill cells (raw leachate) is sent to a basin to regulate and homogenize the flow. The biological treatment starts in the activated sludge reactor, which allows the partial oxidation of leachates. After that, a biological decantation is performed and some of the sludge is recycled. The following physico-chemical treatment consists in the addition of iron (III) chloride (FeCl₃) and sulphuric acid (H₂SO₄) to the effluent. FeCl₃ promotes coagulation and H₂SO₄ aims to decrease pH. Then, the leachate is decanted and lime is introduced to pH correction. Subsequently the effluent is pumped to the municipal sewage. Biological and physico-chemical sludge are directed to a thickener and then, after adding a polymer to remove the water, mechanical dehydration is carried out before disposing the dehydrated sludge at the landfill.

3. STATE OF THE ART

The interest on Fenton-like processes with ZVI methodology has been growing in recent years. In this context, the present chapter aims to give an overview of the applications of such technology on the depuration of liquid effluents, which comparing to traditional Fenton is a barely new approach.

3.1. LEACHATES OF MUNICIPAL SOLID WASTES LANDFILLS

Despite of the high pollutant load associated with leachates, landfilling still is one of the most applied methods to waste disposal due to its economic advantages (Lopez *et al.*, 2004). The fact of leachates presenting a high range of variability in terms of COD and BOD₅, among others parameters already mentioned at previous sections, allied with the variations on its production flows, it is difficult to choose the best treatment option. The most usual treatments applied were object of an overview and were discussed at section 2.3.

3.2. FENTON-LIKE PROCESSES WITH ZERO-VALENT IRON

Zero-valent iron or Fe⁰ has been considered in several studies, in the last two decades. ZVI is efficient to degrade diverse contaminants, like the dechlorination of chlorinated solvents in contaminated groundwaters, reduction of nitrate to atmospheric N₂, immobilization of numerous inorganic cations and anions, reduction of metallic elements, and the reduction of aromatic azo dye compounds and other organics such as pentachlorophenol and haloacetic acids (Joo and Cheng, 2006).

Numerous reports have been using Fenton-like processes for the remediation of water and soil contaminated with high organic load. Table 3.1 summarizes studies that have been done since 1996, for the Fenton-like ZVI processes. As is can be seen, the spectrum of study in this area covers specially dye wastewaters. Other effluents with trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), Reactive Black 5 (RB5), ethylenediaminetetraacetic acid (EDTA) and 4-chloro-3-methyl phenol (CMP) have been studied. Moreover, pesticides, like dichlorodiphenyltrichloroethane (DDT), were reported as well. Since 2009, this methodology

has been applied to wastewaters rich in phenolic compounds, such as olive mill wastewaters. The first preliminary results about leachates appeared only in 2011, showing that Fenton-like ZVI systems have a lot to offer at this field.

Hundal *et al.* (1997) proved that combining ZVI with H_2O_2 to destroy specific contaminants (RXD and TNT) is more efficient than using ZVI alone. Some papers centered on the study of alternative iron sources, like iron powder. Barbusiński and Majewski (2003) concluded that Fenton-like process with ZVI has advantages in comparison with the traditional Fenton, because increasing the amount of iron powder, the reaction final's pH increase as well, decreasing the costs of pH correction at the end of the reaction. Tang and Chen (1996) concluded that coupling iron powder with H_2O_2 leads to faster dyes decolorization than when classic Fenton reagents ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) are applied due to the continuous dissolution of iron powder and the dye adsorption on iron powder surface.

This new treatment approach has been extended to UV/ H_2O_2 oxidation processes by Chang *et al.* (2006), helping in decolorization and mineralization of dyes wastewater. Kallel *et al.* (2009a) proved that this treatment system is as an effective alternative solution for the depuration of olive mill wastewater and may be coupled with biological processes to improve the quality of the resulting wastewater. Beyond that, Kallel *et al.* (2009b) improved the biodegradability of olive wastewaters and the total degradation of phenolic compounds. Nano zero-valent iron (nano ZVI) was applied to Fenton-like recently by Xu and Wang (2011) and Shafieiyoun *et al.* (2011). They conclude that nZVI have potential to treat wastewaters due their large specific surface area, reaching into zones that are difficult to get in. Shafieiyoun *et al.* (2011) showed that nZVI increases the reaction molar ratio, increasing efficiency of the method.

Usually the selected operating conditions optimized are H_2O_2 , Fe^0 and contaminants concentrations, as well as pH. In fact, these factors show a high impact in this methodology. The optimal pH is, generally, in the range of 2 – 4, but the others parameters have extended results depending on the type of wastewater. From literature results, it can be conclude that Fenton-like ZVI processes are not able to achieve total removal of organic compounds, but COD removals superior to 78 % to the mentioned pollutants have been reported.

The state of the art shows that the Fenton-like processes with ZVI are a promising methodology and may be an efficient alternative for wastewater treatment.

Table 3.1 - Literature overview of Fenton-like ZVI processes.

Ref.	Pollutant	Variables analysed	Conclusions
Tang and Chen (1996)	Commercial dyes: Reactive Red 120, Direct Blue 160 and Acid Blue 40.	Effects of pH, iron powder, H ₂ O ₂ and dye concentrations.	Optimal pH ranged from 2 – 3 and optimal ratio of H ₂ O ₂ to iron powder was 0.001 M to 1 g/L. Complexes are formed to dyes concentrations above 75 mg/L.
Hundal <i>et al.</i> (1997)	2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	Effect of Fe ⁰ concentration.	Reduction of 5200 mg of TNT to 17.2 mg and 6400 mg of RDX/kg to 5.8 mg with 10 % Fe ⁰ . 70 mg/L of TNT spiked with ¹⁴ C-TNT, treated with 5 % of Fe ⁰ and 1 % of H ₂ O ₂ completely destroyed TNT and removed 94 % of the ¹⁴ C from solution, 48 % of which was mineralized to ¹⁴ CO ₂ in 8 h.
Barbusiński and Majewski (2003)	Commercial azo dye Acid Red 18	Effect of H ₂ O ₂ and Fe ⁰ dosages, pH, iron powder dosage on final pH and time between the addition of Fe ⁰ and H ₂ O ₂ .	The optimal conditions were 60 mg/dm ³ of H ₂ O ₂ and 50 mg/dm ³ of Fe ⁰ , pH = 3 and at 15 min. Iron powder can be used repeatedly in the process.
Chang <i>et al.</i> (2006)	C.I. Acid Black 24 wastewater	Effect of ZVI dosage, reaction time and pH.	100 g/L of ZVI with UV/H ₂ O ₂ had a TOC removal of 98 %. In 30 min of ZVI reaction and 11 - 50 min of UV/H ₂ O ₂ process, were obtained 90 % of decolorization and mineralization of dye wastewater, respectively. The optimal pH range is 3 – 5.15.
Boussahel <i>et al.</i> (2007)	4,4-DDT (dichlorodiphenyltrichloroethane) and 2,4-DDT	Effects of pH, iron powder dosage and Fe ⁰ /H ₂ O ₂ ratio.	50 % of 4,4-DDT and 60 % of 2,4-DDT were removed with 40 g of iron powder, at pH = 2 and with a 1/0.5 Fe ⁰ /H ₂ O ₂ ratio in 90 min.
Kallel <i>et al.</i> (2009a)	Olive mill wastewater	Effects of H ₂ O ₂ and Fe ⁰ dosages, pH, initial COD concentration and color.	pH range of 2 - 4, 9.5 M of H ₂ O ₂ and 20 g/L of Fe ⁰ . COD removal reaches 78 % with 4 g/L of initial COD. Coloration disappeared and phenolic compounds decreased to 50% of initial concentration after 3 h.
Kallel <i>et al.</i> (2009b)	Olive mill wastewater	Effects of H ₂ O ₂ dosage, initial pH on COD removal and effluent biodegradability.	With 20 g/L of Fe ⁰ , the optimal conditions were 0.95 M of H ₂ O ₂ , pH range of 2 – 4 with a maximum COD removal of 92 %. After 24 h of reaction, BOD ₅ /COD ratio improves from 0.14 to 0.53, due to the phenolic compounds removal.

Table 3.1 -Literature overview of Fenton-like ZVI processes (continuation).

Ref.	Pollutant	Variables analysed	Conclusions
Zhou <i>et al.</i> (2009)	Simulated textil wastewater	Decolorization and degradation of the wastewater, initial Reactive Black 5 (RB5) concentration, Fe ⁰ and ethylenediaminetetraacetic acid (EDTA), dosages, pH, atmospheres and degradation with external energy.	After 3h, a rapid decolorization was obtained and complete degradation of EDTA. A 68.6 % TOC and 92.2 % COD were achieved at a neutral pH condition. Fe ⁰ , RB5 and EDTA concentrations were 25 g/L, 100 mg/L and 0.4 mM, respectively. Optimal pH is 2. Open to air showed to be the best atmosphere. Ultrasound improved the decolorization rate of the effluent but ultraviolet inhibit it.
Xu and Wang (2011)	4-chloro-3-methyl phenol (CMP)	Effects of pH, initial concentration of CMP, pH, ZVI and H ₂ O ₂ concentration.	In 15 min were obtained a complete degradation of CMP with 0.5 g/L of ZVI, 3.0 mM of H ₂ O ₂ , 0.70 mM of CMP at pH = 6.1. 63 % of TOC removal was achieved at 60 min of reaction.
Shafieiyoun <i>et al.</i> (2011)	Landfill leachates	Effects of initial pH, H ₂ O ₂ /Fe ⁰ molar ratio, dosage of Fenton reagents and temperature.	pH = 2, H ₂ O ₂ /Fe ⁰ molar ratio of 39, 2.7 M of H ₂ O ₂ , 0.07 M of NZVI and 40 °C were the best operating conditions to remove 87 % of leachates COD in 1 h.

4. EXPERIMENTAL METHODOLOGY

In this chapter it will be described the experimental methodology applied in the treatment of urban landfill leachates. Firstly, an approach about the sampling of the effluents is given, followed by the experimental procedures and a description about the analytical techniques that were used.

4.1. SAMPLING OF EFFLUENTS

Fig. 4.1 represents a flow-sheet of the landfill leachate treatment plant, where the effluents samples were collected in different phases, in order to evaluate the new methodology approach of this thesis and the best location to implement it. E_{Raw} sample was obtained before the aerobic bio-reactor, the $E_{Post-Bio}$ was taken before the physico-chemical treatment and after the biological treatment, and the E_{Treat} after the biological and physico-chemical treatments, just before leachate is released to the municipal wastewater treatment plant. The samples were collected in plastic containers and were stored in a laboratory refrigerator.

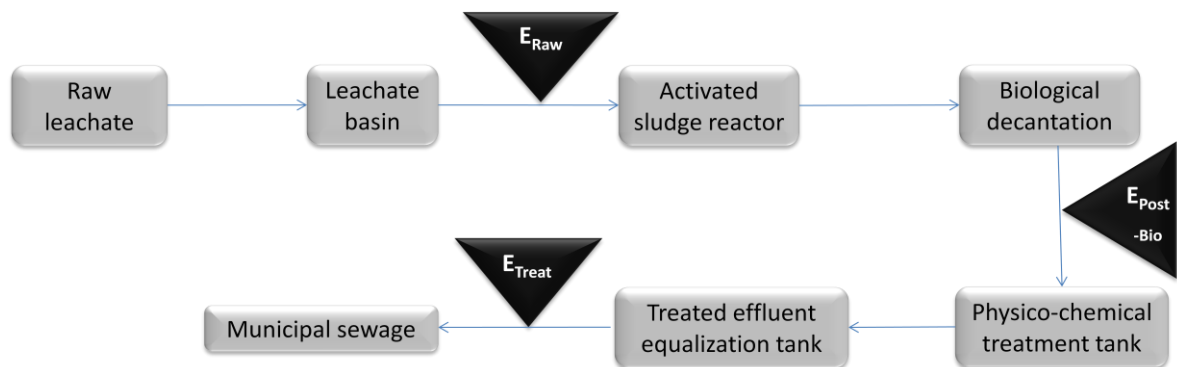


Fig. 4.1 - Adapted flow-sheet of the landfill leachate treatment plant in the sanitary landfill under study, with the local of effluent's collection.

