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LANDFILL LEACHATE TREATMENT THROUGH THE INTEGRATION OF AIR-STRIPPING, MEMBRANE BIOREACTOR, ADVANCED OXIDATIVE PROCESS AND NANOFILTRATION

Belo Horizonte
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The burden is in proportion to strength, as the reward will be in proportion to resignation and courage.

Allan Kardec

RESUMO

Esta pesquisa avalia a integração dos processos de *air-stripping*/absorção (AS/AB), biorreator com membranas inoculado com *Saccharomyces cerevisiae* (BRM_{LEV}), POA/Fenton e nanofiltração (NF), visando a remoção/recuperação da amônia e reuso do lixiviado de aterro sanitário (LFL). O lixiviado estabilizado se destaca pela alta concentração de demanda química de oxigênio (DQO), nitrogênio amoniacal ($N\text{-}NH_3$) e compostos recalcitrantes. Inicialmente, foi avaliado o desempenho do BRM_{LEV} em diferentes razões DQO/N. A menor relação DQO/N favoreceu o crescimento da levedura no líquido reacional, mesmo sob condições adversas. Em maior relação DQO/N, alta remoção de matéria orgânica em termos de DQO (71 ± 4%) e remoção de amônia (97 ± 3%) foi observada. A análise da aplicação dos processos de AS/AB como pré- ou pós-tratamento do BRM_{LEV} no âmbito técnico e econômico demonstrou que a melhor forma de integrar os processos AS/AB é como pré-tratamento do BRM_{LEV} (AS/AB – BRM_{LEV}). Essa rota permitiu a recuperação de 7 kg de amônia por m^3 de lixiviado tratado. A concentração de amônia na alimentação do processo AS/AB foi um fator chave para atingir as especificações do mercado em termos da comercialização do fertilizante obtido. A operação do AS em altas temperaturas (60°C) foi a que apresentou maior taxa de remoção de amônia (99%). Portanto, a integração AS/AB – BRM_{LEV} permite a obtenção de um permeado com concentração final de 2.902 ± 374 mg L^{-1} de DQO e 9 ± 7,5 mg L^{-1} de amônia. Apesar de ter sido possível atingir o padrão de lançamento para amônia, não foi possível atingir o padrão para DQO, em que a fração remanescente se refere a matéria orgânica recalcitrante, necessitando da aplicação de uma etapa de polimento para este efluente. Os polimentos do permeado do BRM_{LEV} tanto por (I) NF – Fenton quanto por (II) Fenton – NF foram avaliados, em que a NF permitiu que o LFL obtivesse concentração final de DQO de 177 mg L^{-1} e 88 mg L^{-1}, respectivamente. Além de terem alcançado os padrões estabelecidos pela legislação vigente, o efluente final representa uma boa alternativa de reuso dentro da planta de aterro para contenção de poeira, terraplenagem e em canteiros de obras. O concentrado da NF foi tratado por Fenton (BRM_{LEV} – NF – $Fenton_{(concentrado)}$), em condições otimizadas, atingindo remoção de 87% de DQO. Por fim, com a realização de uma análise econômica preliminar foi verificado que a rota BRM_{LEV} – NF – $Fenton_{(concentrado)}$ foi a mais vantajosa devido a menor demanda por reagentes químicos e área de membrana. Desta forma, esta rota apresenta-se como uma alternativa para subsidiar projetos de sistemas de tratamento de lixiviado em aterros sanitários, uma vez que tem sido observado o crescimento do uso de BRM e NF para o tratamento desse efluente.

Palavras-chave: lixiviado aterro sanitário; brm_{LEV}; poa/fenton; nanofiltração; recuperação de amônia; tratamento do concentrado da nf; reuso.

ABSTRACT

This research evaluates air-stripping/absorption (AS/AB), membrane bioreactor inoculated with *Saccharomyces cerevisiae* (MBRy), AOP/Fenton and nanofiltration (NF) integration processes, aiming the ammonia removal/recovery and landfill leachate (LFL) reuse. The stabilized leachate stands out for its higher chemical oxygen demand concentration (COD), ammoniacal nitrogen ($N\text{-}NH_3$) and recalcitrant compounds. Initially, the MBRy performance was evaluated in different COD/N ratios. The lower COD/N ratio favored the yeast growth in the mixed liquor, even under adverse conditions. In higher COD/N ratios, high organic matter removal in terms of COD (71 ± 4%) and ammonia removal (97 ± 3%) was observed. The analysis of the application of AS/AB processes as pre- or post-treatment of MBRy in the technical and economic aspect showed that the best way to integrate AS/AB processes is as pretreatment of MBRy (AS/AB – MBRy). This route allowed the recovery of 7 kg of ammonia per m^3 of treated leachate. The ammonia concentration in the AS/AB process feed was a key factor to achieve the market specifications in terms of commercialization of the fertilizer obtained. The AS operation at high temperatures (60°C) showed the highest ammonia removal rate (99%). Therefore, the integration of AS/AB with MBRy allows obtaining a permeate with a final concentration of 2,902 ± 374 mg L^{-1} of COD and 9 ± 7.5 mg L^{-1} of ammonia. Although it was possible to achieve the release standard for ammonia, it was not possible to achieve the standard for COD, in which the remaining fraction refers to recalcitrant organic matter, requiring the application of a polishing step for this wastewater. The polishing of the MBRy permeate by both (I) NF – Fenton and (II) Fenton – NF were evaluated, in which the NF allowed the LFL to obtain a final COD concentration of 177 mg L^{-1} and 88 mg L^{-1}, respectively. In addition to having reached the standards established by current legislation, the final effluent represents a good alternative for reuse within the landfill plant for dust arrestment, earthworks and in construction sites. The NF concentrate was treated by Fenton in optimized conditions (MBRy – NF – $\text{Fenton}_{(\text{concentrate})}$), achieving 87% COD removal. Finally, with a preliminary economic analysis it was verified that the MBRy - NF - $\text{Fenton}_{(\text{concentrate})}$ route was the most advantageous due to the lower requirement with chemical reagents and membrane area. Thus, this route presents itself as an alternative to subsidize projects of leachate treatment systems in landfills, since the growth in the use of MBR and NF for the treatment of this effluent has been observed.

Keywords: landfill leachate; mbr_y; aop/fenton; nanofiltration; ammonia recovery; nf concentrate treatment; reuse.

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μ	– Dynamic water viscosity
A	– Area
AB	– Absorption
ANOVA	– Analysis of variance
AOP	– Advanced oxidation process
AOP/Fenton	– Advanced oxidation process for Fenton reagent
AS	– Air-stripping
BOD	– Biochemical oxygen demand
CCD	– Central composite design
CERH	– Conselho Estadual de Recursos Hídricos
COD	– Chemical oxygen demand
COD/N	– Chemical oxygen demand/nitrogen ratio
CODS	– Chemical oxygen demand soluble
COPAM	– Conselho Estadual de Política Ambiental
DOC	– Dissolved organic carbon
EC_{50}	– Median effective concentration
EPS	– Extracellular polymeric substances
EPS-COD	– COD of Extracellular polymeric substances
EPS-P	– Proteins of Extracellular polymeric substances
FSS	– Fixed suspended solids
FTS	– Fixed total solids
GE	– Global efficiency
HA	– Humic acid
HRT	– Hydraulic retention time
HS	– Humic substances
J	– Permeate flux
K	– Membrane permeability in distilled water
K_a	– Mass transfer
LFL	– Landfill leachate

MBR	– Membrane bioreactor
MBRy	– MBR inoculated with *Saccharomyces cerevisiae*
MCWO	– Molecular weight cut off
MF	– Microfiltration
MLVSS	– Mixed liquor volatile suspended solids
MSP	– Membrane separation process
MSW	– Municipal solid waste
NF	– Nanofiltration
NOM	– Natural organic matter
$N\text{-}NH_3$	– Ammoniacal nitrogen
PTFE	– Polytetrafluoroethylene
PVC	– Polyvinyl chloride
PVDF	– Polyvinylidene fluoride
Q_P	– Permeate flowrate
R_f	– Fouling resistance
R_m	– Membrane resistance
RO	– Reverse osmosis
S	– Sulfur
SAAR	– Specific ammonium removal rate
SMP	– Soluble microbial products
SMP-COD	– COD of Soluble microbial products
SMP-P	– Proteins of Soluble microbial products
SRT	– Solid retention time
TC	– Total carbon or total cost
TN	– Total nitrogen
TMP	– Transmembrane pressure
TOC	– Total organic carbon
TS	– Total solids
TSS	– Total suspend solids
UASB	– Upflow anaerobic sludge blanket

UF – Ultrafiltration

VOC – Volatile organic compounds

VSS – Volatile suspended solids

VTS – Volatile total solids

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1 CHAPTER 1: INTRODUCTION

1.1 Literature review

1.1.1 Landfill leachate

The improvement in the economy and in the population lifestyle have led to an increase in municipal solid waste (MSW) generation. The world generates about 2.01 billion tons of waste per year, which is expected to increase to 3.40 billion tons in 2050. In addition, the per capita generation is expected to increase by 19% in high-income countries and 40% in low-income countries, where the amount of waste generated in low-income countries is expected to triple (KAZA et al., 2018). According to ABRELPE (2019), Brazil produced approximately 217 tons of MSW daily in 2018, which is equivalent to 1.039 kg per inhabitant per day. Regarding the MSW disposal and treatment, there are different methods such as incineration, composting and landfill, among others. In Brazil, the waste disposal in sanitary or controlled landfills, or open dumps are one of the main forms of MSW disposal (COSTA et al., 2019). The landfill is the most used technique, in which about 59.5% (118.631 tons day^{-1}) of the generated residues were destined to these sites (ABRELPE, 2019).

The landfill is a technique of waste disposal in the soil, which does not cause damage to public health and safety, minimizing environmental impacts by using engineering principles to confine solid waste to the lowest possible area and reduce it to the minimum permissible volume (ABNT, 1992). However, the conditioning MSW in landfills does not ensure their inactivation since they are influenced by natural agents (rain and microorganisms). This activates biochemical transformation processes, and the bioconversion of organic matter into soluble and gaseous forms is the main factor of waste degradation, thus leading to the formation of biogas and leachate (CASTILHOS JR. et al., 2003). Although landfill is considered a suitable technique from an environmental point of view, the by-products generated need to be drained, collected and treated effectively so that they are not disposed in the environment, causing negative environmental impacts on air, soil and water bodies. One ton of solid waste can produce 0.2 m^3 of landfill leachate along the decomposition processes (CHRISTENSEN et al., 2005).

Landfill leachate (LFL) can be defined as the liquid from the moisture in the waste; the infiltration water in the cover layer; the products resulting from the biological degradation of the organic matter present; and the materials dissolved in the waste mass (MORAVIA et al., 2011). Also known as slurry or percolate, the LFL presents high values of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), ammoniacal nitrogen ($N\text{-}NH_3$), and dark color (AZZOUZ et al., 2018). It is noteworthy that in tropical climate regions like Brazil, these concentrations occur in the early stages of degradation. The presence of humic substances (HS) is also reported in LFL (KANG et al., 2002). In addition, their liquid composition can be divided into four groups of pollutants: (a) dissolved organic material (volatile organic acids and refractory organic compounds such as humic and fulvic acids), (b) inorganic macro components (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, Fe^{2+}, Mn^{2+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}), (c) heavy metals (Cd^{2+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}), and (d) xenobiotic organic compounds from domestic waste and chemicals present in low concentrations (aromatic hydrocarbons, phenols, pesticides, among others) (KJELDSEN et al., 2002).

According to Renou et al. (2008), the characteristics of leachate are variable, which depend mainly on the composition and compaction of the waste, precipitation rate, climate, hydrology, and age of the landfill. The latter characteristic is related to the LFL biodegradability, as organic fractions are replaced by non-biodegradable compounds according to the landfill age (SANGUANPAK et al., 2015). Landfills can be classified according to their age: young (under 5 years), medium (5-10 years) and old (over 10 years) (EL-GOHARY and KAMEL, 2016). The characteristic of old leachate is due to its recalcitrant composition, which makes its degradation by microorganisms difficult or impossible. The LFL recalcitrance is inherent to the presence of HS, which are compounds of high molecular weight and complex structure (KANG et al., 2002). Stabilized LFL, besides being characterized by ubiquitous presence of recalcitrant substances, are rich in $N\text{-}NH_3$ (SCHIOPU and GAVRILESCU, 2010). It should be noted that the main source of $N\text{-}NH_3$ in leachate comes from the protein’s degradation, which can constitute 0.5% of the dry mass of the residue (JOKELA et al., 2002).

However, it is important to note that in tropical climate regions (high temperatures) the process of waste degradation can be favored, making the leachate stabilization faster due to higher biological activity (TRÄNKLER et al., 2005), when compared to the leachate generated in temperate climate regions. Thus, it is expected that the concentrations of recalcitrant substances in the leachate from tropical climate regions will be higher, and that these conditions can be achieved in up to 1.5 years of operation (CHEN, 1996). Table 1.1 shows the leachate composition at different ages and locations.

Inadequate disposal of leachate without prior treatment can cause negative environmental impacts such as eutrophication of the receiving water bodies, toxicity to biota present in the soil and affected aquatic communities, in addition to decreased dissolved oxygen. Therefore, the implementation of treatment processes for this wastewater is of utmost importance in order to promote environmental protection and adequate sanitary conditions for the population.

1.1.2 Landfill leachate treatment

Conventional biological (activated sludge, stabilization ponds, UASB reactor) and physicochemical (coagulation-flocculation, chemical precipitation, adsorption) treatments were considered for many years as the most appropriate technologies for LFL treatment. With respect to young leachate, i.e., with higher biodegradable organic load, moderate levels of organic matter removal and $N\text{-}NH_3$ can be achieved using these treatment techniques (RENOU et al., 2008). However, due to more rigorous discharge standards, the variation in quality and quantity of LFL, and the difficulty of removing COD and recalcitrant compounds in old LFL with conventional treatments, resulted in the need to study the treatment of this effluent in several stages (AHMED and LAN, 2012).

In Minas Gerais, the legislation that provides the conditions and standards for effluent discharge is the COPAM/CERH-MG Joint Normative Deliberation No. 01, of May 5, 2008, which was defined by the State Environmental Policy Council (COPAM) and the State Water Resources Council of Minas Gerais (CERH-MG). Municipal landfill leachate must have a COD of up to 180 mg L^{-1} or treatment with reduction efficiency of at least 55% and an annual average of 65% or more, and a maximum $N\text{-}NH_3$ concentration of 20 mg L^{-1}.

Table 1.1 - Physico-chemical characterization of leachate in different locations and landfill ages.

Landfills locations	Parameters								References
	Landfill age (years) [1]	pH	BOD ($mg\ L^{-1}$)	COD ($mg\ L^{-1}$)	BOD/COD	TN [2] ($mg\ L^{-1}$)	$N-NH_3$ ($mg\ L^{-1}$)	True color ($mg\ L^{-1}$)	
Brazil (Paraná)	7	7.7	443	2,265	0.19	-	410	1,060	(SCANDELAI et al., 2018)
Poland (Northern region)	8	7.2	1,500	2,791	-	906	790	-	(FUDALA-KSIAZEK et al., 2018)
Brazil (Paraná)	11	9.1	55	1,819	0.03	-	859	4,180	(KAWAHIGASHI et al., 2014)
Brazil (Minas Gerais)	12	8.5	-	6,861	-	2,331	2,027	13,271	(AMARAL et al., 2017)
Portugal (Vila Real)	15	7.8	400	5,700	0.07	-	-	-	(AMOR et al., 2015)
Spain (Orís)	15	8.4	182	3,350 [3]	0.05	555	693	-	(RIBEIRA-PI et al., 2020)
China (Shenzhen and Beijing)	18	8.5	34	1,330	0.03	-	-	400	(LI et al., 2016)
Malasya (Penang)	19	8.7	100	2,615	0.04	-	2,010	5,545	(BASHIR et al., 2010)
Brazil (Pernambuco)	27	7.9	136	6,077	0.02	257.8	153.6	-	(RODRIGUES FILHO et al., 2012)
Brazil (Minas Gerais)	33	8.3	99	2,990	0.03	1,250	-	1,374	(MORAVIA et al., 2013)
France (Saint-Nazaire)	35	7.5	7.1	500	0.01	-	430	-	(TREBOUET et al., 2001)

[1] Total nitrogen
[2] In the year the study was published
[3] COD soluble

1.1.2.1 Ammonia removal/recovery

According to Table 1.1, old LFL has in its composition a high concentration of N-NH_3, which can cause toxicity to the microorganisms responsible for the biological degradation. In addition, high concentration of N-NH_3 in the post-treatment effluent may promote depletion of dissolved oxygen in water bodies due to stimulus to algae growth (DOS SANTOS et al., 2020). Cheung et al. (1993) found that the toxicity present in LFL is due to high ammonia concentration. Amaral et al. (2018) observed that the COD removal and the N-NH_3 concentration had a negative correlation, in which the reduction of COD removal in the LFL was caused by the increase in the concentration of N-NH_3 in the MBRy feed. The COD/N ratio is a parameter that influences the biological treatment of LFL. Previous studies from Kim et al. (2003), Wichitsathian et al. (2004) and Smaoui et al. (2020) found that the higher the COD/N ratio, the higher are the organic matter removal efficiencies in leachate.

Air-stripping (AS) is the treatment technique most used in the N-NH_3 removal in LFL (GUO et al., 2010), which consists in transferring the mass of a gas, which is in the liquid phase, to the gas phase, through contact of the liquid with the injected gas (usually air) (METACALF and EDDY, 2003). AS is based on the volatilization of non-ionized ammonia with increased pH (GOMES et al., 2009). According to Equation 1.1, ammonia is ionized in aqueous media, giving rise to the ammonium ion:

$$\begin{gathered} NH_4^+{}_{(aq)} + OH^- \leftrightharpoons NH_{3(aq)} + H_2O \\ K_a(25°C) = 5.70 \cdot 10^{-10} \end{gathered} \tag{1.1}$$

The NH_3 form is called free ammonia, and the NH_4^+ form is called ionized ammonia, and only NH_3 is capable of being removed by volatilization. These two forms of ammonia are in chemical equilibrium, and the proportion between them will depend on the pH of the media (DOS SANTOS et al., 2020). With the pH increase, the equilibrium shifts to the left, favoring a higher presence of NH_3, while the pH around the neutrality all ammonia is, practically, in the NH_4^+ form. At pH close to 9.5, approximately 50% of ammonia is in free form and 50% in ionized form, and at pH above 11 the ammonia is practically all in free form. Since the pH of the old leachate is in the range 7.7 - 8.7, pH adjustment may be necessary to promote higher ammonia volatilization. Besides the pH, the temperature is also a factor that influences the N-NH_3 removal, where for the same pH value, the proportion of NH_3 will be higher the higher the temperature of the liquid. Consequently, the temperature rise may favor an increase in LFL toxicity. Campos et al. (2013) achieved N-NH_3 removal higher than 91% in LFL at 60°C and 7 hours test, regardless of pH value. Hossini et al. (2015) achieved N-NH_3 removal of 84.11% at 36°C and 10.7 pH. Smaoui et al. (2020) applied AS as pre-treatment of LFL anaerobic digestion at pH 11 and ambient temperature (25°C) and achieved N-NH_3 removal of 85%. Although AS is a suitable technology for the N-NH_3 removal from LFL, the ammonia release into the atmosphere is still common, and may cause air pollution, and depending on the level of contact and period of exposure, respiratory, eye and throat irritation (DOS SANTOS et al., 2020). The ammonia removed by the AS can be recovered through chemical absorption in an acidic solution, forming ammonium salt (ammonium sulfate), according to Equation 1.2:

$$2NH_{3\,(g)} + H_2SO_{4\,(l)} \rightarrow (NH_4)_2SO_{4(l)} \tag{1.2}$$

Ammonium sulfate ($(NH_4)_2SO_4$) is a fertilizer that can be obtained as a by-product of industrial processes, such as gas purification. This fertilizer provides essential nutrients for plants in the form of nitrogen (N) and sulfur (S), with benefits compared to other nitrogen-based fertilizers. Some examples are: (i) no loss of N by volatilization when applied to acid or neutral soils; (ii) best source of N for saline soils, and (iii) no contribution of CO2 emissions to greenhouse gases (CHIEN et al., 2011). According to these authors, ammonium sulfate has 21 and 24% of N and S in its composition, respectively. However, it is observed the commercialization of this fertilizer with the composition of 20% of N.

According to Saab and Paula (2008), ammonium sulfate is the third most imported intermediary fertilizer, with an external dependence of 86.6%. Silva (2019) shows the increase in Brazilian dependence on imported nitrogen fertilizers, making this a limiting factor to meet national demand. This fact reflects the relevance of new studies that can meet the demand for this fertilizer.

1.1.2.2 Membrane bioreactor, advanced oxidation process and nanofiltration

Biological processes combined with membrane separation processes (MSP), such as membrane bioreactors (MBR), have proven appropriate for the biological treatment of recalcitrant LFL. In addition, there has been an increasing use of MBR in the treatment of this effluent (SONG et al., 2020). Ahmed and Lan (2012) conducted a review of LFL treatment with MBR and found that this technology has a high potential for COD, BOD and N-NH3 removal, regardless of the leachate age. Furthermore, Abuabdou et al. (2020) showed that leachate treatment in anaerobic membrane bioreactors (AnMBR) can achieve up to 95% COD removal, in addition to the benefit of biogas production, which can be used within the plant to reduce energy costs.

MBR is a hybrid process that combines the conventional biological process with membrane filtration, which can be ultrafiltration (UF) or microfiltration (MF) membrane (LUONG et al., 2016). Due to the biomass retention in the system, besides the low sludge production, the MBR operates with high biomass concentration and sludge age (XUE et al., 2015). Complete biomass retention also benefits the acclimatization of microorganisms to extreme conditions such as high salinity, temperature, and toxicity, as well as the enrichment of microorganisms that can degrade specific pollutants in the wastewater (SONG et al., 2020). The MBR has the capacity to support large operational variations in terms of the composition of the affluent leachate, without affecting the quality of the final effluent. Alvarez-Vazquez et al. (2004), compared MBR and conventional biological process in LFL treatment, and observed that MBR was able to achieve higher COD removal in old leachate.

The bacterial sludge used in MBR, both under aerobic and anaerobic conditions, has limitations regarding the removal of recalcitrant compounds in the leachate (BRITO et al., 2019). The use of fungi is an alternative for the treatment of LFL in MBR, because according to Harms et al. (2011), these microorganisms present high breakage and assimilation capacity of recalcitrant pollutants.

The application of fungal sludge in MBR must consider the membrane fouling phenomenon, being one of the main phenomena resulting from MSP. Filamentous fungi have extensive mycelium mesh, which can contribute to the fouling. Yeasts, on the other hand, are unicellular fungi that do not present flagellos or any locomotion structures (ROSE and HARRISON, 1987), making their application in MBR possible. The ideal growth range of these microorganisms is 20 to 30°C and they can withstand temperatures from 0 to 47°C (WICHITSATHIAN, 2004). In addition, yeasts prefer a slightly acidic environment for their growth, between 4.5 and 5.5, but can withstand a wide pH range between 3 and 10 (DEAK, 2006).

The species *Saccharomyces cerevisiae* stands out for its easy reproduction (sexually and asexually), becoming the most economically relevant species of the fungal group (GUIMARÃES, 2005). It is widely used in fermentation processes in industries, which grow under high concentrations of sugars and ethanol, withstanding the stress imposed by osmotic pressure, lack of water and the harmful effect of ethanol (TANGHE et al., 2006). There are studies that used MBR inoculated with *Saccharomyces cerevisiae* (MBRy) in the LFL treatment. Amaral et al. (2018) and Reis et al. (2017) found that, compared to MBR with bacterial sludge, MBRy provided greater removal of COD, color, $N\text{-}NH_3$, and phosphorus, in addition to presenting lower fouling potential.

However, Amaral et al. (2017) verified that the COD removal obtained in MBRy (72 ± 3%) corresponds to the biodegradable fraction, and the remaining COD refers to the recalcitrant fraction. Reis et al. (2017) found the persistence of recalcitrant compounds after LFL treatment in MBRy, and the production of new compounds in MBRy that have the potential to promote toxicity in the permeate. These results reinforce the importance of polishing this effluent after biological treatment.

The integration of MBR with physico-chemical methods for polishing, such as advanced oxidative processes (AOP) and MSP, is an alternative for the LFL treatment, aiming both its framework to legislation and its reuse. According to Lin et al. (2012), the integration of MBR with physico-chemical methods is expected to promote higher removal efficiencies than conventional treatment technologies.

Advanced oxidative processes (AOP) consist in producing hydroxyl radicals ($^{\bullet}OH$) from a highly reactive strong oxidizer for complete mineralization producing CO_2 and H_2O, or partial degradation, increasing the biodegradability of organic pollutants (MORAVIA et al., 2011). The leachate treatment by AOP is justified by the presence of recalcitrant, toxic, and low biodegradability compounds in this wastewater. According to Deng and Zhao (2015), one of the goals of treating LFL by AOP is to assist in the degradation of organic matter as a posttreatment of other technologies.

The Fenton reagent (AOP/Fenton) is among the AOP techniques that has greater removal of organic matter due to the use of catalysts. This process uses hydrogen peroxide (H2O2) as an oxidizing agent and iron in reduced form (Fe^{2+}) as a catalyst for $^{\bullet}OH$ production under acid conditions (AMOR et al., 2015). According to Moreira

(2009), the H_2O_2 concentration will depend on the amount of organic matter present in the system for the formation of $^{\bullet}OH$ and, consequently, oxidation of organic matter. Regarding iron dosage, it is pertinent that it is not too high to avoid excessive sludge formation and the need for an additional step in the process to remove ferrous ions (KIM et al., 1997).

Deng (2009), based on 24 data from 17 studies, reported that the efficiency of COD removal in leachate using Fenton varies from 35 to 90%, with an average of 71 ± 13%. Lima et al. (2017) applied Fenton in the LFL treatment and obtained 88 and 85% HS removal for the leachate from the Gericinó and Gramacho landfills, respectively, both located in the state of Rio de Janeiro.

Moreover, although Fenton can decrease the leachate toxicity (DA COSTA et al., 2018), increased toxicity can also be observed due to the formation of toxic products, which may be more toxic than the original compounds (GOTVAJN et al., 2011). Huang and Wang (2007) pointed out that toxicity, when present, can have causes such as the presence of residual chemical oxidants (such as H2O2), which can be present due to inadequate dosages, in addition to the low pH and intermediate compounds formed during the degradation process. It is worth noting that although Fenton is considered an alternative for the removal of residual organic matter, the application of this process alone may not be sufficient for LFL polishing. Besides organic matter, there is the presence of high concentration of compounds such as chloride (150-4,500 mg L^{-1}), sulfate (8-8,870 mg L^{-1}), sodium (70-7,700 mg L^{-1}), potassium (50-3,700 mg L^{-1}), calcium (10-7,200 mg L^{-1}) and magnesium (30-15,000 mg L^{-1}) (KJELDSEN et al., 2002), which are not effectively removed in MBR or Fenton.

In this way, although AOP can remove recalcitrant compounds and increasing biodegradability, LFL may be toxic due to the presence of toxic chemical oxidants or the formation of by-products. Since leachate is a complex wastewater, which has no way to define a universal form of treatment, the search for treatment routes that enable its compliance with legislation and reuse becomes relevant.

MSP can be combined with both MBR and AOP to increase the efficiency of LFL treatment. MF, for example, can be used to remove the sludge generated in Fenton. In addition, nanofiltration (NF) has been used as a polishing in LFL treatment to remove residual organic matter, toxic by-products that may be formed during Fenton and dissolved ions. It is used for this purpose since the NF membrane is quite susceptible to fouling. The NF process occurs basically by two principles: rejection of neutral species by size (molecules larger than 200-300 g mol^{-1} are rejected), and rejection of inorganic ions due to electrostatic interactions between - the ions and the membrane (LINDE and JONSSON, 1995). Still according to the same authors, the NF membrane has the ability to remove recalcitrant compounds and heavy metals from the LFL.

