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Reduction of phenols in the effluent of the Sines Refinery catalytic cracking complex for water reuse

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“If you know what you’re worth, go out and get what you’re worth, but you gotta be willing to take the hits”

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RESUMO

A implementação de tecnologias para reutilização de água em refinarias de petróleo tem ganho particular interesse ao longo da última década devido a pressões ambientais associadas ao uso eficiente de recursos de água e descarga de efluentes aquosos. A necessidade de recorrer a grandes quantidades de água na indústria do petróleo têm incentivado a procura de soluções para a sua reutilização através de uma gestão apropriada e sustentável.

O presente projeto foca na melhoria da gestão relacionada com o impacto ambiental de uma classe de poluentes relevantes, os fenóis, e à reutilização de água na Galp, na maior refinaria de petróleo portuguesa, em Sines. O primeiro passo foi identificar a corrente de efluente que contribui de forma mais significativa para a emissão de compostos fenólicos na refinaria e destacá-la como efluente-alvo a ser tratada.

O efluente-alvo foi sujeito a um tratamento usando filtração com membranas, incluindo nanofiltração e osmose inversa. As tecnologias com membranas têm sido estudadas na indústria do petróleo como um tratamento físico eficiente, com baixo consumo energético, baixa pegada de carbono e a possibilidade de recuperação compostos de valor acrescentado presentes no efluente original.

A garantia do uso seguro da água tratada para reutilização na refinaria tornou-se decisiva para evitar interferências no atual sistema de gestão de água industrial. Assim, foram realizados estudos de compatibilidade física e química, usando técnicas de eletroquímica para medir a corrosão da água tratada e avaliar a adequabilidade da sua reutilização.

Foi realizado um estudo detalhado de tratamento por osmose inversa à escala piloto, testando seu o desempenho técnico e energético, permitindo a realização preliminar de uma avaliação económica e de sustentabilidade. Foi igualmente realizado um estudo de análise de dados, executado através do desenvolvimento de uma ferramenta de previsão de fenóis, baseado nas variáveis do processo de refinação e o seu impacto no atual circuito de tratamento de efluentes.

Palavras-chave: Águas ácidas tratadas, Fenóis, Osmose Inversa, Reutilização de água, Gestão Ambiental

ABSTRACT

Technologies for wastewater reclamation and water reuse in oil refineries have been gaining particular attention over the past decade due to legislative pressures associated with the efficient use of water resources and wastewater discharge. Having to constantly rely on access to great amounts of water, the oil and gas industry has been seeking opportunities to reclaim water using sustainable and efficient management procedures.

The present project focuses on improving the management procedures related to the wastewater-related environmental impact of a relevant class of pollutants, phenolic compounds, and water reuse at Galp, at the largest Portuguese oil refinery, located in Sines. The first step was to identify the wastewater stream that contributed the most in terms of phenolic compounds and highlight it as the key-effluent to be treated.

The key-effluent was subjected to treatment using membrane filtration, including nanofiltration and reverse osmosis. Membrane technology in the petrochemical industry has been reviewed as a physical and efficient treatment with the ongoing commercialization of membranes with a competitive cost, low energy consumptions, low carbon footprint and allowing the recovery of added value components.

Ensuring the safe use of the treated water samples to be reused in the refinery came to be decisive to avoid interference with the current water management system. Therefore, a physical and chemical compatibility test was conducted through electrochemical means to measure the corrosivity of the treated water and evaluate its feasibility for reuse.

A reverse osmosis pilot scale study on the wastewater was performed to test its technical performance and an energy consumption, economical assessment and sustainability preliminary evaluation were conducted. A data analysis approach was also performed to develop a useful tool to predict the phenolic content in stripped sour water, based on the relevant refinery process variables, and assess the impact on the current wastewater circuit.

Keywords: Stripped sour water, Phenols, Reverse Osmosis, Water Reuse, Environmental Management

ABBREVIATIONS

BOD – Biochemical Oxygen Demand

CAPEX – Capital Expenditure

CIP – Cleaning in Place

COD – Chemical Oxygen Demand

CPI - Coalescing Plate Interceptors

CWB – Clean Water Basin

DAF – Dissolved Air Flotation

EU – European Union

ETP – Ecotoxicity Potential

EPA – Environmental Protection Agency

ERD – Energy Recovery Device

FCC – Fluid Catalytic Cracking

GWP – Global Warming Potential

HDS – Hydrodesulphurization units

MR – Matosinhos Refinery

MM – Molecular Mass

MWCO – Molecular Weight Cut Off

MW – Make-up water

NF – Nanofiltration

O&G – Oil & Grease

OPEX – Operating Expenditure

RAT – Atmospheric Residue

RO – Reverse Osmosis

SCE – Saturated Calomel Electrode

SR – Sines Refinery

SWS – Sour Water Stripper

TDS – Total Dissolved Solids

TMP – Transmembrane Pressure

TOC – Total Organic Carbon

TSS – Total Suspended Solids

UCO – Unconverted Oil

UF – Ultrafiltration

VCF – Volume Concentration Factor

VGO – Vacuum Gas Oil

WWTP - Wastewater Treatment Plant

ZLD – Zero Liquid Discharge

CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 State of the art

Crude oil processing and effluent generation have been an issue over the past few years from the increase of global energy needs. Environmental constraints and regulations, such as discharge limits, have also become more stringent to encourage industries to adopt new strategies for effluent treatment and water reuse. From a technological, environmental, and economic point of view, these changes are challenging, requiring the development of sustainable, efficient and economically viable technologies to treat the effluents and enable the reuse of resources. Conventional processes have become increasingly obsolete and can no longer meet the imposed restrictions.

The present project aims at increasing the knowledge on technologies that allow an efficient treatment of a particularly relevant and persistent class of organic pollutants, phenols, at the source and, ultimately, increase the quality of the final effluent to fulfil the legal regulations and decrease the wastewater discharge costs. The objective is to use this knowledge to ultimately remove phenols from the most relevant stream and apply the treatment process at a pilot scale. The treatment highlighted in this project incorporates the possibility of water reuse which would be an added value in industry and in the quest for sustainability.

Galp, a Portuguese company with over 40 years of existence in the national and international market, operates in the energy sector with two refineries, Matosinhos (MR) and Sines (RS). The present work focuses on the latter being the largest and most complex Portuguese refinery, with about 12.5 million ton of processed crude oil/year (Galp Energia, 2015), and a wide range of final added value products (gases, petrol, jet/kerosene, diesel fuels, among others).

1.2 Crude oil refineries and the adverse effects of effluents

Oil refineries are complex industrial facilities, composed of numerous operations whose process conditions depend on the type of crude oil to be processed and the desired end-products. Oil refinery processes are known to be highly dependent on water, with the required amount of water depending on plant size, type of crude, products and complexity of the operations involved. Refining processes for oil and sweetening of gases produce large amounts of wastewater, generally referred to as “process water” [1], which has been in close contact with hydrocarbons. Contaminated wastewater is typically sent to a wastewater treatment plant, located at the facility, or undergoes through a pre-treatment process and later sent to the municipal sewer system for further treatment.

The large consumption of water leads to significant volumes of generated wastewater, reported to reach, for the petroleum refinery, 0.4–1.6 times the amount of the crude oil processed [2]. In the case of RS at Galp and based on the average internal data from 2016 to 2019, approximately 320 to 420 m^3/h of effluent was discharged to the wastewater treatment plant (WWTP). This corresponds to up to 63000 bpd (barrels per day) of generated effluent. Considering the typical 220000 bpd of oil processed at RS, this means that the volume of generated wastewater reaches up to 30% of the amount of oil processed.

Global oil demand is expected to rise to 107mbpd (million barrels per day) over the next twenty years, oil accounting for 32% of the world's energy supply by 2030. Biofuels are expected to account for 5.9 mbpd by the same year, data that clearly indicate that effluents from the oil industry will continually be generated and discharged into the world's main water bodies [3].

Oil refinery effluents are considered priority pollutants due to their high polycyclic aromatic content, which is toxic and tend to be more persistent in the environment [4, 5]. The minimum amount of dissolved oxygen necessary for normal aquatic environment life is about 2 ppm [6] and the release of high organic matter, contained in wastewaters, leads to an excessive consumption of oxygen by bacteria during the oxidation of the effluent. This diminishes oxygen from the water faster than it can be dissolved back into the water from the air with dire consequences to the ecosystems. Furthermore, oxygen availability is a key aspect regarding the end products of chemical and biochemical reactions, in anaerobic systems, which often produce aesthetically displeasing colours, tastes and odours to the water.

Oil and grease (O&G) encompass non-polar and polar hydrocarbon compounds, where the former consists of linear and branched chain hydrocarbons, being insoluble in water, and the latter organic compounds, such as heterocyclic, aromatic and unsaturated substances and elements that have polar arrangements like naphthenic acids. Knowing to have a sticky nature, non-polar O&G compounds tend to interfere with unit operations in municipal wastewater treatment plants as they float as a layer on top of the water, sticking onto pipes and walls, blocking filters [7]. They also aggregate, clogging drainpipes and sewer lines, causing unfriendly odours and corroding sewer lines under anaerobic conditions.

Furthermore, the effluent also contains nitrogen and sulphur compounds, in the form of ammonia and hydrogen sulphide (H_2S), respectively, that are highly toxic. In aqueous form, H_2S exists in equilibrium with bisulphide (HS^-) and sulphide (S^{2-}), with the sulphide being the most reduced form. Sulphide has a high oxygen demand of 2mol of O_2/L mol S^{2-} thus significantly contributing to oxygen depletion [8], resulting in mass fish mortality when the edge limit exceeds 0.5 ppm for both freshwater and saltwater fish [9]. Phenolic compounds pose a substantial threat to the environment due to their high toxicity, stability, bioaccumulation and ability to remain in the environment for long periods. They generally are carcinogenic, causing considerable damage and threaten the eco-system in water bodies along with human health [10].

The degradation of water quality through oil refinery effluent discharges and the pursuit for a cleaner environment caused by the increased awareness of the hazardous composition has resulted in several environmental protection agencies setting maximum discharge limits for each of the abovementioned components on the effluent. The composition of the wastewater generated from a refinery depends greatly on the complexity of the process. Refineries can be classified as either hydro skimming, comprising distillation, reforming and desulfurization processes, or complex, which include a catalytic cracking unit additional to the hydro skimming refinery. Table 1.1 indicates the typical wastewater parameters in the characterization and assessment of refinery wastewaters along with a wide range of compositions, which vary according to refining processes involved.

Table 1.1 Typical compositions of some oil refinery effluents [2].

pH	COD	BOD	O&G	Suspended solids	Ammonia	Phenols	Sulphides
8	80 - 120	40.25	NR	-	-	13	-
7.9	300 – 600	150 – 360	≤50	≤150	15	-	-
6-7	300 – 800	150 – 350	3000	-	-	20 – 200	-
8 – 8.2	200	-	23	-	70	3.7	-
6.5	850 – 1020	570	12.7	-	5.1 – 21.1	98 – 128	15 – 23
8.1 – 8.9	800	-	3000	-	-	8	17

1.3 Sines Refinery wastewater treatment circuit, discharges and costs

In the largest and most complex Portuguese refinery, there are different wastewater circuits according to the type of effluent generated, such as oily wastewater, storm waters, saline effluent and accidentally contaminated wastewater.

Oily wastewater is referred to the process water that has been in direct contact with crude oil and its fractions along the refining process units. After decantation, crude oil received in the refinery tanks contains a percentage of bottom water and residues. The bottoms of the tanks are drained out continuously to reduce the inert volume of the tanks and to guarantee the feedstock's specifications. Bottom residues and water are sent to primary gravity separators, such as CPI (Coalescing Plate Interceptors), which are designed to physically separate gross amounts of oil and suspended solids greater than 150 µm. Slop tanks store the recovered oil, while water with emulsified oils and smaller oil droplets is pumped to an equalization basin.

Water directly used in refining units generates oily wastewaters generally referred to sour waters or process waters. Sour waters are treated in sour water stripping units (SWS), where stripping steam is injected in counter-current to extract soluble ammonia, sulphides and volatile compounds. The Claus units receive the sour gas formed, while stripped wastewater and process waters are sent to a desalter and then on to the CPI equipment and wastewater equalization basin. The equalization basin acts as a volume buffer to downstream treatment units as well as to correct the alkaline wastewaters to pH 7-9 with carbon dioxide. Homogenized wastewater is pumped to a dissolved air flotation unit (DAF), where air and coagulants/flocculants are injected to promote the aggregation of emulsified oils and the accumulation at the wastewater surface, which can be scrapped off and sent to the slop tank.

Saline effluent is produced in the purges of cooling water towers as a result of maintaining the cooling water's analytical parameters within the required operation range, after being subjected to demineralization in ion exchange columns. These streams are collected in a saline effluent basin and analysed on a regular basis, in order to ensure that the quality of the water is in line with the environmental legislation, prior to direct discharge into the sea. In case of contamination, the effluent overflows to the accidentally contaminated wastewater route, and goes on to the effluent treatment system.

Accidentally contaminated wastewater includes storm water collected through the process areas, service water used for pavement cleaning and the contaminated saline effluent. Due to traces of oil or other chemical substances, this wastewater is collected in a devoted basin for decantation of oils that are removed with an oil skimmer and sent to a slop tank for reprocessing in an atmospheric distillation unit mixed with crude oil. Wastewater with a lower content of oil is directed to an equalization basin that also receives oily wastewater after primary clarification.

Storm waters are collected within the area where the likelihood of contamination with hydrocarbons or other chemicals is low, such as roads or administrative and storage areas. Rain is collected in a dedicated drainage network and routed to a clean water basin (CWB) and can be discharged to a riverside after laboratory control analysis to ensure environmental regulations. The stream is routed to a local wastewater treatment plant (WWTP) in case of contamination traces for further treatment.

Regarding the process units, RS is composed of Plant I, which focuses on the production of gases, gasoline, aviation fuel, diesel and fuel oil with emphasis given on atmospheric and vacuum distillation, Merox and Platforming; Plant II which highlights the production of gasoline and alkylates, involving process units such as Fluid Catalytic Cracker, Visbreaker, Vacuum Distillation and Alkylation; Plant III, with diesel being the main added value product with the most recent Hydrocracking unit. Figure 1.1 shows a simplified wastewater circuit of the Sines Refinery (RS) focusing on the effluent treatment prior to discharge to the external WWTP.

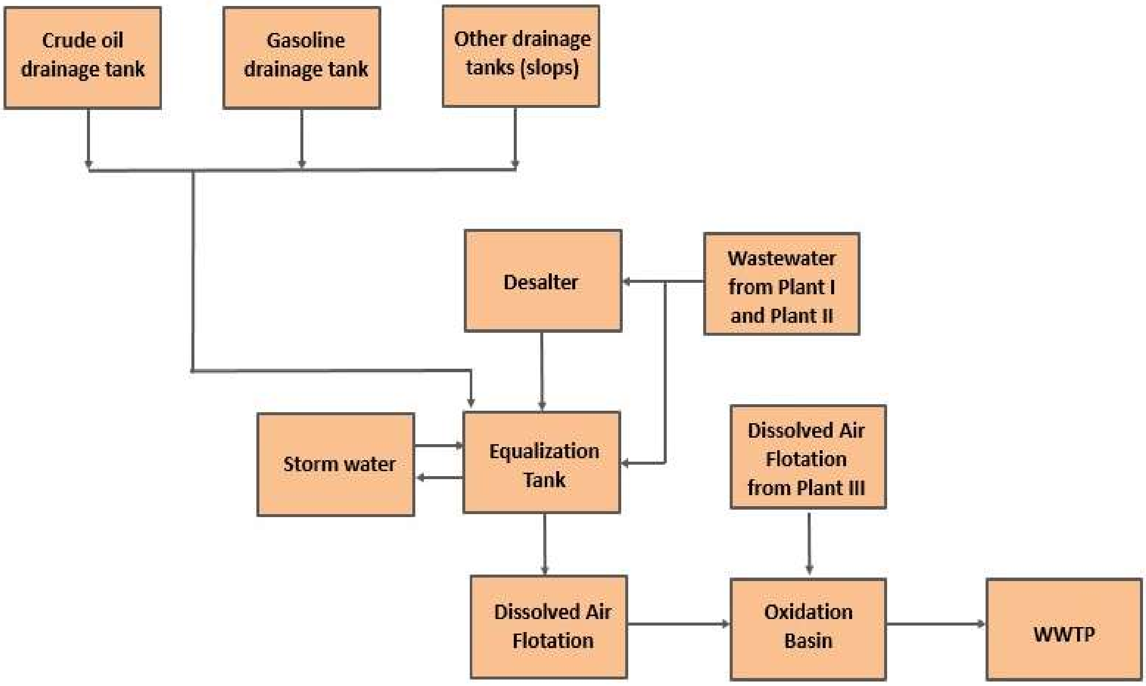


Figure 1.1 Simplified wastewater circuit of the Sines Refinery

Following the primary and secondary treatment, wastewater is discharged to an external WWTP for final treatment before release into a water receiving medium. This effluent discharge is subjected to rules defined by the municipal water company, Águas de Santo André, which among different considerations, establishes the cost charges to be applied based on the wastewater volume and quality. The wastewater analytical composition is determined twice a week with samples collected with an automatic sampler located between the refinery and the treatment plant. The parameters analysed include pH, chemical oxygen demand (COD), sulphides, phenolic compounds, oil and grease (O&G), ammonia and total suspended solids (TSS).

The effluent is then classified, in different classes, according to the matrix presented in Table 1.2. The final wastewater classification is then defined by the parameter that falls in the highest class. For instance, if all the parameters have analytical values that define them as Class 1, but phenols indicate a Class 3, the effluent is defined as Class 3 for charging. An additional 15% penalty is imputed to the charges, in the following 45 days, if the effluent exceeds Class 5 (or Class 1 in case of ammonia) with the charge of the effluent being proportional to the quantity sent to the WWTP.

Table 1.2 Matrix for classification and charge of the wastewater sent to external WWTP (Santos, 2015)

Parameter	Class 1	Class 2	Class 3	Class 4	Class 5
Sulphides (ppm)	]LOQ[1]; 2]	]2;4]	]4;7]	]7;10]	]10;20]
Phenols (ppm)	]LOQ.; 5]	]5;10]	]10;15]	]15;20]	]20;40]
COD (mgO_2/L)	]LOQ.; 150]	]150;300]	]300;600]	]600;1000]	]1000;2000]
O&G (ppm)	]LOQ.; 5]	]5;20]	]20;35]	]35;50]	]50;100]
Ammonia (ppm)	]LOQ.; 125]	N/A	N/A	N/A	N/A
pH		N/A	N/A	N/A	]4.5;10]
TSS (ppm)	]LOQ.; 100]	]100;200]	]200;300]	]300;500]	]500;1000]

[1] – Limit of Quantification

Figure 1.2 shows the historical wastewater treatment costs charged by the municipal water company WWTP in Ribeira de Moinhos. It can be observed that 2010-2013 showed a significant aggravation on the effluent's treatment costs. A previous study (Santos, 2015) showed that this was due to the ammonia and polar O&G contamination in the wastewater circuit by inadequate routing of sour gas from the sour water stripping unit and consequently to high concentrations in the kerosene caustic washing unit. This unusual contamination led to many Class 5 occurrences during that period and thus, to the reported costs.

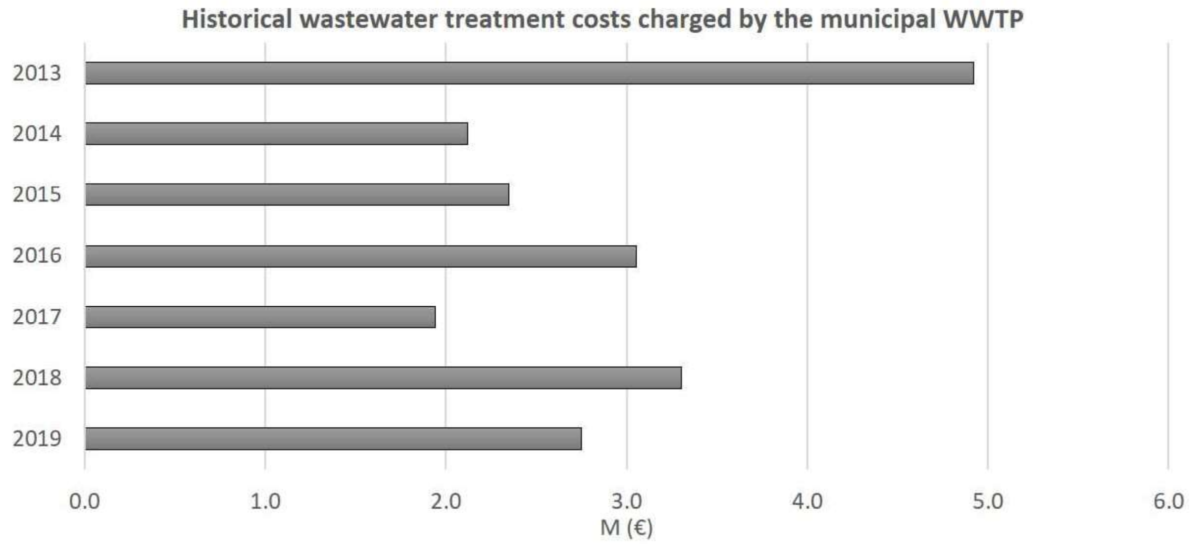


Figure 1.2 – Historical wastewater treatment costs charged by the municipal WWTP

1.4 Phenols

Phenols, often referred to as phenolics, are organic compounds that contain phenol in their chemical structure. Being involved in many industries, such as coke, oil refineries, resin manufacturing, pharmaceuticals, pesticides, dyes and plastics, phenols play an important role to what concerns environment impact. Phenolics play a part in some of the major hazardous compounds in industrial wastewater due to their poor biodegradability, high toxicity and ecological aspects, mainly on the aquatic environment [11]. This led to many national and international environmental regulatory bodies to set stricter discharge limits, which have been fostering the development and implementation of more efficient treatments and sustainable processes. Phenol has been designated as a priority pollutant by the US Environmental Protection Agency (EPA) and the EU, with these agencies establishing limits for wastewater discharge of 0.5 ppm for surface waters and 1 ppm for the sewage system [12, 13]. Figure 1.3 shows the phenolic compounds structures considered priority pollutants by the EPA.

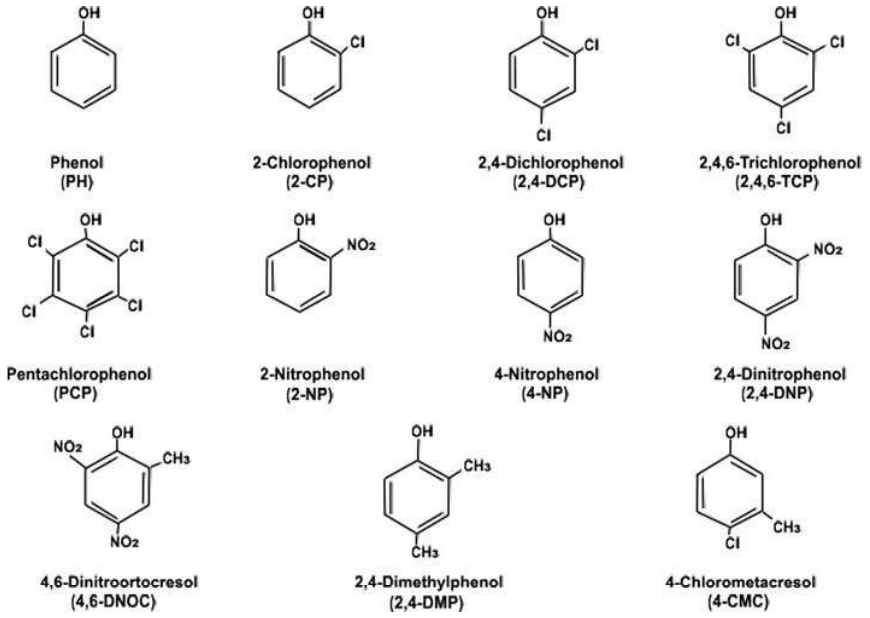


Figure 1.3 Phenolic compounds considered priority pollutants by the EPA [14]

1.5 Phenols in refinery wastewater

Refineries use great amounts of raw water with different quality specifications depending on the purpose of the use. The main types of water in oil refineries include boiler feed water, required for the generation of steam, cooling water, for water-cooled condensers and product-cooled heat exchangers, utility water for washing operations and process water. The latter is defined as water that has been in intimate contact with hydrocarbons in the refining process and can be subdivided into the following groups [15]:

- Sour water and process condensates
- Desalter effluent
- Tank bottoms
- Spent caustic

Due to a great fraction of the water used in refining that is in direct contact with the processed oil, contaminants such as hydrocarbons, sulphides, ammonia and phenolic compounds are carried over and solubilized into the 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.

1.5.1 Sour water and process condensates

Oily wastewaters resulting from water use in refining units are usually referred to sour waters or process waters. Sour waters are treated in sour water stripping units (SWS), shown in Figure 1.4, where stripping steam is injected in a counter current operation mode to extract soluble ammonia, sulphide, and volatile compounds.

It has been reported that there are more sources of sour water from refining than there are in gas processing applications [16]. These sources include distillation, wash systems, water from knockouts and amine systems.

The largest source of sour water has been identified [16] as being that from the steam stripping of the crude in the atmospheric and vacuum tower processing units. Fluid catalytic crackers (FCC), hydrodesulphurization units (HDS) and hydrocrackers also generate a significant amount of sour water. Sour water comes from the steam, the demineralized water used for thermal cracking and hydrotreating. As heavy products are cracked, sulphur is converted into H_2S and mercaptans and nitrogen compounds are converted into NH_3. Phenol is produced from the reaction between cyclic hydrocarbons and steam. By-products are present in the water such as H_2S, NH_3, phenolics and hydrogen cyanide [17]. Table 1.3 and Table 1.4 show the typical sour water contaminants in the feed and treated water concentrations and with a more detailed description of stripped sour water., respectively.

