Universidade do Minho
Escola de Engenharia

Susana Maria Ribeiro Cortez

Landfill Leachate Treatment in Rotating Biological Contactors

Agosto de 2010

Universidade do Minho
Escola de Engenharia

Susana Maria Ribeiro Cortez

Landfill Leachate Treatment in Rotating Biological Contactors

Doutoramento em Engenharia Química e Biológica

Trabalho efectuado sob a orientação do
Professor Doutor Manuel José Magalhães Gomes Mota
e da
Professora Doutora Domingas do Rosário Veríssimo Jacinto Tavares de Oliveira

Agosto de 2010

AUTOR:

Susana Maria Ribeiro Cortez
E-mail: susana_cortez@deb.uminho.pt
Telf: +351 965 159 192
BI: 11449347

LANDFILL LEACHATE TREATMENT IN ROTATING BIOLOGICAL CONTACTORS

ORIENTADORES:

Professor Doutor Manuel José Magalhães Gomes Mota
Professora Doutora Domingas do Rosário Veríssimo Jacinto Tavares de Oliveira

ANO DE CONCLUSÃO:

2010

DOUTORAMENTO EM ENGENHARIA QUÍMICA E BIOLÓGICA

É AUTORIZADA A REPRODUÇÃO INTEGRAL DESTA TESE/TRABALHO APENAS PARA EFEITOS DE INVESTIGAÇÃO, MEDIANTE AUTORIZAÇÃO ESCRITA DO INTERESSADO, QUE A TAL SE COMPROMETE.

Universidade do Minho, 17 de Agosto de 2010

AGRADECIMENTOS

As palavras que se seguem são, sem dúvida, as que me parecem mais fáceis e espontâneas de escrever. E é com grande satisfação que desejo manifestar o meu profundo reconhecimento e gratidão a todos que me acompanharam e apoiaram no decorrer dos últimos anos.

Em primeiro lugar, gostaria de agradecer aos meus orientadores científicos, Professor Manuel Mota e Professora Rosário Oliveira, pela confiança que depositaram em mim, pelos meios que colocaram à minha disposição, disponibilidade, apoio, incentivo e constantes desafios. Indiscutivelmente, as suas excepcionais qualidades científicas e humanas foram determinantes para a concretização deste trabalho.

Agradeço à Doutora Pilar Teixeira os ensinamentos que me transmitiu, a disponibilidade, apoio e palavra amiga.

Ao Doutor António Vicente agradeço ter disponibilizado o Laboratório de Instalações Piloto.

Estou muito grata aos técnicos do Departamento de Engenharia Biológica: Eng.ª Madalena, Sr. Santos e Dona Adelaide, pela preciosa ajuda laboratorial.

Aos “lipinhos” e investigadores do LBA agradeço terem-me adoptado como “uma deles”; agradeço a troca de impressões e incentivo que tanto me ajudaram nos momentos de ansiedade e desmotivação e a boa disposição com que me acompanharam ao longo dos trabalhos tornando cada dia no laboratório mais azul.

Gostaria de estender os agradecimentos aos meus amigos de longa data (cauminhos, biológicos, carpediem’s e CABes) por tornarem a minha vida bem mais feliz e preenchida, assim como pelas oportunas manifestações de encorajamento e companheirismo.

Finalmente, agradeço à minha Família, especialmente aos meus pais, a quem devo tudo o que sou, e a quem dedico esta tese, pelo amor, exemplo, dedicação e apoio que sempre me deram.

Um “obrigado” especial e com muito carinho ao Miguelzinho, pela compreensão, força e entusiasmo com que me brinda todos os dias, lembrando-me constantemente que “o essencial é invisível aos olhos”.

This research was financially supported by the research grant SRFH/BD/24715/2005 from the Fundação para a Ciência e Tecnologia (FCT).

ABSTRACT

Sanitary landfilling is the most used and accepted method to eliminate municipal solid waste worldwide due to its economic advantages. The generation of leachate is an inevitable consequence of this practice. Landfill leachate is a high-strength wastewater with great chemical complexity and diversity. In order to avoid discharges to the environment causing negative impacts to the biota or public health, it must be properly collected and treated before being discharged.

In Portugal, in many leachate treatment plants, the leachate after withstanding a series of biological and physico-chemical processes, still presents very high concentrations of nitrate (NO_3^-).

The main objective of this work was to evaluate the removal of nitrate from a landfill leachate with high NO_3^- load by denitrification in an anoxic rotating biological contactor (RBC). Accordingly, the study began by assessing the denitrification process in an anoxic RBC, for the treatment of synthetic wastewater, under two carbon to nitrogen ratios (C/N) (1.5 and 3). For the tested conditions, the ratio C/N=1.5 was the most advantageous. The anoxic RBC showed a very high performance in reducing the nitrate concentration working with a relatively short hydraulic retention time. Moreover, the increase of carbon-acetate and nitrogen-nitrate influent concentrations had only a slight negative effect in terms of substrate removal. As the biofilm structure and activity are determinant to the reactor performance, at the end of the continuous experiment, biofilm characteristics, composition and activity were evaluated. It was verified that, in spite of a lower thickness, the biofilm grown under a carbon/nitrogen ratio of 1.5 was more active than the biofilm grown at C/N=3.

After that, the denitrification performance of the biofilm grown on the reactor disks using pre-treated landfill leachate with high nitrate load was evaluated and the effect of initial nitrate load, phosphorus concentration and C/N ratio assessed. Under a C/N=2, the reactor achieved N-NO_3^- removal efficiencies above 95% for nitrate loads up to 100 mg N-$NO_3^- \cdot L^{-1}$. The highest observed denitrification rate was 55 mg N-$NO_3^- \cdot L^{-1} \cdot h^{-1}$ at a nitrate load of 560 mg N-$NO_3^- \cdot L^{-1}$. Although the reactor has revealed a very good performance in terms of denitrification, effluent chemical oxygen demand (COD) concentrations were still high for direct discharge. The results obtained in a subsequent experiment at constant nitrate load (220 mg N-$NO_3^- \cdot L^{-1}$) and lower C/N ratios (1.2 and 1.5) evidenced that the organic matter present in the leachate was non-biodegradable. A phosphorus concentration of 10 mg P-$PO_4^{3-} \cdot L^{-1}$ promoted autotrophic denitrification, revealing the importance of phosphorus concentration on biological nitrate removal processes.

In order to improve the biodegradability of the pre-treated landfill leachate, Fenton's oxidation (Fe^{2+}/H_2O_2) and different ozone-based Advanced Oxidation Processes (AOPs) (O_3, O_3/OH^- and O_3/H_2O_2) were also tested. The effect of initial pH, oxidant agents concentration and reaction time on the performance of each AOP tested was evaluated in terms of COD, total organic carbon (TOC), BOD_5, nitrogenous compounds and aromaticity. The results indicated that Fe^{2+}/H_2O_2, O_3/OH^- and O_3/H_2O_2 processes, comparatively to ozone at natural and neutral pH values, resulted in higher COD, TOC and UV_{254} removal efficiencies and improvement of landfill leachate biodegradability. These results confirm the enhanced production of hydroxyl radical under such conditions. Although Fe^{2+}/H_2O_2 is the most economical system to treat the landfill leachate, for practical purposes O_3/OH^- was chosen for further work.

Finally, the performance of the sequence of treatments, leachate ozonation followed by RBC denitrification was analyzed. The pre-ozonation led to a TOC removal of 28%. The global system did not affect the denitrification efficiency, which remained close to 100%. In fact, it was possible to attain a denitrification rate of 123 mg $N\text{-}NO_3^- \cdot L^{-1} \cdot h^{-1}$. The moderate decrease in the carbon load of the final effluent indicated that some recalcitrant compounds were still present after ozonation. These results were confirmed by the denitrifying activity tests carried out at the end of the continuous experiment.

From the experiments performed with landfill leachate, considering the nitrate load applied, nitrate removal efficiencies and the negligible accumulation of intermediates, the anoxic rotating biological contactor showed to be extremely efficient and constitutes a promising technology for removing nitrate from landfill leachate.

Keywords: Advanced Oxidation Processes (AOPs), biodegradability, biofilm, carbon to nitrogen ratio (C/N), denitrification, Fenton's oxidation, landfill leachate, ozonation, phosphorus, rotating biological contactors (RBCs)

SUMÁRIO

A deposição final de resíduos sólidos urbanos em aterro sanitário é o método de tratamento mais usado e aceite em todo o mundo devido às suas vantagens económicas. A produção de lixiviado é uma consequência inevitável deste método. O lixiviado de aterro sanitário é uma água residual com elevada carga poluente e com grande complexidade química. Para evitar descargas que causem impactos negativos ao ambiente ou à saúde pública, o lixiviado deve ser recolhido e tratado adequadamente antes da descarga.

Em Portugal, em muitas estações de tratamento de águas lixiviantes, tem-se verificado que o lixiviado tratado, após suportar uma série de processos biológicos e físico-químicos, continua a apresentar elevadas concentrações de nitrato (NO_3^-).

O objectivo principal do trabalho experimental conducente a esta dissertação consistiu em avaliar a remoção de nitrato de um lixiviado de um aterro sanitário com elevada carga de NO_3^- por desnitrificação num reactor anóxico de discos biológicos rotativos. Com este propósito, começou-se por estudar o processo de desnitrificação no reactor anóxico para o tratamento de uma água residual sintética, sob duas razões carbono/azoto (C/N) (1.5 e 3). Para as condições testadas observou-se que a razão C/N=1.5 era a mais vantajosa. O reactor apresentou uma grande eficácia na redução da concentração de nitrato num tempo de retenção hidráulico baixo e o aumento das concentrações de carbono-acetato e azoto-nitrato do influente tiveram apenas um ligeiro efeito negativo em termos de remoção de substrato. Como a estrutura e a actividade do biofilme são determinantes para o desempenho do reactor, no final da experiência em contínuo, tanto as características do biofilme como a sua actividade foram avaliadas. Constatou-se que, apesar de uma espessura menor, o biofilme desenvolvido com uma razão C/N=1.5 era mais activo do que o biofilme crescido a C/N=3.

Seguidamente, estudou-se o desempenho desnitrificante do reactor usando lixiviado pré-tratado com elevada carga de nitrato e foram avaliados os efeitos da carga inicial de nitrato, da concentração de fósforo e da razão C/N.

Com uma razão C/N=2, o reactor atingiu eficiências de remoção de $N\text{-}NO_3^-$ acima de 95% para cargas superiores a 100 mg $N\text{-}NO_3^- \cdot L^{-1}$. A maior taxa de desnitrificação observada foi de 55 mg $N\text{-}NO_3^- \cdot L^{-1} \cdot h^{-1}$ para uma carga de nitrato de 560 mg $N\text{-}NO_3^- \cdot L^{-1}$. Embora o reactor tenha demonstrado um desempenho muito bom em termos de desnitrificação, as concentrações da carência química de oxigénio no efluente eram ainda elevadas para descarga directa. Os resultados obtidos numa experiência posterior, com uma carga constante de nitrato (220 mg

N-NO_3^-·L^{-1}) e valores inferiores de C/N (1.2 e 1.5), evidenciaram que a matéria orgânica presente no lixiviado era não-biodegradável. Uma concentração de fósforo 10 mg P-PO_4^{3-}·L^{-1} estimulou a desnitrificação autotrófica, revelando a importância da concentração de fósforo nos processos de remoção biológica de nitrato.

De forma a melhorar a biodegradabilidade do lixiviado pré-tratado foram estudados, o processo de oxidação de Fenton (Fe^{2+}/H_2O_2) e vários processos de oxidação avançada com ozono (O_3, O_3/OH^- e O_3/H_2O_2). O efeito do pH inicial, concentração dos agentes oxidantes e tempo de reacção no desempenho de cada um dos processos foi analisado em termos de carência química de oxigénio, carbono orgânico total, biodegradabilidade, compostos azotados e aromaticidade. Os resultados indicaram que os processos Fe^{2+}/H_2O_2, O_3/OH^- e O_3/H_2O_2, comparativamente com ozonização a pH natural ou neutro, resultaram em eficiências de remoção superiores e aumentaram a biodegradabilidade do lixiviado. Estes resultados confirmam o aumento da produção do radical hidroxilo em tais condições. Apesar do sistema Fe^{2+}/H_2O_2 ser o mais económico, por motivos práticos o processo O_3/OH^- foi o escolhido para trabalho posterior.

Por fim, analisou-se o desempenho da sequência de tratamentos: ozonização do lixiviado seguida de desnitrificação no reactor. A pré-ozonização removeu cerca de 28% do carbono orgânico total. O sistema global não afectou a eficiência de desnitrificação, que se manteve próxima de 100%. De facto, foi mesmo possível alcançar uma taxa de desnitrificação de 123 mg N-NO_3^-·L^{-1}·h^{-1}. A diminuição moderada na carga de carbono do efluente final indicou que alguns compostos recalcitrantes continuavam presentes após ozonização. Estes resultados foram confirmados pelos testes de actividade desnitrificante realizados no final da experiência em contínuo.

Pelas experiências realizadas com lixiviado, considerando a carga de nitrato aplicada, as eficiências de remoção de nitrato e a acumulação insignificante de intermediários, o reactor anóxico de discos biológicos rotativos demonstrou ser extremamente eficiente e uma tecnologia promissora para a remoção de nitrato de lixiviados de aterros sanitários.

Palavras chave: biodegradabilidade, biofilme, desnitrificação, fósforo, lixiviado de aterro sanitário, oxidação de Fenton, ozonização, Processos de Oxidação Avançada (POAs), razão carbono/azoto (C/N), reactor de discos biológicos rotativos

TABLE OF CONTENTS

6A Ozonation as Polishing Treatment of Mature Landfill Leachate

6B EVALUATION OF FENTON'S OXIDATION AND OZONE-BASED ADVANCED OXIDATION PROCESSES AS MATURE LANDFILL LEACHATE PRE-TREATMENTS

LIST OF FIGURES

1. GENERAL INTRODUCTION

2. OVERVIEW OF LANDFILL LEACHATE TREATMENTS

3. ROTATING BIOLOGICAL CONTACTORS: A REVIEW ON MAIN FACTORS AFFECTING PERFORMANCE

4. EFFECT OF OPERATING PARAMETERS ON DENITRIFICATION IN AN ANOXIC ROTATING BIOLOGICAL CONTACTOR

5. DENITRIFICATION OF A LANDFILL LEACHATE WITH HIGH NITRATE LOAD IN AN ANOXIC ROTATING BIOLOGICAL CONTACTOR

6. Landfill Leachate Polishing Treatments: Ozonation and Fenton's Oxidation

7. Mature Landfill Leachate Treatment by Denitrification and Ozonation

LIST OF TABLES

2. OVERVIEW OF LANDFILL LEACHATE TREATMENTS

3. ROTATING BIOLOGICAL CONTACTORS: A REVIEW ON MAIN FACTORS AFFECTING PERFORMANCE

4. EFFECT OF OPERATING PARAMETERS ON DENITRIFICATION IN AN ANOXIC ROTATING BIOLOGICAL CONTACTOR

5. DENITRIFICATION OF A LANDFILL LEACHATE WITH HIGH NITRATE LOAD IN AN ANOXIC ROTATING BIOLOGICAL CONTACTOR

6. LANDFILL LEACHATE POLISHING TREATMENTS: OZONATION AND FENTON'S OXIDATION

7. MATURE LANDFILL LEACHATE TREATMENT BY DENITRIFICATION AND OZONATION

LIST OF SYMBOLS AND ABBREVIATIONS

AD	Anaerobic Digester
AOP	Advanced Oxidation Process
AS	Activated Sludge
BF	Biological Filter
BOD_5	5-day Biochemical Oxygen Demand
$C\text{-}CH_3COO^-$	Carbon-acetate
CH_3COO^-	Acetate
C/N	Carbon to Nitrogen ratio
COD	Chemical Oxygen Demand
DL	Decree-Law
DO	Dissolved Oxygen
dS	Specific substrate consumption rate
GAC	Granular Activated Carbon
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
HRT	Hydraulic Retention Time
MBR	Membrane bioreactor
MF	Microfiltration
MSW	Municipal Solid Waste
$N\text{-}NH_4^+$	Nitrogen-ammonium
NH_4^+	Ammonium
$N\text{-}NO_2^-$	Nitrogen-nitrite
NO_2^-	Nitrite
$N\text{-}NO_3^-$	Nitrogen-nitrate
NO_3^-	Nitrate
NF	Nanofiltration
NTP	Normal Temperature and Pressure Conditions
O_3	Ozone
$O_{3G,i}$	Ozone concentration in the gas stream at the inlet
$O_{3G,o}$	Ozone concentration in the gas stream at the outlet
OC	Ozone Consumption
PAC	Powdered Activated Carbon
PMMA	Polymethylmethacrylate
Q_G	Gas flow rate
RBC	Rotating Biological Contactor
rpm	rotations per minute
S_0	Substrate concentration at the beginning of the batch test
S_t	Substrate concentration at the end of the batch test
SBR	Sequencing Batch Reactor
SCBR	Suspended Carrier Biofilm
SCOD	Soluble Chemical Oxygen Demand
SOL	Superficial Organic Load
t	time
TDS	Total Dissolved Solids
TF	Trickling Filter
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon

TS	Total Solids
UASB	Upflow Anaerobic Sludge Blanket
UF	Ultrafiltration
UV_{254}	Ultraviolet absorbance at 254 nm
V_L	Liquid volume
VS	Volatile Solids
VSS	Volatile Suspended Solids
w/w	weight/weight

Chapter 1

General Introduction

This chapter presents information on municipal solid waste management and treatment in the world, highlighting sanitary landfills, which is the most common treatment method in Portugal. The national legislation concerning sanitary landfills is provided. In addition, the importance of landfill leachate treatment and one of the main current problems of many leachate treatment or pre-treatment plants, such as the inefficiency in removing nitrate, are pointed out. The motivation to evaluate landfill leachate treatment is therefore presented. Finally, the research aims and the outline of the dissertation are described.

1. GENERAL INTRODUCTION

1.1 MUNICIPAL SOLID WASTE MANAGEMENT

During the past decades, the population growth combined with changes in productivity, consumption habits and lifestyles yielded an increase of municipal and industrial solid waste generation (RENOU ET AL., 2008; FOO & HAMEED, 2009). For instance, municipal solid waste reached 222 million tones in 2005 in the European Union (EU), 20% higher than 10 years before (OECD, 2008).

In general, municipal solid waste (MSW) refers to waste collected and treated by or for municipalities. MSW includes waste from households, commerce and trade, office buildings, institutions and small businesses, yard and garden waste, street sweepings, contents of litter containers and industrial cleansing waste. The definition excludes waste from municipal sewage networks and treatment, as well as municipal construction and demolition waste.

As society and technology has developed, the management of waste became a very organized, specialized and complex activity. Figure 1.1 (a) and (b) show the generation rate of MSW and some contrasting examples of waste management practices in different countries during 2008.

According to this data, Denmark and the USA were the countries with the highest MSW generation rates: 802 and 747 kg of MSW per person per year, respectively (EPA, 2009; EUROSTAT, 2010). The lowest value of 320 kg of MSW per person was found in Poland (EUROSTAT, 2010).

The treatment methods differ substantially. In 2008, USA landfilled 54% of MSW, incinerated 13%, recycled 24% and composted 9% (EPA, 2009). The percentage of MSW disposed at landfills was 44% in Italy, 87% in Poland, 65% in Portugal, 36% in France, 4% in Denmark and 1% in German and in the Netherlands (EUROSTAT, 2010). Incineration dominated in Denmark (54%), while recycling and composting was most common in Germany (65%) and in the Netherlands (60%) (EUROSTAT, 2010).

The type of waste management practices adopted in each country is not only a function of economic considerations, but is also a reflection of the country environmental legislation, the energy policy, the technical aspects and capabilities due to the type of waste to be handled, and the education and environmental awareness of its citizens.

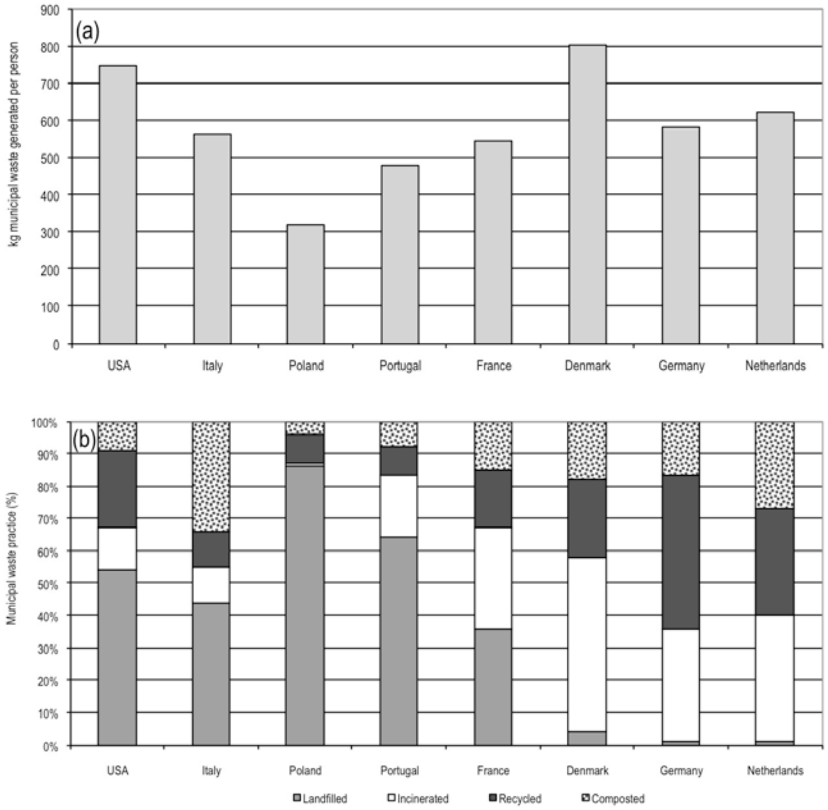

Figure 1.1 (a) Municipal solid waste generated per person and (b) waste management practices in different countries (source: EPA, 2009; EUROSTAT, 2010).

A number of serious and highly publicized pollution incidents associated with incorrect waste management practices, led to public concern regarding the lack of controls, inadequate legislation and environmental and human health impact. This in turn forced many national and federal governments to introduce new regulatory frameworks to deal with hazardous and unsustainable waste management operations (GIUSTI, 2009). A waste management hierarchy was introduced stipulating waste reduction, re-use and recycling over waste disposal. The European Commission adopted the Council Directive 1999/31/EC on the landfill of waste, known as the Landfill Directive. This Directive imposes, among others, the reduction of biodegradable organic waste in MSW disposed in landfills, aiming at reducing environmental pollution generated by landfills (EUROPEAN COMMISSION, 1999). Under this policy, landfilling should be used only when all the other treatment methods have been explored. As a result, the sanitary landfill as a strategic option declined and the diversion of organic matter to composting or incineration rapidly increased in some member states, such as Netherlands, Denmark, and Germany (Figure 1.1). Other EU countries still rely heavily on sanitary landfills.

In other parts of the world (Australia, Canada, China, New Zealand, Korea, South Africa, South America), sanitary landfilling is still the most widely applied option for MSW disposal. Sanitary landfilling is also increasing in developing countries, particularly close to the main cities, mainly due to economic advantages and also to the opportunities offered by the *Clean Development Mechanism* for methane recovery projects (COSSU, 2009). Therefore, disposal in landfill remains, and by far, the principal mode of waste elimination in the world (SALEM ET AL., 2008).

1.2 LEGAL FRAMEWORK IN PORTUGAL

The management of municipal solid waste in Portugal experienced a tremendous evolution of character political, legislative and strategic character, in late 1990s, with emphasis on institutional reorganization and the strategic measures adopted (MINISTÉRIO DO AMBIENTE, DO ORDENAMENTO DO TERRITÓRIO E DO DESENVOLVIMENTO REGIONAL, 2007).

The approval of the Strategic Plan for Municipal Solid Waste (PERSU I), in July 1997, generated a great impact in the management of MSW in the country. Based on the Waste Framework Directive 1975/442/EC (EUROPEAN COMMISSION, 1975), PERSU I was the first strategic planning document released for municipal waste establishing a comprehensive set of concrete actions to be undertaken in order to improve the sector in the period 1997-2006 (ERSAR, 2010). It defined the application of a hierarchy of principles namely prevention (reduction and reuse), recovery (recycling and recovery) and the safe disposal, in order of importance.

In the course of implementation of the strategic plan PERSU I, until 2002 a total of 341 dumpsites were closed in Portugal, a network of collection and recycling of waste was implemented, multi and intermunicipal systems were organized and new infrastructures were built for the appropriate treatment and confinement of MSW (MINISTÉRIO DO AMBIENTE, DO ORDENAMENTO DO TERRITÓRIO E DO DESENVOLVIMENTO REGIONAL, 2007).

When sanitary landfills started to be built, appeared the need of ensuring the issues related to environmental protection and human health associated with construction, operation and closure of these facilities as well as uniforming the conditions to be applied to the different stages of their life cycle. As a consequence of these assumptions, on 23 May 2002, the Landfill

Directive was transposed to the national legislative system – DL 152/2002, establishing the legislative pattern for the licensing, installation, exploration, closing and aftercare of landfills (MINISTÉRIO DO AMBIENTE E DO ORDENAMENTO DO TERRITÓRIO, 2002). The same directive established national targets concerning the reduction of biodegradable waste landfilling, based on the amount of biodegradable MSW produced in 1995, which was 2 252 720 tons. The limits of biodegradable municipal waste admissible for landfilling in Portugal were 1 689 540, 1 126 360 and 788 452 tons for January 2006, 2009 and 2016, respectively.

According to the Portuguese Environmental Agency (APA) in 2006, 459 kg per capita of municipal waste were generated in Portugal (APA, 2008). Of this, 66% was landfilled, 18% was incinerated, 10% recycled and only 6% was organically recovered. The European Commission opinion was that additional efforts were needed in order to reach the 2010 targets. Therefore, a new strategic plan for municipal solid waste, PERSU II, was approved for the period 2007-2016 in Portugal. This strategic plan continues the former policy of waste management taking into account the new (more ambitious) requirements formulated at national and Community level. In particular, it focuses on ensuring the compliance with the European Union (EU) objectives of deviating biodegradable waste from landfill, recycling and recovering packaging waste and reducing greenhouse gas emissions (MINISTÉRIO DO AMBIENTE, DO ORDENAMENTO DO TERRITÓRIO E DO DESENVOLVIMENTO REGIONAL, 2007).

So, a scenario of change and evolution in the MSW sector is expected in the near future. New opportunities and challenges to different waste management practices such as mechanical-biological waste pre-treatment, incineration, composting and anaerobic digestion are strong potential options and it is anticipated that the number of landfills will decrease. Even so, whatever the alternative treatment and recovery of waste, landfilling of MSW will always be, and is today, an essential practice in a waste management system, as destination of the scrap produced in the other treatment practices (incineration, composting, anaerobic digestion), which ultimately must be landfilled, or even as the only option of treatment.

In this context and in order to strengthen measures to promote recycling and recovery, as well as to adapt the operation of waste disposal in landfills to high standards of environmental quality, it was necessary to revise the national law (DL 152/2002). The review work culminated with the publication on August 2009 of a new law – DL 183/2009, which establishes the new legal regime of waste disposal in landfills, as well as the general requirements to be followed in the design, construction, operation, closure and post-closure of landfills (MINISTÉRIO DO AMBIENTE, DO ORDENAMENTO DO TERRITÓRIO E DO DESENVOLVIMENTO REGIONAL, 2009). In the purpose of this diploma, among others, are subjacent major concerns about minimizing and mitigating the negative impacts on the environment at local level, particularly with regard to emissions of greenhouse gases and landfill leachate.

The discharge of leachate into the aquatic environment is ruled by a different law (DL 236/1998, of August 1), which sets standards, including the emission limit values, for discharge of wastewater into surface and groundwater and into soil, aiming to promote the quality of aquatic environment and protect public health and soil (MINISTÉRIO DO AMBIENTE, 1998).

The discharge of leachate into sewers for subsequent treatment in a wastewater treatment plant usually obeys to the municipal regulations established for the reception of wastewater in the sewers network, involving the participation throughout the process of the organizations coordinating licensing.

1.3 CURRENT PROBLEMATIC OF LEACHATE TREATMENT IN PORTUGAL

The production of leachate is an inevitable consequence of the deposition of MSW in landfills. Typically, landfill leachate is a complex and strongly polluted wastewater with varying characteristics. An inadequate leachate management entails considerable risks, namely contamination of surface and groundwater and soil underlying the landfill and in many situations posing more costs for the waste management system. It is therefore essential to collect and treat the leachate correctly, not only from the perspective of prevention and control of pollution, but also from the viewpoint of economic sustainability.

Even after its closure, the landfill continues to generate leachate and according to the law DL 183/2009 it is necessary to continue the leachate monitoring and treatment during the following 30 years (MINISTÉRIO DO AMBIENTE, DO ORDENAMENTO DO TERRITÓRIO E DO DESENVOLVIMENTO REGIONAL, 2009).

Currently there are 24 MSW management systems in Portugal, of which 12 are multimunicipal systems and 12 are intermunicipal systems (Figure 1.2). These systems exploit 34 MSW landfills presently in operation and 15 already closed, which give rise to considerable quantities of landfill leachate.

Most of these MSW landfills began its operation in the early 2000s. Almost all of these facilities have leachate treatment or pre-treatment plants with direct disposal into the aquatic environment or into sewer for subsequent treatment in a wastewater treatment plant, respectively. This difference is mainly due to the existence, or not, of drainage networks in the vicinity of municipal landfill, which determines the type of treatment to employ.

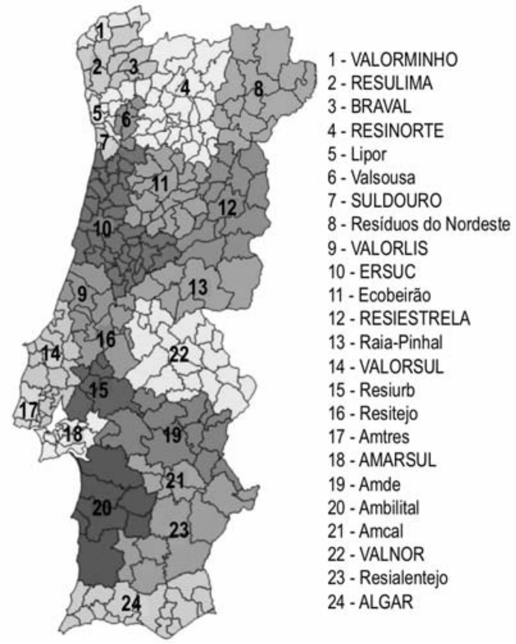

Figure 1.2 Distribution of waste management systems in Portugal: uppercase letters represent multimunicipal management systems; lowercase letters represent intermunicipal management systems (source: APA, 2010).

The current problematic of leachate management in Portugal is intimately connected with the inefficiency of the systems in operation, with subsequent discharge into sewers and water streams of effluents still with high levels of contamination. More specifically, many leachate treatment or pre-treatment plants have been experiencing difficulties in the removal of nitrate.

The removal of nitrogenous compounds is very important since, high concentrations of nitrogen-ammonium (N-NH_4^+) or nitrogen-nitrate (N-NO_3^-), can be toxic to aquatic life, deplete dissolved oxygen (DO) levels, cause eutrophication in receiving water bodies and affect the suitability of wastewater for reuse (Kumar & Lin, 2010; Paredes et al., 2007). Furthermore, N-NO_3^- in the gastrointestinal tract can be reduced to nitrogen-nitrite (N-NO_2^-) causing health problems like methemoglobinemia in infants or form nitrosamines and nitrosamides, potentially human carcinogenic compounds (Aslan & Cakici, 2007; Ghafari et al., 2008).

Biological processes (nitrification and denitrification) have been shown to be the most economical and useful approaches among all methods for removing nitrogenous compounds from water and wastewater.

The failure of the existing treatment systems in reducing leachate nitrate load and the good denitrification performance of biological processes were the starting-point for studying landfill leachate treatment in a closed rotating biological contactor.

1.4 RESEARCH AIMS

The main goal of this work was to evaluate the removal of nitrate from a landfill leachate with high NO_3^- load by denitrification in an anoxic rotating biological contactor. To fulfill this purpose different studies were performed to assess:

- the effect of several environmental parameters that influence denitrification such as the carbon to nitrogen ratio (C/N), phosphorus concentration and nitrate and carbon influent concentrations;
- the degradation of the leachate refractory compounds into biodegradable organic matter through Fenton's oxidation and ozone-based processes;
- the performance of a system comprising an ozonation step before biological treatment.

1.5 OUTLINE OF THE DISSERTATION

This dissertation reports the experimental work performed to attain the proposed scientific goals and is organized in eight chapters.

The present section (CHAPTER 1) provides information on municipal solid waste management and treatment in the world, giving particular emphasis to sanitary landfills, which is the most common treatment method in Portugal. The national legislation concerning sanitary landfills is presented, being also indicated one of the main current problems in the treatment of landfill leachate, such as the inefficiency in removing nitrate, which was the motivation to study landfill leachate treatment in rotating biological contactors. Finally, the aims and the organization of this dissertation are also presented.

In CHAPTER 2, the evolution of sanitary landfills along time and the major parameters affecting leachate production and composition are presented, as well as, the main conventional treatment systems, emerging processes and the national leachate treatment or pre-treatment plants.

A description of rotating biological contactors, historical evolution, advantages, application fields and the main factors affecting their performance are reviewed in CHAPTER 3.

In CHAPTER 4, the denitrification process in an anoxic bench-scale RBC, for the treatment of a synthetic wastewater under two C/N ratios is evaluated. The effect of different HRTs and different carbon and nitrate influent concentrations on the reactor performance, keeping C/N constant are analyzed and the characteristics and the activity of the biofilm grown in those conditions are compared.

In CHAPTER 5, the study of denitrification of a landfill leachate with high nitrate load in an anoxic rotating biological contactor is reported. The effect of initial nitrate load on the reactor performance is evaluated, as well as the effect of phosphorus concentration and C/N ratio.

Landfill leachate polishing treatment through Fenton's oxidation and ozone-based processes, in order to improve the biodegradability of its recalcitrant organic matter for subsequent biological treatment, is described in CHAPTER 6.

In CHAPTER 7, the removal of nitrate from landfill leachate with high nitrate load by denitrification in an anoxic RBC, previously ozonated to favor the biodegradability of the refractory organic load is described. In the beginning of the experiment, some operational parameters that affect denitrification efficiency, such as phosphorus concentration and C/N ratio were optimized. After stopping the reactor, in order to clarify the results obtained with the combined treatments in continuous mode, substrate removal rate was evaluated through batch experiments.

CHAPTER 8 contains the most significant conclusions withdrawn from the described experiments as well as some perspectives for further investigation in this field of research.

1.6 REFERENCES

APA (2008) Caracterização da Situação dos Resíduos Urbanos em Portugal continental em 2006-Resumo. Agência Portuguesa do Ambiente (APA), Ministério do Ambiente, do Ordenamento do Território e do Desenvolvimento Regional. [<http://www.apambiente.pt/politicasambiente/Residuos/gestaoresiduos/RU/Paginas/default.aspx>] (accessed 06.08.2010).

APA (2010) Sistemas de Gestão de Resíduos Sólidos Urbanos-Situação actual. Agência Portuguesa do Ambiente (APA), Ministério do Ambiente, do Ordenamento do Território e do Desenvolvimento Regional. [<http://www.apambiente.pt/politicasambiente/Residuos/gestaoresiduos/RU/Paginas/default.aspx>] (accessed 06.08.2010).

ASLAN, S. & CAKICI, H. (2007) Biological denitrification of drinking water in a slow sand filter.

Journal of Hazardous Materials, 148, 253-258.

COSSU, R. (2009) Driving forces in national waste management strategies. *Waste Management*, 29, 2797-2798.

EPA (2009) Municipal Solid Waste Generation, Recycling, and Disposal in the United States-Detailed Tables and Figures for 2008. U.S. Environmental Protection Agency Office of Resource Conservation and Recovery.
[<http://www.epa.gov/osw/nonhaz/municipal/msw99.htm>] (accessed 07.06.2010).

ERSAR (2010) Relatório Anual do Sector de Águas e Resíduos em Portugal-2008. Entidade Reguladora dos Serviços de Águas e Resíduos (ERSAR), [<www.ersar.pt>] (accessed 22.07.2010).

EUROPEAN COMMISSION (1975) Council Directive 1975/442/EEC of 25 July 1975 on Waste. *Official Journal of the European Communities*, L194, 39-49.

EUROPEAN COMMISSION (1999) Council Directive 1999/31/EC of 26 April 1999 on the Landfill of Waste. *Official Journal of the European Communities*, L182, 1-19.

EUROSTAT (2010) Environment in the EU 27,
[<http://epp.eurostat.ec.europa.eu/portal/page/portal/statistics/search_database>] (acessed 12.06.2010)

FOO, K. & HAMEED, B. (2009) An overview of landfill leachate treatment via activated carbon adsorption process. *Journal of Hazardous Materials*, 171, 54-60.

GHAFARI, S., HASAN, M. & AROUA, M.K. (2008) Bio-electrochemical removal of nitrate from water and wastewater-A review. *Bioresource Technology*, 99, 3965-3974.

GIUSTI, L. (2009) A review of waste management practices and their impact on human health. *Waste Management*, 29, 2227-2239.

KUMAR, M. & LIN, J. (2010) Co-existence of anammox and denitrification for simultaneous nitrogen and carbon removal-Strategies and issues. *Journal of Hazardous Materials*, 178, 1-9.

MINISTÉRIO DO AMBIENTE (1998) DL 236/1998. *Diário da República*, I Série-A, nº 176 de 1 de Agosto de 1998, 3676-3722.

MINISTÉRIO DO AMBIENTE E DO ORDENAMENTO DO TERRITÓRIO (2002) DL 152/2002. *Diário da República*, I Série-A, nº 119 de 23 de Maio de 2002, 4680-4699.

MINISTÉRIO DO AMBIENTE, DO ORDENAMENTO DO TERRITÓRIO E DO DESENVOLVIMENTO REGIONAL (2007) Plano Estratégico para os Resíduos Sólidos Urbanos 2007-2016 (PERSU II). Ministério do Ambiente, do Ordenamento do Território e do Desenvolvimento Regional [<www.maotdr.gov.pt/Admin/Files/Documents/PERSU.pdf>] (accessed 22.07.2010).

MINISTÉRIO DO AMBIENTE, DO ORDENAMENTO DO TERRITÓRIO E DO DESENVOLVIMENTO REGIONAL (2009) DL 183/2009. *Diário da República*, Série I, nº 153 de 10 de Agosto de 2009, 5170-5198.

OECD (2008) Environment Data: Compendium 2006-2008. Organization for Economic Co-operation and Development. [<http://oecd.org/env/>] (accessed 03.05.2010).

PAREDES, D., KUSCHK, P., MBWETTE, T.S.A., STANGE, F., MULLER, R.A. & KOSER, H. (2007) New aspects of microbial nitrogen transformations in the context of wastewater treatment - a review. *Engineering in Life Sciences*, 7, 13-25.

RENOU, S., GIVAUDAN, J., POULAIN, S., DIRASSOUYAN, F. & MOULIN, P. (2008) Landfill leachate treatment: review and opportunity. *Journal of Hazardous Materials*, 150, 468-493.

SALEM, Z., HAMOURI, K., DJEMAA, R. & ALLIA, K. (2008) Evaluation of landfill leachate pollution and treatment. *Desalination*, 220, 108-114.

Chapter 2

Overview of Landfill Leachate Treatments

In the last few decades, waste generation and the need for environmental preservation has become a major global concern. In line with the growing pressure for the use of environment-friendly technologies, various research and development efforts have been deployed for landfill leachate treatment. This chapter outlines the origin, properties and environmental impacts of landfill leachate. Biological, physico-chemical and combined leachate treatment technologies are discussed and their operating conditions such as pH, required dose, characteristics of leachate in terms of chemical oxygen demand (COD), biodegradability and N-NH_4^+ concentration and treatment efficiency are compared. The leachate treatment complexity makes it very difficult to formulate general recommendations of universal validity. Each of the presented methods offers inherent advantages and drawbacks. Particular attention is focused to the national leachate treatment or pre-treatment plants. Finally, major challenges and prospects concerning landfill leachate treatment are highlighted.

The information presented in this Chapter is from the following review, which has been submitted to an international scientific journal:

CORTEZ S., TEIXEIRA P., OLIVEIRA R. & MOTA M. Landfill leachate: generation, composition, management and treatment.

2. OVERVIEW OF LANDFILL LEACHATE TREATMENTS

2.1 SANITARY LANDFILLS

Not so long ago, uncontrolled dumping was the main system used in the final disposal of waste worldwide. In the 1960s, the use of uncontrolled dumping was gradually replaced in several industrialized countries by controlled tipping, encoded by the first series of technical guidelines on municipal solid waste disposal (COSSU, 2010). In these landfills, waste was deposited in thin, uncompacted layers covered with inert materials (preferably clay) to enhance the establishment of aerobic conditions and to avoid contact between waste and animals. Landfilled putrescible waste causes gas and leachate production. Collection of leachate and biogas was not provided for; leachate was allowed to infiltrate into the ground, whilst biogas production was not considered due to the presence of aerobic conditions, which were meant (optimistically) to prevent this phenomenon. In the majority of cases, things did not go exactly as planned, since little attention was paid to monitoring the ground and air circulation between the waste layers. As a consequence, the operation of this type of landfill resulted in the contamination of the surrounding air, soil, groundwater and even surface water (DING ET AL., 2001). The repeated occurrence of incidents and an increased public awareness of environmental issues, together with technical and scientific progress in the field and the enforcement of legislation, led to the improvement of the design, planning, operation and management of the sanitary landfills in the 1980s. Since then, these structures are constructed in carefully selected sites, which restrict the type of waste allowed to be landfilled, and include waste pre-treatment and compaction prior to disposal, multi-barrier lining systems, biogas collection (for energy production), leachate drainage, collection and treatment systems, management of the landfill. Finally, after closure, monitoring of the landfill leachate is mandatory and proper vegetation cover and landscape recovery is demanded. Figure 2.1 presents a scheme of a modern sanitary landfill.

A new emerging waste management trend operates a landfill as a bioreactor. Bioreactor landfills differ from conventional landfills in that they are operated in a controlled mode with the intent of creating an *in situ* environment favorable to the microbial degradation of waste. Creation of a biologically active environment is generally accomplished by injecting leachate and/or air in to the landfill (BERGE ET AL., 2009; ZHONG ET AL., 2009).

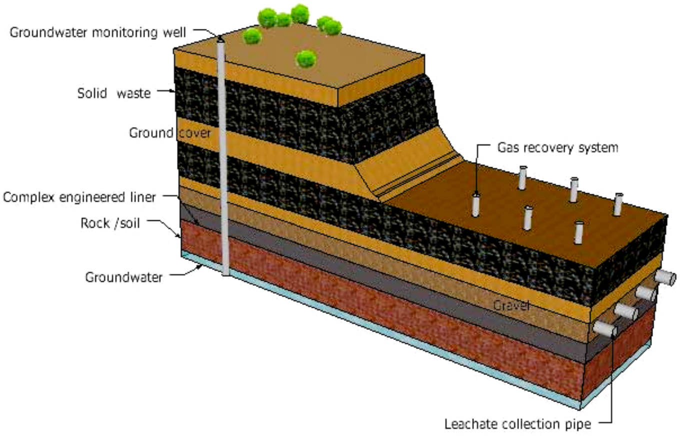

Figure 2.1 Sanitary landfill scheme.

Effective operation of bioreactor landfills involves careful operation and construction of an infrastructure not present in traditional landfills. Thus, investment capital and operating costs of such systems are greater than those associated with traditional landfills. These additional costs, however, may be offset by numerous economic advantages resulting from bioreactor landfill operation.

Despite the evolution of landfill technology, from open uncontrolled dumps to highly engineered facilities designed to eliminate or minimize the potential adverse impact of the waste on the surrounding environment, the generation of leachate remains inevitable (WISZNIOWSKI, ROBERT, ET AL., 2006). Moreover, landfills constructed and filled in the past still produce leachate and will probably do so for several decades (WALL & ZEISS, 1995; KYLEFORS ET AL., 2003; KURNIAWAN ET AL., 2006A), which still requires monitoring and treatment.

Therefore, the treatment of landfill leachate is and will be in the foreseeable future a major environmental concern. This is evident from the increasing number of publications on the generation, collection, storage, composition and treatment of landfill leachate during the period between 1980 and 2009. From Figure 2.2 it can be seen that in the 1980s, there were less than 25 related articles published annually. Recently, the number in the ISI Web of Knowledge database rose to over 300 articles.

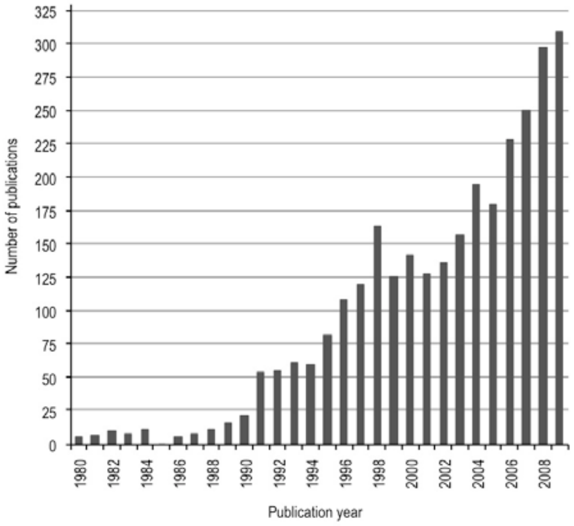

Figure 2.2 Number of publications concerning landfill leachate during the period 1980-2009 (source: ISI Web of Knowledge).

2.2 Landfill Leachate Definition, Production and Composition

Landfill leachate can be defined as the liquid resulting from percolation of water and liquid waste through deposited solid waste, containing a cocktail of organic and inorganic compounds, biodegradable or non-biodegradable, in dissolved or suspended forms. Around 100 hazardous compounds have been identified in the landfill leachate. Some of them may be found at extremely high concentrations, presenting a cumulative, threatening and detrimental effect to the surrounding environment. Put in simply, those compounds can be divided into four main groups: dissolved organic matter; inorganic macro-components, such as ammonium (NH_4^+), calcium (Ca^{2+}), sodium (Na^+), iron (Fe^{2+}), sulphate (SO_4^{2-}), chloride (Cl^-); heavy metals, such as cadmium (Cd^{2+}), chromium (Cr^{3+}), copper (Cu^{2+}), lead (Pb^{2+}), nickel (Ni^{2+}); and xenobiotic organic compounds (XOCs). Dissolved organic matter covers a wide range of organic species, from methane (CH_4), volatile fatty acids (VFA) to more recalcitrant humic substances found in landfill leachate and is quantified as chemical oxygen demand (COD) and/or total organic carbon (TOC). Xenobiotic organic compounds resulting from household or industrial chemicals are present in very low concentrations (usually lower than one milligram per liter level). These compounds include, among others, a variety of aromatic hydrocarbons, phenols and chlorinated aliphatics (Kjeldsen et al., 2002).

Landfill leachate flow rate varies from site to site, seasonally within each site (LEMA ET AL., 1988), and is influenced by many factors: climatic and hydro-geological conditions, site operations and management, refuse characteristics and internal landfill processes. These factors can be divided into those that contribute directly to leachate production (rainfall, snowmelt, surface runoff, evaporation, evapotranspiration, groundwater intrusion, initial waste water content, irrigation, recirculation, liquid waste co-disposal and refuse decomposition) and those that affect leachate distribution within the landfill (refuse pre-treatment, compaction, permeability, particle size, density, settlement, vegetation, cover, sidewall, liner material, gas and heat generation and transport) (EL-FADEL ET AL., 1997). The volume of landfill leachate produced is small compared to other wastewaters (SILVA ET AL., 2004).

The composition of landfill leachate is closely related to the quantity produced, and can exhibit considerable spatial and temporal variations depending upon site operations and management practices (such as refuse pre-treatment, irrigation, and recirculation), refuse characteristics (composition and age) and internal landfill processes (such as hydrolysis, adsorption and biodegradation) (LEMA ET AL., 1988; EL-FADEL ET AL., 1997). The physicochemical and biological processes that occur within the waste and landfill age are usually the major determinants of leachate composition (KULIKOWSKA & KLIMIUK, 2008).

In general, the composition of the landfill leachate is characterized by the basic parameters: COD, TOC, five-day biochemical oxygen demand (BOD_5), BOD_5/COD ratio (biodegradability), total Kjeldahl nitrogen (TKN), nitrogen-ammonium ($N\text{-}NH_4^+$), pH, total dissolved solids (TDS), turbidity, alkalinity, color, conductivity, salts, xenobiotic organic substances and/or heavy metals content. Leachate toxic composition may also be evaluated by different toxicological tests, which provide indirect information on the content of pollutants that may be harmful to severe test organisms (such as micro-algae, duckweed, rotifers or luminescent bacteria).

Table 2.1 summarizes the major characteristics of leachate according to landfill site and landfill age.

Table 2.1 Mean composition of leachate at different landfill sites and ages.

Landfill site	Spain		China		Greece	
	(Hermosilla et al., 2009)		(Huo et al., 2008)		(Tatsi et al., 2003)	
Parameter \ Landfill age	Young	Mature	Young	Mature	Young	Mature
pH	8.3	8.5	6.7	8.8	6.2	7.9
Conductivity (mS·cm^{-1})	32.7	8.0	31.5	29.1	29.5	18.3
TDS (g·L^{-1})	16	4	-	-	51	9.6
BOD_5 (mg·L^{-1})	1000	43	39900	149	26800	1050
COD (mg·L^{-1})	6119	837	53200	1863	70900	5350
BOD_5/COD	0.2	0.05	0.75	0.08	0.4	0.2
TOC (mg·L^{-1})	1481	223	-	-	-	-
TKN (mg·L^{-1})	-	-	-	-	3400	1100
N-NH_4^+ (mg·L^{-1})	1965	200	2760	796	3100	940
Alkalinity (mg $CaCO_3$·L^{-1})	14443	2204	-	-	12880	4950
Color (units PtCo)	-	-	-	-	10550	7600
Turbidity (NTU)	-	-	-	-	1700	340
PO_4^{3-} (mg·L^{-1})	-	-	1.63	1.86	nd	3.0
SO_4^{2-} (mg·L^{-1})	-	-	163	18	1600	210
Cl^- (mg·L^{-1})	4430	1335	6150	8250	3260	4120

nd: not detected

After being landfilled, the solid waste decomposes through different phases. The first one, which only lasts a few days or weeks, corresponds to the aerobic degradation of organic matter. As soon as the oxygen is depleted, the degradation proceeds anaerobically (Kurniawan et al., 2006a; Salem et al., 2008). In young landfills containing substantial amounts of biodegradable organic matter, a rapid anaerobic fermentation takes place, resulting in low molecular weight compounds such as volatile fatty acids (VFAs) (Welander et al., 1998). This early phase of a landfill's lifetime is called the acidogenic phase and, besides the high organic fraction of VFAs, the leachate produced presents weak to strongly acidic pH, high COD and TOC concentrations, and high biodegradability (BOD_5/COD ratio in the range 0.4-0.7) (Chen, 1996; Kurniawan et al., 2006a; Salem et al., 2008). N-NH_4^+ and heavy metals concentrations also rise during this period (Salem et al., 2008). It has been established that the acidogenic phase may last one to four years. With the landfill maturation, the methanogenic phase begins. During this phase, VFAs are degraded decreasing the organic strength in the leachate, biogas is produced (CH_4, CO_2) and leachate becomes neutral or alkaline. With the increasing of age (>10 years), the matured leachate evolves towards a high strength of ammonium nitrogen, a moderate strength in COD, low concentrations of heavy metals and a low BOD_5/COD ratio (most often close to 0.1) (DE MORAIS & ZAMORA, 2005; KURNIAWAN ET AL., 2006A). Typically, most of the organic materials present in the mature leachate have a high molecular weight and are recalcitrant compounds such as humic- and fulvic-like acids (WELANDER ET AL., 1998). It is important to note that the different degradation phases are not definitive, since dynamic variations in the environmental conditions result in changes in their distribution and rates within the landfill. For example, under certain conditions, the acid-formers may outgrow methane-formers, leading to acidification and interruption of the anaerobic digestion process (BARLAZ ET AL., 1989).

Recently, it has been observed that even leachate from young landfills contains low organics (COD and TOC) concentration (CHEN, 1996; AZIZ ET AL., 2007). This can be due to leachate recirculation that started to be practiced in many landfills.

The data presented in Table 2.1 prove that landfill leachate constitutes a serious pollution hazard to the surrounding soil, and ground or surface water. The understanding, monitoring, management and treatment of quantity and quality of landfill leachate during operation and after landfill closure are of great importance.

2.3 LANDFILL LEACHATE MANAGEMENT AND TREATMENT TECHNOLOGIES

The selection and design of the management and treatment of a landfill leachate is governed by factors such as leachate characteristics, effluent discharge alternatives, technological options, final discharge requirements and economical aspects (QASIM & CHIANG, 1994; CHATURAPRUEK ET AL., 2005).

The most common options of leachate management include recirculation and recycling of the leachate back into the landfill, combined treatment with municipal wastewater, use of systems such as constructed wetlands, leachate evaporation or evapotranspiration (through vegetation) and on-site treatment followed by discharge. Leachate recirculation is being increasingly used since it accelerates the stabilization of the landfilled municipal solid waste and increases methane production. However, recycling leachate invariably results in accumulation of ammonia, which is nearly inert under anaerobic conditions. This high-strength wastewater requires intensive treatment before its safe disposal (BERGE ET AL., 2006; SHAO ET AL., 2008). The treatment of landfill leachate together with municipal wastewater is not recommended since it may contribute to increase total pollutant load in sewage (such as XOCs and nitrogen-ammonium), which can be adsorbed into sludge particles and transferred to the sludge processing systems (MARTTINEN ET AL., 2003). Furthermore, landfills are generally located far from metropolitan areas and sewage treatment plants, making this option increasingly expensive. Where land is available at low-cost, systems such as constructed wetlands, are attractive alternatives for landfill leachate management. Constructed wetlands are not likely to provide pollutants removal below detection for the major constituents of a specific leachate, but may very well do so for trace constituents (KADLEC & ZMARTHIE, 2010). Leachate evaporation or evapotranspiration (through vegetation) during warm periods may produce a high quality condensate, residuals being a small fraction of the original leachate volume (BIRCHLER ET AL., 1994).

Careful site management can reduce the quality and pollution potential of the formed leachate, without attaining total pollutant removal. The application of a general strategy for on-site landfill leachate treatment is hampered by its great diversity. Techniques successfully developed for one site might not necessarily being applicable elsewhere. In addition, treatment methods that work well at young landfills are likely to become progressively less effective with the tip's age (LEMA ET AL., 1988). Biological treatments of landfill leachate have been shown to be very effective in removing organic matter in the early stages when the BOD_5/COD ratio of the leachate is high, but this ratio decreases with the age of the landfill and the process is less effective with time, when the presence of recalcitrant organic matter is higher. Accordingly, a variety of physico-chemical processes have been developed and used to treat leachate with this type of matter (RODRIGUEZ ET AL., 2004). Therefore, the leachate treatment system must be flexible enough to produce the same effluent quality despite the sudden and large variations in the leachate strength (SMITH, 1995; KOCHANY & LIPCZYNSKA-KOCHANY, 2009). Currently, the treatment systems used for leachate treatment include biological, physico-chemical and a combination of these processes. ALVAREZ-VAZQUEZ ET AL. (2004) estimated that the treatment systems used for leachate treatment were 72% biological, 11% flocculation/coagulation, 5% membrane filtration, 4% air stripping, 4% chemical oxidation and 4% adsorption on activated carbon. It is important to note that, previously to any process, landfill leachate treatment plants usually possess entrance units that allow the removal of suspended and floating debris, oils or sand and stabilization lagoons. The latter are responsible for the homogenization and regularization of the leachate flow that is produced in the landfill. Furthermore, these units ensure the removal of some pollutant load, as there is some degradation and sedimentation. Given the variability of the quantity and quality of leachate, stabilization lagoons, therefore, perform a very important step, whatever the treatment or pre-treatment system used.

The enforcement of environmental discharge rules and the aging of landfill sites with more and more stabilized leachate in different countries have put pressure on operators to implement better processes for the reduction of pollutants (HAGMAN ET AL., 2008). New treatment alternatives and conventional technology improvements, mainly specialized on tertiary treatment, have been developed in recent years. This chapter provides an up to date overview of landfill leachate treatment.

2.3.1 BIOLOGICAL TREATMENT SYSTEMS

Biological treatment technologies have been shown to be feasible, simple, effective and economical methods to degrade biodegradable organic and nitrogenous matter of landfill leachate (NECZAJ ET AL., 2005; KURNIAWAN ET AL., 2006A; LIANG & LIU, 2008). In aerobic processes, microorganisms degrade leachate organic compounds to carbon dioxide, water and microbial biomass and reduce nitrogen-ammonium to nitrogen-nitrate by nitrification. Nitrogen-nitrate is then oxidized to nitrogen gas under an anoxic environment and with external carbon addition during denitrification. Biological anaerobic processes are also used for removal of organic pollutants, mainly from high strength leachate, presenting some advantages such as biogas (mainly methane and carbon dioxide) generation and low biomass production, and for the conversion of ammonium to nitrogen gas in a process called ANAMMOX (anaerobic ammonium oxidation), which is a recent finding and allows energy and cost savings (WANG ET AL., 2010).

It is worth mentioning that parameters such as food-microorganisms ratio (F/M), hydraulic retention time (HRT) and environmental factors such as pH or mixing are usually controlled to insure the optimum growth of the complex mixed microbiological populations and, consequently, to optimize biological treatment (WISZNIOWSKI, ROBERT, ET AL., 2006). For instance, phosphorus deficiency in leachate hampers the production of microorganisms and consequently the treatment performance (JOKELA ET AL., 2002). It is thus common to overcome this deficiency by adding phosphorus. Likewise, since most denitrifiers are heterotrophs, external carbon is usually added following nitrification, mainly when treating mature leachate, whose organic load is resistant to biodegradation.

Biological treatment of landfill leachate includes suspended-growth biomass systems such as lagooning, activated sludge (AS) and sequencing batch reactors (SBRs), as well as attached-growth biomass systems such as trickling filters (TFs), rotating biological contactors (RBCs) and suspended carrier biofilm reactors. The latter mentioned systems, using biofilm, present some advantages such as higher volumetric conversion rates, lower hydraulic retention time, higher resistance to toxic agents, lower sensitivity to environmental conditions (such as temperature, pH and metabolic products) and less sludge production (WISZNIOWSKI, ROBERT, ET AL., 2006; RENOU ET AL., 2008; KULIKOWSKA ET AL., 2010). The attached-growth biomass systems are of particular interest for landfill leachate nitrification due to a high resistance to shock of organics and nitrogen loadings.

2.3.1.1 Suspended-growth biomass systems

2.3.1.1.1 Activated sludge

Conventional activated sludge (AS) processes use an aerobic and/or anoxic biological tank followed by a settlement chamber for sludge separation. Part of this sludge is then recycled to the tank to provide biomass to treat the new leachate. In the past, these traditional treatment schemes, proved to exhibit satisfactory and consistent leachate treatment performance in terms of biodegradable organic carbon and nutrients removal, providing enough hydraulic residence time (TSILOGEORGIS ET AL., 2008). However, over time and with landfill aging, many operational problems such as control of biomass settling, loss of slow growing organisms (for example, nitrifiers) able to remove the biodegradable pollutants at low kinetics, high-energy consumption, excess of sludge production and microbial inhibition by toxic compounds led to the abandonment of this type of reactor for landfill leachate treatment (QASIM & CHIANG, 1994; DI IACONI ET AL., 2006; WISZNIOWSKI , ROBERT ET AL., 2006). There are very few recent works available concerning landfill leachate treatment by conventional activated sludge methods (Table 2.2).

Increasing attention has been given on the inclusion of plastic carriers (WELANDER ET AL., 1998), bentonite (WISZNIOWSKI ET AL., 2006) or granular activated carbon (LOUKIDOU & ZOUBOULIS, 2001) into the AS reactor. Such modifications can improve settling sludge properties, allowing retaining the microorganisms in the system and, in the case of activated carbon, enhancing adsorption of the substrate, resulting in more effective nitrogen-ammonium, metal and COD removal. Nevertheless, the operational cost of leachate treatment by this modified activated sludge system is notably increased (WISZNIOWSKI, ROBERT, ET AL., 2006).

Table 2.2 Landfill leachate treatment using activated sludge reactors.