Moravia et al. (2013) assessed the integration of Fenton with MF and NF in LFL treatment and obtained a final concentration of 45 ± 13 mg L^{-1} for COD and 78 ± 7 mg L^{-1} for N-NH_3. Reis et al. (2020) verified the importance of NF application as a polishing in two leachate treatment routes, where global removals above 88% for COD and 80% for N-NH_3 could be achieved, in addition to toxicity removal. The final concentration reached by the parameters with the leachate polishing through the MSP application may allow its reuse within the landfill. Some forms of reuse are in dust arrestment, in earthworks and in construction site works. In Brazil there are examples of landfills using MSP for full-scale leachate polishing. The Gramacho landfill, located in Rio de Janeiro (RJ), uses NF as a polish for the biological leachate process (MANNARINO et al., 2006), and the landfills of São Gonçalo (RJ) and Campos (RJ) use reverse osmosis (RO) after the pre-filtration (SOARES, et al., 2017). In Minas Gerais, two landfills in Macaúbas, operated by Vital Ambiental in partnership with AST Ambiente, use RO to treat leachate. Table 1.2 presents the final characterization from the integration of AS, MBR, Fenton and MSP in LFL treatment.

Table 1.2 - Effluent characterization after the combination of processes involving MBR, Fenton and MSP in LFL treatment.

LFL treatment process	Parameters								References
	pH	COD (mg L^{-1})	BOD (mg L^{-1})	Total N (mg L^{-1})	$N\text{-}NH_3$ (mg L^{-1})	Color (mg L^{-1})	HS (mg L^{-1})	Acute toxicity (TU)	
AS + MBRy (1) + NF	5.7	77	-	230	58	-	-	0	(REIS et al., 2017)
AS + MBRb (2) + NF	6.7	457	-	699	126	-	-	8	(REIS et al., 2017)
AS (3) + MBRy + NF	-	482	-	620	116	6	109	0	(AMARAL et al., 2016)
AS + MBRb + NF	7.8	404	73	-	116	3	106	-	(AMARAL et al., 2015)
AS + MBRy + NF	8.64	84	-	24.31	-	53	-	-	(SILVA et al., 2019)
MBRb + NF	-	1,145	-	-	268	12	-	-	(CAMPAGNA et al., 2013)
AS + MBR + NF	7.4	464	-	714	131	2.7	-	<1	(REIS et al., 2020)
MBR + NF	7.05	22.67	2.21	13	0.26	-	-	-	(FUDALA-KSIAZEK et al., 2018)
Fenton + MF (4) + NF	8.1	278	-	623	331	-	-	<1	(REIS et al., 2020)
Fenton + MF + NF	-	106	-	-	-	11	-	-	(SANTOS et al., 2019)
SBR (5) + Coagulation + Fenton + BAF (6)	-	75	6	35.6	6	8	-	-	(WU et al., 2011)
Coagulation/flocculation + Fenton	-	620	-	-	-	-	-	-	(AMOR et al., 2015)
Coagulation/flocculation + Fenton (7)	-	408	-	-	-	270	160	-	(LIMA et al., 2017)
Coagulation/flocculation + Fenton (8)	-	590	-	-	-	481	245	-	(LIMA et al., 2017)
AS + Fenton + SBR + Coagulation	-	317.4	114	-	50.6	-	-	-	(LIU et al., 2015)

(1) Membrane bioreactor inoculated with yeast
(2) Membrane bioreactor inoculated with bacteria
(3) Air-stripping
(4) Microfiltration
(5) Sequencing batch reactor
(6) Biological aerated filter
(7) Gericinó landfill
(8) Gramacho landfill

The production of concentrated LFL using MSP is the main disadvantage of this process, which is characterized by a dark color, refractory pollutants, and high salinity (ZHANG et al., 2009). Because it contains high COD concentration (1,100-6,800 mg L^{-1}) and low BOD concentration (3-29 mg L^{-1}), the LFL concentrated by NF becomes an untreatable effluent by biological processes (KEYIKOGLU et al., 2020). According to Zhang et al. (2013), HS are the largest fraction of dissolved organic matter in concentrated LFL, ranging from 60 to 75%. An alternative for the treatment of concentrated LFL is the application of physico-chemical processes to remove refractory pollutants such as AOPs. As the leachate concentrated by NF has a low BOD_5/COD ratio (0.094), the Fenton process has been applied to increase its biodegradability (HE et al., 2015).

Wu et al. (2020), after a literature review on the studies that used Fenton in the LFL treatment, showed that the pH range for concentrated leachate treatment by RO is 3-5.08, and H_2O_2:Fe^{2+} ratio of 6.545. Table 1.3 shows some studies that applied Fenton to concentrated MSP leachate.

Table 1.3 - Concentrated leachate treatment by NF from Fenton.

Process	Wastewater characteristics	Experimental conditions	Treatment efficiency	References
Fenton	COD: 3,060 mg L^{-1} BOD: 288 mg L^{-1} BOD_5/COD: 0.09	pH: 3 H_2O_2: 65.43mM Fe^{2+}: 7.27 Mm H_2O_2/Fe^{2+}: 9 Reaction time: 120 min	COD: 63.5%	(HE et al., 2015)
Fenton	COD: 3,300 mg L^{-1} TOC: 1,080 mg L^{-1} BOD_5/COD: 0.014	pH: 3 H_2O_2: 45 mM Fe^{2+}: 15 mM H_2O_2/ Fe^{2+}: 3 Reaction time: 40 min	COD: 78.9% TOC: 70.2% BOD_5/COD: 0.106	(TENG et al., 2020)
Fenton	COD: 3,450 mg L^{-1} TOC: 1,426 mg L^{-1} BOD5/COD: 0.01	pH: 5 H_2O_2: 10 mM Fe^{2+}: 8 mM H_2O_2/Fe^{2+}: 1.25 Reaction time: 120 min	COD: 68.7% TOC: 68.5% BOD_5/COD: 0.04	(LI et al., 2016)
Coagulation + Fenton	COD: 4,500 mg L^{-1} TOC: 1,600 mg L^{-1}	pH: 2 H_2O_2: 1000 mM Fe^{2+}: 17 mM H_2O_2/Fe^{2+}: 58.82 Reaction time: 180 min	COD: 69.6% TOC: 68.9%	(XU et al., 2017)

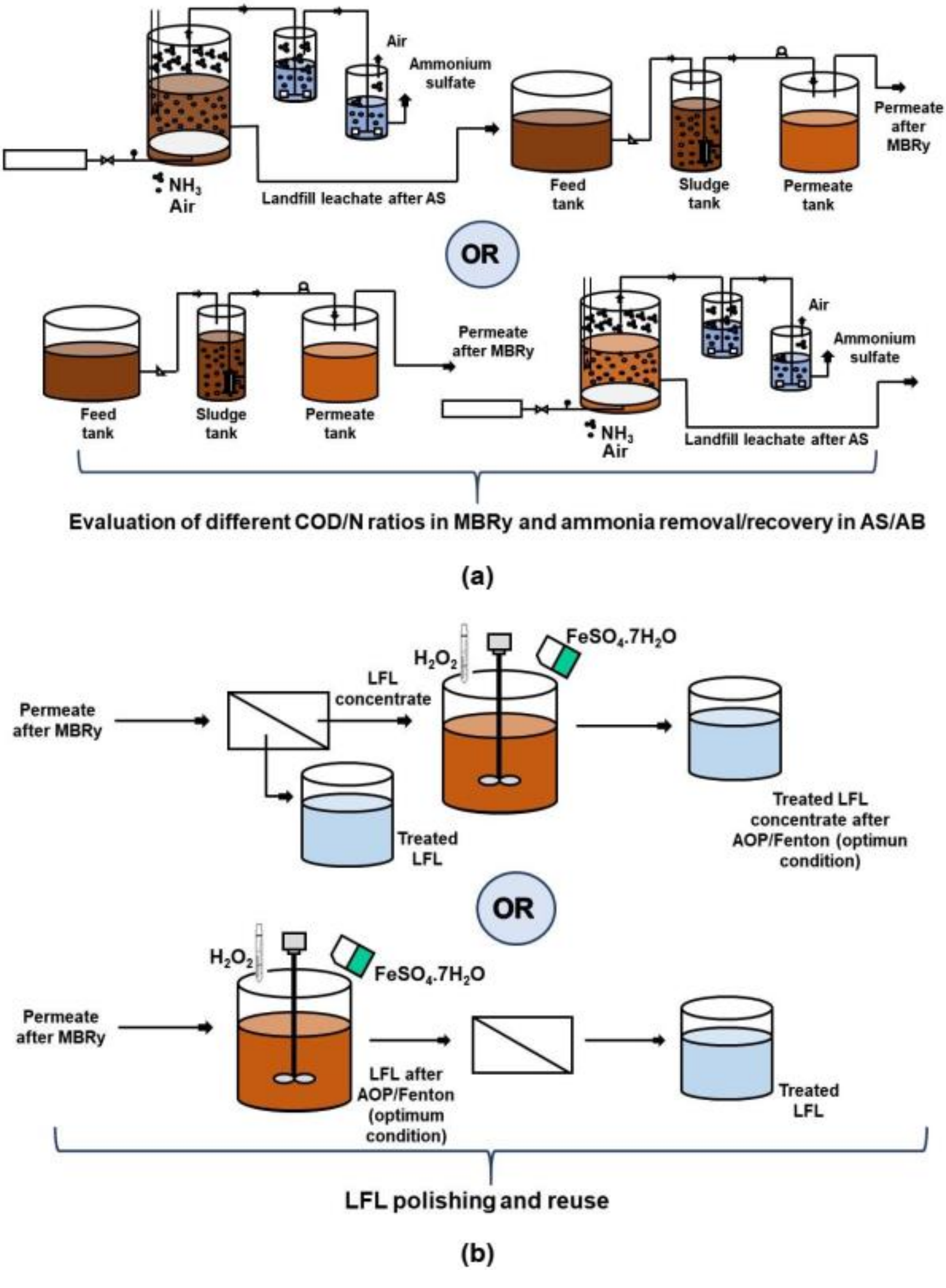
1.2 Integration of processes aiming ammonia recovery and reuse in landfill leachate treatment

Considering the landfill age and the faster biological stabilization of leachate due to climatic conditions (tropical climate in Brazil), it is necessary to apply treatment routes that are able to remove the high concentration of ammonia and recalcitrant compounds.

In addition to meeting legislation, it is of extreme importance that the treatment route provides the recovery of value-added by-products. The ammonia recovery can be done through the application of the air-stripping/absorption process (AS/AB) in the ammonium sulphate form, a nitrogen fertilizer with high national demand. MBRy is an alternative for the biological treatment of LFL and considerable removals of organic matter can be achieved. It is relevant to analyze the AS/AB process application as pre- or post-treatment of MBRy taking into consideration technical (initial ammonia concentration) and economical (amount of recovered ammonia) aspects.

However, it is important to apply other processes for leachate polishing, such as AOP and NF, for the remaining recalcitrant compounds removal from biological degradation. The leachate polishing can also allow its reuse inside the landfill. Fenton and NF can be integrated in different ways for the polishing of MBRy treated leachate: (I) NF – Fenton or (II) Fenton – NF (Figure 1.1).

Figure 1.1 - Proposed treatment routes for LFL evaluating a) ammonia removal and different COD/N ratio in MBRy and b) polishing and reuse.



The advantages of the first conjugation (Figure 1.1b) Fenton would be applied in the NF concentrated compartment treatment, since there are treatment plants that use NF or RO as LFL polishing that recirculate the concentrate to the landfill. There are studies that show the problems caused by this recirculation such as alteration of the physico-chemical composition of the leachate (decrease in the BOD_5/COD ratio, increase volatile fatty acids concentration, ammonia nitrogen and COD), and decrease the membrane performance due to higher fouling, leading to increased energy consumption (KEYIKOGLU et al., 2020). The advantages of the second conjugation consist in the removal of the remaining organic matter and ions, in addition to by-products formed in Fenton that may confer toxicity. The indication of the best alternative of process integration for LFL polishing will depend on the application and importance of the study, and the choice should be based on technical and economic criteria.

There are several studies regarding the processes integration for LFL treatment. On the other hand, it was observed the absence of research that evaluated the performance of MBRy, inoculated with *Saccharomyces cerevisiae*, in different COD/N ratio regarding the COD, NNH_3, toxicity removal and membrane fouling, without adjusting the feed pH. In addition, a study evaluating the best alternative of process integration for LFL polishing has not been seen in the literature, since there are works that evaluate MBRy – Fenton – NF integration in an individualized way.

Therefore, this dissertation aims to establish routes for the LFL treatment taking into consideration the AS/AB, MBRy, Fenton and NF processes aiming at the removal/recovery of $N\text{-}NH_3$ and effluent reuse.

1.3 Objective

1.3.1 General objective

To evaluate treatment routes for LFL landfill leachate taking into consideration airstripping/absorption, MBRy, Fenton and NF processes aiming at the removal/recovery of NNH_3 and effluent reuse.

1.3.2 Specific objectives

- To evaluate the MBRy performance in the LFL treatment in different COD/N ratios;

- To evaluate the air-stripping/absorption process in N-NH_3 removal/recovery and its integration as pre-treatment or post-treatment of MBRy considering technical and economic aspects; and
- To evaluate the MBRy permeate polishing through Fenton – NF and NF – Fenton taking into consideration technical and economic aspects.

1.4 Document structure

This dissertation is divided into 4 chapters: Chapter 1 consists of the introduction, which contains the literature review, objectives, and the document structure; Chapter 2 presents the discussion on the technical and economic feasibility of integrating the AS/AB process as a pre- (ammonia recovery) or post-treatment (polishing step) of the MBRy, in addition to the evaluation of the MBRy in different COD/N ratios; Chapter 3 evaluates the MBRy permeate polishing by both Fenton-NF and NF-Fenton; and finally, Chapter 4 presents the final considerations of this work in an integrated way. It should be noted that even though Chapters 2 and 3 are presented in article format, and presenting interdependence among themselves, they can be clearly understood separately.

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2 CHAPTER 2: LANDFILL LEACHATE TREATMENT FROM INTEGRATION OF MEMBRANE BIOREACTOR AND AIR-STRIPPING/ABSORPTION PROCESS: TECHNICAL AND ECONOMIC ASSESSMENT

2.1 Introduction

Landfill leachate (LFL) has a high biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), ammoniacal nitrogen (N-NH_3), and dark color (AZZOUZ et al., 2018). Improper disposal of leachate without prior treatment can cause negative environmental impacts such as eutrophication of the receiving water bodies, toxicity to biota present in the soil and in the affected aquatic communities.

According to Renou et al. (2008), the leachate characteristics vary and depend mainly on the composition and compaction of the waste, precipitation rate, hydrology, and the landfill age. The latter characteristic is related to the biodegradability of LFL, as organic fractions are replaced by non-biodegradable compounds according to the aging of the landfill (SANGUANPAK et al., 2015). The old LFL is characterized by its recalcitrant composition, which is related to the presence of humic substances (HS), which are compounds of high molecular mass and complex structure (KANG et al., 2002). The presence of HS in the old LFL leachate hinders or makes impossible the wastewater degradation by microorganisms. Moreover, the mineralization of organic matter in landfills installed in tropical climate regions occurs faster compared to temperate climate regions due to higher biological activity under warmer conditions, reducing the LFL biodegradability (CHEN, 1996).

Conventional treatments, both biological (activated sludge, stabilization ponds, upflow anaerobic sludge blanket (UASB) reactor) and physicochemical (coagulation-flocculation, chemical precipitation, adsorption), have been considered for many years as the most suitable technologies for LFL (RENOU et al., 2008). However, stricter standards of discharge, variation in quality and quantity of LFL, difficulty in removing COD and recalcitrant compounds in old LFL with conventional treatments resulted in the need to study the treatment of this wastewater using other technologies.

Biological processes combined with membrane separation processes (MSP), such as membrane bioreactors (MBR), have proven to be appropriate for the biological treatment of recalcitrant LFL (LUONG et al., 2016). Biomass retention in the MBR associated with low sludge production provides system operation with high biomass concentration and sludge age (XUE et al., 2015). According to Ahmed and Lan (2012) aerobic MBR has a high potential for removing COD, BOD and N-NH_3 of LFL, regardless of the leachate composition. Also, the MBR supports great operational variations in terms of the composition of the affluent leachate, without affecting the quality of the final effluent (BOVE et al., 2015). Although few researches have been conducted in the treatment of LFL by anaerobic membrane bioreactors (AnMBR), lab-scale studies showed COD removal efficiencies of up to 95% (ABUABDOU et al., 2020). The biogas production is among the main benefits of the wastewater treatment by AnMBR, being able to supply the energy demand required for the operation of the treatment plant (SONG et al., 2018).

However, the typical sludge used in the MBR, both under aerobic and anaerobic conditions, has limitations regarding the removal of recalcitrant compounds in the leachate (BRITO et al., 2019). The use of fungi is an alternative for the LFL treatment in MBR, where the species Saccharomyces cerevisiae stands out for its easy reproduction (sexually and asexually), becoming the most economically relevant species of the fungal group (GUIMARÃES, 2005). Table 2.1 shows the characteristics of yeast required for growth.

Table 2.1 - Characteristics that influence the yeast growth.

Temperature (°C)	0 – 47 [(1)]
pH	3 – 10 [(2)]
Carbon and energy source	Carbohydrates, alcohols, organic acids [(2)]
Nitrogen source	Ammonia, nitrite, nitrate, amino acids, urea [(3)]

[(1)] WICHITSATHIAN (2004)
[(2)] DEAK (2006)
[(3)] DAN (2001)

Amaral et al. (2018) and Reis et al. (2017) verified that, if compared with MBR with bacterial sludge, the MBR inoculated with Saccharomyces cerevisiae (MBRy) provided higher removal of COD, color, N-NH_3 and phosphorus, besides presenting lower potential of membrane fouling.

Besides the organic matter removal, the LFL treatment should also include a step for N-NH_3. The COD/N ratio is a parameter that influences the biological treatment of LFL.

In works performed by Kim et al. (2003) and Smaoui et al. (2020) it was found that the higher the COD/N ratio, the higher are the efficiencies of organic matter removal in leachate. Wichitsathian et al. (2004) also verified that higher COD removals were obtained in higher COD/N ratio. This study evaluated the performance of an MBR inoculated with a mixture of wild yeasts in the treatment of medium age LFL using or not air-stripping (AS) as pre-treatment. The pH of the leachate in AS was adjusted to 11-12, and no increase in COD concentration after AS was mentioned. The pH of the MBR feed was adjusted to acid (3.5-3.8) to avoid contamination by bacteria.

Air-stripping (AS) is the most widely used treatment technique for N-NH_3 removal in LFL (GUO et al., 2010). Although AS is a suitable technology for removing N-NH_3 from the LFL, it is still common, mainly in low-income country, the ammonia release into the atmosphere causing air pollution (DOS SANTOS, et al., 2020). The ammonia removed by the AS can be recovered by chemical absorption in an acidic solution, producing ammonium salt (ammonium sulphate), which can be commercialized as fertilizer, providing essential nutrients in the form of nitrogen (N) and sulfur (S). The use of air-stripping/absorption (AS/AB) as pre-treatment has the advantage of increasing the performance of microorganisms in the removal of organic matter due to the reduction of N-NH_3 concentration in the medium, besides allowing greater N recovery. However, if ammonia recovery is not a technical (low concentration of ammonia in solution, for example) or economically feasible, it is more suitable to use as post-treatment. Hence, the amount of N-NH_3 to be removed will be lower on AS/AB, implying lower cost in the process. In general, the application of the AS/AB process as pre- or post-treatment will enable the framing of the release standards.

The main objective of this study was to investigate the overall performance of MBRy inoculated with commercial baker's yeast (*Saccharomyces cerevisiae*) at different COD/N ratios by long-term operation. The technical and economically viability of ammonia recovery from LFL by AS/AB was also investigated. The results were used to establish the best way to integrate AS/AB and MBRy processes. It should be noted that there was no pH adjustment in the mixed liquor of MBRy to prevent bacterial growth. Besides this initiative to reduce the cost with chemicals, it assumed that the bacteria that would grow in the mixed liquor had as origin the leachate itself, and that the consortium between the yeasts and these bacteria could be beneficial. This is the first study in the literature that evaluates the effect of ammonia concentration and the viability of its recovery considering the market specifications. No studies have been found in the literature addressing the performance of membrane fouling in different COD/N ratios in the treatment of LFL using MBRy.

2.2 Material and Methods

2.2.1 Landfill leachate samples

Samples of raw LFL were collected in the equalization tank of a landfill located in the city of Sabará/Minas Gerais - Brazil. The landfill operates since 2005, generates around 600 m³ day^{-1} of leachate and receives, on average, 3,400 t day^{-1} of urban waste, non-hazardous industrial waste, civil construction waste and waste from health service. The leachate collections at the landfill were performed in February and June 2016 and were kept in cold storage (~ 4°C) for a maximum of 120 days. The physico-chemical characterization of the wastewater is shown in Table 2.2. The analyses were performed according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2017).

Table 2.2 - Physico-chemical characterization of the raw leachate (n = 26 samples).

Parameter	Unit	Minimum	25% quartile	Average	Median	75% quartile	Maximum
COD_T	mg L^{-1}	5,454	6,188	6,597	6,714	6,861	7,915
COD_S	mg L^{-1}	4,279	5,592	5,858	5,957	6,330	6,887
TOC	mg L^{-1}	1,321	1,661	1,796	1,831	1,908	2,227
Cl^-	mg L^{-1}	2,402	2,423	2,472	2,448	2,484	2,642
Alkalinity	mg L^{-1}	20,009	20,185	20,590	20,392	20,691	22,008
TN	mg L^{-1}	2,230	2,789	3,040	3,062	3,442	3,744
HS	mg L^{-1}	3,527	4,244	5,668	5,197	7,304	8,290
$N\text{-}NH_3$	mg L^{-1}	1,402	2,035	2,249	2,309	2,516	2,921
Conductivity	mS cm^{-1}	20.16	21.98	23.24	23.1	23.82	25.94
pH	-	8.01	8.18	8.33	8.36	8.47	8.59
True color	uH	9,175	9,970	11,578	10,862	12,089	18,837
Turbidity	NTU	117	138	170	152	173	361
Sulfate	mg L^{-1}	406	470	537	571	588	627
VSS	mg L^{-1}	190	285	402	425	496	683
TS	mg L^{-1}	8,280	11,200	11,776	12,470	12,800	13,185

COD_T = total COD; COD_S = soluble COD; TOC = total organic carbon; HS = humic substances; VSS = volatile suspend solids; TS = total solids

2.2.2 Experimental setup and operational conditions of MBRy for different COD/N ratios

The MBRy was operated for 130 days, being fed with leachate with $N\text{-}NH_3$ concentration of 236 ± 52 mg L^{-1} (range I) for the first 66 days and with leachate with $N\text{-}NH_3$ concentration of 2,512 ± 200 mg L-1 (range II) for the remaining 64 days. For the leachate to achieve the ammonia concentration for range I, the AS process was adopted. The AS system was fed with 10 L of raw leachate (without pH adjustment and at room temperature), with an aeration flow rate of 4 L min^{-1} and a hydraulic retention time (HRT) of 48 hours.

The MBRy was inoculated with commercial baker's yeast (*Saccharomyces cerevisiae*) purchased from Fleischmann®, and the startup and details of the MBR used are found in the work of Amaral et al. (2017). The reactor operated with high sludge age (278 days), HRT of 48 hours, average permeate flow rate of 0.1 L h^{-1} and backwash flow rate of 0.3 L h^{-1}. Backwash was performed every 15 minutes of filtration for 15 seconds. The biological tank received constant aeration of 1.67 L min^{-1} without acidification of the mixed liquor and was equipped with a submerged ultrafiltration (UF) module (PVDF hollow fiber membrane, average pore size of 0.04 µm, total surface area of 0.047 m^2, ZeeWeed 500D - GE). The UF membrane was also aerated constantly at a flow rate of 8.33 L min^{-1}. pH, permeate flow, filtration and backwash pressure were monitored daily. Membrane chemical cleaning occurred weekly in order to recover membrane permeability using citric acid solution (pH 3.0) and sodium hydroxide solution (NaOH) 0.4% w/w. The chemical cleaning was performed for 20 minutes in ultrasound bath (Unique USC 2800–40 kHz) with each solution.

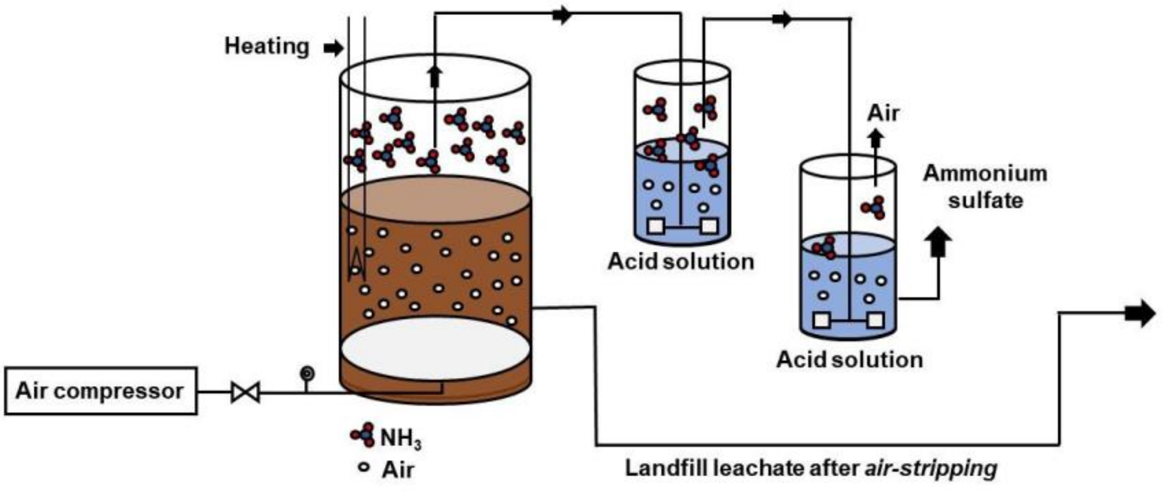
The pollutant removal efficiency of the MBRy was evaluated by monitoring the parameters COD and $N\text{-}NH_3$ in the collected feed and permeate samples. For biomass monitoring, samples of the mixed liquor were collected for analysis of volatile suspended solids (VSS). The specific ammonium removal rate (SAAR) was calculated by dividing the mass of $N\text{-}NH_3$ removed on the day with the biomass present in the reactor.

For the investigation of membrane fouling, hydraulic permeability, filtration resistance, and quantification of soluble microbial products (SMP) and extracellular polymeric substances (EPS) were evaluated. For the evaluation of the filtration resistance the series resistance model was used (LEE et al., 2003). SMP and EPS were determined using the method described by Morgan et al. (1990). The SMP and EPS samples obtained were analyzed according to the protein and COD parameters.

2.2.3 Ammonia removal/recovery through air-stripping/absorption processes

The air-stripping and absorption processes were used for ammonia removal and recovery, varying the operational parameters pH and temperature. Ammonia-stripping was performed in a PVC tank (effective height = 31.5 cm, internal diameter = 29 cm, total volume = 20 L), operated on a bench-scale and in a batch mode. The system consisted of a heater, a fine bubble aerator plate (diameter = 25 cm), a rotameter for air, a needle valve and an air compressor. The gas from the ammonia-stripping tank was continuously conducted to two sealed PVC gas scrubbers. Two gas scrubbers were used in series in order to ensure that all the ammonia carried by the carrier gas was recovered in the acid solution. The carrier gas, after being bubbled in the gas scrubbers in series, was released into the atmosphere. The schematic diagram is shown in Figure 2.1.