Table 1.3 Typical sour water contaminants with feed and stripped water concentration [16, 18, 19]

Pollutant	Feed (ppm)	Stripped water (ppm)
H_2S	300 – 12000	< 10 (often < 1)
NH_3	100 – 8000	< 100 (often < 30)
HCN	26	22
Phenols	Up to 200	Up to 200

Table 1.4 Stripped sour water contaminants [15]

Pollutant	Expected concentration (ppm)
Chemical Oxygen Demand (COD)	600 – 1200
Free hydrocarbons	<10
Suspended solids	<10
Phenols	Up to 200
Benzene	0
Sulphides	<10
Ammonia	<100

It can be observed that phenols are not removed in the sour water stripping units. The non-strippable nature of phenols is most likely due to its high affinity to water, as phenol has a relatively high solubility in water (8.4% w/w at 20 ºC) [20]. This issue in sour water stripping is present in refining, such as cokers, crude units and FCC, along with other contaminants such as cyanide and colloidal sulphur [18], unlike hydrotreaters and desulfurization units, where phenols are not usually an issue in the wastewaters generated, as they are not formed.

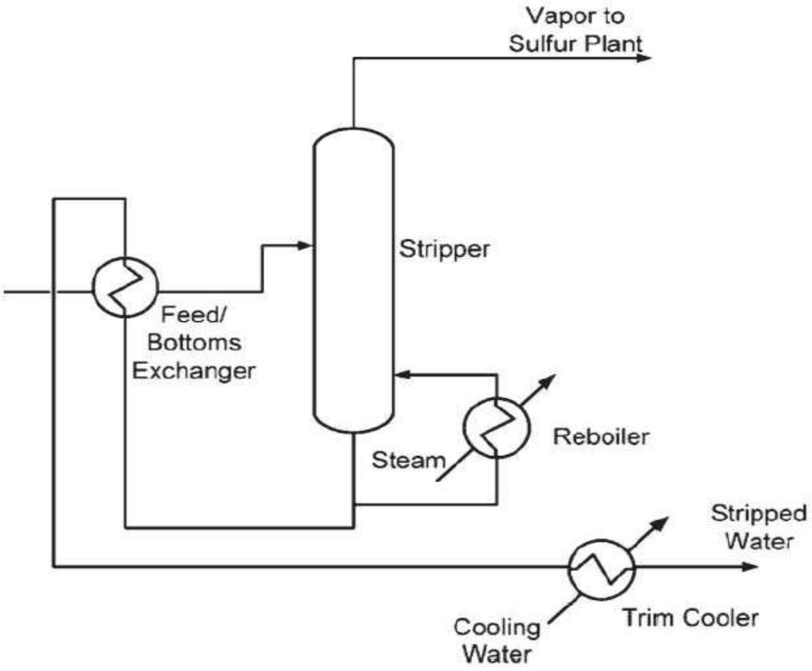


Figure 1.4 Schematic representation of a Sour Water Stripping Unit [15]

Phenols have been found in stripped sour water in concentrations ranging between 300-537 ppm [21, 22] and 190-220 ppm [23], indicating the presence of a very high phenolic contaminated wastewater generated which, if discharged without adequate treatment, will contribute to a low-quality effluent. However, most refineries use a well-known and reported treatment [22] to overcome this issue by reusing the stripped water as wash water for desalters that in turn results in a portion of the phenol being extracted lowering its content in the wastewater stream.

Process condensates are wastewater streams that result from the condensation of vapours that have been in contact with oil products. They can be divided into distillation condensates, sour water from FCC, hydrocracking and hydrodesulphurization processes and steam cracking. Atmospheric distillation condensates come from steam stripping of distilled products and represent about 3.5 wt% of the feed flow rate, whereas vacuum distillation condensates approximately 4 wt% of the feed. Table 1.5

shows an example of the composition of several process condensates, including atmospheric distillation, vacuum distillation and FCC.

Table 1.5 Example of the composition of some process condensates in parts per million (ppm) [24]

	Atmospheric distillation	Vacuum distillation	FCC
%wt of the feed	2.5-3.5	3-4	6-12
pH	6-7	6-7	8-9.5
HS^-, RSH	20-200	10-50	500-3000
Cl^-	5-100	5-50	10-50
CN^-	-	-	5-200
NH_4^+	10-60	5-30	300-3000
Phenols	10-30	5-10	80-300
Hydrocarbons	30-60	5-20	5-60

1.5.2 Desalters

Crude oil is washed in desalination units after decantation and water drainage in order to remove inorganic salts that are present, mostly sodium chloride but also found in the form of other chlorides, such as magnesium and calcium. Desalting is typically the first operation in a refinery crude unit, being fundamental to avoid plugging and fouling of downstream units by salt deposition and reduce corrosion due to hydrochloric acid formation from the chloride salts during crude processing. The wash water is usually injected into the second stage of the desalter after being heat exchanged with the hot effluent, being then sent to the first stage, contacting the incoming crude. The hot brine is then discharged to effluent treatment after being cooled.

One of the sources of wash water, previously mentioned, is the stripped sour water in which the phenol content of the effluent is lowered by being extracted into the crude and being sent back into the refining system. The advantages of this approach consist of lowering the capital and operating costs for wastewater treatment. However, this process does not necessarily remove or degrade phenolics, but rather creates a closed phenolic circuit throughout the refining process as the washed crude with adsorbed phenols feeds the crude tower and goes on to the following refining units.

Al Hashemi et al. [25] reported a characterization study of condensate-oil refinery wastewater at the first oil refinery in the Emirate of Dubai, UAE, in which phenols were given emphasis and were characterized in different effluents of the refinery. The company is a condensate splitter refinery with various plants including Merox sulphur removal and sulphur recovery units and has little environmental emissions when compared to crude oil refineries, which have other units such as hydrocrackers, vacuum distillation, and coking units. The authors reported up to 2.6 ppm of total phenols in the desalter effluent, having the lowest phenol content of the troublesome waste streams studied. Richard J. Metcalf [22] reported 24.5 ppm of phenols in the desalter wastewater in the well-known patent of recycling the phenolic stripped sour water into desalter units, where phenols were present in the feed streams of the desalter at concentrations of 156 ppm and 537 ppm for the vacuum distillation wastewater and treated water from the fluidized catalytic cracking unit, respectively. The results show a major influence of catalytic cracking and vacuum distillation units, in complex oil refineries, on the phenolic content in the wastewater generated, indicating that although desalter units show promising results in reducing phenols in stripped sour water, the effluent quality in desalters may vary depending on the catalytic cracking processes, which in turn could lead to the formation of phenolic by-products, contributing therefore to the increase of phenols in sour waters, overcoming the limited phenol adsorbent capability of crude oil in the desalters.

1.5.3 Tank bottoms

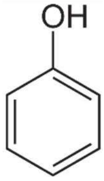
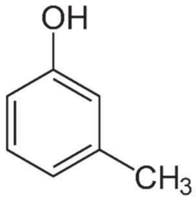
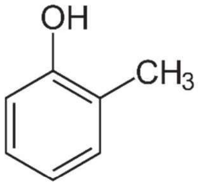
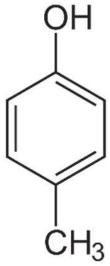
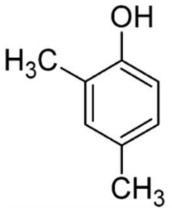
Categories of tanks that may require water draws in refineries often include crude oil tanks and gasoline tanks, resulting from a percentage of bottom water and sediments that they contain, upon storage. The water draws are normally sent to either the wastewater treatment or to a separate tank where the solids are separated from the oil and water. Although the amount of water that is drained from these tanks is significantly lower than other forms of process water, it still comes into direct contact with hydrocarbons and still presents many of the typical contaminants previously mentioned. Many different phenolics were detected in tank drains, where the total phenolic content has found to be, in average, 6.7 ppm [25], indicating that crude oil itself contains phenols. The contribution of the flow rate of these wastewater streams to effluent treatment is, nonetheless, low compared to other forms of process water.

1.5.4 Spent caustic

Spent caustic is formed upon the extraction of acidic components from hydrocarbon streams which include residual H_2S, phenols, organic acids, hydrogen cyanide and carbon dioxide. These compounds are absorbed into the reagent, and the resulting spent caustic solution cannot be regenerated and is purged intermittently or continuously from the caustic treating system. The discharge to the sewer system is common but other treatments are often put into practice, such as wet air oxidation under high temperatures and pressures, depending on the type of spent caustic produced.

Al Zarooni et al. [26] conducted a characterization and assessment of refinery wastewater of the Ruwais refinery at UAE, a hydro skimmer refinery with no catalytic cracking processes involved. Phenols in the spent caustic characterized the feed that undergoes the sweetening process, where the feed is kerosene and the type of phenolic compounds are those typically present in kerosene. In the authors' analysis, an average concentration of 21.7 ppm of phenols was detected in the spent caustic stream. Table 1.6 shows the main phenols found in the wastewater stream.

Table 1.6 Major phenols found in refinery wastewater [25]

Compound	Chemical structure
Phenol	
m-cresol	
o-cresol	
p-cresol	
2,4-dimethylophenol (xylenol)	

1.6 Motivation & Strategy

In order to overcome the issue related with phenolic compounds and their impact on the effluent treatment at the refinery, it is important to determine the key effluent which represents the largest contribution in terms of phenolic content within the wastewater treatment circuit. This identification of the key-effluent will allow a treatment targeted to phenols, allowing the treatment of lower volumes than the entire volume of wastewater generated at the refinery, lowering therefore capital expenses, while removing one of the most relevant pollutants emitted at the refinery. Moreover, strategies regarding the possibility of water reuse while assuring an efficient phenol removal will positively impact costs associated with fresh industrial water as a utility. Therefore, the two main points that contribute to the motivation of this project are as follows:

- Removing phenolic compounds at the source which would provide capital expense advantages in treating smaller volumes.
- Improving the quality of the final effluent (free of phenols) sent to the municipal WWTP.
- Resorting to a treatment that allows water reuse, reducing costs of using fresh industrial water as a utility.

The application of membrane separation processes in the petrochemical industry has been widely reviewed as an advanced and efficient treatment technology with the ongoing commercialization of economical membranes, operating under low energy consumptions, with minimal environmental impacts and allowing the recovery of added value components from a main stream [1, 27]. The most important membrane technologies studied to remove organics from wastewater are membrane-based solvent extraction (MBSE) (known as liquid membranes), NF/RO, pervaporation (PV), and membrane distillation (MD) [28]. Both NF and RO have been used as good treatment methods for removal of organic pollutant in order to produce purified water [36]. Table 1.7 shows literature results from several membrane techniques regarding the removal of phenolic/poly-phenolic compounds in water or wastewater streams in laboratory and pilot scale studies.

Table 1.7 Nanofiltration and reverse osmosis processes for phenolic removal in water or wastewater streams

Component	Apparent rejection (%)	Permeate flux (L/(m^2.h))	Ref.
NF membrane			
NF-97	20-40 (10-20 bar TMP)	180-360 (10-20 bar)	[29]
NF-99	10-15(10-20 bar TMP)	72-216 (10-20 bar)	
DSS-HR98PP	80-85(10-20 bar TMP)	54-72 (10-20 bar)	
NF99HF	86-88 (20-40 bar TMP)	80-140 (20-40 bar TMP)	[30]
NF97	85-86 (20-40 bar TMP)	25-50 (20-40 bar TMP)	
UTC60	20-47 (3bar TMP)		[31]
NTR729HF	80-99 (3bar TMP)		
UTC70	98-99 (3bar TMP)		
NF90	55-60 (15 bar TMP)		[32]
NF-1	75-90 (5-15 bar TMP)	100 (15bar TMP)	[33]
NF-2	68-75 (5-15 bar TMP)	295 (15bar TMP)	
NF-3	72-85 (5-15 bar TMP)	130 (15bar TMP)	
NF-20	70-80 (5-15 bar TMP)	125 (15bar TMP)	
RO membrane			
RO98pHt	92-95 (20-40 bar TMP)	20-30 (20-40 bar TMP)	[30]
ES10C	97-99 (3bar TMP)		[31]
LF10	98-99 (3bar TMP)		

AG 2514 TF	60-70 (5-15bar TMP)	[34]

Advanced Oxidation Processes (AOPs) have also been attracting considerable attention over the past few years as techniques for removal of organic pollutants and become highly relevant when the contaminants have low biodegradability and therefore are named as persistent organic pollutant, remaining in the environment for long periods of time. In water treatment using AOPs, oxidative dissolution of organic pollutants in wastewater is achieved using hydroxyl (•OH) radicals generated using possible combinations between ozone, UV light, a semiconductor photocatalyst, hydrogen peroxide and a Fenton reagent. Table 1.8. shows literature results from several oxidation and advanced oxidation laboratory techniques regarding the degradation of phenolic/poly-phenolic compounds in water or wastewater streams.

Table 1.8 Several oxidation and advanced oxidation techniques for phenolic degradation

Oxidation/AOP process	Results	Ref
O3-UV-TiO_2	100% decomposition of 50 ppm phenol was reached within 120 min; 80% decomposition of 200ppm phenol within 225 min	[35]
UV; UV/H_2O_2; O_3/H_2O_2	Degradation rates: $k=0.528\ h^{-1}$ for UV; $k=6.26h^{-1}$ for UV/H_2O_2; $k= 2.13\ h^{-1}$	[36]
Fenton and Photo -ferrioxalate	Phenol removal > 99% with Fenton's + photo-ferrioxalate with 60-90 min reaction time	[37]
Fenton+H_2O_2	92% degradation of 100ppm phenol within 30 min	[38]

1.7 Thesis outline

Chapter 1 gives an overview of crude oil refineries, the adverse effects of effluents, a description of the current Sines Refinery wastewater treatment circuit and the role played by phenols in the oil and gas industry, including environmental impact and how they are generated.

Chapter 2 describes the methodology used for identifying the key-effluent to be treated and the development of a tool that predicts phenols in the wastewater at hand using refining process variables. The effluent was characterized over a 24-month period which was the basis for a data analysis approach.

Chapter 3 goes into technical detail regarding the membrane treatment performance of the key-effluent using nanofiltration and reverse osmosis at laboratory scale in order to determine the most efficient membrane and evaluate the fluid dynamics involved and its effect on performance and phenol retention.

Chapter 4 provides a complete reclamation study of the treated water to be reused at the refinery. A physical and chemical compatibility test was performed using electrochemical methods to determine the corrosivity of the reclaimed water and its effect on the current water system implemented at the refinery.

Chapter 5 takes one step further in the scale-up of the proposal, by means of a reverse osmosis pilot scale study on-site at the refinery and determining performance in efficacy, energy consumption and a preliminary economic and sustainability evaluation.

Chapter 6 gives a final conclusion about the overall assessment on the feasibility of the proposed project, and important points to be considered in the management of the concentrate stream. Future work is also put forward in how an opportunity can arise in the recovery of the phenolic compounds present to be used as potential added-value products in some applications within the oil and gas industry and take another step towards sustainability.

CHAPTER 2

PREDICTING THE CONCENTRATION OF HAZARDOUS PHENOLIC COMPOUNDS IN REFINERY WASTEWATER – A MULTIVARIATE DATA ANALYSIS APPROACH

Submitted as: ***Pedro D.A. Bastos****, Cláudia F. Galinha, Maria António Santos, Pedro J. Carvalho, João G. Crespo, Predicting the concentration of hazardous phenolic compounds in refinery wastewater - a multivariate data analysis approach, to Environmental Science & Pollution Research. The author Pedro D.A. Bastos was involved in the research, visualization and writing of the original manuscript.*

2.1 State of the art

The present study focused on the methodology for identification of the wastewater stream that presents the highest phenolic impact at a large oil refinery. As a case-study the oil refinery, Petrogal S.A., in Sines, Portugal, was selected. Firstly, stripped sour water from the cracking complex was identified as the most relevant wastewater stream concerning phenolic emission. Secondly, multivariate data analysis was used, through projection to latent structures (PLS) regression, to find existing correlations between process parameters and phenols content in stripped sour water, for the first time at the Sines refinery. The models developed allowed the prediction of phenols concentration with predictive errors down to 20.16 ppm (corresponding to an 8.2% average error), depending on the complexity of the correlation used, and R^2 values as high as 0.85 for the training and validation sets of the model. The studied data analysis approach showed to be useful as a tool to predict the phenolic content in stripped sour water. Such prediction would help improve the wastewater management system, especially the units responsible for phenol degradation. The methodology shown in this work can be used in other refineries containing catalytic cracking complexes, providing a tool which allows the online prediction of phenols in stripped sour water and the identification of the most relevant process parameters. An optimized system at any refinery leads to an improvement in the wastewater quality and costs associated with pollutant discharge.

2.2 Introduction

2.2.1 Phenols at the Sines Refinery

Phenols have had a relatively steady behaviour over the past 4 years regarding their discharge to the external WWTP and costs associated, as it can be seen in Figure 2.1, which shows the history of phenols in the final effluent prior to discharge. However, there is still room for improvement regarding phenols content reduction by analysing the matrix classification from strict environmental regulations (Table 1.2) and the average phenolic content historical emissions (Figure 2.1), where phenols have hardly exceeded Class 3 since 2014. Although a relatively steady behaviour over the past few years can be seen, the existence of outliers (>20 ppm) originate from unexplained or unpredictable occurrences, which generate an effluent richer in phenols with higher costs for the refinery associated with pollutant discharge. It should be taken into account that any unpredictable behaviour of phenols discharge, whether due to the decrease in desalter efficiency or the complex nature of the FCC feed and catalytic cracking process that originate phenols or even the type of crude oil mix processed, will lead to an increase in phenol concentration in the wastewater, affecting the overall Class that is charged to the refinery by the WWTP.

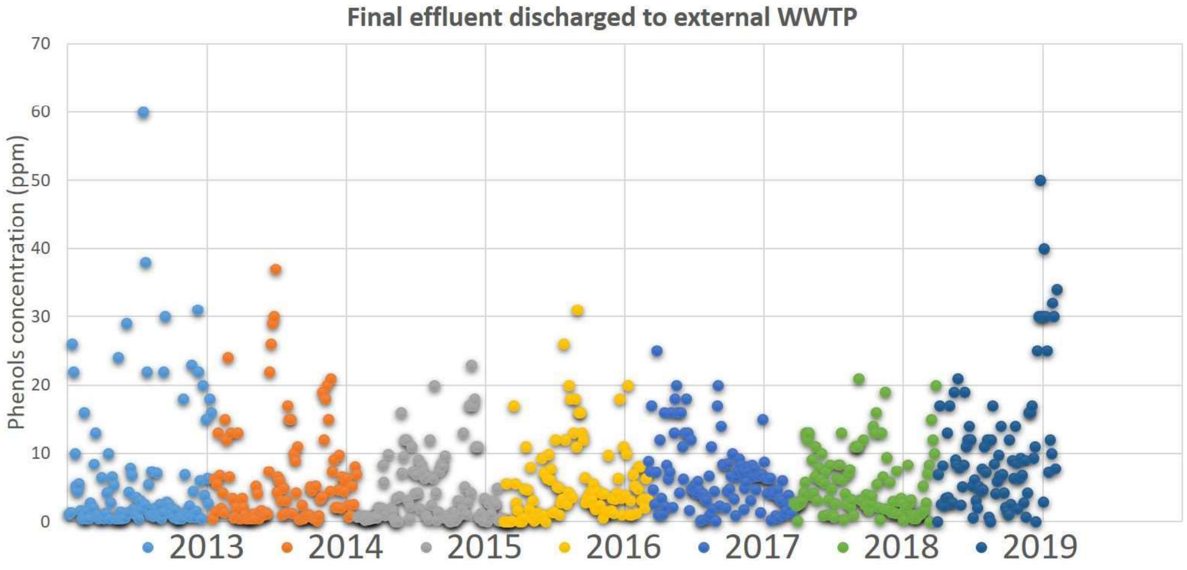


Figure 2.1 Historical data of phenols discharged to external WWTP

As previously described, the effluents generated in the different processes of crude oil refining are collected in a retention basin, homogenized, pre-treated by dissolved air flotation and oxidized in an aerated basin, and then sent to the local WWTP. Figure 2.2 shows a schematic representation of the wastewater circuit at the RS with emphasis given on the effluents generated from Plant II (highlighted in green blocks).

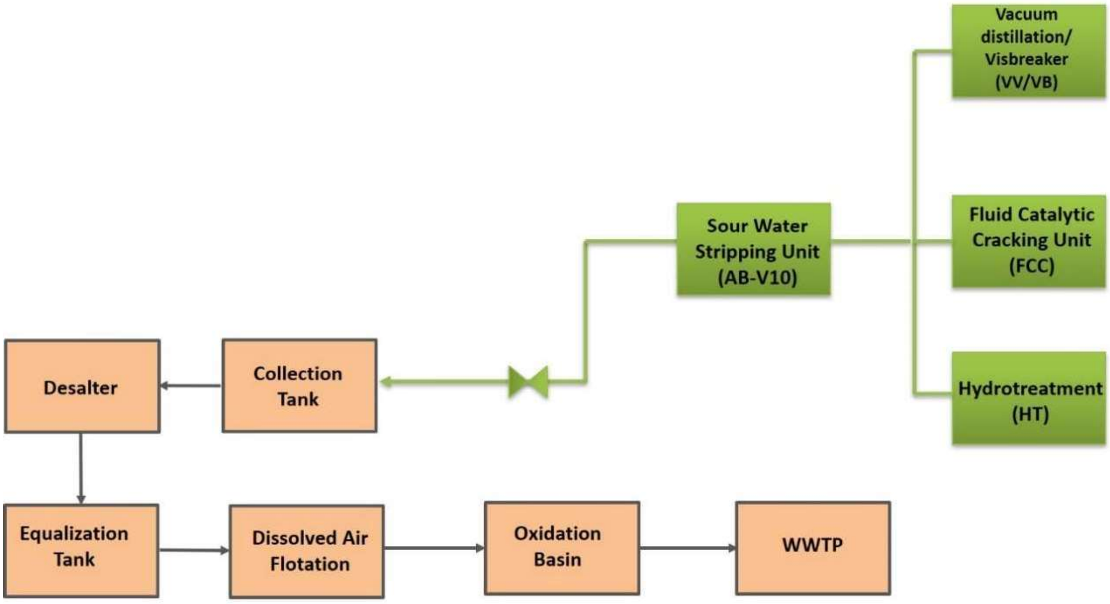


Figure 2.2 Schematic representation of the wastewater circuit with emphasis on Plant II (green blocks)

Sour water generated from the refining processes in Plant II, passes through a stripping process at a Sour Water Stripping Unit where practically all the sulphur and ammonia are stripped leaving the treated water with residual concentrations of these contaminants, compared to the feed. A Process Flow Diagram of the Sour Water Stripping Unit (AB-V-10) from the Sines Refinery Cracking Complex is shown in Figure 2.3. However, as previously mentioned, the phenolic content of the stripped water remains approximately the same as in the feed, showing the non-strippable behaviour of phenols, leaving the treated water with a phenolic contribution of over 60% of the pollutants present, as it can be observed from Table 2.1, leading to this effluent being often denoted as phenolic stripped water.

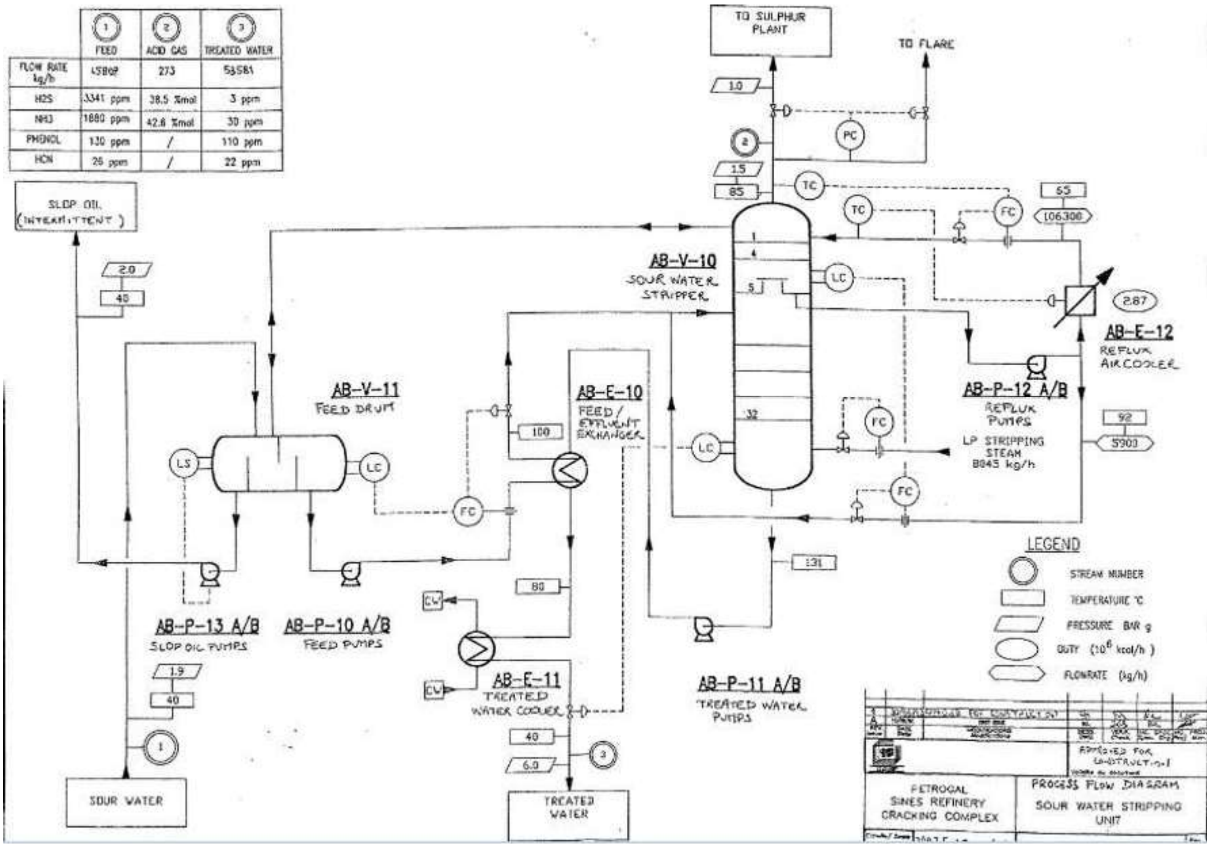


Figure 2.3 Process Flow Diagram of the Sour Water Stripping Unit (AB-V-10) from the cracking complex of the Sines Refinery

Table 2.1 Pollutants present in the Sour Water Stripping Unit (AB-V10) [19]

	Feed	Acid gas	Stripped water
Flow rate (kg/h)	45807	273	53581
H_2S	3341 ppm	38.5 %mol	3 ppm
NH_3	1880 ppm	42.6 %mol	30 ppm
Phenols	130 ppm	-	110 ppm
HCN	26 ppm	-	22 ppm

The stripped water from AB-V-10 is pumped to a collection tank (CC-V7), which collects a large portion of all the refinery aqueous effluents, including from Plant I. This effluent then goes on to feed the desalter at a flowrate of approximately 45-65 m^3/h where most of the phenol is adsorbed in the oil phase and sent back into the refining system. This suggests that phenolic stripped water from Plant II is completely dependent of the desalter contributing to a large portion of its total feed flowrate (about 65%).

