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Master in Chemical Engineering

## **Optimization of Wastewater Quality in the Sines Refinery**

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## **Optimization of wastewater quality in Sines Refinery**

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*Life is like a marathon...*

*It doesn't matter how it starts, but how it ends!*

Carlos Santos



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# Abstract

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In order to address and resolve the wastewater contamination problem of the Sines refinery with the main objective of optimizing the quality of this stream and reducing the costs charged to the refinery, a dynamic mass balance was developed and implemented for ammonia and polar oil and grease (O&G) contamination in the wastewater circuit.

The inadequate routing of sour gas from the sour water stripping unit and the kerosene caustic washing unit, were identified respectively as the major source of ammonia and polar substances present in the industrial wastewater effluent. For the O&G content, a predictive model was developed for the kerosene caustic washing unit, following the Projection to Latent Structures (PLS) approach. Comparison between analytical data for ammonia and polar O&G concentrations in refinery wastewater originating from the Dissolved Air Flotation (DAF) effluent and the model predictions of the dynamic mass balance calculations are in a very good agreement and highlights the dominant impact of the identified streams for the wastewater contamination levels. The ammonia contamination problem was solved by rerouting the sour gas through an existing clogged line with ammonia salts due to a non-insulated line section, while for the O&G a dynamic mass balance was implemented as an online tool, which allows for prevision of possible contamination situations and taking the required preventive actions, and can also serve as a basis for establishing relationships between the O&G contamination in the refinery wastewater with the properties of the refined crude oils and the process operating conditions. The PLS model developed could be of great asset in both optimizing the existing and designing new refinery wastewater treatment units or reuse schemes.

In order to find a possible treatment solution for the spent caustic problem, an on-site pilot plant experiments for NaOH recovery from the

refinery kerosene caustic washing unit effluent using an alkaline-resistant nanofiltration (NF) polymeric membrane were performed in order to evaluate its applicability for treating these highly alkaline and contaminated streams. For a constant operating pressure and temperature and adequate operating conditions, 99.9% of oil and grease rejection and 97.7% of chemical oxygen demand (COD) rejection were observed. No noticeable membrane fouling or flux decrease were registered until a volume concentration factor of 3. These results allow for NF permeate reuse instead of fresh caustic and for significant reduction of the wastewater contamination, which can result in savings of 1.5 M€ per year at the current prices for the largest Portuguese oil refinery. The capital investments needed for implementation of the required NF membrane system are less than 10% of those associated with the traditional wet air oxidation solution of the spent caustic problem. The operating costs are very similar, but can be less than half if reusing the NF concentrate in refinery pH control applications. The payback period was estimated to be 1.1 years. Overall, the pilot plant experimental results obtained and the process economic evaluation data indicate a very competitive solution through the proposed NF treatment process, which represents a highly promising alternative to conventional and existing spent caustic treatment units.

An alternative wastewater treatment solution for contamination by O&G was tested by employing a spent catalyst from a FCC industrial unit. The wastewater and catalyst were contacted in different ratios and in reactors of different configurations. The results indicated that the treatment of the wastewater in an arrangement with a fluidized catalyst bed with air in countercurrent with wastewater results in a reduction of more than 90% of the initial soluble O&G compounds. The results also indicated that the decontamination process occurs by a catalytic process rendering the proposed treatment a more valuable alternative to the use of activated carbon or other adsorbents.

**Keywords:** Petroleum refinery; Refinery wastewater; Oil and Grease (O&G); Ammonia; Spent caustic; PLS modeling; Nanofiltration; FCC catalyst; Zeolite

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## Resumo

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A otimização da qualidade das águas residuais da Refinaria de Sines tinha como principal objetivo reduzir os custos cobrados pela Estação de Tratamento de Águas Residuais pela descarga de efluente contaminado. Com essa motivação um balanço de massa dinâmico foi implementado para os teores de amónia e óleos polares no circuito de águas residuais.

O encaminhamento do gás ácido obtido nas unidades de *stripping* de águas ácidas e o efluente produzido na unidade de lavagem cáustica do querosene, ou petróleo, foram identificados, respetivamente, como as principais fontes de amónia e de substâncias polares no efluente dado que eram descarregados no sistema de águas residuais da refinaria. Para os óleos e gorduras um modelo preditivo foi desenvolvido para a unidade de lavagem cáustica do queroseno, seguindo a metodologia de Projeção para Estruturas Latentes (PLS). A comparação entre os dados analíticos para a amónia e óleos polares no efluente da unidade flotação (DAF) e as previsões dos balanços de massa dinâmicos demonstraram uma correspondência bastante elevada, destacando o impacto dominante dos fluxos identificados para os níveis de contaminação de águas residuais. A contaminação do efluente com amónia foi resolvida através do encaminhamento do gás ácido por meio de uma linha existente, colmatada com sais amoniacais devido a uma seção de linha não isolada, enquanto que para o teor de óleos um balanço de massa dinâmico foi implementado, servindo como uma ferramenta on-line, que permite a previsão de possíveis situações de contaminação e tomar as medidas preventivas necessárias. Pode igualmente servir como uma base para o estabelecimento de relações entre a contaminação do efluente com óleos e as propriedades dos crudes refinados e as condições operacionais do processo. O modelo PLS desenvolvido apresenta-se como uma ferramenta importante, tanto para

otimizar as unidades de tratamento de águas residuais existentes como para permitir uma adequada projeção de novos sistemas ou sistemas de reutilização.

Com o objetivo de encontrar uma solução possível para o tratamento da soda exausta, foi realizado um teste através de uma planta piloto para recuperação de NaOH da unidade de lavagem cáustica do petróleo, usando uma membrana de nanofiltração, polimérica e alcalino-resistente. Para uma pressão de operação constante e temperatura e condições operacionais adequadas, observou-se uma taxa de rejeição de óleos de 99,9% e uma taxa de rejeição de 97,7% para a Carência Química de Oxigénio. Não se observou *fouling* ou diminuição de fluxo até um fator de concentração volumétrica de 3. Estes resultados permitem a reutilização do permeado ao invés de utilização de soda cáustica fresca e antecipam uma significativa redução da contaminação das águas residuais, o que pode resultar numa economia de 1,5 M € por ano a preços correntes. O capital necessário para um sistema de membrana de NF são inferiores a 10% relativamente à solução tradicional através de oxidação térmica com ar. Os custos operacionais são muito semelhantes, mas podem ser otimizados e reduzidos a menos de metade através da reutilização do concentrado em aplicações de controlo de pH na refinaria. O período de retorno é de 1,1 anos. No geral, os resultados obtidos na unidade piloto e os dados de avaliação económica do processo indicam uma solução muito competitiva por meio do processo de tratamento com membranas de NF proposto, o que representa uma alternativa altamente promissora face às unidades de tratamento de sodas exaustas convencionais que representam custos de investimento superiores.

Foi igualmente testada uma segunda solução de tratamento para a contaminação com óleos polares no efluente, através da utilização de catalisador gasto de uma unidade industrial FCC. A água residual e o catalisador foram contactados em diferentes proporções e em reatores de diferentes configurações. Os resultados indicam que o tratamento das águas

residuais, com um reator de leito fluidizado e injeção de ar em contra-corrente com as águas residuais a tratar apresenta uma redução de mais de 90% dos óleos solúveis. Os resultados também indicam que o processo de descontaminação ocorre por um processo catalítico pelo que o tratamento proposto apresenta-se como uma alternativa à utilização de carvão ativado ou outros adsorventes.

**Palavras-chave:** Refinaria; Água residual industrial; Óleos e Gorduras; Amónia; Soda Exausta; Modelos PLS; Nanofiltração; Catalisador de FCC; Zeólitos

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# Contents

<b>1.</b>	<b>INTRODUCTION .....</b>	<b>- 1 -</b>
1.1.	WORK MOTIVATION AND OBJECTIVES.....	- 1 -
1.2.	THESIS STRUCTURE.....	- 2 -
1.3.	CRUDE OIL REFINING PROCESS .....	- 4 -
1.4.	SINES REFINERY WASTEWATER CIRCUIT .....	- 7 -
1.5.	WASTEWATER CHARGES.....	- 10 -
<b>2.</b>	<b>CONTAMINANTS IDENTIFICATION .....</b>	<b>- 15 -</b>
2.1.	OIL AND GREASE.....	- 15 -
2.2.	AMMONIA .....	- 23 -
<b>3.</b>	<b>PREDICTION OF POLAR OIL AND GREASE CONTAMINATION LEVELS IN REFINERY WASTEWATER THROUGH MULTIVARIATE STATISTICAL MODELING .</b>	<b>- 37 -</b>
3.1.	INTRODUCTION .....	- 37 -
3.2.	MATERIALS AND METHODS .....	- 40 -
3.3.	RESULTS AND DISCUSSION .....	- 45 -
<b>4.</b>	<b>AN ON-SITE PILOT SCALE RECOVERY OF PETROLEUM REFINERY SPENT CAUSTICS BY NANOFILTRATION: PROCESS VALIDATION AND ECONOMIC EVALUATION .....</b>	<b>- 55 -</b>
4.1.	INTRODUCTION .....	- 55 -
4.2.	MATERIALS AND METHODS .....	- 58 -
4.3.	RESULTS AND DISCUSSION .....	- 62 -
<b>5.</b>	<b>SOLUBLE OIL AND GREASE REMOVAL OF PETROLEUM REFINERY WASTEWATER USING SPENT FCC CATALYST .....</b>	<b>- 75 -</b>
5.1.	INTRODUCTION .....	- 75 -
5.2.	MATERIALS AND METHODS .....	- 76 -
5.3.	RESULTS AND DISCUSSION .....	- 79 -
<b>6.</b>	<b>CONCLUSIONS AND FUTURE WORK.....</b>	<b>- 87 -</b>



# Figures list

FIGURE 1. 1 – CRUDE DESALINATION UNIT SCHEME [4].....	- 5 -
FIGURE 1. 2 – WASTEWATER TREATMENT COSTS CHARGED BY EXTERNAL WWTP.....	- 12 -
FIGURE 1. 3 – NUMBER OF OCCURRENCES OF CLASS 5 IN THE WASTEWATER BY PARAMETER.....	- 12 -
FIGURE 1. 4 – NUMBER OF OCCURRENCES OF PENALIZATIONS IN THE WASTEWATER BY PARAMETER.....	- 13 -
FIGURE 2. 1 – SCHEMATIC REPRESENTATION OF WASTEWATER CIRCUIT IN THE LARGEST PORTUGUESE OIL REFINERY, WITH IDENTIFICATION OF SAMPLE COLLECTION POINTS FOR O&G ANALYSIS.....	- 17 -
FIGURE 2. 2 – HYDROCARBON AND SOLUBLE OIL CONCENTRATION IN THE DISCHARGE POINT FOR THE EXTERNAL WWTP BETWEEN 2010 AND 2012.....	- 19 -
FIGURE 2. 3 – AVERAGE POLAR O&G MASS FLOW RATE CONTRIBUTION OF DIFFERENT EMISSION POINTS FOR O&G WASTEWATER CONTAMINATION AT THE DISCHARGE POINT FOR EXTERNAL WWTP.....	- 20 -
FIGURE 2. 4 – SCHEMATIC REPRESENTATION OF SOUR WATER STRIPPER (SWS) [3].....	- 23 -
FIGURE 2. 5 – SCHEMATIC REPRESENTATION OF WASTEWATER CIRCUIT IN THE LARGEST PORTUGUESE OIL REFINERY, WITH IDENTIFICATION OF SAMPLE COLLECTION POINTS FOR AMMONIA ANALYSIS.....	- 25 -
FIGURE 2. 6 – AVERAGE MASS CONTRIBUTION OF DIFFERENT EMISSION POINTS FOR AMMONIA WASTEWATER CONTAMINATION AT THE DISCHARGE POINT FOR THE EXTERNAL WWTP.....	- 26 -
FIGURE 2. 7 – AVERAGE MASS CONTRIBUTION OF SLOP OIL, DIESEL AND CRUDE OIL TANKS FOR AMMONIA WASTEWATER CONTAMINATION AT THE OIL SEPARATOR FOR CRUDE OIL TANK AREA.....	- 28 -
FIGURE 2. 8 – AMMONIA MASS BALANCE ESTIMATION COMPARED WITH ANALYTICAL RESULT AT THE DISCHARGE POINT FOR EXTERNAL WWTP DURING NOVEMBER 2011.....	- 29 -
FIGURE 2. 9 – MASS CONTRIBUTIONS OF DESALTER EFFLUENT, SLOP OIL TANK BOTTOMS AND OTHER EMISSION POINTS FOR THE ESTIMATED AMMONIA VALUE AT THE DISCHARGE POINT FOR EXTERNAL WWTP IN NOVEMBER 2011.....	- 30 -
FIGURE 2. 10 – SIMPLIFIED SCHEME OF A FLARE SYSTEM [25].....	- 31 -
FIGURE 2. 11 – COMPARISON BETWEEN SLOP OIL FLOW ESTIMATION AND TANK INVENTORY VARIATIONS IN DECEMBER 2011.....	- 32 -
FIGURE 2. 12 – VOLUMETRIC CONTRIBUTIONS TO SLOP OIL FLOW ESTIMATIONS OF DIFFERENT SOURCES UPSTREAM OF SLOP OIL TANK, WITH INDICATION OF FLARE KNOCKOUT DRUMS (FL-V1 AND FL-V5) AND PRIMARY SEPARATION WASTEWATER EQUIPMENT (API, CPI AND DAF) IN DECEMBER 2011.....	- 32 -
FIGURE 2. 13 – CORRELATION BETWEEN SOUR GAS VALVE OPENING TO FLARE CIRCUIT AND AMMONIA CONTENT IN REFINERY WASTEWATER AT THE DISCHARGE POINT FOR THE EXTERNAL WWTP.....	- 34 -
FIGURE 2. 14 – AMMONIA AVERAGE CONCENTRATION IN DISCHARGE POINT TO EXTERNAL WWTP AND NUMBER OF PENALIZATIONS OCCURRENCES (AMMONIA > 125 PPM).....	- 35 -
FIGURE 3. 1 – REGRESSION COEFFICIENTS OF MODEL INPUTS FOR POLAR OIL AND GREASE CONTAMINATION LEVEL IN THE EFFLUENT OF THE KEROSENE CAUSTIC WASHING UNIT.....	- 46 -

FIGURE 3. 2 – COMPARISON BETWEEN PLS MODEL ESTIMATIONS AND EXPERIMENTAL DATA FOR POLAR OIL AND GREASE CONTENT IN THE KEROSENE CAUSTIC WASHING UNIT EFFLUENT, WITH SLOPE AND QUADRATIC ERROR, FOR THE TRAINING AND VALIDATION DATA SETS.....	47 -
FIGURE 3. 3 – COMPARISON OF DYNAMIC MASS BALANCE ESTIMATION LINE OF POLAR OIL AND GREASE CONTENT IN THE EFFLUENT OF THE DISSOLVED AIR FLOTATION UNIT WITH EXPERIMENTAL DATA POINTS.....	49 -
FIGURE 3. 4 – COMPARISON OF DYNAMIC MASS BALANCE ESTIMATION LINE OF POLAR OIL AND GREASE CONTENT AT DISCHARGE POINT FOR EXTERNAL WWTP WITH ANALYTICAL VALUES. ....	53 -
FIGURE 4. 1 – NOMINAL DIMENSIONS FOR THE PROPRIETARY COMPOSITE NANOFILTRATION MEMBRANE, FROM KOCH, TESTED FOR SPENT CAUSTIC FILTRATION [58].....	59 -
FIGURE 4. 2 – PERMEATE FLUX ACROSS ULTRAFILTRATION CERAMIC MEMBRANE FOR DEMINERALIZED WATER BEFORE AND AFTER FILTRATION USING WASTEWATER AND CLEANING WITH A 2%NaOH SOLUTION, FOR WASTEWATER SAMPLE #1.....	63 -
FIGURE 4. 3 – EFFECT OF TRANSMEMBRANE PRESSURE ON PERMEATE FLUX, AND HYSTERESIS EFFECT WITH WASTEWATER SAMPLE #1.....	65 -
FIGURE 4. 4 – EFFECT OF CROSSFLOW VELOCITY ON PERMEATE FLUX AT A TRANSMEMBRANE PRESSURE OF 0.5 BAR FOR WASTEWATER SAMPLE #1.....	66 -
FIGURE 4. 5 – EFFECT OF CROSSFLOW VELOCITY ON PERMEATE FLUX AT A TRANSMEMBRANE PRESSURE OF 1 BAR FOR WASTEWATER SAMPLE #1.....	66 -
FIGURE 4. 6 – PERMEATE FLUX ACROSS NF MEMBRANE FOR DEMINERALIZED WATER BEFORE AND AFTER FILTRATION OF SPENT CAUSTIC SAMPLE #1 .....	69 -
FIGURE 4. 7 – APPARENT NF MEMBRANE REJECTION VALUES FOR O&G, COD, SULFUR AND SODIUM, WITH CONCENTRATION FACTOR, FOR SPENT CAUSTIC SAMPLE #1.....	70 -
FIGURE 4. 8 – PERMEATE FLUX ACROSS NF MEMBRANE FOR DEMINERALIZED WATER BEFORE AND AFTER NANOFILTRATION USING SPENT CAUSTIC AND CLEANING WITH A 2%NaOH SOLUTION, AND FOR SPENT CAUSTIC SAMPLE #2. ....	71 -
FIGURE 4. 9 – APPARENT NF MEMBRANE REJECTION VALUES FOR O&G, COD, SULFUR AND SODIUM IN PERMEATE, WITH CONCENTRATION FACTOR, FOR SPENT CAUSTIC SAMPLE #2 .....	72 -
FIGURE 5. 1 – SCHEMATICALLY REPRESENTATION OF THE GLASS CHROMATOGRAPH COLUMN USED FOR THE WASTEWATER TREATMENT TESTS IN FIXED AND FLUIDIZED BED ARRANGEMENT.....	78 -
FIGURE 5. 2 – POLAR OIL AND GREASE CONCENTRATION REDUCTION FOR FILTRATION OF REFINERY WASTEWATER SAMPLE IN A FIXED BED CATALYST TEST.....	79 -
FIGURE 5. 3 – POLAR OIL AND GREASE CONCENTRATION REDUCTION FOR FILTRATION OF REFINERY WASTEWATER SAMPLE IN A NON-AERATED CATALYST BED (INITIAL 2000 ML) AND IN A FLUIDIZED CATALYST BED TEST (AFTER INITIAL 2000 ML).....	81 -
FIGURE 5. 4 – POLAR OIL AND GREASE CONCENTRATION REDUCTION IN WASTEWATER SAMPLE FOR DIFFERENT CATALYST TO WASTEWATER RATIOS, AFTER 3H30 MIXING BATCHES WITH SPENT FCC CATALYST.....	82 -
FIGURE 5. 5 – POLAR OIL AND GREASE CONCENTRATION REDUCTION IN WASTEWATER SAMPLE, FOR DIFFERENT MIXING TIME BATCHES WITH 50 G OF SPENT FCC CATALYST.....	83 -
FIGURE 5. 6 – POLAR OIL AND GREASE CONCENTRATION REDUCTION IN WASTEWATER SAMPLES, FOR DIFFERENT INITIAL POLAR OIL AND GREASE CONCENTRATIONS, WITH A MIXING TIME OF 15 MINUTES AND 50G OF SPENT FCC CATALYST.....	84 -

# Tables list

TABLE 1. 1 – MATRIX FOR CLASSIFICATION AND CHARGE OF THE WASTEWATER SENT TO EXTERNAL WWTP .....	11 -
TABLE 2. 1 – TYPICAL COMPOSITION OF A NAPHTHENIC SPENT CAUSTIC FROM A KEROSENE CAUSTIC WASHING UNIT [18, 21] .....	21 -
TABLE 2. 2 – AMMONIA ANALYTICAL RESULTS IN KNOCKOUT DRUM FL-V5 AND SLOP OIL TANK BOTTOMS IN DECEMBER 2011 .....	33 -
TABLE 3. 1 – PROCESS DATA USED AS INPUTS FOR PLS MODEL DEVELOPMENT FOR PREDICTION OF SPENT CAUSTIC CONTAMINATION WITH POLAR OIL AND GREASE .....	42 -
TABLE 3. 2 – PLS MODELS, CAPTURED VARIANCE AND CORRELATION COEFFICIENTS FOR VALIDATION AND TRAINING SETS.....	45 -
TABLE 4. 1 – AVERAGE COMPOSITION OF SPENT CAUSTIC EFFLUENT [21, 44].....	56 -
TABLE 4. 2 – ANALYTICAL RESULTS FOR WASTEWATER SAMPLES BEFORE AND AFTER ULTRAFILTRATION.....	64 -
TABLE 4. 3 – ANALYTICAL RESULTS OF SPENT CAUSTIC SAMPLES BEFORE AND AFTER NANOFILTRATION.....	68 -
TABLE 4. 4 – ECONOMIC DATA FOR A SPENT CAUSTIC TREATMENT INSTALLATION WITH POLYMERIC MEMBRANES, ASSUMING A DIRECT EXTRAPOLATION OF PILOT PLANT RESULTS.....	73 -
TABLE 5. 1 – AVERAGE PROPERTIES OF THE SPENT FCC CATALYST USED FOR OIL AND GREASE REMOVAL FROM WASTEWATER SAMPLES .....	77 -



# Abbreviations

AdSA	Águas de Santo André
APA	Portuguese Environmental Agency
API	American Petroleum Institute
BAL	Clean Water Basin
BAT	Best Available Technology
CDU	Crude Distillation Unit
CF	Volume Concentration Factor
COD	Chemical Oxygen Demand
CPI	Coalescence Plate Interceptor
DAF	Dissolved Air Flotation
FCC	Fluid Catalytic Cracking
LEL	Lowest Emission Limit
LPG	Liquefied Petroleum Gas
l.q.	Quantification Limit
n.a.	non applicable
NF	Nanofiltration
O&G	Oil and Grease
OSPAR	Oslo and Paris Conventions for the Protection of the Marine Environment of the North-East Atlantic
PLS	Partial Least Square

PO&G <sub>SC</sub>	Polar Fraction of Oil and Grease in Spent Caustic of Kerosene Caustic Washing Unit (ppm)
ppb	part per billion ( $\mu\text{g.l}^{-1}$ )
ppm	part per million ( $\text{mg.l}^{-1}$ )
$Q_K$	Kerosene flow ( $\text{m}^3.\text{h}^{-1}$ )
RARISA	Wastewater Collection and Treatment Rules in Santo André System
RMSECV	Root Mean Square Error of Cross Validation
RMSEP	Root Mean Square Error of Prediction
RSH	Kerosene Mercaptan content (ppm)
%S	Kerosene sulfur content (%m/m)
SWS	Sour Water Stripper
$\text{TAN}_C$	Naphthenic Oil Acidity ( $\text{mg}_{\text{KOH}}.\text{g}^{-1}$ )
$\text{TAN}_K$	Naphthenic Kerosene Acidity ( $\text{mg}_{\text{KOH}}.\text{g}^{-1}$ )
TSS	Total Suspended Solids
UF	Ultrafiltration
WWTP	Wastewater Treatment Plant
$\rho_C$	Crude Oil Density ( $\text{kg m}^{-3}$ )
$\rho_K$	Kerosene Density ( $\text{kg m}^{-3}$ )



# 1. Introduction

## 1.1. Work motivation and objectives

Crude oil refining employs the use of significant quantities of fresh water. A great fraction of this water contacts intimately with the processed oil and, as consequence, the contaminants present, such as hydrocarbons, sulfides, ammonia, phenolic compounds, among others are carried over and solubilized by water due to diffusion mechanisms that occur in oil/water interface. Refinery wastewater contamination is mainly associated with feedstock's quality and the technological level of refining process units [1]. Despite the possibility to find in the literature several ranges for contaminants level, to the best of the author's knowledge, no correlation between feedstock's quality, process operating conditions and the concentration of different substances in the industrial liquid effluent have been reported so far in the available literature.

In the largest and most complex Portuguese oil refinery, a wastewater pretreatment system exists, while the final correction and adjustment of the contaminants levels is done in an external WWTP. To discharge wastewater, the refinery is charged according to its quantity and quality, suffering a penalization each time when there is a documented contamination.

Therefore the work developed within the frame of this PhD thesis, was devoted to identifying and studying the different phenomena involved in the production of the refinery wastewater and their impacts on the wastewater pretreatment system, especially targeting optimizing the wastewater circuits, improving the wastewater quality and, through all this; reducing of the costs charged by the WWTP to the refinery.

The research strategy followed consisted in identifying the sources of water contamination for the main analytical parameters responsible for the costs charged: O&G and ammonia; and developing possible source reduction and/or

wastewater treatment solutions or in order to mitigate or eliminate their impacts. This was accomplished by developing a mass balance to the refinery wastewater circuit for prediction and identification of contamination sources of ammonia and O&G.

The important relevance of spent caustic discharge to O&G contamination was clearly demonstrated and a predictive model based on Projection to Latent Structures (PLS) was developed for the kerosene caustic washing unit. The O&G concentration was set as an output of the PLS model and was used as an input for the refinery wastewater mass balance. In order to reduce the impact of this stream on the wastewater contamination, a pilot plant nanofiltration unit was built and installed on site in order to test the feasibility of nanofiltration to remove and/or significantly reduce the water pollution caused by spent caustic at the source.

Laboratory tests were also performed to explore the possibility for reduction of oil and grease concentration in the wastewater effluent after its clarification in the dissolved air flotation unit, by passing it through a fluidized FCC spent catalyst bed, injecting air in the wastewater in a countercurrent operating mode.

## **1.2. Thesis structure**

The sections presented throughout this PhD thesis are arranged according to the following structure:

In the first chapter, work is framed within the crude oil refining industry, with a brief description of the typical process units and the usual products obtained. The wastewater circuit of the largest Portuguese oil refinery, in Sines, is described as well as the historical evolution of the main water contaminants and their impacts on the costs charged to the refinery for treating the discharged wastewater into a nearby located wastewater treatment plant. The context presented in this first chapter allows to identify the problems and to

define the motivation, the main objectives and research strategy followed to execute the work performed during this PhD project.

Chapter 2 is dedicated to detail the wastewater contamination problems, focusing on the description of the origin and importance of each contaminant, the problems which it causes in the effluent quality and its impact on the charged costs. The sources of emission of each contaminant are identified.

Chapter 3 explains the developed mass balance for polar oil and grease content prediction. Herein the methodology employed and the results obtained, which have validated the model and allowed for actions that created immediate benefits to the refinery, in terms of reducing the associated charged costs, are presented

Chapter 4 presents the on-site spent caustic nanofiltration pilot tests performed and the promising results obtained for contamination reduction at the source. Also an economic evaluation was performed indicating the feasibility of this solution to be scaled-up and developed as a large-scale spent caustic treatment option.

Chapter 5 describes the potential for using a residue like spent FCC catalysts as a way for wastewater treatment and correction of oil and grease concentration after primary treatment units like API/CPI and DAF, by using a fluidized bed of spent FCC catalyst, injecting air, in a countercurrent mode, into the effluent to be treated.

Finally, Chapter 6 enounces the main conclusions withdrawn from the work developed throughout the thesis and suggests some guidelines for future work, which may allow for a significant reduction of the contamination and further improvement in the quality of wastewater, generated in the refineries.