Figure 2.1 - Schematic diagram of the AS/AB system.



The operational conditions of the AS/AB system were based on the work developed by Magalhães (2014), which are shown in Table 2.3. For each operational condition, two samples with different concentrations of $N\text{-}NH_3$ corresponding to raw leachate (tests 1 and 2) and permeate from MBRy (tests 3 and 4) were evaluated.

Table 2.3 - Operational conditions of AS/AB tests.

Test	pH	Temperature (°C)	$N\text{-}NH_3$ initial concentration (mg L^{-1})
1	8	60	1,910
2	10	30	1,968
3	8	60	880
4	10	30	870

The leachate pH adjustment was performed with hydrated lime. The AS system was fed with 9 L of raw leachate (tests 1 and 2) and permeate (tests 3 and 4), and submitted to aeration for 9 hours, with air flow rate of 4.32 L min^{-1} $L^{-1}_{leachate}$. In the absorption process, 6 L of 0.1 M sulfuric acid solution were added to each gas scrubber tank, and an air flow of 6.48 L min^{-1} $L^{-1}_{absorbent}$ was used. Therefore, the ratio between the volume of effluent and the volume of absorbent solution was 1.5. Samples were collected during the tests at the AS tank and evaluated in relation to pH and $N\text{-}NH_3$ concentration. After the ammonia-rich gas stream passed through the gas scrubbers, the acid solution was analyzed for $N\text{-}NH_3$ concentration.

The ammonia removal and absorption efficiencies were calculated according to Equations 2.1 and 2.2, respectively:

$$N - NH_{3(removal)}(\%) = \frac{N - NH_{3(initial)} - N - NH_{3(final)}}{N - NH_{3(initial)}} \cdot 100 \qquad (2.1)$$

$$N - NH_{3(absorption)}(\%) = \frac{N - NH_{3(absorption)}(g)}{N - NH_{3(stripped)}(g)} \cdot 100 \qquad (2.2)$$

It is worth mentioning that in the calculation of the absorbed ammonia only the first gas scrubber was considered, since the final ammonia concentration (% w/w) in the acid solution of the second scrubber was less than 0.5%.

In addition, the mass transfer coefficient was determined according to Quan et al. (2009), as well as the ammonia removal reaction rate (Equation 2.3) for each operational condition in AS process.

$$\ln[C] = -k \cdot t \qquad (2.3)$$

where C is the ammonia concentration at time t (h), and k is the constant of the ammonia removal rate (h^{-1}). The first order kinetic model is represented by plotting the graph $\mathbf{ln}[\boldsymbol{N}-\boldsymbol{NH_3}]$ *versus* **time,** in which the reaction rate is given by the slope of the line obtained.

2.2.4 Analytical methods

The parameters electrical conductivity (EC) (2510-B - Hach 44600), color (2120-B – Hach 2100AN), turbidity (2130-B - turbidimeter Hach 2100AN), COD (5220–D), ammonia nitrogen (4500-NH_3-B, 4500-NH_3-C), sulfate (4500-SO_4^{2-}-D), chloride (4500-Cl^--B), alkalinity (2320-B), pH (4500-B - Digimed DM-22), and solids series (2510-B; 2540-B, 2540-C) were analyzed according to Standard Methods for the Examination of Water and Wastewater (APHA, 2017). The parameters total organic carbon (TOC) and total nitrogen (TN) were analyzed in the Shimadzu TOC-V equipped with CNP, and Shimadzu TNM-1, respectively. The ions concentration was determined by ion chromatography (4110 - Dionex ICS-1000 ion chromatography, equipped with column type IonPac AS22 and IonPac CS12A). Proteins were analyzed according to the method of Lowry et al. (1951) and HS were analyzed according to the method of Lowry et al. (1951) modified by Frolund et al. (1995).

The acute toxicity test was performed with the marine luminescent bacterium Aliivibrio fischeri, using the MICROTOX® equipment model 500 Analyzer. The tests were performed in accordance with the ABNT NBR 15411-3 standard and following the protocol established by the software (MICROTOX® Omni Software, version 4.1). Acute toxicity was expressed as Median Effective Concentration (EC_{50}), representing the effective concentration of the toxic agent responsible for the adverse effects in 50% of observed individuals determined from the measurement of the bacterium luminescence in a maximum time of 30 minutes.

2.2.5 Economic analysis

The cost estimate was based on the results obtained from AS/AB tests, extrapolated to a real system with leachate flow rate of 20 $m^3\ h^{-1}$. The costs were represented by capital expenditure (CapEX), operational expenditure (OpEX) and total cost (TC) normalized per unit of volume of leachate treated. Some considerations were made for the preliminary estimation of the process costs:

a) In the calculation of CapEX was considered the implementation of tanks, pumps, aeration system, heating system, civil construction, instrumentation, engineering and project management, with leachate flow rate of 20 $m^3 h^{-1}$;
b) The residual heat of the raw leachate of 42 °C measured in an equalization tank (LANGE et al., 2006) was considered in test 1 in calculating the cost of heating the effluent;
c) The treatment cost with only one gas scrubber was considered, considering that most of the ammonia is recovered in the first scrubber; and
d) The treatment plant would operate 365 days a year and would be out of operation only during periods of routine maintenance, chemical cleaning and integrity tests.

For the OpEX calculation were considered the energy costs (aeration, pumps and wastewater heating), chemicals (lime and sulfuric acid), water, labor (one engineer and two technicians), and maintenance of the facilities (5% of CapEX). The total cost (Equation 2.4) includes the amortization (C_{am}), OpEX (C_{op}) and the annual volume treated. For the estimation of the C_{am} (Equation 2.5), the CapEX (C_{in}) was considered, the current national (Brazilian) investment rate (ir, 2% for November 2020) and a project time (ls) of 15 years.

$$TC(US\$/m^3) = \frac{C_{am} + C_{op}}{V_{total}} \tag{2.4}$$

$$C_{am} = C_{in}\left(\frac{ir}{1-(1+ir)^{-ls}}\right) \tag{2.5}$$

The revenue was obtained from the sale of ammonium sulfate obtained from recovered ammonia (US$ 0.63 kg^{-1} of ammonium sulfate, with 21% $N\text{-}NH_3$, Brazilian fertilizer brand Agroadubo), and the environmental valuation was considered when the ammonia was removed more than required by legislation. In this case, a valuation of US$ 9.59 kg^{-1} was considered (MOLINOS-SENANTE et al., 2010). This value was obtained through the shadow prices valuation methodology approached by these authors, which was calculated with the objective of valuing the gain with the non-disposal in the environment of pollutants such as organic matter, phosphorus, and nitrogen existing in the effluents.

2.2.6 Statistical analysis

The existence of differences between the parameters monitored in the two ranges (I and II) in the MBRy was investigated. The Mann-Whitney U test was used for two independent samples, checking the significance difference by means of the hypothesis test. The existence of correlations between the parameters evaluated during the MBRy monitoring in the two ranges (I and II) was also evaluated. The Spearman correlation coefficient (R) was used with further correlation significance analysis by means of the hypothesis test. All statistical analyses were performed using STATISTICA 10.0 software, at a significance level (α) of 5%.

2.3 Results and discussions

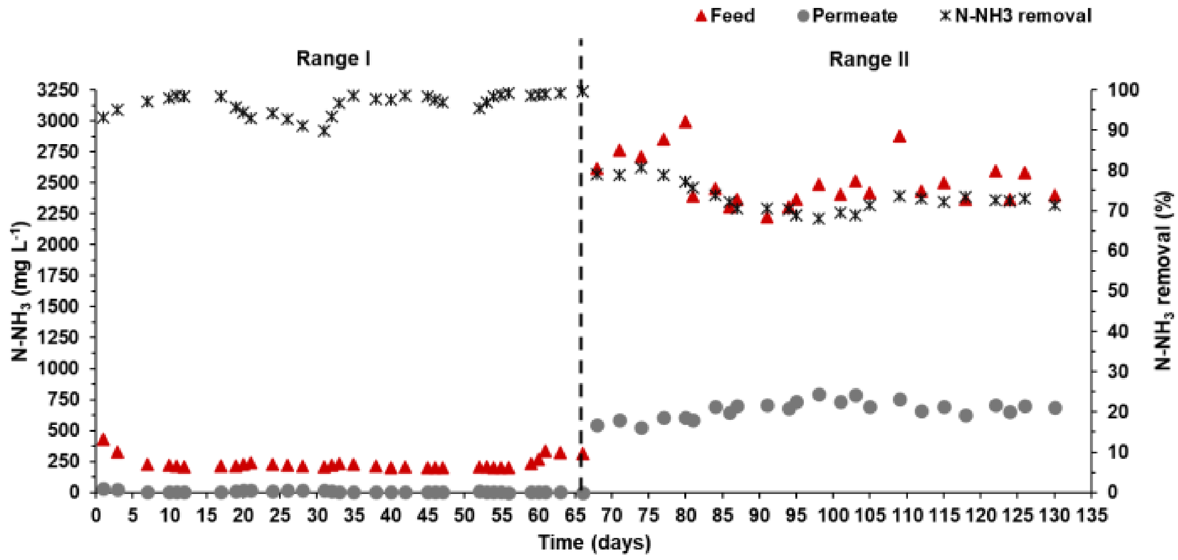
2.3.1 MBRy performance

2.3.1.1 Removal of N-NH_3 and organic matter

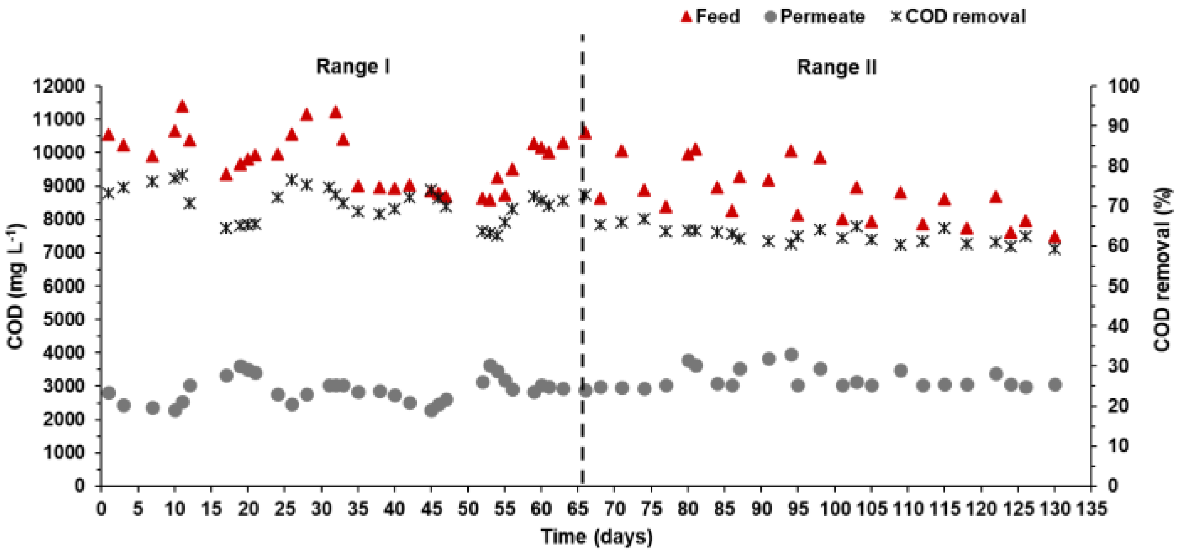
Figure 2.2 shows the N-NH_3 and COD concentrations in the feed and MBRy permeate and their removal efficiencies in both ranges (I and II). It is noted that the COD concentration in range I is higher (9,868 ± 895 mg L^{-1}) than in range II (8,732 ± 827 mg L^{-1}), where this increase may be associated with the evaporation of the liquid fraction present in the leachate during the AS process. The N-NH_3 concentration in the LFL might influence the removal efficiency of both N-NH_3 and COD in the MBRy. Spearman correlation test confirmed a negative correlation between N-NH_3 concentration in the feed and COD removal, with Spearman coefficient of -0.51, indicating that the higher the N-NH_3 concentration in the mixed liquor, lower COD removal efficiency by MBRy.

N-NH_3 removal was higher in range I (97 ± 3%) than in range II (73 ± 4%). The concentration of N-NH_3 in the permeate in range I (9 ± 7.5 mg L^{-1}) complied with the Brazilian legislation in relation to the discharge standard established for this wastewater (COPAM, 2008), differently from N-NH_3 concentration in range II permeate (671 ± 71 mg L^{-1}). According to Mann-Whitney U test, significant differences (p-value <0.05) were found for both COD and N-NH_3 concentration in the permeate in ranges I and II. The mass of COD removed by g mixed liquor volatile suspended solids (MLVSS) was 1.22 ± 0.44 for range I and 0.51 ± 0.07 for range II. For N-NH_3, the mass removed by g_{MLVSS} was 0.04 ± 0.02 for range I and 0.17 ± 0.02 for range II.

Figure 2.2 - MBRy performance in ranges I and II for a) N-NH_3 and b) COD.



(a)



(b)

According to the Mann-Whitney U test, significant differences were found between the mass of N-NH_3 removed by g_{MLVSS} in the two ranges, with the highest values being found for range II (0.17 ± 0.02). These results indicate that even in the highest concentrations of N-NH_3 in the feed, the microorganisms were able to remove the compound. Yeasts absorb nitrogen both in inorganic (ammonia, ammonium, nitrite and nitrate) and organic (amino acids, urea, vitamins, etc.) forms (DAN, 2001), with ammonia nitrogen being the nitrogen source most used by fungi generally (CARLILE et al., 2001). The same was observed for COD, where the significant highest values of COD mass removed by g_{MLVSS} were found in range I, showing that organic matter removal mechanisms were more sensitive in this scenario.

It is observed that *Saccharomyces cerevisiae* is a promising yeast in the wastewater treatment because, even at high concentrations of organic matter and N-NH_3, it was possible to achieve high removal efficiencies. Brito et al. (2013) found that inert COD for bacterial sludge was 13% higher than inert COD with yeast sludge in the LFL treatment.

The pH is an operational parameter that can influence the removal efficiency of the N-NH_3. According to Equation 2.6, ammonia (NH_3) is ionized in an aqueous media giving rise to the ammonium ion (NH_4^+):

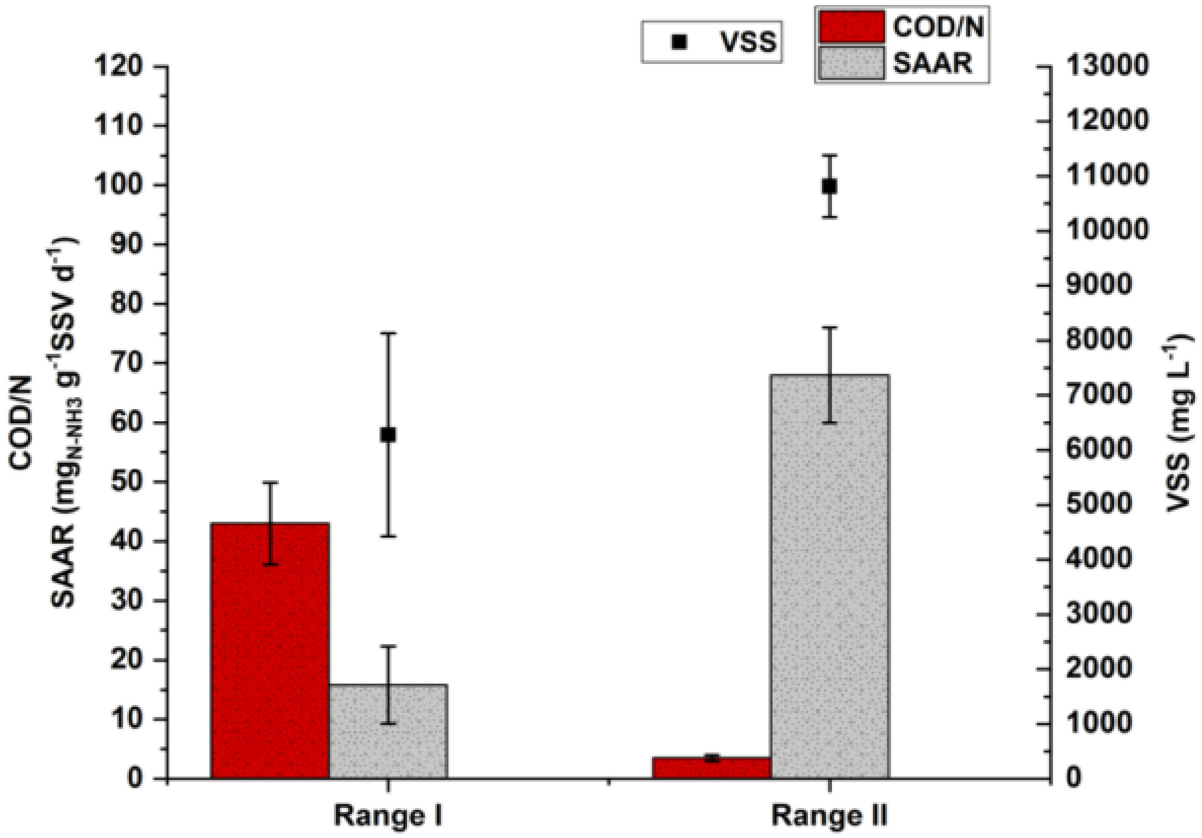
$$NH^+_{4(aq)} + OH^-_{(aq)} \leftrightarrow NH_{3(aq)} + H_2O \qquad (2.6)$$

The pH of the sludge in the MBRy in the range II was 8.89 ± 0.15, suggesting that even being in the form of NH_4^+, a fraction of the ammonia could be in the form of NH_3, since the pH of the sludge was close to the pH of NH_3 formation (>9.25) (BENJAMIN, 2002). Thus, it can be inferred that a portion of the N-NH_3 removal may have occurred by volatilization favored by the aeration in the sludge tank and by high sludge retention time. The pH of the sludge in the studies conducted by Reis et al. (2017), Amaral et al. (2018) and Brito et al. (2019) was about 3.5, suggesting that the ammonia removal by volatilization was negligible, leading to lower removal efficiencies.

As in the study conducted by Wichitsathian et al. (2004), an increase of 9% and 25% in COD and N-NH_3 removal efficiency was observed, respectively, in lower N-NH_3 concentrations in the MBRy. It is also important to note that even though the N-NH_3 removal in the MBRy was increased with the application of AS previously, the ammonia removal per g of MLVSS in the MBRy was greater in range II, reinforcing that there were no critical conditions of toxicity to yeast. Figure 2.3 shows the COD/N ratio, SAAR and VSS for ranges I and II.

According to Dan (2001), the demand for nutrients, represented by the C/N/P ratio, for yeasts is 100/4/1. Assuming that all carbon and nitrogen are in COD and N-NH_3 form, respectively, in range I the MBRy operated with a deficiency of about 160 mg L^{-1} of nitrogen. On the other hand, in range II the bioreactor operated with an excess of nitrogen of approximately 2,160 mgL^{-1}. This may justify the high $N\text{-}NH_3$ removal percentage in range I, because as the nutrient was a limiting factor for yeasts, they used practically all available nitrogen for their metabolism. Even with the nutrient deficiency in the mixed liquor, the performance of the MBRy, in terms of organic matter removal, was not affected, demonstrating that the yeasts are resistant and appropriate for the treatment of high organic load wastewater.

Figure 2.3 - COD/N, SAAR and VSS for ranges I and II.



It is important to note that the sludge tank receives constant aeration and that the sludge pH in range II is close to the value tested in AS (without pH adjustment and HRT of 48 hours). Thus, it can be inferred that besides the removal by biological mechanism, it can also be occurring the ammonia removal by AS in the MBRy. However, considering these two removal mechanisms, the $N\text{-}NH_3$ removal obtained in range II (73 ± 4%) was smaller than the removal obtained only in the AS process (92 ± 7%). A justification for this is due to the aeration flow of the sludge tank being lower (1.67 L min^{-1}) than the aeration flow of the AS tank (4 L min^{-1}), besides the physical property of the raw leachate, such as the viscosity, being distinct from the mixed liquor due to the presence of yeasts, which can make it difficult to release the gaseous ammonia into the air. Therefore, even if the SAAR was larger in range II (Figure 2.3), possibly an N-NH_3 fraction may have been removed by volatilization.

In range II, the excess nutrient may have favored the increase of microorganisms in the mixed liquor (Figure 2.3), since in this range the VSS concentration was higher (10,815 ± 566 mg L^{-1}) than in range I (6,278 ± 1,851 mg L^{-1}). Spearman correlation test confirmed a positive correlation between N-NH_3 concentration in the feed and VSS, with Spearman coefficients of 0.73, indicating that the higher the N-NH_3 concentration in the mixed liquor, the higher the VSS concentration. According to ter Schure et al. (2000), *Saccharomyces cerevisiae* has a higher growth rate in nitrogen sources such as asparagine, glutamine and N-NH_3. As the concentration of N-NH_3 was higher in range II, it can be inferred that *Saccharomyces cerevisiae* had a higher nitrogen source for its growth than in range I, explaining the higher VSS concentrations and higher N-NH_3 consumption in range II.

Taking into account that 30% of LFL COD is inert (BRITO et al., 2013) and the permeate concentrations in ranges I and II, it can be assumed that almost all biodegradable organic matter was removed by microorganisms, since the inert COD in ranges I and II was 2,961 ± 268 and 2,620 ± 248 mg L^{-1}, respectively. This suggests that the higher concentration of N-NH_3 in the feed in range II did not restrict the removal efficiency of COD by microorganisms. In addition, it is important to apply physico-chemical techniques as a polishing step of the MBRy to remove recalcitrant organic matter.

Feed and permeate leachate samples of ranges I and II were analyzed in relation to acute toxicity test (Table 2.4). The results of EC_{50} that present values lower or equal to 81.9% in 30 minutes are attributed toxic character to the sample. It is worth mentioning that the toxicity expressed decreased with the increase of the EC_{50} value.

Table 2.4 - EC_{50} of feed and permeate in ranges I and II.

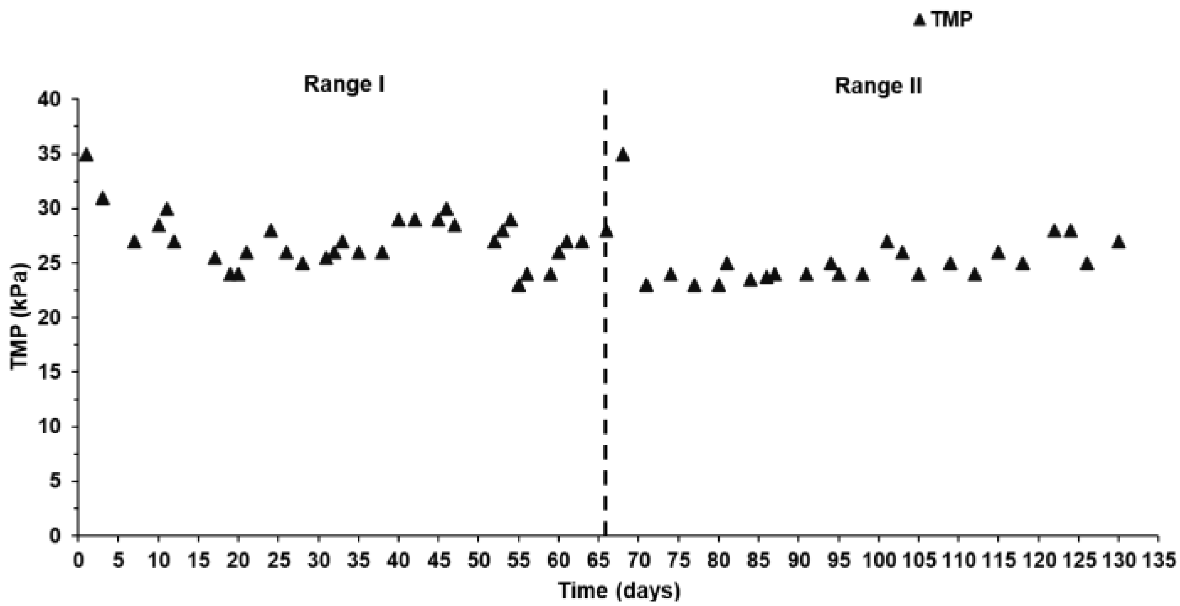
Ranges	Feed (%)	Permeate (%)
I	16.38 ± 7.68	65.85 ± 18.42
II	10.73 ± 1.56	34.01 ± 7.83

EC_{50} in feed was 16.4 ± 7.68% and 10.7 ± 1.6% in ranges I and II, respectively. Range II showed higher toxicity due to higher ammonia concentration in the mixed liquor. Reis et al. (2017) verified that high ammonia concentration in the media has contributed to LFL toxicity. A significant difference was found between the acute toxicity of feed in both ranges. In addition, a negative correlation between EC_{50} and N-NH_3 concentration in feed was verified through the Spearman correlation test, with a coefficient of -0.5. There was also a significant difference between permeate toxicity in ranges I and II, which showed values of 65.9 ± 18.4% and 34.0 ± 7.8%, respectively. The permeate toxicity was higher in range II since the concentration of NNH_3 in the permeate was higher, as seen in Figure 2.2.

2.3.1.2 Membrane fouling

Since the MBRy was operated with constant permeate flow (2.1 L h^{-1} m^{-2}), the transmembrane pressure (TMP) was directly related to membrane fouling. TMP for ranges I and II are found in Figure 2.4.

Figure 2.4 - TMP for ranges I and II.



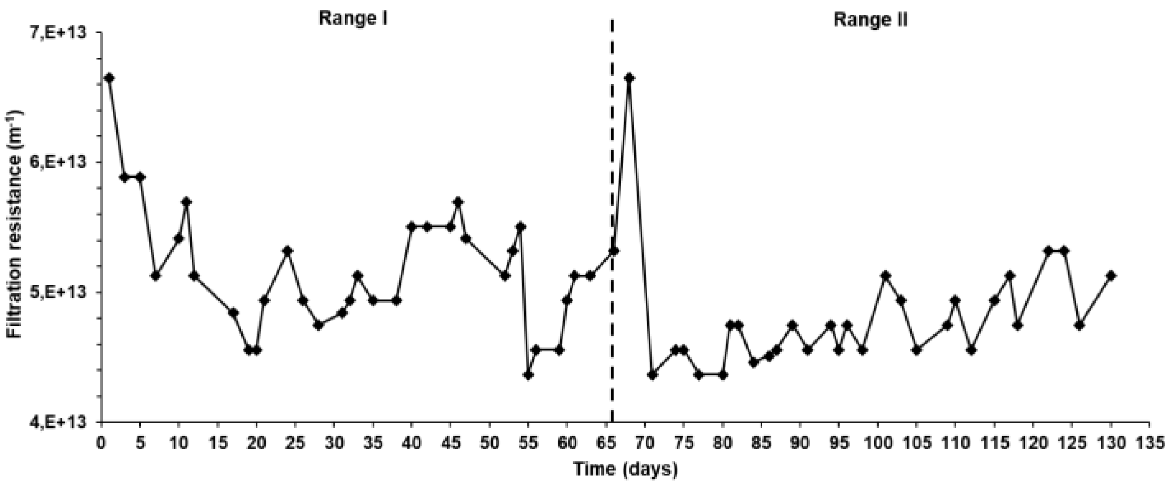
The transmembrane pressure in range II (25 ± 1.5 kPa) was lower than in range I (27.3 ± 2.5 kPa). No significant difference was found in the TMP for the two ranges according to the Mann-Whitney U test (p-value > 0.05). Also, the fouling resistance was lower in range II, demonstrating that in range I the membrane fouling was higher (Table 2.5). It is important to emphasize that the chemical cleaning of the membrane was performed weekly. Although no significant difference was found in the membrane resistances, a significant difference was found for the fouling resistances in ranges I and II.