Therefore, reducing the feed to the desalter through rerouting the stripped water to an adequate and sustainable treatment technology could decrease the effluent that the desalter discharges to the rest of the wastewater treatment within the refinery, reducing final costs associated with volume treated by the local WWTP.

A study that shows correlations between the refinery process conditions and concentration of phenols in refinery wastewater arises, thus, as a potential useful anticipation tool to overcome such unpredictable and complex behaviours that could affect the wastewater treatment process downstream. Different modelling approaches can be great statistical resources in order to prompt additional inputs in advanced control systems of refining units. The use of multivariate data analysis allows to reveal patterns between input data (process conditions) and the output (phenols contamination in refinery wastewater). As shown in a previous work, this multivariate data analysis approach allowed a better understanding of the source of polar oil and grease compounds that are emitted into the wastewater stream and affect the quality of the final effluent discharged to the external WWTP and costs associated [39]. In that study, the developed model was successfully applied to feed mass balance estimation to the refinery wastewater circuit and validated through analytical monitoring. Furthermore, the implemented online mass balance has ever since been used by the refinery environmental department to predict polar oil and grease contamination peaks upstream and act on the optimization of the wastewater treatment units downstream, such as in the dissolved air flotation unit and oxidation basin.

In the present work, a phenolic emission evaluation was performed throughout the wastewater circuit of the Sines Refinery to identify the wastewater stream that contributed the most in terms of phenols. A detailed physico-chemical characterization of the most relevant stream was conducted over a representative operational period. After identifying the key-stream, multivariate data analysis was used, through projection to latent structures (PLS) regression, to find existing correlations between oil refining process parameters and phenols content in stripped sour water, for the first time at the Sines refinery.

2.3 Materials and methods

2.3.1 Characterization and assessment of Sines Refinery wastewater streams and emission of phenols

An initial evaluation of the phenols present in the wastewater circuit at the refinery was conducted. Figure 2.4 shows a schematic representation of several sampling collection points based on the process water involved in relevant refining process as described in Chapter 1.6. Samples were collected in one litre glass bottles and either readily analysed within 4h after sampling or preserved and stored upon acidification with 2 mL H_2SO_4/L, shown to be the most effective method of preserving phenols in wastewaters [40].

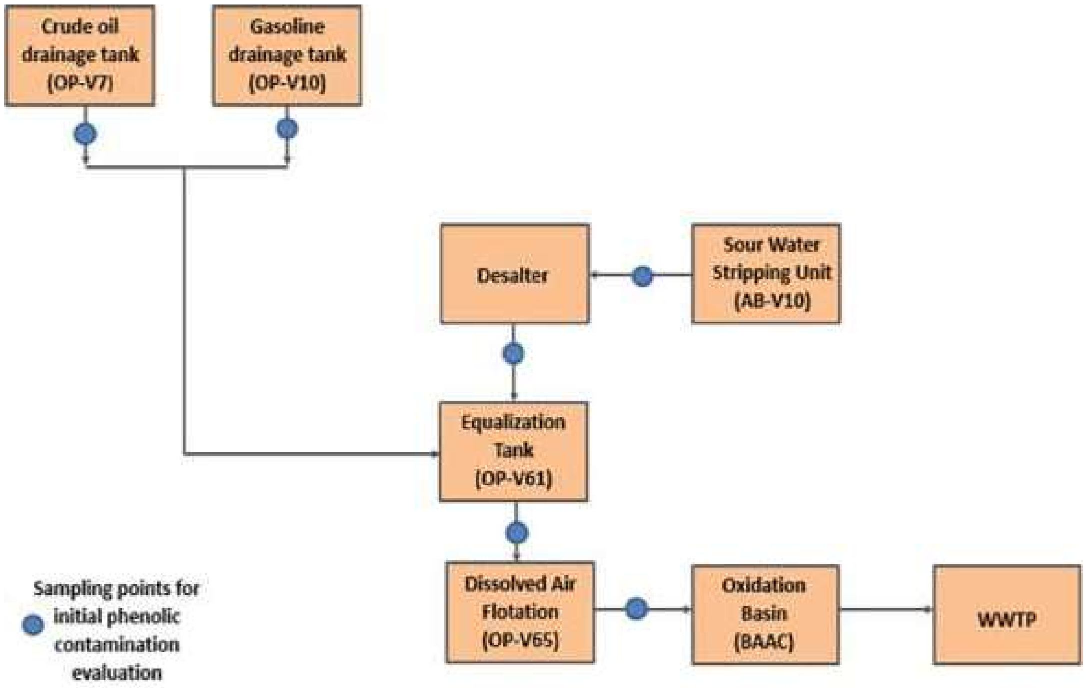


Figure 2.4 Schematic representation of wastewater circuit at RS with sampling points for phenol analysis

Samples of the stripped sour water from the cracking complex of the RS were withdrawn and characterised over a 24-month period in terms the most relevant parameters that compose a key effluent prior to treatment. A continuous characterisation of the wastewater over a representative operational period shows potential advantages in terms of planning, control and treatment of the wastewater, allowing the possibility of witnessing variations in the effluent that could affect treatment performance.

Standard methods were used for phenols and oil and grease concentration (O&G) (SMEWW 5530D and SMEWW5520 C/F, respectively) and COD was analysed using and a LCI 500 cuvette kit (Hach Lange, GmbH, Germany) in agreement with ISO 15705 using the standard method SWEWW 5220 B. Total dissolved solids (TDS) and conductivity measurements were obtained by means of a WTW portable conductivity meter and pH measurements were conducted using a Basic 20 pH meter (Hach).

The determination of phenolic content was performed using the standard methods approved by legislation, such as SMEWW 5530D upon the general principle that steam-distillable phenolic compounds react with 4-aminoantipyrine at pH 7.9 ± 0.1 in the presence of potassium ferricyanide to form a coloured antipyrine dye. The dye is kept in aqueous solution and the absorbance is measured at 507 nm. Interferences are eliminated or reduced to a minimum by using the distillate from the preliminary distillation procedure [41].

2.3.2 Refinery process data

Acquisition of operational information regarding the refining process was accomplished through the online control system of the refinery, namely the data regarding the mass quantities of steam injected in the FCC catalyst stripper coupled to the riser reactor (*VAPreact*). Data regarding the quality of the crudemix processed, such as crudemix acidity (*CMacid*) and crudemix density (ρ_{CM}), as well as the FCC feedstock quality, namely density (ρ_{feed}), levels of sulfur (%S) and mass flowrate (Qm_{feed}) were collected from an existing linear model for the refinery that reports [39] mass quantities and several properties of the crude oil processed, including its acidity and density, and different feedstock qualities fed to the units of the cracking complex.

The parameters initially assessed as possible contributors (inputs) to phenols contamination in wastewater are summarized in Table 2.2. Data regarding process was collected for the same refining program period, in which a sample of treated water of the sour water stripping unit of the cracking complex was withdrawn, for a total of 62 statistical observations. These collections have been reported to be typically in line with the minimum number of observations necessary for adequate industrial data modelling [42].

Table 2.2 Variables studied as inputs for PLS modeling of phenolic concentration in stripped sour water (output)

Model role	Variables	Parameter abbreviation	Range	Average	Standard deviation
Inputs	FCC feedstock density (kg.m^{-3})	ρ_{feed}	[0.913;0.927]	0.92	0.0034
	FCC feedstock mass flowrate (ton/d)	Qm_{feed}	[6083;6186]	6135	22.26
	Steam injected in FCC catalyst stripper (ton/h)	VAP_{react}	[0.56;5]	2.4	1.19
	RAT in FCC feedstock (ton/d)	RAT_{feed}	[617;4390]	3265	790
	VGO in FCC feedstock (ton/d)	VGO_{feed}	[1554;5511]	2676	776

	UCO in FCC feedstock (ton/d)	UCO_{feed}	[72;431]	109	63
	Crudemix acidity (mg KOH.g^{-1})	CM_{acid}	[0.05;0.42]	0.19	0.09
	Naphtha in FCC feedstock (ton/d)	$NAPH_{feed}$	[56;88]	72	9.8
	Naphtha density fed to FCC (kg.m^{-3})	ρ_{NAPH}	[0.67;0.675]	0.67	0.0012
	Crudemix density (kg.m^{-3})	ρ_{CM}	[0.82;0.87]	0.85	0.014
Output	Phenols concentration in stripped sour water (ppm)	$Phenols_{SWS}$	[112;376]	196	59.8

2.3.3 *Sour water stripping unit – Development of PLS models*

Projection to latent structures (PLS) regression was used to correlate process parameters (the inputs) with phenols contamination (the output). PLS regression results in multilinear models able to describe one output based on the inputs. In this work the data collected was divided in two sets, the training set (75% of the observations were used to calibrate the model) and the external validation set (25% of the observations were used to validate the model). These data sets were divided randomly, while it was ensured that the validation set was well distributed and within the training set range of values to avoid extrapolation. The same data sets of training and validation were used to develop the and optimise the models developed using different input approaches. All data used in PLS models was previously normalised through autoscaling (subtracting the average and dividing by standard deviation).

The calibration of the models and the selection of the latent variables (LV) was done through leave-one-out cross-validation, using only the training data set. To assess the quality of the models the root mean squared error of cross-validation (*RMSECV*) was used (Eq 2.1):

$$RMSECV = \sqrt{\frac{\sum_{i=1}^{N}(y_{mod}-y_{exp})^2}{N}} \qquad \text{(Eq 2.1)}$$

where y_{mod} was the output value from the model and y_{exp} the output experimental value for each observation leaved out during cross-validation, and N the total number of experimental observations in the training data set. Cross-validation also allowed the calculation of the uncertainty associated with each input, for each model, through Jackknife standard deviations [43].

External validation of the models was done through the assessment of the root mean squared error of prediction (*RMSEP*), calculated as the *RMSECV*, but for the external validation data set (where *N* is the number of observations in the validation data set). Optimisation of the mathematical models was done through the selection of inputs. This was done aiming at improving the quality of the model and to assess which inputs have a real impact for the output prediction. Selection of useful inputs was performed initially based on the regression coefficient of the model (inputs with higher impact on the output prediction have higher regression coefficient). Subsequently, quadratic and interaction terms were also added to the models to improve prediction. Therefore, instead of a multilinear regression, the models obtained were in the form of (Eq 2.2):

$$y = ax_1 + bx_2 + cx_3 + \cdots + dx_1^2 + ex_2^2 + fx_3^2 + \cdots + gx_1x_2 + hx_1x_3 + ix_2x_3 + \cdots \qquad \text{(Eq 2.2)}$$

where *y* is the output and x_i the inputs. Selection of quadratic and interaction terms was done by running all combinations of inputs with 5 to 12 inputs, and the models selected based on *RMSECV* and *RMSEP*.

2.4 Results and discussion

2.4.1 Characterization and assessment of Sines Refinery wastewater streams and emission of phenols

In order to determine the wastewater stream representing the major source of phenols emission within the refinery, different relevant sampling points were withdrawn throughout the wastewater treatment circuit and were analysed in terms of their phenolic content. Figure 2.5 shows the mass contribution of the phenols (kg/h) emitted in each of the referred sampling points, calculated resorting to the experimentally determined concentration of phenols in wastewater (mg/L) and the corresponding flowrates (m^3/h), using average values over a 6-month period. This allows a comparison of different contributions of phenols in terms of mass within relevant points of the wastewater treatment circuit, in order to identify the most relevant wastewater stream.

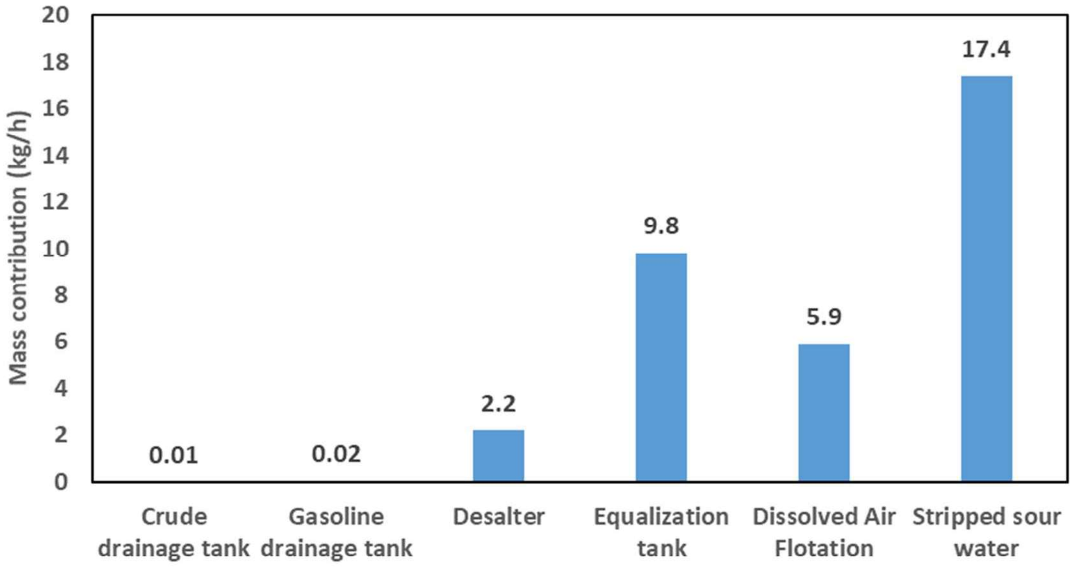


Figure 2.5 Mass contribution of phenols emitted in the studied wastewater circuit sampling points

It can be observed that the effluent that has the greatest phenolic contribution of the sampling points studied is the treated water of the sour water stripping unit (AB-V-10) with mass flow rates reaching over 17.4 kg/h. These large phenol contributions are in line with the refining processes that generate sour water rich in phenols, as explained in Chapter 1.6, such as FCC, visbreaking and vacuum distillation (Table 1.5), which are all routed to a stripping process but have negligible effect on phenol removal.

Table 2.3 shows the physico-chemical characterization of the Sines Refinery stripped sour water from the cracking complex in terms of pH, TDS, conductivity, phenols and COD over a 24-month sampling period from 2017 to 2019. It is possible to observe, from the lower standard deviations and standard errors that pH, TDS and conductivity were the parameters that showed the most consistent behaviour over the 2 years, compared with phenols and COD, with pH values hardly dropping below 7 or exceeding 9, giving the wastewater neutral characteristics. This may be due to the amount of residual ammonia (basic) and sulphides (more acidic) that remain in the wastewater, after stripping, cancelling each other out in terms of pH. The constantly low value of dissolved solids and conductivity compared with the other types of wastewater in the refinery are due to the fact that the water that constitutes sour water generated in the cracking complex, is originated from the demineralized water used in the overhead column of the FCC unit. Demineralized water is always used to avoid fouling due to deposition of ammonia salts on the top of the column. Therefore, the amount of salts in the stripped sour water is practically non-existent and the dissolved solids are mainly due to dissolved phenols present. Phenols concentration ranged between 112 ppm and 376 ppm, presenting an average concentration of 195.7 ppm and a standard deviation of 59.8 ppm. This low variability, in comparison for instance with the amount of polar oil and grease compounds reported [39] in the kerosene spent caustic of the Sines

Refinery, could show a potential advantage of a trustworthy wastewater treatment process which can operate at steady performance without fluctuations in feedstock that could eventually affect optimum treatment. The behaviour of the experimentally determined phenols concentration in stripped sour water throughout the years of 2017-2019 can be found in Figure S1, Supporting Information.

Table 2.3 Experimental characterization of the Sines Refinery stripped sour water from the cracking complex for sampling from 2017 - 2019

	pH	TDS (ppm)	Conductivity (μS.cm^{-1})	COD (mgO$_2$/L)	Phenols (ppm)
Min	6.70	38	85.8	525	112
Max	10.42	144	335.0	6067	376
Average	8.03	65.45	159.4	1241.9	195.7
Standard deviation	0.71	17.29	56.4	1029.4	59.8
Standard error	0.10	2.33	7.61	176.54	7.59

2.4.2 Sour water stripping unit – PLS modelling for phenolic content

Once the stripped sour water stream was identified as having the greatest phenolic contribution of the refinery, a PLS model was developed in order to predict the content of phenolic compounds in the effluent of the sour water stripping unit. A multilinear combination of the inputs chosen was attempted in the development of a PLS model. These inputs were selected based on the process variables related to upstream units that are directly related to the stream fed to the sour water stripping unit of the cracking complex. Most of the inputs focus on the FCC feedstock quality and steam injected in the riser reactor stripper, where phenols are primarily formed from the reaction between cyclic hydrocarbons and steam [17, 24]. In a first approach, over 50 different inputs combinations were selected as screening in the study of their relevance and usefulness to develop a PLS model based only on multilinear combinations. The best model obtained through these combinations is shown in Table 2.4, where it is possible to observe that the linear model only captured 55% of the data variance and the poor predictive ability of the model for the training and validation set. However, the screening study allowed to narrow down some of the inputs initially selected, where variables related to the FCC feedstock quality and steam injected in the catalyst stripper indeed ended up playing a major role. A graph of the best linear PLS model obtained with the variables chosen can be found in Figure S2, Supporting Information.

Table 2.4 Linear PLS model analysis of captured variance and training set and validation set correlation coefficients

Model role	Variables	Captured variance (%)	*RMSECV* (ppm)	*RMSEP* (ppm)	Training set coefficient of determination	Validation set coefficient of determination
Inputs	VGO_{feed} UCO_{feed} VAP_{react} Qm_{feed} ρ_{CM} CM_{acid}	55.3	48.33	31.10	0.55	0.62
Output	$Phenols_{SWS}$					

RMSECV – root mean squared error of cross-validation; *RMSEP* – root mean squared error of prediction.

Considering these results, in a second approach, it was decided to include quadratic and interaction terms of these operational input data values aiming to improve the prediction correlation in the development of the PLS model. Additionally, two more inputs were added to the ones selected by the linear model: FCC feedstock density and the atmospheric residue (RAT) of FCC feedstock. Despite these two inputs not being selected by the multilinear modelling approach, they were found to be of high relevance for output estimation when used in other input combinations (data not shown). Table 2.5 shows the best two non-linear models achieved through inputs selection, where it is possible to clearly observe an improvement in the captured variance and coefficients of determination in training and validation sets. Although the number of terms increased compared to the multilinear model, they resulted from the multiplication or squared of the existing variables (7 input variables), not by new data inputs. Such increase in the number and complexity of terms used in the model allowed the extraction of the information (relative to the output) contained in the inputs. One of the inputs that was initially included in the linear model (crudemix density) ended up being withdrawn from the multilinear model, as it showed to have a minor impact in the improvement of model and is not directly related to the FCC process but rather the very first stream fed to the refining process, that could affect the feedstock quality downstream.

Figure 2.6 shows the comparison between the PLS model estimations and the experimental data for the concentration of phenols in stripped sour water of the cracking complex, for the most accurate PLS model obtained using quadratic terms (the model with 11 terms shown in Table 2.5). A graph of the non-linear PLS model with 9 terms obtained can be found in Figure S3, Supporting Information.

An interesting agreement was found, where a coefficient of determination of 0.85 was obtained for the training and validation set. Furthermore, the training and validation set presented slopes of 0.849 and 0.976, respectively, indicating an interesting correlation even though data showed to be relatively dispersed. As was witnessed for the linear model, practically all of the most relevant inputs originated from the FCC feedstock quality, with atmospheric residue (RAT) [44, 45] and vacuum gas oil (VGO) composing over 80% wt. of the highly complex stream fed to the FCC unit. Apart from the cyclic hydrocarbons that exist in heavy coke accumulated on the FCC spent catalyst and that in the presence of steam are stripped and form phenols, phenolic compounds may also exist in FCC feedstock [46], most likely due to oxygen atoms being naturally bonded to cyclic hydrocarbons that compose the feed. The inputs that showed the most relevance for the model (atmospheric residue (RAT) and vacuum gas oil (VGO)) are part of the FCC feedstock quality and can easily be obtained from the manufacturing programs of refineries whenever a certain type of crudemix is processed, and therefore be directly used for these types of models, without the need of extra characterizations or lab work.

The usefulness of the model obtained as a predictive anticipation tool arises from the route that stripped sour water takes (Figure 2.4) before being sent to the municipal WWTP. The first and most decisive step of the route is using the effluent as wash water for the desalters, where 75-88% of the phenols (experimentally determined, based on phenolic concentration in desalter effluent) are absorbed back into the crude phase. However, heavier loads of phenols lead to a higher phenolic content at the final effluent (as it can be seen from the outliers in Figure 2.1), which can lead to a sensible assumption that a decrease in desalter efficiency occurs whenever a greater emission of phenols takes place in stripped sour water. The model would allow the prediction of the concentration of phenols in stripped sour water before it is fed to the desalter and in case of a heavier load, alert the wastewater treatment units downstream. The downstream unit most responsible for degrading the phenols is the oxidation basin, where hydrogen peroxide is fed to oxide the pollutants present. Depending on the amount of phenols emitted, the adjustment of hydrogen peroxide can be optimized, leading to an improved management of such reagent, which from a sustainable point of view, can be worthwhile.

Although other refineries may present other forms of wastewater treatment for the effluents generated, it is safe to affirm that the methodology developed in this work can be applied to refineries that contain a catalytic cracking complex, and can provide useful information regarding the phenolic content in stripped sour water, without the need of phenolic determination through lab work, thus avoiding the use of resources while saving time.

Table 2.5 Non-linear PLS model analysis of captured variance and training set and validation set coefficients of determination

Nº of terms	Captured variance (%)	*RMSECV* (ppm)	*RMSEP* (ppm)	Training set coefficient of determination	Validation set coefficient of determination
9	82.7	30.98	22.74	0.827	0.832
11	84.8	30.89	20.16	0.848	0.845

RMSECV – root mean squared error of cross-validation; RMSEP – root mean squared error of prediction

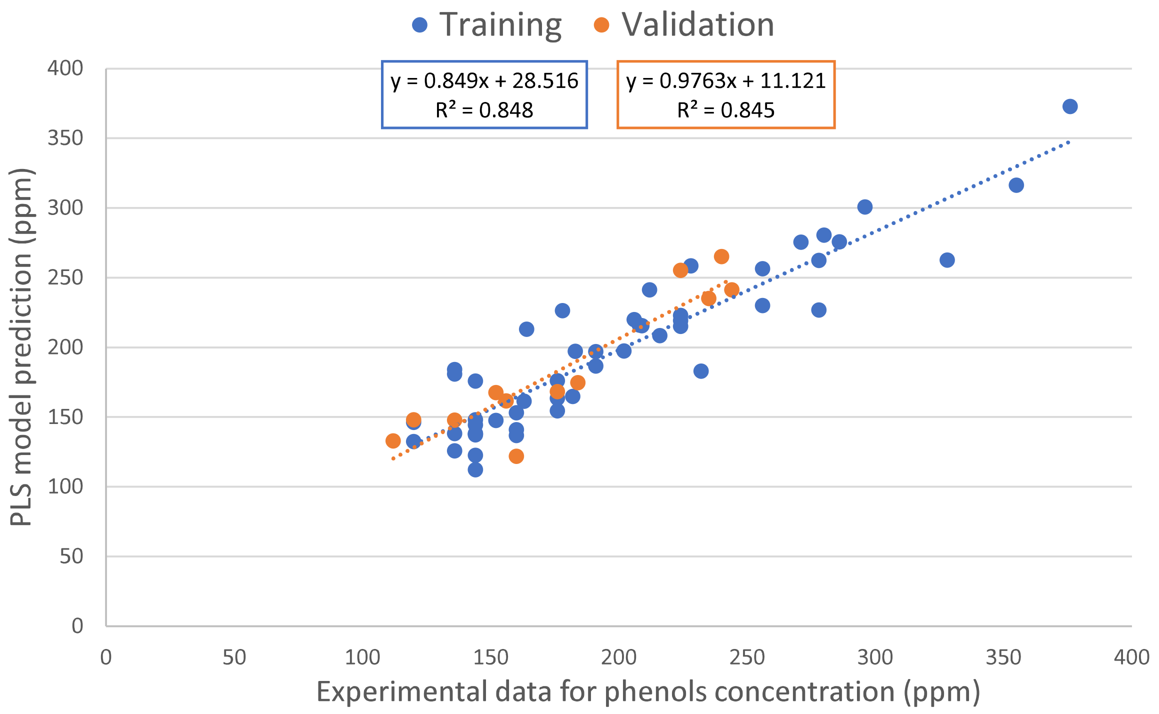


Figure 2.6 Non-linear PLS model, with 11 terms, predictions as a function of the experimental data for phenols concentration in stripped sour water from the refinery cracking complex

Figures 2.7 (a) and 2.7 (b) show the regression coefficients (for normalised data) of the model inputs for the model with 9 terms and 11 terms, respectively. The low uncertainty found for all inputs (error bars in Figure 2.7) show low variability of the correlation between each input and the output across training data, which results in robust models. It is possible to observe that, for both models, the mass flowrate of RAT (*RATfeed*) and its combination with the VGO mass flowrate (*VGOfeed*) that compose the FCC feedstock flowrate showed to be the most relevant, presenting greater regression coefficients than the remaining inputs studied. The mass flowrate of the feedstock that enters the FCC unit itself (*Qmfeed*) also showed a particular relevance for the best model obtained. An interesting observation that can also be withdrawn is that the amount of steam injected in the FCC catalyst stripper (*VAPreact*), that is known to be directly related to the formation of phenol upon stripping of heavy coke, ended up playing a less active role in comparison with the FCC feedstock quality itself. It is therefore possible that most of the phenolic compounds emitted in the stripped sour water actually originated from the cyclic hydrocarbons with oxygen atoms naturally bonded to them that compose the stream fed to the FCC unit, and not so much from the phenols formed from the reaction occurring in the FCC catalyst stripper.