### **1.3. Crude oil refining process**

Crude oil is a complex mixture that comprises hydrocarbons from methane to asphalt. The different types of hydrocarbons are normally classified into paraffins, naphthenes and aromatics. Crude oil is also composed of variable quantities of sulfur compounds, nitrogen, oxygen and heavy metals such as nickel, iron or vanadium, among others. Crude is extracted in oil fields in different locations around the globe, and is shipped to refineries where is separated and converted into fuels daily used, like gasoline, diesel, kerosene, butane and propane. Other refined streams are the base for the development of chemical products synthetized in petrochemical industries [2].

In Galp Energia, Sines Refinery the crude oil is received by ships and kept in 100.000 m<sup>3</sup> tanks, prior to its refining in the process units. After decantation and water drainage, the crude is washed in a desalination unit. In its composition, inorganic salts of sodium, chloride, magnesium and calcium, are removed with water and chemical products in the presence of an electrostatic field in order to agglomerate the oil particles dispersed in the water. Salts removal is a fundamental step to prevent their deposition in the downstream units, and to avoid corrosion due to hydrochloric acid formation from chloride ions [3]. A schematic representation of a typical desalination unit is shown on Figure 1. 1.

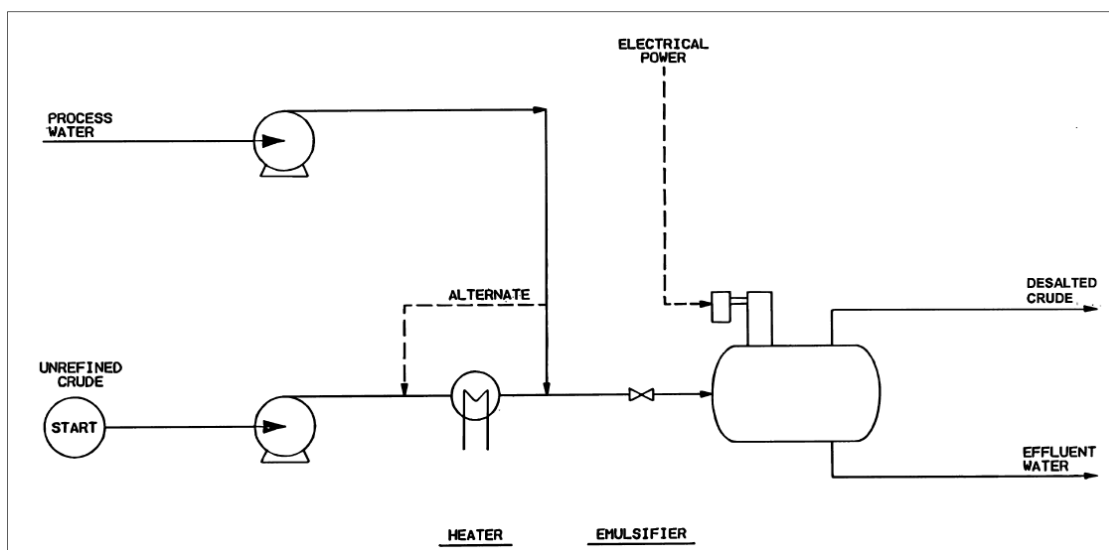


Figure 1. 1 – Crude desalination unit scheme [4].

Due to the intimate contact between wash water and crude oil, the desalter water effluent can carry free oil, suspended solids, phenolic compounds, sulfides and ammonia [3, 4]. After salt removal, oil is fed to atmospheric distillation unit to be fractionated in light hydrocarbons ( $C_1 - C_4$ ), naphtha/gasoline, kerosene, diesel and atmospheric residue. Splitted hydrocarbon fractions are drawn from the column as side cuts with fractions from other products entrained. In order to separate and adjust the properties of each product, they are routed to side strippers where steam is injected, carrying the lighter fractions back to the distillation column [5].

Stripping steam is condensed and separated from the lighter hydrocarbons in an overhead drum. The liquefaction occurs in the presence of sulfides and ammonia, formed by hydrogenation of sulfur and nitrogen present on crude oil, which are solubilized by the water. This effluent is normally designated as sour water.

The different products obtained in the crude distillation unit (CDU) are routed to other downstream process units in order to improve their chemical, environmental and economic properties, namely the reduction of sulfur

content, improving gasoline octane number and upgrading of heavier hydrocarbon fractions into more valuable lighter fractions employing different cracking processes. Gas from the top of the CDU is separated in C1-C2, which are incorporated in the refinery fuel gas network and burned in the refinery furnaces; and propane and butane, which are used as Liquefied Petroleum Gas (LPG). Naphta cut is used as feedstock for petrochemical industry in order to obtain olefins and aromatic compounds, or for gasoline production in naphta cracking units or catalytic reformers. Kerosene can be used as a diesel blending component, but its mainly used as aviation fuel.

In order to be used as fuel, kerosene should be treated for removal of acidic and sulfur compounds, in extraction and oxidation units employing caustic, ammonia or ionic liquids. Another option is kerosene hydro-treatment in a hydrogen desulfurization unit. So far, the most common technology is the MEROX process from UOP with caustic. Fresh caustic after an intimate contact with kerosene is spent and saturated with mercaptans, sulfides, inorganic salts, phenolic compounds and organic acids, such as naphthenic acids. Spent caustic is continuously produced and normally routed to wastewater circuit, which poses serious difficulties for the industrial effluent treatment [3, 6]. Mercaptan extraction and oxidation units are also used to upgrade LPG and gasoline cuts.

Distillate diesel is normally routed to desulfurization units in order to adjust its sulfur content to each country environmental legislation norm. Other hydrocarbon fractions, such as gasoline, vacuum gasoil, and fuel can also be processed in desulfurization units, where the stream containing sulfur and hydrogen are sent to a catalytic reactor. Besides the desulfurized stream, a gas stream composed of light hydrocarbons, hydrogen and sulfides is also produced. Sulfides are separated from the combustible gas employing an amine solution in gas treating units. Sulfidic gas is separated from the amine in a regeneration unit, and is sent to thermal catalytic oxidation units for

transformation in molecular sulfur: Claus process units. This reaction avoids SO<sub>x</sub> emissions to the atmosphere.

Atmospheric residue, collected in the bottoms of the CDU, contains significant quantities of valuable hydrocarbons, which are not recovered at operating temperatures employed in this unit, since a higher temperature severity will lead to cracking reactions, increase of operating pressure and products degradation. In order to reduce residue production and improve distillates yields, CDU bottoms is further processed in vacuum distillation units, thermal or catalytic conversion units. Conversion units like Visbreaker, Fluid Catalytic Cracker (FCC), Hydrocracker or Coker, are fed with heavier products from atmospheric and vacuum distillation units. Heavier hydrocarbons with longer carbon streams and reduced commercial value are cracked into smaller chain hydrocarbons like gas, naphtha, gasoline, diesel and kerosene. The bottoms production normally comprises the higher fraction of fuel oil, used as ship or furnace fuel. In conversion units water and steam are used to improve separation between different fractions, to improve flow of heavier products and as cooling media. Due to the intimate contact between water and hydrocarbons, wastewater with a high content of sulfides, ammonia, phenolic compounds is generated and also carries over some oil [4].

#### **1.4. Sines Refinery wastewater circuit**

In the biggest and most complex Portuguese refinery, there are different wastewater circuits accordingly to the type of effluent generated: storm waters, saline effluent, oily wastewater, accidentally contaminated wastewater, chemical effluent and sanitary.

Storm waters are collected within the zones where the risk of contamination with hydrocarbons or chemical products is negligible, such as roads, administrative or storage areas. Water from rain is collected in a dedicated

drainage network and routed to a 31000 m<sup>3</sup> clean water basin (BAL). Further to decantation this water can be discharged to a riverside, after laboratory analyzes attesting that the water quality corresponds to the environmental legislation and a previous communication to the Environmental Portuguese Agency (APA). If the analytical values show eventual traces of contamination, this stream is routed to a wastewater treatment plant (WWTP) external to the refinery, for further treatment. Rain water is also used as a make-up stream of the Fire water basin, and the possibility of upgrading this water as cooling water towers make-up is being studied.

Saline effluent is generated in the purges of cooling water towers, to maintain cooling water analytical parameters within the required operation range, and after the regeneration of water demineralization ion exchange columns. These streams are collected in a saline effluent basin and analyzed on a regular basis in order to guarantee that the quality of the water prior to discharge directly into the sea respects the environmental legislation norms. In case of an eventual contamination, effluent sags by overflow to accidentally contaminated wastewater circuit, in order to avoid contamination of the water receiving media.

Accidentally contaminated wastewater comprises storm water collected in process areas, service water used for pavement cleaning and contaminated saline effluent. This wastewater can contain traces of oil or other chemical substances, and for that reason, a risk of contamination exists that inhibits the direct discharge to a water receiving media. Wastewater is therefore collected in a dedicated basin for decantation of carryover solids and oils. Oils are removed with an oil skimmer and sent to a slop oil tank for reprocessing in CDU mixed with crude oil. Wastewater with a lower content of oil is routed to an equalization basin that receives also oily wastewater after primary clarification.

Oily wastewater is the process water that has been in intimate contact with crude oil and its fractions along the refining process units. A fraction of this



effluent is generated in the storage area. Crude oil received in the refinery tanks after decantation contains a percentage of bottom water and sediments. Distillate products carry over some process water. The bottoms of the tanks are drained continuously to reduce the inert volume of the tanks and in order to guarantee the specifications of the feedstock's and products. Bottom sediments and water are routed to primary gravity separators, normally designated as API (American Petroleum Institute) and CPI (Coalescence Plate Interceptor), which are designed to recover non-emulsified oil droplets greater than 150  $\mu\text{m}$ , by physical separation. Recovered oil is sent to a slop tank, while water with emulsified oil and smaller oil droplets is pumped to an equalization basin, where accidentally contaminated waters are also received. Oily wastewaters resulting from water utilization in refining units is normally referred to sour waters or process waters. Sour waters are treated in sour water stripping units (SWS), where stripping steam is injected in a countercurrent operation mode with sour water to extract soluble ammonia, sulfide, and volatile compounds. Sour gas resulting from sour water stripping is sent to Claus units, while stripped wastewater and process waters are pumped to API/CPI equipment's and then to the wastewater equalization basin.

The main purpose of the equalization basin is to act as a volume buffer to downstream treatment units and also to correct the alkaline pH of wastewater, , to values ranging from 7 to 9 with carbon dioxide. Homogenized wastewater is then pumped to a dissolved air flotation unit (DAF) where air and coagulant/flocculant chemical preparation is injected to promote aggregation of emulsified oils and their accumulation on the surface of the wastewater in order to be scrapped off and sent to the slop tank. Clarified water with less than 5-10 ppm of free oil flows to an aerated basin with oxygen gas injection for oxidation and biological treatment of sulfides, phenolic compounds and organic dissolved substances. Further pH correction to 6 to 9 can be also accomplished in this basin by injection of carbon dioxide. After the possible correction of the

physical and chemical properties, wastewater is discharged to an external WWTP for improvement and rectification before being sent to the sea.

Sanitary wastewater from domestic utilization and chemical effluents from the laboratory are collected in distinct circuits and pumped directly to an aerated lagoon.

### **1.5. Wastewater charges**

After primary and secondary treatment, wastewater is discharged to an external WWTP, for final treatment of the stream before discharging it to a water receiving medium. The discharge of the refinery effluent to this external WWTP is subjected to rules defined in RARISA that among different considerations indicates the tariffs to be applied based on the discharged wastewater quantity and quality. The wastewater analytical composition is determined twice per week with composed samples collected with an automatic sampler located between the refinery and the treatment plant. The parameters analyzed are sulfides, phenolic compounds, Chemical Oxygen Demand (COD), Oil and Grease (O&G), ammonia, Total Suspended Solids (TSS) and pH. Based on the results obtained, the total amount of the effluent prior to that sample is classified according to the matrix presented in Table 1. 1.

The wastewater classification is defined by the parameter that presents the highest class in the analyses of the composed sample, e.g. if all the parameters have analytical values that define them as class 1, but phenolic compounds indicate a class 3, the effluent is defined as class 3 for charging.

If the class 5 limits are exceeded, or class 1 in case of ammonia, the discharged wastewater will be in a situation of penalization, and an extra factor of 15% will be applied to the charges in the following 45 days. The extra factor is cumulative up to a maximum of 5 events, i.e. 75% of extra charge. The charge of the effluent is proportional to the quantity sent to the WWTP.

**Table 1. 1 – Matrix for classification and charge of the wastewater sent to external WWTP**

<b>Parameter</b>	<b>Unity</b>	<b>Class 1</b>	<b>Class 2</b>	<b>Class 3</b>	<b>Class 4</b>	<b>Class 5</b>
<b>Sulfides</b>	mg.l <sup>-1</sup>	]l.q. <sup>1</sup> ; 2]	]2; 4]	]4; 7]	]7; 10]	]10; 20]
<b>Phenolic compounds</b>	mg.l <sup>-1</sup>	]l.q.; 5]	]5; 10]	]10; 15]	]15; 20]	]20; 40]
<b>COD</b>	mgO <sub>2</sub> .l <sup>-1</sup>	]l.q.; 150]	]150; 300]	]300; 600]	]600; 1000]	]1000; 2000]
<b>O&amp;G</b>	mg.l <sup>-1</sup>	]l.q.; 5]	]5; 20]	]20; 35]	]35; 50]	]50; 100]
<b>Ammonia</b>	mg.l <sup>-1</sup>	]l.q.; 125]	n.a	n.a.	n.a.	n.a.
<b>pH</b>	Sorensen scale	[6; 9]	n.a.	n.a.	n.a.	[4,5; 10]
<b>TSS</b>	mg.l <sup>-1</sup>	]l.q.; 100]	]100; 200]	]200; 300]	]300; 500]	]500; 1000]

<sup>1</sup> l.q.: Quantification Limit

Since 2009 until 2013, as shown on Figure 1. 2, there was a tendency of aggravation of wastewater charged cost. Since then, and due to the work performed throughout this PhD project that will be described in the following sections, there was a reduction in the charged costs, back to the same values seen in 2009.

The higher costs charged between 2009 and 2013 have been due to the increase of contamination, mainly oil and grease, and ammonia, since COD can be correlated with these two parameters, which have contributed to a higher classification of the wastewater and also to more penalization situations as shown on Figure 1. 3 and Figure 1. 4.

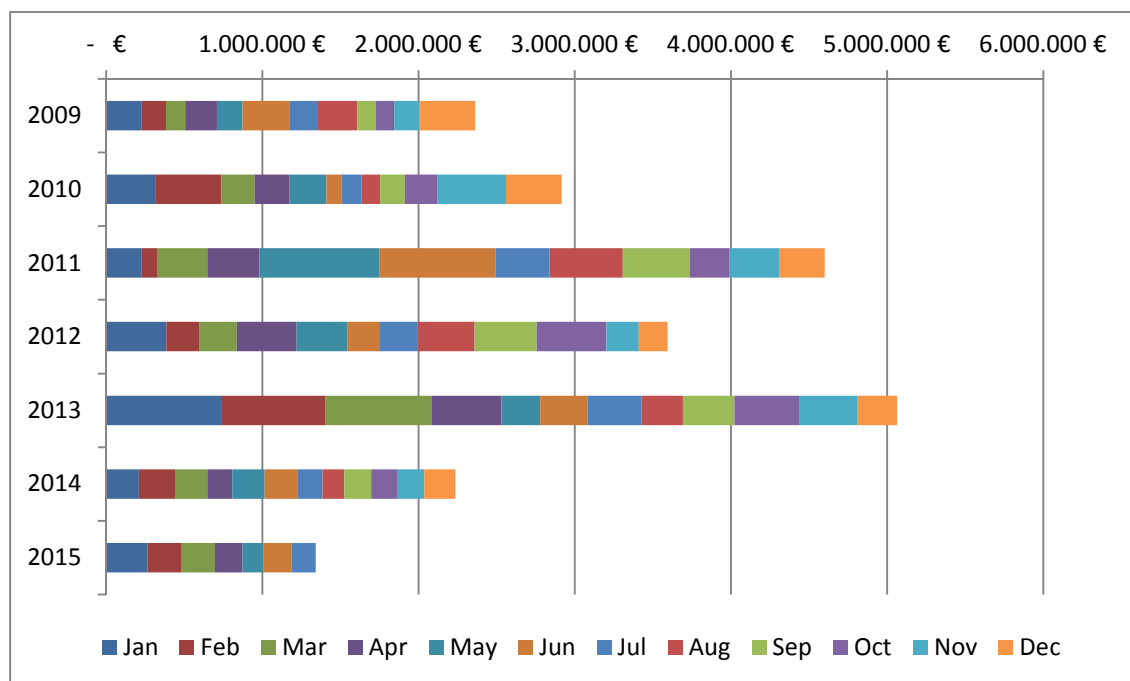


Figure 1. 2 - Wastewater treatment costs charged by external WWTP.

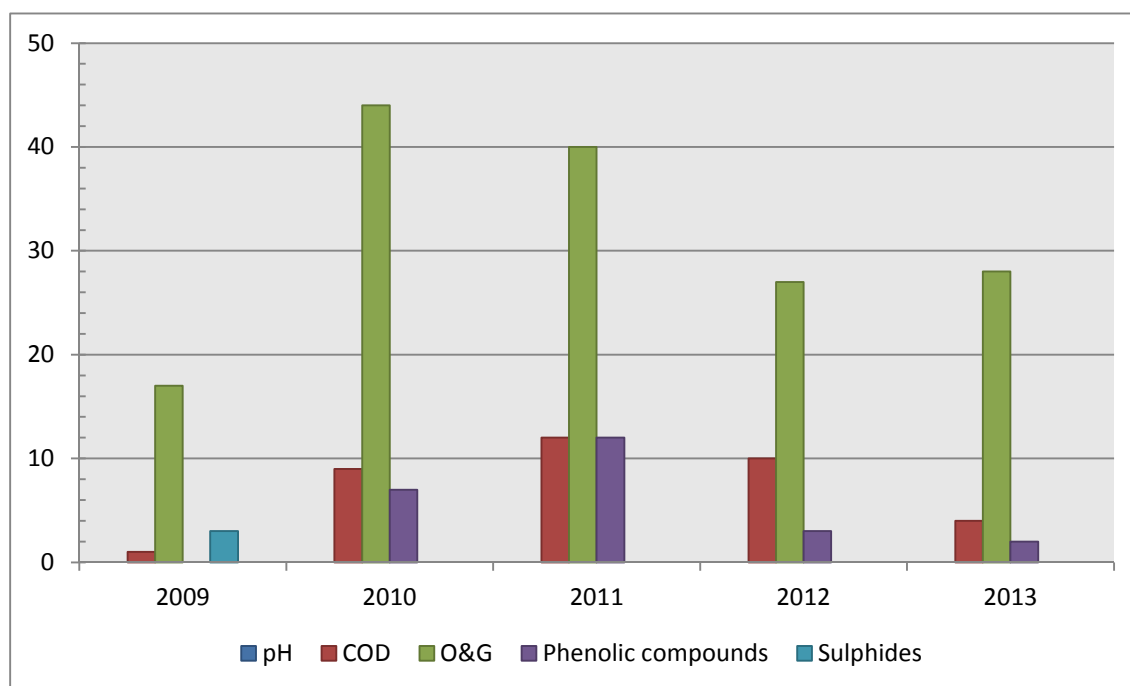
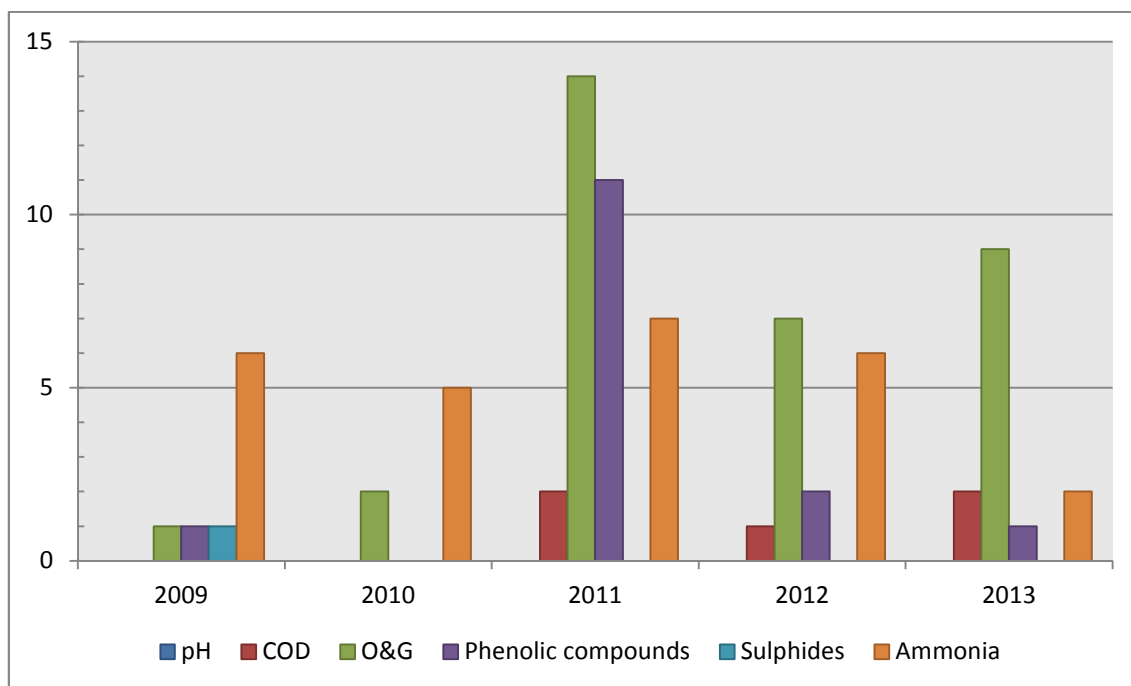


Figure 1. 3 - Number of occurrences of class 5 in the wastewater by parameter.



**Figure 1. 4 - Number of occurrences of penalizations in the wastewater by parameter.**



## **2. Contaminants identification**

The wastewater from the largest Portuguese oil refinery is most significantly affected by the high concentrations of oil and grease and ammonia, due to their strongest impacts on the costs charged by the external WWTP.

### **2.1. Oil and Grease**

#### **2.1.1. Introduction**

Among the different wastewater contaminants, oil and grease is the most critical one in terms of its impact on the receiving media and requires dedicated treatment. The substances that are comprised by the O&G parameter are less biodegradable when compared with other organic substances [7], therefore the presence of significant amounts of O&G may interfere with the biological treatment, seriously reducing its efficiency [8]. The discharge of these substances into water media and their deposition causes important problems and risks for the environment and for the people health, such as introduction of unpleasant flavor, smell and color in the water, formation of a surface oily film in water bodies, which blocks the absorption of atmospheric oxygen and the entrance of sunlight, thus harming the marine fauna and flora [1, 8]. The disastrous impact of this pollutant on the marine environment has led to the emission of stringent recommendations and legislations in order to remove it from the receiving media. The Oslo and Paris Conventions for the protection of the marine environment of the North-East Atlantic (OSPAR) recommends a maximum discharge concentration value for oil in wastewater of 5 ppm [9]. Therefore, the value of 5 ppm, is the maximum limit in class 1 for oil and grease discharge into external WWTP as defined in RARISA and Table 1. Still, according to the Portuguese law the maximum emission limit for the O&G content in wastewater is 15 ppm [10].

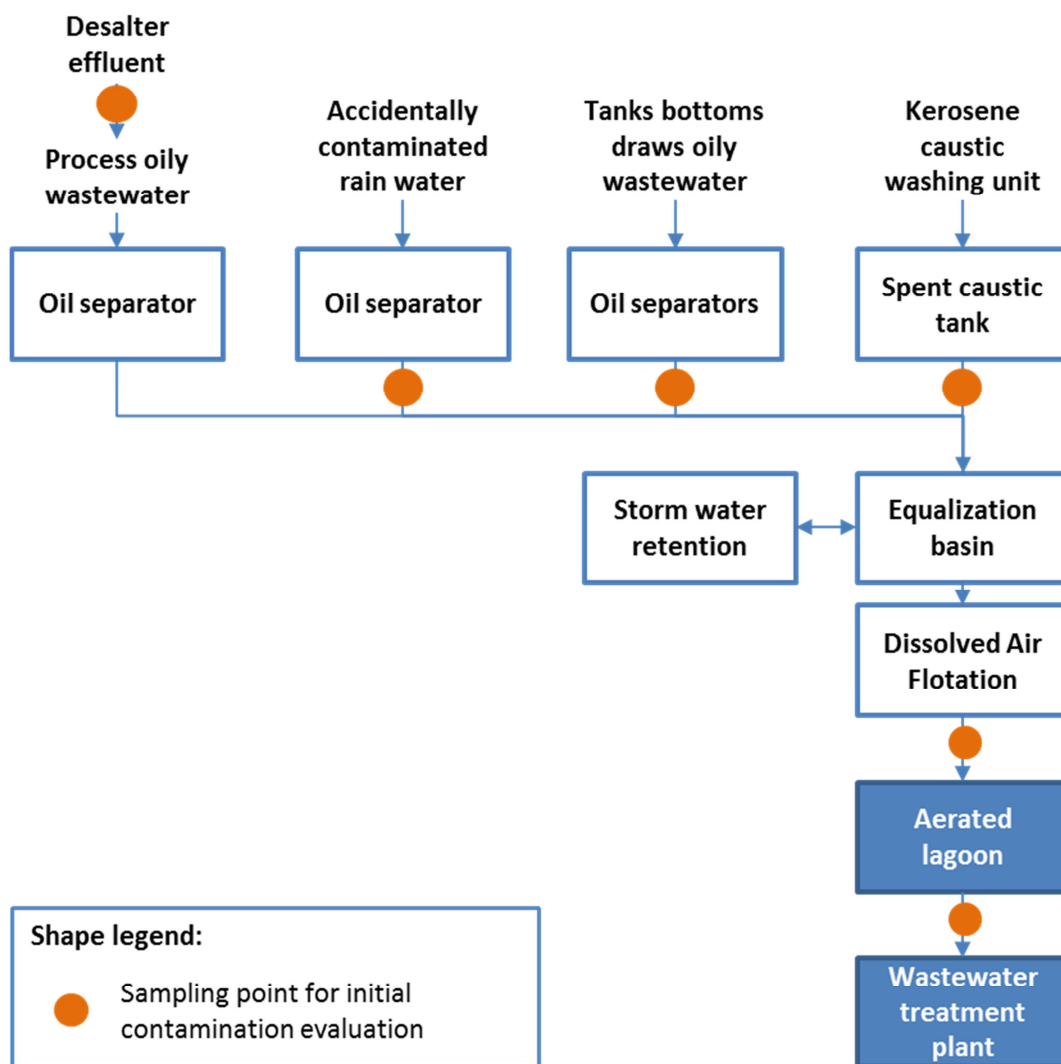
The standard methods used for oil and grease determination in waters, do not allow for the quantification of a particular substance. Instead, groups of compounds with similar chemical characteristics, that are extracted from the water sample by a certain organic solvent, are measured [8]. When hydrocarbons are extracted into the organic solvent, the analytical result can be affected by the presence of sulfur and/or nitrogen compounds, organic dyes, vegetable oil, animal fat, waxes and other substances with similar properties [8, 11]. O&G can be polar or non-polar substances. The polar fraction accounts for heterocyclic, aromatic and phenolic substances that are present in crude oil composition, and for aromatic compounds, unsaturated substances and elements that have polar arrangements by the presence of distinct atoms such as chlorine, oxygen, nitrogen or sulfur [11]. Naphthenic acids are important polar substances. Polar oil and grease can be removed from the organic extract by absorption into silica gel, which allows for the determination of their fraction for the total oil and grease. Non-polar oil and grease fraction, or hydrocarbons content, measures the presence of simple and ramified chain hydrocarbons [8, 11]. The non-polar substances are insoluble in water and can be removed through the utilization of chemical and physical separation, such as gravity decantation, centrifugation, coagulation and/or flotation. On contrary, the polar compounds are soluble in aqueous media, and their presence in wastewater will lead to high values of oil and grease, (even after chemical and/or physical separation treatment), that may lead to an increase in water toxicity levels, with devastating impacts for the water environment and its users [12-14].