Landfill site, age, reference	Leachate feeding characteristics				Reactor operational parameters					Performance
	pH	COD ($mg \cdot L^{-1}$)	BOD_5/COD	$N\text{-}NH_4^+$ ($mg \cdot L^{-1}$)	T (ºC)	Type of operation and scale	HRT (d)	SRT (d)	OLR (g $COD \cdot L^{-1} \cdot d^{-1}$)	
Moyer (Philadelphia, USA), mature leachate, (Dzombak et al., 1990)	7	733	0.02	354	-	Aerobic, lab-scale (6L aeration tank+1.4L settling tank)	2	30	-	100 and 40% for $N\text{-}NH_4^+$ and COD removal, respectively
Burns Bog (British Columbia, USA), mature leachate, (Shiskowski & Mavinic, 1998)	7.5	-	-	200-1200	20	Anoxic/aerobic, pilot-scale (5L anoxic tank+10L aeration tank+4L settling tank)	0.14	13	-	-
Kimpo (Korea), mature leachate, (Bae et al., 1999)	-	3130	0.44	-	rt	Aerobic, lab-scale	3	-	-	69 and 98% for COD and BOD_5 removal, respectively
Djebel Chekir (Tunisia), young leachate, (Ellouze, M. et al., 2008)	7.8	3200	0.51	1750	rt	Aerobic, pilot-scale (14L aeration tank+settling tank)	5.5	-	4.5	92 and 75% for $N\text{-}NH_4^+$ and COD removal, respectively

SRT: sludge retention time; OLR: organic loading rate; rt: room temperature

2.3.1.1.2 Sequencing batch reactors

The sequencing batch reactor (SBR) is a variation of the conventional activated sludge system in which biological oxidation and sludge separation are carried out in the same tank and environmental conditions are controlled using fill and draw operations at distinct time intervals (Neczaj et al., 2005; Tsilogeorgis et al., 2008). The periodic and controlled change of process conditions, such as concentration of oxygen, makes the SBR technology attractive for aerobic, anoxic and anaerobic processes and has resulted in a wide application for landfill leachate treatment. Typical performances of SBRs are reported in Table 2.3.

Table 2.3 Landfill leachate treatment using sequencing batch reactors.

Landfill site, age, reference	Leachate feeding characteristics				Reactor operational parameters					Performance
	pH	COD (mg·L^{-1})	BOD$_5$ /COD	N-NH$_4^+$ (mg·L^{-1})	T (ºC)	Type of operation and scale	HRT (d)	SRT (d)	Cycle	
Jiangmen (China), mature leachate, (Li, Zhou, et al., 2009)	8.8	3000	0.22	1200	et	Aerobic, full-scale (1200 m^3)	-	20	24 h (1 h feed, 4 h mixing, 5 h aeration, 2 h mixing, 3 h aeration, 8 h settle and 1 h decant)	99 and 76% for N-NH$_4^+$ and COD removal, respectively
Wysieka (Poland), mature leachate, (Klimiuk & Kulikowska, 2004)	-	680	0.16	312	rt	Aerobic /anoxic, lab-scale (6 dm^3)	3	-	24 h (0.25 h feed, 20.5 h aeration, 3 h settle and 0.25 h decant)	100, 49 and 93% for N-NH$_4^+$, COD and BOD$_5$ removal, respectively
	-	680	0.16	312	rt	Aerobic /anoxic, lab-scale (6 dm^3)	2	-	12h (0.25 h feed, 10 h mixing, 1.5 h settle and 0.25 h decant)	100, 48 and 93% for N-NH$_4^+$, COD and BOD$_5$ removal, respectively; occasionally a higher amount of N-NH$_4^+$ was observed
Turkey, mature leachate, previously coagulated and air stripped, (Uygur & Kargi, 2004)	7-7.5	5750	-	185	25	Anaerobic /aerobic /anoxic, lab-scale (5 dm^3)	-	10	21 h (1 h anaerobic, 1 h anoxic, 2 h aerobic, 1 h anoxic and 1 h aerobic × 3 cycles)	31 and 62% for COD and BOD$_5$ removal, respectively
Thessaloniki (Greece), mature leachate, (Zouboulis et al., 2001)	7.5	15000	0.37	1800	40-50	Aerobic /anoxic, lab-scale (8 dm^3)	20	-	16 h (2 h feed and mixing, 6 h aeration, 1 h mixing, 6 h aeration, 1 h settle and decant)	60-70, 40 and 70% for N-NH$_4^+$, COD and BOD$_5$ removal, respectively
Heimifeng (China), mature leachate, (Xu et al., 2010)	7.7	3876	0.14	1451	30	Anaerobic /aerobic /anoxic, lab-scale (3 dm^3)	-	-	12 h	90, <6.7 and >95% for N-NH$_4^+$, COD and BOD$_5$ removal, respectively

et: environmental temperature

To enhance the degradation of organic constituents, as well as to reduce the nitrogen content of a landfill leachate, small improvements to the SBR system have been tried: ZOUBOULIS ET AL. (2001) analyzed the addition of enzymes while UYGUR & KARGI (2004) studied the introduction of powdered activated carbon (PAC) in a SBR. Both solutions achieved interesting results but, inevitably, represent additional costs.

2.3.1.1.3 Lagooning

Aerated and non-aerated lagoons are interesting options for on-site treatment of landfill leachate since they offer low operational and maintenance costs, can effectively remove pathogens, organic and inorganic compounds and support significant fluctuations of influent concentration and strength, typical of landfill leachate (FRASCARI ET AL., 2004). Aerated lagoon systems are similar to activated sludge systems except that no recycle is used. In many cases lagoons are operated as a leachate pre-treatment step prior to disposal into municipal sewers, other on-site leachate treatments or recycling into landfills.

Although a considerable amount of lagoons has been employed on biological leachate treatment, few studies relative to the utilization of these systems for this purpose are available in the current literature (Table 2.4).

Table 2.4 Landfill leachate treatment using aerated and non-aerated lagoons.

Landfill site, age, reference	Leachate feeding characteristics				Lagoon operational parameters			Performance
	pH	COD ($mg \cdot L^{-1}$)	BOD_5/COD	$N\text{-}NH_4^+$ ($mg \cdot L^{-1}$)	T (ºC)	Type of operation and scale	HRT (d)	
Penzberg (Germany), mature leachate, (SCHWARZENBECK ET AL., 2004)	-	136-1980	-	-	et	(1) Aerobic, full-scale (2000 m^3)	-	≈50% for $N\text{-}NH_4^+$
Tre Monti (Italy), mature leachate, (FRASCARI ET AL., 2004)	8.4	5050	0.25	1330	et	(2) Anaerobic lagoons (4.4 and 5.2m depths) (3) facultative aerobic lagoons (1.5 and 2.1 depths), full-scale	32 (anaerobic lagoons) 148 (facultative aerobic lagoons)	77, 40 and 64% for $N\text{-}NH_4^+$, COD and BOD_5 removal, respectively
Colchester (United Kingdom), mature leachate, (MEHMOOD ET AL., 2009)	7.2	1740	-	965	et	(4) Facultative aerobic lagoons, full-scale (60-80 m^3)	11-254	99 and 75% for $N\text{-}NH_4^+$ and COD removal, respectively

2.3.1.1.4 Anaerobic digesters

The anaerobic digestion (AD) treatment of leachate enables the process initiated in the landfill to be concluded (LEMA ET AL., 1988). An interesting feature of anaerobic treatment is the possibility of using the biogas produced to warm the digester that usually works at 35 ºC.

The performance of some conventional anaerobic suspended-growth reactors is presented in Table 2.5.

Table 2.5 Landfill leachate treatment using conventional anaerobic digesters.

Landfill site, age, reference	Leachate feeding characteristics				Reactor operational parameters				Performance
	pH	COD ($mg \cdot L^{-1}$)	BOD_5 /COD	$N\text{-}NH_4^+$ ($mg \cdot L^{-1}$)	T (ºC)	Scale	HRT (d)	OLR (g $COD \cdot L^{-1} \cdot d^{-1}$)	
Coruña (Spain), young leachate, (MENDEZ ET AL., 1989)	7.3	4100	-	800	37	Lab-scale (0.9 L)	4	1.1	47% COD removal
	7.3	4100	-	800	20	Lab-scale (0.9 L)	4	1.1	29% COD removal
Kaushung (Taiwan), young leachate, (LIN, 1991)	6.3 - 6.4	22750	0.7	171	35	Lab-scale (2 L)	15	1.51	93 and 97% for COD and BOD_5 removal, respectively; 770 mg $N\text{-}NH_4^+ \cdot L^{-1}$ in the effluent
Shiraz (Iran), young leachate, (KHERADMAND ET AL., 2010)	6.3	50534	0.7	1460	32	Pilot-scale (150 L)	15	3.37	79 and 75% for COD and BOD_5 removal, respectively

The efficiencies reported in Table 2.5 demonstrate that the anaerobic digester is an economic and reliable process, particularly suitable for dealing with high organic matter concentration from young landfills. Obviously, anaerobic processes do not remove ammonium and therefore always need downstream stripping or, more frequently, nitrification (ALVAREZ-VAZQUEZ ET AL., 2004).

2.3.1.1.5 Upflow anaerobic sludge blanket reactors

In the upflow anaerobic sludge blanket (UASB) reactor, a high concentration of active anaerobic biomass is held in suspension in the reactor by hydraulic design and occurs formation of granular biomass. The upward motion of methane and carbon dioxide gas bubbles imparts mixing in the sludge bed.

Over the years, several UASB reactors have been shown to be efficient in the treatment of the MSW leachate (LIU ET AL., 2010). From Table 2.6 it can be seen that the average performance of COD removal efficiency was always higher than 69% for temperatures in the range 19-42 ºC.

Table 2.6 Landfill leachate treatment using UASB reactors.

Landfill site, age, reference	Leachate feeding characteristics				Reactor operational parameters				Performance
	pH	COD ($mg \cdot L^{-1}$)	BOD_5/COD	$N\text{-}NH_4^+$ ($mg \cdot L^{-1}$)	T (ºC)	Scale	HRT (d)	OLR (g $COD \cdot L^{-1} \cdot d^{-1}$)	
Nepean (Canada), young leachate, (Kennedy & Lentz, 2000)	6.9-9.0	4800-9840	0.86	-	35	Lab-scale (6.2 L)	1	4.8-9.8	78% COD removal
Turkey, young leachate, (Agdag & Sponza, 2005)	-	20000	-	679	37-42	Lab-scale (2.5 L)	1.25	16	27 and 79% for $N\text{-}NH_4^+$ and COD removal, respectively
Bucaramanga (Colombia), young leachate, (Castillo et al., 2007)	6.5-7.5	3273	>0.5	-	-	Lab-scale (5 L)	2.3	0.33	62% COD removal
Asturias (Spain), young leachate, (Castrillón et al., 2010)	-	11939	-	1679	35	Lab-scale (2 L)	1.6	7.5	80% COD removal; 1665 mg $N\text{-}NH_4^+ \cdot L^{-1}$ in the effluent
Quito (Ecuador), young leachate, (Kettunen & Rintala, 1998)	7.1	26000	0.5	-	19	Lab-scale (2.5 L)	1.2	21	69% COD removal
	7.1	26000	0.5	-	30	Lab-scale (2.5 L)	1.2	21	72% COD removal

Kettunen & Rintala (1998) observed similar COD removal efficiency at low temperatures (13-23 ºC), and in the treatment of landfill leachate in a UASB reactor. This surprising result suggests that high treatment efficiency can be achieved without heating the reactor, providing an interesting cost-effective option.

Recently, Liu et al. (2010) applied a modified reactor of the traditional UASB, the expanded granular sludge bed (EGSB), which operates at much higher superficial velocities and height/diameter ratio for the treatment of a fresh leachate. Under the proposed optimal conditions (HRT=2.83 d and OLR=22.5 g $COD \cdot L^{-1} \cdot d^{-1}$) and at 35 ºC, the lab-scale EGSB reactor removed 94-96% of the COD from the raw leachate (COD=66000-68000 $mg \cdot L^{-1}$).

2.3.1.1.6 Membrane bioreactors

There is a growing interest in using the membrane bioreactor (MBR), which comprises a bioreactor generally containing suspended microorganisms combined with a membrane module (Alvarez-Vazquez et al., 2004; Bohdziewicz et al., 2008; Hasar et al., 2009). The MBR has a low footprint, can be operated at very long sludge age (SRT) and with high biomass concentration, and can achieve an excellent clarified effluent with low sludge waste production (Alvarez-Vazquez et al., 2004; Canziani et al., 2006). Contrary to conventional systems, organisms such as nitrifiers or organisms that are able to degrade slowly biodegradable substances are not washed out of the system and no loss of process activity occurs. Such advantages turn the MBR an attractive alternative for organic matter removal and nitrification of young and even mature landfill leachate (ALVAREZ-VAZQUEZ ET AL., 2004; CANZIANI ET AL., 2006; HASAR ET AL., 2009). Naturally, the denitrification process will also occur in the MBR if an intermittent aeration it is adapted to the system.

MBRs use ultrafiltration (UF) and/or microfiltration (MF) membranes for the complete retention of sludge (BOHDZIEWICZ ET AL., 2008). The membrane can be fitted either outside or within (submerged) the bioreactor tank, and both configurations have been employed for landfill leachate treatment (ALVAREZ-VAZQUEZ ET AL., 2004). The major disadvantages of membrane bioreactors are the high capital and operating costs. Operational data and performance of different kinds of MBRs are detailed in Table 2.7.

PIRBAZARI ET AL. (1996) tested the combination of a lab-scale MBR with powdered activated carbon, blending adsorption, biodegradation and membrane filtration processes for the treatment of landfill leachate. The process efficiencies were in the range of 95-98% in terms of TOC reduction and exceeded 97% for specific organic pollutants.

2.3.1.2 Attached-growth biomass systems

2.3.1.2.1 Fixed-bed reactors

Trickling filters (TFs) and submerged biological filters (BFs) represent the main fixed-bed reactors that have been investigated for organic and nitrogen removal from MSW leachate. In these reactors, biological reactions take place in the biofilm developed on the immobilized support material. Trickling filters are commonly aerobic systems whereas biofilters operate under aerated or non-aerated conditions (Table 2.8). Biofilters are being increasingly used instead of TFs.

As part of biofilm technology, fixed-bed reactors provide good removal efficiencies, even with effluents with low BOD_5/COD ratio, are resistant to toxic substances and tolerate many of the inhibitors usually contained in leachate (GÁLVEZ ET AL., 2009). Under certain conditions, a biofilm, with a great diversity of microorganisms performing nitrification and denitrification, occurs in the same reactor. Furthermore, biological treatment and solids separation occur in the same reactor eliminating the requirement for separate secondary clarification and minimizing footprint. An important drawback of fixed-bed reactors is the added cost of the support.

Table 2.7 Landfill leachate treatment using MBRs.

Landfill site, age, reference	Leachate feeding characteristics				Reactor characteristics		Membrane properties		Operational parameters				Performance
	pH	COD (mg·L^{-1})	BOD$_5$/COD	N-NH$_4^+$ (mg·L^{-1})	Type of reactor	Type of operation and scale	Type of membrane, module and configuration	Operated pressure (bar)	T (ºC)	HRT (d)	SRT (d)	OLR	
Thessaloniki (Greece), mature leachate, (TSILOGEORGIS ET AL., 2008)	8.4	2456	-	238	Sequencing batch reactor (cycle 12 h)	Aerobic/anoxic, lab-scale (5L)	Polymeric ultrafiltration, hollow fiber submerged	0.1-0.5	-	10	No waste sludge removal took place	-	≈100% for N-NH$_4^+$ and N-NO$_3^-$, 40-60% for COD removal
Italy, mature leachate, (CANZIANI ET AL., 2006)	7.8-8.2	4224	0.33	1547	Activated sludge	Aerobic, pilot-scale (500 L)	Ceramic ultrafiltration, tubular external	1.5	30-37	-	>45	-	45% COD removal
Jebel Chakir (Tunisia), young leachate, (ZAYEN ET AL., 2010)	7	41000	-	-	Activated sludge	Anaerobic, pilot-scale (50 L)	Polymeric ultrafiltration, tubular external	0.2-3	37	7	-	6.27 g COD·L^{-1}·d^{-1}	91% COD removal
Thailand, young leachate, (VISVANATHAN ET AL., 2007)	6.8-7.0	12000	0.65	1000	Activated sludge	Aerobic, lab-scale (6 L)	Ceramic ultrafiltration, hollow fiber submerged	0.18-0.6	45	1	-	7.2-8.5 g BOD·L^{-1}·d^{-1}	79 and 76% for N-NH$_4^+$ and COD removal, respectively

Table 2.8 Landfill leachate treatment using fixed-bed reactors.

Landfill site, age, reference	Leachate feeding characteristics				Reactor characteristics		Support material properties		Operational parameters			Performance
	pH	COD (mg·L^{-1})	BOD$_5$ /COD	N-NH$_4^+$ (mg·L^{-1})	Type of reactor, mode of operation	Type of operation and scale	Type of material and media	Media dimensions	T (ºC)	HRT (d)	OLR (g COD·L^{-1}·d^{-1})	
Essex (United Kingdom), mature leachate, (KNOX, 1985)	≥7.5	-	-	233	TF, leachate continuously recirculated	Aerobic, pilot-scale (16.5 m^3)	Corrugated plastic cylinders	Diameter-3 cm; specific surface area-230 m^2·m^{-3}	19.7	0.2-0.6	-	≈100, 87 and 86% for N-NH$_4^+$, BOD$_5$ and SS removal, respectively
France, mature leachate, (GOURDON ET AL., 1989)	8.0-8.5	850-1350	0.1-0.2	295	TF, leachate continuously recirculated	Aerobic, full-scale (16500 dm^3)	Plastic fragments	Particles size-10-10 mm	20	4.5	-	52% COD removal
Coruña (Spain), young leachate, (MENDEZ ET AL., 1989)	8.2	4200	-	700	BF, continuously recirculated	Anaerobic, lab-scale (2 dm^3)	Corrugated plastic rings	Specific surface area-500 m^2·m^{-3}	37	1.8	1.92	65% COD removal
Jyväskylä (Finland), mature leachate, (JOKELA ET AL., 2002)	6.5-7.0	230-510	-	60-170	Upflow BF, leachate semi-continuously fed	Aerobic, lab-scale (9.4 dm^3)	Ceramic fragments	Particles size-16-32 mm	25	3.8	-	60-90 and 26-62% for N-NH$_4^+$and COD removal, respectively
United Kingdom, mature leachate, (STEPHENSON ET AL., 2004)	7.8	787	0.1	581	BF, leachate continuously recirculated	Aerobic, pilot-scale (770 dm^3)	Crystal quartz sand	Diameter-1.5-2.2 mm	15-19	-	0.1	99, 36, 93 and 73% for N-NH$_4^+$, COD, BOD$_5$ and SS removal, respectively
Granada (Spain), mature leachate, (GÁLVEZ ET AL., 2006)	7.8	787	0.1	581	BF, continuously recirculated	Aerated, leachate lab-scale (5.7 dm^3)	Ceramic fragments	Diameter-6-8 mm	-	0.7	25.1	67, 87 and 27% for COD, BOD$_5$ and VSS removal, respectively
	7.8	787	0.1	581	BF, continuously recirculated	Non-aerated, leachate lab-scale (5.7 dm^3)	Ceramic fragments	Diameter-6-8 mm	-	0.7	25.1	18, 16 and 38% for COD, BOD$_5$ and VSS removal, respectively

As it can be seen in Table 2.8, GÁLVEZ ET AL. (2006) observed that the aerated biofilter was more effective than the non-aerated reactor in the removal of COD and BOD_5. Anaerobic biological treatment is generally more susceptible to poisoning by toxic substances, especially heavy metals, phenols, ammonium and chlorinated organic compounds. Aerobic microorganisms have the capacity to acclimatize to the presence of certain toxic organic substances, which can oxidize in some cases, and even to the presence of heavy metal ions, although in the latter case the toxic substances are not biologically oxidized, but rather absorbed by the biological flocks. DI IACONI ET AL. (2006) used a biofilter with aerobic granular biomass working in the fill and draw mode - a sequencing batch biofilter granular reactor- for the treatment of a mature landfill leachate. This system revealed to be an effective technology, removing about 80% at least up to 1.1 g COD$\cdot L^{-1}\cdot d^{-1}$.

The hybrid bed filter (HBF) is another relevant modification of biofilters. It consists of an upflow sludge blanket at the bottom and an anaerobic filter on top, combining the advantages of UASB and BF reactors, while minimizing their limitations. The filter zone in the HBF reactor, in addition to its physical role for biomass retention, has some biological activity contributing to COD reduction in a zone, which, in a classical UASB reactor, biomass is scarce (TILCHE & VIEIRA, 1991). NEDWELL & REYNOLDS (1996) reported steady-state COD removal efficiencies of 81-97% up to 3.75 g COD$\cdot L^{-1}\cdot d^{-1}$, under methanogenic digestion of a landfill leachate at 30 ºC. KETTUNEN & RINTALA (1996) observed lower COD reductions (52-60%) with a young leachate load of 1.0-1.2 g COD$\cdot L^{-1}\cdot d^{-1}$ but at an unusual temperature digestion, 11 ºC.

2.3.1.2.2 Moving-bed reactors

2.3.1.2.2.1 Rotating biological contactors

The treatment of landfill leachate has also been carried out in rotating biological contactors (RBCs) (EGLI ET AL., 2003; CEMA ET AL., 2007; KULIKOWSKA ET AL., 2010). For instance, until 1985, Japan had 1323 plants with RBC arrangements, of which 10% were utilized for bioremediation of leachates generated in municipal landfills (CASTILLO ET AL., 2007). In a RBC unit, the pollutants contained in the leachate are removed by the biofilm that is established on the entire surface area of the support material (typically flat or corrugated disks), which continually rotates (CORTEZ ET AL., 2008). RBCs have been applied for removal of ammonium and organic substances from landfill leachate with high performance (Table 2.9).

If the support material is completely submerged in the leachate to be treated and the reactor tightly closed to avoid air entrance, they can also be used for leachate denitrification (SPENGEL & DZOMBAK, 1991).

2.3.1.2.2.2 Suspended carrier biofilm reactors

The suspended carrier biofilm (SCBR) is a completely mixed reactor where the biomass is grown on small carrier elements that have a density close to the water density and are kept in movement along with a water stream inside a reactor (LOUKIDOU & ZOUBOULIS, 2001; CHEN ET AL., 2008). The fluidization inside a reactor can be caused by aeration in an aerobic reactor and by a mechanical stirrer in an anaerobic or anoxic reactor. The treatability of landfill leachate by this process is given in Table 2.10.

2.3.2 PHYSICO-CHEMICAL SYSTEMS

The advantages of physico-chemical systems in general include immediate start-up, easy automation, insensivity to temperature changes and, in most cases, simplicity of the materials and of the plant required. Commonly, however, these advantages are outweighed by the drawbacks: the operation costs and the secondary pollution (such as the large quantities of waste sludge generated by the addition of flocculants). As a result, physico-chemical methods are mainly suitable for the pre- or post-treatment of landfill leachate to complement biological degradation techniques (LEMA ET AL., 1988). In this role, they are especially useful in the treatment of mature leachate (containing recalcitrant substances) and for the elimination of specific pollutants such as ammonium, heavy metals, suspended solids, colloidal particles and color. Conventional physico-chemical systems include coagulation-flocculation, chemical precipitation, air stripping, adsorption and flotation. Pressure-driven membrane technologies and advanced oxidation processes have emerged as the most promising options for leachate treatment (KURNIAWAN ET AL., 2006A; MARIAM & NGHIEM, 2010).

2.3.2.1 Conventional physico-chemical technologies

2.3.2.1.1 Coagulation-flocculation

Table 2.9 Landfill leachate treatment using RBCs. (SOL:superficial organic load)

Landfill site, age, reference	Leachate feeding characteristics				Reactor characteristics		Support material properties		Operational parameters			Performance
	pH	COD ($mg\cdot L^{-1}$)	BOD_5/COD	$N\text{-}NH_4^+$ ($mg\cdot L^{-1}$)	Type of operation and scale	No. stages, rotational speed (rpm)	Type of material, media and quantity/stage	Media dimensions	T (ºC)	HRT (d)	SOL (g $COD\cdot m^{-2}\cdot d^{-1}$)	
Moyer (Philadelphia, USA), mature leachate, (Spengel & Dzombak, 1991)	7.5-8	358	-	154	Aerobic, lab-scale (3.42 dm^3)	3; 2.3	Flat plastic disks, 2 disks/stage	Diameter-23.8 cm; area of disks/stage-0.187 m^2	22	1.05	6.1 g $COD\cdot m^{-2}\cdot d^{-1}$	≈97, 36 and 81% for $N\text{-}NH_4^+$, COD and BOD_5 removal, respectively; 140 mg $N\text{-}NO_3^-\cdot L^{-1}$ in the effluent
Bucaramanga (Colombia), young leachate, (Castillo et al., 2007)	7.8-8.8	2500-9000	-	-	Aerobic, pilot-scale (20 dm^3)	4; 6	Perforated acetate disks, 10 disks/stage	Diameter-30 cm	-	1	24.7 g $COD\cdot m^{-2}\cdot d^{-1}$	52% COD removal
Bartoszyce (Poland), mature leachate, (Kulikowska et al., 2010)	-	-	-	243	Aerobic, pilot-scale	2; 7	-	Area of disks/stage-0.67 m^2	20	1	-	≈100% $N\text{-}NH_4^+$ removal; 222 mg $N\text{-}NO_3^-\cdot L^{-1}$ in the effluent

Table 2.10 Landfill leachate treatment using suspended carrier biofilm reactors.

Landfill site, age, reference	Leachate feeding characteristics				Reactor characteristics		Support material properties		Operational parameters			Performance
	pH	COD ($mg\cdot L^{-1}$)	BOD_5/COD	$N\text{-}NH_4^+$ ($mg\cdot L^{-1}$)	Type of operation and scale	Mode of operation	Type of material, media and quantity	Media dimensions	T (ºC)	HRT (d)	OLR (g $COD\cdot L^{-1}\cdot d^{-1}$)	
Hyllstofta (Sweden), mature leachate, (Welander et al., 1997)	7.5	800-1300	-	460-600	Aerobic, lab-scale (0.6 dm^3)	Continuous mode	Plastic cylinders, 60% of reactor volume	Diameter-9.1 mm; length-7.2 mm; specific surface area-500 $m^2\cdot m^{-3}$	20	5	-	99% $N\text{-}NH_4^+$ removal
Japan, mature leachate, (Isaka et al., 2007)	7.5-8.0	-	-	150	Aerobic, lab-scale (1.2 dm^3)	Continuous mode, air-lift	Plastic gel cubes, 15% of reactor volume	Size-3 mm	10	0.2	-	83% $N\text{-}NH_4^+$ removal; 90 mg $N\text{-}NO_2^-\cdot L^{-1}$, 15 mg $N\text{-}NO_3^-\cdot L^{-1}$ in the effluent
Harbin (China), young leachate, (Chen et al., 2008)	7.5	15993	-	350-400	Anaerobic, lab-scale (4.2 dm^3)	Continuous mode	Plastic cylinders, 40% of reactor volume	Diameter-7 mm; length-9 mm; specific surface area-900 $m^2\cdot m^{-3}$	35	1.5	10.66	12 and 91% for $N\text{-}NH_4^+$ and COD removal
Greece, mature l, (Loukidou & Zouboulis, 2001)	7.5	5000	0.2	1800	Aerobic/anoxic, lab-scale (8 dm^3)	Sequencing batch mode	Plastic cubes, 50% of reactor volume	Size-1 cm	-	20	-	95, 65 and 90% for $N\text{-}NH_4^+$, COD and BOD_5 removal

Table 2.11 Landfill leachate treatment by coagulation-flocculation.

Landfill site, age, reference	Leachate feeding characteristics				Coagulation-flocculation operation					Performance
	pH	COD ($mg \cdot L^{-1}$)	BOD_5/ COD	$N\text{-}NH_4^+$ ($mg \cdot L^{-1}$)	Scale	Reaction mode	pH	Coagulant type and dose	Flocculant type and dose	
Gaziantep (Turkey), young leachate, (Cecen & Gursoy, 2000)	8	2431	0.21	1379	Lab-scale (1 L)	Rapid mixing-20 min, 100 rpm, flocculant addition; slow mixing-40 min, 40 rpm; settle-60 min	8	4000 mg $Al_2(SO_4)_3 \cdot L^{-1}$	8 mg anionic polyelectrolyte- SF-380 $\cdot L^{-1}$	≈40, 12, 40, 55 and 3% for COD, Cu, Fe, Mn and Ni removal, respectively
	8	2431	0.21	1379	Lab-scale (1 L)	Rapid mixing-20 min, 100 rpm, flocculant addition; slow mixing-40 min, 40 rpm; settle-60 min	8	4000 mg $Al_2(SO_4)_3 \cdot L^{-1}$ + 16000 mg $Ca(OH)_2 \cdot L^{-1}$	8 mg anionic polyelectrolyte- SF-380 $\cdot L^{-1}$	≈40, 85, 47, 95 and 7% for COD, Cu, Fe, Mn and Ni removal, respectively
Chongqing (China), mature leachate, (Guo et al., 2010)	7.9	3000-4500	0.09-0.22	1000-1750	Lab-scale (1 L)	Rapid mixing-2 min, 250 rpm, flocculant addition; slow mixing-15 min, 80 rpm; settle-60 min	4, 5, 6	600 mg $Fe_2(SO_4)_3 \cdot L^{-1}$	1mL polyacrylamide (0.1% v/v) per liter of leachate	28, 32 and 24% COD removal for pH=4, 5 and 6, respectively
	7.9	3000-4500	0.09-0.22	1000-1750	Lab-scale (1 L)	Rapid mixing-2 min, 250 rpm, flocculant addition; slow mixing-15 min, 80 rpm; settle-60 min	5	600, 800, 1000 mg $Fe_2(SO_4)_3 \cdot L^{-1}$	1mL polyacrylamide (0.1% v/v) per liter of leachate	32, 36 and 30% COD removal for 600, 800 and 1000 mg $Fe_2(SO_4)_3 \cdot L^{-1}$, respectively
Mexico city (Mexico), mature leachate, (Monje-Ramirez & Velásquez, 2004)	8-8.5	4580	<0.01	-	Lab-scale (1 L)	Rapid mixing-30 sec, 100 rpm; slow mixing-30 min, <50 rpm; settle-30 min	6	3000 mg $Fe_2(SO_4)_3 \cdot L^{-1}$	-	65 and 97% for COD and color removal, respectively
	8-8.5	4580	<0.01	-	Lab-scale (1 L)	Rapid mixing-30 sec, 100 rpm; slow mixing-10 min, <50 rpm; settle-30 min	6	3000 mg $Fe_2(SO_4)_3 \cdot L^{-1}$	-	58.2 and 97.1% for COD and color removal, respectively
Asturias (Spain), young leachate, (Castrillón et al., 2010)	8.3	18352	0.6	2445	Lab-scale (1 L)	Rapid mixing-3 min, 180 rpm; slow mixing-17 min, 40 rpm; settle-30 min	3.8	1200 mg $FeCl_3 \cdot L^{-1}$	-	28, 78 and 90% for COD, color and turbidity removal, respectively
	8.3	18352	0.6	2445	Lab-scale (1 L)	Rapid mixing-3 min, 180 rpm; slow mixing-17 min, 40 rpm; settle-30 min	6	5000 mg $Al_2(SO_4)_3 \cdot L^{-1}$	-	27, 84 and 93% for COD, color and turbidity removal, respectively
	8.3	18352	0.6	2445	Lab-scale (1 L)	Rapid mixing-3 min, 180 rpm; slow mixing-17 min, 40 rpm; settle-30 min	6.5	4000 mg aluminum polychloride $\cdot L^{-1}$	-	35, 91 and 90% for COD, color and turbidity removal, respectively
Asturias (Spain), mature leachate, (Castrillón et al., 2010)	8.3	4814	0.14	2950	Lab-scale (1 L)	Rapid mixing-3 min, 180 rpm; slow mixing-17 min, 40 rpm; settle-30 min	5.2	1700 mg $FeCl_3 \cdot L^{-1}$	-	73, 98 and 100% for COD, color and turbidity removal, respectively
	8.3	4814	0.14	2950	Lab-scale (1 L)	Rapid mixing-3 min, 180 rpm; slow mixing-17 min, 40 rpm; settle-30 min	6	3200 mg $Al_2(SO_4)_3 \cdot L^{-1}$	-	60, 95 and 92% for COD, color and turbidity removal, respectively
	8.3	4814	0.14	2950	Lab-scale (1 L)	Rapid mixing-3 min, 180 rpm; slow mixing-17 min, 40 rpm; settle-30 min	7	6000 mg aluminum polychloride $\cdot L^{-1}$	-	62, 97 and 98% for COD, color and turbidity removal, respectively

Coagulation-flocculation is a relative simple technique that has been employed for the removal of suspended solids (SS), colloidal particles, color, non-biodegradable organic matter and heavy metals from landfill leachate (KURNIAWAN ET AL., 2006; MARAÑÓN ET AL., 2008). The coagulation process destabilizes colloidal particles by the addition of a coagulant. To increase the particle size, coagulation is usually followed by aggregation of the unstable particles into bulky flocks thereby promoting easier settling. The type and concentration of coagulant, pH, velocity gradient, rapid and slow mixing, settling time and flocculant addition play major roles in increasing the probability of the settling of colloidal particles (TATSI ET AL., 2003; KURNIAWAN ET AL., 2006). Iron and aluminum salts have been widely used as coagulants as shown in Table 2.11.

Occasionally, it is observed that the addition of flocculants does not improve COD, color and turbidity removal. However, settling conditions are substantially improved by the formation of flocks that settle better and more quickly (MARAÑÓN ET AL., 2008).

Some drawbacks of the coagulation-flocculation system include high operational cost due to high chemical consumption, the generation of sludge, the sensitivity of the process to pH and in certain cases, the increase on the concentration of aluminum and iron in the resulting effluent (MARAÑÓN ET AL., 2008). This is why it has been proposed mainly as a pre-treatment method for young leachate, prior to a biological or membrane step, reducing leachate turbidity and counteracting the problem of membrane fouling (CASTRILLÓN ET AL., 2010). It is also often used as a post-treatment technique for mature leachate, in order to reduce non-biodegradable organic matter (TATSI ET AL., 2003).

Recently, MARIAM & NGHIEM (2010) compared conventional chemical coagulation with electro-coagulation, using aluminum electrodes, for the treatment of landfill leachate. At the optimum reaction time, TOC and turbidity removals by the electro-coagulation process were 67% and 80%, respectively, while at the optimum dosage of $Al_2(SO_4)_3$, TOC and turbidity removals by the chemical coagulation process were only 10% and 65%, respectively.

2.3.2.1.2 Chemical precipitation

During chemical precipitation, dissolved ions in the solution are transferred to the insoluble solid phase via chemical reactions. Struvite (magnesium ammonium phosphate (MAP)) or lime are usually employed as the precipitant, depending on the target of the removal: $N\text{-}NH_4^+$ or heavy metals (KURNIAWAN ET AL., 2006).

LI & ZHAO (2001) investigated the removal of ammonium ions from landfill leachate by applying struvite precipitation and observed that the $N\text{-}NH_4^+$ content could be reduced from 5618 $mg \cdot L^{-1}$

to 112 $mg \cdot L^{-1}$ in 15 min with a $Mg^{2+}:NH_4^+:PO_4^{3-}$ molar ratio of 1:1:1 and a pH between 8.5 and 9. Thereafter, a number of reports on the application of struvite precipitation as a leachate pre- or post-treatment have been published, exploring influence of factors such as pH, molar ratio of $Mg^{2+}:NH_4^+:PO_4^{3-}$ or the initial concentration of the reagents (Table 2.12).

Table 2.12 Landfill leachate treatment by chemical precipitation.

Landfill site, age, reference	Leachate feeding characteristics				Chemical precipitation operation				Performance
	pH	COD ($mg \cdot L^{-1}$)	BOD_5 /COD	$N\text{-}NH_4^+$ ($mg \cdot L^{-1}$)	Scale	Reaction mode	pH	Precipitant type and molar ratio	
Gaziantep (Turkey), young leachate, (Cecen & Gursoy, 2000)	8	37024	0.4	2430	Lab-scale (1 L)	Rapid mixing-20 min, 100 rpm; slow mixing-40 min, 40 rpm; settle-60 min	9.5-10	$Ca(OH)_2$	59, 67, 76 and 29% for Cu, Fe, Mn and Ni removal, respectively
Komurcuoda (Turkey), young leachate, biologically pre-treated, (Calli et al., 2005)	6.2-8.4	20700	0.6	2330	Lab-scale (0.5 L)	Rapid mixing of magnesium and phosphate-1 min; pH adjustment; settle-30 min	7.5	$Mg^{2+}:NH_4^+:PO_4^{3-}$ = 1:1:1	98 and 20% for $N\text{-}NH_4^+$ and COD removal, respectively
Nanjing (China), mature leachate, (Zhang et al., 2009)	8.1	7200	0.2	1960	Lab-scale	Rapid mixing of magnesium and phosphate-30 min; pH adjustment; settle-30 min	8.5, 9.5, 10.5	$Mg^{2+}:NH_4^+:PO_4^{3-}$ = 1:1:1	45, 79 and 75% $N\text{-}NH_4^+$ removal for pH 8.5, 9.5 and 10.5, respectively
	8.1	7200	0.2	1960	Lab-scale	Rapid mixing of magnesium and phosphate-30 min; pH adjustment; settle-30 min	9.5	$Mg^{2+}:NH_4^+:PO_4^{3-}$ = 1:1:0.9; $Mg^{2+}:NH_4^+:PO_4^{3-}$ = 1:1:1.1	69 and 83% $N\text{-}NH_4^+$ removal for $Mg^{2+}:NH_4^+:PO_4^{3-}$ =1:1:0.9; and $Mg^{2+}:NH_4^+:PO_4^{3-}$ = 1:1:1.1, respectively
Apulia (Italy), mature leachate, (Di Iaconi et al., 2010)	8.5	9700	0.15	2600	Lab-scale (1 L)	Rapid mixing of magnesium and phosphate; pH adjustment; slow mixing-30 min; settle-60 min	9	$Mg^{2+}:NH_4^+:PO_4^{3-}$ = 1:1:1; $Mg^{2+}:NH_4^+:PO_4^{3-}$ = 1.5:1:1; $Mg^{2+}:NH_4^+:PO_4^{3-}$ = 2.5:1:1.1	67, 87 and 98% $N\text{-}NH_4^+$ removal for $Mg^{2+}:NH_4^+:PO_4^{3-}$ =1:1:1; $Mg^{2+}:NH_4^+:PO_4^{3-}$ =1.5:1:1 and $Mg^{2+}:NH_4^+:PO_4^{3-}$ =2.5:1:1.1

Drawbacks of struvite precipitation include the sensitivity of the process employed to pH, the low effectiveness for COD removal and the high dose of precipitant required associated to a high operative cost. In fact, leachates are characterized by low concentrations of magnesium and phosphorus and external sources of these compounds are demanded. Nevertheless, in the case of mature leachates, known by high ammonium concentrations and very low BOD_5/COD ratios, the process could potentially compete even with the cheapest existing method (i.e. biological removal) since in the latter an amount of carbon from an expensive external source is required (DI IACONI ET AL., 2010). Another concern associated to struvite precipitation is the generation of sludge and the need for further disposal. However, if the leachate does not contain any heavy metals, struvite can be used as a valuable fertilizer since it is a slow release source of nitrogen, magnesium and phosphorus (LI ET AL., 1999).

2.3.2.1.3 Air stripping

Air stripping has been widely used for removing high concentrations of $N\text{-}NH_4^+$ from landfill leachate. In this process, $N\text{-}NH_4^+$ is transferred from the leachate into the air and is then absorbed from the air into a strong acid such as HCl or H_2SO_4. The air stripping rate is expected to be somewhat lower with low strength leachate than with concentrated leachate (MARTTINEN ET AL., 2002). The process is further dependent of pH and temperature. Raising the pH (above 7), $N\text{-}NH_4^+$ turns into nitrogen-ammonia ($N\text{-}NH_3$). Since $N\text{-}NH_3$ is more easily removed by air stripping, high pH values must be employed (HASAR ET AL., 2009; GUO ET AL., 2010). Additionally, as the solubility of nitrogen-ammonia increases at low ambient temperatures, high temperatures favor the air stripping efficiency (HASAR ET AL., 2009).

A synthesis of recent works on treatment of landfill leachate using air stripping is presented in Table 2.13.

Some of the drawbacks associated to air stripping are foaming, which imposes the use of bigger stripping reactors and the generation of carbonate precipitate that may cause severe operation and maintenance problems (LI ET AL., 1999). Moreover, the high operational pH needs further neutralization, which increases leachate salinity and operational costs (CANZIANI ET AL., 2006).

Table 2.13 Landfill leachate treatment by air stripping.

Landfill site, age, reference	Leachate feeding characteristics				Air stripping operation						Performance
	pH	COD (mg·L^{-1})	BOD$_5$/COD	N-NH$_4^+$ (mg·L^{-1})	Scale	Air source	T (ºC)	Chemical for pH adjustment, dose	pH	Time (h)	
Komurcuoda (Turkey), young leachate, (Calli et al., 2005)	6.2-8.4	20700	0.6	2330	Lab-scale	Air flow	15; 20	Ca(OH)$_2$, 13 g·L^{-1}	11	12	87 and 15; 94 and 15% for N-NH$_4^+$ and COD removal, respectively, at 15 and 20 ºC
Dyarbakir (Turkey), young leachate, (Hasar et al., 2009)	6.5-7.5	8500-19200	0.4-0.7	1100-2150	Lab-scale	Air flow rate- 0 L·h^{-1}, stirring- 400 rpm	rt	-	9, 10, 11, 12	6	15, 26, 28 and 30% N-NH$_4^+$ removal for pH 9, 10, 11 and 12, respectively
	6.5-7.5	8500-19200	0.4-0.7	1100-2150	Lab-scale	Air flow rate- 2 L·h^{-1}, stirring- 400 rpm	rt	-	9, 10, 11, 12	6	48, 76, 91 and 93% N-NH$_4^+$ removal for pH 9, 10, 11 and 12, respectively
Asturias (Spain), young leachate, (Castrillón et al., 2010)	8.3	7624	-	1750	Lab-scale	Stirring	rt	Ca(OH)$_2$, 18.6 g·L^{-1}	13	24	86 and 23% for N-NH$_4^+$ and COD removal, respectively
Asturias (Spain), young leachate, biologically pre-treated, (Castrillón et al., 2010)	6.9	3484		2156			rt	Ca(OH)$_2$, 10 g·L^{-1}	12		94 and 46% for N-NH$_4^+$ and COD removal, respectively
Chongquing (China), mature leachate, (Guo et al., 2010)	7.9-8.5	3000-4500	0.09-0.22	1000-1750	Lab-scale (10 L)	Air flow rate- 900 L·h^{-1}	rt	-	11	18	97% N-NH$_4^+$ removal

2.3.2.1.4 Adsorption

Adsorption is a mass transfer process by which a substance is transferred from the gas or liquid phase of a mixture to the surface of a solid adsorbent to which becomes bound via physical and/or chemical interactions (Kurniawan et al., 2006; Foo & Hameed, 2009). Due to its inherent physical properties, large surface area, microporous structure, high adsorption capacity and surface reactivity, adsorption using granular activated carbon (GAC) in columns or powdered activated carbon (PAC) is a well-recognized means of leachate treatment (KURNIAWAN ET AL., 2006; FOO & HAMEED, 2009; HALIM ET AL., 2010). In general, the application of activated carbon adsorption (GAC or PAC) is effective for the removal of color, heavy metals, biodegradable and non-biodegradable organic compounds from landfill leachate (WISZNIOWSKI , ROBERT ET AL., 2006; CASTRILLÓN ET AL., 2010). It is easy to operate and has low energy demand, however the frequent need to regenerate the column or the equivalent replacement of powdered activated carbon makes this option expensive (LEMA ET AL., 1988; KURNIAWAN & LO, 2009). Furthermore, activated carbon generally does not have sufficient adsorption capacity for the removal of N-NH_4^+ (HALIM ET AL., 2010). So, over the last few years, this method has been used mainly for polishing the mature leachate, for treatment of leachate from biological units or alongside with biological treatment as was previously mentioned. Accordingly, other materials, such as zeolite, coconut shell charcoal or municipal waste incinerator bottom ash have been chemically modified and tested as low-cost absorbents for landfill leachate treatment.

Table 2.14 presents some lab-scale experiments reporting landfill leachate treatment via adsorption.

KURNIAWAN & LO (2009) investigated the combination of granular activated carbon adsorption with H_2O_2 in a low biodegradable leachate. This system achieved substantially higher removal (82% COD, N-NH_4^+ 59%) than the GAC adsorption (58% COD) or H_2O_2 oxidation (33% COD, N-NH_4^+ 4.9%) systems at optimized experimental conditions. The addition of a Fe^{2+} dose at 1.8 mg$\cdot L^{-1}$ further improved the removal of refractory compounds by the integrated treatment from 82 to 89%.

2.3.2.1.5 Flotation and dissolved air flotation

Flotation in wastewater treatment and especially dissolved air flotation (DAF), offer advantages over precipitation, adsorption and membrane filtration processes. Advantages include better effluent quality, rapid start-up, high rate operation, and a thicker sludge (RUBIO ET AL., 2007). However, very few studies have so far been devoted to the application of flotation for landfill leachate treatment.

ZOUBOULIS ET AL. (2003) employed flotation in a column, as a post-treatment stage for removing residual humic acids (recalcitrant compounds) from simulated landfill leachates.

Table 2.14 Landfill leachate treatment by adsorption.

Landfill site, age, reference	Leachate feeding characteristics				Adsorption operation					Performance
	pH	COD ($mg{\cdot}L^{-1}$)	BOD_5/COD	$N\text{-}NH_4^+$ ($mg{\cdot}L^{-1}$)	Scale	Operation mode	Adsorbent type and dose	Adsorbent characteristics	Time (h)	
Chania (Greece), mature leachate previously coagulated, (Papastavrou et al., 2009)	4.6	500	-	-	Lab-scale	Continuous stirring-100 rpm	Coconut shell: -GAC, 1.25 g YAO M200 W20 $\cdot L^{-1}$; -PAC, 1.25 g YAO 30x60 $\cdot L^{-1}$	GAC: size-0.6 mm, BET surface area-1250 $m^2{\cdot}g^{-1}$; PAC: size-0.15 mm, BET surface area-1250 $m^2{\cdot}g^{-1}$	2	25 and 35% COD removal for GAC and PAC, respectively
Hong Kong (China), mature leachate, (Kurniawan & Lo, 2009)	8.0	8000	0.08	2595	Lab-scale (0.25 L)	Continuous stirring-200 rpm	Coconut shell: GAC, 15 $g{\cdot}L^{-1}$	Particle diameter-0.5 mm; BET surface area-900-1100 $m^2{\cdot}g^{-1}$	1	58% COD removal
Slovenia, mixed leachate, (Cotman & Gotvajn, 2010)	8.2	1396	0.01	388	Lab-scale	Column, 0.12 $L{\cdot}h^{-1}$	Zeolite: Clinoptiolite	-	1.67	100, 32, 48 and 50% for $N\text{-}NH_4^+$, COD, Fe and Mn removal
Asturias (Spain), young leachate, biologically pre-treated, (Castrillón et al., 2010)	6.9	3484	-	2156	Lab-scale	Continuous stirring	Coal: -GAC, 10 g Organosorb 10 MB $\cdot L^{-1}$; -GAC, 10g Filtracarb CC65/1240 $\cdot L^{-1}$	-GAC: size-0.4-1.7 mm, BET surface area-1020 $m^2{\cdot}g^{-1}$; -GAC: size-0.4-1.7 mm, BET surface area-1050 $m^2{\cdot}g^{-1}$	5	48 and 31; 43 and 27% for COD and color removal, for GAC Organosorb and GAC Filtracarb, respectively
	6.9	3484	-	2156	Lab-scale	Continuous stirring	Coal: -GAC, 20 g Organosorb 10 MB $\cdot L^{-1}$	-GAC: size-0.4-1.7 mm, BET surface area-1020 $m^2{\cdot}g^{-1}$	5	63 and 45% for COD and color removal, respectively

Under optimized conditions, the treatment performance was very efficient reaching almost 99%, indicating that flotation can serve as a possible alternative technology for the removal of humic acids. Recently, PALANIANDY ET AL. (2010) investigated the feasibility of treating a mature landfill leachate with DAF and proved that the coagulation process enhanced the removal of color, COD and turbidity. In fact, in the case of DAF without coagulation, low percent removals of 36%, 33%, and 32% were observed for color, COD, and turbidity, respectively. In turn, with coagulation followed by DAF, the removals were 70%, 79% and 42% for color, COD, and turbidity, respectively.

2.3.2.2 Pressure-driven membrane technologies

Pressure-driven membrane technologies (microfiltration, ultrafiltration, nanofiltration, reverse osmosis) can be used to remove a wide range of components, ranging from suspended solids (microfiltration) to small organic compounds and ions (reverse osmosis). In these processes, a pressure exerted on the solution at one side of the membrane serves as a driving force to separate the solution into a permeate and a retentate. The permeate is the treated effluent, whereas the retentate is a concentrated solution that must be disposed of or treated by other methods (BRUGGEN ET AL., 2003).

Microfiltration, ultrafiltration, nanofiltration and reverse osmosis have been found to be highly effective in the treatment of landfill leachate (LINDE ET AL., 1995; AHN ET AL., 2002; USHIKOSHI ET AL., 2002). The selection of the appropriate membrane for leachate treatment depends on a number of factors such as the nature and concentration of materials present in the leachate and pH.

2.3.2.2.1 Microfiltration and Ultrafiltration

Microfiltration (MF) and ultrafiltration (UF) membranes have a porous structure that retains components by a sieving mechanism. In microfiltration, the pore size of the membrane is provided by the manufacturers and serves as a reference for the size of the retained particles. For ultrafiltration, the concept of molecular weight cut-off of the membrane is often used. Rejection increases with the reduction of membrane cut-off (BRUGGEN ET AL., 2003).

MF and UF membranes are mainly used as pre-treatment stage for another membrane process (nanofiltration or reverse osmosis) or in combination with chemical processes. The former are appropriate to remove suspended solids, colloids and bacteria while the latter are effective in eliminating large dissolved molecules. Landfill leachate purification by MF and UF membranes is shown in Table 2.15.

Recently, several hybrid systems including MF and UF membranes have been studied. For instance, INCE ET AL. (2010) applied a microfiltration-powdered activated carbon unit to a biologically treated landfill leachate and when 8 g PAC·L^{-1} was used a COD removal above 50% was achieved. This result was better than the achieved with a nanofiltration membrane. Likewise, PIRBAZARI ET AL. (1996) used an ultrafiltration-powdered activated carbon system and observed TOC removals of 95-97% for a previously coagulated leachate.

UF membranes have further been successfully employed in membrane bioreactors as detailed in Table 2.7.

2.3.2.2.2 Nanofiltration

Nanofiltration (NF) membranes have smaller pores than MF and UF membranes, which make them suitable for the removal of color, biodegradable and non-biodegradable organic micropollutants with a molecular weight above 200 Da. Furthermore, NF membranes also have a surface charge allowing the retention of ionic species and even the retention of ions with a size below the pore size of the membrane.

Due to its unique properties, NF is able to remove recalcitrant organic compounds and heavy metals, being considered one of the best techniques for landfill leachate treatment (BRUGGEN ET AL., 2003). Nanofiltration membranes, compared to reverse osmosis membranes, have many advantages such as, lower operational pressure, high flux, high rejection of polyvalent ions, relatively low investment, operational and maintenance costs (INCE ET AL., 2010). All these advantages increased the use of nanofiltration technologies in the last years (Table 2.16).

2.3.2.2.3 Reverse Osmosis

In reverse osmosis (RO), permeation is slower and rejection is not a result of sieving but of a solution-diffusion mechanism. The low permeability of reverse osmosis membranes requires high pressures and, consequently, relatively high-energy consumption (BRUGGEN ET AL., 2003).

RO membranes have been applied to remove the organic and non-organic fraction of young and mature landfill leachates with very good performances, both at lab (BOHDZIEWICZ ET AL., 2001; LI, WICHMANN, ET AL., 2009) and full scales (LINDE ET AL., 1995; AHN ET AL., 2002; USHIKOSHI ET AL., 2002) (Table 2.16).

Among the reverse osmosis membrane modules applied for leachate treatment, the commonly used modules are the tubular membrane modules (LINDE ET AL., 1995) and the disk tube module (USHIKOSHI ET AL., 2002). Recently, a treatment system equipped with the newly developed open channel spiral wound modules for leachate purification was studied (LI, WICHMANN, ET AL., 2009).

In spite of being promising technologies in the treatment of leachate, pressure-driven membrane processes, particularly reverse osmosis, have obvious drawbacks, which remain unsolved: extensive application is inhibited due to the expensive facilities and European patents, membrane fouling frequently reduces membrane lifetime and decreases productivity, and the large quantity of unusable residual concentrate generated needs further treatment (LI, ZHOU, ET AL., 2009).

2.3.2.3 Chemical oxidation

Chemical oxidation is being considered for its potential in converting harmful organics into innocuous substances without the production of concentrated residues, which require further disposal, often as hazardous waste. Chemical oxidation of landfill leachate based on chlorine (Cl_2), potassium permanganate ($KMnO_4$) or calcium hydrochlorine ($Ca(ClO)_2$) resulted in COD removals between 20 and 50% (LEMA ET AL., 1988; WISZNIOWSKI, ROBERT ET AL., 2006).

Due to its ability to eliminate color, reduce the organic load and improve the biodegradability of recalcitrant contaminants, advanced oxidation processes (AOPs) have increasingly been studied and applied in the treatment of mature leachate (KURNIAWAN ET AL., 2006A). The main purpose of AOPs is to enhance chemical oxidation efficiency by increasing the production of highly free radicals, mainly the hydroxyl radical ($^{\bullet}OH$), a non-selective, very reactive oxidant. These radicals can be produced in reactions without irradiation involving the presence of strong oxidants such as O_3, H_2O_2 and/or a catalyst, or with irradiation employing the energy of ultraviolet's (UV), ultrasounds (US) or electron beams (EB) associated or not to strong oxidants and/or a catalyst. AOPs are affected by many factors such as the amount of constituents in the solution, concentration of oxidants, reaction time, pH, reaction by-products and temperature.

2.3.2.3.1 AOPs without irradiation

Among AOPs, the Fenton process, which is based on the electron transfer between hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}) in acidic medium, seems to be the best compromise because the process is technologically simple, there is no mass transfer limitation, and both hydrogen peroxide and iron are cheap and non-toxic (GUO ET AL., 2010).

Table 2.15 Landfill leachate treatment using MF or UF.

Landfill site, age, reference	Leachate feeding characteristics				Membrane filtration operation						Performance
	pH	COD (mg·L^{-1})	BOD$_5$/COD	N-NH$_4^+$ (mg·L^{-1})	Scale, kind of process	Type of membrane, model and module type	Pore size (μm), surface area (m^2), cut-off (kDa)	Velocity (m·s^{-1}), flux (L·m^{-2})	Operated pressure (bar)	T (ºC)	
Lubna (Poland), mature leachate, (Piatkiewicz et al., 2001)	7.3	2300	0.3	12.6	Pilot-scale, MF	Polymeric, Accurel PP, S6/2, tubular	0.2-0.6, 0.11, -	4.1-4.3, 35-40	-	20	26, 30 and 86% for COD, BOD$_5$ and TSS removal, respectively
Wuhan (China), mature leachate, (Pi et al., 2009)	6.3	20015	0.16	369	Pilot-scale, UF	Polymeric, YM3, tubular	-, -, 3	-	6	-	28 and 83% for N-NH$_4^+$ and COD removal, respectively
Lipówka (Poland), mature leachate, biologically pre-treated, (Bohdziewicz et al., 2001)	8.6	1660	-	-	Pilot-scale, UF	Polymeric, PSf-15, tubular	-, 0.025, 300	2.5, -	3	25	49 and 100% for COD and SS removal, respectively
France, mature leachate, (Renou et al., 2009)	8.6	1339	0.06	364	Pilot-scale, UF	Ceramic, KERASEP, tubular	-, -, 15 and 5	-	-	20	47 and 63% COD removal

Table 2.16 Landfill leachate treatment using NF and RO.

Landfill site, age, reference	Leachate feeding characteristics				Membrane filtration operation						Performance
	pH	COD (mg·L^{-1})	BOD$_5$/COD	N-NH$_4^+$ (mg·L^{-1})	Scale, kind of process	Type of membrane, model and module type	Surface area (cm^2), cut-off (Da)	Velocity (m·s^{-1}), flux (L·h^{-1})	Operated pressure (bar)	T (ºC)	
Istanbul (Turkey), mature leachate biologically pre-treated, (Ince et al., 2010)	9.3	2070	-	2180	Lab-scale, NF	Polymeric, FM NP030, -	80, 400	1.1, -	20	25	37 and 41% for N-NH$_4^+$ and COD removal, respectively
Wollongong (Australia), mature leachate, (Mariam & Nghiem, 2010)	7.3	635.8 (TOC)	-	918.3 (TN)	Lab-scale, NF	Polymeric, NF 270, -	21.2, 300	-, -	5	-	10 and 90% for TN and TOC removal, respectively
Gujarat (India), mature leachate, (Chaudhari & Murthy, 2010)	5	56521	0.33	196	Pilot-scale, NF	Polymeric, NF-300, flat sheet	150, 300	-, 900	20	-	52, 94, 67, 86, 84, 98, 95, and 93% N-NH$_4^+$, COD, BOD$_5$, TDS, color, Cr^{3+}, Ni^{2+} and Cu^{2+} removal, respectively
Hanover (Germany), -, (Li, Wichmann, et al., 2009)	6-6.5	3100	-	1000	Full-scale, RO	Polymeric, FT-30, open channel spiral wound	25.6 m^2, -	-, 8000	20-40	-	99; 100; 100; 99; 100 and 100% for N-NH$_4^+$, COD, TSS, Cl$^-$, Fe^{2+} and Cu^{2+} rem

Therefore, the Fenton process has been widely applied on the remediation of young and mature landfill leachate directly, as post- or pre-treatment (DENG & ENGLEHARDT, 2006). For instance, DI IACONI ET AL. (2006) reported that, when mature leachate was pre-treated by a biological process, the Fenton process achieved an additional COD removal of 85%, while KOCHANY & LIPCZYNSKA-KOCHANY (2009) applied the Fenton process as pre-treatment and observed 66% of SCOD removal and an increase in the leachate BOD_5/COD ratio from 0.63 to 0.88.

Regardless its high COD removal efficiency and environmental friendliness, Fenton treatment of wastewater results in the production of ferric hydroxide sludge, which requires an additional separation process and disposal. In order to deal with this problem, it has been suggested that the conventional Fenton process could be modified by the combined application of electricity, i.e. electro-Fenton (ZHANG ET AL., 2006; ATMACA, 2009; MOHAJERI ET AL., 2010). The electro-Fenton process, in which either or both of H_2O_2 and Fe^{2+}can be generated electrochemically *in situ*, is an indirect electrochemical oxidation that employs $^{\bullet}OH$ produced by the Fenton reaction to oxidize organic compounds (DENG & ENGLEHARDT, 2006). Since more $^{\bullet}OH$ radicals are produced, the oxidation of the organics is enhanced (MOHAJERI ET AL., 2010). In a 43 min electro-Fenton study, MOHAJERI ET AL. (2010) achieved 94% of COD and 96% of color removal of a mature leachate at pH 3 and H_2O_2/Fe^{2+} molar ratio 1, while current density was 49 $mA \cdot cm^{-2}$.

In spite of its advantages, conventional Fenton and Fenton-based processes require low pH and a modification of this parameter is necessary for further treatment or disposal, and deal with H_2O_2, which is very aggressive and can cause corrosion. Furthermore few ammonium is oxidized (DENG & ENGLEHARDT, 2006).

Molecular ozone is a strong oxidant having high reactivity and selectivity towards organic pollutants such as humic substances (CHATURAPRUEK ET AL., 2005). WANG ET AL. (2004) achieved removal efficiencies of 70, 90 and 67% for COD, color and ammonium, respectively, and an increase in the BOD_5/COD ratio from 0.04 to 0.22, applying ozone directly to a mature leachate, at the natural pH of the leachate (8.3) and consuming 12.5 g $O_3 \cdot L^{-1}$. Occasionally, as a single process, ozonation has not been very effective. Due to the complexity of the leachate, high doses are required and the reaction takes a long time (MONJE-RAMIREZ & VELÁSQUEZ, 2004). Therefore, in the last years, ozonation has increasingly been studied and used for leachate remediation as a pre-treatment or as a polishing step. The use of ozone at high pH (O_3/OH^-) or the combination with H_2O_2 (O_3/H_2O_2) have also become attractive options to oxidize the complex leachate mixtures since they favor the production of the hydroxyl radical, a oxidant even stronger than that of ozone (TIZAOUI ET AL., 2007). For instance, HAGMAN ET AL. (2008) reported that when the same ozone dose was applied, ozone alone ensured a COD removal of about 22%, while the combination of O_3 and H_2O_2 (1 $g \cdot L^{-1}$) increased COD removal up to 50%.