Table 2.5 - Membrane and fouling resistances for the ranges I and II.

Resistance (m^{-1})	Range	
	I	II
Membrane	$4.27 \times 10^{12} \pm 1.56 \times 10^{12}$	$5.06 \times 10^{12} \pm 1.10 \times 10^{12}$
Fouling	$5.02 \times 10^{13} \pm 2.36 \times 10^{12}$	$4.18 \times 10^{13} \times 1.90 \times 10^{12}$

Figure 2.5 shows the filtration resistance performance in ranges I and II. Gradual increases in filtration resistance were observed, with the highest peaks being observed in range I, which can be justified by the higher membrane fouling. Furthermore, it is observed that the chemical cleaning was effective in terms of membrane permeability recovery.

Figure 2.5 - Filtration resistance in the ranges I and II.



There is no agreement in the literature about the influence of VSS concentration in the mixed liquor on membrane fouling. The most important factor to be considered are the characteristics of the sludge, not its concentration. According to Iorhemen et al. (2016), the increase of suspended solids in the bioreactor is associated with the increase of membrane fouling. However, in the present study the fouling was lower in range II, which had a higher VSS concentration when compared to the VSS concentration in range I. In some instances, a higher concentration of VSS promotes a rapid cake formation on the membrane surface, preventing fouling by pore blockage or adsorption on the membrane surface. In this case, a higher VSS concentration would be benefic for the membrane performance.

The higher membrane fouling in range I can also be justified by the nitrogen deficiency in the mixed liquor. Guo et al. (2000) reported that *Saccharomyces cerevisiae* carries five adhesive genes, four of which are responsible for cell-cell adhesion, and one gene (FLO11) responsible for yeast adhesion to a substrate. The adhesion genes are activated by diverse environmental triggers, one of them being the deficiency of nitrogen (VERSTREPEN et al., 2003). Nitrogen starvation allows the activation of the FLO11 gene, causing fungi to adhere and penetrate the substrates in an effort to search for new nutrients (GAGIANO et al., 2002). Moreover, according to the same authors, the abundance of carbon source can also activate the FLO11 gene. Thus, due to the higher carbon concentration and lower nitrogen concentration in range I, *Saccharomyces cerevisiae*, as a response to these factors, may have activated this gene. Consequently, they adhered to the membrane surface and provided higher membrane fouling. The Spearman test indicated a significant negative correlation between $N\text{-}NH_3$ feed and TMP, with the R coefficient of -0.4, i.e., lower concentration of $N\text{-}NH_3$ in the feed is related to increased TMP.

Table 2.6 presents the production of SMP and EPS, according to COD, for ranges I and II. According to Mann-Whitney U test, there was a significant difference between the production of SMP-COD between the two ranges evaluated (p-value <0.05). However, there was no significant difference in EPS-COD production. Although SMP-COD production was higher in range II, fouling and filtration resistance was higher in range I. Thus, the potential release of the FLO11 gene by *Saccharomyces cerevisiae*, due to the low nitrogen concentration in the mixed liquor, may have caused a greater effect on membrane fouling than the SMP and EPS concentration.

Table 2.6 - SMP and EPS (COD) production for the ranges I and II.

Ranges	**SMP-COD ($mg\ L^{-1}$)**	**EPS-COD ($mg\ L^{-1}$)**	**SMP-COD/VSS ($g\ g^{-1}$)**	**EPS-COD/VSS ($g\ g^{-1}$)**
I	21,602.82 ± 2,542.64	850.00 ± 259.52	3.64 ± 0.73	0.14 ± 0.02
II	24,146.35 ± 547.85	992.18 ± 27.61	2.24 ± 0.11	0.09 ± 0.01

The highest production of SMP-COD and EPS-COD in range II may be related to the low COD/N ratio. According to Table 2.5, the higher SMP concentration in range II may be associated with higher VSS concentration in this range, since these compounds are associated with microorganism metabolism. This is reinforced by the lower ratio between SMP production and VSS concentration in the mixed liquor in range II. The ratio between EPS production and VSS concentration in the mixed liquor was higher in range I, indicating higher EPS release in this range, reinforcing the higher membrane fouling. The higher EPS release in the media is associated with the cellular lysis of microorganisms.

The protein concentration in the SMP and EPS fractions (SMP-P and EPS-P) was higher in range II (4,186 ± 79.39 mg L^{-1}), compared to range I (4,089 ± 28.53 mg L^{-1}). The EPS-P production in range I and II was 695.85 ± 387.85 mg L^{-1} and 1,272.15 ± 48.94 mg L^{-1} respectively. A significant difference was found between SMP-P and EPS-P concentrations in ranges I and II (p-value <0.05). The ratio between SMP-P and VSS for ranges I and II was 0.71 ± 0.20 g g^{-1} and 0.39 ± 0.02 g g^{-1}, respectively. The ratio between EPS-P and VSS found was 0.10 ± 0.03 g g^{-1} and 0.12 ± 0.01 g g^{-1} for ranges I and II, respectively. Although the EPS-P/VSS ratio was higher in range II, which had lower fouling, it is important to note that the SMPP/VSS ratio is considerably higher in range I, which may have had greater influence on membrane fouling.

For systems that operate with high sludge age and low F/M ratio, the protein concentration is high due to cell lysis (LEE et al., 2003), as seen in range II (F/M ratio of 0.32 ± 0.04). According to Yigit et al. (2008), the increase in EPS-P concentration was accompanied by an increase in VSS concentration, corroborating the results of the present study, since both the highest concentration of EPS-P and VSS was observed in range II. According to the Spearman correlation test, positive correlation was found both between SMP-P and VSS and between EPS-P and VSS, both with a coefficient of 0.8. Also, the results found by Hao et al. (2016) support the results found in this research, which verified that the production of SMP-P and EPSP was higher in lower COD/N ratios. A positive correlation was found between SMP-P and EPS-P with the N-NH_3 concentration in the feed, both with R coefficients of 0.6.

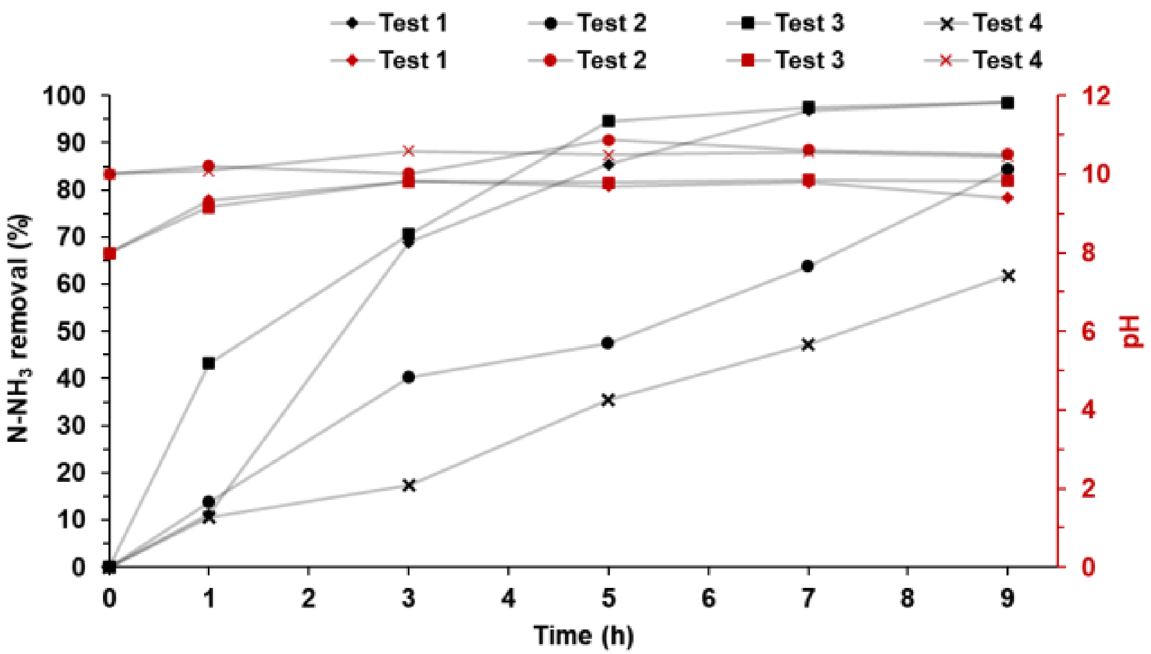
2.3.2 Ammonia removal/recovery in the landfill leachate through airstripping/absorption processes

According to the results presented in the discussion of the MBRy performance, an additional step for the N-NH_3 removal is necessary, being this step integrated as pre-treatment of the effluent, that is, before the MBRy, or as post-treatment for the effluent polishing after the biological treatment. The integration as pre- or post-treatment depends mainly on the technical and economic feasibility of the ammonia recovery present in the leachate. If this recovery is viable economically, the AS should be considered as pre-treatment, reducing the concentration of N-NH_3 in the effluent that will be fed into the MBRy. However, if there is no economic feasibility, the integration of ammonia removal as post-treatment should be considered, since a considerable portion of this compound will be removed during the biological process. As observed in the previous item, the removal efficiency of this compound was higher than 70% in range II, which was operated in the highest concentrations of N-NH_3 in the LFL. This will reduce the ammonia concentration to be removed by AS and consequently reduce the posttreatment process cost. It is noteworthy that the oxygen supply in an MBRy is superior to the biological demand, since aeration also acts as membrane fouling control. Therefore, the MBRy operation, even in higher concentrations of N-NH_3 in the LFL will not imply in the reduction of oxygen that will be destined to the process.

Since the removal of N-NH_3 using AS depends on parameters such as pH, temperature and initial concentration of N-NH_3, four tests were performed evaluating these operational parameters. Tests 1 and 2 were performed using raw leachate (higher N-NH_3 concentration), and tests 3 and 4 using MBRy permeate (lower N-NH_3 concentration). Figure 2.6 shows the N-NH_3 removal for the tests performed.

It is observed that, independent of the initial N-NH_3 concentration, the highest removals were achieved in tests 1 and 3 (99%), at pH 8 and temperature of 60°C. These results are similar to the results found by Ata et al. (2017), where ammonia removals above 99% were identified at temperatures above 50°C. In contrast, in tests 2 and 4, which were performed at pH 10 and temperature of 30°C, the initial ammonia concentration in the LFL influenced its removal, which was higher in test 2. El-Gohary et al. (2016) found ammonia removal of approximately 80% in 9 hours of leachate testing using AS at pH 10 with an initial concentration of 5,208 mg L^{-1}. This result is similar to the one found in the present study, since the ammonia removal found in test 2 was 84% at pH 10, with a higher initial N-NH_3 concentration.

Figure 2.6 - N-NH_3 removal and pH values in tests 1, 2, 3 and 4 for 9 hours (4.32 L min^{-1} $L^{-1}_{leachate}$).



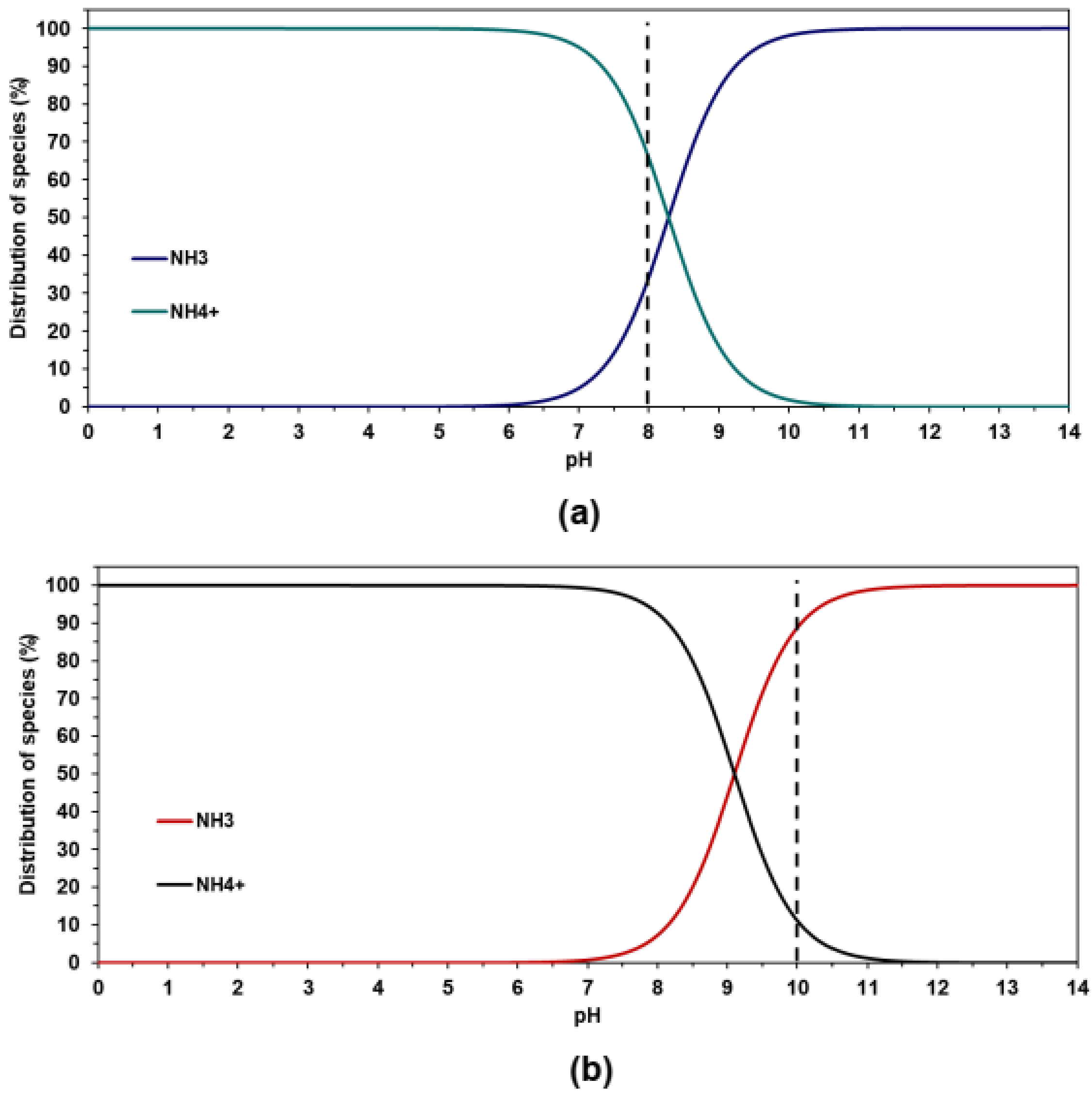
Note:
Test 1 - pH = 8, temperature = 60°C, N-NH_3 concentration = 1,910 mg L^{-1}, raw leachate.
Test 2 - pH = 10, temperature = 30°C, N-NH_3 concentration = 1,968 mg L^{-1}, raw leachate.
Test 3 - pH = 8, temperature = 60°C, N-NH_3 concentration = 880 mg L^{-1}, MBRy permeate.
Test 4 - pH = 10, temperature = 30°C, N-NH_3 concentration = 870 mg L^{-1}, MBRy permeate.

According to Değermenci et al. (2012), the increase in ammonia removal due to its higher initial concentration may be due to the increased driving force required for ammonia mass transfer. In addition, the pH increase was evidenced throughout the tests (Figure 2.6), probably due to the removal of carbon dioxide (CO_2) before the equilibrium conditions were reached (COTMAN and GOTVAJN, 2010). It is important to note that out of the four tests performed, only test 3 was in accordance with the discharge limit of 20 mg L^{-1} for N-NH_3 at the end of the test (COPAM, 2008), presenting a final concentration of 13 mg L^{-1}.

Although the percentage of NH_3 at pH 10 and temperature of 30°C is higher (88.92%) (Figure 2.7), the highest ammonia removals occurred at pH 8 and temperature of 60°C, where the NH_3 percentage is 34.19%. Furthermore, it is observed that after 3 hours from the beginning of tests 1 and 3, the removal was approximately 70%, while the ammonia removals in tests 2 and 4 for the same time were 40 and 17%, respectively.

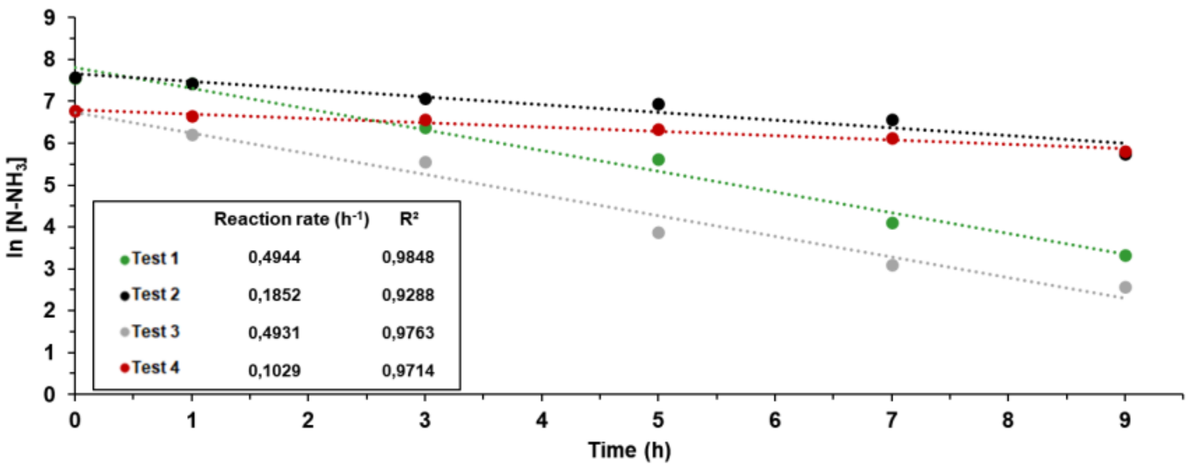
Thus, from the results obtained, it can be inferred that the temperature had a higher influence on the N-NH_3 removal than the pH. The higher removal of N-NH_3 at higher temperatures can be justified by considering the Henry constants for NH_3 at temperatures of 30 and 60°C: 1.68 and 4.44 atm, respectively. The higher the Henry constant, the higher the release of the gas from liquid (METCALF and EDDY, 2003). This may have favored the AS process, promoting higher ammonia removals and in a shorter time. Campos et al. (2013) found that regardless of the leachate pH (8.3, 9.5 and 11.0) in the AS process, the temperature of 60°C was also the one that promoted the highest ammonia removals (above 95% in 7-hours test).

Figure 2.7 - Distribution of NH_3 and NH_4^+ species as a function of pH at a) 60°C and b) 30°C.



The reaction kinetic was evaluated for the four tests performed. According to Figure 2.8, the highest reaction rates were found for tests 1 and 3, which confirmed that the highest temperature was the determining factor in the $N\text{-}NH_3$ removal in the LFL. El-Gohary et al. (2013) found that the reaction rate for the raw leachate (0.210 h^{-1}) (initial concentration of $N\text{-}NH_3$ of 5,572 mg L^{-1}) was higher than for the diluted leachate (0.109 h^{-1}) (initial concentration of $N\text{-}NH_3$ of 2,800 mg L^{-1}). This demonstrates that the higher initial ammonia concentration promoted the higher removal. However, in this study, the initial ammonia concentration was not a factor that influenced its removal, because the reaction rates for tests 1 (initial $N\text{-}NH_3$ concentration of 1,910 mg L^{-1}) and 3 (initial $N\text{-}NH_3$ concentration of 880 mg L^{-1}) were 0.4944 h^{-1} and 0.4931 h^{-1}, respectively. Furthermore, corroborating the studies of Jurczyk et al. (2020), Hossini et al. (2016), and El-Gohary et al. (2013), the ammonia removal using the AS process followed a first-order kinetics. Liu et al. (2015) found a reaction rate of 0.493 h^{-1} at the ammonia removal in urine, a temperature of 60°C and pH 10, similar to that found in test 1. However, it is important to note that the same reaction rate was achieved without the requirement of the leachate pH correction.

Figure 2.8 - Reaction rate for tests 1, 2, 3 and 4 for 9 hours (4.32 L min^{-1} $L^{-1}_{leachate}$).



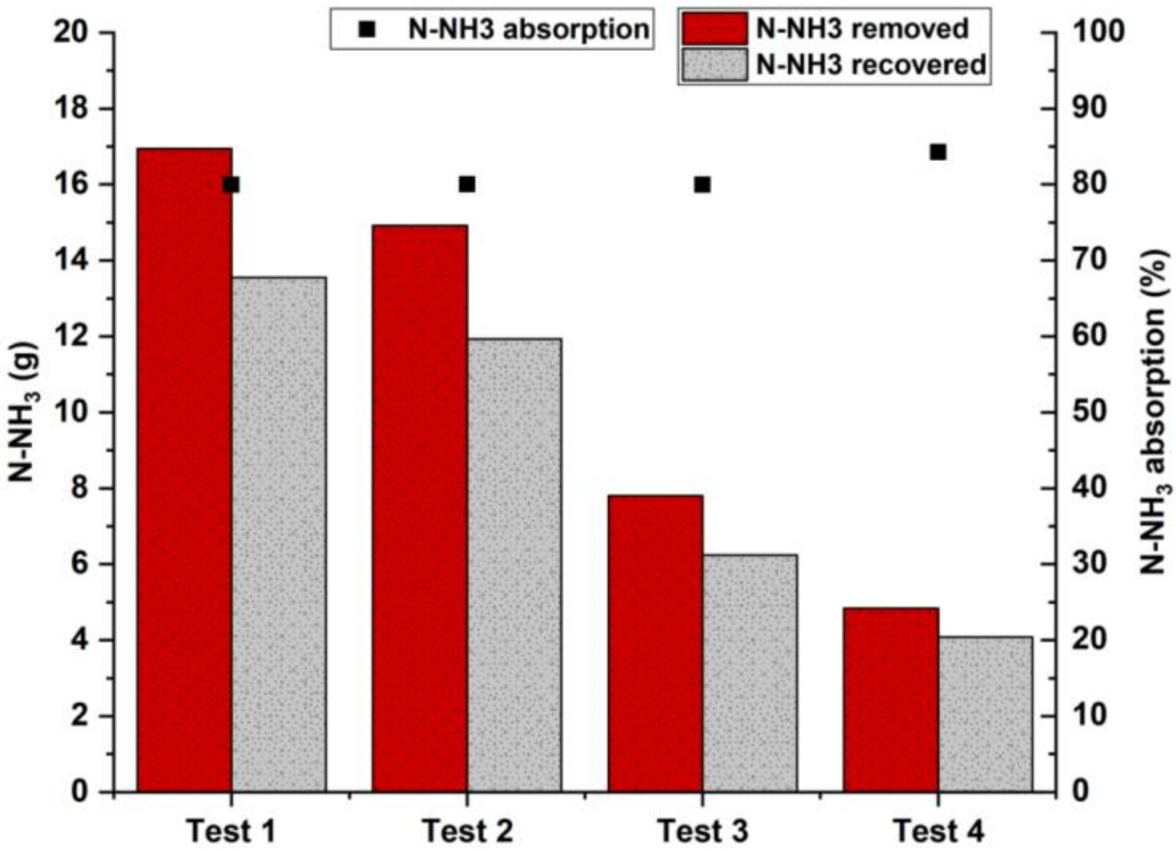
The mass transfer coefficient (K_a) for tests 1, 2, 3 and 4 were 6.74, 2.52, 6.72 and 1.40 cm h^{-1}, respectively. As well as the reaction rate, the mass transfer coefficient for tests 1 and 3 were higher. The temperature increase causes the viscosity and surface tension of the liquid phase to decrease, in addition to the increase of ammonia diffusion coefficients and heat transfer rates in the gaseous and liquid phases (LI et al., 2020). Additionally, both the ammonia removal efficiency and the mass transfer coefficient increased with the temperature rise using AS, according to the study conducted by Quan et al. (2009). Considering that the ammonia distribution in the liquid and gas phase is pH and temperature dependent, Quan et al. (2009) showed that the mass transfer coefficient increases widely at high temperatures accompanied by a sufficiently high pH (such as 11).

However, according to the results obtained in this study, a high pH was not necessary to achieve high ammonia removals. This shows that the addition of alkalinizing agents to correct the pH in the leachate was not necessary in the AS process, and that only the increase in the wastewater temperature was sufficient. In addition, it is important to note that leachate can be generated at higher temperatures due to temperature variation in the waste mass. Lange et al. (2006) verified that the leachate temperature collected from the equalization tank was 42 °C. In this way, the residual heat from the leachate can be used in the process and consequently reduce costs. These results demonstrate the benefit from the economic point of view of the process. The ammonia removed by AS was recovered through chemical absorption in the sulfuric acid solution (H_2SO_4) forming ammonium sulfate ($(NH_4)_2SO_4$), a nitrogen-based fertilizer (Equation 2.7).

$$2NH_{3\,(gas)} + H_2SO_{4\,(liquid)} \leftrightarrow (NH_4)_2SO_{4\,(liquid)} \qquad (2.7)$$

According to Figure 2.9 it is observed that both the removal and recovery of N-NH_3, in mass, were higher in tests 1 and 2 because they were performed with an initial concentration of N-NH_3 higher than the other tests. However, taking into account only the operational parameters pH and temperature, the highest removals and recoveries were verified in tests with high leachate temperature (tests 1 and 3). In addition, although the values of removal and recovery were different, the rate of ammonia absorbed in the acid solution was similar for the 4 tests, being approximately 80%. Since the concentration of H_2SO_4 solution was the same for all tests (0.1 M), it was in excess for all tests to ensure maximum ammonia recovery. However, the recovery was not complete, and may be due to ammonia volatilization during pH adjustment (tests 2 and 4), ammonia loss due to applied air flow (all tests), and by the ammonia absorption by condensed water inside the AS tank before NH_3 reached the absorption tank (tests 1 and 3) (LIU et al., 2015).

Figure 2.9 - Removal and recovery of N-NH_3, in mass, for tests 1, 2, 3 and 4 in 9 hours (4.32 L min^{-1} $L^{-1}_{leachate}$).



Ferraz et al. (2013) recovered 80% N-NH_3 from LFL in a 0.4 mol L^{-1} H_2SO_4 solution in 12 days for an initial N-NH_3 concentration of 1,966.5 ± 19 mg L^{-1}. In the current study, considering the tests with initial N-NH_3 concentrations similar to those of these authors (tests 1 and 2), it was possible to achieve the same recovery rate in a 9-hours test using a lower H_2SO_4 concentration, representing an economic advantage.

The final concentration of N-NH_3 in ammonium sulfate solution for tests 1, 2, 3 and 4 was 23.02, 20.28, 10.60 and 6.93% w/w, respectively. Although the N-NH_3 absorption in the acid solution was high for all the tests, only in tests 1 and 2 it was attended the percentage of nitrogen in the N-NH_3 form (20-21%) practiced on the market for ammonium sulphate. In this case, it can be inferred that the higher initial concentration of N-NH_3 in the leachate was of paramount importance to promote higher percentages of ammonia mass in the ammonium sulfate solution. From a technical point of view, the application of AS as pre-treatment, which consists in the use of raw leachate (tests 1 and 2), presents some advantages in terms of higher concentration of N-NH_3 in the effluent, besides the utilization of the leachate residual heat. However, these benefits will only be important if the N-NH_3 recovery is economically viable.

2.3.2.1 Air-stripping/absorption processes as pre- or post-treatment: Preliminary economic analysis

In order to evaluate the feasibility of the application of the AS/AB process as pre- or posttreatment of MBRy a preliminary economic analysis was performed. Regarding costs, both CapEX and OpEX of the four tests were estimated, considering a leachate flow of 20 m^3 h^{-1}, i.e., annual volume of 175,200 m^3 of leachate. Table 2.7 shows the characteristics of the AS/AB system considered for the calculation, as well as the CapEX for all tests.