#### **2.1.2. Materials and methods**

In order to address the problem of O&G contamination in the wastewater circuit of the largest Portuguese refinery, samples were collected in several points, as schematically shown on Figure 2. 1. Samples were collected in one



liter glass bottles in different refinery location sites during 24 months, and readily analyzed after sampling. The historic records before that period were also used for framing and contamination evolution comparison.



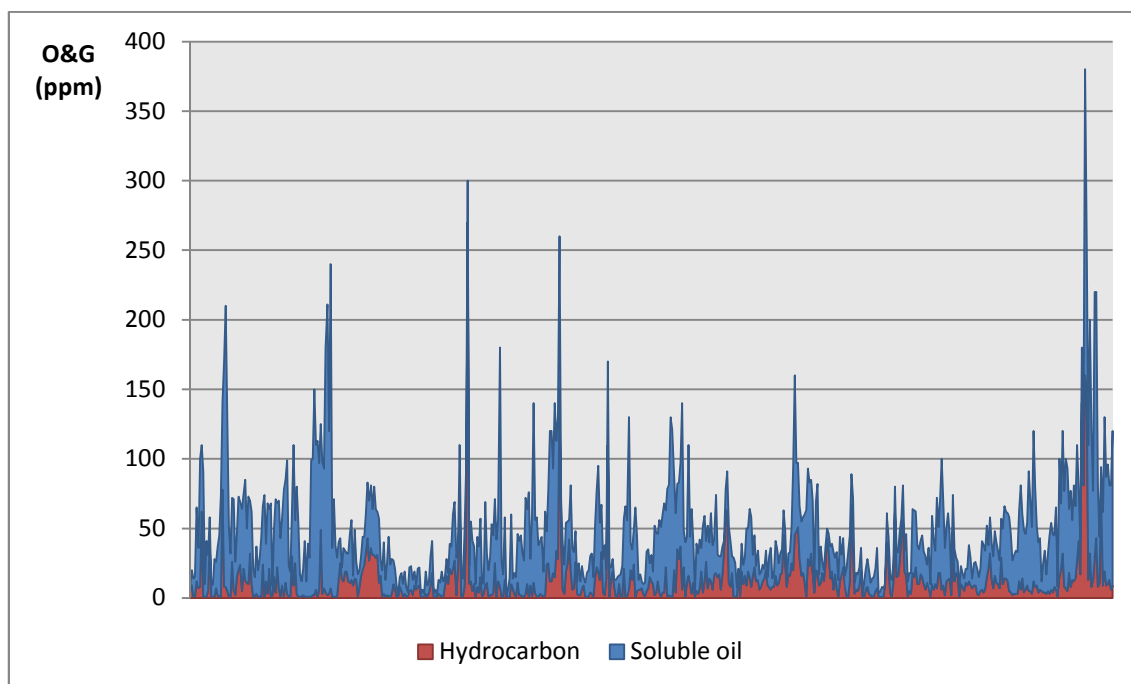
**Figure 2. 1 – Schematic representation of wastewater circuit in the largest Portuguese oil refinery, with identification of sample collection points for O&G analysis.**

The determination of O&G content and polar and non-polar fractions, were done using the standard methods already applied in the refinery, namely SMEWW 5520 C and SMEWW 5520 F. The method 5520 C allows for the

determination of total O&G concentration, and is the most suitable for application in water samples that may contain volatile hydrocarbons and oil content below 10 ppm. The standard method 5520 F determines the O&G non-polar fraction, i.e. the presence of hydrocarbons that can be recovered by physical and/or chemical treatment. The remaining quantity which is not removed by primary or secondary treatments, accounts for the soluble oil content [8, 11].

### **2.1.3. Emission source identification**

The O&G emission source identification was performed by sampling wastewater in different points located along the effluent circuit as shown on Figure 2. 1. Based on the average flow rate of the different wastewater emission points, the mass contributions of each point in the total O&G concentration in the effluent were estimated. As an initial evaluation step observation of historic results for O&G at the discharge point for external WWTP, between 2010 and 2012, was performed. These data are presented on Figure 2. 2.



**Figure 2. 2 – Hydrocarbon and soluble oil concentration in the discharge point for the external WWTP between 2010 and 2012.**

The analysis of the data indicated that the polar fraction of oil and grease has accounted for more than 73% of the system contamination with oil. Also, it was identified that the appearance of higher concentrations of hydrocarbons was due to upsets in the upstream treatment equipment's, e.g. a mechanical failure in the dissolved air flotation unit. Based on these considerations, the analytical work regarding the samples taken from the upstream points was focused in identification of contamination by polar substances. The results obtained are presented on Figure 2. 3 and show that the major contribution for soluble oil concentration in wastewater is due to the emission of highly contaminated spent caustic, which accounts for more than 92 wt%. The desalter effluent accounts for more than 6 wt%, and the remaining points have negligible impacts. Spent caustic is a by-product resulting from the kerosene caustic washing for mercaptan extraction and oxidation [1, 3, 6]. The most common

process, which is also applied in the Sines refinery is the Merox process from UOP.

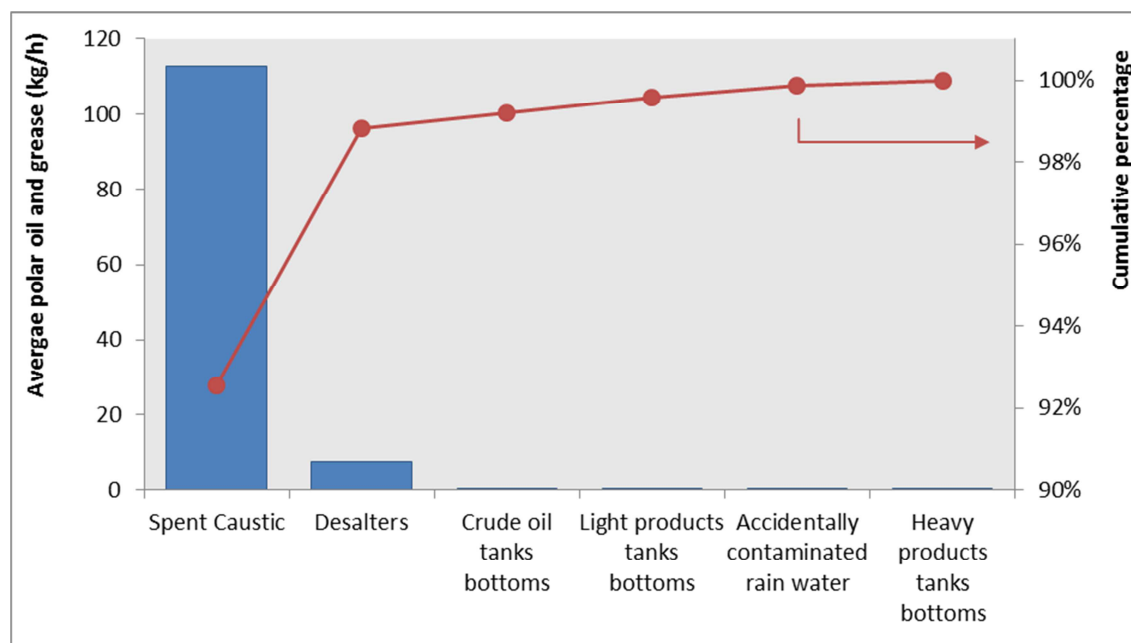


Figure 2.3 - Average polar O&G mass flow rate contribution of different emission points for O&G wastewater contamination at the discharge point for external WWTP.

#### 2.1.4. Kerosene caustic washing unit

The global fossil fuel consumption has increased significantly and the degradation of crude oils with higher concentrations of sulfur and acidic compounds which are responsible for strong unpleasant odors, corrosion and degradation of products, has led to the need of more upgrading process units for removal and elimination of the contaminants from the hydrocarbon streams [REF.]. Among the different possible technologies, the extraction and oxidation process with caustic is the most commonly used one. The efficiency of the system, which is associated with the relatively low cost of caustic, when compared with hydrogen, is the major reason for its popularity [15-17]. The MEROX process developed from UOP is one of the technologies widely used worldwide in the refineries for mercaptan and acidic compounds removal from

LPG, naphtha, gasoline or kerosene. The kerosene cut is one of the most sensitive operations, since in this hydrocarbon fraction most of the acidic compounds, namely naphthenic acids, concentrates, etc. are present [18]. In caustic washing unit, kerosene cut from CDU is sent to a pre-wash drum for extraction of acidic compounds. In the downstream sections, mercaptans are removed and the caustic used is firstly heated in order to promote the oxidation of sulfur compounds into sulfides [17]. Caustic used in the pre-wash section is continuously drawn off from the unit and after contact with kerosene is saturated in acidic compounds and is designated as naphthenic spent caustic. This caustic is very hazardous for the environment due to the presence of sodium hydroxide based compounds that make this stream extremely alkaline and corrosive [17], as well as toxic due to the presence of dissolved organic compounds such as mercaptans, sulfides, cresylic acids and naphthenic acids [19]. The typical composition of spent caustic solution is presented on Table 2.

1.

**Table 2. 1 – Typical composition of a naphthenic spent caustic from a kerosene caustic washing unit [18, 21]**

<b>Parameter</b>	<b>Range</b>	<b>Unity</b>
<b>NaOH</b>	1-4	%(m/m)
<b>Sulfides (S<sup>-</sup>)</b>	0-0.1	%(m/m)
<b>Mercaptans (S<sup>+</sup>)</b>	0-0.5	%(m/m)
<b>Naphthenic acids</b>	2-15	%(m/m)
<b>Cresylic acids</b>	0-3	%(m/m)
<b>pH</b>	12-14	Sorensen scale

The presence of polar compounds in spent caustic, interferes with the O&G analytical quantification. If this stream is diluted in the refinery effluent, the oil

content will still be extremely high, even after primary and secondary chemical/physical separations. Besides the environmental problems, the fact that spent caustic has no economic value, the difficulties in its neutralization and the higher associated treatment costs, imposes a great impact on the financial refinery margins [16, 20].

#### **2.1.5. Mitigation**

The management and disposal of the spent caustics originating from kerosene caustic washing units, is the main challenge for the largest and most complex Portuguese refinery, but also for the refineries all around the world [16, 20, 21]. As the first step to validate and identify the contamination source, a mass balance to the refinery wastewater system was developed, in order to estimate the soluble oil content in different points located along the circuit. This mass balance was fed by a predictive model based on a multivariate statistical method, which results are presented in Chapter 3. Due to the strong impact of this stream on the wastewater contamination, and consequently, on the costs charged to the refinery, different treatment solutions were tested. A spent caustic nanofiltration pilot plant test for source contamination elimination was performed in an industrial environment, and an economic analysis was elaborated in order to validate the feasibility of scaling up this solution. The results are presented in Chapter 4. A treatment solution for O&G reduction after clarification in dissolved air flotation units, using FCC spent catalyst in a fluidized catalyst bed arrangement, injecting air in a countercurrent mode, with the effluent was tested under laboratory conditions, with results being shown in Chapter 5.

## 2.2. Ammonia

### 2.2.1. Introduction

The formation of ammonia in crude oil refining results from the hydrogenation of nitrogen compounds present in crude oil chemical formulation. Due to the affinity of these substances to water, ammonia is normally solubilized by aqueous stream, when it is in an intimate contact with hydrocarbon streams. The same mass transport phenomenon occurs with sulfides, formed by hydrogenation of sulfur compounds. The presence of ammonia and sulfides in aqueous solutions results in sour water, which dependently on feedstock quality and refining process units can have more than 20000 ppm of ammonia [1]. Sour waters are normally routed to treatment in SWS with injection of air or steam into the column. An alternative configuration is the vaporization of the liquid in the bottom of the column in a reboiler, which is schematically represented in Figure 2. 4.

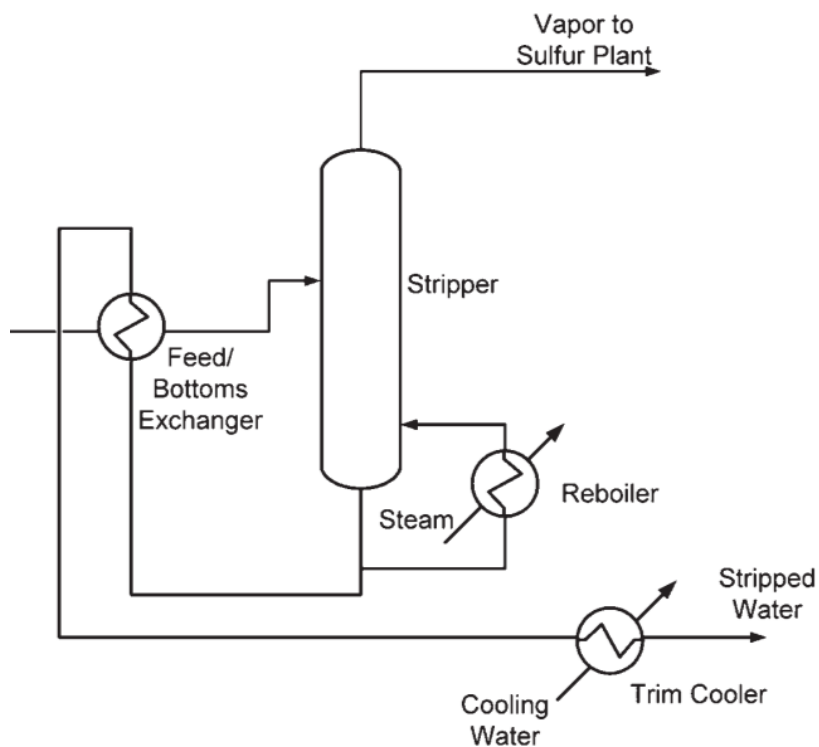


Figure 2. 4 - Schematic representation of Sour Water Stripper (SWS) [3].

In SWS, contaminants are transported from liquid media into gas, thus originating a sour gas, to which 80 to 99% of ammonia is transferred. Sour gas is routed to Claus reactors, incinerators or flaring, to oxidize ammonia and sulfides. Stripped water with ammonia traces can be reused in refining units or disposed to an wastewater treatment plant [1, 3].

Wastewater treatment plants normally have equipment to reduce the ammonia concentration in the wastewater. The most common technologies are based on biological denitrification, chemical precipitation or electrochemical conversion. More recent technologies apply microwaves [22] or ion exchange [23]. The presence of significant amounts of ammonia can affect biological treatment systems, due to high toxicity and consumption of available oxygen, and may represent a significant fraction of COD [24]. Ammonia, due to its noxious effects in the environment is one of the target pollutants for European Union, within the water conservation policy 2000/60/CE. The Portuguese legislation defines a maximum discharge value of 10 ppm to water bodies [10], and the rules for wastewater discharge from the refinery to the external WWTP recommends a maximum value of 125 ppm. Above this value a penalization situation occurs involving increased costs charged to the refinery.

### **2.2.2. Materials and methods**

For identification and quantification of ammonia in refinery wastewater, samples were collected in the same points used for O&G, as schematically represented in Figure 2. 1. Due to the need of acquiring data from additional points, the sampling network was extended, as indicated in Figure 2. 5. Samples in different points were collected and analyzed during 11 months. Available historic data was also gathered in order to study the evolution of the ammonia contamination in the refinery.



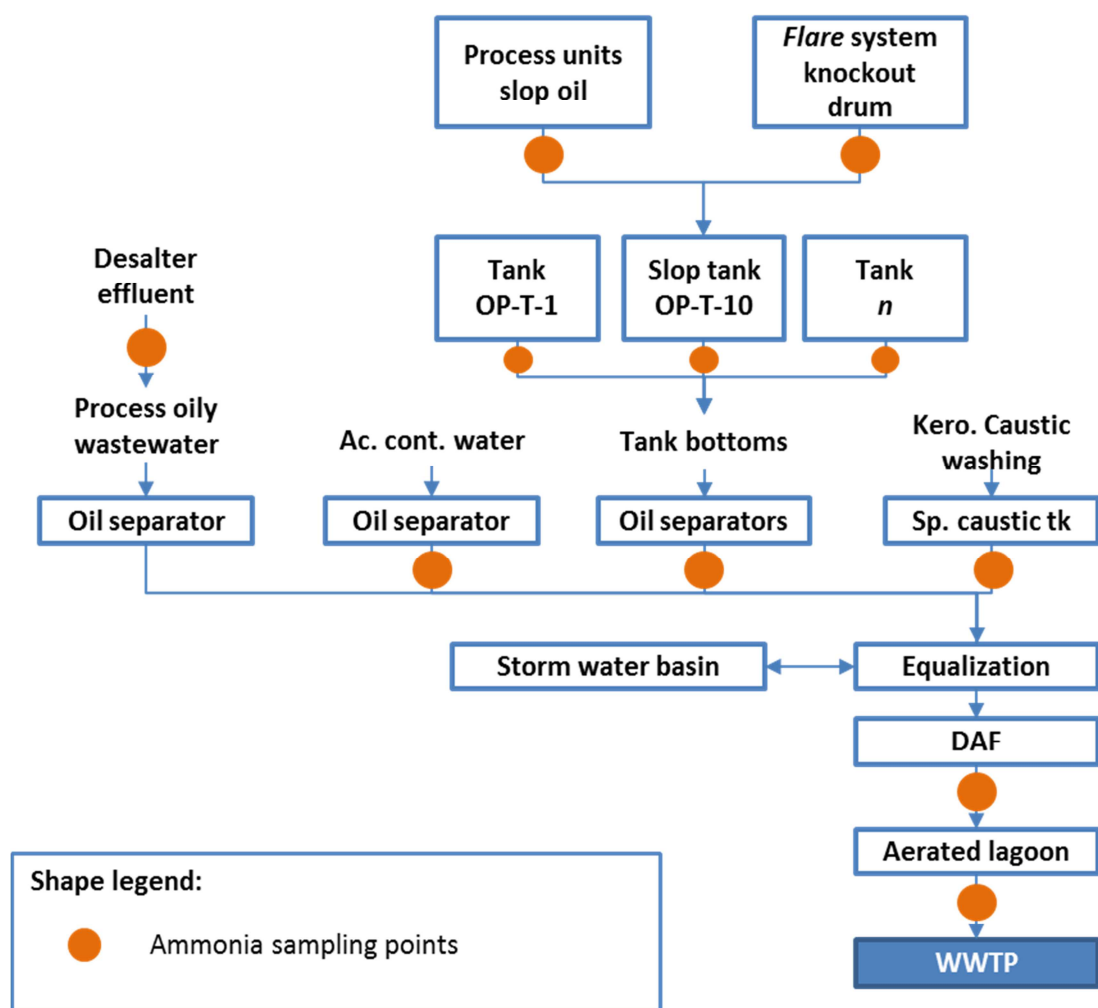
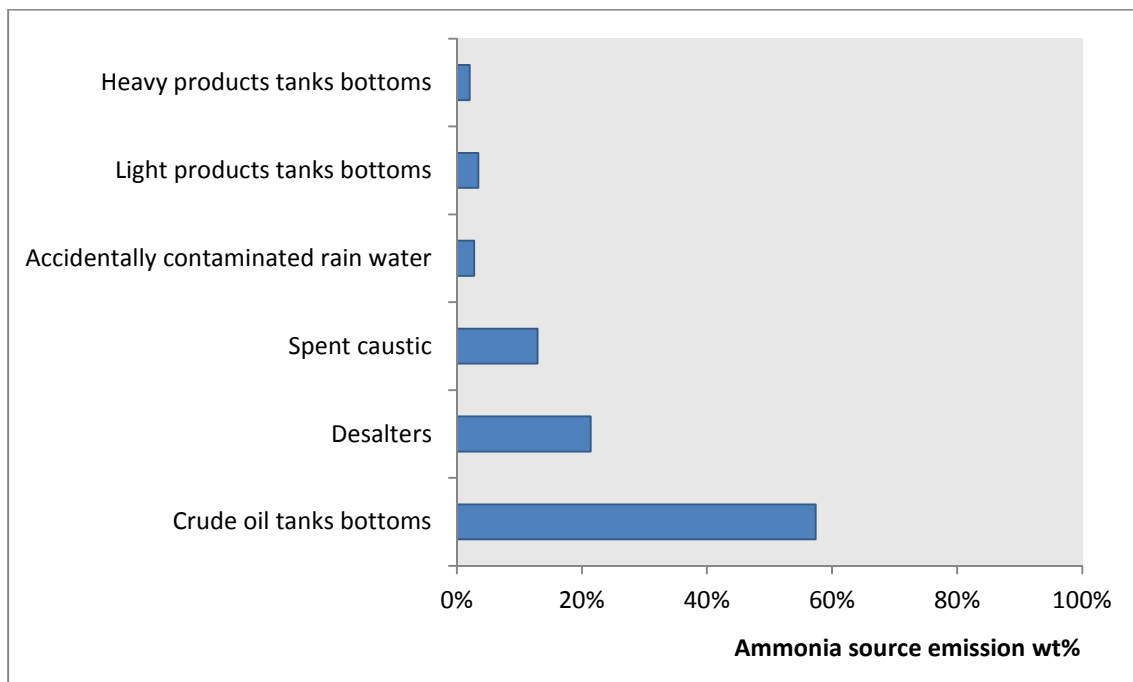


Figure 2. 5 – Schematic representation of wastewater circuit in the largest Portuguese oil refinery, with identification of sample collection points for ammonia analysis.

Ammonia quantification was done in laboratory using an existing standard method SMEWW 4500-NH<sub>3</sub> F. This method is based on the formation of a blue coloration in the sample due to reaction between ammonia present in aqueous solution and hypochlorite and phenol which are added to the solution. This method does not suffer interference from other ammoniac species and therefore is highly precise [8].

### 2.2.3. Emission source identification

The historic data from wastewater quality discharged to the external WWTP between 2009 and 2013, indicates an average ammonia concentration of 91 ppm. Although this average value is lower than the maximum limit for a penalization, accordingly to the RARISA matrix, shown on Table 1. 1., along these 5 years this limit has been violated in 20% of the analyses performed for wastewater classification and charging. The analytical data obtained with samples combined with the average mass flows in each point, have indicated ammonia emission distribution between the analyzed point sources presented in Figure 2. 6.

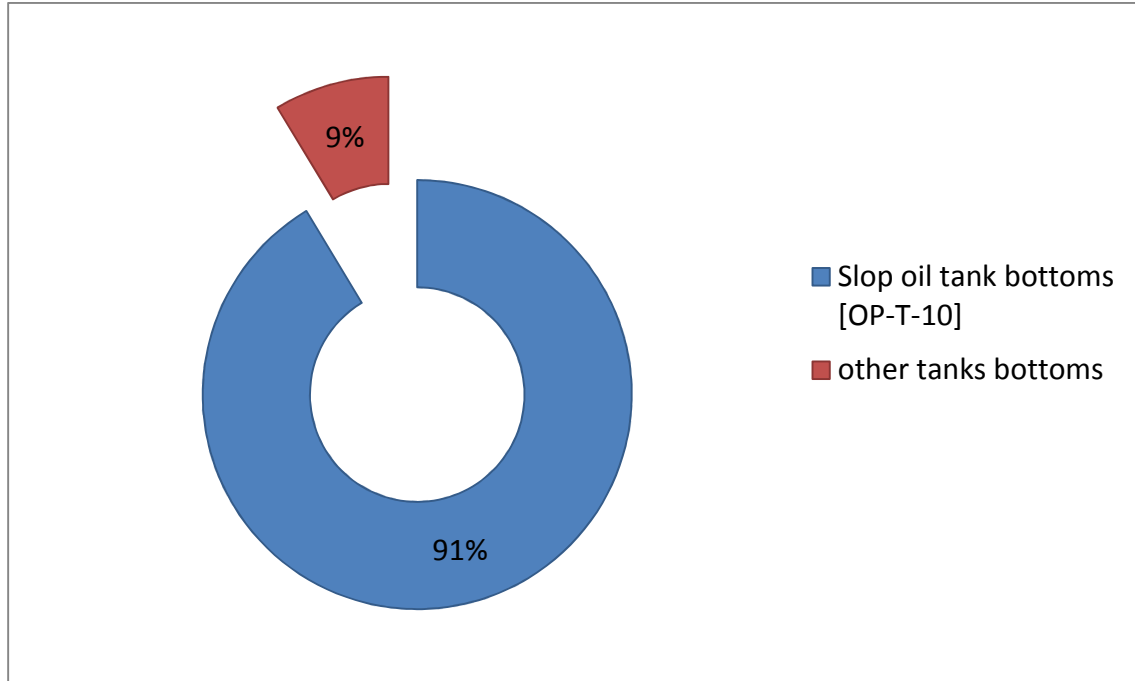


**Figure 2. 6 – Average mass contribution of different emission points for ammonia wastewater contamination at the discharge point for the external WWTP.**

The data indicates as major contributions the drainage from crude oil tanks bottoms – 57 wt% - desalter effluent – 21wt% - and spent caustic -13 wt%.

In the Sines refinery there are 17 crude oil tanks with a nominal capacity of 100000 m<sup>3</sup> initially designed to store the feedstock of the refining process. However, due to scheduling, logistics and inventory reasons, 4 of the tanks are used to store diesel and one of these tanks serves as slop oil tank. The crude oil received in a refinery contains a certain amount of solids and water, which are extracted from the wells together with the crude. Since water and sediments have a higher densities when compared with hydrocarbons, they tend to settle and, thus, can be periodically drained through the bottoms of the tanks [3]. The accumulation of water in diesel tanks is minor and is only due to carryover of some process water. The main accumulation of water occurs in the slop oil tank. Slop oil is mainly produced at start-up and shutdown of the refining units and in the wastewater primary treatment by recovering the carryover oil in API/CPI gravity separators and DAF unit. The scrapping of oils from the surface of water in these separators results in significant amount of water that is sent to the slop oil tank.

As shown on Figure 2. 5, samples were collected in the drain of the 17 tanks. The analytical results, presented on Figure 2. 7, have identified the slop oil tank as the major contributor for ammonia contamination in the wastewater system.



**Figure 2. 7 – Average mass contribution of slop oil, diesel and crude oil tanks for ammonia wastewater contamination at the oil separator for crude oil tank area.**

Based on these results, a mass balance was developed for wastewater contamination with ammonia, based on the emissions of desalter, slop oil tank and spent caustic streams. Daily samples were collected in these 3 points assuming that the analytical data obtained were valid during the entire day. The remaining emission points were assumed to have a negligible effect on the ammonia concentration. Mass balance for determination of ammonia concentration in ppm ( $C_{NH_3}$ ) at the outlet of the wastewater basins ( $V_{basin}$ ) shown on Figure 2. 5, was based on the equation (2. 1), which was used with analytical values of ammonia ( $C_i$ ) in ppm and estimated flows ( $Q_i$ ) in  $m^3.h^{-1}$  for the different emission points for each basin.