The main limitation of using ozone or ozone-based advanced processes lies in the high-energy consumption.

Electrochemical oxidation has been used for landfill leachate treatment over the past 10 years and, under appropriate conditions, has been proved to remove almost all ammonium, most COD and color. During the electro-oxidation of landfill leachate, reduction of pollutants appears to be primarily due to indirect oxidation, utilizing chlorine or hypochlorite, metals mediators such as Ag^{2+}, hydrogen peroxide or ozone, formed by anodic oxidation and originally existing or added in the leachate. Direct anodic oxidation may also occur to some extent, destroying pollutants adsorbed on the anode surface (DENG & ENGLEHARDT, 2007). In order to increase the efficiency of the method and optimize energy consumption, the influence of pre-treatment methods, pH, current density, leachate composition, electrolytes added and anode materials has been studied.

With mature leachate MORAES & BERTAZZOLI (2005) found removal efficiencies of 73, 86 and 49% for COD, color and nitrogen-ammonium, respectively, by employing a electrochemical reactor using TiO_2 anode and Ti cathode at 1160 $A \cdot m^{-2}$ with a flow rate of 2000 $L \cdot h^{-1}$ during 3 h while CABEZA ET AL. (2007) used boron doped diamond as anode and stainless steel as cathode at 900 $A \cdot m^{-2}$ with a flow rate of 660 $L \cdot h^{-1}$ and after 6 h got 100% both of COD and nitrogen-ammonium removal, respectively. These authors also reported that half of the initial ammonium nitrogen was oxidized to $N\text{-}NO_3^-$.

Wide application of electro-oxidation in landfill leachate treatment is limited by its high-energy consumption and potential production of chlorinated organics. Especially because of its expensive operating costs compared with other available technologies, electro-oxidation will be favored as a finishing step in a combined process or an auxiliary unit in emergency situations, instead of a full treatment for landfill leachate.

Wet air oxidation is defined as an oxidation technology carried out in the liquid phase under moderately elevated temperature and pressure. The oxidizing agent is oxygen usually added as pressurized air or pure oxygen. The presence of a catalyst or oxidation promoters has resulted in higher oxidation efficiencies.

Table 2.17 Landfill leachate treatment using AOPs without irradiation.

Landfill site, age, reference	Leachate feeding characteristics				AOP without irradiation operation					Performance
	pH	COD (mg·L^{-1})	BOD$_5$/ COD	N-NH$_4^+$ (mg·L^{-1})	Scale, kind of process	Oxidants concentration, reaction details	pH	Time (h)	T (ºC)	
Italy, mature leachate, (LÓPEZ ET AL., 2004)	8.2	10540	0.2	5210	Lab-scale, Fenton	H_2O_2=97 mmol·L^{-1}, Fe_2^+=4.924 mmol·L^{-1}, molar H_2O_2/Fe_2^+=19.7	3	2	rt	25% COD removal, BOD$_5$/COD=0.5
Jiangmen (China), mature leachate biologically pre-treated, (WANG ET AL., 2009)	5-8	600-700	0.01	<3	Lab-scale, Fenton	H_2O_2=7.2 mmol·L^{-1}, Fe_2^+=6 mmol·L^{-1}, molar H_2O_2/Fe_2^+=1.2	5	3	rt	47% COD removal
Madrid (Spain), young leachate, (HERMOSILLA ET AL., 2009)	8.3	6119	0.02	1965	Lab-scale, Fenton	H_2O_2=0.15 mol·L^{-1}, Fe_2^+=0.1 mol·L^{-1}, molar H_2O_2/Fe_2^+=1.5	2.5	1	25	80% COD removal
Wuhan (China), young leachate, (ZHANG ET AL., 2006)	6.4	5000	-	650	Lab-scale, electro-Fenton	H_2O_2=0.34 mol·L^{-1}, Fe_2^+=0.028 mol·L^{-1}, molar H_2O_2/Fe_2^+=12, Ti/RuO_2-IrO_2 anode and cathode plates, electrode distance=2.1 cm, I=3 A	3	1.25	rt	81% COD removal
Sivas (Turkey), young leachate, (ATMACA, 2009)	8.4	2350	-	310	Lab-scale, electro-Fenton	H_2O_2=58.8 mmol·L^{-1}, cast-iron anode and cathode plates, electrode distance=1.3 cm, I=3 A	3	0.33	rt	28, 72, 90 and 87% for N-NH$_4^+$, COD, color and P-PO$_4^{3-}$ removal, respectively
Estonia, young leachate, (GOI, VERESSININA, ET AL., 2009)	8.1	14000	0.44	-	Lab-scale, O_3	O_3 dose=33.6 g·L^{-1} leachate, O_3 consumed=14 g·L^{-1} leachate	8.1	4	20	29% COD removal BOD$_5$/COD=0.41
	8.1	14000	0.44	-	Lab-scale, O_3/OH^-	O_3 dose=33.6 g·L^{-1} leachate, O_3 consumed=18 g·L^{-1} leachate	11	4	20	41% COD removal, BOD$_5$/COD=0.5
Tunis (Tunisia), mature leachate, (TIZAOUI ET AL., 2007)	8.7	5230	0.01	-	Lab-scale, O_3	O_3 dose=4.3 g·L^{-1} leachate, O_3 consumed=3.5 g·g^{-1} COD	8.7	0.67	20	19% COD removal, BOD$_5$/COD=0.19
					Lab-scale, O_3/H_2O_2	H_2O_2=58.8 mmol·L^{-1}, O_3 dose=4.3 g·L^{-1} leachate, O_3 consumed=1.5 g·g^{-1} COD				48% COD removal, BOD$_5$/COD=0.64
Penang (Malaysia), mature leachate, (BASHIR ET AL., 2009)	8.9	1414	0.04	-	Lab-scale, electro-oxidation	Na_2SO_4=7 mmol·L^{-1}, graphite anode and cathode plates, electrode distance=1.5 cm, I=799 A·m^{-2}	8.9	4	rt	68, 70 and 84% for COD, BOD$_5$ and color removal, respectively
Italy, mature leachate, (GOI, DI GIORGIO, ET AL., 2009)	5-7	2000	-	-	Lab-scale, wet air oxidation	O_2 from pressurized air, P=35 bar, H_2O_2=0.88 mol·L^{-1}	5-7	2	227	55% COD removal

Few experimental data are available on wet air oxidation of leachate (GOI, DI GIORGIO, ET AL., 2009). RIVAS ET AL. (2005) applied wet air oxidation using HSO_5^- as promoter to a mature leachate and at pH 8.8, T=250 ºC, P=51 bar and after 2.5 h of reaction verified 60% of COD depletion. This result was better than the one achieved with the unpromoted wet air oxidation system or even using hydrogen peroxide as promoter.

Although wet air oxidation offers some advantages such as a small plant for operations and its ability to deal with varying flow rates and composition of the effluent, this process is not cost-effective for leachate treatment with a COD concentration of less than 5000 $mg \cdot L^{-1}$(KURNIAWAN ET AL., 2006A).

Table 2.17 lists the performance of some AOPs without irradiation in the treatment of landfill leachate.

2.3.2.3.2 AOPs with irradiation

Photochemical technology such as UV irradiation has been applied for leachate treatment, mainly in combination with other strong oxidants.

WU ET AL. (2004) observed that among O_3, UV/H_2O_2 and UV/O_3 processes, the latter was found to be the most effective in enhancing the biodegradability and eliminating the color of a mature leachate.

SHU ET AL. (2006) applied a thin gap annular UV/H_2O_2 photo reactor for the treatment of landfill leachate. At the maximum UV dosage and 0.233 mol $H_2O_2 \cdot L^{-1}$ the authors achieved 72 and 65% of color and COD removal efficiencies, respectively, in 300 min.

Concerning the UV/H_2O_2/O_3 process, QURESHI ET AL. (2002) reported that this combination slightly favored the biodegradability, the removal of organic compounds and color in comparison with the UV/O_3 and UV/H_2O_2 systems, as can be seen in Table 2.18.

The combination of UV irradiation with H_2O_2 and Fe^{2+} (UV/H_2O_2/Fe^{2+}), the so-called photo-Fenton process, is a promising AOP for the treatment of landfill leachate, as UV light may promote photo decarboxylation of ferric carboxylates and reduce ferric to ferrous iron yielding additional hydroxyl radicals by photolysis. Furthermore, the amount of catalytic iron required, and consequently the volume of sludge produced could be strongly reduced in comparison to the conventional Fenton. Due to the fact that this process can be driven by low energy photons, it can also be achieved using solar irradiation (PRIMO ET AL., 2008; HERMOSILLA ET AL., 2009).

In a recent study HERMOSILLA ET AL. (2009) found that the photo-Fenton treatment of landfill leachate yielded the same COD removal result than a conventional Fenton treatment, but consumed 32 times less iron and produced 25 times less sludge volume. An important drawback of the UV/H_2O_2/Fe^{2+} process is the need to operate under acidic conditions.

Photo electrochemical oxidation has been proven to be a better method for the treatment of complex matrixes, in comparison with individual electrolysis and photocatalysis methods. TAUCHERT ET AL. (2006) reported that, when applied to untreated mature leachate, the photo electrochemical system was significantly hindered on account of the characteristic dark coloration of the samples. In these conditions, the degradation process was essentially electrochemical permitting typical color and COD removal of about 50% and 20%, respectively. When a previous chemical precipitation process was applied aiming at the elimination of colored species (mainly humic substances), the discoloration and COD removal increased to 90% and 60%, respectively.

There has been little investigation into photochemical technologies using UV irradiation in spite of it being highly effective, and its application to leachate treatment is scarce due to its high operational costs. Therefore, the determination of optimum operational conditions is one of the primary concerns for the future development and potential application of these processes.

Ultrasonication is considered as a new possibility in wastewater treatment for several decades. Sonochemical decomposition of pollutants results from the rapid formation, growth, and violent collapse of cavitation bubbles or the reduction and oxidation due to the generation of $^{\bullet}H$ and $^{\bullet}OH$ radicals (NECZAJ ET AL., 2007). There are few reports about the sonochemical treatment of heavily polluted wastewater like landfill leachate. Recently, after 180 minutes of ultrasound irradiation in a mature leachate, with a power input of 150 W and at pH 11, WANG ET AL. (2008) obtained up to 96% of nitrogen-ammonium reduction. NECZAJ ET AL. (2007) used effectively ultrasonication on leachate degradation as pre-treatment of a biological process.

BAE ET AL. (1999) applied electron-beam irradiation to a biologically treated landfill leachate and found that this process was very efficient principally in removing humic substances.

Among the AOPs reviewed, ozone-based and Fenton oxidation processes are the most frequently studied and widely applied methods for the treatment of landfill leachate. A limitation of the AOPs is that they are affected by some chemicals, such as carbonates/hydrocarbonates, phosphate and chloride ions, or aliphatic alkyl compounds, since these compounds can interrupt the chain reaction of the generation of hydroxyl radicals (MONJE-RAMIREZ & VELÁSQUEZ, 2004).

Table 2.18 Landfill leachate treatment using AOPs with irradiation.

Landfill site, age, reference	Leachate feeding characteristics				AOP without irradiation operation					Performance
	pH	COD ($mg \cdot L^{-1}$)	BOD_5/ COD	$N\text{-}NH_4^+$ ($mg \cdot L^{-1}$)	Scale, kind of process	Oxidants concentration, reaction details	pH	Time (h)	T (ºC)	
Taegu (Korea), mature leachate, (QURESHI ET AL., 2002)	7.8	25950	0.11	1854	Lab-scale, UV/O_3	O_3 dose=70.3 $mg \cdot min^{-1}$, O_3 consumed=28.9 $mg \cdot min^{-1}$, 20 cm synthetic quartz tube UV lamp, I=0.69 $W \cdot cm^{-2}$, 1500 W	7.8	5	20	63 and 88% for TOC and color removal, respectively, $BOD_5/COD=0.35$
	7.8	25950	0.11	1854	Lab-scale, UV/H_2O_2	H_2O_2=0.2 * COD, 20 cm synthetic quartz tube UV lamp, I=0.69 $W \cdot cm^{-2}$, 1500 W	3	5	20	79 and 96% for TOC and color removal, respectively, $BOD_5/COD=0.37$
	7.8	25950	0.11	1854	Lab-scale, $UV/H_2O_2/O_3$	H_2O_2=0.2 * COD, O_3 dose=50.3 $mg \cdot min^{-1}$, O_3 consumed=28.1 $mg \cdot min^{-1}$, 20 cm synthetic quartz tube UV lamp, I=0.69 $W \cdot cm^{-2}$, 1500 W	7.8	5	20	88 and 92% for TOC and color removal, respectively, $BOD_5/COD=0.39$
Curitiba (Brazil), mature leachate, (DE MORAIS & ZAMORA, 2005)	8.4	5200	0.13	-	Lab-scale, UV/H_2O_2	H_2O_2=0.1 $mol \cdot L^{-1}$, quartz bulb UV lamp, I=3.2*10^{-3} Einstein $\cdot L^{-1} \cdot s^{-1}$, 125 W	8.4	1	-	56 and 97% for COD and TOC removal, respectively, $BOD_5/COD=0.4$
	8.4	5200	0.13	-	Lab-scale, $UV/H_2O_2/Fe^{2+}$	H_2O_2=0.06 $mol \cdot L^{-1}$, Fe^{2+}=0.18 $mmol \cdot L^{-1}$, quartz bulb UV lamp, I=3.2*10^{-3} Einstein $\cdot L^{-1} \cdot s^{-1}$, 125 W	2.8	1	-	58 and 90% for COD and TOC removal, respectively, $BOD_5/COD=0.4$
Cantabria (Spain), mature leachate, (PRIMO ET AL., 2008)	7.9	3824	0.18	2017	Lab-scale, $UV/H_2O_2/Fe^{2+}$	H_2O_2=0.44 $mol \cdot L^{-1}$, Fe^{2+}=55.6 $mmol \cdot L^{-1}$, TQ 150 UV lamp, I=8.8*10^{-5} Einstein $\cdot s^{-1}$, 150 W	3-3.5	1	-	78% COD removal
Beijing (China), mature leachate biologically pre-treated, (ZHAO ET AL., 2010)	7.8	560	0.07	700	Lab-scale, photo electrochemical oxidation	$Ti/TiRuO_2$ anode and stainless steel cathode, glass quartz tube UV lamp, I=671 $A \cdot m^{-2}$, 20 W	7.8	2.5	rt	94.5, 74.1 and 41.6% for $N\text{-}NH_4^+$, COD and TOC removal, respectively, $BOD_5/COD=0.6$

Another common drawback of AOPs is the high operational cost due to the high-energy consumption of devices such as ozonizers, UV lamps and ultrasounds and/or due to high oxidant doses required for complete degradation (mineralization). Although being expensive to operate, AOPs application is inevitable for the treatment of recalcitrant organic pollutants. Therefore, AOPs have been mainly applied for landfill leachate as post- or pre-treatment together with a physico-chemical and/or a biological technique. A combination of two AOPs in an integrated system may also enhance the formation of $^{\bullet}OH$ radicals, improving the removal efficiency. For instance, in the study of single AOPs such as O_3, O_3/H_2O_2, Fenton and several combined treatment schemes for landfill leachate, GOI, VERESSININA, ET AL. (2009) found that the best results in COD removal were achieved by the application of combined Fenton and ozonation processes.

2.3.3 COMBINED TREATMENT SYSTEMS

Although many different treatments can be applied, not one of the individual biological or physico-chemical techniques described in the previous sections is universally applicable or highly effective for landfill leachate treatment. In general, to set up satisfactory removal of pollutants from the leachate, a combination of several treatment systems is applied. The integrated systems ameliorate the drawbacks of individual processes contributing to a higher efficacy of the overall treatment. It must be noted, however, that the combination of treatment processes must be adjusted to each specific landfill leachate. Table 2.19 shows the performance of different combined systems on landfill leachate treatment. Though the conclusions should be carefully balanced due to different testing conditions (pH, temperature, strength of leachate, seasonal climate, and hydrology site), this comparison is useful to evaluate the overall treatment performance of each technique to assist the decision-making process.

As seem from Table 2.19, $N\text{-}NH_4^+$ removal was in the range 49–99% and COD removal was in the range 70–100%. Among the combined treatments reviewed above, it is observed that the combination of activated sludge, coagulation-flocculation and reverse osmosis demonstrated outstanding treatment performances in the removal of $N\text{-}NH_4^+$ (99%) and COD (100%).

Table 2.19 Landfill leachate treatment using combined systems.

Landfill site, age, reference	Combined system	Scale	Leachate feeding characteristics			Performance
			COD (mg·L^{-1})	BOD$_5$/COD	N-NH$_4^+$ (mg·L^{-1})	
Chen-Shi-Li (Taiwan), mature leachate, (Wu et al., 2004)	Coagulation-flocculation + ozonation + UV irradiation	Lab-scale	6500	0.06	5500	85% COD removal, BOD$_5$/COD=0.5
Apulia (Italy), mature leachate, (Di Iaconi et al., 2006)	Struvite + aerobic sequencing batch granular biofilter + Fenton	Lab-scale	24400	-	3190	99 and 97% for N-NH$_4^+$ and COD removal, respectively
Estonia, young leachate, (Goi, Veressinina, et al., 2009)	Coagulation-flocculation + Fenton	Lab-scale	14000	0.44	-	70% COD removal, BOD$_5$/COD=0.65
Hong Kong, mature leachate, (Kurniawan et al., 2006b)	Ozonation + adsorption	Lab-scale	8000	0.09	2620	92 and 86% for N-NH$_4^+$, and COD removal, respectively, BOD$_5$/COD=0.47
Wollongong (Australia), -, (Mariam & Nghiem, 2010)	Coagulation-flocculation + NF	Lab-scale	636 (TOC)	-	-	92% TOC removal
Diyarbakir (Turkey), young leachate, (Hasar et al., 2009)	Coagulation-flocculation + air stripping + aerobic/anoxic MBR + RO	Lab-scale	8500-19200	>0.3	1100-2150	100% COD removal
Jiangmen (China), mature leachate, (Li, Zhou, et al., 2009)	SBR + coagulation-flocculation + Fenton + upflow biological aerated filter	Full-scale	3000	0.22	1200	99 and 97% for N-NH$_4^+$, and COD removal, respectively
Chongqing (China), mature leachate, (Guo et al., 2010)	Air stripping + Fenton + SBR + coagulation-flocculation	Lab-scale	4150	0.18	1169	98 and 93% for N-NH$_4^+$ and COD removal, respectively, BOD$_5$/COD=0.41
Shiraz (Iran), young leachate, (Kheradmand et al., 2010)	AD+ AD + AS	Lab-scale	55351	0.81	1460	49-65 and 94% for N-NH$_4^+$ and COD removal, respectively
Kolenfeld (Germany), mature leachate, (Li, Wichmann, et al., 2009)	AS + coagulation-flocculation + RO	Full-scale	3100	-	1000	99 and 100% for N-NH$_4^+$ and COD removal, respectively

2.4 Landfill Leachate Treatment Costs

The adoption of the optimal treatment process in the industrial environment ultimately depends on favorable process economics. Estimating a reliable treatment cost for landfill leachate is difficult due to many cost components such as collection system, pumping equipment and treatment facility. In addition, changes in the quality and quantity of leachate due to seasonal variations also contribute to the inconsistency of treatment costs data. For this reason, information on the treatment cost of landfill leachate is rarely reported.

From the reviewed literature, only LI, ZHOU, ET AL. (2009) estimated the operating treatment cost of leachate using a combined system. According to the economical analysis performed, using combined SBR, coagulation-flocculation, Fenton and upflow biological aerated filter processes would cost US$ 2.7 per m^3 of the treated effluent. The cost covered the reagents required and energy consumption. The same authors stated that the cost of advanced treatment employing a membrane is always up to \$5-7 $\cdot m^{-3}$.

ALTINBAŞ ET AL. (2002) reported that, depending on the type of precipitation and chemicals employed, the treatment cost of struvite precipitation varies between US$ 2 and \$4 $\cdot m^{-3}$. TIZAOUI ET AL. (2007) achieved operating costs of US$ 3.1 and 2.3 per kg of COD removed from leachate using O_3 and O_3/H_2O_2 systems, respectively, while RIVAS ET AL. (2003) obtained an operating cost of US$ 0.008 per m^3 of the treated leachate and $mg \cdot L^{-1}$ of COD removed using Fenton oxidation.

It is important to note that, in the case of advanced oxidation processes, fine-tuning of the operating conditions could change radically the operating costs. Since the biological methods are more financially profitable and more environmental friendly, they should be preferred whenever possible.

Although it is unknown the cost component of leachate treatment in the overall cost of managing a landfill, it is thought that treatment of leachate from MSW will absorb more and more, a significant share of the total cost of MSW treatment.

2.5 LANDFILL LEACHATE TREATMENT IN PORTUGAL

The first leachate treatment plants in Portugal were designed similar to the domestic wastewater treatment plants, using the same parameters of scaling and assuming the same degree of efficiency. The analytical control of the treated effluent of these plants during the first years revealed much lower efficiency levels than expected mainly due to an incorrect water balance and the consequent inability to fit the flow, the high pollutant load of landfill leachate and/or its low biodegradability compared with domestic municipal wastewater (LEVY & SANTANA, 2004). Therefore, most of these structures have already changed or improved the sequence of treatment initially deployed.

According to the Environment Portuguese Agency and from a data survey carried out by our group, in the first half of 2008, of the 34 municipal solid waste sanitary landfills in operation, 31 had their own leachate treatment or pre-treatment plant while 3 led the produced leachate for the municipal sewer or directly to the wastewater treatment plant. The leachate treatment or pre-treatment plants of the sanitary landfills in operation were based on the systems presented in Table 2.20.

Of the 31 leachate treatment plants operating in Portugal sanitary landfills, in the first half of 2008, 12 performed the pre-treatment and discharged the pre-treated effluent in the municipal sewer, 18 had treatment systems that allowed the discharge of treated leachate in the aquatic environment and one did not generate any discharge. However, two of these facilities were inoperative for failing to comply with the parameters of discharge in the surface water or due to the inadequate adjustment of the system to the leachate quantity to be treated. It should be noted that in both cases, was under investigation, or already in test phase, a different treatment solution or an optimization of the system already deployed.

Most of leachate treatment plants included lagoons. Excluding lagoons, the treatment systems described in Table 2.20 present great diversity. Some of them are very simple and only remove some organic load because leachate is discharged in the municipal sewer and subsequently is treated in a wastewater treatment plant. This is the case, for example, of the Valsousa system. Other schemes are very complex and robusts allowing the discharge in the aquatic environment, such as the Lipor, REBAT, RESIDOURO, Ecobeirão, RESIESTRELA, Raia-Pinhal, Ecolezíria, Resitejo, Gesamb and ALGAR systems, which integrate in the treatment plant the reverse osmosis process, the Resíduos do Nordeste system, which employs a sophisticated evaporation and condensation process or the Resialentejo system, which utilizes physico-chemical tuning of the final effluent with activated carbon. Naturally, the complexity of the treatment is reflected in its cost, which ranges, for instance from 0.25 € per liter of treated leachate with the AMARSUL system to 6 € per liter of treated leachate with the ALGAR systems (operating costs).

The processing of the sludge produced during treatment has consisted, mainly, on their dehydration followed by disposal in the landfill, which is not environment-friendly and does not meet the requirements stipulated by law. Likewise, the concentrates resulting from the treatment by reverse osmosis, rich in nitrogenous compounds and heavy metals, cannot be MSW landfilled. However, this is a recurring practice in national and European landfills due to the costs associated with their treatment and blanketing.

The removal of recalcitrant carbonaceous and nitrogenous compounds (mainly ammonium and nitrate) to values below the discharge limits has been one of the major problems in leachate treatment plants operating in Portugal, as all over the world.

Table 2.20 Landfill leachate treatment or pre-treatment plants of the sanitary landfills in operation in Portugal (June 2008).

Management system	Landfill site and operation start	Treatment or pre-treatment system	Final leachate discharge
VALORMINHO	Valença, August 1998	Retention tank + Fast mixing tank (pH adjustment and/or phosphorus addition) + AS + decanting + stabilization tank	Municipal sewer
RESULIMA	Viana do Castelo, December 1998	Stabilization lagoon (and emergency lagoon) + anaerobic lagoon + anoxic tank + aerated lagoon + decanting + Fenton oxidation + decanting	Municipal sewer
BRAVAL	Póvoa de Lanhoso, July 1998	Stabilization lagoon + sand filter + AS + coagulation-flocculation + decanting	Municipal sewer
Amave	Santo Tirso, February 2000	Does not have leachate treatment or pre-treatment plant	Municipal sewer
Lipor	Maia, June 2001	Stabilization lagoon + AS + UF + RO	Surface water
Valsousa	Lousada, November 1998	Entrance structure + stabilization lagoon + AS + decanting stabilization lagoon	Municipal sewer
	Penafiel, April 1999	Stabilization lagoon + aerated lagoon + stabilization and aerated lagoon (and emergency lagoon)	Municipal sewer
SULDOURO	Vila Nova de Gaia, March 1999	Stabilization lagoon (and emergency lagoon) + fast mixing tank (coagulant addition and pH adjustment) + decanting + AS + decanting + flotation + stabilization lagoon	Municipal sewer
RESAT	Boticas, November 2001	Entrance structure + stabilization lagoon + coagulation-flocculation + decanting	Municipal sewer
Vale do Douro Norte	Vila Real, August 2000	Stabilization and aerated lagoon + coagulation-flocculation + decanting	Surface water - inoperative
Resíduos do Nordeste	Mirandela, September 1997	Fast mixing tank (acid addition, anti-foaming and anti-fouling) + evaporation + condensation + pH adjustment + air stripping + pH adjustment + AS + decanting + stabilization tank	Water resource
REBAT	Celorico de Basto, November 2001	Stabilization lagoon + aerated lagoon + AS + sand filter + cartridge filter + RO	Surface water
RESIDOURO	Lamego, January 2002	Aerated lagoon + stabilization lagoon + sand filter + cartridge filter + RO	Surface water
VALORLIS	Leiria, September 1998	Stabilization lagoon + aerated lagoon + retention lagoon + decanting + constructed wetlands system	Municipal sewer
ERSUC	Aveiro, December 1998	Fast mixing tank (pH adjustment and/or phosphorus addition) + retention lagoon + aerated lagoon + Fenton oxidation + lamellar decanting + aerated tank + sand filter	Municipal sewer
	Coimbra, September 1998	Stabilization lagoon + AS (Carrousel system) + decanting + Fenton oxidation + decanting + pH adjustment	Municipal sewer
	Figueira da Foz, September 1998	Does not have leachate treatment or pre-treatment plant	Municipal sewer
Ecobeirão	Tondela, May 1999	Two distinct treatment sequences: Stabilization lagoon + AS + decanting + AS + UF + RO + aerated lagoon Stabilization lagoon + aerated lagoon + decanting + sand filter + cartridge filter + RO + aerated lagoon	Surface water
RESIESTRELA	Fundão, November 2001	Stabilization lagoon + AS + UF + RO	Surface water

Table 2.20 Landfill leachate treatment or pre-treatment plants of the sanitary landfills in operation in Portugal (June 2008). *Continuation*

Management system	Landfill site and operation start	Treatment or pre-treatment system	Final leachate discharge
Raia-Pinhal	Castelo Branco, April 1999	Entrance structure + stabilization and aerated lagoon (and emergency lagoon) + decanting + AS + decanting + sand filter + cartridge filter + RO + stabilization lagoon	Surface water
RESIOESTE	Cadaval, November 2001	Stabilization and aerated lagoon + AS + decanting + sand filter + cartridge filter + RO	Surface water
Ecolezíria	Almeirim, July 2000	Retention lagoon + decanting + AS + decanting + sand filter + cartridge filter + RO	Surface water
Resitejo	Chamusca, May 1999	Retention lagoon + stabilization lagoon + electro-coagulation + decanting + RO	Surface water
VALORSUL	Vila Franca de Xira, June 1998	Entrance structure + fast mixing tank (phosphorus addition) + aerated lagoon + coagulation-flocculation + decanting + pH adjustment	Municipal sewer
AMARSUL	Palmela, January 1997	Entrance structure + aerated lagoon + decanting	Municipal sewer
	Seixal, July 1995	Does not have leachate treatment or pre-treatment plant	Municipal sewer
Gesamb	Évora, January 2002	Stabilization lagoon + sand filter + cartridge filter + RO+ e stabilization tank	Surface water
Ambilital	Santiago do Cacém, April 2000	Retention lagoon + entrance structure + aerated lagoon 1 + aerated lagoon 2 + retention lagoon + evaporation lagoon	No discharge - inoperative
Amcal	Cuba, June 1999	Entrance structure + anaerobic lagoon + facultative lagoon + aerated lagoon 1 + aerated lagoon 2 + decanting + constructed wetlands system + stabilization tank	Surface water or no discharge
VALNOR	Avis, May 2000	Entrance structure + stabilization tank + anaerobic lagoon 1 + anaerobic lagoon 2 + aerated lagoon + AS + decanting + coagulation-flocculation + decanting + pH adjustment	Surface water
	Abrantes, June 1998	Entrance structure + anaerobic lagoon + aerated lagoon 1 + aerated lagoon 2 + stabilization tank + anaerobic lagoon 1 + anaerobic lagoon 2 + aerated lagoon + AS + decanting + coagulation-flocculation + decanting + pH adjustment	Surface water
Resialentejo	Beja, December 2001	Stabilization lagoon + decanting + sand filter + AS (2 SBR) + coagulation-flocculation + decanting + sand filter + activated carbon	Surface water
ALGAR	Portimão, February 1998	Retention lagoon + stabilization and aerated lagoon + sand filter 1 + sand filter 2 + microfilter + RO	Surface water
	Loulé, July 2000	Retention lagoon + stabilization and aerated lagoon + sand filter 1 + sand filter 2 + microfilter + RO	Surface water

NOTE: In the first column, uppercase letters represent multimunicipal management systems; lowercase letters represent intermunicipal management systems

With respect to denitrification, required to reduce the total nitrogen and nitrate, all treatment plants adopted a pre-anoxic process followed by a nitrification stage with activated sludge and installed a circuit for leachate internal recirculation. The monitoring of the treated leachate has shown that this system is not satisfactory and the concentrations of those parameters exceed the discharge limits. Apparently, only a part of the nitrogen-ammonium is nitrified, and only a part of nitrogen-nitrate is denitrified. For instance, in a leachate treatment plant where the influent had concentrations of about 2500 mg $N\text{-}NH_4^+ \cdot L^{-1}$ and 25 mg $N\text{-}NO_3^- \cdot L^{-1}$, after pre-treatment and before being discharged in the municipal sewer the effluent had 435 mg $N\text{-}NH_4^+ \cdot L^{-1}$ and 1165 mg $N\text{-}NO_3^- \cdot L^{-1}$. This issue is even more pertinent for the treatment systems that allowed the discharge in the aquatic environment since, in order to avoid negative impacts to the biota or public health, according to the DL 236/98, of August 1 (MINISTÉRIO DO AMBIENTE, 1998), the emission limit value for nitrate for the receiving environment of discharge the effluent is 11.3 mg $N\text{-}NO_3^- \cdot L^{-1}$, for ammonium is 7.8 mg $N\text{-}NH_4^+ \cdot L^{-1}$ and for total nitrogen is 15 mg $N \cdot L^{-1}$.

The introduction of an oxidation step after biological treatment, namely the Fenton's oxidation, allows reducing the concentration of recalcitrant compounds. However, in many cases, it has been observed a significant increase of nitrogen-nitrate concentration.

Reverse osmosis units have also been effective in removing refractory substances from leachate. Regarding total nitrogen and nitrate, values exceeding the discharge limits were detected in many facilities.

Therefore, the improvement of nitrification-denitrification after the oxidation or before the reverse osmosis steps must be considered. To achieve this amendment, adequate dissolved oxygen content must be ensured in the aeration tank. Furthermore, the recirculation flow must be performed at a proper rate. The addition of a carbon source, such as methanol, in the anoxic tank, may also be needed, as verified in the Asturias leachate treatment plant (CASTRILLÓN ET AL., 2010). In addition to these measures, a different denitrification reactor can be used.

In order to optimize existing nitrate removal strategies and to find new ways to respond to stricter legislation concerning nitrogen discharge, this research focused on the denitrification of a landfill leachate with high nitrate load in an anoxic rotating biological contactor.

2.6 MAJOR CHALLENGES AND PROSPECTS

In order to fully reduce the negative impact on the environment, optimal leachate treatment is still facing various challenges.

Due to the EU Landfill Directive, which requires that the amount of biodegradable municipal waste deposited at landfill progressively been reduced, over a 15-year period, to only 35% of the total amount produced in 1995, the pre-treatment of MSW, has started to be widely used in Germany and Austria and is quickly developing in Italy and the UK. It is expected that this tendency will be adopted soon not only in the other European countries but also worldwide. The pre-treatment of MSW include mechanical and biological treatment (MBT). MBT of solid waste improves waste settlement characteristics, reduces clogging of leachate drainage systems and accelerates organic degradation in landfills, shortening the monitoring period of the landfill and minimizing the quantity of landfill gas generated (ZHANG ET AL., 2010; ROBINSON ET AL., 2005). However, the fresh leachate generated from pre-treated MSW, contains large amounts of contaminants and a high COD concentration. As a consequence, its treatment has become a new challenge (LIU ET AL., 2010).

The continuous hardening of the discharge standards in most countries, the aging of landfill sites with more and more stabilized leachate and the increasingly practiced leachate recirculation in the landfill with consequent modifications in leachate composition demand different treatment solutions.

Therefore, it can be anticipated that several new landfill leachate treatment alternatives will be proposed in the next several years. We are still far from the end of the landfills and even more distant from the end of leachate production.

2.7 CONCLUSIONS

During the next years, sanitary landfills will continue to be used as a solid waste management strategy for disposal and elimination of MSW, releasing landfill leachate. The leachate treatment complexity makes it very difficult to formulate general recommendations of universal validity. Each of the presented methods offers inherent advantages and drawbacks.

The choice of the most suitable treatment strategy depends mainly on the initial leachate quality, the discharge limits required by local authorities, the effluent discharge alternatives, the overall treatment performance compared to other technologies, the technical applicability, the plant flexibility and reliability, the environmental impact and the capital and operating costs.

Some challenges were identified and a widespread and great progress in this area can be expected in the future.

2.8 REFERENCES

AGDAG, O.N. & SPONZA, D.T. (2005) Anaerobic/aerobic treatment of municipal landfill leachate in sequential two-stage up-flow anaerobic sludge blanket reactor (UASB)/completely stirred tank reactor (CSTR) systems. *Process Biochemistry*, 40, 895-902.

AHN, W.Y., KANG, M.S., YIM, S.K. & CHOI, K.H. (2002) Advanced landfill leachate treatment using an integrated membrane process. *Desalination*, 149, 109-114.

ALTINBAŞ, M., YANGIN, C. & OZTURK, I. (2002) Struvite precipitation from anaerobically treated municipal and landfill wastewaters. *Water Science and Technology*, 46, 271-278.

ALVAREZ-VAZQUEZ, H., JEFFERSON, B. & JUDD, S.J. (2004) Membrane bioreactors vs conventional biological treatment of landfill leachate: a brief review. *Journal of Chemical Technology and Biotechnology*, 79, 1043-1049.

ATMACA, E. (2009) Treatment of landfill leachate by using electro-Fenton method. *Journal of Hazardous Materials*, 163, 109-114.

AZIZ, H.A., ALIAS, S., ADLAN, M.N., ASAARI, F.A.H. & ZAHARI, S. (2007) Colour removal from landfill leachate by coagulation and flocculation processes. *Bioresource Technology*, 98, 218-220.

BAE, B., JUNG, E., KIM, Y. & SHIN, H. (1999) Treatment of landfill leachate using activated sludge process and electron-beam radiation. *Water Research*, 33, 2669-2673.

BARLAZ, M.A., SCHAEFER, D.M. & HAM, R.K. (1989) Bacterial Population Development and Chemical Characteristics of Refuse Decomposition in a Simulated Sanitary Landfill. *Applied Environmental Microbiology*, 55, 55-65.

BASHIR, M.J., ISA, M.H., KUTTY, S.R.M., AWANG, Z.B., AZIZ, H.A., MOHAJERI, S. & FAROOQI, I.H. (2009) Landfill leachate treatment by electrochemical oxidation. *Waste Management*, 29, 2534-2541.

BERGE, N.D., REINHART, D.R. & BATARSEH, E.S. (2009) An assessment of bioreactor landfill costs and benefits. *Waste Management*, 29, 1558-1567.

BERGE, N.D., REINHART, D.R., DIETZ, J. & TOWNSEND, T. (2006) In situ ammonia removal in bioreactor landfill leachate. *Waste Management*, 26, 334-343.

BILA, D.M., MONTALVÃO, A., SILVA, A.C. & DEZOTTI, M. (2005) Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement. *Journal of Hazardous Materials*, 117, 235-242.

BIRCHLER, D.R., MILKE, M.W., MARKS, A.L. & LUTHY, R.G. (1994) Landfill Leachate Treatment by Evaporation. *Journal of Environmental Engineering*, 120, 1109-1131.

BOHDZIEWICZ, J., BODZEK, M. & GÓRSKA, J. (2001) Application of pressure-driven membrane techniques to biological treatment of landfill leachate. *Process Biochemistry*, 36, 641-646.

BOHDZIEWICZ, J., NECZAJ, E. & KWARCIAK, A. (2008) Landfill leachate treatment by means of anaerobic membrane bioreactor. *Desalination*, 221, 559-565.

BRUGGEN, B.V.D., VANDECASTEELE, C., GESTEL, T.V., DOYEN, W. & LEYSEN, R. (2003) A review of pressure-driven membrane processes in wastewater treatment and drinking water production. *Environmental Progress*, 22, 46-56.

CABEZA, A., PRIMO, O., URTIAGA, A. & ORTIZ, I. (2007) Definition of a clean process for the treatment of landfill leachates integration of electrooxidation and ion exchange technologies. *Separation science and technology*, 42, 1585-1596.

CALLI, B., MERTOGLU, B. & INANC, B. (2005) Landfill leachate management in Istanbul: applications and alternatives. *Chemosphere*, 59, 819-829.

CANZIANI, R., EMONDI, V., GARAVAGLIA, M., MALPEI, F., PASINETTI, E. & BUTTIGLIERI, G. (2006) Effect of oxygen concentration on biological nitrification and microbial kinetics in a cross-flow membrane bioreactor (MBR) and moving-bed biofilm reactor (MBBR) treating old landfill leachate. *Journal of Membrane Science*, 286, 202-212.

CASTILLO, E., VERGARA, M. & MORENO, Y. (2007) Landfill leachate treatment using a rotating biological contactor and an upward-flow anaerobic sludge bed reactor. *Waste Management*, 27, 720-726.

CASTRILLÓN, L., FERNÁNDEZ-NAVA, Y., ULMANU, M., ANGER, I. & MARAÑÓN, E. (2010) Physico-chemical and biological treatment of MSW landfill leachate. *Waste Management*, 30, 228-235.

CECEN, F. & GURSOY, G. (2000) Characterization of landfill leachates and studies on heavy metal removal. *Journal of Environmental Monitoring*, 2, 436-442.

CEMA, G., WISZNIOWSKI, J., ZABCZYNSKI, S., ZABLOCKA-GODLEWSKA, E., RASZKA, A. & SURMACZ-GORSKA, J. (2007) Biological nitrogen removal from landfill leachate by deammonification assisted by heterotrophic denitrification in a rotating biological contactor (RBC). *Water Science and Technology*, 55, 35-42.

CHATURAPRUEK, A., VISVANATHAN, C. & AHN, K.H. (2005) Ozonation of membrane bioreactor effluent for landfill leachate treatment. *Environmental Technology*, 26, 65-73.

CHAUDHARI, L.B. & MURTHY, Z. (2010) Treatment of landfill leachates by nanofiltration. *Journal of Environmental Management*, 91, 1209-1217.

CHEN, P.H. (1996) Assessment of leachates from sanitary landfills: Impact of age, rainfall, and treatment. *Environment International*, 22, 225-237.

CHEN, S., SUN, D. & CHUNG, J. (2008) Simultaneous removal of COD and ammonium from landfill leachate using an anaerobic-aerobic moving-bed biofilm reactor system. *Waste Management*, 28, 339-346.

CORTEZ, S., TEIXEIRA, P., OLIVEIRA, R. & MOTA, M. (2008) Rotating biological contactors: a review on main factors affecting performance. *Reviews in Environmental Science and Biotechnology*, 7, 155-172.

COSSU, R. (2010) Technical evolution of landfilling. *Waste Management*, 30, 947-948.

COTMAN, M. & GOTVAJN, A.Z. (2010) Comparison of different physico-chemical methods for the removal of toxicants from landfill leachate. *Journal of Hazardous Materials*, 178, 298-305.

DENG, Y. & ENGLEHARDT, J.D. (2006) Treatment of landfill leachate by the Fenton process. *Water Research*, 40, 3683-3694.

DENG, Y. & ENGLEHARDT, J.D. (2007) Electrochemical oxidation for landfill leachate treatment. *Waste Management*, 27, 380-388.

DI IACONI, C., PAGANO, M., RAMADORI, R. & LOPEZ, A. (2010) Nitrogen recovery from a stabilized municipal landfill leachate. *Bioresource Technology*, 101, 1732-1736.

DI IACONI, C., RAMADORI, R. & LOPEZ, A. (2006) Combined biological and chemical degradation for treating a mature municipal landfill leachate. *Biochemical Engineering Journal*, 31, 118-124.

DING, A., ZHANG, Z., FU, J. & CHENG, L. (2001) Biological control of leachate from municipal landfills. *Chemosphere*, 44, 1-8.

DZOMBAK, D., LAGNESE, K., SPENGEL, D. & LUTHY, R. (1990) Comparison of activated sludge and RBC treatment of leachate from a solid waste landfill. In *Proceedings of the Water Quality Management of Landfills Conference* (eds. Water Pollution Control Federation), pp. 4-39-4-58, Alexandria, Virginia.

EGLI, K., BOSSHARD, F., WERLEN, C., LAIS, P., SIEGRIST, H., ZEHNDER, A. & VAN DER MEER, J. (2003) Microbial composition and structure of a rotating biological contactor biofilm treating ammonium-rich wastewater without organic carbon. *Microbial Ecology*, 45, 419-432.

EL-FADEL M., FINDIKAKIS A.N. & LECKIE J.O. (1997) Modeling leachate generation and transport in solid waste landfills. *Environmental Technology*, 18, 669-686.

ELDYASTI, A., CHOWDHURY, N., NAKHLA, G. & ZHU, J. (2010) Biological nutrient removal from leachate using a pilot liquid-solid circulating fluidized bed bioreactor (LSCFB). *Journal of Hazardous Materials*, 181, 289-297.

ELLOUZE, M., ALOUI, F. & SAYADI, S. (2008) Performance of biological treatment of high-level ammonia landfill leachate. *Environmental Technology*, 29, 1169-1178.

FOO, K. & HAMEED, B. (2009) An overview of landfill leachate treatment via activated carbon adsorption process. *Journal of Hazardous Materials*, 171, 54-60.

FRASCARI, D., BRONZINI, F., GIORDANO, G., TEDIOLI, G. & NOCENTINI, M. (2004) Long-term characterization, lagoon treatment and migration potential of landfill leachate: a case study in an active Italian landfill. *Chemosphere*, 54, 335-343.

GÁLVEZ, A., GIUSTI, L., ZAMORANO, M. & RAMOS-RIDAO, A. (2009) Stability and efficiency of biofilms for landfill leachate treatment. *Bioresource Technology*, 100, 4895-4898.

GÁLVEZ, A., ZAMORANO, M., HONTORIA, E. & RAMOS, A. (2006) Treatment of Landfill Leachate with Aerated and Non-Aerated Submerged Biofilters. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, 41, 1129.

GOI, A., VERESSININA, Y. & TRAPIDO, M. (2009) Combination of ozonation and the Fenton processes for landfill leachate treatment: evaluation of treatment efficiency. *Ozone: Science and Engineering*, 31, 28-36.

GOI, D., DI GIORGIO, G., CIMAROSTI, I., LESA, B., ROSSI, G. & DOLCETTI, G. (2009) Treatment of landfill leachate by H_2O_2 promoted wet air oxidation: COD-AOX reduction, biodegradability enhancement and comparison with a Fenton-type oxidation. *Chemical & Biochemical Engineering Quarterly*, 23, 343-349.

GOURDON, R., COMEL, C., VERMANDE, P. & VERON, J. (1989) Fractionation of the organic matter of a landfill leachate before and after aerobic or anaerobic biological treatment. *Water Research*, 23, 167-173.

GUO, J., ABBAS, A.A., CHEN, Y., LIU, Z., FANG, F. & CHEN, P. (2010) Treatment of landfill leachate using a combined stripping, Fenton, SBR, and coagulation process. *Journal of Hazardous Materials*, 178, 699-705.

HAGMAN, M., HEANDER, E. & JANSEN, J.L.C. (2008) Advanced oxidation of refractory organics in leachate – potential methods and evaluation of biodegradability of the remaining substrate. *Environmental Technology*, 29, 941-946.

HALIM, A.A., AZIZ, H.A., JOHARI, M.A.M., ARIFFIN, K.S. & ADLAN, M.N. (2010) Ammoniacal nitrogen and COD removal from semi-aerobic landfill leachate using a composite adsorbent: Fixed bed column adsorption performance. *Journal of Hazardous Materials*, 175, 960-964.

HASAR, H., UNSAL, S.A., IPEK, U., KARATAS, S., CINAR, O., YAMAN, C. & KINACI, C. (2009) Stripping/flocculation/membrane bioreactor/reverse osmosis treatment of municipal landfill leachate. *Journal of Hazardous Materials*, 171, 309-317.

HERMOSILLA, D., CORTIJO, M. & HUANG, C.P. (2009) Optimizing the treatment of landfill leachate by conventional Fenton and photo-Fenton processes. *Science of The Total Environment*, 407, 3473-3481.

HUO, S., XI, B., YU, H., HE, L., FAN, S. & LIU, H. (2008) Characteristics of dissolved organic matter (DOM) in leachate with different landfill ages. *Journal of Environmental Sciences*, 20, 492-498.

INCE, M., SENTURK, E., ONKAL ENGIN, G. & KESKINLER, B. (2010) Further treatment of landfill leachate by nanofiltration and microfiltration-PAC hybrid process. *Desalination*, 255, 52-60.

ISAKA, K., YOSHIE, S., SUMINO, T., INAMORI, Y. & TSUNEDA, S. (2007) Nitrification of landfill leachate using immobilized nitrifying bacteria at low temperatures. *Biochemical Engineering Journal*, 37, 49-55.

JOKELA, J., KETTUNEN, R., SORMUNEN, K. & RINTALA, J. (2002) Biological nitrogen removal from municipal landfill leachate: low-cost nitrification in biofilters and laboratory scale in-situ denitrification. *Water Research*, 36, 4079-4087.

KADLEC, R.H. & ZMARTHIE, L.A. (2010) Wetland treatment of leachate from a closed landfill. *Ecological Engineering*, 36, 946-957.

KENNEDY, K.J. & LENTZ, E.M. (2000) Treatment of landfill leachate using sequencing batch and continuous flow upflow anaerobic sludge blanket (UASB) reactors. *Water Research*, 34, 3640-3656.

KETTUNEN, R.H. & RINTALA, J.A. (1998) Performance of an on-site UASB reactor treating leachate at low temperature. *Water Research*, 32, 537-546.

KHERADMAND, S., KARIMI-JASHNI, A. & SARTAJ, M. (2010) Treatment of municipal landfill leachate using a combined anaerobic digester and activated sludge system. *Waste Management*, 30, 1025-1031.

KJELDSEN, P., BARLAZ, M.A., ROOKER, A.P., BAUN, A., LEDIN, A. & CHRISTENSEN, T.H. (2002) Present and long-term composition of MSW landfill leachate: A review. *Critical Reviews in Environmental Science and Technology*, 32, 297-336.

KLIMIUK, E. & KULIKOWSKA, D. (2004) Effectiveness of organics and nitrogen removal from municipal landfill leachate in single- and two-stage SBR systems. *Polish Journal of Environmental Studies*, 13, 525-532.

KNOX, K. (1985) Leachate treatment with nitrification of ammonia. *Water Research*, 19, 895-904.

KOCHANY, J. & LIPCZYNSKA-KOCHANY, E. (2009) Utilization of landfill leachate parameters for pretreatment by Fenton reaction and struvite precipitation--A comparative study. *Journal of Hazardous Materials*, 166, 248-254.

KULIKOWSKA, D., JÓZWIAK, T., KOWAL, P. & CIESIELSKI, S. (2010) Municipal landfill leachate nitrification in RBC biofilm - Process efficiency and molecular analysis of microbial structure. *Bioresource Technology*, 101, 3400-3405.

KULIKOWSKA, D. & KLIMIUK, E. (2008) The effect of landfill age on municipal leachate composition. *Bioresource Technology*, 99, 5981-5985.

KURNIAWAN, T.A., LO, W.H. & CHAN, G.Y. (2006) Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate. *Journal of Hazardous Materials*, 129, 80-100.

KURNIAWAN, T.A. & LO, W. (2009) Removal of refractory compounds from stabilized landfill leachate using an integrated H2O2 oxidation and granular activated carbon (GAC) adsorption treatment. *Water Research*, 43, 4079-4091.

KURNIAWAN, T.A., LO, W. & CHAN, G. (2006a) Radicals-catalyzed oxidation reactions for degradation of recalcitrant compounds from landfill leachate. *Chemical Engineering Journal*, 125, 35-57.

KURNIAWAN, T.A., LO, W. & CHAN, G.Y. (2006b) Degradation of recalcitrant compounds from stabilized landfill leachate using a combination of ozone-GAC adsorption treatment. *Journal of Hazardous Materials*, 137, 443-455.

KYLEFORS, K., ANDREAS, L. & LAGERKVIST, A. (2003) A comparison of small-scale, pilot-scale and large-scale tests for predicting leaching behaviour of landfilled wastes. *Waste Management*, 23, 45-59.

LEMA, J., MENDEZ, R. & BLAZQUEZ, R. (1988) Characteristics of landfill leachates and alternatives for their treatment - A review. *Water Air and Soil Pollution*, 40, 223-250.

LEVY, J.Q. & SANTANA, C. (2004) Funcionamento das estações de tratamento de águas lixiviantes e acções para a sua beneficiação. Centro de Sistemas Urbanos e Regionais, CESUR, IST

Lisboa.
[<http://www.ecoservicos.pt/page.jsp?section=cientificos&page=pubs>]
(accessed 15.07.2010).

LI, F., WICHMANN, K. & HEINE, W. (2009) Treatment of the methanogenic landfill leachate with thin open channel reverse osmosis membrane modules. *Waste Management*, 29, 960-964.

LI, H., ZHOU, S., SUN, Y., FENG, P. & LI, J. (2009) Advanced treatment of landfill leachate by a new combination process in a full-scale plant. *Journal of Hazardous Materials*, 172, 408-415.

LI, X.Z. & ZHAO, Q.L. (2001) Efficiency of biological treatment affected by high strength of ammonium-nitrogen in leachate and chemical precipitation of ammonium-nitrogen as pretreatment. *Chemosphere*, 44, 37-43.

LI, X., ZHAO, Q. & HAO, X. (1999) Ammonium removal from landfill leachate by chemical precipitation. *Waste Management*, 19, 409-415.

LIANG, Z. & LIU, J. (2008) Landfill leachate treatment with a novel process: Anaerobic ammonium oxidation (Anammox) combined with soil infiltration system. *Journal of Hazardous Materials*, 151, 202-212.

LIN, C. (1991) Anaerobic digestion of landfill leachate. *Water S.A.*, 17, 301-306.

LINDE, K., JÖNSSON, A. & WIMMERSTEDT, R. (1995) Treatment of three types of landfill leachate with reverse osmosis. *Desalination*, 101, 21-30.

LIU, J., ZHONG, J., WANG, Y., LIU, Q., QIAN, G., ZHONG, L. ET AL. (2010) Effective bio-treatment of fresh leachate from pretreated municipal solid waste in an expanded granular sludge bed bioreactor. *Bioresource Technology*, 101, 1447-1452.

LÓPEZ, A., PAGANO, M., VOLPE, A. & DI PINTO, A.C. (2004) Fenton's pre-treatment of mature landfill leachate. *Chemosphere*, 54, 1005-1010.

LOUKIDOU, M. & ZOUBOULIS, A. (2001) Comparison of two biological treatment processes using attached-growth biomass for sanitary landfill leachate treatment. *Environmental Pollution*, 111, 273-281.

MARAÑÓN, E., CASTRILLÓN, L., FERNÁNDEZ-NAVA, Y., FERNÁNDEZ-MÉNDEZ, A. & FERNÁNDEZ-SÁNCHEZ, A. (2008) Coagulation-flocculation as a pretreatment process at a landfill leachate nitrification-denitrification plant. *Journal of Hazardous Materials*, 156, 538-544.

MARIAM, T. & NGHIEM, L.D. (2010) Landfill leachate treatment using hybrid coagulation-nanofiltration processes. *Desalination*, 250, 677-681.

MARTTINEN, S., KETTUNEN, R., SORMUNEN, K., SOIMASUO, R. & RINTALA, J. (2002) Screening of physical-chemical methods for removal of organic material, nitrogen and toxicity from low strength landfill leachates. *Chemosphere*, 46, 851-858.

MARTTINEN, S.K., KETTUNEN, R.H. & RINTALA, J.A. (2003) Occurrence and removal of organic pollutants in sewages and landfill leachates. *The Science of The Total Environment*, 301, 1-12.

MEHMOOD, M., ADETUTU, E., NEDWELL, D. & BALL, A. (2009) In situ microbial treatment of landfill leachate using aerated lagoons. *Bioresource Technology*, 100, 2741-2744.

MENDEZ, R., LEMA, J., BLAZQUEZ, R., PAN, M. & FORJAN, C. (1989) Characterization, digestibility and anaerobic treatment of leachates from old and young landfills. *Water Science and Technology*, 21, 145-155.

MINISTÉRIO DO AMBIENTE (1998) DL 236/1998. *Diário da República*, I Série-A, nº 176 de 1 de Agosto de 1998, 3676-3722.

MOHAJERI, S., AZIZ, H.A., ISA, M.H., ZAHED, M.A. & ADLAN, M.N. (2010) Statistical optimization of process parameters for landfill leachate treatment using electro-Fenton technique. *Journal of Hazardous Materials*, 176, 749-758.

MONJE-RAMIREZ, I. & VELÁSQUEZ, M.T.O.D. (2004) Removal and transformation of recalcitrant organic matter from stabilized saline landfill leachates by coagulation-ozonation coupling processes. *Water Research*, 38, 2359-2367.

MORAES, P.B. & BERTAZZOLI, R. (2005) Electrodegradation of landfill leachate in a flow electrochemical reactor. *Chemosphere*, 58, 41-46.

DE MORAIS, J.L. & ZAMORA, P.P. (2005) Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates. *Journal of Hazardous Materials*, 123, 181-186.

NECZAJ, E., KACPRZAK, M., LACH, J. & OKONIEWSKA, E. (2007) Effect of sonication on combined treatment of landfill leachate and domestic sewage in SBR reactor. *Desalination*, 204, 227-233.

NECZAJ, E., OKONIEWSKA, E. & KACPRZAK, M. (2005) Treatment of landfill leachate by sequencing batch reactor. *Desalination*, 185, 357-362.

NEDWELL, D.B. & REYNOLDS, P.J. (1996) Treatment of landfill leachate by methanogenic and sulphate-reducing digestion. *Water Research*, 30, 21-28.

PALANIANDY, P., ADLAN, M.N., AZIZ, H.A. & MURSHED, M.F. (2010) Application of dissolved air flotation (DAF) in semi-aerobic leachate treatment. *Chemical Engineering Journal*, 157, 316-322.

PAPASTAVROU, C., MANTZAVINOS, D. & DIAMADOPOULOS, E. (2009) A comparative treatment of stabilized landfill leachate: Coagulation and activated carbon adsorption vs. electrochemical oxidation. *Environmental Technology*, 30, 1547.

PI, K., GAO, L., FAN, M., GONG, W. & WAN, D. (2009) Two-stage biodegradation coupled with ultrafiltration for treatment of municipal landfill leachate. *Process Safety and Environmental Protection*, 87, 336-342.

PIATKIEWICZ, W., BIEMACKA, E. & SUCHECKA, T. (2001) A polish study: treating landfill leachate with membranes. *Filtration and Separation*, 38, 22-23.

PIRBAZARI, M., RAVINDRAN, V., BADRIYHA, B.N. & KIM, S. (1996) Hybrid membrane filtration process for leachate treatment. *Water Research*, 30, 2691-2706.

PRIMO, O., RIVERO, M.J. & ORTIZ, I. (2008) Photo-Fenton process as an efficient alternative to the treatment of landfill leachates. *Journal of Hazardous Materials*, 153, 834-842.

QASIM, S.R. & CHIANG, W. (1994) Sanitary landfill leachate - generation, control and treatment. Technomic Publishing Company, Inc., Lancaster, Pennsylvania.

QURESHI, T.I., KIM, H. & KIM, Y. (2002) UV-catalytic treatment of municipal solid-waste landfill leachate with hydrogen peroxide and ozone oxidation. *Chinese Journal of Chemical Engineering*, 10, 444-449.

RENOU, S., GIVAUDAN, J., POULAIN, S., DIRASSOUYAN, F. & MOULIN, P. (2008) Landfill leachate treatment: review and opportunity. *Journal of Hazardous Materials*, 150, 468-493.

RENOU, S., POULAIN, S., GIVAUDAN, J. & MOULIN, P. (2009) Amelioration of ultrafiltration process by lime treatment: Case of landfill leachate. *Desalination*, 249, 72-82.

RIVAS, F.J., BELTRÁN, F., GIMENO, O. & CARVALHO, F. (2003) Fenton-like Oxidation of Landfill Leachate. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, 38, 371.

RIVAS, F.J., BELTRÁN, F.J., CARVALHO, F. & ALVAREZ, P.M. (2005) Oxone-Promoted Wet Air Oxidation of Landfill Leachates. *Industrial and Engineering Chemistry Research*, 44, 749-758.

ROBINSON, H., KNOX, K., BONE, B. & PICKEN, A. (2005) Leachate quality from landfilled MBT waste. *Waste Management*, 25, 383-391.

RODRIGUEZ, J., CASTRILLON, L., MARANON, E., SASTRE, H. & FERNANDEZ, E. (2004) Removal of non-biodegradable organic matter from landfill leachates by adsorption. *Water Research*, 38, 3297-3303.

RUBIO, J., CARISSIMI, E. & ROSA, J. (2007) Flotation in water and wastewater treatment and reuse: recent trends in Brazil. *International Journal of Environment and Pollution*, 30, 197 - 212.

SALEM, Z., HAMOURI, K., DJEMAA, R. & ALLIA, K. (2008) Evaluation of landfill leachate pollution and treatment. *Desalination*, 220, 108-114.

SCHWARZENBECK, N., LEONHARD, K. & WILDERER, P. (2004) Treatment of landfill leachate - high tech or low tech? A case study. *Water Science and Technology*, 48, 277-284.

SHAO, L.M., HE, P.J. & LI, G.J. (2008) In situ nitrogen removal from leachate by bioreactor landfill with limited aeration. *Waste Management*, 28, 1000-1007.

SHISKOWSKI, D. & MAVINIC, D. (1998) Biological treatment of a high ammonia leachate: influence of external carbon during initial startup. *Water Research*, 32, 2533-2541.

SHU, H., FAN, H., CHANG, M. & HSIEH, W. (2006) Treatment of MSW landfill leachate by a thin gap annular UV/H2O2 photoreactor with multi-UV lamps. *Journal of Hazardous Materials*, 129, 73-79.

SILVA, A.C., DEZOTTI, M. & SANT'ANNA, G.L. (2004) Treatment and detoxification of a sanitary landfill leachate. *Chemosphere*, 55, 207-214.

SMITH, D. (1995) Submerged filter biotreatment of hazardous leachate in aerobic, anaerobic, and anaerobic/aerobic systems. *Hazardous Waste and Hazardous Materials*, 12, 167-183.

SPENGEL, D. & DZOMBAK, D. (1991) Treatment of a landfill leachate with rotating biological contactors: bench-scale experiments. *Research Journal Water Pollution Control Federation*, 63, 971-981.