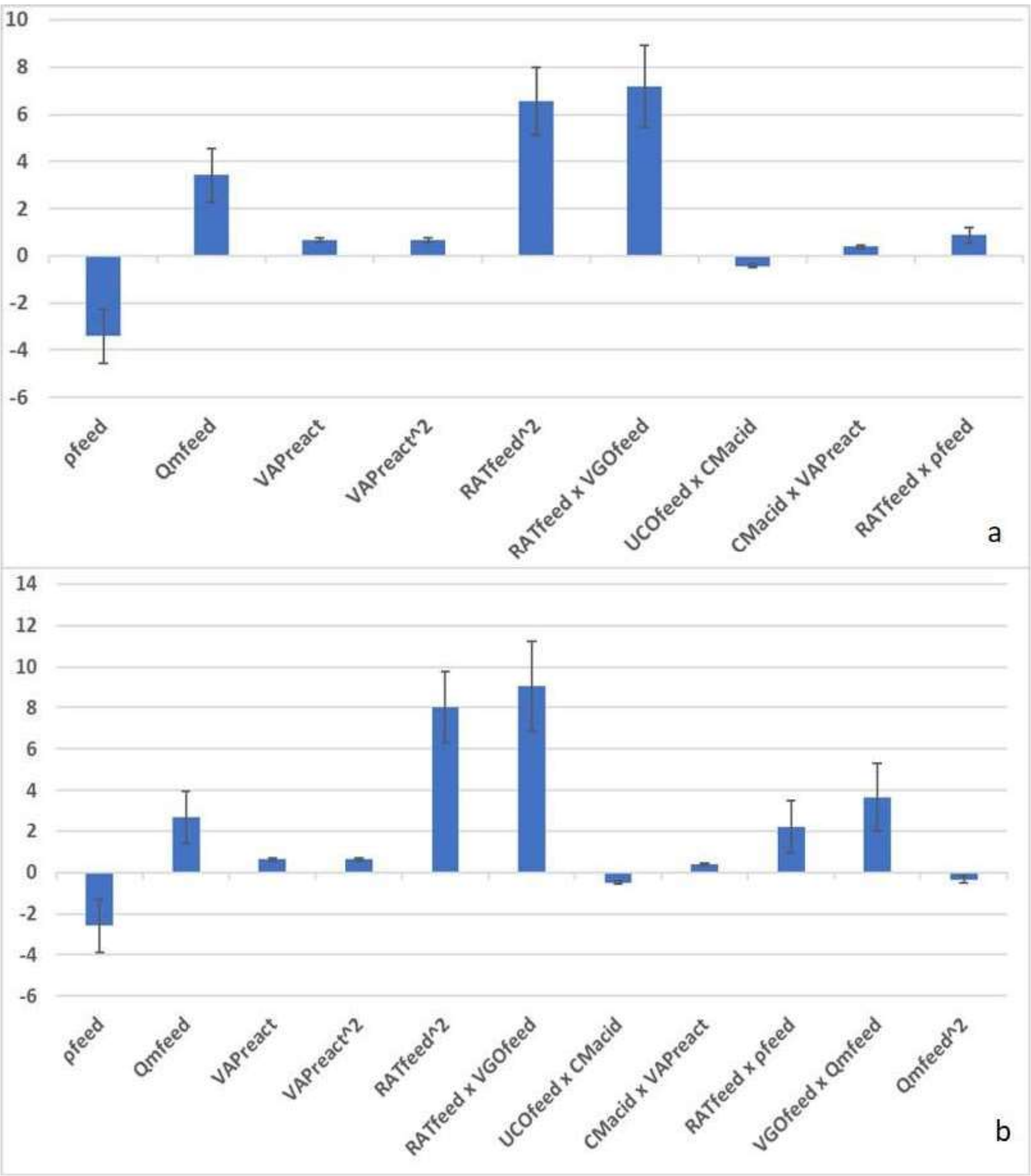


Figure 2.7 Regression coefficients of the model inputs with the 9-term model (a) and 11-term model (b) for phenols concentration in stripped sour water, for normalized data

The use of non-linear inputs for an insightful PLS model proved to be inevitable, as the inclusion of only linear inputs (such as *VGOfeed*, *UCOfeed* and *CMacid*) did not improve the model. However, the results achieved with the use of quadratic and interaction terms (of the same input parameters) in non-linear models show that the relationship between the output and the inputs studied is complex and not easily disclosed by linear correlations. One of the inputs that varied the most in terms of relevance and regression coefficient was the mass flow rate of atmospheric residue in the FCC feedstock

(*RATfeed*), which greatly improved the model when added to the model as new input composed of its squared value, with coefficients of determination increasing from 0.77 (data not shown) to 0.84.

2.5 Conclusions

The present study allowed the evaluation and identification of the most relevant wastewater stream in terms of phenolic impact at the largest Portuguese oil refinery, Petrogal S.A. in Sines, Portugal. It was observed that the effluent presenting the greatest phenolic contribution was the stripped sour water stream of the cracking complex. The large phenolic contributions showed to be in line with the typical refining processes that generate sour water rich in phenols. After identifying the most relevant stream, multivariate data analysis was successfully used to correlate the process parameters with the concentration of phenols in stripped sour water. Seven process parameters, mostly representing the FCC feedstock quality and steam injected in the riser reactor, were identified as necessary to estimate phenols in non-linear correlations. These models can predict phenols concentration with a predictive error of 22.74 or 20.16 ppm, depending on the complexity of the correlation used. The modelling work allowed the selection of the most relevant operating parameters contributing to the phenol concentration in stripped sour water. Above all, the study allowed the development of an anticipation tool through prediction of phenols in the referred wastewater which would help control and optimize the efficiency of the current effluent treatment units. Such optimization leads to an improvement in the quality of the final wastewater stream and reduces costs associated with the discharge to the external wastewater treatment plant. Furthermore, the work developed in the present study arises as useful for other refineries which contain catalytic cracking complexes, as it provides the methodology to develop a tool specific to a certain refinery, which allows the determination of phenols in the stripped sour water and the impact of different input process parameters. The usefulness of such information ranges from the possibility of optimizing the on-site conditions for an efficient phenol degradation, to the avoidance of using resources associated with lab work for the determination of phenols in stripped sour water.

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CHAPTER 3

REVERSE OSMOSIS PERFORMANCE ON STRIPPED PHENOLIC SOUR WATER TREATMENT – A STUDY ON THE EFFECT OF OIL AND GREASE AND OSMOTIC PRESSURE

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3.1 State of the art

Technologies that allow water recycling within oil refineries have been gaining interest at an extensive rate due to the large volume of wastewater generated, high dependency of water and the progressive scarcity of this valuable resource. Phenols are part of a specific class of organic pollutants that have been contributing to a low-quality effluent in oil refineries due to their hazardous nature and strict environmental legislations associated. The reuse of stripped sour water within refineries is often blocked due to its rich phenolic content.

This study presents the retention of phenols in refinery wastewater through reverse osmosis (RO) at its major source of emission for water reclamation. The RO membrane exhibited rejections of up to 98% of phenols and 99% of both chemical oxygen demand (COD) and total organic carbon (TOC). Permeate quality remained intact despite flux decline caused by phenolic and hydrocarbon adsorption when the oil content in feed reached 771 ppm. The poor ionic nature of the effluent due to lack of salts and low conductivity led to minor osmotic pressures (less than 2.5 bar at a volume concentration factor of 3), therefore showing appealing performances of reverse osmosis filtration. Characterization of all permeates obtained from cross-flow filtration experiments showed COD levels in line with water reuse quality standards for make-up water in cooling processes.

3.2 Introduction

Many technologies have been reviewed over the past few years [11,30] regarding phenol removal from wastewaters, ranging from traditional methods such as distillation, extraction, adsorption, chemical oxidation, and biodegradation to advanced methods namely photo oxidation processes and membrane separation technologies, where the latter has been given particular attention due to low energy consumption, low operating cost, and easy scale up by membrane modules.

Phenolic wastewaters from paper mill industries [30] and coke-oven wastewaters [33] are examples of industrial effluents that have undergone phenol removal through membrane filtration processes. However, studies regarding direct reverse osmosis or nanofiltration technologies on stripped phenolic sour water from refineries are yet to be thoroughly explored, especially regarding membrane performance on phenol removal itself upon feed quality variations such as pH and oil and grease contamination levels.

Regarding the Sines Refinery, sour waters from the cracking complex, after being stripped, undergo a series of pre-treatment steps which minimize phenolic impact before being discharged to an external WWTP. Figure 3.1 shows an alternative proposal involving membrane treatment at the source of phenol emission. The proposed technology leads to the possibility of both reducing the volume discharged to the external WWTP and reusing water within the refinery, contributing to lowering the costs of raw water as a utility, such as in make-up water in cooling towers.

Therefore, a lab study on real stripped phenolic sour water treatment, over a representative operational period was conducted, where it was possible to witness the variability of the feed regarding its physico-chemical characteristics, such as oil and grease and explore their influence on the treatment performance using nanofiltration (NF) and RO membranes through analysis of permeate flux and overall rejections.

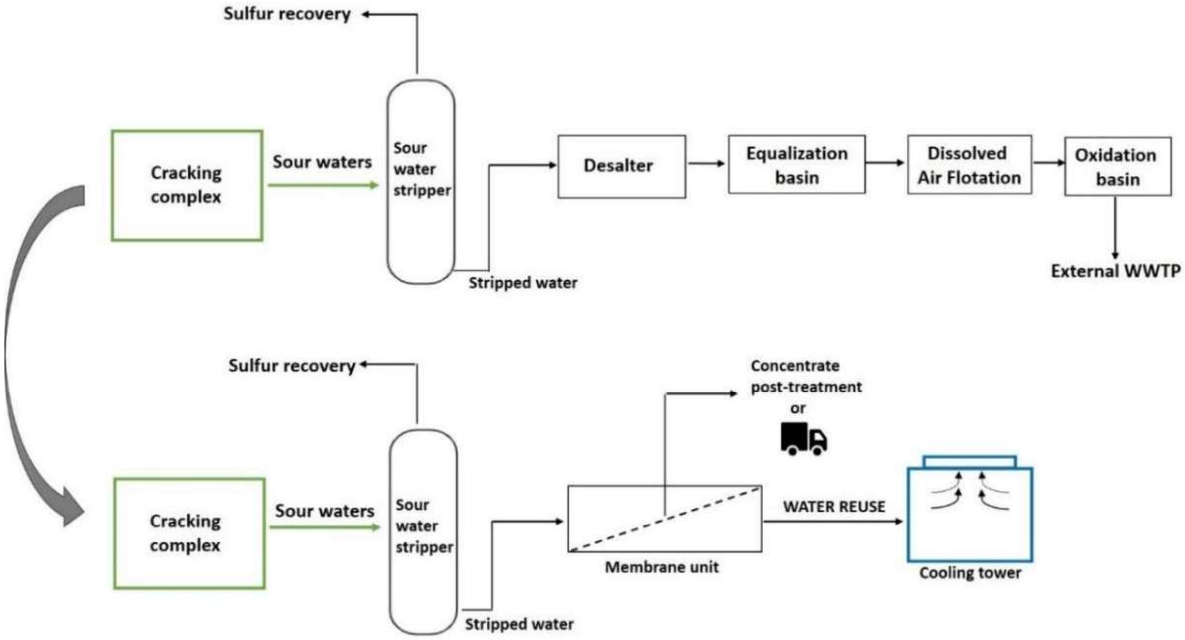

Figure 3.1 Simplified wastewater treatment circuit of Sines Refinery and proposed membrane treatment

3.3 Materials and methods

Stripped sour water samples were collected directly from the effluent of the sour water stripping unit of the cracking complex at the Sines refinery. Samples from the initial wastewater and permeates obtained after NF and RO were analysed by standard methods for oil and grease and phenols concentration (SMEWW 5520 C/F and SMEWW 5530D, respectively). COD was analysed by the LCI 500 cuvette kit (Hach Lange, GmbH, Germany) in agreement with ISO 15705 and TOC was determined through a total carbon analyser TOC-VCSH (Shimadzu, Japan). Ammonia and phosphates content were analysed by a SKALAR analyser. Turbidity values were acquired through a portable turbidity meter (Hanna Instruments, USA). Total dissolved solids (TDS) and conductivity measurements were obtained by means of a WTW portable conductivity meter. Salinity measurements were performed using a Sension+ EC7 Laboratory Conductivity Meter, (Hach, USA).

3.3.1 Membrane screening for nanofiltration and reverse osmosis assays

Membrane screening assays were conducted to address the difference in efficiencies of using nanofiltration and reverse osmosis regarding rejections of COD from the stripped sour water. The membranes used in this study along with their main characteristics are described in Table 3.1 and were chosen based on the major phenolics found in real refinery wastewater streams [26] which were identified having molecular weights of up to 122 Da. Filtration experiments were conducted in a stainless steel dead-end stirred-cell (Membrane Extraction Technology Ltd., UK) with an effective membrane area of 54 cm^2. The nanofiltration experiment was conducted at 15 bar whereas reverse osmosis assays were performed at 50 bar, all at room temperature (22± 1 °C) and feed solutions were stirred at 900 rpm to lessen concentration polarization. Samples of permeates were withdrawn throughout the experiments to measure COD and calculate apparent rejections as,

$$Apparent\ rejection\ (\%) = (1 - \frac{Cp}{Cf}) \times 100 \qquad \text{(Eq. 3.1)}$$

where Cp and Cf are the COD in the permeate and feed, respectively.

Table 3.1 Main characteristics of membranes used in the study

Manufacturer	Membrane	Material	Type of membrane	Molecular weight cut-off (MWCO) (Da)	Temperature/Maximum pressure	pH
GE Osmonics	Desal DK	Polyamide Selective Layer Thin Film Composite	Nanofiltration	150-300	50 ˚C/ 41 bar	3-9
DOW	SW30 BW30	Polyamide Selective Layer Thin Film Composite	Reverse Osmosis	NaCl rejection = 99,4%	45 ˚C/ 69 bar	2-11

3.3.2 Cross-flow filtration assays through reverse osmosis

The filtration experiments were carried out in a cross-flow membrane filtration unit (Sepa CF II Membrane Cell system, SUEZ Water Technologies and Solutions) with effective membrane area of 140 cm^2. Figure 3.2 shows a schematic representation of the system. The unit was equipped with a permeate and feed tank, a high-pressure diaphragm pump (Hydra-Cell, Wanner Engineering, Inc.), a valve to regulate pressure and an electronic balance coupled to a computer for on-line mass acquisition. The studies were carried out in concentration mode, where the permeate was collected and continuously weighed over time into a clean tank with the concentrate being recirculated back into the feed tank. All filtration assays were performed at constant transmembrane pressure (50 ± 1 bar) and feed flow rate (360 $L.h^{-1}$). The transmembrane pressure was calculated as the arithmetic average of the pressure difference between the feed circuit and the permeate circuit, at the entrance and the outlet of the module [47]. Feed temperature was maintained at 22 ± 2 °C by cooling the concentrate through counter current heat exchange before returning to the feed tank. Permeate fluxes (Jv) were calculated based on the permeate flowrate (Qv) per unit membrane area (A) as,

$$Jv = \frac{Qv}{A} \qquad \text{(Eq. 3.2)}$$

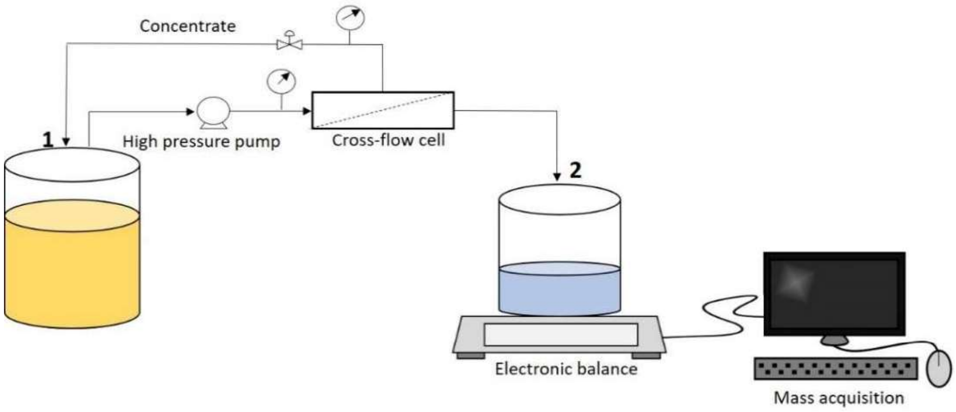

Figure 3.2 Schematic diagram of the membrane filtration system; 1 – Feed tank; 2 – Permeate collection tank

3.4 Results and discussion

3.4.1 Membrane screening experiments through nanofiltration and reverse osmosis

In order to select the efficiency of the most adequate membrane for the treatment of stripped phenolic sour water, known for its high phenolic content, a nanofiltration membrane (Desal DK) and two reverse osmosis membranes (SW30 and BW30) were tested in a dead-end filtration setup aiming at an evaluation of their performance regarding rejection of the organic pollutants at hand. Samples of permeate were withdrawn throughout the filtration experiments and COD was measured and compared with that of the inlet feed. For the screening assays, COD measurements were chosen as a straightforward and efficient method of determining the amount of organic pollutants that permeate the membrane, showing to be a useful parameter to assess water quality. Figure 3.3 shows the COD apparent rejection as a function of the volume concentration factor (VCF) for the three membranes studied at a transmembrane pressure applied of 15 bar for Desal DK and 50 bar for SW30 and BW30, calculated by Eq. 3.1. It can be seen that COD apparent rejections were no greater than 40% when the feed was processed through the Desal DK nanofiltration membrane and decreased throughout the filtration, indicating that most of organic pollutants composing the feed, including phenols as the most abundant, are not retained by the membrane. It can be suggested that most of the phenols constituting the feed have molecular weights that are lower than the membrane's MWCO (150 – 300 Da). A reported study on the pilot processing of a phenolic-rich wastewater using the same membrane [48] also found generally unimpressive rejections of low molecular weight phenols identified in the feed. This study along with the major phenols found in real refinery wastewater streams [26], such as phenol, cresol and xylenol, strongly support that the nanofiltration membrane Desal DK is not suitable for the retention of phenols in the stripped phenolic sour water studied, unlike other industrial effluents of high organic load where nanofiltration was successfully implemented [49]. The molecular weight of phenolic compounds plays a decisive role in the type of membrane required for a successful separation, where nanofiltration may present interesting rejections if the total phenols constituting the feed are of high molecular weight [50]. On the other hand, the reverse osmosis membranes BW30 and SW30 showed COD rejections of up to 83 and 97%, respectively, with minimal loss of rejection (no greater than 12% for SW30) compared to Desal DK (approx. 40% loss of rejection) at a concentration factor of 3.2, showing that the nanofiltration membrane could be more sensitive to concentration polarization, inevitably formed due to dead-end filtration, compared to the reverse osmosis membranes. An accumulated reduction in COD of 21.5% was observed for Desal DK and 83.2% and 86.1% reduction for BW30 and SW30 membranes, respectively, as it can be seen in Table 3.2.

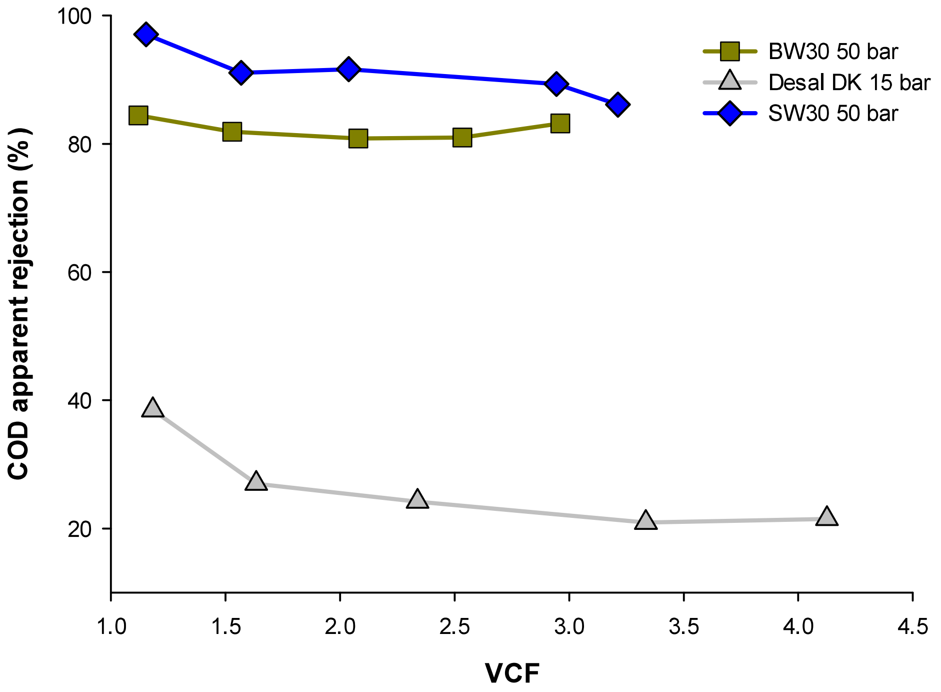

Figure 3.3 Apparent rejection (%) of COD as a function of volume concentration factor (VCF) for the membranes studied

Table 3.2 Feed and permeate COD and overall COD reduction for membranes studied

		Nanofiltration	Reverse Osmosis	
		DESAL DK	BW30	SW30
COD (mgO$_2$/L)	Feed	793.3	782.3	740.3
	Final permeate	622.8	131.7	103.0
Overall reduction (%)		21.5	83.2	86.1

As the SW30 membrane showed the best results regarding COD reduction, a further characterization of the permeate was performed, regarding relevant parameters concerning water reuse, such as pH, conductivity and TDS and compared with the water quality standards with results are presented in Table 3.3. It can be observed that the permeate quality is line with the standards regarding most of the routinely controlled parameters such as pH, TDS and conductivity. The COD value for the final permeate was higher than the reported quality standards for water reuse, mainly affected by the loss of rejection throughout the filtration due to concentration polarization that can hardly be eliminated in dead-end filtration processes.

Therefore, a study regarding reverse osmosis performance in cross-flow filtration using the SW30 membrane was conducted to study the effect on rejection loss of organic compounds by the membrane, while scaling-up the wastewater treatment and allowing control of the fluid dynamics involved.

Table 3.3 Characterization of feed and permeate from SW30 membrane and water reuse quality standards

Parameter			Water reuse quality standards [51]
	Feed	Permeate	Cooling water
pH	8.44	7.66	6.5 – 9.0
TDS (ppm)	70.9	20.5	500
Conductivity ($\mu S.cm^{-1}$)	141.4	41.5	b
COD (mgO_2/L)	740.3	103	75
TOC (ppm)	293.4	41.4	-
Phosphates (ppm)	< LOQ	< LOQ	b
Ammonia (ppm)	13.5	2.86	b

[b] Accepted as received

3.4.2 Cross-flow assays through reverse osmosis

3.4.2.1 RO membrane performance on flux and rejection

Based on the membrane screening experiments conducted, where it was possible to observe that the SW30 reverse osmosis showed the most appealing results of the membranes studied, a cross-flow filtration of the wastewater was performed, in concentration mode. This method of filtration allows an interesting scale-up, while permitting control of fluid dynamics such as feed flow rate, overcoming flux declines associated with concentration polarization.

Three wastewater samples of stripped phenolic sour water were collected over a representative operational period, throughout distinct production plans of the refinery, to study feed quality variations that could occur based on different types of crude oil processed.

A physico-chemical characterization of the feed samples is presented in Table 3.4 where it is possible to observe the distinct variations between wastewaters, such as pH and oil and grease concentration. The identification of the experiments performed on each batch sample, was set according to the oil and grease content found and is identified as follows: Assay 1 - Low O&G content (4 ppm); Assay 2 – Intermediate O&G content (98 ppm); Assay 3 – High O&G content (771 ppm).

Samples of instantaneous permeates where collected throughout each filtration experiment at different VCF and were analysed in terms of phenols, COD and TOC. Apparent rejections were calculated based on and adapted from Eq.3.1. Fig.3.4. represents the apparent rejections (phenols and COD) and corresponding normalized permeate fluxes (Jv/Jv_0) for all assays, where Jv_0 represents the initial permeate flux as a function of the VCF for each assay. It is possible to that the normalized permeate flux remained constant throughout the filtration in Assay 1 and Assay 2, respectively. Opposingly, Assay 3 shows a sharp flux decline up to a VCF of 1.5 and a gradual flux decline for VCF up to 2.94 where the final permeate flux dropped to approximately 53% of its initial value. Regarding phenols retention, it can be seen that the apparent rejections show negligible decreases throughout the filtration up to a concentration factor of 3, from 97.2 - 96.5% for Assay 1, 97.4 - 95.7% for Assay 2 and 98.1 - 96.6% for Assay 3. COD rejections remain clearly constant for all assays, reaching values of 97.4% for Assay 1 and Assay 2, and 99.4% for Assay 3. The fact that the major contributors of COD are phenols and O&G supports the higher COD rejection for the feed rich in O&G compared to the feed poor in O&G. Nevertheless, it is possible to highlight from the overall results that the flux decline showed no effect on the phenol/COD rejections, suggesting that potential fouling by oil and grease contributes to the rejection of smaller solutes. In this study, such high molecular weight compounds encompass heavy non-polar hydrocarbons that exist in the feed.