$C_{NH_3} = \frac{\sum_{i=1}^n (Q_i \times C_i) - V_{basin} \times \frac{dC_{NH_3}}{dt}}{\sum_{i=1}^n Q_i}$	<b>(2. 1)</b>
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In Figure 2. 8, the mass balance estimation to ammonia is compared with the analysis at the discharge point for the external WWTP. As can be seen, the estimations for ammonia follow reasonably well the tendency of the analytical results obtained during the observed period, which validates the initial assumptions. The observed deviations in November 12<sup>th</sup> and 16<sup>th</sup> are possibly due to the fact that the ideality assumptions of the system of perfectly mixing and non-preferred paths are not always verified and the system is dynamic, since the high ammonia value expected for the November 16<sup>th</sup> was only observed in the following day. Major contributions for the ammonia mass balance are indicated in Figure 2. 9, from which it can be seen that the slop oil tank has the most significant impact for the final result.

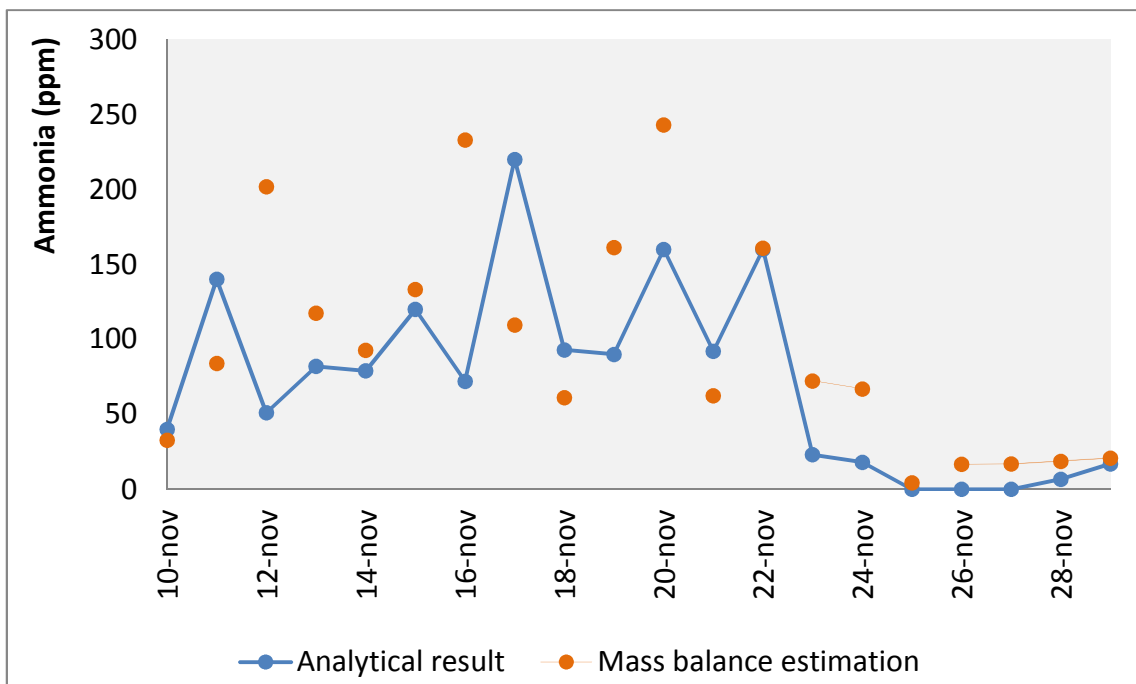
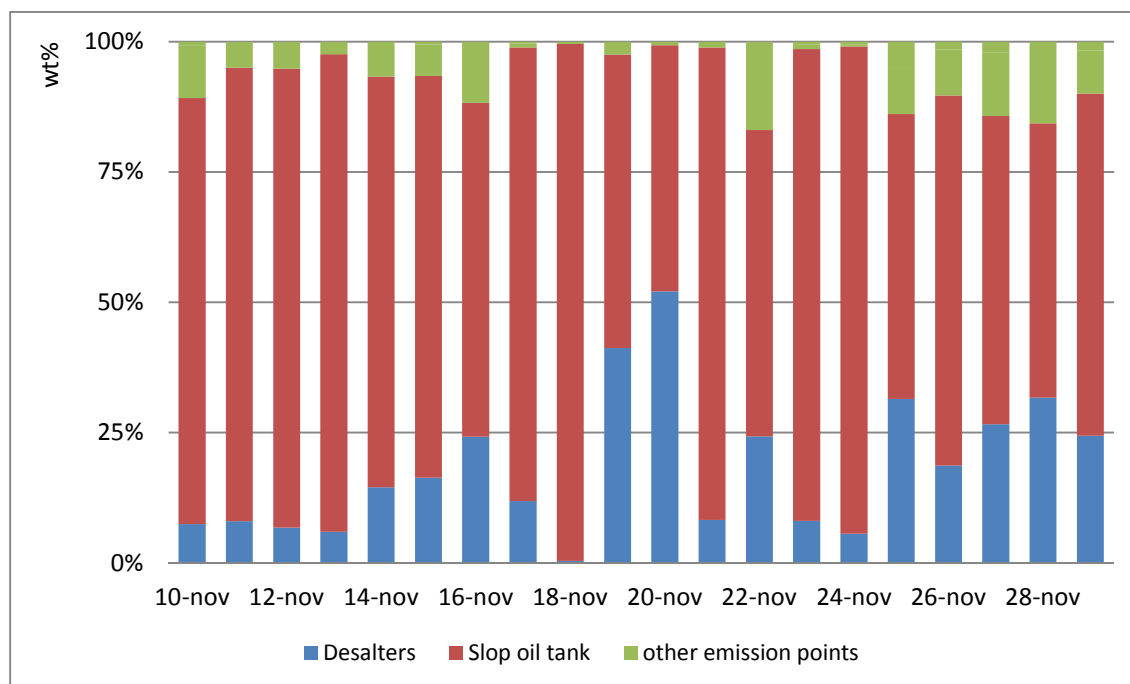


Figure 2. 8 – Ammonia mass balance estimation compared with analytical result at the discharge point for external WWTP during November 2011.



**Figure 2. 9 – Mass contributions of desalter effluent, slop oil tank bottoms and other emission points for the estimated ammonia value at the discharge point for external WWTP in November 2011.**

#### **2.2.4. Slop oil tank**

A slop oil tank is integrated in a system designed for recovering the crude derivate products, which are generated in the refining process, but don't fulfill the product specifications and cannot be used or distributed without previous reprocessing or upgrading. Slop oil is generated in oil that is carried with water in tank drainage procedures, hydrocarbons that are drained from equipment's that are going to be maintained, oil resulting from equipment cleaning, off spec products from units startup and shutdown procedures, and hydrocarbons recovered in knockout drums in flare systems [1, 3, 6].

Flare system is composed by a knockout drum for recovering of liquid hydrocarbons and for an incineration torch. Flare acts as safety system, which is used for environmental control of hazardous products discharge in emergency situations or operational problems in refining units [25]. A schematic representation is shown on Figure 2. 10.

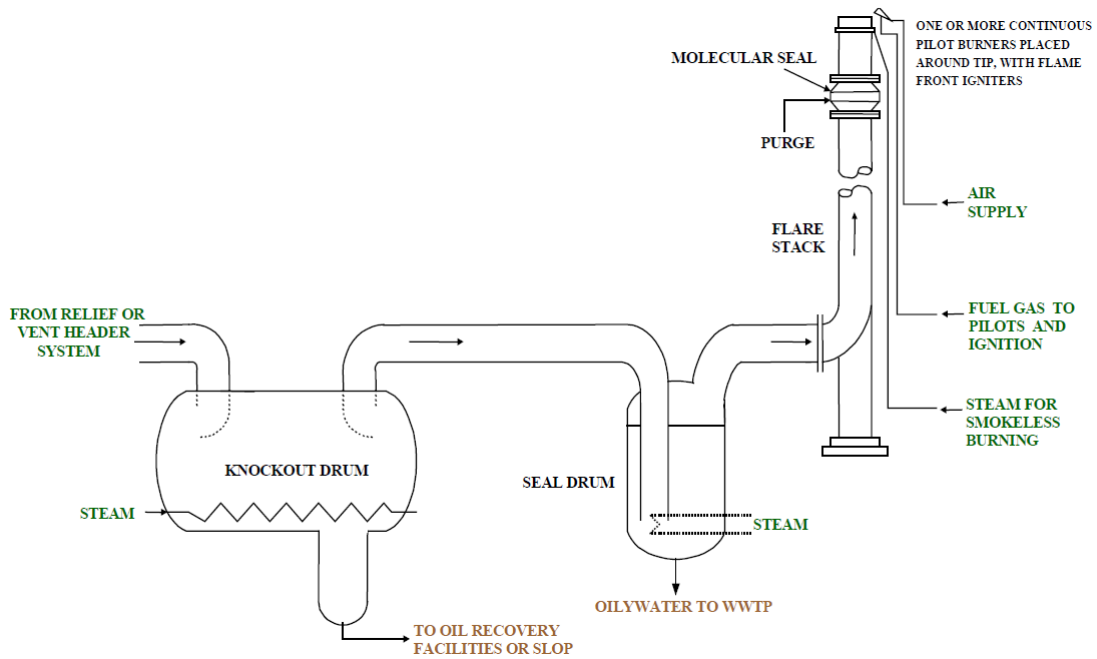


Figure 2. 10 – Simplified scheme of a flare system [25].

Based on the results presented on Figure 2. 9, which indicate the major contribution of slop oil tank to ammonia contamination, the upstream equipment were identified and the daily slop oil production of each equipment estimated with the number of working hours of slop oil pumps. The estimated flow was cross checked with the inventory variation of slop oil tank as indicated in Figure 2. 11. The results show a good agreement between the estimated flow of the different sources, indicated on Figure 2. 12, and the variation of tank level, being the daily differences explained by accumulations in interconnecting lines.

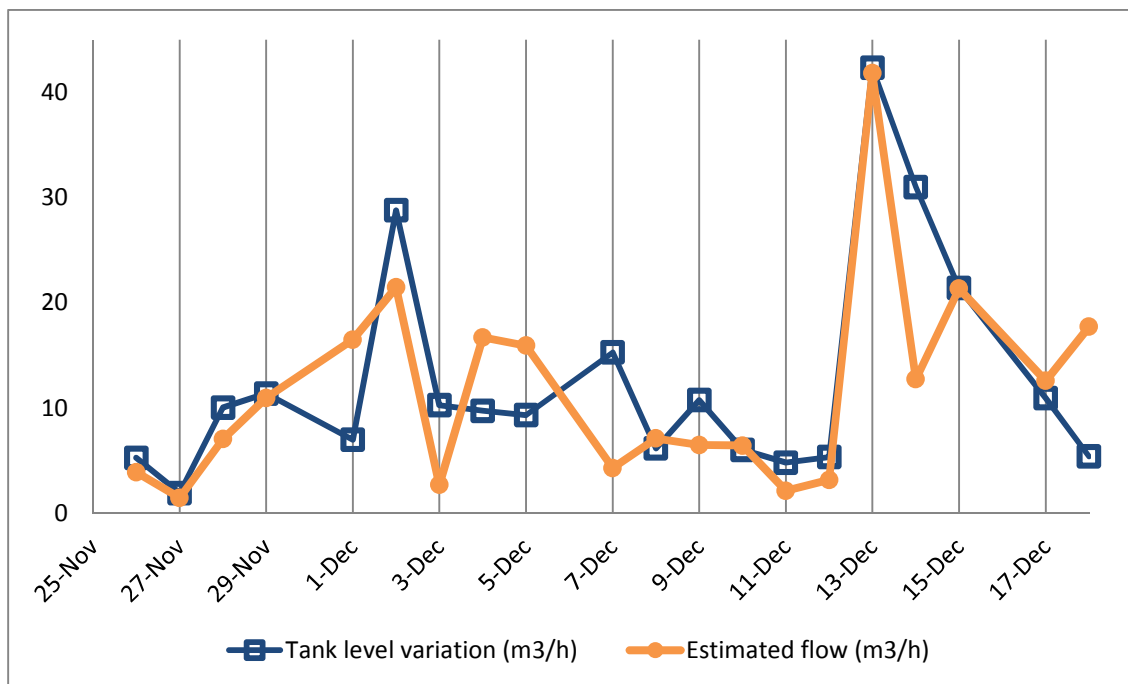


Figure 2. 11 - Comparison between slop oil flow estimation and tank inventory variations in December 2011.

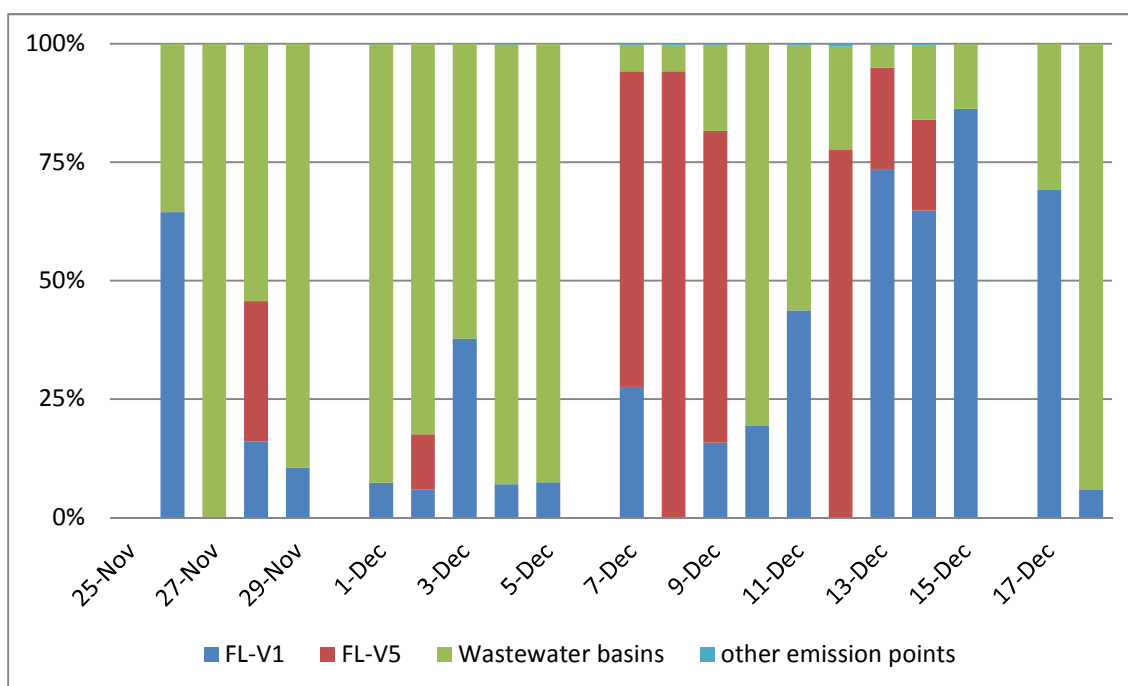


Figure 2. 12 - Volumetric contributions to slop oil flow estimations of different sources upstream of slop oil tank, with indication of flare knockout drums (FL-V1 and FL-V5) and primary separation wastewater equipment (API, CPI and DAF) in December 2011.



It becomes clear from Figure 2. 12 that the main contributors to slop oil production are the primary separators like API, CPI and DAF, in the wastewater circuit, which recover the oil carryover from tanks and equipment drainages. Still in primary separators there is no generation of ammonia, and so the possible emissions points are most likely related to knockout drums from flare system. Samples were collected in knockout drum FL-V5, but due to safety reasons, it was not possible to sample the knockout drum FL-V1. The results obtained are presented in Table 2. 2.

**Table 2. 2 – Ammonia analytical results in knockout drum FL-V5 and slop oil tank bottoms in December 2011**

<i>NH<sub>3</sub></i> (ppm)	7-Dec	8-Dec	9-Dec	10-Dec	11-Dec	12-Dec	13-Dec	14-Dec	15-Dec	16-Dec
FL-V5	701	701	670	510	630	590	760	720	760	970
Slop oil tank bot.	1700	1700	3100			1500	3200	3400		

A critical analysis of the results suggests that knockout drum FL-V5 is not the most responsible one for the ammonia contamination levels observed in slop oil tank. It was therefore assumed that the major ammonia contribution was due to the other knockout drum FL-V1, and that emission source was a unit upstream of this drum. An operational investigation was developed in the upstream circuit in order to identify the ammonia source emission point. During the investigation, an interconnection between the flare gas line circuit with knockout drum FL-V1 and a sour gas line coming from a SWS, was identified. This interconnection was in service, since the normal operation line that routes the sour gas to incineration in a sour gas flare line was obstructed, possibly due

to precipitation of ammonia salts. Such precipitation of ammonia salts could have been provoked by the absence of insulation in a section of the line, which causes a sharp variation of the gas temperature. Also the reduced and occasional sour gas flow in that line, since normally it is routed to the Claus reactors for sulfur recovery, has led to that situation [26].

### 2.2.5. Mitigation

In face of the results, an action was immediately triggered to divert the sour gas path from the normal flare gas line and clear the obstruction in the sour gas flare line, by passing steam to clear the line. The line was readily insulated during August 2012, and in Figure 2. 13, it is possible to observe the evolution in wastewater ammonia content prior to the described actions in August 2012, which was correlated with the routing of sour gas to flare, and since this period, when sour gas is sent to sour gas flare circuit.

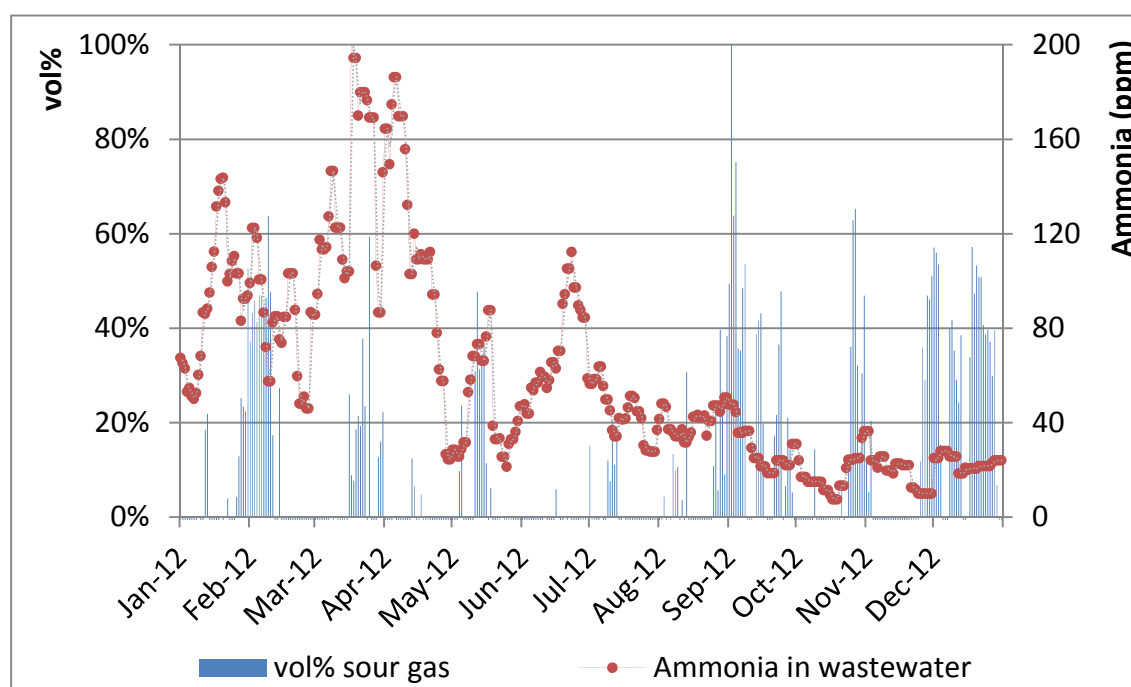
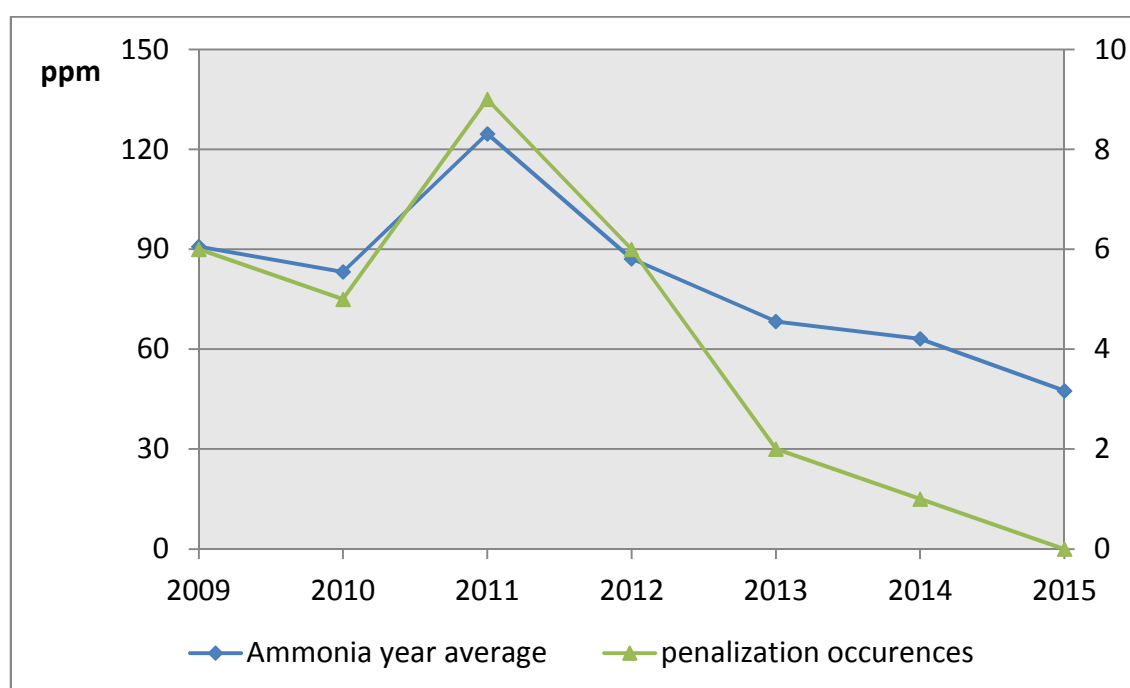


Figure 2. 13 – Correlation between sour gas valve opening to flare circuit and ammonia content in refinery wastewater at the discharge point for the external WWTP.

The impact of modifications performed during the summer of 2012 were immediately observed in the reduction of the average ammonia content in the wastewater and, consequently, in the decreased number of the occurrence of penalizations, resulting from a discharge of more than 125 ppm of ammonia. These observations are presented in Figure 2. 14.



**Figure 2. 14 – Ammonia average concentration in discharge point to external WWTP and number of penalizations occurrences (Ammonia > 125 ppm).**

The observed results in Figure 2. 14 show that the developed worked during this PhD has resulted in great economic savings just after 2012, since in the following 3 years (2013 to 2015) the sum of penalization occurrences was smaller than the total number of situations verified yearly between 2009 and 2012. The penalizations that have occurred since 2012 are due to emergency shutdowns of the refinery, which causes the absence of steam to adequately treat the sour waters sent to SWS. The routing of the sour gas to a dedicated flaring system allows to adequate treatment and avoids wastewater contamination with ammonia.



# **3. Prediction of polar oil and grease contamination levels in refinery wastewater through multivariate statistical modeling<sup>1</sup>**

## **3.1. Introduction**

The goal of the works described in this chapter was to build up and implement a mass balance to the largest Portuguese refinery wastewater circuit. In order to fulfill this goal, a PLS model was developed to predict the polar O&G concentration in the effluent of the kerosene caustic washing unit, due to its major impact to this pollutant concentration in the system. The results of the PLS model are used as inputs to the mass balance.

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<sup>1</sup> This chapter was partially published as a scientific article with the reference: Santos, B., Galinha, C. F., Crespo, J. G., Santos, M. A., Velizarov, S., Prediction of Polar Oil and Grease Contamination Levels in Refinery Wastewater Through Multivariate Statistical Modeling, Separation and Purification Technology, 119, 51-57 (2013).

### **3.1.1. Spent caustic impact**

The production, management and treating of spent caustics are a subject of growing interest due to the hazard and toxic nature of this byproduct. The level of spent caustic contamination is related with the chemical composition of the treated hydrocarbon in caustic washing units, and with the process operating conditions. As described in previous sections, the discharge of spent caustic directly to wastewater circuit contributes to increase the pollution levels. In the particular case of the refinery, this augmentation is observed in COD and polar O&G with significant impact in classification and costs of the discharged wastewater to external WWTP. The market presents several solutions to mitigate the noxious effects of spent caustics. However its application depends on the contamination degree of caustic, the refinery dimension and configuration, and the maximum accepted toxicity for existing biological treatment solutions downstream [21]. Therefore is of great interest the development of contamination models that can predict the impact of spent caustic discharge and establish a relation with operating conditions and properties of the feedstock. Still, and despite the relevance of this topic, I was neither able to find in the open literature correlations or models for prediction of polar O&G pollution, nor for any other of the analytical parameter considered in this thesis. The literature only provides some anticipated values or range of values [1, 3, 4, 6, 21].

### **3.1.2. Multivariate statistical methods**

The description of any dynamic system can be done by using different type of models, such as mechanical, black box, qualitative and statistical models.

Mechanical models are obtained through the application of state equations that describe the chemical and physical behavior of the system, which implies a deep knowledge of its characteristics and its behavior [27]. The application of

mechanical models to industrial systems with wide and constant variations in operating conditions is of difficult implementation [28].

Black box models describe simply the functional relations between inputs and outputs. Parameters used by this type of models do not have any physical or chemical significance, like mass transfer coefficients or reaction rates [29].

The application of qualitative methods is preferred when the nature of the process is more embracing than the simple mathematical description, e.g. the processes which physical limits present discontinuity points. In these cases “If-Then-Else” rules are introduced [29].

The need for statistical models results from the uncertainties and variability of certain processes, like industrial processes. This type of models allow to overcome the limitations of mechanical models using process data bases in order to develop a correlation between the different inputs to obtain a prediction of the output [27, 28]. Among the different methodologies to develop statistical models, PLS is one of the most popular ones. This mathematical tool can be used to identify and obtain information from the most significant process variables and their relation with the behavior of a certain output [30]. PLS as the advantage that can be used with extended process database that normally have some co-linearity between the different variables, missing values, noise and variables of different magnitude [31, 32].

### **3.1.3. Projection to Latent Structures (PLS)**

The working principle of PLS models is the establishment of linear relations between the process available data and the output variables which are intended to be predicted. The connections are established through selection and weighting of different model inputs and are used to predict the desired outputs [33]. The  $n$  observations collected for the  $k$  different variables which are intended to be used in output prediction, are structured in a matrix  $X$  with

dimensions  $n \times k$ . The same  $n$  events are collected for the  $j$  dependent variables, which are intended to be the output of the model, and organized into a matrix  $Y$  with dimensions  $n \times j$ . The PLS methodology decomposes matrixes  $X$  and  $Y$  into a product of groups of orthogonal factors with a matrix of specific weightings [34]. Independent variables are presented accordingly with equation (3. 1), into a product of a weighting matrix  $T$  by a loadings matrix  $P^T$ .