As the pH of the raw leachate is approximately 8 (Table 2.2), it was necessary to adjust the pH to 10 only for tests 2 and 4, corresponding to the additional costs with hydrated lime. On the other hand, the energy requirement is higher for tests 1 and 3 since the operating temperature is higher (60°C) compared to tests 2 and 4 (30°C). However, it is worth noting that the residual heat of the raw leachate was considered in test 1 (42°C), resulting in a lower energy cost than in test 3. For tests 2 and 4 it was not necessary to heat the effluent, justifying lower energy cost. In addition, the cooling cost for this condition was not considered, since the use of an equalization tank can help in temperature control. The amount of water and acid required is the same since the acid solution concentration is similar (0.1 M) for all tests, making these costs similar.

Of all the utility costs considered in the OpEX calculation, the energy cost was the main contributor in tests 1 and 3 (Figure 2.10), due to effluent heating. In test 3 the cost for heating corresponds to approximately 68% of the energy cost (Figure 2.11), demonstrating that consideration of the residual heat of raw leachate is an alternative for reducing process costs. It should be noted that in addition to the LFL heating, the energy cost for the aeration system of both air-stripping and absorption was also considerable. Regarding the cost with chemicals, tests 2 and 4 had higher expenses, corresponding to 28% of OpEX, since in these tests lime is used for pH adjustment. However, the cost for heating the effluent in tests 1 and 3 corresponds to 36.7 and 53% of OpEX, respectively. Dos Santos et al. (2020) found that the operating cost of

AS is high due to electricity consumption, and that the use of sulfuric acid in the absorber also conferred high cost in the LFL treatment process.

Figure 2.10 - Operating expenses and total costs for tests 1, 2, 3 and 4.

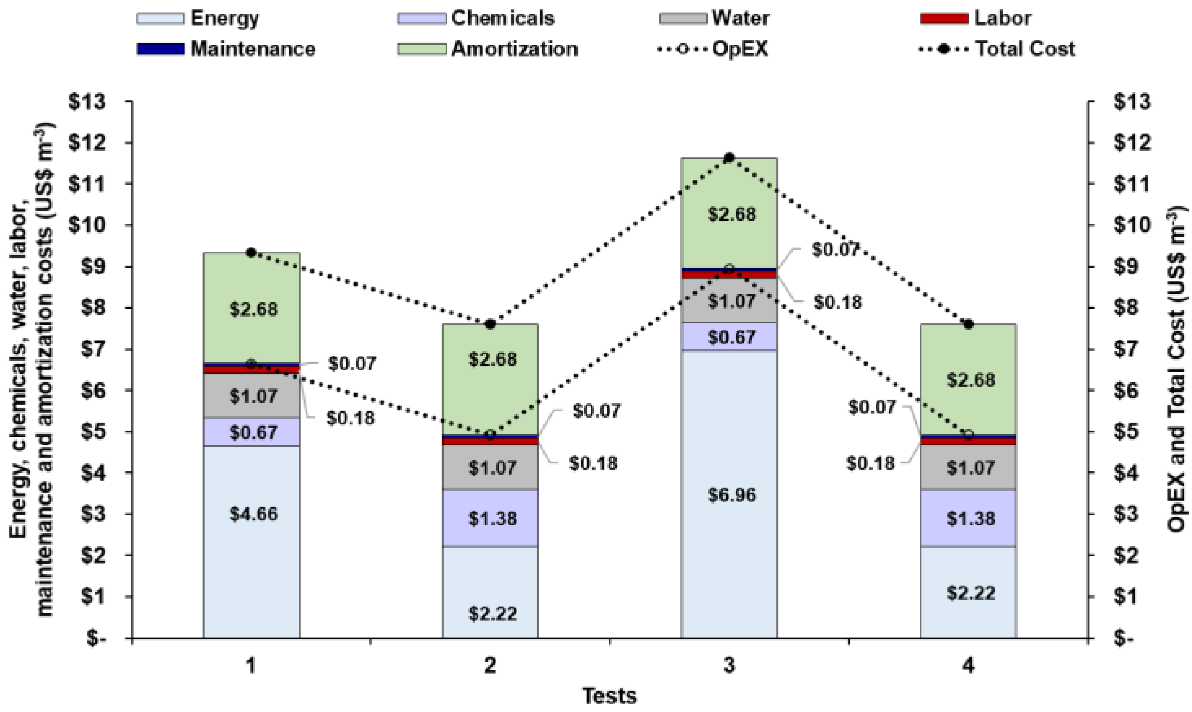


Figure 2.11 - Energy costs (thermal and others).

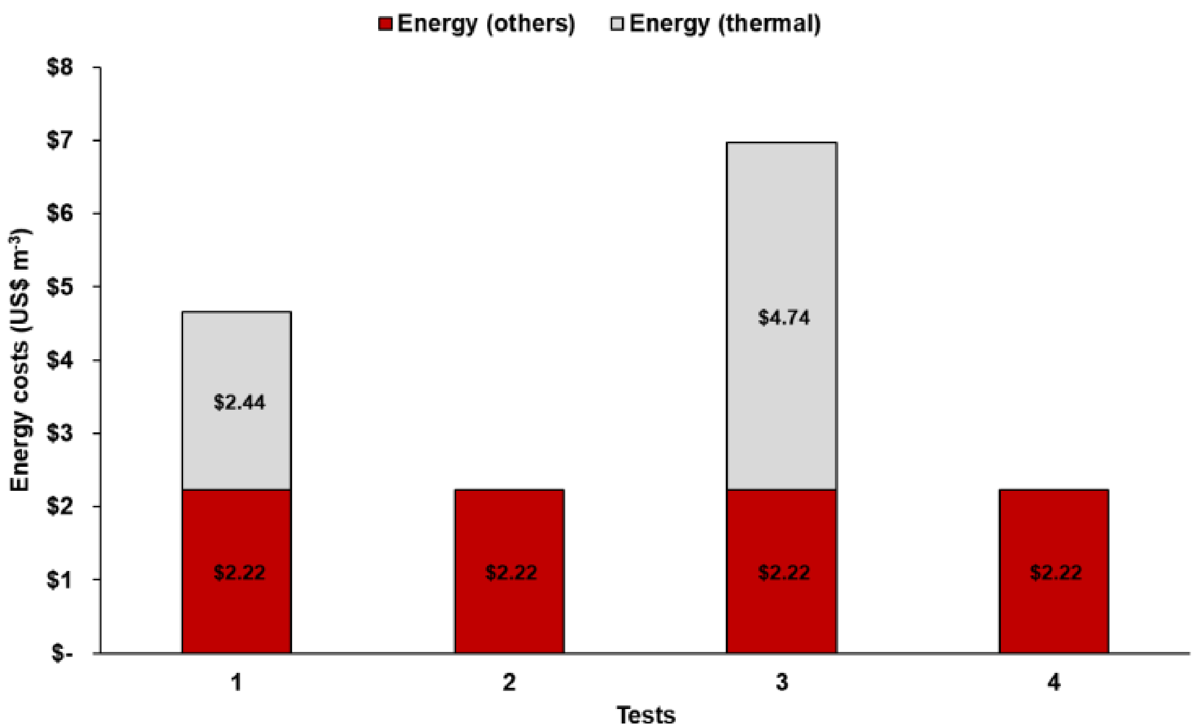
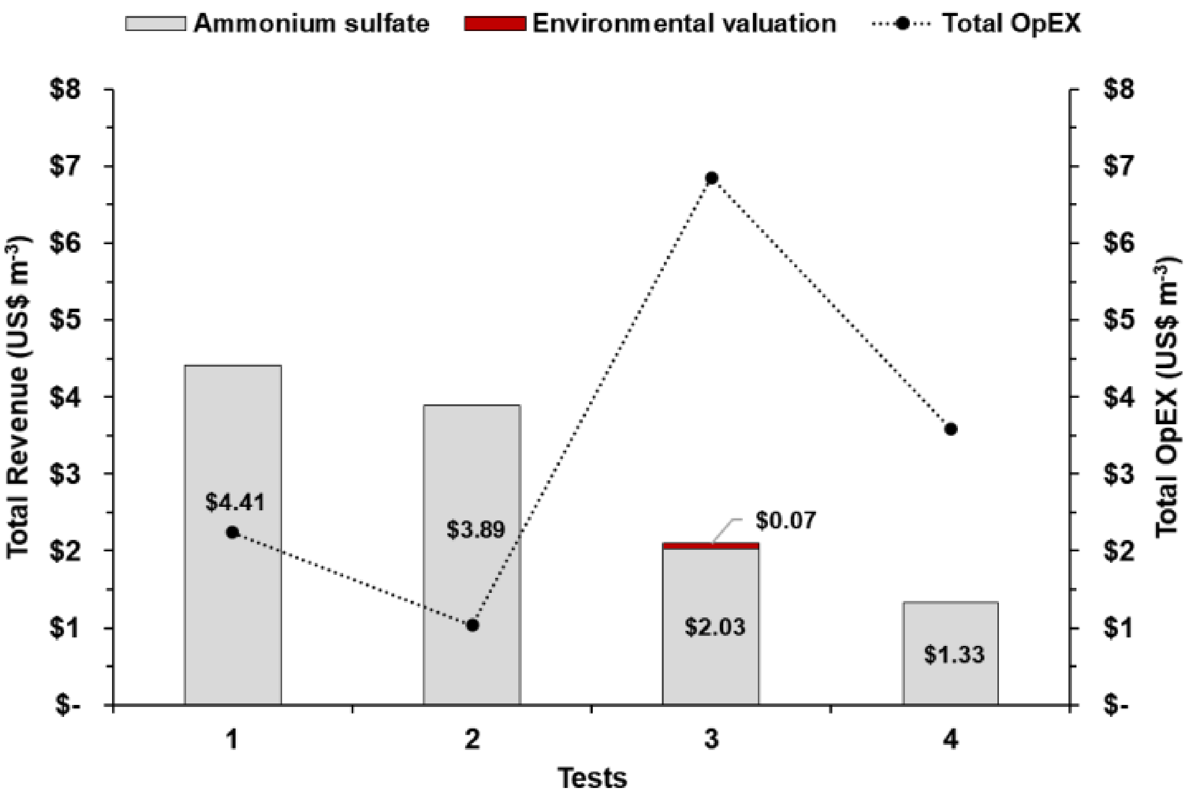


Table 2.7 - Features considered for the cost estimation of the AS/AB system for the tests performed and the CapEX obtained.

	Description	Values				Units
		Test 1	Test 2	Test 3	Test 4	
Summary of the system's characteristics	Annual System Capacity	175,200	175,200	175,200	175,200	m^3 $year^{-1}$
	Operating temperature	60	30	60	30	°C
	Design Plant Life	15	15	15	15	years
	Brazil Investment Rate	2	2	2	2	%
	pH adjustment cost	-	0.71	-	0.71	US\$ m^{-3}
	Maintenance cost	0.07	0.07	0.07	0.07	US\$ m^{-3}
	Energy requirement	39.29	18.74	58.69	18.74	Kwh m^{-3}
	Energy cost	4.66	2.22	6.96	2.22	US\$ m^{-3}
	Water requirement	0.66	0.66	0.66	0.66	m^3 water m^{-3} LFL
	Water cost	1.07	1.07	1.07	1.07	US\$ m^{-3}
	Sulfuric acid requirement	0.0036	0.0036	0.0036	0.0036	m^3 sulfuric acid m^{-3} LFL
	Sulfuric acid cost	0.67	0.67	0.67	0.67	US\$ m^{-3}
	Labor cost	31,486.62	31,486.62	31,486.62	31,486.62	US\$ $year^{-1}$
CapEX	Treatment System	235,019.83	235,019.83	235,019.83	235,019.83	US$

For the process revenue, it was considered the commercialization of the recovered ammonium sulfate and the environmental valuation if it was removed $N\text{-}NH_3$ beyond what was required by legislation. In Figure 2.12, it is observed that the revenue was higher for tests 1 and 2 because they were the tests that had a higher initial ammonia concentration, and consequently, higher mass recovery. The commercialization of ammonium sulfate of the lower concentration tests (tests 3 and 4) would not be viable, since the market specification regarding the mass concentration of nitrogen in the form of $N\text{-}NH_3$ (20-21%) was not attended. An alternative would be the addition of an ammonia concentration step with acid recovery to make the sale of the solution as fertilizer viable. The environmental valuation was estimated only in test 3, because at the end of the test the concentration of $N\text{-}NH_3$ of 13 mg L^{-1} was reached, that is, a concentration lower than that required by the legislation (20 mg L^{-1}), corresponding to a value of US$ 0.07 m^{-3} of leachate.

Figure 2.12 - Total revenue and total OpEX for tests 1, 2, 3 e 4.



Although the residual heat of the raw leachate was considered in test 1, the OpEX was higher than the revenue in all scenarios. The use of renewable energies, such as solar energy and the biogas generated in the landfill itself from the anaerobic digestion of the waste, for example, are alternatives that can be considered to minimize the energy cost of both the wastewater heating and the aeration system of the air-stripping and absorption.

According to Townsend et al. (2015), landfills have the potential to install photovoltaic panels because they have large areas. In addition, countries such as Germany, France, Japan, Portugal, Italy, Taiwan and the United States (USA) already have solar installations in landfills or at least have been planned (LOPES et al., 2019). Szabó et al. (2017) highlighted that closed landfills have high potential for installing solar systems for power generation. The use of biogas also shows as an opportunity to reduce costs. Dos Santos et al. (2020) claim that landfills are increasingly implementing Clean Development Mechanism projects aimed at the sale of carbon credits, either by the reuse of biogas for energy or by burning it. This alternative, besides making possible the reduction of energy costs, also makes possible the increase of the revenue with the sale of credits. Lopes et al. (2019) evaluated the possibility of using biogas for energy purposes and installing a solar photovoltaic system in a landfill, which presented economic viability.

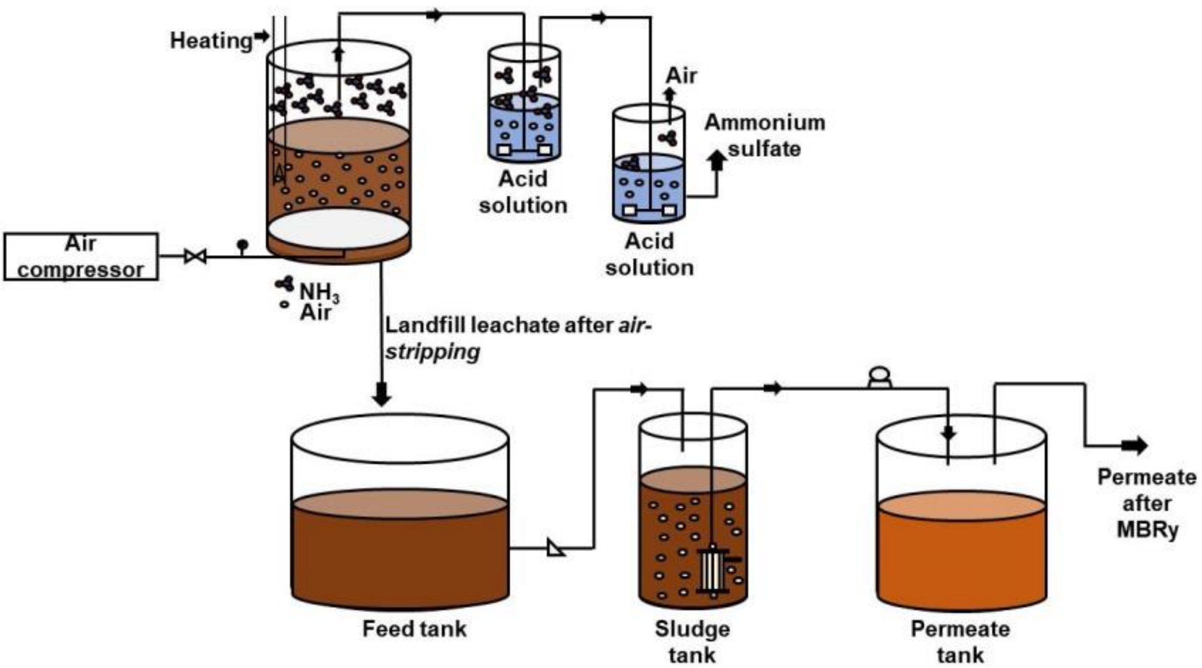
The LFL treatment is of paramount importance, regardless of existing costs, since it is necessary to meet legal requirements and promote environmental protection. The commercialization of ammonium sulfate and the consideration of environmental valuation are ways to minimize LFL treatment expenses, where the existence of profit in the proposed process is not necessarily mandatory. Moreover, the commercialization of ammonium sulfate obtained from renewable sources is satisfactory for Brazil, since the importation of nitrogen-based fertilizers has increased (SILVA, 2019), being an alternative for reducing the dependence on the international market.

2.3.3 Feasibility of air-stripping/absorption application as pre- or posttreatment of MBRy

Faced with the evaluation of the MBRy performance in different ammonia concentrations in the LFL, the results obtained both from the removal and recovery of N-NH_3 by AS/AB process, and the preliminary economic analysis, it was found that the best alternative is the application of this process as pre-treatment of the MBRy.

Regarding the technical feasibility of $N\text{-}NH_3$ recovery, the initial concentration of $N\text{-}NH_3$ was the most important factor, since regardless of the condition (pH or temperature increase) a solution with economic value was obtained. For the MBRy feeding there would be no negative impacts since the residual value of this compound in both scenarios was low (28 and 310 mg L^{-1} of $N\text{-}NH_3$ for tests 1 and 2, respectively). Although the cost for heating is higher than the cost of chemicals to adjust the pH of the leachate, the revenue in test 1 was higher. The use of renewable energies, such as biogas generated in the landfill itself, or even solar energy, can be an alternative for reducing energy costs. Thus, one possibility of treatment route for LFL, aiming the treatment and recovery of ammonia, is the application of AS/AB followed by MBRy (Figure 2.13). However, the LFL ammonia removal in the AS/AB processes should not occur completely, in order to maintain the appropriate amount of nutrients for the yeasts in the MBRy. Studies are needed to define the appropriate COD/N ratio for *Saccharomyces cerevisiae*.

Figure 2.13 - Integration of AS/AB process at pH 8 and temperature of 60°C and MBRy at higher COD/N ratio for LFL treatment.



According to Campos et al. (2013), the temperature of 60°C is not a very high value if one considers the temperature of tropical countries like Brazil, where temperatures of 40°C can occur in summer. The development of studies evaluating the effect of MBRy operation at higher temperatures would be relevant. It is also important to consider the heat exchanger in the biological tank operated with high residence time (48h).

This route allowed the recovery of 7 kg of ammonia per m³ of treated leachate. For comparison with other studies, the recoveries obtained by the AS/AB process were extrapolated to a real system with effluent flow rate of 20 m³ h^{-1}. Errico et al. (2017) obtained 28.5 kg ammonia per m³ of biogas digestate, while Tao and Ukwuani (2015) obtained 16.7 kg ammonia per m³ of dairy manure. It is observed that the different recoveries obtained for these effluents can be justified mainly by the initial ammonia concentration, and by the operational factors of the AS/AB process such as pH, temperature, TDH and concentration of the H_2SO_4 solution.

2.4 Conclusions

The evaluation of the MBRy performance in different COD/N ratios allowed to verify that the highest removals of organic matter and ammonia were achieved in higher COD/N ratio. However, it is important to point out that even at a lower COD/N ratio *Saccharomyces cerevisiae* was able to multiply, besides reaching considerable ammonia and organic matter removal efficiencies.

As far as AS/AB tests are concerned, removals of 99% N-NH_3 were verified at pH 8 and temperature of 60°C. However, the ammonia concentration in the AS/AB process feed was a key factor to achieve the market specification. Therefore, the proposed route for the treatment of the raw LFL was using the AS/AB process as pre-treatment of MBRy in higher COD/N ratio. This route allowed only the ammonia concentration in the permeate to reach the discharge standard (9 ± 7.5 mg L^{-1}), since the remaining COD concentration (2,902 ± 374 mg L^{-1}) is a recalcitrant organic matter, requiring the integration of a physico-chemical process. The energy cost for wastewater heating can be mitigated with the use of biogas generated in landfill and solar energy use. It should be noted that the proposed route allowed recovery 7 kg of ammonia per m³ of treated leachate.

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3 CHAPTER 3: INTEGRATED ROUTES FOR LANDFILL LEACHATE TREATMENT AND REUSE WATER RECLAMATION: MBR FOLLOWED BY FENTON AND NANOFILTRATION PROCESSES

3.1 Introduction

Among the existing techniques for the solid waste management, landfilling is the most used practice due to the economic advantages and environmental sustainability (TOWNSEND et al., 2015). In contrast, the by-products generated need to be drained, collected and effectively treated to not allow their disposal in the environment, which avoids damage to the air, soil and water bodies. The landfill leachate (LFL) is one of the by-products formed, which has in its composition a high concentration of ammonia (N-NH_3), heavy metals, humic acids (HA), nitrogen, inorganic salts, and xenobiotics (ABUABDOU et al., 2020). In addition, according to Christensen et al. (2005), it is estimated that each ton of solid waste generates 0.2 m^3 of LFL.

According to Renou et al. (2008), leachate treatments can be divided into three main groups: (a) leachate transfer: recycling and treatment with domestic sewage, (b) biodegradation: anaerobic and aerobic processes and (c) physico-chemical: chemical oxidation, adsorption, chemical precipitation, coagulation/flocculation, sedimentation, flotation, and air-stripping. However, the most appropriate technique for LFL treatment will depend on its physicochemical composition, which is related to the landfill age, the leachate stabilization, and the climate. Regarding climate, in tropical regions the leachate stabilization occurs faster (up to 1.5 years of operation (CHEN, 1996) due to the greater biological activity under warmer conditions, when compared to the leachate generated in temperate regions. Therefore, it is expected a higher concentration of recalcitrant substances in the leachate from tropical regions.

Stabilized LFL is characterized by its recalcitrance, which hinders or prevents its degradation by microorganisms (biodegradation). The LFL recalcitrance is inherent to the presence of humic substances (HS), which are compounds with high molecular weight and complex structure (KANG et al., 2002). Membrane bioreactor (MBR) is an advanced hybrid process consisting of a biological treatment combined with membrane separation processes (MSP) for a solid-liquid physical separation. The MBR has advantages such as shorter hydraulic retention time (HRT), longer solids retention time (SRT), and lower sludge production (IORHEMEN et al., 2016). The increasing use of

MBR in the LFL treatment is observed (SONG et al., 2020a), in which the use of yeasts in membrane bioreactors (MBRy), such as *Saccharomyces cerevisiae*, has proven promising in the LFL treatment. The higher removal of COD, color, ammoniacal nitrogen, phosphorus, and lower membrane fouling was verified in MBRy compared to MBR inoculated with bacterial sludge for the LFL treatment (REIS et al., 2017; AMARAL et al., 2018). Amaral et al. (2017) verified that the COD removal obtained in the MBRy (72 ± 3%) corresponds to the biodegradable fraction, and the remaining COD refers to the recalcitrant fraction. Reis et al. (2017) found that the LFL COD removal performance was higher using MBRy (69 ± 7%) than MBR inoculated with bacteria (27 ± 5%). Although the COD removal was satisfactory in MBRy, showing that the remaining organic fraction (1,403 ± 374 mg L^{-1}) is only inert COD (BRITO et al., 2013), it is important polishing this effluent to remove the recalcitrant compounds. Moreover, the MBRy permeate in COD/N ratios of 43.0 ± 6.9 and 3.5 ± 0.4 treating the same effluent showed acute toxicity of 65.85 ± 18.42% and 34.01 ± 7.83%, respectively, reinforcing the relevance of applying a polishing step.

Advanced oxidation processes (AOPs) consist in the production of hydroxyl radicals ($^{\bullet}OH$) from a highly reactive and strong oxidizer for complete mineralization – producing CO_2 and H_2O, or partial degradation – increasing the biodegradability of organic pollutants (MORAVIA et al., 2011). According to Deng and Zhao (2015), one of the objectives of treating LFL by AOP is to complement the organic matter degradation as a polishing step to other technologies. The Fenton reagent is among the AOP techniques with greater organic matter removal due to the use of catalysts, substances that increase the reaction rate to achieve chemical equilibrium without being altered chemically. This process uses hydrogen peroxide (H_2O_2) as an oxidizing agent and iron in reduced form (Fe^{2+}) as a catalyst for $^{\bullet}OH$ production under acid conditions (AMOR et al., 2015).

Deng (2009), based on 24 data from 17 studies, reported that the efficiency of COD removal in leachate using Fenton has an average of 71 ± 13%. Lima et al. (2017) applied Fenton in LFL treatment and obtained removal of more than 85% of HS from the Gericinó and Gramacho landfills. However, according to Bokare and Choi (2014), Fenton is limited by the sludge formation containing iron hydroxides, and its separation from the treated effluent is necessary. Sludge removal is one of the challenges of this process due to the time required, and usually a neutralization/precipitation step is applied for sludge separation, which presents low sedimentability (MORAVIA et al., 2011).

Since the cost of Fenton can be high, its integration with other processes is interesting. In this way, Fenton can be used to remove only the recalcitrant fraction, reducing the treatment cost. It is worth noting that although Fenton is considered an alternative for the removal of residual organic matter, the application of this process alone may not be sufficient for LFL polishing. Besides organic matter, there is the presence of high concentration of compounds such as chloride (150-4,500 mg L^{-1}), sulfate (8-8,870 mg L^{-1}), sodium (70-7,700 mg L^{-1}), potassium (50-3,700 mg L^{-1}), calcium (10-7,200 mg L^{-1}) and magnesium (30-15,000 mg L^{-1}) (KJELDSEN et al., 2002), which are not effectively removed in MBR or Fenton.

MSPs can be increase the efficiency of LFL treatment. Microfiltration (MF), for example, can be used to remove the sludge generated in Fenton. The MF application allowed the removal of 91.2% and 92.3% of solids and phosphorus in the post-Fenton LFL, respectively (MORAVIA et al., 2013). In addition, nanofiltration (NF) has been used as a polishing in LFL treatment to remove residual organic matter, toxic by-products that may be formed during Fenton and dissolved ions. The NF process occurs basically by two principles: rejection of neutral species by size (molecules larger than 200-300 g mol^{-1} are rejected), and rejection of inorganic ions due to electrostatic interactions between the ions and the membrane (LINDE and JONSSON, 1995). Also, according to the same authors, the NF has the ability to remove recalcitrant compounds and heavy metals from LFL. In Brazil, the Gramacho landfill, located in Rio de Janeiro (RJ), uses NF as a polishing step for the biological process employed for leachate treatment. In developed countries, NF has also been used in the LFL treatment (KEYIKOGLU et al., 2020).

Fenton and NF can be integrated in different ways for the polishing of MBRy treated leachate: (I) Fenton – NF or (II) NF – Fenton. The advantages of the first route consist in the removal of the remaining organic matter and ions, in addition to by-products formed in Fenton that may confer toxicity. Regarding the second route, Fenton would be applied in the NF concentrated compartment treatment, since there are treatment plants that use NF or reverse osmosis (RO) as LFL polishing that recirculate the concentrate to the landfill. There are studies that show the problems caused by this recirculation such as alteration of the physico-chemical composition of the leachate (decrease in the BOD_5/COD ratio, increase volatile fatty acids concentration, ammoniacal nitrogen and COD), and decrease in the membrane performance due to higher fouling, leading to increase the energy consumption (KEYIKOGLU et al., 2020). The indication of the best alternative of process integration for LFL polishing will depend on the application and importance of the study, and the choice should be based on technical and economic criteria.