Before each filtration experiment, deionized water was passed through the fresh membrane to determine the pure water permeability at 50 bar and room temperature. The following clean water fluxes at 22 ± 2 °C were experimentally obtained: 35.42 $L.h^{-1}.m^{-2}$, 50 bar; 26.93 $L.h^{-1}.m^{-2}$, 40 bar; 19.53 $L.h^{-1}.m^{-2}$, 30 bar; 11.90 $L.h^{-1}.m^{-2}$, 20bar, which showed that the membrane was properly compacted.

Table 3.4 Physico-chemical characterization of stripped sour water samples fed to filtration system

Feed characterization			
Parameter	**Assay 1**	**Assay 2**	**Assay 3**
pH	8.83	10.41	9.35
Conductivity (µS.cm^{-1})	222	335	86.3
TDS (ppm)	71	101	46
Turbidity (NTU)	-	14.5	16.8
COD (mgO$_2$/L)	857	1577	1605
TOC (ppm)	273.3	664.7	399.4
Phenols (ppm)	160	184	128
Polar O&G (ppm)	1	1	37
Non-polar O&G (ppm)	3	97	734
Total O&G (ppm)	4	98	771
Ammonia (ppm)	13.62	37.84	9.47
Phosphates (ppm)	< LOQ	< LOQ	< LOQ

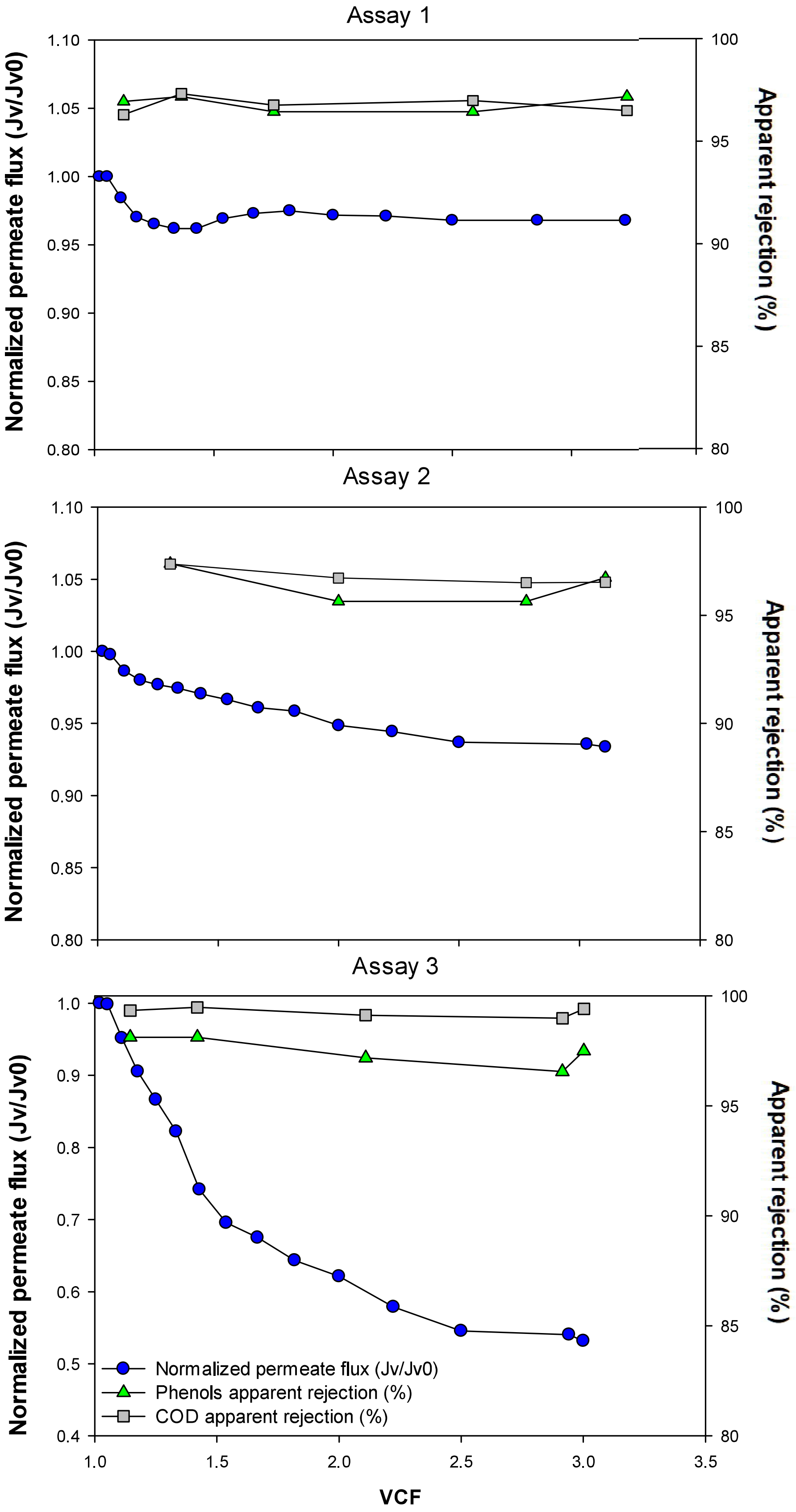

Figure 3.4 Cross-flow filtration evolution of apparent rejection of phenols and COD with volume concentration factor and normalized permeate fluxes for all assays

3.4.2.2 Osmotic pressure estimation and adsorption

For nanofiltration and reverse osmosis processes, the osmotic pressure difference ($\Delta\pi$) between the retentate and permeate normally plays a major impact on permeate flux (Jv), when operating in concentration mode, due to the driving force decrease, according to,

$$Jv = Lp\ (TMP - \ \Delta\pi) \qquad \text{(Eq.3.3)}$$

where Lp represents the membrane permeability and TMP the transmembrane pressure. Therefore, an estimation of the impact of low molecular weight solutes on the driving force was conducted in order to study the causes of the flux decline observed in Assay 3. The osmotic pressure difference between the concentrate and permeate side was determined using the Van't Hoff equation, as

$$\Delta\pi = (Cm - Cp)RT \qquad \text{(Eq.3.4)}$$

where Cm is the molar concentration of the solutes in the concentrate, Cp their molar concentration in the permeate, R is the gas constant and T is the absolute temperature. As far as contribution to osmotic pressure difference, it was assumed that only molecules with low molecular weight showed the highest relevance such as phenols, salts and small non-polar hydrocarbons. Therefore, the following components in the wastewater were considered the key compounds for osmotic pressure estimation: phenol (MM, 94.11 $g.mol^{-1}$), cresol (MM, 108.14$g.mol^{-1}$), xylenol (MM, 122.16 $g.mol^{-1}$), heptane (MM, 100.21 $g.mol^{-1}$), octane (MM, 114.23 $g.mol^{-1}$), nonane (MM, 128.26 $g.mol^{-1}$), decane (MM, 142.29 $g.mol^{-1}$) and sodium chloride (MM, 58.44 $g.mol^{-1}$). Molar concentrations in the concentrate were calculated through a mass balance using the molar concentrations in permeate and feed as well as their respective volumes. The experimentally obtained mass concentrations were used to calculate feed and permeate molar concentrations. Figure 3.5 shows the evolution of the estimated osmotic pressure difference as a function of the volume concentration factor, as opposed to the transmembrane pressure.

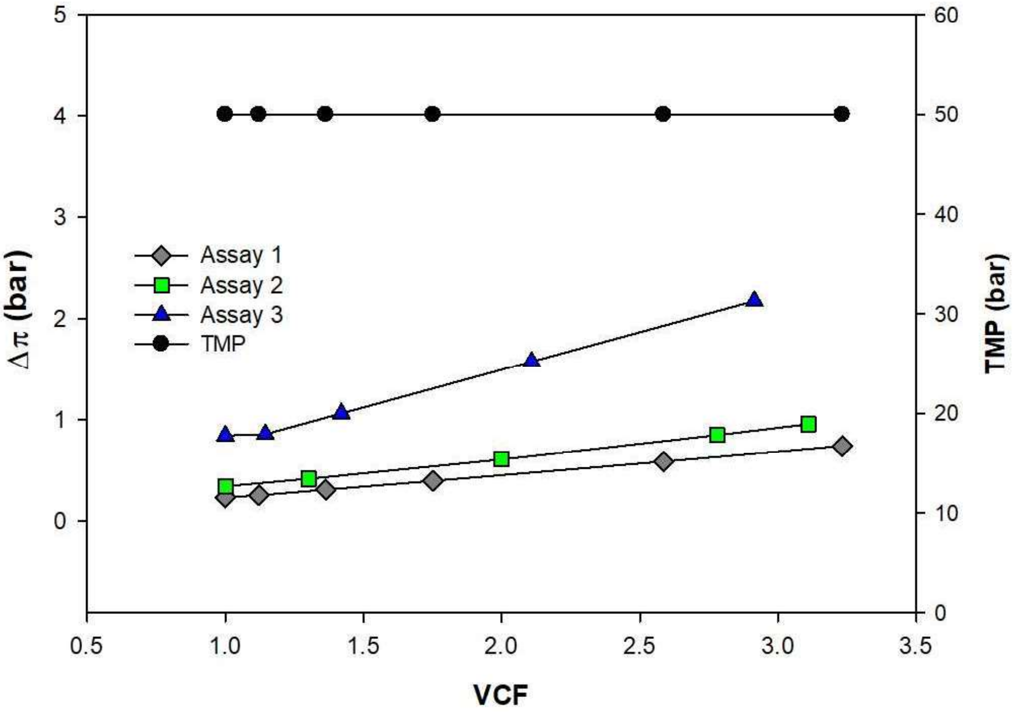

Figure 3.5 Evolution of the estimated osmotic pressure difference for the filtration experiments operating in concentration mode

It can be clearly seen that the increase in osmotic pressure difference in Assay 3 is greater than the increase in the remaining assays, ranging from less than 1 bar up to 2.2 bar at a concentration factor of 3, whereas the slight increase for Assay 1 and Assay 2 ranged from 0.3 bar to less than 1 bar for the same VCF. For the feed with low and intermediate O&G content (Assay 1 and 2, respectively), phenols played the most relevant part with the largest contribution to osmotic pressure difference, showing the highest molar concentrations, whereas for the feed rich in O&G (Assay 3), low molecular weight non-polar hydrocarbons overcame phenols in terms of osmotic pressure contribution, due to the O&G content being about 7x as high as the feed with intermediate O&G content. The salts contribution (in terms of sodium chloride) ended up playing a minor role in the osmotic pressure difference, due to the original wastewater being poor in salts with average salinity concentrations of 113mg.L^{-1} leading to nevertheless low molar concentrations. The low TDS and conductivity values of all wastewater samples fed to the filtration system also supports the lack of salinity of the feed. In all scenarios, however, it can be highlighted that compared to the transmembrane pressure, the total osmotic pressures of the experiments are negligible, suggesting that flux declines can hardly be caused by this phenomenon which usually poses challenges towards reverse osmosis performance, especially regarding overall recovery rates.

Therefore, the most likely explanation of the flux decline observed leans on membrane adsorption. It is of high importance to minimize fouling in reverse osmosis processes to achieve maximum recoveries while maintaining rejection performances, which is why designers tend to use proper modules to optimize operational conditions such as temperature, transmembrane pressure and crossflow velocity [52].

Adsorption (Ads) on the membrane is one of the contributing parameters of rejection of compounds and can be calculated as,

$$Ads\ (\%) = (1 - \frac{m_p + m_r}{m_f}) \times 100 \qquad \text{(Eq. 3.5)}$$

where m_p, m_r and m_f are the mass of a given compound in the permeate, retentate and feed, respectively, which were calculated from the concentrations and volumes of the streams at hand. Total rejections and adsorption percentages were determined for COD and phenols in Assay 2 and Assay 3 and can be seen in Figure 3.6. Phenols showed to have a relatively constant adsorption percentage (15 to 17%) regardless of the permeate flux obtained with high total rejections (96.7 to 97.5%) whereas COD values only showed adsorption (21.4%) when flux decline was observed, nevertheless presenting appealing rejections (97 to 99.4%). Since the observed flux decline presented practically no effect on phenols adsorption, it is plausible that oily matter, which greatly contributes to COD, played a relevant role in membrane adsorption as the feed rich in oil and grease led to flux decline.

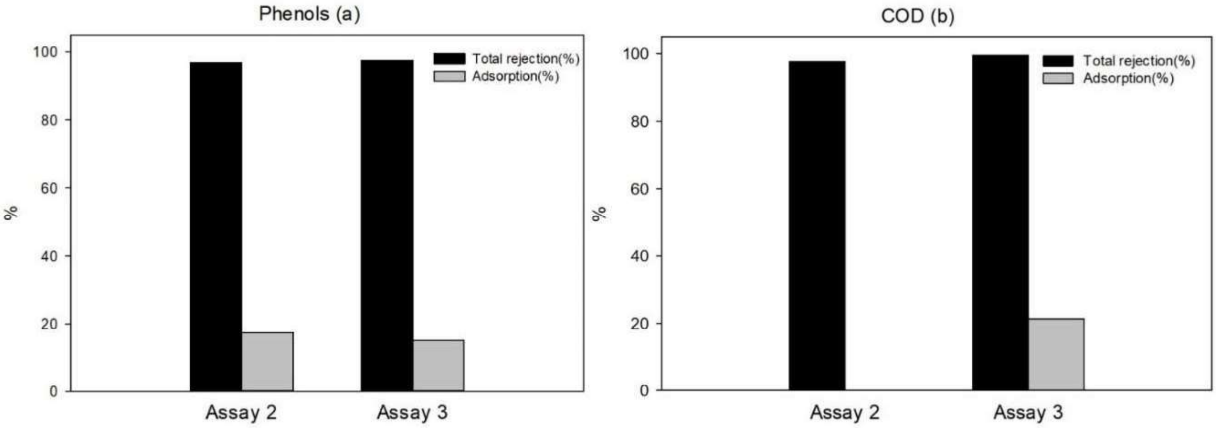

Figure 3.6 Percentages of total rejection and adsorption determined in Assay 2 and Assay 3 for phenols (a) and COD (b)

For filtration assays with low O&G content, membrane rinsing with hot deionized water (35 – 45 °C) for 30 min sufficed to recover hydraulic permeability. A cleaning-in-place protocol (CIP) with P3-Ultrasil 75 (2%) for 1h followed by 30min rinsing with water recovered hydraulic permeability for a heavier load of oily matter in the feed.

Overall, it is to be highlighted that the specific wastewater studied possesses promising advantages regarding its pyshico-chemical characteristics, in that its salinity is negligible and therefore osmotic pressure is extremely low compared to the transmembrane pressure applied. This shows that from a process point of view, reverse osmosis could be applied efficiently at high recoveries with fewer stages, lowering capital costs associated with membrane modules used. However, a balanced trade-off should be considered between the need of a RO pre-treatment for cases in which flux decline caused by hydrocarbon membrane adsorption might show damaging consequences to the membrane and the simple adjustment and process optimization of the fluid dynamics involved, namely cross-flow velocity, temperature and working at controlled permeate flux. Sour water is always sent to a flash drum and fed to a Feed Stabilization Tank before entering the stripping unit so that the residence time of the sour water is increased for longer mixing and homogenization of the feed composition and for further removal of hydrocarbons. Therefore, O&G content remained low in the stripped phenolic sour water in the Sines Refinery with concentrations ranging from 0 – 155 ppm with an average concentration of 22 ppm in 2017.

Nevertheless, a combination of monitoring the RO performance and monitoring the O&G content of the wastewater fed to the treatment system could lead to promising results when operational upsets arise. Careful monitoring could therefore be coupled to a ceramic ultrafiltration (UF) membrane system for such cases and that have been reported to have had 99.8% rejection of non-polar hydrocarbons in refinery wastewater treatment [53].

3.5 Permeate characterization and water reuse

As referred, no flux decline observed led to any significant rejection loss of the organic matter within the wastewater. Therefore, final permeates characteristics for all experiments were compared to the water quality requirements for cooling systems for water reuse as well as a sample of the make-up water from the Sines Refinery cooling tower. The analytical data and permeates and wastewaters and presented in Table 3.5. It can be seen that all COD values fit the water quality standards for water reuse as well as pH values. TDS and conductivity values were well below the Sines Refinery cooling tower make-up water and quality standards which show that they are fit for reuse as such referred parameters are usually controlled due to being correlated with salinity, which in turn are correlated with corrosion rates.

Table 3.5 Analytical data for feed and permeate characterization from cross-flow filtration studies and water reuse quality standards

Parameter	Assay 1		Assay 2		Assay 3		Water reuse quality standards [51]	Sines Refinery cooling tower
	Feed	Permeate	Feed	Permeate	Feed	Permeate	Cooling water	Make-up water
pH	8.83	6.61	10.41	7.79	9.35	6.84	6.5 – 9.0	7.81
Conductivity (μS.cm^{-1})	222	7.77	335	109.1	86.3	8.82	[a]	1095
TDS (ppm)	71	3.77	101	54.63	46	4.59	500	548
Turbidity (NTU)	-	2.21	14.5	1.18	16.8	1.02		1.76
COD (mgO$_2$/L)	857	29.5	1577	54.7	1605	9.5	75	5.34
TOC (ppm)	273.3	8.48	664.7	13.3	399.4	3.72		
Phenols (ppm)	160	4.4	184	6	128	3.2		
Total O&G (ppm)	4	< LOQ	98	< 1	771	< LOQ		
Ammonia (ppm)	13.62	0.58	37.84	9.45	9.47	0.65	[a]	
Phosphates (ppm)	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	[a]	

[a] Accepted as received

3.6 Conclusions

In the present study, a specific refinery effluent with a rich phenolic content, stripped phenolic sour water, was processed through a nanofiltration membrane as a wastewater treatment. Low COD rejections after using a Desal DK NF membrane led to observation that nanofiltration was not suitable for an efficient treatment by retention of the most abundant organic contaminant, phenols. Therefore, two reverse osmosis membranes, BW30 and SW30 were tested without any pre-treatment, in which the latter showed appealing overall rejections of COD (up to 99%) and phenols (up to 98%) when being processed in a cross-flow filtration mode. Three different wastewater samples were processed over a representative operational period, two of which experienced no flux decline up to a concentration factor of 3. Flux decline due to hydrocarbon and phenolic adsorption was observed in the case where O&G content in feed exceeded regular values. No loss of rejection, however, was observed in any of the cross-flow experiments and all permeates characterized were within the water quality standards for water reuse in cooling systems. The minor osmotic pressures (less than 2.5 bar at a concentration factor of 3) due to poor salinity of the wastewater show potential advantages of using reverse osmosis with appealing performances and high recoveries. Careful monitoring and fluid dynamics control should be considered to minimize flux decline whenever operational upsets arise in order to protect the lifetime of the reverse osmosis plant.

Acknowledgments

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CHAPTER 4

A CORROSION EVALUATION OF MILD CARBON STEEL IN RECLAIMED REFINERY STRIPPED SOUR WATER

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4.1 State of the art

Reclaiming water for cooling systems in oil refineries has been strongly encouraged over the past years for decreasing the large consumption of fresh water, thus contributing to the efficient use of this valuable resource. In a recent study [Journal of Environmental Management 261 (2020) 110229], some of the authors studied the retention of phenols in refinery wastewater through reverse osmosis (RO) and found rejections of up to 98% of phenols and 99% of both chemical oxygen demand (COD) and total organic carbon (TOC). The permeates complied with the quality standards for make-up water in cooling processes. A missing aspect, important for the water to be used in the oil and gas industry, was the level of corrosivity of the new permeates. In this work the corrosion of mild carbon steel in the permeates and in the original cooling tower make-up water was studied by electrochemical techniques. The corrosion rate of steel in the permeates in aerated conditions was lower (between 0.053 ± 0.006 and 0.123 ± 0.011 mm year^{-1}) than in the make-up water (0.167 ± 0.030 mm year^{-1}), confirming their suitability for replacing make-up water in the cooling towers. The low corrosion of carbon steel was attributed to the low conductivity and absence of oxidizing species in the fluids, compared to fresh water.

4.2 Introduction

Oil refineries are known examples of water-intensive industries, as they rely on the ready availability of large quantities of water. As water demand in these industries is constant all year-round, compared to other activities such as agricultural irrigation, opportunities arise for reclaiming water to mitigate the necessity of fresh water, thus reducing costs and lowering the environmental impact. For the past two decades industries have been subjected to environmental and legislative pressures regarding wastewater discharges, by setting a long-term goal of completely abolishing waste discharges to natural water bodies, a concept known as zero liquid discharge (ZLD) [51]. The challenges associated with ZLD goals, together with the high costs of water and effluent discharge, have stimulated the reuse of wastewater. New environmental and economically viable options and internal water recycling practices are been gradually adopted [54]. Oil and gas industries have the potential to significantly reduce the load of freshwater supplies by implementing wastewater treatment and reuse technologies [55]. In petroleum refineries the volume of wastewater has been reported to be 0.4 – 1.6 times the amount of crude oil processed [2]. Cooling water is one of the largest water demanding units in the petroleum industry and a clear example where reclaimed water can be directly used if the appropriate operational conditions are achieved. Controlling the accumulation of dissolved minerals and organic compounds constitutes a major water quality problem for an appropriate cooling water system operation. Since a portion of the water evaporates during the cooling process, an increase in concentration of total dissolved solids (TDS) occurs and the addition of fresh auxiliary water (known as make-up water) is required. In order to remove higher TDS water, a blowdown is also applied. Therefore, using reclaimed water for direct use as make-up water in cooling towers appears as a viable possibility to reduce fresh water costs and overcome water depletion.

Wastewater generated from crude oil refining processes incorporates an assorted range of pollutants such as oil and grease, phenols, sulphides and ammonia. Regarding environmental impact, phenols are amongst the major hazardous compounds in industrial wastewater due to their low biodegradability, toxicity and ecological effects on the aquatic environment [11, 28] as well as remaining in the environment for long periods of time and rapidly contributing to high chemical oxygen demand (COD). The presence of a heavy organic load of phenols in refinery stripped sour water often blocks the possibility for internal reuse. Moreover, even residual amounts of sulphides and ammonia (often < 1 and < 30 ppm, respectively) [16] may pose threats to water quality regarding corrosion or biological growth if reused in cooling processes. Therefore, a treatment technology that allows the retention of these pollutants, while generating water for direct reclamation, is required for the internal reuse of stripped sour water.

Among the technologies for phenol removal from wastewaters that have been reviewed over the past few years [11, 28], membrane separation technologies have been given particular attention due to low energy consumption, low operating cost, and easy scale up by membrane modules. Reverse Osmosis (RO), for instance, has been widely used at water reclamation plants where high purity water is indispensable, such as in boiler feedwater systems, with some systems designed to remove 99% of the dissolved minerals and provide high-quality water to the boiler [56]. Reverse osmosis processes have also been recently studied as stand-alone proposals [57] in water treatment processes, avoiding capital costs associated with pre-treatment steps, if the appropriate conditions are met.

In a recent study [58] membrane filtration through RO was applied over a 6-month period to the stripped sour water from the cracking complex of the largest Portuguese oil refinery, located in Sines. The resulting permeates showed a reduction of up to 98% of phenolic content and 99% of both chemical oxygen demand (COD) and total organic carbon (TOC) from the original wastewater, therefore, chemically complying with the water reuse quality standards for cooling processes. However, a complete wastewater reclamation study should involve not only the compliance of chemical and physical parameters to the standards, but also the corrosivity of the fluid towards the materials it will contact in future reuse [59, 60]. Corrosion is, in fact, a problem in our metals based society, with costs ranging 3–5% of gross domestic product (GDP) every year in each country [61, 62]. Preventing corrosion, as well as scaling and biological fouling are key aspects in cooling systems, and a requisite for any new technology for reclaiming water [51]. The presence in the reclaimed water of aggressive ions such as chlorides, sulphides and sulphates facilitate the corrosion process either uniform or localized, such as pitting, crevice or stress corrosion cracking, depending on water parameters like pH, conductivity, alkalinity and dissolved oxygen.

The present work complements the previous membrane filtration wastewater treatment performance [58] by comparing the corrosion of the carbon steel used in the cooling towers of the Sines refinery when immersed in the RO permeates or in the original fresh make-up water, therefore providing a complete evaluation of the wastewater reclamation at the oil refinery. The crude oils processed in the refinery can vary significantly and so varies the composition of the wastewater. However, the studied RO filtration process was able to produce permeates with close compositions, despite the variations in the feed wastewater. In any case, for this work three permeates were collected over a 6-month period, from winter to spring, in such a way that they could fully comprehend the limits of the wastewater composition oscillations that were registered during 2 years of refinery operation and wastewater sampling and characterization. Hence, it was possible to warrant the representativeness of the permeate solutions used for the corrosion testing

4.3 Materials and methods

4.3.1 Refinery wastewater, make-up water and chemical analyses

Refinery wastewater samples were directly withdrawn from the effluent of the sour water stripping unit of the cracking complex at the Sines refinery. Samples from the initial wastewater and permeates obtained after reverse osmosis were analysed by standard methods for oil and grease and phenols concentration (SMEWW 5520 C/F and SMEWW 5530D, respectively). Chemical oxygen demand (COD) was analysed by the LCI 500 cuvette kit (Hach Lange, GmbH, Germany) in agreement with ISO 15705 and total organic carbon (TOC) was determined through a total carbon analyser TOC-VCSH (Shimadzu, Japan). Ammonia and phosphates content were measured by a San^{++} Continuous Flow Analyzer (Skalar, The Netherlands). Turbidity values were acquired through a portable turbidity meter (Hanna Instruments, USA). Total dissolved solids (TDS), pH and conductivity measurements were obtained with Mettler Toledo Seven Multi Equipment with Inlab Expert Pro and Inlab 731 electrodes. A sample of make-up water (MW) was collected from the refinery cooling tower and was analysed in terms of pH, TDS, conductivity, turbidity and COD through the methods referred above.