$X = T \cdot P^T$	(3. 1)
-------------------	--------

The dependent variables matrix is similarly decomposed as shown on equation (3. 2).

$Y = T \cdot B \cdot C^T$	(3. 2)
---------------------------	--------

Using PLS methodology the matrix  $T$  is built in order to allow for an adequate description of the input matrix  $X$  at the same time that allows for an adequate estimation of the output results matrix  $Y$ . With this arrangement, is possible the determination and interpretation of the used variables for modeling the desired predicted values.

## 3.2. Materials and methods

### 3.2.1. Wastewater sampling and analysis

A wastewater sampling campaign was performed to allow for the determination of soluble oil emission points, which methodology has been described in section **Error! Reference source not found.** As observed in previous sections, the spent caustic effluent from the kerosene caustic washing



unit is the main contamination source of the refinery wastewater. With the goal of developing a statistical model based on PLS for the kerosene caustic washing unit, 60 spent caustic samples were collected in the continuous effluent from this unit, during a representative period of 7 months. The distribution of sampling along the time allowed to have samples from diverse operating conditions and different feedstock properties. After development of the models, samples from the clarified effluent of dissolved air flotation unit were collected during 2 years in order to prove the adequacy of the predictive tools. Oil and grease concentration in wastewater and spent caustic samples was determined employing standard method SMEWW 5520 C. The quantification of polar and hydrocarbon fraction was made with the analysis SMEWW 5520 F [8, 11].

### **3.2.2. Process data**

For the buildup of the models and mass balances, several process data was acquired through the refinery process control system, namely kerosene density ( $\rho_K$ ), kerosene flow to caustic washing unit ( $Q_K$ ), crude oil density ( $\rho_C$ ) and wastewater flow in the wastewater circuit. Other relevant properties of the feedstock and products were obtained in the existing refinery linear model. The linear model performs refining simulations to the different process units and retrieves information about products yields and chemical parameters of distilled products, based on the processed feedstock. Selected data was the mass composition of crude oil mix fed to CDU, the naphthenic acidity of the crude mix ( $TAN_C$ ) and the kerosene cut ( $TAN_K$ ), the expected values of kerosene sulfur (%S) and mercaptans (RSH). The selected variables for PLS model development are indicated in Table 3. 1. For the identified independent variables 60 observations were retrieved at the same time that a spent caustic sample was collected for polar oil and grease laboratory analysis. The number of selected statistical events is within the recommended range for the development of a statistical model based on industrial data [35].

**Table 3. 1 – Process data used as inputs for PLS model development for prediction of spent caustic contamination with polar oil and grease**

Type	Parameter	Used in PLS model	Symbol	Source	Unit	Range	Average	Standard deviation
Input	Crude oil density	No	$\rho_C$	Online analyser	kg.m <sup>-3</sup>	[0.82; 0.88]	0.84	0.02
	Kerosene density	No	$\rho_K$	Online analyzer	kg.m <sup>-3</sup>	[0.79; 0.81]	0.80	0.004
	Crude oil naphthenic acidity	Yes	TAN <sub>C</sub>	Linear model	mg <sub>KOH</sub> .g <sup>-1</sup>	[0.06; 0.77]	0.39	0.24
	Kerosene sulfur content	Yes	%S	Linear model	wt%	[0.04; 0.23]	0.12	0.05
	Kerosene mercaptan content	Yes	RSH	Linear model	ppm	[43; 399]	262	66
	Kerosene naphthenic acidity	Yes	TAN <sub>K</sub>	Linear model	mg <sub>KOH</sub> .g <sup>-1</sup>	[0.02; 0.32]	0.20	0.12
	Kerosene flow	Yes	Q <sub>K</sub>	Online analyzer	m <sup>3</sup> .h <sup>-1</sup>	[67; 134]	114	26
Output	Polar oil and grease in spent caustic	---	PO&G <sub>SC</sub>	PLS model	ppm	[32; 31254]	15874	10688

### 3.2.3. PLS modeling of the kerosene caustic washing unit

The statistical events data gathered, for the variables indicated on Table 3. 1, has been used to create a statistical correlation for prediction of soluble oil content in the spent caustic effluent. Data was previously normalized by subtracting to each set of variables the average value of that variable, and divide by the standard deviation of the same variable. The normalization allows for each set

of data to be evenly distributed and that the initial weighting is the same for different variables. The data matrix obtained after normalization was randomly split in 75%/25% matrixes. The greater matrix was used for training the PLS model. The remaining data was used as a validation set and to adjust the weight of each variable. Despite the random distribution, the training and validation set were verified in order to assure that the events used for validating PLS model were representative of the training set, i.e. to avoid an extrapolation in results prediction using validation data. The PLS model for kerosene caustic washing unit has followed a methodology previously employed in biological membrane bioreactors modeling [31], which was adapted in order to correspond to the requisites of this work.

Multivariate statistical models developed with PLS methodology use a combination of  $x$  independent variables that are weighted with  $a$  factors accordingly their relation with the desired output  $y$ , as described by equation (3. 3).

$y = a.x_1 + b.x_2 + c.x_3 + \dots$	(3. 3)
-------------------------------------	--------

In order to improve the predictive capacity of multivariate model and in order to explain possible additional relations, interaction and quadratic variations of the parameter listed in Table 3. 1 have been used. This approach results in a statistical model described by equation (3. 4), which can have complex interactions and non-linear terms.

$y = a.x_1 + b.x_2 + c.x_3 + \dots + d.x_1^2 + e.x_1.x_2 + f.x_1.x_3 + \dots$	(3. 4)
---	--------

The introduction of quadratic and interaction parameters leads to a significant increase in the model inputs. However, from the group of the independent variables used as inputs, some of them do not have any utility in the prediction

of polar oil and grease concentration in spent caustic. In order to eliminate the unnecessary data, 3 different selection mathematical methodologies were used: ISE method based on iterative elimination step-by-step [36], elimination step-by-step [37], and Martens uncertainty test [35], using the jackknife methodology [38]. Application of these methods allows for the elimination of the unnecessary variables to output estimative, which as the advantage to have a better prediction with less parameters. Each methodology has resulted in a model with a different number of parameters. Multivariate equations were compared based on slope and correlation coefficients ( $R^2$ ) of the tendency lines obtained in parity graphs, that plots the predicted value and the analytical result, for the training and validation sets. For the evaluation of the predictive capacity of each obtained model it was also used the Root Mean Square Error of Prediction (RMSEP) which indicates the error of the prediction by the validation set. The selection of the optimum number of latent variables in PLS regression was based in the lower value of the RMSECV: Root Mean Square Error of Cross Validation. RMSECV indicates the error of the training set by cross validation calculation as indicated in equation (3. 5) where  $y_i$  is the experimental value for the statistical event  $i$ ,  $\hat{y}_i$  is the estimated value by the PLS model for the same event  $i$ , using a data set of  $N-i$  events, where  $N$  is the total number of observations used for PLS model development.

$RMSECV = \sqrt{\frac{\sum_{i=1}^N (\hat{y}_i - y_i)^2}{N}}$	(3. 5)
--	--------

In this work there were 60 observations. PLS models were developed in *Matlab* by using the *N-way toolbox* [39].

### 3.3. Results and discussion

#### 3.3.1. Modeling of polar oil and grease content in the spent caustic effluent

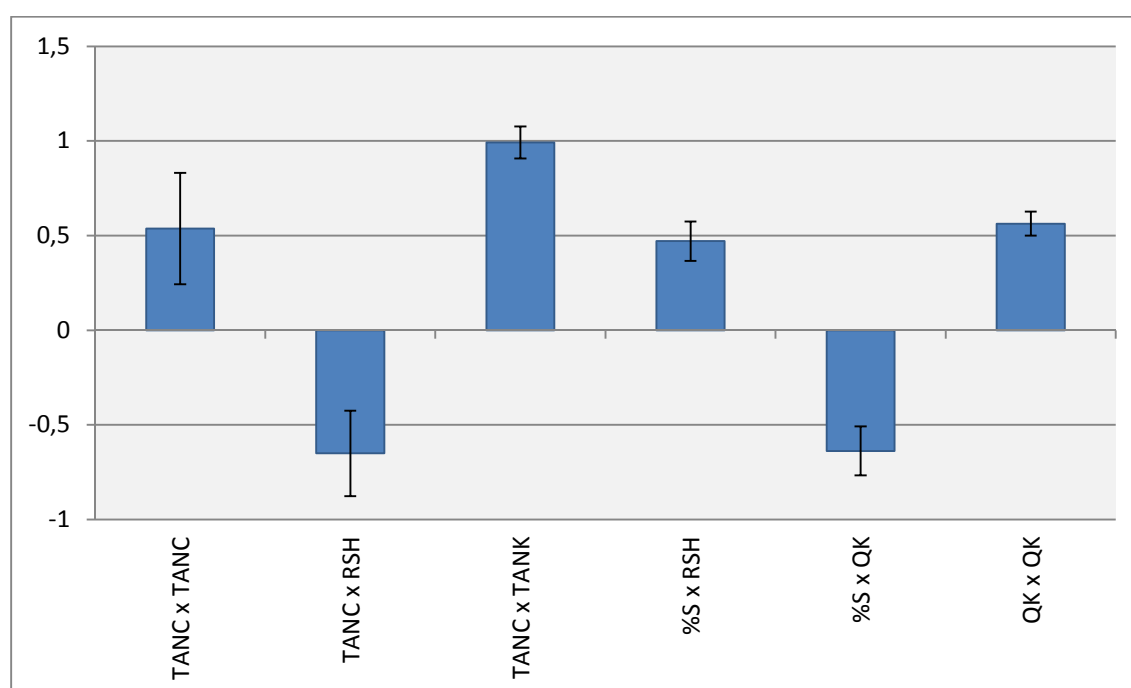
The 60 observations gathered for the variables indicated in Table 3. 1, were used for the development of a multivariate statistical model for polar oil and grease prediction in spent caustic effluent from a kerosene caustic washing unit. In order to allow for a simple interpretation of the relation between latent variables and the estimate contamination of wastewater by soluble oil, it has been developed a model based only on linear combinations between independent variables. The evaluation terms for the best model obtained accordingly with this principle, are presented on Table 3. 2.

**Table 3. 2 – PLS models, captured variance and correlation coefficients for validation and training sets**

PLS model	Captured variance (%)	RMSEP (ppm)	Validation set correlation coefficient	Training set correlation coefficient
Only linear terms	76.5%	3014	0.94	0.76
Interaction and quadratic terms	96.1%	2582	0.94	0.96

The analysis of the table data indicates that despite the PLS model with only linear terms allow for an adequate representation of the observations included on validation set, it fails to predict adequately the training set data, since the correlation coefficient for this set is only 0.76. Based on this low predictive capacity a PLS model with interaction and quadratic combinations of the initial terms was developed in order to upgrade the precision of correlation prediction. Accessory and unnecessary terms were eliminated with the selection methodologies, resulting in an equation with only 6 weighted terms from the initial 35. The most robust PLS model was obtained using the selection

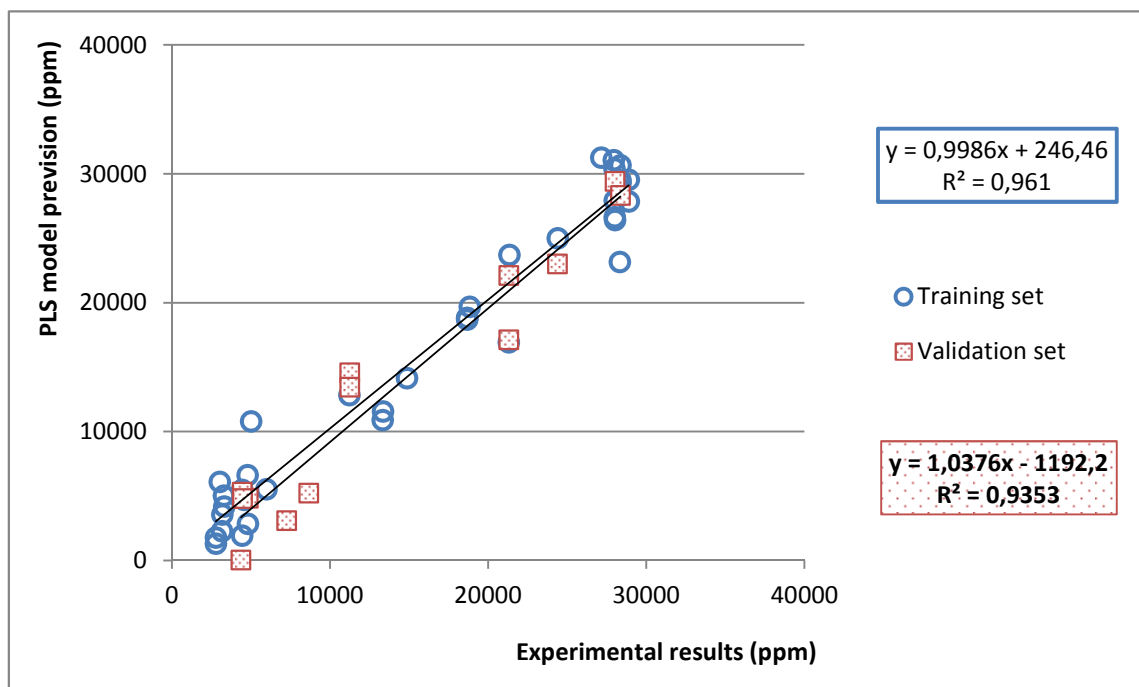
method ISE, which regression coefficients are indicated in Figure 3. 1. The observation of the selected variables shows that none of the terms related with crude oil and kerosene density was selected to polar oil and grease prediction model. The lack of this parameters could be related with the small variation range of the product densities during gathering of experimental values, which have no impact on spent caustic quality.



**Figure 3. 1 - Regression coefficients of model inputs for polar oil and grease contamination level in the effluent of the kerosene caustic washing unit.**

Regression coefficients selected to PLS model indicate that a higher concentration of soluble oil in spent caustic occurs with the increase of kerosene flow to caustic washing unit, which could be related with the higher turbulence in prewash column and greater contact efficiency between kerosene and caustic. An intimate contact between hydrocarbons and aqueous phase promotes the extraction of pollutants from the product. Also, the data suggests that an increase of spent caustic contamination is associated with higher values

of crude oil and kerosene naphthenic acidity, sulfur and mercaptan concentration in the kerosene. This behavior is expectable since naphthenic acids, sulfur and mercaptans are polar substances which interfere with the determination of oil and grease in waters [8, 15]. The PLS model comparison with analytical values for polar oil and grease in spent caustic is shown on Figure 3. 2, and indicates that training and validation sets have high correlation coefficients, respectively 0.96 and 0.94.



**Figure 3. 2 – Comparison between PLS model estimations and experimental data for polar oil and grease content in the kerosene caustic washing unit effluent, with slope and quadratic error, for the training and validation data sets.**

As indicated on Table 3. 2, the statistical equation, used for polar oil and grease concentration prediction in spent caustic, with interaction and quadratic terms describes 96% of the data variation and presents a prediction error, RMSEP, 15% lower when compared with the correlation obtained only with linear combinations of the variables. The results show the capability of the predictive model to follow up and adapt to the changes and fluctuations in the process

variables and feedstock properties and reflect them in spent caustic contamination. It should be noticed that the PLS model was developed based only on process data and variables obtained in other prediction model, the refinery linear model, and despite that they allow for an adequate representation of the soluble oil content in naphthenic spent caustic.

### **3.3.2. Wastewater mass balance**

Following the excellent results obtained with PLS predictive model for polar oil and grease in spent caustic, and being the main goal the estimation of this pollutant at discharge point for external WWTP, a mass balance to refinery wastewater circuit was developed. As referred in previous sections, the high concentration of polar species in the system is responsible for the augmentation of the charged costs, based on the existent classification system. A mass balance to the system schematically represented on Figure 2. 1 was buildup assuming that the only emission point for polar substances was the kerosene caustic washing unit effluent, for which a PLS prediction model was available. It was also assumed that due to the wastewater basins dimensions and volumetric flows, there was a perfect mixing inside the basins and no dead volumes or preferential paths exist in the system. To validate the mass balance estimations, samples were collected in the clarified effluent from the dissolved air flotation unit. Comparison between mass balance and analytical values is presented on Figure 3. 3.



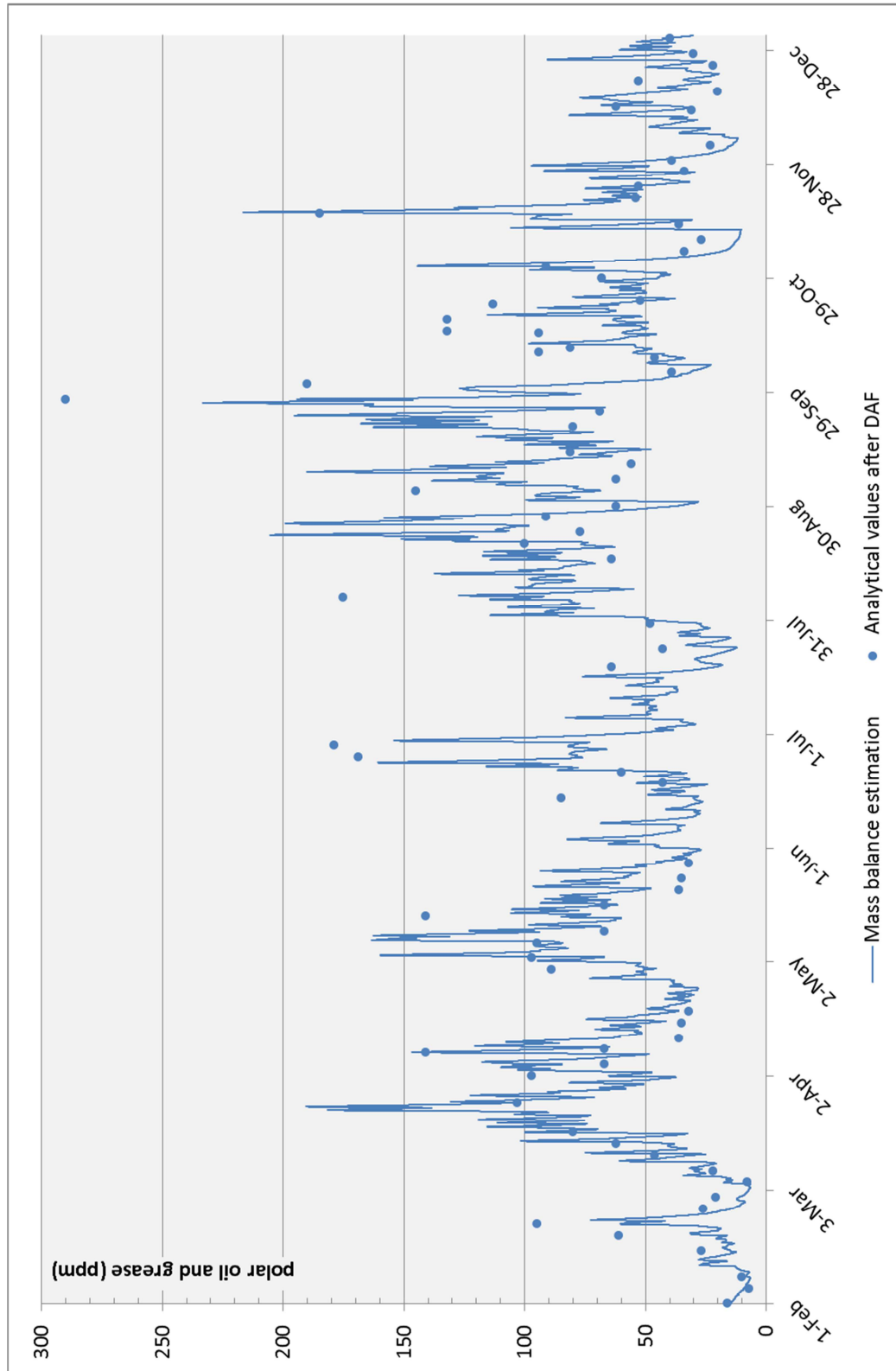


Figure 3. 3 - Comparison of dynamic mass balance estimation line of polar oil and grease content in the effluent of the dissolved air flotation unit with experimental data points.

Analyzing the data we can conclude that the assumptions used for wastewater mass balance buildup were corrected, in particular the hypothesis of the spent caustic as being the single emission point. It is important to notice that despite the estimations could be affected by deviations to the perfect system theory, namely non turbulent flow, preferential paths or incorrect PLS predictions, the mass balance is capable of reproducing accurately the experimental dynamic behavior of the system. The predictive capacity of the mass balance is more important because it was only started after the PLS tool development, and since the start of the estimations, the PLS equation was never updated or corrected, despite the fact that during the considered period, different feedstock qualities from the used in training and validation, have been processed. The wastewater mass balance and kerosene caustic washing unit PLS model are effective and robust tools for prediction of wastewater polar oil and grease contamination in the largest Portuguese oil refinery and in any other refinery with similar complexity and specially with a kerosene spent caustic unit, which spent caustic is discarded to wastewater treatment system.

### **3.3.3. Optimization of kerosene caustic washing unit in refinery framework**

The results obtained in the previous section, have demonstrated the great estimation capability of the developed wastewater mass balance, and based on the daily observations and correlations with processed feedstock's, an optimization of kerosene caustic washing unit functioning within refinery framework was developed. As previously described, the increase in crude oil and kerosene naphthenic acidity leads to higher contamination of the wastewater with O&G and consequently to a greater impact in charged costs to the refinery. Acid crude oils are gaining significant importance since they are a cheaper feedstock when compared with crudes with lower naphthenic acidity. Faced with this evidence it was proposed to refinery planning that during

processing of acid crude oils, the kerosene cut was diverted from caustic washing unit and sent to treatment in existing hydrogenation unit. In hydrogenation unit, the spent caustic effluent is not produced. Instead a sour gas stream is generated which is routed to Claus reactors. Hydrogenation units are normally operated near their maximum capacity, so there is the need to storage the products normally sent to this units, like diesel, which causes a planning and logistic problem and can lead to accumulation of high sulfur products with a lower market value. During the first trimester of 2014, the described operational strategy for kerosene caustic washing unit was implemented. The comparison of charged costs along the different years since 2009, was presented on Figure 1. 2.

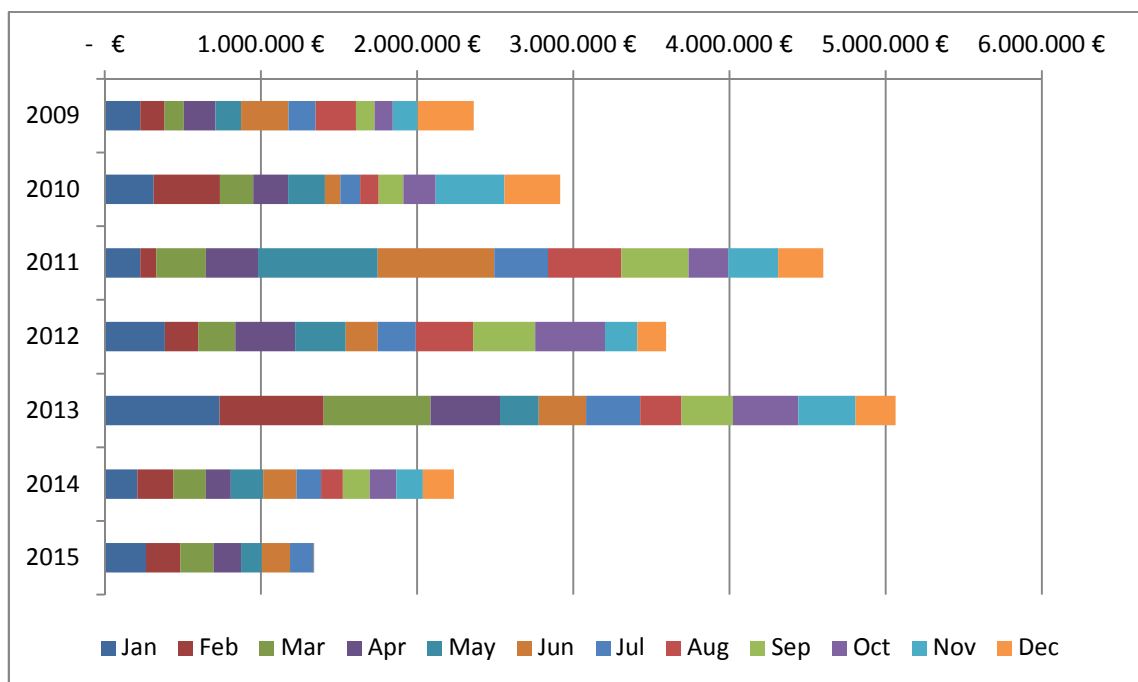


Figure 1. 2 – Wastewater treatment costs charged by external WWTP

It is possible to observe that with the implementation of the new operating strategy, along with the development of other corrections like in ammonia pollution reduction, as allowed to reduce significantly the effluent charged costs from 5 M€ to almost 2 M€. Also the economic analysis performed with

refinery linear planning model has shown that when facing an excess capacity situation in hydrotreating units, the economic interest in acid crude oil processing and the savings generated in wastewater charged costs can compensated the increase in kerosene treatment costs from a caustic washing unit to an hydrogenation unit.

Nevertheless, treatment solutions were studied with the goal of developing a cheap technology capable to eliminate or mitigate the noxious effects of spent caustic discharge in wastewater refinery circuit. Results are presented in Chapter 4 and Chapter 5.

#### **3.3.4. Aerated lagoon operational tests**

In refinery aerated lagoon, with a volume of 7000 m<sup>3</sup>, wastewater is aerated with surface air and injection of oxygen in the bottoms with the goal of sulfides and phenolic compounds oxidation. Since 2005 bacteria and activated carbon were bought and added in an attempt to reduce O&G content. Using the developed wastewater mass balance the impact of stopping the addition of this two substances, was evaluated starting on August 2013. Results at the discharge point for the external WWTP presented on Figure 1. 4, show that between May 2013 and August 2013, prior to the modification, significant differences between mass balance estimations and analytical values were observed. Based on the accurate predictions for polar oil and grease concentration in wastewater, upstream of the aerated lagoon, the fluctuations were assumed to be related with the fact that activated carbon acts like a toxic substance adsorbent, such as phenolic compounds and carboxylic acid. However the adsorption of the toxic substances, combined with dynamic operation basin could create a situation of sudden increase in wastewater pollution which could be explained by the simple fact that samples are not prior filtrate to O&G analysis, and in the presence of an organic substance, adsorbed compounds in activated carbon are extracted [40].