4.2. EXPERIMENTAL PROCEDURE

Fenton-like ZVI process was generally carried out in dark glass bottles, where 40 mL of effluent were introduced and agitated in an orbital shaker (Heidolph – Reax 20 shaker at 16 rpm). Hydrogen peroxide (industrial grade, 50 % w/w) and iron powder (-325 mesh, 97 %, Aldrich) were added in some experiments. Iron powder has 0.868 ± 4.42 m²/g of surface area and a pore size of 37.50 Å.

When iron shavings (obtained from a metal turner) were tested as catalyst, 1 L reactor with 500 mL of landfill leachate was used. Samples were periodically withdrawn and the reaction was stopped by raising pH to 12, with NaOH (3 M).

All tests were repeated, at least 2 times to guarantee the repeatability of results and, in general, the deviations were less than to 10 % in COD, TPh and 20 % in BOD₅.

An important note is that not all BOD₅ values in this study were performed due to the short time to accomplish them. Despite of the all BOD₅ values on this thesis were evaluated with the standard control solution of glucose-glutamic acid, some BOD₅ values were negative and were despised. This happened because the dissolved oxygen were lower than the limit detection of the equipment used (2 mg/L), meaning that the samples are highly biodegradable.

4.3. ANALYTICAL TECHNIQUES

COD was determined by the sample digestion method with dichromate using a thermoreactor CR3000, during 2 h at 150 °C and COD was measured in Photometer MPM 3000, at 605 nm. Total suspended solids (TSS) and total dissolved solids (TDS) were determined according to the Standard Methods (Greenberg *et al.*, 1985), with a 0.45 µm pore filter under vacuum conditions and a CARBOLITE stove, respectively. BOD₅ was determined by the difference between the oxygen dissolved before and after the 5 incubation days. Activated sludge was obtained from the industrial bio-reactor. The dissolved oxygen was measured with a WTW inoLab Terminal 740 Stirrox. To ensure the accuracy of the BOD₅ test, a mixture of 7.5 mg of glucose and 7.5 mg of glutamic acid, previously dried during 1 h at 103 °C were dissolved in a 50 mL volumetric flask. The BOD₅ range of this standard mixture should be 198 ± 30.5

mg/L. pH and oxidation reduction potential (ORP) were measured by CRISON micro pH 2002. Total phenolic content (TPh) was quantified by Folin-Ciocalteu method described in bibliography (Silva *et al.*, 2007), using a T60 spectrophotometer. Chlorides were measured by the Mohr method with AgNO_3 (0.1 M), dried at 120 °C for 2 h, and K_2CrO_4 (0.257 M), according to Quina (2005). Colour will change to a low red-brown, at the equivalence point. The concentration of iron in the leachates composition was determined by atomic absorption spectrophotometry (FAAS – Perkin–Elmer 3000). Surface areas, S_{BET} , of iron powder and iron shavings were determined with an accelerated surface area analyzer (*ASAP 2000*, *Micromeritics*). Hydrogen peroxide concentration was measured after the treatment by Precision Laboratories Peroxide Test Strips (0 – 100 ppm).

5. RESULTS AND DISCUSSION

In this chapter, laboratory results are presented and discussed with the objective to determine if the Fenton-like methodology is appropriated to improve the industrial landfill leachates treatment. This chapter is divided in 4 sections: the characterisation of effluents collected at landfill and its comparison with legal limits values for discharge to a local municipal sewage; a set of preliminary tests to choose the best option for the leachates treatment; the Fenton-like process with ZVI, will be considered to study the effects of operational conditions; Fenton-like process with iron shavings will be to analysed.

It is important to note that TSS and TDS were determined to each pre-test and test of this chapter. Nevertheless, the fact of this work was made with a real effluent and the lack of time to repeat the solids experiments, increasing the experimental errors associated, made the TSS and TDS values not conclusive. These tests were only made for the characterisation of effluents.

5.1. CHARACTERISATION OF EFFLUENTS

At 4th April 2011 (1) E_{Raw} and E_{Treat} were collected and at 2nd May 2011 (2) a second sample of both E_{Raw} and E_{Treat} was obtained, whereas $E_{Post-Bio}$ was also collected. Their physico-chemical characterisation can be seen in Table 5.1.

Table 5.1 - Characterisation of both effluents collected at 4th April (1) and 2nd May (2) in 2011.

Parameters	E_{Raw}		$E_{Post-Bio}$	E_{Treat}		LLD
	1	2		1	2	
pH	8.0	8.0	7.0	6.9	4.7	5.5 – 9.5
Redox Potential (mV)	-154	-316	120	212	432	*
COD (mg O ₂ /L)	2047±15	2030±72	1540±20	1573±6	1065±64	1000
BOD ₅ (mg O ₂ /L)	1253±193	n.d.	65±58	18±4	n.d.	800
BOD ₅ /COD	0.61	n.d.	0.04	0.01	n.d.	*
Chloride (mg/L)	2049±191	2340±20	2326±20	3106±120	2815±70	750
Iron (mg/L)	28±0.1	15.9±0.1	13.8±0.1	85±0.1	0.9±0.1	20
TSS (mg/L)	200±42	300	500	150±14	50	1000
TDS (mg/L)	8040±424	7600	5150	7960±57	56000	*
TPh (mg GAeq/L)	291±3	336±8	106±5	142±7	31±10	*

n.d.- not determined; LLD – Legal limit of discharge throughout the local municipal sewage.

* This values are not stipulated in legislation of discharge throughout the local municipal sewage.

The difference between the results obtained for E_{Raw} and E_{Treat} from (1) to (2) reveals the leachates composition variability, which is mainly due to the atmospheric conditions, and the variations of the waste disposed into the landfill, in terms of quantity and type of waste (Renou *et al.*, 2008). In general, the highest differences were attained for E_{Treat} . This can be explained by the differences on the atmospheric conditions between April and May; and by the fact that the industrial treatment is not working properly at 4th April (1). In fact, at 2nd May (2) by simple observation of the sample, it was evident that the plant was working in a more efficient way.

The first tests in our laboratory were performed by using the E_{Raw} (1) and E_{Treat} (1), so that to maintain the consistence of values, all the experiments carried out in this thesis were performed with (1).

It is important to refer that E_{Treat} (1) shows a higher COD value than $E_{\text{Post-Bio}}$ even if, theoretically it was subjected to a secondary treatment. However, the inlet leachate is constantly changing affecting thus the depuration efficiency. In this context, since E_{Treat} (1) and $E_{\text{Post-Bio}}$ were not collected in the same date it is probable that the pollutant character of the raw effluents giving rise to both samples was completely different.

The pH of E_{Treat} (2) is comparably lower than the one observed for (1). This is related with an increase on the H_2SO_4 load introduced at the physico-chemical treatment stage at the landfill leachate treatment plant.

The landfill treatment applied to these effluent decreased COD in 23 % in E_{Raw} (1) to E_{Treat} (1) and 47.5 % E_{Raw} (2) to E_{Treat} (2). At 2nd May, the biological treatment showed a COD removal efficiency, comparing E_{Raw} (2) with $E_{\text{Post-Bio}}$, of 25 %. However, in any case E_{Treat} fulfilled the legal limits of COD for direct discharge throughout the local municipal sewage.

Even though the high biodegradability observed for the raw leachate ($\text{BOD}_5/\text{COD} = 0.61$), the activated sludge treatment system is not able, by itself, to totally depurate it. Moreover, a dramatic decrease on the biodegradable load of the effluent is observed after the bio-reactor ($\text{BOD}_5/\text{COD} = 0.04$) and after the physico-chemical process ($\text{BOD}_5/\text{COD} = 0.01$). Within this context, it seems that further bioremediation will not be possible and the search of more suitable technological solutions is required.

According to the values depicted in Table 5.1, chloride concentration is also a major problem since the determined values along the treatment process largely overpass the legal thresholds for the discharge of leachates to the local municipal sewage.

The quantity of iron present in this raw effluent may be higher than LLD and can increase from $E_{\text{Post-Bio}}$ to $E_{\text{Treat}} (1)$ due to the physico-chemical treatment at the landfill leachate treatment plant, which consists in the addition FeCl_3 to the leachate. In case of $E_{\text{Treat}} (2)$, the amount of iron is lower when compared with $E_{\text{Treat}} (1)$, probably because a lower amount of FeCl_3 was added or due to an efficient coagulation process.

TSS of E_{Treat} and $E_{\text{Post-Bio}}$ fulfils the legal limit value. The 500 mg/L of $E_{\text{Post-Bio}}$ TSS are due to sludge from the biological decantation.

At 4th April, discharges did not fulfilled the COD, chloride and iron, but in 2nd May failed in terms of pH, COD and chloride. It seems that the treated effluent rarely accomplishes the legal COD threshold for discharge, thus, this thesis aims to optimize a new treatment approach.

There was an opportunity to compare some of our characterisation values with the ones obtained by the laboratory of the landfill leachate treatment plant. One more time, the variability of landfill leachates parameters was proved. Fig. 5.1 compares the results of April and May of 2008 to 2010 from the industrial plant, with the ones obtained at DEQ-FCTUC in 2011. Additional industrial data can be found in the Annex.

The COD values of E_{Raw} reveal high variability. It can be observed that the COD values determined in DEQ-FCTUC are always lower than the ones reported by the landfill laboratory. For example, in April of 2011 COD values of 2047 mg O_2/L and 8000 mg O_2/L were obtained by the former and the latter laboratory, respectively. The E_{Raw} values obtained at DEQ-FCTUC laboratory (2011) for both April and May were more similar than the ones obtained by the landfill laboratory. The difference between COD from April and May are, probably, due to the different amount of waste disposal at the landfill and due to atmospheric conditions. E_{Treat} showed to be more stable than E_{Raw} , but April values were bigger than May, which is normal considering that E_{Raw} , in April, showed a larger organic load. At 2011, E_{Treat} increased from 1200 mg O_2/L to 1573 mg O_2/L (April) and from 170 mg O_2/L to 1065 mg O_2/L (May).

BOD₅ values for April 2011, were 130 mg O₂/L and 18 mg O₂/L attained by the landfill laboratory and DEQ-FCTUC, respectively. This difference could be associated with the method of BOD₅ determination at the landfills laboratory, which was not revealed, and the experimental errors associated with this methodology. For the May sample, there was not sufficient time to do the BOD₅ test and it cannot be compared with the others obtained till 2010.