4.3.2 Corrosion measurements

The corrosivity of the original refinery make-up water (MW) and of the permeates P1, P2 and P3 towards mild carbon steel was assessed by electrochemical methods. In addition, to simulate the case where the cooling fluid is a mixture of the reclaimed water and MW, each permeate P1, P2 and P3, was mixed with MW in a 50/50 (wt%) proportion, giving origin to mixtures Mix 1, Mix 2 and Mix 3.

Mild carbon steel pieces of 1x1 cm^2 were electrically connected to copper wire and embedded in epoxy resin. The surface of the mounts was abraded with SiC paper down to 1200 grit, rinsed in distilled water, followed by ethanol. The measurements were performed with a PGSTAT302N Potentiostat (Autolab Metrohm), in electrochemical cells with a three-electrode arrangement, consisting of the working electrode (resin mounted steel sample), a platinum counter electrode and a saturated calomel electrode (SCE) as reference. Polarization curves were measured after 1 hour of immersion either in aerated conditions or after bubbling with argon for 30 minutes to remove dissolved oxygen. Independent anodic and cathodic sweeps were obtained with a scan rate of 1 mV s^{-1}. Four replicate measurements were acquired for each condition.

4.4 Results and discussion

4.4.1 Reverse osmosis tests and permeates characterization

The analytical data obtained for the wastewater samples, as well as the final permeates, are presented in Table 3.5 and compared against quality standards for reused water and with the make-up water from the Sines Refinery cooling tower. All permeates are in line with the quality standards for water reuse, regarding the most relevant parameters in water quality management, including pH, conductivity and TDS. The COD values are below the specifications, which leads to the assumption that the remaining vestigial organic matter will not compromise water quality upon reuse. Moreover, scaling or biofouling phenomena are not likely to occur, due to lack of salts or nutrients for microbial growth, such as phosphate-based compounds. Evidently, the make-up water also lies within the water quality standards regarding all parameters studied, since the facility resorts to fresh industrial water for cooling processes.

4.4.2 Corrosion tests

Since the RO permeates complied with the specifications for reuse as make-up water in cooling towers, a corrosion evaluation was performed to verify their compatibility with the carbon steel used in the cooling towers. The make-up water currently in use was also tested and served as control.

Figure 4.1 presents polarization curves measured after 1 hour of immersion. The cathodic sweeps (Figure 4 a) reveal the response of species in the environment that can promote the oxidation of steel. The reduction of dissolved oxygen dominates the curves from the corrosion potential (E_{corr}) down to about -0.9 V_{SCE} and then the reduction of water becomes dominant for more negative potentials. The distinct shapes of these two regions are more evident in the curve of MW. The anodic sweeps show the current of steel oxidation as the potential gets more positive than E_{corr}. The current is smaller in the permeates than in the MW reference. This is an indication of a lower corrosion rate of the steel when exposed to the new permeate waters.

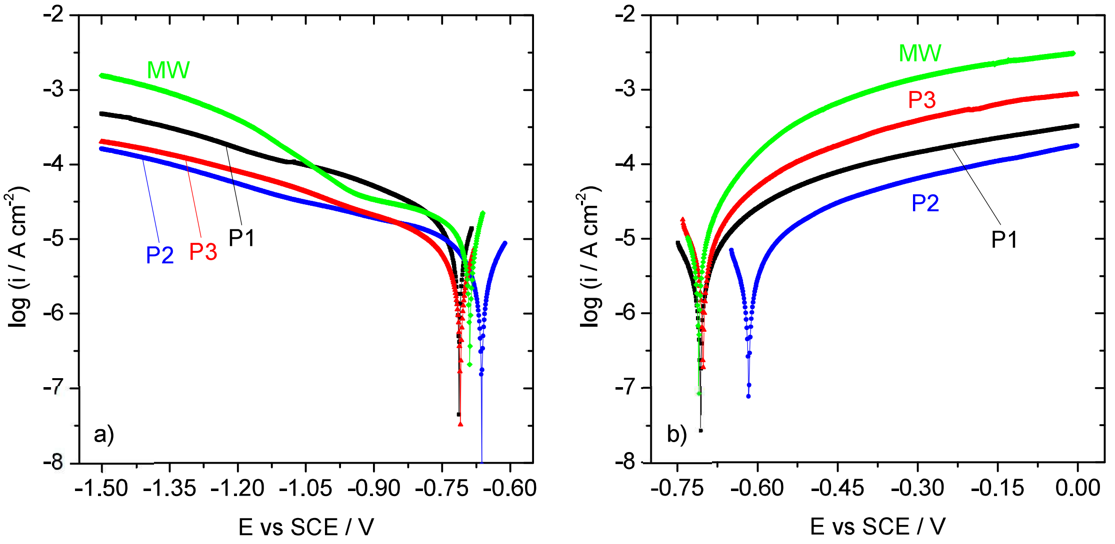

Figure 4.1 a) cathodic and b) anodic polarization curves of carbon steel after 1 hour of immersion in make-up water (MW) and permeates P1, P2 and P3.

Quantitative values could have been obtained by the Tafel extrapolation method, but the abnormal inclination of the curves (due to the ohmic drop in solution resulting from the low conductivity of the tested waters) would lead to an erroneous estimation of the corrosion rates. Consequently, the polarization resistance method was preferred because it just needs a small polarization around E_{corr} and the involved currents are very small (in the μA cm^{-2} range) leading to a much more reduced ohmic drop in solution. The experimental plots are shown in Figure 4.2 where, for a better comparison of the different curves, the potential axes depict overpotentials ($\eta = E_{applied} - E_{corr}$) instead of E_{corr}. Mixtures of the permeates P1, P2 and P3, with MW in a 50/50 (wt%) proportion were also tested to simulate the case where the cooling fluid is a mixture of the reclaimed water and MW. The mixtures of permeates and make-up water were prepared and studied considering that treating the phenolic stripped sour water using reverse osmosis on an industrial scale would generate a permeate flow rate that would meet about half of the make-up water demand of one of the refinery cooling towers. Therefore, a study of the corrosion evaluation using the prepared mixtures was considered relevant for a realistic assessment of the final water to be reused for the cooling tower.

Tests with the permeates and MW were repeated in deaerated conditions (after bubbling argon for 30 minutes) in order to determine whether oxidant species, other than oxygen from the air, exist in the samples that could cause corrosion to the steel. Notice the fivefold decrease in the current scale units.

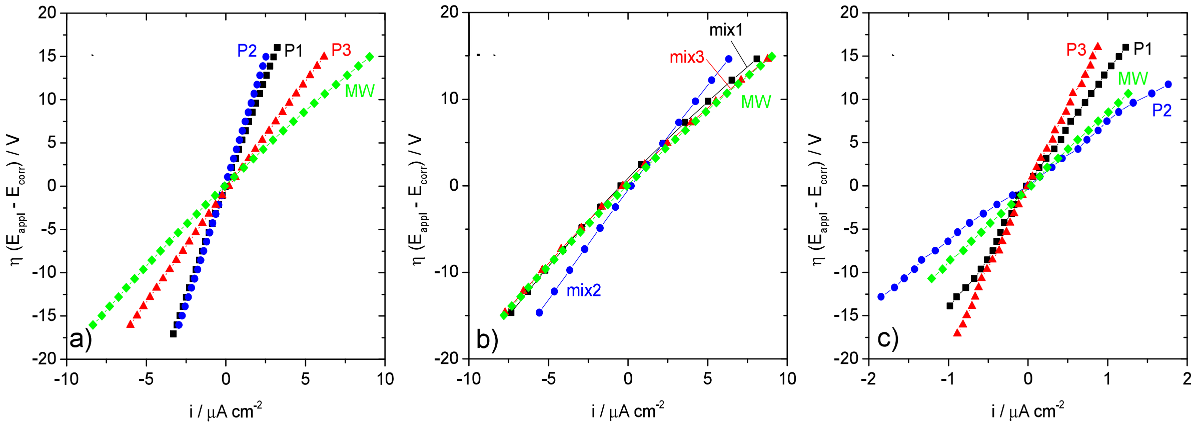

Figure 4.2 Polarization resistance plots of steel after 1 hour of immersion in: a) MW, P1, P2 and P3; b) mixes of MW with P1, P2 and P3 in a 50:50 (vol%) proportion; c) MW, P1, P2 and P3 in deaerated conditions

The polarization resistance values ($R_p = \Delta E_{appl} / \Delta i$) are presented in Table 2 and Table 3. The corrosion current (i_{corr}) can be calculated from the R_p values using the Stern-Geary equation, (Equation 4.1) [63],

$$i_{corr} = \frac{B}{R_p}\ , \quad B = \frac{\beta_a \beta_c}{2.3\ (\beta_a + \beta_c)} \qquad \text{(Eq. 4.1)}$$

where β_a and β_c are the Tafel constants of the anodic and cathodic reactions, respectively. Since the curves in Figure 1 are strongly affected by the ohmic drop in solution, the slopes of the Tafel lines are unreliable and, in this case, it is advisable to use a value of B = 26 mV [64]. This procedure is commonly adopted when the electro-kinetics parameters are unknown and is based on the fact that most Tafel slopes lie within well-defined limits [64]. Using mean values for β_a and β_c gives B = 26 mV which yields corrosion rates differing by no more than a factor of 3 from the actual rates, when applied in equation (1) [64]. More importantly, since the metal and solutions are similar, the reactions are the same and so are the kinetic parameters. Hence, the error in using an approximate value of B will be the same for all systems and will not affect their relative rates. The corrosion rate in the form of corrosion current can be presented in the units of mass loss per unit time per unit area after applying the Faraday laws of electrolysis (Equation 4.2),

$$\frac{m}{A\,t} = \frac{M}{n\,F} i_{corr} \qquad \text{(Eq 4.2)}$$

where m is the mass loss during time t in a surface area A, M is the molar mass of iron, n is 2 (for the reaction $Fe \rightarrow Fe^{2+} + 2e^-$), F is the Faraday constant (96485 C mol^{-1}) and i_{corr} is the corrosion current determined before. The direct application of equation (7) gives the mass loss per second in 1 cm^2. Dividing by the iron density gives the corrosion rate in the form of thickness reduction. The corrosion rates in the three different units are presented in Table 4.1 and Table 4.2.

The corrosion rates were higher for the MW than for the permeates which confirms that the RO process yields water with less corrosivity. The reason is attributed to the lower conductivity of the permeates resulting from the purification process. The higher resistive medium increases the global resistance of the corrosion cell and decreases the corrosion current by introducing a fraction of resistance control to the polarization [65]. Hilbert et.al. has discussed the importance of low conductivity water for the low corrosion of carbon steel piping in district heating systems [66]. Lee et al. compared the effects of tap water and reclaimed water on the corrosion of the inner surface of pipes and observed that the reclaimed water with higher ionic content showed higher corrosion rate than tap water [60]. As the permeates are mixed with MW the conductivity increases and the corrosion rates become closer to that of the original MW. Another important result is that upon removing the dissolved oxygen the corrosion rate decreases substantially, a fact expected because no noticeable evidences of corrosion are observed with the MW in use today in the Sines refinery. Being a closed system, no substantial oxygen is in the fluid to feed the corrosion of steel. The importance of oxygen in the corrosion of steel cannot be overstated. An investigation of the effect of dissolved oxygen (DO) on internal corrosion of water pipes reported that a reduction of DO concentration from 9 ± 0.5 mg/L to 2 ± 0.5 mg/L leads to a 75% decrease of the corrosion rate of carbon steel (from 133 to 32 mg cm^{-2} y^{-1}) and concluded that DO could be used as a major parameter in controlling the corrosion of water pipes [67]. In another study, steel coupons after 1 day immersed in aerated and deaerated synthetic RO platform water (215 ppm Cl^-, 18 ppm SO_4^{2-}, 148 ppm Na^+, pH=5.65, conductivity = 766 µS cm^{-1}) were corroding at 200 µm y^{-1} (with oxygen), while in the same solution deaerated with ultra-high purity nitrogen (99.999%) the corrosion rate was only 5 µm y^{-1}, 40x slower [68]. It is also noticeable that, with the exception of oxygen from the air, no oxidant agents are present in the permeates that could cause significant damage, as their corrosion rates also greatly decreased and showed a response similar to MW, upon removal of oxygen. These results show that the trace contaminants remaining in the permeates have negligible effect on the corrosion of steel. It is important to restate that the permeates used in this study represent effluents from RO purification of the most compositionally diverse wastewaters produced in a two-year period in the refinery operation and wastewater sampling and characterization.

As a final conclusion of these experiments, the corrosion of steel in contact with the permeates was lower than the MW, confirming the suitability and safe use of the permeates in the cooling system of the refinery.

Table 4.1 Corrosion potential, polarization resistance and corrosion rates for electrochemical experiments exposed to air

			Corrosion rates		
	E_{corr} **/ V *vs.* *SCE***	R_p **/ Ω.cm^2**	i_{corr} **/ A.cm^{-2}**	**Mass loss /mg.cm^{-2}. yr^{-1}**	**Thickness reduction / mm. yr^{-1}**
Make-up water (MW) (control)	-0.677 ± 0.043	1802 ± 235	14.4 ± 2.6	131.3 ± 23.4	0.167 ± 0.030
Permeate 1 (P1)	-0.670 ± 0.036	4927 ± 650	5.28 ± 0.70	48.0 ± 6.3	0.061 ± 0.008
Permeate 2 (P2)	-0.610 ± 0.043	5662 ± 812	4.59 ± 0.66	41.8 ± 6.0	0.053 ± 0.008
Permeate 3 (P3)	-0.661 ± 0.051	2453 ± 211	10.6 ± 0.90	96.5 ± 8.3	0.123 ± 0.011
Mix 1	-0.719 ± 0.033	2388 ± 722	11.7 ± 3.5	106.6 ± 31.9	0.135 ± 0.040
Mix 2	-0.637 ± 0.039	2441 ± 245	10.7 ± 1.1	96.9 ± 9.7	0.123 ± 0.012
Mix 3	-0.734 ± 0.036	1880 ± 263	14.0 ± 1.9	127.9 ± 17.0	0.162 ± 0.021

Table 4.2 Corrosion potential, polarization resistance and corrosion rates for electrochemical experiments under argon

			Corrosion rates		
	E_{corr} **/ V *vs.* *SCE***	R_p **/ Ω.cm^2**	i_{corr} **/ A.cm^{-2}**	**Mass loss /mg.cm^{-2}. yr^{-1}**	**Thickness reduction / mm. yr^{-1}**

Make-up water (MW) (control)	-0.778 ± 0.032	22392 ± 4980	1.16 ± 0.26	10.61 ± 2.36	0.0135 ± 0.0030
Permeate 1 (P1)	-0.734 ± 0.044	35477 ± 6829	0.73 ± 0.14	6.70 ± 1.29	0.0085 ± 0.0016
Permeate 2 (P2)	-0.727 ± 0.039	42387 ± 10370	0.61 ± 0.15	5.60 ± 1.37	0.0071 ± 0.0017
Permeate 3 (P3)	-0.759 ± 0.041	30218 ± 6101	0.86 ± 0.17	7.86 ± 1.59	0.0108 ± 0.0022

4.4 Conclusions

This study evaluated the corrosion of mild carbon steel in the permeates from the reverse osmosis filtration of stripped phenolic sour water to determine the feasibility of their use as make-up water in cooling towers. The corrosion of steel in the permeates was compared against the corrosion of steel in fresh industrial water used daily at the refinery. The linear polarization resistance method showed that, in aerated conditions, the corrosion rate of steel in the permeates varied between 0.053 ± 0.006 and 0.123 ± 0.011 mm y^{-1} while 0.167 ± 0.030 mm y^{-1} was obtained for the make-up water. These rates are largely controlled by the low conductivity of the permeates and the absence of oxidizing species in the fluids, apart from oxygen. The lower corrosion rate found in all permeates confirms their adequacy and safe use in the cooling system of the refinery. These findings, together with the chemical composition of the permeates compared with the feed water and the make-up water, lead to the final conclusion that reverse osmosis showed to be a suitable stand-alone technology for generating water from phenolic refinery wastewater for direct use as make-up water in cooling towers.

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CHAPTER 5

PILOT SCALE REVERSE OSMOSIS REFINERY WASTEWATER TREATMENT – A TECHNO-ECONOMICAL AND SUSTAINABILITY ASSESSMENT

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5.1 State of the art

Technologies for wastewater reclamation and water reuse within oil refineries have been gaining particular attention over the past decade due to legislative pressures associated with the efficient use of water resources and wastewater discharge. Having to constantly rely on access to great amounts of water, the oil and gas industry has been seeking opportunities to reclaim water using sustainable and efficient management procedures. In the present study, an on-site pilot plant treatment study on real refinery stripped sour water using reverse osmosis was conducted with the goal of removing the main pollutant blocking the possibility for water reuse in the refinery cooling tower, phenols. A technical and energy evaluation was performed where 90% of the initial wastewater was recovered without loss of permeate quality with 98% rejection of phenols. The installation of an Energy Recovery Device with the reverse osmosis plant could drop the energy input demand to 1.2kWh/m^3, allowing the operating costs to decrease from 1.37€/m^3 to 0.41€/m^3. Treatment on an industrial scale would allow the refinery to save up to about 375 000 m^3/year in water and up to approximately 417 000 m^3/year in wastewater volume discharged, translating into net savings of up to 286 000€/year and a payback period of down to 4 years. The current treatment proposed showed low carbon footprint and negligible waste generation, based on green metric tools, however careful consideration should be taken in the management and treatment of the concentrate stream.

5.2 Introduction

Oil refinery effluents are aqueous forms of waste generated from crude oil refining processes. Being composed of a diverse range of toxic compounds, such as oil and grease, phenols, sulphides and ammonia, such forms of wastewater are a major source of aquatic pollution [2, 4]. Moreover, oil refineries are considered a highly water demanding industry, relying on a constant amount of industrial water throughout the year. Therefore, environmental regulations, as well as strict wastewater discharge limits have encouraged many industries to adopt efficient strategies for effluent treatment and water reuse, aiming at the minimization of environmental impact. A promising opportunity for water reclamation aims at reusing water for cooling towers, since they are among the largest water demanding units in the petroleum industry. Legislative pressures to go the extra mile have even involved a long-term goal of total abolishment of any form of waste discharge to water receiving bodies through a concept described as zero liquid discharge (ZLD) [51].

Among the several pollutants that are controlled in the wastewater generated at the largest Portuguese oil refinery, located in Sines, phenols have recently been given more attention. The presence of a heavy organic load of phenolic compounds at its major source of origin in the refinery, stripped sour water from the cracking complex, is currently blocking the opportunity for water reuse in the cooling towers, and limits its use as wash water for desalters, to minimize phenolic impact in the refinery's pre-treatment wastewater circuit. Phenols play a key role in environmental impact, being among the major hazardous pollutants in industrial wastewater resulting from their poor biodegradability, high toxicity and significant contribution to high chemical oxygen demands [5, 11, 28]. Phenols have been reported in refinery wastewater in a wide range of concentrations (6-500 mg/L) [28] and specifically in stripped sour water (190-537 ppm) from cracking complexes [21-23]. Most refineries reuse stripped sour water as wash water for desalters, using a well-known and reported procedure, [22] where most of the phenols are adsorbed into the crude phase, redirecting them back into the refining process, and thus, lowering its content in the wastewater. Although this form of reuse has proved to be a straightforward, cost-effective and relatively efficient way of overcoming phenolic impact in the effluent, it doesn't take into account possible fluctuations in the type or amount of phenols that are formed in catalytic cracking processes and that are not removed in sour water stripping units [18, 24]. Moreover, desalter effluent treatment for recycling involves challenges on its own already, with its general approach focusing more on de-oiling and de-mineralizing [69, 70].

Many technologies have been reviewed for phenol removal from different types of wastewater over the past few years [11, 28, 33, 71]. Membrane separation technologies have been highlighted due to low energy consumption, and easy scale up by membrane modules, leading to convenient operation procedures [72, 73]. Reverse Osmosis (RO), for example, has been frequently used at water reclamation plants for cases where high purity water is required, such as in boiler feedwater systems, reported to remove 99% of the dissolved minerals [56] and up to 95% phenols from wastewater [29, 30]. RO has also been recently studied for water reuse in coal seam gas associated water, focusing on the improvement of the economics involved [74]. Despite the advances in improving pump efficiencies and energy costs, high energy demand remains a drawback in RO processes, with electricity accounting for at least 35% of the total operating costs in seawater desalination systems [75]. Therefore, determining the energy consumed in any RO treatment, is of major importance, including refinery wastewater treatment, to ensure a proper insight regarding its economic feasibility.

The last published study of refinery stripped sour treatment through RO focused on the removal of a particularly relevant pollutant at the refinery at hand, selenium, with some pre-treatment steps being involved [23]. The present study focuses on the removal of phenols, pollutant which has been behind the reason blocking the reuse of stripped sour water within refineries that contain catalytic cracking complexes, the main emitter of phenols. A technical and energy evaluation was performed for on-site stripped sour water treatment through stand-alone RO, at pilot scale. The pilot plant results were the basis of an economic and sustainability evaluation in the projection to an industrial scale and the potential to recover energy was evaluated based on reported energy recovering methods and the specific physico-chemical nature of the effluent studied.

5.3 Materials and methods

5.3.1 Pilot scale experimental setup

To assess the technical performance of the RO membrane at pilot scale for refinery stripped sour water treatment, a membrane filtration experiment was set up as shown in Figure 5.1. The phenomena of fluid dynamics control play a major role in a spiral-wound module configuration, which match the conditions at an industrial scale. The pilot unit was equipped with a permeate and feed tank, a high-pressure diaphragm pump (Hydra-Cell, Wanner Engineering, Inc.) and a valve to regulate pressure. The pilot assays were performed in concentration mode where the concentrate stream was recirculated back to the feed tank, while permeating the treated water into a clean tank. In order to calculate the energy consumption of the pilot installation, a 324 Plus True RMS Clamp Meter (FLUKE CORPORATION) was used to measure the voltage and current during the filtration, allowing an instantaneous and accumulated measurements. The electrical readings were then converted to pump power (kW) and translated into energy consumption (kWh) considering the total duration of each assay [76]. The data obtained was used to estimate the average energy consumption in treating 1 m^3 of stripped sour water.

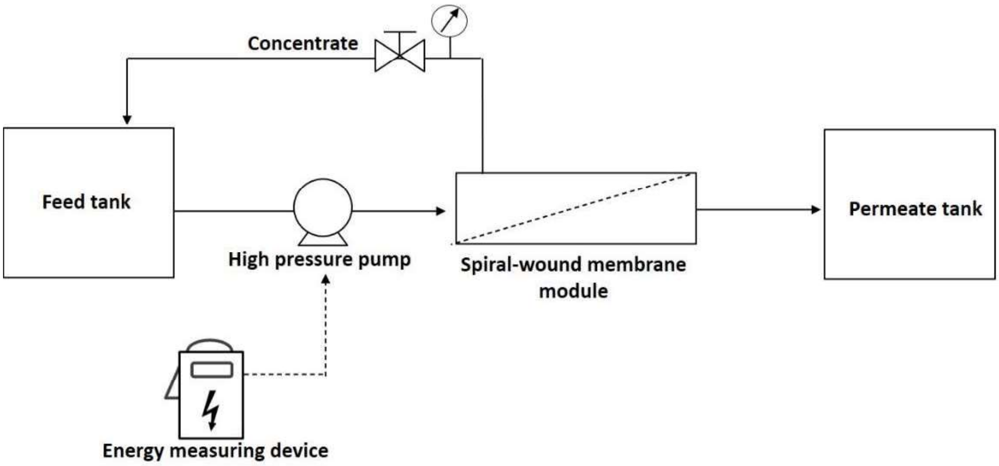

Figure 5.1 Schematic representation of the reverse osmosis pilot unit coupled to energy measuring device

5.3.2 Membrane and chemicals

A polyamide thin-film composite spiral-wound FILMTEC SW30 – 2540 Reverse Osmosis membrane element was used for the filtration assays. The membrane has an active area of 2.8 m^2, stabilized salt rejection of 99.4%, a maximum operating temperature and pressure of 45 °C and 69 bar, respectively and a pH range of 2 – 11. P3-ultrasil® 73 (Ecolab, Lenntech) was used for membrane chemical cleaning after the reverse osmosis filtration experiments. This membrane integrates the features that proved to be the most appropriate and efficient for phenol retention for the wastewater studied, as concluded from preliminary laboratory studies [58]. Although brackish water membranes may lead to higher permeate fluxes, the laboratory studies showed an 80% phenol rejection, generating permeates unsuitable to be reused, based on the water reuse quality standards.

5.3.3 Refinery wastewater and reverse osmosis pilot assays

Two batches of stripped sour water were consecutively collected from the effluent of the sour water stripping unit of the cracking complex, at the Sines refinery. While the laboratory studies [58] allowed the assessment of membrane treatment performance over a 6-month representative operational period, the pilot scale studies involved an energy consumption evaluation upon operating at different transmembrane pressures. Therefore, to avoid feed quality variations, the batches were successively withdrawn and processed for treatment.

Samples from the initial wastewater and permeates obtained after reverse osmosis were analysed by standard methods for oil and grease and phenols concentration (SMEWW 5520 C/F and

SMEWW 5530D, respectively). COD was analysed by the LCI 500 cuvette kit (Hach, Germany) in agreement with ISO 15705. Ammonium and sulphides concentration were determined using the LCK 304 and LCK 653 cuvette test, respectively (Hach, Germany). Total dissolved solids (TDS) and conductivity measurements were obtained by means of a WTW portable conductivity meter. Table 5.1 shows a physico-chemical characterization of the feed batch.

Table 5.1 Refinery wastewater characterization for pilot scale treatment

Stripped sour water characterization	
Parameter	
pH	7.2
TDS (ppm)	74
Conductivity ($\mu S.cm^{-1}$)	122.1
COD (mgO_2/L)	1179
Phenols (ppm)	257
Polar O&G (ppm)	38
Non-polar O&G (ppm)	179
Total O&G (ppm)	217
Ammonium (ppm)	23
Sulphides (ppm)	0.18

Before the experiment, the membrane was rinsed and compacted with tap water at 51 ± 1 bar for about 2h until constant permeability was achieved. The hydraulic permeability of the spiral wound reverse osmosis membrane was measured before the filtration assay at around 21 °C.