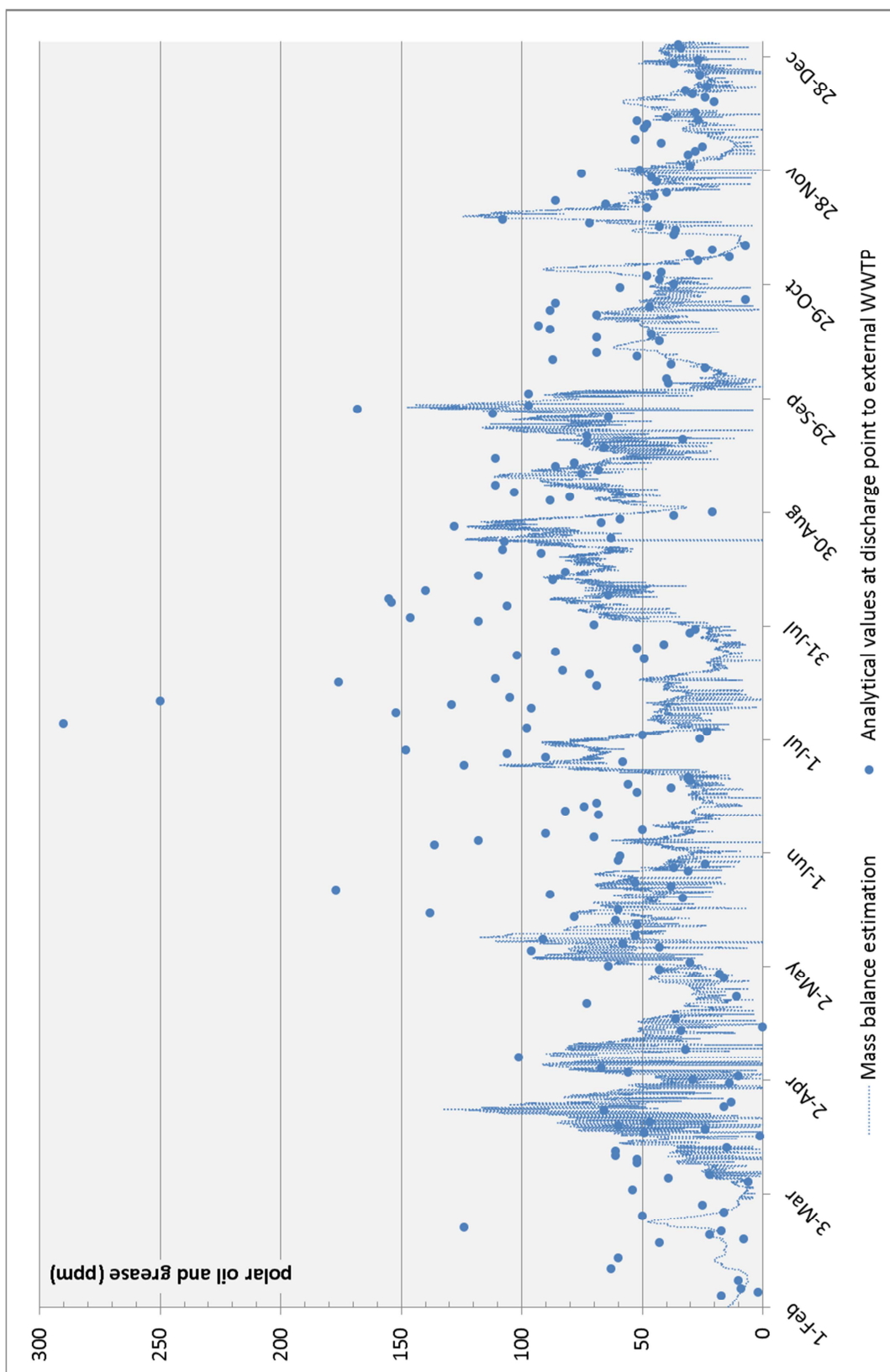


Figure 3. 4 - Comparison of dynamic mass balance estimation line of polar oil and grease content at discharge point for external WWTP with analytical values.

Since August 2013, as observed on Figure 3. 4 is evident the improvement in the analytical results which validates the anticipated assumption that bacteria and activated carbon addition have a placebo effect on polar O&G contamination reduction.

The addition of commercial bacteria, despite their synthesis in alleged identical conditions, may not reflect the nature, dynamic and temporal distribution of microorganism population within the aerated lagoon. This possible mismatch of the added cultures may be one of the causes for the apparent inefficiency [41]. Other negative factor that may contribute to the apparent inaction of added bacteria, could be the relative low residence time of the aerated lagoon and the severe fluctuations in effluent quality, flow and dissolved oxygen value, which can prematurely inhibit the development of introduced biological strains [42].

The developed PLS model and wastewater mass balance, despite the validation of kerosene caustic washing unit as single oil and grease emission point, as also allowed to test the non-utilization of activated carbon and bacteria inoculum and consequently proves the placebo effect of these addition. These conclusions allows the refinery to save more than 200,000 € every year at current prices from 2013.

## **4. An on-site pilot scale recovery of petroleum refinery spent caustics by nanofiltration: Process validation and economic evaluation <sup>2</sup>**

### **4.1. Introduction**

In the previous sections, it has been demonstrated that wastewater treatment costs, charged by the WWTP external to the refinery are mainly influenced by the polar oil and grease content. The implementation of a mass balance to wastewater circuit, using as input a PLS model developed for kerosene caustic washing unit, has shown clearly the enormous impact of this parameter in the refinery wastewater pollution. Results indicated by standard methods SMEWW 5520 C and SMEWW 5520 F suggests the possible presence of heterocyclic, aromatic and phenolic substances, but also unsaturated compounds and substances that have in its structure polar atoms like chlorine, oxygen, sulfur or nitrogen [11]. One of the most important substances that interferes with soluble oil content is naphthenic acid that remains in the wastewater even after gravity separations or chemical treatments such as coagulation or flocculation [15]. The

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significant presence of this specie in the effluent from the kerosene caustic washing unit is the reason for the denomination: “naphthenic spent caustic” [21].

Spent caustics poses very serious difficulties to refineries operation in terms of its handling, treatment and disposal, due to its highly toxic nature as indicated in Table 4. 1. The relatively high concentrations of various pollutants, make these streams toxic to bacteria used in wastewater treatment units, and may cause discharges of wastewater with pollutants levels above the limits defined by environmental legislations [43]. In order to mitigate the negative impacts of spent caustics, the respective streams can be reduced on source, reused within the refineries, recycled outside the facilities, or appropriately treated and disposed.

**Table 4. 1 - Average composition of spent caustic effluent [21, 44]**

<b>Component</b>	<b>Units</b>	<b>Range</b>
<b>Sodium hydroxide</b>	wt%	1-15
<b>Inorganing sulfides, as S</b>	wt%	0-4
<b>Mercaptide, as S</b>	wt%	0-4
<b>Cresylicacids</b>	wt%	0-25
<b>Naphthenic acids</b>	wt%	2-15
<b>Phenols</b>	mg.l <sup>-1</sup>	0-2000
<b>Total organic carbon (TOC)</b>	mg.l <sup>-1</sup>	6000-20000
<b>Chemical oxygen demand (COD)</b>	mg.l <sup>-1</sup>	20000-60000
<b>Biochemical oxygen demand (BOD)</b>	mg.l <sup>-1</sup>	5000-15000
<b>pH</b>	Sorensen scale	12-14



A reduction of the spent caustic volume, on source, can be accomplished by choosing a caustic-free process like hydrotreatment or replacing the caustic with ammonia, or an ionic liquid as have been recently investigated [45]. In case of existing processes, the reduction is essentially accomplished through optimizing the procedure of caustic washing, or when possible by maximizing caustic strength. However, there will be always a caustic-containing stream resulting from the process. Reuse of spent caustics, within refineries, normally targets the fresh caustic uses for pH control like: pH control in crude desalting process or pH control of wastewater treatment units [21, 46-48]. Nevertheless, reuse of spent caustics is often limited in quantities and should be done in a controlled manner in order to avoid possible adverse impacts. An undesirable impact often reported is corrosion on overhead distillation column, when spent caustics is used for pH control in the crude desalting process without adequate follow up due to the fact that spent caustic has less buffer effect than fresh caustic solution, however the sodium content remains the same. Care must be taken in order to avoid the deposition of high quantities of sodium in overhead circuits [46]. The recycling of spent caustics outside the refineries, so far has been reported in pulp and paper, tannery, mining and wood preservatives industries, for replacing some of the fresh caustic using in these industries. However, in what concerns refineries, such a recycling has either not been yet performed or additional treatment has been suggested for spent caustics conditioning inside the refinery [21]. Some treatment technologies such as chemical oxidation/precipitation using hydrogen peroxide or chlorinated copperas, neutralization/acidification employing sulfuric acid and wet oxidation and are available for treating spent caustic. Despite their efficiencies, the main disadvantages are the high capital and operating costs, which represent a fixed monetary fee for the refinery. One of the most used technologies, indicated as a Best Available Technology (BAT), can represent an investment cost around 10 million US dollars and operation expenditures around 1 million US dollars [49, 50].

So far, the use of membrane filtration has been applied in oil refineries for concentration and clarification of oily wastewater, as an alternative to the conventional methods [51]. The high degrees of oil and COD removal, the elimination of chemical additives, the comparatively lower energy costs and the minimal space requirements are the drivers for membrane processes preference [52]. Newly emerging membrane applications allow for a police of pollution reduction at source and effluent reusing towards a target of zero discharge. New resources such as desalination and wastewater reuse already account for 0,5% of the worldwide water consumption [53]. Food and beverage industries, are an example of effluent reusing. Dilute caustic solutions used for cleaning the process equipment, are recovered with membranes with the primary objective of reducing chemical disposal and reusing the caustic in the process [54, 55]. A reduction in COD content from 76% to almost 100% off the caustic washing has been reported using nanofiltration membrane systems [56, 57]. The reduction of caustic consumption in the cleaning process and the corresponding minimization of discharged spent caustic allow for significant savings and a payback time in less than 2 years when using micro-, ultra- or nanofiltration membrane systems [55]. However, and despite the generation of big amounts of highly contaminated spent caustics in oil refineries, to the best of my knowledge, there is still no studies reported for membrane applications to refinery spent caustic. Therefore, the main goal of this work, which is described in the following sections was to investigate the feasibility of spent caustic recovery using nanofiltration as an alternative to currently applied treatment options such as wet air oxidation.

## **4.2. Materials and methods**

The performance of two types of membranes was studied with the objective of reducing the impact and contamination caused by spent caustic in the refinery

wastewater. A tubular ceramic UF membrane with an inner diameter of 6 mm and a filtration area of 0.013 m<sup>2</sup> manufactured by Tech-Sep, type Carbosep M2 with a claimed molecular weight cut-off 15000 Da (Rhône-Poulenc Group, Miribel, France), was tested for global refinery aqueous effluent treatment. The membrane is composed of a thin perm-selective skin layer of zirconium oxide and titanium dioxide spread on the interior (lumen) surface of a tubular porous carbon support. The membrane was tested in a concentration operation mode, i.e. the permeate being collected and the concentrate recycled. The membrane was tested at different transmembrane pressures ranging between 0.5 and 1.4 bar. The operating temperature was around 24°C since the experiments were performed in an air-conditioned room at this temperature. After filtration, the membrane was washed with water and cleaned with a 2%(m/m) aqueous caustic soda solution. A proprietary composite polymeric nanofiltration membrane SeIRO®, model MPS-34 2540 A2Z in a spiral-wound module configuration from Koch was then tested for its potential to filtrate spent caustic samples taken from a kerosene caustic washing unit. This alkaline resistant membrane has a molecular weight cut-off of 200 Dalton and 1.2 m<sup>2</sup> of membrane area. The dimensions of the NF module tested are shown on Figure 4. 1.

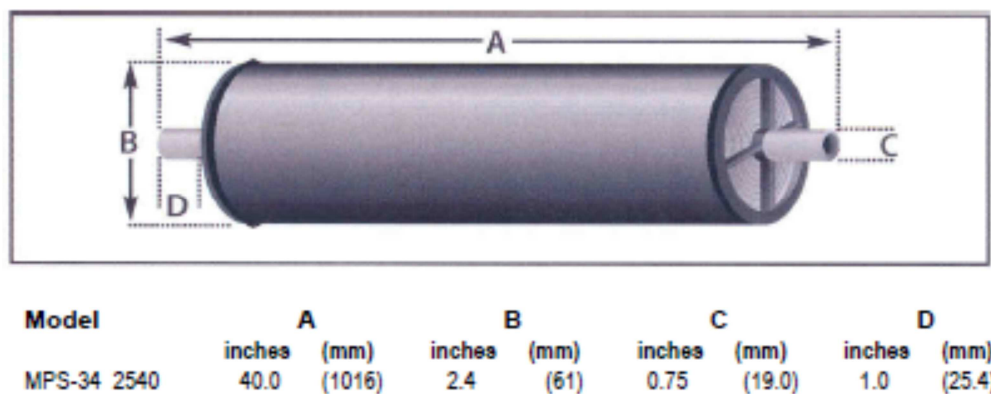


Figure 4. 1 – Nominal dimensions for the proprietary composite nanofiltration membrane, from Koch, tested for spent caustic filtration [58]

An important characteristic of the membrane is its broad allowable pH operation range, which is between 0 and 14. The composite element is designed to work at a maximum pressure of 35 bar and up to 50°C. For a lower pressure, of 15 bar, the temperature can be increased up to 70°C [58].

Spent caustic was filtrated in a concentration operation mode. The operating pressure was set up at 15 bar. The concentrate was not thermostated, as its temperature remained around 25°C during the duration of the tests. In order to assess the energy consumption of the pilot installation for spent caustic filtration, an energy measuring device, Brennenstuhl PM 231E, was plugged in the electric circuit, thus allowing for an instantaneous and accumulated registration of the electric energy consumption. This data obtained was used to estimate the average electric consumption for treating 1 m<sup>3</sup> of spent caustic. After the tests, the NF element was washed with water and cleaned with a 2%(m/m) caustic solution for 8 hours. The osmotic pressure gradient between the concentrate and permeate solutions in the presence of caustic, was calculated using the data for demineralized water flux ( $J_w$ ) and operating pressure gradient ( $\Delta P$ ). With these variables the hydraulic permeability constant of the filtration element ( $A$ ) was estimated using equation (4. 1).

$J_w = A \times \Delta P$	(4. 1)
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The osmotic pressure gradient ( $\Delta\pi$ ) through the membrane with the caustic containing solutions was estimated using the observed permeate flux ( $J$ ), as defined by equation (4. 2).

$J = A \times (\Delta P - \Delta\pi)$	(4. 2)
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Refinery wastewater was collected after the refinery equalization basin and before the dissolved air flotation unit, as schematically represented on Figure 2. 1. Spent caustic was collected from the effluent of the kerosene caustic washing unit. The samples of refinery wastewater were filtered by the UF ceramic membrane, and the NF polymeric membrane was applied for the samples of spent caustic. Initial wastewater, spent caustic samples, and samples from the permeates obtained after filtration were collected and analyzed with standard methods for polar oil and grease (SMEWW 5520 C/F), COD (SMEWW 5220 B), pH (SMEWW 4500 H+) and conductivity (SMEWW 2510 B). For the spent caustic treatment, sodium and sulfur were also analyzed in the samples using an ICP-AES (Ultima model, Horiba Jobin-Yvon, France) equipped with a radio-frequency (RF) generator of 40.68 MHz a Czerny–Turner type monochromator with 1.00 m (sequential), AS500 autosampler and data acquisition software.

The economic evaluation, for a hypothetical spent caustic industrial treatment unit equipped with the investigated NF composite membrane was based on extrapolation of the NF pilot plant data obtained. The calculations are based on the expected annual production of spent caustic, from a refinery caustic washing unit, and consider that 2/3 of the spent caustic effluent will be permeated, corresponding to a volume concentration factor (CF) of 3 as defined by the equation (4. 3).

$CF = \frac{Vol_{initial}}{Vol_{initial} - Vol_{permeate}}$	<b>(4. 3)</b>
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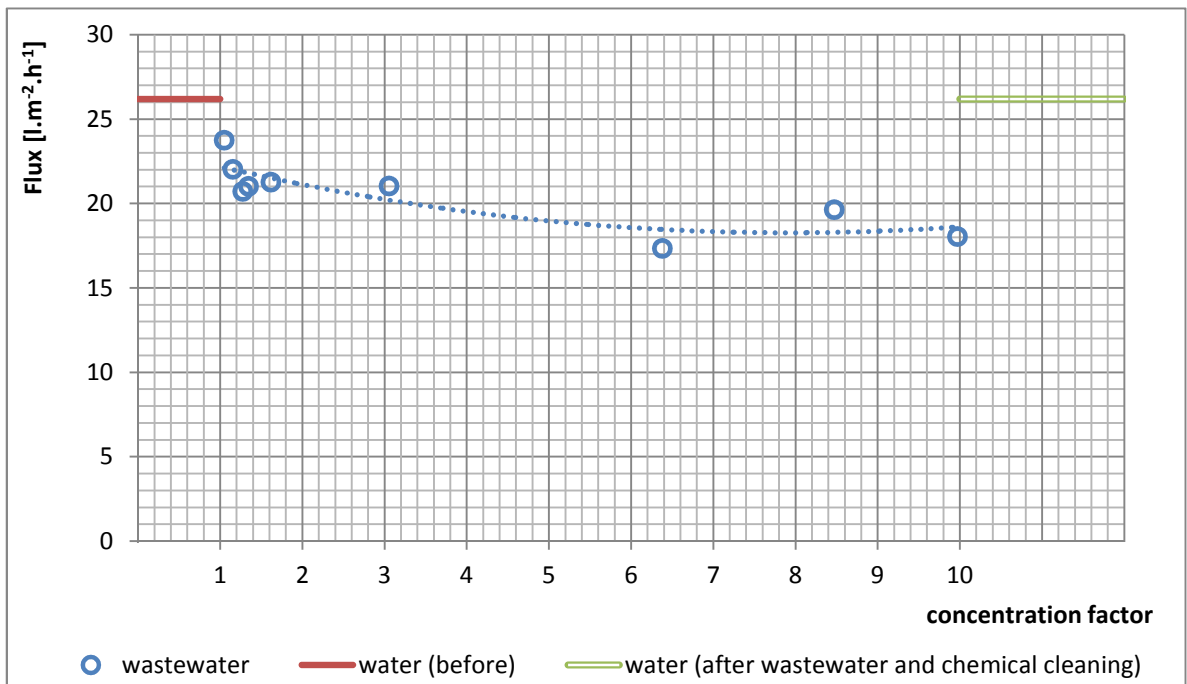
For the associated capital costs (CAPEX), a constant membrane flux along the lifecycle of each filtration element was assumed. Based on pilot plant data, each module is capable to permeate 74.5 m<sup>3</sup> per year. In the biggest oil Portuguese refinery around 14982 m<sup>3</sup> of spent caustic are produced every year. For a

concentration factor of 3, the caustic permeate will be 9928 m<sup>3</sup> per year. Therefore each filtration element is able to permeate 0.75% of the total caustic recovered volume, thus 133 modules are needed. For royalties, engineering and construction, 75% of the total membrane costs were estimated for the economic evaluation. A conservative reference value of 1558.5€ per filtration element, with a membrane area of 1.2 m<sup>2</sup> was used based on the purchasing price of a single element. The estimated operating costs were the energy consumption, installation maintenance, membrane replacement and treatment costs associated with the concentrated spent caustic. The energy index cost was extrapolated for 133 filtration elements, from the measured energy consumption of the pilot unit. The energy cost used is the reference value for industrial consumers in Portugal in 2015. The annual installation maintenance cost was assumed to be 40% of the capital invested and membrane lifetime was assumed to be 1.5 years [59, 60]. For the concentrated spent caustic transport and treatment outside the refinery, an approximated quote for handling this kind of hazardous residues by the current Portuguese refinery service provider, was obtained. Costs related with manpower, land acquisition, insurances or any other related costs were not considered, since it is assumed that the installation will be built within the refinery. Benefits from caustic reuse and reduction of wastewater contamination, have been estimated to be equal to 1.8 M€ based on the current refinery operational costs. An interest rate of 33% and an update factor of 11.9%, for a plant lifetime of 5 years were considered. Finally, a sensitive analysis was performed varying the operating costs by +/- 15%.

### **4.3. Results and discussion**

The tests with UF membrane were initially deployed with the objective of evaluating the potential of this solution to reduce the oil and grease

contamination of refinery wastewater, which is mainly caused by spent caustic, formed on kerosene caustic washing unit as discussed in previous sections. This approach was inspired by the reported investigations on oil and grease reduction, using ceramic membrane filtration, which have resulted in removal rates greater than 95% [61-64]. Also it could be a treatment alternative to dissolved air flotation unit or a complementary technology to reach the target result of 5 ppm, indicated to be in compliance to discharge to final water body media [9]. Refinery effluent samples collected after the wastewater equalization basin were fed to ceramic UF membrane and filtered in a concentration operation mode. Results compiled on Figure 4. 2, show a slight tendency for decreasing flux with the increase of the concentration factor.



**Figure 4. 2 –** Permeate flux across ultrafiltration ceramic membrane for demineralized water before and after filtration using wastewater and cleaning with a 2%NaOH solution, for wastewater sample #1

When 90% of the initial volume was filtered, the flux decrease reached almost 25%. Still, the membrane properties were completely restored after a chemical cleaning with a solution of 2 % NaOH, for a transmembrane pressure of 1.4 bar.

Analytical results obtained for two different wastewater samples and for clarified wastewater are presented in Table 4. 2. Results indicated almost 100% reduction in non-polar oil and grease, which is coherent with the data reported in the literature. However, the polar oil and grease fraction, which is the main responsible one for the effluent toxicity, remained to a great extent in the wastewater, since its reduction was variable and not effective. For the samples tested, it ranged between 30% and 60%, possibly due to different molecular masses of the compounds present. Therefore, these results cannot guarantee an adequate treatment of the refinery wastewater, which possessed an oil and grease content above the maximum desirable range of 5 to 20 ppm of the classification matrix, in order to be on the lowest tax range.

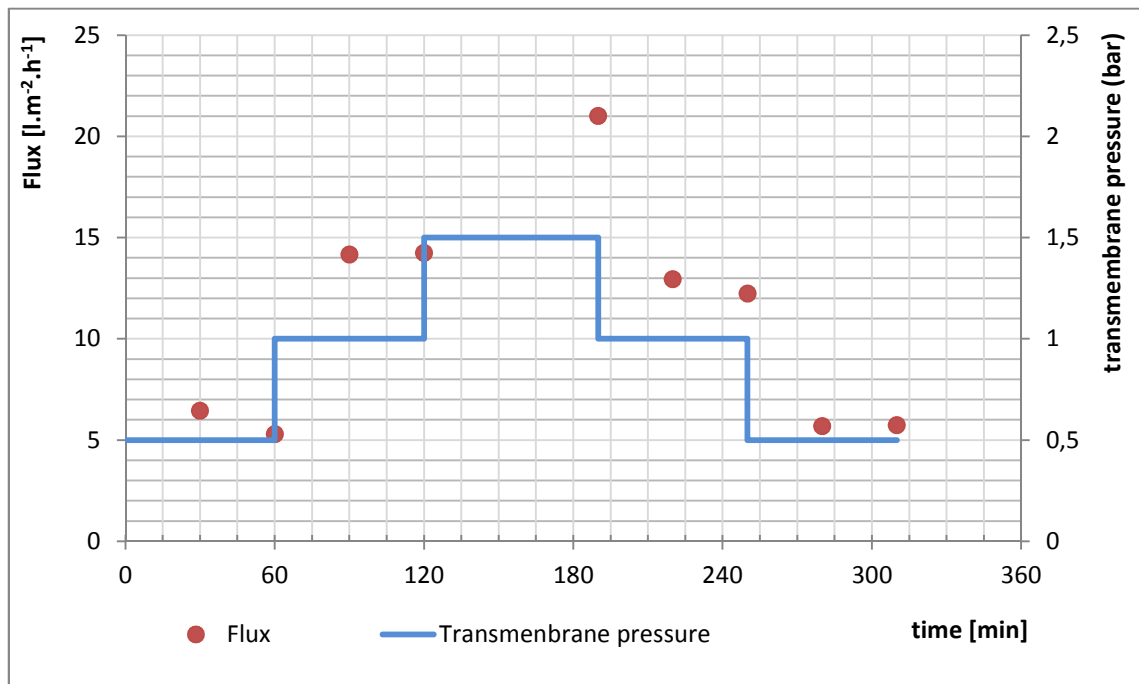
**Table 4. 2** – Analytical results for wastewater samples before and after ultrafiltration

Parameter	Unity	Sample #1		Sample #2	
		wastewater	permeate	wastewater	permeate
Conductivity	$\mu\text{S.cm}^{-1}$	2400	2100	2500	2000
pH	Sorensen	9.4	9.3	9.6	9.6
Ammonia	$\text{mg.l}^{-1}$	53	53	81	85
COD	$\text{mg.l}^{-1}$	2000	800	2100	860
O&G	$\text{mg.l}^{-1}$	470	74	310	81
<i>O&amp;G Polar fraction</i>	$\text{mg.l}^{-1}$	110	74	190	79
<i>O&amp;G non polar fraction</i>	$\text{mg.l}^{-1}$	360	<1	120	<2

The impact of transmembrane pressure on permeate flux was evaluated by performing a step test in a closed concentrate re-circulation mode, at 3 different pressures: 0.5, 1 and 1.4. The hysteresis of the UF membrane flux recovery by performing the opposite steps, decreasing the pressure to its initial value was



also evaluated, as shown on Figure 4. 3. The increase of transmembrane pressure from 0.5 to 1 bar increased the permeate flux about two times, which as expected indicates that a higher pressure favors the velocity of filtration. Also the flux across the UF ceramic membrane was recovered, when the pressure increase was reverted, which indicates that, during the test time, there was no irreversible fouling on the membrane [65].



**Figure 4. 3 - Effect of transmembrane pressure on permeate flux, and hysteresis effect with wastewater sample #1.**

The impact of crossflow velocity on the permeate flux, was also investigated by varying the velocity in a step test and re-circulation of the concentrate , at two different transmembrane pressures: 0.5 and 1 bar, which data is plotted on Figure 4. 4 and Figure 4. 5, respectively.

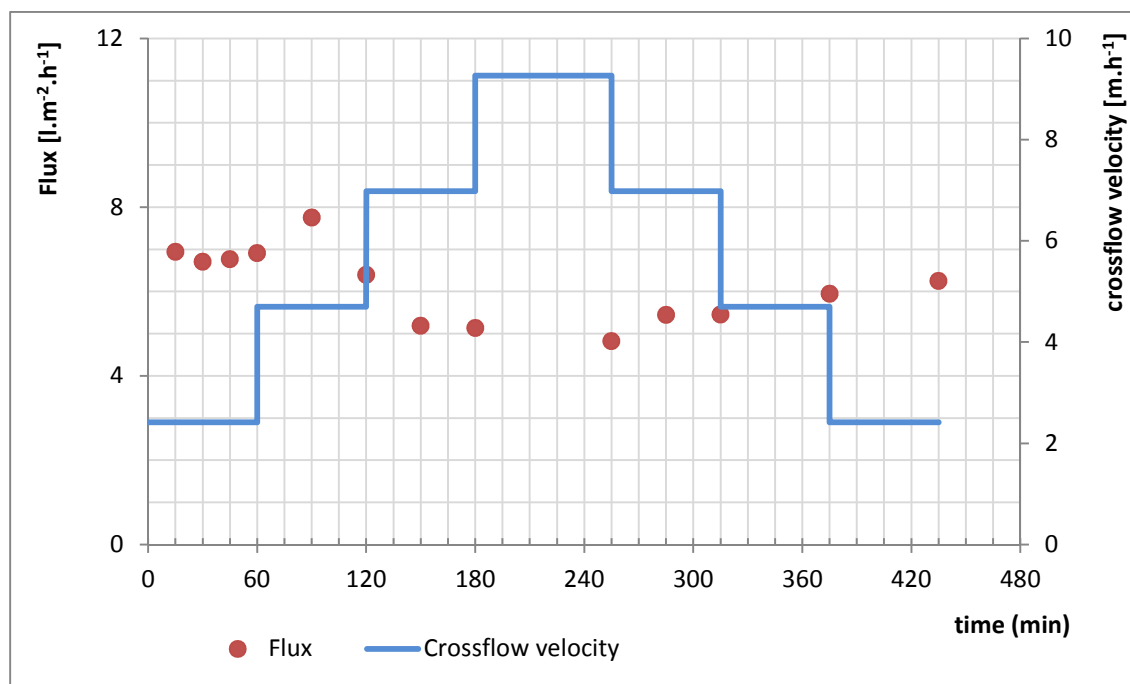


Figure 4. 4 – Effect of crossflow velocity on permeate flux at a transmembrane pressure of 0.5 bar for wastewater sample #1.