Therefore, the main objective of this study was to investigate the best way to integrate Fenton and NF for the polishment of MBRy permeate aiming to comply with legislation and wastewater reuse. One of the uses of the treated effluent in the landfill plant can be for dust arrestment, in earthworks and in construction site works. Two treatment after MBRy by Fenton process followed by NF (MBRy – Fenton – NF), and polishing of MBRy permeate by NF with concentrated compartment treatment (MBRy-NF-$\text{Fenton}_{\text{(concentrate)}}$) were evaluated in relation to the pollutants removal and the membrane fouling. This is the first study that evaluates the best alternative of process integration for LFL polishing, since there are works that evaluate MBRy – Fenton – NF in an individual way. Moreover, this study aims to subsidize the best design of the treatment system, since it has been seen the growth in the use of MBR and NF for the leachate treatment.

3.2 Materials and methods

3.2.1 Landfill leachate samples

The raw LFL samples were collected in the equalization tank of a landfill located in the municipality of Sabará/Minas Gerais - Brazil, and stored at 4°C. The effluent is characterized by a high organic matter concentration (COD: 5,858 ± 605 mg L^{-1}), ammoniacal nitrogen (2,249 ± 454 mg L^{-1}), color (11,578 ± 2,401 mg L^{-1}), HS (5,668 ± 1,853 mg L^{-1}) and alkalinity (20,590 ± 649 mg L^{-1}). The LFL was subjected to an air-stripping treatment (aiming at $N\text{-}NH_3$ removal) followed by a yeast-inoculated membrane bioreactor (MBRy), which was operated with a submerged ultrafiltration (UF) membrane. The MBRy operated at constant temperature (23 ± 2°C), a hydraulic retention time (HRT) of 48 hours, without a feed pH adjustment, and with a COD/N ratio of 43 ± 6.9. A detailed description of the experimental apparatus employed was previously described in Chapter 2. The physico-chemical characterization of the MBRy permeate is shown in Table 3.1.

Table 3.1 - Physico-chemical characteristics of the MBRy permeate.

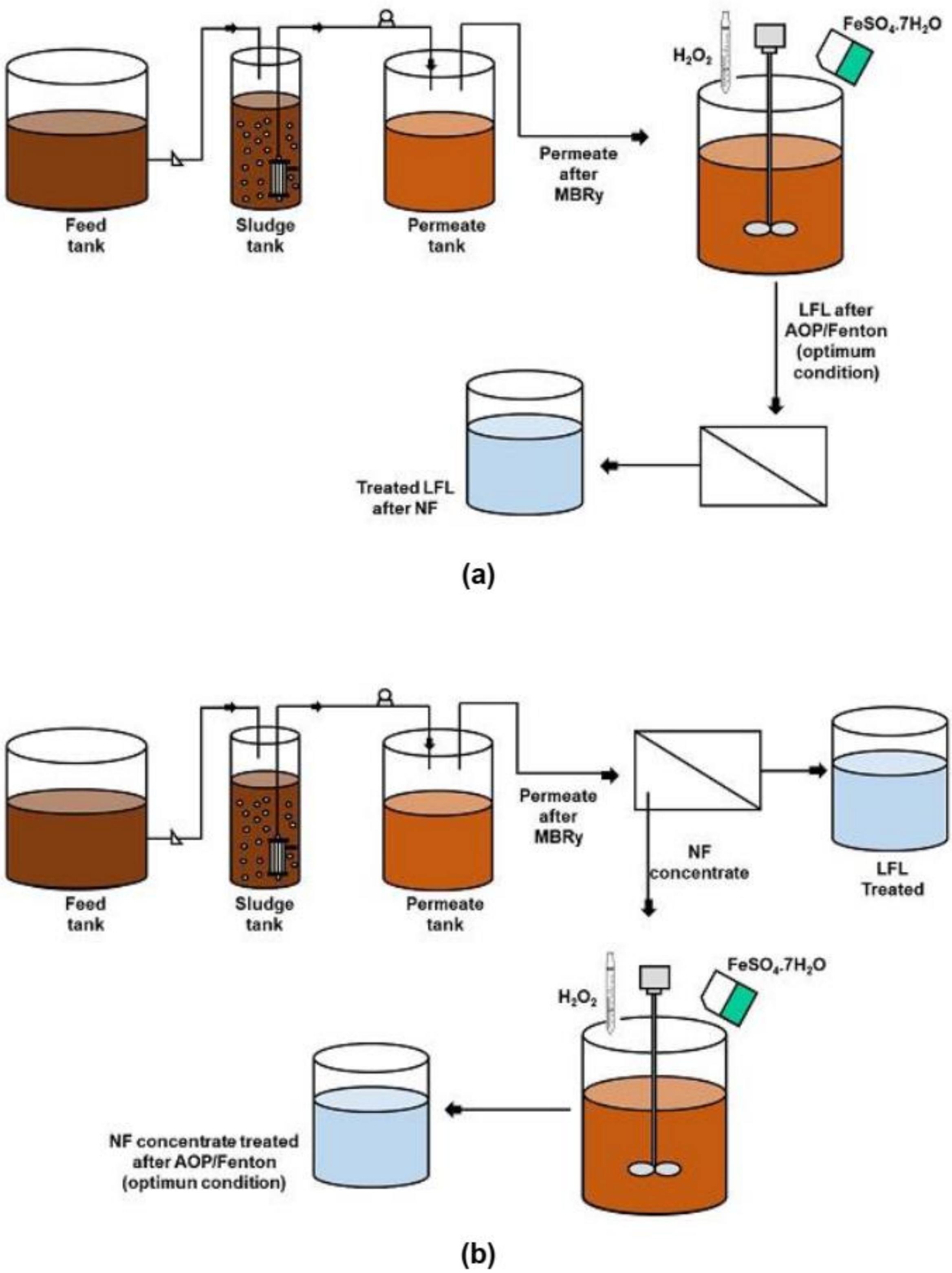
Parameter	Unit	Median ± Std	Parameter	Unit	Median ± Std
COD	mg L^{-1}	2,910 ± 44	Phosphate	mg L^{-1}	189.79 ± 14.79
TOC*	mg L^{-1}	1,003 ± 50	Bromide	mg L^{-1}	181.70 ± 0.43
HS*	mg L^{-1}	2,150 ± 108	Sodium	mg L^{-1}	1,920.68 ± 97.93
pH	-	8.82 ± 0.17	Potassium	mg L^{-1}	1,898.87 ± 170.25
True color	uH	8,816 ± 772	Magnesium	mg L^{-1}	68.08 ± 34.09
Conductivity	mS cm^{-1}	17.09 ± 4.8	Calcium	mg L^{-1}	77.11 ± 14.13
Alkalinity	mg L^{-1}	1,796 ± 90	TS*	mg L^{-1}	9,253 ± 802
$N\text{-}NH_3$	mg L^{-1}	0.17 ± 0.15	VTS*	mg L^{-1}	1,670 ± 544
Turbidity	NTU	4.37 ± 0.77	FTS*	mg L^{-1}	7,583 ± 1,285
Cl^-	mg L^{-1}	4,403 ± 470	TSS*	mg L^{-1}	16.17 ± 1.89
NO_2^-	mg L^{-1}	79.83 ± 1.40	VSS*	mg L^{-1}	11.50 ± 4.09
NO_3^-	mg L^{-1}	197.02 ± 4.13	FSS*	mg L^{-1}	4.67 ± 2.52
Sulphate	mg L^{-1}	206.01 ± 33.72			

TOC – total organic carbon; HS – humic substances; TS – total solids; FTS – fixed total solids; VTS – volatile total solids; TSS – total suspended solids; FSS – fixed suspended solids; VSS – volatile suspended solids

3.2.2 MBRy, Fenton and nanofiltration processes integration

Two treatment routes were proposed for LFL treatment (Figure 3.1), comparing their efficiency in pollutants removal and compliance with the discharge limits for treated LFL. In Figure 3.1a it is represented a membrane bioreactor inoculated with yeast and integrated with Fenton and nanofiltration (MBRy – Fenton – NF) processes for polishing. Figure 3.1b represents a membrane bioreactor inoculated with yeasts integrated with nanofiltration, which the concentrate underwent to a Fenton process for its treatment (MBRy – NF – $\text{Fenton}_{(\text{concentrate})}$).

Figure 3.1 - (a) MBRy – Fenton – NF and (b) MBRy – NF – Fenton$_{(concentrate)}$ routes.



3.2.3 Fenton optimization

The MBRy permeate was subjected to Fenton process, optimized by a central composite design (CCD - Table 3.2). The COD removal efficiency was chosen as a response variable, assumed to be affected by three independent factors: C:H_2O_2 (A; molar ratio), Fe:H_2O_2 (B; molar ratio) and pH (C). These experiments were conducted in a jar test equipment at a constant reaction time (30 min) and agitation (60 rpm), according to recommendations from previous studies (MORAVIA et al., 2013). Oxidation occurred with pH adjustment with sulfuric acid (H_2SO_4) in 1 L of MBRy permeate, followed by the addition of ferrous sulfate solid heptahydrate ($FeSO_4.7H_2O$) and addition of 30% hydrogen peroxide solution (v/v). At reaction time, the samples were neutralized (pH 7) with sodium hydroxide solution (10 mol L^{-1}) and filtered by a syringe filter (0.45 μm PTFE - Polytetrafluoroethylene) for residual COD measurements. For the optimal operational condition, the test was carried out for 120 min with agitation of 60 rpm. The interference of residual H_2O_2 on residual COD measures were corrected following the procedure recommended by Nogueira et al. (2005). Statistical analysis was carried out at 95% confidence level in the Design-Expert® software (Stat-Ease, Inc. 2017 - version 11), and the optimal value for the evaluated factors was obtained by solving the quadratic equation associated to the Fenton process. The Fenton kinetics was evaluated based on the COD using the first order kinetic model plotting **ln[COD]** *versus* **time**, in which the inclination of the obtained linear equation is the reaction rate.

Fenton was performed with 4 L of MBRy permeate according to the operational parameters found in the optimal condition, under agitation of 60 rpm for 30 minutes for NF tests. At the end of the oxidation step, sodium hydroxide solution was added to adjust the pH to 7, followed by homogenization and sedimentation to sludge removal. The supernatant was filtered with AP40 filter. It should be noted that the optimal condition was applied both in the treatment of the MBRy permeate and in the NF concentrate treatment to evaluate the best way to integrate the processes.

Table 3.2 - Coded and real values defined in the experimental design, experimental and predicted COD removal efficiency. Note that the signs +, -, 0 and α are coded values for the factors.

Run	Coded and (real) value			COD removal (%)		
	A - C:H_2O_2	B - Fe: H_2O_2	C - pH	Actual	Predicted	Residual
1	- (1: 1.125)	-(1:2.82)	-3,4	74	75,2	-1,2
2	+ (1: 3.125)	-(1:2.82)	-3,4	77	75,2	1,8
3	- (1: 1.125)	+(1:8.18)	-3,4	68,5	69,8	-1,3
4	+ (1: 3.125)	+(1:8.18)	-3,4	48	48	0
5	- (1: 1.125)	-(1:2.82)	4,6	38	36,3	1,7
6	+ (1: 3.125)	-(1:2.82)	4,6	71,8	73,6	-1,8
7	- (1: 1.125)	+(1:8.18)	4,6	70	69,7	0,3
8	+ (1: 3.125)	+(1:8.18)	4,6	34,2	34,3	-0,1
9	-α (1: 0.45)	0 (1:5.5)	0 (4.0)	62	63,9	-1,9
10	+α (1: 3.8)	0 (1:5.5)	0 (4.0)	66,4	66,2	0,2
11	0 (1: 2.125)	-α (1:10)	0 (4.0)	91,5	90,3	1,2
12	0 (1: 2.125)	+α (1:1)	0 (4.0)	45,5	45,5	-0,1
13	0 (1: 2.125)	0 (1:5.5)	-α (3.0)	11.7	12	-0,3
14	0 (1: 2.125)	0 (1:5.5)	+α (5.0)	62.0	60,8	1,3
15	0 (1: 2.125)	0 (1:5.5)	0 (4.0)	69,2	69,7	-0,5
16	0 (1: 2.125)	0 (1:5.5)	0 (4.0)	82	80,8	1,2
17	0 (1: 2.125)	0 (1:5.5)	0 (4.0)	75	75,2	-0,2

3.2.4 Nanofiltration process

The NF experimental conditions were based on a previous study developed by Silva et al. (2019), which applied NF for the treatment of a MBRy permeate employed for LFL treatment. According to the authors, a transmembrane pressure of 10 bar and recirculation flowrate of 2.4 L min^{-1} was the one that exhibit the greatest pollutants removal, highest permeate flux and the lowest fouling potential. The authors also defined a recovery rate of 40%, in which a high-quality permeate was obtained without compromising its physico-chemical quality.

The NF tests were performed with a FilmTec NF90 nanofiltration membrane module with an effective membrane area of 75 cm^2, with recirculation of the concentrate to the feed tank (Figure 3.2). Table 3.3 summarized the membrane characteristics. The NF module was fed with 3 L of MBRy permeate and MBRy – Fenton effluent. Prior to each test, the membrane was chemically cleaned with 0.1% NaOH solution (pH 11) and citric acid (2%) for 20 minutes in ultrasound bath for each solution.

Figure 3.2 - Schematic diagram of the NF module.

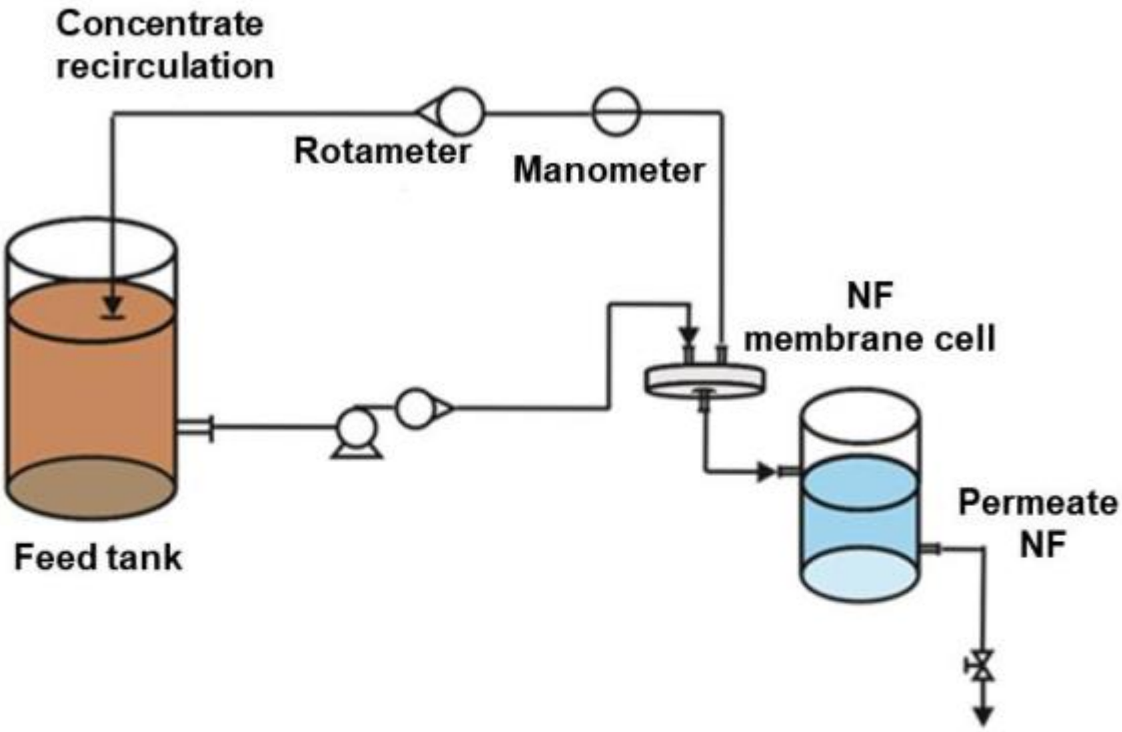


Table 3.3 - NF membrane characteristics.

Manufacture	DOW/Filmtec
Membrane material	Polyamide
Molecular weight cut off (Da)	200 – 400
Maximum temperature (˚C)	45
Maximum pressure (bar)	41
pH range	2 - 11
Pure water permeability (L m^{-2} h^{-1} bar^{-1}) [(1)]	6.4
Salt rejection (%)	90-96 (NaCl) [(2)]
	98 (MgSO4) [(2)]

[(1)] INCE et al. (2010)
[(2)] NaCl: Sodium chloride; $MgSO_4$: Magnesium sulfate

3.2.5 Calculation

The permeate flux (J, L m^{-2} h^{-1}) was calculated by the ratio between the permeate flowrate (Qp, L h^{-1}) and NF membrane area (A, m²), as represented in Equation 3.1.

$$J = \frac{Q_p}{A} \tag{3.1}$$

The fouling resistance (R_f) was estimated as in Equation 3.2, where P_{ef} (m^3 m^{-2} s^{-1} Pa^{-1}) is the membrane permeability obtained at the end of each filtration experiment, R_m is the NF membrane resistance, and μ (Pa s) is the dynamic water viscosity at 25°C (LEE et al., 2003).

$$R_f = \frac{1}{P_{ef} \cdot \mu(25°C)} - R_m \tag{3.2}$$

The membrane resistance (R_m) was calculated according to Equation (3.3), where K (m^3 m^{-2} s Pa) is the membrane permeability measured before each experiment with distilled water.

$$R_m = \frac{1}{K \cdot \mu(25°C)} \tag{3.3}$$

The mechanisms responsible for membrane fouling were assessed by the filtration models developed by Hermia (Table 3.4) using the experimental flux data. The models describe four different mechanisms which are correlated to: (a) complete blocking, (b) standard blocking, (c) intermediate blocking and (d) cake filtration (HERMIA, 1982). The k values correspond to mass transfer coefficients.

Table 3.4 - Linearized equations from Hermia's model.

Model	**Equation**
Complete blocking	$ln(J^{-1}) = ln\,(J_O)^{-1} + k.t$
Standard blocking	$J^{-1/2} = J_0^{-1/2} + k.t$
Intermediate blocking	$J^{-1} = J_0^{-1} + k.t$
Cake filtration	$J^{-2} = J_0^{-2} + k.t$

The removal efficiency was calculated considering the feed (C_f, mg L^{-1}) and permeate (C_p, mg L^{-1}) concentrations of a given pollutant, as represented in Equation 3.4.

$$R(\%) = \left(\frac{C_f - C_p}{C_f}\right) \cdot 100 \tag{3.4}$$

3.2.6 Analytical methods

The parameters electrical conductivity (EC) (2510-B - Hach 44600), color (2120-B – Hach 2100AN), turbidity (2130-B - turbidimeter Hach 2100AN), COD (5220–D), ammoniacal nitrogen (4500-NH_3-B, 4500-NH_3-C), sulfate (4500-SO_4^{2-}-D), chloride (4500-Cl^--B), alkalinity (2320-B), pH (4500-B - Digimed DM-22), and solids (2510-B; 2540-B, 2540-C) were analyzed according to Standard Methods for the Examination of Water and Wastewater (APHA, 2017). The parameters total organic carbon (TOC), total carbon (TC) and total nitrogen (NT) were analyzed in the Shimadzu TOC-V equipped with CNP, and Shimadzu TNM-1, respectively. The ions concentration was determined by ion chromatography (4110 - Dionex ICS-1000 ion chromatography, equipped with column type IonPac AS22 and IonPac CS12A). Humic substances were analyzed according to the method of Lowry et al. (1951) modified by Frolund et al. (1995). A Perkin Elmer UV/Vis Lambda XLS spectrophotometer was used to measure the absorbance at 254 nm (Abs254) in the MBRy permeate and in the effluent after Fenton in the optimum condition.

The acute toxicity tests were performed with the luminescent marine bacteria *Aliivibrio fischeri*, using the MICROTOX® model 500 Analyzer. The tests were performed according to the ABNT NBR 15411-3 standard and following the protocol established by the software (MICROTOX® Omni Software, version 4.1). The samples were kept at -20ºC, and their pH were adjusted with sodium hydroxide (NaOH; 0.001 mol L^{-1}) and hydrochloric acid (HCl; 0.001 mol L^{-1}) to maintain their pH between 6.0 and 8.0 - the standardized range for testing. The tests were performed based on serial dilution of the samples, in a 2% NaCl diluent solution. Acute toxicity was expressed in Median Effective Concentration (EC50), which represents the concentration of the toxic agent responsible for an adverse effect in 50% of the individuals, determined from a luminescence measurement of the bacteria after 30 minutes.

3.2.7 Preliminary economic analysis

Capital and operating expenditures (CapEX and OpEX, respectively) were estimated based on a treatment capacity of 20 m^3 h^{-1}. The investment cost for MBR (C_{in}) was calculated using the six-tenths factor rule (Equation 3.5), where P_{base} is the price for the installed MBR (MBR: US$ 4,751.00; V_{base}: 5 m³) and V_r is the volume of the installed reactor (PÉREZ et al., 2013).

$$IC_{MBR} = P_{base} \cdot \left(\frac{V_r}{V_{base}}\right)^{0.6} \tag{3.5}$$

The amortization cost (C_{am}, US\$ m^{-3}) was calculated from Equation 3.6 taking into account the project lifespan (ls, 15 years), the CapEX (C_{in}), and the current national investment rate (i_r, 2% per year; November 2020). Further detailing of assumptions made for CapEX and OpEX estimation for both systems is presented in Table 3.5.

$$C_{am} = C_{in} \cdot \left(\frac{i_r}{1-(1+i_r)^{ls}}\right) \quad (3.6)$$

Table 3.5 - System characteristics and assumptions made for CapEx and OpEx estimation for the MBRy – Fenton – NF and MBRy – NF – Fenton$_{(concentrate)}$.

	Descriptions	MBRy – Fenton efluente	MBRy permeate
System description	Wastewater flowrate (m^3 h^{-1})	20	
	UF permeate flux (L m^{-2}.h^{-1})	2.13	
	UF operating pressure (bar)	0.26	
	NF permeate flux (L m^{-2}.h^{-1})	5.49	9.21
	NF recovery rate (%)	40	
	NF operating pressure (bar)	10	
Chemicals and utilities	Cleaning agent requirement (kg/3,000 m^2 of membrane)	3	
	Cleaning agent: NaOH (US\$ kg^{-1})	0.12	
	Cleaning agent: Citric acid (US\$ kg^{-1})	0.65	
	Cleaning frequency	weekly	
	AOP: $FeSO_4 \cdot 7H_2O$ cost (US\$ kg^{-1})	0.15	
	AOP: H_2O_2 cost (US\$ kg^{-1})	0.48	
	Pump efficiency	0.85	
	Energy costs (US\$ kWh^{-1})	0.04	
Capital expenditures (CapEX)	MBR base price (US\$)	4.751	
	MBR base volume (m^3)	5	
	MBR installed reactor volume (m^3)	1.248	
	POA base price (US\$) (1)	57.749	
	Energy POA (kWh m^{-3})	0.776	
	NF base price (US\$/m^3/h)	6,400	
Operating expenditures (OpEX)	Average UF membrane cost (US\$ m^{-2})	9.7	
	Average NF membrane cost (US\$ m^{-2})	17.3	
	Concentrate disposal (US\$ m^{-3}) (2)	3	
	Project lifespan (year)	15	
	Membrane lifespan (year)	7	
	Maintenance rate (% from CapEX)	5	

(1) Turton et al. (2008)
(2) Vergili et al. (2012)

3.3 Results and discussions

3.3.1 Optimization of Fenton applied to MBRy permeate

From the experimental runs in the CCD design, four different models were fitted to the experimental data. The linear, two factor interaction (2FI), quadratic and cubic model's summary statistics is shown in Table 3.6. Comparing their adequacy, it can be noted that the cubic and 2FI models showed p-values higher than 0.05, thus considered as non-significant. On the contrary, the linear and quadratic models showed p-values <0.05, the latter with a higher R^2 (0.997) among the two. Furthermore, the difference between the R^2 predicted and the adjusted R^2 is less than 0.2, which shows that the quadratic model is not overfitted by the increase in factors and coefficients in the model. For those reasons, the quadratic model was chosen to describe the Fenton process.

Table 3.6 - Models summary statistics.

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	p-value
Linear	13.27	0.644	0.561	0.396	3874.2	0.003
2FI	13.11	0.732	0.571	0.500	3207.2	0.391
Quadratic	1.72	0.997	0.992	0.979	134.1	<0.001
Cubic	1.92	0.998	0.990	0.779	1413.8	0.661

The quadratic model chosen for describing the Fenton was presented in Equation 3.7 (in terms of coded variable), along its analysis of variance in Table 3.7. The model and all variables were statistically significant, except the interaction between C:H_2O_2 and pH (coded: AC). COD removal efficiency seems to be directly affected by the Fe:H_2O_2 (coded: B), whereas high values of C:H_2O_2 (coded: A) and pH (coded: C) would be disadvantageous to the process. A lower H_2O_2 concentration means in an also lower hydroxyl radicals' concentration, reducing the oxidation rate of organic compounds. As pH increases, the iron species responsible for hydroxyl radicals' generation precipitates, being also disadvantageous to an effective COD removal (KARTHIKEYAN et al., 2011; CLARIZIA et al., 2017). In addition, higher H_2O_2 concentrations and pH less than 2.5 causes parallel reactions to occur, slowing down the reaction rate for hydroxyl radical production. Complementarily to a significant model, the lack of fit was considered non-significant (p-value = 0.472), which reinforces a proper model fit to the experimental data and the significant effect of the independent variables (C:H_2O_2, Fe:H_2O_2 and pH) on the output response (COD removal). The quadratic model explains 99.2% of the variations, and presented an adequacy precision value 59.38, greater than the reference value of 4 (DEAN et al., 2017).

The confidence for predictive purposes was further assured by a residual analysis related to the quadratic model (

The 3-D response surfaces shown in Figure 3.4 can be used to better understand the effects of the independent variables (C:H_2O_2, Fe:H_2O_2 and pH) on the COD removal. In Figure 3.4a, where the effect of C:H_2O_2 and pH were assessed, higher COD removal are attained at the lower level for pH (-1, pH 3.4) and central level for C: H_2O_2 (0, 1:2.125). One aspect that may have led the increase in COD removal in lower pH levels is that the Fe^{3+} is increased, on the contrary, in higher pH levels, the increase in hydroxyl ions concentration within the medium favors the Fe^{3+} precipitation (KARTHIKEYAN et al., 2011).

Figure 3.3). It is expected from an adequate model a normal distribution of the residues (

The 3-D response surfaces shown in Figure 3.4 can be used to better understand the effects of the independent variables (C:H_2O_2, Fe:H_2O_2 and pH) on the COD removal. In Figure 3.4a, where the effect of C:H_2O_2 and pH were assessed, higher COD removal are attained at the lower level for pH (-1, pH 3.4) and central level for C: H_2O_2 (0, 1:2.125). One aspect that may have led the increase in COD removal in lower pH levels is that the Fe^{3+} is increased, on the contrary, in higher pH levels, the increase in hydroxyl ions concentration within the medium favors the Fe^{3+} precipitation (KARTHIKEYAN et al., 2011).

Figure 3.3a), their random distribution between the predicted values (

The 3-D response surfaces shown in Figure 3.4 can be used to better understand the effects of the independent variables (C:H_2O_2, Fe:H_2O_2 and pH) on the COD removal. In Figure 3.4a, where the effect of C:H_2O_2 and pH were assessed, higher COD removal are attained at the lower level for pH (-1, pH 3.4) and central level for C: H_2O_2 (0, 1:2.125). One aspect that may have led the increase in COD removal in lower pH levels is that the Fe^{3+} is increased, on the contrary, in higher pH levels, the increase in

hydroxyl ions concentration within the medium favors the Fe^{3+} precipitation (KARTHIKEYAN et al., 2011).