STEPHENSON, T., POLLARD, S.J.T. & CARTMELL, E. (2004) Feasibility of biological aerated filters (bafs) for treating landfill leachate. *Environmental Technology*, 25, 349.

TATSI, A.A., ZOUBOULIS, A.I., MATIS, K.A. & SAMARAS, P. (2003) Coagulation-flocculation pretreatment of sanitary landfill leachates. *Chemosphere*, 53, 737-744.

TAUCHERT, E., SCHNEIDER, S., DE MORAIS, J.L. & PERALTA-ZAMORA, P. (2006) Photochemically-assisted electrochemical degradation of landfill leachate. *Chemosphere*, 64, 1458-1463.

TILCHE, A. & VIEIRA, S.M. (1991) Discussion report on reactor design of anaerobic filters and sludge bed reactors. *Water Science and Technology*, 24, 193-206.

TIZAOUI, C., BOUSELMI, L., MANSOURI, L. & GHRABI, A. (2007) Landfill leachate treatment with ozone and ozone/hydrogen peroxide systems. *Journal of Hazardous Materials*, 140, 316-324.

TSILOGEORGIS, J., ZOUBOULIS, A., SAMARAS, P. & ZAMBOULIS, D. (2008) Application of a membrane sequencing batch reactor for landfill leachate treatment. *Desalination*, 221, 483-493.

USHIKOSHI, K., KOBAYASHI, T., UEMATSU, K., TOJI, A., KOJIMA, D. & MATSUMOTO, K. (2002) Leachate treatment by the reverse osmosis system. *Desalination*, 150, 121-129.

UYGUR, A. & KARGI, F. (2004) Biological nutrient removal from pre-treated landfill leachate in a sequencing batch reactor. *Journal of Environmental Management*, 71, 9-14.

VISVANATHAN, C., CHOUDHARY, M., MONTALBO, M. & JEGATHEESAN, V. (2007) Landfill leachate treatment using thermophilic membrane bioreactor. *Desalination*, 204, 8-16.

WALL, D. & ZEISS, C. (1995) Municipal landfill biodegradation and settlement. *Journal of Environmental Engineering*, 121, 214-224.

WANG, C., LEE, P., KUMAR, M., HUANG, Y., SUNG, S. & LIN, J. (2010) Simultaneous partial nitrification, anaerobic ammonium oxidation and denitrification (SNAD) in a full-scale landfill-leachate treatment plant. *Journal of Hazardous Materials*, 175, 622-628.

WANG, F., EL-DIN, M.G. & SMITH, D.W. (2004) Oxidation of aged raw landfill leachate with O_3 only and O_3/H_2O_2: treatment efficiency and molecular size distribution analysis. *Ozone: Science and Engineering*, 26, 287-298.

WANG, S., WU, X., WANG, Y., LI, Q. & TAO, M. (2008) Removal of organic matter and ammonia nitrogen from landfill leachate by ultrasound. *Ultrasonics Sonochemistry*, 15, 933-937.

WANG, X., CHEN, S., GU, X. & WANG, K. (2009) Pilot study on the advanced treatment of landfill leachate using a combined coagulation, Fenton oxidation and biological aerated filter process. *Waste Management*, 29, 1354-1358.

WELANDER, U., HENRYSSON, T. & WELANDER, T. (1997) Nitrification of landfill leachate using suspended-carrier biofilm technology. *Water Research*, 31, 2351-2355.

WELANDER, U., HENRYSSON, T. & WELANDER, T. (1998) Biological nitrogen removal from municipal landfill leachate in a pilot scale suspended carrier biofilm process. *Water Research*, 32, 1564-1570.

WISZNIOWSKI, J., ROBERT, D., SURMACZ-GORSKA, J., MIKSCH, K. & WEBER, J. (2006) Landfill leachate treatment methods: A review. *Environmental Chemistry Letters*, 4, 51-61.

WISZNIOWSKI, J., SURMACZ-GORSKA, J., ROBERT, D. & WEBER, J. (2006) The effect of landfill leachate composition on organics and nitrogen removal in an activated sludge system with bentonite additive. *Journal of Environmental Management*, 85, 59-68.

WU, J.J., WU, C.C., MA, H.W. & CHANG, C.C. (2004) Treatment of landfill leachate by ozone-based advanced oxidation processes. *Chemosphere*, 54, 997-1003.

XU, Z., ZENG, G., YANG, Z., XIAO, Y., CAO, M., SUN, H. ET AL. (2010) Biological treatment of landfill leachate with the integration of partial nitrification, anaerobic ammonium oxidation and heterotrophic denitrification. *Bioresource Technology*, 101, 79-86.

ZAYEN, A., MNIF, S., ALOUI, F., FKI, F., LOUKIL, S., BOUAZIZ, M. & SAYADI, S. (2010) Anaerobic membrane bioreactor for the treatment of leachates from Jebel Chakir discharge in Tunisia. *Journal of Hazardous Materials*, 177, 918-923.

ZHANG, D.Q., TAN, S.K. & GERSBERG, R.M. (2010) Municipal solid waste management in China: Status, problems and challenges. *Journal of Environmental Management*, In Press, Corrected Proof.

ZHANG, H., ZHANG, D. & ZHOU, J. (2006) Removal of COD from landfill leachate by electro-Fenton method. *Journal of Hazardous Materials*, 135, 106-111.

ZHANG, T., DING, L. & REN, H. (2009) Pretreatment of ammonium removal from landfill leachate by chemical precipitation. *Journal of Hazardous Materials*, 166, 911-915.

ZHAO, X., QU, J., LIU, H., WANG, C., XIAO, S., LIU, R. ET AL. (2010) Photoelectrochemical treatment of landfill leachate in a continuous flow reactor. *Bioresource Technology*, 101, 865-869.

ZHONG, Q., LI, D., TAO, Y., WANG, X., HE, X., ZHANG, J. ET AL. (2009) Nitrogen removal from landfill leachate via ex situ nitrification and sequential in situ denitrification. *Waste Management*, 29, 1347-1353.

ZOUBOULIS, A., LOUKIDOU, M. & CHRISTODOULOU, K. (2001) Enzymatic treatment of sanitary landfill leachate. *Chemosphere*, 44, 1103-1108.

ZOUBOULIS, A.I., JUN, W. & KATSOYIANNIS, I.A. (2003) Removal of humic acids by flotation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 231, 181-193.

Chapter 3

Rotating Biological Contactors: a Review on Main Factors Affecting Performance

Rotating Biological Contactors (RBCs) constitute a very unique and superior alternative for biodegradable matter and nitrogen removal on account of their feasibility, simplicity of design and operation, short start-up, low land area requirement, low energy consumption, low operating and maintenance cost and treatment efficiency. The objective of this chapter is to present an overview of scientific literature on rotating biological contactors. Particular attention is given on parameters that affect performance like rotational speed, organic and hydraulic loading rates, retention time, biofilm support media, staging, temperature, influent wastewater characteristics, biofilm characteristics, dissolved oxygen levels, effluent and solids recirculation, step feeding and medium submergence. Some rotating biological contactors scale-up and design considerations, operational problems and comparison with other wastewater treatment systems are also reported.

The information presented in this Chapter has been published in: CORTEZ S., TEIXEIRA P., OLIVEIRA R. & MOTA M. (2008). Rotating biological contactors: a review on main factors affecting performance. *Reviews in Environmental Science and Biotechnology*, 7 (2), 155-172.

3. ROTATING BIOLOGICAL CONTACTORS: A REVIEW ON MAIN FACTORS AFFECTING PERFORMANCE

3.1 INTRODUCTION

A rotating biological contactor (RBC) is an attached growth bioreactor that offers an alternative technology to the conventional activated sludge process.

The first RBC system was used in the early 1900s and consisted of a cylinder with wooden slats (MATHURE & PATWARDHAN, 2005). The availability of polystyrene marked the beginning of commercial application of RBCs with the first full-scale system being installed in Germany in 1958 (RODGERS & ZHAN, 2003). Significant refinements in media type and equipment configuration occurred during the 1960s and early 1970s (TCHOBANOGLOUS & BURTON, 1991; GRADY ET AL., 1999). Currently, there are many thousands of units operating worldwide and several different designs available depending upon specific requirement criteria (MBA ET AL., 1999).

A RBC unit typically consists of a series of closely spaced large flat or corrugated disks that are mounted on a common horizontal shaft and are partially or completely submerged in wastewater (Figure 3.1).

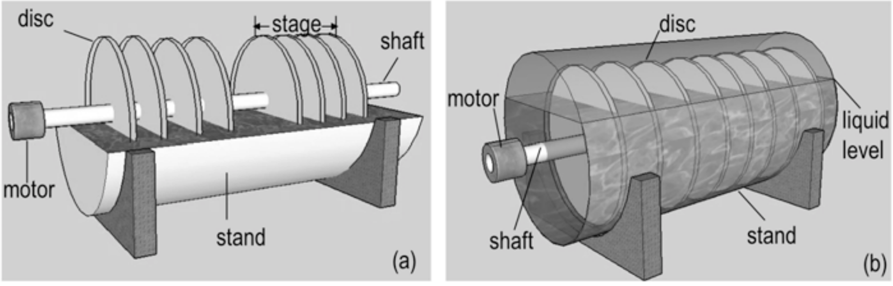

Figure 3.1 Schematic diagram of RBC units: (a) conventional RBC with two-stages (b) single-stage closed RBC with high submergence level.

A drum filled with some lightweight packed supports can also be used in place of conventional disks. The shaft continually rotates by a mechanical motor or a compressed air drive and a biofilm is established onto the entire surface area of the media, which metabolizes the organic materials contained in the wastewater. In aerobic processes the rotation of the media promotes oxygen transfer and maintains the biomass in aerobic conditions. The rotation also provides turbulence in the mixed liquor surface and enables the removal of excess solids from the media (PATWARDHAN, 2003; RODGERS & ZHAN, 2003). Biomass clarification is used to remove these solids.

RBC systems due to their advantages (Table 3.1) constitute a very unique and superior alternative for biodegradable matter and nitrogen removal.

Table 3.1 General advantages and drawbacks of the RBC process.

Advantages	Drawbacks
Land requirement relatively small	Difficult scale-up
Easy construction and expansion	Slow process start-up
Compact design with separate compartments	Adequate primary treatment and secondary clarifier required
Simple process control and monitoring	Limited process flexibility
Low operating and maintenance cost	
Short hydraulic retention times	
High oxygen transfer efficiency	
High biomass concentration per volume reactor	
Low sludge volume index values in the second clarifier	
No requirement of sludge recirculation	
Resistance to shock and toxic loads	
No problems with bad odors and flies	

Over the years rotating biological contactors have been successfully used to provide secondary treatment to municipal wastewater from small units serving residential dwellings to large ones treating flows of up to several million liters per day (BANERJEE, 1997B). They have also been used to nitrify municipal wastewater, either in combined carbon oxidation and nitrification applications or in separate stage nitrification applications, denitrification and phosphorus removal. In addition, decolorization of wastes like textile dyes (AXELSSON ET AL., 2006) and colored sugar refinery effluents (GUIMARÃES ET AL., 2005); bioremediation of landfill leachates (CEMA ET AL., 2007) or organopollutants such as of chlorophenols (RADWAN & RAMANUJAM, 1997; MAJUMDER & GUPTA, 2007) and thrichloroethylene (BRAR & GUPTA, 2000); treatment of effluents from wineries (MALANDRA ET AL., 2003), bakeries (NAHID ET AL., 2001), food processors (NASR ET AL., 2006), pulp and paper mills (SELVAM ET AL., 2002), leather tanneries (ZAO-YAN & ZHEN-SAN, 1990) and other biodegradable industrial discharges can be performed by the RBC system.

In the last decade, RBC facilities tightly closed to avoid air entrance started to be used for anoxic (denitrification) (TEIXEIRA & OLIVEIRA, 2001) or anaerobic processes (LU & YEH, 1995; LU, LI, ET AL., 1997; LU, LIN, ET AL., 1997).

The RBC system optimization and adaptability under different environmental conditions and influent characteristics remain challenging tasks for the efficient design and use of this technology.

3.2 FACTORS AFFECTING PERFORMANCE

The performance of rotating biological contactors depends upon several design parameters. Particularly significant are: rotational speed, organic and hydraulic loading rates, hydraulic retention time, RBC media, staging, temperature, wastewater and biofilm characteristics, dissolved oxygen levels, effluent and solids recirculation, step-feeding and medium submergence.

3.2.1 ROTATIONAL SPEED

The rotational speed of the RBC media is a very important parameter that affects nutrient and oxygen mass transfer in the biofilm and consequently substrate removal. Table 3.2 summarizes some studies on the effect of rotational speed in the performance of RBC systems.

Usually an increase on the speed of rotation increases the dissolved oxygen concentration available to the microorganisms and as a result they are able to degrade the substrate at a higher rate (ISRANI ET AL., 2002). However, increasing the rotational speed leads to higher power consumption, which may not be economical for wastewater treatment applications (RAMSAY ET AL., 2006). Besides, if the rotational speed gets too high, the microorganisms will be stripped off the media, deteriorating the effluent quality and lowering the biodegradation rate in the reactor.

Packed supports will provide considerably more oxygenation than disk RBCs at the same rotational speed, but they will require greater power consumption (HOCCHEIMER & WHEATON, 1998).

Thus, the guiding principle is to adopt the minimum speed commensurate with acceptable treatment. According to (MATHURE & PATWARDHAN, 2005), typically rotational speeds are 1-10 rpm for RBC media in disk form with disks with 1-4 m diameter mounted on shafts around 5-10 m long.

Table 3.2 Experimental details and summary of results of different studies on the effect of rotational speed in the performance of RBC systems.

Type of operation and scale	Reactor specifications				Type of wastewater	Modified parameters			Performance	Reference
	Type of material and media	Media dimensions	No. of stages/no. of disks or filling ratio	Submergence (%)		Hydraulic loading/ influent flow rate	Inlet organic loading/ substrate concentration	Rotational speed		
Aerobic lab-scale	Stainless steel disks covered with cloth	Diameter: 0.09 m	1/9	50	Synthetic phenolic wastewater	8.77-23.42 dm^{3}·m^{-2}·h^{-1}	1754-3508 mg phenol·m^{-2}·h^{-1}	40-175 rpm	For 23.42 dm^{3}·m^{-2}·h^{-1}and 3508 mg phenol·m^{-2}·h^{-1}at: -40 rpm: 30.9 mg phenol removed·dm^{-3} -150 rpm: 114 mg phenol removed·dm^{-3}	ISRANI ET AL. (2002)
	Lightweight clear plastic disks	Diameter: 0.35 m	3/54	-	Food cannery wastewater	-	22.13 g COD·m^{-2}·d^{-1}	3 and 11 rpm	At: -3 rpm: 1.03 g SCOD removed·dm^{-3}·d^{-1} and 62.67% SCOD removed -11 rpm: 1.76 g SCOD removed·dm^{-3}·d^{-1} and 93.70% SCOD removed	NAJAFPOUR ET AL. (2006)
	Propylene Pallrings	Diameter: 2.54 cm	3/85%	40	Bakers yeast wastewater	-	210 g COD·m^{-2}·d^{-1} 456 mg COD·dm^{-3}	15 and 17 rpm	At: -15 rpm: 77% COD removed -17 rpm: 78% COD removed	NAHID ET AL. (2001)
Aerobic pilot-scale	Hard polyethylene disks	Diameter: 0.5 m	6/16	37	Industrial wastewater	0.013 and 0.017 m^{3}·m^{-2}·d^{-1}	5.3-7.8 mg SBOD·m^{-2}·d^{-1}	8 and 11 rpm	No effect was observed on RBC performance. Perhaps the range of the rotational speed studied was greater than the optimum.	TORKIAN ET AL. (2003)
Anaerobic lab-scale	Acrylic plastic disks	Diameter: 0.12 m	4/60	100	Synthetic high-strength organic wastewater	6.3 kg COD m^{-3}·d^{-1}	52.8 g COD·m^{-2}·d^{-1}	0-60 rpm	For the first stage at: -0 rpm: 26% COD removed -24 rpm: 45% COD removed -48 rpm: 32% COD removed -60 rpm: 28% COD removed	LU ET AL. (1997a)
Anoxic full-scale	-	Diameter: 3 m	1/91	40	Municipal wastewater		9.80-12.40 mg N-NO_3^-·dm^{-3}	0.67-2.1 min^{-1}	At: 0.67 min^{-1}-1.53 g N-NO_3^-removed·m^{-2}·d^{-1} and 7.0% denitrifying capacity 1.4 min^{-1}-1.16 g N-NO_3^- removed·m^{-2}·d^{-1} and 7.5% denitrifying capacity 2.1 min^{-1}-1.29 g N-NO_3^-removed·m^{-2}·d^{-1} and 7.5% denitrifying capacity	HANHAN ET AL. (2005)

3.2.2 ORGANIC LOADING

The organic loading of a RBC reactor must be accurately defined during planning and designing. The variation of the organic loading rate is generally accomplished by changing the inlet flow rate or the hydraulic retention time, which also results in a change in the hydraulic loading (NAJAFPOUR ET AL., 2005). Table 3.3 summarizes the experimental details and performance results of different works to study the effect of organic loading on the performance of some RBC systems.

Available data show that, for a given system, as the applied organic loading rate increases, the substrate removal rate increases and removal efficiency decreases. Reduction in substrate removal efficiency may be an indication of limitation in dissolved oxygen.

Under normal operating conditions, carbonaceous substrate is mainly removed in the first-stage of the RBC. To avoid oxygen transfer limitations the first-stage design load must be limited to a BOD_5 load of about 30 g $BOD_5 \cdot m^{-2} \cdot d^{-1}$ or to a soluble BOD_5 load of 12-20 g $BOD_5 \cdot m^{-2} \cdot d^{-1}$ according to WEF & ASCE (1998). The use of higher first-stage organic loadings will increase the probability of developing problems such as excessive biofilm thickness, depletion of dissolved oxygen, deterioration of process performance, appearance of H_2S odors and excessive growth of nuisance organisms such as *Beggiatoa* (TCHOBANOGLOUS & BURTON, 1991; GRADY ET AL., 1999). Overloading problems can be overcome by removing baffles between the first and second-stages to reduce surface loading and increase oxygen transfer. Other approaches include supplemental air systems, step-feed, or recycle from the last stage (SURAMPALLI & BAUMANN, 1997).

The organic loading affects nitrification in a RBC unit. In the initial stages, where the organic load is high, heterotrophic bacteria offer strong competition to nitrifiers displacing them within the bioreactor (BRAZIL, 2006). Therefore, the maximum nitrification rate occurs when the soluble BOD load reduces sufficiently, which always takes place in the latter stages of the RBC set-up. In the case of full-scale RBCs for nitrification of municipal wastewater with four units in series, the German ATV guideline (ATV, 1989) proposes a design value of 5 g $BOD_5 \cdot m^{-2} \cdot d^{-1}$. NOWAK (2000) has investigated nitrification in full-scale RBCs (with disks and plastic packages) and proposed that the surface-loading rate should not exceed 2.5 g $BOD_5 \cdot m^{-2} \cdot d^{-1}$ to keep the effluent ammonium concentration below 5 mg $N\text{-}NH_4^+ \cdot L^{-1}$, at temperatures above 13 ºC. In the same investigation nitrification rates of 1.5 g N oxidized$\cdot m^{-2} \cdot d^{-1}$ at 8 ºC and of 1.8 g N oxidized$\cdot m^{-2} \cdot d^{-1}$ at 13 ºC were obtained in tertiary full-scale RBCs with ammonium effluent concentrations mostly below 4 mg $N\text{-}NH_4^+ \cdot L^{-1}$.

Table 3.3 Experimental details and summary of results of different studies on the effect of organic and hydraulic loading in the performance of RBC systems.

Type of operation and scale	Reactor specifications					Type of wastewater	Modified parameters			Performance	Reference
	Type of material and media	Media dimensions	No. of stages/no. of disks or filling ratio	Submer-gence (%)	Rotational speed (rpm)		Hydraulic loading/ influent flow rate	Inlet organic loading/ substrate concentration	HRT (h)		
Aerobic lab-scale	Acrylic disks	Diameter: 0.25 m	3/42	32	5	High strength municipal wastewater	20-32 $dm^3 \cdot m^{-2} \cdot d^{-1}$	10-32 g $COD \cdot m^{-2} \cdot d^{-1}$ 1.1-3.3 g $N \cdot m^{-2} \cdot d^{-1}$	24-15	For HRT= 24 h and HLR= 20 $dm^3 \cdot m^{-2} \cdot d^{-1}$, at: -20 g $COD \cdot m^{-2} \cdot d^{-1}$ and 2.2 g $N \cdot m^{-2} \cdot d^{-1}$: 19.4 g $COD \cdot m^{-2} \cdot d^{-1}$ removed in the 1st stage and 99.45% $N\text{-}NH_4^+$ overall removed; -10 g $COD \cdot m^{-2} \cdot d^{-1}$ and 1.1 g $N \cdot m^{-2} \cdot d^{-1}$: 8.7 g $COD \cdot m^{-2} \cdot d^{-1}$ removed in the 1st stage and 90.50% $N\text{-}NH_4^+$ overall removed	GUPTA & GUPTA (2001)
	Lightweight clear plastic disks	Diameter: 0.35 m	1/60	-	10	Palm oil mill wastewater	1.1-6 $dm^3 \cdot h^{-1}$	38-210 g $COD \cdot m^{-2} \cdot d^{-1}$ 1 – 6.2 g $N \cdot m^{-2} \cdot d^{-1}$	55-10	At: - 38 g $COD \cdot m^{-2} \cdot d^{-1}$ and 10 h: 88% COD removed and 80 g COD $removed \cdot m^{-2} \cdot d^{-1}$; - 210 g $COD \cdot m^{-2} \cdot d^{-1}$ and 55 h: 35% COD removed and 72 g COD $removed \cdot m^{-2} \cdot d^{-1}$ At: - 1 g $N \cdot m^{-2} \cdot d^{-1}$ and 55 h: 80% TKN removed and 0.8 g N $removed \cdot m^{-2} \cdot d^{-1}$; - 6.2 g $N \cdot m^{-2} \cdot d^{-1}$ and 10 h: 68% TKN removed and 4 g N $removed \cdot m^{-2} \cdot d^{-1}$	NAJAFPOUR ET AL. (2005)
	Propylene square rings	Diameter: 68 mm	1/-	40	3	Synthetic food industrial wastewater	0.6-1.2g $BOD_5 \cdot dm^{-3} \cdot d^{-1}$	2.04-4.07 g $BOD_5 \cdot m^{-2} \cdot d^{-1}$	16-8	At: -2.04 g $BOD_5 \cdot m^{-2} \cdot d^{-1}$ and 0.6 g $BOD_5 \cdot dm^{-3} \cdot d^{-1}$: 91.7, 92.5 and 47.4 for COD, BOD_5 and TKN removal, respectively; -4.07 g $BOD_5 \cdot m^{-2} \cdot d^{-1}$ and 1.2 g $BOD_5 \cdot dm^{-3} \cdot d^{-1}$: 87.4, 90.0 and 44.1 for COD, BOD_5 and TKN removal, respectively	SIRIANUNTAPIBOON (2006)

Table 3.3 Experimental details and summary of results of different studies on the effect of organic and hydraulic loading in the performance of RBC systems. *Continuation*

Type of operation and scale	Reactor specifications					Type of wastewater	Modified parameters			Performance	Reference
	Type of material and media	Media dimensions	No. of stages/no. of disks or filling ratio	Submer-gence (%)	Rotational speed (rpm)		Hydraulic loading/ influent flow rate	Inlet organic loading/ substrate concentration	HRT (h)		
Aerobic pilot-scale	Hard polyethylene disks	Diameter: 0.5 m	6/16	37	8	Industrial wastewater	0.013 $m^3 \cdot m^{-2} \cdot d^{-1}$	5.3-17.8 mg $SBOD_5 \cdot m^{-2} \cdot d^{-1}$	16	At: -5.3 mg $SBOD_5 \cdot m^{-2} \cdot d^{-1}$: 76, 75 and 85% for COD, BOD_5 and $SBOD_5$ removal, respectively; -17.8 mg $SBOD_5 \cdot m^{-2} \cdot d^{-1}$: 59, 65 and 74% for COD, BOD_5 and $SBOD_5$ removal, respectively	Torkian et al. (2003)
Aerobic full-scale	Disks	-	4/-	-	-	Municipal wastewater	3785 $m^3 \cdot d^{-1}$	18-42 mg $N\text{-}NH_4^+ \cdot dm^{-3}$ Lower loading period: 164.4 mg $SCOD \cdot dm^{-3}$ Higher loading period: 430 mg $SCOD \cdot dm^{-3}$	-	At: -164.4 mg $SCOD \cdot dm^{-3}$: 72.7 and 20.2% for SCOD and $N\text{-}NH_4^+$ removal, respectively; -430 mg $SCOD \cdot dm^{-3}$: 67.4 and 25.6% for SCOD and $N\text{-}NH_4^+$ removal, respectively	Surampalli & Baumann (1997)

NOTE: – Denotes that the particular information is unavailable; BOD_5: 5-day biochemical oxygen demand; COD: chemical oxygen demand; HLR: hydraulic loading rate; HRT: hydraulic retention time; SCOD: soluble chemical oxygen demand; $SBOD_5$: 5-day soluble biochemical oxygen demand; TKN: total Kjeldahl nitrogen

3.2.3 HYDRAULIC LOADING

The performance of RBCs has historically been correlated with hydraulic loading. Increasing the flow rate through the bioreactor reduces the liquid retention time in the system and results in a reduction in removal efficiency (Table 3.3). In defined conditions increasing hydraulic loading also leads to an increase of attached biomass on RBC media surface (ALEMZADEH & VOSSOUGHI, 2001).

Hydraulic loading rates vary widely depending on the design, the substrate being removed and the effluent concentration desired (HOCCHEIMER & WHEATON, 1998). Some RBC manufacturers developed design relationships for municipal wastewater in which effluent quality is plotted as a function of hydraulic loading, at a given temperature. These relationships are very useful for characterizing full-scale RBC facilities performance. However, since in these relationships the intrinsic biodegradation constants and hydrodynamics of the system are not taken into consideration and equipment manufacturers provide optimistic estimates, care should be exercised in the selection and application of such empirical relationships (GRADY ET AL., 1999).

Typical hydraulic loading rate range recommended by RBC manufacturers (full-scale) is 1.292 – 6.833 $dm^3 \cdot m^{-2} \cdot h^{-1}$ (TCHOBANOGLOUS & BURTON, 1991).

Due to the large amount of biological mass present (low operating feed/microorganisms) rotating biological contactors offer good stability under high or toxic hydraulic and organic loadings (SIRIANUNTAPIBOON, 2006).

3.2.4 HYDRAULIC RETENTION TIME

Studies with RBC systems have revealed that longer contact times improve the diffusion of the substrate into the biofilm and its consequent removal of the influent (HANHAN ET AL., 2005; NAJAFPOUR ET AL., 2006). This trend is also verified with toxic and heavy metals substrates (COSTLEY & WALLIS, 2000; MAJUMDER & GUPTA, 2007; SIRIANUNTAPIBOON & CHUAMKAEW, 2007).

Too short a hydraulic retention time (HRT) will result in low removal rates, whereas too long a HRT will not be economically feasible. In order for a biological system to compete successfully with conventional physicochemical methods of treatment, the shortest possible hydraulic retention time associated with the most efficient removal rates is required (COSTLEY & WALLIS, 2000).

A significant advantage offered by full-scale RBCs is to require short hydraulic retention periods (generally less than one hour) (BENEFIELD & RANDALL, 1980).

3.2.5 RBC MEDIA

RBC systems have evolved considerably from the original design of several rotating disks. Many variations now exist, ranging from simple flat disks through corrugations to cellular meshes all of which are designed to give extra surface area per unit volume (Figure 3.2). However, as the supporting medium gets more complex its cost increases (WARE ET AL., 1990).

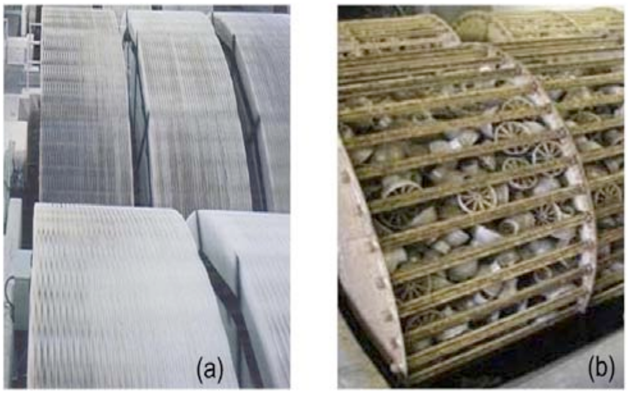

Figure 3.2 (a) Closely spaced disks in a full-scale RBC [<http://www.dmw.co.jp>] (b) RBC with a random packed medium [<http://www.wateronline.com>].

The media used for RBCs are actually produced from Styrofoam, polycarbonate sheets or high-density polyethylene (HDPE) and others (Table 3.2 and Table 3.3). HDPE containing UV inhibitors such as carbon black is the material most commonly used and is provided in different configurations or corrugation patterns (WARE ET AL., 1990; RODGERS & ZHAN, 2003). Corrugations enhance structural stability, improve mass transfer and increase the available surface area (GRADY ET AL., 1999). The types of biofilm supporting media are classified on the basis of surface area provided and are commonly termed low- (or standard-) density, medium-density and high-density. Standard-density media are defined as having a surface area of about 115 $m^2 \cdot m^{-3}$ of reactor, with larger spaces between media layers and are normally used in the lead stages of a RBC process train. Medium and high-density media have surface areas of about 135 to 200 $m^2 \cdot m^{-3}$ of reactor and are used typically in the middle and final stages of a RBC system where thinner biological growth occurs (TCHOBANOGLOUS & BURTON, 1991; PATWARDHAN, 2003). Standard-density media must be used in the first's two stages that are highly loaded or where

Beggiatoa growth is possible because excess biological growths are more difficult to remove from high-density media (GRADY ET AL., 1999).

Some modifications of conventional RBCs media have been explored at laboratory-scale with positive results concerning substrate removal. In order to enhance biofilm area and volume, RADWAN & RAMANUJAM (1997) modified RBC disks by attaching porous netlon sheets. GUIMARÃES ET AL. (2005) also attached a layer of polyurethane foam on plastic disks in order to enhance the adhesion of filamentous organisms.

At the laboratory and pilot-scale, random packed media have been successfully used as substitutes for disks. Such media provide more area for attachment of the biofilm within the same RBC reactor size, contributing to higher mass transfer efficiency due to increased turbulence. Besides they have low energy consumption and the fabrication cost is nearly one third that of disks (WARE ET AL., 1990; MATHURE & PATWARDHAN, 2005). Different types of packing such as Pallrings, saddles and cylindrical plastic elements with distinctive sizes have been applied in random packed RBC systems presenting attractive results (NAHID ET AL., 2001; MATHURE & PATWARDHAN, 2005; SIRIANUNTAPIBOON, 2006).

Whilst the use of random packed media is not new, few manufacturers are commercially exploiting it. On large-scale, like with conventional disks, some operational problems can occur, leading to a lot or any biofilm growth. With careful design it may be possible to develop packing media with the appropriate orientation and movement allowing the development of a suitable biofilm in a full-scale packed cage (WARE ET AL., 1990).

As recommendation, at the design stage of a particular RBC system, it is necessary to evaluate the characteristics of the wastewater being treated, the treatment objectives and to compare the various types of biofilm supporting media reported in the literature in terms of costs, the interfacial area offered, mass transfer coefficients, and power consumption. This will enable the process design engineer to choose the most appropriate type of medium (PATWARDHAN, 2003).

3.2.6 STAGING

Staging of RBC media is recommended to maximize removal of BOD_5 and nitrogen-ammonium ($N\text{-}NH_4^+$). Stages are accomplished by using baffles in a tank or using a series of tanks. Typical RBC staging arrangements are illustrated in Figure 3.3.

In secondary treatment applications, rotating biological contactors shall be designed and operated in a series of three stages per flow. For combined BOD_5 and $N\text{-}NH_4^+$ removal a minimum of four stages is recommended per flow. For small plants, multiple stages are acceptable on a single shaft oriented in parallel to the direction of flow. In larger installations, shafts are mounted perpendicular to flow with several stages in series (TCHOBANOGLOUS & BURTON, 1991).

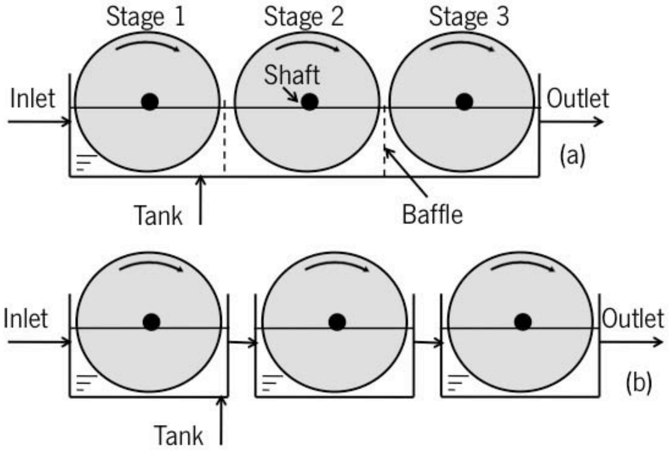

Figure 3.3 Staging arrangements of RBC units accomplished by (a) baffles in a tank (b) using a series of tanks, both with flow perpendicular to shaft.

As the wastewater flows through the system, each subsequent stage receives an influent with an organic concentration lower than the previous stage. Because heterotrophic bacteria grow faster than nitrifiers the first stage tends to be primarily an organic removal device, unless the wastewater organic content is very low. As the wastewater moves to the second and subsequent stages the RBC tends to first removing ammonium and then nitrite with the final product being nitrate, assuming that the RBC is sized and operated correctly (HOCCHEIMER & WHEATON, 1998). When there is recycling of wastewater from the last stage to the first one, denitrification may be achieved in the first stage, where there is high organic loading and low dissolved oxygen content.

Experimental results of BANERJEE (1997B) justify the use of staging in a RBC reactor, since mixing decreases gradually along the reactor, better approximating the system to the plug-flow regime. RADWAN & RAMANUJAM (1997) concluded that staging in the design of RBC systems is especially important at higher organic loadings and also if high effluent treatment quality is required. Moreover, according to TAWFIK ET AL. (2002) staging of RBC decreases the detrimental effect of shock load on the performance of the system.

Different numbers of stages have been used in several applications (Table 3.2 and Table 3.3). The number of stages to be used depends on the organic content of the influent, flow rate and several other variables (HOCCHEIMER & WHEATON, 1998). Staging calculations, based on COD and N-NH_4^+ effluent concentrations, can be done using literature tables (GRADY ET AL., 1999), with the appropriate adaptations.

3.2.7 TEMPERATURE

Temperature is one of the most important factors that affect the rate of biological processes and consequently influences RBCs performance. At limited conditions, an increase in the influent temperature leads to an increase in the microbial activity and a higher substrate removal can be observed in all RBC stages (BANERJEE, 1997A; ISRANI ET AL., 2002). Low influent temperatures can adversely affect biofilm establishment, particularly in its early stages (COSTLEY & WALLIS, 2000). When wastewater temperatures less than 13 ºC are expected, organic and nitrogen removal rates may decrease.

Temperature correction factors need to be taken into account in design criteria and can be obtained from the equipment manufacturers or from pilot studies. Generally, when the temperature drops from 13 to 5 ºC, nearly 2.5 times more media surface area is required for achieving the same performance (RODGERS & ZHAN, 2003).

In biofilms the nitrification process is less temperature-dependent than in activated sludge. The nitrification rate increases by about 4.5% per ºC (NOWAK, 2000).

Year-round operation requires that rotating contactors be covered to protect the biological growth from freezing temperatures or excessive heat gain, which accelerates media deterioration. Covers also reduce heat loss, allow the off gas to be collected for odor control, and minimize algae growth. Individual covers are preferable than entire installations being placed in buildings (TCHOBANOGLOUS & BURTON, 1991).

3.2.8 WASTEWATER CHARACTERISTICS

The influent substances and its concentration levels may play a significant role in the operation of rotating biological contactors. For example, the flux into the biofilm may be smaller for large and slowly biodegradable compounds. The presence of particulate organic matter can reduce the flux of soluble substrate since the particulate matter occupies space within the biofilm, which decreases the rate of biodegradation (GRADY ET AL., 1999).

When sulphide is present, either in the influent wastewater or by its production deep within the biofilm, sulphide-oxidizing bacteria such as *Beggiatoa* will grow on the biofilm surface. The production of sulphide within the biofilm is due to oxygen depletion. *Beggiatoa* will compete with heterotrophic organisms for oxygen and in extreme cases will take over the first-stage of an overloaded RBC, shifting the load to the next stage and progressively taking over the system (MBA ET AL., 1999).

RBC units properly designed and supplemented with essential nutrients consistently produce the best effluents and maintain biofilm on the media with better adhesion characteristics, especially when treating industrial wastewater.

3.2.9 BIOFILM CHARACTERISTICS

To optimize the removal of organic matter and nitrogen compounds from wastewater in a RBC, an adequate understanding of the dynamic nature and characteristics of the biofilm, the major constituent of the process, is essential.

A biofilm is a living microbial system composed mainly of microorganisms, extracellular polymers, and water. The spatial distribution of these components within the biofilm matrix may influence the biofilm functions and the relationship to the immediate aquatic environment. This, in turn, depends on the operating conditions. For example, biofilm thickness depends on applied organic loading and shearing forces (GRIFFIN & FINDLAY, 2000).

Observations of full-scale RBCs biofilms treating municipal wastewaters report that biofilms from the initial stages have a gelatinous aspect, being usually grayish and may present some white zones probably due to filamentous bacteria like *Beggiatoa*. Biofilms of the last stages appear more compact: are always thinner than the first's stages and have a brown-like color or sometimes reddish. In addition, the main limiting factor of microfauna growth is the degree of pollution in the influent expressed in terms of COD or BOD_5. As long as this parameter decreases along the RBC, its effect as a limiting factor decreases too, resulting in an increase in the majority of existing species. Initial stages are almost entirely constituted by species of ciliates, whereas the last stages show more diversified communities, not only in species of ciliates but also in flagellates, amoebae and metazoa (MARTÍN-CERECEDA ET AL., 2001; SALVADÓ ET AL., 2004).

Microscopic studies reveal that the outer biofilm layer of a full-scale RBC is very heterogeneous and complex, mainly composed of filamentous bacteria, protozoa, green eukaryotic algae and small metazoans. The inner layer is more uniform and compact (MARTÍN-CERECEDA ET AL., 2001).

In aerobic RBC units for carbonaceous oxidation, during the initial stages, heterotrophs compete with nitrifiers in the outermost biofilm layer for oxygen and space. The microbial density is reduced in the innermost biofilm layer, which has a larger percentage of non-viable bacteria than the outer layer (RODGERS & ZHAN, 2003). The active metabolic cell fraction decreases from 35±13% in the outermost to 15±4% in the innermost biofilm (OKABE ET AL., 1996). When the depth of the biofilm is large and the concentration of dissolved oxygen (DO) in air is low, the outer layer acts aerobically and the inner side acts anoxic or anaerobically (NAHID ET AL., 2001). The filamentous organisms frequently present in the biofilm are *Beggiatoa* ssp. and *Sphaerotilus natans* (GALVAN ET AL., 2000). The development of *Beggiatoa*, as mentioned before, is always taken as a warning for the performance of RBC units because its blooming prevents the sloughing of thick biofilm from the disks, which can lead to overload on the media supports (RODGERS & ZHAN, 2003).

Biofilm ranging from 0.5 to 4.5 mm in thickness have been found in full-scale disk RBCs treating municipal wastewater. The biofilm thickness control is very important to avoid clogging or material fatigue stresses (GRIFFIN & FINDLAY, 2000). A positive mechanism to strip excessive biofilm growth from the media such as variable rotational speeds, supplemental air, air or water stripping or the ability to reverse shaft rotation must be provided to the RBC units (TCHOBANOGLOUS & BURTON, 1991).

3.2.10 DISSOLVED OXYGEN LEVELS

In an aerobic RBC system the biofilm is allowed to form on the medium, which is partly submerged in the wastewater and partly exposed to the air. The rotation alternately exposes this biofilm to atmospheric oxygen and wastewater. Oxygen transfers from the air to the RBC unit in three ways: by oxygen absorption at the liquid film over the biofilm surface when the biofilm is in the air; by direct oxygen transfer at the air-water interface; and by direct oxygen absorption by the microorganisms during the air exposures (GRADY, 1982).

Usually, as a consequence of an active respiration in the initial stages, the oxygen concentration reaches minimal levels, increasing along the reactor where substrate concentration is low.

An increase in the speed of rotation, at a given level of submergence, leads to an increase in the oxygen transfer capacity of a RBC, in terms of the overall oxygen transfer coefficient, K_La (RODGERS & ZHAN, 2003). At a particular rotational speed, as submergence increases the K_La decreases (MATHURE & PATWARDHAN, 2005). Figure 3.4 shows this behavior. Some researchers have attempted to develop empirical/mathematical models for the estimation of K_La in RBC reactors. It is very difficult, however, to model the oxygen transfer because these systems are very complex and include biofilm growth and detachment, the participation of suspended biomass, etc.

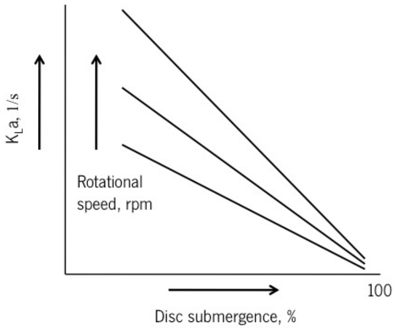

Figure 3.4 KLa values versus submergence level and rotational speed of RBC media.

ISRANI ET AL. (2002) and MATHURE & PATWARDHAN (2005) evaluated the performance of pilot-scale RBC systems in terms of the oxygen transfer efficiency (OTE). They observed that the OTE per unit energy consumed decreased rapidly with an increase in rotational speed and increased with a decrease in hydraulic loading rate. MATHURE & PATWARDHAN (2005) also compared the oxygen transfer efficiencies of a conventional RBC and a RBC with different packings such as rings, superintalox saddles and a wiremesh spiral bundle. The OTE values for the typical RBC were found to be 1-2 $kg{\cdot}kWh^{-1}$, which were poor in comparison with the values found with packings (2-5 $kg{\cdot}kWh^{-1}$).

Dissolved oxygen is very important in carbonaceous oxidation and nitrification being the most important design factor for aerobic RBCs. During operation oxygen levels must be properly controlled and to prevent from becoming a limiting factor, initial stages should have at least 2 mg $DO{\cdot}L^{-1}$ (NOWAK, 2000). If the rotating motion does not supply sufficient oxygen, a supplemental aeration system should be installed (SURAMPALLI & BAUMANN, 1997; RODGERS & ZHAN, 2003). Usually this promotes a remarkable performance of the RBC, with an established thinner and active aerobic biomass, allowing considerable cost savings in design and construction of RBC units.

Denitrification occurs if the oxygen in the liquid inside of the RBC media is depleted as well as in the liquid, which surrounds the fixed-film. Primary clarifier effluent is the carbon source for denitrification (NEU, 1994).

3.2.11 EFFLUENT AND SOLIDS RECIRCULATION

Effluent or solids recirculation is an attractive solution for existing RBC plants that need to be upgraded to meet stricter effluent limits or for increased performance. Improved COD, BOD_5 and ammonium removal efficiencies have been reported when recirculation is applied, increasing with recirculation ratios (KLEES & SILVERSTEIN, 1992; NEU, 1994). Improved nitrification with recirculation has been attributed to the dilution of influent biodegradable organic carbon.

In spite of being optional, recirculation should be considered in the RBC design for adverse conditions. The rate of recirculation recommended is approximately 25% of the average design flow (LE GROUP TEKNIKA, 1988).

3.2.12 STEP-FEEDING

To increase the process capacity, to have a more robust performance and to reduce or prevent overloads, the capability to step-feed RBC stage(s) should be provided. Working in a step-feed mode JANCZUKOWICZ & KLIMIUK (1992) and SAIKALY & AYOUB (2003) improved the removal rates and found higher dissolved oxygen values. The combined effect of step-feed and effluent recirculation in increasing RBC activity was reported by AYOUB & SAIKALY (2004), but for a simple soluble substrate.

Besides step feeding and recirculation other alternative modes of operation can be implemented. For example, to avoid the excessive fungal biofilm growth in the first-stage of the RBC system, after 17 days of operation, GUIMARÃES ET AL. (2005) reversed the feed inlet. With this simple modification it was possible to double the active biofilm lifetime, improving the removal efficiency.

3.2.13 RBC MEDIUM SUBMERGENCE

The percentage of RBC medium submergence depends on several factors, namely the operation type, microorganisms and characteristics of the effluent to be treated. Typically in aerobic processes of municipal wastewater treatment the submergence is about 40%, although in nutrients removal it can attain 60%. However, due to the diversity of industrial wastewater there is no reference value for disk submergence.

Increased submergence was developed to reduce shaft and bearing loads and to improve equipment reliability (TCHOBANOGLOUS & BURTON, 1991). Submerged biological contactors (SBCs), as are called, operate at 70-90% submergence providing the advantages of larger medium volume available and fewer SBC units required (SCHWINGLE ET AL., 2005). Submergence in excess of 50% will decrease the rate of oxygen transfer in the system, thereby if the SBC is used to treat wastewater aerobically, additional air drive units to provide oxygen and rotation must be used (RODGERS & ZHAN, 2003). The increased submergence combined with the air drive rotation of the SBC has dramatic economic and operating benefits (SCHWINGLE ET AL., 2005).

The deeper submerged RBCs can also be applied as anaerobic rotating biological contactors (LU & YEH, 1995; LU, LI, ET AL., 1997; LU, LIN, ET AL., 1997) or used for denitrification (TEIXEIRA & OLIVEIRA, 2001). In these applications the RBC units are completely closed to avoid air entrance.

At bench-scale various aspects of the anaerobic RBC process have been exploited (LU & YEH, 1995; LU, LI, ET AL., 1997; LU, LIN, ET AL., 1997). According to LAQUIDARA ET AL. (1986), this system combines advantages of the aerobic RBC reactor with the anaerobic process (no oxygen transfer limitations, low quantities of waste biological solids and recovery of the usable energy in the form of methane). Due to these advantages, the anaerobic RBC process appears to be well suited for treating both medium-strength and high-strength organic wastewater (LU, LI, ET AL., 1997).

There is a great scope of application for anaerobic RBCs in industrial wastewater treatment, which are presently considered suitable for treatment by other anaerobic processes. It is in anaerobic degradation that RBCs could prove to be even more successful than they have been in aerobic treatment (WARE ET AL., 1990).

The use of deeper submerged RBCs in denitrification is not very widespread. TEIXEIRA & OLIVEIRA (2001) investigated the effect of disk submergence on the performance of lab-scale RBCs, in terms of the denitrification process. For an influent $N\text{-}NO_3^-$ concentration of 50 $mg \cdot L^{-1}$, at 26 ºC and 2 rpm, using citrate as carbon source the higher efficiency (36.71 g $N\text{-}NO_3^- \cdot m^{-3} \cdot m^{-2}$ removed) was attained with a completely submerged reactor. With the partially (64.5%) submerged RBC only 16.97 g $N\text{-}NO_3^- \cdot m^{-3} \cdot m^{-2}$ were removed. Using a pilot-scale RBC with ethanol as carbon source, at 2 rpm and with a plastic package, MOHSENI-BANDPI & ELLIOTT (1996) achieved a maximum nitrate removal rate of 168 mg $N\text{-}NO_3^- \cdot m^{-2} \cdot h^{-1}$ for an influent of 130 mg $N\text{-}NO_3^- \cdot L^{-1}$.

3.3 RBC SCALE-UP

Effective design of full-scale rotating biological contactors based on data from bench and small pilot-scale studies has proven to be difficult because of the widespread use of an inappropriate scale-up procedure. Scale-up based only on criteria such as equal tip speed, same hydraulic loading, equal number of disks, would alter, for example, the stresses experienced by the microorganisms, as well as the biomass loading and the thicknesses of the biofilm and the liquid film. As a result, the RBC performance is likely to be affected. The influence of various geometries, hydrodynamics and chemical (mass transfer) processes need to be considered in the scale-up of RBCs, and it is not yet clear which of these should drive RBC scale-up (SPENGEL & DZOMBAK, 1992; PATWARDHAN, 2003).

Design relationships and curves developed by RBC manufacturers and pilot studies and/or full-scale data from similar systems provide the basis to optimize the expansion of an existing RBC system. A mechanistic model is also a useful tool for this purpose. Investigation of the dependence of disk biomass thickness and density on the shear force distribution appears to be the appropriate next step for improving RBC mechanistic models and resolving the RBC scale-up dilemma (SPENGEL & DZOMBAK, 1992).

3.4 OPERATIONAL PROBLEMS

In spite of all of the referred advantages, rotating biological contactors have some operating problems such as difficulty in maintenance of an appropriate biofilm thickness under adverse conditions (SIRIANUNTAPIBOON, 2006). Mechanical failures are also commonly pointed to RBCs. The most common are shaft, bearing and media support structure failures. These may arise due to overloading conditions, excess of biofilm growth, microbiologically influenced corrosion, low frequency corrosion fatigue, improper greasing and inadequate locking of nuts and bolts or poor engineering design (MBA ET AL., 1999).

A reputation for mechanical failures has restricted the growth of RBC technology (GRIFFIN & FINDLAY, 2000). With a thorough understanding of the mechanisms of mechanical failure and with the development of improved RBC biofilm supports and bearings and stronger shafts, among others, a new approach to RBC design has resulted in units with an expected operational life of twenty years. Also, the improved design could revolutionize applicability of RBCs to high flow/highly populated regions (MBA ET AL., 1999; BRAZIL, 2006).

3.5 RBCS *VERSUS* OTHER WASTEWATER TREATMENT SYSTEMS

RBCs provide a higher level of treatment than conventional high-rate packed-bed reactors. The efficiency of these two systems for the treatment of a UASB reactor effluent was compared by VAN BUUREN (1991): at a HRT of 3.3 hours, the packed-bed reactor removed 50% of COD while the RBC removed 70%. Moreover, at much shorter HRT of 0.24h the RBC still achieved 40-80% COD removal.

The RBC and activated sludge processes can produce high degrees of treatment. However, RBCs are generally less susceptible to upset due to loading changes and constitute a technology less complicated than activated sludge. NASR ET AL. (2007) compared, at laboratory-scale, these two biological processes for the treatment of chemical industrial wastewater (5239 mg $COD \cdot L^{-1}$ and 2615 mg $BOD_5 \cdot L^{-1}$). As both proved to be effective, producing effluents within the permissible limits, the engineering design of each treatment system (full-scale) was developed and the cost estimate indicated that the construction cost was similar for both systems, while the running cost of activated sludge was almost twice of the RBC. Thus, the use of the RBC system is recommended.

Although it is not possible to find easily comparable values in the literature between RBCs and other biological processes, Table 3.4 presents the characteristics and performance of several rotating biological contactors and of other aerobic biofilm and activated sludge processes.

Estimations reveal that RBCs require only about 25% of the energy consumption of an activated sludge system (US Filter, 1998) and 70-80% of a packed-bed reactor (RODGERS & ZHAN, 2003).

Manufacturers of full-scale conventional RBCs specify an energy consumption of 1 to 1.5 $kWh \cdot kg^{-1}$ of BOD_5 removed (MSE, 2006). WANNER ET AL. (1990) described an energy usage of 1.6$kWh \cdot kg^{-1}$ of BOD_5 removed in a full-scale RBC packed with cylindrical PVC off cuts. WATANABE ET AL. (1994) referred that the electrical power consumption of the pilot RBC was 0.005 $kWh \cdot m^{-2} \cdot d^{-1}$ at a rotational speed of 1 rpm.

Table 3.4 Performance of different aerobic wastewater treatment systems.

Type of reactor	Type of material and media	Type of wastewater	pH	HRT (h)	Hydraulic loading/influent flow rate	Inlet organic loading/ substrate concentration	Other related data	Performance	Reference
Lab-scale									
Attached growth reactors									
Rotating biological contactor									
	PVC disks	Food industry wastewater	5.2	-	0.03 Kg COD $\cdot m^{-3} \cdot d^{-1}$		Four-stage RBC	95, 94, 78, 94 and 87% for COD, BOD_5, TON, TSS and oil and grease removal, respectively	Nasr et al. (2006)
	Polypropylene square packed rings	Synthetic food industrial wastewater	6.8	12	-	2.72 g $BOD_5 \cdot m^{-2} \cdot d^{-1}$	One-stage RBC	89.4, 92.0, 78 and 45.2% for COD, BOD_5 and TKN removal, respectively	Sirianuntapiboon (2006)
Packed-bed reactor									
	Plastic corrugated cylindrical tubes with 2 cm length and 1.5 cm diameter	Food industry wastewater	4.6-5.0	-	0.31 $m^3 \cdot m^{-2} \cdot d^{-1}$ 0.45 Kg BOD $\cdot m^{-3} \cdot d^{-1}$ 0.03 Kg N $\cdot m^{-3} \cdot d^{-1}$			87, 93, 65, 78 and 73% for COD, BOD_5, TKN, TSS and oil and grease removal, respectively	Abou-Elela et al. (2008)
Moving-bed biofilm reactor									
	Kaldnes carrier elements with 7 mm length and 10 mm diameter	Thermomechanical pulping whitewater	7.0	17.9	2.7 Kg SCOD $\cdot m^{-3} \cdot d^{-1}$		Reactor temperature: 55 ºC	44 and 64% for COD and BOD_7 removal, respectively	Jahren et al. (2002)
Suspended growth reactors									
Activated sludge									
		Chemical industry wastewater	7.2	24			3 g MLSS $\cdot dm^{-3}$	93, 95, 92, 98 and 89% for COD, BOD_5, TON, TSS and oil and grease removal, respectively	Nasr et al. (2007)
		Food industry wastewater	5.2	3 (SRT)			3 g MLSS $\cdot dm^{-3}$	96, 98, 41, 94 and 74% for COD, BOD_5, TON, TSS and oil and grease removal, respectively	Nasr et al. (2006)

Table 3.4 Performance of different aerobic wastewater treatment systems. *Continuation*

Type of reactor	Type of material and media	Type of wastewater	pH	HRT (h)	Hydraulic loading/influent flow rate	Inlet organic loading/ substrate concentration	Other related data	Performance	Reference
Large-scale									
Attached growth reactors									
Rotating biological contactor									
Pilot-scale	Polystyrene foam disks	Municipal wastewater	6.7-7.1	5	-	22 g COD $\cdot m^{-2} \cdot d^{-1}$	Two-stage RBC	77, 20 and 31% for COD, N-NH_4^+, and TKN removal, respectively	Tawfik et al. (2006)
Full-scale	Disks	Leather and fur wastewater	9.0	-	-	15 – 20 g BOD $\cdot m^{-2} \cdot d^{-1}$ 50 – 65 g COD $\cdot m^{-2} \cdot d^{-1}$	Four-stage RBCs	52.69% and 76.36% for COD and BOD_5 removal, respectively	Zao-yan & Zhen-san (1990)
Full-scale	Plastic packed rings	Food industry wastewater	5.2	-	0.02 $m^3 \cdot m^{-2} \cdot d^{-1}$		Four-stage RBC	86, 88, 71, 73 and 77% for COD, BOD_5, TON, TSS and oil and grease removal, respectively	Nasr et al. (2006)
Moving-bed biofilm reactor									
Pilot-scale	Polypropylene corrugated cylinders with 20-30 mm length and 15-20 mm diameter	Municipal wastewater	-	-	0.61 kg COD $\cdot m^{-3} \cdot d^{-1}$	5.5 g COD $\cdot m^{-2} \cdot d^{-1}$	Filling ratio: 70% Two reactors in series	76 and 92% for COD and N-NH_4^+ removal, respectively	Andreottola et al. (2000a)
Full-scale (upgrading)	Polypropylene corrugated cylinders with 20-30 mm length and 15-20 mm diameter	Municipal wastewater	-			7.9 g COD $\cdot m^{-2} \cdot d^{-1}$	Filling ratio: 53%	73, 83 and 72% for COD, BOD_5 and N-NH_4^+ removal, respectively	Andreottola et al. (2000b)
Suspended growth reactors									
Activated sludge									
Pilot-scale		Municipal wastewater	-	-	0.61 kg COD $\cdot m^{-3} \cdot d^{-1}$	5.5 g COD $\cdot m^{-2} \cdot d^{-1}$	Sludge recirculation	84 and 98% for COD and N-NH_4^+ removal, respectively	Andreottola et al. (2000a)

NOTE: – Denotes that the particular information is unavailable; BOD_5: 5-day biochemical oxygen demand; COD: chemical oxygen demand; MLSS: mixed liquor suspended solids; SCOD: soluble chemical oxygen demand; SRT: sludge retention time; TKN: total Kjeldahl nitrogen; TN: total nitrogen; TON: total organic nitrogen; TSS: total suspended solids

3.6 RBC DESIGN HINTS

Empirical observations form the basis of the design relationships and curves that are usually used to design RBCs for treatment of domestic and some common industrial wastewaters. RBC manufacturers have each developed their own empirical design curves, equations and guidelines based on treatment data collected using their equipment. However, empirical models cannot be relied on to predict the concentration profile of a substrate through an RBC for conditions other than those studied experimentally. In addition, available RBC design curves and equations are not useful for the treatment of leachates or industrial wastewaters that differ in composition from the well-characterized wastewaters for which they were developed. Thus, the relatively slow acceptance and use of RBCs has been attributed, in part, to the lack of a standardized design procedure (SPENGEL & DZOMBAK, 1992).

In the RBC process design it has to be determined the type and dimensions of medium and degree of submergence, the rotational speed, number of stages, among other parameters, to achieve the optimal degree of treatment. Accordingly, the physical facilities, including the motor, gear system, etc., have to be designed. Moreover, the RBC configuration so established must be such that the overall operation becomes economically viable and attractive (PATWARDHAN, 2003). The process design of a RBC system must also take into consideration the underlying hydrodynamics, biodegradation kinetics, oxygen transfer, development and detachment of the biological film. Thus, the first step in the overall design process should be to carry out laboratory or pilot-scale experiments to determine the biodegradation kinetics over a wide range of operating conditions with the particular wastewater. With this kinetics it is possible to design the large-scale RBC system. A step-wise process design algorithm is presented by PATWARDHAN (2003).

RBC treatment plants must contain a primary sedimentation tank (for effective removal of grit, debris and grease), the biological chamber and a secondary clarifier. RBC media should be constructed of noncorrosive materials. Disk shafts, bearing and drives should be designed for heavy-duty use. Some RBC design recommendations, like not use high-density media in the first-stage or prevent that the first-stage keeps an organic surface loading below 30 g $BOD_5 \cdot m^{-2} \cdot d^{-1}$, along with many others, were referred along this review and should be respected. Further RBC process recommendations can be found in a design manual produced by WEF & ASCE (1998).

The performance of a rotating biological contactor will be favored if it is designed to withstand normal and unusual operation conditions. The use of supplemental aeration, step-feed or removable baffles (between stages) may increase operational flexibility of RBCs.

3.7 CONCLUSIONS

Rotating biological contactors have been widely used in different treatment applications. However, due to the complex flow patterns where aeration, nutrient and oxygen mass transfer, biofilm growth and detachment, and the participation of suspended biomass must be considered, few mathematical models and with many limitations have been proposed to describe the performance of this type of reactors. Thus, RBCs design is not yet fully mastered and further studies on hydrodynamics, biochemical kinetics and biofilm properties should be carried out.

RBCs have been mainly used in aerobic processes since they provide high oxygen transfer efficiency. In this field RBC media evolved considerably from the original design of several rotating disks into a unit filled with some lightweight packed supports. As RBCs with packings are relatively recent, there are not many studies on the influence of physical characteristics of the process in these reactors performance. Besides, studies on power consumption, hydrodynamics, mass transfer and biofilm properties also need to be investigated for each type of packing material. Such studies should have an important bearing on scale-up.

More recently, submerged aerobic biological contactors started to be used successfully at full-scale to treat high strength industrial wastewaters, constituting a promising technology. Nevertheless, several improvements can be expected in terms of biofilm supporting media.

Until now few experiments were carried out with anaerobic and anoxic RBCs. Results obtained at laboratory-scale suggest that anaerobic RBCs are effective for the treatment of high-strength organic wastewaters and possible competitors with conventional anaerobic processes. On the other hand, lab-scale studies with anoxic RBCs have been showing high nitrate removal efficiencies. The application of anoxic RBCs, at full-scale, with conventional or packing media, can have an important role in secondary treatment and must be encouraged.