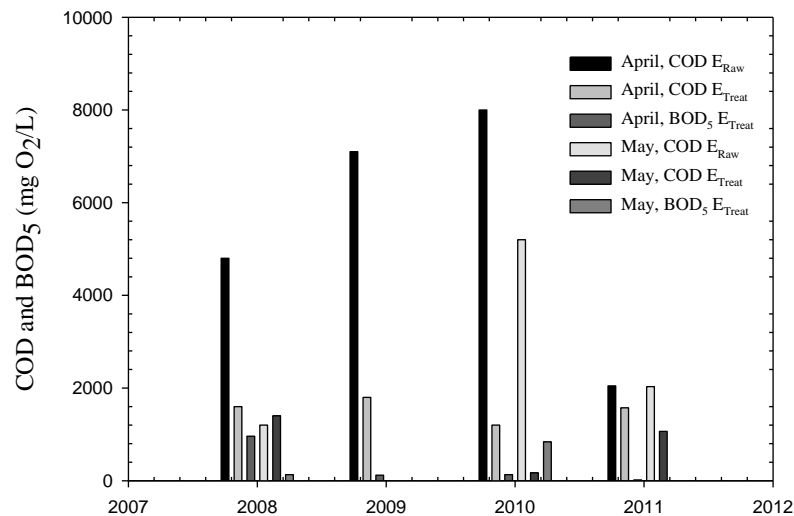


Fig. 5.1 - Landfill data for COD and BOD₅ in April and May, since 2008.

5.2. PRELIMINARY TESTS

Before Fenton-like process with zero-valent iron, ZVI, some preliminary tests were performed. The purpose was to evaluate the leachate behaviour to ZVI methodology, Fenton-like and Fenton-like with ZVI process in order to choose the best treatment to this kind of effluent. These experiments were denominated in this section as preliminary tests, which include the addition of Fe⁰ and H₂O₂ separately (T1 and T2, respectively) and both reactants together (T3). All tests were made under the experimental conditions showed in Table 5.2.

Table 5.2 - Experimental conditions of the preliminary tests.

Experimental conditions	T1		T2		T3	
	E_{Treat}	E_{Raw}	E_{Treat}	E_{Raw}	E_{Treat}	E_{Raw}
Temperature	Room temp.	Room temp.	Room temp.	Room temp.	Room temp.	Room temp.
Initial pH (raw pH)	6.9	8.0	6.9	8.0	6.9	6.9
Concentration of Fe^0 (g/L)	125	-	-	125	125	125
Concentration of H_2O_2 (g/L)	-	3.35	3.35	3.35	3.35	3.35
Volume of effluent sample (mL)	40	40	40	40	40	40
Residence time at the orbital shaker	2 h	2 h	2 h	2 h	2 h	2 h
Analysed tests	COD and BOD_5	COD and BOD_5	COD and BOD_5	COD and BOD_5	COD and BOD_5	COD and BOD_5

Table 5.3 resumes the COD and BOD_5 values attained before and after each treatment.

Table 5.3 - Preliminary tests to E_{Raw} and E_{Treat} .

Parameters	T1		T2		T3		LLD
	E_{Treat}	E_{Raw}	E_{Treat}	E_{Raw}	E_{Treat}	E_{Raw}	
COD after treatment test (mg O_2/L)	1483±3	2030±20	1342±32	1957±4	1283±3	1000	1000
COD Removal (%)	5.7	0.8	14.7	4.4	18.4	-	-
BOD_5 after treatment test (mg O_2/L)	58±31	n.d.	3±0	-	-	800	800
BOD_5 after treatment test/ BOD_5 before treatment test	322.2	n.d.	0.2	-	-	-	-
BOD_5/COD after treatment test	0.04	n.d.	0.002	-	-	-	-

n.d.- not determined; LLD – Legal limit of discharge throughout the local municipal sewage.

The ZVI treatment (T1) was only applied to E_{Treat} . According to Bell *et al.* (2003), the mass of iron powder used to degrade organic matter was 125 g/L.

The COD value of E_{Treat} was tested with a gas stream of N_2 to guarantee that ZVI was not oxidized by the O_2 and the obtained value was 1510 mg O_2/L , which is very similar compared with the E_{Treat} COD, 1483 mg O_2/L . Therefore, it may be concluded that reducing conditions were not important in this case.

According to Table 5.3, in this case, the addition of Fe^0 reduces COD in 5.7 %, which is not significant. Fe^0 , by itself, do not have the capacity to abate the organic matter present in E_{Treat} . In fact, ZVI is reported to be efficient in the reduction of nitrogenated and chlorinated compounds (Agrawal and Tratnyek, 1996; Ma and Zhang, 2008). However, in what regards

COD abatement, which is our goal, it probably require an oxidant agent. Moreover, a slight BOD₅ increased was observed after the application of ZVI process, which means that some bio-refractory matter was transformed into biodegradable matter. Even so, the BOD₅/COD ratio is below 0.4, which is the commonly accepted threshold to consider an effluent as biodegradable (Esplugas *et al.*, 2004). This treatment improve biodegradability from 0.01 to 0.04.

According to Table 5.2, Fenton-like process was implemented in T2 by adding 3.35 g H₂O₂/L to the effluents, E_{Raw} and E_{Treat}. This amount was based on the stoichiometry value theoretically required to totally oxidize E_{Treat}. The stoichiometry value was obtained by Eq. (5.1) (Eckenfelder, 2000):

$$H_2O_2 \text{ stoichiometry demand (mg } H_2O_2/L) = 2.13 \times COD \quad (5.1)$$

where *COD* is the chemical oxygen demand that characterize the effluent under analysis (E_{Treat}=1573 mg O₂/L).

The same amount of hydrogen peroxide was used for both effluents, E_{Raw} and E_{Treat}, for comparative purposes. It is important to note that classic Fenton's process requires a source of iron as catalyst and, according to Table 5.1, the wastewaters encompass a high amount of this metal in their composition (28±0.1 mg/L for E_{Raw} and 85±0.1 mg/L for E_{Treat}). Thus, in order to minimize operational costs, the ability of this residual iron to enhance H₂O₂ oxidant power was tested. T2 was performed with the experimental conditions showed in Table 5.2.

According to Table 5.3, a COD removal of 14.7 % was observed for the E_{Treat} whereas E_{Raw} did not even reach 1 % of COD depletion. This means that adding only H₂O₂ is not a good approach to E_{Raw}, since it has much more organic matter than the treated one, 2047 mg O₂/L, besides a lower amount of iron and H₂O₂ did not produce enough HO· radicals to oxidize the organic matter with the iron present in leachates (Fe³⁺). Moreover, it is probable that a higher efficiency would be attained if a more active catalyst was used, in fact, the iron present in the effluents it is much probably Fe³⁺ which is reported a less proficient than Fe²⁺ or Fe⁰ (Deng and Englehardt, 2006). Even though the 14.7 % of COD removed for E_{Treat}, this abatement is

still not significant to fulfill the 1000 mg O₂/L legal limit for discharge throughout the local municipal sewage.

In general, AOP can be envisaged as pre-treatments to improve effluents biodegradability by increasing BOD₅. However, in this particular case, it was achieved lower BOD₅ values (according to Table 5.3) what means that the microorganisms will probably be unable to remove more organic matter.

Fenton-like process with ZVI (T3) was tested under the operational conditions referred in Table 5.2. Table 5.3 shows that 4.4 % of COD removal was attained for E_{Raw} with T3 showing an improvement comparatively with T2 (0.8 %). For E_{Treat}, 18.4 % of COD was abated in T3, when compared with T1 (5.7 %) and T2 (14.7 %). This means that adding a strong catalyst, Fe⁰, helps H₂O₂ to oxidize more organic matter than ZVI (T1) or Fenton-like (T2). However, T3 do not fulfil the limit of COD discharge.

According to Fig. 5.2, T3 is the best treatment in terms of COD removal, in a general way, in spite of none of the treatments applied was able to fulfil the legal COD value for discharge throughout the local municipal sewage.

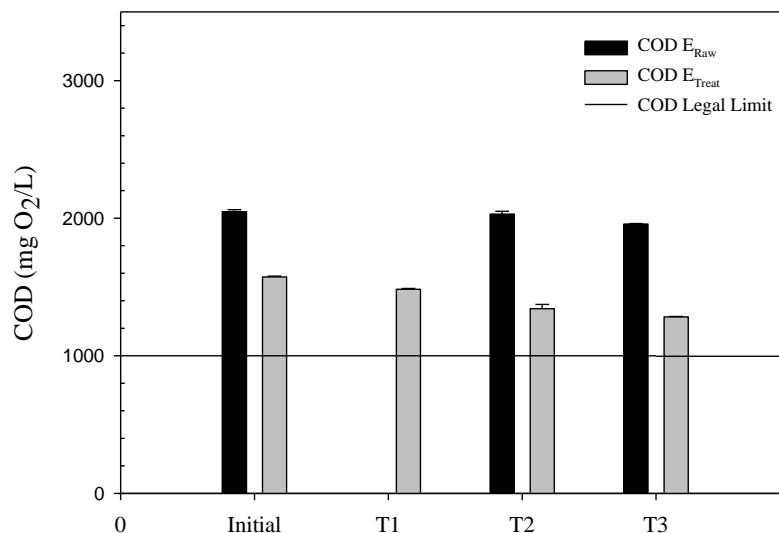


Fig. 5.2 - Comparison of COD removal for the preliminary tests, T1, T2 and T3.

5.3. FENTON-LIKE PROCESSES WITH ZERO-VALENT IRON

To optimize the new methodology of leachates treatment, a set of operating parameters variations were performed and analysed, like the effect of pH, concentration of H_2O_2 , concentration of Fe^0 and residence time. The experiments involved E_{Raw} and E_{Treat} because at the time that these were tested, $E_{Post-Bio}$ had not been collected yet. All the experiments were performed at room temperature.

5.3.1. EFFECT OF pH

pH variation was held for T2 (only H_2O_2) and T3 ($H_2O_2 + Fe^0$), within a range between 2 and 9.3. Other experimental conditions are mentioned in Table 5.2, but at this time for T2, besides the COD and BOD_5 tests, TPh was also analysed.

At a first approach, T2 was applied to E_{Raw} and E_{Treat} under operational conditions mentioned at Table 5.2 . Fig. 5.3. shows the effect of pH E_{Raw} and E_{Treat} COD abatement.

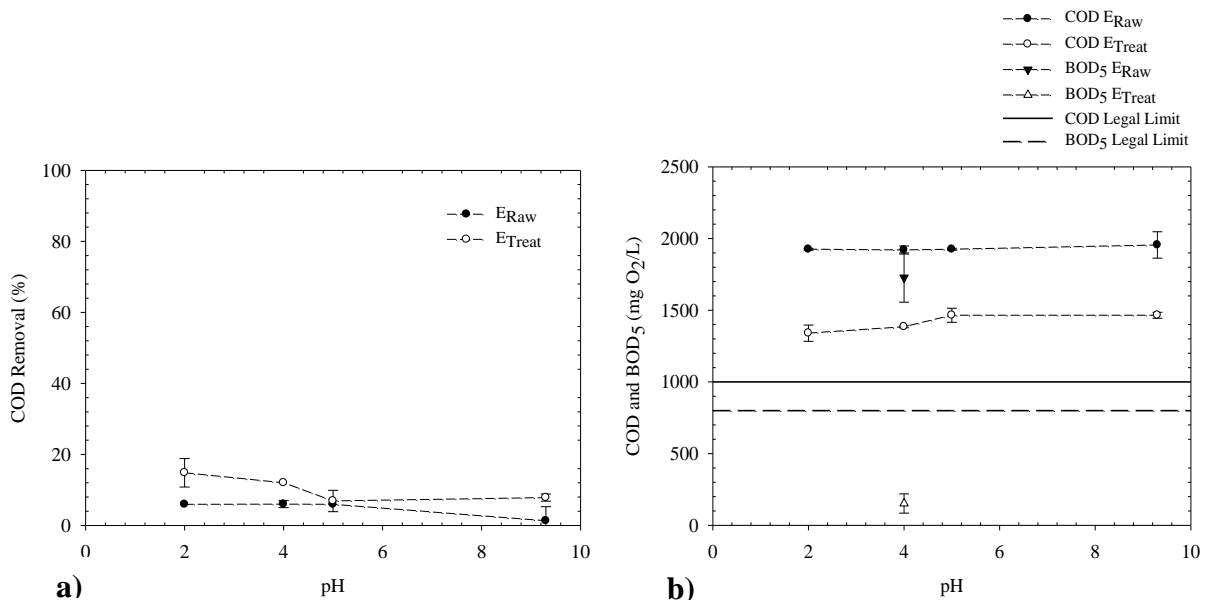


Fig. 5.3 - Effect of pH in E_{Raw} and E_{Treat} remediation by Fenton-like process T2, with 3.35 g/L of H_2O_2 for 2 h. **a)** COD removal (%); **b)** COD and the Legal Limit for discharge throughout the local municipal sewage (mg O_2/L).