The performance of the reverse osmosis filtration was carried out by measuring the permeate flux throughout the filtration time and collecting instant permeate samples at different volume concentration factors, for chemical analysis. The wastewater was concentrated until the instantaneous permeates started to lose chemical quality regarding water reuse standards. The first and second filtration assays were performed in concentration mode at constant transmembrane pressure of 50 ± 1 bar and 35 ± 1 bar, respectively and a feed flowrate of around 420 L/h. For pilot plant studies, operation under concentration mode is a practical alternative to continuous operation with a defined recovery rate, with the advantage of requiring lower feed volumes. A volume reduction factor of 10 corresponds to a 90% permeate recovery, which is considered a rather ambitious target.

Some temperature variations occurred throughout the assays, as they were carried out outdoors. The temperature of the feed was continuously measured over time until the end of the experiment. The permeate fluxes calculated for both assays were corrected for a reference temperature of 22 °C. Apparent rejections of phenols and COD were calculated using the same equation as in the laboratory studies (Eq 3.1).

5.3.4 An economic study evaluation

An average of 50 m^3/h of stripped sour water from the cracking complex at the Sines Refinery is generated and sent as wash water to the desalters. The stream then undergoes a series of pre-treatment steps until a final accumulated effluent, averaging 350 m^3/h based on 2017-2019 data, is discharged to the external Wastewater Treatment Plant (WWTP). This means that the key-effluent of this project represents about 14% of the total wastewater discharged. Therefore, an economic evaluation which focuses on the volume reduction as well as the reduction of fresh make-up water demand for the cooling tower is essential to determine the economic feasibility of the technology proposed.

An economic evaluation of treating 1200 m^3/day (50 m^3/h, 24 h/day) of stripped sour water by reverse osmosis was performed. The calculations were based on a direct projection of the pilot plant data obtained onto an industrial RO treatment unit, considering an overall 90% recovery rate, therefore generating 1080 m^3/day of permeate. Bearing in mind that energy consumption in RO is typically the major contributor of operating costs, different scenarios were studied, extrapolating different energy demands based on the possible energy recovered through an Energy Recovery Device (ERD) and the real data obtained in the pilot plant assays. Recent studies go into detail regarding technical efficiencies of ERD in large desalination plants, from turbines to pressure exchangers which have reported yields of up to 90%, reducing specific energy consumptions down to 3 – 4 kWh/m^3 [77-79]. As electricity generally accounts for the largest portion of the operating costs of a RO plant, different energy recovery scenarios allow a sensitivity analysis regarding total operating expenses as an added insight for economic evaluation. A sensitivity analysis related to the frequency of the RO unit shutdowns for membrane cleaning and maintenance was also conducted, which allows an overview of the economic assessment for cases where changes in the refining process upstream might lead to wastewater feed variations.

Final operating and capital costs were directly compared with the savings in fresh water and the reduction of the volume discharged per year, in order to evaluate the economic feasibility of the treatment.

Finally, an environmental and sustainability assessment was conducted through analysis of relevant parameters, such as global warming potential, ecotoxicity potential and impact of water saving.

5.4 Results and discussion

Stripped sour water from the cracking complex, at the Sines refinery, is currently subjected to a sequence of pre-treatment steps, to diminish the phenolic levels before the final effluent is sent to a municipal WWTP (Wastewater Treatment Plant). Figure 5.2 shows the current route taken by the wastewater stream and an alternative route through membrane treatment, at the source of phenolic emission. Such proposed technology results from the motivation of both reducing the volume discharged to the WWTP and saving water through reclamation as make-up water in cooling towers.

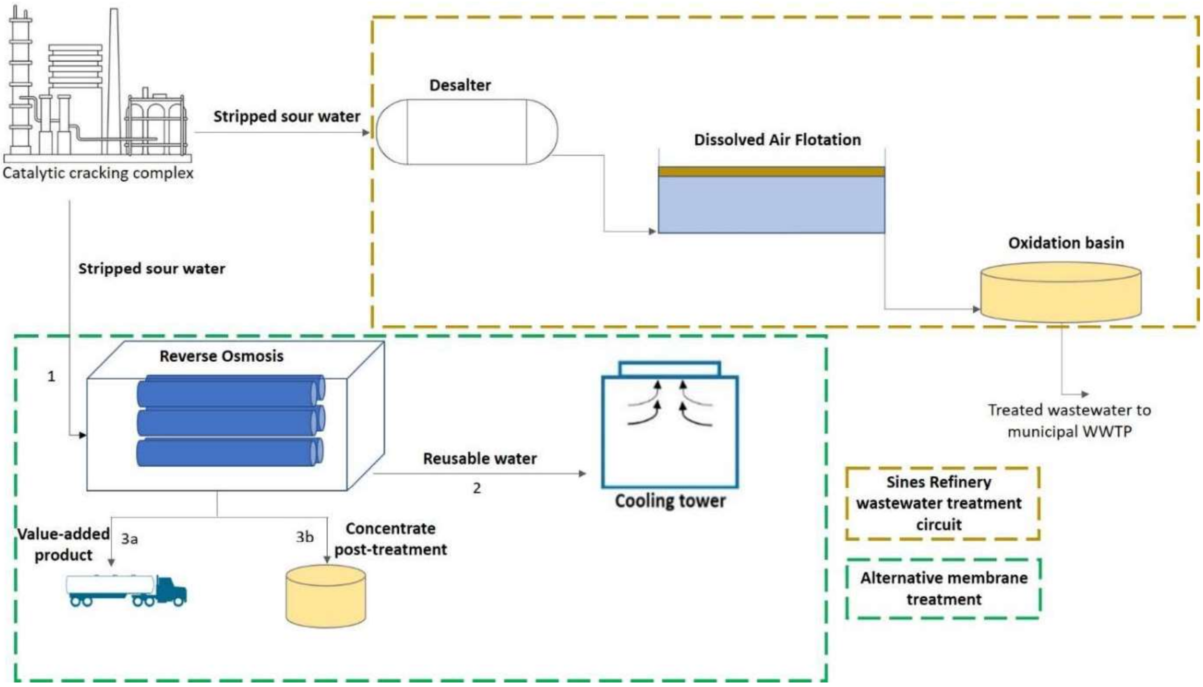

Figure 5.2 Schematic representation of wastewater route taken by stripped sour water from cracking complex at Sines refinery and alternative membrane treatment

5.4.1 Performance of pilot scale RO filtration – permeate fluxes and rejections

A first batch of 600 L of stripped sour water was processed in concentration mode, operating at the highest volume concentration factor possible. This allows a technical evaluation of the process, while avoiding the generation of a large volume of concentrate, which needs to be adequately disposed. The wastewater was processed at 50 bar until a final concentrate volume of 52 L, leading to an approximate volume concentration factor of 11.5. The second batch of 400L was identically processed, but at a transmembrane pressure of 35 bar. The final concentrate volume was approximately 95 L, reaching a volume concentration factor of 4.2.

Figure 5.3 shows the profile of the normalized permeate fluxes obtained as a function of the volume concentration factor (VCF). It is possible to observe that while operating at 35 bar, the flux decline is significantly lower throughout filtration than the permeate flux in the experiment operating at a transmembrane pressure (TMP) of 50 bar. At a VCF of 2, an approximate 20% drop from the initial flux was felt at TMP = 50 bar, whereas only a 5% drop was felt at TMP = 35 bar. This could be generally attributed to membrane fouling being less severe at milder operating pressures. Higher transmembrane pressures generate higher permeate fluxes, but also push foulants strongly towards the membrane surface, leading to a more extensive adsorption on the membrane faster and, ultimately, to flux decline throughout filtration. It can also be observed that permeate flux remained practically constant from VCF = 2 to VCF = 10, with permeate flux declines ranging from 2 to 6%. An overall flux decline of around 47% was felt, at a concentration factor of 10. This means by the time the flux had dropped by almost half, 90% of the initial feed wastewater volume had already been converted into clean permeate. This is due to the relatively high permeate fluxes encountered (up to 44 $L.h^{-1}.m^{-2}$), which has only been found to be reported in studies with a looser RO membrane and lower salt rejections, after UF treatment, in a similar phenolic industrial wastewater [30]. As was observed in previous lab studies [58] the low osmotic pressure of the feed plays the most decisive role in the high permeate flux obtained in the present pilot study, due to low conductivity resulting from the lack of salts with average reported salinities measuring down to 113 mg/L and conductivities no greater than 335 µS/cm.

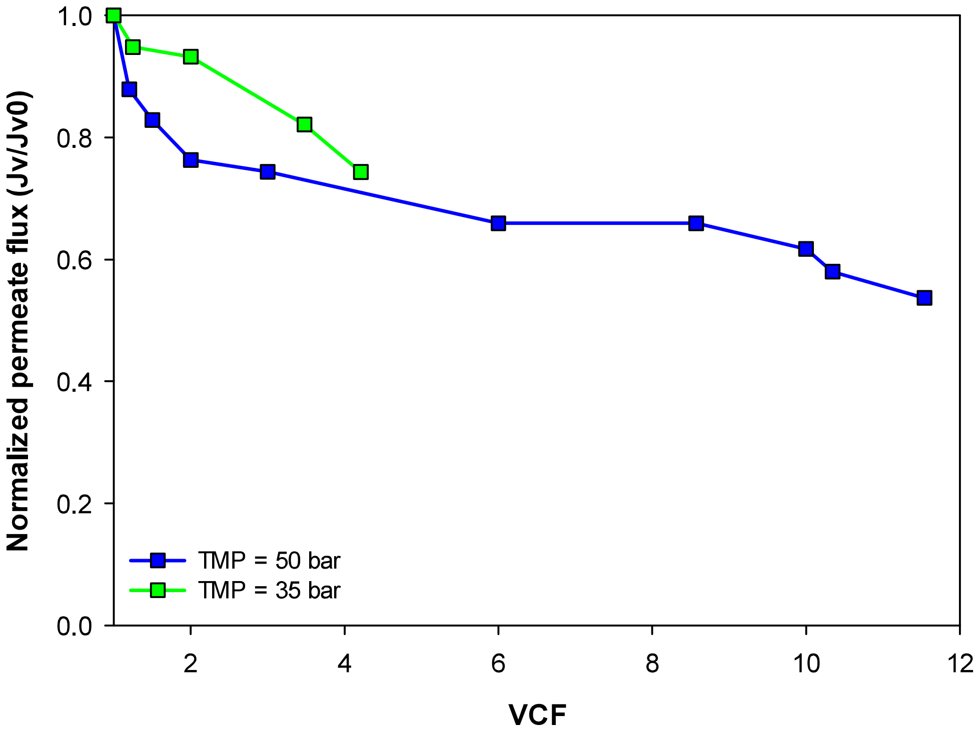

Figure 5.3 Normalized permeate fluxes at pilot scale as a function of volume concentration factor

The goal of testing the system at a transmembrane pressure of 35 bar was to evaluate the impact in energy consumption, as lower consumptions would decrease operational costs related to electricity, at an industrial scale. As previously mentioned in the Materials and Methods section, the voltages and currents were continuously measured throughout the filtration. The instantaneous and accumulated values that were recorded were actually not lower than those obtained while operating at 50 bar. Therefore, gains related to energy savings ceased to exist when operating at the lower TMP and thus, it was decided not to concentrate the wastewater any further than a VCF of 4.2, matching the total filtration times for both assays.

Figure 5.4 shows the membrane performance regarding apparent rejection of phenols and COD for both assays, along with the corresponding permeate fluxes as a function of the VCF. High rejections of phenols and COD were obtained (approximately 97.5% and 98%, respectively at a VCF of 3) with phenol rejections remaining high throughout the entire assay up to a VCF of 10 (>92%). A slight loss of rejection started to take place at a VCF of 6 (2.5% drop in rejection) and 4% drop at VCF of 10. Regarding COD, a similar behaviour was witnessed with instant rejections remaining over 94% even after 90% of the wastewater was filtered. At a VCF of 10.3, the permeate started to lose quality regarding COD values, according to the quality standards for water reuse (COD < 75 mgO_2/L) described and used as main reference in Chapter 3 and Chapter 4 shown in Table 3.5.

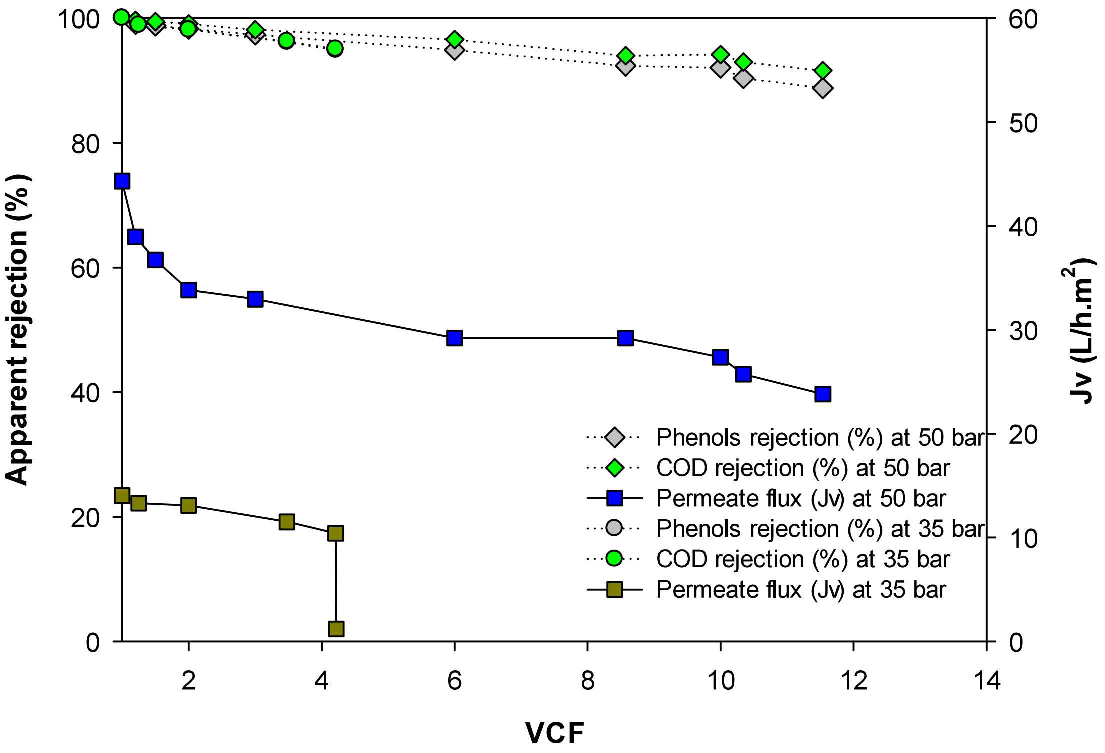

Figure 5.4 Reverse osmosis membrane performance in stripped sour water treatment at pilot scale (rejections hardly changed between assays; points are overlapped)

Table 5.2 shows the final rejection and permeate quality regarding the parameters studied for both assays, where it possible to observe the consistency in complete rejection (100%) of O&G, as was seen in the previous lab studies. The fact that almost all O&G compounds in the feed are insoluble (non-polar hydrocarbons) provides a potential advantage in a highly efficient removal of O&G, since applying a high cross flow velocity, allows the formation of a second or dynamic membrane on the surface, which maintains a reasonable flux and high rejection of phenols.

Ensuring the safe use of the final permeates arises as a decisive procedure for water reclamation in any industry, after wastewater treatment. Since cooling water plays a large role in water demand in the oil and gas industry, an opportunity emerges for water reclamation as make-up water in the refinery cooling towers, where most industries resort to fresh industrial water. Using reclaimed water for make-up water also appears as a feasible possibility, since the quality of make-water required for safe use is lower than most forms of water at refineries, such as boiler feedwater. The final permeates where therefore characterized and compared with water reuse quality standards [51] for cooling processes, showing chemical compatibility for the most relevant parameters, such as pH, TDS, conductivity and COD. The permeates should also show physical compatibility with the material in which the reclaimed water will come in contact with, to prevent corrosion phenomena in the cooling systems. The authors previously reported [80] a corrosion evaluation in mild carbon steel for permeates generated with the same wastewater treatment as the present study, with a wide range of physico-chemical qualities for water reclamation through means of electrochemical methods. The final permeates shown in Table 5.2, therefore showed chemical and physical compatibility for reclamation as make-up water in the cooling towers.

Table 5.2 Final permeate characterization of pilot assays and overall rejections

		TMP = 50 bar (VCF=11.5)		**TMP = 35 bar (VCF=4.2)**	
Parameter	**Feed**	**Final permeate**	**Overall rejection (%)**	**Final permeate**	**Overall rejection (%)**
pH	7.2	6.2		6.2	
TDS (ppm)	74	6	91.9	6	91.9
Conductivity (μS.cm^{-1})	122.1	10.9	91.1	10.9	91.1
COD (mgO$_2$/L)	1179	19.9	98.3	21	97.9
Phenols (ppm)	257	5.4	97.9	4.5	98.2
Polar O&G compounds (ppm)	38	0	100	0	100
Non-polar O&G (ppm)	179	0	100	0	100
Total O&G (ppm)	217	0	100	0	100
Ammonium	23	3.3	86	3.3	86
Sulphides	0.18	0	100	0	100

5.4.2 Hydraulic permeability and membrane cleaning

Before and after each pilot assay, the hydraulic permeability of the reverse osmosis membrane was determined on site, in order to evaluate the degree of reversible and irreversible membrane fouling, based on the permeability recovery after chemical cleaning. Figure 5.5 shows the hydraulic permeability of the membrane before and after the assay and after chemical cleaning. The initial hydraulic permeability obtained was 1.22 L.h^{-1}.m^{-2}.bar^{-1}. It can be observed that rinsing the membrane with warm tap water (30 – 35 °C) for 30 min allowed a 70% permeability recovery (0.86 L.h^{-1}.m^{-2}.bar^{-1}). Although a

30% drop in permeability is significant as far as membrane performance goes, it can be assumed that most of the fouling is reversible and can be corrected with warm water rinsing. After chemical cleaning for about 1h, almost complete permeability recovery (> 90%) was achieved.

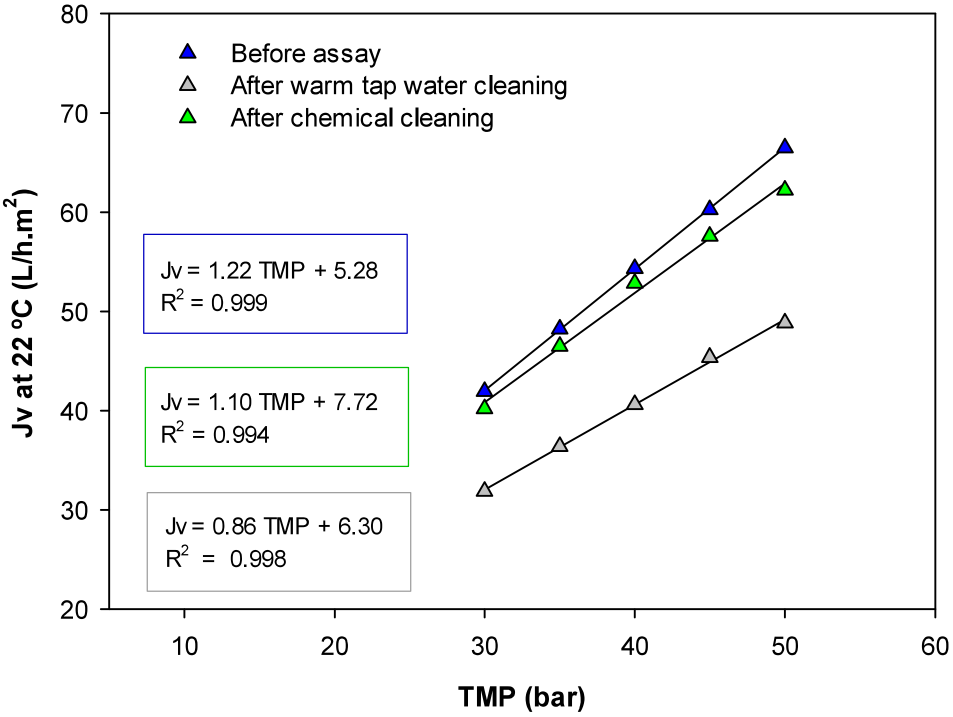

Figure 5.5 Hydraulic permeabilities of reverse osmosis membrane before and after filtration at pilot scale

5.4.3 Flux decline, fouling and the influence of O&G content in wastewater

Proper membrane protection procedures are of great importance when upscaling to an industrial wastewater treatment program resorting to reverse osmosis, in order to extend the lifetime of the membrane and allowing maximum efficiency of the treatment, regarding permeate fluxes and solute rejections. Therefore, many industries use a RO pre-treatment using microfiltration or ultrafiltration, that has the main goal of removing suspended solids from the feed before entering the RO unit.

In the present study, two experimental procedures were chosen in order to test the system to the limit. The first was working in concentration mode, in which the concentrate stream is sent back to the feed tank, increasing the volume concentration factor as much as possible, while maintaining permeate quality. The second was avoiding the use of a pre-treatment, as it was observed that throughout the years 2017 – 2019 (as seen in Chapter 2, Figure 2.10) stripped sour water remained mostly free of O&G compounds, except for a few cases in 2018. The design of the sour water stripper unit itself justifies the naturally "clean" aspect of the wastewater, due to separation of oily matter in the feed drum before entering the stripper, as previously explained in Chapter 2, Figure 2.3. A photograph of the wastewater studied in a best-case scenario and a worst-case scenario regarding the existence of suspended solids and oily matter is shown in Figure 5.6. Operating in concentration mode is most often used where the feed stream is not continuous and is low, whereas operating in continuous mode is mostly used in industrial scale membrane applications, where a concentrate stream is continuously generated [81] and not sent back into the RO unit. This allows a more constant feed quality continuously entering the RO plant.

Figure 5.6 Photograph of stripped sour water samples in a) best-case scenario and b) worst-case scenario regarding suspended solids and oily matter content

Figure 5.7 shows the normalized apparent permeate fluxes (*Jv/Jv0*) as a function of the VCF, which allows the observation of the influence of oily matter on permeate flux. The greatest flux decline took place in feed with a high O&G content (>98 ppm). For lower concentrations, the real permeabilities remain approximately constant compared to feed containing O&G greater than 98 ppm, for the same volume concentration factor (VCF = 3). Real permeabilities were calculated, already taking into account the osmotic pressure difference, which in turn was calculated using the Van't Hoff equation [48]. It was observed that the osmotic pressure difference ended playing a minor role, even at high concentration factors (5.8 bar obtained at a VCF of 11.5). Low osmotic pressures in the pilot assays were in line with the laboratory studies previously published, where the explanation of flux declines due to osmotic pressure differences was discarded [58], leading to fouling phenomena having the highest relevance to explain flux decline. Fouling due to membrane adsorption from non-polar hydrocarbons was hardly felt whenever the feed contained less than 98 ppm of O&G. As the O&G content increased in the feed, fouling was greatly felt, causing significant flux decline.

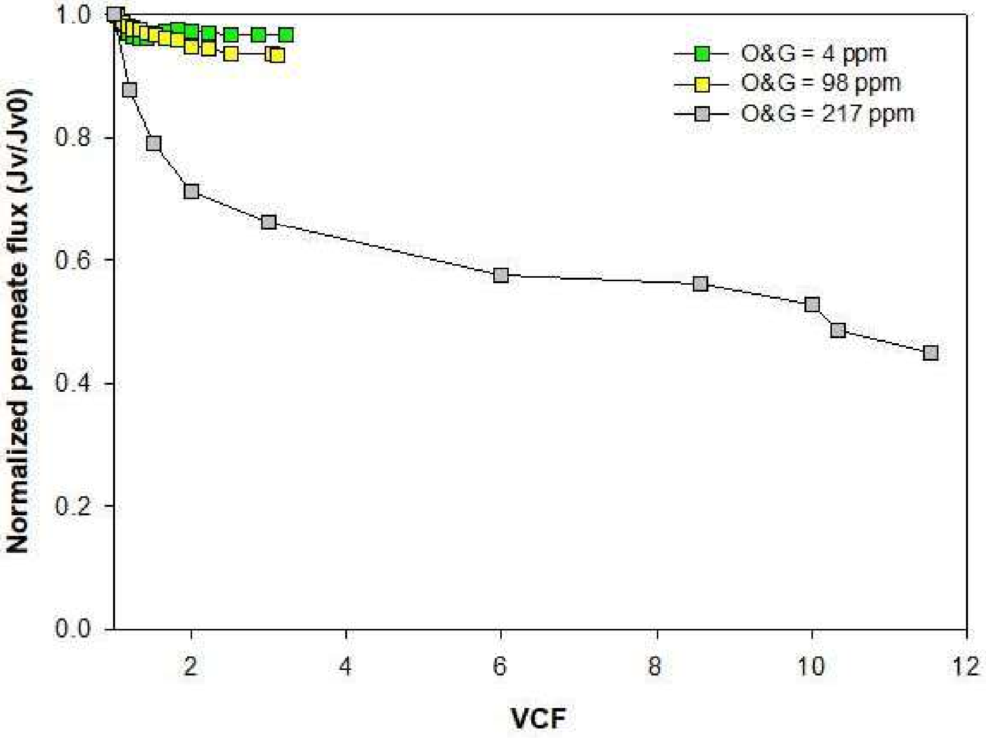

Figure 5.7 Normalized apparent permeate fluxes as a function of VCF for feed with different O&G contents.

5.4.4 *Energy consumption evaluation of RO treatment at pilot scale*

The main drawback associated with the use of reverse osmosis processes in major desalination plants resides on the frequent high energy input demand. This is mainly due to the high hydraulic pressure required to overcome the osmotic pressure of seawater feed. Although there have been advances in technologies to overcome the high energy demand, a typical RO plant still uses around 3-10 kWh of electricity to produce one cubic meter of freshwater from seawater [82].