Several modifications can still be expected, specifically concerning recycling and supplemental aeration or step feeding, in order to improve RBCs performance.

3.8 REFERENCES

ABOUB-ELELA, S.I., NASR, F.A. & EL-SHAFAI, S.A. (2008) Wastewater management in small- and medium-size enterprises: case studies. *The Environmentalist*, 28, 289-296.

ALEMZADEH, I. & VOSSOUGHI, M. (2001) Biodegradation of toluene by an attached biofilm in a rotating biological contactor. *Process Biochemistry*, 36, 707-711.

ANDREOTTOLA G., FOLADORI P., RAGAZZI M. & TATÀNO F (2000A) Experimental comparison between MBBR and activated sludge system for the treatment of municipal wastewater. *Water Science and Technology*, 41, 375–382.

ANDREOTTOLA G., FOLADORI P. & RAGAZZI M. (2000B) Upgrading of a small wastewater treatment plant in a cold climate region using a moving bed biofilm reactor (MBBR) system. *Water Science and Technology*, 41, 177–185.

ATV (1989) Arbeitsblatt A135: Grundsätze für die Bemessung von Tropfkörpern und Tauchkörpern mit Anschlußwerten über 500 Einwohnergleichwerten, 2, AuflageAbwassertechnischeVereinigung. St Augustin, Germany.

AXELSSON, J., NILSSON, U., TERRAZAS, E., ALIAGA, T. & WELANDER, U. (2006) Decolorization of the textile dyes Reactive Red 2 and Reactive Blue 4 using *Bjerkandera* sp. Strain BOL 13 in a continuous rotating biological contactor reactor. *Enzyme and Microbial Technology*, 39, 32-37.

AYOUB, G. & SAIKALY, P. (2004) The combined effect of step-feed and recycling on RBC performance. *Water Research*, 38, 3009-3016.

BANERJEE, G. (1997A) Treatment of phenolic wastewater in RBC reactor. *Water Research*, 31, 705-714.

BANERJEE, G. (1997B) Hydraulics of bench-scale rotating biological contactor. *Water Research*, 31, 2500-2510.

BENEFIELD L.D. & RANDALL, C. (1980) Biological process design for wastewater treatment. Prentice-Hall Inc., Englewood Cliffs, NJ.

BRAR, S.K. & GUPTA, S. (2000) Biodegradation of trichloroethylene in a rotating biological contactor. *Water Research*, 34, 4207-4214.

BRAZIL, B.L. (2006) Performance and operation of a rotating biological contactor in a tilapia recirculating aquaculture system. *Aquacultural Engineering*, 34, 261-274.

VAN BUUREN (1991) Post-treatment methods for effluent of UASB reactors treating domestic sewage. Wageningen University, Department of Environmental Technology, The Netherlands.

CEMA, G., WISZNIOWSKI, J., ZABCZYNSKI, S., ZABLOCKA-GODLEWSKA, E., RASZKA, A. & SURMACZ-GORSKA, J. (2007) Biological nitrogen removal from landfill leachate by deammonification assisted by heterotrophic denitrification in a rotating biological contactor (RBC). *Water Science and Technology*, 55, 35-42.

COSTLEY, S. & WALLIS, F. (2000) Effect of flow rate on heavy metal accumulation by rotating biological contactor (RBC) biofilms. *Journal of Industrial Microbiology and Biotechnology*, 24, 244-250.

GALVAN A., URBINA, P. & DE CASTRO, F. (2000) Characterization of filamentous microorganisms in rotating biological contactor biofilms of wastewater treatment plants. *Bioprocess Engineering*, 22, 257-260.

GRADY, C. (1982) Modelling of biological fixed films - A state of the art review. In *Proceedings of the First International Conference on Fixed-Film Biological Processes*, pp. 344-403, University of Pittsburgh, Pittsburgh.

GRADY, C., DAIGGER, G. & LIM, H. (1999) Rotating Biological Contactor. In *Biological Wastewater Treatment*, pp. 907-947, 2nd edition. Marcel Dekker Inc., New York.

GRIFFIN, P. & FINDLAY, G. (2000) Process and engineering improvements to rotating biological contactor design. *Water Science and Technology,*, 41, 137-144.

GUIMARÃES, C., PORTO, P., OLIVEIRA, R. & MOTA, M. (2005) Continuous decolourization of a sugar refinery wastewater in a modified rotating biological contactor with *Phanerochaete chrysosporium* immobilized on polyurethane foam disks. *Process Biochemistry*, 40, 535-540.

GUPTA A.B. & GUPTA S.K. (2001) Simultaneous carbon and nitrogen removal from high strength domestic wastewater in an aerobic RBC biofilm. *Water Research*, 35, 1714–1722.

HANHAN, O., ORHON, D., KRAUTH, K. & GUNDER, B. (2005) Evaluation of denitrification potential of rotating biological contactors for treatment of municipal wastewater. *Water Science and Technology*, 51, 131-139.

HOCCHEIMER, J. N. & WHEATON, F. (1998) Biological filters: trickling filters and RBC design. In *12nd International Conference on Recirculation Aquaculture*, pp. 291-318. Libey GS & Timmons MB, Roanoke, VA.

ISRANI, S., KOLI, S., PATWARDHAN, A., MELO, J. & D'SOUZA, S. (2002) Phenol degradation in rotational biological contactors. *Journal of Chemical Technology and Biotechnology*, 77, 1050-1057.

JAHREN S.J., RINTALA J.A. & ØDEGAARD H. (2002) Aerobic moving bed biofilm reactor treating thermomechanical pulping whitewater under thermophilic conditions. *Water Research*, 36, 1067–1075.

JANCZUKOWICZ, W. & KLIMIUK, E. (1992) The influence of the raw wastes dosing system on technological parameters of the rotating biological disc (RBC) process. *Bioresource Technology*, 42, 241-245.

KLEES, R. & SILVERSTEIN, J. (1992) Improved biological nitrification using recirculation in rotating biological contactors. *Water Science and Technology*, 26, 545-553.

LAQUIDARA, M., BLANC, F. & O'SHAUGHNESSY, J. (1986) Development of biofilm, operating characteristics and operational control in the anaerobic rotating biological contactor process, *Journal Water Pollution Control Federation*, 58, 107-114.

LE GROUP TEKNIKA (1988) Les disques pour le traitement des eaux usées des petites et moyennes municipalités. Project de développement technologique, No. DT87.001.

LU, C. & YEH, A. (1995) Treatment of high-strength organic wastewaters using an anaerobic rotating biological contactor. *Environment International*, 21, 313-323.

LU, C., LI, H. & LEE, L. (1997) Effects of disc rotational speed and submergence on the performance of an anaerobic rotating biological contactor. *Environment International*, 23, 253-263.

LU, C., LIN, M., LI, H. & LEE, L. (1997) Temperature effects on the performance of an anaerobic rotating biological contactor. *Environmental Technology*, 18, 711-720.

MAJUMDER, P.S. & GUPTA, S. (2007) Removal of chlorophenols in sequential anaerobic-aerobic reactors. *Bioresource Technology*, 98, 118-129.

MALANDRA, L., WOLFAARDT, G., ZIETSMAN, A. & VILJOEN-BLOOM, M. (2003) Microbiology of a biological contactor for winery wastewater treatment. *Water Research*, 37, 4125-4134.

MARTÍN-CERECEDA M., ALVAREZ A.M., SERRANO, S. & GUINEA, A. (2001) Confocal and light microscope examination of protozoa and other microorganisms in the biofilms from a rotating biological contactor wastewater treatment plant. *Acta Protozoologica*, 40, 263-272.

MARTÍN-CERECEDA, M., SERRANO, S. & GUINEA, A. (2001) Biofilm communities and operational monitoring of a rotating biological contactor system. *Water, Air, and Soil Pollution*, 126, 193-206.

MATHURE, P. & PATWARDHAN, A. (2005) Comparison of mass transfer efficiency in horizontal rotating packed beds and rotating biological contactors. *Journal of Chemical Technology & Biotechnology*, 80, 413-419.

MBA, D., BANNISTER, R. & FINDLAY, G. (1999) Mechanical redesign of the rotating biological contactor. *Water Research*, 33, 3679-3688.

MOHSENI-BANDPI, A. & ELLIOTT, D. (1996) Nitrate removal from ground water using an anoxic-aerobic rotating biological contactor. *Water Science and Technology*, 34, 323-330.

MSE (ME TALLERIE DU SUD EST) (2006) Filières d'épuration adaptées aux petites collectivités: les disques biologiques. MSE. Journées Techniques de l'Ascomade, France, [<http:// www.dklik.planetb.fr/ascomade_demo/upload/ouvrage/ 1145352132.PDF>] (acessed 12.2007)

NAHID, P., VOSSOUGHI, M. & ALEMZADEH, I. (2001) Treatment of bakers yeast wastewater with a Biopack system. *Process Biochemistry*, 37, 447-451.

NAJAFPOUR, G., ZINATIZADEH, A. & LEE, L. (2006) Performance of a three-stage aerobic RBC reactor in food canning wastewater treatment. *Biochemical Engineering Journal*, 30, 297-302.

NAJAFPOUR, G., YIENG, H.A., YOUNESI, H. & ZINATIZADEH, A. (2005) Effect of organic loading on performance of rotating biological contactors using Palm Oil Mill effluents. *Process Biochemistry*, 40, 2879-2884.

NASR, F., BADR, N. & DOMA, H. (2006) Flavour Industry Wastewater Management Case Study. *The Environmentalist*, 26, 31-39.

NASR, F., DOMA, H., ABDEL-HALIM, H. & EL-SHAFAI, S. (2007) Chemical industry wastewater treatment. *The Environmentalist*, 27, 275-286.

NEU, K. (1994) Upgrading of rotating biological contactor (RBC) systems to achieve higher effluent quality, including biological nutrient enrichment and reduction techniques. *Water Science and Technology*, 29, 197-206.

NOWAK, O. (2000) Upgrading of wastewater treatment plants equipped with rotating biological contactors to nitrification and P removal. *Water Science and Technology*, 41, 145-153.

OKABE, S., HIRATIA, K., OZAWA, Y. & WATANABE, Y. (1996) Spatial microbial distributions of nitrifiers and heterotrophs in mixed-population biofilms. *Biotechnology and Bioengineering*, 50, 24-35.

PATWARDHAN, A. (2003) Rotating Biological Contactors: A Review. *Industrial Engineering of Chemical Research*, 42, 2035-2051.

RADWAN, K. & RAMANUJAM, T. (1997) Studies on organic removal of 2,4-dichlorophenol wastewaters using a modified RBC. *Bioprocess and Biosystems Engineering*, 16, 219-223.

RAMSAY, J., SHIN, M., WONG, S. & GOODE, C. (2006) Amaranth decoloration by Trametes versicolor in a rotating biological contacting reactor. *Journal of Industrial Microbiology and Biotechnology*, 33, 791-795.

RODGERS, M. & ZHAN, X. (2003) Moving-medium biofilm reactors. *Reviews in Environmental Science and Biotechnology*, 2, 213-224.

SAIKALY, P. & AYOUB, G. (2003) Ammonia nitrogen removal in step-feed rotating biological contactors. *Water, Air, and Soil Pollution*, 150, 177-191.

SALVADÓ, H., PALOMO, A., MAS, M., PUIGAGUT, J. & GRACIA, M. (2004) Dynamics of nematodes in a high organic loading rotating biological contactors. *Water Research*, 38, 2571-2578.

SCHWINGLE, T., LEPAK, A. & WENTA, R. (2005) Refining applications. *Hydrocarbon Engineering*, 10, 97-98.

SELVAM, K., SWAMINATHAN, K., SONG, M. & CHAE, K. (2002) Biological treatment of a pulp and paper industry effluent by Fomes lividus and Trametes versicolor. *World Journal of Microbiology and Biotechnology*, 18, 523-526.

SIRIANUNTAPIBOON, S. (2006) Treatment of wastewater containing Cl2 residue by packed cage rotating biological contactor (RBC) system. *Bioresource Technology*, 97, 1735-1744.

SIRIANUNTAPIBOON, S. & CHUAMKAEW, C. (2007) Packed cage rotating biological contactor system for treatment of cyanide wastewater. *Bioresource Technology*, 98, 266-272.

SPENGEL, D. & DZOMBAK, D. (1992) Biokinetic modeling and scale-up considerations for rotating biological contactors. *Water Environment Research*, 64, 223-235.

SURAMPALLI, R.Y. & BAUMANN, E. (1997) Role of supplemental aeration in improving overloaded first-stage RBC performance. *Water, Air, and Soil Pollution*, 98, 1-15.

TAWFIK, A., KLAPWIJK, B., EL-GOHARY, F. & LETTINGA, G. (2002) Treatment of anaerobically pre-treated domestic sewage by a rotating biological contactor. *Water Research*, 36, 147-155.

TCHOBANOGLOUS, G. & BURTON, F. (1991) Wastewater engineering: Treatment, Disposal and Reuse, 3rd edition. Metcalf and Eddy, Inc., McGraw-Hill Inc., New York.

TEIXEIRA, P. & OLIVEIRA, R. (2001) Denitrification in a closed rotating biological contactor: effect of disk submergence. *Process Biochemistry*, 37, 345-349.

TORKIAN A., HASHEMIAN S.J. & ALINEJAD K. (2003) Posttreatment of upflow anaerobic sludge blanket-treated industrial waste- water by a rotating biological contactor. *Water Environment Research*, 75, 232–237.

US FILTER (1998) Applying the rotating biological contactor process. US Filter. Bulletin No. USF 315-13A6, [<http:// www.waow.net/Brochures/RBC.pdf>] (acessed 12.2007)

WANNER, J., SYKORA, M., KOS, M., MIKLENDA, J. & GRAU, P. (1990) Packed-cage RBC with combined cultivation of suspended and fixed-film biomass. *Water Science and Technology*, 22, 101-111.

WARE, A., PESCOD, M. & STORCH, B. (1990) Evaluation of alternatives to conventional disc support media for rotating biological contactors. *Water Science and Technology*, 22, 113-117.

WATANABE, Y., BANG, D., ITOH, K. & MATSUI, K. (1994) Nitrogen removal from wastewaters by a bio-reactor with partially and fully submerged rotating biofilms. *Water Science and Technology*, 29, 431-438.

WEF & ASCE (1998) Design of municipal wastewater treatment plants, WEF Manual of practice No. 8, ASCE Manual and report on engineering practice No. 76. Water Environment Federation and American Society of Civil Engineers. Alexandria and Reston, USA.

ZAO-YAN, Y. & ZHEN-SAN, F. (1990) Treatment of leather and fur wastewater by a rotating biological contactor. *Water Science and Technology*, 22, 119-126.

Chapter 4

Effect of Operating Parameters on Denitrification in an Anoxic Rotating Biological Contactor

In this study the effect of two carbon/nitrogen (C/N) ratios (1.5 and 3) (weight/weight) on denitrification, using acetate as a carbon source, was investigated in an anoxic bench-scale RBC, treating synthetic wastewater. The effect of different hydraulic retention times (HRT) and different nitrogen and carbon influent concentrations on the reactor performance, at constant C/N, were also analyzed. The average removal efficiency in terms of nitrogen-nitrate was about 90% at C/N=1.5, lowering to 74% at C/N=3. Considering carbon-acetate removal, overall efficiencies of 82% and 64% were attained at C/N ratios of 1.5 and 3, respectively. The increase of nitrogen-nitrate (from 50 to 100 mg $N\text{-}NO_3^-\cdot L^{-1}$) and carbon-acetate influent concentrations and the decrease of hydraulic retention time (HRT), keeping C/N constant, had a slight negative effect in terms of substrate removal. It was found that, for the tested conditions, the use of C/N=1.5 is advantageous to denitrification. The anoxic RBC was significantly effective to reduce nitrate concentrations within a relatively short hydraulic retention time. These reactors may be a feasible option for the treatment of nitrate-rich wastewater.

The results presented in this Chapter have been published in: CORTEZ S., TEIXEIRA P., OLIVEIRA R. & MOTA M. (2009). Effect of operating parameters on denitrification in an anoxic rotating biological contactor. *Environmental Technology* 30 (13): 1381-1389.

4. EFFECT OF OPERATING PARAMETERS ON DENITRIFICATION IN AN ANOXIC ROTATING BIOLOGICAL CONTACTOR

4.1 INTRODUCTION

The traditional physico-chemical methods used to eliminate nitrate from water and wastewater are ion exchange, reverse osmosis and electrodialysis (ZHOU ET AL., 2007). However, these approaches present some drawbacks such as concentrated waste disposal issues, cost and susceptibility to fouling (in the case of reverse osmosis) (ASLAN & CAKICI, 2007). Biological nitrate reduction (denitrification) has been shown to be more economical, practical and the most versatile approach among all methods to remove nitrate from water and wastewater (MATEJU ET AL., 1992). Anoxic rotating biological contactors (RBCs) are a novel promising technology for nitrate removal.

An anoxic RBC unit typically consists of a series of closely spaced disks that are mounted on a common horizontal shaft and are partially or completely submerged in wastewater and inserted in a tightly closed case to avoid air entrance. Similarly to an open RBC, the shaft continually rotates and a biofilm is established onto the entire surface area of the media, which metabolizes the organic materials contained in the wastewater. Due to its advantages, such as, low land area requirement, easy construction, compact design, simplicity of operation, low operating and maintenance costs, short hydraulic retention time (HRT) and high biomass concentration per reactor volume, RBCs constitute a very unique and superior alternative technology for carbon oxidation, nitrification, denitrification and phosphorus removal (CORTEZ ET AL., 2008).

In municipal wastewater treatment processes most denitrifying bacteria are heterotrophic and so, an organic carbon source is required (ISAACS ET AL., 1994; BEAUBIEN ET AL., 1995; TEIXEIRA & OLIVEIRA, 2000). Methanol, acetate, citrate, propionate, ethanol and glucose, are some of the carbon sources that have been used. Acetate has been reported to give high denitrification rates in most cases (MOHSENI-BANDPI ET AL., 1999; SANCHEZ ET AL., 2000; HALLIN ET AL., 2006). Besides the type of carbon source, denitrification rate is strongly susceptible to concentration of carbon source and carbon to nitrogen ratio (C/N) (GÁLVEZ ET AL., 2003; VAN RIJN ET AL., 2006). This can vary for different microorganisms, water streams and environmental conditions (CHIU & CHUNG, 2003).

Although in the last decade anoxic RBCs have started to be used for denitrification, few studies have still been conducted with this type of reactors. Therefore, the aim of this work was to evaluate the denitrification process in an anoxic bench-scale RBC, for the treatment of a synthetic wastewater under two C/N ratios (1.5 and 3) and to compare the characteristics and the activity of the biofilm grown in those conditions. The effect of different hydraulic retention times (HRT) and different organic and nitrate influent concentrations in the reactor performance, keeping C/N constant, were also analyzed.

4.2 MATERIALS AND METHODS

4.2.1 EXPERIMENTAL SETUP

A single-stage bench-scale anoxic RBC reactor with 8 polymethylmethacrylate (PMMA) disks was used in the experiments. The details are given in Table 4.1.

Table 4.1 Summary of the dimensions of the anoxic RBC experimental unit.

Parameter	Value
No. of stages	1
No. of disks/stage	8
Internal unit diameter	140 mm
Disk diameter	130 mm
Disk thickness	3 mm
Disk spacing	20 mm
Shaft diameter	16 mm
Submergence	93.5 %
Useful volume	0.0025 m^3
Unit length	210 mm
Type of material	Acrylic
Rotational speed	4 rpm

The temperature was maintained at 28 ºC by means of a heating jacket. The reactor was covered and sealed and no special precaution was taken to maintain anoxic conditions. An influent feed tank was coupled to a previously calibrated peristaltic pump used to supply the synthetic wastewater flow rate into the anoxic RBC in a direction parallel to the rotating shaft. A dynamic head tube resembling a vented inverted siphon on the effluent line was used to control the liquid level. The treated effluent was collected in a receiving tank. A Ritter MilliGascounter measured the produced gas flow rate.

4.2.2 ACCLIMATIZATION OF BIOMASS

A volume of concentrated biological sludge was collected from an activated sludge tank at Esposende Wastewater Treatment Plant, Portugal. In order to get a suitable consortium, the fresh biomass was acclimatized during one month in a denitrifying medium, in anoxic conditions, at room temperature and 150 rpm, using acetate as a carbon source and a phosphorus concentration of 10 mg $P{\cdot}L^{-1}$. According to the experiment (C/N=1.5 or C/N=3 (weight/weight)) the consortium was enriched in a denitrifying medium with the composition shown in Table 4.2.

The trace elemental solution contained: 242 mg $Na_2MoO_4{\cdot}2H_2O$, 56 mg $FeSO_4{\cdot}7H_2O$, 8.1 mg $MnCl_2{\cdot}2H_2O$, 390 mg $CaCl_2{\cdot}2H_2O$ and 409.2 mg $MgSO_4{\cdot}7H_2O$ per liter of tap water. Due to the medium buffering capacity, no pH adjustment was performed.

The acclimatized sludge was then used for seeding into the anoxic RBC.

Table 4.2 Chemical composition of the denitrifying medium used for acclimatization of biological sludge.

Compound	Concentration (mg L^{-1})	
	C/N = 1.5	C/N = 3
$CH_3COONa.3H_2O$	425.3	850.5
KNO_3	360.9	360.9
$K_2HPO_4.\ 3H_2O$	60.9	60.9
KH_2PO_4	9.0	9.0
Trace element solution	100 mL	100 mL

4.2.3 SYNTHETIC WASTEWATER

The anoxic rotating biological contactor was fed continuously with synthetic wastewater. The synthetic influent had a composition similar to the denitrifying medium. The nitrogen-nitrate range selected is typical of concentrations found in agricultural and industrial wastewaters (BICKERS & VAN OOSTROM, 2000).

To evaluate the reactor efficiency and biofilm development the carbon and nitrate loads were doubled on the 8th day of operation (at constant C/N ratio), in both experimental conditions (C/N=1.5 or C/N=3).

4.2.4 REACTOR INOCULATION, START-UP AND OPERATION

The bench-scale reactor was inoculated with 2.5 L of the adapted consortium of sludge and microbial attachment onto the disks was allowed to occur in batch mode. The initial biomass concentration in the system was 2.63 and 2.21 g of volatile suspended solids (VSS)$\cdot$L^{-1}, for C/N=1.5 and C/N=3, respectively. A visible attachment of biomass on the disks was noticed after 4 days of inoculation. On day 6, the anoxic RBC mixed liquor was removed, the reactor was re-filled with the synthetic wastewater and started to operate in a continuous mode. The hydraulic retention time, very high at the beginning, was gradually reduced. The time “zero” of operation was considered when the hydraulic retention time was adjusted to 10 hours. Two days after that, samples started to be collected.

The study was conducted for a period of 28 days (for each C/N ratio). During the assay, carbon-acetate and nitrogen-nitrate concentrations were doubled and the hydraulic retention time was changed from 10 h to 5.68 h as shown in Table 4.3. Whenever a parameter was changed, the reactor was allowed to stabilize for a period of at least two times the corresponding retention time before taking any sample.

Table 4.3 Operating parameters of the anoxic RBC.

Days of operation	HRT (h)	N-NO_3^- (mg L^{-1})	C/N = 1.5	C/N = 3
			C-CH_3COO^- (mg L^{-1})	
0 - 8	10.00	50	75	150
8 - 15	10.00	100	150	300
15 - 22	6.84	100	150	300
22 – 28	5.68	100	150	300

4.2.5 BIOFILM DENITRIFYING ACTIVITY

At the end of each experiment, the biofilm formed on the disks was carefully removed (along the whole depth). The scrapped biofilm was used in additional batch assays to evaluate the specific substrate consumption rates and biofilm activity as well. These assays were performed in 160 mL serum flasks containing 90 mL of the denitrifying medium referred above and were inoculated with 1g of biofilm (wet weight). In order to evaluate the activity along the reactor, the biofilm samples used as inoculum corresponded to a mixture of biofilm removed from the first and second disks, from the three middle disks, and from the three last disks. Flasks were closed with butyl rubber stoppers and aluminum caps. To obtain anoxic conditions, the flasks were flushed with helium gas. Finally, the flasks were incubated at 28 ºC and 150 rpm. Aliquots of 2.5 mL were removed from each bottle, along the time, and immediately analyzed for various parameters.

Specific substrate consumption rates of nitrate and acetate were determined according to the following equation:

$$dS = \frac{(S_0 - S_t)}{VSS \cdot t} \qquad \text{Equation 4.1}$$

where dS is the specific substrate consumption rate, S_0 and S_t are the substrate concentration at the beginning and at the end of the batch test, respectively, and *VSS* is the concentration of solids during the denitrification batch test time *t*.

4.2.6 SAMPLING AND ANALYTICAL METHODS

During the course of continuous operation, samples of the RBC influent and effluent were collected routinely and analyzed for various parameters such as pH, chemical oxygen demand (COD), nitrate, nitrite and acetate. Dissolved oxygen was not measured. pH was immediately read after the collection of the sample and measured with a Metrohm 620 pH meter. COD was determined according to the closed reflux colorimetric method (APHA ET AL., 1989). For the determination of nitrate, nitrite and acetate ions concentration, samples were filtered through a 0.2 µm membrane filter in order to remove interfering suspended particles. Nitrite-nitrogen concentration was determined by a colorimetric method using N-(1-naphthyl)-ethylene-diamine, according to Standard Methods (APHA ET AL., 1989). Nitrate and acetate concentrations were measured by high-performance liquid chromatography (HPLC), using a Varian Metacarb column (type 67H, 9 µm, 300 mm long, 6.5 mm internal diameter) and a mobile phase of 0.005 M sulphuric acid (H_2SO_4) at 0.7 mL·min^{-1}. Column temperature was set at 60 ºC and nitrate and acetate were detected by UV at 210 nm. Periodically, gas samples were analyzed by a gas chromatograph (GC) equipped with a thermal conductivity detector and a Porapak Q column (2 mm internal diameter, 80-100 µm mesh, 1 m length) in series with a Molecular Sieve column (2 mm internal diameter, 5 Aº, 80-100 µm mesh, 2 m length). Helium was used as the carrier gas at a flow rate of 17 mL·min^{-1}. Temperatures of the injector port, columns and detector were 110 °C, 35 °C and 110 °C, respectively.

In order to separate the polymeric matrix from the cells, portions of biofilm from the three defined sections of the reactor (for each experiment) were submitted to an extraction procedure, according to AZEREDO ET AL. (1999). The protein content was determined by a Lowry modified method, using the Bicinchoninic Acid Protein Assay Kit (BCA) (BCA-PIERCE Cat. No. 23225). Polysaccharide concentration was estimated colorimetrically by means of the phenol – sulphuric acid method of DUBOIS ET AL. (1956) - using glucose as standard. Biofilm thickness was measured with a Vernier caliper. Density was calculated in terms of dry mass per unit of wet volume (TEIXEIRA & OLIVEIRA, 2001).

4.3 RESULTS AND DISCUSSION

One of the most important parameters of control to achieve high denitrifying efficiencies, under heterotrophic conditions, is the carbon/nitrogen ratio. The C/N ratio required for complete nitrate reduction to nitrogen gas by denitrifying bacteria depends on the nature of the carbon source. Carbon limitation will result in incomplete denitrification and a concomitant accumulation of intermediate products, such as NO_2 and N_2O. Conversely, an excess of carbon constitutes an extra cost and will promote dissimilatory nitrate reduction to ammonia and the presence of carbon in the denitrified effluent (HER & HUANG, 1995; VAN RIJN ET AL., 2006). Therefore, the type of carbon source should be selected and the C/N ratio properly controlled.

Stoichiometric relationships of heterotrophic denitrification with acetate have been referred to in the literature (CONSTANTIN & FICK, 1997; REYES-AVILA ET AL., 2004) but in many cases cell synthesis is not considered. All bacterial reactions (except photosynthesis) are the result of a synthesis of biomass reaction and an energy production reaction, being both oxidation–reduction reactions. Considering denitrification as a two-step process, using acetate as the carbon and energy source, using the half reactions given in MCCARTY ET AL. (1969) and normalizing to one mole of nitrate, the following reaction can be written:

$$NO_3^- + 0.826CH_3COO^- + 1.816H^+ \rightarrow 1.302CO_2 + 0.07C_5H_7O_2N + 1.9H_2O + 0.467N_2$$

Equation 4.2

According to Equation 4.2 the theoretical acetate consumption for denitrification (including the requirements for biomass growth) is 1.416 mg of C-CH_3COO^- per mg of N-NO_3^-.

The C/N ratio required for complete denitrification depends, among other factors, on the nature of the bacterial species (VAN RIJN ET AL., 2006). Therefore, taking into account that the inoculum used was activated sludge – a consortium of microorganisms, and considering that some acetate is necessary for the removal of oxygen from the system, it was decided to investigate the performance of the anoxic RBC and the characteristics of the biofilm grown under two carbon/nitrogen ratios: 1.5 and 3. The first mentioned ratio is almost identical to the ratio given by the stoichiometric equation while the second one is about twofold the reference value.

The two continuous experiments were carried out along the same time (28 days) and under the same conditions, except the acetate and nitrate loads. As pointed in Table 4.3, four periods can be distinguished. These periods are differentiated in Figure 4.1, Figure 4.2 and Figure 4.3 by vertical lines, which indicate process disturbances.

4.3.1 PERFORMANCE OF THE ANOXIC RBC REACTOR

4.3.1.1 Effect of influent C/N ratio

Variations in the removal efficiencies of nitrogen-nitrate (N-NO_3^-), carbon-acetate (C-CH_3COO^-) and chemical oxygen demand (COD) as a function of operating time are shown in Figure 4.1 (a), (b) and (c), respectively. From the observation of this figure it is clear that, as the C/N ratio increased from 1.5 to 3, the substrate removal efficiencies decreased.

Considering nitrogen-nitrate removal (Figure 4.1 (a)), an overall efficiency of about 90% was obtained with a C/N=1.5, which reveals a good performance and indicates that, with this ratio and using acetate as a carbon source, the tested anoxic RBC is a convenient and reliable process for the removal of nitrate from wastewater. For a ratio C/N=3 the nitrogen-nitrate overall removal efficiency lowered to 74%.

The bench-scale RBC achieved carbon-acetate overall removal efficiencies of 82% and 64%, and COD overall removal efficiencies of 70% and 54% with C/N ratios of 1.5 and 3, respectively (Figure 4.1 (b) and (c)).

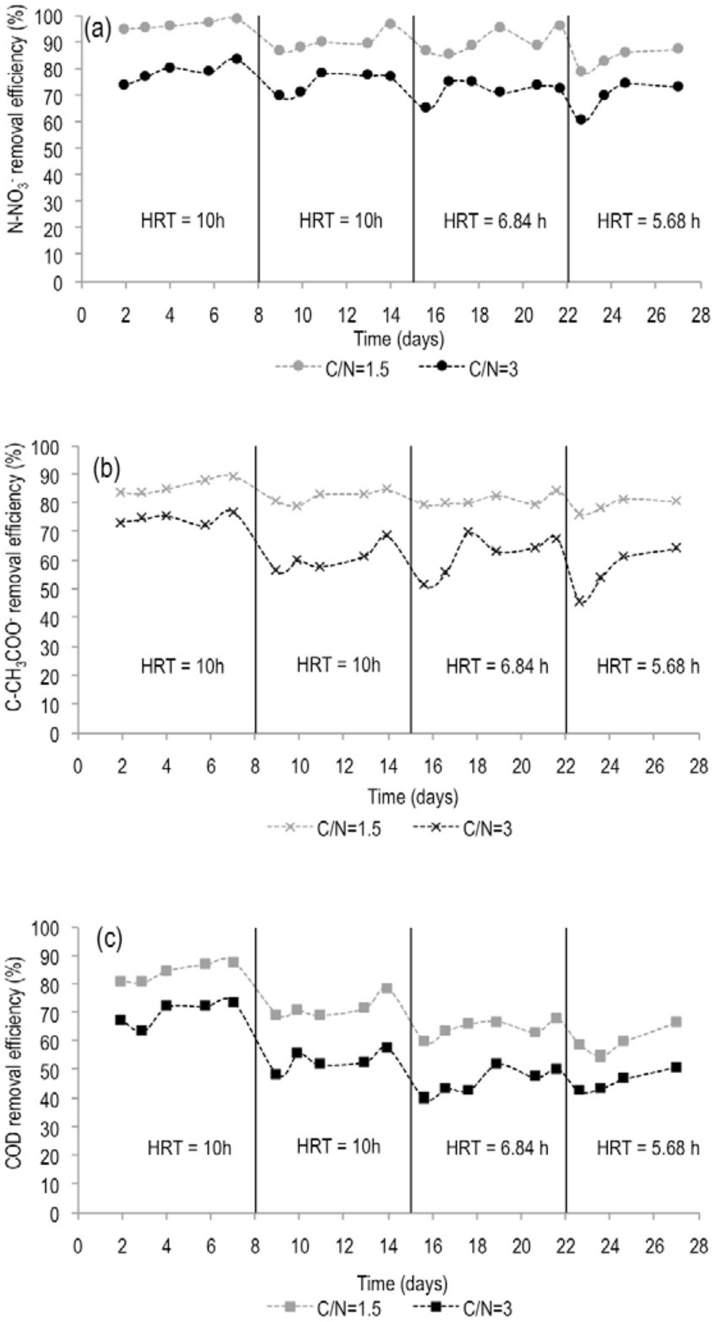

Figure 4.1 Nitrogen-nitrate (a), carbon-acetate (b) and COD (c) removal efficiency over time at C/N=1.5 and C/N=3.

These values reveal that applying a carbon/nitrogen ratio of 1.5 is appropriate. The use of a C/N=3 is excessive, for this denitrification system, inducing excess of carbon and nitrogen in the final effluent, which is not desirable for economical and environmental reasons. A possible explanation for the differences found in the efficiency of the reactor when the C/N ratio was increased can be the occurrence of inhibition of the denitrifying sludge activity.

Figure 4.2 presents nitrogen-nitrite (N-NO_2^-) concentration profile in the reactor effluent for the two C/N ratios applied.

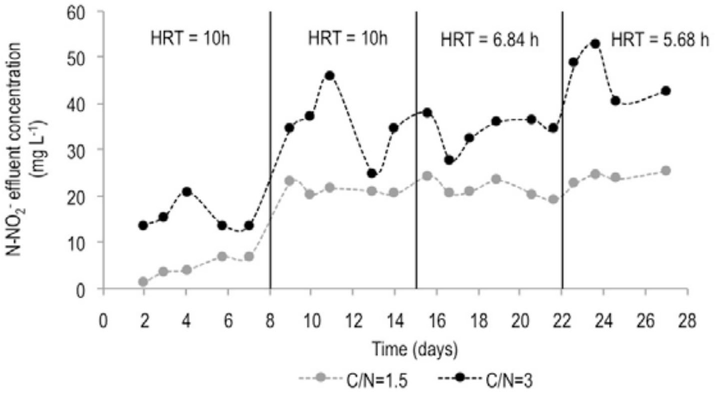

Figure 4.2 Nitrite-nitrogen effluent concentration over time at C/N=1.5 (●) and C/N=3 (●).

The nitrite produced during the continuous experiments was not completely consumed in the reactor and an accumulation of nitrite can be observed for both tested carbon/nitrogen ratios. The use of a C/N=3 generated much more accumulation of nitrite than the use of a C/N=1.5, which traduces, again, an inefficient denitrification process. Accumulation of nitrite has been frequently found in biological denitrification processes. Several factors such as oxygen concentration, temperature, biofilm composition, toxic substances, influent nitrate concentration, available and type of carbon source and carbon to nitrogen ratio influence nitrite accumulation (HER & HUANG, 1995; MORENO ET AL., 2005). It is very important to avoid nitrite accumulation because it can lead to inhibition of the bacterial development (CONSTANTIN ET AL., 1996). Moreover, high nitrite concentration is highly undesirable once nitrite is more toxic than nitrate (HUNTER, 2003).

Different microorganisms show different patterns of nitrite accumulation, pointing out that this phenomenon is strongly influenced by the microbial species present (BLASZCZYK, 1992). DHAMOLE ET AL. (2007) underlined the difference between true denitrifiers, that reduce nitrate to nitrogen gas, and nitrate respirators, that only have the enzymatic ability to reduce nitrate to nitrite. According to ROBERTSON & KUENEN (1992) most of the denitrifying bacteria in aquatic systems are only capable of incomplete denitrification. In mixed cultures like activated sludge, if population of nitrate respirators is higher than true denitrifiers it will result in nitrite build-up. In the present work the accumulation of nitrite can be the result of the microbial population present inside the RBC rich in nitrate reducing bacteria.

An insufficient phosphate level leads also to nitrite accumulation (REISINGER ET AL., 1989). In order to reduce the formation of nitrite TEIXEIRA & OLIVEIRA (2000) increased the phosphorus concentration tenfold (from 2 mg P L^{-1} to 20 mg P L^{-1}), which resulted in a drastically decrease in the accumulation of nitrite and induced a good anoxic RBC performance. Accordingly, the low phosphate concentration can have limited the conversion of nitrite to harmless nitrogen gas and most probably it had been advantageous to increase the phosphorus concentration.

According to ZHOU ET AL. (2007) acidic and alkaline environment is not convenient for denitrification and pH value plays an important role on nitrite accumulation. The main reason is that pH influences the enzyme activity of bacteria. Thus, an alkaline environment can also be the explanation to nitrite build-up, once the pH of the effluent (approximately 7.8 at C/N=1.5 and 9.0 at C/N=3) was considerably higher than the pH of the influent (approximately 6.6).

The gas production rate can be used to evaluate the metabolic activity of denitrifying microorganisms (BEAUBIEN ET AL., 1995). The differences in gas production between a carbon/nitrogen ratio of 1.5 and 3 are presented in Figure 4.3. Due to a gas leakage from the reactor, at C/N=3, which was corrected on day 7, the produced gas flow rate is only presented from that moment onwards. Increasing C/N ratio from 1.5 to 3 resulted in a significant decrease in gas production, which agrees with the nitrogen-nitrite (N-NO_2^-) concentration profile.

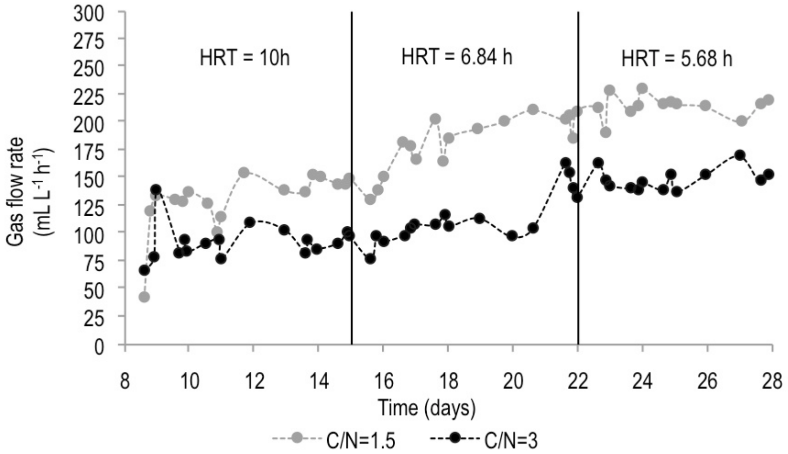

Figure 4.3 Gas production rate over time at C/N=1.5 (●) and C/N=3 (●).

Relatively to gas composition at C/N=1.5 in average it was measured 93% of N_2, 2% CO_2, 0.2% N_2O and 3% O_2 and at C/N=3 there was a slight decrease of N_2 to 92%. Evolution of CO_2 from acetate was low because it was mainly solubilized in the medium promoting an increase of alkalinity. In fact, in both experiments, the pH of the effluent was considerably higher than the pH of the influent. Production of N_2O was below 0.2% (minimum detection value). A small concentration of O_2 (approximately 3%) was detected in the gas composition analyzed. It is important to note that, initially, biological denitrification was considered to be strictly anoxic (PAYNE, 1973), with O_2 below 0.5 mg L^{-1} (VAN DER HOEK ET AL., 1994). However, with a certain number of bacteria, denitrification occurs in the presence of O_2 (LUKOW & DIEKMANN, 1997). If methane gas was produced that would be detected by the used system.

4.3.1.2 Effect of nitrogen and carbon load

To study the effect of the influent nitrogen and carbon load on the removal efficiency, on the 8th day of operation the influent nitrogen-nitrate and carbon-acetate concentrations were doubled, while the C/N ratio and the HRT were kept constant. It can be seen from Figure 4.1 that nitrogen-nitrate, carbon-acetate and COD removal efficiencies decreased but not very significantly. The increase of nitrogen-nitrate and carbon-acetate influent concentrations, keeping C/N constant, had, therefore, a slight negative effect in terms of substrate removal. Similarly, nitrite build-up rose with an increase in influent nitrogen and carbon concentrations (Figure 4.2).

The maximum substrate removal efficiencies were obtained in the first period of operation with an influent nitrogen-nitrate concentration of 50 mg $N\text{-}NO_3^-$ L^{-1} and a hydraulic retention time of 10 h.

4.3.1.3 Effect of hydraulic retention time

It is very important to determine the appropriate hydraulic retention time for the reactor because the performance of denitrification is associated with HRT, obviously. A HRT too short will result in low removal rates, whereas a too long HRT will not be economically feasible. For a biological system to compete successfully with conventional physicochemical methods of treatment, the shortest possible hydraulic retention time associated with the most efficient removal rates is required (COSTLEY & WALLIS, 2000). The influence of the hydraulic retention time on the anoxic RBC performance is shown in Figure 4.1 taking into account the three last periods (when nitrogen and carbon loads were maintained constant). As expected, nitrogen-nitrate, carbon-acetate and

COD removal decreased with the decrease of the HRT and increase of flow rate, however, this decrease was not very pronounced. So, for an influent nitrogen-nitrate concentration of 100 mg $N\text{-}NO_3^- L^{-1}$, it can be economically advantageous to use the anoxic RBC with a hydraulic retention time lower than 10 h. Generally, a decrease of the hydraulic retention time stimulated also a slightly increase in nitrite accumulation (Figure 4.2).

DAHAB & LEE (1988) successfully used acetic acid as carbon source to remove nitrate from a simulated groundwater using anoxic bench-scale static-bed upflow reactors. They reported that nearly 100% nitrate removal efficiency was achieved with an influent nitrogen-nitrate concentration of 100 mg $N\text{-}NO_3^- L^{-1}$ and 9 h of retention time. Additionally they found that a carbon to nitrogen ratio of 1.5 was optimal for denitrification in that research.

It is important to note that in spite of C/N=1.5 presenting an overall COD removal of 70%, with an influent carbon-acetate load of 150 mg $C\text{-}CH_3COO^- L^{-1}$ and at a HRT lower than 10 h, the COD concentration value in the denitrified effluent was about 200 mg $O_2 L^{-1}$, which exceeds the legal European Union upper limit of 125 mg $O_2 L^{-1}$ (EUROPEAN COMISSION, 1991). It can be speculated that at higher flow rates more biofilm was detached from the disks and was quantified in the COD measurement.

It is also relevant to emphasize that with a C/N ratio of 1.5, excluding the period of operation when HRT was 5.68 h, it was possible to reduce effluent nitrate concentrations to levels below the admissible value required by the European Union wastewater discharge standards considering that the receiving environment will be, for example, fresh water (10 - 30 mg $N\text{-}NO_3^- L^{-1}$) (EUROPEAN COMISSION, 1991). Under a carbon/nitrogen ratio of 3 the overall average value of effluent nitrate concentration was about 26.0 mg $N\text{-}NO_3^- L^{-1}$ and the required limit was only attained in the first period of operation.

4.3.2 BIOFILM PROPERTIES

To optimize the removal of nitrate and organic matter from wastewater in a RBC, an adequate understanding of the dynamic nature and characteristics of the biofilm, the major constituent of the process, is essential. The biofilm character that develops on a RBC can significantly affect its performance. This, in turn, depends on the operating conditions (CORTEZ ET AL., 2008).

For both carbon/nitrogen ratios assayed, some days after the reactor inoculation, the development of the biofilm on the disks of the RBC was clearly observable, displaying a lighter-yellow tone that was maintained until the end of the experiment. When the reactor was stopped and opened, in both cases, the biofilm was easily removed. For a C/N=1.5 the biofilm was very uniform, while for C/N=3 the biofilm presented some roughness (its surface was not homogeneous). After biofilm collection some physical characteristics such as thickness, density and humidity were determined, which are summarized in Table 4.4.

Table 4.4 Physical properties of the biofilm developed in the anoxic RBC at C/N=1.5 and C/N =3.

Biofilm	Thickness (mm)		Density (g TS L^{-1})		Wet weight/Dry weight		% Water	
	C/N=1.5	C/N=3	C/N=1.5	C/N=3	C/N=1.5	C/N=3	C/N=1.5	C/N=3
First disks	2.8 ± 0.3	3.5 ± 0.2	7.9 ± 0.1	9.1 ± 3.3	41.2 ± 7.3	29.8 ± 0.8	97.5 ± 0.4	96.6 ± 0.1
Middle disks	1.6 ± 0.1	1.9 ± 0.2	4.6 ± 0.1	7.7 ± 1.5	44.9 ± 3.5	30.5 ± 1.1	97.8 ± 0.2	96.7 ± 0.1
Last disks	0.7 ± 0.1	0.8 ± 0.1	3.9 ± 0.4	4.5 ± 1.6	50.0 ± 5.7	34.4 ± 3.1	98.0 ± 0.2	97.1 ± 0.2

It can be observed that the biofilm thickness obtained in both continuous experiments vary with the position of the disk in the reactor, being greater at the entrance and smaller at the exit of the reactor. Biofilms of wastewater treatment systems are characterized by being rather thick (>0.6 mm) (BISHOP, 1996) and these results also prove that (even in the last disks the thickness was above 0.7 mm).

For both experiments biofilm density decreased along the reactor which can be attributed to a more sparse growth of biomass on media surface. This is in accordance with the hydration values given by the ratio between wet weight and dry weight of biofilm and percentage of water, which show that on the final disks the biofilm was more hydrated.

The biofilm formed under C/N=1.5 was less dense and more hydrated than biofilm grown with a ratio C/N=3. This means that for a C/N=3 more biomass was formed. Taking into account the previously presented removal results, this can indicate that, at this condition, the whole biofilm was not entirely active and biofilm activity was not proportional to the quantity of fixed biomass, as referred by LAZAROVA & MANEM (1995). This also leads to the conclusion that biofilm activity must be always considered and studied. Moreover, higher biomass might be due to an increase in biofilm matrix.

Biofilms are formed by bacterial cells embedded in a polymeric matrix. The main components of the matrix are polysaccharides and proteins. Matrix specific composition for any biofilm depends upon the organism(s) present, their physiological status, the nature of the growth environment, bulk fluid-flow dynamics, the substratum and the prevailing physical conditions. Thus, it is probable that biofilm matrices, even those produced by identical organisms, will vary greatly in their composition and in their physical properties (ALLISON, 2003).

The composition of the polymeric matrix of biofilms formed under C/N=1.5 and C/N=3 is presented in Table 4.5. Proteins and polysaccharides content can only be considered in comparative terms, on account of the standards used in their quantification, BCA and glucose, respectively, which do not allow the expression of absolute values. The protein content of the biofilm grown under C/N=3 presented values higher than the one formed at C/N=1.5. On the contrary, the matrix polysaccharides were produced in higher quantity at C/N=1.5. An increase in the protein content was observed along the reactor for both C/N ratios. On the other hand the polysaccharides content did not change significantly (Table 4.5). This behavior is probably due to higher degree of cell lyses in the last disks.

Table 4.5 Composition of the polymeric matrix of biofilms formed at C/N=1.5 and C/N=3.

Biofilm	Matrix protein (mg BCA g^{-1}TS)		Matrix polysaccharides (mg glucose g^{-1}TS)	
	C/N=1.5	C/N=3	C/N=1.5	C/N=3
First disks	2.34 ± 0.09	5.15 ± 0.62	9.89 ± 0.11	6.64 ± 0.36
Middle disks	4.39 ± 0.08	5.50 ± 0.10	8.47 ± 0.23	4.67 ± 0.13
Last disks	6.41 ± 0.08	9.57 ± 0.22	9.82 ± 0.08	6.82 ± 0.44

4.3.3 BIOFILM ACTIVITY

A key parameter in water and wastewater treatment technology is microbial activity, expressed in terms of substrate removal ability. However, this parameter is not always linearly correlated with the conventional biofilm descriptors as dry weight, COD or biofilm thickness (ALLISON, 2003). In order to determine the denitrifying biofilm activity, for both C/N ratios, batch tests were performed using biofilm samples removed from the continuous denitrifying reactor. In these activity tests, nitrate was completely consumed in 7 h and 10 h for a carbon/nitrogen ratio of 1.5 and 3, respectively. The nitrite formed during the batch assays, if any, was completely consumed at the end of the experiment.

The activity of the biofilm portions removed from first and second disks, three middle disks and three last disks for both experiments was expressed as specific consumption rates for nitrate and acetate (Figure 4.4 and 4.5).

As it can be observed in Figure 4.4 and 4.5, the biofilm of the first disks presented specific acetate and nitrate consumption rates higher than in the other disks. A biofilm with superior activity in the first disks should be expected due to higher substrate concentration in the inlet zone. Specific acetate consumption for C/N=3 was almost constant along the reactor. The activity of the biofilm formed under C/N=1.5 was always higher than under C/N=3, which is in agreement with the results of nitrate, acetate and COD removal. It must be noted that, in this case, thicker biofilms were the less active. Thus, in spite of a lower thickness, the biofilm grown under a carbon/nitrogen ratio of 1.5 was constituted by very active cells. It is then reinforced the importance of biofilm activity in terms of denitrification rate.

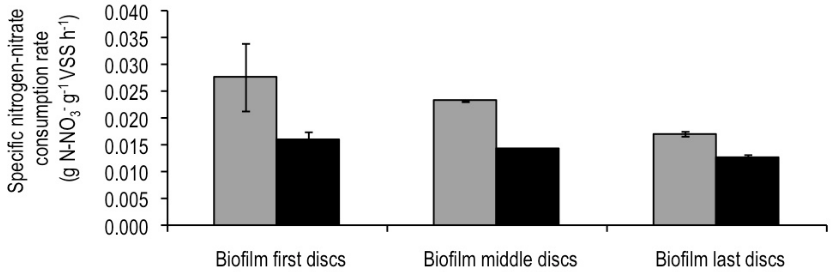

Figure 4.4 Specific nitrogen-nitrate consumption rate of biofilm portions removed from first disks, three middle disks and three last disks at C/N=1.5 (■) and C/N =3 (■).

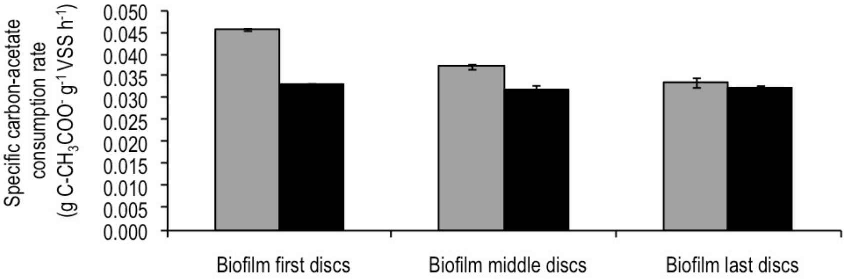

Figure 4.5 Specific carbon-acetate consumption rate of biofilm portions removed from first disks, three middle disks and three last disks at C/N=1.5 (■) and C/N =3 (■).

Specific acetate and nitrate consumption rates are influenced by several parameters and are expressed in the literature in different ways, making difficult their comparison, mainly when referring to a heterogeneous culture of microorganisms, as it is the case of activated sludge.

4.4 CONCLUSIONS

The results of nitrogen-nitrate, acetate and COD removal efficiencies indicate good performance of the anoxic RBC, using acetate as carbon source. The average removal efficiency in terms of nitrogen-nitrate was about 90% at a C/N=1.5 lowering to 74% at a C/N=3. Considering carbon-acetate removal, overall efficiencies of 82% and 64% were attained at C/N ratios of 1.5 and 3, respectively. These results evidence that, for the tested conditions, the use of C/N=1.5 is more economically and environmentally advantageous than a ratio C/N=3. Additionally, it was observed that the increase of nitrogen-nitrate and carbon-acetate influent concentrations, keeping C/N constant, and the decrease of hydraulic retention time (HRT) had a slight negative effect in terms of substrate removal. The RBC proved, therefore, to be very robust in coping with changes in substrate loads. The accumulation of nitrite occurred in both experiments, which could probably be lowered with an increase in phosphorus influent concentration. Based on experimental results of this study, it can be concluded that the tested anoxic RBC is a potential and convenient process for the removal of nitrate from wastewater.

4.5 REFERENCES

ALLISON, D. (2003) The biofilm matrix. *Biofouling*, 19, 139-150.

APHA, AWWA & WPCF (1989) Standard methods for the examination of water and wastewater, 17th edition. American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC.

ASLAN, S. & CAKICI, H. (2007) Biological denitrification of drinking water in a slow sand filter. *Journal of Hazardous Materials*, 148, 253-258.

AZEREDO, J., LAZAROVA, V. & OLIVEIRA, R. (1999) Methods to extract the exopolymeric matrix from biofilms: a comparative study. *Water Science and Technology*, 39, 243-250.

BEAUBIEN, A., HU, Y., BELLAHCEN, D., URBAIN, V. & CHANG, J. (1995) Monitoring metabolic activity of denitrification processes using gas production measurements. *Water Research*, 29, 2269-

2274.

BICKERS, P. & VAN OOSTROM, A. (2000) Availability for denitrification of organic carbon in meat-processing wastestreams. *Bioresource Technology*, 73, 53-58.

BISHOP, P. (1996) Biofilm structure and kinetics. In *Proceedings of the 3rd International IAWQ Special Conference on Biofilm Systems*. Copenhagen.

BLASZCZYK, M. (1992) Comparison of denitrification by *Paracoccus denitrificans*, *Pseudomonas stutzeri* and *Pseudomonas aeruginosa*. *Acta Microbiologica Polonica*, 41, 203-210.

CHIU, Y. & CHUNG, M. (2003) Determination of optimal COD/nitrate ratio for biological denitrification. *International Biodeterioration and Biodegradation*, 51, 43-49.

CONSTANTIN, H. & FICK, M. (1997) Influence of C-sources on the denitrification rate of a high-nitrate concentrated industrial wastewater. *Water Research*, 31, 583-589.

CONSTANTIN, H., RAOULT, S., MONTIGNY, W. & FICK, M. (1996) Denitrification of concentrated industrial wastewater: microorganism selection and kinetic studies. *Environmental Technology*, 17, 831-840.

CORTEZ, S., TEIXEIRA, P., OLIVEIRA, R. & MOTA, M. (2008) Rotating biological contactors: a review on main factors affecting performance. *Reviews in Environmental Science and Biotechnology*, 7, 155-172.

COSTLEY, S. & WALLIS, F. (2000) Effect of flow rate on heavy metal accumulation by rotating biological contactor (RBC) biofilms. *Journal of Industrial Microbiology and Biotechnology*, 24, 244-250.

DAHAB, M. & LEE, Y. (1988) Nitrate removal from water supplies using biological denitrification. *Journal Water Pollution Control Federation*, 60, 1670-1678.

DHAMOLE, P.B., NAIR, R.R., D'SOUZA, S.F. & LELE, S. (2007) Denitrification of high strength nitrate waste. *Bioresource Technology*, 98, 247-252.

DUBOIS, M., GILLES, K., HAMILTON, J., REBERS, P. & SMITH, F. (1956) Colorimetric method for determination of suggars and related substances. *Analytical Chemistry*, 28, 350-355.

EUROPEAN COMISSION (1991) Council Directive 1991/271/EEC of 21 May 1991 on Urban Waste Water Treatment. *Official Journal of the European Communitie*, L135, 40-52.

GÁLVEZ, J., GÓMEZ, M., HONTORIA, E. & GONZÁLEZ-LÓPEZ, J. (2003) Influence of hydraulic loading and air flowrate on urban wastewater nitrogen removal with a submerged fixed-film reactor. *Journal of Hazardous Materials*, 101, 219-229.

HALLIN, S., THROBACK, I.N., DICKSVED, J. & PELL, M. (2006) Metabolic profiles and genetic diversity of denitrifying communities in activated sludge after addition of methanol or ethanol. *Applied and Environmental Microbiology*, 72, 5445-5452.

HER, J.J. & HUANG, J.S. (1995) Influences of carbon source and C/N ratio on nitrate/nitrite denitrification and carbon breakthrough. *Bioresource Technology*, 54, 45-51.

HUNTER, W. (2003) Accumulation of nitrite in denitrifying barriers when phosphate is limiting. *Journal of Contaminant Hydrology*, 66, 79-91.

ISAACS, S., HENZE, M., SOEBERG, H. & KUMMEL, M. (1994) External carbon source addition as a means to control an activated sludge nutrient removal process. *Water Research*, 28, 511-520.

LAZAROVA, V. & MANEM, J. (1995) Biofilm characterization and activity analysis in water and wastewater treatment. *Water Research*, 29, 2227-2245.

LUKOW, T. & DIEKMANN, H. (1997) Aerobic denitrification by a newly isolated heterotrophic bacterium strain TL1. *Biotechnology Letters*, 19, 1157-1159.

MATEJU, V., CIZINSKA, S., KREJEI, J. & JANOCH, T. (1992) Biological water denitrification: a review. *Enzyme and Microbial Technology*, 14, 170-183.

MCCARTY, P., BECK, L. & AMANT, P. (1969) Biological denitrification of wastewaters by addition of organic materials. In *Proceedings of the 24th Purdue Industrial Waste Conference* (ed. Purdue University), pp. 1271-1285. Indiana, USA.

MOHSENI-BANDPI, A., ELLIOTT, D. & MOMENY-MAZDEH, A. (1999) Denitrification of groundwater using acetic acid as a carbon source. *Water Science and Technology*, 40, 53-59.

MORENO, B., GOMEZ, M., GONZALEZ-LOPEZ, J. & HONTORIA, E. (2005) Inoculation of a submerged filter for biological denitrification of nitrate polluted groundwater: a comparative study. *Journal of Hazardous Materials*, 117, 141-147.

PAYNE, W. (1973) Reduction of nitrogenous oxides by microorganisms. *Bacteriological Reviews*, 37, 409-452.

REISINGER, C., BRAUN, R. & MOSER, A. (1989) Cybernetic and technical aspects for advanced biological drinking water treatment. In *Workshop -Strategies for Closed Cycle Production* p. 10. Department of Biotechnology, Technical University of Graz, Austria.

REYES-AVILA, J., RAZO-FLORES, E. & GOMEZ, J. (2004) Simultaneous biological removal of nitrogen, carbon and sulfur by denitrification. *Water Research*, 38, 3313-3321.

VAN RIJN, J., TAL, Y. & SCHREIER, H.J. (2006) Denitrification in recirculating systems: theory and applications. *Aquacultural Engineering*, 34, 364-376.

ROBERTSON, L. & KUENEN, G. (1992) Nitrogen removal from water and waste. In *Microbial Control of Pollution* (eds J.C: Fry, G. Gadd, R. Herbert, C.W: Jones & I. Watson-Craik), pp. 227-267. Society for General Microbiology Ltd, Cambridge, England.

SANCHEZ, M., MOSQUERA-CORRAL, A., MENDEZ, R. & LEMA, J. (2000) Simple methods for the determination of the denitrifying activity of sludges. *Bioresource Technology*, 75, 1-6.

TEIXEIRA, P. & OLIVEIRA, R. (2000) Denitrification by *Alcaligenes denitrificans* in a closed rotating biological contactor. *Biotechnology Letters*, 22, 1789-1792.

TEIXEIRA, P. & OLIVEIRA, R. (2001) Denitrification in a closed rotating biological contactor: effect of disk submergence. *Process Biochemistry*, 37, 345-349.

VAN DER HOEK, J., KAPPELHOF, J. & SCHIPPERS, J. (1994) The use of vacuum daeration in biological nitrate removal processes. *Journal of Water Supply: Research and Technology-Aqua*, 43, 84-94.

ZHOU, M., FU, W., GU, H. & LEI, L. (2007) Nitrate removal from groundwater by a novel three-dimensional electrode biofilm reactor. *Electrochimica Acta*, 52, 6052-6059.