In spite of pH do not have considerable effect in E_{Raw} COD removal till $pH = 5$, the optimal pH to remediate E_{Raw} by the Fenton-like process is $pH = 4$, with 6.0 % of COD removal, as observed in Fig 5.3 a). In fact, from $pH = 5$ to $pH = 9.3$, COD removal of raw leachate decreased in 4.7 %. It is clear that COD removal decrease with the increase of pH when E_{Treat} depuration is taken into account, but its maximal COD removal (14.8 %) corresponds to $pH = 2$.

Fig. 5.3 b) shows the final COD and BOD_5 achieved after treatment as function of pH as well as the legal thresholds for discharge into the local sewage. In all cases, effluents cannot be disposed into local municipal sewage. Concerning to BOD_5 of the effluents, the initial value was 1253 mg O_2/L to E_{Raw} , and 18 mg O_2/L to E_{Treat} . At $pH = 4$, these initial values increased to 1728 mg O_2/L and 152 mg O_2/L to E_{Raw} and E_{Treat} , respectively.

Total phenolic compounds removal variation with pH for E_{Raw} and E_{Treat} is demonstrated in Fig. 5.4, only for treatment T2.

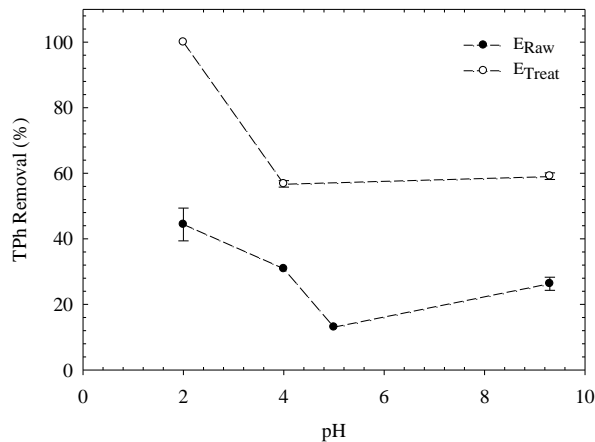


Fig. 5.4 - Effect of pH in E_{Raw} and E_{Treat} with T2 on TPh removal (%), with 3.35 g/L of H_2O_2 for 2 h.

Total phenolic compounds removal was only tested at T2 due to reasons already mentioned in relation with iron powder.

At $pH = 2$, E_{Treat} reached 100 % of TPh removal but then decreased to 56.8 % ($pH = 4$) probably due to the formation of intermediary compounds. From $pH = 4$, there were no significant changes on TPh removal. The optimal pH to E_{Raw} was $pH = 2$, as well. To E_{Raw} ,

from pH range 2 - 5, T2 reduced its efficiency to a minimum of 13.0 % for TPh abatement. Then, the percentage of phenolic removal increased when pH = 9.3 was used (26.3 %). This probably happened due to the formation of intermediary compounds with phenolic characteristics when high pH values are applied. Phenolic characteristics of E_{Treat} revealed to be more easily removed maybe because as this effluent has been already treated, its compounds are less refractory, so easier to be removed by the treatment applied.

Secondly, E_{Raw} and E_{Treat} were submitted to T3 pre-treatment, according to Table 5.2. COD abatement as function of the medium pH is given in Fig. 5.5.

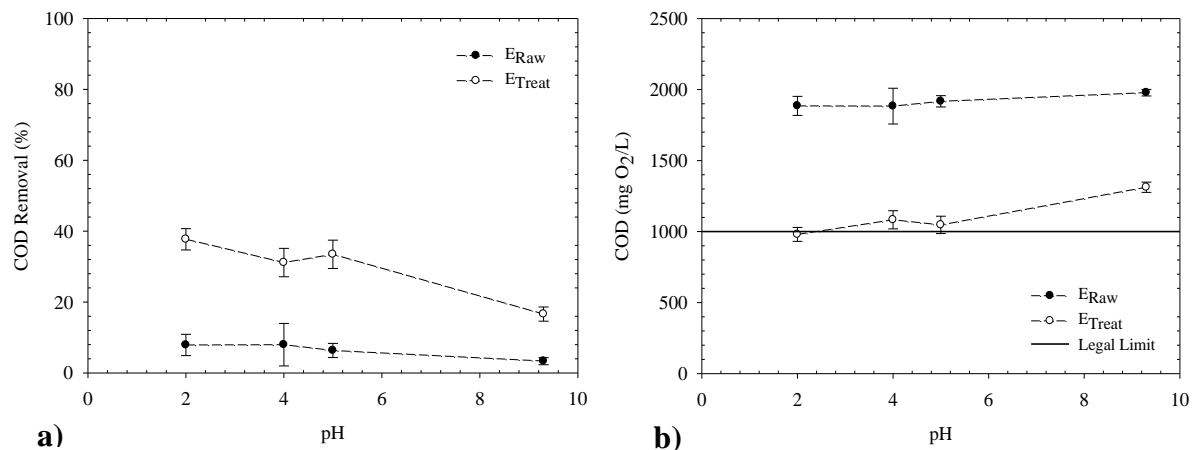


Fig. 5.5 - Effect of pH in E_{Raw} and E_{Treat} remediation by $\text{H}_2\text{O}_2 + \text{Fe}^0$ T3, with 125 g/L of Fe^0 and 3.35 g/L of H_2O_2 , for 2 h. **a)** COD removal (%); **b)** COD and the Legal Limit for discharge throughout the local municipal sewage (mg O₂/L).

According to Fig. 5.5 a), pH reveals a slightly effect on E_{Raw} COD abatement. Even so, pH = 4 seems to be the best choice leading to a global removal of 8.0 %. In a general way, it is clear that COD removal decreases with the increase of pH when E_{Treat} depuration is taken into account, Fig. 5.5 a), reaching a maximum of 37.7 % at pH = 2. In fact, as it can be observed in Fig. 5.5 b) the legal limit of 1000 mg O₂/L is only fulfilled for E_{Treat} when the process is carried out at pH = 2. For higher pH values it is notorious that a Fenton-like ZVI process losses its efficiency because of the fact that there are less HO· radicals in solution due to the formation of ferric-hydroxo complexes (Kallel *et al.*, 2009b).

By comparing Fig. 5.3. a) with Fig. 5.5. a), it is important to note that similar trends for E_{Raw} COD removal as function of pH are observed even if higher removal values are attained for T3. In what regards E_{Treat} depuration, the process involving H_2O_2 and Fe^0 (T3) (Fig. 5.5) leads to higher efficiencies than when only H_2O_2 is applied (T2) (Fig. 5.3). In fact, for example for $pH = 2$, 14.8 % of COD removal were attained for T2 when compared with up to 37.7 % for T3. It should be referred that BOD_5 values obtained for T2 cannot be compared yet with T3, because given the short time it was not possible to conduct all the BOD_5 tests. The BOD_5/COD ratio to $pH = 4$ was 0.90 to E_{Raw} and 0.11 to E_{Treat} , which demonstrating that E_{Raw} leachate is very biodegradable contrarily to E_{Treat} .

Gathering up all the results attained by performing variations in the pH, it seems preferable to conduct E_{Treat} and E_{Raw} treatment at $pH = 2$ and $pH = 4$, respectively, in T2 or T3. These results are consistent with the optimal pH range to Fenton's process found in literature, which indicates values within 2 – 4 (Ahmadi *et al.*, 2005).

5.3.2. EFFECT OF H_2O_2 CONCENTRATION

The study of the impact of hydrogen peroxide concentration over Fenton like process efficiency was performed using H_2O_2 loads within the range of 0.84 – 13.40 g/L. The operating pH was fixed in 3 because this value is between the optimal pH range to Fenton's reaction (Ahmadi *et al.*, 2005). The samples were agitated in a orbital shaker for 2 h. From the moment that H_2O_2 was not present in the solution, COD, BOD_5 and TPh tests were performed. Fig. 5.6. represents COD and BOD_5 of the treated effluents.

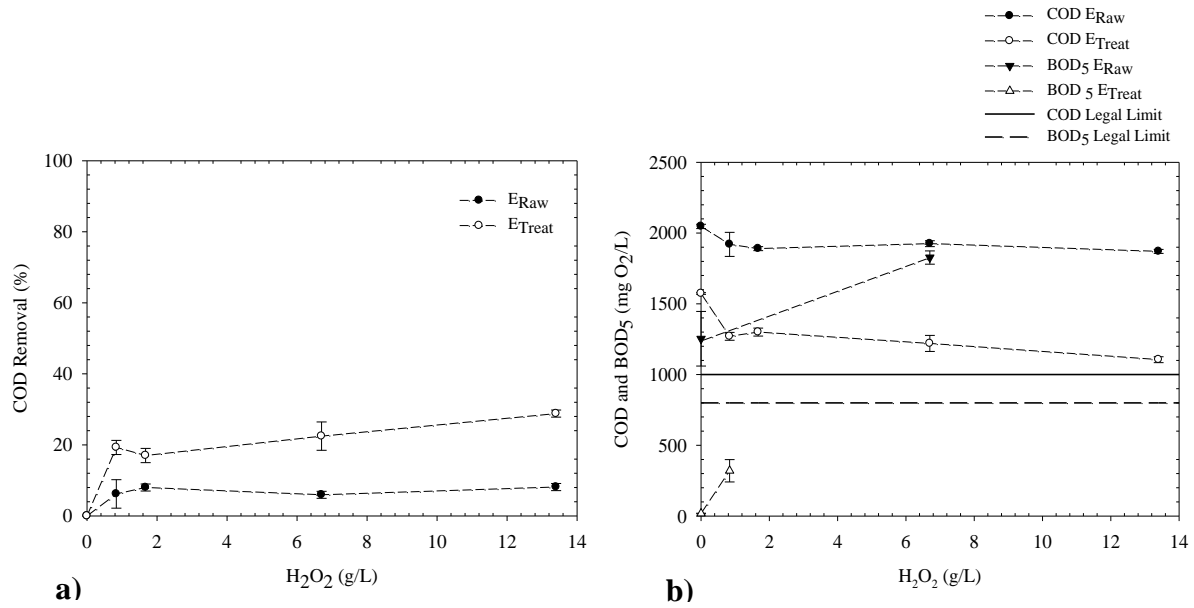


Fig. 5.6 - Effect of concentration of H₂O₂ in E_{Raw} and E_{Treat} with T2, pH = 3 for 2 h. **a)** COD removal (%); **b)** COD, BOD₅ and their Legal Limit of discharge throughout the local municipal sewage (mg O₂/L).

According to Fig. 5.6 a), by increasing the concentration of H₂O₂ leads to higher COD removal except when the concentration of H₂O₂ is 1.67 g/L to E_{Treat} and 6.70 g/L to E_{Raw}. In fact, H₂O₂ concentration should be carefully selected since the production of HO· radicals increase with the concentration of H₂O₂, but if its amount is excessive in the reaction this reactant reveals a radical scavenger effect inhibiting the organic matter oxidation.