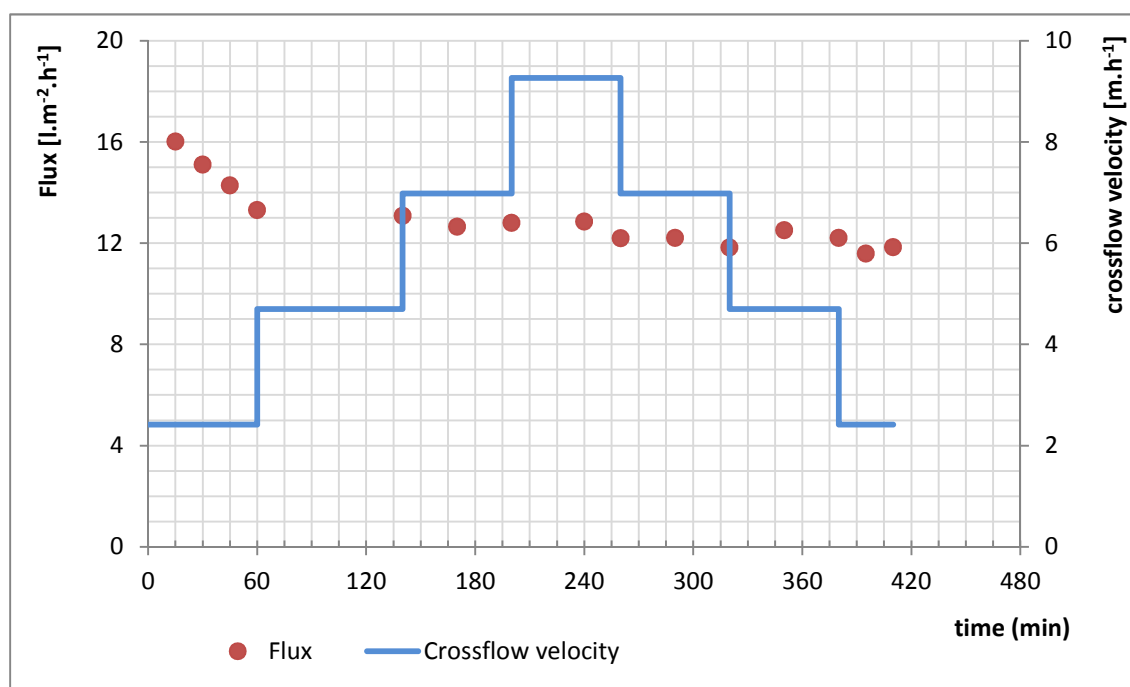


Figure 4. 5 – Effect of crossflow velocity on permeate flux at a transmembrane pressure of 1 bar for wastewater sample #1.

At operating pressure of 0.5 bar, as shown on Figure 4. 4, a reduction in permeate flux was observed at a higher crossflow velocity, which is contrary to what has been described in other studies [51, 66, 67]. This effect was also observed at an increased pressure of 1 bar (Figure 4. 5). Overall, the effect of increasing the crossflow velocity within the investigated range was found to be unable to improve the transmembrane volumetric flux, which may suggest that the transmembrane pressure impact overlaps the greater turbulence inside the lumen of the tubular membrane that , in general, is expected to reduce the formation of deposits on the inner membrane surface and clogging of the membrane pores. A possible explanation of this behavior could be that an increase in crossflow velocity could cause a reduction of the particles size due to shearing of the larger particles [68]. This phenomenon could increase fouling through favoring membrane pores clogging and/or obtaining a more compacting gel layer on the membrane surface thus causing a reduction in the permeate flux.

The results obtained with the UF membrane and presented on Table 4. 2 indicate its relatively good capability and robustness to reject hydrocarbons or non-polar oil and grease from refinery wastewater. Still, the presence of polar compounds limits the applicability of this solution, when a kerosene caustic washing units technology is used in a crude oil refinery, and spent caustics are discharged to the wastewater treatment circuit.

It was therefore decided to investigate the potential of using alkaline resistant NF membrane with a claimed molecular cut off of 200 Da. Since the spent caustic is the main contributor for polluting the refinery wastewater circuit with polar oil and grease, the membrane performance was studied with an effluent from the kerosene caustic washing unit. This option was based on the idea of eliminating the contamination at its source, since this can allows for a significant reduction in the dimensions of the membrane filtration installation. First, demineralized water was passed through the membrane in order to

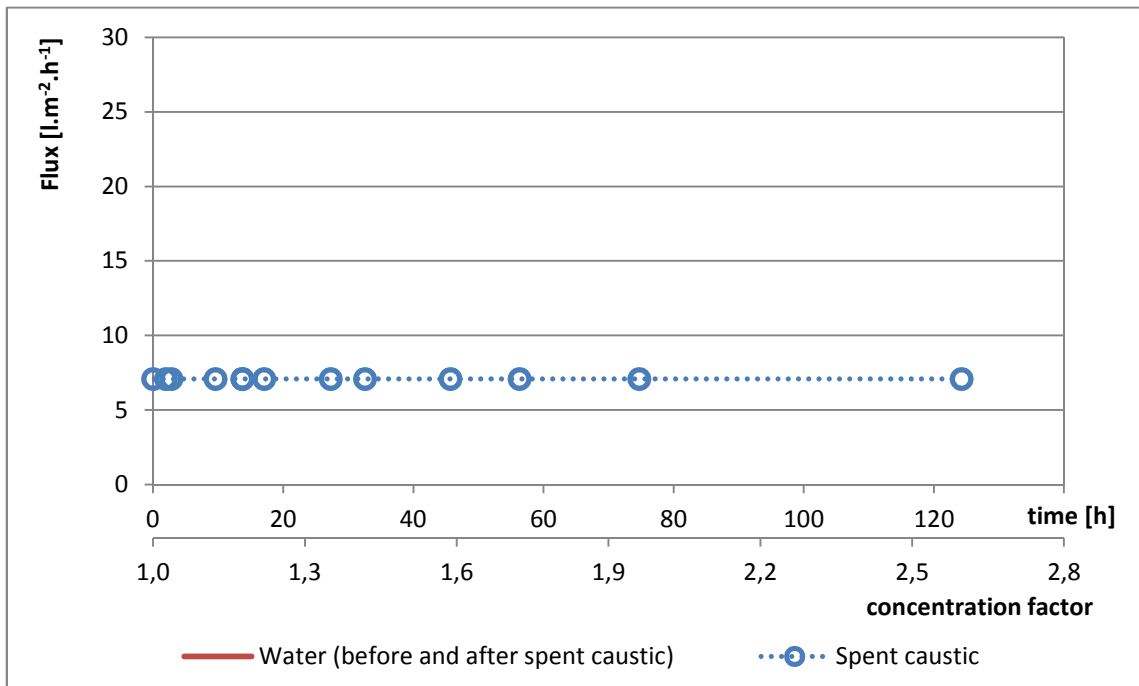
evaluate its pure water permeability. The volumetric water flow rates obtained at 15 and 30 bar were 0.72 and 1.44 m<sup>3</sup> per day, respectively, or 25.0 and 50.0 l.m<sup>-2</sup>.h<sup>-1</sup> at 25°C. Then, 1.7 m<sup>3</sup> of spent caustic, which properties are summarized in Table 4. 3, was filtered at 15 bar and a temperature of 25°C.

**Table 4. 3 – Analytical results of spent caustic samples before and after nanofiltration**

<b>Parameter</b>	<b>Unity</b>	<b>Spent caustic #1</b>	<b>Spent caustic #2</b>
<b>Conductivity</b>	mS.cm <sup>-1</sup>	110	97
<b>pH</b>	Sorensen	13.7	13.7
<b>COD</b>	mg.l <sup>-1</sup>	81571	25780
<b>Sulfur</b>	mg.l <sup>-1</sup>	275.6	242.5
<b>O&amp;G [100% polar]</b>	mg.l <sup>-1</sup>	11300	3900

In order to assess the feasibility of using the membrane with this type of stream, the solution was concentrated only 1.6x. After that, and without any cleaning, the membrane water permeability was checked again. The results shown in Figure 4. 6, indicate that in the presence of spent caustic the permeate flux was reduced to less than 1/3 that when demineralized water was used. The same result was observed when a solution of fresh caustic solution with the same sodium concentration than that in the spent caustic sample, was tested in the pilot installation. This observation suggests that the contaminants present in the spent caustic do not affect the membrane performance. Contrariwise the observation that membrane permeability was reduced with a solution of sodium hydroxide is consistent with previous studies [69, 70]. The explanation could be related with a change in the membrane pore size due to polymer matrix shrinking caused by an increase in ion concentration in the membrane matrix. Other proposed explanation is an increase in the frictional coefficients inside the membrane. Also, higher pH and higher salt concentrations lead to a

reduction in permeate flux [69]. It's noticeable that after permeating 1.05 m<sup>3</sup> from the initial 1.7 m<sup>3</sup>, the average flux was still maintained. Also no fouling was detected since the membrane permeability for demineralized water, measured after using spent caustic, was the same as before. The osmotic pressure gradient between the concentrate and permeate solutions in the presence of caustic, was calculated using equations (4. 1) and (4. 2). The estimated osmotic pressure gradient is 10.75 bar and is significant compared to the applied operating pressure of 15 bar. This justifies the flux decrease when introducing caustic in the filtration element.

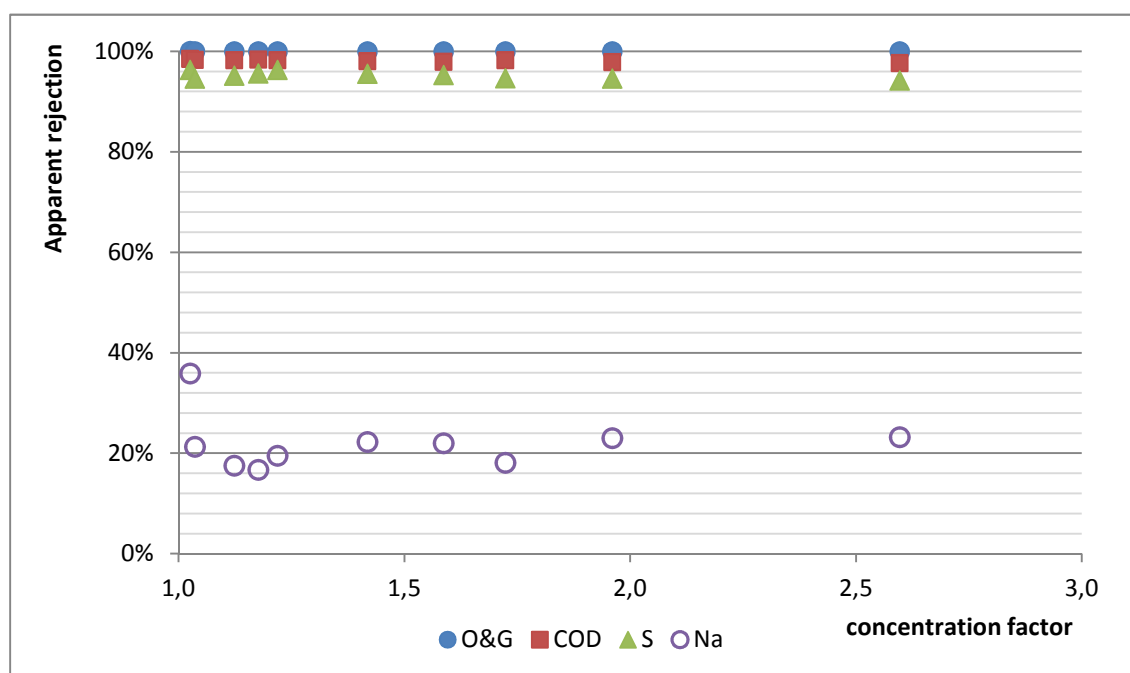


**Figure 4. 6 - Permeate flux across NF membrane for demineralized water before and after filtration of spent caustic sample #1**

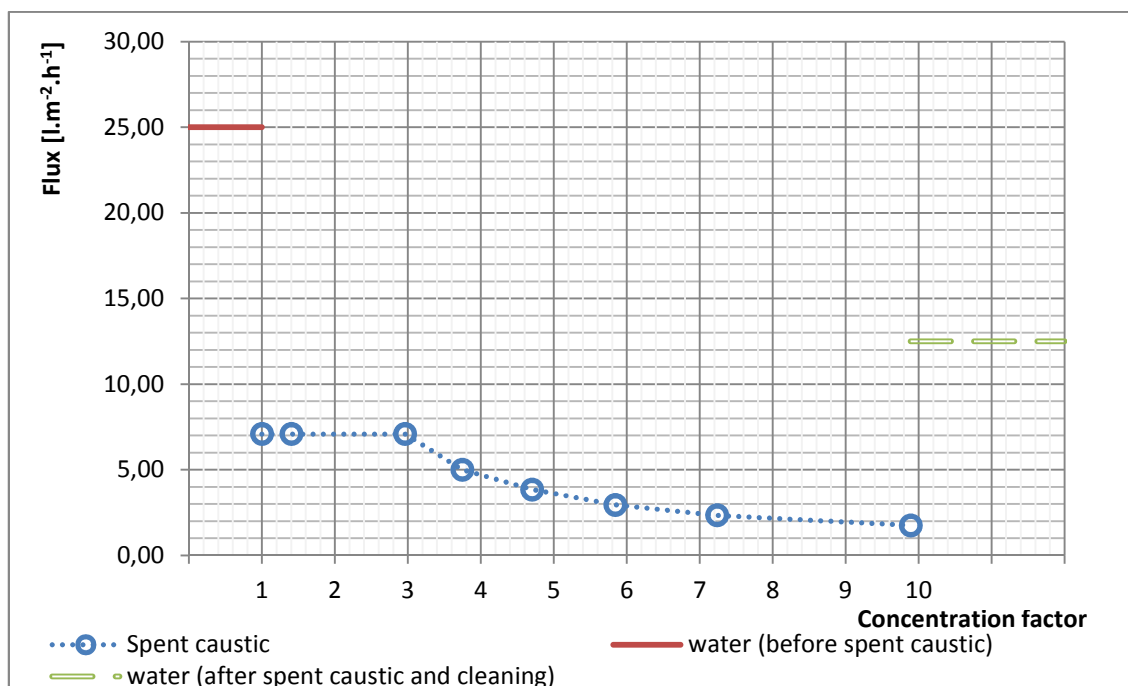
The COD, O&G and sulfur rejection results obtained, which are presented in Figure 4. 7, show that despite the slight increase in the permeate concentrations of the analyzed species at higher concentration factors, the rejection values were all above 94%. Most importantly, for polar oil and grease, which is the most

relevant contaminant due to its high contribution to the wastewater toxicity, its rejection, even at the end of the filtration test, was higher than 99.9%.

Following these encouraging results, a second sample of 0.17 m<sup>3</sup> of spent caustic, was filtered in order to test the membrane limits in terms of maximizing the volume concentration factor. The test was terminated when no permeate flux was noticeable. This second sample, due to the feedstock's quality processed in the refinery, was less contaminated than sample #1, as indicated in Table 4. 3. The results presented in Figure 4. 8, indicate a validation of the results obtained with spent caustic sample #1 (CF = 1.6). When the solution a reached a CF higher than 3 the permeate flux started to decrease being less than the half of the initial when the spent caustic solution was concentrated 6 times.

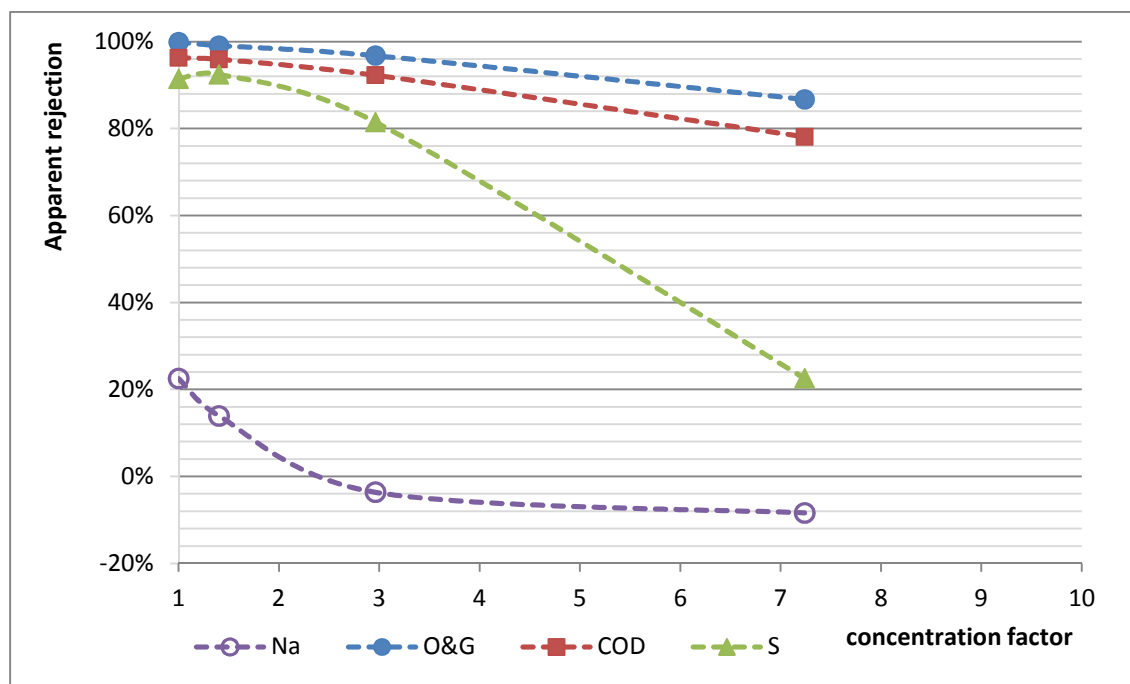


**Figure 4. 7 – Apparent NF membrane rejection values for O&G, COD, sulfur and sodium, with concentration factor, for spent caustic sample #1**



**Figure 4. 8** – Permeate flux across NF membrane for demineralized water before and after nanofiltration using spent caustic and cleaning with a 2%NaOH solution, and for spent caustic sample #2.

The apparent rejection for the species analyzed also dropped, as indicated on Figure 4. 9, but even for a concentration factor of more than 7, above 78% for COD and above 86% for O&G were still rejected, resulting in acceptable COD and O&G levels in the permeate, for the refinery wastewater system and thus allowing for an adequate reduction of the wastewater pollution. Nevertheless, their augmentation in the concentrate solution until a volume CF of 10 has most probably led to fouling on the membrane since the demineralized water flux after the experiment with sample #2, as can be observed in Figure 4. 9, was reduced to 12.5 l.m<sup>-2</sup>.h<sup>-1</sup>, which is half of its initial value. The original value of 25 l.m<sup>-2</sup>.h<sup>-1</sup> was not restored even after cleaning with water and 2% NaOH aqueous solution.



**Figure 4. 9 – Apparent NF membrane rejection values for O&G, COD, sulfur and sodium in permeate, with concentration factor, for spent caustic sample #2**

This result could be explained by accumulation of contaminants in the spent caustic for high volume concentration factors, since it is known that polymeric membranes are sensitive to both polar substances and oil fractions [51, 52]. It can be therefore concluded that the treatment should be performed to spent caustic volume CF's equal to about 3, for which the results obtained showed a stable and restorable membrane flux operation. Besides, at this CF the Na rejection was negative, which is beneficial from the point of view of reutilizing the recovered purified permeate caustic solution in the kerosene washing unit.

In order to assess the feasibility of nanofiltration as an alternative to currently available technologies for spent caustic treatment, its economics was estimated based on the pilot tests results, presented in Table 4. 4.



Table 4. 4 – Economic data for a spent caustic treatment installation with polymeric membranes, assuming a direct extrapolation of pilot plant results

Operating data				
Volume concentration factor (CF)	3			
Spent caustic produced	14892	m <sup>3</sup> per year		
Permeate	9928	m <sup>3</sup> per year		
Concentrate	4964	m <sup>3</sup> per year		
Economic data (CAPEX)			363.650	€
Filtration element cost	1558.5	€ per element		
Filtration element flux	74.46	m <sup>3</sup> per year and element		
Filtration element needed	133	---		
			207.800	€
Civil and engineering costs	75%	(of elements cost)		
			155.850	€
Economic data (OPEX)			931.124	€ per year
Concentrate treatment cost	80	€.m <sup>-3</sup>		
			397.120	€ per year
Filtration element duration	1.5	years		
Installation maintenance	40%	(of CAPEX)		
			397.120	€ per year
Energy index	117.65	kWh.m <sup>-3</sup>		
Energy cost	0.1427	€.kWh <sup>-1</sup>		
			250.010	€ pe year

The scenario assumes NF membrane operation, to a CF assuring no noticeable decline in permeate flux and does not account for scale price reductions and/or commercial contracts for membrane modules or energy supply. The economic data for such a case indicate that the NF membrane treatment, when compared with available data for spent caustic wet air oxidation, is a very competitive solution. Namely the CAPEX of the NF installation is less than 4% of the cost of a wet air oxidation system, while the operating costs are similar. The main operating cost of the membrane installation is related with the concentrate

treatment, but this item can be drastically reduced if, for example, the concentrated caustic could be routed to pH control in crude desalting units, with adequate control and follow up in order to avoid corrosion in the crude distillation columns [21, 47, 48]. The economic evaluation of the solution presented in Table 4. 4 was done, assuming that the gains from the treatment of spent caustic, which allows for a reduction in effluent contamination and caustic reuse, can arise to 1.5 M€, based on the current data from the refinery operation. Taxes were assumed to be 33%, at an annual update factor 11.9% for a lifetime of the plant of 5 years. The economic analysis indicates a payback time of 1.1 years while the investment ratio is more than 355%. A sensitivity analysis was also performed, changing the operating costs by +/- 15%. Assuming for example that a NF element lifespan is reduced to 9 months (+15% OPEX) the payback period increases to 1.38 years. Reversely and assuming that spent caustic concentrate cost treatment after negotiation can decrease by 35% (-15% OPEX), the payback period can drop to less than 1 year: 0.91 years. A reduction in the benefits to less than 1 M€ or an increase by more than 57% of the operational costs will compromise the project. Finally it has to be mentioned that due to the configuration of the pilot system, the NF performance at higher temperatures has not been tested. Such an increase in temperature could lead to a greater permeate flux [71] and to a reduction in the dimensions of an industrial installation, which will clearly make the proposed NF treatment process even more competitive solution for treatment / recovery of spent caustic in petroleum refineries.

## **5. Soluble oil and grease removal of petroleum refinery wastewater using spent FCC catalyst <sup>3</sup>**

### **5.1. Introduction**

In the chapters 3 and 4 a description of the work developed to identify wastewater contamination by polar oil and grease in the largest crude oil refinery in Portugal, which greatly impacts charged costs to refinery due to high pollutant concentration when wastewater is discharged to the external WWTP, were presented. The work developed and described in the previous chapter has defined an innovative solution based on the use of a NF membrane to filtrate spent caustic originating from kerosene caustic washing unit, which is the most responsible for emission of soluble oil to wastewater circuit.

In any case, other treatment solutions also exist that have been already applied to remove dissolved oil and grease from industrial wastewaters [72]. They usually involve the use of adsorbents, like activated carbon [73-75] or zeolites [14], UF ceramic membrane filtration [76, 77] and/or biological treatment [78], but different methods have also been tested, including temperature changes and ultra-sound assistance [79, 80].

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Zeolites are natural or synthetic microporous crystalline aluminosilicates, built up of a 3 dimensional framework of silica and alumina oxides tetrahedra, linked by sharing oxygen atoms and cations that are present in the microporous space to compensate for the aluminum in the framework. Due to their unique properties, zeolites have several applications as catalysts, adsorbents, molecular sieves and ion exchangers with a market that represented about 4 million tons in 2010 [81]. One of the major applications for zeolites in oil refineries is as catalyst for Fluid Catalytic Cracking - FCC - units. Spent FCC catalyst is removed from the unit when its activity drops, and fresh catalyst is continuously added in order to maintain proper conversion. Although the FCC continuously regenerated the catalyst, the spent catalyst cannot be regenerated and is normally routed to landfill or reused as filler for asphalt or cement [82].

Due to their high adsorption capacity, zeolites have been investigate as adsorbents for treating refinery wastewater. Results have shown good efficiencies in removing ammonia, hydrocarbons, COD and BOD [83-85]. More precisely, spent FCC catalysts have shown great capability in removing naphthenic acids [85], phenolic compounds [86] and heavy metals like copper [87] and mercury [88].

The goal of the work here described was the evaluation of spent catalyst from a FCC unit as an adsorbent or catalyst for polar oil and grease removal from refinery wastewater, which can be an alternative or complementary solution to spent caustic nanofiltration.

## **5.2. Materials and methods**

Wastewater samples were collected from the equalized effluent produced in the largest oil refinery in Portugal, after removal of the major portion of oil and grease in a dissolved air flotation unit. Wastewater samples and treated effluent were analyzed for concentrations of polar oil and grease, using standard

method SMEWW 5520C. Polar and non-polar fractions of oil and grease were separated employing silica gel that has the ability of removing polar materials, as described in standard method SMEWW 5520 F [8, 11]. Spent catalyst was obtained in a FCC unit with the average properties indicated in Table 5. 1, which were determined in an outsourced German laboratory. Catalyst matrix and carbon content were determined by employing ICP-OES: Inductively Coupled Plasma - Optical Emission Spectroscopy. Pore volume was determined by weighting catalyst dry and after addition of water and removal of water excess. Apparent bulk density was estimated by weighting 25 ml of catalyst with a tared glass cylinder. Particle size was measured with the principle of laser diffraction (low angle laser light scattering). Surface area value was a result of the adsorption of nitrogen in an amount of catalyst employing Langmuir adsorption model.

**Table 5. 1 - Average properties of the spent FCC catalyst used for oil and grease removal from wastewater samples**

<b>Properties</b>	<b>Surface area (m<sup>2</sup>.g<sup>-1</sup>)</b>	<b>Particle size (µm)</b>	<b>Pore volume (cm<sup>3</sup>.g<sup>-1</sup>)</b>	<b>Bulk density (g.cm<sup>-3</sup>)</b>	<b>Catalyst matrix</b>	<b>Carbon (wt%)</b>
<b>FCC spent catalyst</b>	135	90	0.38	0.85	Al <sub>2</sub> O <sub>3</sub> & SiO <sub>2</sub>	0.04

In order to test the removal of soluble or polar oil and grease from wastewater samples, different assays were performed at a laboratory scale.