Chapter 5

Denitrification of a Landfill Leachate with High Nitrate Load in an Anoxic Rotating Biological

The denitrification performance of a lab-scale anoxic rotating biological contactor (RBC) using landfill leachate with high nitrate load was evaluated. Under a carbon to nitrogen ratio (C/N) of 2, the reactor achieved $N\text{-}NO_3^-$ removal efficiencies above 95% for loads up to 100 mg $N\text{-}NO_3^- \cdot L^{-1}$. The highest observed denitrification rate was 55 mg $N\text{-}NO_3^- \cdot L^{-1} \cdot h^{-1}$ at a nitrate load of 560 mg $N\text{-}NO_3^- \cdot L^{-1}$. Although the reactor has revealed a very good performance in terms of denitrification, effluent chemical oxygen demand (COD) concentrations were still high for direct discharge. The results obtained in a subsequent experiment at constant nitrate load (220 mg $N\text{-}NO_3^- \cdot L^{-1}$) and lower C/N ratios (1.2 and 1.5) evidenced that the organic matter present in the leachate was non-biodegradable. A phosphorus concentration of 10 mg $P\text{-}PO_4^{3-} \cdot L^{-1}$ promoted autotrophic denitrification, revealing the importance of phosphorus concentration on biological denitrification processes.

The results presented in this Chapter are from the following paper, which has been submitted to an international scientific journal:

CORTEZ S., TEIXEIRA P., OLIVEIRA R. & MOTA M. Denitrification of a landfill leachate with high nitrate load in an anoxic rotating biological contactor.

5. DENITRIFICATION OF A LANDFILL LEACHATE WITH HIGH NITRATE LOAD IN AN ANOXIC ROTATING BIOLOGICAL CONTACTOR

5.1 INTRODUCTION

The generation of leachate remains an inevitable consequence of the practice of waste disposal in sanitary landfills (WANG ET AL., 2010). Landfill leachate may contain a high concentration of organic matter such as volatile fatty acids, humic and fulvic compounds; inorganic contaminants such as ammonium, sulphate and chloride; heavy metals and xenobiotic organic substances (WANG ET AL., 2010; XU ET AL., 2010). In many cases, after withstanding a series of oxidation processes in the treatment plant at the sanitary landfill the leachate still presents a high nitrate load.

Nitrate contamination constitutes an environmental and health problem all over the world due to its harmful effects. Since increasingly stringent effluent discharge standards are being established, there is a great need to find new solutions and to improve the existing technologies. Biofilm technology has been shown to be an economic and effective method to degrade nitrate (MORENO ET AL., 2005). Biological nitrate reduction (denitrification) is based on a dissimilatory mechanism by which denitrifying bacteria use nitrate as terminal electron acceptor in their respiratory process in the absence of dissolved oxygen or under limited oxygen concentrations (GHAFARI ET AL., 2008; GIBERT ET AL., 2008). Heterotrophic denitrifiers, using organic carbon compounds as a source of biosynthetic carbon and electrons, are the most common denitrifiers in nature. Such compounds include carbohydrates, organic alcohols, amino acids and fatty acids. Elemental nitrogen (N_2) is the end product of this process, however intermediate accumulation of nitrite (NO_2), nitric oxide (NO) and nitrous oxide (N_2O), that are undesirable compounds and indicators of an imperfect denitrification, may take place. In some reduced environments low in dissolved carbon, autotrophic denitrifiers are the prevalent denitrifiers using reduced inorganic compounds, such as Fe^{2+}, sulfur and H_2 as electron sources and inorganic carbon as a biosynthetic carbon source (GHAFARI ET AL., 2008). The availability and type of organic carbon compounds and the oxidation/reduction state of wastewater, dictate to a large extent the occurrence of nitrate reduction (VAN RIJN ET AL., 2006). Influence of microbial growth and composition and microbiota type in the biofilm are also significant factors that affect the effluent quality and the application of a biofilm technology for water and wastewater treatment (LAZAROVA & MANEM, 1995). In turn, microbial growth is regulated by many factors, being the availability of phosphorus one of the most important (TEIXEIRA & OLIVEIRA, 2000).

An anoxic rotating biological contactor (RBC) typically consists of a series of closely spaced disks that are mounted on a common horizontal shaft and are partially or completely submerged in the wastewater to be treated and inserted in a tightly closed case to avoid air entrance. It is a reactor simple to operate with low operating and maintenance costs, high biomass concentration, high specific surface area, short hydraulic retention time (HRT), resistance to toxic loads and relatively small accumulation of sloughed biofilm. Similarly to an open RBC, the pollutants contained in the wastewater are removed by the biofilm that is established on the entire surface area of the disks, which continually rotate. Because of their advantages, RBCs constitute an attractive technology for carbon oxidation, nitrification, denitrification and phosphorus removal (CORTEZ ET AL., 2008). Aerobic RBCs have been used for removal of ammonium and organic substances from landfill leachate with high performance (EGLI ET AL., 2003; CASTILLO ET AL., 2007; CEMA ET AL., 2007; KULIKOWSKA ET AL., 2010). Anoxic RBC units have been applied for denitrification of groundwater and synthetic wastewater (MOHSENI-BANDPI ET AL., 1999; TEIXEIRA & OLIVEIRA, 2000; CORTEZ ET AL., 2009). Although in the last decade anoxic RBCs have started to be used for denitrification, there are very few studies reported in the literature.

The aim of this study was to evaluate the performance of an anoxic lab-scale RBC in terms of denitrification of a landfill leachate with high nitrate load. Accordingly, the effect of initial nitrate load on the reactor performance was assessed, as well as the effect of phosphorus concentration and C/N ratio.

5.2 MATERIALS AND METHODS

5.2.1 EXPERIMENTAL LAB-SCALE REACTOR

The single-stage anoxic RBC consisted of 8 polymethylmethacrylate (PMMA) disks mounted on a rotating shaft. The reactor working volume was 2.5 L. Further details are given in Table 5.1. The disks were completely immersed. The anoxic RBC was covered and sealed and no special precaution was taken to maintain anoxic conditions. The temperature was kept at 28 ºC by means of a heating jacket. Substrate was fed by a peristaltic pump at a constant hydraulic retention time (HRT) of 10 h and a flow rate of 0.25 L·h^{-1}. The treated effluent was collected in a receiving tank. Flow through disks was parallel to the rotating shaft. A Ritter MilliGascounter was used to measure the rate of produced gas.

Table 5.1 Summary of the characteristics of the anoxic RBC experimental unit

Parameter	Value
No. of stages	1
No. of disks/stage	8
Internal unit diameter (mm)	140
Disk diameter (mm)	130
Disk thickness (mm)	3
Disk spacing (mm)	20
Shaft diameter (mm)	16
Unit length (mm)	210
Type of material	Acrylic
Rotational speed (rpm)	4

5.2.2 EXPERIMENTAL PROCEDURE

The study consisted of two experiments. In both of them, for biofilm development, the lab-scale reactor was inoculated with acclimatized sludge and was operated in batch mode for 5 days. After that time, the anoxic RBC mixed liquor was removed, the reactor was re-filled with fresh substrate and started to operate in a continuous mode. The hydraulic retention time, very high at the beginning, was gradually reduced during 8 days. The time “zero” of operation was set two days after having the HRT stabilized at 10 h, when samples started to be collected.

Throughout the study, considering the low carbon content of the leachate tested and since acetate is known to give the highest denitrification rates (TAM ET AL., 1992; ELEFSINIOTIS & WAREHAM, 2007), sodium acetate was added as supplementary carbon source. The amount of sodium acetate needed to attain the desired C/N (w/w) was calculated taking into account the total organic carbon present in the landfill leachate.

The first experiment – Experiment 1- was designed to evaluate the effect of initial nitrate concentration on reactor performance and lasted for 26 days. Nitrate influent concentration was gradually increased (by reducing leachate dilution), while all other operating parameters were kept constant, as listed in Table 5.2. At the beginning of the experiment the reactor was fed with synthetic wastewater, having a composition similar to the denitrifying medium described below.

Table 5.2 Operating conditions of the anoxic RBC during the study of the effect of initial nitrate concentration on the reactor performance (Experiment 1).

Days of operation	Type of influent	C/N	N-NO_3^- (mg·L^{-1})
0-6	Synthetic wastewater	2.0	100
6-13	Landfill leachate		140
13-20			280
20-26			560

Another experiment – Experiment 2 – followed Experiment 1 to evaluate the influence of carbon to nitrogen ratio (C/N) and phosphorus concentration on denitrification (Table 5.3). Experiment 2 was performed using a five-fold diluted landfill leachate and lasted for 42 days. The required phosphorus concentration was achieved adding to the influent a calculated amount of K_2HPO_4 and KH_2PO_4.

Table 5.3 Operating conditions of the anoxic RBC during the study of the C/N effect and phosphorus concentration on the reactor performance (Experiment 2).

Days of operation	Type of influent	C/N	N-NO_3^- (mg·L^{-1})	P-PO_4^{3-} (mg·L^{-1})
0-13	Landfill leachate	1.5	220	0.3
13-20		1.2		0.3
20-27		1.2		10
27-36		1.5		10
36-42		2.0		10

5.2.3 INOCULUM

A volume of concentrated biological sludge was collected from an activated sludge tank at Esposende Wastewater Treatment Plant, Portugal. In order to work with a suitable consortium, in both experiments, the fresh biomass was acclimatized for one month in a denitrifying medium, under anoxic conditions, at room temperature, in conical flasks stirred at 150 rpm, using acetate as carbon source and a phosphorus concentration of 10 mg P·L^{-1}. The denitrifying medium composition was 1134.0 or 850.6 mg $CH_3COONa·3H_2O$·L^{-1} according to the former or the latter experiment, respectively, 721.8 mg $KNO_3 \cdot L^{-1}$, 60.9 mg $K_2HPO_4 \cdot 3H_2O \cdot L^{-1}$, 9.0 mg $KH_2PO_4 \cdot L^{-1}$ and 100 mL of trace elemental solution, which contained: 242 mg $Na_2MoO_4 \cdot 2H_2O$, 56 mg $FeSO_4 \cdot 7H_2O$, 8.1 mg $MnCl_2 \cdot 2H_2O$, 390 mg $CaCl_2 \cdot 2H_2O$ and 409.2 mg $MgSO_4 \cdot 7H_2O$ per liter of tap water. Due to the medium buffering capacity, no pH adjustment was performed.

5.2.4 LANDFILL LEACHATE CHARACTERISTICS

Landfill leachate was collected from a municipal landfill in the North of Portugal, in operation since 1998, after having been treated in the treatment plant existing in the sanitary landfill, which comprises stabilization and anaerobic ponds, an anoxic tank, aerated ponds and a biological decantation unit, together with an oxidation tank and two chemical precipitators. The collected leachate was stored in closed containers at 4 ºC until use. The characteristics of the undiluted leachate used in the experiments are summarized in Table 5.4.

Table 5.4 Landfill leachate average characteristics

Parameter	Experiment 1	Experiment 2
pH	5.72±0.03	4.13±0.06
COD ($mg \cdot L^{-1}$)	453±8	866±16
TOC ($mg \cdot L^{-1}$)	172±5	366±8
$N\text{-}NO_3^-$ ($mg \cdot L^{-1}$)	1118±50	1103±24
$N\text{-}NO_2^-$ ($mg \cdot L^{-1}$)	0.08±0.05	0.19±0.06
$N\text{-}NH_4^+$ ($mg \cdot L^{-1}$)	197±7	470±6
$P\text{-}PO_4^{3-}$ ($mg \cdot L^{-1}$)	1.03±0.07	1.50±0.53

From Table 5.4 it can be seen that the major problem associated with the already treated leachate is its extremely high nitrogen-nitrate load.

5.2.5 PROCESS MONITORING

During the course of operation, samples of the RBC influent and effluent were regularly collected and analyzed for pH, chemical oxygen demand (COD), nitrogen-nitrate ($N\text{-}NO_3^-$), nitrogen-nitrite ($N\text{-}NO_2^-$), nitrogen-ammonium ($N\text{-}NH_4^+$) and carbon-acetate ($C\text{-}CH_3COO^-$). pH values were immediately measured after the collection of the sample with a pH meter. COD, nitrogen-nitrite, and nitrogen-ammonium were determined according to the standard methods (APHA ET AL., 1989). Nitrate and acetate concentrations were measured by high-performance liquid chromatography (HPLC), using a Varian Metacarb column (type 67H, 9 μm, 300 mm long, 6.5 mm internal diameter) and a mobile phase of 0.005 M sulphuric acid (H_2SO_4) at 0.7 $mL \cdot min^{-1}$. Column temperature was set at 60 ºC and nitrate and acetate were detected by UV at 210 nm. Periodically, gas samples were analyzed by a gas chromatograph (GC) equipped with a thermal conductivity detector and a Porapak Q column (2 mm internal diameter, 80-100 μm mesh, 1 m length) in series with a Molecular Sieve column (2 mm internal diameter, 5 Aº, 80-100 μm mesh, 2 m length). Helium was used as the carrier gas at a flow rate of 17 $mL \cdot min^{-1}$. Temperatures of the injector port, columns and detector were 110 °C, 35 °C and 110 °C, respectively. Total organic carbon (TOC) analyses were performed using a Dohrmann DC-190 total organic carbon analyzer.

5.3 RESULTS AND DISCUSSION

5.3.1 EFFECT OF INFLUENT NITRATE CONCENTRATION

The influence of initial nitrate concentration on denitrification efficiency was investigated by changing the nitrogen-nitrate concentration (from about 100 to 560 mg $N\text{-}NO_3^- \cdot L^{-1}$), keeping a C/N ratio of 2. This ratio is slightly higher than the theoretical value of 1.4 obtained considering the approach of MCCARTY ET AL. (1969) when acetate is the carbon source, given by the stoichiometric equation:

$$NO_3^- + 0.826CH_3COO^- + 1.816H^+ \rightarrow 1.302CO_2 + 0.07C_5H_7O_2N + 1.9H_2O + 0.467N_2$$

Equation 5.1

However, some carbon is used for the removal of oxygen from the system. Therefore, a conservative assumption was made to ensure complete denitrification during the experiment. Fine-tuning of carbon dosages were investigated in a later experiment.

Figure 5.1 shows the effect of influent nitrate-nitrogen concentration on nitrate removal and $N\text{-}NO_2^-$ and $N\text{-}NH_4^+$ effluent concentrations. The reactor presented a very good performance in terms of nitrate removal when synthetic wastewater was used as influent. The change from synthetic wastewater to leachate and the slight increase in nitrate load (day 6) caused initially a decrease in nitrate removal efficiency to 75%. This was certainly a transient response to the change of influent, corresponding to biofilm acclimatization phase. Nitrate removal efficiency recovered fast and was kept around 99% as on day 10. When the nitrate load was doubled on day 13 and again on day 20, the nitrate reduction remained approximately constant.

Throughout the experiment, the actual amount of nitrate removed increased, which indicates that the denitrification rate increased with the initial nitrate loading. This fact might be explained by the increase in electron acceptor when the nitrate concentration increased.

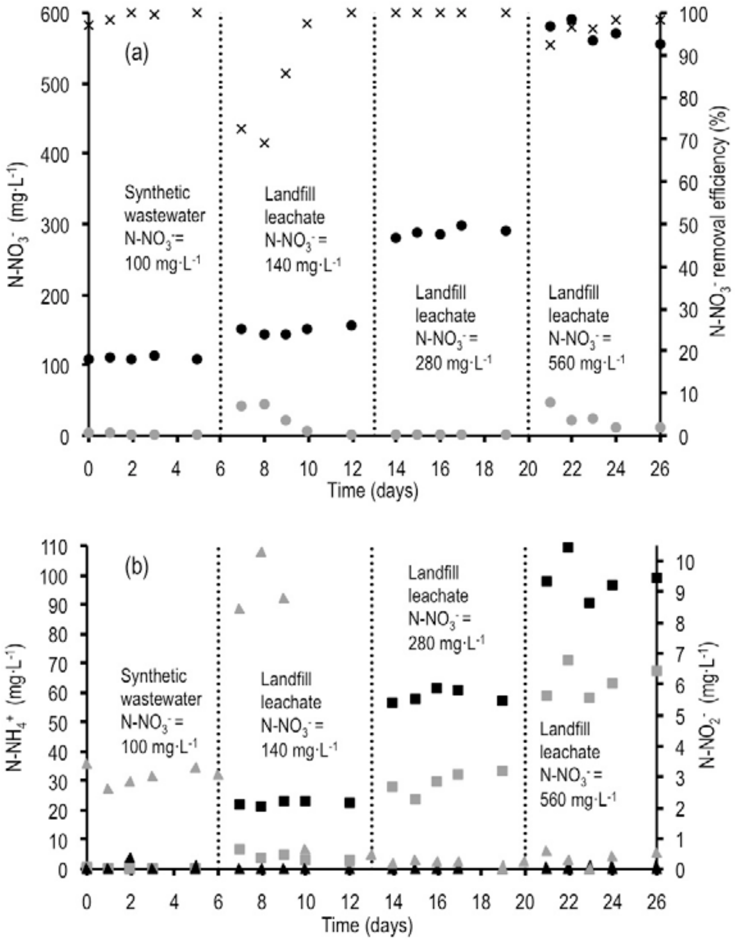

Figure 5.1 Effect of influent nitrate concentration on nitrogenous compounds. (a) Influent (●) and effluent (●) $N\text{-}NO_3^-$ concentration and $N\text{-}NO_3^-$ removal efficiency (×); (b) Influent (■) and effluent (■) $N\text{-}NH_4^+$ concentration, influent (▲) and effluent (▲) $N\text{-}NO_2^-$ concentration.

Excluding the biofilm adaptation periods, even for the greatest influent nitrate concentration tested, effluent $N\text{-}NO_3^-$ concentration was less than or equal to 10 mg·L^{-1}, being below the established limit for discharge into fresh water (10-30 mg $N\text{-}NO_3^-$·L^{-1}) (EUROPEAN COMISSION, 1991). Regarding the results achieved with landfill leachate, the denitrification rate increased from

13 to 55 mg $N\text{-}NO_3^- \cdot L^{-1} \cdot h^{-1}$ when the initial nitrate increased from 140 to 560 mg $N\text{-}NO_3^- \cdot L^{-1}$. In a previous study, CALLI ET AL. (2005) obtained denitrification rates in the range 33.3-120.8 mg $N\text{-}NO_X^- \cdot L^{-1} \cdot h^{-1}$ ($N\text{-}NO_X$-nitrogen from nitrate and nitrite compounds) in the treatment of a young landfill leachate with sodium acetate as carbon source. A denitrification rate of 55 mg $N\text{-}NO_3^- \cdot L^{-1} \cdot h^{-1}$ was achieved by WELANDER ET AL. (1998) in a suspended carrier biofilm reactor, treating leachate but using methanol as external carbon source. The denitrification rates obtained in the present work are similar to the best values reported in the literature. The selected retention time of 10 h was adequate to assure the nitrate removal performance. Also, the obtained results demonstrate the viability of the anoxic RBC in the denitrification of a pre-treated landfill leachate.

Nitrite accumulation during denitrification of landfill leachates has been observed in many studies (MARTIENSSEN & SCHOPS, 1997; SUN ET AL., 2009; CHEN ET AL., 2009). However, it is very important to avoid nitrite accumulation because it can lead to inhibition of bacterial development (MARTIENSSEN & SCHOPS, 1997). Moreover, high nitrite content is highly undesirable as nitrite is more toxic than nitrate (WELANDER ET AL., 1998). It can be seen from Figure 5.1 (b) that effluent $N\text{-}NO_2^-$ was around 3 mg $\cdot L^{-1}$ when the influent was synthetic wastewater. By changing the influent to leachate, an increase in nitrogen-nitrite accumulation was noted followed by a rapid and significant drop. A plausible explanation for this behavior may be related with the activity of the enzyme nitrite reductase present in the microbial biofilm community, which is only stimulated when a considerable nitrite concentration is produced. Another possible explanation for this phenomenon is the sudden increase of ammonium in the reactor, which might have inhibited temporarily the growth of nitrite oxidizing bacteria, although followed by a rapid recovery (TERADA ET AL., 2003). The increase in nitrate load had no significant influence in nitrite effluent concentration.

Ammonium is also an undesirable compound since it can be toxic to aquatic microorganisms. As illustrated in Figure 5.1 (b) a significant ammonium removal was observed when landfill leachate was fed to the reactor. This is probably due to ammonium reduction by nitrite to form gaseous nitrogen. In fact, in the beginning there was some nitrite accumulation and a low ammonium reduction but when the ammonium reduction rises to about 50% nitrite accumulation is almost negligible.

The changes in COD and $C\text{-}CH_3COO^-$ concentrations throughout the experiment are shown in Figure 5.2 (a) and (b), respectively. Until the sixth day of operation COD influent values were only due to the addition of acetate. From day 6 onwards, these data correspond to the contribution of added acetate and carbon content from the landfill leachate.

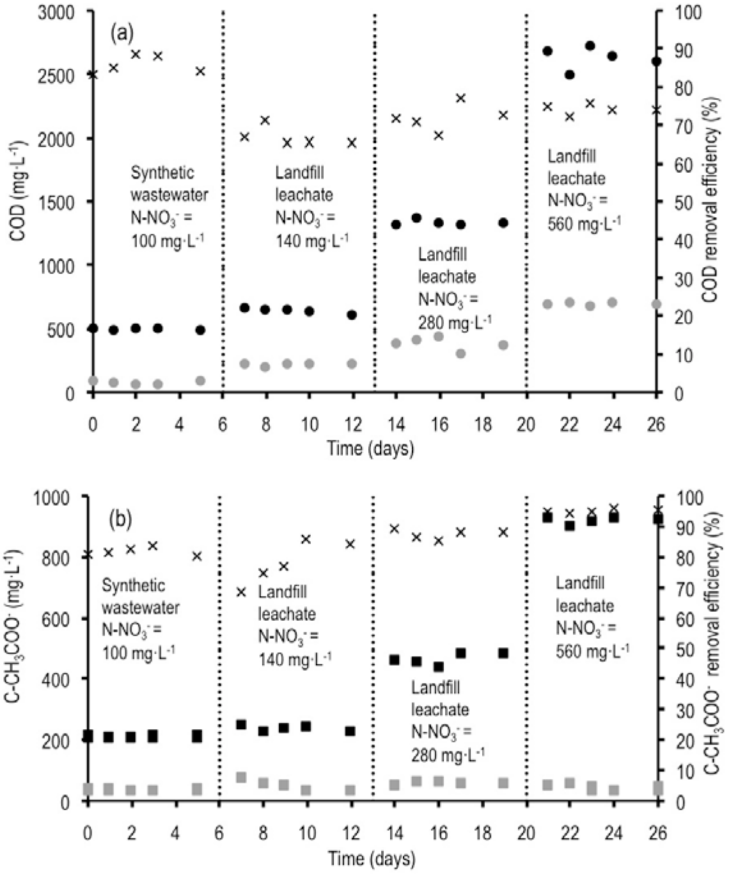

Figure 5.2 Effect of influent nitrate concentration on carbonaceous compounds. (a) Influent (●) and effluent (●) COD concentration and COD removal efficiency (×); (b) Influent (■) and effluent (■) C-CH$_3$COO$^-$ concentration and C-CH$_3$COO$^-$ removal efficiency (×).

During the first experimental period, around 82% of carbon-acetate was consumed and showed to be enough to assure 99% of nitrogen-nitrate removal. This implies that the reactor was not carbon limited and was receiving enough carbon to promote the denitrification process. Effluent COD concentration was approximately 71 mg·L^{-1}. After the shift to leachate and the corresponding biofilm acclimatization phase, small variations in COD removal values were observed until the end of the experiment. The carbon-acetate removal efficiency slightly increased with the increasing nitrate load. This trend may be due to the lower amount of acetate fed to the reactor when leachate was used as influent, thereby remaining less acetate in the effluent. The carbon content of the leachate is most probably less degradable than acetate, which might also explain the observed differences. The effluent COD concentrations reached values greater than 125 mg·L^{-1}, which is the discharge standard value. Therefore, in order to fulfill environmental regulations, for high nitrate loads, the acetate load should be adjusted and biodegradability studies concerning the landfill leachate must be carried out.

pH values increased from 6.4-7.3 in the influent to 7.8-9.4 in the effluent. The observed pH trend might be attributed to the conversion of N-NO_3^- to nitrogen gas in the reactor, which consumed hydrogen ions. This effect was more relevant as the inlet nitrate load increased. The optimum pH for most environmental strains of denitrifying bacteria was reported between 7.0 and 8.0 (TCHOBANOGLOUS & BURTON, 1991). In the present study high nitrate removals were even possible for pH above 9.0, which leads to the conclusion that the increased pH was not inhibitory.

The produced gas flow rate, as expected, increased with the increasing nitrate load, in agreement with the nitrogen-nitrate removal efficiency profile (Figure 5.3 (a)).

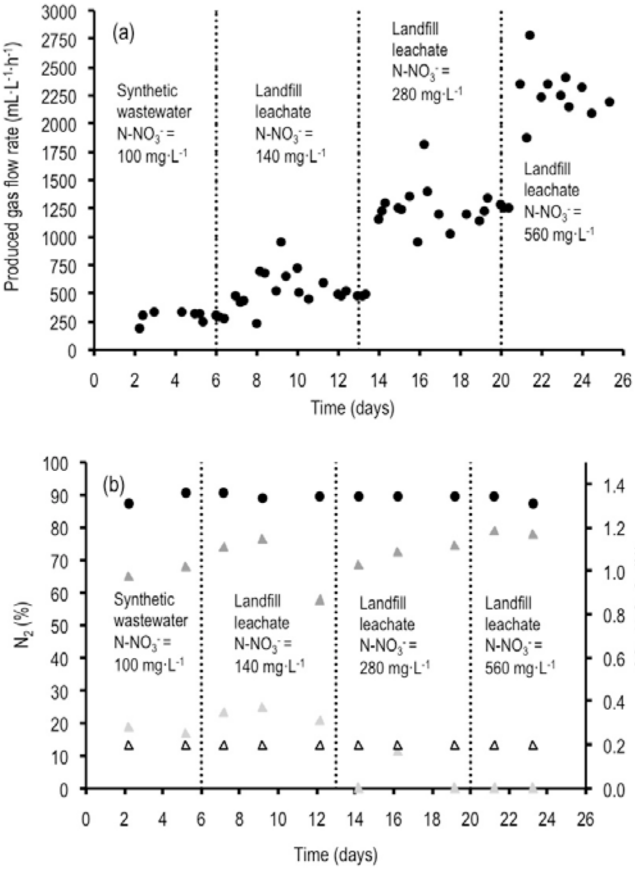

Figure 5.3 Effect of influent nitrate concentration on (a) produced gas flow rate; (b) produced gas composition: N_2 (●); CO_2 (▲); N_2O (△) and O_2 (▲).

Gas composition was measured at NTP conditions as a percentage by volume and data are shown in Figure 5.3 (b). The gas composition remained almost unchanged with the increasing nitrate concentration. Nitrogen (N_2) was the main compound in the analyzed gas composition (around 90%). Release of CO_2 was low because it was mainly solubilized in the medium, promoting an increase in alkalinity. Production of N_2O was below 0.2% (minimum detection value). A small concentration of O_2 (approximately 0.3%) was detected in the gas composition analyzed until day 13. It is important to note that biological denitrification was considered before to be strictly anoxic (PAYNE, 1973). However, the present results confirm that, as reported by LUKOW & DIEKMANN (1997), with a certain number of bacteria, denitrification occurs in the presence of O_2. No methane or hydrogen sulfide gases were detected by the measuring system.

During this experiment, the anoxic RBC presented a very good denitrification performance. Almost all nitrate was reduced to nitrogen gas and no nitrite accumulation was found. The biofilm attached to the disks was slightly sensitive to variations in substrate, which is a desirable characteristic when landfill leachate with such high nitrogen-nitrate content is being treated. The main drawback of the system was the unused carbon remaining in the treated effluent with increased COD discharge. Therefore, an efficient acetate dosage strategy is required, which was considered in the following experiment (Experiment 2).

5.3.2 EFFECT OF C/N RATIO AND INFLUENT PHOSPHORUS CONCENTRATION

Dosage of external carbon source is a tricky parameter to control in a denitrification process. A poor C/N ratio leads to incomplete denitrification resulting in a significant increase in the effluent nitrate concentration or accumulation of intermediate products, such as NO_2 and N_2O. On the other hand a high C/N ratio is an extra cost and may promote dissimilatory nitrate reduction to ammonia and the presence of carbon in the denitrified effluent (HER & HUANG, 1995). Therefore, the C/N ratio must be properly controlled.

The nature and concentration of influent substrates may affect biofilm growth and composition. Under a high substrate loading rate, the biofilm accumulation is higher. The limitation in some nutrients, as phosphorus, may enhance polysaccharide production instead of cell formation in the biofilm and consequently the concentration of active biomass (VEIGA ET AL., 1992).

The influence of C/N on denitrification efficiency was investigated by changing the carbon concentration, keeping constant the nitrate load (220 mg $N\text{-}NO_3^-\cdot L^{-1}$). A range of C/N between

1.45 and 2 is reported in the literature (Mohseni-Bandpi et al., 1999; Reyes-Avila et al., 2004; Hamlin et al., 2008) for denitrification using acetate as carbon source. Based on the data from the previous trial, this experiment started with a C/N ratio almost identical to the ratio given by the stoichiometric equation: 1.5.

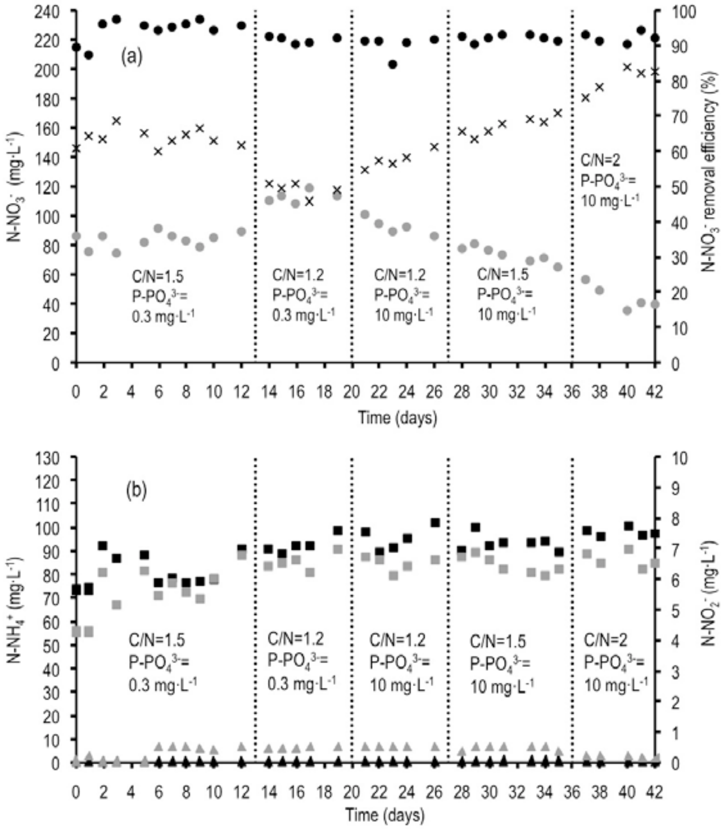

Figure 5.4 Effect of C/N ratio and phosphorus concentration on nitrogenous compounds. (a) Influent (●) and effluent (●) N-NO$_3^-$ concentration and N-NO$_3^-$ removal efficiency (×); (b) Influent (■) and effluent (■) N-NH$_4^+$ concentration, influent (▲) and effluent (▲) N-NO$_2^-$ concentration.

It can be seen in Figure 5.4 that, under the running conditions of C/N=1.5 and 0.3 mg P-PO$_4^{3-}$·L^{-1}, the nitrogen-nitrate removal efficiency was around 63%. Considering the concentration of N-NO$_3^-$ in the effluent, this removal was relatively low, however some acetate still remained in the treated leachate (Figure 5.5), showing that the reactor was not carbon limited. After 13 days of operation, the C/N ratio was adjusted from 1.5 to 1.2, which is below the theoretical value. The aim of this change in the C/N ratio was to reduce the concentration of COD in the effluent and to examine into what extent the organic matter in the leachate could be used as carbon source for the denitrification process.

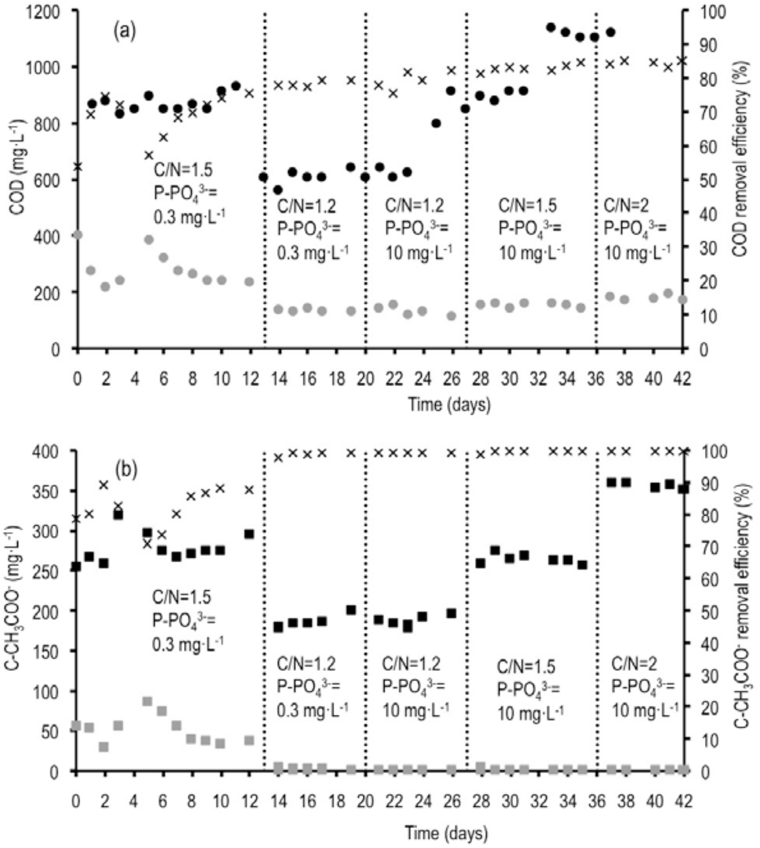

Figure 5.5 Effect of C/N ratio and phosphorus concentration on carbonaceous compounds. (a) Influent (●) and effluent (●) COD concentration and COD removal efficiency (×); (b) Influent (■) and effluent (■) C-CH_3COO^- concentration and C-CH_3COO^- removal efficiency (×).

As a consequence, acetate was completely consumed and effluent COD concentration remained near the reference value of 125 mg·L^{-1} but N-NO_3^- removal efficiency decreased to 48%. Since all acetate was consumed and effluent COD was not, these results suggest that the organic matter present in the leachate should be non-biodegradable and the denitrifying biofilm could not use it. The C/N of 1.2, composed of carbon from sodium acetate and landfill leachate, was insufficient for the denitrification process.

Considering that influent phosphorus concentration can significantly affect the denitrifying process (TEIXEIRA & OLIVEIRA, 2000; ALVES ET AL., 2002), in an attempt to make the microbial community consume the leachate organic matter, P-PO_4^{3-} influent concentration was changed to 10 mg·L^{-1}, from day 20 onwards. Phosphorus concentration was selected according to WELANDER ET AL. (1998). The shift to a higher phosphorus load, keeping C/N=1.2, led to a moderately increase in nitrogen-nitrate removal efficiency, while no effect was detected on COD removal efficiency. A possible explanation might be that a high phosphorus concentration led to the growth of autotrophic denitrifying microorganisms. A higher activity of autotrophic denitrifying microorganisms usually occurs in environments with low C/N ratios (KIM & SON, 2000). KOENIG & LIU (1996) showed that a decrease in the nitrate concentration was coupled with an increase in the sulphate concentration due to autotrophic denitrification.

Taking into account the positive effect of phosphorus concentration on nitrate removal, the high effluent $N\text{-}NO_3^-$ concentration and the poor biodegradability of the landfill leachate, the C/N ratio was increased again to 1.5 on day 27 and finally to 2 on day 36 keeping on working with 10 mg $P\text{-}PO_4^{3-}\cdot L^{-1}$. Nitrogen-nitrate removal efficiency notably increased, while small differences in COD and carbon-acetate removal values were noted under those conditions. High C/N ratios with 10 mg $P\text{-}PO_4^{3-}\cdot L^{-1}$ may have stimulated the growth of autotrophic and heterotrophic denitrifying bacteria in the biofilm and thus promoting a higher nitrate removal rate. The C/N ratio required for complete denitrification, besides the nature of the carbon source, depends on the nature of the bacterial species (VAN RIJN ET AL., 2006).

The results suggest that for a nitrate load of 220 mg $N\text{-}NO_3^-\cdot L^{-1}$, a better reactor performance was achieved with C/N=2 and 10 mg $P\text{-}PO_4^{3-}\cdot L^{-1}$. At these conditions, the highest denitrification rate was 18.5 mg $N\text{-}NO_3^-\cdot L^{-1}\cdot h^{-1}$.

Probably a further increase of the C/N ratio would have allowed the complete removal of nitrate, as observed by ALVES ET AL. (2002). In addition, it may be possible to optimize the phosphorus concentration in the range 0.3-10 mg $P\text{-}PO_4^{3-}\cdot L^{-1}$.

Nitrite accumulation was not observed, even when the C/N ratio was lower than the stoichiometric value. The effluent ammonium concentrations were always lower than the input values.

pH values increased from 6.4-7.1 in the influent to 8.6-9.4 in the effluent.

The produced gas flow rate varied following the profile of nitrogen-nitrate removal efficiency (Figure 5.6 (a)).

The reactor was operated with approximately 0.4% of O_2 (Figure 5.6 (b)). CO_2 production remained around 1%. Gas was mainly composed of N_2. N_2O accumulation was observed when C/N ratio was 1.2. HONG ET AL. (1993) reported that a low C/N ratio could result in N_2O

production. N_2O is a potent greenhouse gas with high ozone depletion potential, therefore, it is important to minimize its emission.

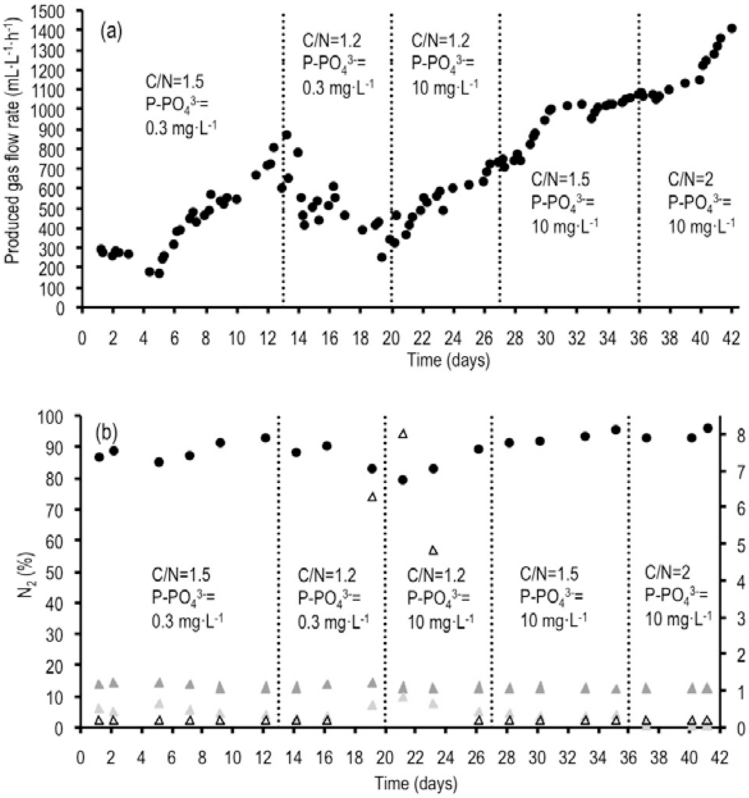

Figure 5.6 Effect of C/N ratio and phosphorus concentration on (a) produced gas flow rate; (b) produced gas composition: N_2 (●); CO_2 (▲); N_2O (△) and O_2 (▲).

The results obtained in this experiment showed that a limited C/N ratio (less than the theoretical 1.4) resulted in an increase of effluent nitrate concentration and N_2O production. The landfill leachate used was non-biodegradable, rich in refractory compounds and the denitrifying biofilm could not use its carbon content. Probably, to meet the maximum allowable organic matter concentration for discharge, advanced oxidation processes, such as ozone or Fenton oxidation should be applied before biological treatment.

The shift to a higher concentration of phosphorus seemed to favor the activity of autotrophic denitrifiers and therefore, nitrate removal. This result emphasizes the importance of phosphorus concentration on the denitrification process. Better denitrification conditions were achieved with C/N=2 and 10 mg $P\text{-}PO_4^{3-}\cdot L^{-1}$. Considering the nitrate load applied (220 mg $N\text{-}NO_3^{-}\cdot L^{-1}$) and since no nitrite accumulation was detected, the anoxic RBC showed an efficient performance in terms of denitrification.

5.4 CONCLUSIONS

Considering the nitrate load applied, nitrate removal efficiencies and the negligible accumulation of intermediates in both experiments, the anoxic rotating biological contactor showed to be very efficient and is a promising technology for removing nitrate from landfill leachate.

In order to improve leachate biological treatability, future research should focus on the removal and change of the recalcitrant organic matter by an advanced oxidation process, which must be applied before the biofilm reactor. Considering the ammonium content of the treated leachate, a system involving denitrification and nitrification followed by recirculation to the first unit should also be evaluated.

5.5 REFERENCES

ALVES, C., MELO, L. & VIEIRA, M. (2002) Influence of medium composition on the characteristics of a denitrifying biofilm formed by Alcaligenes denitrificans in a fluidised bed reactor. *Process Biochemistry*, 37, 837-845.

APHA, AWWA & WPCF (1989) Standard methods for the examination of water and wastewater, 17th edition. American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC.

CALLI, B., MERTOGLU, B. & INANC, B. (2005) Landfill leachate management in Istanbul: applications and alternatives. *Chemosphere*, 59, 819-829.

CASTILLO, E., VERGARA, M. & MORENO, Y. (2007) Landfill leachate treatment using a rotating biological contactor and an upward-flow anaerobic sludge bed reactor. *Waste Management*, 27, 720-726.

CEMA, G., WISZNIOWSKI, J., ZABCZYNSKI, S., ZABLOCKA-GODLEWSKA, E., RASZKA, A. & SURMACZ-

GORSKA, J. (2007) Biological nitrogen removal from landfill leachate by deammonification assisted by heterotrophic denitrification in a rotating biological contactor (RBC). *Water Science and Technology*, 55, 35-42.

CHEN, Y., WU, S., WU, W., SUN, H. & DING, Y. (2009) Denitrification capacity of bioreactors filled with refuse at different landfill ages. *Journal of Hazardous Materials*, 172, 159-165.

CORTEZ, S., TEIXEIRA, P., OLIVEIRA, R. & MOTA, M. (2008) Rotating biological contactors: a review on main factors affecting performance. *Reviews in Environmental Science and Biotechnology*, 7, 155-172.

CORTEZ, S., TEIXEIRA, P., OLIVEIRA, R. & MOTA, M. (2009) Effect of operating parameters on denitrification in an anoxic rotating biological contactor. *Environmental Technology*, 30, 1381-1389.

EGLI, K., BOSSHARD, F., WERLEN, C., LAIS, P., SIEGRIST, H., ZEHNDER, A. & VAN DER MEER, J. (2003) Microbial composition and structure of a rotating biological contactor biofilm treating ammonium-rich wastewater without organic carbon. *Microbial Ecology*, 45, 419-432.

ELEFSINIOTIS, P. & WAREHAM, D. (2007) Utilization patterns of volatile fatty acids in the denitrification reaction. *Enzyme and Microbial Technology*, 41, 92-97.

EUROPEAN COMISSION (1991) Council Directive 1991/271/EEC of 21 May 1991 on Urban Waste Water Treatment. *Official Journal of the European Communities*, L/135, 40-52.

GHAFARI, S., HASAN, M. & AROUA, M.K. (2008) Bio-electrochemical removal of nitrate from water and wastewater--A review. *Bioresource Technology*, 99, 3965-3974.

GIBERT, O., POMIERNY, S., ROWE, I. & KALIN, R.M. (2008) Selection of organic substrates as potential reactive materials for use in a denitrification permeable reactive barrier (PRB). *Bioresource Technology*, 99, 7587-7596.

HAMLIN, H., MICHAELS, J., BEAULATON, C., GRAHAM, W., DUTT, W., STEINBACH, P. ET AL. (2008) Comparing denitrification rates and carbon sources in commercial scale upflow denitrification biological filters in aquaculture. *Aquacultural Engineering*, 38, 79-92.

HER, J.J. & HUANG, J.S. (1995) Influences of carbon source and C/N ratio on nitrate/nitrite denitrification and carbon breakthrough. *Bioresource Technology*, 54, 45-51.

HONG, K., HU, L.F. & SHEN, D.S. (1993) Greenhouse gas - N2O production during denitrification in wastewater treatment. *Water Science and Technology*, 28, 203-207.

KIM, I. & SON, J. (2000) Impact of COD/N/S ratio on dentrification by the mixed cultures of sulfatereducing bacteria and sulfur denitrifying bacteria. *Water Science and Technology*, 42, 69-76.

KOENIG, A. & LIU, L.H. (1996) Autotrophic denitrification of landfill leachate using elemental sulphur. *Water Science and Technology*, 34, 469-476.

KULIKOWSKA, D., JÓZWIAK, T., KOWAL, P. & CIESIELSKI, S. (2010) Municipal landfill leachate nitrification in RBC biofilm - Process efficiency and molecular analysis of microbial structure. *Bioresource Technology*, 101, 3400-3405.

LAZAROVA, V. & MANEM, J. (1995) Biofilm characterization and activity analysis in water and wastewater treatment. *Water Research*, 29, 2227-2245.

LUKOW, T. & DIEKMANN, H. (1997) Aerobic denitrification by a newly isolated heterotrophic bacterium strain TL1. *Biotechnology Letters*, 19, 1157-1159.

MARTIENSSEN, M. & SCHOPS, R. (1997) Biological treatment of leachate from solid waste landfill sites-Alterations in the bacterial community during the denitrification process. *Water Research*, 31, 1164-1170.

MCCARTY, P., BECK, L. & AMANT, P. (1969) Biological denitrification of wastewaters by addition of organic materials. In *Proceedings of the 24th Purdue Industrial Waste Conference* (ed. Purdue University), pp. 1271-1285. Indiana, USA.

MOHSENI-BANDPI, A., ELLIOTT, D. & MOMENY-MAZDEH, A. (1999) Denitrification of groundwater using acetic acid as a carbon source. *Water Science and Technology*, 40, 53-59.

MORENO, B., GOMEZ, M., GONZALEZ-LOPEZ, J. & HONTORIA, E. (2005) Inoculation of a submerged filter for biological denitrification of nitrate polluted groundwater: a comparative study. *Journal of Hazardous Materials*, 117, 141-147.

PAYNE, W. (1973) Reduction of nitrogenous oxides by microorganisms. *Bacteriological Reviews*, 37, 409-452.

REYES-AVILA, J., RAZO-FLORES, E. & GOMEZ, J. (2004) Simultaneous biological removal of nitrogen, carbon and sulfur by denitrification. *Water Research*, 38, 3313-3321.

VAN RIJN, J., TAL, Y. & SCHREIER, H.J. (2006) Denitrification in recirculating systems: theory and applications. *Aquacultural Engineering*, 34, 364-376.

SUN, H., YANG, Q., PENG, Y., SHI, X., WANG, S. & ZHANG, S. (2009) Nitrite accumulation during the denitrification process in SBR for the treatment of pre-treated landfill leachate. *Chinese Journal of Chemical Engineering*, 17, 1027-1031.

TAM, N., WONG, Y. & LEUNG, G. (1992) Effect of exogenous carbon sources on removal of inorganic nutrient by the nitrification-denitrification process. *Water Research*, 26, 1229-1236.

TCHOBANOGLOUS, G. & BURTON, F. (1991) Wastewater engineering:Treatment, Disposal and Reuse., 3rd edition. Metcalf and Eddy, Inc., McGraw-Hill Inc., New York.

TEIXEIRA, P. & OLIVEIRA, R. (2000) Denitrification by Alcaligenes denitrificans in a closed rotating biological contactor. *Biotechnology Letters*, 22, 1789-1792.

TERADA, A., HIBIYA, K., NAGAI, J., TSUNEDA, S. & HIRATA, A. (2003) Nitrogen removal characteristics and biofilm analysis of a membrane-aerated biofilm reactor applicable to high-strength nitrogenous wastewater treatment. *Journal of Bioscience and Bioengineering*, 95, 170-178.

VEIGA, M.C., MENDEZ, R. & LEMA, J.M. (1992) Development and stability of biofilms in bioreactors. In *Biofilms – Science and Technology* pp. 421-434, L.F. Melo, T.R. Bott, M. Fletcher and B. Capdeville. Kluwer Academic Publishers, Netherlands.

WANG, C., LEE, P., KUMAR, M., HUANG, Y., SUNG, S. & LIN, J. (2010) Simultaneous partial nitrification, anaerobic ammonium oxidation and denitrification (SNAD) in a full-scale landfill-leachate treatment plant. *Journal of Hazardous Materials*, 175, 622-628.

WELANDER, U., HENRYSSON, T. & WELANDER, T. (1998) Biological nitrogen removal from municipal landfill leachate in a pilot scale suspended carrier biofilm process. *Water Research*, 32, 1564-1570.

XU, Z., ZENG, G., YANG, Z., XIAO, Y., CAO, M., SUN, H. ET AL. (2010) Biological treatment of landfill leachate with the integration of partial nitrification, anaerobic ammonium oxidation and heterotrophic denitrification. *Bioresource Technology*, 101, 79-86.

Chapter 6

Landfill Leachate Polishing Treatments: Ozonation and Fenton’s Oxidation

Mature landfill leachate is typically resistant to biological processes. Fenton’s oxidation (Fe^{2+}/H_2O_2) and different ozone-based Advanced Oxidation Processes (AOPs) (O_3, O_3/OH^- and O_3/H_2O_2) were evaluated as pre-treatment of a mature landfill leachate, in order to improve the biodegradability of its recalcitrant organic matter for subsequent biological treatment. The results are presented in two subchapters. The best results were achieved with Fe^{2+}/H_2O_2, O_3/OH^- and O_3/H_2O_2 processes, confirming the enhanced production of hydroxyl radical under such conditions. Although Fe^{2+}/H_2O_2 is the most economical system to treat the landfill leachate, for ease of operation, the system O_3/OH^- was chosen for further work.

Some of the results presented in this Chapter have been published in:

CORTEZ S., TEIXEIRA P., OLIVEIRA R. & MOTA M. (2010) Ozonation as polishing treatment of mature landfill leachate. *Journal of Hazardous Materials* 182 (1-3): 730-734.

Other results presented in this Chapter are from the following paper, which has been submitted to an international scientific journal:

CORTEZ S., TEIXEIRA P., OLIVEIRA R. & MOTA M. Evaluation of Fenton's oxidation and ozone-based advanced oxidation processes as mature landfill leachate pre-treatments.

6. LANDFILL LEACHATE POLISHING TREATMENTS: OZONATION AND FENTON'S OXIDATION

6A OZONATION AS POLISHING TREATMENT OF MATURE LANDFILL LEACHATE

6A.1 INTRODUCTION

Sanitary landfilling is still the most used and accepted method to eliminate municipal solid wastes worldwide due to its economic advantages (RENOU ET AL., 2008). Given the great chemical complexity and diversity of the leachate produced, sanitary landfills have searched for innovative leachate treatment technologies, in order to avoid discharges to the environment causing negative impacts to the biota or public health (HAGMAN ET AL., 2008).

Leachate generated from mature landfills (with more than 10 years) is typically characterized by high ammonium (NH_4^+) content, a low five-day biochemical oxygen demand (BOD_5) to chemical oxygen demand (COD) ratio (BOD_5/COD generally below 0.1), and high fraction of refractory and large organic molecules (humic substances) (KURNIAWAN ET AL., 2006; HAGMAN ET AL., 2008) . Humic substances consist of a structure of alkyl/aromatic units, mainly cross-linked by oxygen and nitrogen groups with the major functional groups being carboxylic acid, phenolic and alcoholic hydroxyls, as well as ketone and quinone groups (SCHULTEN ET AL., 1991).

Since biological treatments are not effective for the removal of refractory compounds and physico-chemical processes such as reverse osmosis and adsorption are non-destructive, innovative technologies have focused on advanced oxidation processes (AOPs) (GEENENS ET AL., 2001; RENOU ET AL., 2008). AOPs are attractive methods to eliminate the color, to reduce the organic load and to improve the biodegradability of recalcitrant contaminants of mature leachate (DE MORAIS & ZAMORA, 2005; RENOU ET AL., 2008; KOCHANY & LIPCZYNSKA-KOCHANY, 2009). These processes involve the production of powerful oxidizing agents, mainly the hydroxyl radical ($^{\bullet}OH$), from single oxidants, such as ozone (DI IACONI ET AL., 2006), or from a combination of strong oxidants, e.g. O_3 and OH^- (HAAPEA ET AL., 2002), H_2O_2 (WANG ET AL., 2004), irradiation, e.g. ultraviolet (WU ET AL., 2004), ultrasound (WANG ET AL., 2008) or electron beam (BAE ET AL., 1999), and catalysts, e.g. transition metal ions or photocatalyst (CHO ET AL., 2004).

Molecular ozone is a strong oxidizer having high reactivity and selectivity towards organic pollutants such as humic substances (CHATURAPRUEK ET AL., 2005). The use of ozone at high pH (O_3/OH^-) or in combination with H_2O_2 (O_3/H_2O_2), both favoring the production of hydroxyl radicals that have an oxidation potential higher than that of ozone molecule, are attractive processes to oxidize the complex leachate mixtures (TIZAOUI ET AL., 2007). It is expected that the use of such processes as pre-treatment, to reduce and convert the large refractory organic molecules, found in mature leachates, into smaller more biodegradable intermediates, followed by biological oxidation of these intermediates would result in economical savings and improvement of the treatment efficiency (IMAI ET AL., 1998; WU ET AL., 2004).

The treatment of mature landfill leachate using ozone, ozone at alkaline pH or ozone with hydrogen peroxide has been demonstrated in the literature. For instance, TIZAOUI ET AL. (2007) reported that ozone alone ensured a COD removal of about 27% after 60 min of ozonation, while the O_3 and H_2O_2 combination increased COD removal up to 48%. HAGMAN ET AL. (2008) verified the same tendency obtaining an improvement in COD reduction from 22% for ozone alone to 50% when hydrogen peroxide was added. GOI ET AL. (2009) studied the effect of pH on ozonation of a landfill leachate, achieving COD removal efficiencies of 24%, 29% and 41% at initial pH 4.5, 8.1 and 11, respectively. Many researchers (IMAI ET AL., 1998; MONJE-RAMIREZ & VELÁSQUEZ, 2004; WU ET AL., 2004; BILA ET AL., 2005; TIZAOUI ET AL., 2007) observed a significant enhancement in biodegradability, defined as the BOD_5/COD ratio, after ozonation. However, none of these reports evaluated the effect of different O_3 concentrations, O_3 at different pH values and O_3 with different H_2O_2 concentrations on leachate COD, BOD_5, pH, ultraviolet absorbance at 254 nm (UV_{254}) and nitrogenous compounds.

Therefore, the objective of this study was to investigate the ozonation of a mature landfill leachate, in order to transform refractory compounds and improve leachate biodegradability. Experiments were conducted at different ozone concentrations, contact time, initial pH and H_2O_2 concentrations in a lab-scale column. The leachate under study had already been treated in the treatment plant of the sanitary landfill, which comprises stabilization, anaerobic ponds, an anoxic tank, aerated ponds and a biological decantation unit, together with an oxidation tank and two chemical precipitators. In spite of that, at the end of the process the leachate still did not meet the maximum allowable nitrogen and organic matter concentrations for direct or indirect discharge. Previously we developed a biological process using an anoxic rotating biological contactor to remove nitrate. Despite its high efficiency in nitrate removal, it was not able to remove any of the refractory organic compounds still present, and an external carbon source had to be added, which represents an additional cost.

6A.2 MATERIALS AND METHODS

6A.2.1 LANDFILL LEACHATE

The landfill leachate was collected from a municipal landfill in the North of Portugal before being discharged to the municipal sewer. This landfill has been in operation since 1998. The collected leachate was stored in closed containers at 4 ºC until use. The characteristics of the leachate used in the investigated period are listed in Table 6.1. Taking into account the extremely low value of the BOD_5/COD ratio (0.01) and the high content of nitrogen-ammonium ($N\text{-}NH_4^+$), this leachate can be considered mature and rich in refractory compounds. Another important feature of this leachate is the high nitrogen-nitrate ($N\text{-}NO_3^-$) content.

Table 6.1 Landfill leachate characteristics.

Parameter	Value
pH	3.5±0.1
Conductivity ($mS \cdot cm^{-1}$)	4.45±0.03
COD ($mg \cdot L^{-1}$)	743±14
BOD_5 ($mg \cdot L^{-1}$)	10±1
TOC ($mg \cdot L^{-1}$)	284±6
UV_{254}	2.614±0.023
$N\text{-}NO_3^-$ ($mg \cdot L^{-1}$)	1824±103
$N\text{-}NO_2^-$ ($mg \cdot L^{-1}$)	<0.01
$N\text{-}NH_4^+$ ($mg \cdot L^{-1}$)	714±23
VSS ($mg \cdot L^{-1}$)	79±3

6A.2.2 OZONATION

The ozonation experiments were conducted in an acrylic column, semi-batch reactor, with a height of 69.5 cm and an internal diameter of 8.2 cm. Ozone was produced from pure and dry oxygen by corona discharge using an ozone generator (Anseros Peripheral Com-AD-02), capable of producing up to 8 g O_3 h^{-1}. The ozone and oxygen mixture was continuously introduced into the column through a ceramic diffuser placed at the bottom and was allowed to react with each sample for 60 min. The inlet and outlet concentrations of ozone in the gas phase were measured at 254 nm using an ozone analyzer (Anseros Ozomat GM-6000-OEM), throughout the experiments. The residual gas was vented through the catalytic ozone destruction unit. A needle valve and a gas flow meter were placed before the column to control and measure the ozone and oxygen mixture flow rate in $L \cdot h^{-1}$. For every experiment the reactor was filled with one liter of leachate. Effluent samples were taken during reaction at the bottom of the column.

The effect of initial pH was studied adjusting the pH of the leachate with NaOH. In O_3/H_2O_2 experiments, the required amount of H_2O_2 was injected in a single-step to the column at time zero. The samples collected from these trials were treated with a saturated solution of NaOH to quench the reaction of residual H_2O_2.

All experiments were carried out at room temperature (20 ºC ± 2 ºC), performed in duplicate and the results were averaged.

6A.2.3 ANALYTICAL METHODS

The leachate was characterized before and after ozonation, through analyses of pH, chemical oxygen demand (COD), total organic carbon (TOC), five-day biochemical oxygen demand (BOD_5), nitrogen-nitrate ($N\text{-}NO_3^-$), nitrogen-nitrite ($N\text{-}NO_2^-$), nitrogen-ammonium ($N\text{-}NH_4^+$), and UV absorbance at 254 nm. COD, BOD_5, $N\text{-}NO_2^-$, and $N\text{-}NH_4^+$ concentrations were determined according to Standard Methods (APHA ET AL., 1989). Nitrate concentration was measured by high-performance liquid chromatography (HPLC), using a Varian Metacarb column (type 67H, 9 μm, 300 mm long, 6.5 mm internal diameter) and a mobile phase of 0.005 M sulphuric acid (H_2SO_4) at 0.7 $mL \cdot min^{-1}$. Column temperature was set at 60 ºC and nitrate was detected by UV at 210 nm. Ultraviolet absorbance at 254 nm (UV_{254}) was monitored with a Jasco V-560 spectrophotometer. TOC measurements were performed using a Dohrmann DC-190 TOC Analyzer.

6A.3 RESULTS AND DISCUSSION

6A.3.1 EFFECT OF INLET OZONE CONCENTRATION AND CONTACT TIME

The effect of inlet ozone concentration was investigated at 63, 74 and 112 $mg \cdot L^{-1}$ NTP, corresponding to a gas flow rate of 2.5, 1.67 and 0.83 $L \cdot min^{-1}$, respectively. These experiments were carried out at the natural pH of the landfill leachate (pH=3.5). Table 6.2 presents the results of ozone consumption, COD, TOC, and UV_{254} removal efficiencies, as well as N-NO_2^-, N-NO_3^- and N-NH_4^+ variations throughout time at different O_3 concentrations. Ozone consumption (OC) was calculated according to Equation 6.1:

$$OC\left(g.O_3\cdot L^{-1}liquid\right)=\frac{Q_G}{V_L}\int_0^t\left(\left[O_{3G,i}\right]-\left[O_{3G,o}\right]\right)\cdot\,dt \quad \text{Equation 6.1}$$

where Q_G is the gas flow rate (L·min^{-1}), V_L the liquid volume (L), and [$O_{3G,i}$] and [$O_{3G,o}$] are the ozone concentrations (g·L^{-1} NTP) in the gas stream at the inlet and outlet, respectively. The inlet ozone concentration remained constant over time for each experiment.