Small oscillations in COD removal were obtained in Fig. 5.6 a). For E_{Treat}, the COD removal decreased from 19.3 % (0.84 g H₂O₂/L) to 17 % (1.68 g H₂O₂/L), increasing again to 22.5 % (6.70 g H₂O₂/L). The same behavior happens to E_{Raw}: COD removal decreased from 8.0 % (1.68 g H₂O₂/L) to 5.9 % (6.70 g H₂O₂/L), increasing again to 8.1 % (13.40 g H₂O₂/L).

Based on these results, it was considered that the optimal concentration of H₂O₂ is 13.40 g/L which corresponds to a COD removal of 28.8 % to E_{Treat} and 8.1 % to E_{Raw}. The lower organic matter removal observed for E_{Raw} is probably due to its more complex constitution encompassing highly refractory pollutants.

In Fig. 5.6 b), it can be observed that none of the concentrations of H₂O₂ values led to effluent with legal characteristics to be discharged throughout the municipal sewage. The nearest point of COD legal value is 1105 mg O₂/L attained when 13.40 g H₂O₂/L were used to E_{Treat}. The few determinations of BOD₅ possible to attain were those related to a concentration of H₂O₂

of 0.84 g/L at E_{Treat} and 6.70 g/L at E_{Raw} . Only for the case of E_{Treat} the legislative limit was not exceeded and in both cases BOD_5 increased comparatively with the initial effluents, which mean that Fenton-like process was able to increase the wastewater biodegradability. A BOD_5/COD ratio of 0.95 was determined for E_{Raw} whereas for E_{Treat} that ratio was 0.25, which shows a high increase when compared with the initial value (0.61 to E_{Raw} and 0.01 to E_{Treat}).

The total phenolic content removal results for both effluents as function of hydrogen peroxide concentration are depicted in Fig. 5.7.

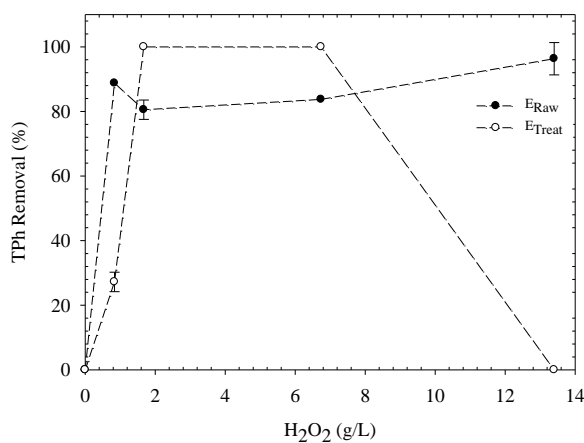


Fig. 5.7 - Effect of concentration of H_2O_2 in E_{Raw} and E_{Treat} with T2 on TPH removal (%), pH = 3 for 2 h.

As it can be seen by the Fig. 5.7, for E_{Treat} , the total of phenolic compounds removal increases with the concentration of H_2O_2 , until 1.68 g/L of H_2O_2 , where the maximum of 100 % of degradation was reached. E_{Raw} never achieved the 100 % of removal probably due to its more complex composition. E_{Raw} have many pollutants, as humic acids, chlorinated organic compounds, among others, which are difficult to remove. These pollutants, especially the humic acids, may react with the phenolic compounds and promote the formation of intermediate compounds with phenolic content, which are difficult to remove entirely (Renou *et al.*, 2008).

5.3.3. EFFECT OF Fe^0 CONCENTRATION

In order to test the effect of Fe^0 load on the leachates treatment by ZVI based Fenton's process, were added to 40 mL of effluents a range of 12.5 – 125 g/L of iron powder and 3.35 g H_2O_2 /L. E_{Raw} pH was fixed at 4 and E_{Treat} at 2 due to the fact that these are the optimal pH values of each leachate as determined before. The samples were agitated for 2 h. After the H_2O_2 were no longer at the samples, COD, BOD_5 and TPh were quantified. Fig. 5.8 represents the effect of Fe^0 mass over the treatment efficiency regarding COD and BOD_5 , between a range of 12.5 – 125 g/L of iron powder.

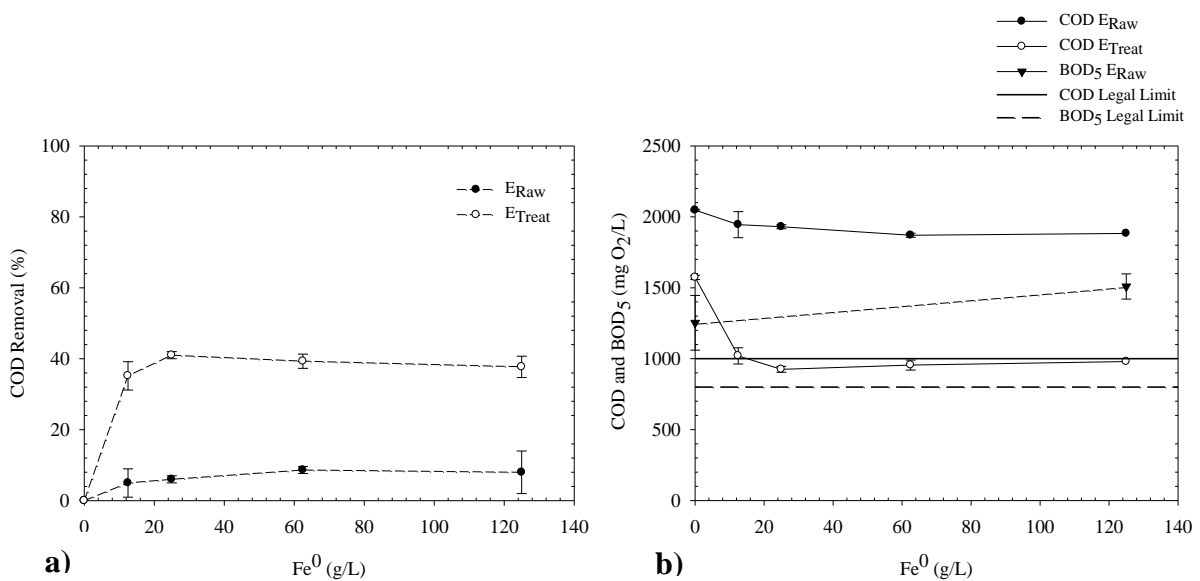


Fig. 5.8 - Effect of concentration of Fe^0 in E_{Raw} and E_{Treat} with T3, with 3.35 g H_2O_2 /L, pH = 4 to E_{Raw} and pH = 2 for E_{Treat} , for 2 h. **a)** COD removal (%); **b)** COD, BOD_5 and their Legal Limit of discharge throughout the local municipal sewage (mg O_2 /L).

In the considered Fenton-like process, to produce $\text{HO}\cdot$ radicals it is very important to have Fe^0 at the solution. In fact, this solid catalyst helps at the organic matter oxidation with H_2O_2 , however, the presence of high loads can lead to a radical scavenger effect. There was a slightly increase of iron from the maximum points of COD removal, this may be related with radical scavenger. Without this catalyst as it was seen in 5.3.2. section of this thesis, by adding only H_2O_2 to the leachates, not enough $\text{HO}\cdot$ radicals are produced to oxidize much organic matter. When H_2O_2 reacts with Fe^0 , the degradation of organic matter is much more efficient.

The addition of Fe^0 to the effluents allows to have two oxidation stages: the passage from Fe^0 to Fe^{2+} and from Fe^{2+} to Fe^{3+} . This enables to oxidize more organic matter than if only Fe^{2+} is used (Kallel *et al.*, 2009a), and the reactions involved were indicated in Eqs. (2.9) and (2.1).

Fig. 5.8 a) shows that there is a strong increase of COD removal in what regards E_{Treat} when Fe^0 is introduced into the system whereas a much slight improvement is observed for E_{Raw} .

The optimal concentration of Fe^0 for the depuration of E_{Raw} is 62.5 g/L with 8.6 % of COD removal while in what regards E_{Treat} 41.0 % of COD abatement was attained using 25 g/L of Fe^0 . After those maximum points of organic matter removal, there is a decline on efficiency probably due to the radical scavenger effect already mentioned. In Fig. 5.8 b) it can be seen that only E_{Treat} fulfils the legal value when 12.5 g/L of Fe^0 is used. The COD value at 125 g/L corresponds to 980 mg O_2/L . However, with further increase on iron load, the legal limit of 1000 mg O_2/L will be exceeded due to radical scavenger.

In terms of the BOD_5 , it was only possible to obtain results for E_{Raw} treated with 125 g/L of Fe^0 , where an increase on BOD_5 from 1253 mg O_2/L to 1509 mg O_2/L was observed, which means that the effluents biodegradability improved from 0.61 to 0.81. Fig. 5.9 shows TPh removal behaviour as function of the concentration of Fe^0 :

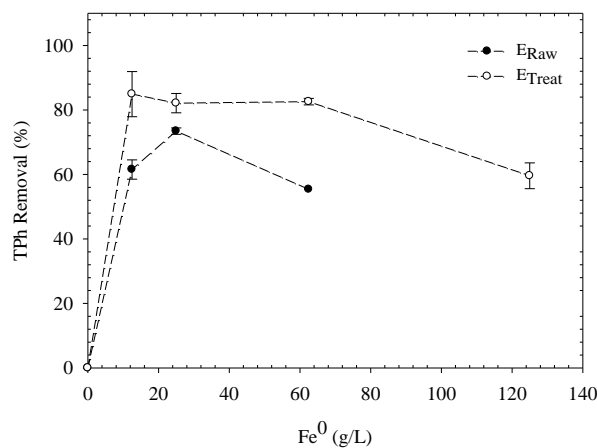


Fig. 5.9 - Effect of concentration of Fe^0 in E_{Raw} and E_{Treat} with T3 on TPh removal (%), with 3.35 g $\text{H}_2\text{O}_2/\text{L}$, pH = 2 for E_{Treat} and pH = 4 to E_{Raw} , for 2 h.

As it can be observed, both effluents never achieve the 100 % of total phenolic content removal, in 2 h of oxidation. Optimal elimination value of 73.4 % was attained when E_{Raw}

was treated with 25 g/L of iron powder. However, the removal percentage decreased afterwards to 55.4 %. E_{Treat} achieved better results, reaching a maximum of 84.9 % with 12.5 g/L of Fe^0 . From this maximal removal point on, the depuration efficiency decreased to 59.6 %, this means that probably there were intermediary compounds with phenolic content formed. It is visible that to high Fe^0 concentrations, TPh removal decreased, which can be related with the increasing of dissolved iron that leads to an orange coloration, and thus affecting the absorbance measurements during the Folin-Ciocalteu methodology.

5.3.4. EFFECT OF THE RESIDENCE TIME

Some experimental tests regarding the impact of the reaction time were performed using 40 mL of each effluent, E_{Raw} and E_{Treat} , with 13.40 g/L of H_2O_2 , which is the optimal concentration of H_2O_2 tested previously, and leachates $\text{pH} = 3$, by the reason enunciated in 5.3.2 section. Despite the best results were obtained for Fenton-like with Fe^0 , iron powder was run out at the time of these experiments. The bottles were placed at a shaker for different times of residence: 15, 30, 60, 90, 120, 150 and 180 min. COD, BOD_5 and TPh tests were carried out, after H_2O_2 was no longer present in solution to not affect the values of COD. Fig. 5.10 shows the COD and BOD_5 values attained after each experiment, from 15 to 180 min of experimental tests.