Figure 3.3b) and each experiment (

The 3-D response surfaces shown in Figure 3.4 can be used to better understand the effects of the independent variables (C:H_2O_2, Fe:H_2O_2 and pH) on the COD removal. In Figure 3.4a, where the effect of C:H_2O_2 and pH were assessed, higher COD removal are attained at the lower level for pH (-1, pH 3.4) and central level for C: H_2O_2 (0, 1:2.125). One aspect that may have led the increase in COD removal in lower pH levels is that the Fe^{3+} is increased, on the contrary, in higher pH levels, the increase in hydroxyl ions concentration within the medium favors the Fe^{3+} precipitation (KARTHIKEYAN et al., 2011).

Figure 3.3d), preferably without outliners and constrained in between a 95% confidence interval (range: ± 4.81963), complemented by an agreement between the predicted and experimental values (

The 3-D response surfaces shown in Figure 3.4 can be used to better understand the effects of the independent variables (C:H_2O_2, Fe:H_2O_2 and pH) on the COD removal. In Figure 3.4a, where the effect of C:H_2O_2 and pH were assessed, higher COD removal are attained at the lower level for pH (-1, pH 3.4) and central level for C: H_2O_2 (0, 1:2.125). One aspect that may have led the increase in COD removal in lower pH levels is that the Fe^{3+} is increased, on the contrary, in higher pH levels, the increase in hydroxyl ions concentration within the medium favors the Fe^{3+} precipitation (KARTHIKEYAN et al., 2011).

Figure 3.3c). That is the case observed in Figure 3.4, which reinforces the model capability for predictive purposes and allows for the obtainment of 3D response surfaces for Fenton optimization.

$$R_{COD}(\%) = 75.24 - 1.74 \cdot A + 17.27 \cdot B - 2.21 \cdot C - 2.87 \cdot A \cdot B + 0.127 \cdot A \cdot C - 7.94 \cdot B \cdot C + 2.98 \cdot A^2 - 12.14 \cdot B^2 - 1.89 \cdot C^2 \tag{3.7}$$

Table 3.7 - Analysis of variance (ANOVA) for the quadratic model.

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	6402.54	9	711.39	240.88	< 0.001
A - $C:H_2O_2$	41.56	1	41.56	14.07	0.007
B - $Fe:H_2O_2$	4025.14	1	4025.14	1362.90	< 0.001
C - pH	66.94	1	66.94	22.67	0.002
AB	66.12	1	66.12	22.39	0.002
AC	0.13	1	0.13	0.044	0.839
BC	504.03	1	504.03	170.67	< 0.001
A^2	100.19	1	100.19	33.92	0.001
B^2	1662.41	1	1662.41	562.89	< 0.001
C^2	40.29	1	40.29	13.64	0.007
Residual	20.67	7	2.95		
Lack of Fit	16.01	5	3.2	1.37	0.47

The 3-D response surfaces shown in Figure 3.4 can be used to better understand the effects of the independent variables ($C:H_2O_2$, $Fe:H_2O_2$ and pH) on the COD removal. In Figure 3.4a, where the effect of $C:H_2O_2$ and pH were assessed, higher COD removal are attained at the lower level for pH (-1, pH 3.4) and central level for C: H_2O_2 (0, 1:2.125). One aspect that may have led the increase in COD removal in lower pH levels is that the Fe^{3+} is increased, on the contrary, in higher pH levels, the increase in hydroxyl ions concentration within the medium favors the Fe^{3+} precipitation (KARTHIKEYAN et al., 2011).

Figure 3.3 - Residual analysis for the quadratic model chosen for describing the Fenton process. (a) Normal probability plot, (b) Externally studentized residuals; (c) Predicted and actual responses; (d) Deviation of predicted values from experimental values.

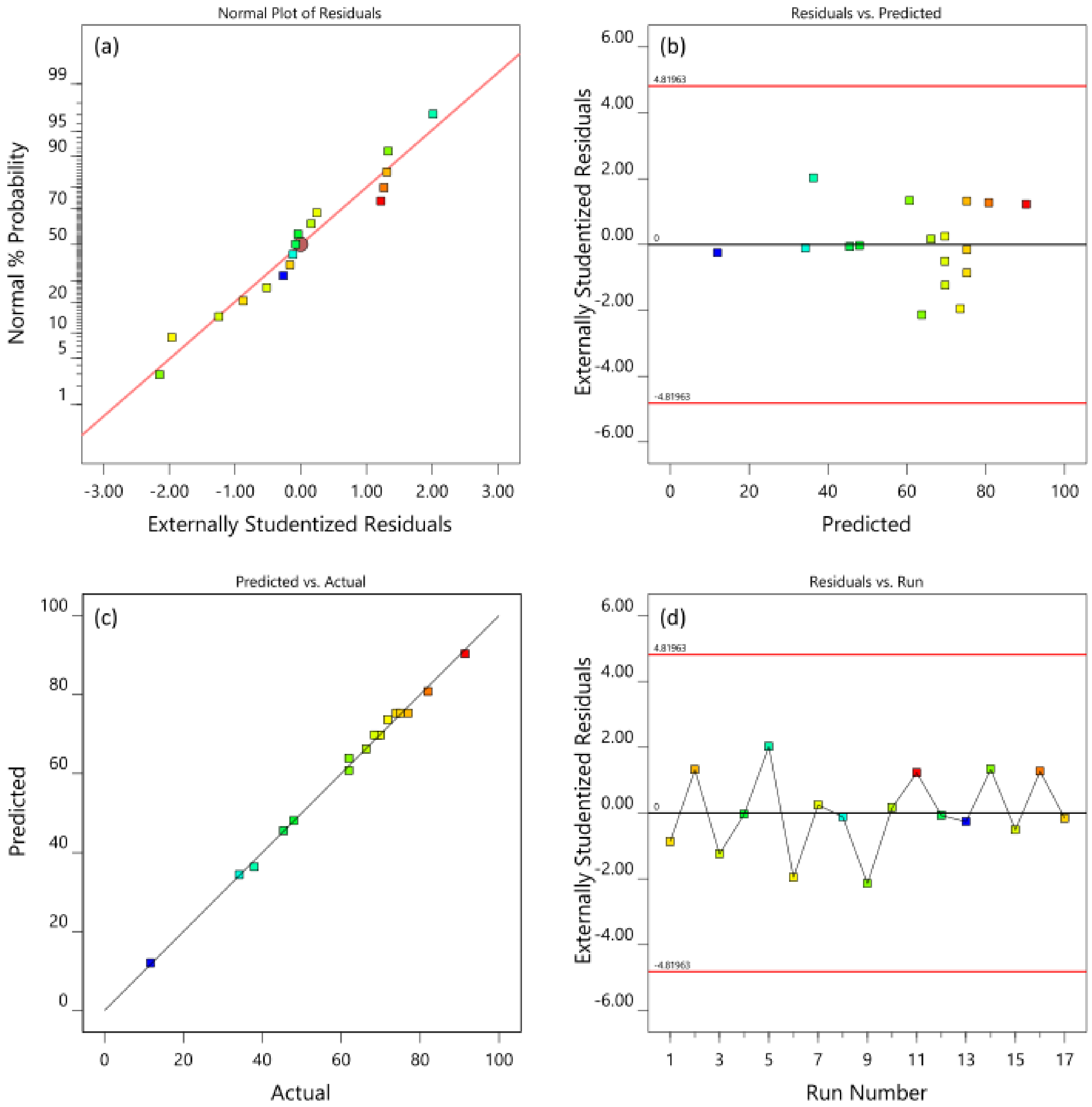
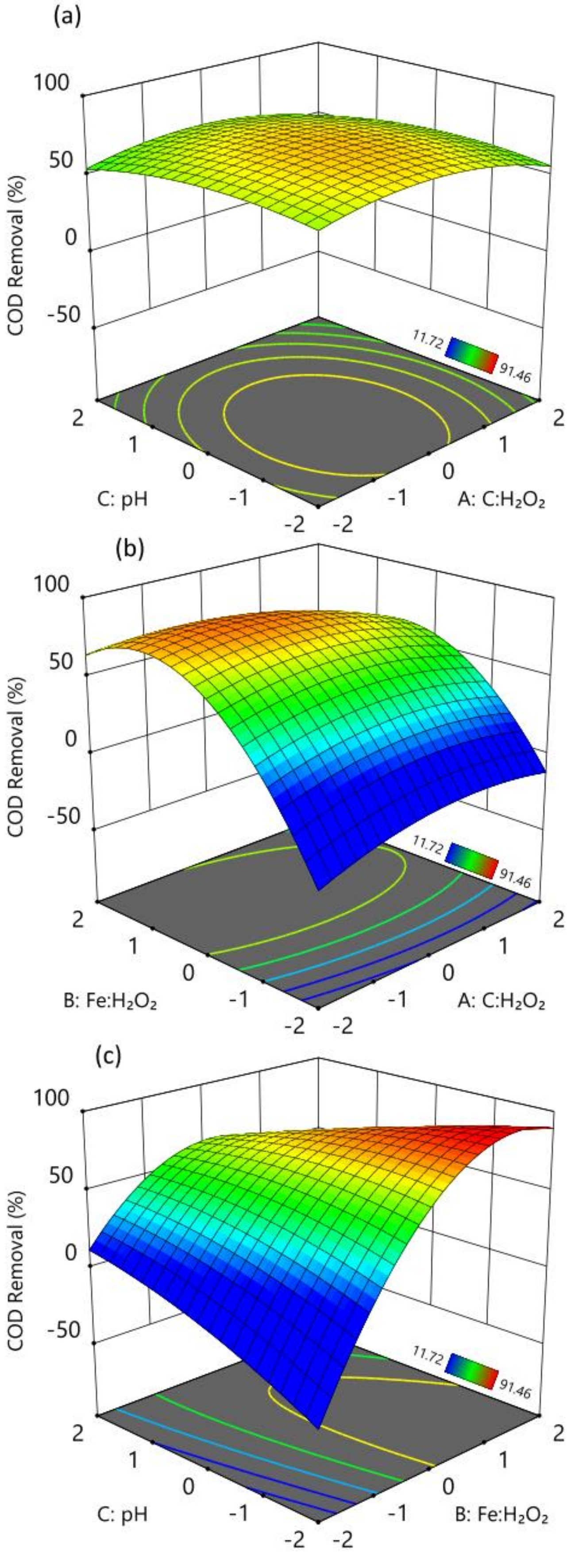


Figure 3.4 - 3D response surfaces correlating COD removal with (a) pH and C:H_2O_2; (b) Fe: H_2O_2 and C: H_2O_2; and (c) pH and Fe: H_2O_2.



The Figure 3.4b shows the relationship between Fe:H_2O_2 and C: H_2O_2 ratio, whereas the pH was fixed at its central level (pH = 4). In this case, the increase in Fe: H_2O_2 led to increase in COD removal efficiency up until the +1 level (1:8.18), from then on, an increase in the Fe: H_2O_2 led to a decrease in COD removal efficiency. According to Karthikeyan et al. (2011), the increase in H_2O_2 concentration could favor the precipitation of Fe^{3+}. Furthermore, increased concentrations of H_2O_2 could favor the $^{\bullet}OH$ scavenging, which leads to a dimerization of both hydroxyl and per hydroxyl radicals, ultimately inhibiting the COD removal (CLARIZIA et al., 2017). In addition, a higher H_2O_2 concentration may shift the chemical equilibrium towards the production of H_2O_2 rather than the hydroxyl radical (Equation 3.8). Lastly, the combined effects here discussed can be seen in Figure 3.4c, whereas lower pH levels favor the Fe^{3+} is increased and the Fe: H_2O_2 increase the $^{\bullet}OH$ radicals up until a level (+1, 1:8.18), both scenarios favoring the COD removal.

$$Fe^{2+} + H_2O_2 \leftrightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \qquad k = 76M^{-1}s^{-1} \tag{3.8}$$

It is important to note that the COD removal efficiency may have been influenced by the presence of chloride anions in MBRy permeate (4,403 mg L^{-1}, Table 3.1), which can act as $^{\bullet}OH$ scavengers (ZHANG et al., 2012) and formation of less reactive inorganic radicals ($Cl^{\bullet}$, $Cl_2^{\bullet-}$) according to Equations 3.9 to 3.12.

$$Cl^{-} + {}^{\bullet}OH \rightarrow [ClOH]^{\bullet-} \qquad k = 4.3 \cdot 10^{9}\ M^{-1}s^{-1} \tag{3.9}$$

$$[ClOH]^{\bullet-} \rightarrow Cl^{-} + {}^{\bullet}OH \qquad k = 6.0 \cdot 10^{9}\ M^{-1}s^{-1} \tag{3.10}$$

$$[ClOH]^{\bullet-} + H^{+} \rightarrow Cl^{\bullet} + H_2O \qquad k = 2.4 \cdot 10^{10} M^{-1}s^{-1} \tag{3.11}$$

$$Cl^{\bullet} + Cl^{-} \rightarrow Cl_2^{\bullet-} \qquad k = 8.5 \cdot 10^{9}\ M^{-1}s^{-1} \tag{3.12}$$

Another reasons are complexation reactions with Fe^{2+} and Fe^{3+}, which can affect the distribution and the reactivity of the iron species (Equations 3.13 to 3.15), H_2O_2 decomposition due to less reactive chloride radicals, increasing the reagent consumption (Equations 3.16 to 3.18) and oxidation reactions involving these inorganic radicals (SILVA et al., 2015).

$$Fe^{2+} + Cl^{-} \leftrightarrow FeCl^{+} \qquad k = 2.88\ M^{-1} \tag{3.13}$$

$$Fe^{3+} + Cl^{-} \leftrightarrow FeCl^{2+} \qquad k = 6.61\ M^{-1} \tag{3.14}$$

$$Fe^{3+} + 2Cl^{-} \leftrightarrow FeCl^{2+} \qquad k = 10.47\ M^{-1} \tag{3.15}$$

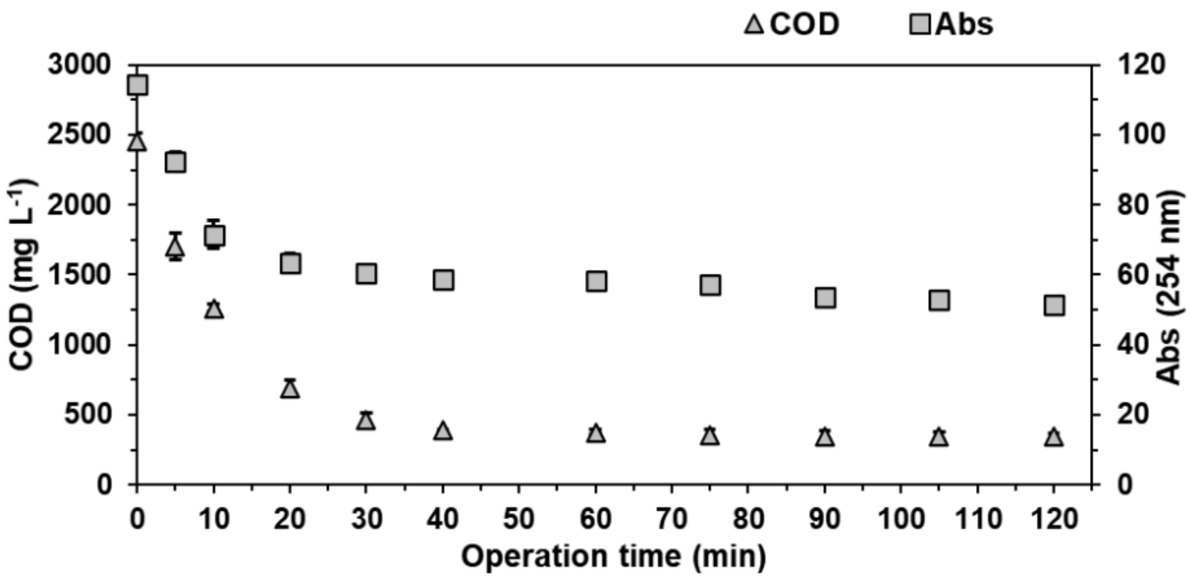
$$Cl^{\bullet} + H_2O_2 \rightarrow Cl^- + H^+ + HO_2^{\bullet} \qquad k = 1.0 \cdot 10^9\ M^{-1}s^{-1} \qquad (3.16)$$

$$Cl_2^{\bullet-} + H_2O_2 \rightarrow 2Cl^- + H^+ + HO_2^{\bullet} \qquad k = 1.0 \cdot 10^9\ M^{-1}s^{-1} \qquad (3.17)$$

$$Cl_2^{\bullet-} + HO_2^{\bullet} \rightarrow 2Cl^- + H^+ + O_2 \qquad k = 1.0 \cdot 10^9 M^{-1}s^{-1} \qquad (3.18)$$

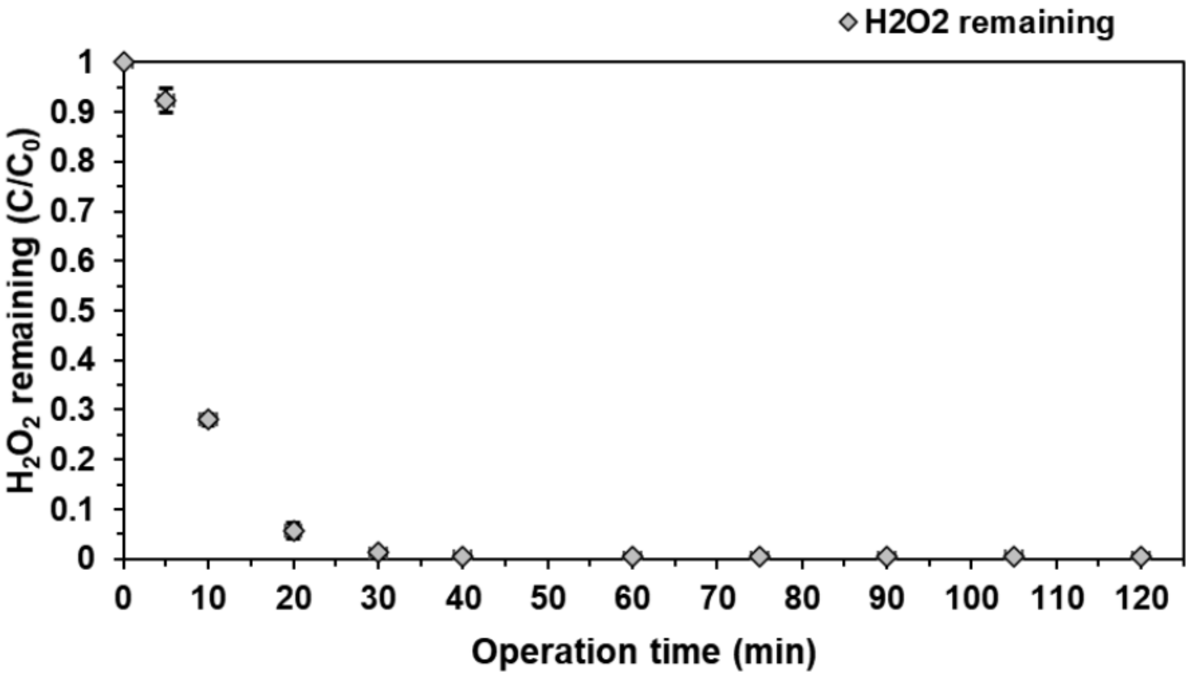
The process was finally optimized aiming for a maximum COD removal efficiency whereas the independent variables varied between their experimental range (+α, -α; Table 3.2). The optimum COD removal efficiency possible to be obtained corresponded to 85.5% for a 1:1.14 C:H_2O_2, 1:9.81 Fe: H_2O_2 and a pH 3.0. The Fenton test was performed under optimal conditions, where at the end of the reaction it was possible to obtain the COD concentration of 341 ± 31 mg L^{-1} (Figure 3.5). Absorbance at 254 nm (Abs_{254}) is a parameter that indicates the presence of complex structured organic compounds such as HS and aromatic compounds (ZHANG et al., 2013). In this study, the MBRy permeate showed Abs254 of 114 ± 1.4, with 69 ± 0.12% removal by Fenton.

Figure 3.5 - Decay curve of COD and Abs_{254} for MBRy permeate by Fenton. Conditions: pH = 3, Fe^{2+}:H_2O_2 molar ratio = 1:9.81 and C:H_2O_2 molar ratio = 1:1.14.



The residual peroxide was measured during the Fenton optimum condition test for the MBRy permeate (Figure 3.6). It can be seen that in the first 10 minutes approximately 92% of the H_2O_2 was consumed. According to Zhang et al. (2005), this means that the reaction between the ferrous ions and the H_2O_2 for the $^{\bullet}OH$ production was practically complete within 10 minutes of reaction.

Figure 3.6 - H_2O_2 remaining for MBRy permeate by Fenton. Conditions: pH = 3, Fe^{2+}: H_2O_2 molar ratio = 1:9.81 and C: H_2O_2 molar ratio = 1:1.14.



The reaction rate for the COD removal by Fenton in the optimized condition was 0.056 min^{-1} (R^2 = 0.99), following a first order kinetics model. Da Costa et al. (2018) found reaction rates of 0.009 and 0.03 min^{-1} for the leachate from the Gramacho and Seropédica landfills, respectively. The authors stated that the reaction rate was lower for Gramacho leachate because it came from an older landfill and because of the type of waste received (urban and industrial over time). In the present study, even the leachate coming from an old landfill (since 2005), because it had been submitted to a biological treatment, may have made it change the behavior of the COD removal by Fenton, increasing the reaction rate.

In this study the sludge generation by Fenton was not evaluated. Even if in Brazil the sludge generated in a leachate treatment plant is returned to the landfill (DA COSTA et al., 2018), it is relevant to evaluate both the amount of sludge generated and the study of the impact of sludge disposal on the landfill.

Even with the high COD removal achieved, it is extremely important to assess toxicity. The EC_{50} in the MBRy – Fenton effluent was 2.45, with a high toxicity (≤ 81.9%). This be associated with the fact that the oxidizing agent can contribute to the formation of toxic by-products, in addition to the residual concentration of H_2O_2 in the medium, in which in Table 3.8 it is possible to observe the increased toxicity with the Fenton application.

Table 3.8 - EC_{50} of raw LFL, MBRy permeate and MBRy-Fenton effluent.

	Raw LFL	MBRy permeate	MBRy-Fenton effluent
EC_{50}(%)	9.74 ± 0.10	65.85 ± 18.42	2.45 ± 0.57

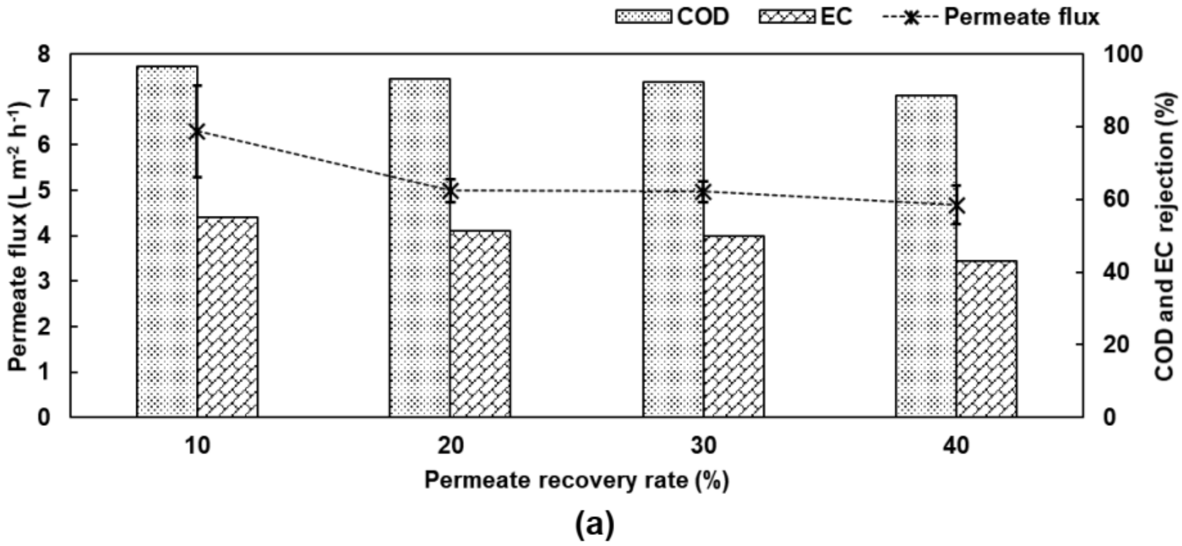
Even with the considerable organic matter removal promoted by Fenton, the effluent after the application of this process still presents high toxicity, which needs to be removed. Reis et al. (2020) obtained a 100% toxicity retention by applying NF as a polishing step of the MBRy permeate. In this sense, the stream generated under these experimental conditions were further polished by NF as will be further discussed in section 3.3.2. The same experimental conditions were also employed for NF concentrate polishing, which results are presented in section 3.3.2.

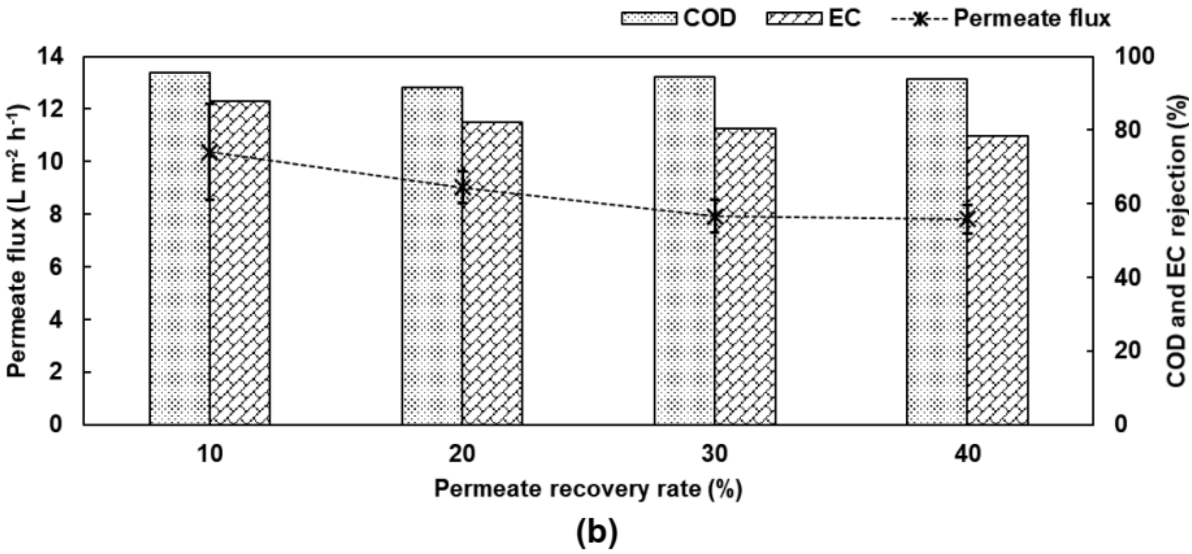
3.3.2 Nanofiltration

The nanofiltration was applied to the treatment of MBRy permeate and the effluent from Fenton process (optimal condition, topic 3.3.1). Figure 3.7 shows the COD and EC rejection and the permeate flux for NF treating both matrix.

The values for COD removal by NF were similar in the treatment of MBRy permeate (94 ± 1.7%) and MBRy – Fenton effluent (93 ± 3.3%). According to Tahiri et al. (2016), HS, fulvic acids and compounds containing carboxyl and aromatic hydroxyl groups are the major contributors for LFL organic matter. They generally have a molecular weight <1,445 Da, a value greater than molecular weight cut off the NF membrane, which contribute considerably to the COD removal efficiency by size exclusion in both routes (CHEN and LIU, 2006). Reis et al. (2017) performed the identification of compounds in the MBRy permeate treating the same leachate of the present study, and verified that the NF membrane was able to promote the retention of both persistent compounds in the MBRy (4-Chloro-2-methyl-2-butanol, N-ethyl-4-methylbenzenesulfonamide, N-butylbenzenesulfonamide) and compounds that were formed in the MBRy (2,6,10-trimethyltetradecane, bis (2-ethylhexyl) hexanedioate, 2-Methylphenyl isocyanate, phenanthrene, 2,4- dimethylquinoline) which may have contributed to the membrane fouling.