It was observed that COD and TOC removal efficiencies increased with contact time and ozone concentration. The highest ozone consumption was observed for the highest ozone concentration tested, suggesting a more effective use of the ozone supplied to the system. This fact is due to the higher ozone partial pressure that provides higher solubility of ozone, achieving maximum ozone mass transfer and consequent availability.

It is difficult to compare the removal efficiency values obtained herein with the ones presented in the literature because these depend on many factors (such as the type of reactor, pH and temperature). Furthermore, the landfill leachate used in this study had the particularity of having been previously treated.

COD removal efficiency increased faster initially leveling off after 30 min (Table 6.2). The COD degradation was rapid during the initial period probably due to the availability of easily oxidizable compounds, such as phenols, quinones and aromatic acids. Further increase in reaction time led to a slow change in organic removal rate, indicating the formation of by-products such as aliphatic acids and aldehydes, which were difficult to further degrade (CHATURAPRUEK ET AL., 2005; TIZAOUI ET AL., 2007). A similar tendency was observed with TOC removal efficiency. WANG ET AL. (2004) and CHATURAPRUEK ET AL. (2005) also reported two kinetic periods in the COD and TOC removal efficiencies of a mature landfill leachate. Therefore, it is not always worthwhile to increase the ozone contact time.

The degree of carbon mineralization (TOC removal) was lower than COD removal throughout the study. This phenomenon is probably related with the generation and accumulation of carboxylic acids and aldehydes as final products, rather than CO_2 (MONJE-RAMIREZ & VELÁSQUEZ, 2004; WU ET AL., 2004).

Table 6.2 Effect of ozone concentration and contact time on OC, COD, TOC and UV_{254} removal efficiencies; $N\text{-}NO_2^-$, $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$ concentrations.

O_3 concentration (mg·L^{-1} NTP)	Parameter	Contact time (min)					
		0	5	15	30	45	60
63	OC (g O_3·L^{-1} effluent)		0.44	1.25	2.19	3.01	3.89
	COD removal (%)		4	6	7	10	10
	TOC removal (%)		2	4	5	6	7
	UV_{254} removal (%)		10	14	16	18	19
	$N\text{-}NO_2^-$ (mg·L^{-1})	0.01	0.04	0.04	0.03	0.03	0.03
	$N\text{-}NO_3^-$ (mg·L^{-1})	2045	2078	2088	2109	2106	2096
	$N\text{-}NH_4^+$ (mg·L^{-1})	690	675	659	637	622	650
74	OC (g O_3·L^{-1} effluent)		0.55	1.39	2.35	3.24	4.07
	COD removal (%)		6	10	14	16	17
	TOC removal (%)		3	8	9	11	11
	UV_{254} removal (%)		9	15	18	19	21
	$N\text{-}NO_2^-$ (mg·L^{-1})	0.01	0.03	0.03	0.03	0.03	0.03
	$N\text{-}NO_3^-$ (mg·L^{-1})	2089	2100	2129	2152	2157	2162
	$N\text{-}NH_4^+$ (mg·L^{-1})	767	764	746	725	711	699
112	OC (g O_3·L^{-1} effluent)		0.61	1.42	2.40	3.37	4.38
	COD removal (%)		10	13	17	20	23
	TOC removal (%)		5	8	10	13	14
	UV_{254} removal (%)		9	17	19	21	22
	$N\text{-}NO_2^-$ (mg·L^{-1})	0.01	0.03	0.04	0.03	0.03	0.03
	$N\text{-}NO_3^-$ (mg·L^{-1})	2059	2075	2123	2144	2154	2162
	$N\text{-}NH_4^+$ (mg·L^{-1})	785	763	743	713	699	690

The molecular ozone is very effective in the oxidation of aromatic compounds susceptible to electrophilic attack. Thus, ozonation can easily alter the molecular structure of the leachate organics from aromatic and unsaturated constituents to saturated intermediates (IMAI ET AL., 1998; LIN ET AL., 2009). The absorbance at 254 nm (UV_{254}) has been reported to be a qualitative indicator of aromatic and unsaturated compounds present in wastewater (IMAI ET AL., 1998; SEVIMLI, 2005). From Table 6.2 it can be observed that UV_{254} removal efficiency increased with contact time and slightly improved with the increase of inlet ozone concentration. A rapid increase of the UV_{254} removal efficiency was noted during the first 30 min, but the oxidation rate decreased as the reaction proceeded. UV_{254} removal was, in general, higher than COD and TOC removal efficiencies. These results support the hypothesis that molecular ozone reacted promptly with aromatic and unsaturated compounds inducing the decrease of aromaticity, but generated compounds that react more slowly and are resistant to further oxidation such as carboxylic acids and aldehydes instead of CO_2, as mentioned above.

Mature landfill leachate typically presents high concentrations of nitrogenous pollutants. During these experiments only about 10% of nitrogen-ammonium was converted to nitrogen-nitrate due to the acidic conditions assayed (pH=3.5). In fact, previous studies (LIN & WU, 1996; TANAKA & MATSUMURA, 2003) showed that this oxidation is negligible in acidic solutions because at pH lower than 7, ammonia (NH_3) exists in the aqueous solution essentially in its ionized form (NH_4^+), which is not reactive toward ozone. Nevertheless, it should also be noted that species such as bromide are known to favor ammonia removal (TANAKA & MATSUMURA, 2003).

Once ammonium removal consumes ozone, it would be interesting to determine whether or not N-NH_4^+ should be removed before oxidation, by a biological nitrification process or by air stripping.

A slight decrease in pH from 3.5 to 3.0 was observed in these experiments (data not shown).

The biodegradability of an effluent can be described in terms of BOD_5/COD ratio. In order to assess the effect of different ozone concentrations on leachate biodegradability, BOD_5 measurements after 60 min of treatment were carried out and the results obtained are compiled in Figure 6.1.

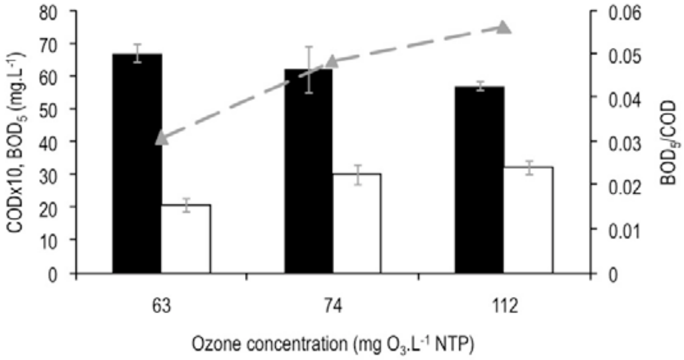

Figure 6.1 Effect of ozone concentration on COD (■), BOD_5 (□), and BOD_5/COD ratio (▲) after 60 min of treatment.

After ozonation, BOD_5 increased by about 80% at 63 mg $O_3 \cdot L^{-1}$ NTP, 160% at 74 mg $O_3 \cdot L^{-1}$ NTP, and 180% at 112 mg $O_3 \cdot L^{-1}$ NTP. Consequently, BOD_5/COD ratio increased with the increase of the ozone concentration from 0.03 at 63 mg $O_3 \cdot L^{-1}$ NTP to 0.06 at 112 mg $O_3 \cdot L^{-1}$ NTP.

According to the results, a gas flow rate of 0.83 L·min^{-1} and an inlet ozone concentration of about 112 mg·L^{-1} NTP were chosen for further experiments.

6A.3.2 EFFECT OF INITIAL PH

The effect of initial pH on ozone consumption and degradation of the landfill leachate pollutants by ozonation is given in Table 6.3. OC, COD and TOC removal efficiencies increased as the pH raised because under basic pH higher number of ozone molecules are decomposed to generate OH^- and $^{\bullet}OH$ radicals and a less selective and more powerful hydroxyl oxidation dominates (LIN ET AL., 2009; SOMENSI ET AL., 2010). UV_{254} removal efficiency was not affected by pH.

Table 6.3 Effect of initial pH on OC, COD, TOC and UV_{254} removal efficiencies; $N\text{-}NO_2^-$, $N\text{-}NO_3^-$, and $N\text{-}NH_4^+$ concentrations after 60 min of ozonation with an ozone concentration of 112 mg O_3·L^{-1} NTP.

Parameter	pH=3.5[a]	pH=7	pH=9	pH=11
OC (g O_3·L^{-1} effluent)	4.38	4.89	5.05	5.14
COD removal (%)	23	30	36	40
TOC removal (%)	14	21	28	32
UV_{254} removal (%)	22	22	22	22
$N\text{-}NO_2^-$ (mg·L^{-1})	0.03	0.06	0.13	0.08
$N\text{-}NO_3^-$ (mg·L^{-1})	2162	2188	2228	2263
$N\text{-}NH_4^+$ (mg·L^{-1})	690	619	565	548

[a] pH 3.5 was the natural pH of the landfill leachate.

The results show that ozonation at high pH values favored the conversion of ammonium (in the un-ionized form) to nitrate (Table 6.3), as also observed by SINGER & ZILLI (1975).

In these experiments, after 60 minutes of reaction only a slight decrease in pH values was noticed (data not shown). The maximum drop (2.2 units) was observed at initial pH 7. Probably carbonates accumulated in the treated leachate as a result of mineralization at basic pH, while carboxylic acids and aldehydes (WANG ET AL., 2004) were produced by direct ozonation reactions at pH=7.

Figure 6.2 depicts the results of COD, BOD_5, and BOD_5/COD as a function of initial pH, after ozonation. BOD_5 increased about 180% at pH 3.5, 230% at pH 7, 275% at pH 9 and 455% at pH 11. The raise in BOD_5 can be due to the transformation of the refractory large compounds into smaller and more biodegradable products (WANG ET AL., 2004).

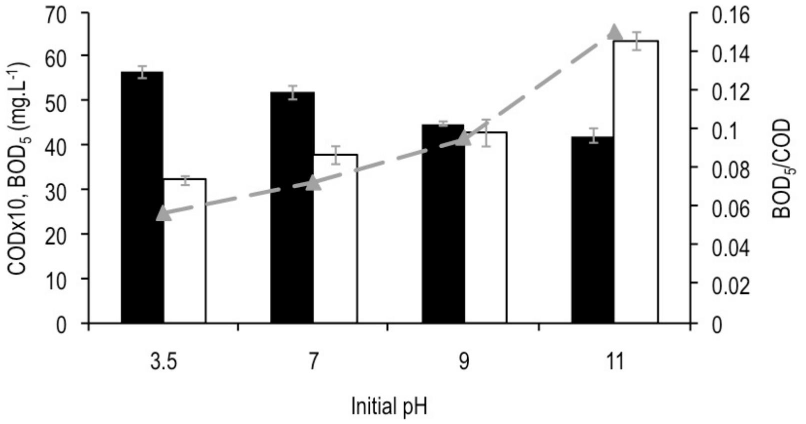

Figure 6.2 Effect of initial pH on COD (■), BOD5 (□), and BOD5/COD ratio (▲) after 60 min of ozonation with an ozone concentration of 112 mg $O_3 \cdot L^{-1}$ NTP.

6A.3.3 EFFECT OF HYDROGEN PEROXIDE CONCENTRATION

The AOP experiments associating ozone and hydrogen peroxide (O_3/H_2O_2) were performed with H_2O_2 at 200, 400 and 600 mg$\cdot L^{-1}$. According to STAEHELIN & HOIGNÉ (1982), the lower limit for the effectiveness of the H_2O_2/O_3 process is in a pH range of 5 to 7, therefore, the O_3/H_2O_2 process was applied to leachate, after correction to pH 7.

Table 6.4 presents the results of ozone consumption, COD, TOC, and UV_{254} removal efficiencies, as well as nitrogenous compounds concentrations after ozonation at different H_2O_2 concentrations. Additionally, and as a control, landfill leachate was treated with hydrogen peroxide only at the same concentrations for 60 min and during the experiments no changes of parameters were detected since the hydrogen peroxide alone is not a strong oxygen transfer agent (data not shown).

The O_3/H_2O_2 process enhanced the degradation of the landfill leachate compared to O_3 only. In the O_3/H_2O_2 system the production of hydroxyl radicals is significantly high, thus these results confirmed that the oxidation of this effluent was mainly due to these chemical species. In addition, they also promoted an increase in UV_{254} removal.

Some authors (AKMEHMET BALCIOGLU & ÖTKER, 2003; TIZAOUI ET AL., 2007; LIN ET AL., 2009) report that an increase in hydrogen peroxide concentration will not always increase organic compounds degradation. In effect, supplying hydrogen peroxide in excess will change its role from being the initiator for the production of $^{\bullet}OH$ radicals to inhibitor of ozone decomposition through free radical reactions. As a consequence, degradation of the organic matter in the leachate diminishes. In this work, since for the tested amounts of H_2O_2 the oxidation rate increased as the hydrogen peroxide concentration increased, that trend was not observed and perhaps the optimum hydrogen peroxide dose was not found.

Table 6.4 Effect of hydrogen peroxide concentration on OC, COD, TOC and UV_{254} removal efficiencies; $N\text{-}NO_2^-$, $N\text{-}NO_3^-$, and $N\text{-}NH_4^+$ concentrations after 60 min of ozonation with an ozone concentration of 112mg $O_3 \cdot L^{-1}$ NTP at pH7.

Parameter	0 mg $H_2O_2 \cdot L^{-1}$	200 mg $H_2O_2 \cdot L^{-1}$	400 mg $H_2O_2 \cdot L^{-1}$	600 mg $H_2O_2 \cdot L^{-1}$
OC (g $O_3 \cdot L^{-1}$ effluent)	4.89	5.19	5.30	5.40
COD removal (%)	30	47	57	63
TOC removal (%)	21	38	50	53
UV_{254} removal (%)	22	30	36	42
$N\text{-}NO_2^-$ ($mg \cdot L^{-1}$)	0.06	0.08	0.14	0.12
$N\text{-}NO_3^-$ ($mg \cdot L^{-1}$)	2188	2191	2171	2166
$N\text{-}NH_4^+$ ($mg \cdot L^{-1}$)	619	621	632	632

Considering nitrogenous pollutants, as is shown in Table 6.4, nitrogen-ammonium was converted to nitrogen-nitrate and it was not verified a significant difference between the treatments with O_3 only and O_3/H_2O_2, for the different amounts of H_2O_2 assayed.

Results of the effect of O_3 only and O_3/H_2O_2 on biodegradability are presented in Figure 6.3. Biodegradability improved in both systems; however, the O_3/H_2O_2 process presented noticeable higher BOD_5/COD values. A BOD_5/COD ratio of about 0.17 was achieved for the different concentrations of peroxide.

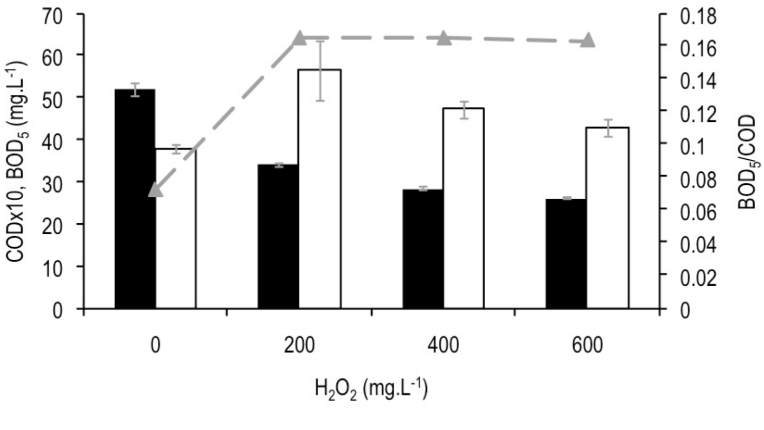

Figure 6.3 Effect of hydrogen peroxide concentration on COD (■), BOD_5 (□), and BOD_5/COD ratio (▲) after 60 min of ozonation with an ozone concentration of 112 mg $O_3 \cdot L^{-1}$ NTP at pH 7.

A simplistic economical analysis of the operating costs associated to each AOP studied, such as expenses of reagents and energy, was performed. The calculated costs, based on 60 min of operating time and considering 0.09 € · kWh^{-1}; 0.35 €·kg^{-1} NaOH, 0.33 €·L^{-1} H_2O_2 (35%) and 0.08 €·m^{-3} O_2, are summarized in Table 6.5.

Table 6.5 Operating costs for the AOPs studied.

AOP	Operating costs (€·m^{-3}·g^{-1} of COD removed)
O_3/pH=3.5[a]	64.0
O_3/pH=7	49.4
O_3/pH=9	41.7
O_3/pH=11	38.2
O_3/ 200 mg H_2O_2 ·L^{-1}	31.9
O_3/400 mg H_2O_2·L^{-1}	26.6
O_3/ 600 mg H_2O_2·L^{-1}	24.7

[a] pH 3.5 was the natural pH of the landfill leachate.

The lowest operating cost was 24.7 €·m^{-3}·g^{-1} of COD removed for the experiment carried out with the O_3/H_2O_2 system at 600 mg H_2O_2·L^{-1}. Considering the operating costs of O_3 alone, significant reductions in the treatment costs were obtained under basic pH and with hydrogen peroxide. It is important to note that a fine-tuning of the operating conditions could considerably change the operating costs obtained for each treatment process.

Though there was a significant improvement in biodegradability, a BOD_5/COD ratio higher than 0.4, which is the minimum value considered appropriate for the efficient application of a biological treatment (TCHOBANOGLOUS & BURTON, 1991) was never achieved, for all processes tested, emphasizing the highly recalcitrant properties of the landfill leachate studied.

Probably coupling one of O_3/H_2O_2 conditions tested with other physico-chemical treatment process would ensure a BOD_5/COD ratio higher than 0.4 before the biological treatment, without increasing significantly the operation costs. For instance, in the treatment of a landfill leachate, MONJE-RAMIREZ & VELÁSQUEZ (2004) and BILA ET AL. (2005) also applied ozonation preceded by the coagulation/flocculation of colloids and found significant biodegradability improvement.

6A.4 CONCLUSIONS

In the polishing treatment of a mature landfill leachate, the combined effect of ozone with hydrogen peroxide induced higher COD and TOC removal efficiencies as well as higher leachate biodegradability, comparatively to ozone alone at natural pH. These results are related with the enhanced production of hydroxyl radicals in the presence of H_2O_2. For comparison purposes only, estimates of operating costs were calculated. It was found that O_3/H_2O_2 at 600 mg $H_2O_2 \cdot L^{-1}$ was the most economical process (24.7 € $\cdot m^{-3} \cdot g^{-1}$ of COD removed) to treat the leachate tested. Since before being discharged the leachate must be denitrified, which demands the presence of a carbon source, future studies are planned to optimize the O_3/H_2O_2 system in order to obtain even more biodegradable compounds, which could be used in the biological process.

6A.5 REFERENCES

AKMEHMET BALCIOGLU, I. & ÖTKER, M. (2003) Treatment of pharmaceutical wastewater containing antibiotics by O_3 and O_3/H_2O_2 processes. *Chemosphere*, 50, 85-95.

APHA, AWWA & WPCF (1989) Standard methods for the examination of water and wastewater, 17th edition. American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC.

BAE, B., JUNG, E., KIM, Y. & SHIN, H. (1999) Treatment of landfill leachate using activated sludge process and electron-beam radiation. *Water Research*, 33, 2669-2673.

BILA, D.M., FILIPE MONTALVAO, A., SILVA, A.C. & DEZOTTI, M. (2005) Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement. *Journal of Hazardous Materials*, 117, 235-242.

CHATURAPRUEK, A., VISVANATHAN, C. & AHN, K.H. (2005) Ozonation of membrane bioreactor effluent for landfill leachate treatment. *Environmental Technology*, 26, 65-73.

CHO, S.P., HONG, S.C. & HONG, S. (2004) Study of the end point of photocatalytic degradation of landfill leachate containing refractory matter. *Chemical Engineering Journal*, 98, 245-253.

DI IACONI, C., RAMADORI, R. & LOPEZ, A. (2006) Combined biological and chemical degradation for treating a mature municipal landfill leachate. *Biochemical Engineering Journal*, 31, 118-124.

GEENENS, D., BIXIO, B. & THOEYE, C. (2001) Combined ozone-activated sludge treatment of landfill leachate. *Water Science and Technology*, 44, 359-365.

GOI, A., VERESSININA, Y. & TRAPIDO, M. (2009) Combination of ozonation and the Fenton processes for landfill leachate treatment: evaluation of treatment efficiency. *Ozone: Science and Engineering*, 31, 28-36.

HAAPEA, P., KORHONEN, S. & TUHKANEN, T. (2002) Treatment of industrial landfill leachates by chemical and biological methods: ozonation, ozonation hydrogen peroxide, hydrogen peroxide and biological post-treatment for ozonated water. *Ozone: Science and Engineering*, 24, 369-378.

HAGMAN, M., HEANDER, E. & JANSEN, J.L.C. (2008) Advanced oxidation of refractory organics in leachate – potential methods and evaluation of biodegradability of the remaining substrate. *Environmental Technology*, 29, 941-946.

IMAI, A., ONUMA, K., INAMORI, Y. & SUDO, R. (1998) Effects of pre-ozonation in refractory leachate treatment by the biological activated carbon fluidized bed process. *Environmental Technology*, 19, 213-221.

KOCHANY, J. & LIPCZYNSKA-KOCHANY, E. (2009) Utilization of landfill leachate parameters for pretreatment by Fenton reaction and struvite precipitation--A comparative study. *Journal of Hazardous Materials*, 166, 248-254.

KURNIAWAN, T.A., LO, W.H. & CHAN, G.Y. (2006) Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate. *Journal of Hazardous Materials*, 129, 80-100.

LIN, A.Y., LIN, C., CHIOU, J. & HONG, P.A. (2009) O_3 and O_3/H_2O_2 treatment of sulfonamide and macrolide antibiotics in wastewater. *Journal of Hazardous Materials*, 171, 452-458.

LIN, S.H. & WU, C.L. (1996) Removal of nitrogenous compounds from aqueous solution by ozonation and ion exchange. *Water Research*, 30, 1851-1857.

MONJE-RAMIREZ, I. & VELÁSQUEZ, M.T.O.D. (2004) Removal and transformation of recalcitrant organic matter from stabilized saline landfill leachates by coagulation-ozonation coupling processes. *Water Research*, 38, 2359-2367.

DE MORAIS, J.L. & ZAMORA, P.P. (2005) Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates. *Journal of Hazardous Materials*, 123, 181-186.

RENOU, S., GIVAUDAN, J., POULAIN, S., DIRASSOUYAN, F. & MOULIN, P. (2008) Landfill leachate treatment: review and opportunity. *Journal of Hazardous Materials*, 150, 468-493.

SCHULTEN, H.R., PLAGE, B. & SCHNITZER, M. (1991) A chemical-structure for humic substances. *Naturwissenschaften*, 78, 311-312.

SEVIMLI, M.F. (2005) Post-Treatment of pulp and paper industry wastewater by advanced oxidation processes. *Ozone: Science and Engineering*, 27, 37-43.

SINGER, P.C. & ZILLI, W.B. (1975) Ozonation of ammonia in wastewater. *Water Research*, 9, 127-134.

SOMENSI, C.A., SIMIONATTO, E.L., BERTOLI, S.L., WISNIEWSKI JR., A. & RADETSKI, C.M. (2010) Use of ozone in a pilot-scale plant for textile wastewater pre-treatment: Physico-chemical efficiency, degradation by-products identification and environmental toxicity of treated wastewater. *Journal of Hazardous Materials*, 175, 235-240.

STAEHELIN, J. & HOIGNÉ, J. (1982) Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide. *Environmental Science and Technology*, 16, 676-681.

TANAKA, J. & MATSUMURA, M. (2003) Application of ozone treatment for ammonia removal in spent brine. *Advances in Environmental Research*, 7, 835-845.

TCHOBANOGLOUS, G. & BURTON, F. (1991) Wastewater engineering: Treatment, Disposal and Reuse, 3rd edition. Metcalf and Eddy, Inc., McGraw-Hill Inc., New York.

TIZAOUI, C., BOUSELMI, L., MANSOURI, L. & GHRABI, A. (2007) Landfill leachate treatment with ozone and ozone/hydrogen peroxide systems. *Journal of Hazardous Materials*, 140, 316-324.

WANG, F., EL-DIN, M.G. & SMITH, D.W. (2004) Oxidation of aged raw landfill leachate with O_3 only and O_3/H_2O_2: treatment efficiency and molecular size distribution analysis. *Ozone: Science and Engineering*, 26, 287-298.

WANG, S., WU, X., WANG, Y., LI, Q. & TAO, M. (2008) Removal of organic matter and ammonia nitrogen from landfill leachate by ultrasound. *Ultrasonics Sonochemistry*, 15, 933-937.

WU, J.J., WU, C.C., MA, H.W. & CHANG, C.C. (2004) Treatment of landfill leachate by ozone-based advanced oxidation processes. *Chemosphere*, 54, 997-1003.

6B EVALUATION OF FENTON'S OXIDATION AND OZONE-BASED ADVANCED OXIDATION PROCESSES AS MATURE LANDFILL LEACHATE PRE-TREATMENTS

6B.1 INTRODUCTION

The generation of leachate remains an inevitable consequence of the practice of waste disposal in sanitary landfills (WANG ET AL., 2010). Leachate from mature landfills is typically characterized by high ammonium (NH_4^+) content, low biodegradability (low BOD_5/COD ratio) and high fraction of refractory and large organic molecules such as humic and fulvic acids (DE MORAIS & ZAMORA, 2005; DENG & ENGLEHARDT, 2006). In many cases, after treatment by a series of oxidation processes, mature landfill leachate still presents high concentrations of recalcitrant and nitrogenous compounds. Biological processes are not effective for this type of leachate.

In the last two decades, AOPs have been considered an attractive means to eliminate color, reduce the organic load and improve the biodegradability of recalcitrant contaminants of mature leachates (DENG & ENGLEHARDT, 2006; RENOU ET AL., 2008; KOCHANY & LIPCZYNSKA-KOCHANY, 2009). These processes involve the production of free radical species, mainly the hydroxyl radical ($^{\bullet}OH$). The hydroxyl radical is produced from single oxidants such as ozone (O_3), or from a combination of strong oxidants such as O_3 and hydroxide (OH^-), O_3 and hydrogen peroxide (H_2O_2), or ferrous ions (Fe^{2+}) with H_2O_2 (ROSENFELDT ET AL., 2006; RENOU ET AL., 2008). The combination of Fe^{2+} and H_2O_2 is called Fenton's oxidation.

Fenton's oxidation has been extensively studied for the treatment of mature landfill leachates. In this advanced oxidation technology, under optimum pH, ferrous ions react with hydrogen peroxide to generate the hydroxyl radical in a very simple and cost-effective manner (DENG & ENGLEHARDT, 2006).

Ozone (not decomposed, pH<6) is a strong oxidizer having high reactivity and selectivity towards organic pollutants such as aromatic compounds (LIN ET AL., 2009; LUCAS ET AL., 2010). Furthermore, as the standard oxidation potential of the hydroxyl radical ($E_0 = 2.80$ V) is much higher than that of ozone ($E_0 = 2.07$ V), the use of ozone at high pH (O_3/OH^-) or in a combination with H_2O_2 (O_3/H_2O_2) favors the production of hydroxyl radicals and accelerates the removal of recalcitrant organic matter from complex wastewater matrices (TIZAOUI ET AL., 2007; LUCAS ET AL., 2010). Ozonation under alkaline conditions and the combination of ozone with hydrogen peroxide have proved to be effective advanced oxidation processes for landfill leachate (HAAPEA ET AL., 2002; TIZAOUI ET AL., 2007).

Although AOPs are very effective for the treatment of refractory organic pollutants, if they are applied as the only treatment process, they will be expensive. A promising economical alternative to complete the oxidation of refractory compounds is the use of an advanced oxidation technology as pre-treatment to convert initially biorecalcitrant compounds into more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biomass and water (LIN & KIANG, 2003).

This research was conducted to investigate the efficacy and feasibility of Fenton's oxidation and different ozone-based advanced oxidation processes (O_3, O_3/OH^- and O_3/H_2O_2) as pre-treatment steps of a mature landfill leachate, in order to improve its biodegradability for subsequent biological treatment. The effects of initial pH, oxidant agents concentration and reaction time on the performance of each AOP tested were evaluated in terms of COD, total organic carbon (TOC), BOD_5, nitrogenous compounds and aromaticity. A rough estimate of the operating costs involved in each type of pre-treatment was also performed to compare their economical feasibility.

6B.2 MATERIALS AND METHODS

6B.2.1 LANDFILL LEACHATE

Landfill leachate was collected from a municipal landfill in the North of Portugal, in operation since 1998. The current treatment plant in the sanitary landfill comprises stabilization, anaerobic ponds, an anoxic tank, aerated ponds and a biological decantation unit, together with an oxidation tank and two chemical precipitators. However, even after the post-treatment at the end of the process, the leachate still does not meet the maximum allowable nitrogen and organic matter concentrations for direct or indirect discharge. The characteristics of the undiluted leachate are listed in Table 6.6.

The low value of the BOD_5/COD ratio (0.01) and the high content of nitrogen-ammonium (N-NH_4^+), indicate that this leachate is mature and must be rich in refractory compounds. Another important feature of this leachate is the high nitrogen-nitrate (N-NO_3^-) content. An economical approach to treat this leachate can be achieved by combining an advanced oxidation process with the degradation of the refractory compounds into biodegradable organic matter, and using these products as a carbon source for removal of nitrogenous compounds in biological processes.

Table 6.6 Landfill leachate characteristics.

Parameter	Value
pH	3.5±0.1
Conductivity ($mS \cdot cm^{-1}$)	4.45±0.03
COD ($mg \cdot L^{-1}$)	743±14
BOD_5 ($mg \cdot L^{-1}$)	10±1
TOC ($mg \cdot L^{-1}$)	284±6
$N\text{-}NO_3^-$ ($mg \cdot L^{-1}$)	1824±103
$N\text{-}NO_2^-$ ($mg \cdot L^{-1}$)	<0.01
$N\text{-}NH_4^+$ ($mg \cdot L^{-1}$)	714±23
VSS ($mg \cdot L^{-1}$)	79±3
UV_{254}	2.614±0.023

6B.2.2 FENTON'S OXIDATION PROCEDURE

Fenton's oxidation experiments were carried out at room temperature (20 ± 2 °C) and atmospheric pressure in magnetically stirred batch reactors with two-fold diluted leachate. The pH of the leachate was adjusted using H_2SO_4 95-97% (w/w). The predetermined Fe^{2+} dosage was achieved by adding the necessary amount of solid $FeSO_4 \cdot 7H_2O$. A calculated volume of 35% (v/v) H_2O_2 solution was added in a single step. After the fixed oxidation time (120 min), sodium hydroxide was added to increase the pH above 7 and mixed for 10 min. Stirring was turned off and the sludge was allowed to settle for one hour. Finally the supernatant was centrifuged for 10 min at 10000 rpm and the samples were analyzed. Experiments were conducted in duplicate and the results were averaged.

6B.2.3 OZONATION PROCEDURE

Ozonation experiments were performed in an acrylic column, 69.5 cm high and 8.2 cm internal diameter. Ozone was produced from pure oxygen using an ozone generator (Anseros Peripheral Com-AD-02). The ozone and oxygen mixture was continuously introduced into the column through a ceramic diffuser placed at the bottom and 1 L of two-fold diluted leachate was treated for 60 min. The inlet and outlet concentrations of ozone in the gas phase were measured at

λ=254 nm using an ozone analyzer (Anseros Ozomat GM-6000-OEM) throughout the experiments. The gas flow rate was 50 $L \cdot h^{-1}$ and the input ozone concentration was about 0.112 g $O_3 \cdot L^{-1}$. The residual gas was vented through the catalytic ozone destruction unit. Effluent samples were withdrawn regularly and analyzed.

Ozonation experiments were carried out at adjusted pH values of 7, 9, and 11. These pH values were achieved using sodium hydroxide (NaOH). Advanced oxidation with hydrogen peroxide and ozone was also studied. In these tests the pH of the leachate was adjusted to 7 (STAEHELIN & HOIGNÉ, 1982) and, before ozone was supplied, H_2O_2 at concentrations of 100, 200 or 400 $mg \cdot L^{-1}$ was injected in a single-step to the column. The samples collected from these experiments were treated with NaOH to quench the reaction of residual H_2O_2.

All experiments were carried out at room temperature in duplicate and the results were averaged.

6B.2.4 ANALYTICAL METHODS

The leachate was characterized before and after oxidation experiments. COD, BOD_5, nitrogen-nitrite ($N\text{-}NO_2^-$), and nitrogen-ammonium ($N\text{-}NH_4^+$) concentrations were determined according to Standard Methods (APHA ET AL., 1989). It is important to note that during this work, since acidic and basic pH can affect microbial activity, BOD_5 measurements were done after neutralizing the pH of the sample, as recommended in Standard Methods (APHA ET AL., 1989).

Nitrate (NO_3^-) concentration was measured by high-performance liquid chromatography (HPLC), using a Varian Metacarb column (type 67H, 9 µm, 300 mm long, 6.5 mm internal diameter) and a mobile phase of 0.005 M sulphuric acid (H_2SO_4) at 0.7 $mL \cdot min^{-1}$. Column temperature was set at 60 ºC and nitrate was detected by UV at 210 nm. Ultraviolet absorbance at 254 nm (UV_{254}) was obtained with a Jasco V-560 spectrophotometer using a 1 cm quartz cell. TOC analyses were performed using a Dohrmann DC-190 TOC Analyzer.

6B.3 RESULTS AND DISCUSSION

The mature landfill leachate was treated in order to decompose its recalcitrant compounds and increase its biodegradability using different advanced oxidation systems: Fenton's oxidation, ozone, ozone at alkaline pH and ozone combined with H_2O_2. The efficiency of the selected methods depends on many factors including the presence of inorganic and organic substances in the leachate, pH, reaction time and oxidant agents concentration. Treatability studies were carried out to determine the optimum conditions of each process and its effects on biodegradability. Removal of carbonaceous and nitrogenous compounds, and ultraviolet absorbance at 254 nm was also evaluated. The results obtained are useful to select the best-advanced oxidation process and optimum conditions to be applied to the mature landfill leachate before biological treatment. These data might also lead to a better understanding of the chemical oxidation by Fenton's oxidation and ozonation, as well as the role of pH, ferrous ion and hydrogen peroxide concentrations and contact time during degradation of recalcitrant wastewater.

6B.3.1 FENTON'S OXIDATION

Degradation of pollutants by Fenton's oxidation is most effective in acidic environments due to higher production of hydroxyl free radicals ($^{\bullet}OH$) (DE MORAIS & ZAMORA, 2005; KOCHANY & LIPCZYNSKA-KOCHANY, 2009). Optimal pH values reported for conventional Fenton processes for landfill leachate treatment typically range between 2 and 4.5 (DENG & ENGLEHARDT, 2006). This is evidenced in Table 6.7, which reports the results of the process under different initial pH.

In accordance with literature (LÓPEZ ET AL., 2004; DENG, 2007), pH 3 resulted in the highest COD and TOC removal efficiencies. At lower pH (<3), the COD removal efficiency decreased, primarily due to the lower reaction rate of $[Fe(H_2O)]^{2+}$ and H_2O_2 (SZPYRKOWICZ ET AL., 2001), the increased scavenging of $^{\bullet}OH$ by H^+ (GALLARD ET AL., 1998), and/or the inhibition of the reaction between Fe^{3+} and H_2O_2 due to high concentrations of H^+ (TANG & HUANG, 1996). By contrast, COD removal efficiency dropped mainly as the pH exceeded 5, due to the increasing rate of auto decomposition of H_2O_2, deactivation of iron ions into iron oxyhydroxides, the increased scavenging effect of carbonate and bicarbonate on $^{\bullet}OH$, and/or the decreased oxidation potential of $^{\bullet}OH$.

As can be seen in Table 6.7, the effect of pH on mineralization (TOC removal) is similar to COD removal efficiency, although slightly lower, under the same operating conditions. This phenomenon was observed throughout Fenton's oxidation and is probably related with the accumulation of carboxylic acids as final products (CAÑIZARES ET AL., 2009). Therefore, further data related to TOC in the Fenton study will be not shown.

The absorbance at 254 nm (UV_{254}) could represent the degree of aromaticity and unsaturated compounds present in wastewater (SEVIMLI, 2005). Thus, a decrease in the UV absorbance might reflect a decrease of recalcitrant compounds and an increase in the BOD_5/COD ratio. From Table 6.7 it can be observed that UV absorbance removal was also favored at pH 3. The lower COD removal compared to UV_{254} removal can be explained by incomplete or partial oxidation of organic materials.

Table 6.7 Effect of initial pH on COD, TOC and UV_{254} removal efficiencies; $N\text{-}NO_2^-$, $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$ concentrations in Fenton treatment of a mature leachate (conditions: reaction time=120 min; $H_2O_2/Fe^{2+}=3$; $Fe^{2+}=4$ mmol·L⁻¹; mean initial COD=340 mg·L^{-1}).

Parameter	Initial pH					
	2	3	4	5	6	7
COD removal (%)	38	46	43	42	38	34
TOC removal (%)	35	42	41	39	37	31
UV_{254} removal (%)	55	62	60	58	53	51
$N\text{-}NO_2^-$ (mg·L^{-1})	0.003	0.004	0.004	0.003	0.005	0.003
$N\text{-}NO_3^-$ (mg·L^{-1})	1066	1061	1072	1063	1072	1071
$N\text{-}NH_4^+$ (mg·L^{-1})	372	361	377	374	386	369

As mentioned before, mature landfill leachate typically presents high concentrations of nitrogenous pollutants, which is undesirable since these compounds are harmful to environment and human health. In our experiments, $N\text{-}NO_2^-$, $N\text{-}NO_3^-$, and $N\text{-}NH_4^+$ concentrations practically did not change after the Fenton process, for the different pH values tested (Table 6.7). This is in agreement with the results of WANG ET AL. (2001). Other studies reported that only high H_2O_2 concentrations in the Fenton process eliminate ammonium and the main by-products are gaseous N_2 and nitrate (GOI & TRAPIDO, 2002). Therefore, further data related to nitrogenous compounds in Fenton treatment will be not shown.

To assess the effect of different pH on leachate biodegradability, BOD_5 measurements were carried out after 120 min of Fenton treatment. The results of COD, BOD_5 and BOD_5/COD as a function of pH are depicted in Figure 6.4. It can be seen that Fenton's oxidation led to an increase in BOD_5 concentrations for all pH values tested. BOD_5 improvement may be attributed to the presence of oxidation by-products with small molecular weights and thus more easily biodegradable, and/or the reduction of the toxicity effect of some organic compounds due to their degradation. BOD_5 increased from 5 to 28 mg·L^{-1} at pH 3. The increase in BOD_5 and the decrease in COD led to an increase in the BOD_5/COD ratio. The biodegradability improvement also confirms the occurrence of a partial oxidation process.

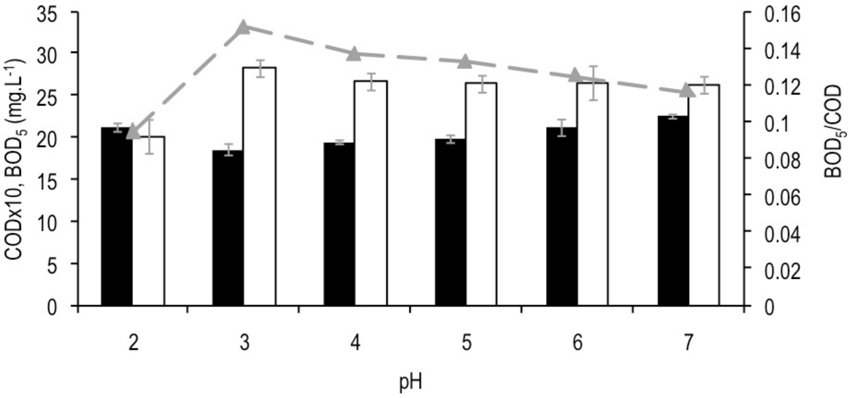

Figure 6.4 Effect of initial pH on COD (■), BOD$_5$ (□) and BOD$_5$/COD ratio (▲) after 120 min of Fenton treatment at $H_2O_2/Fe^{2+}=3$, $Fe^{2+}=4$ mmol·L^{-1} and mean initial COD=340 mg·L^{-1}.

Based on the results, further experiments were performed at pH 3.

In Fenton's oxidation neither H_2O_2 nor Fe^{2+} must be overdosed, to ensure that the maximum amount of $^{\bullet}OH$ radicals is available for the oxidation of organic compounds (TANG & HUANG, 1996). Thus, the H_2O_2 to Fe^{2+} molar ratio (H_2O_2/Fe^{2+}) is an important operational parameter to control. The effect of H_2O_2/Fe^{2+} on COD and UV$_{254}$ removal efficiencies was examined under Fe^{2+} concentrations of 1, 2, and 4 mmol·L^{-1}. The results are shown in Table 6.8.

Table 6.8 Effect of H_2O_2/Fe^{2+} and Fe^{2+} concentration on COD and UV$_{254}$ removal efficiencies in Fenton treatment of a mature leachate (conditions: initial pH 3; reaction time=120 min; mean initial COD=340 mg·L^{-1}).

Fe^{2+} (mmol·L^{-1})	Removal (%)	H_2O_2/Fe^{2+}					
		1	1.5	2	2.5	3	3.5
1	COD	12	14	15	18	25	22
	UV$_{254}$	14	17	21	22	29	25
2	COD	26	29	31	32	36	34
	UV$_{254}$	22	29	34	39	44	40
4	COD	29	31	35	41	46	44
	UV$_{254}$	35	43	52	56	62	59

For the three concentrations of ferrous iron tested, the maximum oxidation efficiency occurred at $H_2O_2/Fe^{2+}=3$. Further increase in this ratio did not show significant removal improvement. This result might be attributed to the scavenging effect of peroxide on the hydroxyl radicals, which presumably became stronger as the ratio H_2O_2/Fe^{2+} increased. Another explanation can be the formation of hydroperoxyl radicals ($HO_2^{\bullet}$), which are less reactive in attacking the recalcitrant compounds in the liquid phase (KURNIAWAN & LO, 2009). At a ratio $H_2O_2/Fe^{2+}<3$ oxidation efficiency decreased probably because iron salt scavenged $^{\bullet}OH$. DENG (2007) also found an optimal H_2O_2/Fe^{2+} molar ratio of 3 in the Fenton treatment of a mature landfill leachate, although as a pre-treatment.

An increase in the initial ferrous iron amount added raised the COD and UV_{254} removal efficiencies (Table 6.8). This indicates that the leachate did not contain sufficient amount of metal ions to keep the process going at a significant rate. The scavenging effect of Fe^{2+} on hydroxyl radicals was not observed.

The effect of Fe^{2+} concentration on leachate biodegradability was also studied under a fixed $H_2O_2/Fe^{2+}=3$. Figure 6.5 shows that Fenton's oxidation resulted in an increase in BOD_5 values for all Fe^{2+} concentrations assayed however, the maximum biodegradability increase occurred at $Fe^{2+}=4$ mmol·L^{-1}.

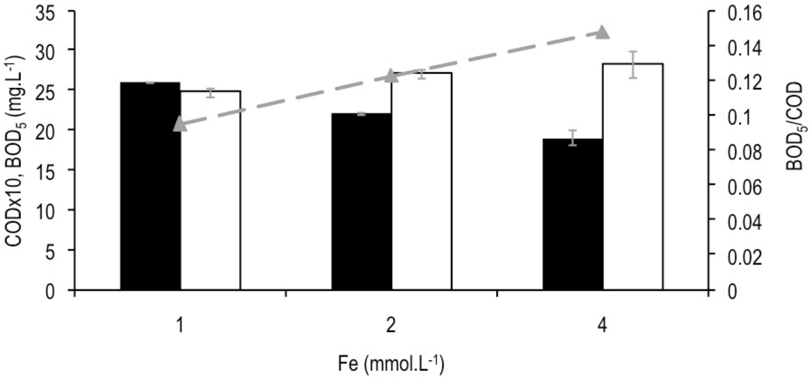

Figure 6.5 Effect of Fe^{2+} concentration on COD (■), BOD_5 (□) and BOD_5/COD ratio (▲) after 120 min of Fenton treatment at $H_2O_2/Fe^{2+}=3$, initial pH 3 and mean initial COD=340 mg·L^{-1}.

Further tests were carried out, at initial pH 3, $H_2O_2/Fe^{2+}=3$ and $Fe^{2+}=4$ mmol·L^{-1}, to find whether reaction times smaller than 120 min, i.e. the time fixed during the whole investigation, would reduce the extent of leachate oxidation. Table 6.9 shows that organic matter was rapidly degraded by Fenton's oxidation. Most organic removal occurred in the first 40 min, after which the change of organic compounds became insignificant. Therefore, 40 min of Fenton's oxidation for this mature landfill leachate would be enough to obtain approximately the same results as obtained in the full two hours.

Table 6.9 Effect of reaction time on COD and UV_{254} removal efficiencies in Fenton treatment of a mature leachate (conditions: initial pH 3; $H_2O_2/Fe^{2+}=3$; $Fe^{2+}=4$ mmol·L⁻¹; mean initial COD=340 mg·L⁻¹).

Parameter	Reaction time (min)					
	20	40	60	80	100	120
COD removal (%)	42	46	45	46	46	46
UV_{254} removal (%)	54	61	62	63	63	62

Results of BOD_5 and residual COD indicated that BOD_5/COD ratio increased from 0.01 for the two-fold diluted leachate to 0.15 after 40 min of Fenton's oxidation, and further reaction did not improve the biodegradability (Figure 6.6).

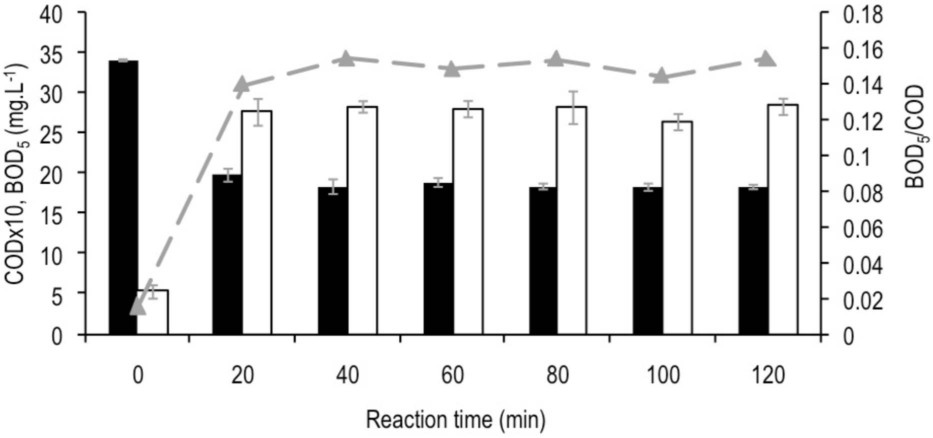

Figure 6.6 Effect of reaction time on COD (■), BOD_5 (□) and BOD_5/COD ratio (▲) after Fenton treatment at $H_2O_2/Fe^{2+}=3$, initial pH 3, $Fe^{2+}=4$ mmol·L⁻¹ and mean initial COD=340 mg·L⁻¹.

The optimum conditions for the Fenton process studied were as follows: initial pH 3, H_2O_2 to Fe^{2+} molar ratio of 3, Fe^{2+}at 4 mmol·L⁻¹, and reaction time of 40 min. For a two-fold diluted leachate, under these conditions, COD removal efficiency was 46%; UV_{254} removal was 62% and BOD_5/COD ratio increased from 0.01 to 0.15.

6B.3.2 OZONATION

To demonstrate the effect of pH on ozonation process, landfill leachate was subjected to ozonation at pH 5.5, 7, 9 and 11 for 60 min. Table 6.10 presents overall COD, TOC and UV_{254} removals, as well as $N\text{-}NO_2^-$, $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$ variations at four different pH values.

The results of COD, TOC and UV_{254} removal efficiencies indicate that ozonation is more effective at degrading the leachate pollutants under basic pH. It is known that under acidic conditions ozonation allows direct oxidation by molecular ozone, while at high pH values a less selective and faster radical oxidation (mainly hydroxyl radical) becomes dominant as a consequence of OH^- accelerated O_3 depletion and $^{\bullet}OH$ radicals production (LANGLAIS ET AL., 1991). Since the oxidation potential of hydroxyl radicals is much higher than the ozone molecule, indirect oxidation is more powerful than ozone oxidation. Thus, the average efficiency for COD removal increased from 18% at pH 5.5 to 49% at pH 11. GOI ET AL. (2009) obtained similar results when treating a landfill leachate with COD removal efficiencies of 24, 29 and 41% at initial pH 4.5, 8.1 and 11, respectively, with 2.5 g $O_3 \cdot h^{-1}$ and after 240 min of ozonation. TOC removal was lower than COD removal but followed the same tendency. Therefore, further data related to TOC in ozonation will be not shown.

Table 6.10 Effect of initial pH on COD, TOC and UV_{254} removal efficiencies; $N\text{-}NO_2^-$, $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$ concentrations in ozonation of a mature leachate (conditions: reaction time=60 min; 5.6 g $O_3 \cdot h^{-1}$; mean initial COD=340 mg$\cdot L^{-1}$).

Parameter	Initial pH			
	5.5	7	9	11
COD removal (%)	18	27	45	49
TOC removal (%)	12	21	37	41
UV_{254} removal (%)	42	44	51	57
$N\text{-}NO_2^-$ (mg$\cdot L^{-1}$)	0.085	0.111	0.142	0.193
$N\text{-}NO_3^-$ (mg$\cdot L^{-1}$)	1109	1135	1150	1174
$N\text{-}NH_4^+$ (mg$\cdot L^{-1}$)	335	319	296	269

As with Fenton treatment, the lower COD removal compared to UV_{254} removal can be explained by incomplete or partial oxidation of organic materials.

By increasing pH, nitrogen-nitrate concentration increased while nitrogen-ammonium decreased, indicating that ammonium was converted to nitrate. SINGER & ZILLI (1975) also reported that at higher pH values nitrate formation is enhanced by the direct oxidation of ammonium (in the un-ionized form) by ozone. It would be of interest to determine whether or not $N\text{-}NH_4^+$ should be removed before oxidation once ammonium removal spends ozone. Nitrogen-nitrite concentration moderately increased with the initial pH value and is of no concern.

Figure 6.7 depicts the evolution of COD, BOD_5 and BOD_5/COD as a function of pH during ozonation. BOD_5 increased from to 5 to approximately 18, 23, 24 and 25 mg·L^{-1} at initial pH 5.5, 7, 9 and pH 11, respectively. The biodegradability values obtained at pH 11 are very close to those obtained after 120 min of Fenton treatment at initial pH 3, H_2O_2 to Fe^{2+} molar ratio of 3 and Fe^{2+} at 4 mmol·L^{-1}.

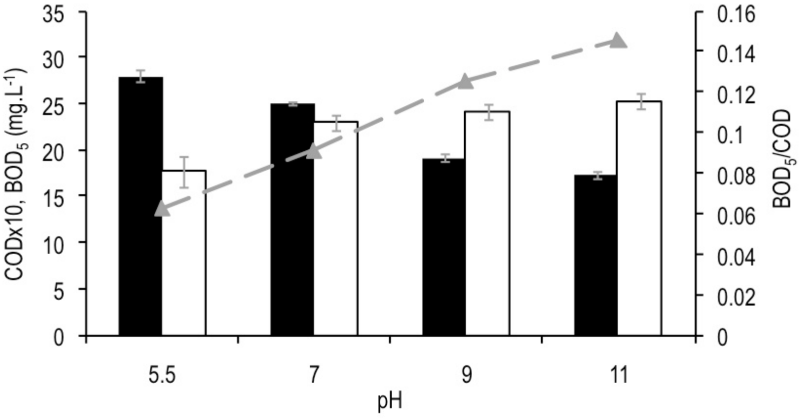

Figure 6.7 Effect of initial pH on COD (■), BOD_5 (□) and BOD_5/COD ratio (▲) after 60 min of ozonation at 5.6 g O_3·h^{-1} and mean initial COD=340 mg·L^{-1}.

The effect of ozone and hydrogen peroxide combination on leachate treatment was explored by adding different amounts of H_2O_2 prior to the start of ozonation, as presented in Table 6.11. According to STAEHELIN & HOIGNÉ (1982), the lower limit for the effectiveness of the H_2O_2/O_3 process is in a pH range of 5 to 7, therefore the H_2O_2/O_3 process was applied to leachate at pH 7. The application of H_2O_2/O_3 enhanced the oxidation rate of the landfill leachate compared to ozone alone. These results confirmed that the oxidation of this effluent was mainly due to hydroxyl radicals. COD and aromaticity removals were enhanced from 27% and 44% with ozone only to 72% and 66%, respectively, in the presence of ozone and 400 mg·L^{-1} of hydrogen peroxide, at 5.6 g O_3·h^{-1} and pH 7.

Table 6.11 Effect of H_2O_2 concentration on COD and UV_{254} removal efficiencies; N-NO_2^-, N-NO_3^- and N-NH_4^+ concentrations in ozonation of a mature leachate (conditions: reaction time=60 min; 5.6 g $O_3 \cdot h^{-1}$; initial pH=7; mean initial COD=340 mg·L^{-1}).

Parameter	$[H_2O_2]$=0 mg·L^{-1}	$[H_2O_2]$=100 mg·L^{-1}	$[H_2O_2]$=200 mg·L^{-1}	$[H_2O_2]$=400 mg·L^{-1}
COD removal (%)	27	41	57	72
UV_{254} removal (%)	44	48	52	66
N-NO_2^- (mg·L^{-1})	0.111	0.057	0.068	0.071
N-NO_3^- (mg·L^{-1})	1135	1159	1135	1128
N-NH_4^+ (mg·L^{-1})	319	291	314	318

Some authors (TIZAOUI ET AL., 2007; LIN ET AL., 2009) report that an increase in hydrogen peroxide concentration will not always improve oxidation. In effect, when the applied hydrogen peroxide dose is above the optimum value, H_2O_2 acts as radical scavenger, suppressing the removal of UV_{254} and COD. In this research, that phenomenon was not observed maybe because the optimum hydrogen peroxide dose was not found. This fact indicates the importance of optimizing ozonation for a specific leachate.

Considering nitrogenous pollutants, as is shown in Table 6.11, nitrogen-nitrate increased and nitrogen-ammonium decreased after 60 min of treatment, confirming that ammonium was oxidized to nitrate. There is not a significant difference between the treatments with O_3 only and with O_3 combined with H_2O_2. WANG ET AL. (2004) used ozone, and ozone in conjunction with hydrogen peroxide for the treatment of a landfill leachate and found a similar behavior. Nitrogen-nitrite concentration after ozonation proved to be of no concern.

Results of the effect of O_3 only and H_2O_2/O_3 on biodegradability are presented in Figure 6.8. Biodegradability improved in both systems; however, the H_2O_2/O_3 process presented noticeable higher BOD_5/COD values. The higher the H_2O_2 dose, more $^{\bullet}OH$ radicals might have been formed and more organic compounds might have been completely oxidized, thus leading to a lower BOD_5 after oxidation with H_2O_2/O_3. The highest BOD_5/COD ratio was attained with the highest H_2O_2 concentration tested (400 mg·L^{-1}). Other studies have also reported improvements in BOD_5 and biodegradability after leachate treatment with ozone and hydrogen peroxide (TIZAOUI ET AL., 2007; HAGMAN ET AL., 2008).

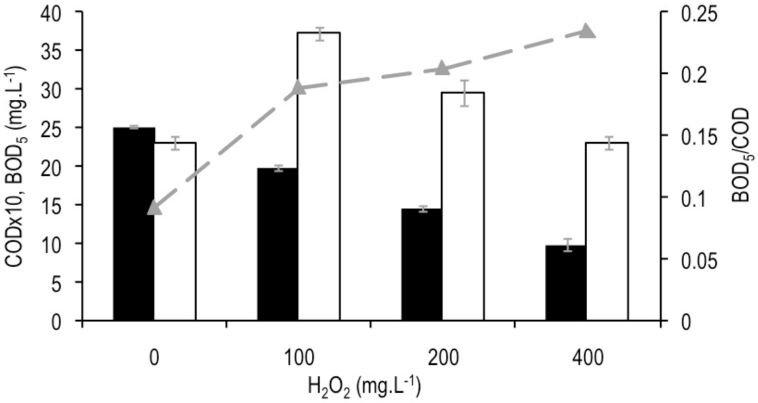

Figure 6.8 Effect of H_2O_2 concentration on COD (■), BOD_5 (☐) and BOD_5/COD ratio (▲) after 60 min of ozonation at 5.6 g $O_3 \cdot h^{-1}$, initial pH=7, and mean initial COD=340 mg$\cdot L^{-1}$.

Table 6.12 presents pollutants removal as a function of the ozonation time applied to the landfill leachate.

Table 6.12 Effect of reaction time on COD and UV_{254} removal efficiencies; $N\text{-}NO_2^-$, $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$ concentrations in ozonation of a mature leachate (conditions: 5.6 g $O_3 \cdot h^{-1}$; initial pH=7; mean initial COD=340 mg$\cdot L^{-1}$).

Parameter	Reaction time (min)					
	0	5	15	30	45	60
COD removal (%)	-	15	21	25	27	27
UV_{254} removal (%)	-	18	23	34	40	44
$N\text{-}NO_2^-$ (mg$\cdot L^{-1}$)	0.005	0.067	0.084	0.100	0.108	0.111
$N\text{-}NO_3^-$ (mg$\cdot L^{-1}$)	1063	1078	1090	1122	1134	1135
$N\text{-}NH_4^+$ (mg$\cdot L^{-1}$)	373	363	351	332	323	319

The results indicate that COD and UV_{254} removal efficiencies increased faster initially, leveling off after 30 min. It can be hypothesized that in the beginning of the reaction, the easily oxidizable substances are removed. As the oxidation continues, the organic compounds that can be easily oxidized became less available and some generated intermediates become increasingly important scavengers of hydroxyl radicals. Further increase in reaction time leads to a slow change in removal rate and a tendency to attain a plateau indicating the presence of recalcitrant compounds. Therefore, it is not always worthwhile to increase the ozone contact time. The continual decrease in absorbance beyond 30 min, when most organic compounds were significantly removed, might be due to continued degradation of intermediates and organic fragments from the organic compounds.

6B.3.3 COMPARISON OF PRE-TREATMENTS

From the data reported in sections 3.1 and 3.2, it is possible to assert that both pre-treatments reduced the recalcitrant organic load of the landfill leachate, described in terms of COD, TOC and UV_{254} removal efficiency, and increased the BOD_5/COD ratio. These results indicate that refractory compounds were converted into lower molecular weight substances, which could be easily degraded biologically. Though there was a significant improvement in biodegradability, a BOD_5/COD ratio higher than 0.4, which is the minimum value considered appropriate for the efficient application of a biological treatment (TCHOBANOGLOUS & BURTON, 1991), was not achieved for all processes tested, emphasizing the highly recalcitrant properties of the landfill leachate studied.

The Fenton treatment and ozonation at adjusted pH 9 and pH 11 showed very similar results, excluding the fact that in ozonation experiments $N\text{-}NH_4^+$ was reduced to $N\text{-}NO_3^-$. The simplicity of operation and design as well as the capital and operating costs of Fenton's oxidation are very attractive compared with other advanced oxidation processes such as ozonation. However, the process presents some drawbacks such as the requirement of acidification and subsequent neutralization after oxidation is completed, which increases the salinity of the treated leachate and produces sludge, with the subsequent requirement of sludge disposal, all of which may influence operational costs.

The best COD, TOC and UV_{254} removal efficiencies, and higher BOD_5/COD ratios were achieved by the application of ozone combined with hydrogen peroxide, for concentrations of 200 and 400 mg $H_2O_2 \cdot L^{-1}$.

Probably, coupling Fenton's oxidation and ozonation with other treatment technologies would ensure a BOD_5/COD ratio higher than 0.4 before the biological treatment, without significantly increasing operation costs. In the treatment of a landfill leachate, GOI ET AL. (2009) applied Fenton's oxidation followed by ozonation, as well as coagulation combined with the Fenton treatment, and obtained high BOD_5/COD values. BILA ET AL. (2005) and WANG ET AL. (2009) also applied ozonation and Fenton's oxidation, respectively, proceeded by the coagulation/flocculation of colloids and found significant biodegradability improvements.

6B.3.4 OPERATING COSTS

A rough economic analysis of the operating costs associated to each AOP studied, such as costs of reagents and energy, was performed. It is important to note that this analysis is just an approximate tool to differentiate the trends in the operating costs associated to the use of each oxidation system. A rigorous economic analysis should consider the initial investment, prices at plant scale, maintenance and labor costs, etc.