Non-aerated - 8.5 ml.min<sup>-1</sup> of refinery wastewater was filtered through approximately 100 grams of FCC catalyst arranged in a fixed bed using a glass chromatograph column with 4 cm internal diameter, schematically shown on , and a liquid holdup of 10 cm. Filtered samples were collected and analyzed for oil and grease.



**Figure 5. 1 – Schematically representation of the glass chromatograph column used for the wastewater treatment tests in fixed and fluidized bed arrangement**

Aerated - a similar experiment to the previous one was conducted, but air was injected in countercurrent to wastewater in order to partial fluidized the catalyst bed in the chromatograph column. Filtered samples were collected and analyzed.

Batch tests - batch tests were also performed by mixing in a glass cup, employing a magnetic stirrer, 500 ml of wastewater and spent FCC catalyst during a certain period of time varying between 5 minutes and 3.5 hours. Mixing times and the ratio between wastewater and FCC catalyst were adjusted in order to maximize the removal of oil and grease from wastewater. After decantation, treated clarified wastewater was removed and analyzed. Some of these experiments were performed using “fresh” catalyst but the re-use of catalyst was also tested. In the latter, the wet catalyst was mixed again with an additional sample of 500 ml of wastewater. All experiments were conducted at around 20°C in a laboratory with controlled air temperature. The initial pH of tested wastewater samples was around 13.

### 5.3. Results and discussion

The basis of this work were the previous investigations in wastewater treatment employing FCC catalyst, that have indicated the capability of FCC catalyst to reduce wastewater contamination [85, 89]. As a starting point of this study, approximately 30 ml.min<sup>-1</sup> of refinery wastewater was passed through a fixed bed of 100 g of spent FCC catalyst. Treated samples were collected along the filtering in volumes of 1 liter and analyzed for polar oil and grease content. Results presented in Figure 5. 2, show that the spent FCC catalysts is capable of reducing the organics content by as much as 80 % but the removal of soluble oil content decreases with the volume of wastewater filtered.

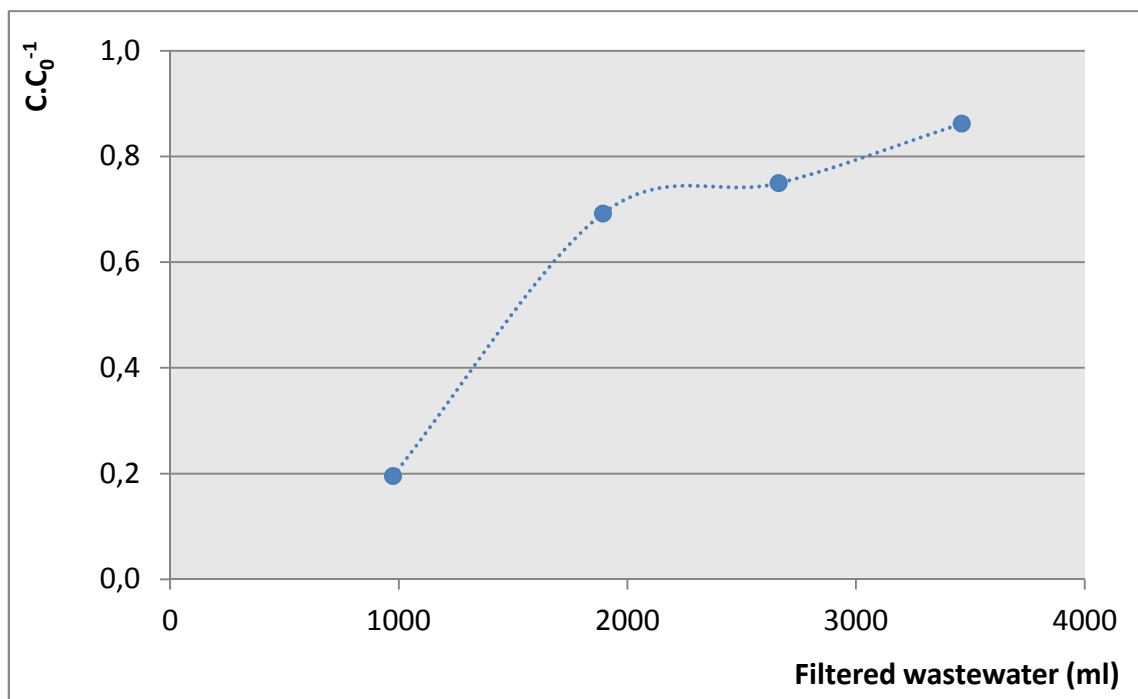


Figure 5. 2 – Polar oil and grease concentration reduction for filtration of refinery wastewater sample in a fixed bed catalyst test

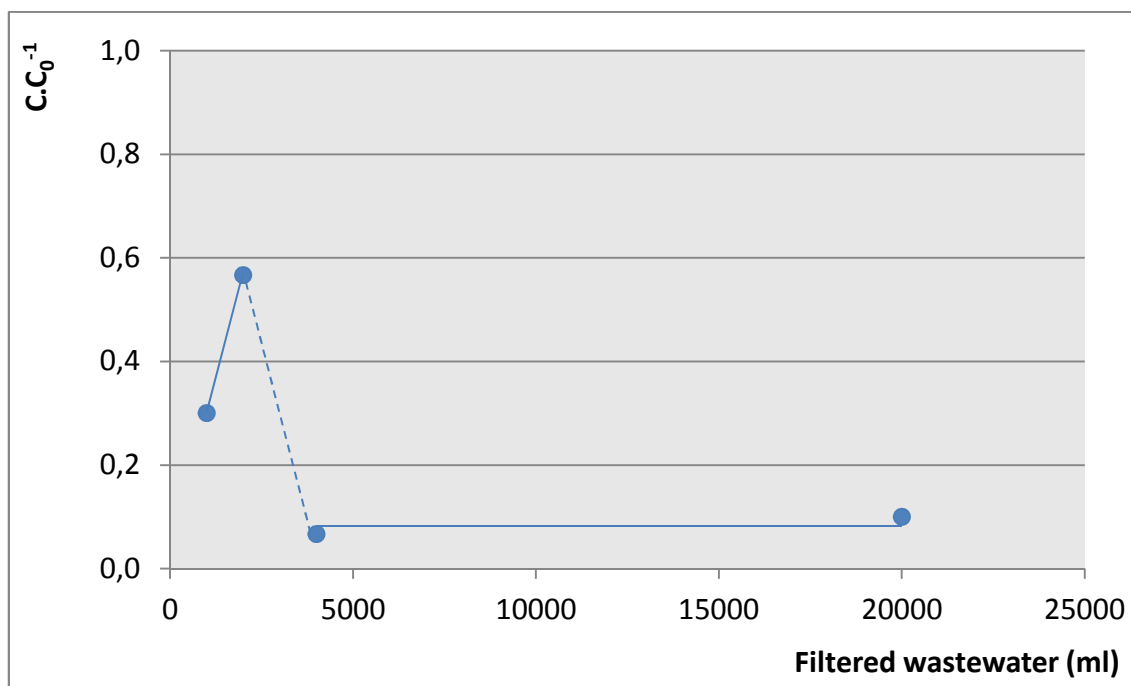
This results are in accordance with previous works [85] and suggest a possible adsorption effect and, thus, a saturation of the catalyst and consequently a

significant reduction of oil and grease removal capacity, after filtering less than 4 liters of wastewater sample. It was also observed an increase in filtration time along the test, caused by a reduction in wastewater flow, which suggests there is some clogging, or partial obstruction, of the catalyst bed possibly due to the presence of suspended solids in the wastewater.

Previous studies have identified the possibility of regenerating the saturated zeolites using a hydrocarbon stream [89] or by employing air to strip adsorbed substances [90]. There is also the indication that a fluidized catalyst bed, instead of a fixed bed, allows for a reduction of the clogging [91]. This possibility was evaluated by introducing an air flow from the bottom of the catalyst bed, fed in countercurrent with the wastewater flux in order to create a partially fluidized catalyst bed. The run was started as before with the sample of wastewater initially fed downwards in the fixed bed; after 2 liters of effluent had been passed through the bed, an air flow was simultaneously introduced into the catalyst bed, from below, in counter-current with the wastewater to be processed.

As presented in Figure 5. 3, while air was not injected the tendency in reduction of polar oil and grease content was identical to the previous test in fixed bed. However when the catalyst was fluidized by the air flow, the capacity for treating the wastewater was restored, and even increase in relation to the first 2 liters, reaching reduction values as high as 90%. The capacity for removal was subsequently maintained. Even after filtering around 20 liters of wastewater, the reduction in the contaminant was maintained above 90%. The fact that there is a higher treatment capacity relative to the non-fluidized bed can be partially explained by the increase in mass transfer rate, due to enhancement of solid-fluid contact interfacial area promoted by the fluidized bed [91]. However, if an adsorption effect was the only one operating in this process, the ability for the reactor to maintain its removal ability for a long time could not be explained.



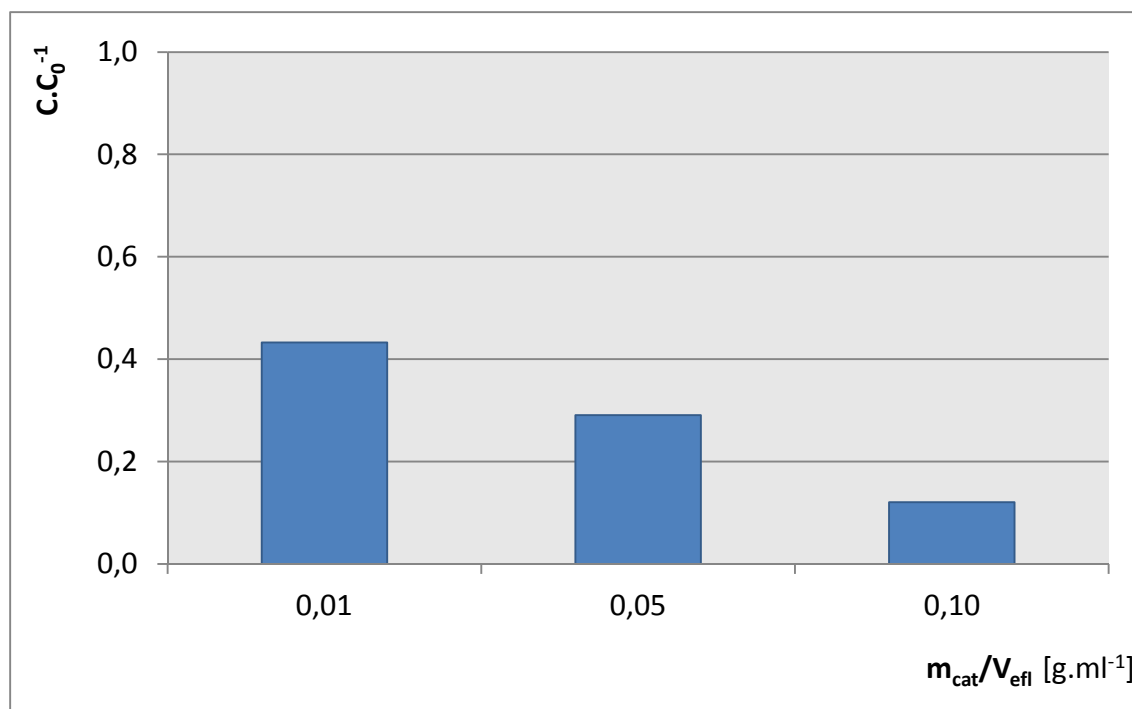


**Figure 5. 3 – Polar oil and grease concentration reduction for filtration of refinery wastewater sample in a non-aerated catalyst bed (initial 2000 ml) and in a fluidized catalyst bed test (after initial 2000 ml)**

The recovery of capacity for the removal of organic compounds could be attributed to the regeneration by the air flow, as indicated in previous studies [90], albeit under different circumstances and with different zeolites. Still, since the air flow is simultaneous with the wastewater to be treated, this is highly unlikely. Thus, these results indicate that there is possibly a catalytic mechanism involved, whereby the hydrocarbons are oxidized, on the catalyst surface, by the air.

Some batch tests were also performed in order to check the variation on different variables, namely catalyst to wastewater ratio, mixing time and the influence of polar oil and grease initial concentration, in the reduction of wastewater contamination. 500 ml of wastewater were mixed in a beaker, with magnetic stirring, with a certain amount of spent FCC catalyst; three different quantities were used: 5, 25 and 50 g. The mixture was stirred for around 3h30 and the test was performed in the controlled environment of a laboratory.

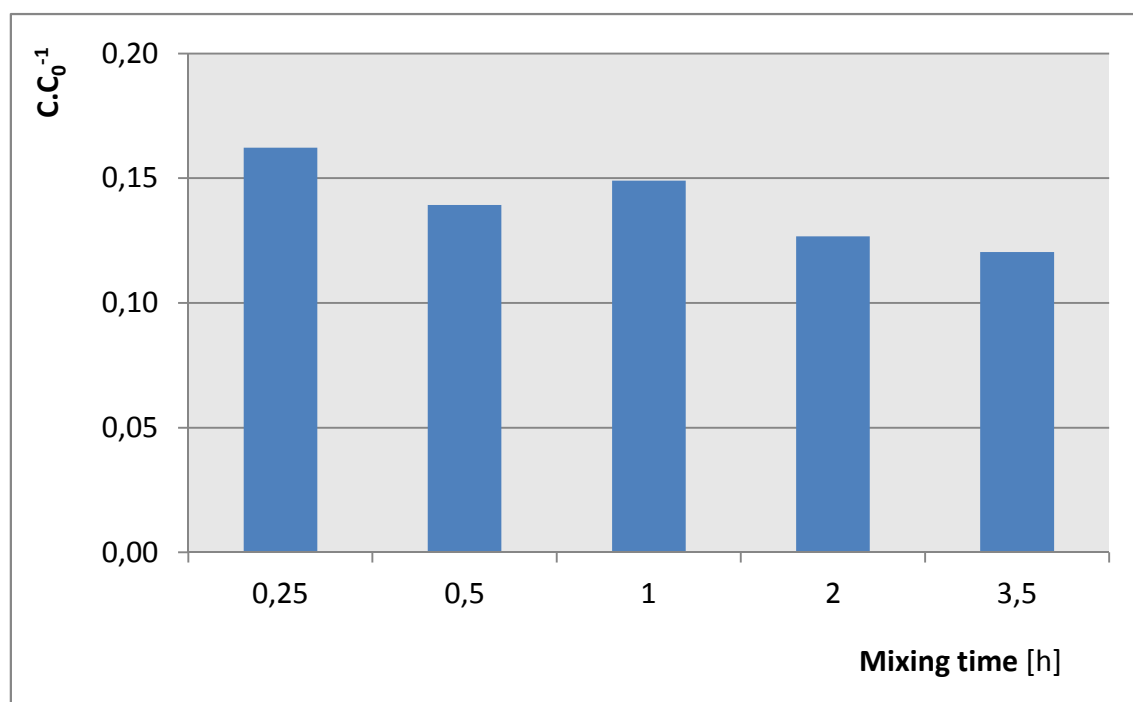
Results presented in Figure 5. 4, indicated that an increase of the catalyst to wastewater ratio from 0.01 to 0.1, results in a greater reduction of polar oil and grease from the wastewater tested samples, from 56% to almost 90%. This fact can be explained by the increase of surface contact area, and has also been observed in previous studies [81, 85, 88, 89].



**Figure 5. 4 – Polar oil and grease concentration reduction in wastewater sample for different catalyst to wastewater ratios, after 3h30 mixing batches with spent FCC catalyst**

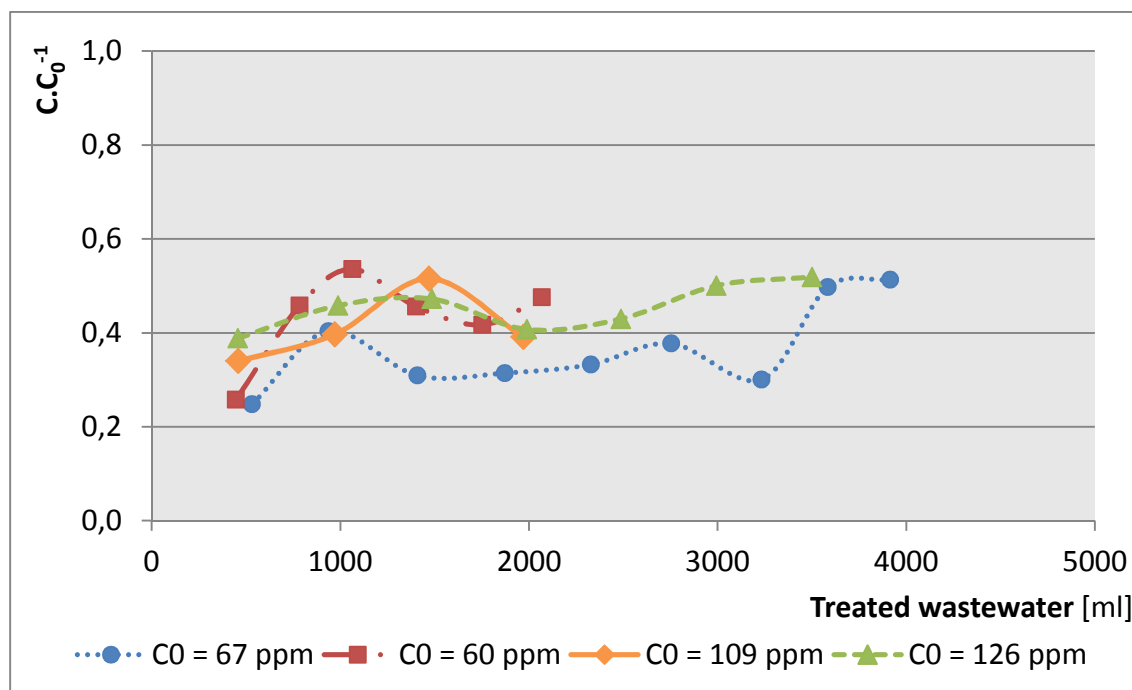
The impact of the mixing time between 500 ml of wastewater and 50 g of spent FCC catalyst, in the reduction of polar oil and grease content, was evaluated by analyzing wastewater after mixing for variable times, between 0.25 hours and 3.5 hours. Results on Figure 5. 5, show that the reduction of contamination occurs very rapidly in the beginning (80% after only 15 minutes of mixing) with a much slower progression afterwards, reaching 88% after 3.5 hours of mixing to. This indicates an excellent performance of the treatment capacity of the spent FCC catalyst, which is consistent with the fact that the continuous tests,

which have a contact time of about 15 minutes, show significant reductions in the oil content.



**Figure 5. 5 – Polar oil and grease concentration reduction in wastewater sample, for different mixing time batches with 50 g of spent FCC catalyst**

The effect of the initial concentration of oil and grease in the treatment capacity by the spent FCC catalyst was also observed, by performing some batch tests mixing, during 15 minutes, using 50g of catalyst and 500 ml of wastewater with different initial concentrations ranging from 60 to 126 ppm. The results, presented in the first data points in Figure 5. 6, indicate that with the increase of contamination the reaction rate increases somewhat, since doubling the concentration does not imply a proportional reduction in contaminant reduction percentage but, nevertheless, the reduction in the first batch slightly decreases from 75% when the soluble oil content is 60 ppm to a little over 61% when the concentration is more than doubled to 126 ppm.



**Figure 5. 6 – Polar oil and grease concentration reduction in wastewater samples, for different initial polar oil and grease concentrations, with a mixing time of 15 minutes and 50g of spent FCC catalyst**

The reuse of the catalyst has also been checked by mixing it with additional portions of wastewater, in the same amount and with the same quality of the initial batch. Results also presented on Figure 5. 6, show that even after mixing 8 times the same catalyst with wastewater the contamination reduction capacity is maintained around 50%, both for the lowest and highest initial concentration of soluble oil and grease. Following the results obtained in the aerated bed experiments, this retained activity is likely due to the natural aeration of the catalyst during the procedure to change the effluent sample in contact with the catalyst. Still, as demonstrated for the fluidized catalyst bed assays, the injection of the air within the mixture of zeolite and wastewater allows for a greater reduction on the contamination.

Lastly, the air effect in polar oil and grease reduction was also tested, with 500 ml of wastewater being mixed in a beaker, with magnetic stirring, without any

catalyst during 1 hour. It was observed that no reduction of the oil and grease content before and after this experiment, concluding that the effect of air is negligible in the absence of catalyst.

These results have proven the capability of spent FCC catalyst to be used in the treatment of refineries wastewater, especially in an arrangement of fluidized catalyst bed with air injection in countercurrent relative to the wastewater feed. The results indicate that aeration of the catalyst bed allows it to maintain its activity for relatively long periods of time.

The availability of relatively large amounts of this spent catalyst in industrial plants with FCC units, makes these treatment a very interesting alternative to the use of other materials, like adsorbents, namely activated carbon, since it doesn't require an additional investment.

Although the lifetime of the spent FCC catalyst in this application has not been fully ascertained in this study, and further long term studies are required, the non-destructive characteristic of the proposed treatment does not preclude the possibility of the catalyst, after it has been used in the polar oil abatement, to be used in other reuse solutions like filler for asphalt or cement.



## 6. Conclusions and future work

The developed work presented in this thesis has targeted at optimizing the Sines refinery wastewater quality. It was identified that the ammonia and the polar fraction of oil and grease have been the main pollutants responsible for the wastewater quality degradation in the Sines refinery, and, consequently, have most impacted the costs charged to the refinery, when wastewater has been discharged to an external wastewater treatment plant.

In order to develop and validate appropriate mitigation solutions for the problems associated with these contaminants, a mass balance to the wastewater circuit was initially developed in order to identify the responsible emission sources, which was compared with analytical sampling data taken along the wastewater circuit within the refinery, as well as with available historical analytical records.

For ammonia contamination, a detailed operational investigation allowed to detect an inadequate routing of sour gas from sour water stripping units to a flaring line, instead of for incineration in Claus reactors for sulfur recovery. This situation was due to clogging of the line, which had resulted from precipitation of ammonia salts in a non-insulated section of the line. Due to solving this issue in August 2012, the occurrence of penalization situations because of higher than the maximum allowable concentration of ammonia in the wastewater has dropped exponentially, since only 3 situations have been observed between years 2013 and 2015. This allows the refinery to save more than 2 million euros per year in wastewater charged costs by the external WWTP.

The wastewater contamination by polar oil and grease was identified as being caused by the spent caustic effluent of the kerosene caustic washing unit. A PLS model was developed in order to predict the levels of polar oil and

grease contamination in the effluent of the spent caustic unit, based on analytical data for the processed crude oils and the unit operating conditions. The model allows for an adequate representation of polar oil and grease mass levels in the spent caustic. The developed PLS model was successfully applied to feed a mass balance estimation to the refinery wastewater circuit, which was validated with analytical monitoring, and allowed for a notoriously good capture of the observed system behavior. The implemented online mass balance is currently being used in order to predict polar oil and grease contamination peaks prior to biological wastewater treatment and to identify which processed feedstocks are responsible for high levels of polar oil and grease in the system. It also allows to operate the kerosene caustic washing unit in a way that minimizes the adverse impacts of spent caustic on the wastewater system.

Following these excellent results, it was observed that addition of bacteria inoculum alongside with activated carbon did not have any effect on the wastewater treatment efficiency, and therefore these additions were stopped, which has resulted in additional costs savings of more than two hundred thousand euros per year. Furthermore, the results obtained in this work can be further applied as an additional tool for evaluating the increase in wastewater treatment costs against higher throughputs of target refined products for every crude oil and for defining maximal oil and grease levels for specific treatment units or reuse schemes.

Succeeding in identifying the mean reason of a high contamination of oil and grease as associated with the kerosene caustic washing unit, dedicated treatment solutions by membrane filtration and catalytic/adsorption treatment with FCC spent catalyst were investigated.

A 15 kDa UF ceramic membrane and a 200 Da NF polymeric alkali resistant membrane were tested in order to evaluate the possibility of purifying, respectively, refinery wastewater and a kerosene caustic washing unit effluent.



The ceramic UF membrane studied showed high removal of non-polar and COD, but was not capable of removing toxic polar O&G to below 20 ppm in the UF permeate, in order to be in accordance with the lower classification levels of RARISA matrix for avoiding wastewater treatment associated taxes.

The NF membrane was successfully tested for spent caustic filtration, demonstrating 99.9% reduction in O&G and almost 98% reduction in COD, without any observed membrane fouling and permeate flux decrease until a volume concentration factor of 3. The economic analysis performed, based on the results obtained through dedicated on-site installed NF pilot plant tests, showed that the investment capital needed for installation of an industrial membrane system is a small fraction, when compared to available investment capital data for a wet air oxidation system. The operating costs are also highly competitive and could be still further optimized. The payback is 1.1 years without any scale price reductions and/or commercial contracts for membrane modules or energy supply. Also reuse of the concentrated spent caustic and/or increase of the lifespan of the NF elements can further reduce the payback of the installation to less than 1 year. Overall, the results obtained with this work developed during the PhD thesis project can be applied for the development and optimization of industrial membrane installations for spent caustic treatment, as a feasible novel alternative to other treatment solutions.

Reduction of wastewater contamination by polar oil and grease was also addressed by a test using spent catalyst from an industrial FCC plant, in different conditions and arrangements. It was observed that the increase on the catalyst to treated wastewater ratio allows for a greater reduction in soluble oil and grease concentration due to the higher contact area. Treatment in a catalyst fluidized bed arrangement with air in countercurrent with wastewater allows for a greater reduction when compared to a catalyst fixed bed since mass transfer rate increase due to enhancement of solid-fluid contact interfacial area. Treatment of wastewater in a fluidized bed results for a reduction of polar oil

and grease higher than 90% after filtering more than 20 liters of contaminated wastewater. The proposed treatment method can be an alternative to the use of activated carbon or other adsorbents. Also, since it's a non-destructive solution allows for the catalyst to still be routed to reuse solutions like filler of asphalt and cement.

The work developed during this PhD can be further expanded in future investigations and for other possible applications. The PLS model has shown great robustness and adjustment to different operation conditions, and therefore can be subsequently used to other refinery wastewater systems.

The membrane tests can be pursued in future works by increasing the temperature and pressure, at which the membrane modules are operated in order to evaluate a possible further optimization of the process conditions within the framework of the kerosene spent caustic filtration. Also, the maintaining and cleaning issues related with the membrane installation need to be addressed and investigated in detail in order to define a chemical solution that may allow for increasing the volume concentration factor and thus to reduce the volume of the NF concentrate without being clarified. Another possible future investigation line can explore a possible combination of UF/NF membranes for a spent caustic filtration or a combination with chemical treatment/NF membrane in order to extend the lifespan of the membrane employed.

For the tests developed with FCC spent catalyst, work around the reaction/adsorption mechanism in fluidized bed configuration can be explored in following works. It will be also interesting to develop and operate a pilot scale unit in order to evaluate the spent catalyst cycles and separation from the reaction media. A parallel system with two or more fluidized reactors could be an option in order for the exhaust catalyst in the standby reactor to be removed

and routed to habitual destinations. Regarding the possible difficulties in the logistic of the system, a more operational work can be developed to check if the catalyst can be routed wet to the habitual destinations, or if a pretreatment needs to be accounted.



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