Figure 3.7 - EC, COD and permeate flux for (a) MBRy – Fenton effluent and (b) MBRy permeate. COD MBRy permeate = 2,910 mg L^{-1}. EC MBRy permeate = 20.50 mS cm^{-1}. COD MBRy – Fenton effluent = 466 mg L^{-1}. EC MBRy – Fenton effluent = 33.20 mS cm^{-1}.





The EC removal by the NF treating MBRy permeate was greater (82 ± 4.2%) than in the NF treating MBRy – Fenton effluent (50 ± 5.0%). In Fenton new ions are added to the effluent, mainly iron (Fe) and sulfate (DA SILVA et al., 2018). Thus, the lower EC removal in the MBRy – Fenton effluent is justified by the higher concentration of ions in the feed, and consequently, higher solute flow and lower rejection, since the solute flow through the membrane is proportional to the concentration of the same in the feed. This may also explain the decrease in COD and EC removal efficiencies with the increased recovery rate. As the NF concentrate is recirculated to the feed tank, the ion concentration increases over time, causing lower rejection.

According to Bellona and Drewes (2005), the isoelectric point of the NF90 membrane is 4, i.e., above this pH the membrane has a negative surface charge. Taking into consideration, the Fe and sulfate addition and the pH of the MBRy – Fenton effluent (8.86), a higher rejection for sulfate is expected because it has a negative charge, with the occurrence of an electrostatic repulsion between the membrane and the sulfate. Silva et al. (2019) found a 90% removal for this ion using the same leachate from this study. Thus, it can be inferred that less rejection may have occurred for Fe, which is positively charged, contributing to less conductivity removal in the MBRy – Fenton effluent.

According to Figure 3.7, the NF treating MBRy – Fenton effluent had a lower flux compared to the NF treating MBRy permeate. It can be inferred that the osmotic pressure was higher in the MBRy – Fenton effluent, which showed higher EC (33.20 mS cm^{-1}) compared to EC in the MBRy permeate (20.50 mS cm^{-1}). In this way, higher osmotic pressure reduces the effective pressure, and consequently, the flux reduction. The lower permeate flux of NF treating MBRyFenton effluent can be associated to the greater membrane fouling potential. In Figure 3.8, it is noted that the fouling resistance was higher for the NF treating the MBRy – Fenton effluent. As Fenton contributes new ions to the effluent, they may have contributed to increased fouling of the NF membrane. For a better comprehension of the fouling mechanisms and further discussion about the differences observed in terms of flux decay when both routes were compared, the flux data were fitted to Hermia's models and the results are shown in Table 3.9.

Figure 3.8 - Fouling resistances for MBRy-Fenton effluent and MBRy permeate.

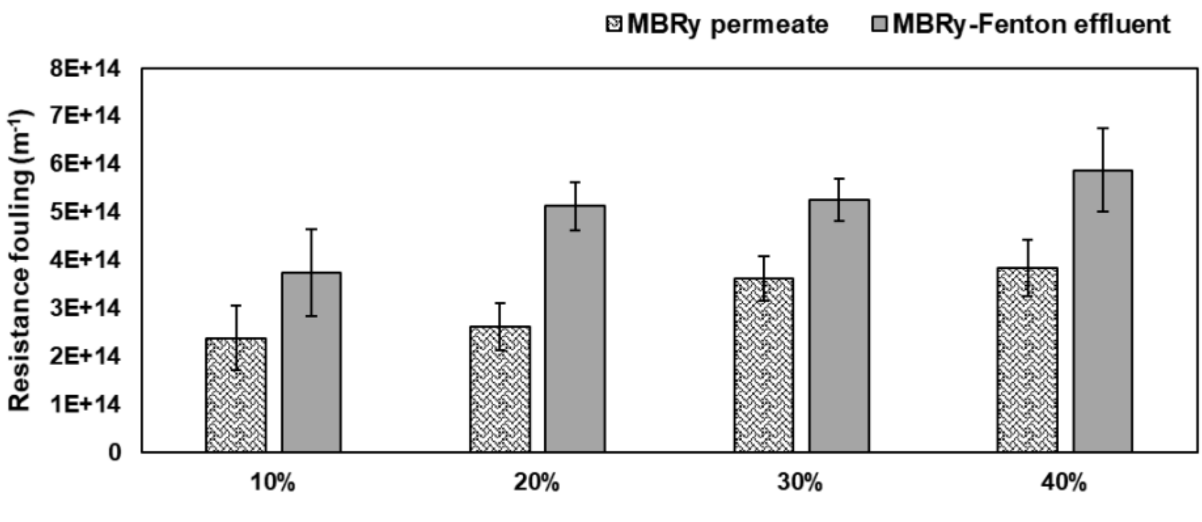


Table 3.9 - Hermia fit and parameters obtained for MBRy – Fenton effluent and MBRy permeate.

Treatment routes	Standard blocking filtration		Intermediate blocking filtration		Cake filtration		Complete blocking filtration	
	k ($m^{-0.5}min^{0.5}$)	R^2	k (m^{-1})	R^2	k (min m^{-2})	R^2	k (min^{-1})	R^2
MBRy – Fenton effluent	4.1 10^{-5}	0.907	3.55 10^{-5}	0.917	1.37 10^{-5}	0.935	1.85 10^{-4}	0.895
MBRy permeate	5.7 10^{-5}	0.947	3.85 10^{-5}	0.956	8.77 10^{-6}	0.969	3.42 10^{-4}	0.936

Table 3.10 - Removal efficiency and physico-chemical parameters for MBRy – Fenton effluent and MBRy permeate (40% recovery rate).

Treatment route		pH	Color (uH)	TOC (mg L^{-1})	TC (mg L^{-1})	TN (mg L^{-1})	Calcium (mg L^{-1})	Magnesium (mg L^{-1})
MBRy – Fenton effluent	LFL after Fenton	8.86	149.8	252.58	273.21	119.18	25	12.5
	Permeate	8.75	<1	73.60	110.50	8.15	3.21	1.40
	Concentrate	-	249.05	348.33	369.69	193.6	39.7	20.0
	Rejection (%)	-	>99.9	70.9	59.5	93.2	>87.16	>88.8
MBRy permeate	LFL after MBRy	8.82	8,816	1,003	1,041	293	77.11	68.08
	Permeate	7.94	39.33	36.90	114.86	52.78	2.50	10.05
	$Rejection_{MBRy\ permeate}$(%)	-	99.6	96.3	88.9	82.0	>96.8	85.2
	Concentrate from NF treating MBRy permeate	9.12	11,160	1,558.20	1,964.66	442.8	125.94	154.86
	Concentrate from NF after Fenton	-	258.67	139.04	160.22	81.59	5.49	35.37
	$Removal_{Fenton(NF\ concentrate)}$ (%)	-	97.7	91.1	91.8	81.6	95.7	77.2

The cake filtration and intermediate blocking filtration were the ones with the best fit in both MBRy – Fenton effluent and MBRy permeate (higher R2 values). According to CorbatónBáguena et al. (2015), the intermediate blocking model describes a fouling mechanism based on solutes settling over those already deposited onto the membrane surface, whereas the cake filtration occurs due to the deposition and accumulation of molecules larger than the membrane pores onto its surface. Complementarily, higher *k* values in the Hermia model suggests a higher obstruction of the membrane. From that, according to Table 3.9 and considering the models that obtained greater adjustments, the *k* value is higher for the MBRy-Fenton effluent, which may justify the lower flux in Figure 3.7.

The fouling layer formed by MBRy – Fenton effluent and MBRy permeate was composed of organic and inorganic compounds. However, it is suggested that the fouling layer of the MBRy – Fenton effluent had a higher contribution of inorganic compounds since the organic matter concentration in this stream is six lower than in the MBRy permeate, besides the increase of Fe and sulfate in the effluent. Jarusutthirak et al. (2007) verified that sulfate promotes the NF membrane fouling, causing the flux decline. Hiemstra et al. (1999) found that both Fe^{2+} and Fe^{3+} cause incrustation in the NF membrane, impairing the performance of the process due to the flux decline. Regarding the MBRy permeate, the composition of the fouling layer had a higher organic contribution. Furthermore, the presence of divalent ions (like Ca^{2+} and Mg^{2+}) could have promoted the natural organic matter (NOM) aggregation, leading to an additional contribution to a cake layer formation (SONG et al., 2020b). It should be noted that the LFL has NOM in the form of HS, a parameter that is directly associated with the presence of color in this effluent (MORAVIA et al., 2013). Since the MBRy did not achieved a complete color removal (8,816 mg L^{-1}, MBRy permeate), and consequently, HS, it is reasonable to assume that cake layer in the MBRy permeate may have formed through the NOM agglomeration, favored by the presence of Ca^{2+} and Mg^{2+}. According to Table 3.10, the concentration of Ca^{2+} and Mg^{2+} after MBRy was 77.11 and 68.08 mg L^{-1}, respectively.

An additional contribution flux decline and membranes pore blockage may be due to byproducts formation during the Fenton process, which would have a lower molecular weight, and therefore would penetrate the membrane more easily (LEBRON et al., 2021). Concomitant to this, Yu et al. (2018) stated that the organic matter degradation can result either in byproducts of size similar to the NF membrane MCWO, or substantially different, which can cause different fouling behavior. Zhu et al. (2010) applied ozonation prior to a NF process in domestic effluent, and observed an increase in phenolic and carboxylic groups, which may have aggravated the NF membrane fouling.

It is noted from Table 3.10 that the NF is capable to generate a high quality permeate regardless of the feed physico-chemical composition (MBRy – Fenton effluent or MBRy permeate), achieving high removal efficiencies for the parameters analyzed. The high color removal for both routes (>99%) can be justified due to its relationship with HS and their retention in the membrane. The removal of TN was higher in the MBRy – Fenton effluent (93.2%), which can be explained by a possible blockage of the membrane pores by the molecules of lower molecular weight obtained after the Fenton, which would serve as an additional barrier to the passage of nitrogen molecules. In addition, the Fenton process changes the speciation of nitrogen species, converting mainly to nitrate (ZOH and STENSTROM, 2002). The cake formed by the MBRy – Fenton effluent may also have contributed to the TN removal, promoting the adsorption of nitrate. Reis et al. (2020) found lower values for TN removal (60%) in a MBRy – NF treatment LFL, which reinforces the idea that the application of the Fenton process previously to NF favored a greater removal rate of TN. It is also observed that the Ca^{2+} and Mg^{2+} removal was high, demonstrating the efficiency of the NF membrane in the retention of these ions.

The investigation of strategies capable to effectively treat the NF concentrate becomes evident after an analysis of its physico-chemical characteristics (Table 3.10 and Table 3.11). The concentrate stream is characterized by a higher pollutant concentration. The NF promotes the recalcitrant and inert substances concentration. Long et al. (2017) reported values of COD, TOC and EC of 4,135 mg L^{-1}, 1,440 mg L^{-1} and 25.3 mS cm^{-1}, respectively, in the NF concentrate after LFL was treated by MBR. These concentration values are close to those obtained for the NF concentrate in the present study. It is observed that the concentrate generated in MBRy – Fenton effluent and MBRy permeate are distinct, since the first has lower concentration of the evaluated parameters due to the Fenton application. Moreover, the COD concentration for these integrations are 593.42 and 3,555.82 mg L^{-1}, respectively. This demonstrates the importance of the treatment of NF concentrate by MBRy permeate, since its recirculation to the landfill cells can lead to problems such as a change in the characteristic of the leachate generated and the membranes performance of the treatment system (KEYIKOGLU et al., 2020).

Fenton was applied in the concentrate treatment which was performed with the MBRy permeate. The Fenton efficiency for the concentrate treatment was considered satisfactory since the initial concentrations for all parameters were reduced, with an emphasis on color, TOC and TC removal, which were greater than 90% (Table 3.10). The process also showed a high removal efficiency for COD, as well as for TOC and TC (Table 3.10 and Table 3.11). He et al. (2015) obtained a COD removal of 63.5% at pH 3, H_2O_2: 65.43 mM and Fe^{2+}: 7.27 mM treating concentrated LFL. Teng et al. (2020) treated a NF concentrate treating a MBR permeate employed for LFL treatment and obtained a COD removal of 78.9% at pH 3, H_2O_2: 45 mM and Fe^{2+}: 15 mM. It is observed that the COD removal in the present study (87.24%) was greater than the removals found in these studies. Although the experimental pH was the same (pH = 3), the H_2O_2 and Fe^{2+} concentrations were different (95 and 9.7 mM, respectively), demonstrating that for the leachate concentrate in question, the highest doses of H_2O_2 favored a greater removal of organic matter. The concentration of Fe and H_2O_2 required in a given effluent treatment depends on its physico-chemical composition. Even though the CCD was not performed with the NF concentrate, the optimized variables still contributed to a high removal efficiency of COD.

Table 3.11 - EC and COD of the concentrate of NF treating MBRy permeate by Fenton.

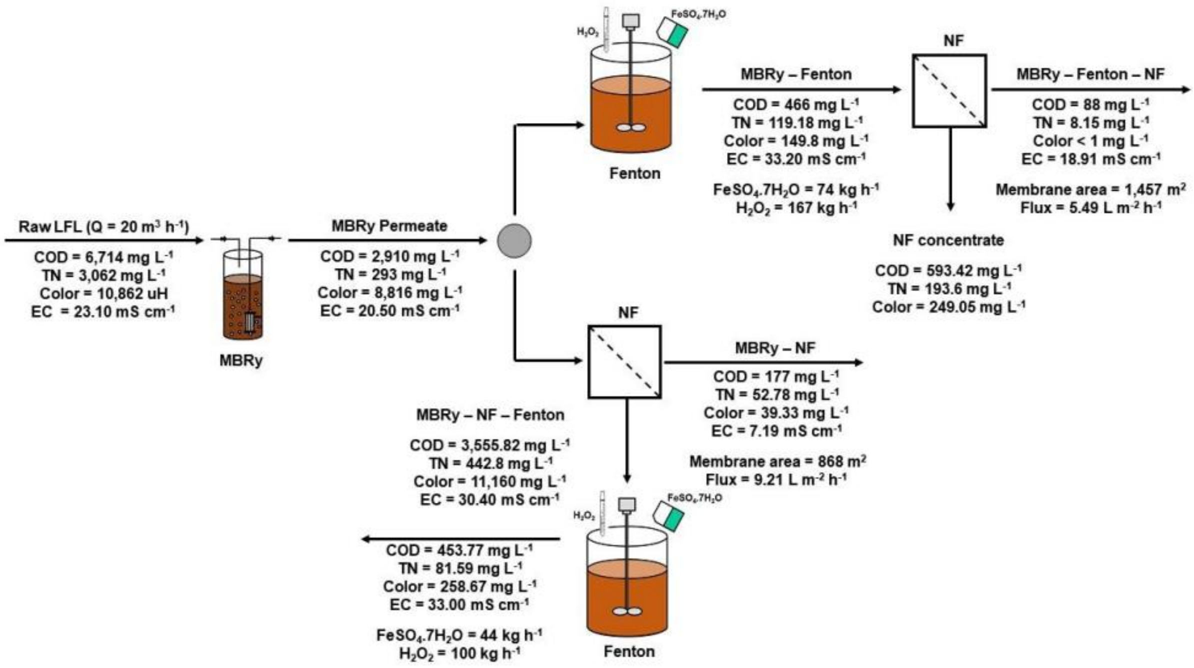
Parameter	**Inicial**	**Final**	**Removal (%)**
Conductivity (mS cm^{-1})	30.40	33.00	-
COD (mg L^{-1})	3,555.82	453.77	87.24

From that, it is noted that the integration way of Fenton and NF processes has implications for the flux, permeate and concentrate quality.

3.3.3 How to integrate the processes?

The NF application for MBRy permeate and MBRy – Fenton effluent showed that both integrations behaved in different ways with respect to compound removal and membrane fouling. For selection of the best integration to subsidize leachate treatment systems in landfills, it is necessary to take into consideration both technical and economic aspects. Figure 3.9 presents a flow chart with the proposed integrations with the current concentrations, chemical dosage and membrane area required.

Figure 3.9 - Flowchart of the proposed routes.



COD and color removal by Fenton were considered high (90%), which suggests that this was an efficient process for the degradation of refractory compounds. It was also verified a high removal for these parameters by the NF in the MBRy – Fenton effluent and MBRy permeate, evidencing that the NF is adequate for effluent polishing. In terms of overall removal efficiency (NF permeate), both routes have achieved removals greater than 97% for COD, TN and color. The final COD concentrations in the NF permeate reached the parameter required by the current legislation (COPAM, 2008) on the investigated routes, with 88 mg L^{-1} for MBRy-Fenton effluent and 177 mg L^{-1} for MBRy permeate.

The final concentrations of COD indicate that the treated LFL can be reused. In Brazil there is no specific legislation establishing standards and parameters for water reuse. One of the uses of the treated effluent in the landfill plant can be for dust arrestment, in earthworks and in construction site works. Sautchuk et al. (2005) suggest that the standards for this reuse are fecal coliforms ≤ 1000 mL^{-1}, pH between 6 and 9, unpleasant odor and appearance, oils and greases ≤1 mg L^{-1}, biochemical oxygen demand (BOD) ≤30 mg L^{-1}, absence of volatile organic compounds (VOC), and TSS ≤ 30 mg L^{-1}. The pH meets the required range for both routes. Even if the oil and grease and fecal coliform (CF) concentration has not been measured, there is no record of significant oil and grease presence in the LFL, and it is expected that the NF membrane has been able to retain CF (ACERO et al., 2010). Likewise, although the BOD, VOC and TSS concentrations were not measured in the NF permeate, according to the DOC results obtained and taking into consideration the capacity of solids retention by the membrane, it is inferred that the standards were achieved for reuse.

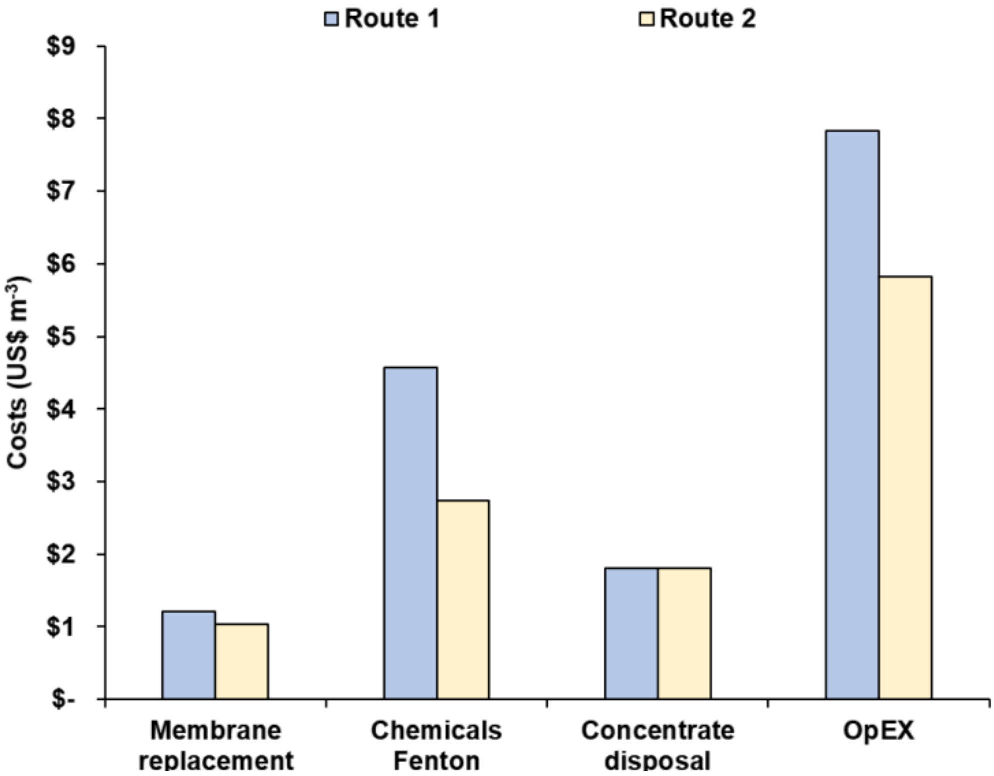
With respect to the leachate quality in the concentrated compartment, the COD concentration obtained by MBRy – Fenton effluent was 593.42 mg L^{-1}. In the Fenton treated concentrated compartment (MBRy permeate) the COD concentration was 453.77 mg L^{-1}. The COD concentration of NF concentrated leachate varies between 1,100 and 6,800 mg L^{-1} (KEYIKOGLU et al., 2020). Even if the COD concentrations found in this study are relatively far from this range, it is difficult to state that in these concentrations there would be no changes in the physico-chemical composition of the leachate if the concentrate were recirculated to the landfill cells. However, as the COD concentration and the volume to be recirculated are lower reduced changes can be observed both in the characteristic of the leachate and in the existing treatment system in the landfill.

Considering that both integrations were able to reach the limits established by legislation, which can be reused, and that the final concentrate has similar characteristics, a preliminary economic analysis was carried out to support the choice of the best integration.

The preliminary economic results were summarized in Figure 3.10 and Figure 3.11. The MBRy – Fenton – NF had a higher OpEX (7.83 US$ m^{-3}) in comparison with the MBRy-NFFenton$_{(concentrate)}$ (5.83 US$ m^{-3}). The factors that led to the higher OpEX in the MBRy – Fenton – NF effluent was the greater contributions from the chemicals required by Fenton (4.57 US$ m^{-3}; 58% of the total OpEX) (Figure 3.10). On the other hand, when Fenton was applied to the NF concentrate, the lower volume to be treated implied in a lower chemical requirement (Figure 3.11).

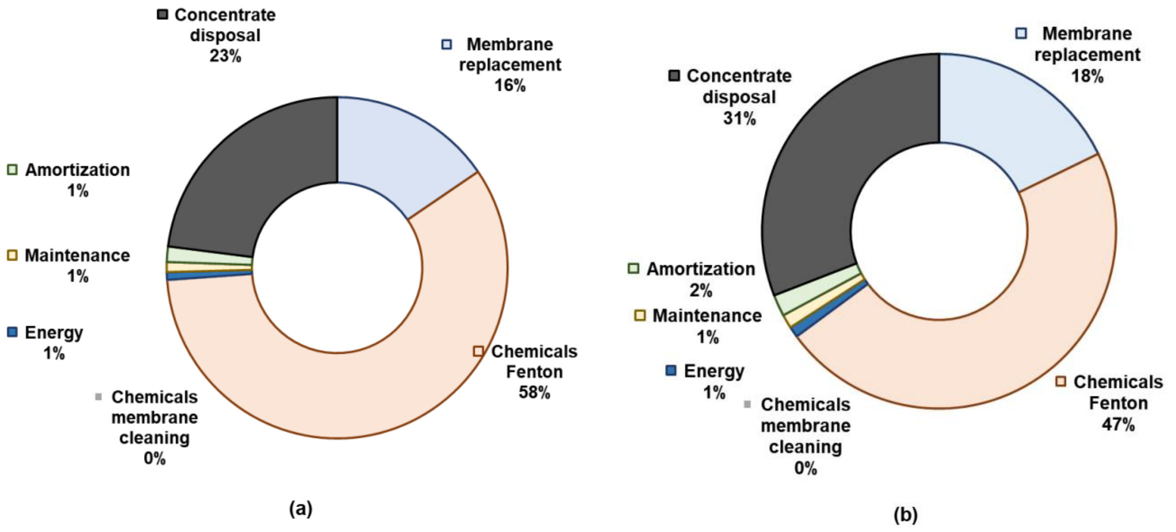
For a given treatment capacity, the MBRy – Fenton – NF integration would still have a greater demand for NF membrane area given its lower permeate flux. This was also a contributor to the higher operating costs for this integration, since the expenses related to the membrane replacement would be higher.

Figure 3.10 - Costs for MBRy – Fenton – NF (Route 1) and MBRy – NF – Fenton$_{(concentrate)}$ (Route 2).



Considering the technical and economic aspects, it is observed that the best integration for the MBRy polishing is through its treatment by NF with Fenton concentrate treatment, due to the lower cost of reagents, smaller membrane area required, and also by the final effluent (NF permeate) reaching the limits established by COPAM (2008) and being suitable for reuse.

Figure 3.11 - OpEX distribution for a) MBRy – Fenton – NF and b) MBRy – NF – Fenton$_{(concentrate)}$.



3.4 Conclusions

The MBRy – Fenton effluent treatment by NF was efficient in removing organic matter and color, reaching removals of 93 and >99%, respectively. The removal efficiencies for these parameters were similar to the MBRy permeate treatment. Although the final COD concentration in the MBRy – Fenton effluent treatment (88 mg L^{-1}) was different in the MBRy permeate treatment (177 mg L^{-1}), both were able to meet the discharge limits for COD. The NF permeate represents a good alternative for water reuse within the landfill plant for dust arrestment, earthworks and in construction sites.

The NF concentrated compartment treatment by Fenton (MBRy – NF – Fenton(concentrate)) promoted 87% of COD removal. Although it is not possible to state that in the COD concentration reached (453.77 mg L^{-1}) no changes in the physico-chemical composition of the leachate would be observed if the treated concentrate were recirculated to the landfill cells, it can be inferred that the observed changes would be reduced since the COD concentration and the volume to be recirculated are smaller.

The preliminary cost analysis of the proposed integrations showed that the treatment of MBRy permeate by NF with Fenton concentrate treatment is more advantageous due to the lower requirement with chemical reagents and membrane area. In this way, considering the final effluent reaches the limits established by the legislation, besides being able to be reused, it can be stated that this route presents itself as an alternative for the treatment of leachate in landfills.

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4 CHAPTER 4: FINAL CONSIDERATIONS

The integration of AS/AB, MBRy, NF and Fenton processes allowed the landfill leachate to reach the limits established by COPAM (2008), besides the ammonia recovery as fertilizer (ammonium sulphate), and effluent reuse.

Regarding the MBRy performance, higher removals of organic matter in terms of COD (71 ± 4%) and ammonia (97 ± 3%) were observed in higher COD/N ratio. In addition, the growth of yeasts was verified even under adverse conditions (lower COD/N ratio).

The results of ammonia removal and recovery, and economic analysis demonstrated that the best way to integrate the AS/AB processes is as pre-treatment of MBRy. The ammonia concentration in the AS/AB process feed was a key factor to achieve the market specification. The route AS/AB – MBRy allowed recovery 7 kg of ammonia per m^3 of treated leachate. However, the final COD concentration reached (2,902 ± 374 mg L^{-1}) did not reach the limit specified by the legislation (COD < 180 mg L^{-1}), and a polishing step is required.

Both the polishing of the MBRy permeate by Fenton – NF and NF – Fenton allowed the effluent to reach a final COD concentration of 88 mg L^{-1} and 177 mg L^{-1}, respectively, meeting the limit established by legislation. The NF permeate represents a good alternative for water reuse within the landfill plant for dust arrestment, earthworks and in construction sites.

With the preliminary economic analysis, it was observed that the MBRy – NF – $Fenton_{(concentrate)}$ route presented the lowest costs due to the smaller membrane area required and the lower requirement with chemical reagents. Therefore, taking into consideration the technical and economic aspects, the MBRy – NF – $Fenton_{(concentrate)}$ route presents itself as an alternative to subsidize the design of the leachate treatment system in landfills, since the growth in the use of MBR and NF for the treatment of this effluent has been observed.