It was assumed that the cost of a power unit was 0.09 € · kWh^{-1}; the cost of reagents was: 0.179 €·kg^{-1} H_2SO_4, 0.35 €·kg^{-1} NaOH, 0.134 €·kg^{-1} $FeSO_4 \cdot 7H_2O$, 0.33 €·L^{-1} H_2O_2 (35%) and 0.08 €·m^{-3} O_2; and the operating time was 40 and 30 min for Fenton (at optimum determined conditions) and ozone experiments, respectively. The calculated cost figures are summarized in Table 6.13.

Table 6.13 Operating costs for the AOPs studied.

AOP	Operating costs (€·m^{-3}·g^{-1} of COD removed)
Fe^{2+}/H_2O_2	8.2
O_3/pH=5.5	101.1
O_3/pH=7	65.5
O_3/pH=9	36.8
O_3/pH=11	36.3
O_3/100 mg · H_2O_2·L^{-1}	41.5
O_3/200 mg · H_2O_2·L^{-1}	30.5
O_3/400 mg · H_2O_2·L^{-1}	25.6

The results show that the Fenton process offers the lowest operating cost for the treatment of the landfill leachate studied. Considering experiments with ozone, the best results were achieved when hydrogen peroxide was added at concentrations of 200 and 400 mg H_2O_2·L^{-1}.

It must be emphasized that ozonation always requires significantly higher initial investment than Fenton's oxidation. However, as stated previously, Fenton's oxidation generates sludge, which can be easily separated from the leachate but requires thickening and, consequently, additional investment and operating costs.

Since fine-tuning the operating conditions could considerably change the operating costs obtained, and probably the optimum hydrogen peroxide dose to the H_2O_2/O_3 process was not determined, it can be supposed that at the finest concentration of H_2O_2, the O_3/H_2O_2 process would compete satisfactorily (in terms of operation costs) with the Fe^{2+}/H_2O_2 system.

6B.4 CONCLUSIONS

The results indicate that Fe^{2+}/H_2O_2, O_3/OH^- and O_3/H_2O_2 processes, comparatively to ozone at natural and neutral pH values (5.5 and 7), resulted in higher COD, TOC and UV_{254} removal efficiencies and improvement of landfill leachate biodegradability. Although these processes produced significant amendment in leachate quality, a BOD_5/COD ratio of 0.4, considered as a minimum to implement an effective biological treatment, was not achieved, which indicates the refractory nature of the landfill leachate. Ozone in combination with hydrogen peroxide 400 $mg \cdot L^{-1}$ was found to be the best oxidation approach tested. COD removal reached 72% and BOD_5/COD ratio increased from 0.01 to 0.24. For comparison purposes only, estimates of operating costs were calculated. It was found that Fe^{2+}/H_2O_2 was the most economical system (8.2 $€ \cdot m^{-3} \cdot g^{-1}$ of COD removed) to treat the used landfill leachate.

Future work should focus on optimizing the mature landfill leachate pre-treatment, including the Fenton treatment and/or ozonation at alkaline pH or combined with hydrogen peroxide, in order to obtain a more biodegradable leachate, which could be followed by biological treatment. Evaluation of costs should also be further investigated prior to practical implementation.

6B.5 REFERENCES

APHA, AWWA & WPCF (1989) Standard methods for the examination of water and wastewater, 17th edition. American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC.

BILA, D.M., MONTALVÃO, A., SILVA, A.C. & DEZOTTI, M. (2005) Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement. *Journal of Hazardous Materials*, 117, 235-242.

CAÑIZARES, P., PAZ, R., SÁEZ, C. & RODRIGO, M.A. (2009) Costs of the electrochemical oxidation of wastewaters: A comparison with ozonation and Fenton oxidation processes. *Journal of Environmental Management*, 90, 410-420.

DENG, Y. (2007) Physical and oxidative removal of organics during Fenton treatment of mature municipal landfill leachate. *Journal of Hazardous Materials*, 146, 334-340.

DENG, Y. & ENGLEHARDT, J.D. (2006) Treatment of landfill leachate by the Fenton process. *Water Research*, 40, 3683-3694.

GALLARD, H., LAAT, J.D. & LEGUBE, B. (1998) Influence du pH sur la vitesse d'oxydation de composés organiques par FeII/H2O2. Mécanismes réactionnels et modélisation. *New Journal of Chemistry*, 22, 263-268.

GOI, A. & TRAPIDO, M. (2002) Hydrogen peroxide photolysis, Fenton reagent and photo-Fenton for the degradation of nitrophenols: a comparative study. *Chemosphere*, 46, 913-922.

GOI, A., VERESSININA, Y. & TRAPIDO, M. (2009) Combination of ozonation and the Fenton processes for landfill leachate treatment: evaluation of treatment efficiency. *Ozone: Science and Engineering*, 31, 28-36.

HAAPEA, P., KORHONEN, S. & TUHKANEN, T. (2002) Treatment of industrial landfill leachates by chemical and biological methods: ozonation, ozonation hydrogen peroxide, hydrogen peroxide and biological post-treatment for ozonated water. *Ozone: Science and Engineering*, 24, 369-378.

HAGMAN, M., HEANDER, E. & JANSEN, J.L.C. (2008) Advanced oxidation of refractory organics in leachate – potential methods and evaluation of biodegradability of the remaining substrate. *Environmental Technology*, 29, 941-946.

KOCHANY, J. & LIPCZYNSKA-KOCHANY, E. (2009) Utilization of landfill leachate parameters for pretreatment by Fenton reaction and struvite precipitation-a comparative study. *Journal of Hazardous Materials*, 166, 248-254.

KURNIAWAN, T.A. & LO, W. (2009) Removal of refractory compounds from stabilized landfill leachate using an integrated H_2O_2 oxidation and granular activated carbon (GAC) adsorption treatment. *Water Research*, 43, 4079-4091.

LANGLAIS, B., RECKHOW, D.A. & BRINK, D.R. (1991) Ozone in Water Treatment: Application and Engineering, 1st edition. Lewis Publishers Inc., Chelsea, MI, USA.

LIN, A.Y., LIN, C., CHIOU, J. & HONG, P.A. (2009) O_3 and O_3/H_2O_2 treatment of sulfonamide and macrolide antibiotics in wastewater. *Journal of Hazardous Materials*, 171, 452-458.

LIN, S.H. & KIANG, C.D. (2003) Combined physical, chemical and biological treatments of wastewater containing organics from a semiconductor plant. *Journal of Hazardous Materials*, 97, 159-171.

LÓPEZ, A., PAGANO, M., VOLPE, A. & DI PINTO, A.C. (2004) Fenton's pre-treatment of mature landfill leachate. *Chemosphere*, 54, 1005-1010.

LUCAS, M.S., PERES, J.A. & LI PUMA, G. (2010) Treatment of winery wastewater by ozone-based advanced oxidation processes (O_3, O_3/UV and O_3/UV/H_2O_2) in a pilot-scale bubble column reactor and process economics. *Separation and Purification Technology*, 72, 235-241.

DE MORAIS, J.L. & ZAMORA, P.P. (2005) Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates. *Journal of Hazardous Materials*, 123, 181-186.

RENOU, S., GIVAUDAN, J., POULAIN, S., DIRASSOUYAN, F. & MOULIN, P. (2008) Landfill leachate treatment: review and opportunity. *Journal of Hazardous Materials*, 150, 468-493.

ROSENFELDT, E.J., LINDEN, K.G., CANONICA, S. & VON GUNTEN, U. (2006) Comparison of the efficiency of OH radical formation during ozonation and the advanced oxidation processes O_3/H_2O_2 and UV/H_2O_2. *Water Research*, 40, 3695-3704.

SEVIMLI, M.F. (2005) Post-Treatment of pulp and paper industry wastewater by advanced oxidation processes. *Ozone: Science and Engineering*, 27, 37-43.

SINGER, P.C. & ZILLI, W.B. (1975) Ozonation of ammonia in wastewater. *Water Research*, 9, 127-134.

STAEHELIN, J. & HOIGNÉ, J. (1982) Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide. *Environmental Science and Technology*, 16, 676-681.

SZPYRKOWICZ, L., JUZZOLINO, C. & KAUL, S.N. (2001) A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent. *Water Research*, 35, 2129-2136.

TANG, W. & HUANG, C. (1996) 2,4-Dichlorophenol oxidation kinetics by Fenton's reagent. *Environmental Technology*, 17, 1371-1378.

TCHOBANOGLOUS, G. & BURTON, F. (1991) Wastewater engineering: Treatment, Disposal and Reuse, 3rd edition. Metcalf and Eddy, Inc., McGraw-Hill Inc., New York.

TIZAOUI, C., BOUSELMI, L., MANSOURI, L. & GHRABI, A. (2007) Landfill leachate treatment with ozone and ozone/hydrogen peroxide systems. *Journal of Hazardous Materials*, 140, 316-324.

WANG, C., LEE, P., KUMAR, M., HUANG, Y., SUNG, S. & LIN, J. (2010) Simultaneous partial nitrification, anaerobic ammonium oxidation and denitrification (SNAD) in a full-scale landfill-leachate treatment plant. *Journal of Hazardous Materials*, 175, 622-628.

WANG, F., EL-DIN, M.G. & SMITH, D.W. (2004) Oxidation of aged raw landfill leachate with O_3 only and O_3/H_2O_2: treatment efficiency and molecular size distribution analysis. *Ozone: Science and Engineering*, 26, 287-298.

WANG, P., LAU, I. & FANG, H. (2001) Electrochemical oxidation of leachate pretreated in an upflow anaerobic sludge blanket reactor. *Environmental Technology*, 22, 373-381.

WANG, X., CHEN, S., GU, X. & WANG, K. (2009) Pilot study on the advanced treatment of landfill leachate using a combined coagulation, Fenton oxidation and biological aerated filter process. *Waste Management*, 29, 1354-1358.

Chapter 7

Mature Landfill Leachate Treatment by Denitrification and Ozonation

The removal of nitrate from a mature landfill leachate with high nitrate load in a lab-scale anoxic rotating biological contactor (RBC) was studied. Under a phosphorus-phosphate concentration of 10 mg $P\text{-}PO_4^{3-}\cdot L^{-1}$ and nitrogen-nitrate concentrations above 530 mg $N\text{-}NO_3^{-}\cdot L^{-1}$ the reactor achieved nitrogen-nitrate removal efficiencies close to 100%, without nitrite or nitrous oxide accumulation. Although the reactor presented a very good denitrification performance, the effluent carbon concentration was still above the legal discharge value. In order to increase the biodegradability of the leachate recalcitrant carbon load, a pre-ozonation was further investigated. The pre-ozonation led to a total organic carbon (TOC) removal of 28%. The sequence of treatments, leachate ozonation followed by RBC denitrification did not affect the denitrification efficiency. In fact, it was possible to attain a denitrification rate of 123 mg $N\text{-}NO_3^{-}\cdot L^{-1}\cdot h^{-1}$. The moderate decrease in the carbon load of the final effluent indicated that some recalcitrant compounds were still present after ozonation. The anoxic RBC showed to be a promising technology for removing nitrate from landfill leachate.

The results presented in this Chapter are forthcoming in the following paper:

CORTEZ S., TEIXEIRA P., OLIVEIRA R. & MOTA M. (in press) Mature landfill leachate treatment by denitrification and ozonation. *Process Biochemistry*.

7. MATURE LANDFILL LEACHATE TREATMENT BY DENITRIFICATION AND OZONATION

7.1 INTRODUCTION

Water and wastewater contamination by nitrate (NO_3^-) constitutes a major environmental concern worldwide. Biological nitrate reduction (denitrification) is the most widely used method to remove nitrate due to the high specificity of denitrifying bacteria, low cost and high denitrification efficiency (WANG ET AL., 2009). In this process, under low oxygen levels, microorganisms first reduce nitrate to nitrite (NO_2^-) and then produce nitric oxide (NO), nitrous oxide (N_2O), and, finally, nitrogen gas (N_2). The production and accumulation of nitrite and other intermediary products is undesirable, since they are toxic, and is often referred to as incomplete denitrification. To ensure complete denitrification, since most denitrifiers are heterotrophs, sufficient carbon must be available. Denitrification efficiency is strongly susceptible to type of carbon source, concentration of carbon source, the carbon to nitrogen molar ratio (C/N) and the biomass activity. Phosphorus has also an important effect on denitrification efficiency (TEIXEIRA & OLIVEIRA, 2000; ALVES ET AL., 2002).

Anoxic rotating biological contactors (RBCs) started to be used for denitrification of groundwater and synthetic wastewaters in the last decade (MOHSENI-BANDPI ET AL., 1999; TEIXEIRA & OLIVEIRA, 2000; CORTEZ ET AL., 2009;). An anoxic RBC unit typically consists of a series of closely spaced disks that are mounted on a common horizontal shaft and are partially or completely submerged in the wastewater to be treated and inserted in a tightly closed case to avoid air entrance. Similarly to an open RBC, the pollutants contained in the wastewater are removed by the biofilm that is established on the entire surface area of the disks, which continually rotate. These reactors offer advantages such as compact design, simplicity of operation, low operating and maintenance costs, short hydraulic retention time (HRT), high biomass concentration, high specific surface area, resistance to toxic loads and relatively small accumulation of sloughed biofilm. RBCs have been applied for removal of ammonium and organic substances in the treatment of landfill leachate with high performance (SPENGEL & DZOMBAK, 1991; CEMA ET AL., 2007; CASTILLO ET AL., 2007). However, to the authors' knowledge, reports of nitrate removal from landfill leachate in anoxic RBCs are not found in the literature.

Landfill leachate has been generally known as a high-strength wastewater that is most difficult to deal with. Leachate generated from mature landfills is typically characterized by high ammonium (NH_4^+) content, low five-day biochemical oxygen demand (BOD_5) to chemical oxygen demand (COD) ratio (BOD_5/COD), or, in other words, low biodegradability and high fraction of refractory and large organic molecules (WANG ET AL., 2003). In many cases, after treatment by a series of oxidation processes, mature landfill leachate still presents high concentrations of recalcitrant compounds and nitrate. When treating this type of leachate, biological methods are ineffective, while physico-chemical and advanced oxidation processes are expensive. By combining several treatment technologies, economical savings and process optimizations could be achieved due to the degradation of the refractory compounds into biodegradable organic matter and the use of these products as a carbon source for denitrification.

Ozone (O_3) has proved to be an effective oxidant for landfill leachate, due to its oxidation potential (HAAPEA ET AL., 2002). During ozonation, organic compounds with long chains can be fragmented in lower chains, with an increase of their biodegradability, or degraded to carbon dioxide. GEENENS ET AL. (2001) used a combined treatment comprising ozonation before the biological process and verified that landfill leachate biodegradability increased after ozonation, resulting in a higher carbon removal by the biological process.

The purpose of this investigation was to evaluate the removal of nitrate from a mature landfill leachate with high nitrate load by denitrification in a lab-scale anoxic RBC, with previous ozonation to favor the biodegradability of the refractory organic load. Previously, the anoxic reactor was operated to optimize some parameters that affect denitrification efficiency such as phosphorus concentration and C/N ratio. In order to clarify the results obtained with the combined treatments in continuous mode, batch experiments were also performed to evaluate the substrate removal rate.

7.2 MATERIALS AND METHODS

7.2.1 LANDFILL LEACHATE CHARACTERISTICS

The landfill leachate was collected at the end of the treatment plant of a municipal landfill in the North of Portugal, in operation since 1998. This means that the leachate had already withstood a series of treatments including: stabilization and anaerobic ponds, an anoxic tank, aerated ponds, decantation unit together with an oxidation tank and two chemical precipitators. The collected leachate was stored in closed containers at 4 ºC until use. The characteristics of the undiluted leachate used in the experiments are summarized in Table 7.1.

Table 7.1 Landfill leachate average characteristics.

Parameter	Value
pH	3.5±0.1
Conductivity ($mS \cdot cm^{-1}$)	4.45±0.03
COD ($mg \cdot L^{-1}$)	743±14
BOD_5 ($mg \cdot L^{-1}$)	10±1
TOC ($mg \cdot L^{-1}$)	284±6
$N\text{-}NO_3^-$ ($mg \cdot L^{-1}$)	1824±103
$N\text{-}NO_2^-$ ($mg \cdot L^{-1}$)	<0.01
$N\text{-}NH_4^+$ ($mg \cdot L^{-1}$)	714±23
$P\text{-}PO_4^{3-}$ ($mg \cdot L^{-1}$)	0.88±0.05
VSS ($mg \cdot L^{-1}$)	79±3

The extremely low BOD_5/COD ratio (0.01) and the high content of nitrogen-ammonium ($N\text{-}NH_4^+$) (714 $mg \cdot L^{-1}$) show that this leachate is mature and must be rich in refractory compounds. Another important feature of this already treated leachate is its high nitrogen-nitrate ($N\text{-}NO_3^-$) (1824 $mg \cdot L^{-1}$) content.

7.2.2 DENITRIFYING REACTOR SETUP AND OPERATION

The single-stage anoxic RBC consisted of 8 polymethylmethacrylate (PMMA) disks (13 cm in diameter) mounted on a rotating shaft (1.6 cm in diameter). The reactor working volume was 2.5 L. The disks were completely immersed. The anoxic RBC was covered and sealed and no special precaution was taken to maintain anoxic conditions. The rotational speed was 4 rpm and the temperature was kept at 28 ºC by means of a heating jacket. Substrate was fed by a peristaltic pump at a constant hydraulic retention time (HRT) of 10 h. The treated effluent was collected in a receiving tank. Flow through disks was parallel to the rotating shaft. A Ritter MilliGascounter was used to measure the rate of produced gas. A schematic description of the reactor is presented in Figure 7.1.

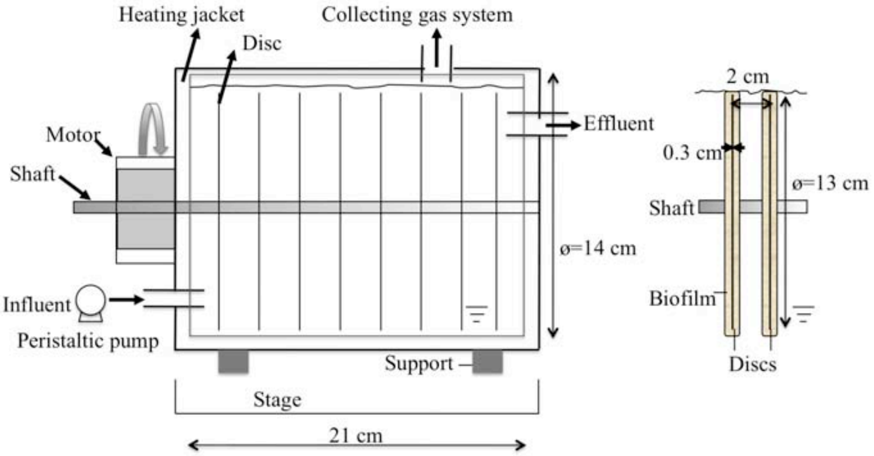

Figure 7.1 Schematic diagram of the anoxic RBC.

The reactor was inoculated with sludge collected from an activated sludge tank at a municipal wastewater treatment plant and previously acclimatized. Sludge acclimatization lasted approximately one month and occurred in anoxic conditions, at room temperature and 150 rpm, using two-fold diluted leachate supplemented with acetate (C/N=2) and involved decanting and washing steps every 5-days.

To allow for biofilm development the reactor was operated in batch mode for 5 days. On day 6, the anoxic RBC mixed liquor was removed, the reactor was re-filled and started to operate in a continuous mode. The hydraulic retention time, very high at the beginning, was gradually reduced. The time “zero” of operation was set two days after having the HRT stabilized at 10 h, when samples started to be collected.

The study was conducted for a period of 21 days. During the assay, the landfill leachate load, C/N ratio and phosphorus concentration were changed, while all other operation parameters were kept constant. Landfill leachate previously ozonated was fed to the reactor in the final period of the continuous experiment, as listed in Table 7.2.

Throughout the study, to overcome the low biodegradable carbon content of the leachate tested, sodium acetate was added as supplementary carbon source, since acetate is known to give the highest denitrification rates (TAM ET AL., 1992; ELEFSINIOTIS & WAREHAM, 2007). The amount of sodium acetate needed to attain the desired C/N (w/w) was calculated taking into account the total organic carbon present in the landfill leachate. The required phosphorus concentration was achieved adding to the influent a calculated amount of K_2HPO_4 and KH_2PO_4. Due to the medium buffering capacity, no pH adjustment was performed.

Table 7.2 Operating conditions of the anoxic RBC.

Days of operation	Type of influent	C/N	$N\text{-}NO_3^-$ ($mg \cdot L^{-1}$)	$P\text{-}PO_4^{3-}$ ($mg \cdot L^{-1}$)
0-2.2	Two-fold diluted leachate	2	912	0.44
2.2-6.4	Four-fold diluted leachate	2	456	0.21
6.4-10.4	Four-fold diluted leachate	2	456	10
10.4-14.2	Four-fold diluted leachate	1.4	456	10
14.2-17.2	Two-fold diluted leachate	1.4	912	10
17.2-21.4	Two-fold diluted and ozonated leachate	1.4	912	10

7.2.3 OZONATION

Ozonation of the leachate was performed in an acrylic column 69.5 cm height and 8.2 cm internal diameter. Ozone was generated from pure oxygen using an ozone generator (Anseros Peripheral Com-AD-02). The inlet and outlet concentrations of ozone in the gas phase were measured at 254 nm using an ozone analyzer (Anseros Ozomat GM-6000-OEM). The ozone and oxygen mixture was continuously introduced into the column through a ceramic diffuser placed at the bottom and one liter of two-fold diluted leachate was treated in batch mode during 60 minutes. The operation was conducted at adjusted pH 9, at room temperature (20 ºC ± 2 ºC) with a gas flow rate of 0.83 $L \cdot min^{-1}$ and an inlet ozone concentration of about 112 $mg \cdot L^{-1}$ NTP.

7.2.4 BIOFILM DENITRIFYING ACTIVITY

At the end of the anoxic RBC operation, the biofilm formed on the disks was carefully removed and used in batch assays to evaluate the biofilm denitrifying activity. The assays were carried out in 160 mL vials using 90 mL of denitrifying medium. The denitrifying medium for a two-fold diluted leachate was different from the two-fold diluted and ozonated leachate, both with C/N=1.4 and 10 mg $P\text{-}PO_4^{3-} \cdot L^{-1}$. Each vial was inoculated with 5 g of biofilm (wet weight). Abiotic tests were also performed to determine abiotic losses of nitrogen and carbon, using similar conditions but without inoculum addition. Assays in the absence of carbon-acetate were also conducted. In any case, the vials were closed with butyl rubber stoppers and aluminum caps. To obtain anoxic conditions, the vials were flushed with helium. Finally, the vials were incubated at 28 °C and 150 rpm. All the assays were performed in duplicate. Samples from each vial were collected at regular intervals and immediately analyzed for several parameters.

7.2.5 CHEMICAL ANALYSES

pH values were measured with a pH meter. Chemical oxygen demand (COD), nitrogen-nitrite (N-NO_2^-) and nitrogen-ammonium (N-NH_4^+) concentrations were determined according to Standard Methods (APHA ET AL., 1989). COD was estimated using the closed reflux titrimetric method. N-NO_2^- and N-NH_4^+ concentrations were determined spectrophotometrically using N-(1-naphthyl)-ethylene-diamine and Nessler's reagent, respectively. Nitrogen-nitrate (N-NO_3^-) and carbon-acetate (C-CH_3COO^-) concentrations were measured by high-performance liquid chromatography (HPLC), using a Varian Metacarb column (type 67H, 9 μm, 300 mm long, 6.5 mm internal diameter) and a mobile phase of 0.005 M sulphuric acid (H_2SO_4) at 0.7 $mL \cdot min^{-1}$. Column temperature was set at 60 ºC and nitrate and acetate were detected by UV at 210 nm. Periodically, gas samples were analyzed by a gas chromatograph (GC) equipped with a thermal conductivity detector and a Porapak Q column (2 mm internal diameter, 80-100 μm mesh, 1 m length) in series with a Molecular Sieve column (2 mm internal diameter, 5 Aº, 80-100 μm mesh, 2 m length). Helium was used as the carrier gas at a flow rate of 17 $mL \cdot min^{-1}$. Temperatures of the injector port, columns and detector were 110 °C, 35 °C and 110 °C, respectively. Total organic carbon (TOC) analyses were performed using a Dohrmann DC-190 TOC Analyzer.

7.3 RESULTS AND DISCUSSION

7.3.1 PERFORMANCE OF THE ANOXIC RBC

7.3.1.1 Nitrogenous compounds

Figure 7.2 shows the influent and effluent concentrations of nitrogenous compounds and the nitrate removal efficiency in the denitrifying reactor throughout the experiment. The denitrifying reactor was initially operated with a nitrate load of 1090 mg N-$NO_3^- \cdot L^{-1}$ and a carbon to nitrogen ratio (C/N) of 2, using acetate as the additional carbon and energy source. This ratio is slightly higher than the theoretical value of 1.4 obtained considering the approach of MCCARTY ET AL.

(1969) when acetate is the carbon source. However, it is also necessary to consider that some carbon is used for the removal of oxygen from the system. Therefore, a conservative approach was made to insure complete denitrification. In this period, the reactor presented a very low performance in terms of nitrate removal. Considering that the high nitrate concentration could inhibit the microbial biofilm activity, the initial N-NO_3^- concentration was reduced by increasing the influent dilution. However, this adjustment did not cause any change on nitrate removal, indicating that the nitrate load was not the limiting factor.

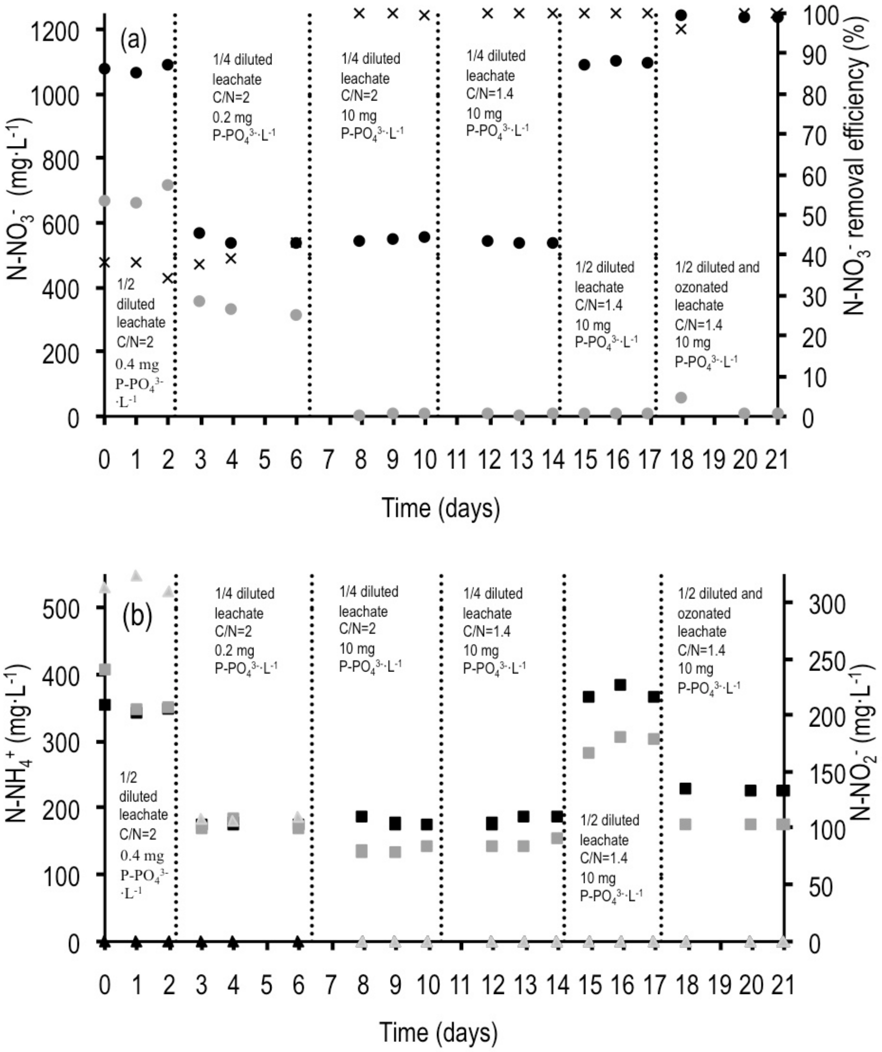

Figure 7.2 Nitrogenous compounds profile in the denitrifying reactor throughout time. (a) Influent (●) and effluent (●) N-NO_3^- concentration and N-NO_3^- removal efficiency (×). (b) Influent (■) and effluent (■) N-NH_4^+ concentration, influent (▲) and effluent (▲) N-NO_2^- concentration.

Considering that influent phosphorus concentration can significantly affect the denitrifying process (TEIXEIRA & OLIVEIRA, 2000; ALVES ET AL., 2002), from day 6 onwards the $P\text{-}PO_4^{3-}$ influent concentration was changed to 10 $mg \cdot L^{-1}$. This phosphorus concentration was selected according to WELANDER ET AL. (1998). The shift to a higher phosphorus load, keeping C/N=2, had a significant effect on nitrogen-nitrate removal efficiency, which became close to 100%. In fact, higher phosphorus concentration stimulates cell production in detriment of extracellular polymers production in the biofilm, consequently increasing biofilm activity. This is corroborated by other authors who reported that a deficiency of some nutrients in the medium could enhance polysaccharide production instead of cell production (VEIGA ET AL., 1992).

After approximately 10 days of operation, the C/N ratio of the culture was modified from 2 to 1.4 (equal to the theoretical value) to adjust the operational conditions to the stoichiometric ones for the nitrate and acetate removal reaction also considering microbial growth. No effect on the nitrate consumption was observed when the C/N ratio decreased, as the removal efficiency remained constant and close to 100%. Taking into account the high performance of the anoxic RBC in terms of nitrate removal, on day 14 the nitrate load was doubled but the nitrate reduction remained constant. Finally, in order to decrease effluent COD concentration, ozonated leachate was fed to the reactor. The nitrate removal slightly decreased, which can be attributed to the biofilm acclimatization to a different type of influent. It was a transitory period since nitrate removal efficiency recovered quickly and was kept around 99% after day 20, indicating that the denitrifying biofilm did not lose its performance. It is worth mentioning that the ozonation of the landfill leachate caused some oxidation of ammonium to nitrate leading to an increase on the fed nitrate load. Excluding the periods with insufficient phosphorus concentration, effluent $N\text{-}NO_3^-$ concentrations were less than 10 $mg \cdot L^{-1}$, being below the established limit for discharge into fresh water (10-30 $mg\ N\text{-}NO_3^- \cdot L^{-1}$) (EUROPEAN COMISSION, 1991). The highest denitrification rate of 123 $mg\ N\text{-}NO_3^- \cdot L^{-1} \cdot h^{-1}$ was achieved under a C/N ratio of 1.4, 10 $mg\ P\text{-}PO_4^{3-} \cdot L^{-1}$ and approximately 1240 $mg\ N\text{-}NO_3^- \cdot L^{-1}$ (ozonated leachate). CALLI ET AL. (2005) obtained denitrification rates in the range of 33.3-120.8 $mg\ N\text{-}NO_X^- \cdot L^{-1} \cdot h^{-1}$ ($N\text{-}NO_X$-nitrogen from nitrate and nitrite compounds) in the treatment of a young landfill leachate with sodium acetate as carbon source. A denitrification rate of 55 $mg\ N\text{-}NO_3^- \cdot L^{-1} \cdot h^{-1}$ was achieved by WELANDER ET AL. (1998) in a suspended carrier biofilm reactor, which treated leachate, but using methanol as external carbon source. So, the denitrification rate found in the present study indicates a very good performance of the anoxic RBC.

From Figure 7.2 (b) it can be seen that, in the beginning of the anoxic experiment, a significant part of nitrate was converted to nitrite, which accumulated in the effluent. Nitrite accumulation during denitrification of landfill leachates has been observed in many studies (MARTIENSSEN & SCHOPS, 1997; SUN ET AL., 2009). However, it is very important to avoid N-NO_2^- accumulation because it can lead to inhibition of the bacterial growth and the denitrification process (MARTIENSSEN & SCHOPS, 1997). Moreover, nitrite is even more toxic than nitrate (WELANDER ET AL., 1998). N-NO_2^- accumulation is probably related with the activity of the nitrite reductase enzyme, which can be inhibited by nitrate or to low oxygen concentrations (MARTIENSSEN & SCHOPS, 1997; VAN RIJN ET AL., 2006). When influent phosphorus concentration was changed to 10 mg P-$PO_4^{3-}\cdot L^{-1}$, all nitrate was reduced to gaseous nitrogen and no nitrite was measured in the effluent. Further changes in the experimental conditions, namely C/N ratio, nitrate load and influent type did not cause nitrite production.

Ammonium is one of the worst polluting agents for aquatic ecosystems and may restrain the microorganisms' activity. Ammonium concentrations in the effluent remained relatively unchanged until approximately 6 days of reactor operation. N-NH_4^+ removal observed onwards was probably due to a higher assimilation of ammonium for biomass growth triggered by the increase in phosphorus concentration. Another explanation might be due to ammonium reduction by nitrite to form gaseous nitrogen. In fact, in the beginning there was some nitrite accumulation and a low ammonium reduction but when the ammonium reduction rose, nitrite accumulation was almost negligible.

No significant effect of C/N ratio, nitrate load or effluent type on ammonium removal was noticed. As previously mentioned, the ozonation of the landfill leachate caused a decrease on initial ammonium load.

The produced gas flow rate varied according to the profile of nitrogen-nitrate removal efficiency (Figure 7.3). Molecular nitrogen (N_2) was the most abundant compound detected in gas composition (around 92%). Production of N_2O remained around 0.2% (minimum detection value) except when the influent was changed to ozonated leachate, which can be due to the biofilm acclimatization, as mentioned before. Dissolved oxygen concentration in the reactor was detected only in the beginning of the experiment, remaining below the limit of detection until the end. Initially, biological denitrification was considered to be strictly anoxic (PAYNE, 1973), however, with a certain number of bacteria, denitrification occurs even in the presence of O_2 (LUKOW &

DIEKMANN, 1997). No methane or hydrogen sulfide gases were detected by the measuring system.

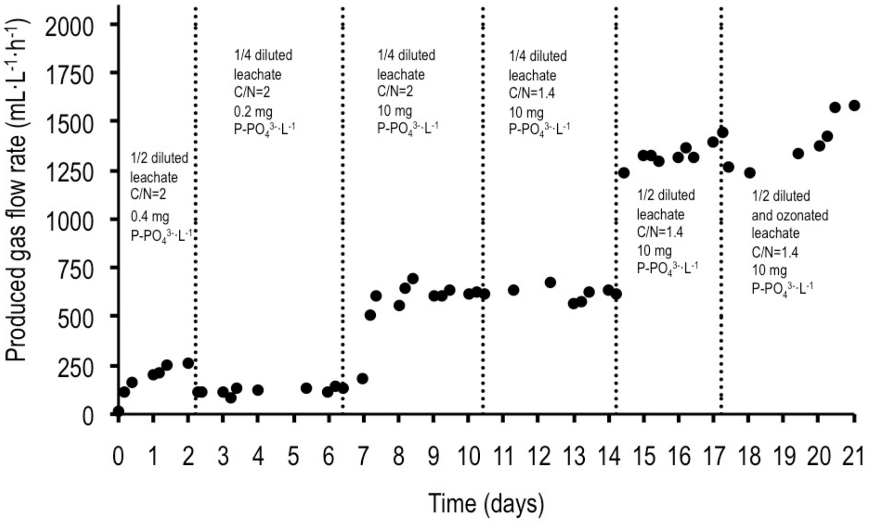

Figure 7.3 Produced gas flow rate in the denitrifying reactor throughout time.

7.3.1.2 Carbonaceous compounds

TOC and carbon-acetate concentration time profile as well as removal efficiencies are shown in Figure 7.4.

During the two first periods of operation the reactor presented an average value of 19.2 and 33.3% for TOC and carbon-acetate removal efficiency, respectively. These low values are due to poor denitrification efficiency. From day 6 onwards, when phosphorus influent concentration was changed to 10 mg $P\text{-}PO_4^{3-}\cdot L^{-1}$, keeping C/N=2, a better reactor performance in terms of nitrate removal was obtained also yielding an increase in carbon consumption, reflecting on effluent TOC and acetate concentrations. In spite of a higher carbon removal, acetate still remained in the effluent flow, which implies that the reactor was receiving enough carbon to facilitate the denitrification process. Under a C/N ratio of 1.4, acetate was completely consumed but TOC was still detected in the effluent. The effluent TOC values corresponded entirely to the contribution of the landfill leachate composition. These results reveal, as expected, that the organic matter present in the leachate was non-biodegradable and the denitrifying biofilm could not use it, preferring the easily biodegradable carbon. Another important conclusion is that, since only carbon from acetate was being used, the reactor operated, in practice, under a C/N ratio below

1.4, and this experimental C/N value (around 1.3) was enough to achieve a nitrate removal of approximately 100%.

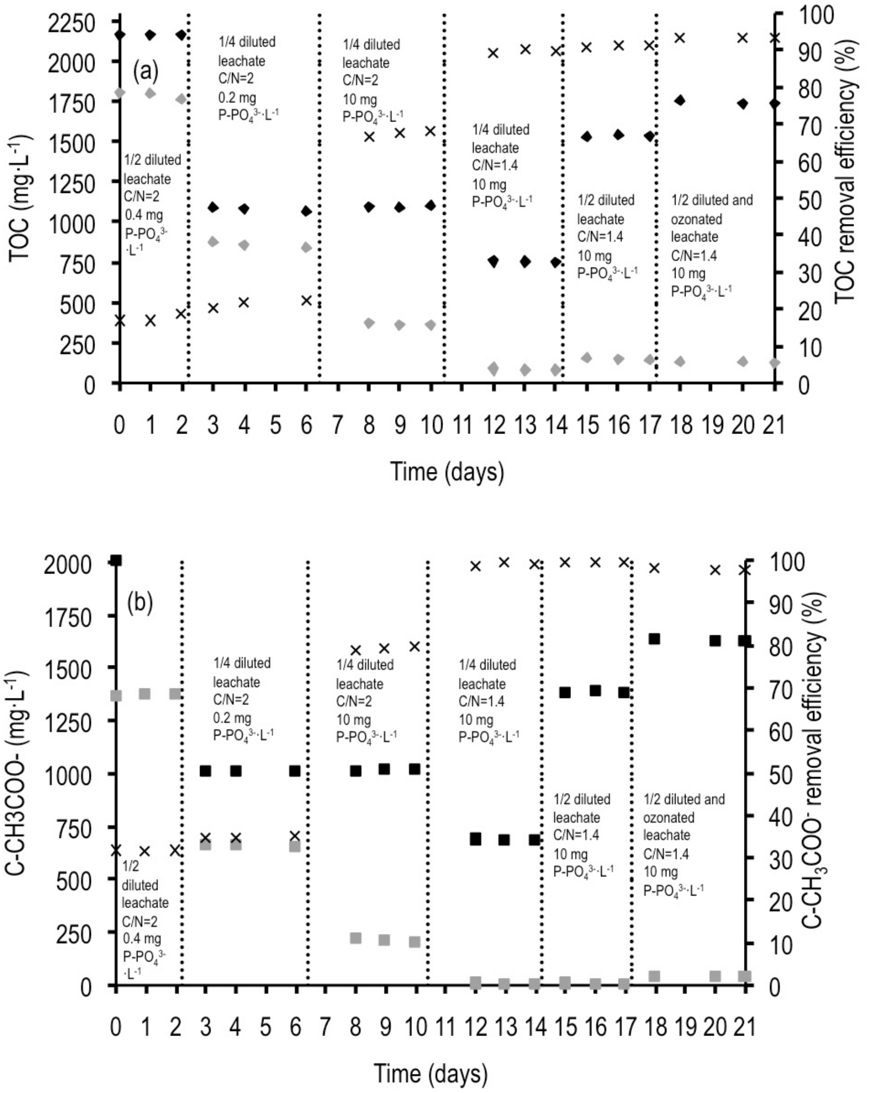

Figure 7.4 Carbonaceous compounds profile in the denitrifying reactor throughout time. (a) Influent (◆) and effluent (◆) TOC concentration and TOC removal efficiency (×). (b) Influent (■) and effluent (■) C-CH_3COO^- concentration and C-CH_3COO^- removal efficiency (×).

In order to increase leachate biodegradability and to reduce the organic content in the biological treated effluent, the two-fold diluted leachate was previously treated by ozonation at pH 9 and with an ozone dose of 0.112 g $O_3 \cdot L^{-1}$. This pre-treatment led to a TOC removal of 28%.

Denitrifying biofilm activity was not affected when the reactor started to be fed with ozonated leachate. The biological treatment of the ozonated effluent resulted in a slight decrease in acetate removal efficiency from about 100 to 98%. There was also a reduction in the total carbon content in the biological treated effluent. These results might indicate that, after ozonation, a small organic fraction of the landfill leachate was transformed into more readily biodegradable compounds, able to be consumed by the biofilm. However, this effluent still contained an organic fraction recalcitrant to biological degradation. The values of soluble COD measured at the inlet and outlet of the reactor indicate that, although not very significantly, ozonation allowed reducing the effluent COD concentration to a value close to the discharge standard value.

7.3.1.3 pH

Throughout the experiment, pH values increased from 6.8-7.1 in the influent to 8.0-9.5 in the effluent. The observed pH trend might be attributed to the conversion of $N\text{-}NO_3^-$ to gaseous nitrogen in the reactor, which consumed hydrogen ion. It is important to note that after ozonation at pH 9, the pH of the landfill leachate dropped around 2 units bringing the ozonated leachate pH to neutral. Therefore, no further pH adjustment was necessary before the biological treatment.

7.3.2 BIOFILM DENITRIFYING ACTIVITY

A key parameter in water and wastewater treatment technology is microbial activity, expressed in terms of substrate removal ability. In order to determine the denitrifying biofilm activity, batch tests were performed using the biofilm removed from the continuous denitrifying reactor. The abiotic tests showed that no nitrate or carbon was removed, indicating that the denitrification process was completely due to biological activity. From Figure 7.5 (a) and (b) it can be seen that, under anoxic heterotrophic conditions, nitrate was completely consumed in 12 h and 14 h for ozonated and non-ozonated landfill leachate, respectively. Some nitrite accumulated, but it was completely consumed until the end of the experiment. N_2 was the main gas produced. The profiles of nitrogenous compounds allow concluding that denitrification was faster with the ozonated leachate. Considering carbon consumption, when ozonated leachate was used some acetate remained in the effluent, while in the non-ozonated leachate acetate was completely consumed. Denitrification of leachate without additional acetate showed that the nitrate reduction was negligible. However, some nitrate and carbon consumption were noticed in the medium with ozonated leachate. These results confirm that ozonation converted some high molecular weight compounds, which were difficult to degrade into easily biodegradable compounds.

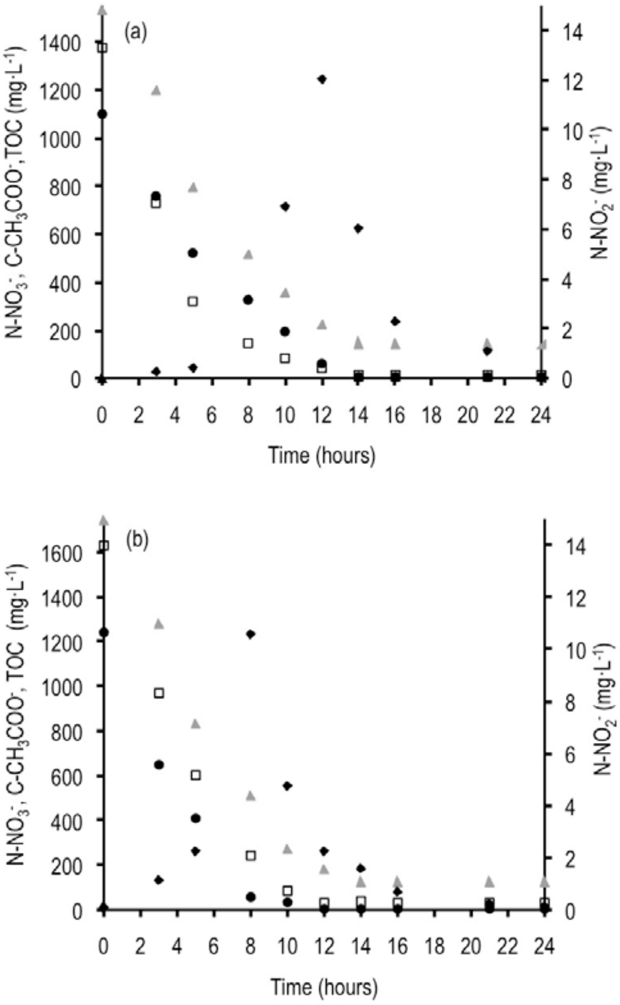

Figure 7.5 Nitrogen-nitrate (●), nitrogen-nitrite (♦), carbon-acetate (□) and total organic carbon (▲) profiles during biofilm denitrifying activity tests of a non-ozonated (a) and ozonated (b) two-fold diluted landfill leachate.

Ammonium was determined in the beginning and at the end of the batch tests and, similarly to the continuous experiment, ammonium removal was verified.

The activity of the biofilm was measured as specific consumption rate for nitrate and acetate. The specific denitrification rate (expressed in g of $N\text{-}NO_3^-$ removed per g of vial VSS per day) and the specific carbon-acetate consumption rate (expressed in g of $C\text{-}CH_3COO^-$ consumed per g of vial VSS per day) are shown in Table 7.3. The specific rates were calculated for the total duration of each run, in order to obtain an overall assessment of the ability of the biofilm to perform under the conditions investigated. The initial nitrate concentration was around 1240 and 1090 mg N-NO_3^- ·L^{-1} for the ozonated and non-ozonated leachate, respectively. When acetate was added, the C/N ratio was 1.4.

Table 7.3 Specific denitrification and acetate consumption rates in biofilm denitrifying activity tests.

	Non-ozonated leachate		Ozonated leachate	
	Without acetate	With acetate	Without acetate	With acetate
Specific denitrification rate (g N-NO_3^- ·g^{-1} VSS · d^{-1})	0.0008± 0.0002	0.830±0.007	0.0016± 0.0001	0.864±0.007
Specific carbon-acetate consumption rate (g C-CH_3COO^- ·g^{-1} VSS · d^{-1})	-	1.043±0.002	-	1.112±0.004

In a previous study, REYES-AVILA ET AL. (2004) reported a specific denitrification rate of 1.9 g N-NO_3^- ·g^{-1} VSS ·d^{-1} and a specific carbon-acetate consumption rate of 1.9 g C-CH_3COO^- ·g^{-1} VSS ·d^{-1} in batch tests using acetate, C/N=1.4 and 73 mg N-NO_3^- ·L^{-1}, but treating a synthetic refinery wastewater. The lower values of substrate consumption rates found in this study might be justified by the complexity of the leachate and the much higher nitrate concentration.

7.4 CONCLUSIONS

The results demonstrate that the anoxic rotating biological contactor is very effective having a great potential in the denitrification of a mature landfill leachate with high nitrate load, using acetate as additional carbon source. The supplementary addition of phosphorus played a determinant role on nitrate removal.

The pre-ozonation of the already treated leachate before RBC denitrification led to a moderate TOC reduction, which indicates the high complexity and refractory nature of this leachate.

Future research should focus on improving the pre-treatment of the leachate before the biological process. Considering the ammonium content of the treated leachate, a system involving nitrification should also be evaluated.

7.5 REFERENCES

ALVES, C., MELO, L. & VIEIRA, M. (2002) Influence of medium composition on the characteristics of a denitrifying biofilm formed by *Alcaligenes denitrificans* in a fluidized bed reactor. *Process Biochemistry*, 37, 837-845.

APHA, AWWA & WPCF (1989) Standard methods for the examination of water and wastewater, 17th edition. American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC.

CALLI, B., MERTOGLU, B. & INANC, B. (2005) Landfill leachate management in Istanbul: applications and alternatives. *Chemosphere*, 59, 819-829.

CASTILLO, E., VERGARA, M. & MORENO, Y. (2007) Landfill leachate treatment using a rotating biological contactor and an upward-flow anaerobic sludge bed reactor. *Waste Management*, 27, 720-726.

CEMA, G., WISZNIOWSKI, J., ZABCZYNSKI, S., ZABLOCKA-GODLEWSKA, E., RASZKA, A. & SURMACZ-GORSKA, J. (2007) Biological nitrogen removal from landfill leachate by deammonification assisted by heterotrophic denitrification in a rotating biological contactor (RBC). *Water Science and Technology*, 55, 35-42.

CORTEZ, S., TEIXEIRA, P., OLIVEIRA, R. & MOTA, M. (2009) Effect of operating parameters on denitrification in an anoxic rotating biological contactor. *Environmental Technology*, 30, 1381-1389.

ELEFSINIOTIS, P. & WAREHAM, D. (2007) Utilization patterns of volatile fatty acids in the denitrification reaction. *Enzyme and Microbial Technology*, 41, 92-97.

EUROPEAN COMISSION (1991) Council Directive 1991/271/EEC of 21 May 1991 on Urban Waste Water Treatment. *Official Journal of the European Communities*, L/135, 40-52.

GEENENS, D., BIXIO, B. & THOEYE, C. (2001) Combined ozone-activated sludge treatment of landfill leachate. *Water Science and Technology*, 44, 359-365.

HAAPEA, P., KORHONEN, S. & TUHKANEN, T. (2002) Treatment of industrial landfill leachates by chemical and biological methods: ozonation, ozonation hydrogen peroxide, hydrogen peroxide and biological post-treatment for ozonated water. *Ozone: Science and Engineering*, 24, 369-378.

LUKOW, T. & DIEKMANN, H. (1997) Aerobic denitrification by a newly isolated heterotrophic bacterium strain TL1. *Biotechnology Letters*, 19, 1157-1159.

MARTIENSSEN, M. & SCHOPS, R. (1997) Biological treatment of leachate from solid waste landfill sites-Alterations in the bacterial community during the denitrification process. *Water Research*, 31, 1164-1170.

MCCARTY, P., BECK, L. & AMANT, P. (1969) Biological denitrification of wastewaters by addition of organic materials. In *Proceedings of the 24th Purdue Industrial Waste Conference* (ed. Purdue University), pp. 1271-1285. Indiana, USA.

MOHSENI-BANDPI, A., ELLIOTT, D. & MOMENY-MAZDEH, A. (1999) Denitrification of groundwater using acetic acid as a carbon source. *Water Science and Technology*, 40, 53-59.

PAYNE, W. (1973) Reduction of nitrogenous oxides by microorganisms. *Bacteriological Reviews*, 37, 409-452.

REYES-AVILA, J., RAZO-FLORES, E. & GOMEZ, J. (2004) Simultaneous biological removal of nitrogen, carbon and sulfur by denitrification. *Water Research*, 38, 3313-3321.

VAN RIJN, J., TAL, Y. & SCHREIER, H.J. (2006) Denitrification in recirculating systems: theory and applications. *Aquacultural Engineering*, 34, 364-376.

SPENGEL, D. & DZOMBAK, D. (1991) Treatment of a landfill leachate with rotating biological contactors: bench-scale experiments. *Research Journal Water Pollution Control Federation*, 63, 971-981.

SUN, H., YANG, Q., PENG, Y., SHI, X., WANG, S. & ZHANG, S. (2009) Nitrite accumulation during the denitrification process in SBR for the treatment of pre-treated landfill leachate. *Chinese Journal of Chemical Engineering*, 17, 1027-1031.

TAM, N., WONG, Y. & LEUNG, G. (1992) Effect of exogenous carbon sources on removal of inorganic nutrient by the nitrification-denitrification process. *Water Research*, 26, 1229-1236.

TEIXEIRA, P. & OLIVEIRA, R. (2000) Denitrification by *Alcaligenes denitrificans* in a closed rotating biological contactor. *Biotechnology Letters*, 22, 1789-1792.

VEIGA, M.C., MENDEZ, R. & LEMA, J.M. (1992) Development and stability of biofilms in bioreactors. In *Biofilms – Science and Technology* pp. 421-434L.F Melo, T.R Bott, M Fletcher and B Capdeville. Kluwer Academic Publishers, Netherlands.

WANG, F., SMITH, D.W. & EL-DIN, M.G. (2003) Application of advanced oxidation methods for landfill leachate treatment - A review. *Journal of Environmental Engineering and Science*, 2, 413-427.

WANG, Q., FENG, C., ZHAO, Y. & HAO, C. (2009) Denitrification of nitrate contaminated groundwater with a fiber-based biofilm reactor. *Bioresource Technology*, 100, 2223-2227.

WELANDER, U., HENRYSSON, T. & WELANDER, T. (1998) Biological nitrogen removal from municipal landfill leachate in a pilot scale suspended carrier biofilm process. *Water Research*, 32, 1564-1570.

Chapter 8

General Conclusions and Suggestions

In this chapter, general conclusions obtained from the present dissertation are addressed. More detailed conclusions can be found at the end of each individual chapter. Also, some suggestions for further research in this field are given.

8. GENERAL CONCLUSIONS AND SUGGESTIONS

8.1 GENERAL CONCLUSIONS

Many landfill leachate treatment plants in Portugal, have been having difficulties in nitrate removal, systematically exceeding the established discharge limits. Accordingly, the main purpose of this work was to evaluate the removal of nitrate from a landfill leachate with high NO_3^- load by denitrification in an anoxic rotating biological contactor (RBC).

The main conclusions that can be withdrawn from the obtained results are listed below.

The study of the effect of some environmental conditions (C/N ratio, hydraulic retention time, carbon-acetate and nitrogen-nitrate load) on the denitrification process in the anoxic RBC, when treating synthetic wastewater (CHAPTER 4) showed that this reactor is effective in reducing nitrate concentration and slightly affected by variations of influent load or hydraulic retention time. From this experiment a hydraulic retention time of 10 h was chosen for further work. Moreover, the characteristics and the activity of the biofilm grown in those conditions were compared and the importance in determining these parameters was ascertained.

The denitrification process proceeded very favorably when the reactor was operated with pre-treated landfill leachate, registering, under a C/N of 2, $N\text{-}NO_3^-$ removal efficiencies above 95% for loads up to 100 mg $N\text{-}NO_3^-\cdot L^{-1}$ (CHAPTER 5). The highest observed denitrification rate was 55 mg $N\text{-}NO_3^-\cdot L^{-1}\cdot h^{-1}$ at a nitrate load of 560 mg $N\text{-}NO_3^-\cdot L^{-1}$. These extremely good results were reinforced by the negligible values of intermediate products such as $N\text{-}NO_2^-$ and N_2O. In a subsequent experiment, at constant nitrate load (220 mg $N\text{-}NO_3^-\cdot L^{-1}$) and lower C/N ratios (1.2 and 1.5), it was found that the organic matter present in the leachate was non-biodegradable. Furthermore, a phosphorus concentration of 10 mg $P\text{-}PO_4^{3-}\cdot L^{-1}$ was needed to promote autotrophic denitrification, revealing the importance of phosphorus concentration on biological nitrate removal processes.

In CHAPTER 6, Fenton's oxidation (Fe^{2+}/H_2O_2) and different ozone-based AOPs (O_3, O_3/OH^- and O_3/H_2O_2) were studied in order to improve the biodegradability of the pre-treated landfill leachate. The best results were achieved with Fe^{2+}/H_2O_2, O_3/OH^- and O_3/H_2O_2 processes, confirming the enhanced production of hydroxyl radical under such conditions. Although Fe^{2+}/H_2O_2 is the most economical system to treat the landfill leachate, for ease of operation O_3/OH^- was chosen for further work.

The combined treatments, leachate ozonation followed by RBC denitrification (CHAPTER 7), showed that the pre-ozonation led to a TOC removal of 28% and the global system did not affect the denitrification efficiency, which remained close to 100%. In fact, it was possible to attain a denitrification rate of 123 mg $N\text{-}NO_3^- \cdot L^{-1} \cdot h^{-1}$. The moderate decrease in the carbon load of the final effluent indicated that some recalcitrant compounds were still present after ozonation. These results were also confirmed by the denitrifying activity tests carried out at the end of the continuous experiment.

In global terms, the acclimatization of the activated sludge consortium to study the denitrification process was a very important step in this work. Currently, in Portugal, there are many leachate treatment plants that use biological treatment with activated sludge for removal of biodegradable organic matter and nitrogenous compounds, however the complete removal of nitrogen compounds is not achieved. The results obtained in this work indicate that this failure is due not to the microorganisms used but to the type of management of the treatment systems or to the type of reactors used.

From the experiments performed with landfill leachate, considering the nitrate load applied, nitrate removal efficiencies and the negligible accumulation of intermediates, the anoxic rotating biological contactor showed to be extremely efficient and constitutes a promising technology for removing nitrate from landfill leachate.

8.2 SUGGESTIONS

In the context of this dissertation further research should be performed.

Considering the ammonium content of the pre-treated leachate, a biological system involving pre-denitrification followed by a nitrification stage and a circuit for leachate recirculation to the first unit should be evaluated.

It would be also of particular interest to improve the advanced oxidation step of the pre-treated leachate before the biological system since, although the tested processes produced significant amendment in leachate quality, a BOD_5/COD ratio of 0.4, considered as a minimum to implement an effective biological treatment, was not achieved, which indicates the high refractory nature of the landfill leachate.

Throughout the work, acetate was used as carbon source to ensure the process of heterotrophic denitrification. Acetate was chosen due to the high rates of denitrification generally obtained.

Methanol and ethanol are commonly used as carbon sources because they are cheap, however, in certain conditions, they can be toxic. Nevertheless, the use of acetate at a full scale could make the denitrification process very expensive. Thus, it would be attractive to use a real effluent as carbon source for the denitrification step. This real effluent could be, for instance, cheese whey or even young landfill leachate, which are usually rich in biodegradable organic matter.

The results at bench-scale allow obtaining indications concerning operational strategies to be applied to perform denitrification of this pre-treated landfill leachate. However, the size of the reactor and the operational conditions do not allow to fully evaluating the process. An interesting next step would be to perform pilot scale studies.

9. SCIENTIFIC OUTPUT

The overall work developed during this PhD thesis originated the following publications:

PAPERS IN JOURNALS WITH PEER REVIEW:

- Cortez S., Teixeira P., Oliveira R. & Mota M. (in press). Mature landfill leachate treatment by denitrification and ozonation. *Process Biochemistry*.

- Cortez S., Teixeira P., Oliveira R. & Mota M. (2010). Ozonation as polishing treatment of mature landfill leachate. *Journal of Hazardous Materials* 182 (1-3): 730-734.

- Cortez S., Teixeira P., Oliveira R. & Mota M. 2010. Denitrifying activity of activated sludge in suspension and in biofilm. *Environmental Engineering and Management Journal* 9 (3): 295-298.

- Cortez S., Teixeira P., Oliveira R. & Mota M. 2009. Effect of operating parameters on denirtification in an anoxic rotating biological contactor. *Environmental Technology* 30 (13): 1381-1389.

- Cortez S., Teixeira P., Oliveira R. & Mota M. 2008. Rotating biological contactors: a review on main factors affecting performance. *Reviews in Environmental Science and Biotechnology* 7 (2): 155-172.

PAPERS SUBMITTED TO JOURNALS WITH PEER REVIEW:

- Cortez S., Teixeira P., Oliveira R. & Mota M. Landfill leachate: generation, composition, management and treatment.

- Cortez S., Teixeira P., Oliveira R. & Mota M. Evaluation of Fenton and ozone-based advanced oxidation processes as mature landfill leachate pre-treatments.

- Cortez S., Teixeira P., Oliveira R. & Mota M. Denitrification of a landfill leachate with high nitrate load in an anoxic rotating biological contactor.

PUBLICATIONS IN CONFERENCE PROCEEDINGS (WITH PEER REVIEW):

-Cortez S., Teixeira P., Oliveira R. & Mota M. (2009) Fenton's oxidation as post-treatment of a mature municipal landfill leachate. In: *Proceedings of the WASET International Conference on Environmental Sciences and Engineering-ICESE,* Amesterdam, 23-25 September 2009, pp. 157-160.

-Cortez S., Teixeira P., Oliveira R. & Mota M. (2008) Denitrification in an anoxic rotating biological contactor under two carbon/nitrogen ratios. In: *Proceedings of the 10th International Chemical and Biological Engineering Conference,* Braga, Portugal, 4-6 September 2008, pp 632-633.

- Cortez S., Teixeira P., Oliveira R. & Mota M.(2008) Denitrifying activity of activated sludge in suspension and in biofilm. In: *IWA Biofilm Technologies Conference,* Singapore, 8-10 January 2008, pp 437-438.