A 324 Plus True RMS Clamp Meter (FLUKE CORPORATION) was used to measure the voltage and current during the filtration which allowed instantaneous and accumulated measurements of such parameters. The electrical readings were then converted to pump power (kW) and translated into energy consumption (kWh) considering the total duration of each assay. The data obtained was used to estimate the average energy consumption in generating 1 m^3 of clean permeate. The input power load was calculated using the following equation [76],

$$Pi = \frac{V \times I \times \cos\varphi}{1000} \qquad \text{(Eq 5.1)}$$

where Pi is the pump power in kW for three phase motors, V is the measured voltage in volts, I is the current obtained in Amp and $\cos\varphi$ represents the pump efficiency as a decimal, indicated in the pump specifications. Table 5.3 shows the results obtained for all parameters measured or calculated for both pilot assays operating in concentration mode and the final energy input required to produce 1 m^3 of clean permeate.

Table 5.3 Energy consumption evaluation at pilot scale for pilot assays

Parameter	**TMP = 50 bar**	**TMP = 35 bar**
Voltage (V)	408	408
Average I (Amp)	2.05 ± 0.02	2.58 ± 0.08
cos(φ)	0.8	0.8
Pi (kW)	1.16	1.46
Filtration time (h)	5.67	5.67
Volume concentration factor	11.5	4.2
Permeate generated (L)	548	305
Feed flowrate (L/h)	420	420
Energy consumption (kWh/m^3)	11.97	27.14

It can be observed that while operating at a transmembrane pressure of 50 bar, the pilot plant required an energy consumption that is approximately in line to that of a typical RO plant to desalinate seawater, at similar operating pressures, deviating slightly from the energy input range of 3 – 10 kWh/m^3. Operating at a transmembrane pressure of 35 bar ended up showing a lower efficiency in terms of the energy consumed to generate the same amount of permeate, which explains why the energy consumption per cubic meter of permeate was higher. Although absolute energy values over time while operating at higher pressures were indeed greater, once the amount of permeate generated due to higher fluxes was taken into account, a more energy-efficient process was witnessed while operating at 50 bar.

5.4.5 An economic study evaluation

Three scenarios were considered for an economic evaluation which allow an insight on the effect that an industrial RO installation equipped with an Energy Recovery Device (ERD) would have on energy consumption. Scenario 1 was studied using the real pilot plant data without any recovery of energy. Scenario 2 assumed a 70% drop in energy demand and was based on a conservative energy reduction assumption compared with the reductions described in the literature for a similar industrial RO desalination application, with energy recovery efficiencies reaching 90% [77-79, 83, 84]. Scenario 3 used a more optimistic 90% drop in energy consumption.

In all scenarios, the RO plant was assumed to operate 24h/day, with 1-day shutdowns occurring for membrane cleaning, maintenance, and plant start-ups every 3 weeks, giving a total of 17 shutdown days and 348 working days per year. The scenarios are presented for a volume reduction factor of 10 (similar to an overall permeate recovery rate of 90%), where larger recovery rates witnessed significant loss in permeate quality based on the pilot plant data obtained.

For a plant capacity of 1080 m^3 of permeate/day, and a constant flux of 25 $L.h^{-1}.m^{-2}$ (based on the average constant permeate flux generated in pilot assays), a total of 1800 m^2 would be required, given an active membrane area per element of 35.2 m^2. Data presented leads to 51 spiral-wound SW30HR-380 elements being therefore required for such a plant capacity.

The capital costs (CAPEX) associated were determined based on the current prices for the equipment cost of the RO plant, from feed pumps, pipelines and valves to pressure regulators and microfilter cartridges for pre-filtration, reaching values of 600€ of (all) equipment per m^2. A reported study involving the evaluation of an ERD application for the treatment of brackish water with a very similar permeate production rate estimated the capital cost of about 150 000€ for a pressure exchanger [83]. Therefore, the acquisition and installation of turbines or pressure exchangers as energy recovery devices could increase the capital costs up to 750€/m^2. Investment in membrane modules was calculated based on the price of one SW30HR-380 element, provided by the manufacturer (672€/element) and the number of modules required for the plant capacity. The cost per membrane unit area was therefore determined as 19€/m^2, which represents less than 5% of the total installation investment. Civil and engineering costs were estimated as 75% of the total elements cost, according to similar reported refinery wastewater treatment projects [53]. The total capital costs (equivalent per year) were calculated considering a lifetime span for the RO installation and membranes of 20 years and 5 years, respectively.

Total operation costs (OPEX) were determined based on energy consumption, membrane replacement, chemical cleaning, concentrate disposal, manpower and repair and maintenance. Energy costs were calculated using the electricity prices for the industry in Portugal based on the relevant annual consumption (0.0891€/kWh) [85].

Table 5.4 shows the total economic data for one year for the RO treatment for all scenarios, assuming a 1080 m^3/day plant capacity operating 348 days per year. It can be clearly seen that energy consumption is the greatest contributor of the operating costs, with energy demand alone reaching almost 80% of the total OPEX for the treatment. Therefore, mild deviations in energy consumption can be clearly felt, when comparing the direct extrapolation of the pilot plant data with the different scenarios assumed. A 90% drop in energy consumption allows a new energy demand of 1.2 kWh/m^3 permeate, leading to a decrease from 1.37 €/m^3 to 0.41 €/m^3 permeate, translating into a reduction of over 300 000€ per year in electricity alone, which showed to be in line with the benefits reported in the use of Energy Recovery Devices [83] for similar projects.

Table 5.4 Economic data per year for the reverse osmosis treatment of refinery stripped sour water

	Scenario 1 Direct extrapolation of pilot plant data (no ERD)	Scenario 2 70% energy recovery	Scenario 3 90% energy recovery
Assumptions			
Capacity (m^3/day)	1080	1080	1080
Membrane area (m^2)	1800	1800	1800
348 days/year; 24h/day			
Capital costs (CAPEX) (€/year)			
Equipment cost of RO plant with ERD (750€/m^2) (€) (including membranes and civil + engineering costs) (20-year lifetime)[a]	63181	78143	78143
Operation costs (OPEX)			
Energy (0.089€/kWh)	400741	120222	40074
Manpower (€)	48000	48000	48000
Membrane chemical cleaning (€) (every 3 weeks)	10710	10710	10710
Concentrate + washing effluent disposal (€)	47608	47608	47608
Repair and maintenance (2% of capital costs) (€)	2408	2978	2978
Membrane replacement (€) (5-year lifetime)	6873	6873	6873
Total operation costs (€/year)	516340	236391	156242
Total operation costs (€/m^3)	1.37	0.63	0.41

[a] – A depreciation over 20 years and 1% annual tax was assumed

The remainder of operation costs include manpower, considering the average monthly payment of employees in the oil and gas industry. Membrane cleaning and replacement was calculated based on the current prices of Ultrasil and its concentration used in the pilot plant assays for chemical cleaning, as well as the current quotes for new membrane modules, assuming a 5-year lifetime. Concentrate and washing effluent disposal costs were estimated based on the external WWTP fees applied to an equivalent wastewater quality and volume, whereas repair and maintenance costs were considered as 2% of the capital costs, as per a similar reported economic evaluation [48]. In order to assess the feasibility of the treatment from a strictly economic point of view, the economic data was compared with the gains that would be generated with the implementation of the project. Such gains represent savings in fresh water and reduction in volume of the final effluent discharged from the Sines Refinery to the external WWTP. The final effluent discharged is classified according to its quality, where the higher the Class, the higher the fee. Therefore, savings in wastewater reduction upon the implementation of the RO treatment are felt quicker in scenarios where the final effluent is inserted in a higher Class, due to the higher fee applied to the refinery per cubic meter. Savings in fresh water were assumed to be constant, as the stripped sour water treatment is expected to operate at 90% recovery, allowing the generation of 1080 m^3/day of reusable permeate.

Table 5.5 shows the results obtained for economic assessment that allows direct comparison of data for the main Classes, for scenarios with energy recovery systems. The different scenarios studied also allowed a sensitivity analysis regarding the parameter that possesses the greatest impact in RO operating expenses, electricity, and the effect the energy recovery can have on net savings and payback periods. The difference between gross savings (fresh water + wastewater volume reduction) and the total costs (operating + capital costs) each year can be classified as the net savings. It can be observed that the Class in which the final wastewater is inserted in, as well as the energy recovery efficiency during the membrane filtration, are key parameters which affect net savings and payback periods. For a fixed Class (for example Class 3), a 20% increase in energy recovery would increase the net savings by almost 10%, which is due to the extremely high contribution of electricity to the total operating costs. However, the same 20% increase in energy recovery would lead to an increase in net savings by almost 50%, if the final wastewater discharged falls in Class 4. The significantly higher fee per cubic meter applied by the WWTP to the refinery for Classes 4 and 5 are behind the explanation of the boost felt in net savings each year as well as the improvement in payback periods. Nevertheless, the inevitably high payback periods for this study lean on the fact that stripped sour water from the cracking complex at the Sines Refinery accounts for 12-14% of the total wastewater flowrate discharged to the WWTP. Net savings with no energy recovery system proved to be always negative (data not shown) and was therefore withdrawn from the economic evaluation. A further sensitivity analysis was performed related to the frequency of RO unit shutdowns for membrane cleaning and maintenance. It was observed that shutdowns for membrane cleaning every 2 weeks led to a 6% drop in total net savings per year and a 6-month increase in the payback period. On the other hand, if membrane cleaning occurs every week, a 20% drop in savings is expected to be felt every year. Therefore, on-site monitoring of the O&G content of the wastewater feed arises as an important tool to avoid frequent shutdowns and to protect the membrane lifetime, as previously reported [58].

Table 5.5 Economic assessment of RO treatment of stripped sour water for different Classes of final wastewater quality for scenarios studied with energy recovery systems

	Scenario 2 – 70% energy recovery		
	Class 3	**Class 4**	**Class 5**
Total CAPEX (€)	1410136	1410136	1410136
Total OPEX (€/year)	236391	236391	236391
Net savings (€/year)	6063	68343	206417
Payback period (years)	18	10	5.1
	Scenario 3 – 90% energy recovery		
	Class 3	**Class 4**	**Class 5**
Total CAPEX (€)	1410136	1410136	1410136
Total OPEX (€/year)	194953	194953	194953
Net savings (€/year)	86212	148492	286566
Payback period (years)	8.9	6.4	3.9

5.4.6 A sustainability analysis for refinery stripped sour water treatment

RO is known to be a mature and solid technology to overcome water shortages through desalination, with more appealing energy input requirements when compared with traditional processes such as distillation [86]. However, when it comes to using RO for industrial wastewater treatment, sustainability assessments arise as vital for a project approval and investment, especially when analysing the carbon footprint, energy sources for electricity consumed in the treatment and the environmental impact of the waste generated from membrane cleaning.

The electricity production mix in mainland Portugal has undergone a boosting shift from the dominated technologies for the past decades [87]. As of May 2020, over 70% of the total mix originated from renewable energy resources, with wind and hydropower averaging 23% and 30% of the total renewables [88]. Some studies have presented sustainability assessments of RO processes aiming primarily at desalination [86, 89, 90], rather than using RO as refinery wastewater treatment. However, the environmental impact through interpretation of the Global Warming Potential (GWP) for RO has been reported, for the same energy demand (3kWh) (considering Scenario 2) as the present manuscript for refinery stripped sour water treatment, as 1.77 kg CO_2-Eq to produce 1m^3 of permeate [89] when resorting to cogeneration for electricity production. Considering the updated energy production mix in Portugal, a promising opportunity arises to drop the GWP to the reported 0.235 kg CO_2-Eq or 0.0335 kg CO_2-Eq [89] if wind or solar power, respectively, are used as energy supply for the industrial RO unit at the refinery.

Regarding the assessment of the waste generated when resorting to RO for refinery wastewater treatment, an analysis of the Ecotoxicity Potential (ETP) is of great importance to predict environmental impact and can result from the chemicals used for membrane cleaning. Based on the number of shutdowns of the RO unit for membrane cleaning, the volume of the effluent resulting from it was calculated as less than 2% of the permeate generated and less than 0.2% of the total wastewater at the refinery. Therefore, a safe assumption of minor ecotoxicity impact from the detergents involved can be made, when considering a realistic scenario within the refinery.

It is also worthwhile to be aware of the energy consumption and chemicals used currently in the refinery wastewater treatment circuit and compare it with the energy consumptions after the implementation of the proposed RO treatment. Bearing in mind that using RO the volume of the final effluent discharged to the municipal WWTP would be reduced by as much as 14% (less 50m^3/h from the total 350m^3/h), a fair indication of energy savings in pumping for the current treatment may arise, as well as milder amounts of chemicals and reagents being required for the flotation and oxidation tanks. Table 5.6 shows the typical energy consumed in dissolved air flotation units (DAF) and common flocculants and coagulants used in oily wastewater treatment, where the former resorts to compounds based on acrylamides and the latter through inorganic metal-based components. Regarding oxidation, many industries use hydrogen peroxide (H_2O_2) due to its appealing efficacy in degrading organic persistent pollutants. However, the auto-oxidation of anthraquinone still dominates as technology to produce H_2O_2 worldwide. Therefore, opportunities associated with milder use of these chemicals and reagents due to smaller volumes of wastewater to be treated should be encouraged.

Table 5.6 Energy consumed in dissolved air flotation units (DAF), common flocculants and coagulants used in oily wastewater treatment and chemicals used for oxidation

	Dissolved Air Flotation (DAF)	Oxidation Basin
Energy	0.02 - 0.04 kWh/m^3 [91] 0.05 - 0.075 kWh/m^3 [92]	-
Chemicals & Reagents	Flocculants: Polyacrylamides derivatives (200mg/L to 6 g/L for optimum results) Coagulants: Aluminium and polyaluminium chloride [93]	Hydrogen peroxide (35%) (H_2O_2) Estimated concentrations (0.56 g/L) (auto-oxidation of anthraquinone as dominating technology for H_2O_2 production worldwide) [94]

Another relevant aspect regarding sustainability evaluation is the effect on fresh industrial water savings upon the implementation of the proposed RO treatment which is expected to work at 90% recovery, generating 1080 m^3/day of reusable water, translating into 375 840 m^3/year of water to be reclaimed in the refinery cooling towers (Figure 5.2, stream 2). As part of an encouragement for industries to efficiently use and reuse water, growing as a scarce resource, the fee applied to the refinery has suffered, on average, a 3% increase every 3 years. This means that besides the savings in water volume, the Sines refinery could actually save up to 163 000 €/year in 6 years' time, rather than the expected 150 000€/year.

A further analysis can be made through the current route taken of stripped sour water from the catalytic cracking complex and the proposed treatment (Figure 5.2). A technical analysis and evaluation on the best way to proceed regarding the management of the concentrate stream should not be overlooked. One of the main advantages of membrane technology in wastewater treatment is the reduction in volume of the effluent, which usually leads to a more practical handling. The expected 120m^3/day of concentrate generated (with phenol concentrations up to 3500mg/L and COD concentrations up to 12000mgO_2/L) can be expected to be treated based on several studies that go into detail regarding treatment and remediation of phenolic wastewaters involving advanced oxidation processes [35-37, 95, 96]. Table 5.7 shows the predicted phenol removal, operating costs, and impact of the treated concentrate regarding discharge, through reported studies for similar highly phenolic refinery wastewaters. The concentrate (Figure 5.2, stream 3b), once treated and discharged into the refinery effluent pre-treatment system, is expected to suffer a dilution effect as it would be mixed with other forms of wastewater (ex: desalter effluent, non-phenolic sour waters, etc). This would mean that the phenolic concentration could decrease as much as 60 times, which will be taken into account for a realistic assessment in the Sines refinery scenario. It can be seen that neutralization/acidification, followed by Fenton is expected to present higher phenolic removal efficiencies (up to 99%) than without acidification, generating a treated concentrate with minimal environmental impact (down to 0.5 mg/L in phenols) compared to the usual effluent quality. However, operating costs associated with AOPs are known to be relatively high, due to the high cost of reagents involved (inorganic compounds for Fenton and H_2O_2) and the need sufficiently high concentrations of H_2O_2 for appropriate oxidation, which also poses challenges in terms of green metrics.

Another option would be to study the possibility of reusing the phenolic compounds as added-value products (Figure 5.2, 3a). Depending on the type of compounds present, its use as jet fuel or lubricant additives could be considered an option, where many forms of branched phenols, such as 2,6-di-tert-butylphenol are applied as jet fuel additives [97]. Moreover, the actual use of additives on different forms of fuel, including diesel and jet fuel, usually lead to a higher quality and more efficient use of fuel, which results in lower consumptions and therefore less greenhouse gas emissions.

Table 5.7 Reported technologies for phenol removal in phenolic refinery wastewaters and predicted impact on concentrate treatment

Technology	Removal efficiency (%)	Expected concentration after treatment (mg/L)	Expected concentration after dilution effect (mg/L)	Average concentration in final effluent discharged[a] (mg/L)	Operating costs (€/m^3)[b]	Ref
Fenton (no neutralization)	up to 65	1225	20.4	3 – 12	4	[37, 98]
Neutralization + Fenton	95 – 99	35 - 175	0.6 - 2.9		4.6	[37, 98]

[a] Based on Sines refinery 2017-2019 data
[b] Based on market values of products involved in 2019 [98]

5.5 Conclusions

The present study involved an on-site pilot plant treatment of stripped sour water originating from the cracking complex at the Sines refinery, Portugal, using reverse osmosis, with the goal of reusing water and reducing wastewater volume. A technical, economic and energy assessment was performed to evaluate the overall feasibility of the treatment. Technical analysis focused on the permeate recovery and rejection of phenols/COD, which was 90% and 98%, respectively. The naturally low osmotic pressure of the wastewater allowed high fluxes (up to 44 $L.h^{-1}.m^{-2}$) and a concentration factor of 10, without loss of permeate quality as quality standards for water reuse. The pilot plant results indicated a relatively high energy demand. However, the installation of an Energy Recovery Device with reported 90% recoveries would allow a decrease in energy input demand to $1.2kWh/m^3$, translating into a drop in OPEX from $1.37€/m^3$ to $0.41€/m^3$. An economic evaluation for different scenarios was performed taking into account savings associated with fresh water and wastewater volume reduction and energy recovery efficiencies. Results showed that it can be possible for the Sines refinery to save up to 375 840 m^3/year in fresh water and up to 417 850m^3/year of wastewater discharges, translating into net savings of up to 286 566€/year and a payback period of down to 4 years. The RO proposal showed a low carbon footprint and negligible waste generation, however, careful consideration should be taken in the management and treatment of the concentrate stream.

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CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

The first study of this PhD thesis (Chapter 2) involved a wide assessment of the Sines Refinery wastewater circuit and the upstream refining processes that generate the wastewater streams that enter the circuit. The main goal was to identify the stream that contributes the most in terms of phenols throughout the refinery, through comparison of phenol mass contribution between the several wastewater streams. Stripped sour water from the cracking complex was identified as the source of phenol emission and key effluent to be treated in order to remove the organic pollutants that contribute to its low quality. The upstream refining process that generates stripped sour water from the cracking complex justifies the high phenolic content, as practically all phenols emitted in refinery wastewater streams, as long as a cracking complex is present, derive from by-products in the Fluid Catalytic Cracking unit due to the reaction between cyclic hydrocarbons and steam. It was concluded that strategies regarding the possibility of water reuse while assuring efficient phenol removal would positively impact costs associated with fresh water as a utility and wastewater volume reduction. Such strategies would therefore highlight the possibility of removing phenols at the source of emission, leading to an improvement of the effluent quality downstream to the external WWTP, while resorting to a treatment that would allow water reuse. Membrane separation technologies were given particular attention in approaching the strategy at hand due being known as having low energy consumption, low operating and capital cost, and easy modular scale up.

Chapter 3 focused on the key effluent at hand from the Sines Refinery being treated for the first time using membrane filtration processes. Laboratory studies focused on processing the wastewater through a nanofiltration membrane as a wastewater treatment. Low COD rejections after using a Desal DK NF membrane led to observation that nanofiltration was not suitable for an efficient treatment by retention of the most abundant organic contaminant, phenols. Therefore, two reverse osmosis membranes, BW30 and SW30 were tested, in which the latter showed appealing overall rejections of COD (up to 99%) and phenols (up to 98%) when being processed in a cross-flow filtration mode. Three different wastewater samples were processed over a representative operational period, two of which experienced no flux decline up to a concentration factor of 3. Flux decline due to hydrocarbon and phenolic adsorption was observed in the case where O&G content in feed exceeded regular values. No loss of rejection, however, was observed in any of the cross-flow experiments and all permeates characterized were within the water quality standards for water reuse in cooling systems. It was concluded that minor osmotic pressure differences were developed (less than 2.5 bar at a concentration factor of 3) due to poor salinity of the wastewater led to potential advantages of using reverse osmosis, with appealing performances and high recoveries, unlike typical desalination processes, where the high osmotic pressure in seawater limits the overall recovery rate to 50% at most, even when multiple stages are implemented.

Chapter 4 highlighted, for the first time, a complete evaluation of the treated water generated from reverse osmosis filtration in order to be reused within the refinery. The goal was to assess the quality of the water to be reused as make-up water in cooling towers, as these units are known to be the highest consumers of industrial water of the oil refining industry. Therefore, a chemical and physical compatibility test was performed, where chemical analysis of the permeate samples were compared with the reported quality standards for water reuse in cooling processes in the industry. The physical evaluation involved an electrochemical compatibility test of the permeate samples, where they were put into direct contact with mild carbon steel and compared with the current safe make-up water used, in order to determine the feasibility of water reclamation. Linear-polarization analysis showed that all permeates lead to the same or even lower corrosion rates as the make-up water. The permeate with the highest COD, still in line with quality standards for water reuse, and highest conductivity showed a corrosion rate of 0.123 mm.year^{-1} while 0.167 mm.year^{-1} was obtained for make-up water. It was concluded that the poor conductivity of all permeates compared with the make-up water played a decisive role in the low corrosion phenomena observed. The reclamation study involving chemical characterization and corrosion evaluation confirmed the adequacy and safe use of the permeates in the cooling system of the refinery.

Chapter 5 focused on an on-site pilot plant treatment of stripped sour water using reverse osmosis, with the goal of reusing water and reducing wastewater volume. A technical, economic and energy assessment was performed to evaluate the overall feasibility of the treatment. Technical analysis focused on the permeate recovery and rejection of phenols/COD, which was 90% and 98%, respectively. The naturally low osmotic pressure of the wastewater allowed high fluxes and a concentration factor of 10, without loss of permeate quality as quality standards for water reuse. The pilot plant results indicated a relatively high energy demand. The installation, however, of an Energy Recovery Device with reported 90% recoveries would allow a decrease in energy input demand to 1.2kWh/m^3, translating into a drop in OPEX from 1.37€/m^3 to 0.41€/m^3. An economic evaluation for different scenarios was performed taking into account savings associated with fresh water and wastewater volume reduction and energy recovery efficiencies.

It was shown that it can be possible for the Sines refinery to save up to 375 840 m^3/year in fresh water and up to 417 850m^3/year of wastewater discharges. This translates into net savings of up to 286 566€/year and a payback period as low as 4 years. The RO proposal showed a low carbon footprint and negligible waste generation, however, careful consideration should be taken in the management and treatment of the concentrate stream.

6.2 Future Work

Reverse Osmosis proved to be a promising stand-alone technology for the upstream treatment of a very specific wastewater stream, rich in hazardous phenols, which presents a unique physico-chemical nature including the lack of salts or suspended solids, giving an unusual advantage in terms of treatment performance with such membranes. However, as explained in Chapter 3, a balanced trade-off should be considered between the need of a RO pre-treatment for the rare cases in which O&G compounds surpass values already shown to be damaging to the membrane and the simple adjustment and process optimization of the fluid dynamics involved. Therefore, future work could involve onsite instrumental monitoring of O&G content in the stream to indicate possible fluctuations in the feed quality. RO pre-treatment would potentially involve an ultrafiltration installation and membranes to remove a colloidal fraction containing O&G compounds, boosting the CAPEX of the investment on an industrial scale. Future work could present an economic insight regarding the most promising option between the increase in CAPEX for pre-treatment and the onsite monitoring of the compounds that could affect the wastewater treatment performance.

Future work would also involve a technical analysis and evaluation on the best way to proceed regarding the management of the concentrate stream. One of the main advantages of membrane technology in wastewater treatment is the reduction in volume of the effluent, which usually leads to a more straightforward handling, whether it be for post-treatment or external disposal. Therefore, a trade-off study would be required between the costs associated for external disposal of the 80m^3/day of concentrate generated in a best-case scenario (with phenol concentrations up to 4g/L and COD concentrations up to 15000mgO_2/L) and costs for a post-treatment within the refinery. Several studies go into detail regarding treatment and remediation of phenolic wastewaters involving advanced oxidation processes, including Fenton processes, ozonation or the use of hydrogen peroxide combined with UV light, some of which with promising results regarding phenol removal using photo-ferrioxalate (up to 100% for 200mg/L of phenols) in oil refinery effluents [35, 37, 95, 96].

Another key advantage of using membrane technology to treat wastewater is the fact that the components that compose the feed are not degraded bur rather concentrated into a smaller volume. In some cases, such a technology is actually considered a process of concentration and recovery of compounds that could lead to added value products, frequently applied to the food industry. A similar insight regarding the oil and gas industry could also be considered, where research in the transformation of waste into raw materials or value are to be highlighted. In the present project, the concentration stream would be primarily rich in phenolic compounds. The quickest and most straightforward application would be in the oil and gas market itself. It is a fact that the world is going through intensive research and investment regarding energy transition in the quest for sustainability and climate change battling. However, such a transition would be more gradual in some forms of transportation over others, particularly air travel and maritime transport, in comparison with car transportation, which has already shown to be on a well-defined route of energy transition involving electric and hydrogen fuel cell technologies. Therefore, the possibility of recovering and purifying the phenolic compounds to be used as fuel or lubricant additives could be considered an investment, where many forms of branched phenols, such as 2,6-di-tert-butylphenol are applied as jet fuel additives [97]. Moreover, the actual use of additives on different forms of fuel, including diesel and jet fuel, usually lead to a higher quality and more efficient use of fuel, which results in lower consumptions and therefore less greenhouse gas emissions.

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