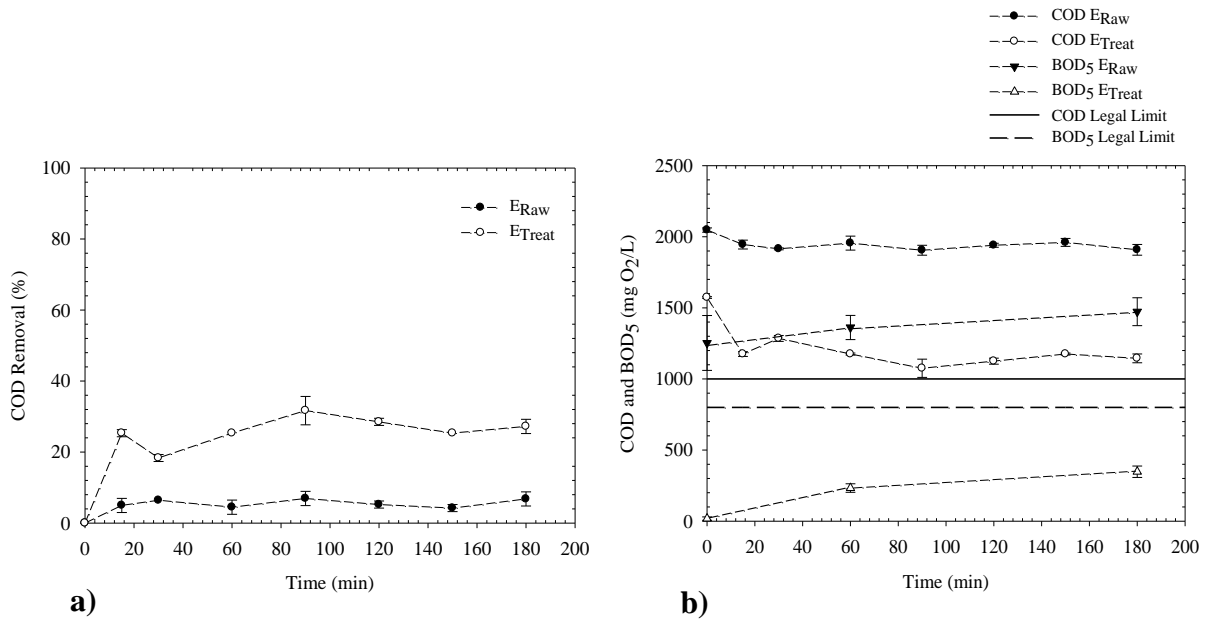


Fig. 5.10 - Effect of concentration of residence time in E_{Raw} and E_{Treat} with T2, pH = 3, with 13.40 g H_2O_2/L . **a)** COD removal (%); **b)** COD, BOD₅ and their Legal Limit of discharge throughout the local municipal sewage (mg O₂/L).

Both effluents demonstrated that at these operating conditions, the reaction of organic matter degradation was fast and there is no need to let it occurring during 2 h. As it can be seen at Fig. 5.10 a), the optimal residence times found with the best COD removal was 90 min for both effluents with a COD removal of 6.9 % and 31.7 % for E_{Raw} and E_{Treat} , respectively. Nevertheless, only 60 min seems to be enough to the reaction occurs since COD removal after this experimental time varied very slightly. For 60 min, 4.5 % and 25.3 % of COD removal was attained for E_{Raw} and E_{Treat} , respectively. It is important to note that lower residence times will allow energy savings for stirring.

In Fig. 5.10 b) can be seen that none of COD values attained, independently of each effluent, fulfils the legal limit for discharge to the local municipal sewage. BOD₅ values were determined to 60 min and 180 min for both streams. For 60 min, E_{Raw} had a 1362 mg O₂/L and E_{Treat} had 233 mg O₂/L. The biodegradability associated at this point, measured as the ratio BOD₅/COD, for 60 min was 0.67 and 0.20 respectively, which represents a good biodegradability of E_{Raw} , as was expected given its characteristics. For 180 min, E_{Raw} shows a BOD₅ of 1473 mg O₂/L and E_{Treat} 348 mg O₂/L, leading to 0.77 and 0.30 for the respective BOD₅/COD. Thus, the biodegradability of leachates reveals to increase with the residence

time probably due to the formation of biodegradable organic by-products. Fig. 5.11 shows the results for TPh abatement by Fenton-like process during 180 min.

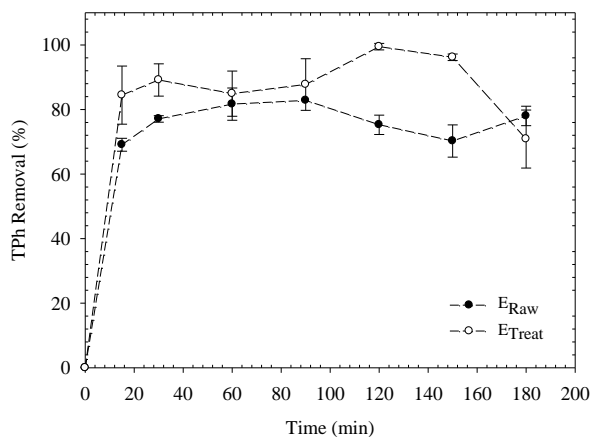


Fig. 5.11 - Effect of concentration of residence time in E_{Raw} and E_{Treat} with T2 on TPh removal (%), pH = 3, with 13.40 g H_2O_2/L .

According to Fig. 5.11, E_{Raw} TPh removal till 90 min shows a gradually increasing behaviour, with the maximal value of 82.8 % (90 min). From 90 min to 150 min, intermediary compounds with phenolic characteristics were probably formed, so that the TPh removal decreased to 70.2 % (150 min). E_{Treat} showed a very oscillating behaviour from 30 min to 180 min of reaction maybe related with the formation and subsequent decomposition of by-products with different phenolic character along the reaction.

5.4. FENTON-LIKE PROCESS WITH IRON SHAVINGS

The effluents tested with Fenton-like process with iron shavings were $E_{Post-Bio}$ and E_{Treat} , since for E_{Raw} the results obtained previously indicated low efficiencies.

5.4.1. PRELIMINARY TESTS

Before the implementation Fenton-like process with iron shavings, $E_{Post-Bio}$ was submitted to the optimal conditions selected to E_{Treat} , which are pH = 2 to all experiments and

concentration of reagents are 25 g Fe⁰/L (T1), 13.40 g H₂O₂/L (T2) and 25 g Fe⁰/L with 13.40 g H₂O₂/L (T3). Those experiments were made at the optimal conditions of E_{Treat} because E_{Post-Bio} is very similar to E_{Treat}, as it can be seen at Table 5.1. The objective was to evaluate the behaviour of this effluent to these set of treatments. Table 5.4 shows the results attained after 2 h of T1, T2 and T3 reactions.

Table 5.4 - Results attained after the preliminary tests performed to E_{Post-Bio}, with the optimal conditions selected to E_{Treat}.

Parameters	T1	T2	T3	LLD
COD after treatment test (mg O ₂ /L)	930±14	1255±28	800±64	1000
COD Removal (%)	39.6	18.5	48.1	-
BOD ₅ after treatment test (mg O ₂ /L)	214.8±62	167.6±48	188±97	800
BOD ₅ after treatment test/BOD ₅ before treatment test	3.3	2.6	2.9	-
BOD ₅ /COD after treatment test	0.23	0.13	0.24	-

LLD – Legal limit of discharge throughout the local municipal sewage.

Comparing COD removals and the BOD₅/COD ratios attained for E_{Post-Bio} (Table 5.4) with the results achieved for E_{Treat} (Table 5.3), in all tests, it is possible to conclude that E_{Post-Bio} is easier to degrad than E_{Treat} or E_{Raw}.

As it was expected, T3 led to superior results with 48.1 % of organic matter removed and a biodegradability of 0.24. Legal limits for discharge throughout the local municipal sewage were fulfilled in this case.

5.4.2. APPLICATION OF IRON SHAVINGS

Iron shavings were used in this thesis because are wastes from other industries and can be bought at a low cost. This idea of an industrial symbiosis, besides having economical advantages, brings environmental benefit, as well. Iron shavings at this test had a surface area of 1.116±1.83 m²/g and a pore size of 74.18 Å. Iron powder was characterized as well with the 0.868±4.42 m²/g of surface area and a pore size of 37.50 Å. Iron shavings used at this experiment were shown in Fig. 5.12.



Fig. 5.12 - Iron shavings (from a metal turner) used in the laboratory experiments.

The experiments involving iron shavings were made for $E_{\text{Post-Bio}}$ and E_{Treat} . The effluent E_{Raw} was not tested because at this point, the objective was to improve E_{Treat} and compare it with $E_{\text{Post-Bio}}$ to find the best location to implement this new approach of treatment at the landfill leachate treatment plant under study.

The experiments were carried out as follows: to 500 mL of each effluent at $\text{pH} = 2$, were added 25 g/L of iron shavings and 13.40 g/L of H_2O_2 , due to the optimal conditions obtained previously. The reactors were putted at the shaker for 60 min and samples were taken at 1, 5, 7, 10, 15, 30, 45 and 60 min. The parameters COD, BOD_5 and TPh were determined, after there was no H_2O_2 in the solution. In Fig. 5.13, the COD removal, COD and BOD_5 values attained are represented.

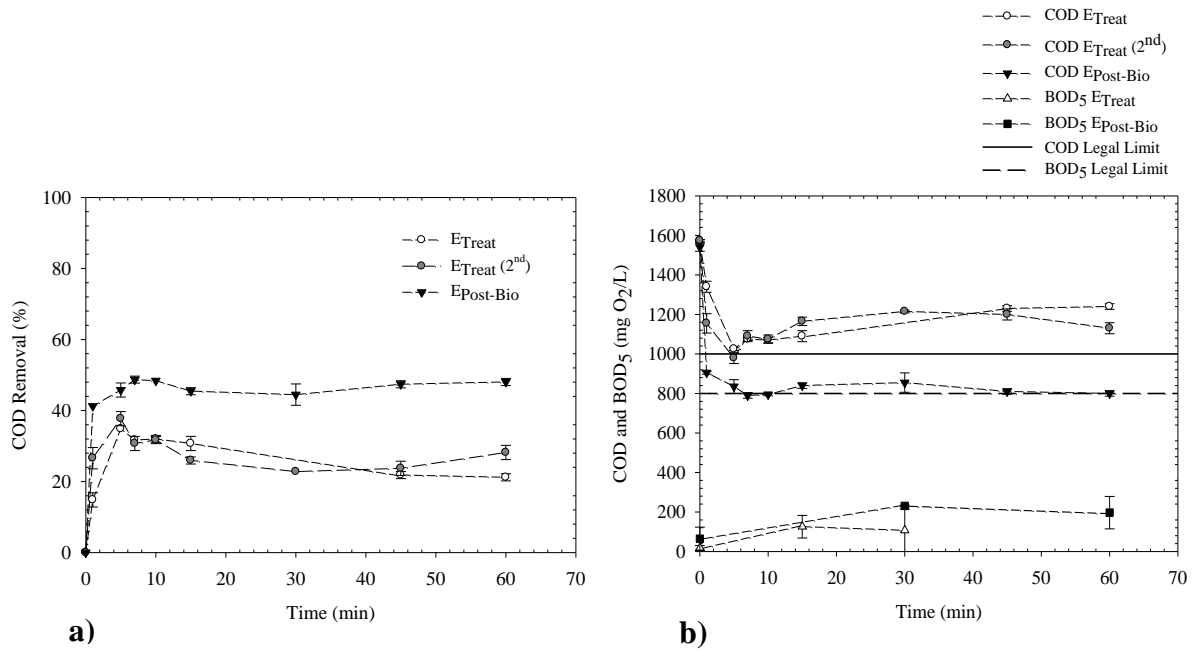


Fig. 5.13 - Evolution of **a)** COD removal (%) and **b)** COD, BOD₅ values during Fenton-like process with iron shavings treatment of E_{Posto-Bio} and E_{Treat}, adding 25 g/L of iron shavings and 13.40 g/L of H₂O₂, pH = 2.

In Fig. 5.13 a) it can be seen that COD removal is very fast within the first 5 min, which means that HO· radicals are produced at a large amount at the beginning of the experimental test. E_{Treat} (2nd) is a repetition of E_{Treat} assay to guarantee the reproducibility of the results. The maximal COD removal for E_{Treat} is 34.9 % attained in 5 min and the results achieved for the second run are very similar (for the exactly same time, 37.7 % of COD removal were attained). These values only vary 2.9 % which means that the experiments are reproducible. After this experimental time COD removals tend to a plateau without significant efficiency increase.

In relation to E_{Post-Bio}, a higher depuration was attained with a maximum COD removal of 48.7 % after 7 min of reaction. This better performance is related with the fact of E_{Post-Bio} had more organic matter than E_{Treat}, because the post-biological effluent did not pass through physico-chemical treatment yet. E_{Post-Bio} has less variations of COD removal over time and its stabilization remains at, more or less, 48.0 % of organic matter removal, comparatively with the results of treated effluent.

It was observed at both leachates that over time, the colour of samples passed from light yellow to an orange-brown and it were formed more and more sludge. The meaning of these

changes over time are related with solid iron solubilisation, and thus more $\text{Fe}(\text{OH})_3$ sludge was formed due to the introduction of NaOH at the end of the experiment.

As it can be observed in Fig. 5.13 b), COD below the 1000 mg O_2/L are attained with this process which allows the direct discharge of the attained effluents throughout the local municipal sewage.

BOD_5 tests were made for the samples withdrawn at 15 min and 30 min, to E_{Treat} and at 30 min and 60 min to $E_{\text{Post-Bio}}$. When compared with the initials BOD_5 values, both effluents tested had significant increases. E_{Treat} passed from 18 mg O_2/L to 106.95 mg O_2/L in 30 min and $E_{\text{Post-Bio}}$ increased from 65 mg O_2/L to 230.70 mg O_2/L , in 60 min. Therefore, every BOD_5 values fulfilled the legal limit of 800 mg O_2/L (Fig. 5.12 b)). The biodegradability was improved from 0.01 to 0.11 (E_{Treat}) and 0.04 to 0.27 ($E_{\text{Post-Bio}}$). Fig. 5.14 shows the TPh removal trends during Fenton-Like over iron shavings.

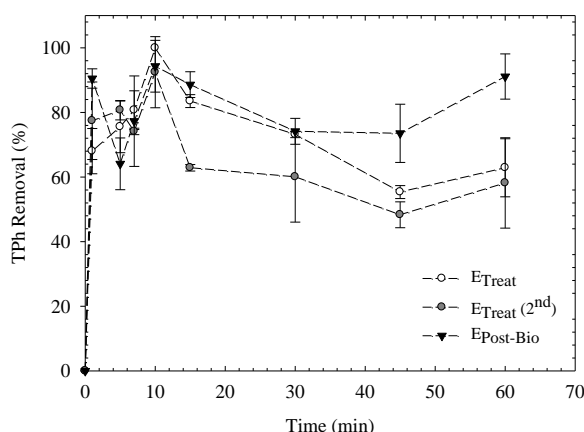


Fig. 5.14 - Evolution of TPh removal (%) during the treatment of $E_{\text{Posto-Bio}}$ and E_{Treat} by Fenton-like process over iron shavings, adding to E_{Treat} and $E_{\text{Post-Bio}}$ 25 g/L of iron shavings and 13.40 g/L of H_2O_2 , pH = 2.

In general, E_{Treat} TPh removal followed the same trend line of the one obtained for $E_{\text{Treat}} (2^{\text{nd}})$, which ensure the reliability of the results. Some oscillations were observed with $E_{\text{Treat}} (2^{\text{nd}})$ between 5 and 10 min, probably due to experimental errors. The maximum of TPh removal obtained was 100 % (10 min) to E_{Treat} and 92.5 % (10 min) to $E_{\text{Treat}} (2^{\text{nd}})$. Before the 10 min, intermediary compounds with phenol character may be formed, decreasing the TPh removal.

$E_{\text{Post-Bio}}$ had a maximum total phenolic content removal of 94.3 % at 10 min. The TPh removal of this effluent decreased till 45 min (73.5 %) and this may be the result of the presence of intermediary compounds increasing until 91.2 % afterwards. Once more, besides some experimental errors associated with the determination, this oscillation is related with the cumbersome composition of these effluents and the different by-products (with more or less phenolic character) formed along the oxidation.

5.4.3. REUSE OF IRON SHAVINGS

To establish the behaviour of iron shavings along several reuses to demonstrate the behaviour of the efficiency of the material in a sequential batch process, it was added to 500 mL of $E_{\text{Post-Bio}}$ at pH = 2, 25 g/L of iron shaving with 13.40 g/L of H_2O_2 , at a start point. $E_{\text{Post-Bio}}$ was chosen to be the effluent of this experimental test, since previous experiments revealed that this leachate is more appealing to treat at the scope of this thesis, due to the high COD removals achieved with it, in comparison with E_{Treat} . The iron shaving's reuse was done in batch conditions, where iron shavings remain the same in 10 repetitions and each reuse lasted 60 min at the shaker. A pre-test was performed, previously, by using iron shavings for 60 min and the resulting solids were weighed on a dry basis to determine the mass lost during the pre-test. The lost of weight of 7 % was considered at each of the 10 tests in cyclic because the reuse test was made to be similar to a industrial process, where is not possible to weigh the mass of iron shavings after each reuse. To guarantee a constant L/S ratio along the 10 trials, it was made a proportion to the volume of effluent and to the concentration of H_2O_2 , at the beginning of each test according to the remaining weight of iron shavings after each cycle. At the end of each test, the reaction was stopped by increasing pH to 12 with NaOH and COD tests were made. Fig. 5.15 shows the COD results.

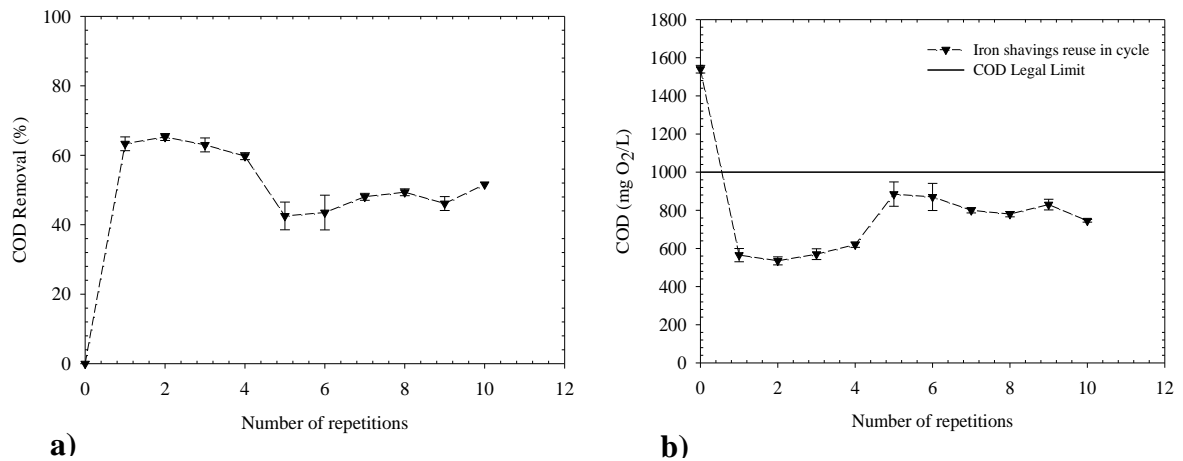


Fig. 5.15 - Evolution **a)** COD removal (%); **b)** COD values after 60 min of Fenton-like reactions for each reuse of the iron shavings, with pH = 2, 25 g/L of iron shaving and 13.40 g/L of H₂O₂.

As it can be seen in Fig. 5.15 a), in the first trial of the sequential experiments, COD removal reached 63.3 %. The maximal COD removal obtained was of 65.3 % at the second trial. From the fourth, the iron shavings efficiency decreased to 42.5 %, but after that a plateau without significant changes is reached. Fig. 5.15 b) reveals that COD values associated with the 10 sequential tests are always below the stipulated value for disposal to the municipal sewage.

Iron shavings behaviour was observed along the cycle tests. At seventh trial, iron shavings demonstrated to be smaller, brittle and sludge had a brown tone (Fig. 5.16). The final mass of iron shavings at the 10th repetition was of 9.10 g, which means that there was a mass reduction of 27.2 %.

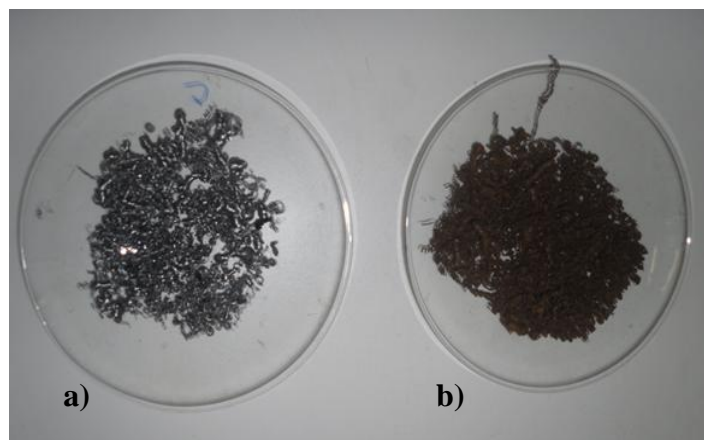


Fig. 5.16 - Iron shavings before **(a)** and after **(b)** the cycle tests (10 repetitions).

The concentration of H_2O_2 after each cycle was monitored and Fig. 5.15 shows its behaviour:

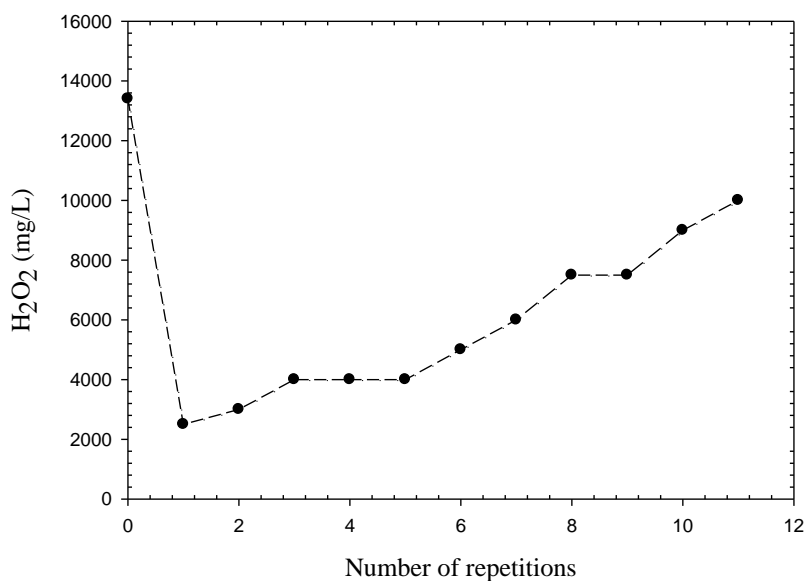


Fig. 5.17 - Amount of H_2O_2 present after each reuse test (mg/L).

The initial concentration decreased due to the consumption of H_2O_2 at the first trial. From this moment on, the concentration of H_2O_2 with the number of repetitions increased consecutively. This happened because over the cycles, the iron shavings will be decomposing, losing their capability to produce $\text{HO}\cdot$ radicals, along with H_2O_2 . The amount of H_2O_2 (13.40 g/L) is introduced for each repetition and cannot react with the old iron shavings, remaining in solution. The decrease of H_2O_2 from the initial value (13400 mg/L) to the first trial (2500 mg/L) showed that 18.7 % of this reagent was added in excess.

6. CONCLUSIONS AND FORTHCOMING WORK

One of the many environmental problems associated with landfills is the leachate production. Due to their pollutant characteristics it is important to investigate others methodologies of treatment, besides the biological treatment, which only by itself generally show to be inefficient.

The main goal of this study was to improve the biodegradability of leachates and bring a new approach to treat them, in a low cost point of view. In our study three different approaches were tested: the ZVI, Fenton-like processes and Fenton-like processes with ZVI. The experimental results showed that the best option studied was the Fenton-like processes with ZVI.

The study of operating conditions revealed that acid conditions (pH in a range of 2 – 4) were more efficient to remove COD. In a general way, rising the H_2O_2 at solution, increases the COD removal and 13.40 g H_2O_2/L was the amount selected. Increasing iron powder concentration, the degradation of organic load increase as well, until to reach the point which radical scavenger starts to decrease the efficiency of the method. In general, after 1 h, the removal of organic matter is stabilized. All tests performed showed that Fenton-like and Fenton-like ZVI are not efficient to treat E_{Raw} due to the fact of its COD removal were always inferior to 8 %.

This methodology was applied with iron shavings, whose reaction demonstrated to be faster. At the firsts 5 and 7 min, a maximal value of 37.7 % at E_{Treat} (2nd) and 48.7 % of $E_{Post-Bio}$, respectively of COD removal were obtained. The use of iron shavings improved the removal of organic matter for both effluents and, for the first time, the COD legal limit for discharge into the local municipal sewage was fulfilled. This treatment was also efficient in terms of biodegradability, because the biodegradability was improved from 0.01 to 0.11 at E_{Treat} case and from 0.04 to 0.27 at $E_{Post-Bio}$, in 30 min. The goal of the biodegradability improvement was accomplished.

A cycle of 10 reuses of iron shavings was performed to $E_{Post-Bio}$. A maximal COD removal was achieved at the second reuse of iron shavings with 65.3 %, which was the best performance attained by this methodology. Iron shavings still showed performance for a COD removal superior than 43 % in all the reuse cycles, which correspond to a good performance

to apply this treatment at industrial scale. Beyond that, an industrial leachate treatment with iron shavings will bring environmental and economic benefits, due to the use of an industrial waste, that can be achieved with a low price. The Fenton-like process with iron shavings, in an industrial scale, could be more economical than the physico-chemical treatment that has been used in the landfill leachates treatment plant, because, in principle, buying FeCl_3 is more expensive than buying iron shavings. Even if the cost of iron shavings and FeCl_3 is the same, the former methodology is better once it is more efficient than the one applied at the landfill leachate treatment plant. Other advantages must be taken into account, as the fact of this experiment was performed at room temperature and the use of H_2O_2 it is environmentally innocuous.

The weak points of this methodology are the production of iron sludge, the phenolic compounds of leachates are difficult to decompose, once there were formed many intermediary compounds with this treatment, the H_2O_2 and pH correction are costs always associated with this process. There is less formation of iron sludge with iron shavings because the iron is in a solid state, unlike it happens with the classic Fenton's process, which uses Fe^{2+} .

It is important to compare the efficiency of iron shavings with iron powder. This comparison may be established according to $E_{\text{Post-Bio}}$ (where the optimal conditions were 25 g Fe^0/L and 13.40 g $\text{H}_2\text{O}_2/\text{L}$) with the preliminary test and the use of this effluent with iron shavings at section 5.4.2. Iron powder had an efficiency of COD removal of 48.1 % in 2 h and iron shavings 48.7 % in 1 h. The time associated with the iron shavings experimental test is not relevant, because it can be seen that from 60 min of reaction, the COD removal do not change over the time. Therefore, since the efficiency of both catalyst are similar, iron shavings should be selected for economical reasons.

Other goal of this thesis was to decide the best place to implement this methodology at the landfill leachate treatment plant in use. Since the best results in terms of COD removal and biodegradability (BOD_5/COD) were attained for $E_{\text{Post-Bio}}$ in 30 min, after the application of this AOP, it seems preferable to implement this process after the biological reactor and before the effluents discharge throughout the municipal sewage, replacing the physico-chemical treatment applied at the landfill treatment plant.

Despite the fact of this study has to be optimized to apply it at an industrial scale, it can be concluded that the objectives of this thesis were achieved and this methodology proved to be efficient to treat leachates.

FORTHCOMING WORK

During this study there have been some experimental tests that were not made for lack of time and some ideas to optimize this new treatment of leachates. In relation to future laboratory tests, is essential to study the effect of the concentration of H_2O_2 with iron powder at first and, after that, with iron shavings. It is important to analyse the effect of pH with iron shavings and the mass as well. These experiments should be made with $E_{Post-Bio}$, since the methodology studied at this thesis should be introduced after the biological treatment and the COD removal obtained had the best results. All BOD_5 tests must be performed. The concentration of iron shavings and H_2O_2 , along with pH, should be optimized using statistical devices based on design of experiments since it is well known that these operating parameters strongly interact. The respirometry test may be carried out to determine the biodegradability and the toxicity of leachates.

To increase iron shavings efficiency, they can be washed with 10 % of HCl (v/v) after some treatment time. This procedure removes the oxides at the surface of the shavings and its contaminants reactivating the catalyst (Agrawal and Tratnyek, 1996). It would be interesting to improve the reactivity of iron shavings by its dopping with other metals, such as copper, nickel, among others noble metals that acts as dopants (Ma and Zhang, 2008).

This methodology should be tested at a pilot-scale to analyse if it is possible to operate in continuous conditions and taking into account the costs of this treatment. The pilot-scale reactor may be similar with the one represented in Fig. 6.1 (Ma and Zhang, 2008).

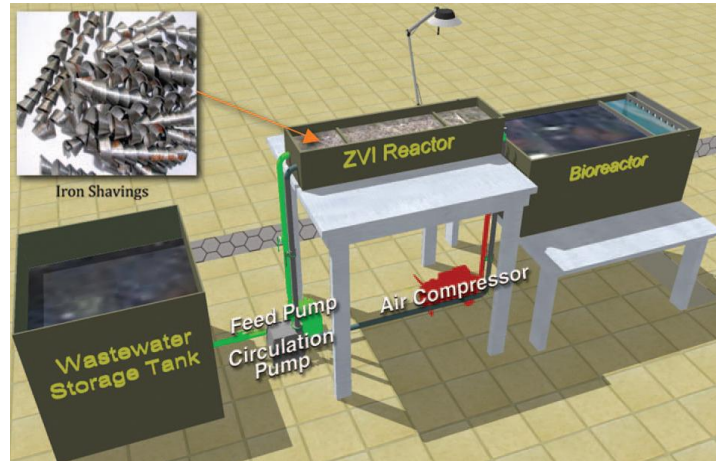


Fig. 6.1 - Pilot-scale reactor with iron shavings (Ma and Zhang, 2008).

In this case, the biological treatment represented in the Fig. as a bioreactor, should be placed before the ZVI reactor due to reasons already mentioned.

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ANNEX

The industrial data from the landfill leachates are mentioned at Tables 1 to 6 in this section. The tables are grouped by years (2008 to 2010) and in each year two types of leachates, E_{Raw} and E_{Treat} , are described.

- **2008 VALUES:**

Table 1 - Industrial values of landfill parameters at E_{Raw} in 2008.

	Jan.	Fev.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
COD (mgO ₂ /L)	3200	2800	4300	4800	1200	4100	5100	6300	7900	11000	7900	2600
pH	8.0	8.2	8.2	8.0	8.1	8.1	8.1	8.1	8.2	8.2	8.2	7.9
Ammonia nitrogen (mg/L)	2200	1500	1200	740	420	2100	2400	2700	3000	2600	3100	1000

Table 2 - Industrial values of landfill parameters at E_{Treat} in 2008.

	Jan.	Fev.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
COD (mgO ₂ /L)	430	700	980	1600	1400	1200	2200	1300	2000	2300	2100	2300
BOD ₅ (mgO ₂ /L)	125	400	200	960	130	110	80	300	200	80	100	220
pH	6.5	7.2	7.1	7.3	7.9	8.2	8.3	7.1	7.4	7.0	6.9	7.2
Iron (mg/L)	17	100	67	15	37	5.8	6.6	22	220	59	110	210
SST (mg/L)	62	310	230	120	180	38	50	190	110	270	640	920
Ammonia nitrogen (mg/L)	5300	780	720	610	960	280	610	140	120	210	730	1200

- **2009 VALUES:****Table 3** - Industrial values of landfill parameters at E_{Raw} in 2009.

	Jan.	Fev.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
COD (mgO ₂ /L)	9200	1300	8300	7100	-	7600	7800	8800	8700	1100	5800	7300
		0								0		
pH	7.8	7.9	8.2	8.3	-	8.3	8.4	8.4	8.2	8.3	8.3	8.1
Ammonia nitrogen (mg/L)	1500	2000	2500	2700	-	2800	2800	2800	2800	2800	1500	1100

Table 4 - Industrial values of landfill parameters at E_{Treat} in 2009.

	Jan.	Fev.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
COD (mgO ₂ /L)	2100	6300	4100	1800	-	3900	1600	380	1700	3100	1400	7000
BOD ₅ (mgO ₂ /L)	240	920	800	120	-	260	80	60	100	320	240	480
pH	7.8	8.3	8.1	7.8	-	7.2	6.3	6.7	6.3	7.9	7.1	7.9
Iron (mg/L)	29	180	37	17	-	140	50	80	140	110	84	1400
SST (mg/L)	170	1300	260	80	-	680	96	13	800	320	410	2600
Ammonia nitrogen (mg/L)	1500	930	2200	2000	-	1500	580	130	380	820	510	1200

- **2010 VALUES:****Table 5** - Industrial values of landfill parameters at E_{Raw} in 2010.

	Jan.	Fev.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
COD (mgO ₂ /L)	4000	6600	4100	8000	5200	5400	6400	6500	6300	7700	1300	15000
pH	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
Ammonia nitrogen (mg/L)	1600	230	1100	1800	1700	2000	2000	2700	2200	1400	1600	1700

Table 6 - Industrial values of landfill parameters at E_{Treat} in 2010.

	Jan.	Fev.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
COD (mgO ₂ /L)	880	1200	1700	1200	1200	170	1300	1100	1600	1200	1100	2900
BOD ₅ (mgO ₂ /L)	240	70	360	130	840	200	80	110	480	110	190	500
pH	8.0	8.0	7.9	8.0	7.4	6.8	7.5	7.3	7.3	7.0	6.5	6.7
Iron (mg/L)	38	21	94	47	25	39	23	49	30	<0.1	52	35
SST (mg/L)	140	43	390	140	130	89	79	52	28	430	190	210
Ammonia nitrogen (mg/L)	4300	1200	1100	770	880	240	91	680	530	350	1100	940